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Risk Assessment and Risk Management in Managed Aquifer Recharge and Recycled Water Reuse: The Case of Sabadell

Maria Neus Ayuso Gabella

Doctorate Program: Environmental Science and Technology
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RISK ASSESSMENT AND RISK MANAGEMENT IN MANAGED AQUIFER RECHARGE AND RECYCLED WATER REUSE: THE CASE OF SABADELL

Thesis submitted to the University of Barcelona in fulfilment of the requirements for the degree of Doctor by Maria Neus Ayuso Gabella

Director: Professor Miquel Salgot de Marçay
Natural Products, Vegetal Biology and Soil Science Department
University of Barcelona

Tutor: Professor Joan Mata Álvarez
Chemical Engineering Department
University of Barcelona

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"I know that I know nothing."
Socrates

“We are all very ignorant but not all ignorant of the same things.”
Albert Einstein

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EXECUTIVE SUMMARY

The increasing practice of water recycling, including or not managed aquifer recharge (MAR), requires to thoroughly assess the risks posed by it in real systems, not only in laboratory and column studies.

The present work has been developed in a case study in Sabadell, Spain. For this site, the treated effluent of the Ripoll River WWTP is discharged into the Ripoll River, thus enhancing the natural infiltration to the alluvial aquifer. Pumping of the groundwater induces a riverbed filtration process (RBF), which is one of types of MAR. The recovered water undergoes further post-treatments, including UV, chlorination and sand filtration. After the post-treatments, the water is used for park irrigation and street cleaning. This site was part of the RECLAIM WATER project, supported by the European Commission and devoted to studying MAR and the use of reclaimed water for it in different locations in Europe, as well as in other countries outside Europe. For Sabadell case study, named "RISMAR" in the present work, a risk assessment and a risk management have been developed. In addition, a quantitative microbial risk assessment (QMRA) has been developed too. QMRA is not as usually applied to recycled water schemes as it is to drinking water ones, and even less to MAR.

In order to develop the risk assessment, it was necessary to gather data on the site. Most of the data used to develop the present work were generated in the framework of the RECLAIM WATER project, and it included not only basic wastewater and surface water regular parameters and microbiological indicators, but also trace compounds, pathogens and antibiotic resistance genes. Other data were available from public institutions and previous works.

The main results of the risk assessment indicate that for the uses considered for the final treated water the risk is low and in some cases medium, with the exception of using the final treated water as drinking water. Currently, this use it is not in place at the site, and it is not expected to be in the near future. The QMRA results additionally indicate that cross-connection, swimming and the immunocompromised population would be in the limit of the acceptable level of risk. Thus, the immunocompromised population should be considered in risk assessments, as the risk for them might be much higher than for the rest of the population. The residual risks that needed to be managed and considered were posed by inorganic compounds, organic compounds, salinity and mobilization of inorganic compounds from the sediments.

Another important result of the work is that the RBF and subsurface treatment proved to be very useful in reducing the risks posed by pathogens, nutrients, organic compounds and particulates. In contraposition, other risks appeared, like the mobilization of inorganic compounds from the aquifer. Then, these positive results support the request by many authors of treating MAR as an additional treatment.

Finally, a risk management plan has been developed, integrating the results of the risk assessment. For this risk management plan, not only the critical control points are identified, as it is typical for risk managements, but the twelve elements of the framework issued by the Australian Government (NRMMC-EPHC–NHMRC, 2009) have been assessed and developed, thus supporting a robust risk management plan. Emphasis is put in corrective and preventive actions for the system, as well as in defining the critical limits, monitoring program and sampling points. Besides, validation is given the importance it has in order to ensure a proper functioning of the system.

ABBREVIATIONS

95th	95th percentile
ACA	Agència Catalana de l'Aigua - Catalonia Water Agency)
AEW	Aquatic Ecosystems Water
AHMC	Australian Health Ministers' Conference
AIDS	Acquired Immunodeficiency Syndrome
ANZECC	Australian and New Zealand Environment and Conservation Council (Note: in 2001, the functions of ARMCANZ and ANZECC were taken up by the Environment Protection and Heritage Council and the Natural Resource Management Ministerial Council)
APHA	American Public Health Association
ARFC	Agricultural Reuse - Food Crops
ARGs	Antibiotic Resistance Genes
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand (Note: in 2001, the functions of ARMCANZ and ANZECC were taken up by the Environment Protection and Heritage Council and the Natural Resource Management Ministerial Council)
ASR	Aquifer Storage and Recovery
ASTR	Aquifer Storage, Transfer and Recovery
ATLL	Aigües Ter-Llobregat (Ter and Llobregat Waters)
ATSDR	Agency for Toxic Substances and Disease Registry
Au	Australian
BOD_5	5 day Biochemical Oxygen Demand
BPA	Bisphenol A
BWSP	Bathing Waters - Swimming Pools
CAC	Codex Alimentarius Commission
CASSA	Companyia d'Aigües de Sabadell S.A. – Sabadell Water company
CCP	Critical Control Point
CDPH	California Department of Public Health
CHD	Departament de Salut de la Generalitat de Catalunya - Catalonia Health Department
cfu	colony-forming unit
CL	Critical Limit
CNE	Centro Nacional de Epidemiología (National Epidemiology Center).
COD	Chemical Oxygen Demand
CSIRO	Commonwealth Scientific and Industrial Research Organization

DALYs	Disability Adjusted Life Years
DBPs	Disinfection By-Products
DECOS	Dutch Expert Committee for Occupational Standards
DME EPA	Danish Ministry of the Environment – Environmental Protection Agency
DW	Drinking Water
EDC	Endocrine Disrupting Compound
EDS	Departament de Sostenibilitat i Gestió d'Ecosistemes de l'Ajuntament de Sabadell - Environmental Department of Sabadell Municipality
EPA	Environment Protection Agency
EPHC	Environment Protection and Heritage Council
ER	Environmental Reuse
FAO	Food and Agriculture Organization
FS	Factor Sensitivity
G	Guidelines
gc	gene copies
GHTF	The Global Harmonization Task Force
GV	Guideline Value
HACCP	Hazard Analysis and Critical Control Points
IARC	International Agency for Research on Cancer
ICP	Inductively Coupled Plasma
ID_{50}	Pathogen dose at which 50% of the population develops a disease
IGME	Instituto Geológico y Minero de España
INE	Instituto Nacional de Estadística (National Statistics Institute)
IPR	Indirect Potable Reuse
IQ	Installation Qualification
IR	Industrial Reuse
IUPAC	International Union of Pure and Applied Chemistry
IW	Irrigation Water
LOAEL	Lowest Observed Adverse Effect Level
LOD	Limit of Detection
LTV	Long-term Value
MAGRAMA	Ministerio de Agricultura, Alimentación y Medio Ambiente (Spanish Ministry of Agriculture, Food and Environment)
MAR	Managed Aquifer Recharge
MASL	Metres Above Sea Level
max	maximum value
med	median value

meq	milliequivalent
min	minimum value
NDBA	N-nitrosodibutylamine
NDEA	N-nitrosodiethylamine
NDMA	N-Nitrosodimethylamine
NHMRC	National Health and Medical Research Council
NMOR	N-Nitrosomorpholine
NOAEL	No Observed Adverse Effect Level
NPIP	N-nitrosopiperidine
NRC	National Research Council
NRMMC	Natural Resource Management Ministerial Council
NTU	Nefelometric Turbidity Unit
NZMOH	New Zealand Ministry of Health
OQ	Operational Qualification
PCR	Polymerase Chain Reaction
PDF	Probability Distribution Function
pfu	plaque forming unit
PhACs	Pharmaceutically Active Compounds or Pharmaceuticals
POA	Point Of Attention
pppy	per person per year
PQ	Performance Qualification
QA	Quality Assurance
QMRA	Quantitative Microbial Risk Assessment
R	Regulation
RBF	Riverbed Filtration
RD	Royal Decree (Spanish Regulation)
RISMAR	Recycled water and Managed Aquifer Recharge scheme based on the Ripoll River in Sabadell
RW	Recreational Water
S1 C	Sampling point secondary effluent of the WWTP composite sample
S1 S	Sampling point secondary effluent of the WWTP grab sample
S2	Sampling point Ripoll River reference point
S3	Sampling point Ripoll River mixture 1
S4	Sampling point water recovered from the aquifer in the mine
S5	Sampling point sprinklers from the Taulí Park (final treated water)
S6	Sampling point Ripoll River mixture 2
SAR	Sodium Adsorption Ratio

SAT	Soil Aquifer Treatment
SCADA	Supervisory control and Data Acquisition System
STV	Short-term Value
SUVA	Specific Ultraviolet Absorption
THM	Trihalomethane
UB	Universitat de Barcelona - University of Barcelona
URR	Unrestricted Recreational Reuse
US EPA	United States Environmental Protection Agency
UUR	Unrestricted Urban Reuse
UV	Ultraviolet
VOCs	Volatile Organic Compounds
WFD	Water Framework Directive
WHO	World Health Organization
WSP	Water Safety Plans
WWTP	Wastewater Treatment Plant

1. LIST OF PUBLICATIONS

1.1. Peer-reviewed journal publications

Ayuso-Gabella, M.N., Page, D., Masciopinto, C., Aharoni, A., Salgot, M. and Wintgens, T. (2011). Quantifying the effect of Managed Aquifer Recharge on the microbiological human health risks of irrigating crops with recycled water. *Agricultural Water Management*, 99: 93-102.

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1.2. Peer-reviewed reports

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*Note: this report was peer-reviewed by the different contributors but previously to its publication the partners involved decided to keep it confidential and not publishing it, as the information included was deemed to be too sensitive to be made public.

1.3. RECLAIM WATER project book

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2. INTRODUCTION

2.1. Water in the World: scarcity

Water is one of the essential human needs. In our changing and heavily populated world, that currently has reached 7 billion inhabitants, water is becoming a precious jewel, unevenly distributed and more and more scarce, and future projections are even worse. In this difficult context, alternative water sources are gaining importance, as part of a requested global solution.

Access to safe drinking-water is essential to health, a basic human right and a component of effective policy for health protection. The importance of water, sanitation and hygiene for health and development has been reflected in the outcomes of a series of international policy forums. At the 2000 UN Millennium Summit, world leaders from rich and poor countries alike committed themselves - at the highest political level - to a set of eight time-bound targets that, when achieved, would end extreme poverty worldwide by 2015 (United Nations, 2012). Goal number seven is devoted to "Ensure Environmental Sustainability", and one of the set targets inside this goal is "Halve, by 2015, the proportion of the population without sustainable access to safe drinking water and basic sanitation". In our world today around 2.5 billion people do not have access to improved sanitation and some 1.2 billion people do not have access to an improved source of water.

In addition of working to supply safe drinking water and basic sanitation to the population, water scarcity requires the use of alternative water sources in order to cope with the demand. Alternative water resources include:

- Water surpluses.
- Seawater desalination.
- Continental saline waters desalination.
- Rainwater and stormwater.
- Condensed/dew water.
- Recycled water/water reuse.

Water reuse has gained importance and is nowadays a great option to increase water resources. One of the most widely extended uses of recycled water is agricultural irrigation, which helps to grow more food and reduce the use of potable water and fertilizers, thus contributing to Millennium Development Goal 1: "Eliminate extreme poverty and hungry" (WHO, 2006b).

Treated wastewater has the advantage of being produced the whole year round. However, this treated wastewater sometimes needs to be stored in order to be used during high demand periods or to cope with strong scarcity periods. One good option for storage is to perform a managed aquifer recharge, which at the same time can improve the water quality. Then, managed aquifer recharge with treated wastewater is a good opportunity to cope with the water scarcity in the world.

2.2. Water reuse and reclamation processes

Global water reuse is primarily driven by two main groups of drivers: first, reuse is a response to an increasing demand for water and limitations on freshwater availability; and second, water reuse is driven by a desire to take advantage of the economic benefits of wastewater (US EPA, 2012).

The first group of drivers for water reuse is typically found in areas of physical water scarcity, such as the Middle East and North Africa region, Australia, Singapore, and parts of southern

Africa. Thus, poor water resources management and climate change may exacerbate conditions of scarcity in some countries and create conditions of scarcity in others. The creation of environmental regulations that limit the quantity of water available for human use and set standards for the quality of the treated effluent has, in turn, promoted greater reuse of existing water rather than development of new water sources.

Economic considerations are also beginning to drive water reuse in high-resource contexts, marketing the reuse of reclaimed water as a way of obtaining a partial return on investment for wastewater treatment. The prospect of water scarcity begins to discourage lower-value uses, such as agricultural irrigation. Economic benefits associated with formal water reuse projects are more likely to be achieved over longer timeframes compared to shorter-term gains from transporting water from distant sources, groundwater mining, and reservoir construction.

2.2.1. Wastewater and reclaimed water reuse

Wastewater reuse has been done since ancient times. The first historical evidence of wastewater used for irrigation goes back to the Middle and Late Bronze Ages (c.3000–1400 BC) in the Minoan Civilization (Angelakis and Spyridakis, 1996). Water reuse was already a common practice in Roman times where water was used several times in the same house. Wastewater has also been used by the Mediterranean civilizations, for example in the 14th and 15th centuries in Milan and Valencia, and also in the North European ones, like in Great Britain, Germany, France, and Poland (Soulié and Tréméa, 1992). The reuse practice was performed without measures of health control and any treatment process. Later on, wastewater was directly disposed into the crop fields, in UK and Germany during the sixteenth and seventeenth centuries (Asano and Levine, 1996). In more recent history, the first large-scale water reuse projects were developed at the beginning of 1800s when “sewage farms”, a technology developed in Germany, were expanded to England and to other European countries until the end of nineteenth century. However, sewage farms were principally operated as disposal sites aiming to maximize the amount of wastewater applied per surface unit rather than to recycle it efficiently for crop irrigation (Paranychianakis *et al.*, 2011). Systems to discharge wastewater into surface water were introduced during the nineteenth century. This led to problems of biological contamination, cholera and typhoid fever during the period 1840-1850. In London, in order to correct these problems, wastewater was discharged downstream of the river catchment area for potable purposes. Gradually, drinking water filtration before use was introduced. The implementation of planning programs for wastewater use started in the early twentieth century. The state of California was the first to establish regulations for the reuse of reclaimed water in 1918, "First regulation for use of sewage for irrigation purposes in California" (Paranychianakis *et al.*, 2011). The pressure on water resources and the benefits of reclaimed water use to crop yield due to the increased concentrations of nutrients stimulated water recycling for irrigation. These regulations encouraged water reuse for irrigation of non-edible crops and for crops cooked before being eaten, while prohibiting the use of raw wastewater for crop irrigation. Since then, the “California Regulations” have been continuously updated to cover new applications and to meet the stringent requirements for public health and of the environment. In 1965 Israel adopted the first water reuse regulations for irrigation, and in 1999 they were revised by the Israeli Ministry of Health. In 1973 the first guidelines for water reuse were published by the World Health Organization addressing health criteria and treatment processes for water reuse applications (WHO, 1973). In 1989 following a meeting in Switzerland the first revision of the WHO guidelines was published (WHO, 1989). Following the publication of the “California Regulations” and the WHO recommendations, many countries and states developed criteria for water reuse that were mainly influenced by these two distinct philosophies (Paranychianakis *et al.*, 2011).

In the late 90's there has been a growing interest in using reclaimed water worldwide. Many communities throughout the world are approaching, or have already reached, the limits of their available water supplies; water reclamation and reuse have almost become necessary for conserving and extending available water supplies. Water reuse may also present communities with an alternate wastewater disposal method as well as provide pollution abatement by diverting effluent discharge away from sensitive surface waters. Already accepted and endorsed by the public in many urban and agricultural areas, properly implemented non-potable reuse projects can help communities meet water demand and supply challenges without any known significant health risks (US EPA, 2012).

Nowadays, untreated wastewater is widely used in developing countries for irrigation. This practice entails serious risks for the human health. However, scarcity obliges them to take action and use any resource possible. In developed countries, untreated wastewater is not used for irrigation, but it is treated in wastewater treatment plants (WWTPs) and in some cases in reclamation plants, in order to reuse it for potable or non-potable purposes.

2.2.2. Uses of the reclaimed water

Reclaimed water can be given many different uses. Table 1 gives a summary of possible uses, and also includes the main limitations that need to be overcome for each use. In the sections below the most important uses of reclaimed water are discussed.

2.2.2.1. Urban uses

Urban uses include a wide variety of possibilities for reclaimed water use, and usually is serving large users. In dual distribution systems, the reclaimed water is delivered to customers through a parallel network of distribution mains separate from the community's potable water distribution system, and taking all available measures to avoid cross-connection. In addition, it is requested to warn consumers of the risks that can be undertaken when reclaimed water is used for potable purposes. Urban uses are currently performed around the world. Initial experiences with urban reuse come from California, USA. The city of Pomona started to reuse water for urban purposes in 1973. In Australia, Mawson Lakes community, in South Australia, has a dual network system and the reclaimed water is used for many urban uses (NRMMC–EPHC–AHMC, 2006). In Spain, one example is Sabadell, Catalonia, which is the focus of the present work. In this case, the final treated water is used for street cleaning and urban park irrigation. Other examples are: a recreational park in Tarragona province (Alcalde, 2012) and green areas irrigation in La China, Madrid (Olcina, 2002).

2.2.2.2. Agricultural uses

Agricultural utilization of reclaimed water is the most widely extended use. Worldwide, it was estimated that irrigation water demands exceeded all other categories of water use, and almost 60 percent of all the world's freshwater withdrawals go towards irrigation uses (US EPA, 2012). Many reuse experiences in the world, then, are devoted to agricultural use. In fact, agricultural irrigation is the predominant application for reclaimed water in Europe with 70 % of the reused volumes devoted to this use (Wintgens and Hochstrat, 2006). The widespread use of reclaimed water for irrigation comes from the high water demands of this sector. In line with the wide use of reclaimed water for irrigation, there has been an active production of guidelines and regulations that refer to this particular water reuse case and it has been extensively studied.

Table 1 Treated wastewater and reclaimed water uses and limitations (modified from Asano *et al.*, 2007; NRMMC–EPHC–AHMC, 2006; Salgot and Angelakis, 2001; US EPA, 2012).

Uses	Limitations
1. Urban uses 1.1. Residential uses: Private gardens irrigation, air conditioning, toilet flushing. 1.2. Irrigation of open access landscape areas: parks, gardens, sport fields, golf courses, school yards, graveyards, highway medians and shoulders, landscaped areas surrounding public buildings and facilities, etc. 1.3. Street cleaning. 1.4. Fire-fighting systems. 1.5. Commercial uses such as vehicle washing facilities, laundry facilities, window washing, and mixing water for pesticides, herbicides, and liquid fertilizers. 1.6. Ornamental landscape uses and decorative water features, such as fountains, reflecting pools, and waterfalls.	- *Legionella* in air conditioning - Pathogens transmission through aerosols - Corrosion, fouling, particles - Salinity and infiltration rate - Implement a piping system separate from potable water - Cross-connection with potable water
2. Agricultural uses 2.1. Crop irrigation. Fodder, cereals, seeds, horticulture, fruit trees, etc. 2.2. Irrigation of pastures for milk or meat animals. 2.3. Aquiculture. 2.4. Irrigation of nurseries and ornamental flowers. 2.5. Production of wood, biofuel, compost.	- Salinity and infiltration rate - Pathogens transmission through aerosols - Public acceptance - Corrosion, fouling, particles - Pollution of continental waters and groundwater - Toxicity for aquatic life, animals or crops - Toxicity for consumers.
3. Industrial uses 3.1. Process water and cleaning. 3.2. Construction, dust control, concrete production. 3.3. Materials transport. 3.4. Cooling water and heating water.	- *Legionella* (cooling water) - Pathogens transmission through aerosols - Corrosion, fouling, particles, scaling - Pathogens transmission through aerosols - Aesthetic (odour)
4. Recreational uses 4.1. Impoundments, lakes, water bodies and streams for recreational uses. 4.2. Artificial snow.	- Pathogens transmission - Eutrophication - Aesthetical (odour) - Adverse effects on flora and fauna
5. Environmental uses 5.1. Irrigation of forested areas, landscape and green areas. 5.2. Environmental flow maintenance (rivers or streams). 5.3. Enhancement of wetlands and marsh.	- Pathogens transmission - Eutrophication - Aesthetical (odour) - Adverse effects on flora and fauna
6. Managed Aquifer Recharge 6.1. Saltwater intrusion barrier. 6.2. Recovery of aquifer water levels and maintenance of groundwater depended ecosystems. 6.3. Storage of recycled water for future uses. 6.4. Recycled water quality improvement. 6.5. Dilution of polluted/saline aquifers. 6.6. Ground subsidence control. 6.7. Water transport. 6.8. Ensure water supply.	- Micropollutants introduction into the aquifer. - Suspended solids, metals, nutrients, nitrate and pathogens in reclaimed water.
7. Potable reuse 7.1. Direct potable reuse by mixture with potable water supply or direct connection to water distribution network. 7.2. Indirect potable reuse by mixing with surface and/or groundwater	- Pathogens transmission - Public acceptance and aesthetical. - Corrosion, fouling, particles - Micropollutants

Crop irrigation requires a good amount of water, which can be reclaimed water thus reducing the stress on potable water use. In developing countries, untreated wastewater is also used for this purpose due to water scarcity and lack of sanitation. When reusing reclaimed water for irrigation, it is important to consider (NRMMC–EPHC–AHMC, 2006; US EPA, 2012; WHO, 2006b):

- The crop: some crops can be sensitive to salinity, heavy metals and other pollutants, so this must be accounted for.
- The soil: some soils can be sensitive to salinity and leaching processes.
- The irrigation type: e.g. sprinklers, drip irrigation, border irrigation. Depending on the kind of irrigation the risk of disease spread due to pathogenic microorganisms varies.
- The quality of the reclaimed water: depending on the crops irrigated, reclaimed water irrigation can be restricted. For instance, if the water contains a high concentration of pathogens, then it is not recommended to be used to irrigate vegetables or crops eaten raw.
- The public acceptance to reuse reclaimed water for crop irrigation: if the consumer will not buy the produce, the system is not useful.

The availability of the water: it is necessary to cover high peak demands and to find a way to store the reclaimed water.

Some well-known water reuse schemes for irrigation purposes in the world are: Dan Region, in Israel; Tula Valley, Mexico; Virginia pipeline scheme and Bolivar ASR, South Australia, Australia; Soukra, Tunisia; Beijing, China; California, USA, among others (Hamilton *et al.*, 2007; Icekson-Tal *et al.*, 2003; Page *et al.*, 2010). Agricultural reuse is also the most commonly found use in Spain, with reuse schemes present in The Costa Brava, Vitoria, Alicante, Gran Canaria, Valencia, Almería and Tenerife (Olcina, 2002), among other implemented.

2.2.2.3. Industrial uses

Industrial use of reclaimed water has increased substantially since the early 1990s. Traditionally, pulp and paper, textile, and other facilities using reclaimed water for cooling tower purposes, have been the primary industrial users of reclaimed water. In the recent years, the industrial use of reclaimed water has been growing in a variety of industries ranging from electronics to food processing, as well as a broader adoption by the power-generation industry. These industries use reclaimed water for purposes ranging from process water, boiler feed water, and cooling tower use to flushing toilets and site irrigation (US EPA, 2012). Some examples around the world are: Coca-Cola, Frito Lay and Intel, USA; Bokod Power Station, Hungary; Samsung, South Korea; Holmen paper mill, Madrid; and different companies in Vitoria, Bilbao and Tarragona, Spain (Blanco *et al.*, 2009; Jiménez and Asano, 2008; Olcina, 2002; US EPA, 2012). Using the reclaimed water as process water entails more risk in the food industry. The highly possible introduction of pathogens when using reclaimed water as process water requests that the reclaimed water used has a high quality standard, with a strict disinfection process. Using the reclaimed water as cooling water entails a risk associated to the presence of *Legionella*, especially in cooling towers.

2.2.2.4. Recreational uses

Uses of reclaimed water for recreational purposes range from landscape impoundments or water hazards on golf courses to full-scale development of water-based recreational impoundments. Artificial snow is also another recreational use, less known. Depending on the degree of contact with the populations, the reclamation treatments will need to be more or less stringent. Examples around the world for water-oriented recreational activities are: Santee Lakes Recreation Preserve (Park), San Diego, USA; Bolivar ASR, South Australia, Australia; and golf courses in the Mediterranean area (Page *et al.*, 2010; Salgot *et al.*, 2012; US EPA, 2012). Snowmaking with reclaimed water is being done in the USA, Canada, and Australia (US EPA, 2012). Examples in Australia include Mt Buller resort (Mt Buller Resort, 2012) and Mount Hotham Resort, both in Victoria (US EPA, 2012). In the USA examples are found in Maine, Pennsylvania, Arizona and California. Recreational examples in Spain include golf courses (water hazards filling), located at Bandama, Gran Canaria, Costa Brava, Catalonia, Balearic Islands and South of Spain, and also Port Aventura park in Tarragona, Catalonia (Alcalde, 2012; Olcina, 2002; Salgot *et al.*, 2012).

2.2.2.5. Environmental uses

Environmental reuse primarily includes the use of reclaimed water to support wetlands and to supplemental stream and river flows (US EPA, 2012). Environmental uses are gaining importance, but not in developing countries where they are not a must. Some examples for environmental uses are: the Orlando Easterly Wetlands, in Florida, USA; Lake Elsinore, California; and flow augmentation for Bell Creek in the city of Sequim, Washington (US EPA, 2012). In Spain interesting cases of rivers and wetlands restoration can be described. Some examples for wetlands are: Aiguamolls de l'Empordà, Costa Brava, Catalonia; Llobregat Delta, Catalonia; and Albufera Natural Park, Valencia (Olcina, 2002). For rivers restoration, Llobregat, Besós and Manzanares are good examples. In Sabadell, the object site of the present work, the treated wastewater is discharged to the Ripoll River for river flow maintenance.

2.2.2.6. Managed Aquifer Recharge uses

Managed aquifer recharge (MAR) will be more in-depth discussed in section 2.2.4.

The purposes of MAR using reclaimed water may be to:

(1) Establish saltwater intrusion barriers in coastal aquifers.

(2) Provide further treatment for future reuse.

(3) Augment potable or non-potable aquifers, recover water levels and maintain groundwater dependent ecosystems.

(4) Provide storage of reclaimed water for subsequent retrieval and reuse.

(5) Control or prevent ground subsidence.

(6) Dilute saline or polluted aquifers.

(7) Use it as a means of moving water from an area to another.

(8) Ensure water supply.

In case MAR is used as storage, transport and/or quality improvement means, the recovered water can be given any of the uses explained in this section, including potable use.

MAR has been gaining more and more importance in the recent years; proof of this is the increase in projects and the last European Commission funded projects "RECLAIM WATER" and "GABARDINE". The present work has been developed in the framework of the RECLAIM WATER project (see section 2.3.3), and Sabadell recycled water scheme was part of it. In Sabadell, the MAR recycled water scheme uses riverbed filtration as means to recharge the alluvial aquifer under the Ripoll River. Some of the sites included in the RECLAIM WATER project have been cited as examples of reuse in the present section 2.2.2. The Orange County case, in California, USA, is one of the most well-known MAR schemes (US EPA, 2012). In Catalonia, it is also well-known the case of the Llobregat Delta, where recharge used to be performed as a barrier against saline intrusion. Other examples of MAR around the world and in Spain are given in section 2.3.1.

2.2.2.7. Potable uses

Direct or indirect potable use of treated wastewater entails a high level of wastewater treatment, including at least advanced tertiary treatments and disinfection, in order to produce "reclaimed water". In the case of direct potable reuse the reclaimed water is directly introduced into the potable distribution network. There are few experiences in this sense, to cite some: Windhoek, Namibia; Big Springs, Texas, USA; Cloudcroft, New Mexico, USA (Leverenz *et al.*, 2011). The main difficulties faced for this direct potable reuse is the high level of treatment required for the wastewater, and the risks posed to the human health. In fact, current regulations in Spain (Spanish Official Bulletin, 2007) and in most countries do not consider/accept the direct potable reuse of reclaimed water. For indirect potable reuse, treated wastewater effluent is discharged into a natural environmental buffer, such as a stream or aquifer (US EPA, 2012). Well-known experiences with indirect potable reuse include: Orange County, California, USA; Atlantis, Cape Town, South Africa; Newater, Singapore; Occoquan County, Virginia, USA; Wulpen/Torreele, Belgium (Leverenz *et al.*, 2011; Page *et al.*, 2010; US EPA, 2012).

2.2.3. Reclamation processes

Raw wastewater needs to follow at least primary and secondary treatments at the WWTP in order to be prepared for reclamation processes. These reclamation processes, also known as tertiary treatments, are mostly intended to reduce the pathogen load still present in the treated wastewater, as well as the salinity, nutrients, organic compounds, trace elements or any other hazardous compounds that would need to be eliminated or decreased depending on the final use of the reclaimed water.

Reclamation processes can be classified in pre-treatments and disinfection treatments. Pre-treatments are usually performed prior to disinfection, with the objective of reducing the solids, organic matter and other contaminant loads of the treated wastewater and prepare it for a more effective disinfection. Disinfection treatments are intended to reduce pathogens concentration, and, some of them, additionally include a residual disinfectant level that persists in the reclaimed water. However, the risk of disinfection by-products generation needs to be considered and reduced as far as possible.

Reclamation technologies, analogously to regular wastewater treatment ones, can be classified in conventional (intensive) and non-conventional (extensive). The most commonly used reclamation technologies are (de Koning *et al.*, 2006, Salgot *et al.*, 2002):

- Pre-treatments:
    - Physical: sand filters and membranes.
    - Physicochemical: dissolved air-flotation, coagulation, flocculation.
    - Physical and biological: infiltration-percolation, wetlands, MAR.
- Disinfection:
    - Physical: ultrafiltration, reverse osmosis, UV radiation.
    - Chemical: chlorination, chloramination, ozonation.
    - Biological: maturation lagooning, constructed wetlands.

It is also important to consider that, apart from the specific reclamation technologies; selected secondary treatments can achieve a good effluent quality, enough to reuse the reclaimed water, as can be the membrane bioreactors. MAR can also be used as a reclamation treatment, and can be integrated in the whole treatment train for the reclaimed water.

2.2.4. Multiple-barrier approach

The multiple-barrier approach is based on the use of more than one barrier to reduce the risks posed by the different hazards in a process, thus making the process more reliable. The strength of this approach is that a failure of one barrier may be compensated by effective operation of the remaining barriers, thus minimizing the likelihood of contaminants passing through the entire system and being present in sufficient amounts to cause harm to consumers (WHO, 2011).

The multiple-barrier approach is universally recognised as the foundation for ensuring the production of safe drinking water, and it was posteriorly applied to wastewater treatment and reclamation processes. No single barrier is effective against all conceivable sources of contamination, is effective all the time or constantly functions at maximum efficiency. Robust barriers are those that can handle a relatively wide range of challenges with close to maximum performance and without suffering major failure. Knowing how many barriers are required to address the level of potential contamination in individual systems is important. This requires a thorough understanding of the nature of the challenges and the vulnerabilities of the barriers in place (NHMRC–NRMMC, 2011; NRMMC-EPHC-AHMC, 2006).

In the case of water reuse, each of the treatments performed to the source water is a barrier that reduces the risk, but also other kinds of barriers are important and need be considered, as for instance source protection or end-user restriction barriers.

The multiple-barrier approach is very important in risk management systems, and it has been developed in section 7.3.1.

2.3. Managed Aquifer Recharge (MAR)

An aquifer is an underground reservoir of water contained by rock or unconsolidated materials (gravel, sand, silt or clay), from which groundwater can be extracted. Aquifers are recharged "naturally" or unintentionally by different means, as pointed out in the MAR guidelines (NRMMC-EPHC–NHMRC, 2009):

- Naturally: rain, rivers, streams, lakes, any superficial water body or other aquifers water.
- Unintentional recharge enhancement: clearing of deep rooted vegetation or soil tillage, leakage from water pipes and sewers, irrigation deep seepage, spraying defoliants, infiltration of run-off from impervious areas.
- Unmanaged recharge (for disposal): stormwater drainage wells and sumps, septic tank leach fields, mining and industrial water disposal to sumps, floodplain water harvesting.

In MAR a water source is used to recharge an aquifer under controlled conditions. The aquifer is used to store surplus water for later use, to improve the water quality or for environmental benefit (see section 2.2.2.6 for the purposes of MAR). Then, citing the MAR guidelines (NRMMC-EPHC–NHMRC, 2009): "Managed aquifer recharge is the purposeful recharge of water to aquifers for subsequent recovery or environmental benefit. It is not a method for waste disposal."

2.3.1. The practice: sources of water and types of MAR

Sources of water that can be used to recharge an aquifer can be:

- Rainwater or stormwater.
- Treated wastewater or reclaimed water.
- Surface water, from rivers, streams and lakes.

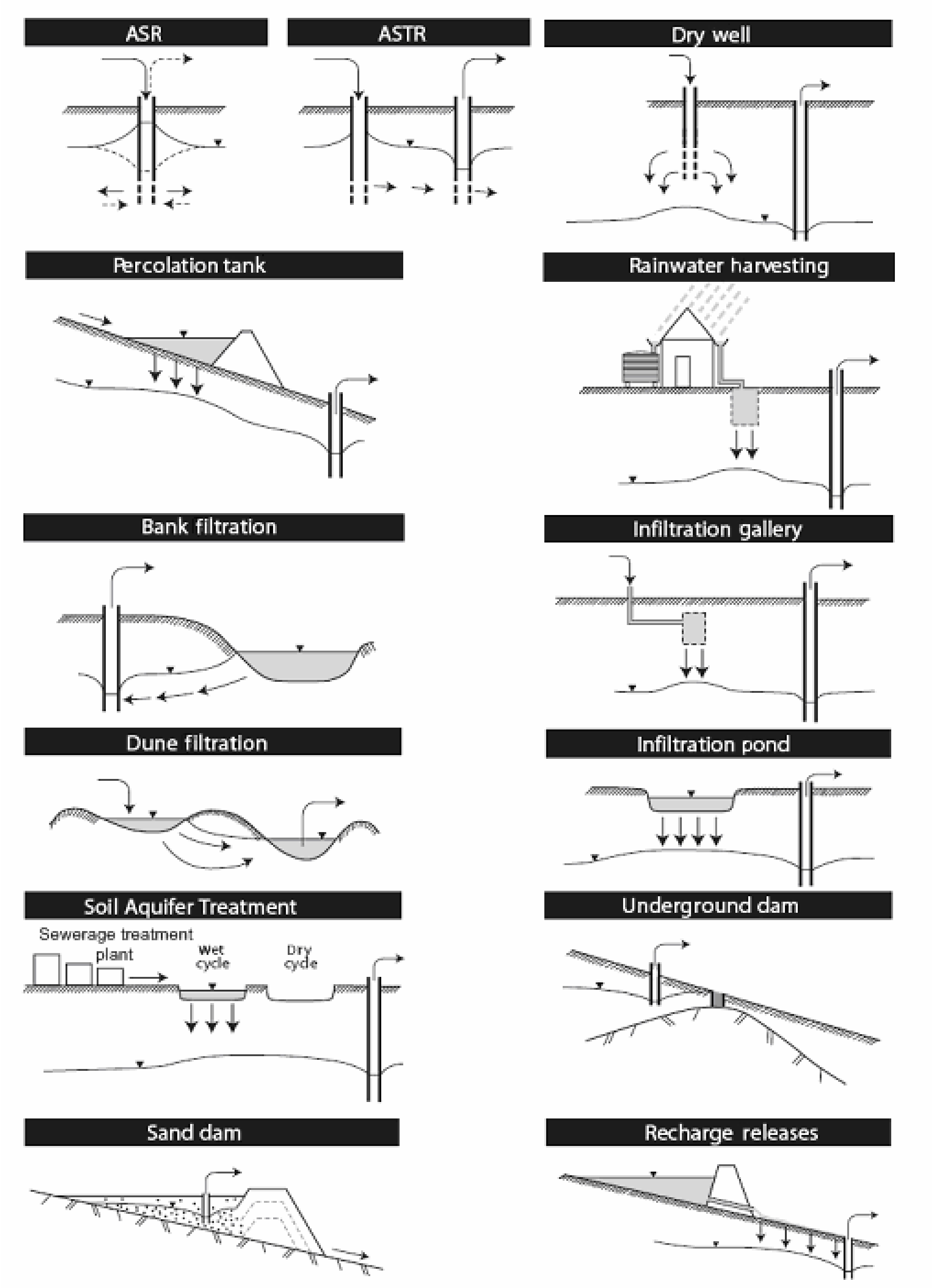
- Groundwater drawn from other aquifers or drawn remotely from the same aquifer.
- Potable water from distribution systems.
- Desalinated water.

MAR can be performed by two means: infiltration/percolation through the soil or direct injection into the aquifer (by constructed wells). Different types of MAR can be differentiated depending on the system used for recharge. The types of MAR, according to Dillon (2005) and NRMMC-EPHC–NHMRC (2009), are summarized below and in Figure 1:

- Aquifer storage and recovery (ASR): injection of water into a well for storage and recovery from the same well. A good example is Bolivar ASR, in Adelaide, South Australia (Ayuso-Gabella *et al.*, 2010; Dillon *et al.*, 2001). Other sites also located in Australia are Perth, Western Australia; Marruwi, Northern Territory (Dillon *et al.*, 2010); Paddocks wetland ASR, in Salisbury, South Australia; ASR into hard rock, Melbourne, Victoria (Dillon, 2009). In the USA ASR is also a common practice for MAR, and many examples are found in the West and East Coasts (Eaton *et al.*, 2009). In Spain examples can be found in Esgueva River, Castilla-León and Llobregat River, Catalonia (Ortuño, 2011; Queralt, 2009).
- Aquifer storage transfer and recovery (ASTR): injection of water into a well for storage and recovery from a different well, generally to provide additional water treatment through aquifer passage. A good example is Parafield Gardens, in Salisbury, South Australia. This case study was part of the RECLAIM WATER project (Dillon *et al.*, 2008). Examples in Spain include Vergel in Alicante, Comunidad Valenciana and Llobregat River, Catalonia (de la Orden, 2009).
- Bank filtration or riverbank filtration (RBF): extraction of groundwater from a well near or under a river or lake to induce infiltration from the surface water body thereby improving and making more consistent the quality of water recovered. By pumping water from the well, a pressure head difference between the river and the aquifer is created and it induces the river water to flow through the riverbed towards the pumping well, that consequently extracts a mixture of groundwater originally present in the aquifer and bank filtrated surface water from the river. The proportions of both kinds of water in the extracted water can vary depending on both extraction rate and river flow (Schmidt *et al.*, 2003). Sabadell, which is the site object of this work, is a good example in Spain, and it was also part of the RECLAIM WATER project. Also in Spain, the Llobregat River is an example of RBF (Ortuño, 2011; Queralt, 2009). Another well-known case study is found in Berlin, Germany, for the lake Tegel (Hoffmann and Gunkel, 2011), which supplies drinking water to the city.
- Dune filtration: infiltration of water from ponds constructed in dunes and extraction from wells or ponds at lower elevation for water quality improvement and to balance supply and demand. A case study from the RECLAIM WATER project is Wulpen/Torreele, in Belgium (Dillon *et al.*, 2008). Examples are also found in the coast of The Netherlands, e.g. Monster, Katwijt, Scheveningen (NRMMC-EPHC–NHMRC, 2009; Stuyfzand, 2009).
- Infiltration galleries are geotechnically-stabilised buried trenches (e.g. with polythene cells), or slotted pipes in permeable media. They allow infiltration through the unsaturated zone to an unconfined aquifer. An example is at Floreat Park, Western Australia, Australia (NRMMC-EPHC–NHMRC, 2009). In Spain, an example is found in the Guadalquivir River (de la Orden, 2009).
- Infiltration ponds: ponds constructed usually off-stream where surface water is diverted and allowed to infiltrate (generally through an unsaturated zone) to the underlying

unconfined aquifer. One example is found on the Burdekin Delta, Queensland, Australia (NRMMC-EPHC–NHMRC, 2009). In Spain, good examples are the Llobregat River, Catalonia; Oja River, Castilla La Mancha; Guadix and Verde River, Andalucía (de la Orden, 2009).

Figure 1 Schematic of types of MAR depending on the recharge means used (extracted from (NRMMC-EPHC–NHMRC, 2009).



- Percolation tanks and recharge weirs: dams built in ephemeral streams (i.e. stream channels that contain water only after rainfall or snowmelt) to retain water that infiltrates through the bed, increasing storage in unconfined aquifers. The water is extracted down-valley. One example is found in Callide Valley, Queensland, Australia

(NRMMC-EPHC–NHMRC, 2009). In Spain one example is found in Jijona, Comunidad Valenciana (de la Orden, 2009).

- Rainwater harvesting: roof run-off is diverted into a well or a caisson filled with sand or gravel and allowed to percolate to the water-table where it is collected by pumping from a well. Examples are common in Perth, Western Australia (NRMMC-EPHC–NHMRC, 2009).
- Soil aquifer treatment (SAT): treated wastewater is intermittently infiltrated through infiltration ponds to facilitate nutrient and pathogen removal during passage through the unsaturated zone for recovery by wells after a certain residence time in the aquifer. A case study from the RECLAIM WATER project is Shafdan (Dan Region) in Israel (Dillon *et al.*, 2008). Examples in Spain are in Santiuste and Carracillo, Castilla-León (Escalante *et al.*, 2009).
- Sand dams: built in ephemeral stream beds in arid areas on low-permeability lithology, sand dams trap sediment when flow occurs, and following successive floods the sand dam is raised to create an “aquifer” which can be tapped by wells in dry seasons. An example is at Kitui, Kenya (NRMMC-EPHC–NHMRC, 2009).
- Underground dams: in ephemeral streams where basement highly constrict flows, a trench is constructed across the streambed keyed to the basement and backfilled with low permeability material to help retain flood flows in saturated alluvium for stock and domestic use. Examples are found in northeast Brazil (NRMMC-EPHC–NHMRC, 2009).
- Vadose zone wells or dry wells: they are typically shallow wells in areas with deep water tables. They allow infiltration of high-quality water through the unsaturated zone to the unconfined aquifer at depth. Examples are found in Phoenix, USA (NRMMC-EPHC–NHMRC, 2009).
- Recharge releases: dams on ephemeral streams are used to retain flood water and uses may include slow release of water into the streambed downstream to match the capacity for infiltration into underlying aquifers, thereby significantly enhancing recharge. An example is Little Para River, South Australia (NRMMC-EPHC–NHMRC, 2009).

2.3.2. Advantages and disadvantages of MAR

One well-known advantage of MAR is that it can be used as a barrier for saline intrusion. In coastal areas, this saline intrusion is developed easily, thus making the aquifer unsuitable as source for potable supply or for other uses where high salt levels are can be a problem. Then, a battery of injection wells can be used to create a hydraulic barrier to control intrusion and reclaimed water can be used for this purpose. This may allow for additional development of inland withdrawals or simply the protection of existing withdrawals.

Aquifers provide a natural mechanism for storage of reclaimed water to ensure a consistent water supply. Irrigation demands of water are often seasonal, requiring either large storage facilities or disposal of the reclaimed water when demands are low. Suitable sites for surface storage facilities may not be available, economically feasible, or environmentally acceptable, and can reduce the land available for crops. Besides, surface storages also have significant evaporation losses, and may allow for algae blooms and creation of odours. MAR overcomes all these problems, as water is stored in the aquifer. However, it must be pointed out that if spreading basins are used, extensive land areas may be needed, which will not be able to be used for crops.

Another question related to MAR is the quality of the water recharged and recovered. MAR can be a double-edged sword in this sense. While in many cases MAR improves the quality of the water recharged, especially when recharge is performed by infiltration/percolation systems, sometimes the infiltrated water can worsen its quality while mixing with the aquifer water. This can be one of the purposes of MAR: dilute brackish and/or polluted aquifers, so the recovered water will have worse quality than the recharged water but the aquifer water quality will have been improved, thus giving an ecological value to the recharge. Then, in case the water quality improves during the aquifer storage time, the treatment achieved in the subsurface environment may eliminate the need for costly advanced wastewater treatment processes, which is clearly an advantage. On the other hand, if the aquifer is pristine, the introduction of reclaimed water can endanger its environmental values and pollute it. The possible effect of MAR, either positive or negative, in the aquifer water will need to be evaluated at the very beginning of the project development.

Disadvantages of MAR are the technical and cost requirements for its implementation. Hydrogeological uncertainties, such as transmissivity, faulting, and aquifer geometry may reduce the effectiveness of the recharge project in meeting water supply demand. Not all recharged water may be recoverable due to movement beyond the extraction well capture zone or mixing with poor-quality groundwater. These disadvantages will be very dependent on the kind of MAR that is desired or feasible to be implemented.

2.3.3. The RECLAIM WATER project

The 6th Framework Programme project RECLAIM WATER focused on understanding water recycling via aquifers and quantifying its effects on human health risk (RECLAIM WATER, 2012). The strategic objective of this project was to develop hazard mitigation technologies for water reclamation providing safe and cost effective routes for artificial groundwater recharge. The work assessed different treatment applications in terms of behaviour of key microbial and chemical contaminants. Nine demonstration sites were included in this project (Dillon *et al.*, 2008), which were: Tula Valley, Mexico; Atlantis, South Africa; Wulpen/Torreele, Belgium; Nardò, Italy; Gaobeidian, China; Parafield Gardens, Australia; Dan Region, Israel; and Sabadell, Spain. Newater project, in Singapur, was also included but no experimental work was done for this site in the RECLAIM WATER project framework. Several sampling campaigns were performed in the eight sites at different sampling points, always including as a minimum the source water, the aquifer and the recovered water. A better understanding on MAR practice, problems, development and necessary pre-treatments and post-treatments was gained.

The present work has been developed in the framework of the RECLAIM WATER project, so more information will be given in further sections.

2.3.4. Recovered water reuse

When MAR is performed, water can be recovered after a certain period of time, and can be reused. MAR has to be considered as another treatment or barrier, by which the water quality can be improved, thus reducing the pollutants and pathogens presence. Then, all uses considered in section 2.2.2 can be given to this recovered water. However, it must be considered that the aquifer can also be a source for other pollutants (e.g. heavy metals) or compounds that were not present in the recharged water, so quality of the recovered water must be evaluated and assessed before any reuse purpose.

2.4. Waterborne diseases

Waterborne diseases are caused by ingestion of water that contains enough quantity of a hazardous component to develop the disease. When waterborne diseases are referred to, they are commonly associated to pathogenic microorganisms present in the water, although the presence of pollutants in the water can also trigger a waterborne disease, being cancer the most common example. Then, in the present section we are going to consider both kinds of hazardous components regarding waterborne diseases.

2.4.1. Pathogens

One of the main hazards that pose obstacles for the implementation of water reuse is the dissemination of waterborne diseases. Outbreaks due to waterborne diseases are usually reported for consumption of drinking water or indirect ingestion of polluted water (e.g. aerosols ingested during a shower). Some of the most well-known waterborne disease outbreaks were reported in North America, being the most famous ones caused by *Cryptosporidium parvum* in USA (MacKenzie *et al.*, 1994) and *Campylobacter* and enterotoxigenic *E. coli* in Canada (Hrudey *et al.*, 2003). These waterborne disease outbreaks were due to the ingestion of contaminated drinking water. Fewer studies exist reporting the relationship between reclaimed water or treated wastewater reuse and waterborne diseases. One of the most important studies is a review by Blumenthal and Peasey (2002), including examples with treated wastewater, untreated wastewater and excreta use for irrigation and fertilization and the relation with waterborne diseases in the population. In this study, it is indicated that guidelines are necessary not only considering that the waterborne diseases are due to crop consumption but also to contact of irrigators, their families and surrounding populations with the irrigation water.

In Table 2 there is a list of identified waterborne pathogens and their related illnesses. It is important to consider that not all the pathogens enlisted will be found everywhere, as there are cases that are specific of a climatology or region.

It is interesting to analyse the major causes for waterborne disease outbreaks, even though those were caused by consumption of drinking water, not by reclaimed water, because failures during the drinking water process treatment can also happen during wastewater treatment. Another point is to consider that outbreaks caused by waterborne disease or food consumption entail the excretion of pathogens to wastewater, contributing to increase the concentration of pathogens in the source water (when wastewater is the source water for reuse).

Table 2 Waterborne pathogens potentially present in wastewater and their related illnesses (Haas *et al.*, 1999; NHMRC–NRMMC, 2011; Rowe and Abdel-Magid, 1995; WHO, 2011a; Yates and Gerba, 1998).

PATHOGEN	RELATED ILLNESS
Bacteria	
Acinetobacter	Nosocomial infections, urinary tract infections, pneumonia, bacteraemia, secondary meningitis, wound infections
Aeromonas	Gastroenteritis, septicaemia, wound infections, respiratory tract infections
Burkholderia pseudomallei	Melioidosis
Campylobacter jejuni, C. coli	Gastroenteritis, Guillain-Barré syndrome
Clostridium perfringens	Gaseous gangrene
E. coli Enterohaemorrhagic (EHEC), of which well-known serotypes are *E. coli* O157:H7 and *E. coli* O111	Gastroenteritis, diarrhoea that ranges from mild and non-bloody to highly bloody, haemolytic uremic syndrome
E. coli Enteroinvasive (EIEC)	Watery and occasionally bloody diarrhoea
E. coli Enteropathogenic (EPEC)	Severe, chronic, non-bloody diarrhoea, vomiting and fever in infants
E. coli Enterotoxigenic (ETEC)	Diarrhoea
Helicobacter pylori	Chronic gastritis
Klebsiella	Invasive infections, pneumonia
Legionella spp.	Legionellosis (Legionnaires' disease and Pontiac

PATHOGEN	RELATED ILLNESS
	fever)
Leptospira interrogans	Leptospirosis
Mycobacterium spp. non-tuberculous	Pulmonary disease, Buruli ulcer, osteomyelitis, septic arthritis
Mycobacterium avium complex	Respiratory illnesses
Plesiomonas shigelloides	Gastroenteritis
Pseudomonas aeruginosa	Dermal, respiratory, ear and urinary infections, folliculitis, septicaemia and meningitis after colonizing damaged sites (wounds, burns, etc.)
Salmonella typhi and *Salmonella paratyphi*	Typhoid fever/enteric fever (sustained fever with or without diarrhoea), gastroenteritis and diarrhoea, bacteraemia or septicaemia
Other salmonellae	Gastroenteritis, salmonellosis
Shigella spp.	Shigellosis (abdominal cramps, fever and watery diarrhoea), bacillary dysentery
Staphylococcus aureus	Gastrointestinal disease (enterocolitis), nosocomial infections (boils, skin sepsis, post-operative wound infections, enteric infections, septicaemia, endocarditis, osteomyelitis and pneumonia)
Tsukamurella	Nosocomial infections (chronic lung infection, necrotizing tenosynovitis with subcutaneous abscesses, cutaneous and bone infections, meningitis and peritonitis)
Vibrio cholerae	Gastroenteritis, diarrhoea, cholera (serotypes O1 and O139), wound infections and bacteraemia
Yersinia enterocolitica	Yersiniosis (acute gastroenteritis with diarrhoea, fever and abdominal pain)
Viruses	
Adenovirus	Gastroenteritis, acute respiratory diseases, pneumonia, pharyngoconjunctival fever, cervicitis, urethritis, haemorrhagic cystitis, epidemic keratoconjunctivitis (shipyard eye), pharyngoconjunctival fever (swimming pool conjunctivitis)
Adenovirus (40 and 41)	Gastroenteritis
Astrovirus	Gastroenteritis, diarrhoea
Calicivirus	Gastroenteritis, diarrhoea
Coxsackievirus	Meningitis
Echovirus	Meningitis
	Mild febrile illness to myocarditis, herpangina, poliomyelitis,meningoencephalitis, hand-footand-mouth disease, neonatal multi-organ failure
Enterovirus (types 68 to 71)	Meningoencephalitis
Hepatitis A	Hepatitis
Hepatitis E	Hepatitis
Noroviruses and Sapoviruses	Gastroenteritis, diarrhoea; dehydration and metabolic acidosis may develop
Poliovirus	Poliomyelitis
Rotavirus	Gastroenteritis

PATHOGEN	RELATED ILLNESS
Small round Virus	Gastroenteritis
Protozoa	
Acanthamoeba spp.	Meningoencephalitis, dermal infection, mental disorders, bronchopneumonia
Balantidium coli	Balantidiasis (dysentery), colitis, diarrhoea
Blastocystis	Diarrhoea
Cryptosporidium parvum	Cryptosporidiosis, diarrhoea
Cyclospora cayetanensis	Diarrhoea
Entamoeba histolytica	Dysentery, colitis, diarrhoea
Giardia intestinalis	Giardiasis, diarrhoea
Microsporidia	Chronic diarrhoea, dehydration
Naegleria fowleri	Amoebic meningoencephalitis
Toxoplasma gondii	Toxoplasmosis (neurological disorders, pneumonia; during pregnancy can cause spontaneous abortion, stillbirth or fetal abnormality)
Helminths	
Ancylostoma duodenale	Anaemia, gastroenteritis
Ascaris lumbricoides	Ascariasis (gastroenteritis), Loeffler's syndrome
Dracunculus medinensis	Dracunculiasis
Fasciola spp.	Fasciolasis (that can entail liver enlargement, obstructive jaundice, cholelithiasis, hepatic lesions, fibrosis and chronic inflammation of the bile ducts).
Schistosoma spp.	Schistosomiasis (Katayama fever), bloody diarrhoea, bilharzial dysentery
Taenia spp	Taeniasis
Trichuris trichiura	Tricuriosis

2.4.2. Chemical compounds

In terms of waterborne diseases, the short-term risk usually considers only the microbiological water quality that it is, in fact, the most important risk when recycling water (Toze, 2006). This is because using the treated wastewater for potable purposes is not an extended practice, and in many countries it is still prohibited. However, it must be also considered that the long-term health risks are usually associated to chemical compounds that can be potentially toxic. Industry, agricultural production and homes are sources of numerous chemical compounds that might pose a risk for the human health if water is recycled, especially for those uses in which there might be direct contact or accidental ingestion (US EPA, 2012; WHO, 2011a). Chemical compounds can have an adverse effect much more important in the environment than in the human health depending on the type and concentrations found (Alcalde, 2012; NRMMC-EPHC-AHMC, 2006; US EPA, 2012). Groups of chemical compounds and their main effects are given below:

- Organic compounds that can be easily degraded (e.g. proteins, carbohydrates…): oxygen concentration decrease in aquatic ecosystems, gaseous compounds generation (odour).
- Organic compounds difficult to be degraded (e.g. grease, phenols, cellulose, lignin…): high COD/BOD, oxygen concentration decrease in aquatic ecosystems.

- Nutrients (nitrogen, phosphorus and carbon): eutrophication, algae blooms, oxygen concentration decrease in aquatic ecosystems, plant toxicity, biodiversity loss.
- Salinity related compounds (e.g. sodium, chloride, sulphate…): salinity (harmful for crops and soils).
- Inorganic compounds (micronutrients: e.g. boron, calcium, copper…): plant toxicity.
- Heavy metals (e.g. cadmium, chromium, lead..): flora and fauna toxicity (by accumulation).
- Micropollutants (e.g. pesticides, PhACs, EDC…): carcinogenic and teratogenic effects, bioaccumulation, flora and fauna toxicity (by accumulation).

In the recent years, there has been a growing interest in the detection of micropollutants in wastewater and reclaimed water. The concept of "micropollutants" encloses organic and inorganic compounds that can be harmful for the human health and are detected in very low concentrations. In the case of inorganic compounds, it is usually heavy metals what are considered/called micropollutants, as they are those that can be more harmful for the human health and that are usually found in very low concentrations. For organic compounds, a wide variety of them are referred: pharmaceutically active compounds, personal care products, endocrine disruptors, disinfection by-products, pesticides, volatile organic compounds and many other. All of them can be harmful for the human health, and can cause waterborne diseases. In addition, many of these compounds are considered to be carcinogenic. Detailed compilations for micropollutants can be found in the Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011), the Australian Guidelines for Water Recycling Phase 1 (NRMMC–EPHC–AHMC, 2006), the Australian Guidelines for Water Recycling Phase 2 (NRMMC–EPHC–AHMC, 2008), the WHO Drinking Water Guidelines (DWG) (WHO, 2011a) and the New Zealand Drinking Water Guidelines (NZ DWG) (NZMOH, 2005).

2.5. Risk assessment

2.5.1. Basic principles

NRC (1983) defines risk assessment as follows: "We use risk assessment to mean the characterization of the potential adverse health effects on human under given exposures to environmental hazards. Risk assessment include several elements: description of the potential health effects based on an evaluation of results of epidemiologic, clinical, toxicological, and environmental research; extrapolation from those results to predict the type and estimate the extent of health effects on human under given conditions of exposure; judgments as to the number and characteristics of persons exposed at various intensities and durations; and summary judgments on the existence and overall magnitude of the public-health problem. Risk assessment also includes characterization of the uncertainties inherent in the process of inferring risk".

In a holistic approach, Haimes (2004) states three risk assessment questions:

- What can go wrong?
- What is the likelihood that it would go wrong?
- What are the consequences?

The same author quotes the criteria for "good" risk analysis:

- Comprehensive.
- Adherent to evidence.

- Logically sound.
- Practical.
- Open to evaluation.
- Based on explicit assumptions and premises.
- Compatible with institutions.
- Conducive to learning.
- Attuned to risk communication.
- Innovative.

More in relation with wastewater reclamation and reuse, Asano *et al.* (2007) define risk assessment as "the qualitative or quantitative characterization and estimation of potential adverse health effects associated with exposure of individuals or populations to hazardous materials and situations".

Haimes (2004) and Asano *et al.* (2007) widely developed the four major steps set by NRC (1983), and Haimes (2004) added an "additional" 5th step:

1. Hazard/risk identification: Characterises the inherent adverse effects (toxicity/ carcinogenicity) of an agent, e.g. causes cancer, birth defects, poisoning, etc. Hazard identification establishes whether exposure to a chemical or microbiological agent can cause harm and is generally based on primary data from human epidemiological studies and animal toxicological studies. Once a health hazard has been identified, the remainder of the process encompasses the description of the properties of the hazardous agent, and the identification of both acute and chronic health effects.
2. Dose response assessment and risk modelling, quantification and measurement: Characterises the relationship between the dose of a hazardous agent (i.e. the amount of the substance taken into the body through inhalation, ingestion and dermal contact) and incidence of an adverse effect in the exposed population.
3. Exposure assessment and risk evaluation: Measures or estimates the intensity, frequency and duration of human contact with a hazardous agent. To determine exposure, it is necessary to combine an estimation of the hazardous agent concentration with demographic or behavioural descriptions of the exposed population.
4. Risk characterization and risk acceptance and avoidance: Provides an indication of the incidence of the health effect under the conditions of exposure described in the exposure assessment and the identified dose-response relationship.
5. Risk management: At this point, it is necessary to define the Critical Control Points (CCP) that are to be prevented and monitored in the system. Usually, the risk management is separated from the assessment, but in fact, it is part of it (NHMRC–NRMMC, 2011; NRMMC–EPHC–AHMC, 2006).

2.5.2. Deterministic versus probabilistic risk assessments

The risk assessment can be undertaken in either a deterministic or probabilistic way. In a deterministic risk assessment, all inputs in the model are point estimates, e.g. mean value or 95th percentile. However, the data can present a wide range of values that are not taken into consideration when dealing with a point estimate. This leads to a high uncertainty in the output result, which will also be a point estimate. To reduce this uncertainty associated with the use of point estimates, a probabilistic risk assessment must be undertaken.

Nowadays, probabilistic risk assessments are more and more used, although its use entails difficulties: it is more complex and requires more data and to adjust the data to a distribution. In any case, a probabilistic approach is preferred when performing microbial risk assessments. For chemical risk assessments it can also be used.

2.5.3. QMRA

Quantitative microbial risk assessment (QMRA) is the application of principles of risk assessment to estimate the consequences from a planned or actual exposure to infectious microorganisms. QMRA aims at numerically quantifying health risks, usually as the probability of infection or illness to consumers, according to Haas *et al.* (1999). In performing a QMRA, the best available information to understand the potential effects from a microbial exposure needs to be used. Usually the information available is incomplete, thus it is necessary to evaluate the potential error involved in the QMRA. The results of the risk assessment will guide the next steps to mitigate and control the risks.

Broadly, QMRA has previously been adapted to assess water supply system performance and integrity (e.g. Crabtree *et al.*, 1997; Glicker and Edwards, 1991; Teunis *et al.*, 1997), theoretically estimate target levels of pathogens in the final treated water product that would constitute an acceptably low health risk and to establish treatment guidelines (e.g. Eisenberg *et al.*, 2002; Macler and Regli, 1993; Rose and Gerba, 1991), and as an appropriate tool with which to identify and prioritise research needs in water treatment (e.g. Gale, 2002). QMRA has been widely applied to drinking water treatment, and has a central role in the WHO Guidelines for Drinking-water Quality (WHO, 2011a) and Australian Drinking Water Guidelines (NHMRC–NRMMC, 2004). Later on was applied to water recycling. QMRA is today used to establish standards, guidelines and other recommendations regarding drinking water, water recycling, food processing and consumer health, etc.

QMRA of recycled water schemes requires the quantification of pathogen occurrence in source water and their removal through various treatment barriers. When pathogen occurrence is combined with exposure scenarios and pathogen dose-response relationships, the risk to human health can be estimated.

2.5.4. Risk assessment as part of a whole risk management approach

Risk assessment will only be useful as long as it is integrated in a whole risk management approach. A risk management approach involves identifying and managing risks in a proactive way, rather than simply reacting when problems arise. In applying this approach to water recycling, the first step is to develop a risk assessment, from which to identify those hazards that represent significant risks for the proposed end use. The next step is to identify preventive measures to control such hazards, and to establish monitoring programs, to ensure that the preventive measures operate effectively. The final step is to verify that the management system consistently provides recycled water of a quality that is fit for the intended use (NRMMC–EPHC–AHMC, 2006).

Risk management systems are seen as the most effective way to assure the appropriate quality of drinking water or recycled water. Risk management has been adopted by the food industry for many years, through application of the Hazard Analysis and Critical Control Point (HACCP) system (CAC, 2003). The HACCP concept was developed in the US in 1959 by the Pillsbury Company to improve food safety for manned space missions by the National Aeronautics and Space Administration (NASA). Since the 1980s the HACCP system has been widely adopted by food and beverage industries worldwide (Jayaratne, 2008). HACCP has been applied to the drinking water (Havelaar, 1994; Jayaratne, 2008; Mullenger *et al.*, 2002) and to the recycled water schemes too (Dewettinck *et al.*, 2001; Swierc *et al.*, 2005; Westrell *et al.*, 2004). The development of risk management systems for water quality is covered in various guidelines, principally endorsed by WHO, Australia, New Zealand, Canada and USA Governments. All approaches incorporate HACCP principles and are consistent with other established systems such as ISO 9001. In all guidelines a risk management framework is described, following similar steps than in the HACCP system. The risk management framework is used to develop a risk management plan that describes the nature of a recycled water scheme and how it should be operated and managed.

2.6. Guidelines and regulations

While there are no provisions in European Union (EU) wide legislation focused explicitly on risk assessment and risk management for MAR, there are many pieces of legislation and policy affecting them. Key regulatory elements having a strong impact on risk assessment and risk management for MAR include the Water Framework Directive (WFD) 2000/60/EC, the Ground Water Daughter Directive 2006/18/EC, the Environmental Impact Assessment Directive 85/337/EEC, the Nitrate Directive 91/676/EEC, and, for water intended for human consumption, the Drinking Water Directive 98/83/EC. Among them, the Water Framework Directive (European Union, 2000) reinforces the well-established requirement of taking into account the precautionary principle, relying in particular on the determination of any potentially adverse effects of the reclaimed water and on a scientific assessment of the risk. It recognises that preventive measures or treatment shall have to be employed in each case consistent with the perceived level of risk. Whilst specifying preventive measures to be employed, the WFD consents also case-by-case assessment where field data or model ecosystems would allow more precise privative measures to be calculated and applied (Page *et al.*, 2012).

Although some MAR schemes are under way in Spain, with experience being gained through pilot studies, a specific regulation is still lacking in the country. Every MAR scheme is regarded as a different case, and different authorisations are required, depending on the environmental matrices involved. In most of the cases, MAR is considered as a treated wastewater reuse case, thus it has to attain the Royal Decree concerning water reuse (R. D. 1620/2007 of 7th December 2007; BOE, 2007b). This Royal Decree defines the quality that the reclaimed water must have depending on its final reuse purpose, considering MAR as one of them.

WHO first set guidelines for the safe use of treated wastewater in agriculture in 1973, building upon the standards for reuse set in the State of California in 1968. These were based on the wastewater quality that could be achieved using the treatment technologies available at the time. In the 1970's and early 1980's, more literature became available on epidemiological and microbiological studies of water reuse. WHO then revised its guidelines for wastewater and excreta use in agriculture, based particularly on the epidemiological evidence in these reviews (Blumenthal and Peasey, 2002). The last version of the guidelines for the safe use of wastewater, excreta and greywater is from 2006, and the guidelines were divided in 4 volumes, devoted to different topics: Volume I, Policy and regulatory aspects (WHO, 2006); Volume II, Wastewater use in agriculture (WHO, 2006b); Volume III, Wastewater and excreta use in aquaculture (WHO, 2006c); and Volume IV, Excreta and greywater use in agriculture (WHO, 2006d). As it can be observed, WHO puts a great emphasis on the reuse for agricultural purposes, while other uses are not considered. USA guidelines for reuse (US EPA, 2012) and Australian Guidelines for Water Recycling (NHMRC–EPHC–AHMC, 2006) consider other possible uses for treated wastewater reuse.

The Australian Guidelines for Water Recycling (Phase 2): Managed Aquifer Recharge (called the MAR guidelines) is the foundational document which describes the approach adopted to risk assessment and management for MAR in Australia. The MAR guidelines focus on the protection of aquifers and the quality of recovered water in MAR projects, as well as assessing the risks associated. Where MAR is part of water recycling schemes, the MAR guidelines should be used in conjunction with the Australian Guidelines for Water Recycling (Phase 1) (NHMRC–

EPHC–AHMC, 2006). If recovered water is intended for use as a drinking water supply, then Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies (NRMMC–EPHC–NHMRC, 2008) should also be used.

3. OBJECTIVES

The present work was developed in the framework of the RECLAIM WATER project and supported by it. RECLAIM WATER was funded by the 6th Framework Programme from the European Commission, under the Priority "Global Change and Ecosystems" (European Union, 2006). This project was devoted to provide effective technologies to monitor and mitigate emerging risks posed by chemical contaminants and pathogens in reclaimed wastewater and other sources of water used for MAR. The necessary data basis were generated from a set of case studies, being one of them located in Sabadell, named "RISMAR" in the present work. One of the sub-objectives of the project was:

> "…directly relate the knowledge obtained on new treatment processes and contaminant behaviour to the question of risk associated to the indicated use. The risk studies cover water intake, treatment, storage and distribution steps, analytical tools, monitoring and control systems, and operational procedures as well as communication procedures. A coherent application of these elements in a number of case studies, that cover important reuse practices, will result in recommendations all the way down to the end-user level, where risk management has to be practiced on a day-to-day basis."

Risk assessment and risk management activities were coordinated by the Hydrology Group from the Soil Science Unit in the Faculty of Pharmacy of the University of Barcelona, which was a partner involved and contracted in the RECLAIM WATER project. Then, one of the main activities undertaken by the Hydrology Group in the framework of the RECLAIM WATER project was to gather information, monitor and evaluate the Recycled water and Managed Aquifer Recharge system based on the Ripoll River in Sabadell (RISMAR scheme) from a risk assessment and management point of view. Thanks to the RECLAIM WATER project a better understanding of the riverbed filtration and recycled water treatment process in place at RISMAR scheme has been gained. The knowledge generated has been reported in the present work and summarized in several publications (see publications list, section 1).

Developing a risk assessment and a risk management system in a MAR scheme is a challenge that needs to be undertaken under different perspectives and adopting a variety of measures. The necessity of reliable indicators in order to validate the system, as well as a set of analyses for operation and verification monitoring had to be adapted. A probabilistic quantitative risk assessment can also aid in the development of the risk management system, reducing the amount of analyses to be performed and also gaining a strong knowledge on the recycled water scheme.

The objectives of the present PhD are:

1. Evaluate the risk associated to the recycled water scheme including MAR. RISMAR is a RBF system, based on the Ripoll River, which crosses Sabadell municipality. Sub-objectives of this risk assessment are:
    a. Assess the suitability of the treatment train in place at RISMAR scheme for the different uses of the recycled water regarding all the hazards and end points considered.
    b. Identify those hazards that still pose a risk after the whole treatment process is applied and that need to be addressed in a risk management plan and/or be further investigated.
2. Application of a probabilistic quantitative microbial risk assessment (QMRA) to the recycled water scheme including MAR, in order to better understand the risks posed by pathogens in the system. Sub-objectives for the QMRA are:

   a. Assess the suitability of the treatment train in place at RISMAR scheme for the different uses of the recycled water regarding hazardous agents (pathogenic microorganisms).
   b. Compare the risk reduction by the treatment train applied.
   c. Assess the suitability of the RBF and subsurface treatment as an extra barrier to reduce the risks in the recycled water scheme.
   d. Assess the efficacy of the other treatments considering the pathogens and indicators data available.

3. Develop a risk management plan for the recycled water scheme including MAR. For the risk management plan it is important to properly integrate the results obtained from the risk assessment, that are direct inputs to define monitoring points, targets and critical limits for the hazards, in order to properly control the system.

4. METHODS

4.1. RISMAR scheme as research site

RISMAR scheme is the object of the present work. This site was selected by different reasons:

- It was part of the RECLAIM WATER project.
- Data on its performance were gathered in the framework of the RECLAIM WATER project.
- Its proximity to the Faculty of Pharmacy (where the Hydrology Group is located) in Barcelona, where the PhD was being developed, facilitating the samplings and visits to it.
- It is a MAR site using a low-cost technology, as water infiltrates through a riverbed instead of other high-cost MAR technologies, e.g. injection into the aquifer.
- All the infrastructures were available for the Hydrology Group in order to perform the investigations, thanks to the support given by CASSA and EDS.

A detailed description on the case study is given in sections 5.1 and 5.3.

4.2. Risk assessment

The risk assessments were performed according to procedures recommended in the MAR guidelines (NRMMC–EPHC–NHMRC, 2009) and Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006). Both guidelines recommend undertaking first a maximal risk assessment and then residual risk assessments (pre-commissioning and operational). The maximal risk assessment is performed considering no barriers present in the reclamation system, so as if the source water was directly used without treatments. The residual risk assessments consider the risks after applying the barriers, which can be engineered treatments, catchment protection measures, etc. In our case, by barriers we consider the engineered treatments and the MAR. The residual risk assessments are recommended to be undertaken during the pre-commissioning and the operational stages (see section 5.2).

For each of the hazards addressed, a brief description of their importance, sources and effects is given, previous to the discussion of the results obtained and the risk assessment. Although the description of their importance, sources and effects could have been developed in the present methods section or in the introduction, it has been considered more useful to put it together with the results and the risk assessment as it helps in understanding the evaluation.

For statistical data treatment and representation purposes, those values below the limit of detection (LOD) were treated and included as the LOD, thus being a very conservative approach. In the Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011) it is recommended to treat the values below the LOD dividing the actual LOD by 2, and this approach is already considered to be a worst-case method. Here we have decided to use directly the LOD, which is also a worst-case method.

In assessing the risk to human health and the environment of using recycled water for different uses, water quality guideline values are needed, in order to compare the water quality data with a set standard. The guideline values used were obtained from different laws and guidelines. First and most important is to fulfil the Spanish regulations in force for recycled water and other kinds of water. The laws that need to be fulfilled and evaluated are the following ones:

- Royal Decree 1620/2007 (Spanish Official Bulletin, 2007): this Royal Decree regulates the minimum quality required for the recycled water considering the different uses that are regulated and permitted in Spain. In Table 4 a summary of the different uses and main requirements for the recycled water quality according to this Royal Decree is given. This Royal Decree is a law that came into force at the end of 2007, and that at RISMAR scheme should be fulfilled for those uses in place (see section 5.1.3). This Royal Decree constitutes the basis for the risk assessment at RISMAR scheme, but other guidelines have been also considered and used as a reference, for several reasons:

  - For some parameters there are no given reference values in the Royal Decree.
  - In the Royal Decree the use of recycled water as drinking water or bathing water it is not considered.
  - To compare the requirements in place in other countries and guidelines.

- Royal Decree 140/2003 (Spanish Official Bulletin, 2003): this Royal Decree regulates the minimum quality required for drinking water and potable uses. Although this use is not allowed for recycled water and not envisaged at RISMAR scheme, it is necessary to evaluate it. First of all, in case of accidental or deliberate final treated water ingestion. Secondly, in case the drought periods extend, the Spanish or Catalan governments may give especial permits or transitory municipal ordinances to use this water for drinking purposes, and only consider the water as recovered water from a well. This has happened, in fact, with the use of the recycled water as bathing water, as it is explained in the paragraph below.
- Royal Decree 742/2013 (Spanish Official Bulletin, 2013): this Royal Decree regulates the minimum quality required for swimming pools. There exists a law for bathing waters, the Royal Decree 1341/2007, that includes marine and fresh waters but explicitly excludes swimming pools. Using the recycled water as bathing water is not permitted but it was proposed at RISMAR scheme to cope with the water scarcity during drought periods, which would require a specific and temporal permit issued by the Catalan government.

In order to compare with the Spanish legislation, obtain guideline values for those hazardous components not regulated in the Spanish legislation and to have an idea of the requested parameters and guideline values set in other countries, guidelines and recommendations from Australia, the United States Environmental Protection Agency (US EPA) and the World Health Organization (WHO) have been used. Many of the European Directives, which are transposed in the Spanish Royal Decrees, are based on the WHO guidelines. WHO guidelines, in its turn, were developed concurringly with Australian guidelines and US EPA guidelines, so they are rather similar, but not exactly the same. Thus, guidelines from the Australian government that have been used to compare and assess the risk are the following ones:

- Australian and New Zealand Guidelines for Fresh and Marine Water Quality (ANZECC and ARMCANZ, 2000): give reference values for several of the considered water recycling uses and receiving environments. Two chapters of the guidelines have been used:
  - Aquatic ecosystems: this chapter gives reference values for fresh and marine waters, to protect the ecosystems present in those waters. These guidelines have been considered regarding the river and aquifer environmental end points. In developing the risk assessment for these environmental end points not only the guideline values set have been used, but the comparison between the river water before and after the discharges, as well as the comparison of the groundwater not affected by the riverbed filtration system and the one affected has been developed as much as possible. This has been done because these environmental

end points might be polluted before the treated wastewater discharges, thus the guideline value would not be fulfilled in any case.

  - Primary industries irrigation: this chapter gives reference values for crop irrigation, and apply to the crops, trees in the Taulí Park and the soil end points. Guideline values are given for both long-term irrigation (100 years) and short-term irrigation (20 years) considering the effect in the crop and the soil, and in addition, specific reference values are also given for the soil in case it is analysed. These different guideline values aim to minimise the build-up of hazardous compounds in soil and also to prevent the direct toxicity of irrigation water to plants. Thus, the soil is protected as long as the irrigation water quality is within the guidelines (ANZECC and ARMCANZ, 2000).

- Guidelines for Managing Risks in Recreational Water (NHMRC, 2008): in these guidelines reference values for recreational waters in order to protect the human health while developing aquatic activities, and to preserve the water quality and aesthetic characteristics, are given.

- Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011): in these guidelines reference values for drinking water in order to protect the human health are given. These guidelines were developed considering Australia as a target country. However, both the Australian and WHO guidelines were developed in parallel and are in agreement in most of the reference values given. Australian Drinking Water Guidelines are considered for those parameters that do not have a set guidelines value in the WHO Drinking Water Guidelines.

WHO has issued several guidelines and specific documents regarding the water quality and the protection of the human health. While in the Australian guidelines focus is put in the human health and the environment protection as well, WHO guidelines are definitely more focused on the protection of the human health. WHO guidelines that have been used to compare and assess the risk are the following ones:

- WHO Drinking Water Guidelines (WHO, 2011a): in these guidelines reference values for drinking water in order to protect the human health are given. As these guidelines were developed by the WHO, they are not specific of a country. However, both the Australian and WHO guidelines were developed in parallel and are in agreement in most of the reference values given.

- WHO Irrigation Water Guidelines (WHO, 2006b): reference values for the irrigation water quality are given and included in the “Guidelines for the safe use of wastewater, excreta and greywater, volume 2: Wastewater use in agriculture” (WHO, 2006b). Guideline values are intended to protect the human health, when consuming the irrigated crops, and also the crop and the soil. However, these guidelines are more devoted to preserve the human health, proposing protection measures for the irrigators and any person coming into contact with the recycled water or consuming the irrigated produce.

- WHO Recreational Water Guidelines (WHO, 2003a): in these guidelines reference values for recreational waters in order to protect the human health while developing aquatic activities, and to preserve the water quality and aesthetic characteristics, are given. Interestingly, in these guidelines only specific values for enterococci and microcystins are given, and for chemical compounds and any other substances of concern, it is referred to the DWG, using a factor of ten times that stipulated in the DWG as the ingested dose of water is considered to be ten times lower.

The US EPA issued guidelines for water recycling (US EPA, 2012), as well as many other guidelines and documents for other kinds of water. Then, in this case, we will consider the water recycling guidelines and the drinking water primary regulations:

- US EPA Water Recycling Guidelines (US EPA, 2012): these water recycling guidelines are very complete, including all uses in place and considered for RISMAR scheme, and they also include regulations in different US states for recycled water.
- US EPA National Primary Drinking Water Regulations (US EPA, 2009): these regulations give guideline values for drinking water, in order to protect the human health. The document is a summary table for quick use.

4.3. Quantitative Microbial Risk Assessment (QMRA) methodology

Epidemiological research is very important for risk assessment, as provide risk estimates and input data for dose-response models. However, in order to predict future risks when designing a water reuse scheme or when evaluating a water reuse scheme in place, epidemiology cannot be used. Besides, epidemiological tools are often not sensitive enough to detect a few cases arising from exposure to pathogens transmitted via the environment (Eisenberg et *al.*, 2002). Quantitative microbial risk assessment (QMRA) can here serve a purpose for estimating infection risks from low exposure to hazardous agents transmitted via the environment and to assess risks in water recycling systems.

Haas *et al.* (1999) define quantitative microbial risk assessment (QMRA) as the application of principles of risk assessment to estimate the consequences from a planned or actual exposure to infectious microorganisms. Risk assessments have also been developed for describing the public health consequences of exposure to pathogens from drinking water, based on its initial use within the food and chemical sectors. Nowadays it has also been widely used to assess risks in other types of water, like recreational water and reclaimed water. QMRA is today applied to establishing standards, guidelines and other recommendations regarding drinking water and consumer health (Bichai and Smeets, 2013; Eisenberg *et al.*, 2002; Kay *et al.*, 2004; Macler and Regli, 1993; Medema, 2007).

The general framework for quantitative microbial risk assessment (QMRA) used is based on the approach described in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) and the WHO guidelines for water reuse (WHO, 2006b).

4.3.1. Deterministic versus probabilistic risk assessments

QMRA can be undertaken at various levels of detail, from a deterministic analysis aiming to characterise, say, worst or best case risk scenarios, to a full scale stochastic analysis. More detail is not always advantageous, but rather the QMRA scope and the perceived risk level of the system should govern what an assessor considers an appropriate level of detail (Petterson *et al.*, 2006).

In a deterministic risk assessment, all inputs in the model are point estimates, e.g. mean value or 95th percentile. However, all inputs in a QMRA model are likely to vary, and they can present a wide range of values that are not taken into consideration when dealing with a point estimate. Understanding the impact of this variability on the end-user risk is important, especially in management terms, as such understanding will aid answering why and how higher risk periods may occur, and provide insight into controlling those effects. The use of point estimates leads to a high uncertainty in the output result, which will be also a point estimate. To reduce this uncertainty associated with the use of point estimates, a probabilistic risk assessment must be undertaken.

The central tool for describing variability is the Probability Density Function (PDF). When a model input is considered to be a variable rather than a constant, the input may be quantified using a PDF, which is the basis for the probabilistic risk assessments. When described by a PDF, the variable may take one of a range of values, each with a known probability of occurrence. Different methods can be used to fit a distribution to data. Frey and Burmaster (1999) describe two equally well-suited methods, maximum likelihood estimation and bootstrap simulation. Maximum likelihood estimation is the method most widely used, and also used in the present work. In addition, this is the method used in the mathematical package @Risk™ (Palisade Corporation, Newfield, NY) for fitting distributions. Maximum likelihood estimation is used for finding the parameter values of a distribution that maximise the probability of obtaining a particular set of data. If several distributions are tested the one with the highest likelihood will accordingly have the best fit (Westrell, 2004).

When adjusting the PDFs for pathogen concentrations, using a lognormal distribution is recommended (NHMRC–NRMMC, 2011; Petterson *et al.*, 2006; Westrell, 2004). However, for some pathogens or depending on the set of data used, other distributions can be fitted that adjust better to the given data. For other inputs, triangular or uniform functions can be used, depending on the amount of data available and how well a distribution can be fit to the data available. When using PDFs to describe the inputs, the final risk result will also be a PDF, and is calculated using a Monte Carlo simulation (Petterson *et al.*, 2006). In Monte Carlo simulations, one value is selected at random for every input PDF, thus creating one possible scenario. This is repeated 10,000 times and gives an output PDF.

4.3.2. General steps to perform a QMRA

Quantitative microbial risk assessment is performed according to the following steps (NRMMC–EPHC–AHMC, 2006; WHO, 2006b):

1. Hazard identification – identification of the pathogens and the associated disease burden on human health; this step also includes consideration of variability in pathogen concentrations.
2. Dose-response – the relationship between the dose of the pathogen and the likelihood of illness.
3. Exposure assessment – determination of the size and nature of the population exposed to the hazard, and the route, volume and duration of exposure.
4. Risk characterisation – integration of data on hazard presence, dose-response and exposure, obtained in the first three steps.

The Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) and the WHO guidelines for water reuse (WHO, 2006b) define a tolerable level of risk as inferior to 10^{-6} DALYs or 1 microDALY (Disability Adjusted Life Years) per person per year (pppy).

4.3.2.1. Hazard identification

There is a large range of known waterborne pathogens representing the different groups; bacteria, viruses, protozoa (unicellular organisms) and helminths (see Table 2). Some, like *Salmonella typhi* or *Vibrio cholerae*, have been known for a long time, while others, like noroviruses and *Escherichia coli* O157, have been discovered quite recently (LeChevallier *et al.*, 1999a,b). Since it is not feasible to assess the potential impact of all waterborne pathogens in a risk assessment, a few are chosen as reference pathogens (NRMMC–EPHC–AHMC, 2006; WHO, 2011a). The choice of reference pathogens in the present work was based on the following criteria/characteristics and on the ones recommended in NRMMC–EPHC–AHMC (2006):

- High occurrence.
- High concentration in water to be recycled.

- High pathogenicity.
- Low removal in treatment.
- Long survival in the environment.

4.3.2.2. Dose-response

Dose-response modelling is the key to microbial risk assessment as it provides a link between exposure dose and the probability of infection (Petterson *et al.*, 2006). Quantitative dose-response models have been developed to estimate the probability of infection based on the average pathogen dose.

Most dose-response models have been based on human feeding trials, i.e. volunteers have been fed with pathogens in different doses and the percentage of subjects seroconverting/excreting the pathogen (or other outcome such as illness) at a certain dose is calculated. In more recent years, information from outbreaks of enteric illness has been used to estimate dose-response parameters. The great advantage of data from a real outbreak is that it demonstrates an actual response to exposure to human pathogens, without the constraints and simplifications necessary for a controlled study; pathogens are native to the system, and those exposed are a true sample from the susceptible population. If well collected, epidemiological data including information such as attack rate (the biostatistical measure of speed of spread in an at risk population) and ingested dose can be an ideal data set (Petterson *et al.*, 2006; Westrell, 2004).

Using the data from human feeding trials or from outbreaks, and by different mathematical methods, dose-response models can be fitted to experimental data (Teunis *et al.*, 1996). The risk of becoming infected depends on two conditional probabilities:

- The probability to ingest the organism (to be exposed to it): this is evaluated in the exposure assessment (see section 4.3.2.3).
- The probability that the organism survives and infects the host once it has been ingested (to be infected considering exposure): this is evaluated in the dose-response assessment.

The environment, the pathogen and the host characteristics play an important role in the probability of infection.

It was previously believed that a threshold number of organisms, or minimum infectious dose, had to be ingested before any infection or adverse effects could occur (Westrell, 2004). In the recent years, latest studies support that infection is theoretically possible from exposure to a single organism, and the use of models based on the 'single-hit' theory of dose-response have increased (Petterson *et al.*, 2006). The assumptions of the single hit model are: that the inoculum is known but for Poisson uncertainty; that organisms act independently, individual probabilities of success do not depend on their numbers (independence); and that any single organism can start infection (Teunis *et al.*, 2002). The probability of infection increases if the pathogen dose increases.

Two models are used to calculate the risk of infection:

- The exponential model is typically used for calculating the risk of infection from protozoan pathognes and is expressed as follows:

  $Pi = 1 - e^{(-rd)}$;

  where

  Pi = probability (risk) of infection

  d = dose or exposure (number of microorganisms)

  r = organism specific parameter describing the probability of infection

This model assumes that all of the ingested organisms have the same probability, r, of causing an infection (Haas *et al.*, 1999).

- The β-distribution model can be used to calculate the probability of infection (Pi) after a single exposure based on dose-response parameters for bacterial and viral pathogens. This model is expressed as follows:

$$Pi = 1 - \left(1 + \frac{d}{\beta}\right)^{-\alpha};$$

where

Pi = probability (risk) of infection

d = dose or exposure (number of microorganisms)

β = median infective dose

α = organism specific parameter describing probability of infection

In the beta-Poisson model, heterogeneity in the organism/host interaction is introduced (Haas *et al.*, 1999).

4.3.2.3. Exposure assessment

To evaluate exposure it is necessary to understand and have information on:

- Routes of exposure.
- Water uses.
- Pathogen concentration in the water.
- Frequency, duration and volumes ingested.

All this information is put together in a so-called “scenario”, where all these inputs need to be evaluated. Usually several scenarios are evaluated, considering different uses of the recycled water, different water intakes, etc.

Exposure assessment typically focuses on the public or consumers to construct or evaluate the different scenarios; for example:

- Consumers of food irrigated with recycled water.
- Users of, and those passing by, areas irrigated with recycled water.
- Swimmers in pools filled in with recycled water.
- Occupiers of homes supplied with recycled water through dual network systems.
- Workers of a laundry service using recycled water.

Exposure assessment uses a wide array of information sources and techniques, to quantify the different inputs and to create the scenario. Most likely, data will not be available for all aspects of the exposure assessment and those data that are available may sometimes be of questionable or unknown quality. In these situations qualified assumptions must be made, based on professional judgments and inferences based on analogy with similar microorganisms or processes.

The main route of exposure to hazardous agents from recycled water is ingestion, including ingestion of droplets or aerosols produced by sprays. Some microorganisms found in recycled water have the potential to cause respiratory illness (e.g. certain types of adenoviruses and enteroviruses) and, for these organisms, inhalation of fine aerosols may be a source of infection.

Dermal exposure to microorganisms is also possible, but there is a lack of evidence of health impacts through this route and it is considered unlikely to cause significant levels of infection or illness in the normal population (Haas *et al.*, 1999; NRMMC–EPHC–AHMC, 2006). Another indirect way to calculate the exposure is to consider the accidental ingestion of soil particles by growers/irrigators or children in the urban parks. This is a typical route of exposure, especially when the soil is dry. Some risk studies have considered this route of exposure instead of the water ingestion (Mara *et al.* 2007).

When considering exposure, intended and unintended uses need to be evaluated. Unintended uses often are related to accidental misuse, for instance cross-connection of water supplies. Deliberate misuses are less frequent, but may happen. An example could be a grower that decides to drink recycled water in the field, as he is thirsty and no other kind of water is available at the moment. Both deliberate and accidental misuse can be reduced by educating stakeholders (irrigators, plumbers, factory workers, etc.), implementing good reuse practices and by managing processes such as auditing.

Pathogen concentration in the recycled water can be directly measured in it, although it is more difficult than in the untreated wastewater as it is always very low and there is a lack of suitable analytical methods. Besides, variations with time can be potentially large. Another possibility is to use literature data, as there are studies reporting the concentration of the different pathogens in treated waters. However, the treatment train applied might not be the same and approximations can be erroneous.

To solve this, QMRA studies regularly start from the occurrence of the pathogen in the raw water and calculate the concentration in drinking water or recycled water considering the removal or inactivation during treatment (Page *et al.*, 2010; Petterson *et al.*, 2006; Signor, 2007; Teunis *et al.*, 1997). The pathogens concentration in the raw water is regularly easy to measure, as long as the raw water is not “extremely clean”, which would make the measurement difficult due to their too low concentration. For untreated wastewater, sometimes the amount of contaminants present in it may interfere with the pathogens quantification. To overcome this, literature data can also be used, as many studies report the concentration of different pathogens in wastewater. In the same line, another approach is to calculate the concentration of pathogens in wastewater from epidemiological data, the excretion of the pathogens from an infected host and the dilution in wastewater (Westrell, 2004). Another possibility is to use indicator organisms. For these organisms is easier to measure their concentrations, and ratios between indicators and pathogens can be used. Their concentration and reduction are often used as surrogate values for pathogens. When the pathogen concentration in the raw water has been determined, then it is necessary to calculate its removal through the different barriers. Regularly, the decimal reduction or $\log_{10}$ removal is calculated, following a simple formula:

$$Log_{10}removal = Log_{10}(C_{in}) - Log_{10}(C_{out})\ ;$$

where

C_{in}: pathogen or indicator concentration in the incoming water

C_{out}: pathogen or indicator concentration in the outgoing water

Depending on the treatment train applied, pathogens concentrations can be measured, although methodological problems are the same as the ones pointed out above. Again, literature data can be used, as well as ratios between indicators and pathogens.

4.3.2.4. Risk characterization

Finally, the risk is characterized accounting for the different pathogens selected in the hazard analysis, the dose-response curves for the different pathogens and the different routes of exposure. During the risk characterization, the risk of infection given exposure to the water or the risk of developing a disease given infection are calculated, in order to have a final risk result.

Infection has been defined as a situation in which the pathogen, after ingestion and surviving all host barriers, actively grows at its target site. Infection may or may not result in illness, as asymptomatic infection can be common for some pathogens (Petterson *et al.*, 2006), but initial work developed in QMRA ended up in the risk of infection probability. In fact, the risk of infection is still the endpoint of many risk assessment studies. US EPA guideline value for the probability of infection acceptable due to drinking water was set to 10^{-4} or a microbial risk of less than 1 infection per 10,000 people per year (Macler and Regli, 1993). The probability of infection can be estimated as the product of the exposure to the water and the probability that exposure to one organism would result in infection (the latter calculated thanks to the dose-response). However, in order to posteriorly calculate DALYs, it is necessary to have an annual probability of infection. Then, the probability of infection per day (P_{id}) is then transformed into a probability of infection per year (P_{iy}), considering a certain number of exposures per year (n) and using the following formula:

$$P_{iy} = 1 - (1 - P_{id})^n$$

In doing so, it is assumed that different exposure events are independent, in that no protective immunity is built up. This is a worst case consideration, as it is well-known that protective immunity can be developed after one or several exposures to a certain pathogen (Westrell, 2004).

As it has been pointed out before, infection is necessary to cause disease, however not all infections will result in the development of a disease. While asymptomatic infections may be important for disease transmission, they do not in themselves contribute to the disease burden on a community. In many QMRA the risk of becoming infected with a specific pathogen after a certain exposure is calculated, however the outcome of these infections is seldom addressed in terms of illness or fatalities. Evaluating the disease burden requires consideration of illness outcomes including the likelihood, severity and duration (Petterson *et al.*, 2006; Westrell, 2004). Then, the use of a health index is recommended. Several health indices exist (McAlearny *et al.*, 1999), among them the Disability Adjusted Life Years (DALY), which is the one recommended in WHO (2006) and NRMMC–EPHC–AHMC (2006).

DALYs have been used extensively by agencies such as the World Health Organization (WHO) to assess disease burdens and to identify intervention priorities associated with a broad range of environmental hazards (WHO, 2011a). DALYs are the sum of life years lost to premature mortality and years lived with disability adjusted for severity (Murray and Lopez, 1997). Then, DALYs conceptually do account for the likelihood of infection and different sequelae and provide means to translate a calculated infection risk into a disease burden estimate. One DALY per million people a year roughly equates to one cancer death per 100000 in a 70 year lifetime (a benchmark often used in chemical risk assessments) (WHO, 2011a). The DALY is calculated as the product of the probability of each illness outcome with a severity factor and the duration (years). In practice, disease burdens per case are used to calculate DALYs. In the work of Havelaar and Melse (2003) a detailed explanation of the calculation of the disease burden per case is given, as well as data on ratios of disease/infection for each pathogen. The advantage of using DALYs over an infection risk end point is that it not only reflects the effects of acute end-points (e.g. diarrhoeal illness) but also the likelihood and severity of more serious disease outcomes (e.g. Guillain-Barré syndrome associated with *Campylobacter*). Besides, DALYs allow comparisons to be made between different health outcomes and also quantification of non-fatal outcomes.

The Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) and the WHO guidelines for water reuse (WHO, 2006b) define a tolerable level of risk as inferior to 10^{-6} DALYs or 1 microDALY per person per year (pppy).

4.3.3. Sensitivity analysis

Often many of the input variables in a QMRA have large statistical variability and uncertainties, which may have a strong effect in the risk outputs of the model. With sensitivity analysis the effects of the input variables on the output risk can be assessed (Frey and Patil, 2002; Zwietering and van Gerwen, 2000). It can therefore be a valuable tool in quantitative risk assessment to:

- Evaluate the events/phenomena guiding the main risks.
- Evaluate the variables that mainly determine the inaccuracy (or spread) in the risk estimate.
- Identify where most effort should be placed in reducing uncertainties.

In our case, which involves the evaluation of a recycled water scheme performance through riverbed filtration, the sensitivity analysis can be used to compare the different treatments applied and their effect in the final risk result, as well as understanding the importance of the riverbed filtration and aquifer/subsurface treatment for reducing the human risks.

The sensitivity analysis procedures used were based on methods described by Frey and Patil (2002), Vose (1996) and Zwietering and van Gerwen (2000). The final risk result for each pathogen and scenario needs to be initially calculated performing Monte Carlo simulations, in the way explained in 4.3.1. Then, for the sensitivity analysis, the QMRA input parameters are assessed one by one by performing Monte Carlo simulations, one at a time, with the value of a parameter of interest held at its modal (or median for uniform PDFs) or at zero values, while leaving all other transformation process model and dose-response function parameters unchanged. Other sensitivity analyses are done increasing the input variables by a certain set percentage (e.g. what would happen if the input pathogen concentration increased by a 25%). The change in the risk output is then taken as an indicator of the sensitivity of that QMRA parameter evaluated to the variability in the input data.

In order to evaluate the change in the risk output, the result obtained removing the factor/treatment, holding it at its modal or increasing/decreasing it by a certain percentage, is compared with the result obtained in the initial risk characterization. This comparison is performed by means of calculating the factor sensitivity (FS) for each barrier. The FS is calculated using the worst-case sensitivity calculation (Zwietering and van Gerwen, 2000), by dividing the new median (50th percentile) risk estimate by the initial median risk estimate with a $\log_{10}$ transformation:

$$FS = \log_{10} (\text{new median risk} / \text{initial median risk})$$

The FS can be also calculated with other statistics, like the mean and the 95th percentile, if it is deemed necessary.

High FS values indicate high sensitivity to variations, and show that changes of factors in process steps have profound effects on the final risk result. For a first analysis every effect smaller than a factor of 10 (FS = 1) can be neglected, in order to search for the factors mainly influencing risks (Zwietering and van Gerwen, 2000). Then, the higher the FS values the larger is the effect of the selected barrier on the overall risk, with a value of 1.0 indicating a tenfold increase in risk. Then, the higher the FS values the more important is the barrier in order to reduce the risks along the treatment train.

4.4. Risk Quotients (RQs) for micropollutants

In order to perform a better risk assessment regarding the micropollutants, the approach selected in the present work is based on the US EPA guidelines for chemical risk assessment (US EPA, 1987, 1998, 2002), also adopted by the Australian Guidelines for Water Recycling phase 2: Augmentation of Drinking Water Supplies (NRMMC-EPHC-NHMRC, 2008). The methodology is based on comparing the amount of a certain chemical compound with a reference value or daily dose intake reported within the US EPA guidelines (US EPA, 1987, 1998, 2002), WHO drinking water guidelines (WHO, 2011a) or other sources of data.

One way of comparing the measured micropollutants concentrations to a guideline value is with risk quotients (RQs). The risk quotients (RQ) method is the most widely used method of assessing risk from trace organic chemicals, and it consists on a ratio between the measured micropollutant concentrations to a guideline value. If the ratio is higher than one, it indicates that the micropollutant can pose a risk for the human health. Health values are concentrations below which no adverse health effects are expected if the water is consumed over a lifetime. If health values (guideline values) are available in any source of information, those are used. In case they are not available, then they have to be calculated. The health values are calculated assuming an average daily intake of 2 litres of water for an individual with a 70kg body weight over 70 years of water consumption. All values were calculated using the equations used in the Australian Guidelines for Water Recycling phase 2: Augmentation of Drinking Water Supplies (NRMMC-EPHC-NHMRC, 2008).

4.5. Risk management: the Guidelines frameworks

Risk management is being widely implemented and adopted in many different organizations, and nowadays is being implemented in the water sector. Risk management systems are seen as the most effective way to assure the appropriate quality of drinking water or recycled water.

Many methodologies and systems can be followed to develop and apply a Risk Management plan. Some well-known methodologies are Hazard Assessment and Critical Control Points (HACCP), ISO 9001 and Water Safety Plans (WHO, 2011a).

The HACCP tool addresses in a logical, ordered and preventive way the identification and evaluation of hazards associated to all steps in the reuse of reclaimed water, its control and the identification of the points where the control is to be critical from different points of view (Ayuso-Gabella *et al.*, 2007). The HACCP system was originally designed to assure food safety in the food industry, but started to be more and more employed in the water industry. The key principles underlying the HACCP approach are adjusted within the WHO water safety plans. The WHO also suggests that a common risk management approach should be applied to drinking water, recycled water and recreational water. When applying HACCP to water management, it fails in areas such as commitment, stakeholder involvement, emergency response, employee training, community consultation, and research and development (NHMRC–NRMMC, 2011).

ISO 9001 provides a generic framework that specifies requirements for quality management systems to address customer satisfaction by assuring a consistent end product. The standard puts emphasis on continuous improvement; it adopts a process model approach that sets out the responsibilities, processes and resources needed to achieve specified objectives with respect to quality (NHMRC–NRMMC, 2011). When applying ISO 9001 to water quality management, it fails to answer specific requirements of water quality management: preventive requirements of system analysis, hazard identification and control, and risk assessment, which are all critical for effective management of water quality.

The Water Safety Plans approach was developed by the WHO to organize and systematize a long history of management practices applied to drinking-water and to ensure the applicability of these practices to the management of drinking-water quality. They represent an evolution of the concept of sanitary surveys and vulnerability assessments that include and encompass the whole of the water supply system and its operation. The Water Safety Plans approach draws on many of the principles and concepts from other risk management approaches, in particular the multiple-barrier approach and HACCP (WHO, 2011a).

Taking as a basis the principles set in HACCP and ISO 9001, the Australian government developed a series of guidelines, focused in drinking water, water reuse, MAR, etc. In all these guidelines, a framework for risk management is given, and the elements of the HACCP and ISO 9001, plus few more elements are given, for a total of twelve elements. In addition, in the different guidelines the hazards related to the specific kind of water are detailed and discussed. Then, as these guidelines are in general more detailed and well adapted to the water discipline, they have been used for developing the risk management. Specifically, the MAR guidelines (NRMMC–EPHC–NHMRC, 2009) and the Australian Guidelines for Water Recycling Phase 1 (NRMMC–EPHC–AHMC, 2006) have been used.

4.6. RISMAR scheme analyses methodology

4.6.1. Analyses performed at the Hydrology group laboratory

Analyses performed at the Hydrology Laboratory included basic wastewater parameters, nutrients, microbiological indicators and salinity related compounds (anions). For other parameters, the samples were treated at the Hydrology Laboratory and measured in external laboratories pertaining to the University of Barcelona. Other specific analyses (pathogens, antibiotic resistance genes and micropollutants) are described in following sections.

In Table 3 there is a summary of the methods used for the analyses and if they were analysed at the Hydrology Group laboratory or in external laboratories.

Table 3 Methods used for the analyses performed at the Hydrology Laboratory.

Parameter	Method used	Laboratory measurement
Suspended solids	Total suspended solids dried at 105ºC APHA (2005) method 2540 D	Hydrology Group laboratory
Alkalinity	Titration method APHA (2005) method 2320 B	Hydrology Group laboratory
pH	Electrometric method APHA (2005) method 4500-H^+ B	Hydrology Group laboratory (field measurements)
Turbidity	Nephelometric method APHA (2005) method 2130 B	Hydrology Group laboratory (field measurements)
Electrical conductivity	Electrical conductivity electrode APHA (2005) method 2510 B	Hydrology Group laboratory (field measurements)
Temperature	Temperature electrode APHA (2005) method 2550 B	Hydrology Group laboratory (field measurements)
Transmittance at 254 nm	Spectrometric method APHA (2005) method 5910 B	Hydrology Group laboratory
Redox potential	Redox electrode APHA (2005) method 2580 B	Hydrology Group laboratory (field

Parameter	Method used	Laboratory measurement
		measurements)
BOD$_5$ (soluble)	5 day BOD test APHA (2005) method 5210 B	Samples treatment and measurements performed by the Specialized Laboratories from the University of Barcelona (Serveis Científico-Tècnics)
COD (total and soluble)	Closed reflux, titrimetric method with dichromate oxidation APHA (2005) method 5220 C	Hydrology Group laboratory
DOC	Wet-oxidation method EPA method 9060 A	Samples filtered and treated at the Hydrology Group laboratory. Measurements performed by the Specialized Laboratories from the University of Barcelona (Serveis Científico-Tècnics)
Surfactants	Kit LCK332 (for anionic surfactants) from Hach-Lange	Hydrology Group laboratory
Cyanide	Kit LCK315 from Hach-Lange	Hydrology Group laboratory
Nitrite	Kit LCK341 from Hach-Lange	Hydrology Group laboratory
Ammonia	Preliminary distillation step followed by titration APHA (2005) method 4500-NH$_3$ C and APHA (2005) method 4500-NH$_3$ D	Hydrology Group laboratory
Total N	Macro-Kjeldahl method: digestion, distillation and titration APHA (2005) method 4500-N$_{org}$ B, APHA (2005) method 4500-NH$_3$ C and APHA (2005) method 4500-NH$_3$ D	Hydrology Group laboratory
Nitrate	Ion chromatography with chemical suppression of eluent conductivity APHA (2005) method 4110 B	Hydrology Group laboratory
Phosphorus		
Fluoride		
Chloride		
Sulphate		
Phenols	Folin Ciocalteau colorimetric method Box, J. D. (1983)	Hydrology Group laboratory
Boron	Inductively coupled plasma/mass spectrometry (ICP/MS) method APHA (2005) method 3125 B	Samples filtered and treated at the Hydrology Group laboratory. Measurements performed by the Specialized Laboratories from the University of
Cadmium		
Chromium		
Cobalt		
Copper		
Iron		
Lead		

Parameter	Method used	Laboratory measurement
Manganese		Barcelona (Serveis Científico-Tècnics)
Molybdenum		
Nickel		
Selenium		
Barium		
Zinc		
Sodium		
Potassium		
Calcium		
Magnesium		
Carbonate/ bicarbonate	Titration method APHA (2005) method 2320 B	Hydrology Group laboratory
Total bacteria count	Membrane filtration and growth on mTGE Broth APHA (2005) method 9215 D	Hydrology Group laboratory
Faecal coliforms	Membrane Filtration and growth on mFC Broth APHA (2005) method 9222D	Hydrology Group laboratory
E. coli	Membrane Filtration and growth on m-ColiBlue24 Broth EPA accepted 40 CFR parts 141, 143	Hydrology Group laboratory
Faecal streptococci	Membrane Filtration and growth on m Enterococcus Agar for faecal streptococci APHA (2005) method 9230 C	Hydrology Group laboratory
***Clostridium* spores**	Membrane Filtration and growth on TSN Agar APHA (2005) method 9222D	Hydrology Group laboratory
Bacteriophages	Enumeration of somatic coliphages. Host culture: *Escherichia coli* WG5 (ATCC 700078). Count plaques of lysed cells on plates ISO 10705-2	Hydrology Group laboratory

4.6.2. Pathogens

Methods used to detect and quantify pathogens in the framework of the RECLAIM WATER project are described in Levantesi *et al.* (2010), Tandoi *et al.* (2012) and reports of the RECLAIM WATER project (La Mantia *et al.*, 2006a; La Mantia *et al.*, 2008b).

For bacterial pathogens, *Campylobacter* was measured by culture method and PNA-FISH, whereas the other bacterial pathogens investigated (*Salmonella* spp., *Yersinia enterocolitica*, *Helicobacter pylori* and *Mycobacterium avium* subsp. *paratuberculosis*) were concentrated in the field by membrane filtration and a pumping system, and posteriorly measured by quantitative PCR. For viruses and protozoa, samples were concentrated in the field, using specific cartridges and a pumping system. Viruses (enteroviruses, Hepatitis A virus, norovirus GGI and GGII) were measured by molecular methods and protozoa (*Giardia* cysts and *Cryptosporidium* oocysts) by staining by fluorescently labelled monoclonal antibodies. Helminth eggs (*Ascaris lumbricoides*, *Trichurus trichiura*, *Ancylostoma duodenale*, *Taenia* spp., among others) were determined using a method that involved sedimentation, flotation and identification and count in an optical microscope.

For samples pre-treatment, a specific report was issued (La Mantia *et al.*, 2006b). At the Hydrology Laboratory the samples were prepared to be sent to the Reclaim Water partner laboratories for its analysis.

4.6.3. Antibiotic Resistance Genes (ARGs)

Methods used to detect and quantify pathogens in the framework of the RECLAIM WATER project are described in Böckelmann *et al.* (2009), Tandoi *et al.* (2012) and a report of the RECLAIM WATER project (Böckelmann *et al.*, 2007).

For ARGs, samples were concentrated in the field, using specific filters and a pumping system. At the Hydrology Laboratory the samples were prepared to be sent to the Reclaim Water partner laboratory for its analysis.

4.6.4. Pharmaceutically Active Compounds (PhACs), Endocrine Disrupting Chemicals (EDCs), Disinfection By-Products (DBPs) and Complexing Agents

Methods used to detect and quantify PhACs, EDCs, DBPs and complexing agents in the framework of the RECLAIM WATER project are described in Ernst *et al.* (2012) and a report of the RECLAIM WATER project (Asmin *et al.*, 2006).

For all these trace organics, samples were concentrated in the laboratory, using specific cartridges and vacuum. For samples pre-treatment, a specific report was issued (Hein *et al.*, 2006b). At the Hydrology Laboratory the samples were prepared to be sent to the Reclaim Water partner laboratory for its analysis.

5. RISK ASSESSMENT OF RISMAR SCHEME (SABADELL)

5.1. Background: Some hints on Sabadell study site

5.1.1. Historical background

Since the 18th century, the main activity of the city of Sabadell, which is located in the southern part of the Vallès Occidental district (Catalonia, Spain), was the textile industry. Factories have been exploiting the Quaternary and Miocene aquifers, as well as the Ripoll River, which crosses the city and which is an affluent to the Besós River (a river passing by Barcelona municipality). Over the years, the industrial activity as well as the urban demand led to a depletion of groundwater levels and also to a high pollution of the river and the aquifers. Furthermore, the riverbed and river banks became an uncontrolled disposal site.

Parallel to the pollution of the area and the depletion of the aquifer levels, a flooding due to the inadequate riverbed and river banks conditions in 1962 resulted in strong damages to many houses close to the river and several victims. Although floodings are not regularly suffered in the area, attention should be paid to them.

In view of this situation, the Environmental Department of Sabadell Municipality decided to restore the area and started a project to create a “Fluvial Park” in the banks of the river. The project is being developed jointly with CASSA, the water company exploiting the water cycle in town. Considering the situation of the area, the restoration project main objectives were:

- The Ripoll River water quality improvement, as it was highly polluted due to the illegal disposals of the factories and other users.
- Landscape ecological reclamation: the riverbed and the river banks were an illegal disposal site, which contributed to the deterioration of the area.
- Water savings: implement aquifer recharge not only for recovering the aquifer levels but also creating an additional source of water which is used for park irrigation and street cleaning, as well as for other minor uses.

5.1.2. Project planning

The restoration project was divided in four units:

- Completion of the wastewater sewerage connections and control system: many companies were not connected to the general sewerage system, thus disposing their effluents directly to the Ripoll River. Besides, the Riu Sec WWTP had not enough capacity to treat the wastewaters from a new industrial area. Thus, it was necessary to construct and implement a new WWTP, the Ripoll River WWTP. Nowadays, only few companies still dispose their effluents directly to the river, and are closely controlled by the local authorities. In order to control these companies and any other disposals to the Ripoll River, an online system was implemented in the sewerage system close to it.
- Indirect water reuse: the water recharged is stored in the aquifer. The water quality is improved thanks to the filtration through the riverbed and it can be legally utilised for non-potable uses, as park irrigation and street cleaning. To fulfil this objective, a pumping system to send the effluent upstream the river as well as emissaries were constructed to discharge the water into three different points of the river.
- Riverbed protection: the riverbanks have been restored, carving a defined path for the river and covering the walls with stones and a metallic net.

- Wetland construction: wetlands in three different points of the river were planned to improve the quality of the river water, expecting a reduction in the organic and the microbial loads. These wetlands were not yet constructed at the time of the RECLAIM WATER project development, but one of the wetland areas is in place nowadays (2014), treating around 10% of the Ripoll River water.

The chronology of the restoration project was as follows (see Figure 2):

- 1994: The project started.
- 2001: Ripoll River WWTP construction finished.
- 2002: Ripoll River WWTP came into operation.
- 2003: Pipes, pumping system and emissaries for the transport of the treated effluent from the WWTP to the river were constructed (1st stage).
- 2004: Water recovery from the mine started. The old facilities were updated, including the pumping system. At this point, the recovered water was naturally infiltrated through the riverbed, but riverbed filtration close to the mine where the water is recovered was not enhanced yet. To increase the riverbed filtration process it was necessary to pump the water upstream the Ripoll River, in order to have a higher amount of water circulating in the area where the riverbed filtration needed to be enhanced: before the recovery area (old gallery system).
- 2005: Piping system came into operation, thus allowing the discharge of the effluent of the Ripoll River WWTP to the Ripoll River. The water started to be discharged downstream the recovery area, close to the Ripoll River WWTP location (Sant Oleguer discharge point).
- 2006: Pumping system to send WWTP effluent upstream the Ripoll River came into operation. The recycled water started to be discharged in two points upstream the Ripoll River: Colobrers area and Torrella Mill area, the latter being located very close to the mine where the water is recovered.
- 2009: Construction of a wetland by the river (downstream Colobrers stream area). Wetland came into operation in 2010. It treats approximately 10% of the water discharged into the Ripoll River, enabling a reduction in nutrients and microorganisms in the water infiltrating through the riverbed to the alluvial aquifer.

Figure 2 Chronology of the restoration project. Red boxes indicate the year when the treatment or element of the system came into operation.

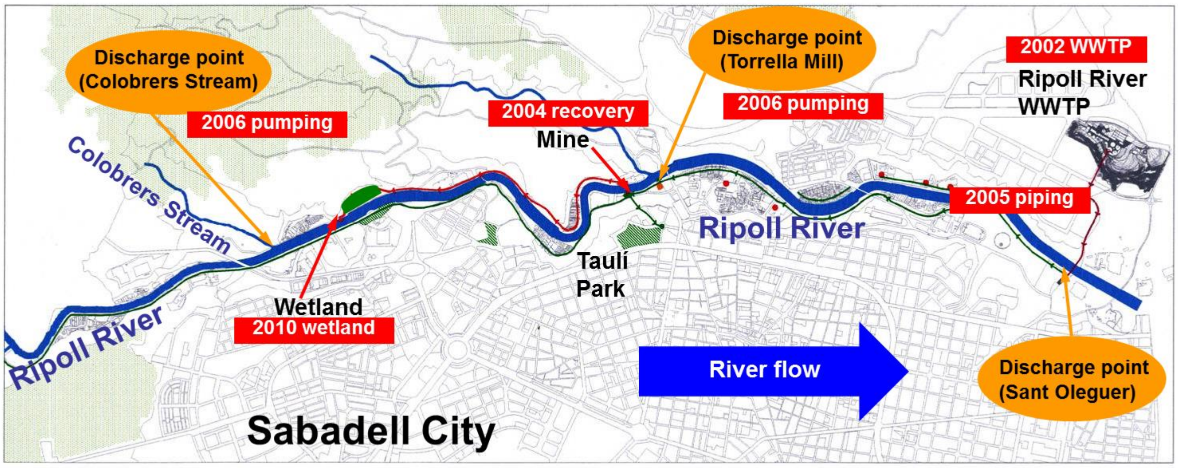


Table 4 Royal Decree 1620/2007 requirements for water reuse (Spain).

Reclaimed water uses	Quality criteria (Maximum value permitted)				
	Helminth eggs	***E. coli*** **(CFU/100 mL)**	**Suspended Solids (mg/L)**	**Turbidity (NTU)**	**Other criteria**
1. Urban uses					
1.1. Residential uses: Private gardens irrigation, toilet flushing.	1 egg/10 L	0	10	2	*Legionella* spp. (1) 100 CFU/L. Other contaminants (2)
1.2. Urban services: Irrigation of open access landscape areas (parks, sport fields…), street cleaning, fire-fighting systems, cars washing (industrial)	1 egg/10 L	200	20	10	*Legionella* spp. (1) 100 CFU/L. Other contaminants (2)
2. Agricultural uses					
2.1. Irrigation of raw consumed crops.	1 egg/10 L	100	20	10	*Legionella* spp. (1) 1000 CFU/L. Other contaminants (2)
2.2. Irrigation of crops for canning industry and crops not raw consumed. Irrigation of pastures for milk or meat animals. Aquiculture.	1 egg/10 L	1,000	35	NLE	*Taenia saginata* and *T. solium* (3) 1 egg/L. Other contaminants (2)
2.3. Irrigation of industrial crops, nurseries, fodder, cereals and oleaginous seeds. Ornamental flowers.	1 egg/10 L	10,000	35	NLE	*Legionella* spp. (1) 100 CFU/L. Other contaminants (2)
3. Industrial uses					
3.1.a. Process water and cleaning, except food industry. Other industrial uses.	NLE	10,000	35	15	*Legionella* spp. 100 CFU/L. Other contaminants (2)
3.1.b. Process water and cleaning in food industry.	1 egg/10 L	1,000	35	NLE	*Legionella* spp. 100 CFU/L. Other contaminants (2)
3.2. Cooling water.	1 egg/10L	0	5	1	*Legionella* spp. 0 CFU/L
4. Recreational uses					
4.1. Irrigation of golf courses.	1 egg/10 L	200	20	10	*Legionella* spp.(1) 100 CFU/L. Other contaminants (2)
4.2. Impoundments, water bodies and streams for recreational uses in which public contact with the water is not permitted.	NLE	10,000	35	NLE	Total Phosphorus (stagnant water bodies): 2 mg/L. Other contaminants (2)
5. Environmental uses					
5.1. Aquifer recharge by localized percolation through the soil.	NLE	1,000	35	NLE	TN: 10 mg/L, NO^{3-}: 25 mg/L. Other contaminants (4)
5.2. Aquifer recharge by direct injection.	1 egg/10L	0	10	2	TN: 10 mg/L, NO^{3-}: 25 mg/L. Other contaminants (4)
5.3. Irrigation of forested areas, landscape and green areas with restricted access	NLE	NLE	35	NLE	Other contaminants (2)
5.4. Other environmental uses (habitat wetlands, enhancement of marsh and similar, environmental flow maintenance)	The quality required will be evaluated case by case.				

NLE: No limit established.

(1) If exists risk of aerosols formation.

(2) See RD 849/1986 Annex II (public disposals to the hydraulic system law), RD 907/2007 Annex IV (hydraulic planning law) and RD 606/2003 (environmental quality law, modification of RD 849/1986).

(3) Pastures used to feed animals producers of meat.

(4) See RD 849/1986 articles 257 to 259 (public disposals to the hydraulic system law).

5.1.3. Authorization procedure and regulations applicable to the system

RISMAR scheme can fall into different uses of the ones detailed in the Spanish Water Reuse Royal Decree 1620/2007 (see Table 4), depending on the point of view used.

MAR is considered as an environmental use of reclaimed water in the Spanish Water Reuse Royal Decree 1620/2007. RISMAR scheme could be included in "5.1: Aquifer recharge by localized percolation through the soil". However, percolation is not exactly "localized", as the water infiltrates all along the riverbed and the shores as well. Besides, the system is not interpreted as a "pure" artificial recharge scheme by the administration, and no authorisation procedure for the recharge of the aquifer has been required to date. It is considered that the WWTP discharges the effluent in the Ripoll River, hence contributing to the preservation of its environmental flow, although it is inevitably recharging the alluvial aquifer through riverbed filtration at the same time.

Then, from the authorities' point of view RISMAR scheme is an "ecological river flow maintenance" site (integrated in "5.4: Other environmental uses"). For this type of reuse application, the water quality and sampling routine required have not been specifically defined yet, and the decree only indicates that "the minimum quality required will be studied case by case". At RISMAR scheme, the Water Catalan administration gave the permit to discharge the WWTP effluent into the Ripoll River, just considering it as a release into the public hydraulic system. In this sense, the quality of Ripoll River WWTP effluent, which is the one discharged into the Ripoll River, is subjected to the requirements of the Royal Decree 509/1996 (Regulations for Urban Wastewater Treatment, see

Table 5). The Ripoll River is declared as a sensitive area and the limits are stricter for the effluent quality.

Another use found at RISMAR scheme is the one integrated in 4.2, "…streams for recreational uses in which public contact with the water is not permitted". In this sense, after the cleaning and recovery of the area, the Ripoll River and the surroundings can be considered as one area for recreational use, and the discharges of the Ripoll River WWTP contribute to increase the flow of the Ripoll River.

The last use found at RISMAR scheme is the one integrated in 1.2, "Urban services: Irrigation of open access landscape areas (parks, sport fields…), street cleaning". The final treated water is used to irrigate the Taulí Park and some trees along the Ripoll River, and it is also use for street cleaning. However, it is not considered as a water reuse by the administration either, but as an extraction of water from the mine, in order to increase the water resources available.

Table 5 Royal Decree 509/1996 requirements.

	RD 509/1996
Scope of the law	WWTP effluent quality
Limits	• $BOD_5 < 25$ mg/L or a red. > 70% • COD < 125 mg/L or a red. > 75% • Suspended solids < 35 mg/L or a red. > 90% Besides, at least one of the following limits must be assured: • Total Nitrogen < 10 mg/L or a red. > 70% • Total Phosphorus < 1 mg/L or a red. > 80%

Thus, considering the present situation, fulfilling the Spanish water reuse RD 1620/2007 limits would be enough, even though not required for some of the uses found at RISMAR scheme, as it has been explained above.

For the purposes of developing the present work, the Australian Guidelines for Managed Aquifer Recharge (MAR guidelines; NRMMC-EPHC–NHMRC, 2009), the Australian Guidelines for Water Recycling Phase 1 and Phase 2 (NRMMC–EPHC–AHMC, 2006; NRMMC–EPHC–NHMRC, 2008), the Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011), the World Health Organization (WHO) Drinking Water Guidelines (WHO, 2011a) and the WHO Guidelines for the safe use of wastewater, excreta and greywater (WHO, 2006b) have been used and followed for the risk assessment development. The Water Safety Plan (WSP) (WHO, 2009b) could have been also used to develop the present work. WSP is a good tool to develop a risk assessment and risk management study, and the steps to be followed are very similar to the ones proposed in the cited guidelines above. However, for the purposes of the present work it was deemed more effective to use the Australian approach. Besides, other guidelines have been also used in order to get reference values for the hazardous components considered, and are cited in their corresponding sections. Although all these guidelines do not need to be fulfilled in Spain, they are of great value for the development of a MAR system and the corresponding risk assessment.

5.1.4. Motivations for recharge and use of recovered water

The primary motivation for the implementation of the aquifer recharge and water reuse scheme was the water scarcity. Specifically for RISMAR scheme, the water stress drivers are:

- The repeated drought episodes experienced in the recent years.
- A high industrial water demand (even though the number of industries has diminished lately).
- The potable water in Sabadell comes from the Llobregat River which is overexploited, as it supplies Barcelona and many other smaller municipalities. Then, there is a risk of lack of supply in dry years.

Other motivations that must be taken into account for the implementation of the MAR and water recycled system in the city are:

- The reduction of the utilisation of potable water in uses when it is not a necessity.
- To have an additional source of water available during the whole year, that can be utilised for non-potable uses as park irrigation or street cleaning.
- Maintenance of the environmental flow of the river. The river flow is usually low, it has a Mediterranean regime, and most of the time the river carries mainly effluents from different WWTPs. The environmental flow of the river remains irregular despite the effluent discharges of the Ripoll River WWTP.
- There is a strong need to improve the quality of the river water.
- To avoid restrictions in the irrigation of public green areas and in street cleaning during dry periods. These are the first uses that experience water restrictions during shortage periods, as the “Catalan Drought Ordinance” (DOGC, 2007) asks for.
- Maintenance and use of old installations already present in the area (the Ripoll River mine, where the water is recovered).

5.2. Risk assessment stages according to MAR guidelines

RISMAR scheme is a case of Managed Aquifer Recharge (MAR) where the recharge is performed through riverbed filtration, thus the risk assessment needs to be performed as a water recycling scheme with MAR. An initial risk assessment of RISMAR scheme was performed during the development of the RECLAIM WATER project, and is summarized in different reports of the project (Ayuso-Gabella, M.N. *et al.*, 2006, 2007, 2008a and 2008b). This risk assessment was initially performed in a qualitative way (Ayuso-Gabella, M.N. *et al.*, 2007 and 2008b), considering events that could possibly occur at the site. Later on, a preliminary quantitative risk assessment was performed (Ayuso-Gabella, M.N. *et al.*, 2008a), that already considered some of the hazards related to a MAR system, but other ones were still lacking and it was incomplete.

In the present work, the risk assessment framework set out in the MAR guidelines (NRMMC-EPHC–NHMRC, 2009) and the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) has been applied to RISMAR scheme, and details on each relevant hazardous component are given in section 5.5. In addition, other guidelines have also been consulted and used in order to further develop the risk assessment and risk management evaluations (see end of section 5.1.3).

The risk assessment framework set in the MAR guidelines encompasses four stages of project development and assessment, with the information required for assessment at each stage increasing in complexity. These four stages are shown in Figure 3 and are summarised below for RISMAR scheme. In case that the project meets the criteria for a simplified assessment, the proponents can contact the local authority for further information about permit requirements and conditions. Sabadell site would not meet all the criteria set in the MAR guidelines for a simplified assessment (see Table 6), but would meet most of it. So it is not clear if it would need to strictly follow the four stages of the risk assessment process, as this would depend on the local authority decision.

Table 6 Qualifying criteria for MAR projects that can follow a simplified assessment (RISMAR scheme example).

Qualifying criteria	Evaluation of RISMAR scheme
Source water is roof run-off from a single dwelling.	**No.** RISMAR scheme uses secondary effluent from a WWTP
Recovered water is for irrigation or other non-drinking uses specified by the local authority.	**Yes.** Recovered water is mainly used for park irrigation and street cleaning, and other uses minor in volume are also non-drinking uses.
An aquifer capable of storing additional water exists.	**Yes.** The aquifer exists and has been traditionally used by industries in the area.
The aquifer has not been identified as being affected by industrial or agricultural contamination to an extent that precludes use.	**Yes.** The aquifer suffered from industrial contamination in the past, but in the recent years the water quality has improved. Its previous industrial contamination has been highly reduced and it does not preclude its use.
The aquifer is not used for drinking water supplies in the area, and is not capable of being used as a drinking water supply based on ambient groundwater quality.	**Yes.** The aquifer is not used for drinking water, and high salinity as well as other characteristics make it not apt for drinking water supply. In case in the future it is considered for drinking water supply,

Qualifying criteria	Evaluation of RISMAR scheme
	further advanced post-treatments would be required and these qualifying criteria would need to be reviewed.
The aquifer is confined and not artesian, or is unconfined and has a watertable deeper than 4 m in rural areas or 8 m in urban areas, or as otherwise specified by the local authority	**Yes.** The aquifer is unconfined and has a watertable deeper than 8 m (it is located in an urban area).

When dealing with RISMAR scheme, it must be taken into consideration that the legislation that applies in Spain and Catalonia does not require such a level of detail as the Australian guidelines (Australian Guidelines for Water Recycling and MAR guidelines). Although such level of detail is not requested in Spain or Catalonia, and that RISMAR scheme follows nearly all the criteria for a simplified assessment as per Table 6, it is still interesting to identify the four stages of the project development and assessment set in the MAR guidelines (see Figure 3).

At RISMAR scheme, the development of the project has not followed straightforwardly the risk assessment stages, rather different stages have been simultaneously developing at the same time.

Stage 1

Stage 1 of the risk assessment framework comprises a desktop study where all available information is collected, and used to undertake an entry level assessment.

At RISMAR scheme, all the information available at the moment of starting the project was gathered, and an entry level assessment was also performed but not exactly following the one recommended in the MAR guidelines. It must be worn in mind that at the onset of the project these guidelines had not been even prepared. An entry level assessment for RISMAR scheme, as it would have been developed, is given in Appendix A and Table A-2. This is intended to reveal the likely degree of difficulty of the MAR project, and hence the extent of field investigations needed in Stage 2.

During this stage, the source water available was considered, which was the treated wastewater. The presence of an available aquifer, as it is the alluvial aquifer, to store the water and to recover it, the already present infrastructures to recover the water and the necessity to treat the wastewaters from factories present in the area were key points to develop the project, as it has been explained in section 5.1.2. The final uses of the recovered water were also considered at this point, as it shows the study by Vinyoles *et al.* (2005). In this study, the economic viability of enhancing the riverbed filtration through WWTP effluent discharges in the Ripoll River was also considered, and also the storage capacity of the alluvial aquifer and the effects on the Ripoll River ecology.

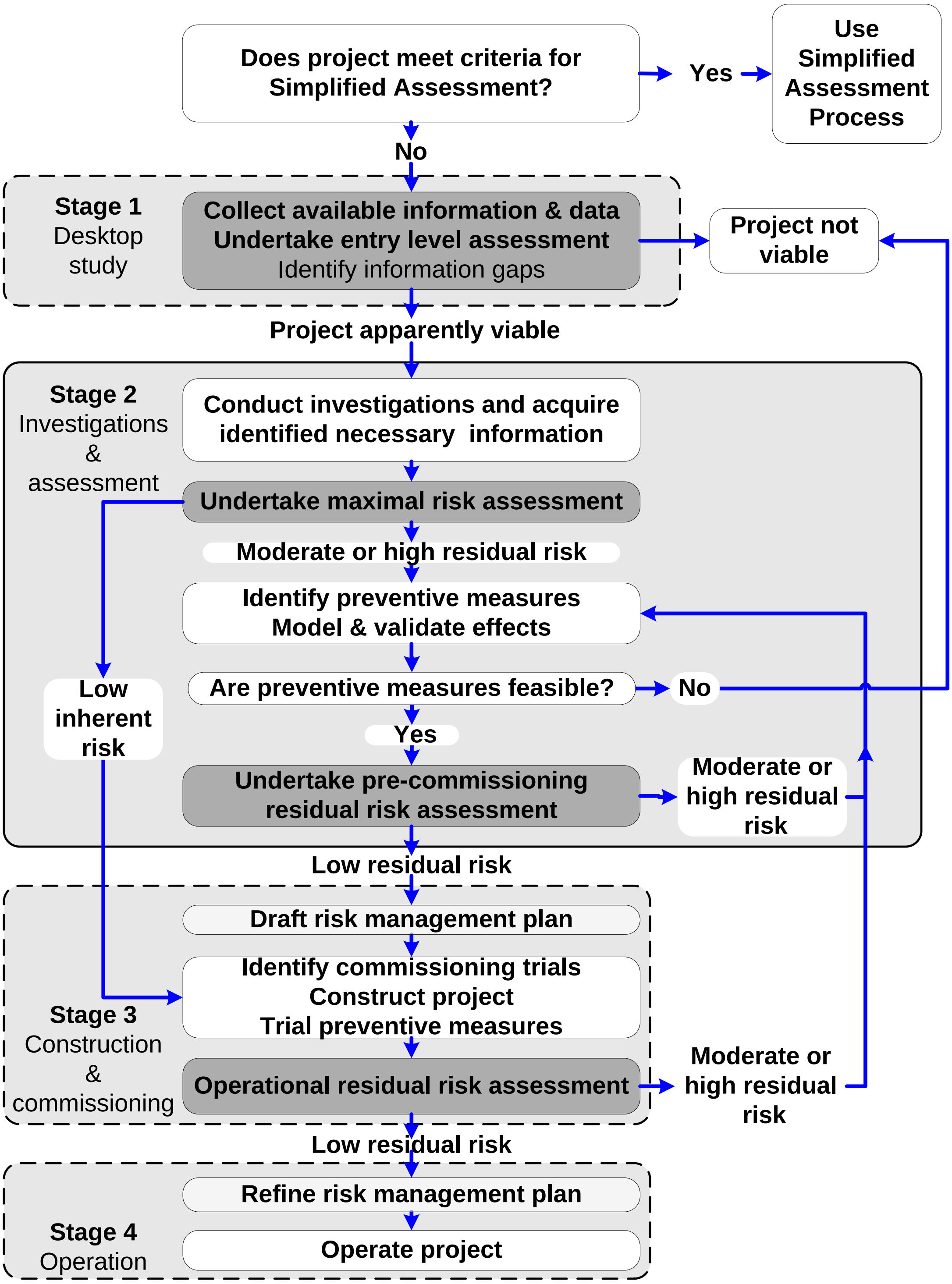
The entry level assessment showed the scheme to be apparently viable, and more detailed investigations were undertaken in Stage 2.

Stage 2

During this stage, laboratory and field studies are being performed to gather more knowledge on RISMAR scheme. Aquifer characterisation and considerations such as river water quality before the discharges, riverbed clogging, efficiency of recovery, fate of recharged water, nutrients, pathogens and microbiota, and interaction of chemical species with the aquifer matrix were addressed by undertaking measurements in the aquifer, the Ripoll River water and at a number of fully penetrating observation wells and piezometers.

Besides, a characterization of the whole RISMAR scheme was undertaken in the framework of the RECLAIM WATER project, sampling the treated effluent, the Ripoll River water, the groundwater, the recovered water and the final treated water (disinfected and sand filtrated). These studies were carried out in the framework of the RECLAIM WATER project and the Hydrogeology Course (Technical University of Catalonia); and as a regular monitoring basis by the Sabadell Town Hall Environmental Department and CASSA.

Figure 3 Risk assessment stages in managed aquifer recharge project development (extracted from MAR guidelines: NRMMC-EPHC–NHMRC, 2009).



Risks associated with discharging treated wastewater into the Ripoll River and recovering the groundwater were qualitatively evaluated (Ayuso-Gabella, M.N. *et al.*, 2007 and 2008b), and have been quantified recently, from the human health point of view (Ayuso-Gabella *et al.*, 2011). A maximal and a residual risk assessment have been performed as part of the present PhD thesis. Identified risks have been managed adequately and are also developed in the risk management section 7. In the same section, corrective and preventive measures, critical limits (CLs), critical control points (CCPs) as well as other operational measures necessary to properly control the system have been widely developed.

The project is under operation nowadays, although Stages 2 and 3 are still under way. The low risk associated to the reuse of water for urban park irrigation and street cleaning prompted its quick implementation before all the stages had been finalised. In addition, riverbed filtration naturally occurs in the riverbed, and the Ripoll River already carries treated wastewater discharges from WWTPs upstream, thus the discharges from the Ripoll River WWTP are not worsening or decreasing the Ripoll River water quality.

Stage 3

After two years of enhancing MAR with the treated wastewater discharges from the Ripoll River WWTP, a residual risk assessment using all the information available has been undertaken, and is summarised in the present chapter. RISMAR scheme was tested for emerging pollutants, pathogens and antibiotic resistance genes, apart of the regular monitoring. A wider hydrogeological study is recommended. This residual risk assessment needs to be evaluated in a regular basis, in order to identify improvements or modifications in the system and to ensure that the risk is kept under a controlled level.

Lately, better technologies have been introduced to improve the recovered water quality. These new post-treatments should be tested and challenged to ensure their good performance and their capability to reduce any risk posed by increases in pollutants or pathogens in the groundwater.

Stage 4

As the project is already in the operational phase, a management plan and regular operational, verification and validation monitoring are required.

Verification monitoring must be performed to assess the quality of the recovered water, and to verify that environmental values of the aquifer, the plants and soils of the park and the areas by the Ripoll River are protected. Furthermore, validation of the treatments is required to ensure a good performance of the system in the future. Operational monitoring is already implemented, and is part of the regular routine of analyses at the WWTP and the recycled water scheme. Verification monitoring was performed in the framework of the RECLAIM WATER project by the University of Barcelona and it will have to be included in CASSA and Sabadell Town Hall environmental department regular monitoring plan. These two partners often perform verification monitoring of the water at the point of use, in this case in the sprinklers of the park irrigated with the final treated water (Taulí Park). However, different parameters and frequency for the monitoring are recommended, as it is summarized in Appendix F. Validation of new treatments is essential to ensure a good performance of the system, and requires a specific monitoring. This is still to be planned, but necessary for an appropriate management of the system. In addition, with the installation of a new UV treatment, it must be ensured that the credited $\log_{10}$ removals for this disinfection treatment are achieved.

5.3. Scope of the risk assessment

In this section the configuration of the RISMAR scheme is presented and its main features and hazards addressed, as well as the historical data available and data generated in the framework of the RECLAIM WATER project. All this information is deemed necessary to perform the risk assessment.

5.3.1. Water recycling system location

Sabadell is a city located 20.6 km North-West of Barcelona, Spain. The riverbed filtration and recycled water scheme is placed by the Ripoll River WWTP, being the latter located in an industrial area of the city (see Figure 4).

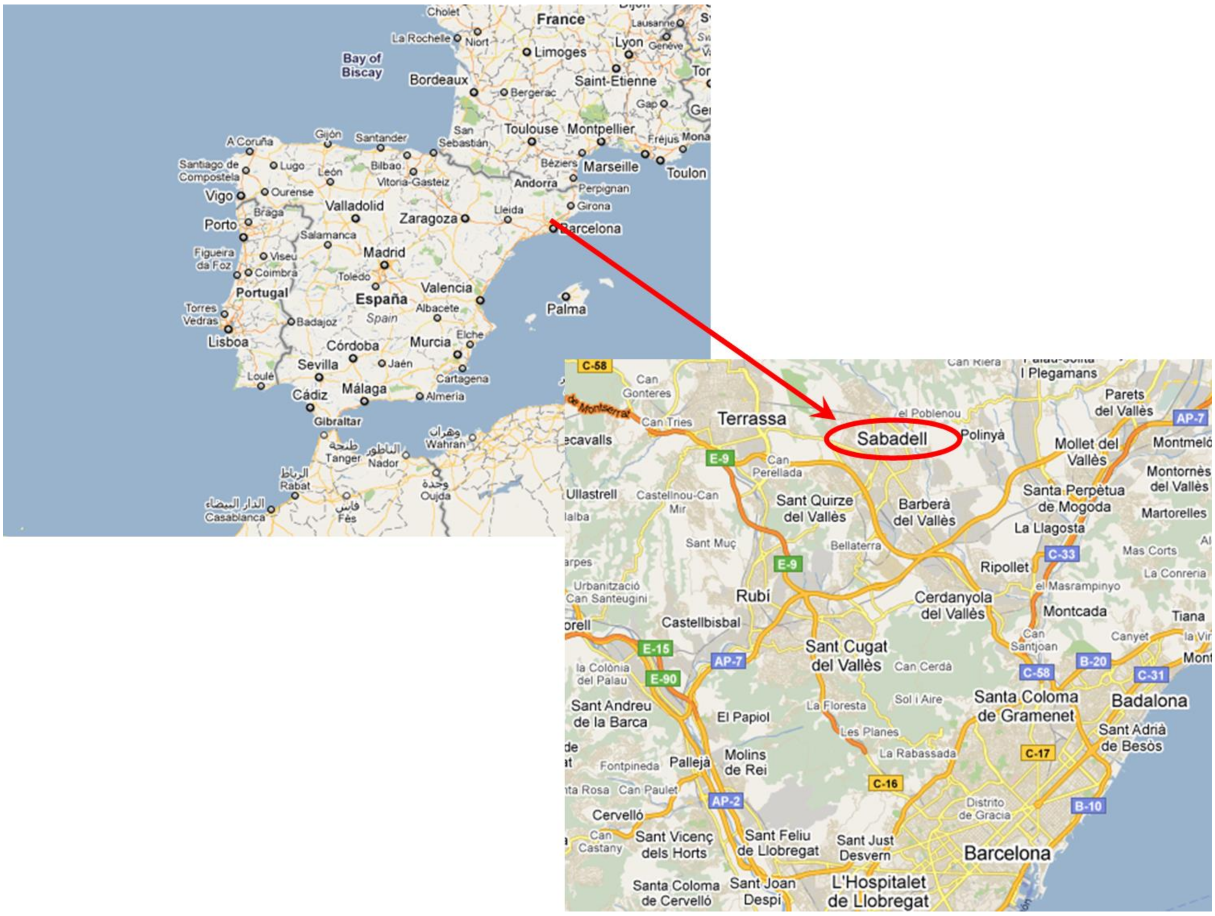
Sabadell has slightly more than 200,000 inhabitants and occupies an area of 37.89 km^2. The average rainfall is of 600-700 mm per year, although in 2007, when the majority of the RECLAIM WATER project sampling campaigns took place, was less than 400 mm. Catalonia region was experiencing a long lasting drought period until April 2008.

The potable water supply in the city of Sabadell is connected to the Ter and Llobregat Waters network. North and central Sabadell receive water from the Llobregat River, while the south of the city receives it from the Ter River. The area close to the Ripoll River is supplied by the Llobregat River.

5.3.2. Source of recycled water

The source of recycled water is the secondary effluent of the Ripoll River WWTP, located in Sabadell (see Figure 2).

Figure 4 Geographical location of Sabadell (© from Google).



Sabadell is divided into two different areas concerning the sewerage and treatment of wastewater: half of the city sends its wastewaters to the Sec River WWTP and the other half to the Ripoll River WWTP. The latter WWTP was also constructed in order to treat the wastewaters from the new industrial area, named Can Roqueta, thus avoiding the discharge of the untreated industrial wastewaters into the Ripoll River (see section 5.1.2 for more information on this). In Figure 5 are depicted both wastewater collecting areas and the placement of the WWTPs to treat them.

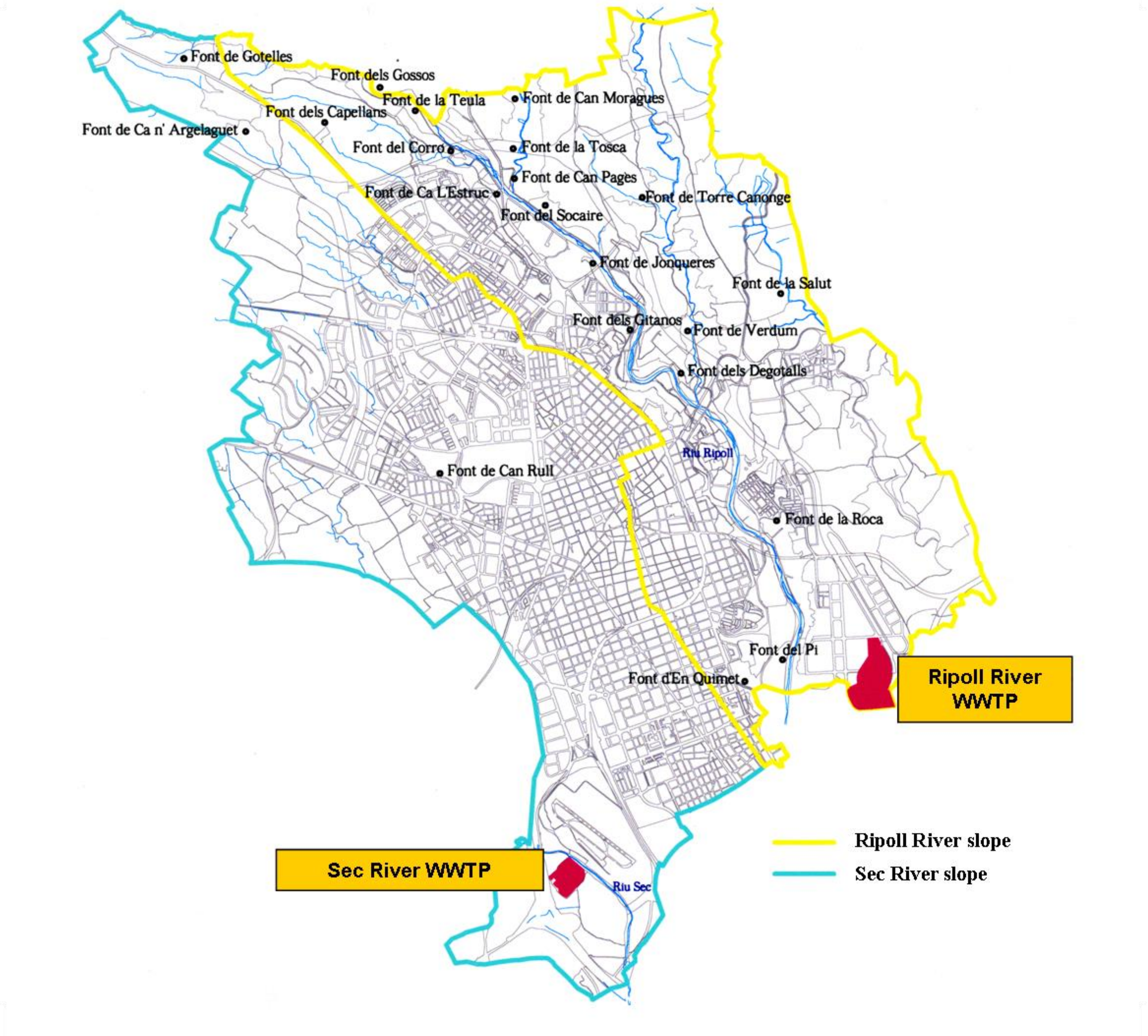
5.3.3. Reclamation process and infrastructure

The reclamation process in place at RISMAR scheme has several steps and treatments, being one of them the riverbed filtration. The different elements of the system are described below and schematized in Figure 6.

5.3.3.1. Ripoll River WWTP

The Ripoll River WWTP has a treatment capacity of 220,000 population equivalent based on conventional activated sludge treatment including nutrient removal. The maximum hydraulic capacity is 30,000 m^3/day, while the average influent amounts were around 16,000 m^3/day during the RECLAIM WATER project development (ACA, 2014). A summary of the WWTP design characteristics is given in Table 7.

Figure 5 Sewerage system and treatment of wastewater at Sabadell (figure modified from EDS).



The wastewater collected in the eastern part of Sabadell (see Figure 5, area marked in yellow) is conveyed by gravity flow to a pumping station, where a pre-treatment is performed for solids removal: the coarse solids are separated and the small ones are sieved. After that, the water is pumped to the Ripoll River WWTP. After an optional pre-treatment, which is usually by-passed and rarely applied, the raw water undergoes an optional physicochemical treatment if necessary. After this, the water enters a primary treatment with settling tanks. Finally, a secondary treatment by activated sludge and additional settling tanks for nutrient removal is undertaken.

In Table 7 the main design characteristics for the Ripoll River WWTP are summarized. The effluent limits set by the RD 509/1996 were adapted by CASSA considering the influent characteristics. For the sludge treatment, the process consists of: primary and secondary thickening, anaerobic digestion, dehydration, centrifugation and storage in silos to be loaded into trucks. The gas produced in the digestion process is used to generate heat and electricity thanks to two power units, of 320 kW each.

All buildings in the WWTP are equipped with an air treatment and air renewal system, using ozone oxidation.

Table 7 Design characteristics for the Ripoll River WWTP.

Characteristics	Influent	Effluent limits set by CASSA	Effluent limits set in the RD 509/1996
Maximum hydraulic capacity	30.000 m^3/day	N/A	N/A
COD	1300 mg/L	≤ 125 mg/L	≤ 125 mg/L or reduction > 75%
BOD_5	440 mg/L	≤ 25 mg/L	≤ 25 mg/L or reduction > 70%
Suspended solids	630 mg/L	≤ 30 mg/L	≤ 35 mg/L or reduction > 90%
Total nitrogen	79 mg/L	≤ 15 mg/L	≤ 10 mg/L or reduction > 70% (*)
Total phosphorus	15 mg/L	≤ 2 mg/L	≤ 1 mg/L or reduction > 80% (*)

(*) RD 509/1996 states that at least one of both limits (Total Nitrogen and Total Phosphorus) needs to be fulfilled.

5.3.3.2. Riverbed filtration (RBF) and Ripoll River

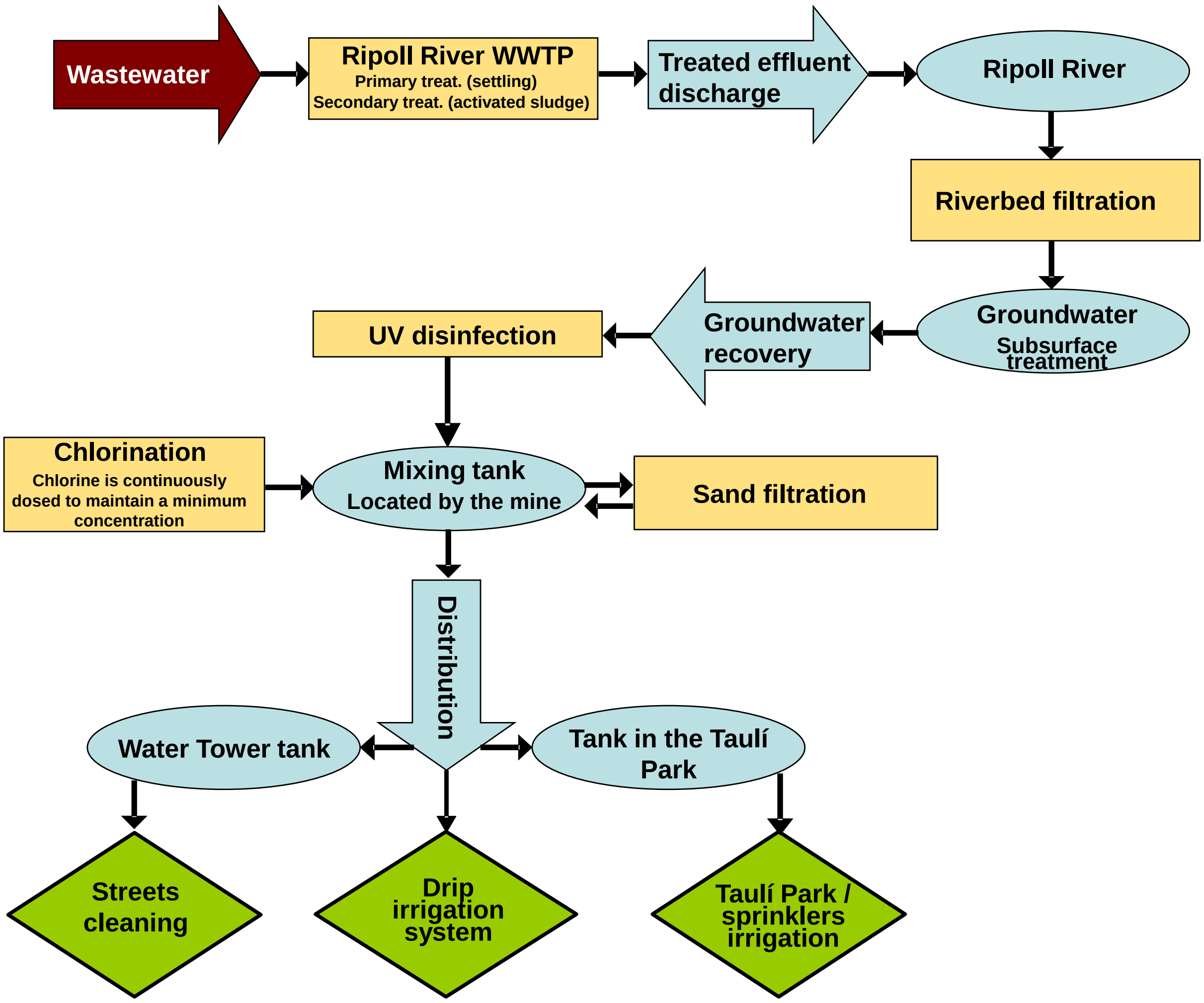
The reuse system is based on the Ripoll River (see Figure 2, Figure 6 and Figure 10), which has a length of 40 km, 7 of them within the limits of the municipality of Sabadell. The river has its source in "Sant Llorenç del Munt i l'Obac" Natural Park, near Sant Llorenç Savall village (Barcelona province).

The secondary effluent of the Ripoll River WWTP is discharged into the Ripoll River in three different points: Colobrers Stream, Torrella Mill and Sant Oleguer (see Figure 2, p. 64). The latter one is only used when the Ripoll River WWTP cannot treat all the influent wastewater, due to heavy rains, or when the pumping upstream the Ripoll River is not available. Once in the river, part of the water infiltrates and reaches the aquifer, which is mainly formed by sand and gravel. The discharges coming from the Ripoll River WWTP increase the Ripoll River flow, and the extraction of water from the well near the river induces infiltration from the surface water body.

There are two more WWTPs upstream of the study area, located in Castellar del Vallès and Sant Llorenç Savall. Castellar del Vallès municipality has 20,000 inhabitants and Sant Llorenç Savall municipality 2,200. Both WWTPs discharge their effluents into the Ripoll River, but the amount of treated wastewater discharged into the river is much smaller than the amount discharged by the Ripoll River WWTP. To allow a sound evaluation of the whole system, a sampling point upstream Colobrers Stream discharge area (the most distant discharge area in the Ripoll River, see Figure 2) was included to measure the water quality of the Ripoll River before arriving to the recharge area. Besides, additional incomes into the Ripoll River that must be considered are:

- Irrigation surpluses (through run-off).
- Groundwater in those areas where the aquifer feeds the Ripoll River.
- Subsurface flows.
- Distribution pipeline losses.
- Partially treated wastewater from a factory (this is a controlled disposal).
- Stormwater (through run-off).
- Wastewater that cannot be treated in the Ripoll River WWTP during heavy rain periods.
- Uncontrolled disposals.

Figure 6 Scheme of the riverbed filtration and recycled system in place at RISMAR scheme during the RECLAIM WATER project (October 2005-December 2008). (Note: in this scheme only appear the most frequent uses given to the final treated water that were in place during the execution of the RECLAIM WATER project; other uses came later on).



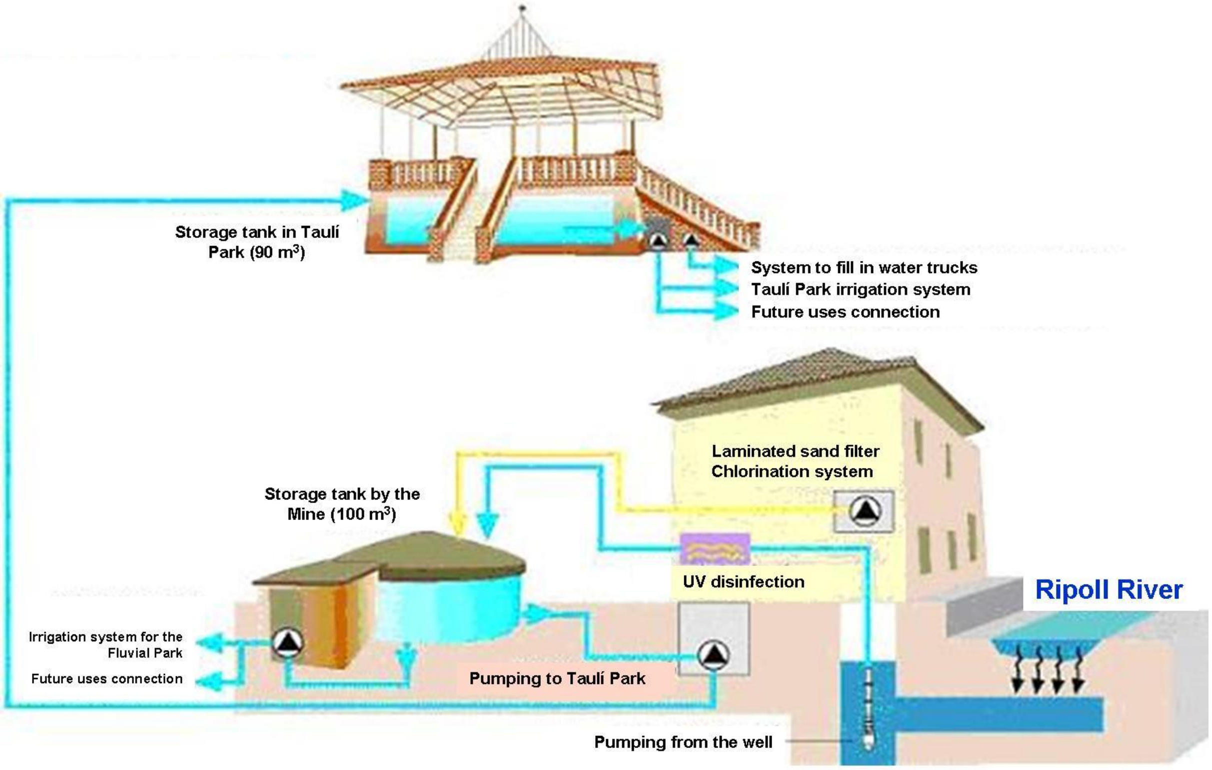
5.3.3.3. Recovery in the mine and in situ post-treatments

The water recovery is performed in a well inside the old mine installations. These old mine installations are located close to the Ripoll River, in the Torrella Mill area.

This well is part of an old constructed gallery, dating back to 1914. The gallery is 1 m wide and 1.5 m deep, and was excavated 7 m under the riverbed, undercrossing the river (see Figure 7, p. 76). In this gallery, the water is collected from the alluvial aquifer and it is carried to a recovery well, where water is pumped. The mine was transferred by Sabadell Municipality to CASSA in 1949, in order to exploit it for irrigation of urban green spaces and loading trucks to clean streets. In 1985 microbiological contamination was detected and the mine was closed, until 2004, when a disinfection system was installed, and the mine was exploited again (Vinyoles *et al.*, 2005). The recovered water, a mixture of groundwater and infiltrated water from the riverbed, is pumped from the alluvial aquifer. In line with the pumping system, a UV treatment disinfects the recovered water. After this, the UV disinfected water is stored in a tank, where chlorine is continuously dosed. A chlorine probe measures the chlorine concentrations in the water tank, and a minimum concentration of 0.5 mg/L is maintained. Besides, there is a laminar sand filter connected to the water tank, which filters the water present in the tank in a continuous way. This laminar sand filter was installed as black precipitates were present in the final treated water (see section 5.5.3.14 for an explanation on this issue). The characteristics of the equipments installed in the mine were:

- The ultraviolet equipment, Wedeco model B120, had a maximum flow of 119.5 m^3/hour and a minimum UV dose of 400 J/L. It worked when water was extracted from the well and can be controlled manually. Currently new UV equipment replaces the one in place when the RECLAIM WATER project was developed.

Figure 7 Scheme for recovery in the mine, post-treatment and distribution system (Modified from EDS, 2012).



- The laminated sand filter, Fiberpool model Z-12-p2-020, was responsible for the removal of suspended solids from the recovered water. Currently a new set of sand filters is in place, much more capable and efficient than the one in place when the RECLAIM WATER project was developed.
- The automated chlorination system consists of a chlorination probe connected to a sodium hypochlorite dispensing system, which maintains a minimum concentration of residual chlorine 0.5 mg/L as indicated.

After the post-treatments on the recovered water are performed, the final treated water is stored in a tank located close to the mine (see Figure 7), and this final treated water can be:

- Used for irrigation of the Fluvial Park on the banks of the Ripoll River. The water is directly taken from the storage tank in the mine, which has a capacity of 100 m^3. In this storage tank there is also an outlet for future different uses.
- Sent to another storage tank in the Taulí Park that has a capacity of 90 m^3. When the Taulí Park storage tank water level substantially decreases, the level probe activates the pumping system located by the mine storage tank, to send water to the Taulí Park storage tank. The water in the Taulí Park storage tank has specific connections to:
    - Irrigate the Taulí Park. This is performed thanks to a sprinkler system.
    - Fill in the tankers for street cleaning.
    - Be used in the future, for other activities not in place yet.
- Sent to the Water Tower tank. This is an old installation that was recovered to distribute water to the tankers for street cleaning.
- Sent to the sports area of La Clota swimming pool. There the water can be used for irrigation of the installations and to fill in the swimming pool during summertime.

During the development of the RECLAIM WATER project, about 70 % of the recovered water was used for park irrigation and 30% for street cleaning. Other uses (irrigation of the sports area and fill in the swimming pool) were not in place.

5.3.4. Intended uses

As indicated, the final treated water was used initially and during the RECLAIM WATER project development to:

- Irrigate the Taulí Park and trees along the Ripoll River: the Taulí Park has trees, bushes and grass, and park irrigation used to be interrupted when drought periods were experienced. The use of the final treated water for irrigation ensures that the Taulí Park is irrigated and has a constant water source, as well as the trees along the Ripoll River.
- Street cleaning: this is another use that permits the reduction of potable water use for uses when potable water is not required.

Only these two uses were in place at the beginning of the RISMAR scheme operation and during the execution of the RECLAIM WATER project.

After a long drought period, it was considered to use the final treated water to fill in a swimming pool and to serve a sports area. Then, after updating and improving the applied post-treatments to the recovered water by means of replacing the UV system and adding manganese and arsenic filters, during summer 2009 the final treated water was used to fill in La Clota swimming pool and to irrigate the fields (football court and athletics track) of the sports area.

It was envisaged that in the future the final treated water could have more uses, as industrial processing waters. To date, this use has not been "officially" implemented and permits have not been requested. However, factories located by the Ripoll River have always used wells that target the alluvial aquifer or the Miocene aquifer. Since MAR was enhanced with the discharges of the Ripoll River WWTP (year 2006, see section 5.1.2), some of those companies have shut down and/or stopped their activities, while others still use their own wells. For the purposes of the risk assessment, a possible direct industrial use will be considered, but currently it is not in place in Sabadell.

To sum up, the real current uses of the final treated water are:

- Urban park irrigation as well as trees along the Ripoll River irrigation.
- Street cleaning.
- Swimming pool fill in and sports area irrigation.

5.3.5. Receiving environments

The receiving environments to be considered at RISMAR scheme include not only the recipients of the final treated water but the Ripoll River and the aquifer themselves. In the recent years, these receiving environments have been described as to providing "ecosystem services", as they present aspects that can be "utilized (actively or passively) to produce human well-being" (Fisher *et al.*, 2009), although there is controversy on the definition of the concept (Boyd and Banzhaf, 2007; Wallace, 2007). In any case, for the purposes of the risk assessment, we are going to consider the different environmental units that receive the treated wastewater directly or indirectly.

5.3.5.1. Ripoll River

The Ripoll River constitutes the means by which to infiltrate the treated wastewater into the aquifer, thanks to the riverbed filtration process, which is a kind of MAR.

The Ripoll River has a moderate ecological value in itself, and it was overpolluted in the past. Then, after restoring and cleaning the area, the birds came back to the river banks, as well as aquatic animals, and it is important to maintain this "improved" ecological status.

The discharges of the treated effluent from the Ripoll River WWTP into the Ripoll River are considered to be very important to maintain the flow of the river, as it is exceptionally very low due to the drought period experienced and usually during summer time. However, it must be ensured that the discharge of the treated wastewater is not damaging or impoverishing the area globally

At the banks of the Ripoll River, the Fluvial Park is still being developed, with paths to walk or bicycle riding.

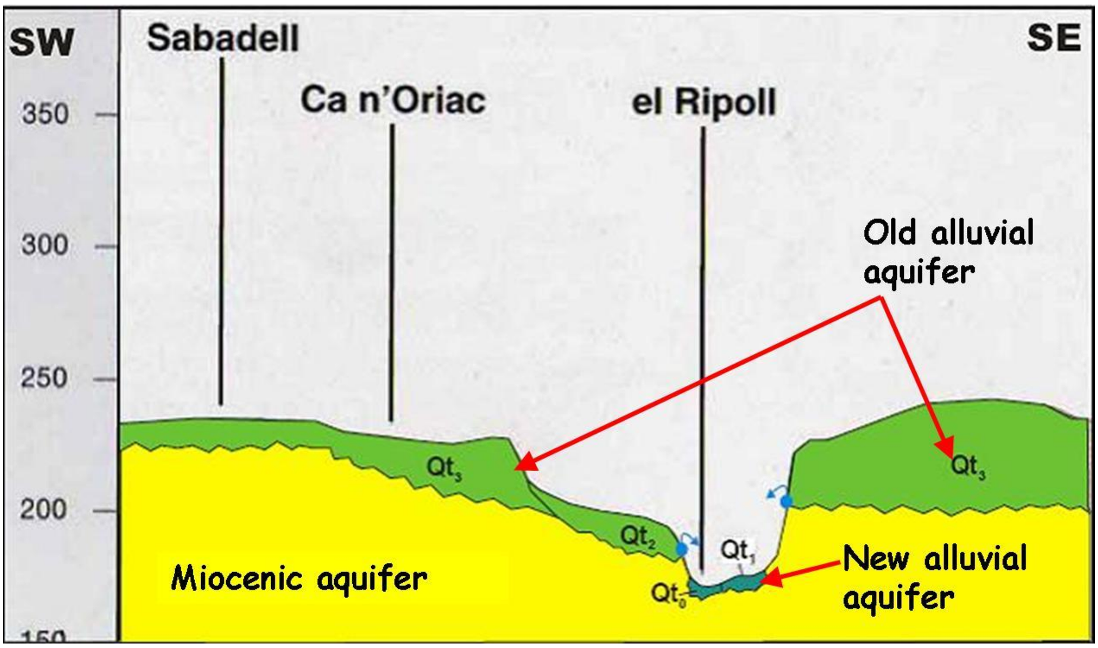
5.3.5.2. Aquifer

The aquifer that is being recharged in Sabadell is unconfined. This aquifer is not used for drinking water uses. Recharge occurs thanks to the natural infiltration through the riverbed. The infiltration water is a mixture of the treated wastewater discharged into the Ripoll River and the water that the Ripoll River already carries.

Three different hydrogeological entities depending on the origin of the sediments in the area can be differentiated (see Figure 8):

- Alluvial aquifer (quaternary origin) corresponding to the old Ripoll River terraces: This aquifer is attached to an area mainly formed of sand and clay, with a little amount of gravels. It is a free aquifer. The recharge is mainly done by the Ripoll River, irrigation surpluses, losses from the distribution system, and rainfall to a minor extent.

Figure 8 Cross section of the aquifer and riverbed at the North area of the city (from Franch, 2007).



- Alluvial aquifer (quaternary origin) corresponding to the new Ripoll River terraces: This aquifer is attached to an area mainly formed of sand and gravel, with little amounts of clay. It is a free aquifer too, with a maximum depth of 5 m, generally. The recharge is mainly done by the Ripoll River, irrigation surpluses, and rainfall to a minor extent.
- Miocene aquifer, under the alluvial aquifers: This aquifer is made of initial materials that were deposited in the Vallès-Penedès depression (Tortonian age). This aquifer is attached to an area mainly formed of conglomerate materials. It is a multi-layered aquifer, with different permeable levels. The recharge is done through the alluvial aquifers.

In practice, and for the purposes of the present work, the aquifer units are referred as alluvial aquifer and Miocene aquifer. As the basin of the river is mainly formed of gravel and sand, with a much lower amount of clay, the river basin is highly permeable, and this greatly influences the groundwater composition.

5.3.5.3. Soils of the Taulí Park and alluvial area

The soils present in the alluvial area (Ripoll River riverbed and banks) are mainly formed of coarse sand and gravel, with patches of fine sands and silty loams. These textures enhance the riverbed filtration through the riverbed. These soils receive the Ripoll River water, as well as the final treated water applied by drip irrigation to the trees along the Ripoll River.

In the Taulí Park the soil has a silty loam texture. This kind of texture can be more easily affected by salinity in the irrigation water, thus in the long-term the soil can be degraded. Then, it is important to monitor the quality of the soils in the area. The soils of the Taulí Park receive the final treated water by sprinkler irrigation.

5.3.5.4. Trees and vegetation of the Taulí Park and trees along the Ripoll River

The trees found along the Ripoll River include chestnut trees and poplars. There is high abundance of reed bed and short bushes. A bit further away from the riverbed, pine trees and other typical Mediterranean trees can be found.

Vegetation in the Taulí Park includes:

- Trees: mainly pine trees, palm trees and poplars; as well as other Mediterranean trees in minor quantities.
- Grass: present everywhere.
- Low bushes and shrubs.
- Aromatic herbs: lavender, rosemary, thyme.

But for the grass, the trees and vegetation are adapted to the Mediterranean climatology and can tolerate fairly well the salinity in the irrigation water. However, as indicated soils salinity still needs to be considered, as well as the beneficial effect of nutrients.

Trees and vegetation of the Taulí Park receive the final treated water by sprinkler irrigation, while the trees along the Ripoll River receive it by drip irrigation.

5.3.5.5. Crops grown by the irrigators of the area

The most typical crops grown in the area are onions, cabbage, tomatoes, beans, chickpeas, wheat and table grapes. Other crops that can be found in the area but in less quantity are almond, eggplant, olive, pepper, chilli, endive, lettuce, carrot, artichoke, cauliflower, courgette and chard, as well as other vegetables. These crops are currently grown in the agricultural park and in other areas of Sabadell; however, the water used is not final treated water of RISMAR scheme. For the purposes of the risk assessment, we are going to consider what would happen if these crops were irrigated with final treated water.

The irrigation methods used for the crops grown in the area are furrow and drip irrigation. Again, tolerance to salinity must be considered, but also the beneficial effect of nutrients present in the water.

5.3.6. Routes of exposure

The routes of exposure to get into contact with the final treated water have been identified according to the end points and the uses given or potentially to be given to this water:

- Human end point.
- Environmental end points: river, aquifer, soil, trees and park vegetation, crops.

5.3.6.1. Human end point

For the human end point three main routes of exposure are considered, which are related to the way a person can come into contact with the recycled water. These routes of exposure will be fully developed and explained in the QMRA section (see section 6.4.1), as they are, in fact, the scenarios used to develop the Monte Carlo simulations and the QMRA. The routes of exposure considered are:

- **Crop consumption**: this is the most typical and well-known route of exposure. For the purposes of the risk assessment, it has been considered what would happen if the crops were irrigated with the final treated water. In this sense, we are considering the irrigation of the crops in the agricultural park in Sabadell, but as it has been explained, these crops are not irrigated with final treated water. (Note: Some growers that have small fields for individual consumption by the Ripoll River use the water that comes from a subsidiary of the Ripoll River, sèquia Monar, and water from wells that target the alluvial aquifer to irrigate their crops, which is illegal. For the purposes of the risk assessment, crop irrigation with Ripoll River water or recovered groundwater has been considered out of the scope of the present work, and would require further investigations).

- **Accidental ingestion of aerosols or a higher volume of water**:
    - Accidental ingestion of aerosols by growers/irrigators: this collective can be easily affected, as they are likely to be close to the irrigation water.
    - Accidental ingestion of aerosols by inhabitants of local communities: local communities can come into contact with the aerosols generated during street cleaning, park irrigation or sports area irrigation. An especial group has been considered that is the immunocompromised population present in the hospital. The immunocompromised are much more sensitive to pathogens and need a smaller dose to develop a disease.
    - Accidental ingestion of aerosols by factory workers, when using the water as process water. (Note: regarding the industrial use of the water as process water, the risk posed by the use of the final treated water in the process itself has not been considered, as there are no food industries in the area, but chemical and textile factories. Only risks to the human health and the environment are considered in the present work. Risks posed to installations and equipments in the factories are out of the scope of this work.)
    - Accidental ingestion of a high volume of water while swimming or developing any kind of aquatic activities in the swimming pool, especially children playing in water.
    - Accidental ingestion of a high volume of water due to cross-connection of the recycled water distribution pipelines with the drinking water distribution pipelines, thus delivering recycled water instead of drinking water: not many information is available to assess how likely it is for a cross-connection to occur, but it is a possible route of exposure. The amount of water ingested should be the same as if it was regular drinking water, but the duration of the cross-connection is considered a short event. At RISMAR scheme, the pipeline system that supplies water to the Taulí Park or to the sports area is rather separated from the population area; it is only close to the hospital, but rather further away from the main population area. The probability that a cross-connection can occur at RISMAR scheme is low. Even though there are many uncertainties related to this route of exposure, it has also been evaluated.
- **Deliberated ingestion of final treated water as potable water (direct/indirect potable reuse)**: Using the final treated water as drinking water is prohibited in the water reuse Royal Decree 1620/2007. However, this route of exposure should be considered in case a strong drought period is suffered in the area. In those kinds of circumstances, the Catalan or the Spanish governments may decide, under an especial and temporal permit, to use the final treated water as potable water, in order to supply the population. Then, the recycled water is to enter the drinking water facility. If not, boiling notices or any hygienic related practice can be issued to reduce health risks to the population.

Another route of exposure for the human end point that could be considered but has not been quantified is the accidental ingestion of soil particles by growers/irrigators or children in the urban parks. This is a possible route of exposure, especially when the soil is dry. However, for the purposes of the risk assessment developed, we have considered enough to calculate the risk of accidental water ingestion. Publications where accidental ingestion of soil particles is studied do not consider water ingestion at the same time; so only one vehicle of transmission is enough for exposure assessment.

5.3.6.2. Environmental end points

The environmental end points are, in fact, the receiving environments explained in section 5.3.5. The routes of exposure for the environmental end points are detailed in section 5.3.6.

5.4. Water quality data used for the risk assessment

In order to develop a risk assessment, a minimum characterization is necessary in terms of water quality data. In the present section, all the information gathered from the site from different sources (CASSA, EDS and ACA) and data generated during the RECLAIM WATER project have been detailed, to give an overview of the RISMAR scheme.

5.4.1. Monitoring program in the RECLAIM WATER project

The monitoring program in RISMAR scheme was based on the requirements set in the RECLAIM WATER project. For the project purposes, it was requested to perform basic analysis monthly or at least three sampling campaigns per year during 2006 and 2007, as part of the so-called “Protocol 1” (see Table 8, p. 82), and specific monitoring campaigns for pathogens and organic compounds, as part of “Protocol 2” (see Table 9, p. 83), a minimum of three sampling campaigns during 2006-2007.

Table 8 Protocol 1 parameters analysed at RISMAR scheme.

Basic wastewater analyses	Microbiological analyses	Trace elements analyses	Salinity related analyses
Suspended solids[4] BOD_5 COD[4] DOC Ammonia[4] Nitrite Nitrate[4] Total Nitrogen[1, 4] Phosphorus[4] Alkalinity pH[4] Turbidity[4] Surfactants Phenols Temperature[2, 4] Redox potential[2, 4]	Total bacteria count at 22º Total bacteria count at 37º Total coliforms[4] *E. coli*[4] Enterococci *Clostridium* spores Bacteriophages	Boron Cadmium Chromium Cobalt Copper Fluoride Iron Lead Manganese Molybdenum Nickel Selenium Barium Cyanide Zinc	Chloride Electrical conductivity[4] Sodium Potassium Calcium Magnesium Carbonate Bicarbonate Sulphate SAR[3]

[1] Total Organic Nitrogen was measured as Total Kjeldahl Nitrogen, and Total Nitrogen was obtained by calculation

[2] Not included in Protocol 1, but also measured during the sampling campaigns.

[3] Not included in Protocol 1, but calculated with the data available.

[4] Also measured in the reduced version of Protocol 1.

Table 9 Organic compounds and pathogens analysed at RISMAR scheme as part of Protocol 2. (Note: specific Protocol 2 campaigns included different sets of analyses, as per Table 10).

ORGANICS							
DBPs	**Pharmaceuticals (PhACs)**					**EDCs**	**Antioxidants**
	Antibiotics	Antiepileptics	Antiphlogistics	Contrast media	Lipid regulator		
N-Nitrosodibutylamine (NDBA) N-Nitrosodiethylamine (NDEA) N-Nitrosodimethylamine (NDMA) N-Nitrosomorpholine (NMOR) N-Nitrosopiperidine (NPIP)	Clarithromycin Erythromycin N-Acetyl-sulfamethoxazole Roxythromycin Sulfamethoxazole Sulfadiazine Sulfadimethoxine Sulfamethazine Trimethoprim	Carbamazepine Primidone	Diclofenac Ibuprofen Mefenamic acid Naproxen	Diatrizoate Iohexol Iomeprol Iopamidol Iopromide	Bezafibrate Clofibric acid	Estradiol E2 Oestrone E1 Ethinylestradiol EE2 Bisphenol-A	4-Tolyltriazole 5-Tolyltriazole Benzotriazole

PATHOGENS and ANTIBIOTIC RESISTANCE GENES (ARGs)				
Protozoa	**Bacteria**	**Viruses**	**Helminth eggs**	**ARGs**
Giardia sp. cysts *Cryptosporidium* sp. oocysts	*Salmonella* sp. *Campylobacter* sp. *Yersinia enterocolitica* *Micobacterium avium* subsp. *Paratuberculosis* *Helicobacter pylori*	Enterovirus Norovirus group I Norovirus group II HAV	*Ascaris* sp. *Trichurus* sp. *Ancylostoma* sp. *Necator* sp. *Strongyloides* sp. *Taenia* sp. *Schistosoma* sp.	*ampC* (ampicillin resistance) *mecA* (methicillin resistance) *blaSHV-5* (extended β-lactam resistance) *ermB* (erythromycin resistance) *tet*(O) (tetracycline resistance) *vanA* (vancomycin resistance)

Note: Clofibric acid is not only a lipid regulator, but an herbicide and also an EC.

Table 10 Sampling campaigns and analyses performed at RISMAR scheme. Note: not all the parameters included in each group (see Table 9) were measured at each sampling campaign, especially for Protocol 2 groups.

Date of the sampling campaign	Protocol 1	Reduced Protocol 1	Protocol 2: DBPs	Protocol 2: PhACs	Protocol 2: EDCs	Protocol 2: Antioxidants	Protocol 2: Protozoa	Protocol 2: Bacteria	Protocol 2: Viruses	Protocol 2: Helminth eggs	Protocol 2: ARGs
06/11/2006		√									
20/11/2006	√										
27/11/2006		√									
04/12/2006		√									
11/12/2006	√										
18/12/2006		√									
08/01/2007		√									
15/01/2007	√										
22/01/2007		√						√			√
05/02/2007	√										
26/02/2007		√									
05/03/2007	√										
19/03/2007		√		√	√						
26/03/2007		√					√	√			√
16/04/2007		√									
23/04/2007	√										
07/05/2007		√									
15/05/2007	√										
21/05/2007		√									
05/06/2007	√										
11/06/2007		√									
25/06/2007		√						√		√	√
02/07/2007		√					√	√	√		
09/07/2007	√										
16/07/2007		√	√	√	√						
20/08/2007		√									
27/08/2007	√										
17/09/2007	√										
15/10/2007		√					√	√	√		
22/10/2007	√										
29/10/2007		√								√	√
12/11/2007	√										
19/11/2007		√		√	√	√					
10/12/2007	√										

The analyses included in Protocol 1 are basic wastewater and potable water analyses: microbiological indicators, trace elements and salinity related parameters. These different groups of parameters tested are not usually analysed in all kinds of water, for instance, basic wastewater analyses are performed in untreated and treated wastewater, but do not regularly include salinity, a full set of trace elements or all microbiological indicators. Thus, it was intended to have a global idea on the water quality, applying all groups of parameters to all kinds of waters involved in the MAR and recycled water schemes included in the RECLAIM WATER project. A reduced version of Protocol 1 (see Table 8) was performed once or twice per month, to gather more basic data on the site, and to have a close monitoring during one full year (2007). A summary of the main statistics for the measurement results generated in Protocol 1 sampling campaigns is given in Appendix B (Table B-1 to Table B-14).

The analyses included in Protocol 2 (see Table 9) go one step further, and are focused on more "sophisticated" analyses that are not usually performed in recycled water facilities. These analyses start to be regular for drinking water, and give information on specific hazardous components.

Table 10 (p. 84) lists all the sampling campaigns performed at RISMAR scheme; the date that the sampling was performed and which set of analyses included.

5.4.2. Reclaim Water sampling points

Considering the characteristics of the case study, the following sampling points were selected to monitor the water quality along the system (see Figure 9 for the location of the sampling points and Figure 10 for a picture of the sampling points area). GPS coordinates for each of the sampling points is given in Table 11.

Figure 9 Location of Ripoll River WWTP, sampling points, discharge areas and recovery well at RISMAR scheme.

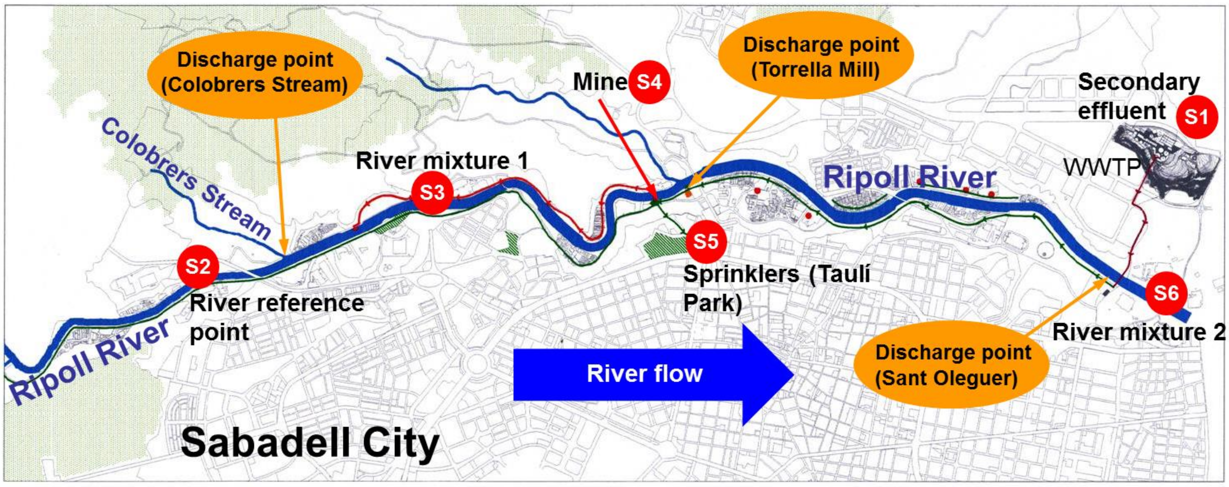


Table 11 GPS coordinates for the sampling points selected.

Sampling points	GPS coordinates
S1: Secondary effluent of the WWTP	41.535133, 2.13727
S2: Ripoll River reference point	41.578101, 2.090857
S3: Ripoll River mixture 1	41.569786, 2.104268
S4: Mine, water recovered from the aquifer	41.558082, 2.113795
S5: Sprinklers from the Taulí Park	41.555738, 2.112422
S6: Ripoll River mixture 2	41.532676, 2.126595

The RECLAIM WATER project asked to monitor a maximum of 5 sampling points, especially regarding Protocol 2 analyses, to fit the budget available. Then, 5 sampling points were selected, but one additional sampling point not reported in the RECLAIM WATER project reports and papers was monitored, in order to understand a bit better how the Ripoll River was affected by the WWTP discharges. This sampling point was S6 (see below).

5.4.2.1. S1: Secondary effluent of the WWTP

This sampling point represents the treated wastewater discharged into the Ripoll River (secondary effluent).

Figure 10 Sampling points selected.


S1: Secondary effluent of the WWTP


S2: Ripoll River reference point


S3: Ripoll River mixture 1


S4: Mine


S5: Sprinklers in the Taulí Park


S6: Ripoll River mixture 2

Grab (S1 S) and composite (S1 C) samples were taken for this sampling point. Composite samples are preferred regarding pollutants (organic and inorganic compounds), but not for microorganisms quantification. Then, in all sampling campaigns a grab and a composite sample were taken. Microbiological parameters were measured only in grab samples, and the other parameters in Protocol 1 with both grab and composite samples. For specific micropollutants sampling campaigns (part of Protocol 2) composite samples were preferred.

It would have been interesting to also monitor the influent of the WWTP, to have a better idea on the WWTP performance. Selected samples from the influent were taken, and information on some basic wastewater parameters was facilitated by CASSA (part of their regular monitoring). WWTP influent data have only been considered in selected sections.

5.4.2.2. S2: Ripoll River reference point

The Ripoll River reference point is located upwards the Colobrers Stream discharge point (see Figure 9).

This sampling point was selected because it is representative of the water that the Ripoll River carries before receiving the treated wastewater discharges. However, at this point, the Ripoll River usually carries a high proportion of water discharged by WWTPs from other municipalities upstream (see section 5.3.3.2). Then, this sampling point it is not indicative of the pristine Ripoll River water quality, but just of the quality right before the Ripoll River WWTP treated wastewater discharges. This sampling point is intended to understand the effect of the treated wastewater discharges on the Ripoll River when it crosses Sabadell municipality and its capacity of diluting/buffering them.

5.4.2.3. S3: Ripoll River mixture 1

The Ripoll River mixture 1 sampling point is located one Km downstream the discharge of treated wastewater in Colobrers Stream area.

This water is a mixture of the water that carries the Ripoll River and the secondary effluent of the Ripoll River WWTP, which is discharged in the Colobrers stream area. Then, this sampling point is intended to be representative of the water that is infiltrated through the riverbed. Although infiltration of Ripoll River water occurs along the whole riverbed, infiltration is increased in the area close to the well location (see section 2.3.1, explanation on RBF process). This is why this sampling point is considered to be representative of the water infiltrated through the riverbed.

On the other hand, the effect of the treated wastewater discharges on the Ripoll River water quality needs to be evaluated too. Then, by comparing the water quality data before the treated wastewater discharge (sampling point S2) against the water quality data after the treated wastewater discharge (sampling point S3) the resulting changes can be determined.

5.4.2.4. S4: Water recovered from the aquifer in the mine

The water is recovered from the aquifer in an old mine installation. This sampling point is representative of the recovered water quality before performing the additional post-treatments. The recovered water is a mixture of the recharged water through the riverbed and the groundwater. The samples were taken before the UV disinfection.

5.4.2.5. S5: Sprinklers from the Taulí Park

This sampling point is representative of the final treated water quality, which is the recovered water after performing the additional post-treatments.

The samples were taken directly from the sprinklers as far as possible, because sprinklers are the final point of use. In some sampling campaigns when sprinklers did not work or there were any other logistic problems, the samples were taken directly from the pipeline sending the water to the storage tank in the Taulí Park. This could be easily done thanks to a tap located close to the chlorine probes.

5.4.2.6. S6: Ripoll River mixture 2

This sampling point is located after the last discharge area, which is close to the Ripoll River WWTP (Sant Oleguer).

This discharge point is only used when there are storm surpluses and/or the Ripoll River WWTP cannot treat all the received water. Nevertheless, untreated wastewater is usually not discharged. This point represents the Ripoll River water quality after all discharges.

This sampling point was not part of the RECLAIM WATER project, but data were gathered in order to have an additional point in the Ripoll River and understand its quality after all discharges. For this sampling point the data available do not include Protocol 2 analyses, just Protocol 1 analyses.

5.4.3. Other sources of data used for the risk assessment

For the purposes of the risk assessment, the data generated in the framework of the RECLAIM WATER project have been used. However, for some hazardous compounds data were not available or they were not enough, and other sources of data have been used. These alternative sources of data were:

- CASSA: They facilitated basic data on the influent and secondary effluent quality, as well as volumes of water treated at the WWTP.
- EDS and CASSA analyses of the groundwater and recycled water: Additionally, and to have data for quality parameters that requested attention and that were not measured in the framework of the RECLAIM WATER project, results from analyses requested by CASSA or EDS to external laboratories have been also used. These results were employed in order to cover some of the hazards evaluated in the risk assessment section and to compare with the data obtained during the Reclaim Water sampling campaigns.
- ACA analyses from Ripoll River water and groundwater: ACA performs periodically analyses from the groundwater and the Ripoll River water, in the framework of its continental waters monitoring. These data are available in ACA's website (ACA, 2013), and have also been used in order to cover some of the hazards evaluated in the risk assessment section and to compare with the data obtained during the Reclaim Water sampling campaigns.

5.5. Risk assessment for the different hazards

A deterministic risk assessment has been performed for all hazards according to procedures recommended in the MAR guidelines (NRMMC–EPHC–NHMRC, 2009) and Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006), considering the recycled water uses explained in section 5.3.4, the routes of exposure identified in section 5.3.6 and the different end points and receiving environments of the recycled water as per section 5.3.5. A separate probabilistic risk assessment has been performed for human pathogens, and is given in section 6.

The hazardous compounds, characteristics and circumstances to human health and/or the environment considered for the purposes of the risk assessment and which are listed and explained in the MAR guidelines (NRMMC–EPHC–NHMRC, 2009) are:

- Pathogens.
- Inorganic chemicals.

- Salinity / Sodicity (for the purposes of the present work, it will be dealt with as SAR and infiltration problems).
- Nutrients.
- Organic chemicals.
- Turbidity / particulates (more widely known as suspended solids).
- Radionuclides.
- Pressure, flow rates, volumes, water levels.
- Contaminant migration through preferential flow paths.
- Aquifer dissolution and stability.
- Aquifer and groundwater dependent ecosystems.
- Energy and greenhouse gases.

The risks arising from these twelve hazardous compounds, characteristics and circumstances are assessed in the present section. It is to consider that not all of the hazardous compounds, characteristics and circumstances apply to all parts of the recycled water scheme and the different end points.

5.5.1. Approach used for the risk assessment

The risk assessments were performed according to procedures recommended in the MAR guidelines (NRMMC–EPHC–NHMRC, 2009) and Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006).

The maximal risk assessment was undertaken considering that the secondary treated wastewater was used instead of the final treated water for the different end uses. The mean and 95th percentile values of each water quality parameter for the secondary treated wastewater (see tables Table B-1 to Table B-4 in Appendix B for these values) were compared with the guideline values explained in this section for each of the different uses and end points and the results are summarised in Table 16. The residual risk assessments were performed in the same way as the maximal risk assessment but considering the different treatment barriers of the recycling system: dilution with the Ripoll River water, infiltration through the riverbed and recovery and post-treatments (see tables Table B-5 to Table B-12 in Appendix B for the mean and 95th percentile values of each water quality parameter in the Ripoll River water before and after the discharges, the groundwater and the final treated water).

For the guideline values used, most of them were taken from regulations and guidelines. In some cases, some search had to be conducted in order to set a guideline value, as they were not available in regular sources. Then, the approach taken for some pharmaceutically active compounds was to use their lower therapeutic dose, available in the vademecum (Vademecum, 2014). For some others, the guideline value has been calculated considering ADIs/NOAELs published and using the formulas and methods explained in the Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies (NRMMC–EPHC–NHMRC, 2008), as noted in section 4.4.

5.5.2. Pathogens, indicators and antibiotic resistance genes

Pathogens pose a risk for the human health, and can also cause havoc in plants, crops and animals. They are one of the most important hazards in a recycled water scheme and need to be monitored and managed. Even though their importance, pathogens monitoring is not an easy task, and it is time consuming and expensive (Salgot and Huertas, 2006). Instead, indicators have been widely used to track the possible presence of pathogens.

The relationship between pathogens and indicator microorganisms present in water has been the object of many studies (e.g. Brookes *et al.*, 2005; Costan-Longares *et al.*, 2008; Ferguson *et al.*, 1996; Harwood *et al.*, 2005; Havelaar *et al.*, 1993; Savichtcheva and Okabe, 2006; Schijven *et al.*, 2003; St-Pierre *et al.*, 2009; Wéry *et al.*, 2008; Wilkes *et al.*, 2009). Although the general opinion is that indicators correlate fairly well with the presence of pathogens, some authors declare not having found any correlation and claim the necessity of performing a direct monitoring of pathogens. In any case, some pathogens and indicators have been monitored at RISMAR scheme, and the results obtained have been discussed and assessed in the present section.

Antimicrobial resistance is a global concern for animal and human health. Antibiotic resistance genes (ARGs) can be detected in wastewater of clinical origin but also in domestic wastewater, so they can be spread in the environment due to the recycled water schemes (Auerbach *et al.*, 2007; Böckelmann *et al.*, 2009; Figueira *et al.*, 2011; Łuczkiewicz *et al.*, 2010; Servais and Passerat, 2009). Recently, there has been increasing interest in resistant bacteria and resistance genes isolated from wildlife and the environment (Allen *et al.*, 2010; Allen *et al.*, 2011). Considering that the use of antibiotics among the population has grown in the recent years, and antibiotics and their metabolites are excreted by their consumers to the wastewaters, ARGs can be easily found in recycled water schemes. Six ARGs were monitored in the framework of the RECLAIM WATER project in the recycled water scheme at RISMAR, and the results obtained are discussed and assessed in the present section.

At RISMAR scheme, indicators were monitored in six sampling points (all but composite samples of the effluent, S1 C), whereas pathogens and ARGs were monitored at five sampling points (all but composite samples of the effluent, S1 C, and river mixture 2, S6). For pathogens and ARGs the RECLAIM WATER project requested to measure a maximum of five sampling points, due to budget adjustments.

5.5.2.1. Human pathogens

Pathogens were investigated at RISMAR scheme as part of the RECLAIM WATER project in two or three sampling campaigns, depending on the pathogen. Results obtained have already been published in Böckelmann *et al.* (2009) and Levantesi *et al.* (2010). Pathogens monitored were:

- Bacteria: *Campylobacter*, *Salmonella* spp., *Yersinia enterocolitica*, *Helicobacter pylori* and *Mycobacterium avium* subsp. *paratuberculosis*.
- Viruses: enteroviruses, Hepatitis A virus, norovirus GGI and GGII.
- Protozoa: *Giardia* cysts and *Cryptosporidium* oocysts.
- Helminth eggs: *Ascaris lumbricoides*, *Trichurus trichiura*, *Ancylostoma duodenale*, *Taenia* spp., among others.

Typical illnesses caused by these pathogens are detailed in Table 2.

5.5.2.1.1. Bacterial human pathogens

Most bacterial pathogens potentially transmitted by water infect the human gastrointestinal tract, typically causing gastroenteritis, diarrhoea that ranges from mild and non-bloody to highly bloody, haemolytic uremic syndrome (produced by Enterohaemorrhagic *E. coli*), fever, nauseas and vomiting among other. To a lesser extent, they can cause respiratory, dermal and nosocomial infections, being these ones considered as caused by opportunistic bacteria (see Table 2 for a detailed list of bacterial pathogens and their related diseases). They are regularly excreted in the faeces of infected humans and other animals. However, there are also some waterborne bacterial pathogens, such as *Legionella*, *Burkholderia pseudomallei* and atypical mycobacteria, which can grow in water and soil. The routes of transmission of these bacteria include inhalation and contact (bathing), with infections occurring in the respiratory tract, skin lesions or brain (WHO, 2011a). Pathogenic bacteria are usually characterised by an elevated infectious dose (10^2–10^9 cells) and are less resistant than protozoa and viruses to traditional disinfection treatments. The bacteria selected for monitoring in this work are well-known by their long-term survival in the environment (Ashbolt, 2004: Lehtola *et al.*, 2007).

Pathogenic bacteria were detected at RISMAR scheme during summer 2007 campaigns: *Campylobacter* was detected in the river water before the discharges (S2; July 2, 2007), while *Salmonella* gene copies were found at all the analysed sampling points (June 25, 2007). *Salmonella* concentration ranged from $1.2\text{x}10^2$ gc/100mL (final treated water, S5) to $2.1\text{x}10^3$ gc/100mL (river mixture 1, S3). *Salmonella* was also found in the secondary treated effluent (S1 S) in March 28, 2007 but the concentration was below the quantification limit. Quantitative PCR can detect the DNA of viable and non-viable cells, as well as the remains of extracellular DNA; therefore, the positive amplification of *Salmonella* genes in all sampling points, even if at high level, does not imply a direct risk for the public health, as they can be not viable cells. It would have been interesting to monitor also *Salmonella* by traditional culture methods, in order to determine the presence of viable cells at RISMAR scheme. Other pathogenic bacteria investigated at RISMAR scheme in the framework of the RECLAIM WATER project (*Mycobacterium avium* subsp. *paratuberculosis, Yersinia enterocolitica* and *Helicobacter pylori*) were not detected.

Legionella is a bacterial pathogen regulated in the Spanish RD for water reuse (BOE, 2007b). This pathogen could pose a risk as it propagates by aerosols, which can be formed due to the sprinkler irrigation systems. *Legionella* was regularly analysed by external laboratories, commissioned by CASSA and EDS. The results were always lower than the LOD, which was 50 cfu/L or 25 cfu/L, depending on the laboratory. Then, these results would fulfil the Spanish water reuse RD requirements for the different uses but for industrial reuse in cooling towers. In this particular case, the Spanish water reuse RD requires absence of the pathogen in 1 L sample, which cannot be ensured with the limit of detection that these laboratories have. Then, in order to use the recycled water for cooling towers, not only an especial permit from the Health Department but also a method with a lower LOD for *Legionella* measurement would be necessary. This use, however, is not in place at RISMAR scheme, so it does not represent a risk.

Pseudomonas aeruginosa is a pathogen requested in the RD for swimming pools water quality (BOE, 2013), and it is requested its absence in 100 mL. This pathogen was not analysed by any external laboratory neither the RECLAIM WATER project. As the RD came into force on October 2013 and the swimming pool where the water is reused is only open during summer, for the next summer 2014 this pathogen should be measured in order to fulfil the RD.

The other bacterial pathogens analysed in the framework of the RECLAIM WATER project are not directly requested in the Spanish legislation. However, in case the guideline values for *Escherichia coli* (a bacterial indicator, see section 5.5.2.2) given in the Spanish water reuse RD are not fulfilled in a certain number of samples, then it is requested to measure *Salmonella* (and other pathogens, even though only *Salmonella* is cited) for agricultural water reuse and industrial use in food industry.

5.5.2.1.2. Viral human pathogens

Viruses associated with waterborne transmission are predominantly those that can infect the gastrointestinal tract, and to a lesser extent, the respiratory one. Similarly to bacterial waterborne pathogens, they cause gastroenteritis and diarrhoea, as well as respiratory diseases. But viruses can cause also other important diseases like meningitis, poliomyelitis and hepatitis (see Table 2 for a detailed list of viral pathogens and their related diseases). They are excreted in the faeces of infected humans, thus can contaminate water and can be ingested through aerosols. With the exception of hepatitis E virus, humans are considered to be the only source of human infectious species. The presence of viruses in reclaimed water is of high concern due to their relatively low infectious dose (1–10 median infectious dose) and their elevated survival in the environment (Asano *et al.* 2007; WHO, 2011a).

For viruses, one sampling campaign performed on October 15, 2007 monitored their presence in the five sampling points selected, and another sampling campaign on July 2, 2007 only in the aquifer (S4) and the final treated water (S5). None of the viruses investigated (enteroviruses, Hepatitis A virus, norovirus GGI and GGII) could be detected in any of the sampling campaigns, even though high volumes of water were filtered and concentrated (up to 500 L in the final treated water).

Virus analysis is not requested in the Spanish legislation. US EPA drinking water regulations (US EPA, 2009) request a 99.99% removal, but not indicating any specific virus or family to investigate. From the analytical point of view this is difficult to demonstrate, as it requires large volumes of water to be analysed. At RISMAR scheme, only the recovered water and the final treated water were analysed, so treated effluent should have been measured, in order to evaluate if this guideline value is fulfilled. However, viral indicators were also analysed, and their removals are discussed in section 5.5.2.2.

5.5.2.1.3. Protozoan human pathogens

The protozoa *Giardia* and *Cryptosporidium* are indicated by the WHO (2011a) as waterborne pathogens of primary concern and are reported as one of the most common causes of waterborne gastroenteritis outbreaks. Typical diseases caused by protozoa are diarrhoea and dysentery (see Table 2 for a detailed list of protozoan pathogens and their related diseases). The control of their waterborne transmission presents real challenges, because most of those pathogens produce cysts and oocysts that are extremely resistant to processes generally used for the disinfection of water and in some cases can be difficult to remove by filtration processes. Besides, their infective dose is regularly low (1-25 oocysts/cysts median infective dose). Among other species *Cryptosporidium parvum* and *Giardia lamblia* are infectious for humans. A large range of animals are reservoirs of *C. parvum*, being humans and livestock, particularly young animals, the most significant source of human infectious organisms (Asano *et al.*, 2007).

Giardia cysts and *Cryptosporidium* oocysts were commonly detected at RISMAR scheme (80% and 66% of the total samples respectively), and both protozoa were detected in the recovered water (S4) at RISMAR scheme. In March 28, and July 2, 2007 *Giardia* cysts were present in the recovered water at concentrations of 0.07 and 0.01 cyst/L respectively, while *Cryptosporidium* oocysts were only found in the recovered water on March 28, 2007 at a concentration of 0.01 oocysts/L. Protozoa cysts and oocysts were never detected in the final treated water (S5) with the volumes tested (at least 100L filtered during each sampling campaign). In addition to groundwater, cysts and oocysts were both detected in all secondary effluent samples and nearly all river water samples.

Measured concentrations could vary one order of magnitude or more in the same sampling point. For instance, *Giardia* cysts in the river water mixture 1 (S3) varied from 0.39 to 6.2 cysts/L, and in the treated wastewater (S1) varied from 0.55 to 5.5 cysts/L. Curiously, in the river reference point (S2) *Giardia* cysts concentrations were more steady, ranging from 1.2 to 4.0 cysts/L, an indication that the presence of protozoan pathogens in the infiltration water it is not only due to the treated wastewater discharges of the Ripoll River WWTP. A different behaviour was found for *Cryptosporidium* oocysts. The treated wastewater (S1) seemed to be the major source for them, and concentrations ranged from 0.091 to 6.5 oocysts/L, while in the river water mixture 1 (S3) the concentrations ranged from no detection in 23.3 L (< 0.043 oocysts/L) to 0.11 oocysts/L, and in the river reference point (S2) from 0.015 to 0.097 oocysts/L. The values obtained indicate a dilution, sedimentation and/or inactivation of the *Cryptosporidium* oocysts when mixing the treated effluent with the river water.

Protozoa analysis is not directly requested in the Spanish legislation. However, in case both guideline values for *Clostridium perfringens* and turbidity given in the Spanish drinking water RD are not fulfilled, then it is requested to measure *Cryptosporidium* and other microorganisms or parasites that Health authorities may request. US EPA drinking water regulations (US EPA, 2009) request to measure *Giardia* and *Cryptosporidium*, and instead of giving a guideline value for them it is requested a 99.9% removal/inactivation for *Giardia lamblia* and a 99% removal for *Cryptosporidium*. Applying these guideline values to our case, the treatment train at RISMAR scheme would fulfil the removals in most of the sampling campaigns, but a much higher volume of final treated water than the one that was analysed (S5, 100L in each sampling campaign) should be considered in those sampling campaigns where the source water (treated wastewater) has already a low concentration of these pathogens, in order to fulfil the removals. Practically, this is very difficult to achieve.

5.5.2.1.4. Helminth eggs human pathogens

Worldwide, enteric worms are one of the principal causative agents of human disease. It is estimated that 133 million people suffer from high intensity intestinal helminths infections, affecting principally underdeveloped countries. They regularly cause gastroenteritis and diarrhoea, and also specific diseases for each of them (see Table 2 for a detailed list of helminthic pathogens and their related diseases). Helminth eggs can be removed by many wastewater-treatment processes such as sedimentation, coagulation and flocculation, filtration, stabilization ponds and wetlands (NRMMC–EPHC–AHMC, 2006). However, some helminth eggs are extremely resistant to environmental stresses and may survive conventional wastewater treatments and disinfection processes. Helminth eggs are more persistent than viruses and bacteria, and immunity generally does not develop readily in early life (Campos, 2006).

Helminth eggs were not detected in any of the three full sampling campaigns and preliminary testing campaigns performed at RISMAR scheme. Helminth eggs were additionally investigated in influent water, in order to prove the efficiency of the recovery method. In that case, many helminth eggs from different species could be detected (data not shown).

Among the different pathogens monitored, helminth eggs are the only ones for which the Spanish water reuse RD sets a guideline value. The limit set for the uses contemplated is 1 helminth egg in 10 L. For all sampling points and sampling campaigns, this guideline value was met, as no helminth eggs were detected in 50 or 100 L (depending on the sampling point evaluated), thus not posing a risk for the human health.

5.5.2.1.5. Overall results for human pathogens

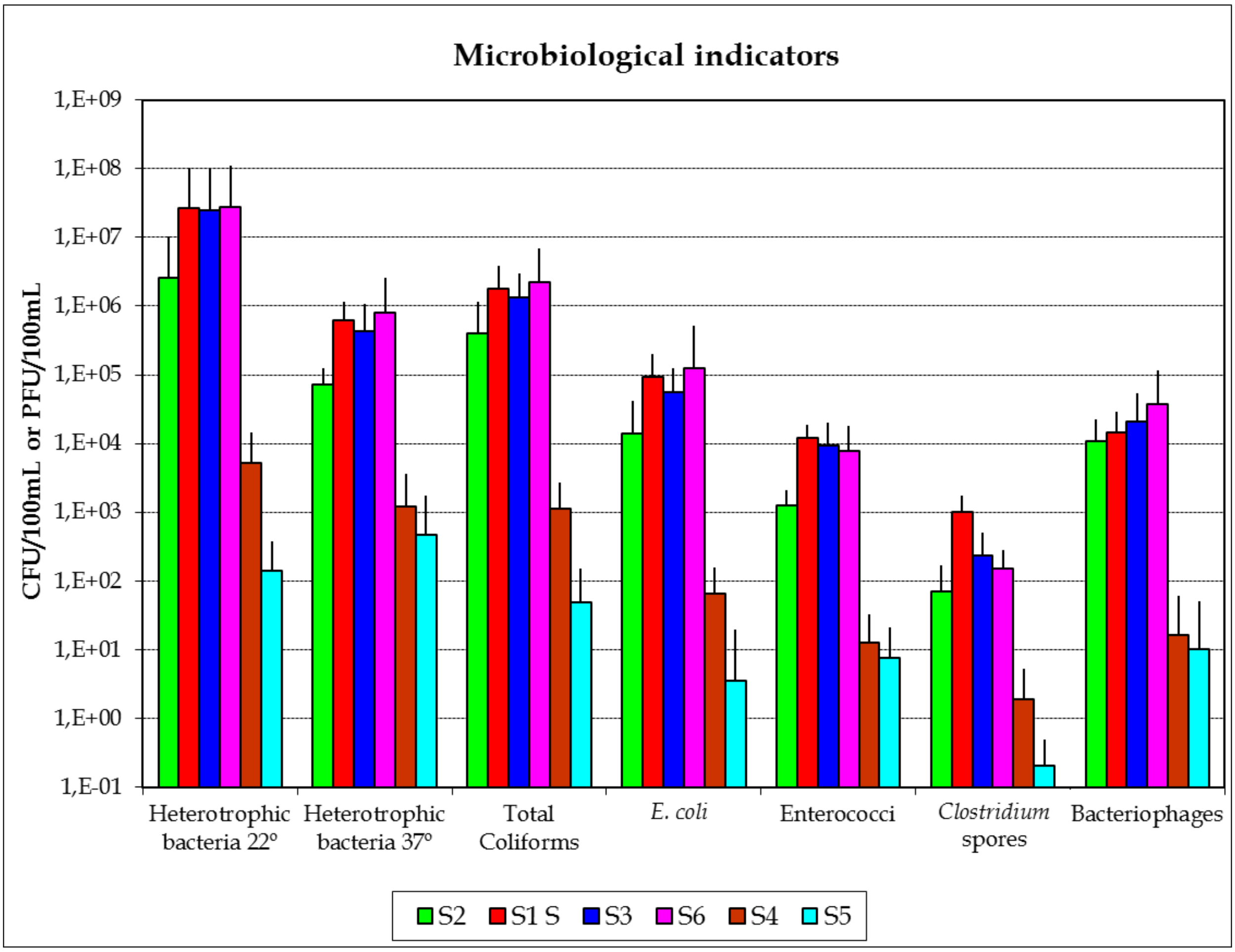
Overall, pathogens analysis showed a low river water quality at the river reference point (S2). The presence of *Salmonella*, *Campylobacter* and parasites in the river water is likely due to the discharge of two WWTPs upstream this sampling point. Only a minor effect on reduction of pathogens concentration was observed by mixing and dilution and/or inactivation of the secondary treated effluent with the river water. Riverbed filtration appeared to have a role in parasite reduction at RISMAR scheme: from SP3 to SP4 several orders of magnitude decrease in (oo)cysts numbers were observed in all the sampling campaigns. Other pathogens measured and not detected were viruses. Then, although all these pathogens are not regulated in the water recycling and drinking water Spanish legislation, it seems clear that further investigation of the RISMAR scheme is necessary, in order to properly evaluate the risk posed to the human health, and to also understand the effect of the different treatments in the pathogens reduction.

5.5.2.2. Indicator microorganisms

As pathogens analysis has an elevated cost and is time-consuming, indicators were measured as well, and they could be measured in a higher number of sampling campaigns. Besides, Spanish legislation and other guidelines set reference values for indicator microorganisms, which need to be fulfilled for the different recycled water uses considered.

Indicators monitored in the framework of the Reclaimed Water project included: heterotrophic plaque counts at 22ºC, heterotrophic plaque counts at 37ºC, total coliforms, *Escherichia coli*, enterococci, *Clostridium* spores and somatic coliphages.

Figure 11 Mean and standard deviation values obtained for the indicator microorganisms measured at the different sampling points.



Results obtained for these microorganisms are graphically summarized in Figure 11. When reporting the results, quite often there were no detections for a certain indicator and sample, especially regarding the final treated water. Then, for the purposes of the graphic and the statistical calculations, the LOD was reported and used instead.

In Figure 11 a similar tendency followed by all indicators tested can be observed: the treated effluent (S1 S) is an important source of microorganisms, presenting a concentration of around one order of magnitude more than the river before the discharges (S2), and the dilution in the river (S2 vs. S3 and S6) does not seem to be strong enough to buffer the discharges, although some dilution is observed. On the other hand, there is a strong decrease after infiltration through the riverbed to the aquifer. Post-treatments, including disinfection, have a different effect depending on the indicator tested.

In order to better evaluate the effect of the different barriers present at RISMAR scheme, in Table 12 their efficacy has been measured by calculating the $\log_{10}$ reductions for each of them and for each indicator. The minimum, average and maximum calculated $\log_{10}$ reductions for each indicator are given in Table 12. Similarly to what it has been observed in Figure 11, when discharging the secondary effluent (S1) to the Ripoll River the mixture water (S3) does not suffer a marked dilution effect, and often the microbiological load increases. Only for

Clostridium spores there is always a dilution when the effluent is discharged into the Ripoll River. Overall, the average log$_{10}$ reductions when discharging the treated wastewater to the river are positive, indicating that indeed certain dilution occurs. Opposite to what happens to the dilution in the river, all of the microbiological indicators evaluated were significantly reduced after aquifer recharge, with average reductions ranging from 2.46 to 3.61 log$_{10}$ units. In this case, the indicators that suffered the highest average reductions were heterotrophic bacteria at 22°, closely followed by total coliforms (that have also the highest maximum reduction, with 6.09 log$_{10}$ units) and bacteriophages. The indicator that suffered the lowest average reductions was *Clostridium* spores (2.46 log$_{10}$ units). Even though the high removal rates obtained during the infiltration, bacteria were still present in the recovered water, so the subsurface treatment itself was not enough to reduce the microbiological load of the recovered water for reuse. Then, the disinfection step is necessary as part of the whole reuse system. The disinfection treatment applied after recharge consists on UV + chlorination, coupled to a sand filter that removes particles and may also reduce some microorganisms at the same time. The whole disinfection treatment is able to reduce between 0.30 and 2.00 log$_{10}$ units on average being the indicators still present in the recovered water. This reduction is relatively low probably due to a not very effective UV treatment and contamination in the distribution system. The highest disinfection log$_{10}$ units removal was observed for the total coliforms, *E. coli* and heterotrophic bacteria at 37°C, but in general, average reductions were low. *Clostridium* spores, which are usually very resistant to UV and chlorination, were barely reduced (0.50 log$_{10}$ units on average). However, it must be also pointed out that the amount of *Clostridium* spores in the recovered water was very low or under the LOD most of the times, which made difficult the removal calculations. Enterococci suffered the lowest reduction by the disinfection process of all the indicators investigated, with an average reduction of 0.31 log$_{10}$ units. Enterococci are in fact good indicators of the efficacy of the disinfection systems, as they are very resistant to them. According to the results obtained, it seems rather clear that the disinfection system should be improved and closely monitored. In fact, after the RECLAIM WATER project, the UV treatment was replaced by a new one including a more potent lamp.

Table 12 Log$_{10}$ removals achieved at the different treatment points (Note: log$_{10}$ differences calculated in each sampling).

Microbiological indicators	**Dilution in the river** **log$_{10}$S1-log$_{10}$S3**			**MAR (riverbed filtration)** **log$_{10}$S3-log$_{10}$S4**			**Disinfection** **log$_{10}$S4-log$_{10}$S5**		
	min	**av**	**max**	**min**	**av**	**max**	**min**	**av**	**max**
Heterotrophic Bacteria (22 °C)	-0.64	0.31	1.53	2.39	3.61	4.87	-0.027	1.45	2.38
Heterotrophic Bacteria (37 °C)	-0.33	0.49	1.90	0.74	2.83	4.47	-1.21	1.02	3.03
Total Coliforms	-0.97	0.23	1.56	1.65	3.44	6.09	-0.61	2.00	4.07
Escherichia coli	-0.99	0.54	3.69	1.20	3.08	4.91	0.00	1.49	3.18
Enterococci	-0.58	0.42	1.85	1.19	3.17	4.36	-1.69	0.31	1.95
Clostridium spores	0.24	0.85	2.17	0.057	2.46	3.50	0.00	0.50	2.04
Bacteriophages	-1.27	0.066	1.46	0.91	3.43	5.14	-0.30	0.96	2.70

Note: negative values indicate that there is not a decrease but an increase in the microorganism concentration.

Escherichia coli is the most widely used indicator in regulations and guidelines. For all the uses contemplated in the Spanish water reuse RD (BOE, 2007b) there is a guideline value set, as shown in Table 4 (p. 65). *E. coli* measured concentrations (see Appendix B) at the secondary effluent of the WWTP (S1 S) and the river water before (S2) and after the discharges (S3, S6) would not be acceptable for any of the uses contemplated. If the mean or median result is considered, the aquifer water (S4) would be acceptable for unrestricted urban reuse, crop irrigation and industrial reuse excluding cooling towers; if the 95th percentile results are considered, only the industrial reuse excluding cooling towers would be acceptable. The final treated water (S5), whether using the mean, the median or the 95th percentile results, would be acceptable for unrestricted urban reuse, crop irrigation and industrial reuse excluding cooling towers. However, the final treated water would not be acceptable as drinking water or bathing water (swimming pools). Thus, regarding *Escherichia coli* indicator, the final treated water would not be suitable for all the uses considered. Other water reuse regulations and guidelines considered (see Appendix E) set similar guideline values for the uses considered, or even more restrictive depending on the case (US EPA, 2012).

Enterococci, *Clostridium perfringens*, heterotrophic bacteria counts at 22° and total coliform indicators are requested in the Spanish drinking water RD (BOE, 2003). The final treated water (S5) would only meet the heterotrophic bacteria counts at 22° guideline value, while the other sampling points would not meet any of the guideline values. It must be considered that in the case study *C. perfringens*, which is the indicator requested in the Spanish drinking water RD, was not measured, but *Clostridium* spores was measured instead. In any case, the final treated water does not meet the Spanish drinking water RD guideline values.

Enterococci are required to be measured in WHO and Australian recreational water guidelines (NHMRC, 2008; WHO, 2003a). The guideline value set in those guidelines (35 and 40 ufc/100 mL, respectively) would be fulfilled by the final treated water (S5) and the aquifer water (S4). For heterotrophic bacteria counts at 22° the guideline value set in the US EPA drinking water regulation is less restrictive than the Spanish RD ($5x10^4$ vs. 10^4 cfu/100 mL), then it would be widely fulfilled by the final treated water.

To sum up, regarding indicators, the final treated water would not meet all the guideline values set in the Spanish regulation for the uses considered at RISMAR scheme, neither for drinking water.

5.5.2.3. Antibiotic resistance genes (ARGs)

Antibiotics are released daily into the natural environment, by means of treated/untreated wastewater and through use in animal husbandry (Auerbach *et al.*, 2007). Many of these antibiotics can now be detected in water resources (Koike *et al.*, 2007; Kolpin *et al.*, 2002; Kümmerer, 2004; Lindsey *et al.*, 2001; Yang and Carlson, 2003) and have been also monitored in the framework of the RECLAIM WATER project (Asmin *et al.*, 2007). The presence of antibiotics in the environment causes increasing concerns, as they can trigger the creation of resistances that will be transferred to populations of pathogenic, commensal and non-pathogenic microorganisms (Auerbach *et al.*, 2007). Then, although antibiotic resistant genes (ARGs) are not the object of any regulation or guidelines, they were monitored in the framework of the RECLAIM WATER project, in order to gather information on their presence in the recycled water and MAR systems.

Six different ARGs with different mechanism of action were selected in the RECLAIM WATER project, due to their abundance and reported increase of their presence in resistant microorganisms in the environment (Auerbach *et al.*, 2007; Chee-Sanford, 2001; Esiobu *et al.* 2002; Ferreira da Silva *et al.* 2006; Kümmerer, 2004; Sengelov *et al.* 2003; Smith *et al.* 2004). The ARGs were monitored in four sampling campaigns (La Mantia *et al.*, 2008a) and the results were published in Böckelmann *et al.* (2009). The following resistance genes were chosen and measured at RISMAR scheme:

- *ampC* (ampicillin resistance): confers resistance to third generation or extended spectrum cephalosporins, e.g. ceftazidime and cefotaxime; additionally, it confers resistance to penicillins.
- *mecA* (methicillin resistance): mecA mediates resistance to methicillin and oxacillin. All methicillin-resistant *Staphylococcus aureus* strains encode the mecA gene.

- *blaSHV-5* (extended β-lactam resistance): encodes an extended spectrum β-lactamase, conferring resistance to expanded spectrum cephalosporins and aminoglycosides. It is often found in multi-resistant *Klebsiella pneumoniae* strains.
- *ermB* (erythromycin resistance): resistance gene conferring macrolide resistance, it is often present in streptococci, e.g. in *S. pneumoniae.*
- *tet(O)* (tetracycline resistance): conferring resistance to tetracyclines, it is commonly found, including environmental samples, and it is present in both Gram-positive and Gram-negative bacteria.
- *vanA* (vancomycin resistance): conferring resistance to vancomycin, the vanA gene is responsible for vancomycin resistance in vancomycin resistant *S. aureus* strains.

All these resistant genes but *vanA* were detected at least once at RISMAR scheme, and three of them (*tetO*, *ermB* and *mecA*) in the final treated water (S5), showing their persistence in the environment. The most common ARG detected at RISMAR scheme was *tetO*, which was present in 70% of the total samples, and it was detected on three out of four sampling campaigns at concentrations ranging from 4.3x10^3 to 9.2 x10^6 gc/100 mL. The second most common ARG was *ermB*, detected in 50% of the samples. It was present in January 22, 2007 in all the samples except the final treated water (S5), in March 28, 2007 in all the samples and in June 25, 2007 only in the treated wastewater (S1 S). For *ermB*, concentrations ranged from 9.5x10^2 to 2.6 x10^6 gc/100 mL. A decrease of *tetO* and *ermB* concentrations was observed along the treatment train at RISMAR scheme. For *mecA* its detection was in the January 22, 2007 sampling campaign in all sampling points (25% of the total samples), being the highest value for the river reference point (S2; 1.4 x10^5 gc/100 mL). The ARG *blaSHV-5* was found in all the samples except the final treated water (S5) in March 28, 2007 with a similar number of copies, and in January 22, 2007 and in June 25, 2007 it was only detected in one sample of each campaign (the aquifer water and treated wastewater, respectively). Finally, *ampC* was only detected in two samples, in the river mixture 1 (S3) on January 22, 2007 and in the treated effluent (S1 S) in June 25, 2007.

By comparing the results from the different sampling campaigns across the year with consumption of antibiotics it appears that there is a correlation with the occurrence of ARGs. Higher consumption rates of antibiotics in winter are consistent with the higher concentrations of ARGs in the water during that period (January and March). Some antibiotics were monitored in the case study (see section 5.5.6.3), but only erythromycin is linked to the ARGs monitored. The highest concentrations were detected in Ripoll River WWTP effluent, with a maximum concentration of 463 ng/L (McArdell *et al.*, 2008), and being below the LOD in the final treated water. In any case, the maximum concentration detected in the secondary effluent is far below concentrations inducing resistance development in bacteria and also far below concentrations increasing gene transfer frequencies. Ohlsen *et al.* (2003) measured erythromycin concentrations up to 0.027 mg/L and ciprofloxacin concentrations up to 0.051 mg/L in wastewater, which are much higher than the ones measured at RISMAR scheme, and at these higher concentrations the plasmid transfer frequencies of staphylococci resistance plasmids did not increase.

Although the measured concentration of erythromycin seems not to be enough to increase the transfer frequencies for plasmids containing resistance genes, three resistance genes could be detected in the final treated water, always at lower number of gene copies than in the secondary effluent, the river water or the aquifer. These resistance genes can come from the Taulí Hospital wastewater, which even though is treated before being discharged to the sewers, may contain these resistance genes in high concentrations as well as very high antibiotic concentrations. Then, the final treated water used for irrigation of the Taulí Park, which is located by the Taulí Hospital, can spread these resistance genes in the population and the environment.

Considering the results obtained, it would be necessary to better understand the gene transfer frequency and the ecology of the bacteria transferring these genes to better evaluate the risk in human population and if antibiotic resistance genes should start to be monitored in recycled water schemes in a regular basis.

5.5.2.4. Plant pathogens

Plant pathogens can cause many problems to crops and trees development. Although there are not guideline values or regulations regarding plant pathogens in recycled water or any other kind of water, it is interesting to dedicate a short section on this.

Examples of specific plant pathogens that may be found in irrigation water are given in Table 9.2.4 of the Australian irrigation guidelines (ANZECC and ARMCANZ, 2000). No guideline values exist for acceptable levels of plant pathogens in irrigation water. However, the irrigation method is more critical than the actual amount present (ANZECC and ARMCANZ, 2000), as most pathogens require high humidity to develop (e.g. *Phytophthora*).

Published data shows presence of plant viruses, bacteria and fungi in wastewater as well as in other kinds of water (Armon *et al.*, 1995; Harrison *et al.*, 2008; Hong and Moorman, 2007; Mehl and Epstein, 2008; Stewart-Wade, 2011). In 1995, Armon *et al.* studied the survival of the bacterium *Erwinia carotovora* in soils after detecting it in reclaimed water used for crop irrigation. Mehl and Epstein (2008) detected the presence of *Fusarium solani*, a fungal pathogen of both humans and plants, in wastewater and community shower drains, although it was undetectable after the basic WWTP processes. Zhang *et al.* (2006) found plant pathogenic viruses in human faeces, suggesting that humans may act as a vehicle for the dissemination of plant viruses. Besides, Rosario *et al.* (2009) proposed the Pepper Mild Mottle Virus as an indicator of human faecal pollution in their work, as this plant pathogen is widespread and abundant in wastewater from the United States.

Although there is no data available on plant pathogens in the riverbed filtration and recycled water scheme at RISMAR scheme, a similar removal to the one suffered for the human pathogens can be expected. For the viruses, a large reduction is expected similar to that observed for human viral pathogens, which could not be detected in huge volumes of final treated water. Hence, for the purposes of the present risk assessment, it is assumed that plant pathogens should pose a low risk for the crops, although no data on plant pathogens is available to support this assumption.

5.5.2.5. Summary of results

Overall, the quality of the final treated water would be adequate for crop irrigation, unrestricted urban reuse (urban park irrigation and street cleaning purposes) and industrial reuse but for cooling towers, considering the requirements of the Royal Decree for water reuse in Spain. The quality of the final treated water would not be enough for drinking water and bathing water purposes, regulated in other Royal Decrees.

Although the pathogens and indicators data obtained are very useful to compare it with the Spanish legislation, it is not possible to quantitatively determine the risks to human health by solely assessing the reduction of the investigated pathogens along the treatment train in three or four sampling campaigns, and the indicators behaviour in several more campaigns. Therefore, a probabilistic quantitative microbial risk assessment was performed to address the risk posed by pathogens. Methodology and results obtained are given in sections 4.3 and 6.

Regarding antibiotic resistance genes and plant pathogens, more information on the recycled water scheme as well as scientific development would be necessary to properly assess the risks posed.

5.5.3. Inorganic compounds

For most of the hazards (both inorganic and organic) found in wastewater there are human health guideline values set, which indicate the acceptable level if found in a drinking water supply. Several of the inorganic elements for which guideline values have been established are recognized to be also essential elements in human nutrition (WHO, 2011a). Then, it is important to have fiable guideline values to consider if they are toxic or not for the human health, the flora and the fauna. For the purposes of the risk assessment, exposure and guideline values used, explanation of its importance, availability and presence in water and soils, as well as other important characteristics, the Australian Irrigation Water Guidelines (ANZECC-ARCAMZ, 2000) have been mostly used. Even though inorganic compounds literature is extense, often it is difficult to find all the information in a document, especially regarding guideline values, which are necessary for the risk assessment purposes. These guidelines, together with other guidelines used, fulfil these requirements.

Salinity related compounds, which are also inorganic compounds, are discussed in section 5.5.4.

5.5.3.1. Aluminium

Aluminium can be toxic to plants, animals and human. Aluminium metal does not occur naturally, but aluminium is found in abundance in the geosphere in complexes with other elements. It is used in many industrial and domestic products including antacids, antiperspirants, food additives and in vaccines. It is commonly used by the food industry for food containers and packaging, and many cooking utensils are made from aluminium. Aluminium may be present in water through natural leaching from soil and rock, or from the use of aluminium salts as coagulants in water treatment (NHMRC-NRMMC, 2011; WHO, 2011a). Aluminium is an important cause of reduced productivity on acid soils, but alkaline soils will precipitate it and eliminate any toxicity (ANZECC-ARCAMZ, 2000). On the other hand, it can be neurotoxic in human, as it has been associated with Parkinson disease and amyotrophic lateral sclerosis, and some studies have hypothesized that aluminium exposure is a risk factor for the development or acceleration of onset of Alzheimer disease in humans. Aluminium also affects kidney dialysis patients accumulating in their blood and resulting in an encephalopathy known as dialysis dementia. However, the major exposure is from food, not from water (NHMRC-NRMMC, 2011; WHO, 2011a).

Aluminium was not measured in the framework of the RECLAIM WATER project, but it was by external laboratories, commissioned by CASSA and EDS, and by ACA. Aluminium measurements commissioned by CASSA and EDS only focused in the final treated water, and the results were always below the LOD (20 µg/L), thus fulfilling the requirements of the Spanish legislation for water reuse and drinking water. ACA measurements were performed from the Ripoll River and the aquifer water, in different wells of the area but in any case in the well used for water recovery at RISMAR scheme. ACA results were always below the LOD or around it (100 µg/L), but for one well ("Aprestos Julià") in which the highest measured value was 234 µg/L, which would be slightly higher than the 200 µg/L guideline value set by the drinking water Spanish legislation and the Australian drinking water guidelines, and also higher than the Australian aquatic ecosystems guidelines (150 µg/L). It must be pointed out that drinking water guideline values are set based on aesthetic considerations, not as health guideline values. Other guideline values considered, set as for instance in the Australian, US EPA or WHO irrigation water guidelines, would be also fulfilled (see Appendix E).

Considering the data evaluated, aluminium does not pose a risk for the human health neither to the plants nor to the crops irrigated.

5.5.3.2. Antimony

Antimony is toxic for animals and human. Antimony is not usually detected in natural source waters; it is used in solders as a replacement for lead. Antimony alloys and compounds are used in semiconductors, batteries, anti-friction compounds, ammunition, cable sheathing and flame-proofing compounds. Antimony salts are used in glass, ceramics and pottery. Antimony can be genotoxic, carcinogenic (only demonstrated by inhalation) and have metabolic effects in human, as well as causing dermatitis and heart problems (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a). However, total exposure from environment, water and food is much lower than the occupational exposure. The most common source of antimony in drinking-water appears to be dissolution from metal plumbing and fittings.

Antimony was not measured in the framework of the RECLAIM WATER project, but it was by external laboratories, commissioned by CASSA and EDS, and by ACA. Antimony measurements commissioned by CASSA and EDS only focused in the final treated water, and measured values ranged from 2.8 to 4.4 µg/L, thus fulfilling the requirements of the Spanish legislation for drinking water (maximum of 5 µg/L). ACA measurements were performed from the Ripoll River and the aquifer water, in different wells of the area but not in the well used for water recovery at RISMAR scheme. ACA results were always below the LOD, which was of 5 µg/L. Other guideline values considered, set as for instance in the Australian irrigation water guidelines, would be also fulfilled (see Appendix E), but for Australian drinking water guidelines, which set a guideline value of 3 µg/L, that would be slightly exceed by part of the measurements done by CASSA and EDS.

Then, considering the data evaluated, antimony does not pose a risk for the human health neither to the plants nor to the crops irrigated, but if in the future the water needs to be used as drinking water, this metal should be considered and more analyses should be performed at RISMAR scheme in order to ensure that it does not pose a risk.

5.5.3.3. Arsenic

Arsenic is toxic to humans, animals and plants. Arsenic is a naturally occurring element, which can be released from the aquifer as part of redox reactions. Agricultural soils can have elevated concentrations of arsenic due to the past use of organoarsenic pesticides, and it can be released by chemically and/or microbiologically mediated oxidation/reduction reactions. In any case, phytotoxicity (destruction of chlorophyll by inhibition of reductase enzymes) can arise from elevated soil arsenic concentrations as well as from its presence in irrigation waters (ANZECC-ARCAMZ, 2000). Arsenic compounds have commercial and industrial uses as alloying agents and in the processing of glass, pigments, textiles, paper, metal adhesives, ceramics, wood preservatives, ammunition and explosives. Apart from occupational exposure, the most important routes of exposure are through food and drinking water. Gastrointestinal problems, skin damage, problems with the circulatory systems and carcinogenicity are effects to human (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a).

Arsenic was not measured in the framework of the RECLAIM WATER project, but it was by external laboratories, commissioned by CASSA and EDS, and by ACA. Arsenic measurements commissioned by CASSA and EDs only focused in the final treated water, and measured values ranged from 11 to 19.5 µg/L, thus fulfilling the requirements of the Spanish legislation for water reuse but not for drinking water. Recommended guideline values in the WHO and Australian drinking water guidelines and the US EPA drinking water regulations regulations are the same as in the Spanish legislation, of 10 µg/L. ACA measurements in the river water and in most of the wells monitored were always below 10 µg/L. However, two wells located close to the well where water is recovered and tapping also the alluvial aquifer presented higher values: "Aprestos Julià"well reached 29 µg/L in one sample, and "Timsa"well values ranged from 11 to 18 µg/L. Other guideline values considered, set as for instance in the US EPA and WHO irrigation water guidelines, or in the Australian guidelines for aquatic ecosystems, would be also fulfilled (see Appendix E).

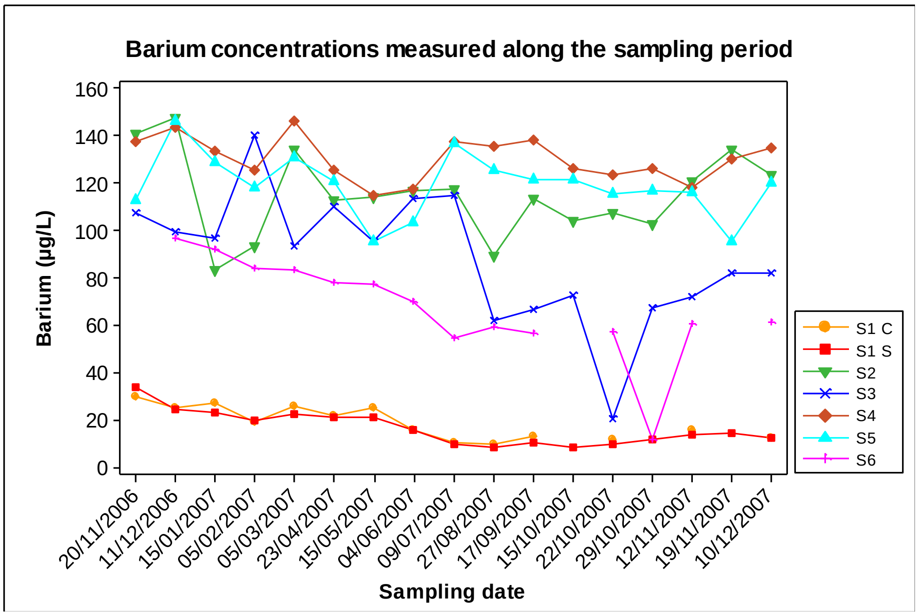
Considering the aerosols ingestion route of exposure, which entails an extremely low water volume ingestion, arsenic does not pose a risk. Considering the ingestion of a higher volume of water while swimming, arsenic does not pose a risk either as the volumes of water ingested are much lower than for drinking water. Then, the only possible problem would arise if the recycled water is used as drinking water.

To sum up, arsenic does not pose a risk for the human health neither to the plants nor to the crops irrigated, but if in the future the water needs to be used as drinking water, this metal should be considered and some additional treatment should be applied to reduce and/or eliminate it. Besides, a more in-depth study of this metal in the aquifer should be developed (see section 5.5.11 for an explanation on the rationale behind this).

5.5.3.4. Barium

Barium is toxic to animals and human. Barium is present as a trace element in both igneous and sedimentary rocks, and barium compounds are used in a variety of industrial applications; however, barium in water comes primarily from natural sources. Barium compounds are used in plastics, rubber, electronics, steel, optical, textile, ceramic glazes, glass, paper making, lubricant additives, pharmaceuticals, cosmetics and as rodenticides. Barium can cause nephropathy and hypertension in human (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a). Food (milk, potatoes, flour, cereals and nuts) is the primary source of barium for the non-occupationally exposed population.

Figure 12 Barium concentrations measured along the sampling period at the different sampling points.



Note: water reuse RD guideline value (20000 µg/L) is not represented in the figure as it much higher than the measured values, so the trends in the data would not be appreciated.

Barium concentration in all water samples is well below the guideline value set in the Spanish water reuse RD (20 mg/L = 20000 µg/L). In Figure 12 the values measured for barium are represented. If drinking water and recreational water guidelines from WHO and Australia, and US EPA drinking water regulations are considered, the measured concentrations are also well below the guideline values set. Barium concentration in the secondary effluent is very stable along time (see Figure 12), and much lower than the concentration in the Ripoll River before the discharges (S1: 19 µg/L mean, vs. S2: 115 µg/L mean), and after the mixture of both waters the concentration is slightly reduced (S3: 88 µg/L mean). In the aquifer, the barium concentration is more similar to the Ripoll River before the discharges (S4: 130 µg/L mean), which indicates the important contribution of the river water to the aquifer water and the possible presence of barium in the sediments of the river, and confirming that barium in water comes primarily from natural sources. Then, none of the end points is affected by the riverbed filtration and recycled water scheme, as the river water is continuously feeding the aquifer and the secondary effluent discharges are not increasing the barium concentration.

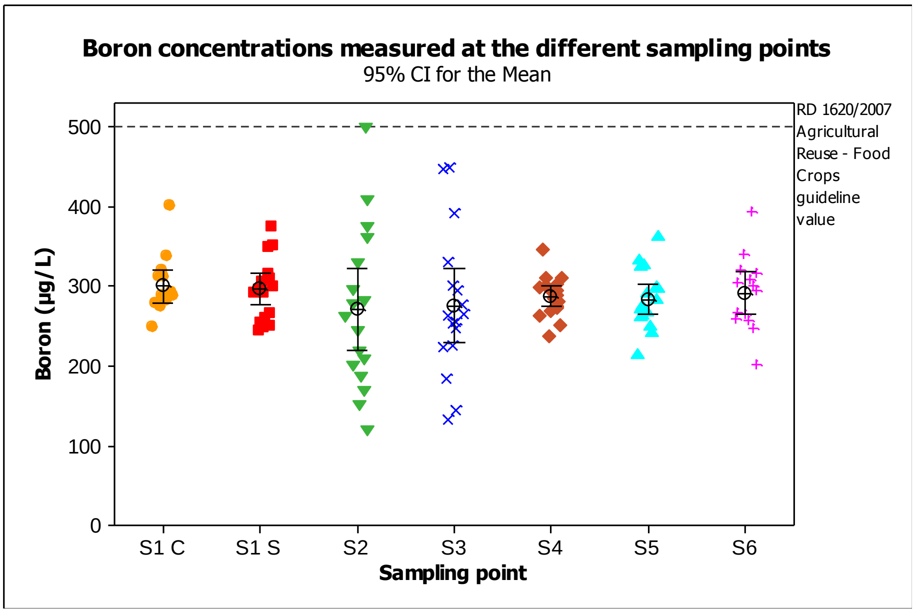
To sum up, barium does not pose a risk for any of the end points evaluated.

5.5.3.5. Boron

Boron in relatively small amounts is essential to the normal growth of all plants, however, it can be toxic when present in excess (ANZECC-ARCAMZ, 2000). It can also be toxic for animals and human, causing problems in development and the reproductive system, and there have been a number of reported cases of poisoning following the ingestion of high doses of boron (NHMRC-NRMMC, 2011; WHO, 2011a). In any case, doses causing toxicity to plants are much lower than doses causing toxicity in human. Naturally occurring boron is present in groundwater primarily as a result of leaching from rocks and soils containing borates and borosilicates. Boron is generally adsorbed onto soil surfaces at alkaline pH values, thus needing an acid pH to be desorbed. Boron compounds are used in the manufacture of glass, soaps, cosmetics, detergents and as flame retardants and occasionally food preservatives; and as agricultural fertilisers, algaecides, herbicides and insecticides. Boron is present naturally in many food products (fruits, leafy vegetables, nuts and legumes), and food is a more important source than drinking water.

Boron average concentration is similar in all sampling points (mean values ranging from 271-300 µg/L in the different water samples), but variability is higher in the river water before the discharges (S2) and in the sampling point S3 (right after the first discharge. Figure 13 shows the individual values measured at the different sampling points and how big are the fluctuations in the river water.

Figure 13 Boron concentrations measured at the different sampling points.



The most sensitive crops to boron toxicity are citrus species and blackberries, which are affected by levels below 0.5 mg/L of boron in water, which is the guideline value set for crop irrigation in the Spanish water reuse RD and other irrigation guidelines. These crop species are not currently grown in Sabadell. Maximum measured boron concentrations in all water samples are below the guideline values set in the Spanish water reuse RD as well as the Spanish drinking water RD, and also below the guideline values set in all the other guidelines considered (see

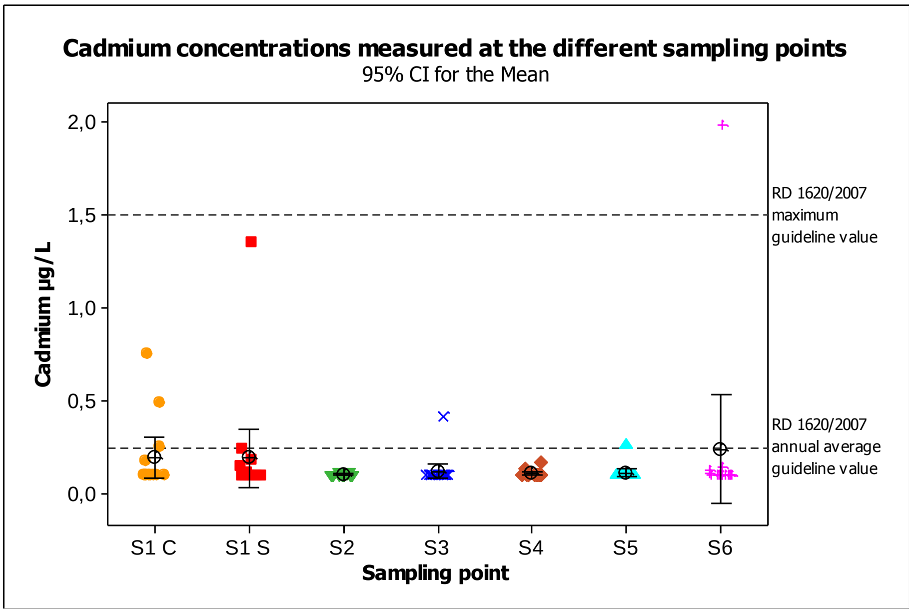
Appendix E). In case boron concentrations in irrigation water increase to values ranging from 500-750 µg/L, crops irrigated in Sabadell that would be affected by a yield reduction would be artichoke, onion, table grapes and beans.

Considering the results obtained, boron does not pose a risk for any of the end points considered.

5.5.3.6. Cadmium

Cadmium is toxic to plants, humans and animals. It can cause kidney damage, accumulating in this organ with a very long half-life, and osteomalacia (softening of the bones) (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a). In plants, cadmium interferes with metabolic processes by blocking zinc binding sites, but its absorption can be minimised by ensuring soils are not acidic or saline (ANZECC-ARCAMZ, 2000). Cadmium is released to the environment in wastewater, coming from metallurgical and plastic industries. Diffuse pollution is caused by contamination from fertilizers and local air pollution. Contamination in drinking-water may also be caused by impurities in the zinc of galvanized pipes, solders and some metal fittings (WHO, 2011a). Cadmium compounds are commonly used as pigments in plastics, batteries and some electrical components. Food is the main source of daily exposure to cadmium, while smoking is a significant additional source of exposure.

Figure 14 Cadmium concentrations measured at the different sampling points.



Note: values below the LOD have been represented as the LOD.

Cadmium is randomly detected in the sampling points. In many samples taken it is under the LOD. In Figure 14 the individual values measured at the different sampling points are shown. Those points below the LOD are represented as the LOD, 0.1 µg/L. The highest values detected were for the treated wastewater effluent and the river water mixture 2 (at S6). Most of the values measured are below the LOD or very low. Cadmium average concentration was always below the guideline values set in the Spanish water reuse RD (0.25 µg/L) as well as in the Spanish drinking water RD (5 µg/L) in all water samples (mean value ranging from <0.10 µg/L to 0.24 µg/L), being often below the LOD. The maximum concentration permitted in the Spanish water reuse RD is 1.5 µg/L, and this value was exceeded in one water sample from Ripoll River mixture 2 (S6: 2.0 µg/L). Similarly, the other guidelines considered (see Appendix E) were always fulfilled, but for the cited value of 2.0 µg/L in sampling point S6 and another maximum value measured in the secondary effluent of the WWTP (S1, grab sample, 1.4 µg/L).

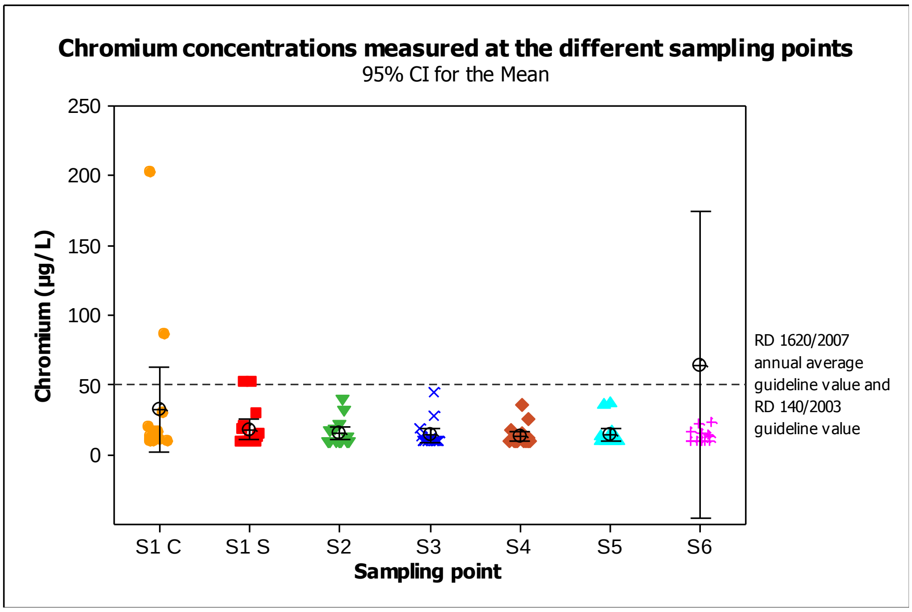
These peak values would not meet the Australian guidelines for aquatic ecosystems, and were probably peaks of contamination, coming from discharges of the factories in the area. In any case, these peak values are close to the set guideline values and are not envisaged to pose a risk for the river water and the species present in it. Besides, water coming from S6 sampling point is not the water taken for the different uses considered at RISMAR scheme.

Considering the results obtained, cadmium does not pose a risk for any of the end points evaluated.

5.5.3.7. Chromium

Chromium is toxic to plants, humans and animals, but traces of chromium are essential for humans and animals. Chromium valence is very important for its mobility in soils, as chromium (VI) remains mobile and available to plants, whereas chromium (III) is adsorbed or complexed and therefore immobile. In plants, chromium can decrease crop yield (ANZECC-ARCAMZ, 2000). In humans, chromium (VI) has proved to be carcinogenic and genotoxic, whereas chromium (III) has not; moreover, it is an essential trace element for humans, with food being the major source of intake (NHMRC-NRMMC, 2011; WHO, 2011a). Chromium can also cause allergic dermatitis (US EPA, 2009). Chromium is used in a wide variety of industrial processes, especially in the metallurgic industry, and in the chemical industry as oxidising agents.

Figure 15 Chromium concentration at the different sampling points.



Note: values below the LOD have been represented as the LOD. A peak value of 725 µg/L in sampling point S6 has not been represented in the figure, in order to properly show the other values measured. The mean and the 95% confidence interval for the mean are clearly shifted due to this peak value.

In Figure 15 the values measured for chromium are represented. Most of the values measured are below the LOD, and are represented in the figure as the LOD, 10 µg/L. Chromium concentration in all samples was below the guideline values set in the Spanish water reuse RD (50 µg/L annual average, but no maximum value given) as well as the Spanish drinking water RD, but for two high values measured in the secondary effluent of the WWTP (S1 C sample: 87 and 202 µg/L) and in the river water mixture 2 (S6: 725 µg/L). These peak concentrations shift the mean value in both sampling points increasing it a lot; otherwise, the mean value would be similar in all sampling points. It is interesting to note that the chromium peak value measured downstream the discharges (S6) coincides with peak values in cadmium, iron, molybdenum and nickel in the same sample (sample taken on June 4, 2007). This may indicate a possible transient pollution in the river, due to discharges from factories not connected to the sewer system or from discharges of WWTPs upstream the river. River water (S2 and S3) and groundwater measured values are very similar (mean value ranging from 13 µg/L to 15 µg/L), then, the aquifer is not affected by the recycled water scheme. Australian and WHO drinking water guideline values are the same as for the Spanish legislation, but US EPA guideline value is more permissive (100 µg/L vs. 50 µg/L). Irrigation, unrestricted urban reuse and recreational water guideline values from US EPA, WHO and Australia are less restrictive than the equivalent in the Spanish legislation (see Appendix E). As chromium VI is the toxic form, and some regulations (including the Spanish water reuse RD) include guideline values specifically for chromium VI, it would have been interesting to measure chromium VI alone, not only total chromium. The peak values detected in the treated wastewater and the river water after all the discharges, then, would have been also put in context.

To sum up, chromium does not pose a risk for the human health neither to the environmental end points considered, but if in the future the water needs to be used as drinking water, this metal should be considered and closely tracked at RISMAR scheme. Illegal discharges in the river water and/or the wastewater can highly increase its concentration at RISMAR scheme, thus potentially increasing its concentration in the aquifer, although in the samples monitored the aquifer concentration was not affected after the peak values detected in the treated wastewater.

5.5.3.8. Cobalt

Cobalt can be toxic to plants, animals and humans, although it is essential in low doses for animals and humans, as it is part of vitamin B_{12}. It is not an essential plant micronutrient, with the exception of legumes involved in symbiotic nitrogen fixation with *Rhizobium*. It is quite stable in soils, and tends to be tightly bound to manganese oxides. When pH decreases to acidic values, it is released and the uptake by the plant is increased (ANZECC-ARCAMZ, 2000). Cobalt occurs naturally in soils but can also come from industries manufacturing or using cobalt alloys, chemicals, batteries, pigments and radioisotopes. In plants, an excess of cobalt reduces vegetative growth. In humans and animals, an excess of cobalt can cause respiratory problems, allergies, contact dermatitis and cardiomyopathies. Studies in animals suggest that nonradioactive cobalt can affect development and can cause cancer (ATSDR, 2004). Cobalt intake is majoritarily from food.

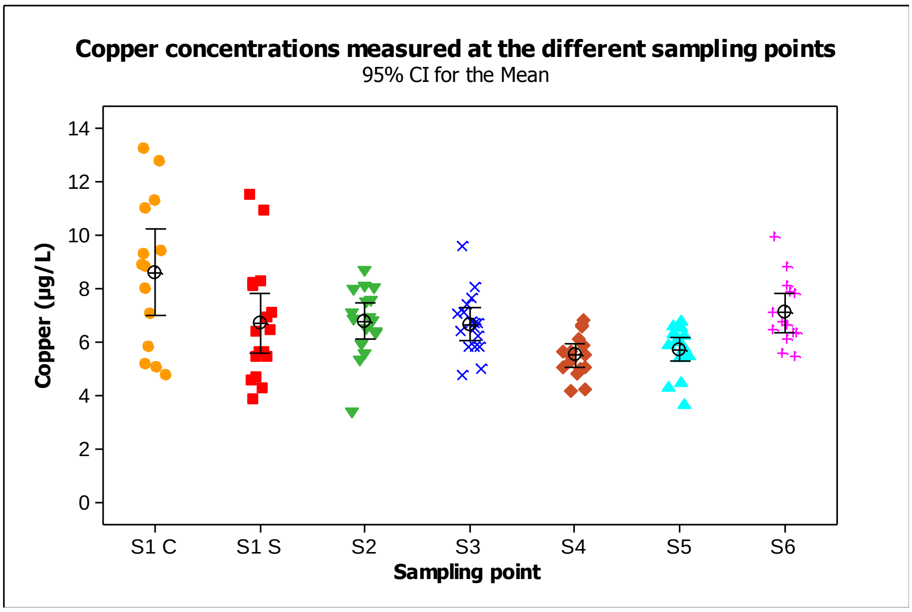
Cobalt concentration was always below the LOD (5 µg/L) in all the samples evaluated, well below the guideline values set in the Spanish water reuse RD and other irrigation guidelines used (see Appendix E), thus not posing a risk for any of the end points considered.

5.5.3.9. Copper

Copper is an essential trace element for humans, animals and plants, but at the same time it can be toxic in higher concentrations. In plants, it can cause growth reductions. Higher concentrations in soils can occur due to application of biosolids, copper-based fungicides (e.g. vineyards) and animal manures, as well as atmospheric deposition in mining areas. Plant uptake of copper occurs more readily in soils with pH less than 5 (ANZECC-ARCAMZ, 2000). In human, copper poisoning can result in cirrhosis and kidney damage, especially in long-term exposures. Other less severe symptoms are gastrointestinal symptoms such as nausea, abdominal pain and vomiting, especially in short-term exposures. Apart from humans, sheep are the most susceptible animals to the toxic effects of copper (NHMRC-NRMMC, 2011; US EPA, 2009). Copper primary source in drinking water is often the corrosion of interior copper plumbing, as it is used to make pipes, valves and fittings and is present in alloys and coatings. Its release increases with acid pH waters or high-carbonate waters with an alkaline pH (WHO, 2011a). Food and water are the primary sources of copper exposure in developed countries, and erosion of natural deposits is a secondary source.

Copper measured concentrations at RISMAR scheme were always very low. In the treated effluent the measured values were a bit higher than in the other sampling points, and present more variability in the results (see Table 17).

Figure 16 Copper concentration at the different sampling points.



Note: water reuse RD guideline value (120 µg/L) and drinking water RD guideline value (2000 µg/L) are not represented in the figure as they are much higher than the measured values, so the trends in the data would not be appreciated.

Copper concentration in all samples was far below the guideline values set in the Spanish water reuse RD (120 µg/L annual average) as well as the Spanish drinking water RD (2000 µg/L) and values set in other regulations considered (see Appendix E). Mean concentrations ranged from 5.5 µg/L to 8.6 µg/L in the different sampling points. Copper concentration fulfilled also other guidelines used for irrigation, drinking water, unrestricted urban reuse and recreational water. However, Australian guidelines for aquatic ecosystems (ANZECC-ARCAMZ, 2000) set a very restrictive value, which would not be met in any case. Curiously, this value is nearly two orders of magnitude lower than the most restrictive of the other guidelines and Spanish regulations values (2.5 µg/L vs. 120 µg/L), and three orders of magnitude lower than the guideline value for drinking water in Australia (2000 µg/L). This value can be whether a typo mistake or not updated to current information available, and has been disregarded for the purposes of the risk assessment.

Considering the results obtained, copper does not pose a risk for any of the end points evaluated.

5.5.3.10. Cyanide

Cyanide is acutely toxic for humans and animals. It can cause nerve damage and thyroid problems (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a). Cyanide can be present in drinking water through the contamination of source water, through the natural decomposition of some plants that synthetize cyanoglycosides and as a metabolic product of some microorganisms. Sodium cyanide is used in the extraction of gold and silver, and for electroplating, steel and chemical industries. Some foods can contain quite high concentrations of cyanide, like green almonds and improperly treated cassava (NHMRC-NRMMC, 2011).

Cyanide concentration was always below the LOD (10 µg/L) in all the samples evaluated, well below the guideline values set in Spanish regulations (40 µg/L in the Spanish water reuse RD and 50 in the Spanish drinking water RD) and other guidelines used (see Appendix E), thus not posing a risk for any of the end points considered.

5.5.3.11. Fluoride

Fluoride toxicity to plants, humans and animals depends on the concentration range. Excessive intake of fluoride can lead to dental and skeletal fluorosis, characterised by hypermineralisation of bones, causing them to become brittle. The margin between beneficial and detrimental concentrations is small (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a). Naturally occurring fluoride concentrations in drinking water depend on the type of soil and rock through which the water drains. Fluoride is widely used in the industry. Virtually all foodstuffs contain traces of fluorine; in particular, high amounts can be found in dried tea leaves. Fluoride is used to protect teeth against dental caries. It is present in most brands of toothpaste, and it is often added to drinking water supplies (NHMRC-NRMMC, 2011). In plants, uptake and toxicity of fluoride are dependent on the ionic species of fluoride in the solution exposed to the plant root (ANZECC-ARCAMZ, 2000).

Fluoride concentration was always below the LOD (0.50 mg/L) in the recovered water (S4) and the final treated water (S5), and in most of the samples from the treated effluent and the river water too. In few samples from the river water and one sample of the treated effluent, fluoride was detected in low concentrations. As it was detected before the treated effluent discharges (S2), this indicates that it might naturally occur in the Ripoll River water, but a pollution effect should not be disregarded. Its absence in the recovered water from the aquifer may be due to a dilution effect of the river water in the groundwater, and that for most samples the results were below the LOD. A different measurement method, with a lower LOD, might help in completely ruling out the absence of fluoride in the aquifer water.

In any case, maximum concentrations detected in the Ripoll River ranged from 0.75 to 1.1 mg/L (S2 and S3 sampling points respectively), and 1.3 mg/L in the only sample of the treated effluent where it was detected, which are well below the Spanish regulations. Irrigation guidelines by US EPA, WHO and Australia recommend a long-term value of 1 mg/L, which was set on the assumption that irrigation water could potentially be phytotoxic to sensitive plants or contaminate stock drinking water (ANZECC-ARCAMZ, 2000). However, fluoride phytotoxicity is not clear, and the guideline value was only exceeded once in one river water sample and once in the treated effluent, never in the recovered water.

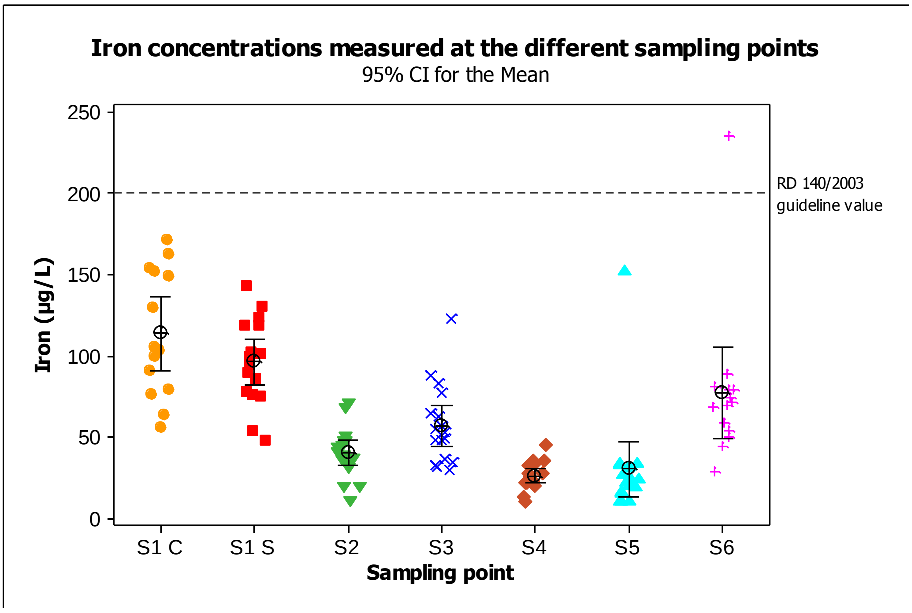
Considering the results obtained, fluoride does not pose a risk for any of the end points evaluated.

5.5.3.12. Iron

Iron is an essential trace element for human, animals and plants. Iron occurs naturally in soil and rocks. Iron has many domestic and industrial applications, ranging from iron and steel products and pigments in paints to food colours and preparations for treating iron deficiency in humans. Ferric chloride and ferric sulphate are used as flocculants in water treatment. Human guideline values are based on aesthetic considerations (precipitation of iron from solution and taste), not on toxicity effects. High iron concentrations give water an undesirable rust-brown appearance and can cause staining, fouling and blockages in irrigation systems (NHMRC-NRMMC, 2011). In plants, iron deficiency results in chlorosis. The soil pH and aeration determine the oxidation state and thus solubility of iron in soil. There is insufficient data to determine a toxicity threshold for plants, but data suggests that above 10 mg/L total iron there might be a reduction in plant growth. This is the short-term value recommended in the Australian irrigation guidelines. The much lower long-term value (0.2 mg/L) is recommended to prevent blocking of the irrigation system, especially using trickle or drip irrigation (ANZECC-ARCAMZ, 2000).

Iron concentration was higher in the secondary effluent (S1 C: mean value of 113 µg/L) than in the river water before the discharges (S2: mean value of 40 µg/L), thus an increase in the river water iron concentration is observed after the WWTP discharges (S3: mean value of 57 µg/L and S6: mean value of 77 µg/L; see Figure 17). However, recovered water mean value (S4: mean value of 26 µg/L) is similar to the river water before the discharges and even lower, so there might be dilution of iron concentration in the infiltrated water when it mixes with groundwater or another possibility is iron deposition in the river sediments. Fluctuations in treated wastewater affect directly the river water concentration after the discharges.

Figure 17 Iron concentration measured at the different sampling points.



Iron measured concentrations in all water samples were well below the Spanish regulations guideline values. Only one peak value in the river water mixture 2 (S6, 235 µg/L) would not fulfil the Spanish drinking water RD, but the given value is based on aesthetic considerations and the human health would not be affected at all. Similarly, other guidelines used (see Appendix E) would be fulfilled but for the long-term irrigation value in Australian guidelines (200 µg/L), which was also set to prevent blocking of the irrigation system. In any case, this was only a peak value in the river water, not representative of the average water quality, and it is not the final treated water used for the different purposes. So neither the plants nor the irrigation systems would be affected.

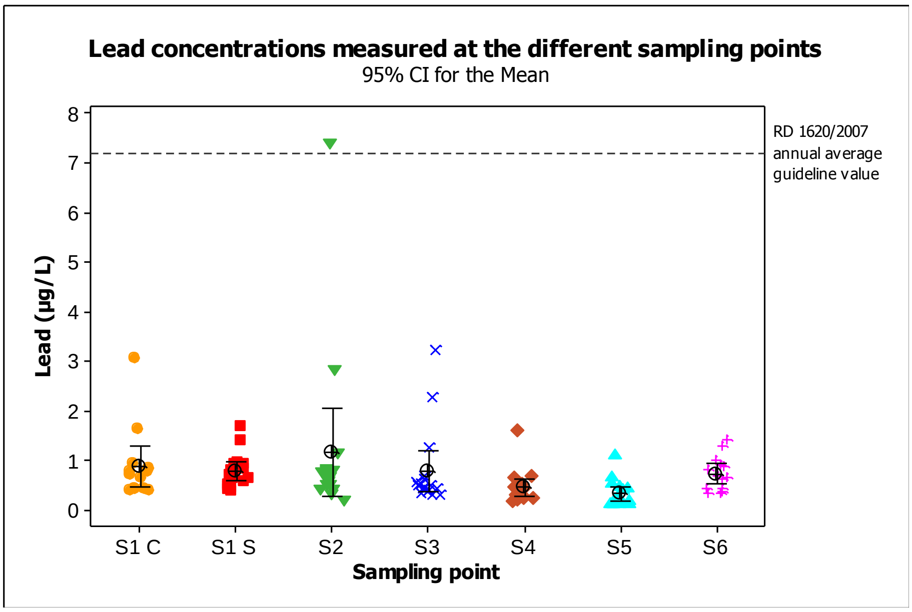
Considering the results obtained, iron does not pose a risk for any of the end points evaluated.

5.5.3.13. Lead

Lead is toxic to plants, humans and animals. Lead is strongly retained by most soils and it is mobilized with low pH (ANZECC-ARCAMZ, 2000). Lead can be present in drinking water as a result of dissolution from natural sources, or from household plumbing systems (pipes or solder used to seal joints) containing lead. Lead is widely used in the industry, and its wastewaters can be a source of it (NHMRC-NRMMC, 2011; WHO, 2011a). Regarding animals, the toxicity of lead depends on the type of animal (including its age), the form of lead and the rate of lead ingestion. Lead is accumulated in the skeleton to a critical maximum level, after which circulating concentrations increase until poisoning occurs. Horses appear to be among the animals most sensitive to lead poisoning (ANZECC-ARCAMZ, 2000). In human, lead can cause delays in physical and mental development in children, cardiovascular diseases, interference with the production of red blood cells, interference with the metabolism of calcium needed for bone formation, hypertension, impaired fertility and adverse pregnancy outcomes (NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a).

Lead was always present in low concentrations in all the samples taken (see Figure 18), and mean concentrations ranged from 0.35 µg/L in the recovered water (S4) to 1.2 µg/L in the river water before the discharges (S2). No tendency can be observed for this heavy metal. It is interesting to note, though, that the highest value detected is in the river water before the discharges (S2: 7.4 µg/L), indicating that there are discharges upstream the river that can affect the quality, and that the treated wastewater discharges from the Ripoll River WWTP that are part of the recycled water scheme are not affecting the aquifer or the river water quality.

Figure 18 Lead concentrations measured at the different sampling points.



Lead measured concentrations in all water samples were well below the Spanish regulations guideline values. It must be considered that the set guideline value in the Spanish regulations is for the annual average of the compound (7.2 µg/L) and there is not a maximum guideline value set. Then, although the highest value measured at RISMAR scheme slightly exceeded the guideline value, this does not pose a risk, as the guideline value is set considering an annual average, not a maximum value. Other guidelines used (see Appendix E) would be also fulfilled.

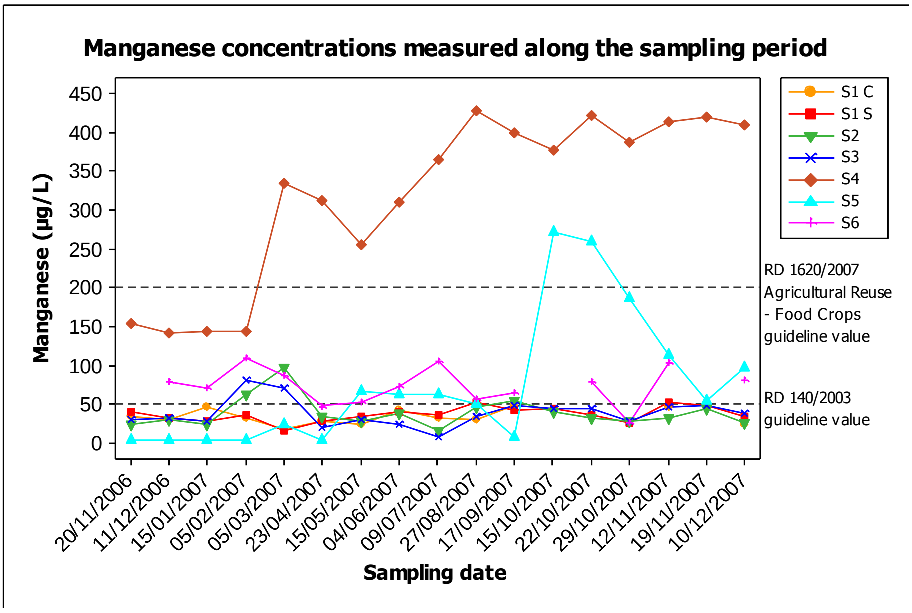
Considering the results obtained, lead does not pose a risk for any of the end points evaluated.

5.5.3.14. Manganese

Manganese is an essential element for humans, animals and plants. It is a constituent of soils and its solubility is controlled by pH and oxidation-reduction reactions (ANZECC-ARCAMZ, 2000). Manganese is naturally occurring in many surface water and groundwater sources, particularly in anaerobic or low oxidation conditions, and this is the most important source for drinking-water. It occurs naturally in many food sources, and the greatest exposure to manganese is usually from food. It is principally used in the manufacture of iron, steel and alloys. In humans, manganese toxicity has occurred mainly as a result of inhalation of manganese dust over long periods. By the oral route, manganese is regarded as one of the least toxic elements. However, at high concentrations in solution, manganese may be highly toxic to plants, especially to root growth in acidic soils (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; WHO, 2011a).

Manganese was found in higher concentrations in the recovered water than in the other sampling points, and increased considerably in the aquifer water during the sampling period (see Figure 19). Manganese concentration was stable and low in the treated wastewater and presented some fluctuations in the river water, but very small comparing to the increase in the aquifer water. Data from ACA of manganese concentrations measured in other wells in the area also present higher values in comparison to measured values in the river, and the same happened for the final treated water measurements performed by CASSA and EDS, that presented high values of manganese (data not shown).

Figure 19 Manganese concentrations measured along the sampling period at the different sampling points.



The increase in manganese concentrations in the aquifer could be due to an increased release of it from the aquifer. Dissolution of manganese from manganese oxides and oxyhydroxides in the sediments occurs by reaction with dissolved oygen or organic matter present in the recharged water, or by changing the pH of the storage zone (Martin, 2005; NRMMC-EPHC–NHMRC, 2009). Then, as the infiltration water has a good amount of organic matter, and may still have some oxygen not consumed, the long-term exposure to this organic matter could have triggered the manganese dissolution.

While manganese measured concentration in the secondary effluent would meet the Spanish regulations, the river water would not meet the drinking water regulations (maximum values of 96 µg/L, 79 µg/L and 106 µg/L for S2, S3 and S6 respectively) and the recovered water from the aquifer would not meet the drinking water neither the water reuse for irrigation guideline values (S4 mean value of 318 µg/L). The final treated water presents lower manganese concentrations than the aquifer water (S5 mean value of 74 µg/L and maximum value of 272 µg/L), due to the precipitation of the dissolved manganese in the recovered water in the form of manganese oxide when it comes into contact with chlorine (a black precipitate was observed in the distribution system and clogged the chlorine probe). Nevertheless, manganese average concentration in the final treated water would still not meet the drinking water guideline value, and the maximum value measured would neither meet the water reuse for irrigation nor the drinking water guideline values.

Comparing the drinking water guideline value set in the Spanish regulation with other guideline values consulted (see Appendix E), Spanish one (50 µg/L) is too restrictive, being one order of magnitude higher than for WHO and Australian drinking water guidelines (400 µg/L and 500 µg/L, respectively). Considering the low toxicity of manganese, the value set in the drinking water Spanish legislation must be related to aesthetic considerations, not to health. Similarly, the guideline value set for irrigation in the Spanish water reuse RD (200 µg/L) is the same given in the Australian irrigation guidelines as a long-term value to prevent blocking of the irrigation equipment, not to prevent phytotoxicity in plants (short-term value) which is much higher (10000 µg/L).

To sum up, this metal does not pose a risk for the human health neither to the plants nor to the crops irrigated, but it can clog the irrigation system. It already caused precipitation problems in the system, clogging the chlorine probe, so a small sand filter was installed to remove it, which was already part of the post-treatments applied to the recovered water during the RECLAIM WATER project sampling period. In case the water needs to be used as drinking water, this metal should be considered and some additional treatment should be applied to reduce and eliminate it, in order to fulfil the Spanish regulations (although the human health is not compromised at any point). Besides, a more in-depth study of this metal in the aquifer should be developed (see section 5.5.11 for an explanation on the rationale behind this).

5.5.3.15. Mercury

Mercury is toxic to animals, human and plants. Natural release of mercury into drinking water is extremely low, because it is strongly retained by soils (especially by those high in organic matter), but contamination can result from industrial emission or spills. Mercury is used widely in electrical components, and it is also used in electrolytic production of chlorine, dental amalgams, fungicides, antiseptics, preservatives and pharmaceuticals. Food is the main source of mercury in non-occupationally exposed populations (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; WHO, 2011a). In rats, inorganic mercury effects include damage to the kidney and the central nervous system. In humans, acute oral poisoning results primarily in haemorrhagic gastritis and colitis; the ultimate damage is to the kidney. Inorganic mercury can be converted into methyl mercury, possibly by the action of bacteria in sediments, and can then readily enter the food chain. Methyl mercury toxic effects are more severe than inorganic mercury effects, as it can cross biological membranes, and it can cause severe irreversible neurological disorder and mental disability.

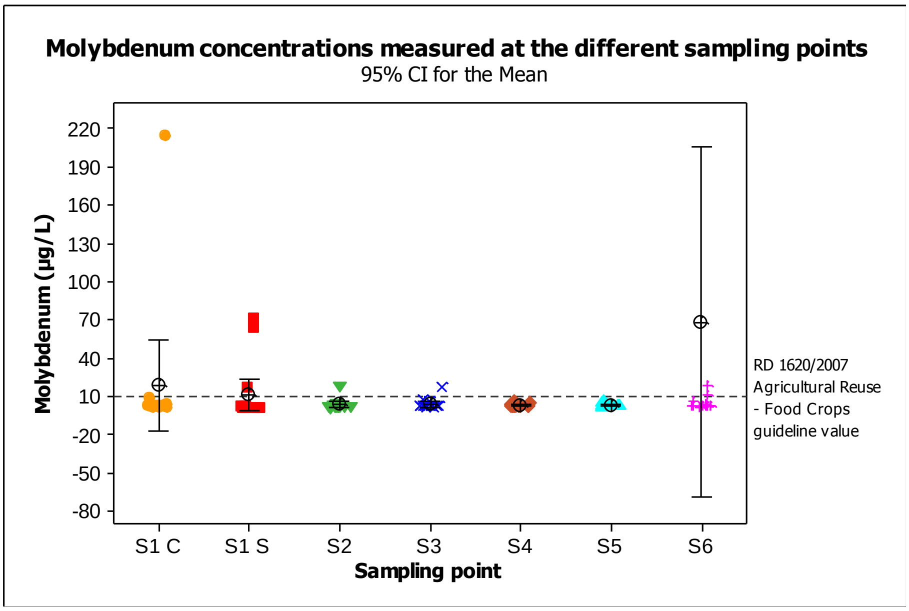
Mercury was not measured in the framework of the RECLAIM WATER project, but it was by external laboratories, commissioned by CASSA and EDS, and by ACA. Mercury measurements commissioned by CASSA and EDS only focused in the final treated water, and measured values were below the LOD (0.1 µg/L to 1.0 µg/L depending on the laboratory and method used), thus fulfilling the requirements of the Spanish legislation for drinking water (maximum of 1 µg/L) and the Spanish water reuse RD. ACA measurements were performed only from the Ripoll River water and the results were always below the LOD (around 0.4 µg/L). The other guidelines considered (see Appendix E) would be fulfilled too.

Considering the data evaluated, this metal does not pose a risk for the human health neither to the plants nor to the crops irrigated.

5.5.3.16. Molybdenum

Molybdenum is an essential element for humans, animals and plants, but it can be toxic in high concentrations. Molybdenum commonly exists as an anion in waters and soils, being very mobile, and less available to plants in acidic conditions (ANZECC-ARCAMZ, 2000). It is used in the production of steel, electrical components and metal alloys. Molybdenum compounds are used as lubricants in oils and greases, and in fertilisers to overcome molybdenum deficiency in soils. Many foods contain significant amounts of molybdenum, like legumes, grains and liver. Data are scarce on the long and short-term toxicity of molybdenum in humans, and studies in animals rendered a wide range of results (skin and fur pigment, enlargement of joints, weight loss, diarrhoea and emaciation) (NHMRC-NRMMC, 2011; WHO, 2011a).

Figure 20 Molybdenum concentrations measured at the different sampling points.



Note: the peak value of 896 µg/L in sampling point S6 has not been represented in the figure, in order to properly show the other values measured. The mean and the 95% confidence interval for the mean are clearly shifted due to this peak value.

Molybdenum concentration presents peak concentrations in several sampling points. The secondary effluent presents in general values below the guideline value set in the Spanish water reuse RD for crop irrigation use, 10 µg/L. This guideline value is in accordance to other irrigation guidelines (Australian, WHO and US EPA). However, few peak concentrations above the guideline value were measured, one in a composite sample (214 µg/L on January 15, 2007) and three in grab samples (being the highest values measured 64 µg/L on January 15, 2007, and 72 µg/L on June 4, 2007). All these peak values were high enough to shift the mean results above the guideline value (see Figure 20). The river mixture 2 (S6) presented three values above the guideline value, being one of them very high (896 µg/L, June 4, 2007). This very high peak value coincides with peak values in cadmium, chromium, iron and nickel for the same sample. As for cadmium, chromium and iron the peak values did not coincide with peak values in the treated wastewater discharged into the Ripoll River, then this very high peak was probably due to transient pollution in the river, due to discharges from factories not connected to the sewer system or to discharges of WWTPs upstream the river, that also receive wastewater from factories in the area. In the other sampling points in the Ripoll River (S2 and S3), one value above the guideline value was measured in each of them, in both cases on June 4, 2007, but for these sampling points the mean results are below the guideline value. As the Ripoll River before the discharges (S2) also presents one value above the guideline value, this reinforces the idea that discharges from factories not connected to the sewer system or discharges of WWTPs upstream the river have an important impact at the RISMAR scheme, and that pollution events cannot be directly linked to the treated effluent of the Ripoll River WWTP.

The results for the recovered water from the aquifer as well as the final treated water show always figures below the irrigation water reuse guideline value. Then, it seems that sporadic pollution events in the secondary effluent and the river water are not affecting the aquifer water quality.

No guideline value is given in the Spanish drinking water RD, but it is in the Australian drinking water guidelines (50 µg/L) and in the WHO drinking water guidelines (70 µg/L). These guideline values as well as other guideline values used (see Appendix E) would be fulfilled, but for the peak values that have been discussed above.

To sum up, this metal does not pose a risk for the human and the environmental end points considered, as the final treated water fulfils all guideline values considered. However, in order to protect the aquifer, illegal discharges in the river as well as the quality of the secondary effluent should be carefully tracked, as they can be a source of this metal and compromise the final treated water quality.

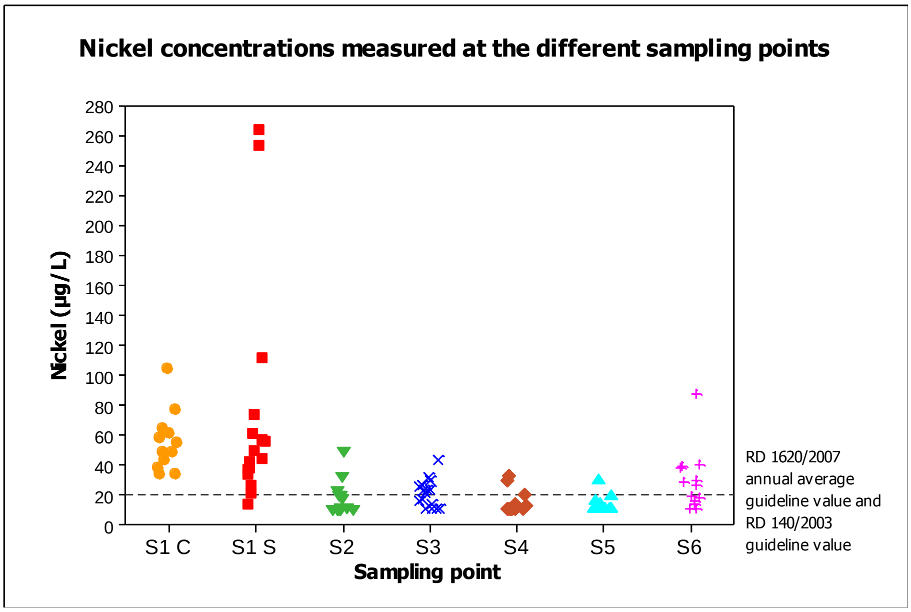
5.5.3.17. Nickel

Nickel is an essential trace element for plants, although it can be toxic at high concentrations for plants, animals and human. Nickel is ubiquitous in the environment, and it is adsorbed strongly to soil components, but below pH=6 the concentration of soluble and exchangeable nickel increases considerably. Concern on its phytotoxicity arises from the use of biosolids of high nickel content on soils (ANZECC-ARCAMZ, 2000). Nickel is used mainly in the production of stainless steel and nickel alloys, as well as a catalyst and for oil refining. Main releases to the environment are from the burning of fossil fuels and in waste discharges from electroplating industries. Food (cocoa, soy beans and some cereals) is the dominant source of nickel exposure in the non-smoking, non-occupationally exposed population; water is generally a minor contributor to the total daily oral intake (NHMRC-NRMMC, 2011; WHO, 2011a). Allergic contact dermatitis is the most prevalent effect of nickel in the general population. A long-term exposure may result in toxic effects to the kidney. Nickel is also carcinogenic, especially when inhaled.

Nickel concentration was in general high in all sampling points. In Figure 21 the values measured for nickel are represented. The secondary effluent presented higher values (S1 C: median value of 55 µg/L and maximum of 886 µg/L) than the river water before the discharges (S2: median value of 11 µg/L and maximum of 49 µg/L) and after the discharges on river mixture 1 (S3: median value of 22 µg/L and maximum of 43 µg/L). However, the river mixture 2 (S6) presented a very high peak value of 3190 µg/L (June 4, 2007), comparing to the median value of 27 µg/L, which was similar to the S3 sampling point. This very high peak value coincides with peak values in cadmium, chromium, iron and molybdenum for the same sample. As for cadmium, chromium and iron the peak values did not coincide with peak values in the treated wastewater discharged into the Ripoll River, then this very high peak was probably due to transient pollution in the river, due to discharges from a factories not connected to the sewer system or to discharges of WWTPs upstream the river, that also receive wastewater from factories in the area. As in the Ripoll River before the discharges (S2) several measured values were above the guideline value (20 µg/L), this reinforces the idea that discharges from factories not connected to the sewer system or discharges of WWTPs upstream the river have an important impact at the RISMAR scheme, and that pollution events cannot be directly linked to the treated effluent of the Ripoll River WWTP.

The recovered water (S4: median value <10 µg/L and maximum of 33 µg/L) and the final treated water (S5: median value <10 µg/L and maximum of 29 µg/L) measured concentrations were most of the time below the LOD, so even lower than in the river water, probably due to a dilution effect with the groundwater present in the aquifer. The median values for the recovered water, the final treated water and the river water before the discharges would meet the Spanish RDs for water reuse and for drinking water, but not the maximum values measured, that are in all cases above the guideline value set of 20 µg/L.

Figure 21 Nickel concentrations measured at the different sampling points.



Note: values below the LOD have been represented as the LOD (10 µg/L). The peak values of 886 µg/L in sampling point S1 C and 3190 µg/L in sampling point S6 have not been represented in the figure, in order to properly show the other values measured. The mean and the 95% confidence interval for the mean are not shown in this case as they would be out of the graph area due to the peak values mentioned.

Other guideline values used are similar to the water reuse and drinking water Spanish RDs (e.g. Australian Aquatic Ecosystems Guidelines: 17 µg/L, Australian Drinking Water Guidelines: 20 µg/L) or less restrictive (e.g. WHO Drinking Water Guidelines: 70 µg/L; Australian Irrigation Water Guidelines: 200 µg/L for the long-term value and 2000 µg/L for the short-term value), so some of these guideline values would be met for samples taken at RISMAR scheme.

Considering the aerosols ingestion route of exposure, which entails an extremely low water volume ingestion, nickel does not pose a risk. Considering the ingestion of a higher volume of water while swimming, nickel neither poses a risk as the volumes ingested are one order of magnitude lower than for drinking water. Then, the risk for the human health would arise if the recycled water was used as drinking water, and in that case a deeper study would be required. Regarding plants and crops, attention should be paid to the frequency and magnitude of peaks in the final treated water, as those peaks could have toxic effects. For the samples measured, peaks detected are slightly higher than the guideline values, and their frequency is low, so they would not pose a direct risk. It must be considered that the guideline values are set for the annual average of the compound (20 µg/L) and there is not a maximum guideline value set. On the other hand, the discharges of treated effluent increase the nickel concentration in the river, thus posing a risk for the species living in it and posing also a potential risk in the aquifer, although this end point has not been affected. Then, disposals in the river must be closely followed, as well as the discharges from the WWTP, in order to prevent any other future problems.

5.5.3.18. Selenium

Selenium is an essential trace element for humans and animals at low concentrations. It is naturally present in soils, in association with sulphur-containing minerals (ANZECC-ARCAMZ, 2000). Food is the major source of selenium in the population (cereals, meat and fish). Selenium is used in electronic components, insecticides, hair shampoos as an anti-dandruff agent, and as a nutritional feed additive for poultry and livestock. Elevated concentrations of selenium in forage crops can lead to toxicity to animals consuming them. In contraposition, plants can absorb relatively large amounts of selenium without displaying any phytotoxicity symptoms. High intakes of selenium are associated with gastrointestinal disturbances, circulatory problems, discoloration of the skin, decayed teeth, hair or nail loss, nail abnormalities, dizziness and changes in peripheral nerves (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; US EPA, 2009; WHO, 2011a).

Selenium concentration was always below the LOD (5 µg/L) in all the samples evaluated, but the guideline value set in the Spanish water reuse RD is of 1 µg/L. The Spanish water reuse RD 160/2007 requests to follow the environmental quality rules, which were previously regulated on RD 995/2000 and are currently set in the RD 60/2011. Curiously, a guideline value of 10 µg/L is set in the Spanish drinking water RD. This discrepancy prompts the evaluation of other guideline values, and among the ones consulted (see Appendix E) 10 µg/L is the most restrictive value set, so they would be fulfilled. Then, considering the guideline value of 1 µg/L, the recycled water could not be said to fulfil it, as the limit of detection of the method used (Inductive Coupled Plasma, ICP) is higher. However, this guideline value of 1 µg/L seems to be a typographic mistake in the RD 995/2000, repeated in the RD 60/2011, as the RD 995/2000 recommended to use also ICP as a reference method and set a limit of detection for this method of 10 µg/L, which is contradiction of setting a guideline value of 1 µg/L.

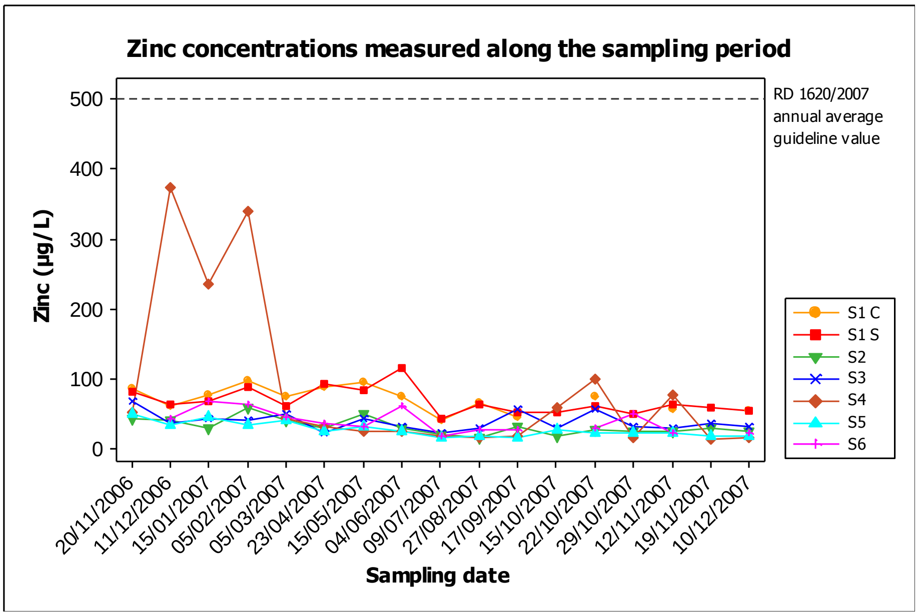
Considering the results obtained, although the discrepancies in the guideline values, selenium does not pose a risk for any of the end points evaluated.

5.5.3.19. Zinc

Zinc is an essential element for plants, animals and human; however, high concentrations in soils may have toxic effects on plants and micro-organisms (ANZECC-ARCAMZ, 2000). Zinc is widely distributed and occurs in small amounts in almost all rocks. It is used as a coating to prevent corrosion of iron and steel products, and it has many other industrial applications. Zinc sulphate, nitrate and halides (except fluorides) are readily soluble in water, while zinc carbonate, oxide, phosphate and silicate are sparingly soluble or insoluble in water. Zinc is more readily available to plants in acid light-textured soils. Food is the major source of zinc intake, as it is present in plant and animal tissues, and drinking water has a very low contribution, unless there exists corrosion of zinc-coated pipes and fittings. Zinc toxicity in plants is evidenced by chlorosis, reduction in leaf size, necrosis of tips and distortion of foliage. In human, zinc deficiency seems to be much more critical than zinc toxicity, and drinking water guideline values set are related to taste, not to toxicity. However, a very high consumption of zinc can result in nausea, vomiting, diarrhoea and abdominal cramps, and in a long-term exposure, it can cause copper deficiency, anaemia and gastric erosion (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; WHO, 2011a).

Zinc concentrations measured at the sampling points were in general low (see Figure 22) and well below the guideline value set in the Spanish water reuse RD. In the recovered water (S4) it is observed how the initial samples taken presented much higher concentrations (ranging from 234 to 373 µg/L) than latter samples, and also higher than the other water samples. This could be due to works in the pumping system performed during those dates or to dissolution of sediments in the aquifer. These higher zinc concentrations in the aquifer water were not present in the final treated water (S5), as the chlorine added probably oxidized the zinc in the recovered water creating a precipitate as happened with the manganese. In general, in the treated effluent (S1 C: mean value of 70 µg/L) the measured values were a bit higher than in the river water (S3: mean value of 38 µg/L).

Figure 22 Zinc concentrations measured along the sampling period at the different sampling points.



Zinc concentrations measured at the sampling points are also well below the other guidelines used (see Appendix E), but for the Australian Aquatic Ecosystems Guidelines, that set a very restrictive value, between 1 and 2 orders of magnitude lower than all the other guideline values (31 µg/L), that would not be met in any of the samples taken. The rationale behind this very restrictive guideline value is not clear, considering that zinc is an essential element and toxicity occurs at very high concentrations.

Considering the results obtained, zinc does not pose a risk for any of the end points evaluated.

5.5.3.20. Beryllium, tin, uranium and vanadium

Beryllium, tin, uranium and vanadium were not measured in the framework of the RECLAIM WATER project, neither by external laboratories commissioned by CASSA and EDS or by ACA. Then, a risk assessment cannot be performed for them. For future work, these inorganic compounds should be considered and measured at least to know in which ranges could be found at RISMAR scheme, as the Spanish water reuse RD requests to follow the environmental quality rules, which were previously regulated on RD 995/2000 and are currently set in the RD 60/2011, and include these compounds.

5.5.4. Salinity, SAR (Sodium Absorption Ratio) and infiltration problems

The salinity is defined here as the contents of salt in water and soils.

For which respects to water, salinity becomes a problem when the total quantity of salts is enough to create problems for plant development. For soils, the problems arise when certain types of salts accumulate in the system and the structure is affected.

There are differences in terms of the salts which affect water and soil, e.g. calcium and magnesium favour soil structure and the creation of aggregates, while sodium generates problems of structure destruction. The excessive quantity of sodium accumulated in the soil, the ionic strength increases in the root area and because the high osmotic pressure, the plant cannot extract any more water from the soil solution. High salinity can affect plants in several ways: water stress as explained, toxicity due to specific ions, nutritional disorders, oxidative stress, alteration of metabolic processes, membrane disorganization, reduction of cell division and expansion, and genotoxicity. Together, these effects reduce plant growth, development and survival. These effects of high salinity may vary with the growth stage and the soil conditions, and in some cases may go entirely unnoticed due to a uniform reduction in yield or growth across an entire field (ANZECC and ARMCANZ, 2000; Carrillo *et al.*, 2011; FAO, 1985; Parida and Das, 2005).

An infiltration problem related to water quality occurs when the normal infiltration rate for the applied water or rainfall is appreciably reduced and water remains on the soil surface too long or infiltrates too slowly to supply the crop with sufficient water to maintain acceptable yields. Although the infiltration rate of water through the soil varies widely and can be greatly influenced by the quality of the irrigation water, soil factors such as structure, degree of compaction, organic matter content and chemical make-up can also greatly influence the intake rate. The adverse influence of sodium on infiltration has been recognized for many years. But in many cases the evaluation of the sodium influence alone has proven to be in error basically because the interaction of both the sodium content and the salinity determine the water's long term influence on the infiltration rate. Then, both SAR (Sodium Absorption Ratio) and salinity need to be evaluated (FAO, 1985):

1. sodium content relative to calcium and magnesium, which is known as Sodium Absorption Ratio (SAR): An infiltration problem related to water quality in most cases occurs in the surface few centimetres of soil and is linked to the structural stability of this surface soil and its low calcium content relative to that of sodium. When a soil is irrigated with high sodium water, a high sodium surface soil develops which weakens soil structure. The surface soil aggregates then disperse to much smaller particles which clog soil pores. The problem may also be caused by an extremely low calcium content of the surface soil.
2. the total salt concentration of the water, typically measured by electrical conductivity: a high salinity water can increase infiltration, and a low salinity water can decrease infiltration, due to the tremendous capacity of pure water to dissolve and remove calcium and other solubles in the soil. Low salinity water (less than 0.5 dS/m and especially below 0.2 dS/m) is corrosive and tends to leach surface soils free of soluble minerals and salts, especially calcium, reducing their strong stabilizing influence on soil aggregates and soil structure. Without salts and without calcium, the soil disperses and the dispersed finer soil particles fill many of the smaller pore spaces, sealing the surface and greatly reducing the rate at which water infiltrates the soil surface. Soil crusting and crop emergence problems often result, in addition to a reduction in the amount of water that will enter the soil in a given amount of time and which may ultimately cause water stress between irrigations.

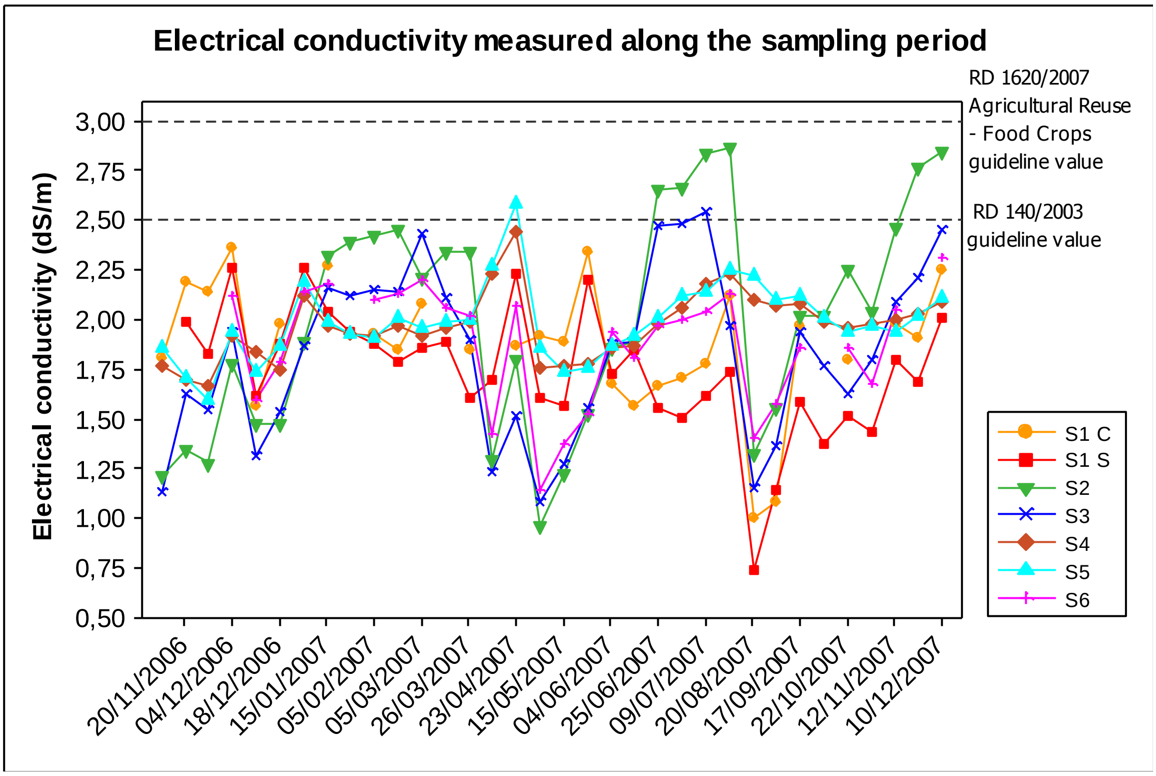
On the other hand, well-drained soils, combined with a proper leaching fraction in the irrigation regime, can tolerate relatively high salinity in the irrigation water, thus infiltration can be controlled (US EPA, 2012).

To assess the salinity, SAR and possible infiltration problems caused by the irrigation water used, a number of interactive factors must be considered, namely: irrigation water quality, soil properties, plant salt tolerance, climate, landscape (including geological and hydrological features) and water and soil management (ANZECC and ARMCANZ, 2000). In 1985, the Food and Agriculture Organization (FAO) published recommendations for agricultural irrigation with degraded water (FAO, 1985); this information provides a guide to making an initial assessment for application of reclaimed water in an agricultural setting, and it has been widely adopted by many organizations and guidelines, as for instance in the WHO water reuse guidelines (WHO, 2006b).

5.5.4.1. Electrical conductivity

The most well-known and widely used measure of salinity is the electrical conductivity, which measures the ability of water to conduct an electric current. This is caused by various anions and cations in solution, such as chloride, sodium, sulphate, nitrate, carbonate, bicarbonate, calcium and magnesium.

Figure 23 Electrical conductivity along the sampling period.



Electrical conductivity is rather high at all sampling points, but for scarce rain episodes that caused a decrease in this parameter in the river water and treated wastewater samples (see Figure 23). The recovered water (S4) and the final treated water (S5) present a more steady behaviour for the electrical conductivity than the river water and the treated wastewater. This is because the river water and the treated wastewater are much more exposed to rain episodes and evapotranspiration, while the groundwater is not exposed to evapotranspiration and is less exposed to rain episodes. Nevertheless, the aquifer is strongly influenced by the infiltration water, as the aquifer where the well is located is an alluvial aquifer and it is naturally fed by the river water. If the mixing with the underlying Miocene aquifer was higher, the recovered water would be expected to have a lower electrical conductivity.

Electrical conductivity guideline values in the Spanish water reuse RD (when the recycled water is used for crop irrigation) and the Spanish drinking water RD are 3 and 2.5 dS/m, respectively. Mean measured concentrations in all sampling points would meet these guideline values (mean measured concentrations ranged from 1.7 to 2.0 dS/m for the different sampling points). For the river water before the discharges (S2), there are few samples that would not meet the drinking water guideline value, as well as one for the river mixture 1 and another one for the final treated water. In any case, if the final treated water would be needed to be used as drinking water, the taste of this water would not be accepted by the consumers, and the salinity contents should be reduced by advanced treatments (e.g. reverse osmosis). Other guidelines for water reuse set ranges of electrical conductivity, as it is the case of the Australian (ANZECC and ARMCANZ, 2000) and WHO (WHO, 2006b) guidelines. For the Australian guidelines, the electrical conductivity ranges are set according to the sensitivity of the crops grown, considering that the most sensitive crops should be irrigated with water presenting an electrical conductivity lower than 0.65 dS/m. For the WHO guidelines, electrical conductivity guideline values are set in relation to SAR, following previous FAO guidelines (FAO, 1985). This option makes much more sense than setting a unique guideline value for electrical conductivity, as salinity problems regarding crop irrigation will arise depending on both the electrical conductivity and the SAR, and both parameters need to be evaluated together, not separately. The final treated water would fulfil the guideline values set in these latter guidelines. Considering the water for drinking purposes, other guidelines set values ranging from 0.75 dS/m (US EPA, 2012) up to 1.56 dS/m (WHO, 2011a). In all cases, the guideline value set is not a health guideline value, and it is only related to taste, but all the guideline values considered are more restrictive than the ones set in the Spanish legislation. Nevertheless, if the final treated water was to be used as drinking water, advanced treatments should be performed, and the electrical conductivity would be reduced.

Agriculturalists define salt tolerance more specifically as the extent to which the relative growth or yield of a crop is decreased when the crop is grown in a saline soil as compared to its growth or yield in a non-saline soil. Salt tolerance is best described by plotting relative crop yield at varying soil salinity levels. Most crops can tolerate soil salinity up to a given threshold. That is, the maximum salinity level at which yield is not reduced. Beyond this threshold value, yield declines in a more or less linear fashion as soil salinity increases (Hanson *et al.*, 2006). Crops grown in Sabadell include: almond, artichoke, bean, cabbage, carrot, cauliflower, chard, chickpea, chilli, courgette, cucumber, endive, eggplant, lettuce, olive, onion, pepper, potatoe, table grape, tomatoe and wheat. Other crops may be grown in the area, but for the purposes of the risk assessment, only these crops have been considered. In Table 13 salinity thresholds (maximum root zone salinity at which 100% yield occurs), slope factors (% reduction in relative yield per increase in soil salinity (dS/m)) of these crops, as well as the yield decrease considering the average and the maximum conductivity of the irrigation water assuming a leaching fraction of 15-20% and a 40-30-20-10 percent water use pattern for the upper to lower quarters of the root zone, are given. Considering the results obtained, bean and chickpea are the most sensitive crops to salinity among the crops grown in Sabadell, and the yield decrease with an average water conductivity of 2.0 dS/cm would be of 38% and 41%, respectively. Other crops to consider would be onion, almond and carrot, with yields of 71- 72% considering the average water conductivity, and crops with a yield close to 80% would be cauliflower, chilli, pepper and lettuce. The rest of the crops would have yields of 80% or higher considering the average water conductivity for the final treated water. The worst case to consider would be irrigation water with a conductivity of 2.6 dS/cm, which was the maximum final treated water (S5) conductivity measured, rendering yields of 44.9% for bean and 26% for chickpea, which would be very low and would suppose a great loss of productivity. Bean and chickpea are typically grown in Sabadell, and for bean, a local variety is grown, that might be especially adapted to the area conditions. The threshold and slope values used represent crop response under experimental conditions, and the threshold value reflects the average root zone salinity the crop encounters during most of the season after the crops have been well established under non-saline conditions, and this might not reflect the reality. Besides, absolute tolerance may vary considerably depending upon climate, soil conditions and cultural practices, and SAR, leaching fraction and other factors need to be considered too. Then, the calculated yields must be taken into consideration in case the final treated water was to be used for irrigation purposes as just an indication of what might happen and which crops would be better adapted to withstand the salinity of the water.

Plants grown in the Taulí Park and trees by the Ripoll River banks irrigated with the final treated water have been detailed in section 5.3.5.4, and include chestnut trees, poplars, reed bed, low bushes, shrubs, pine trees, palm trees, lavender, rosemary, thyme, grass and Mediterranean trees. But for the grass, the trees and vegetation are adapted to the Mediterranean climatology and can tolerate fairly well the salinity in the irrigation water.

Table 13 Salinity effects in crops grown in Sabadell according to ANZECC and ARMCANZ (2000) and data gathered at RISMAR scheme.

Crop	Threshold value (dS/m) (1)	Slope of linear line (%) (2)	Yield potential (%) at ECiw=2.0 dS/m (average ECiw) (3)	Yield potential (%) at ECiw=2.6 dS/m (maximum ECiw) (3)	Chloride sensitivity (mg/L) (4)	Sodium sensitivity (mg/L) (4)
Almond	1.5	19	72	54	<175	<115
Artichoke	6.1	11.5	100	100		
Bean	1.0	19	62	45		
Cabbage	1.8	9.7	88	80		
Carrot	1.0	14	72	59		
Cauliflower	1.5	14.4	78	65	>700	>460
Chard	11.0	5.7	100	100		
Chickpea	1.9	37	59	26		
Chilli	1.5	14	79	66		
Courgette (zucchini)	4.9	10.5	100	100		
Cucumber	2.5	13	94	82	350-700	230-460
Eggplant	1.1	6.9	87	81		
Endive	2.0	15.7	84	70		
Lettuce	1.3	13	78	66		
Olive	4.0	12.0	100	100		
Onion	1.2	16	71	57		
Pepper	1.5	14	79	66	175-350	115-230
Potato	1.7	12	84	74	175-350	115-230
Table grape	1.5	9.6	86	77	<175	<115
Tomato	2.5	9.9	95	86	175-350	115-230
Wheat	6.0	7.1	100	100		

EC_{iw}: electrical conductivity of irrigation water; ECe: root zone salinity (electrical conductivity); MS: moderately sensitive; SAR: Sodium Absorption Ratio.

(1) This value represents the maximum root zone salinity at which 100% yield occurs. This value represents the term A in the yield formula (see comment (3)). Values cited are given in ANZECC and ARMCANZ, 2000; FAO, 2002; De Pascale and Barbieri, 1995; De Pascale *et al.*, 2005; Hanson *et al.*, 2006; Katerji *et al.*, 2003; Shannon and Grieve, 1999.

(2) This value represents the % reduction in relative yield per increase in soil salinity (dS/m). This value represents the term B in the yield formula (see comment (3)). Values cited are given in ANZECC and ARMCANZ, 2000; FAO, 2002; De Pascale and Barbieri, 1995; De Pascale *et al.*, 2005; Hanson *et al.*, 2006; Katerji *et al.*, 2003; Shannon and Grieve, 1999.

(3) Yield potential (%) has been calculated using the formula: Y=100-B(ECe-A). To estimate ECe, the following formula has been used: ECe=1.5ECiw, which assumes a leaching fraction of 15-20% and a 40-30-20-10 percent water use pattern for the upper to lower quarters of the root zone (formulas used appear in FAO, 1985; Hanson *et al.*, 2006).

(4) Values in irrigation water (through sprinkler irrigation) that produce foliar injury (ANZECC and ARMCANZ, 2000; NRMMC–EPHC–AHMC, 2006).

Regarding the grass, it is important to select species tolerating high salinities. In the Australian Guidelines for Water Recycling Phase 1 (NRMMC–EPHC–AHMC, 2006) there is a detailed table including soil salinity tolerance thresholds of turf grasses and estimates for irrigation water (Table A5.12 of the cited guidelines). For a leaching fraction of 17% there are species that could withstand an irrigation water with a very high salinity, like Saltene and Gladstone (17.6 and 16.2 dS/m, respectively), or that could withstand a fairly high salinity water, like Nuttall alkali grass, Weeping alkali grass, Lemon alkali grass, Manila grass and Mascarene grass (9.3 dS/m). However, there are cultivars that for a leaching fraction of 17% could not even withstand a salinity of 1.0 dS/m, like Sea Isle 1 and Velvet bentgrass. Then, it is important to select the most appropriate cultivars in order to tolerate the salinity of the water.

To sum up, as far as salinity is concerned, there are risks for the crops and plants irrigated, as its yield can be reduced, but not for the human health. These risks can be managed by selecting the most appropriate plants and crops to be grown, and also by considering the best irrigation method.

To evaluate the risks for the soils, it is also necessary to consider the Sodium Absorption Ratio (SAR), as sodium plays an important role in soil stability. This has been done in section 5.5.4.7.

5.5.4.2. Bicarbonate and carbonate

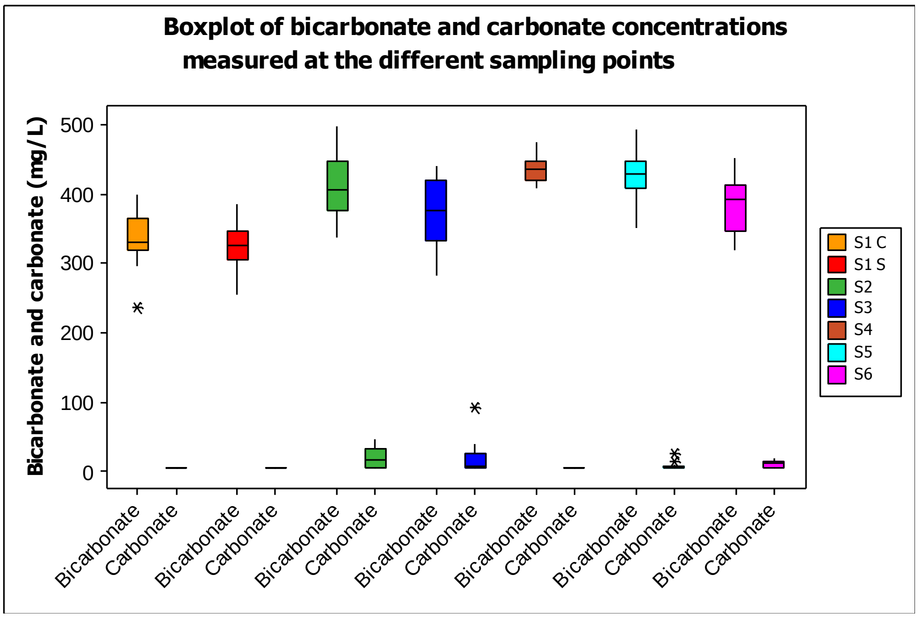
The bicarbonate ion is one of the major contributors to alkalinity in irrigation waters and soil. Bicarbonate is naturally present in rocks and it is widely used in the food industry. In freshwaters, bicarbonate is released as a result of the photosynthetic activity of algae and other plants. Bicarbonate is in equilibrium with carbonate and carbon dioxide, creating a buffering system that is very important in the human body. Carbonate is naturally present in rocks and it is widely used in industry: iron smelting, cement and lime manufacture and ceramic glazes.

Elevated levels of bicarbonate/carbonate in irrigation waters can adversely affect irrigation equipment, soil structure and crop foliage. Prolonged use of irrigation water rich in these species can lead to a high concentration of them in the soil due to evapotranspiration, and there is an increasing tendency for calcium and magnesium to precipitate as insoluble carbonates. Over time, this reduction of calcium and magnesium concentration can result in an increased sodium adsorption ratio (SAR), which may impact adversely on soil structure (see section 5.5.4.7). In fact, for high calcium and/or bicarbonate waters many soil scientists recommend that an adjusted SAR formula be used in place of the regular equation (Lesch and Suarez, 2009) presented in section 5.5.4.7. On the other hand, excessive amounts of bicarbonate can also increase the pH (alkalinity), which can impair plant growth by limiting the uptake of certain ions (ANZECC and ARMCANZ, 2000). Another negative effect of a high concentration of bicarbonates/carbonates is the white scale formation on visible surfaces of the crops, although this is also highly influenced by the irrigation method selected.

Apart from their role in salinity related processes, carbonate and bicarbonate are also measured to track possible releases from rocks forming the aquifer, thus posing a risk of aquifer materials dissolution (see section 5.5.11 for more information on this).

At RISMAR scheme, bicarbonate is the predominant species found, with few samples presenting carbonate (see Figure 24). Bicarbonate concentrations are generally lower in the treated wastewater (S1 S: average of 324 mg/L) than in the river water (S2: average of 411 mg/L) or the aquifer water (S4: average of 436 mg/L). A higher concentration in the river water than in the treated wastewater can be explained by the materials present in the riverbed and dissolved in the water. In the aquifer, a higher bicarbonate concentration needs to come from the infiltrated water or from material released from the sediments. Carbonate was never detected in the treated wastewater neither in the recovered water from the aquifer. However, it was detected in the river water and the final treated water. Regarding the river water, in many of the samples carbonate concentration was below the LOD, and detected concentrations were generally low, with average values ranging from 11-19 mg/L (S2, S3 and S6 sampling points). For the final treated water, most of the samples presented carbonate concentrations below the LOD, and detected concentrations were low too, with an average of 7.5 mg/L, very close to the LOD.

Figure 24 Bicarbonate and carbonate concentrations measured at the different sampling points.



Note: values below the LOD have been represented as the LOD.

There are no guideline values set for these anions in the Spanish regulations, but in the WHO irrigation guidelines bicarbonate is recommended to be between 90-500 mg/L according to slight to moderate restriction in use of the recycled water for irrigation and to an electrical conductivity between 0.7-3.0 dS/m. Measured values in all sampling points would fulfil these recommendations.

Then, considering this, there are chances of scaling build-up in the soils and crops irrigated, and other negative effects in the crops, as bicarbonates are present in high concentrations in the recycled water scheme.

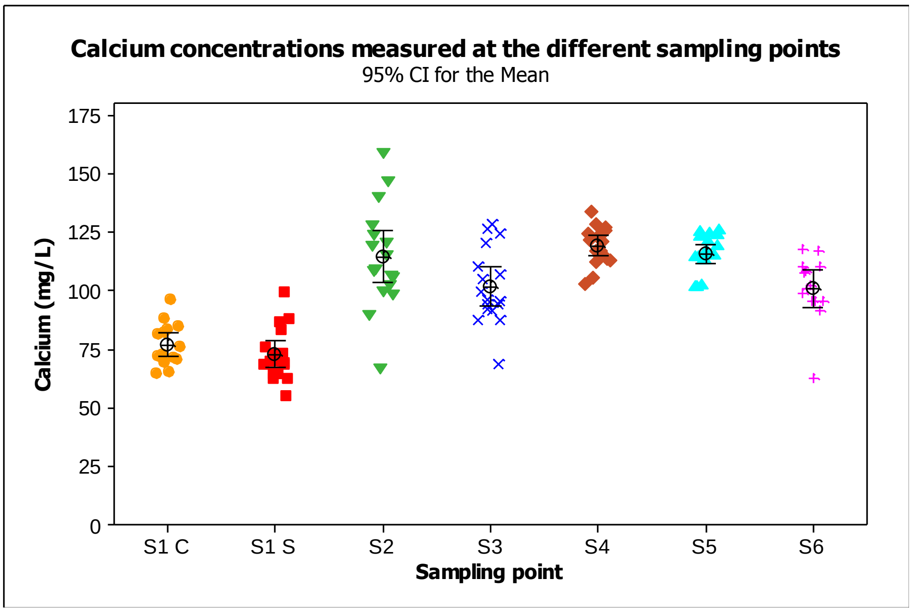
5.5.4.3. Calcium

Calcium is an essential cation for plants, animals and human. In animals and human, it constitutes tissues (e.g. bone), takes part in several biochemical and enzymatic reactions and it has a very important role in the cardiovascular and nervous systems. The main source of calcium is the food, especially milk and dairy products, sardines and green leafy vegetables. Drinking-water can be a contributor to calcium intake (WHO, 2009a). In plants, calcium regulates transport of other nutrients and is also involved in enzymes activation. It is involved in photosynthesis and plant structure, and its deficiency results in stunting. Calcium is naturally present in the earth crust and it is widely used in the metallurgic industry, as well as added to food and medicines. Calcium is also one of the ions highly contributing to water hardness.

Calcium concentration varied in the recycled water at RISMAR scheme, and it was highly influenced by the soils and sediments found in the area. Fluctuations were higher in the river water, especially before the discharge area (S2) (see Figure 25). Treated wastewater presented a lower average calcium concentration (S1 C: 77 mg/L) than river water (S2: 114 mg/L) or recovered water (S4: 114 mg/L). A calcium concentration increase in the recovered water not paired to an increase in the river water or treated wastewater could be a sign of calcium released from aquifer sediments. This has been discussed in section 5.5.11.

No guideline value is set for calcium in the Spanish legislation or in the other guidelines used. Regarding irrigation, SAR is much more commonly used than magnesium or calcium directly, and guideline values are set for SAR. Calcium is much more commonly measured for potable water control, but its measurement is also necessary in order to calculate SAR.

Figure 25 Calcium concentrations measured at the different sampling points.

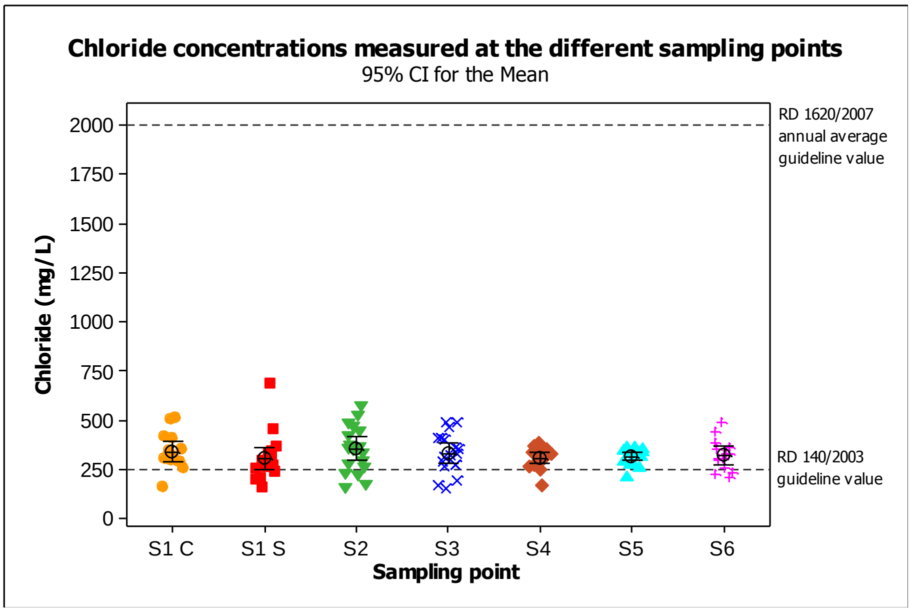


5.5.4.4. Chloride

Chloride is an essential micronutrient in plants, but may be toxic at high concentrations. Chloride is not sorbed to soil clay particles, having permanent negative charge, and therefore is leached to the groundwater by rain and irrigation, and accumulates on the soil surface during evaporation of soil water (Kafkafi, 2011). The toxicity to plants generally occurs at concentrations higher than those that cause salinity and associated osmotic effects; consequently, the toxicity effects are usually secondary to the osmotic effects from salinity. If the chloride concentration in the leaves exceeds the tolerance of the crop, injury symptoms develop such as leaf burn or drying of leaf tissue. Normally, plant injury occurs first at the leaf tips (which is common for chloride toxicity), and progresses from the tip back along the edges as severity increases. Excessive necrosis (dead tissue) is often accompanied by early leaf drop or defoliation (FAO, 1985). Crops grown in soil environments high in chloride can suffer from toxicity, as chloride is taken up by the plant roots, translocates to the shoot, and accumulates in the leaves causing foliar injury and leading to yield decline due to an osmotic effect. Chloride injury can also result from direct leaf absorption during overhead sprinkler irrigation. Sensitive plant species can also suffer associated nutrient imbalances, as chloride interferes with the uptake of other anions such as nitrate, phosphate and sulphate. Chloride can also increase plant uptake of cadmium from soil. Chloride is naturally present in waters from the dissolution of salt deposits, but it can also come from industrial effluents, wastewater and saline intrusion. Sodium chloride is widely used in the production of industrial chemicals such as fertilizers, caustic soda, chlorine, and sodium chlorite and hypochlorite, and it is also used in detergents and in the textile industry to fix the dyes in fabrics. The main source of human exposure is the addition of salt to food, and the intake from this source is usually greatly in excess of that from drinking-water. Excessive chloride concentrations increase rates of metal corrosion in the distribution system, depending on the alkalinity of the water, and this can lead to increased concentrations of metals in the supply (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; WHO, 2011a;).

Presence of chloride at RISMAR scheme was highly influenced by the textile industries present in the area, although their activity has strongly decreased in the recent years, with many of them ceasing their activities. In Figure 26 the individual values measured for chloride at the different sampling points can be observed.

Figure 26 Chloride concentrations measured at the different sampling points.



Chloride suffered strong fluctuations at RISMAR scheme along the sampling period, being these fluctuations smaller in the aquifer water. Overall, measured chloride values at RISMAR scheme are high, and average values are similar in all sampling points, ranging from 307 to 355 mg/L. As the effluent of the WWTP presented similar values than the Ripoll River water before the discharges, the effluent was not impoverishing the Ripoll River water quality for this anion, neither the aquifer water quality which was similar too. Probably, as textile companies were settled close to the Ripoll River in different stretches of it, they were influencing the Ripoll River quality already before the discharge area, through discharges from other WWTPs upstream. Rain events had a strong effect in the chloride concentration, diminishing it considerably (data not shown). The highest peak values were measured in the treated effluent (S1 S: maximum of 687 mg/L) and the river water before the discharges (S2: maximum of 579 mg/L).

Considering the Spanish water reuse RD, all sampling points would meet the guideline values, while any of them would meet the Spanish drinking water RD. In any case, the guideline value set in the Spanish drinking water RD, as well as in other drinking water guidelines considered (see Appendix E), is based on the taste threshold in drinking water, which is of approximately 250 mg/L, and it is not a health guideline value. Other guideline values set for irrigation, like in the Australian Irrigation Water Guidelines, are set to prevent foliar injury (175 mg/L for sensitive plants) and to prevent increased cadmium uptake (350 mg/L). Regarding foliar injury, table grape and almond are cultivated and are very sensitive to foliar injury (sensitive to values <175 mg/L; see Table 13). According to the average chloride concentration in the final irrigation water, which is of 317 mg/L, these crops would be affected. Pepper and tomato are moderately sensitive (ANZECC-ARCAMZ, 2000), and are affected by values ranging from 175-350 mg/L, so these crops would be less affected than table grape and olive, but in the very limit. For cadmium uptake, the risk can be considered low, as the cadmium concentration in the irrigation water is under the limit of detection or very low, and it is not expected that cadmium was accumulated in the soils in the area.

Thus, considering the results obtained, there are risks for the crops grown in the area of foliar injury, thus reducing the crop yield, but there are no risks for the other end points considered.

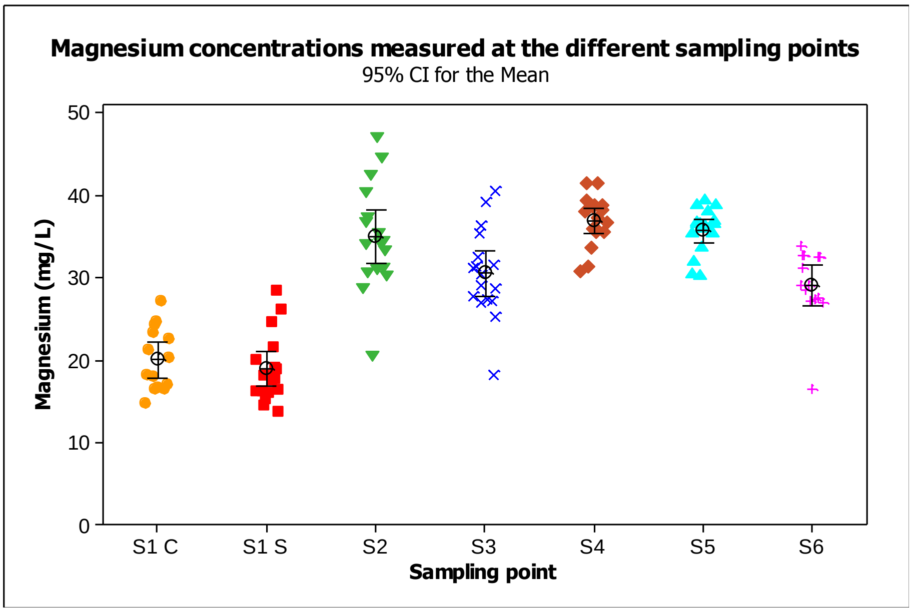
5.5.4.5. Magnesium

Magnesium is an essential cation for plants, animals and human. In animals and human, it constitutes tissues (e.g. bone) and takes part in many metabolic reactions, as well as playing a very important role in the cardiovascular and nervous systems (WHO, 2009a). The main source of magnesium is the food, especially seeds, cereals, legumes and green leafy vegetables. In plants, magnesium is a constituent of the chlorophyll molecule and it is an activator of enzyme reactions. It is naturally present in the earth crust and it has different industrial applications, as a catalyser, to synthetize organic compounds, in alloys and in medicines. Magnesium is also one of the ions highly contributing to water hardness.

Magnesium concentration was highly influenced by the soils and sediments found in the area. The treated wastewater presented a lower average magnesium concentration (S1 C: 20 mg/L) than the river water (S2: 35 mg/L) or the recovered water (S4: 37 mg/L) (see Figure 27).

No guideline value is set for magnesium in the Spanish legislation or in the other guidelines used. Regarding irrigation, SAR is much more commonly used than magnesium or calcium directly, and guideline values are set for SAR. Magnesium is much more commonly measured for potable water control, but its measurement is also necessary in order to calculate SAR.

Figure 27 Magnesium concentrations measured at the different sampling points.

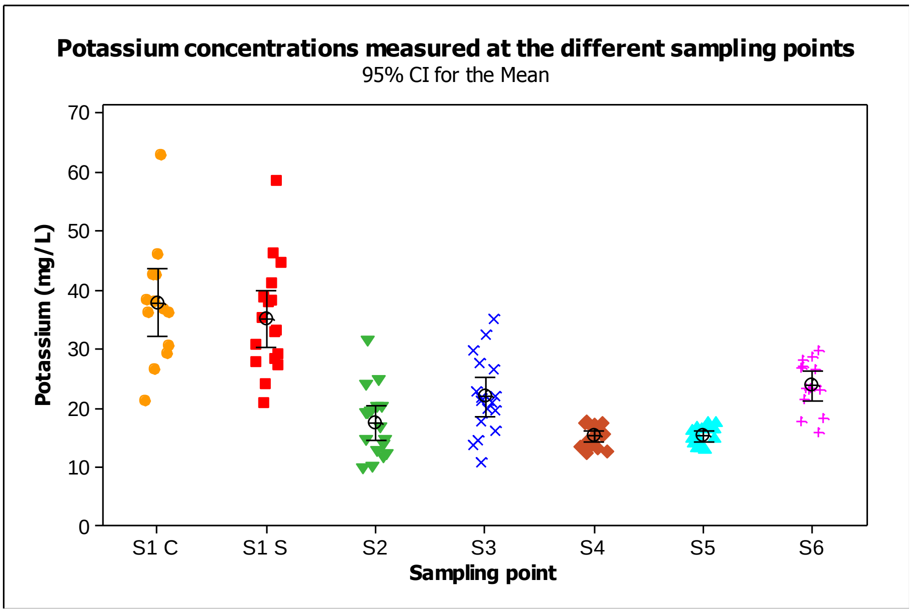


5.5.4.6. Potassium

Potassium is an essential macronutrient for plants, animals and human. It occurs widely in the environment, including all natural waters, and soils are regularly rich in potassium. It can also occur in drinking-water as a consequence of the use of potassium permanganate as an oxidant in water treatment (WHO, 2011a) and for recycled water is used to treat odours. It is usualy added as a fertilizer for plants, so, in general, the concentration in water and soils is not enough. An excess of potassium in the irrigation water can inhibit germination, uptake of other minerals and reduce the quality of the crop. However, potassium is necessary for the formation of carbohydrates and proteins, the regulation of internal plant moisture, as a catalyst and condensing agent of complex substances, as an accelerator of enzyme action, and as contributor to photosynthesis. In animals and human, the diet is the major source of potassium, and it plays an important role in the nervous, circulatory and muscular systems, as well as in the homeostatic function. An excess of potassium can produce problems in the nervous, circulatory and gastrointestinal systems. Potassium is used in fertilizers, soaps, glass, for regeneration of ion exchange water softeners, pyrotechnics and photoelectric cells.

Potassium concentrations varied considerably in the treated wastewater and the river water, while they remained rather constant in the aquifer and the final treated water (see Figure 28). The concentration of potassium was higher in the treated wastewater (S1 C, average of 38 mg/L) than in the river water (S2, average of 17 mg/L; S3, average of 22 mg/L) and the aquifer (S4, average of 15 mg/L), and this could be due to the kind of raw wastewater received at the WWTP. Presence of a higher concentration of potassium in the treated wastewater may be due to industrial discharges in the area.

Figure 28 Potassium concentrations measured at the different sampling points.



There are no guideline values for potassium, but in the WHO drinking water guidelines it is indicated that the daily potassium requirement for humans is of 3000 mg, a quantity that can never be fulfilled only by the drinking water ingested and needs to come from daily food intake. Regarding crops, potassium would probably need to be added, as crop demands are regularly higher (see section 8.1.4, p. 237).

Then, considering the results obtained, potassium does not pose a risk for any of the end points considered.

5.5.4.7. Sodium, SAR and infiltration problems

In small quantities, sodium is beneficial to the growth of some plants, but at higher concentrations it is toxic to many plants. Toxicity generally occurs at concentrations higher than those that cause salinity and associated osmotic effects; consequently, the toxicity effects are usually secondary to the osmotic effects from salinity, similar to chloride. Sodium toxicity is not as easily diagnosed as chloride toxicity, but clear cases of the former have been detected. Typical toxicity symptoms are leaf burn, scorch and dead tissue along the outside edges of leaves in contrast to symptoms of chloride toxicity which normally occur initially at the extreme leaf tip. An extended period of time (many days or weeks) is normally required before accumulation reaches toxic concentrations. Symptoms appear first on the older leaves, starting at the outer edges and, as the severity increases, move progressively inward between the veins toward the leaf centre (FAO, 1985). Many soils, particularly those with a finer texture (clay soil), have naturally elevated sodium levels that may exacerbate toxicities from direct leaf exposure injury (e.g. during overhead sprinkler irrigation) or from recycled water irrigation. The sodium ion is widespread in water due to the high solubility of sodium salts and the abundance of mineral deposits. Proximity to coastal areas, saline intrusion and natural contamination can contribute to the sodium content in recycled waters. Sodium chloride is widely used in the production of industrial chemicals such as fertilizers, caustic soda, chlorine, and sodium chlorite and hypochlorite, and it is also used in detergents and in the textile industry to fix the dyes in fabrics. Sodium is also used in the food industry and for culinary purposes. The main source of human exposure is the addition of salt to food, and the intake from this source is usually greatly in excess of that from drinking-water. The possible association between sodium in drinking-water and the occurrence of hypertension is not clear; however, concentrations higher than 180-200 mg/L may give rise to unacceptable taste (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; WHO, 2011a).

Another important aspect to consider regarding sodium is its proportion relative to calcium and magnesium in the soil or in water, which is calculated as SAR. Excessive sodium in irrigation water promotes soil dispersion and structural breakdown only if sodium exceeds calcium by more than a ratio of about 3:1. Such relatively high sodium content often results in a severe water infiltration problem due to soil dispersion and sealing of the surface pores, in a similar way as does the very low salinity water. Infiltration refers to the entry of water into the soil, which is necessary in order to supply water to the plant and to avoid water run-off, and therefore water loss and soil erosion. The rate at which water enters the soil is referred to as the rate of infiltration. If sodium concentration is high but also is the total salts content, flocculation is favoured and infiltration is still good. Similarly, when calcium and magnesium are the predominant cations adsorbed to the soil, the soil tends to present a flocculated structure, thus enabling infiltration (FAO, 1985; Warrence *et al.*, 2002). In the past, several procedures have been used to predict a potential infiltration problem. The most commonly used method to evaluate the infiltration problem potential has been and probably still is the Sodium Adsorption Ratio (SAR) as indicated. The SAR of a soil extract or water can be calculated as follows:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

where sodium, calcium and magnesium are expressed in meq/L.

It must be taken into consideration that infiltration can be affected by many factors other than the salinity and the sodium to calcium and magnesium ratio, including physical characteristics of the soil, such as soil texture and type of clay minerals, and presence of dissolved organic matter, especially humic substances in high concentrations (FAO, 1985; Levy and Assouline, 2011). Other related problems such as soil crusting, poor seedling emergence, lack of aeration, plant diseases, weed and mosquito control problems caused by the low rate of infiltration may further complicate crop management

As pointed out for chloride (see section 5.5.4.4, p. 123), presence of sodium and chloride at RISMAR scheme was highly influenced by the textile industries present in the area, although their activity has strongly decreased in the recent years, with many of them ceasing their activities. In Figure 29 the individual sodium values measured at the different sampling points can be observed.

Figure 29 Sodium concentrations measured at the different sampling points.

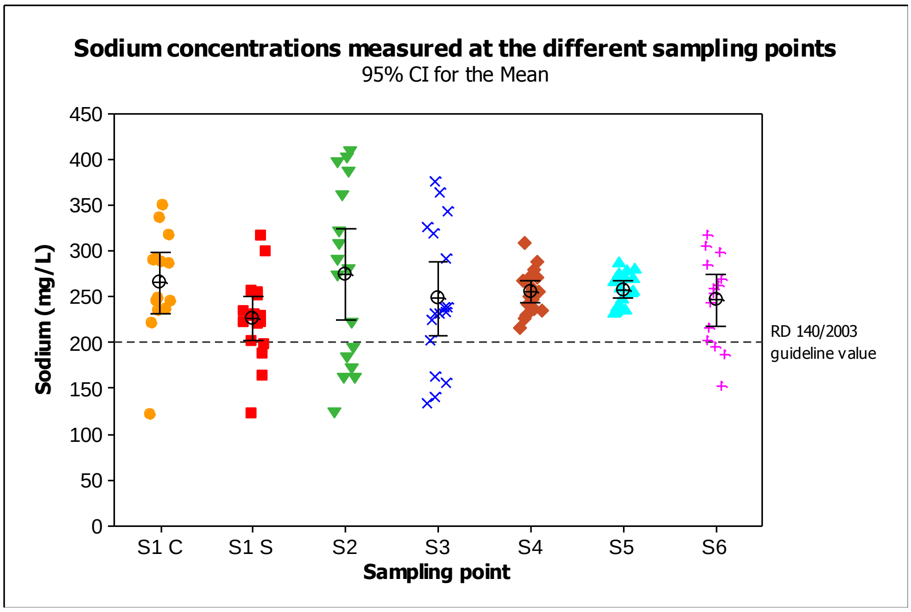
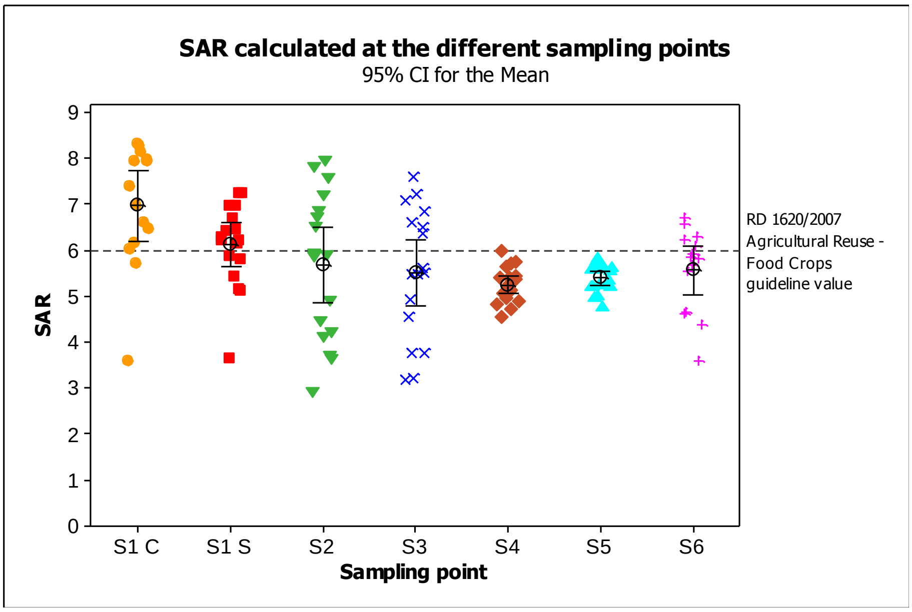


Figure 30 Sodium Absorption Ratio (SAR) calculated at the different sampling points.



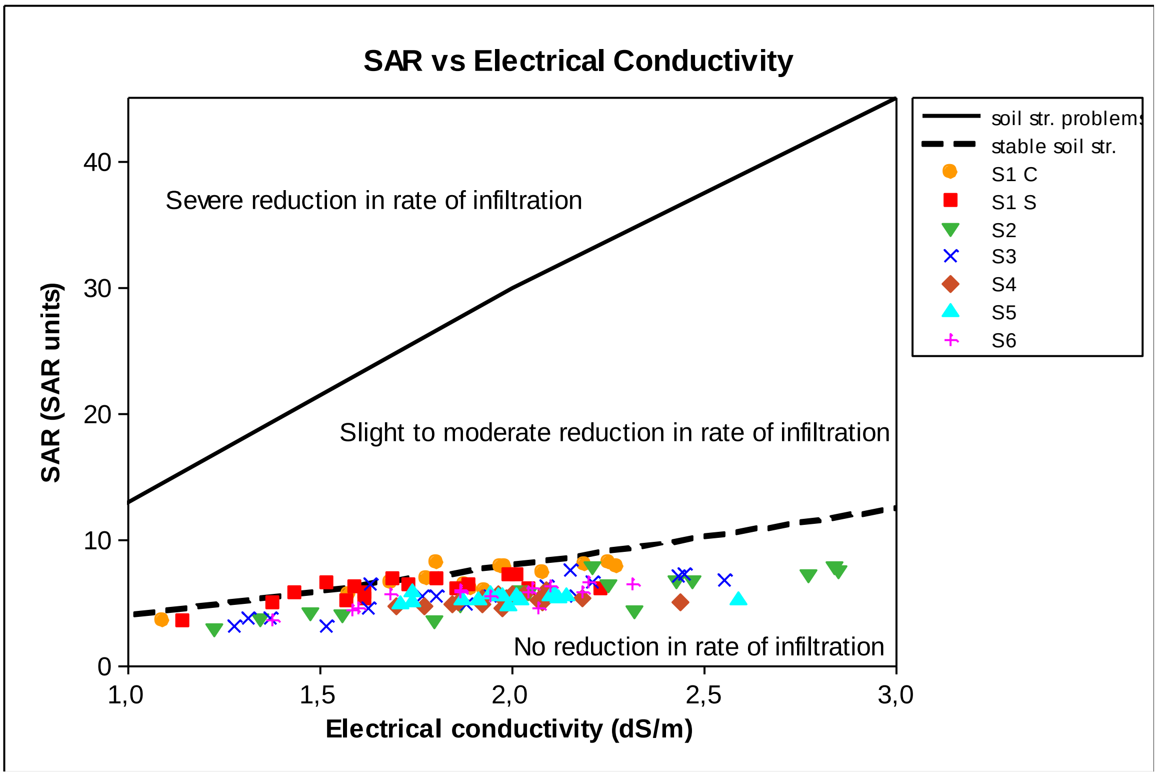
Sodium suffered strong fluctuations in the recycled water and riverbed filtration system along the sampling period, being these fluctuations smaller in the aquifer water, similarly to what happened with chloride. Overall, measured sodium values in the recycled water and riverbed filtration system were rather high, and average values were similar in all sampling points, ranging from 247 to 307 mg/L. As the effluent of the WWTP presented similar values to the Ripoll River water before the discharges, the effluent is not impoverishing the Ripoll River water quality for this cation, neither the aquifer water quality which was similar too. Probably, as textile companies are settled close to the Ripoll River in different stretches of it, they are influencing the Ripoll River quality already before the discharge area, through discharges from other WWTPs upstream. Rain events had a strong effect in the sodium concentration, diminishing it considerably. The highest peak value was measured in the river water before the discharges (S2: maximum of 411 mg/L).

There are no guideline values for sodium in the Spanish water reuse RD, but there are in the Spanish drinking water RD, and none of the sampling points would meet the guideline value. However, the guideline value set in the Spanish drinking water RD, as well as in other drinking water guidelines used (see Appendix E), is based on the taste threshold in drinking water of approximately 180-200 mg/L, and it is not a health guideline value. Other guideline values set for irrigation, like in the Australian Irrigation Water Guidelines (ANZECC-ARCAMZ, 2000), are set to prevent foliar injury if sprinkler irrigation is used (115 mg/L for sensitive plants). Regarding foliar injury, table grape and almond are cultivated in the area, and are very sensitive to foliar injury (sensitive to values <115 mg/L; see Table 13). According to the average sodium concentration in the final treated water, which is of 258 mg/L, these crops would be affected. Pepper and tomato are moderately sensitive (sensitive at values of 115-230 mg/L), so these crops would be also affected, but with a smaller effect than for table grapes. Nevertheless, these values were set to prevent foliar injury in case sprinkler irrigation was used, so this problem may be reduced and avoided if irrigation is performed using methods different than sprinkler irrigation.

Thus, considering the results obtained, sodium could pose a risk of foliar injury for some of the crops grown in the area in case sprinkler irrigation was the system selected to apply the water.

Regarding the soils, in order to evaluate the risk posed by sodium present in the irrigation water, SAR and electrical conductivity need to be evaluated together. SAR measured at the different sampling points rendered a similar average value, but variability in the results was high. Then, while treated wastewater (S1 C, SAR 3.6–8.3) and river water (S2, SAR 3.0 – 8.0) presented strong variations, the aquifer water and the final treated water SAR values span through a much more reduced range (S4, SAR 4.6–6.0; S5, SAR 4.7-5.8). Calculated SAR values for the different sampling points are represented in Figure 30.

Figure 31 Rate of infiltration in function of SAR and Electrical Conductivity.



In the Spanish water reuse RD a guideline value of 6 (maximum) for SAR is given, when the water is used for agricultural irrigation. The recovered water from the aquifer and the final treated water fulfil this guideline value, the river water SAR average fulfils also this value but not the maximum values measured, and the treated effluent does not fulfil this value neither for the maximum nor for the average SAR values. Then, the final treated water would fulfil the guideline value set in the Spanish water reuse RD. In the Australian irrigation water guidelines (ANZECC-ARCAMZ, 2000), it is indicated that a range of 2-8 for SAR in very sensitive crops causes burns in leaf tips. These very sensitive crops include deciduous fruits, which would be the case of table grapes grown in Sabadell. In the same guidelines it is also discussed the relationship between SAR and electrical conductivity in irrigation water for prediction of soil structural stability, and a figure is given to show this relationship. In previous FAO guidelines (FAO, 1985) the importance of SAR and electrical conductivity relationship to predict infiltration problems was already explained, and a similar figure appears. In both guidelines, the figure depicts two lines which separate the likelihood of soil structural problems (ANZECC-ARCAMZ, 2000) or the relative rate of water infiltration (FAO, 1985) in function of SAR and electrical conductivity. Then, in both guidelines the same problem is being discussed, but a different name has been given. A figure has been created (see Figure 31) using the values of electrical conductivity and SAR measured at RISMAR scheme, and considering the ranges set to evaluate the infiltration rate (or likelihood of soil structural problems). Considering the results obtained at RISMAR scheme for SAR and electrical conductivity, the final treated water used for irrigation should not pose a risk for the infiltration rate. In fact, none of waters (sampling points) evaluated at RISMAR scheme would pose a risk. For the WHO guidelines (WHO, 2006b), as it has been explained before (see section 5.5.4.1) electrical conductivity guideline values are set in relation to SAR, following previous FAO guidelines (FAO, 1985). This option makes much more sense than setting a unique guideline value for SAR, as infiltration problems regarding crop irrigation will arise depending on both the electrical conductivity and the SAR, and both parameters need to be evaluated together, not separately. The final treated water would also fulfil the guideline values set in these latter guidelines.

It is also important to consider the texture of the soils in the area to understand to which extent the irrigation water can affect the structure. The soils present in the river banks are mainly formed of coarse sand and gravel, with patches of fine sands and silty loams. These kinds of textures present a good hydraulic conductivity and the salts are perfectly leached, thus reducing the risk of sodium accumulation. In the Taulí Park the soil has a silty loam texture, which has also a good hydraulic conductivity and the salts are leached. Then, the textures of the soils in the area would have a beneficial effect in reducing the possible problems arising from the presence of a high concentration of sodium in the final treated water.

Considering the results obtained for SAR and electrical conductivity, the final treated water should not pose a risk for the infiltration rate, although the SAR guideline values given in the different guidelines considered present discrepancies.

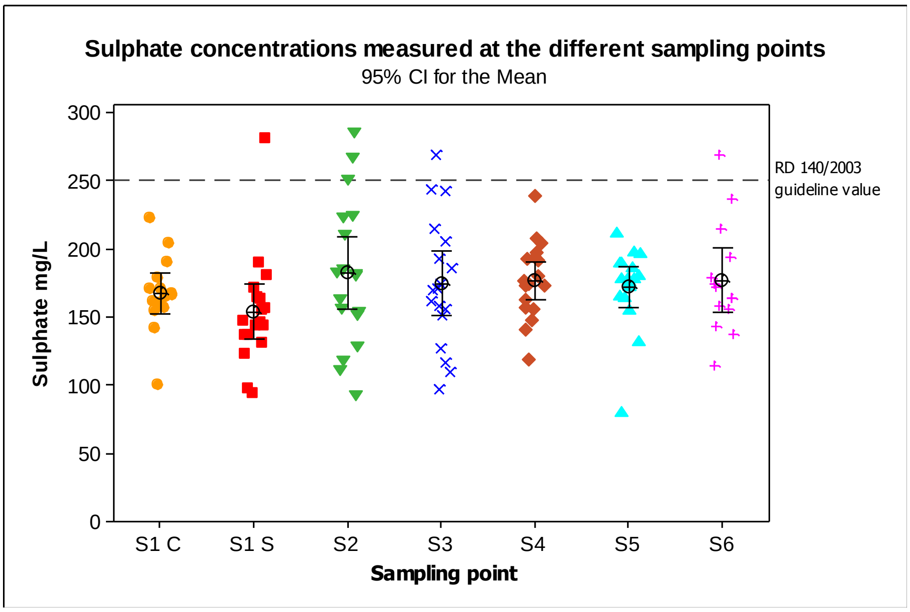
5.5.4.8. Sulphate

Sulphur is a nutrient for plants and is found in all body tissues, concentrating in the metabolically active areas of bone and tooth formation. It can have a laxative effect in animals and human at high concentrations (1000–1200 mg/L). The presence of sulphate in drinking-water may also cause noticeable taste (threshold value of 250-500 mg/L) and may contribute to the corrosion of distribution systems. Sulphate occurs naturally in a number of minerals, and is used commercially in the manufacture of numerous products including chemicals, dyes, glass, paper, soaps, textiles, fungicides and insecticides. In the water industry, aluminium sulphate is used as a flocculant in water treatment, and copper sulphate is used for the control of cyanobacteria in water storages. It is discharged into water in industrial wastes and through atmospheric deposition; however, the highest levels usually occur in groundwater and are from natural sources. In general, the average daily intake of sulphate from drinking-water, air and food is approximately 500 mg, food being the major source. However, in areas with drinking-water supplies containing high levels of sulphate, drinking-water may constitute the principal source of intake. Under anoxic conditions, the reduction of sulphate to sulphide by sulphate-reducing bacteria can result in unpleasant taste and odour due to the release of hydrogen sulphide, and can increase corrosion in pipes (NHMRC-NRMMC, 2011; WHO, 2011a).

Sulphate concentration in the recycled water scheme was in general similar in all sampling points, with average values ranging from 154 to 182 mg/L and marked variations during the sampling period (see Figure 32). For other major ions measured, these variations also occurred but not for the aquifer water (e.g. sodium, magnesium, chloride), which did suffer variations for sulphate. Then, industrial discharges are not affecting the concentration of this anion at RISMAR scheme, and its presence is much more probable to have a natural origin.

Sulphate measured concentrations fulfilled the Spanish water reuse RD guideline value (2000 mg/L) in all sampling points, and the Spanish drinking water RD for the final treated water (S5). River water (S2: maximum of 286 mg/L; S3 and S6: maximum value of 269 mg/L) and secondary effluent (S1 S: maximum of 282 mg/L) presented maximum values a bit higher than the guideline value given in the Spanish drinking water RD, which is of 250 mg/L. Other drinking water guidelines, like WHO and Australian, set a maximum value of 500 mg/L, while the US EPA drinking water guidelines set a maximum value of 250 mg/L, like in the Spanish drinking water RD. In any case, the set drinking water guideline values are not related to human health but to taste, and are fulfilled by the final treated water for reuse.

Figure 32 Sulphate concentrations measured at the different sampling points.



Note: for the purposes of the graphical representation, the Spanish water reuse RD guideline value (2000 mg/L) has not been represented, in order to have a better view of the results obtained, and only the Spanish drinking water RD guideline value has been represented.

Then, considering the results obtained, sulphate does not pose a risk for any of the end points considered.

5.5.5. Nutrients

Plant macronutrients, namely nitrogen, phosphorus and potassium, have been evaluated at RISMAR scheme. Potassium has been discussed in section 5.5.4. Nitrogen and phosphorus, although they are necessary for plant growth, can potentially cause nutrient imbalance in irrigation water, soil eutrophication and toxic effects on terrestrial biota. Nitrogen and phosphorus in the infiltration water will stimulate microbial activity in the subsurface, leading to increasing redox reactions in the aquifer. In turn, this alters the concentration of inorganic and organic compounds in the groundwater, and affects aquifer permeability due to clogging processes (NRMMC-EPHC–NHMRC, 2009). Nutrients can also pose a risk of causing biological clogging in the riverbed filtration system and irrigation systems. In the case of RISMAR scheme, as the riverbed is mainly formed of sand and gravel, the risk of biological clogging can be considered to be very low. However, there is still a risk for the irrigation systems. From the human health point of view, only nitrate and nitrite need to be considered.

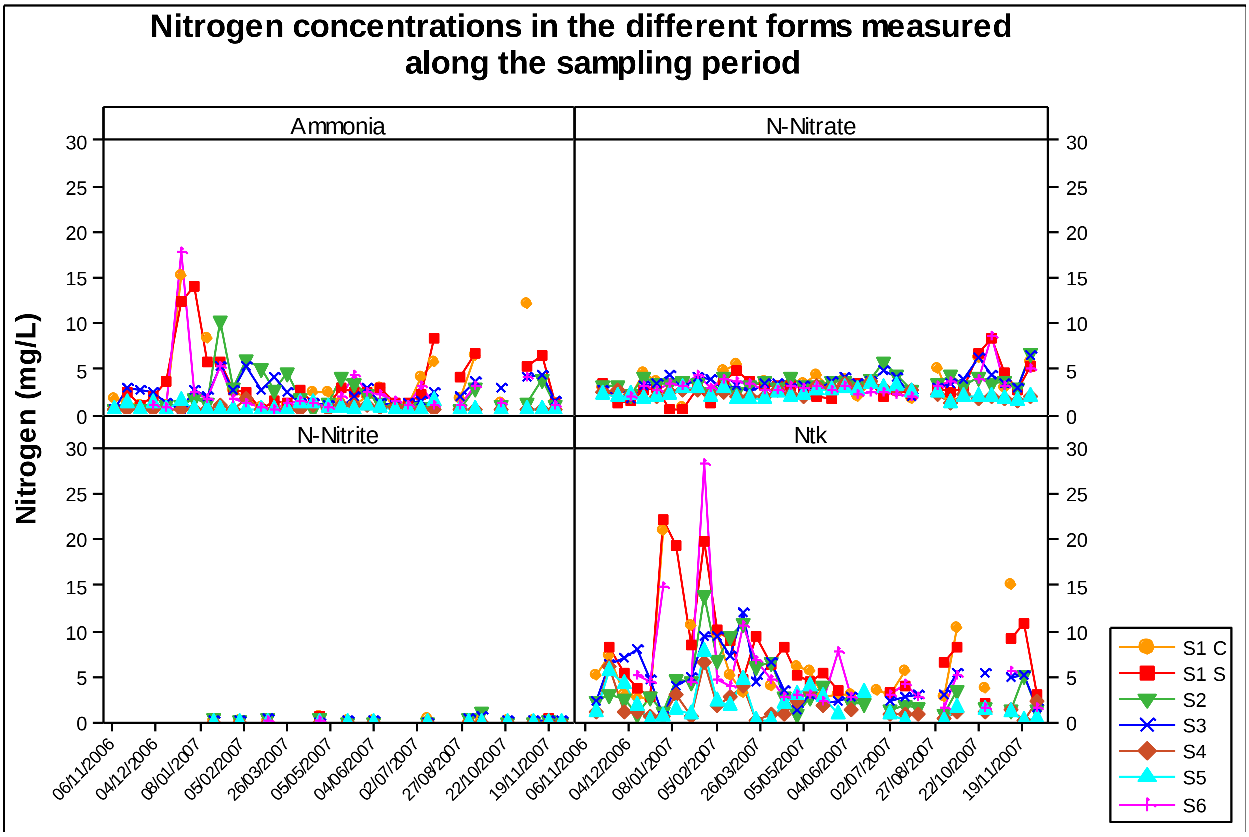
5.5.5.1. Nitrogen

Nitrogen is a necessary macronutrient for plants that can be found in treated wastewater as nitrite, nitrate, ammonia and organic nitrogen. The sum of all these forms is known as total nitrogen. Plants absorb nitrate only, but regularly the other forms are transformed into nitrate in the soil. Nitrogen is usually added for each agricultural cycle. Plants have a high nitrogen demand during initial growth stages, but this demand decreases during flowering and maturation, and excessive concentrations may lead to yield losses. Nitrogen in inorganic fertilizers is added in the form of nitrate. Nitrate is very soluble in water, and it is regularly washed out from agricultural fields and farms or come from wastewaters, reaching continental waters, groundwater and drinking water sources, and playing an active role in eutrophication, although phosphorus is usually the limiting nutrient. Nitrate can also be toxic for animals and human, causing methaemoglobinemia, by its reduction to nitrite in the stomach; however, latest studies indicate that the risk seem to be related to gastrointestinal infections, which increase endogenous nitrite formation. Another potential risk posed by nitrate is the development of gastrointestinal cancer, through the formation of nitrosamines in the human digestive tract, but no causal association between gastric cancer and nitrate in drinking-water has been found to date (NHMRC-NRMMC, 2011; Powlson *et al.*, 2008; WHO, 2011a). The nitrite ion is relatively unstable and can be formed by bacterial reduction of nitrate in poorly oxygenated waters or in vivo in the intestinal tract, but regularly it is rapidly oxidised to nitrate. Food, particularly vegetables and cured meat, is the major source of nitrite intake for humans. The third inorganic form of nitrogen found in water is ammonia, and the term includes the non-ionized (NH_3) and ionized (NH_4^+) species. Ammonia in the environment originates from metabolic, agricultural and industrial processes and from disinfection with chloramine. It is used commercially in animal feeds and fertilisers, and in the manufacture of fibres, plastics and explosives. Ammonia products are widely used as cleaning agents and food additives. It is a major component of the metabolism of mammals. Exposure from environmental sources is insignificant in comparison with endogenous synthesis of ammonia. However, ammonia can compromise disinfection efficiency, result in nitrite formation in distribution systems and cause taste and odour problems. Organic nitrogen may originate from animal, plant and human wastes, and can be also assimilated in the soil through bacterial reactions (ANZECC-ARCAMZ, 2000; NHMRC-NRMMC, 2011; NRMMC–EPHC–AHMC, 2006; US EPA, 2009; WHO, 2006b, 2011a).

Nitrogen in nitrite, nitrate, ammonia forms and organic forms has been measured at RISMAR scheme. Figure 33 shows the different nitrogen species measured along the sampling period and for the different sampling points.

Nitrite was detected in very low concentrations in the measured samples, however, it must be considered that nitrite quickly oxidizes to nitrate. Thus, it is possible that part of the initially present nitrite in the water samples had already been converted to nitrate at the moment of measuring the samples. However, a peak value of 1.2 mg/L (N-nitrite) could be detected in the river water before the discharges (S2), indicating that even though nitrite is quickly oxidized to nitrate it could still be measured in the water samples. Average N-nitrite concentration in the secondary effluent was very similar to average N-nitrite concentration in the river water before and after the discharges, ranging from 0.26-0.30 mg/L. In the recovered water, most of the samples presented nitrite concentrations below the LOD, and average N-nitrite concentration was just above the LOD (S4: 0.081 mg/L). In the final treated water, as it is disinfected by chlorine and it suffers an oxidation process, all measured samples presented nitrite concentrations below the LOD, as the low concentrations detected in the recovered water are readily oxidized to nitrate. The recovered water and the final treated water fulfil the water reuse and the Spanish drinking water RDs regarding nitrite, but the other sampling points would not fulfil the Spanish drinking water RD, which is rather restrictive comparing to other guideline values set by WHO or the Australian authorities (0.03 mg/L in the outlet WWTP and 0.15 mg/L in the distribution network for the Spanish drinking water RD, whereas 0.9 mg/L in the WHO and the Australian drinking water guidelines). In any case, as nitrite is oxidised to nitrate, it is barely detected in the groundwater and the secondary effluent presents similar values than the river water, nitrite does not pose a risk for any of the end-points considered.

Figure 33 Nitrogen concentrations in the different forms measured along the sampling period at the different sampling points.



Note: values below the LOD have been represented as the LOD. “Ntk” stand for “Total Kjeldahl Nitrogen”, which is the sum of ammonia and nitrogen in organic form.

Nitrate concentrations are similar in all sampling points, but a bit lower in the recovered water, and do not present a seasonal fluctuation as it is the case for ammonia and organic nitrogen. Average N-nitrate concentration in the secondary effluent was very similar to average N-nitrate concentration in the river water before and after the discharges, ranging from 3.0 to 3.5 mg/L, and the maximum value measured was in the river water mixture 2 (S6: 8.5 mg/L). In the recovered water, the average N-nitrate concentration was of 2.3 mg/L, with a maximum value measured of 3.5 mg/L. This indicates that the aquifer is not contaminated with nitrate coming from the effluent discharges or agricultural run-off, and that nitrate infiltrated through the riverbed is whether transformed by bacteria (denitrification process) or diluted in the aquifer water. The river water is not affected by the effluent discharges, as values before and after the discharges are similar to the ones measured in the effluent. Measured nitrate concentrations in the recovered water and the final treated water fulfil the water reuse and the Spanish drinking water RDs, as well as other guideline values used for drinking water. However, the other sampling points would not fulfil the Spanish water reuse RD, regarding its use for MAR. The guideline value set for MAR use in the Spanish water reuse RD was probably set in order to minimize build-up of nitrate contamination in the aquifer, and no other guidelines are available to compare. However, the river water that is infiltrated (S2 and S3) only exceeds the guideline value in the maximum value measured, so nitrate concentration in the infiltration water does not pose a risk for the aquifer and any of the environmental points considered. Regarding the human health, the drinking water guideline values are fulfilled, so it would not pose a risk.

Ammonia concentration decreases along the treatment train. While the average concentration of N-ammonia measured in the secondary effluent ranges from 3.1 to 3.5 mg/L (composite and grab samples, respectively), it decreases to 2.1-2.3 mg/L in the river water (S2, S3 and S6 sampling points), and it decreases even more after infiltration and subsurface treatment, being of 0.63 mg/L in the recovered water (S4). Also the maximum value of N-ammonia measured in the recovered water is of 1.7 mg/L, while maximum value measured in the river water is of 18 mg/L (S6) and 15 mg/L in the secondary effluent (S1, composite sample). Then, ammonia seems to suffer a slight reduction in the river, and the most important reduction occurs by infiltration through the riverbed and subsurface treatment. Microorganisms present in the soil and in the river water, as well as algal photosynthetic activity, can degrade or use ammonia. It can also be diluted in the aquifer or oxidised to nitrate under aerobic conditions. Ammonia concentrations also suffer seasonal variations, which can be observed in Figure 33. Maximum ammonia concentrations are measured during the winter period, in the treated wastewater and in the river water as well, and there is a steady decrease until the summer period, when the lowest concentrations are detected. This is directly related to a higher microbial and algal metabolism during summer period, due to higher temperatures and irradiation. This increased metabolic activity during summer consumes more nitrogen and increases the pH in the water. Wastewater treatment, nitrification in this case, is also more efficient in summer than in winter, as microorganisms in the secondary treatment are more active. Then, higher amounts of ammonia and organic nitrogen are discharged into the river during winter. Considering these results, the river water is not very much affected by the treated effluent discharges, as ammonia concentrations before and after the treated wastewater discharges are similar. The groundwater does not seem to be affected either, as the recovered water ammonia concentration is much lower than in the river water, thus not compromising the aquifer. Besides, anaerobic groundwater may contain up to 3 mg/L (WHO, 2011a), and the maximum value measured was of 1.7 mg/L. The recovered and the final treated water fulfil the Spanish water reuse RD, but not the Spanish drinking water RD. In many samples, ammonia concentration is below the LOD (0.5 N-ammonia mg/L), which is already a bit higher than the guideline value set in the Spanish drinking water RD (0.4 N-ammonia mg/L). Considering the information given in other drinking water guidelines used (WHO and Australian), the guideline value is set to avoid corrosion of copper pipes and fittings, but it is not a health guideline value. Then, using the recovered water as drinking water would not pose a risk for the human health, but it might cause problems in the distribution network. The river water before and after the discharges (S2 and S3) would fulfil the Spanish water reuse RD, and the treated wastewater too but for the maximum values measured. Then, the infiltration water (S2 and S3) would fulfil the MAR use requirements. The recovered and the final treated water would also fulfil the Australian aquatic ecosystems and the US EPA environmental reuse guideline values, but not the other sampling points. Then, the ammonia concentrations in the river water could potentially harm the living species in it, but this risk cannot be only attributed to the treated wastewater discharges of the

Ripoll River WWTP, as the values are similar before and after the discharges, but also to discharges upstream the Ripoll River by other WWTPs.

Organic nitrogen indicates the presence of macromolecules in the water, as well as wastes of plant and animal origin, algae and microorganisms. Organic nitrogen was measured by means of the Kjeldahl method, which detects the sum of ammonia and nitrogen in organic form. Total Kjeldahl nitrogen follows the same seasonal trend as ammonia, but more marked due to the higher values measured, and the same reduction along the treatment train. Total Kjeldahl nitrogen average concentration in the secondary effluent ranges from 5.9 to 7.9 mg/L (composite and grab samples, respectively), it decreases to 3.8-5.7 mg/L in the river water (S2, S3 and S6 sampling points), and it decreases even more after infiltration and subsurface treatment, being of 1.8 mg/L in the recovered water (S4). No guideline values are set for this form of nitrogen.

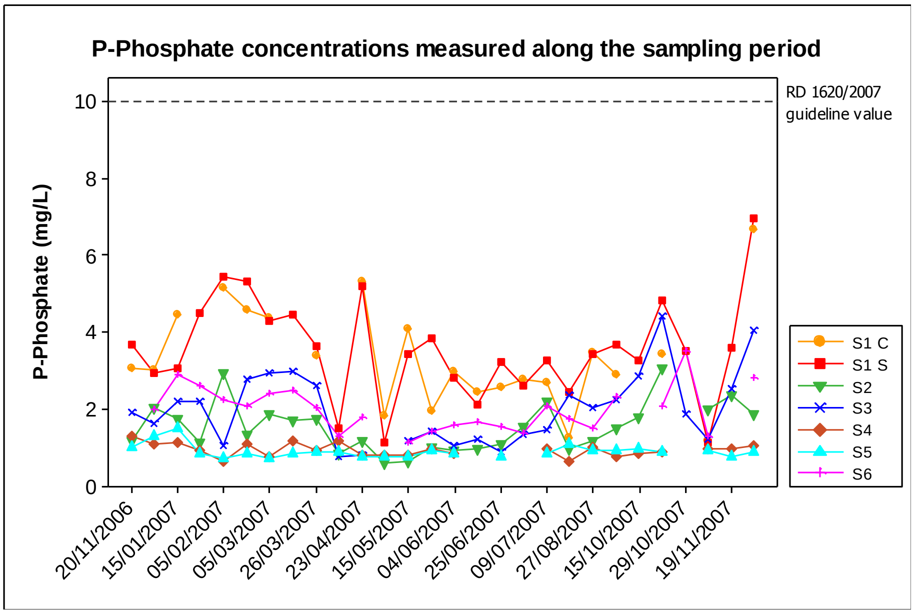
Total nitrogen was calculated by summing up the total Kjeldahl nitrogen (N-ammonia + organic nitrogen), N-nitrate and N-nitrite. As the organic nitrogen represents a high proportion of the total nitrogen, total nitrogen follows a similar trend than the organic nitrogen. Total nitrogen average concentration in the secondary effluent ranges from 9.4 to 11 mg/L (composite and grab samples, respectively), it decreases to 7.4-8.7 mg/L in the river water (S2, S3 and S6 sampling points), and it decreases even more after infiltration and subsurface treatment, being of 4.1 mg/L in the recovered water (S4). Nitrogen removal is a passive water-quality treatment provided by MAR operations, and different processes may take part in it, namely: biodegradation, microbial assimilation, filtration, sorption or precipitation (NRMMC-EPHC–NHMRC, 2009). In the Spanish water reuse RD a guideline value of 10 mg/L of total nitrogen is given for MAR use. The total nitrogen average measured concentrations in the infiltration water would fulfil it; in fact, the guideline value would be fulfilled in 86% of the measured samples. However, this guideline value is the same for MAR performed by infiltration as for MAR performed by injection. Then, this value is probably too restrictive for MAR performed by infiltration, as MAR performed by injection requires a lower content of nitrogen in order to prevent clogging. Besides, it must be taken into consideration that the river water naturally infiltrates to the aquifer, so the MAR process is only enhanced by the treated wastewater discharges, and infiltration would happen in any case. Regarding the final treated water, the average total nitrogen concentration is of 4.2 mg/L, which would fulfil the irrigation guideline values set in the Australian, US EPA and WHO guidelines. However, 22% of the samples measured would not fulfil the WHO and the Australian long-term value of 5 mg/L, set to ensure no decrease in crop yields in sensitive crops or quality due to excessive nitrogen concentrations during flowering and growth stages. Then, this should be taken into consideration if the final treated water is used for crop irrigation, especially considering table grape, as this is one of the sensitive crops cited by FAO (1985). Another use found at RISMAR scheme that should be considered is the Ripoll River flow augmentation (environmental reuse) by the treated wastewater discharges. In the US EPA water reuse guidelines there are total nitrogen values set in regulations of different states, which range from 3 to 6 mg/L. For this reuse scenario, the treated wastewater discharges would not fulfil these regulations. In the Spanish water reuse RD no guideline value is given for environmental use, and it is said that the water quality required will be evaluated case by case, so no guideline value is given.

5.5.5.2. Phosphorus

Phosphorus is a necessary macronutrient for human, animals and plants, which limits productivity in many agricultural systems, and in natural aquatic and terrestrial ecosystems. It is often scarce in soils and it usually needs to be added with fertilizers. Phosphorus does not occur in free in nature and is usually found in the form of phosphates in minerals. It is usually present in irrigation water in two forms: dissolved inorganic phosphate ions and colloidal phosphate (bound with solid minerals and/or organics). Dissolved inorganic phosphate ions (predominantly orthophosphate) are immediately bioavailable. When phosphorus is added to soils it is usually strongly adsorbed, and in contrast to nitrogen, little phosphorus is leached from agricultural soils, except for sandy soils. Excessive phosphorus in irrigation water is not a nutritional problem to plants. Generally, the phosphorus in recycled water greatly benefits the productivity of crops and landscape plants. However, high phosphorus concentrations may stimulate rapid growth of many microorganisms and algae in waters, because phosphorus is often the limiting nutrient for growth, and may trigger algal and cyanobacterial blooms. These algal and cyanobacterial blooms, which predominantly occur in stagnant or very slowly flowing water bodies, may deplete oxygen, increase mortality of biota and create health risks to humans and wildlife due to the production of cyanotoxins (produced by cyanobacteria). Another side effect of high phosphorus concentrations in irrigation water is the possibility of blocking the irrigation equipment. Apart from being added as a fertilizer, other applications of phosphorus are in detergents, nutrient supplements, water softeners, additives in foods and pharmaceuticals, additives in the metallurgic and gas industry, plasticizers and plaguicides (ANZECC-ARCAMZ, 2000; NRMMC–EPHC–AHMC, 2006; WHO, 2006b, 2011a).

Phosphorus was measured as dissolved inorganic phosphate. The average value of phosphorus in the treated wastewater (S1 S: 3.6 mg/L of P-phosphate) is higher than in the river water (S2: 1.5 mg/L of P-phosphate; S3 and S6: 2.0 mg/L of P-phosphate) and also higher than in the recovered water (S4: 1.0 mg/L of P-phosphate). While P-phosphate concentration remains constant and low in the aquifer and the final treated water, it suffers fluctuations in the treated wastewater and the river water, as it can be observed in Figure 34. Variations of P-phosphate concentration in the river water after the discharges (S3 and S6) are highly influenced by fluctuations of P-phosphate concentration in the treated wastewater. Phosphorus increases are observed coinciding with typical fertilization seasons, which are spring and autumn. Then, phosphorus is washed off from orchards and fields, and reaches the river. It is also important the dilution effect while mixing the treated wastewater with the Ripoll River water. Although phosphorus is also an essential nutrient for microbial growth, removal in the aquifer is predominantly through precipitation as highly insoluble calcium phosphate, or by adsorption to iron and aluminium oxides (NRMMC-EPHC–NHMRC, 2009). The precipitation process reduces a great part of the P-phosphate present in the river water, as values in the aquifer and the final treated water are lower and constant.

Figure 34 P-Phosphate concentrations measured along the sampling period at the different sampling points.



The presence of increased phosphorus concentrations in the river water is the driver of the eutrophication observed in it, with macrophytes growing during summer and warmer periods of time. In this case, the treated wastewater contributes to increase the phosphorus concentration in the river water. Although the Ripoll River before the discharges already carries high concentrations of phosphorus, unusual for river water, the phosphorus concentration in the river water increases after the treated wastewater discharges. Nutrients are present in high concentrations in the untreated wastewater (data not shown), and are highly reduced by the treatments performed at the Ripoll River WWTP, especially in the secondary treatment. In the case of nitrogen, the reduction thanks to the secondary treatment is very high, and the discharged water fulfils the requirements set by the administration, with removals always higher than 70%. However, the presence of phosphorus in the treated wastewater is sometimes still high. The performance of the secondary treatment for phosphorus removal was, in general, very variable, ranging from no removal to more than 90% removal, with an average removal of 53% during the period of time when sampling for the RECLAIM WATER project was performed (calculated thanks to data facilitated by CASSA and EDS), and not enough to reduce the phosphorus concentration to less than 1 mg/L, which is the amount set in the RD 509/1996. Nevertheless, as this law states to ensure whether the nitrogen or the phosphorus guideline values and/or reductions, the discharged water would fulfil this law because the nitrogen reductions are attained. However, as it has been explained before, phosphorus is often the limitant nutrient, and efforts should be directed to reduce phosphorus concentrations in treated effluents. In fact, in order to avoid eutrophication, even lower concentrations than 1 mg/L should be achieved, as it is known that concentrations of phosphorus of less than 0.1 mg/L are sufficient to induce a cyanobacterial bloom (WHO, 1999).

The guideline value set in the Spanish water reuse RD is of 10 mg/L for total phosphorus. In this study, dissolved P-phosphate was measured, and all sampling points meet this guideline value. However, if colloidal phosphate had also been measured, the total phosphorus result would have been probably higher, and then not all the sampling points would meet the guideline value, probably only the recovered and final treated waters would meet it. Other guideline values considered are included in the US EPA water reuse guidelines, for environmental reuse (1.0-2.0 mg/L for total phosphorus) and in the Australian irrigation water guidelines (0.05 mg/L for the long-term use for irrigation, 0.8-12 mg/L for the short-term use for irrigation, both for total phosphorus). The US EPA guideline value for environmental reuse is included in regulations of some of the states. It would not be met by the treated wastewater discharged to the Ripoll River, and would not be met by the river water, which is the water that infiltrates to the aquifer. However, the presence of phosphorus in the Ripoll River water before the discharges is already high, and would not meet the guideline values cited. In the case of the Australian irrigation water guidelines, the long-term value for phosphorus has been set to minimise the risk of algal blooms developing in storage facilities, and to reduce the likelihood of biofouling in irrigation equipment, so it should not be seen as a default value for phosphorus in irrigation waters if biofouling of equipment is not a potential issue. The final treated water used for irrigation would not meet this long-term guideline value, and then, there could be a risk of biofouling in the equipment. The short-term irrigation value is considered in the guidelines as an interim range for phosphorus, as this guideline value should be set in after a site-specific assessment. In any case, the final treated water could meet this guideline value, as well as the other sampling points, as the range is very high. As the final treated water presents values in the lower bound of this range (average concentration of 0.91 mg/L of P-phosphate), it could be considered as appropriate for irrigation, although there has not been a site-specific assessment.

Overall, the main risk related to phosphorus at RISMAR scheme is eutrophication of the river water and biofouling of the equipment, and it is necessary to closely monitor the irrigation systems to avoid problems. For the other end-points considered, phosphorus does not pose a risk.

5.5.6. Organic compounds

Organic compounds are a combination of carbon, hydrogen and oxygen, together with nitrogen, phosphorus and sulphur in some cases. In general, the analyses used to measure organic material may be divided into those used to measure gross concentrations of organic matter, greater than about 1.0 mg/L (e.g. BOD_5, COD and TOC), and those used to measure trace concentrations in the range of 10-12 µg/L to 1.0 mg/L (Metcalf and Eddy, 2003). Gross organic matter information is useful to understand the performance of the recycled water scheme, while trace organics, or the so-called micropollutants, are gaining importance from the human health point of view, especially if the recycled water is going to be used for crop irrigation or any other use in which the recycled water is going to be ingested directly or indirectly.

5.5.6.1. Gross organic matter

5.5.6.1.1. Wastewater indices

Gross organic matter has traditionally been measured through BOD_5 (5 day Biological Oxygen Demand), COD Total (Chemical Oxygen Demand), COD Dissolved (obtained through filtration of the sample) and DOC (Dissolved Organic Carbon), to evaluate the performance of the wastewater treatment processes. The differences in the oxygen demand in the different forms indicate the type of the organic matter present in the wastewater and the other waters measured.

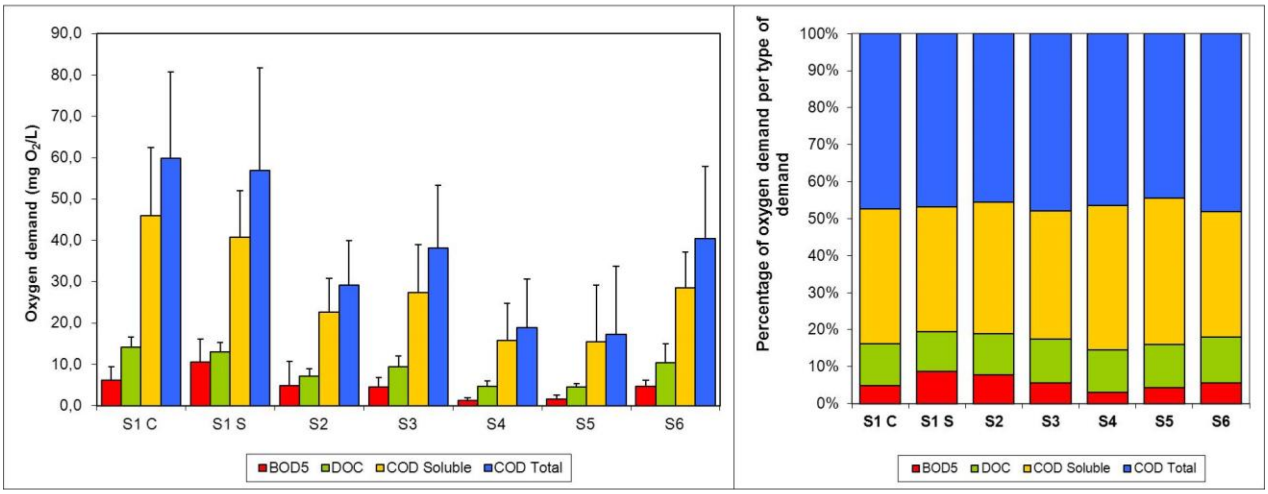
In all sampling points, BOD_5 and DOC represent the smallest proportions of the organic matter, being BOD_5 always a bit lower than DOC. There is little difference between COD Total and COD Dissolved, which indicates that a small proportion of the gross organic matter is present in aggregate form. The higher values obtained for COD (both soluble and total) comparing to BOD_5 and DOC can be due to several factors:

- Presence of organic substances difficult to oxidize biologically, e.g. lignin. This is supported by the high concentrations of phenols from biological origin measured (see section 5.5.6.1.2).
- Inorganic substances that can be oxidized by the dichromate or interact with it, that can mask the result for the COD. In our measurements, the salinity of the tested water may have interfered.
- Presence of toxic substances that could inhibit the growth of the microorganisms and modify the results for BOD_5.

The gross organic matter, whatever is the form measured or tracked, follows a similar pattern in the measured sampling points (see left panel of Figure 35). The highest values are detected in the treated wastewater. After the discharges in the Ripoll River, the river water increases its organic matter presence but for BOD_5, then, a certain dilution of the gross organic matter present in the treated effluent occurs while mixing with the river water. The aquifer and the disinfected water present similar values, lower than in the river water, thanks to the riverbed filtration through the riverbed and the subsurface treatment. The proportion of the gross organic matter in BOD_5, DOC, Total COD and Dissolved COD oxygen demand forms is maintained in all sampling points, as it can be observed in the right panel of Figure 35, which indicates that even though measured values can be higher/lower in the sampling points, the kind of gross organic matter present in the samples is the same.

The BOD_5 measured in composite and grab samples of treated effluent rendered very different results depending on the type of sample. In fresh grab samples measured BOD_5 (average of 11 mg O_2/L) was higher than in composite samples (average of 6.2 mg O_2/L), because in composite samples the organic matter degradation had already started as the sample is taken hourly during 24 hours. In the river water, similar average values were measured before (S2: 4.9 mg O_2/L) and after (S3: 4.5 mg O_2/L; S6: 4.7 mg O_2/L) the treated wastewater discharges, being the highest value measured in a sample of river water before the discharges (S2: 20 mg O_2/L). Then, discharges of treated wastewater do not seem to affect the river water quality. Lower values were measured for the recovered water, with an average of 1.7 mg O_2/L, indicating that the organic matter was whether physically filtered through the riverbed or biologically degraded and metabolized by microorganisms present in the riverbed during the infiltration process. All sampling points fulfil the Spanish water reuse RD guideline value (40 mg O_2/L). The US EPA guideline values for water reuse include values set in state regulations and guideline values proposed by the US EPA, ranging from 5.0 to 60 mg O_2/L, depending on the case. According to this, the recovered water and the final treated water could be used for all the contemplated uses, while the treated effluent and the river water would fulfil the guideline values set by the US EPA but not all the regulations.

Figure 35 Gross organic matter. Left panel: average and standard deviation for oxygen demand; right panel: proportion of oxygen demand per type of gross organic matter.



DOC in the treated wastewater (S1 C: average of 14 mg O_2/L) was higher than in the river water before the discharges (S2: average of 7.1 mg O_2/L). The river water after the discharges has a DOC lower than the treated wastewater and a bit higher than the river water before the discharges (S3: average of 9.4 mg O_2/L). Dilution in the river water represents an average DOC reduction of 34%. In the recovered water, DOC average concentration is of 4.7 mg O_2/L, then, the riverbed filtration and subsurface treatment allows an average DOC reduction of 50%. Organic carbon removal is a passive water-quality treatment provided by MAR operations, and different processes may take part in it, namely: biodegradation, microbial assimilation, filtration, sorption or precipitation (NRMMC-EPHC–NHMRC, 2009). No guideline values are given for DOC in the Spanish legislation. In the US EPA water reuse guidelines, in case of indirect potable reuse, TOC concentration should be on average 0.5-3.0 mg O_2/L, and maximum of 5.0 mg O_2/L as per regulations of different states, and the guidelines set also a recommended value of 2.0 mg O_2/L for TOC. At RISMAR scheme, DOC was measured, and in some sampling campaigns TOC was measured too, but data are not shown for TOC. As higher values were obtained for TOC comparing to DOC, and DOC results were already high, none of the sampling points would meet the guideline values set in the US EPA water reuse guidelines.

COD was measured without sample filtering (total) and with sample filtering (dissolved). The range of values obtained is very high in the treated wastewater, as it depends on the loads received and the performance of the treatment. Values for composite samples range from 21 to 94 mg O_2/L for COD dissolved and 27 to 117 mg O_2/L for COD total. The small difference between dissolved and total COD indicates that most part of the COD is in a dissolved form. COD is lower in the river water before the discharges (S2: average COD total of 29 mg O_2/L) and increases a bit after the treated effluent discharges (S3 and S6: average COD total of 38-40 mg O_2/L, but there is still a reduction (36%) of COD present in the treated wastewater thanks to the dilution in the river water. In the recovered water, COD also decreases after the infiltration through the riverbed, being the average COD total of 19 mg O_2/L (51% reduction). Total COD guideline value set in the Spanish water reuse RD (160 mg O_2/L) is fulfilled in all sampling points. However, COD for the recovered and the final treated water is still high for some of the measured samples, indicating that part of the organic matter cannot be degraded and is still present, which can interfere with the disinfection processes.

According to the results obtained, none of the gross organic matter indices measured would pose a risk for the end points considered, if only the guideline values set in the Spanish legislation are considered. However, the amounts of gross organic matter present at RISMAR scheme are high, and there is risk of eutrophication in the river (as it has been pointed out in the nutrients section 5.5.5), thus posing a risk for the living organisms in it, and there is also risk of recalcitrant pollution presence in the aquifer and inorganic compounds mobilization, due to the presence of organic matter (see section 5.5.11).

5.5.6.1.2. UV-absorbing organic constituents and aromatic character

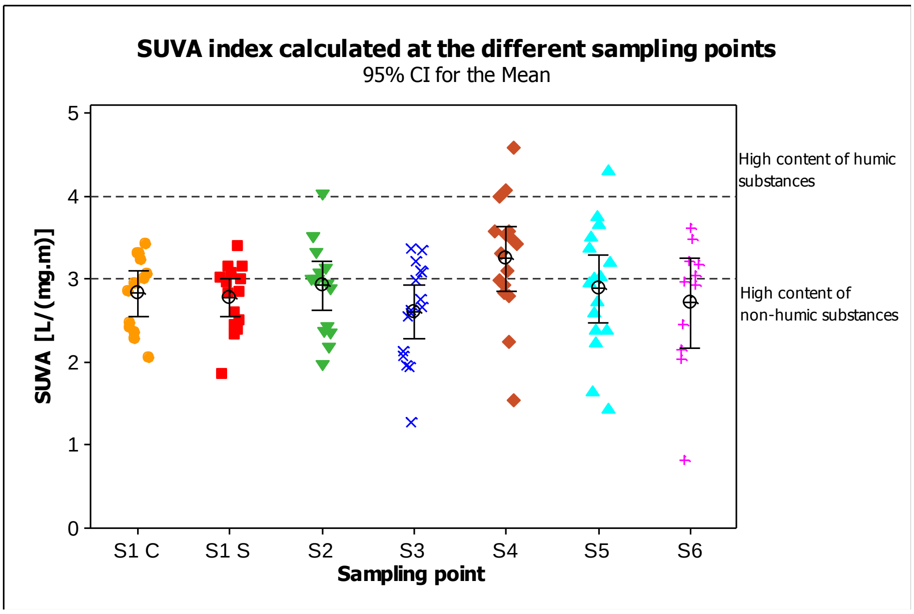
The quantity of organic carbon present in a sample is measured through the DOC, which has been discussed in the previous section. It is not only important the quantity but the type of organic matter present in water samples. Organic matter may have a natural origin (NOM: natural organic matter) or come from a treated effluent, although the treated effluent may also contain a high proportion of NOM. Variations in the amount and nature of organic matter, especially with respect to changes in the aromatic carbon content, have become significant factors for designing strategies for water treatment. UV absorbance at 254 nm is a measure of the aromatic character of the carbon present in a sample. Substances absorbing UV radiation present in the water include humic substances, lignin, tannin and aromatic compounds. Aquatic humic substances within the DOC are generally thought to be the primary precursors for trihalomethanes (THM) and many other disinfection by-products (DBPs). Aquatic humic substances comprise the aromatic fraction of DOC and are amenable to removal from water by coagulation (Weishaar *et al.*, 2003). Specific Ultraviolet Absorption (SUVA) is an index that it is used to characterize the organic matter, calculated as follows:

$$SUVA = \frac{Absorbance_{254nm}}{DOC} \times 100$$

Then, SUVA is also a measure of the extent to which the carbon is aromatic (Metcalf and Eddy, 2003). Natural waters with SUVA values higher than 4 L/(mg.m) have a relatively high content of hydrophobic, aromatic, and high molecular weight NOM fractions, e.g. humic substances. Waters with SUVA values lower than 3 L/(mg.m) contain largely non-humic, hydrophilic and low molecular weight materials, more typical of treated effluent organic matter (Świetlik and Sikorska, 2005).

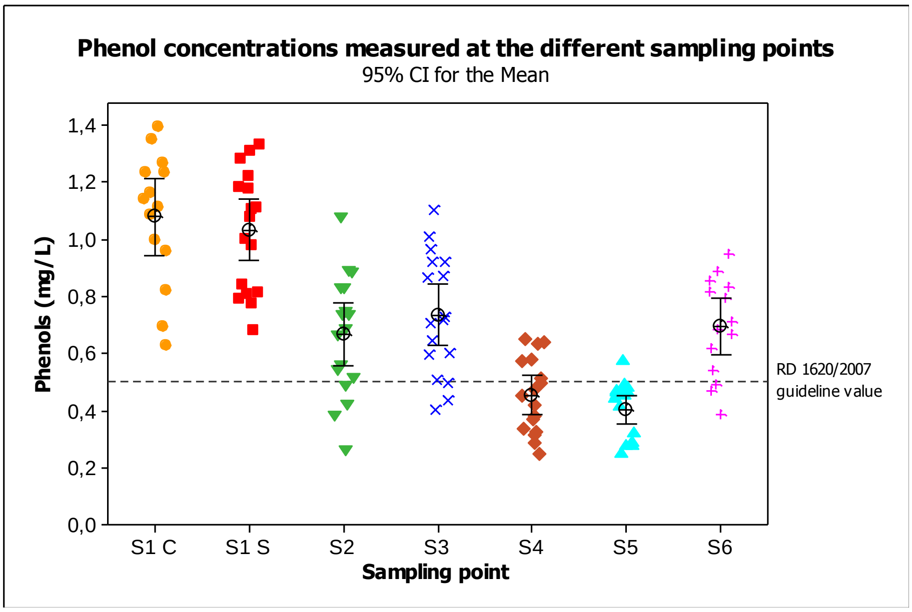
Figure 36 shows the SUVA index calculated at the different sampling points. In most of the samples (54.4%), SUVA was inferior to 3 L/(mg.m); thus these samples contained largely non-humic, hydrophilic and low molecular weight materials, more typical of treated effluent organic matter. In very few samples (3.9%) SUVA was above 4 L/(mg.m), thus indicating that these samples presented a high content of hydrophobic, aromatic, and high molecular weight NOM fractions (humic substances). There are also a good part of the calculated values (41.7%) between 3 and 4 L/(mg.m), thus indicating a mixing of the two kinds of organic matter. Then, in general terms, the organic matter present in the recycled water scheme has an effluent origin, which indicates that the river water and the aquifer are very much influenced by the treated wastewater discharges, not only from Ripoll River WWTP but from other WWTPs upstream the Ripoll River, and the presence of humic substances in the recycled water scheme is low. However, it can be also observed that for the recovered water there was an increase in the average SUVA index, changing from 2.6 L/(mg.m) in the river mixture 1 to 3.2 L/(mg.m) in the recovered water. This indicates that there was a preferential removal of non-humic, hydrophilic and low molecular weight materials (i.e. aliphatic organic matter) during riverbed filtration.

Figure 36 Specific Ultraviolet Absorption (SUVA) index calculated at the different sampling points.



Another way to measure the aromatic character of the organic matter in the samples is to evaluate the presence of phenolic compounds. Phenolic compounds contain at least one group phenol, which is an aromatic ring with a functional group. Many of them are secondary metabolites synthetized by plants. The highest average concentration measured for phenols is in the treated wastewater (S1 C; 1.08 mg/L) and the lowest in the aquifer (S4; 0.45 mg/L) and the final treated water (S5; 0.40 mg/L) (see Figure 37). The guideline value set in the Spanish water reuse RD for phenols is 0.5 mg/L, for the most restrictive values in industrial discharges. This guideline value is in fact given in the RD 849/1986, which is referred to in the Spanish water reuse RD 1620/2007. Considering this, the average phenols concentration in the aquifer and the final treated water would fulfil this guideline value, but not all the individual values measured. The average phenols concentration in the other sampling points would not meet this guideline value. To compare with this guideline value, in the Australian guidelines for aquatic ecosystems the guideline value given is of 1.2 mg/L, less restrictive than the one considered. This guideline value would be fulfilled in nearly all water samples. Phenols were measured by the Folin-Ciocalteu method. This method detects organic compounds with hydroxilated aromatic carbons (e.g. phenols, lignin, tannin, humic acids, proteins), and the method can suffer interferences from other substances (e.g. iron II, cyanide, nitrite, fructose, amines). Another method, that uses 4-aminoantipyrine and would have been more appropriate to detect only phenols, was used at the very beginning of the sampling process, in order to compare with the Folin method, but phenols could not be detected with this method. Then, the phenol concentrations results should be taken cautiously, as the result probably overestimates the phenolic content of the water samples.

Figure 37 Phenolic compounds concentrations measured at the different sampling points.



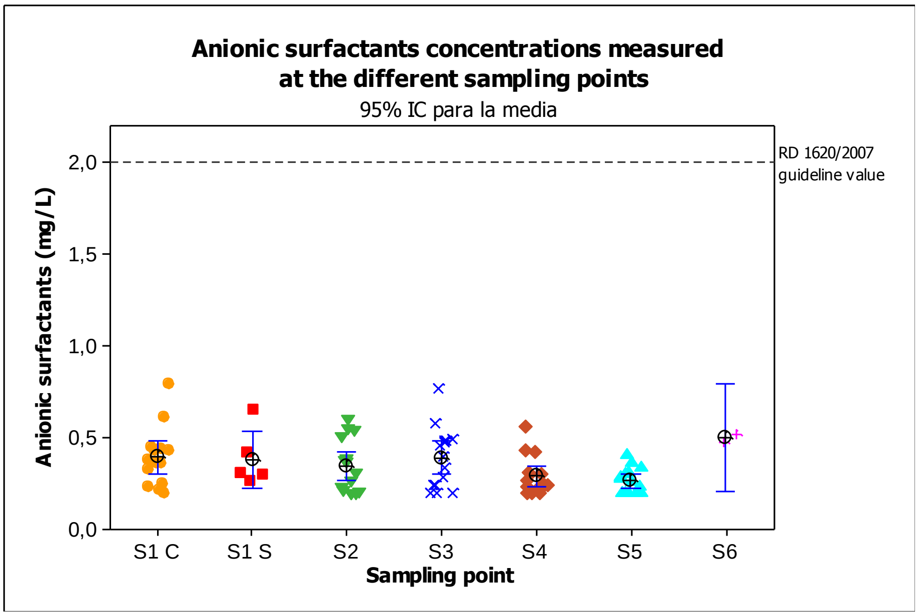
Considering the results obtained for SUVA index and phenols, these compounds would not pose a risk for any of the end points considered, although the phenols concentrations are in general higher than the guideline value set in the Spanish regulation. The measurements performed are indicative of the type of organic matter present in the water samples, but in order to perform an accurate risk assessment and evaluate the effect in the different end points considered, it is necessary to determine other groups of substances, which are discussed in sections 5.5.6.3 and 5.5.6.4.

5.5.6.2. Surfactants

A surfactant is a substance which lowers the surface tension of the medium in which it is dissolved, and/or the interfacial tension with other phases, and, accordingly, is positively adsorbed at the liquid/vapour and/or at other interfaces (IUPAC, 2012). Surfactants can be foaming agents to varying degrees, and cause foaming in WWTPs and surface waters where effluents are discharged (Metcalf and Eddy, 2003). Surfactants are a group of organic chemicals enclosing four subgroups: anionic, cationic, amphoteric and non-ionic surfactants. Surfactants are not categorized as persistent organic pollutants; however, they are typical environmental pollutants widely detected in the water environment because of its abundant usage in our daily lives (Kobuke, 2004). In addition, surfactants can be toxic to plants, animals and human in different degrees (Madsen *et al.*, 2001).

Among the possible surfactants present in the water samples, anionic surfactants were measured using the methylene blue active substances method. Anionic surfactants found in water are usually alkylbenzenesulfonates, a family of compounds that are similar to soap but are more soluble in hard water. The most well-known alkylbenzenesulfonate is the lauryl alkylbenzene sulfonate (LAS), which is the major anionic surfactant used worldwide in detergent and household cleaning product formulations, and is biodegradable (Espinoza, 2004). Anionic surfactants toxicity to human is mostly related to irritation of eyes and skin (Madsen *et al.*, 2001).

Figure 38 Anionic surfactants concentrations measured at the different sampling points.



Average values measured for anionic surfactants are similar in all sampling points, ranging from 0.26 to 0.39 mg/L (see Figure 38), being the lowest values detected in the final treated water, but the reduction through MAR is very low. The river water already carries anionic surfactants concentrations similar to the ones discharged in the treated effluent, thus reduction by dilution with the river water can be considered negligible. River water at sampling point S6 only has 2 measured values. The maximum values measured were around 0.8 mg/L in the treated wastewater and in the river water mixture 1 (S3).

In general, anionic surfactants were detected in low concentrations, and all the values measured are below the guideline value of 2.0 mg/L set in the Spanish water reuse RD. Another guideline value that can be used to compare is given in the Australian guidelines for Aquatic Ecosystems water, where the guideline value is of 2.6 mg/L, similar to the one set in the Spanish legislation. In the US EPA drinking water guidelines, the guideline value is more restrictive (0.5 mg/L). All these guideline values are set for all possible surfactants present in the water, not only anionic surfactants. Considering that anionic surfactants are the most typical surfactants that can be found in domestic wastewaters, and that the final treated water is not nowadays used as drinking water, the risk from the presence of surfactants in the final treated water for the end points evaluated can be considered to be low. If in the future the water is used as drinking water, surfactants should be evaluated carefully and removed using post-treatments for the final treated water. Besides, it would be interesting to determine other surfactants in the sampling points in order to understand the possible harmful effects to the environmental end uses considered.

5.5.6.3. Trace organic contaminants (micropollutants) measured in the framework of the RECLAIM WATER project

The term “trace organics” or the so-called “micropollutants” more specifically refers to a range of emerging chemicals, such as: pharmaceuticals, hormones, personal care products, endocrine disrupters, disinfection by-products, pesticides, flame retardants and other. These emerging contaminants pose a challenge to public health regulation as in many cases there are no toxicological data or guideline values from which to derive the potential human health risk (Page *et al.*, 2012). In addition, they are usually found in very low concentrations in the environment, which avoid the detection of any biological effects with acute toxicity tests. Most of the recent concern and comments regarding trace organic contaminants revolve around pharmaceutically active compounds (PhACs) and endocrine disrupting compounds (EDCs). Both kinds of compounds tend to be present at very low concentrations in recycled water and require the ingestion of large doses over long time periods to produce any clinical effect (Toze, 2006). Besides, they are important for their eco-toxicological activity (Fent *et al.*, 2006). Pharmaceuticals are used for the diagnosis, cure, mitigation, treatment, or prevention of diseases in humans and animals. Certain pharmaceuticals are designed to modulate endocrine and immune systems and cellular signal transduction and as such have obvious potential as endocrine disruptors in the environment. In any case, it must be taken into account that pharmaceuticals are developed with the intention of performing a biological effect, and this is unlike most other chemicals entering the environment, where biological effects generally occur as an unintended consequence of their principal function. Over the years, the consumption of pharmaceuticals has increased, thus increasing their concentrations in the discharges to the environment. The main routes of entry into the environment are from treated patients. The pharmaceutical may enter the environment as the parent compound or as metabolites, via direct release into the sewerage system from manufacturing facilities, hospitals or domestic discharges, and via leaching from terrestrial depositions (e.g. solid waste landfills) (Corcoran *et al.*, 2010). Endocrine disrupting compounds (EDCs) are substances including synthetic and natural chemicals that have the ability to mimic hormones and, thus, are able to interfere or disrupt normal hormonal functions, and they are of concern due to their ecotoxicological and toxicological potentiality. EDCs effect is suspected in the decline of certain species, and change of sex in fish and shellfish. They are also suspected in declining sperm counts in humans (Richardson, 2010).

In the framework of the RECLAIM WATER project, different types of micropollutants were investigated, being most of them PhACs. The objective was to understand the fate of these compounds in the MAR process. Results obtained have been published in McArdell *et al.* (2008). PhACs investigated include antibiotics, anticonvulsants, anti-inflammatories, contrast media, hormones and lipid regulators. Other compounds not belonging to PhACs that have also been investigated were nitrosamines, complexing agents and bisphenol A (an endocrine disruptor).

Antibiotics are used extensively in human and veterinary medicine, as well as in aquaculture, for preventing or treating microbial infections. Then, they are present in municipal wastewater, largely as a result of human or animal excretion, as many active antibiotics are not completely metabolized during therapeutic use. Seasonal variations in wastewater concentrations of antibiotics have also been reported (Le-Minh *et al.*, 2010). Antibiotics are meant to produce direct effects on bacteria, and consequently have the potential to alter the microbial community structure, and select for those few resistant bacteria in any given population, which then reproduce and create an increasingly resistant population through successive generations and build-up of antibiotic resistance genes (Farrell, 2009; Saccà, 2010; see section 5.5.2.3 for more information on antibiotic resistance genes). There are also new concerns that antibiotics will decrease biodegradation of leaf and other plant materials, which serves as the primary food source for aquatic life in rivers and streams (Richardson, 2012).

Anticonvulsants act on the central nervous system by decreasing the overall neuronal activity. Anticonvulsants are very persistent trace compounds (Rauch-Williams *et al.*, 2010), and can act as markers for anthropogenic activity (e.g. carbamazepine). For instance, they can be used to calibrate models of groundwater flow, as reduction of concentration in the aquifer can only be explained by dilution (Gasser *et al.*, 2011). Carbamazepine is a broadly used anticonvulsant, and it is classified as potentially harmful to aquatic organisms. It is considered carcinogenic in rats but is not mutagenic in mammalian cells (Fent *et al.*, 2006).

Anti-inflammatory drugs are commonly used to treat inflammation and pain and to relieve fever in human, and sometimes they are also used for long-term treatment of rheumatic diseases. Since anti-inflammatory drugs inhibit non-specifically prostaglandin synthesis, most side effects, at least after long-term treatment, are related to the physiological function of prostaglandins. Then, these side effects include renal damages and failure, gastric and liver damages, impairment of ion regulation, cardiological abnormalities and reproduction effects. Diclofenac is the compound having the highest acute ecotoxicity among this group of drugs. It was demonstrated that the kidney is a target of diclofenac in trouts and vultures (Corcoran *et al.*, 2010; Fent *et al.*, 2006).

Contrast media are applied in high dosages for medical diagnostics, to enable imaging of soft tissues (e.g. blood vessels) and are designed to be inert substances, with 95% eliminated in urine and faeces unmetabolized within 24 h. They include very persistent trace compounds, and similarly to anticonvulsants, can also be used as markers of anthropogenic activity (Rauch-Williams *et al.*, 2010). Iodinated contrast media have very low toxicity to animals and human, but they must be taken into consideration as precursors of iodinated DBPs, that are highly genotoxic and/or cytotoxic to mammalian cells (Duirk *et al.*, 2011).

Hormones or substances with hormonal effects can act as EDCs. They are used in several therapies (e.g. infertility, prostate cancer, hypoestrogenism) and for contraception. The best knowledge exists for the synthetic steroid EE2 contained in contraceptive pills, showing oestrogenic effects at extremely low and environmentally relevant concentrations. This steroid has been shown in many fish to induce oestrogenic effects, commonly known as feminisation, at extremely low concentrations. Other physiological effects of EE2 in fish include altering mitochondrial function, energy metabolism and cell cycle control (Corcoran *et al.*, 2010; Fent *et al.*, 2006).

Lipid regulators are used to decrease the concentration of cholesterol and triglycerides in the blood plasma. Fibrates, which are the ones that have been investigated in the present study, act by activating the lipoprotein lipase enzyme, thus stimulating cellular fatty acid uptake and reduction in fatty acid and triglyceride synthesis. Increased oxidative stress and hepatic damages may occur after chronic exposure to fibrates in rat, as well as hepatocarcinogenicity in rodents, while this was not observed in humans. Clofibric acid can be classified as harmful to aquatic organisms, affecting reproduction (Corcoran *et al.*, 2010; Fent *et al.*, 2006).

Another relevant group of substances measured but not belonging to PhACs are the complexing agents benzotriazole and its methylated analogues tolyltriazoles, which are compounds used as corrosion inhibitors in many industrial applications, in dishwashing agents and in de-icing fluids for aircraft. Benzotriazole is also used as a chemical intermediate for dyes, pharmaceuticals and fungicides. Derivatives of benzotriazole are used as UV absorbers and as restrainers in photographic emulsions. Benzotriazole was considered of very low toxicity to humans, but it was demonstrated to be toxic to plants. Benzotriazole derivatives were reported to be mutagenic in bacterial systems (DECOS, 2000; DME EPA, 2013). However, in recent fish studies, there is new evidence for oestrogenic effects in vitro, but, so far, not in vivo (la Farré *et al.*, 2008). It is suspected that benzotriazole may be a human carcinogen, but both DECOS (2000) and DME EPA (2013) concluded that there is inconclusive evidence that benzotriazole is carcinogenic.

Nitrosamines were identified as disinfection by-products (DBPs) in chloraminated or chlorinated waters. The danger that they pose to consumer health seems to be much higher than that from chlorinated DBPs (Nawrocki and Andrzejewski, 2011). N-nitrosamines are in general carcinogenic to animals, and probably to human (IARC, 1998). In this group, N-Nitrosodimethylamine (NDMA) is the most widely studied and well-known compound. Although NDMA is much more probably formed after disinfection, other possible sources of NDMA in water are related to its several uses in the industry: industrial solvent, anti-oxidant, rubber vulcanization accelerator, in the preparation of polymers (as an initiator or a plasticiser), to produce rocket fuel, biocide for nematodes and to inhibit nitrification in soils. NDMA can also be formed as a by-product of anion exchange treatment of water (NHMRC-NRMMC, 2011).

The industrial chemical bisphenol A (BPA) is an EDC, used primarily as a component of polycarbonate plastics, epoxy resins and dental sealants. Humans exposure to BPA is primarily through food packaging manufactured using BPA. Among the many health effects associated with BPA exposure, this chemical has been linked with abnormal male and female reproductive organ development in animals and sperm anomalies in humans, and it possibly affects the immunological system (Rees Clayton *et al.*, 2011).

In Table 14 are summarized the results obtained for the different micropollutants investigated (median and maximum values), as well as their corresponding risk quotients (RQs). Nine out of the 33 compounds investigated were not detected in any of the sampling points, which were: N-nitrosodibutylamine (NDBA), N-nitrosodiethylamine (NDEA), N-nitrosopiperidine (NPIP), roxythromycin, sulfadiazine, sulfamethazine, ibuprofen, estradiol E2 and ethynilestradiol EE2. However, from this nine compounds not detected, six of them were only measured in one sampling campaign, which reduces the probabilities of detecting them, as some compounds could be detected in one campaign and not in other ones.

For PhACs, those detected in the treated wastewater were diluted during mixing with the river water, and the reduction increased with the RBF, to the point that some were not detected in the recovered water and the final treated water. None of the antibiotics, anti-inflammatories and hormones could be detected in the final treated water, thus experiencing an estimated 100% reduction in the process. However, the persistent carbamazepine (S5; maximum of 49 ng/L), primidone (S5; maximum of 34 ng/L) and bezafibrate (S5; maximum of 29 ng/L) were still detected in the final treated water, even though they had been reduced along the treatment train. Other PhACs still detected in the final treated water were the X-ray contrast media. High input variations were found for the X-ray contrast media in the treated wastewater, reaching maximum values of 28 µg/L for diatrizoate and 10 µg/L for iopromide. These variations directly affected the concentration in the river water after the discharges (S3), which was less than in the treated wastewater (S1) thanks to the dilution while mixing with the river water (S2), which contained lower concentrations of X-ray contrast media. Further removal occurred during RBF treatment, when X-ray contrast media were considerably reduced, being undetected in some sampling campaigns in the recovered water (S4) or the final treated water (S5). For instance, iohexol was not detected in the recovered water neither in the final treated water in any of the three sampling campaigns.

Five nitrosamines were investigated in the recycled water and riverbed filtration system in one sampling campaign. In the treated wastewater, N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR) were present at low concentrations, 9.6 and 17 ng/L respectively. Both nitrosamines were also detected in the river water before and after the discharges, thus indicating that the treated wastewater was not the only source of them. However, the measured concentration in the river water was lower than in the treated wastewater. The other three nitrosamines were not detected in any of the sampling points (see Table 14). While NDMA was volatilized and/or biodegraded during aquifer passage to levels below the LOQ, NMOR was still present even after UV treatment, which is known that can degrade nitrosamines. This could be explained by two different hypothesis: UV treatment was not performing properly, as it has been pointed out in section 5.5.2.2 according to the microbiological results obtained; or there was formation of new NMOR after the disinfection by chlorination, as it has been observed that UV-irradiated waters may have a high NDMA regeneration potential upon subsequent chlorination (Nawrocki and Andrzejewski, 2011), and this could analogously happen with NMOR. In any case, it must be taken into consideration that these results pertain to only one sampling campaign, and variability in the extraction process or in the samples taken may have influenced the results obtained.

Complexing agents were only measured in one sampling campaign and were detected in all sampling points. These compounds were not reduced at all in the treatment train. Interestingly, 4-tolyltriazole was detected in higher concentrations in the river water after the discharges (S3, 3.9 µg/L) than in the treated wastewater (S1; 0.30 µg/L) and the river water before the discharges (S2; 0.30 µg/L). This can indicate that other sources of pollution may be arriving to the river water, or the values measured were peak values, or it could have been only a mistake in the measurement, as the results correspond to only one sampling campaign. In this line, the concentration in the recovered water (S4; 2.0 µg/L) and the final treated water (S5; 2.4 µg/L) was more similar to the concentration detected in the river water after the discharges.

Bisphenol A (BPA) was measured in two sampling campaigns. The presence of BPA was erratic; it was not detected in the treated wastewater neither in the final treated water. However, it was detected in the river water and the recovered water. Considering the concentrations detected in the river water, BPA was found in higher concentrations in the river water before the discharges (S2; maximum of 0.71 µg/L), and discharges of treated wastewater had a dilution effect (S3; maximum of 0.35 µg/L), being this behaviour very different to the vast majority of compounds investigated. Then, the river upstream must have a source of BPA reaching the water. It seemed to be removed thanks to the RBF treatment, as in the recovered water the concentration was much lower (S4; maximum of 0.054 µg/L), and it was not detected in the final treated water.

In order to evaluate the risk posed by the different micropollutants investigated, RQ values were calculated (see section 4.4 for the calculation of RQ values). For the vast majority of the compounds investigated, only guideline values regarding the human health were available and those have been used, and these guideline values are set considering that the water is used as drinking water. The results obtained for the RQ values are given in Table 14. Calculated RQ values for the PhACs are in general very small, close to zero in many cases, thus indicating that the risk posed by these compounds is negligible. The exception is the hormones, as oestrone E1 was present in high concentrations in the treated wastewater and the river water. RQ value for oestrone E1 in the treated wastewater (S1) is of 2.13 and 1.22 in the river water mixture 1 (S3). This indicates that hormones could potentially pose a risk for the fish and other animals living in the Ripoll River when treated wastewater discharges occur, as oestrone E1 can act as an endocrine disruptor. Oestrone E1 was below the LOD in the recovered water and the final treated water. Bisphenol A RQ values are extremely low (equal or inferior to $1.7x10^{-3}$), to the point that cannot be calculated for those samples with values below the LOD. Complexing agents present low RQ values, however, an eye should be kept to this group of compounds as only one sampling campaign measured them and they were detected in the recovered water and the final treated water. The only group including a compound with a RQ value higher than one in the final treated water is N-nitrosamines. NMOR was the compound with a high RQ value for the final treated water (S5: 7.2), and this compound also presented high RQ values for the other sampling points measured. NDMA RQ value was also higher than one in the treated wastewater (1.65). However, guideline values for N-nitrosamines are under discussion, and the few existing regulations recommend different values for each N-nitrosamine. The guideline value considered for NMOR is of 1 ng/L, given in the Australian Guidelines for Water Recycling phase 2: Augmentation of Drinking Water Supplies (NRMMC–EPHC–NHMRC, 2008), and it is more restrictive than the guideline value recommended by the California Department of Public Health (CDPH), which is of 5 ng/L (CDPH, 2013). The opposite occurs for NDMA, where CDPH sets a more restrictive value (3 ng/L) than the Australian Guidelines for Water Recycling phase 2: Augmentation of Drinking Water Supplies (10 ng/L) or the WHO DWG (100 ng/L) (WHO, 2011a). These differences in the range of the guidelines values indicate that this is an area that requires more investigation in order to set a common guideline value, truly based on toxicity studies.

Table 14 Summary of micropollutants results obtained in the RECLAIM WATER project and calculated corresponding RQ values.

Group	Parameter	units	LOQ	S1C					S2					S3					S4					S5					GV	Reference
				n	min/ med	max	RQ min/ med	RQ max	n	min/ med	max	RQ min/ med	RQ max	n	min/ med	max	RQ min/ med	RQ max	n	min/ med	max	RQ min/ med	RQ max	n	min/ med	max	RQ min/ med	RQ max		
DBPs																														
N-nitrosamines	N-Nitrosodibutylamine (NDBA)	ng/L	3	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	6	US EPA
	N-Nitrosodiethylamine (NDEA)	ng/L	0,3	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	10	AGWR-ADWS
	N-Nitrosodimethylamine (NDMA)	ng/L	0,7	1	16,5	—	**1,7**	—	1	6	—	0,64	—	1	7	—	0,68	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	10	AGWR-ADWS
	N-Nitrosomorpholine (NMOR)	ng/L	1,3	1	9,6	—	**9,6**	—	1	3,6	—	**3,6**	—	1	5,9	—	**5,9**	—	1	3,3	—	**3,3**	—	1	7,2	—	**7,2**	—	1	AGWR-ADWS
	N-Nitrosopiperidine (NPIP)	ng/L	3,2	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	3,5	CDPH
PhACs																														
Antibiotics	Clarithromycin	µg/L	0,01	2	0,201	0,220	8,0E-04	8,8E-04	2	<LOQ	0,181	—	7,2E-04	2	0,093	0,250	3,7E-04	1,0E-03	2	<LOQ	0,012	—	4,8E-05	2	<LOQ	<LOQ	—	—	250	AGWR-ADWS
	Erythromycin	µg/L	0,01	2	0,229	0,463	0,013	0,026	2	0,046	0,238	2,6E-03	0,014	2	0,097	0,419	5,5E-03	0,024	2	<LOQ	0,013	—	7,4E-04	2	<LOQ	<LOQ	—	—	17,5	AGWR-ADWS
	N-Acetilsulfamethoxazole	µg/L	0,01	2	0,073	0,084	2,1E-03	2,4E-03	2	0,021	0,043	6,0E-04	1,2E-03	2	0,014	0,121	4,0E-04	3,5E-03	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	35	AGWR-ADWS
	Roxythromycin	µg/L	0,02	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	150	AGWR-ADWS
	Sulfadiazine	µg/L	0,01	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	35	AGWR-ADWS
	Sulfadimethoxine	µg/L	0,01	2	<LOQ	<LOQ	—	—	2	<LOQ	0,055	—	1,6E-03	2	<LOQ	0,011	—	3,1E-04	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	35	AGWR-ADWS
	Sulfamethoxazole	µg/L	0,01	2	0,167	0,468	4,8E-03	0,013	2	0,065	0,105	1,9E-03	3,0E-03	2	0,080	0,159	2,3E-03	4,5E-03	2	<LOQ	0,053	—	1,5E-03	2	<LOQ	<LOQ	—	—	35	AGWR-ADWS
	Sulfamethazine	µg/L	0,01	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	2	<LOQ	<LOQ	—	—	35	AGWR-ADWS
	Trimethoprim	µg/L	0,01	3	<LOQ	0,264	—	3,8E-03	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	70	AGWR-ADWS
Anticonvulsants	Carbamazepine	µg/L	0,01	2	0,057	0,298	5,7E-04	3,0E-03	2	<LOQ	0,136	—	1,4E-03	2	0,019	0,250	1,9E-04	2,5E-03	2	0,014	0,141	1,4E-04	1,4E-03	2	0,013	0,049	1,3E-04	4,9E-04	100	AGWR-ADWS
	Primidone	µg/L	0,01	2	0,111	0,243	1,8E-03	3,9E-03	2	<LOQ	0,033	—	5,3E-04	2	0,035	0,069	5,6E-04	1,1E-03	2	0,026	0,033	4,2E-04	5,3E-04	2	0,029	0,034	4,6E-04	5,4E-04	62,5	LTD
Anti-inflammatories	Diclofenac	µg/L	0,01	2	0,124	0,187	0,069	0,104	2	0,133	0,336	0,074	0,187	2	0,063	0,185	0,035	0,103	2	0,010	0,027	5,6E-03	0,015	2	<LOQ	<LOQ	—	—	1,8	AGWR-ADWS
	Ibuprofen	µg/L	0,02	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	400	AGWR-ADWS
	Naproxen	µg/L	0,01	3	0,038	0,566	1,7E-04	2,6E-03	3	0,303	0,377	1,4E-03	1,7E-03	3	0,216	0,293	9,8E-04	1,3E-03	3	<LOQ	0,033	—	1,5E-04	3	<LOQ	<LOQ	—	—	220	AGWR-ADWS
X-ray Contrast media	Diatrizoate	µg/L	0,01	3	<LOQ	27,70	—	0,046	3	0,849	0,928	1,4E-03	1,5E-03	3	3,050	4,270	5,1E-03	7,1E-03	3	0,280	1,065	4,7E-04	1,8E-03	3	0,638	1,735	1,1E-03	2,9E-03	600	LTD
	Iohexol	µg/L	0,02	1	0,636	—	8,8E-04	—	3	<LOQ	0,152	—	2,1E-04	3	0,050	0,493	6,9E-05	6,8E-04	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	720	AGWR-ADWS
	Iomeprol	µg/L	0,02	3	0,216	0,339	0,009	0,015	3	<LOQ	0,390	—	0,017	3	0,052	0,354	2,3E-03	1,5E-02	3	<LOQ	<LOQ	—	—	3	<LOQ	0,049	—	2,1E-03	23	LTD
	Iopamidol	µg/L	0,02	3	0,249	0,287	6,2E-04	7,2E-04	3	0,032	0,072	8,0E-05	1,8E-04	3	0,092	0,153	2,3E-04	3,8E-04	3	<LOQ	0,048	—	1,2E-04	3	0,032	0,043	8,0E-05	1,1E-04	400	AGWR-ADWS
	Iopromide	µg/L	0,02	3	6,6	10	8,8E-03	0,013	3	0,909	1,185	1,2E-03	1,6E-03	3	4,915	5,950	6,6E-03	7,9E-03	3	0,059	0,231	7,9E-05	3,1E-04	3	0,155	0,435	2,1E-04	5,8E-04	750	AGWR-ADWS
Hormones	Estradiol E2	ng/L	1	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	175	AGWR-ADWS
	Oestrone E1	ng/L	0,5	1	64	—	**2,13**	—	1	13,5	—	0,450	—	1	36,50	—	**1,22**	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	30	AGWR-ADWS
	Ethinylestradiol EE2	ng/L	0,5	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1	<LOQ	—	—	—	1,5	AGWR-ADWS
Lipid regulators	Bezafibrate	µg/L	0,01	3	0,055	0,129	1,8E-04	4,3E-04	3	0,069	0,281	2,3E-04	9,4E-04	3	0,040	0,177	1,3E-04	5,9E-04	3	0,011	0,019	3,7E-05	6,3E-05	3	0,014	0,029	4,7E-05	9,7E-05	300	AGWR-ADWS
	Clofibric acid	µg/L	0,01	3	0,024	0,026	3,2E-05	3,5E-05	3	<LOQ	0,018	—	2,4E-05	3	0,015	0,022	2,0E-05	2,9E-05	3	<LOQ	<LOQ	—	—	3	<LOQ	<LOQ	—	—	750	AGWR-ADWS
Complexing Agents	4-Tolyltriazole	µg/L	0,1	1	0,300	—	0,015	—	1	0,300	—	0,015	—	1	3,940	—	0,197	—	1	1,990	—	0,100	—	1	2,420	—	0,121	—	20	DME-EPA
	5-Tolyltriazole	µg/L	0,1	1	0,240	—	0,012	—	1	0,240	—	0,012	—	1	0,410	—	0,021	—	1	0,200	—	0,010	—	1	0,290	—	0,015	—	20	DME-EPA
	Benzotriazole	µg/L	0,1	1	2,520	—	0,126	—	1	2,520	—	0,126	—	1	3,120	—	0,156	—	1	1,920	—	0,096	—	1	2,370	—	0,119	—	20	DME-EPA
EDC	Bisphenol-A	µg/L	0,01	2	<LOQ	<LOQ	—	—	2	0,067	0,709	3,4E-04	3,5E-03	2	0,050	0,345	2,5E-04	1,7E-03	2	0,045	0,054	2,3E-04	2,7E-04	2	<LOQ	<LOQ	—	—	200	AGWR-ADWS

AGWR-ADWS: Australian Guidelines for Water Recycling - Augmentation of Drinking Water Supplies; CDPH: California Department of Public Health; DBPs: Disinfection By-Products; DME EPA: Danish Ministry of the Environment – Environmental Protection Agency; EDC: Endocrine Disrupting Compound; GV: Guideline Value; LOQ: Limit Of Quantification; LTD: Lowest Therapeutic Dose; med: median value; max: maximum value; n: number of samples; PhACs: Pharmaceutically Active Compounds; RQ: Risk Quotient; US EPA: United States Environmental Protection Agency. Note: when 2 values were available for the compound, min/med refers to the minimum value; when 3 values were available for the compound, min/med refers to the median value. Similarly for RQ min/med.

To sum up, the nitrosamine NMOR can be considered to pose a risk for the human health in case the final treated water is used as drinking water, and the overall risk posed by N-nitrosamines should be further evaluated with more analyses and with a solid guideline value; and the hormone Oestrone E1 can pose a risk for the fish and other aquatic organisms living in the Ripoll River. These compounds should be further investigated at RISMAR scheme.

5.5.6.4. Trace organic contaminants (micropollutants) measured by CASSA and EDS

CASSA and EDS measured different trace organic contaminants before taking part in the RECLAIM WATER project and in the recent years in order to evaluate the possibility of reusing the final treated water for other purposes than park irrigation and street cleaning. The analyses were performed in the groundwater and in the final treated water. In

Table 15 a summary of the trace organic contaminants measured by CASSA and EDS in the recent years is given.

Most of the compounds investigated are volatile organic compounds (VOCs). VOCs are common air pollutants, but they have been widely found to contaminate groundwater resources. Exposure to them can induce a wide range of acute and chronic health effects, such as sensory irritation, nervous system impairment, haematological changes, asthma and cancer. From the aesthetical point of view, taste and odour complaints from consumers are frequently derived from their presence. VOCs reach water by atmospheric deposition, chemical plant effluent and underground petrol storage tank leakage (Kuster *et al.*, 2010; NHMRC-NRMMC, 2011; WHO, 2011a; Zhou *et al.*, 2011). A reduced number of VOCs could be detected in the groundwater or the final treated water. Tetrachloroethene has been used primarily as a solvent in dry cleaning industries and to a lesser extent as a degreasing solvent. It was detected in the groundwater in a concentration of 5.8 µg/L, and the guideline value set in the Spanish drinking water RD 140/2003 (BOE, 2003) is 10 µg/L for the sum of tetrachloroethene and trichloroethene. As the latter was not detected, tetrachloroethene does not pose a risk for the human health (calculated RQ: 0.58). Another VOC that was detected is c-1,2-dichloroethene, which was previously used as an anaesthetic, being the cis form more frequently found as a water contaminant. In this case, it was detected in the final treated water in concentrations ranging from 2 to 3 µg/L, and there is no guideline value in the Spanish legislation. In the WHO Drinking Water Guidelines, the guideline value set is 50 µg/L (WHO, 2011a), in the Australian Drinking Water Guidelines the guideline value set is 60 µg/L (NHMRC-NRMMC, 2011) and in the US EPA DWG (US EPA, 2009) the guideline value set is 70 µg/L. All of them are fulfilled (worst-case calculated RQ would be 0.06), so this compound does not pose a risk for the human health.

Table 15 Summary of trace organic contaminants measured by CASSA and EDS.

Group of trace organic contaminants investigated	Compounds not detected (under the limit of detection)	Compounds detected, their measured values and sampling point
Aromatic hydrocarbons (VOCs)	benzene, toluene, ethylbenzene, m,p-xylene, o-xylene	
Polycyclic aromatic hydrocarbons (VOCs)	benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, acenaphthene,	

Group of trace organic contaminants investigated	Compounds not detected (under the limit of detection)	Compounds detected, their measured values and sampling point
	acenaphtalene, anthracene, benzo(a)anthracene, dibenzo(a,h)anthracene, chrysene, phenanthrene, fluorene, fluoranthene, naphthalene, pyrene	
Chlorobenzenes (VOCs)	chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, 1,3,5-trichlorobenzene, 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene	
Chloromethanes (VOCs)	1,2-dibromomethane, dichloromethane, bromodichloromethane, dibromomethane, trichlorofluoromethane, tetrachloromethane	
Chloroethanes and chloroethenes (VOCs)	1,1,1-trichoroethane, 1,1,2-trichloroethane, 1,1-dichloroethane, 1,2-dichloroethane, 1,1-dichloroethene, t-1,2-dichloroethene, 1,1,2,2-tetrachloroethane, trichloroethene	tetrachloroethene: S4=5.8 µg/L c-1,2-dichloroethene: S5=2-3 µg/L
Chloropropanes and chloropropenes (VOCs)	1,2-dichloropropane, c-1,2-dichloropropane, t-1,2-dichloropropane, c-1,3-dichloropropene, t-1,3-dichloropropene	
Organochlorine pesticides	hexachlorobenzene, α-HCH, β-HCH, γ-HCH, δ-HCH, aldrin, dieldrin, endrin, endosulfan I, endosulfan II, endosulfan sulphate, heptachlor, β-heptachlor epoxide, α-chlordane, γ-chlordane, chlorobenzilate, chlorpyrifos, DCPA, alachlor, trans-nonachlor, cis-nonachlor, metoxichlor, propachlor, 4,4′-DDD,v4,4′-DDE, 4,4′-DDT, cis-permethrin, trans-permethrin, trifluralin	α-heptachlor epoxide: S4=0.014 µg/L trans-chlordane: S4=0.019 µg/L
Organophosphorus pesticides	demeton-o, demeton-s, diazinon, dichlorvos, disulfoton, ethoprop, fenthion, methyl parathion, mevinphos, naled, phorate, fenchlorfos, tetrachlorvinfos, tokuthion, trichloronate	
Triazine herbicides	simazine, atrazine, atrazine-desethyl, atrizene-desisopropyl, cyanazine,	Prometryn: S4=0.033 µg/L

Group of trace organic contaminants investigated	Compounds not detected (under the limit of detection)	Compounds detected, their measured values and sampling point
	propazine, sebuthylazine, terbuthylazine, ametryn, terbutryn	
Trihalomethanes (THMs)		chloroform: S4=0.2 μg/L; S5=15-28 μg/L bromoform: S5=30-33 μg/L dibromochloromethane: S5=54-70 μg/L bromodichloromethane: S5=35-37 μg/L Total THMs: S5=147-155 μg/L

Another group of compounds investigated were pesticides. Pesticides are widespread in the environment. They are used for pest control, including weeds, insects, nematodes and other animals. Presence of pesticides in water can be explained by agricultural runoff, leaching from soils, atmospheric deposition, industrial discharges and wastes, as well as to accidental spills. It must be taken into consideration that pesticides are widely present in food, which is an important source for human. Pesticides' effects in the human health include affectation of the nervous, reproductive, cardiovascular and hematopoietic systems, as well as hepatic, renal, spleen and ocular damages, skin sensitization, teratogenicity, genotoxicity and carcinogenicity (NHMRC-NRMMC, 2011; WHO, 2011a). Three subgroups were analysed: organophosphorus pesticides, organochlorine pesticides and triazine herbicides. None of the investigated organochlorine pesticides could be detected. Regarding the organophosphorus pesticides, α-heptachlor epoxide and trans-chlordane were detected in the groundwater, being both compounds associated to liver damages. Measured values were below the heptachlor epoxide guideline value of 0.033 μg/L (RQ = 0.42) and the individual pesticide guideline value (set for those pesticides that do not have a specific guideline value) of 0.1 μg/L in the Spanish drinking water RD, that would apply to trans-chlordane (RQ = 0.19). In the Australian Drinking Water Guidelines, heptachlor epoxide guideline value is 0.3 μg/L and for chlordane is 2 μg/L, and in the US EPA DW regulations guideline values are similar (0.2 μg/L and 2 μg/L, respectively). In the WHO Drinking Water Guidelines guideline values are 0.03 μg/L for heptachlor epoxide and 0.2 μg/L for chlordane, similar to the Spanish drinking water RD. In any case, all guideline values considered would be fulfilled. Among triazine herbicides, only prometryn was detected, and similarly to trans-chlordane, below the individual pesticide guideline value (RQ = 0.33). Considering the sum of the detected pesticides, the value is well below the guideline value of 0.5 μg/L set in the Spanish drinking water RD. Then, according to the results evaluated, and the pesticides that have been investigated, pesticides do not pose a risk for the human health.

Trihalomethanes (THMs) are included in the VOCs group, but they are discussed separately, due to its belonging to the DBPs group too. THMs are formed in drinking-water primarily as a result of chlorination of organic matter present in raw water supplies. The rate and degree of THM formation increase as a function of the chlorine and humic acid concentration, temperature, pH and bromide ion concentration. Chloroform is the most common THM and the principal disinfection by-product in chlorinated drinking-water. In the presence of bromides, brominated THMs are formed preferentially, and chloroform concentrations decrease proportionally (WHO, 2011a). The trihalomethanes are rapidly and efficiently absorbed following ingestion; they are fat soluble, and accumulate in tissues such as adipose tissue, brain, kidney and blood. Chloroform and bromoform are known to cause central nervous system depression in humans. Some epidemiological studies have reported associations between the ingestion of chlorinated drinking water (which typically contains THMs) and increased cancer mortality rates, but IARC concluded that the available data for chlorinated water provide inadequate evidence of carcinogenicity in humans (NHMRC-NRMMC, 2011; WHO, 2011a). THMs were measured in the groundwater and the final treated water (that undergoes disinfection by chlorination). In the groundwater, they were detected in very low values (0.2 µg/L for chloroform) or not detected. In the final treated water, the sum of the four THMs ranged from 147 to 155 µg/L, while the guideline value set in the Spanish RD 140/2003 is currently of 100 µg/L (calculated RQ: 1.47-1.55). This guideline value is more restrictive than the one set by the Australian Drinking Water Guidelines, which is of 250 µg/L (calculated RQ: 0.59-0.62), but less restrictive than the one set in the US EPA DWG, of 80 µg/L (calculated RQ: 1.84-1.94). Guideline values for each individual THM are set in the WHO Drinking Water Guidelines, and each THM evaluated separately fulfils them. In any case, the presence of THMs in the final treated water is important enough to consider this group before the use of the final treated water for drinking water purposes, and investigated further their formation, how to prevent it and how to remove them.

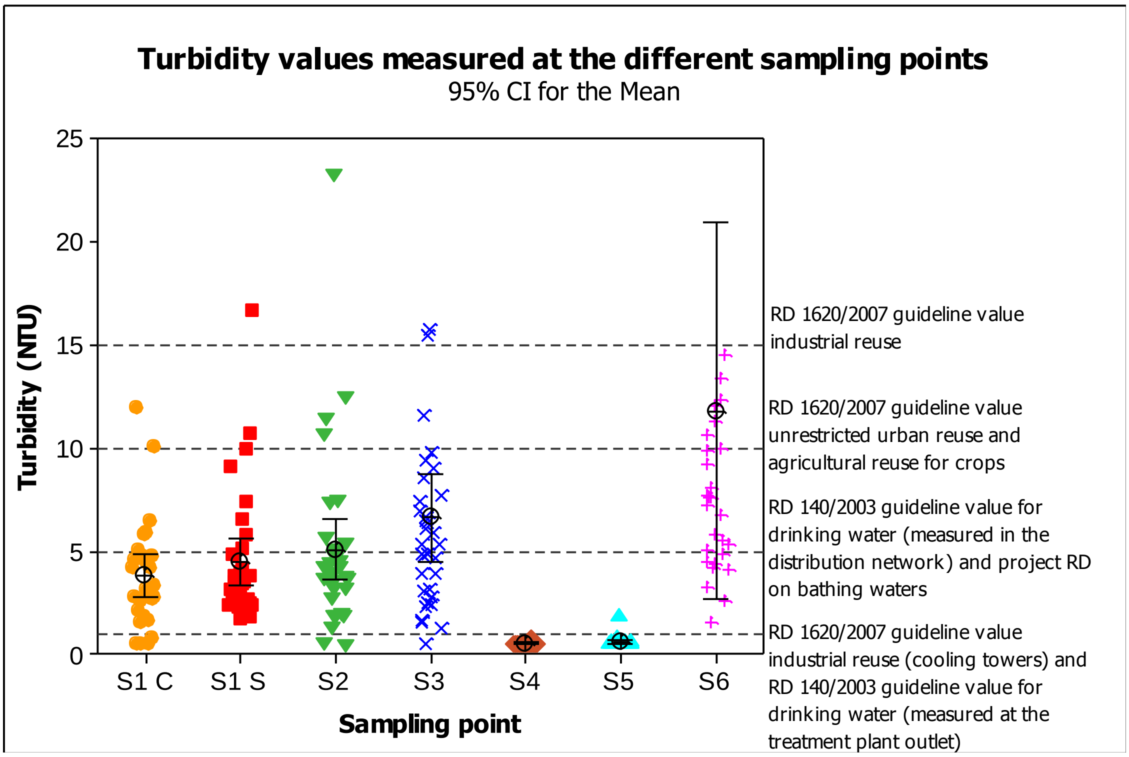
5.5.7. Turbidity and particulates

Turbidity in water is caused by suspended particles or colloidal matter that obstructs light transmission through the water. It may be caused by inorganic or organic matter or a combination of both. The presence of suspended solids/turbidity in groundwater sources is regularly due to inorganic matter, whereas in surface waters it is more likely to include particulate matter of many types, including attached microorganisms. In distribution systems, it can occur as a result of the disturbance of sediments and biofilms but also from mixing of dirty water from outside the system. Suspended solids can clog the irrigation equipment, particularly if sprinkler and drip irrigation are used. The presence of suspended solids/turbidity can seriously interfere with the efficiency of chemical and physical treatments for disinfection by providing protection for organisms, so particulate matter needs to be reduced before disinfection. Besdies, excess organic matter in water can react with disinfection chemicals intended to inactivate microorganisms and can result in an increase in the formation of disinfection by-products. Turbidity can also have a negative impact on consumer acceptability of water as a result of visible cloudiness (NRMMC-EPHC–NHMRC, 2009; WHO, 2006b, 2011a).

The presence of particles in water has been measured at RISMAR scheme in the form of suspended solids and turbidity. Both measurements give an idea of the presence of particulates in water. There is a reasonable relationship between turbidity and total suspended solids for the secondary effluents (Metcalf and Eddy, 2003) and this is extensible to other cleaner water samples. Turbidity has been represented in Figure 39 and suspended solids in Figure 40.

Most of the time, suspended solids and turbidity correlate pretty well, but at some dates and sampling points there is clearly no correlation (data not shown). Then, monitoring both parameters is recommended in order to have the whole picture of the presence of particulates in the system. For the water samples tested, as it could be expected, the aquifer and final treated water barely presented suspended solids neither turbidity (nearly all values measured are below the LOD). Average turbidity for the final treated water was of 0.55 NTU and average suspended solids is 1.0 mg/L. Suspended solids and turbidity were much higher in the river water and in the treated wastewater than in the recovered water, as the riverbed filtration process eliminates most of the particles present in the river water. Average suspended solids removal was 81%, with a maximum removal of 96% (considering the LOD to calculate the removals), and for turbidity, average removal was 85%, with a maximum of 99%. Median turbidity for the river water ranged from 4.2 to 7.4 NTU (S2 and S6, respectively) and median suspended solids ranged from 5.2 to 8.6 mg/L (S2 and S6, respectively), while in the treated wastewater median values were 3.4 NTU and 7.4 mg/L (S1 S). Average is not considered as there were some peak values that shifted it a lot. These peak values, that were removed in the graphs (see graphs footnotes), corresponded to samples taken after a strong rain event. It is interesting how the grab samples taken for the treated effluent (S1 S) tended to present higher values of particulates than the composite samples (S1 C). This is probably due to the fact that the composite samples kept at the WWTP for our measurements were not properly mixed with the total water gathered, so particles had already settled in the tank where the hourly samples are taken. The river water before and after the treated wastewater discharges presented similar values of suspended solids and turbidity for samples taken in the same day, which indicates that the discharges of treated wastewater effluent to the river do not increase the particulates present in the river water.

Figure 39 Turbidity values measured along the sampling period at the different sampling points.

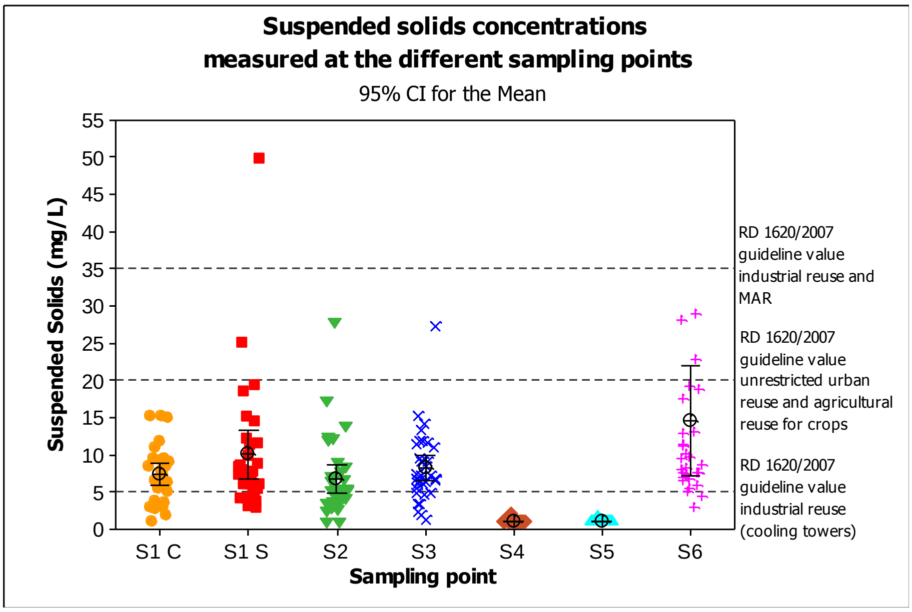


Note: values below the LOD have been represented as the LOD. The peak values of 131 NTU measured in sampling point S6 and 34 NTU measured in sampling point S3 have not been represented in the figure, in order to properly show the other values measured. The mean and the 95% confidence interval for the mean are clearly shifted due to these peak values.

From the results obtained it can be concluded that the river water before and after the treated wastewater discharges, which is the water that infiltrates through the riverbed to the aquifer, would meet the guideline value of 35 mg/L of suspended solids for water to be used for MAR, but for the peak value of 110 mg/L in S6 during a rain event. The excess of particles, in the long-term, could clog the riverbed and reduce the infiltration rate. This could pose a risk for the aquifer, as lower volumes of water would infiltrate, that in the very long-term, could deplete water levels. However, the actual levels of particles measured would not pose a risk for the aquifer. The suspended solids and turbidity values measured in the treated wastewater indicate that there are no big differences with the river water, thus the discharges do not impoverish the quality of the river water regarding particulates and do not pose a risk for the Ripoll River.

Moving to the final treated water, particles do not pose a risk for irrigation or to unrestricted urban reuse, meeting the guideline values given in the RD 1620/2007 for these uses. High amounts of particulates could reduce the permeability of the soil, which would impact the crop growth, and could block the irrigation system, thus reducing the flow of water along the pipeline in the distribution system. In case the final treated water was to be used as drinking water, the guideline value is of 1 NTU in the treatment plant outlet and 5 NTU when measured in the distribution network. These guideline values were set considering that turbidity can reduce the disinfection performance of chlorination or UV, and can transport adsorbed contaminants, that can pose a risk for the human health. As the samples were taken from the distribution network, the guideline value of 5 NTU applies and the final treated water would meet the drinking water guideline value too. However, the maximum value measured regarding turbidity in the final treated water (1.8 NTU) would not meet the guideline value of 1 NTU set for industrial reuse in cooling towers, but all the other samples taken would; so it could be considered that the risk posed is low. Besides, the recovered water values were all below 1 NTU, and this difference between the maximum measured value in the final treated water versus the recovered water can be acknowledged to the presence of manganese precipitates in the final treated water, problem that was already solved by a adding a filtration system.

Figure 40 Suspended solids concentrations measured along the sampling period at the different sampling points.



Note: values below the LOD have been represented as the LOD. The peak value of 110 mg/L measured in sampling point S6 has not been represented in the figure, in order to properly show the other values measured. The mean and the 95% confidence interval for the mean are clearly shifted due to this peak value.

Other guideline values set in different guidelines and legislations are similar to the ones set in the Spanish water reuse RD, although they are a bit more restrictive in the US EPA water reuse guidelines (US EPA, 2012). Guideline values for the different uses oscillate between 2.0 and 5.0 NTU for turbidity and 5.0 and 60 mg/L for suspended solids, depending on if the mean or maximum values are considered. These guideline values would be fulfilled at RISMAR scheme. However, guideline values set for MAR are 2.0 to 5.0 NTU for turbidity, which would not be met in any case by the river water before or after the discharges. States regulations included in the US EPA water reuse guidelines can be much more restrictive, getting to turbidity values of 0.1 and 0.2 NTU, which would be impracticable in most of the reuse schemes and would not be fulfilled at RISMAR scheme. These restrictive regulations require a high level of water treatment in order to reuse the water.

5.5.8. Radionuclides

Radionuclides pose a risk for human health, as they are linked to different kinds of cancer. Radioactivity from several naturally occurring and human-made sources is present throughout the environment. Some chemical elements present in the environment are naturally radioactive. These are found in varying amounts in soils, water, indoor and outdoor air and even within our bodies, so exposure to them is inevitable. In water, they can be found as a result of either natural processes (e.g. absorption from the soil) or technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or phosphate fertilizer production). Radiologically significant natural radionuclides can be ingested with drinking water, transferred to crops through irrigation, be present in stock water, accumulated in food chain (radium and radon) or be inhaled due to gas releases from the water supply. Human-made radionuclides may be present in water from several sources. The use of radiation in medicine for diagnosis and treatment is the largest human-made source of radiation exposure today. The testing of nuclear weapons, routine discharges from industrial and medical facilities and accidents such as Chernobyl have added human-made radionuclides to our environment. Except in extreme circumstances, the radiation dose resulting from the ingestion of radionuclides in drinking-water is much lower than that received from other sources of radiation (ANZECC-ARCAMZ, 2000; NRMMC–EPHC–NHMRC, 2009, WHO, 2011a).

At RISMAR scheme, radionuclides may be present in treated wastewater, and they can also originate from the sediments in the aquifer. No radionuclide data are available for the case study. Then, to evaluate the risk posed by the possible presence of radionuclides at RISMAR scheme the different water sources in the system must be considered.

For the treated wastewater, domestic and industrial wastewater must be evaluated. Regarding industrial wastewater discharges, factories present in the area are mainly textile; there is no mining and processing of mineral sands close to the Sabadell area, neither nuclear power generation facilities, so the risk of radionuclides discharges to the sewerage can be considered to be very low. Tap water, which is the source for domestic wastewater, in Sabadell comes from the Ter and Llobregat Rivers. For the Llobregat River, high values in gross beta activity (more than 1 Bq/L) were found in water samples by Ortega *et al.* (1996). In their study, it was concluded that those were due to high content of ^{40}K content in the water, coming from potassium salts diverted to the river in the mining area situated around the towns of Sallent, Cardona and Súria in the province of Barcelona. Potassium-40 is not considered to be of significance to health because it is present naturally with the stable potassium isotope. Tap water is also analysed by Aigües Ter-Llobregat (ATLL), which is the company that supplies the tap water, in order to fulfil the Spanish Royal Decree (RD) 140/2003 (BOE, 2003) requirements for potable water. The average gross beta activity, as well as the average gross alpha activity and the average tritium, measured by ATLL during the recent years fulfil the guideline values set for them in the Spanish drinking water RD (ATLL, 2008; ATLL, 2010; ATLL, 2012). Then, as the gross beta activity detected in Ortega *et al.* (1996) study of the Llobregat River (that is a source of tap water for Sabadell city) was explained by the high content in ^{40}K, which is not considered to be of significance to health, and the average gross beta activity measured by ATLL in the recent years is below the guideline value set in the RD 140/2003, it can be concluded that the risk due to radionuclides presence in the treated wastewater is low.

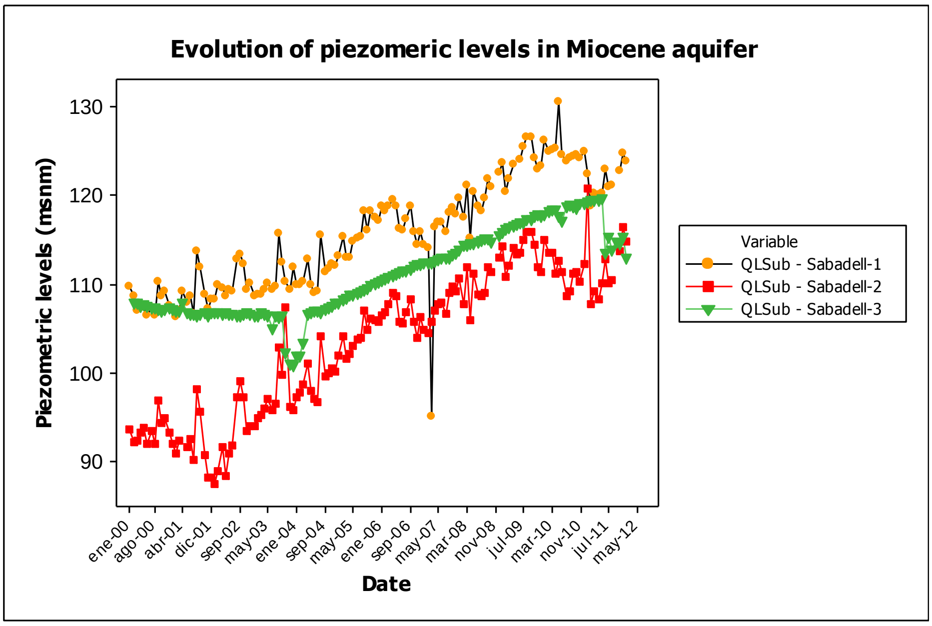
Regarding the groundwater and the Ripoll River water, the sediments present in the riverbed and in the aquifer could be a possible source of radioactivity in the recovered water. The geological characteristics of the area, in which predominates gravel, sand, conglomerates, clay and lime (Sabadell Town Hall, 1986), are not likely to present important natural values of radioactivity. In general, high radionuclide concentrations are found in granitic, fractured rock (crystalline) aquifers and near rich organic coal deposits, and leaching of uranium from carbonate aquifers has also been reported (NRMMC–EPHC–NHMRC, 2009). Then, it is not expected that the groundwater or the Ripoll River water can be a source of radionuclides in the final treated water, thus the risk posed by radionuclides presence can be considered to be low.

Although information on the presence of radionuclides in the recovered water and at RISMAR scheme is not available and should be investigated in the future, especially if the final treated water is intended to be used as drinking water, the risk posed by radionuclides can be considered to be low.

5.5.9. Pressure, flow rates, volumes and groundwater levels

Pressure and flow rates are important to be considered when the MAR is performed through direct injection of water into a confined or semi-confined aquifer, and volumes and groundwater levels need to be evaluated for both MAR performed by infiltration and by direct injection. In the case of RISMAR scheme, MAR is performed by infiltration through the Ripoll River riverbed to an unconfined aquifer, so pressure and flow rates are not considered, but volumes and groundwater levels need to be evaluated. If the watertable is raised too high, recharge of unconfined aquifers may also have adverse impacts, e.g. waterlogging, flooding of basements and effects of anoxia on vegetation root zone. On recovery of stored water, lowering of the watertable may increase pumping costs for other groundwater users and reduce yields of shallow wells, it may also mobilise metals and reduce groundwater discharge to dependent ecosystems at times when this is most needed (NRMMC–EPHC–NHMRC, 2009).

Figure 41 Piezometric levels in the Miocene aquifer in Sabadell.



In Sabadell, the Miocene and the alluvial aquifers suffered depletion in water levels in the past, due to a strong exploitation by the factories present along the Ripoll River banks. Different piezometers pertaining to the ACA have been used to control the water levels in the aquifers. Piezometric levels of the alluvial aquifer measured in a point downstream the Ripoll River area of study in the last decades indicate a slow and steady recovery of the water levels, parallel to a decrease in activity of the factories close to the Ripoll River (Franch, 2007). Piezometric levels of the Miocene aquifer have been measured through three piezometers located in Sabadell. The data available since 2000 to 2011, obtained from ACA website (ACA, 2013), have been represented in Figure 41. These piezometric levels have recovered considerably from 2000 to 2011, especially since 2003. This recovery was produced later than the recovery of the alluvial aquifer, since many of the factories that were still working in the area were using the Miocene aquifer for their processes. In any case, recovery of water from the alluvial aquifer in the framework of the restoration project in Sabadell started in 2004, and none of the aquifers seem to have suffered depletion on their water levels since then, instead, an increase has occurred. This increase is explained by the closure of the factories that were using the aquifers, but not to the increased recharge thanks to the project.

At RISMAR scheme, as the aquifer is unconfined, it is really difficult to calculate the volumes of water that enter the system. Recovered water volumes by CASSA (from the area of study) are known, but not the volumes extracted by companies exploiting the aquifer. Data facilitated by CASSA from the Ripoll River WWTP indicate that the discharges of treated wastewater into the Ripoll River were on average 19.053 m^3/day on 2006, ranging from 11.337 to 61.257 m^3/day, while in 2007 the average decreased to 15.803 m^3/day, ranging from 7.037 to 41.005 m^3/day. The annual volume of water sent to the Ripoll River on 2006 was of 7.0 hm^3, while in 2007 was of 5.8 hm^3. The decrease on discharges to the Ripoll River is explained principally by the climatology, as 2007 was a very dry year, characterized by an extreme drought suffered in Catalonia. Recovered water from the mine (S4) during 2006 was on average 70 m^3/day, that represents a total of 25.550 m^3 (0.026 hm^3) recovered during 2006. This value can be expected to have been higher in 2007, due to the drought suffered in the area (data not available). Then, the volume of treated wastewater sent to the Ripoll River was much higher than the volume of water recovered. However, the volume of water that actually was infiltrated through the riverbed must be considered. In Franch (2007) it was estimated that 1.12 hm^3 infiltrated through the riverbed to the alluvial aquifer all along Ripoll River course. Although this value should be smaller if only the recharge area at RISMAR scheme is considered, it can still be expected that the volume of water recovered is much lower than the volume of water infiltrated. Similarly, in the study of Franch (2007) it was estimated that the overall balances for both the alluvial and the Miocene aquifers were positive, with an increase of 0.40 hm^3 for the alluvial aquifer, and an increase of 0.35 hm^3 for the Miocene aquifer during 2006.

To sum up, for the purposes of the risk assessment, it can be considered that the risk of depleting the water levels in both aquifers was very low, as extractions from factories in the area decreased, the recovered water for reuse purposes did not overexploit the alluvial aquifer, and, at the same time, the water levels in the aquifer have been recovered in the recent years, thus replenishing the aquifers.

5.5.10. Contaminant migration in fractured rock and karstic aquifers

As explained before, the aquifer in Sabadell has two units, the Miocene and the alluvial, so two aquifers are considered. Both units are formed by sedimentary deposits, and as it has been pointed out in section 5.5.8, the materials found are gravel, sand, conglomerates, clay and lime (Sabadell Town Hall, 1986). This aquifer does not present karstic features and hence the residual risk of contaminant migration via fractures is negligible.

5.5.11. Aquifer dissolution and stability of well and aquitard

The source water used in a managed aquifer recharge scheme is unlikely to be in equilibrium with the minerals present in the storage zone. Reactions can occur between the recharged water and the native groundwater, and between the recharged water and the aquifer material. As a result, some dissolution of minerals may occur when the recharge water comes into contact with minerals in the aquifer. The degree of dissolution depends on the solubility of the mineral in the given conditions (e.g. pH, temperature, pressure, ionic strength, contact time). Untreated wastewater has a high amount of organic matter and other substances that can react with the matrix materials in the aquifer. Organic carbon in recharge water may be degraded in the aquifer, producing acidic conditions that result in dissolution of carbonate minerals (predominantly calcite). Carbonate minerals can be a major influence on the quality of water recovered, because carbonate dissolution is a rapid reaction. Dissolution of carbonate minerals will increase aquifer permeability, and the impact on the stability of injection wells and the aquitard must be considered. Although a low rate of calcite dissolution assists in avoiding well clogging, an excessively high rate of aquifer dissolution can collapse uncased wells and the recovered water can become turbid from entrained sand and clay. Preferential flow paths can also develop, which can alter the residence time in the aquifer and cause metal mobilisation. Other subsurface reactions can end up in inorganic compounds increase. Typical inorganic compounds that can be mobilized and take part in subsurface reactions are arsenic, iron and manganese, and to a lesser extent, aluminium, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, fluoride, iron, lead, manganese, molybdenum, nickel, vanadium, uranium and zinc (NRMMC–EPHC–NHMRC, 2009; Custodio and Llamas, 1996). All of these inorganic compounds, most of them trace ions, can pose a human health and/or environmental risk, and have been discussed in section 5.5.3.

The alluvial aquifer in Sabadell is the one where the water is recovered, and it is mainly formed of sand and gravel, with patches of fine sands and silty loams. Presence of limestone is scarce, and it is not a karstic aquifer. Taking these characteristics into consideration, the presence of calcite is probably low. Another point to consider is the acidity and potential for acidification of the recharge water, which could facilitate the dissolution of carbonate minerals, in case they are present. The river water (which is the water that it is being infiltrated) before and after the treated wastewater discharges was always in the neutral and basic range, and it was not acid (see section 5.5.14.2). Another situation that could acidify the groundwater would be the oxidation of the organic carbon present in the recharge water. The recharge water presented a high content of organic carbon (DOC), but the infiltration step retains a big part of the organic matter. Recovered water still had organic carbon, which indicates that the organic carbon that had not been retained through the infiltration step had not been completely oxidized to produce acidic conditions within the aquifer. Finally, considering the results obtained for calcium (see section 5.5.4.3) and carbonate (see section 0), dissolution of calcite does not seem to have happened at RISMAR scheme. Carbonates could not be detected in the recovered at any sampling campaign, but they were detetected in different sampling campaigns in the river water. Then, releases of calcium carbonate from the aquifer materials could not be possible. Regarding calcium, for the recovered water, the average calcium concentration (119 mg/L) is higher than for the river water mixture 1 (102 mg/L) and more similar to the river water reference point (114 mg/L). The river water mixture 1 presents a lower calcium concentration than the river water before the discharges (river water reference point), as it receives the discharges of the treated wastewater which has a much lower concentration of calcium. But the recovered water is much more stable regarding calcium concentrations; in Figure 25 it can be observed that the variabiality in calcium concentrations is much higher in the river reference point than in the recovered water. Taking these results into considerations, it cannot be completely rule out that calcium has not been released from the sediments in the recovered water, but it is clear that in case it was released, it was not released in the form of calcite.

An important point to consider is the possible metals and other organic compounds mobilization. The chemistry of water stored in an aquifer during MAR is affected by chemical reactions, which are dependent on aquifer status (pH, redox state, minerals, organic matter, microbiological activity) and the quality of the recharged water. At RISMAR scheme, manganese mobilization occurred, as explained in section 5.5.3.14. Releases of manganese or iron from the sediments are associated to the presence of organic matter in the water and its oxidation. During the organic matter degradation, the electron donor is the organic matter, and different electron acceptors can be used. The "natural" sequence, which is dominated by the energy required to perform the oxidation, is first to use the dissolved oxygen, then nitrate, after this manganese oxide and then iron oxide. These redox reactions are catalysed by microorganisms, and the most efficient organisms dominate each stage, inhibiting the development of the ones below. Overall, this leads to a natural zonation. Thus, in the aquifer the organic matter is oxidised and the current electron acceptor is the manganese oxide. The increase in DOC in the infiltration water, due to the treated wastewater discharges may have triggered the shift in the redox conditions in the aquifer, thus starting to reduce manganese oxides (Ayuso-Gabella and Salgot, 2012). In any case, mobilization of manganese occurred, and it should be given due consideration. Prior to this manganese mobilization, zinc could have been released too, although for this compound it is not clear if it was mobilization from sediments in the aquifer or transient pollution due to works in the pumping system. Iron mobilization did not occur during the RECLAIM WATER project sampling period.

Considering the data available, the risk of aquifer material dissolution, that could jeopardize the stability of the well and aquitard, is overall very low for RISMAR scheme. However, it is important to follow-up on manganese mobilisation and other possible trace compounds that may be released from the aquifer to groundwater due to changes in redox conditions. Manganese does not pose a risk for the human health, but other trace compounds may pose it.

5.5.12. Aquifer and groundwater-dependent ecosystems

Ecosystems, communities and species are obligate groundwater-dependent if they rely on groundwater to provide all or part of the water supply, pressure, chemistry, or temperature requirements seasonally, intermittently or persistently, or if they rely on a shallow watertable during any time of the year or are restricted to locations of groundwater discharge. In contrast, biota is facultative groundwater-dependent if groundwater maintains their habitat conditions in some locations but not in others. Groundwater-dependent ecosystems can be affected by the recharge of poor quality water into the aquifer or through excessive changes in groundwater levels. They can also benefit from recharge of good quality water or through the increase of water levels thanks to the recharge. Such changes may modify their habitat, or impact directly on the receptor species. The presence and type of groundwater dependent ecosystems needs to be investigated in order to protect them before approaching a MAR project. Groundwater-dependent ecosystems may include: aquifer indigenous microorganisms; stygofauna; wetland, riparian and terrestrial phreatophytic vegetation; and fauna and flora of connected wetlands, streams, lakes, springs, estuaries and marine environments (Dillon *et al.*, 2009; NRMMC–EPHC–NHMRC, 2009).

Aquifer indigenous microorganisms have not been studied at RISMAR scheme. Although there are different processes in the aquifer that are mediated by microorganisms, and it would be interesting to know which populations of microorganisms were living in the “pristine” aquifer, nowadays it is nearly impossible to unravel this question. The many interconnections of the old alluvial aquifer with the new alluvial aquifer, as well as the Miocene aquifer, and the strong historical exploitation of the aquifers and their pollution make it very difficult to identify these microorganisms. An evolution of the microbial populations living in both the alluvial and Miocene aquifers may have occurred, but at this point it cannot be explained. A comprehensive study of the changes in the bacterial communities present in the aquifer was performed during the 2nd cycle of injection at Bolivar Aquifer Storage and Recovery site (Reed, 2008). The results indicated that microbial communities – fermentative, sulphate-reducing and nitrate-reducing bacteria – did change due to the injection of reclaimed water into the aquifer, although they could return to their initial community structures during the storage period, except for the nitrate-reducing bacteria. Although there was not an overall decrease in biodiversity, Reed (2008) found that a different microbial community structure developed in response to the injected water.

Regarding the possible evolution of the microbial populations living in both the alluvial and Miocene aquifer at RISMAR scheme, it can be said that discharges of treated and untreated wastewater into the Ripoll River could have introduced in the aquifer microorganisms of faecal origin, as well as nutrients, that must have contributed to modify the existing populations there.

This happened even before the whole restoration project started (1994) and the piping system to send the treated wastewater to the Ripoll River came into operation (2005). Actually, a well tapping the Miocene aquifer that had been previously exploited by CASSA was sealed and closed due to faecal microorganisms pollution in 1985 (Vinyoles *et al.*, 2005). Right after the amount of water susceptible of being infiltrated was increased thanks to the discharges of treated wastewater coming from the Ripoll River WWTP to the Ripoll River it could be expected that the microbial populations present in the aquifer at that moment were not much different than before of sending the treated wastewater. It must be taken into consideration that the river water quality before and after the treated wastewater discharges is not very different, although nutrients and faecal indicators slightly increase after the treated wastewater discharges. Besides, the infiltration step retains a good amount of microorganisms and nutrients in the riverbed. Then, the risk of affecting the already present microbial communities due to the MAR activities is very low, as probably those microbial communities had already evolved much before the implementation of the restoration project.

The term ‘stygofauna’ encompasses all animals that occur in subsurface waters. Stygofauna have been found in fresh and saline aquifers that have macroporosity, and in pores of alluvial aquifers. Although stygofauna is found in all continents except Antarctica, a large proportion of stygofauna species are highly endemic and localised (NRMMC–EPHC–NHMRC, 2009). Stygofauna has not been investigated in the aquifers of the Ripoll River. No sampling campaigns to recover stygofauna from the aquifer were undertaken in the framework of the RECLAIM WATER project neither out of it. However, the presence of macroinvertebrates and many other organisms, indicators of pollution, in the Ripoll River banks and springs have been investigated as part of several studies on the ecological status of the Ripoll River and the area surrounding (Ecoproges, 2007; Prat *et al.*, 2002) as well as for the Besòs River (Benito, 2007), for which the Ripoll River is a tributary. In the study performed on 2002 by Prat *et al.* different sampling points in Sabadell and upstream and downstream the Ripoll River were investigated regarding the macroinvertebrates communities, as well as a sampling point close to the source. In this sampling point close to the source, the diversity of macroinvertebrates families found was high, with a maximum of 36 different families identified during a summer sampling campaign. This diversity decreased downstream the Ripoll River to 18 different families in Sabadell area, including families very tolerant to pollution. Then, on 2002, much before the piping system to send the treated wastewater to the Ripoll River came into operation (2005), the Ripoll River suffered from pollution. A posterior study by Ecoproges on 2007 showed a similar number of families in the Ripoll River in Sabadell area (15 different families versus 18 in 2002) but a much lower number of families in the sampling point close to the Ripoll River source (14 different families versus 36 families identified in summer 2002). This could be due to a different sampling or identification methodology and skills by the people performing the sampling campaigns, as the source water did not seem to be polluted considering the other data measured by the team. Considering the results of these studies, and that on 2007 the Ripoll River WWTP was already sending the treated wastewater upstream the induced recharge area, the discharges did not seem to impoverish the biological quality of the Ripoll River regarding the macroinvertebrates communities, and no changes can be considered to have occurred.

Riparian and terrestrial phreatophytic vegetation, connected to the Ripoll River and springs, as well as the fauna in the area have been studied in Sabadell since a long time (Ecoproges, 2007; Prat *et al.*, 2002; Sabadell Town Hall, 1986, 2010). In fact, part of the project in place at Sabadell to recover the Ripoll River and the surrounding area is to preserve its ecological value and its historical importance for the city of Sabadell. In the past, the Ripoll River and its banks, as well as the marginal vegetable gardens, were highly polluted. In the work by Sabadell Town Hall (1986) the landscape surrounding the Ripoll River was detailed, and different communities were identified. These were divided in four groups: woods, phreatophytic communities, transition areas and crops. Subgroups and different species in each of them were extensively detailed, in order to understand which were the communities living there and how should be tackled the restoration of the area. A brief summary of the communities identified is given below:

- Woods: holm-oak woods, with or without bushes and lianas; pine woods, with white pine trees, with or without bushes, with more or less density of pine trees, and some of them artificially replanted; underbrush mixed with regenerating pine trees.
- Phreatophytic communities: elm groves, alone or mixed with poplars, plane trees and hazels; bushes of breams; herbaceous communities; mosses and liverleaves; aquatic communities including duckweeds and watercress; ruderal species; hedgerows with different degrees of density.
- Transition areas: Spanish broom mixed with rosemary, furse and bunch grasses; abandoned crop fields with fennel, yellow fleabane, horseweed and bunch grasses; ruderal vegetation; hedgerows with blackberries; redoul; fields of true grasses; parks and gardens.
- Crops: olive trees; almond trees; grape fruit; fruit trees; vegetable gardens; marginal vegetable gardens; ornamental plants plantations; extensive farming (grains and leguminous crops); pastures; abandoned crop fields with or without shrubs; reed beds.

The study concluded that in the area surrounding the Ripoll River the landscape had been strongly transformed, with artificial elements and pollution, and it was identified:

- A strong decrease on woods.
- A degradation of agricultural areas.
- An expansion of marginal activities.
- A strong degradation of the river water quality.
- A degradation of the road and hydraulic networks.
- An excessive proliferation of the transition areas.
- A proliferation of degraded and abandoned areas.

EDS started a project to restore the area in 1994, and commissioned a report on the ecological status of the Ripoll River and its surrounding area. This study, performed by Prat *et al. (*2002), evaluated the ecological evolution of the area from 1996 to 2001, and the results indicated that the status of the area was deplorable and that restoration was required. Prat *et al. (*2002) and EDS made a plan for restoration, and this included:

- To restore and preserve the natural values.
- To reforest uncultivated areas and slopes.
- To preserve agricultural areas of interest.
- To preserve forest areas of interest.
- To improve the Ripoll River in its entirity, avoiding an excessive degradation.
- To enable social uses of the area.
- To integrate industrial and urban areas in the landscape thanks to a green network.

Later on, the study performed by Ecoproges (2007) indicated that all the typical species to be present in phreatophytic communities were identified in the banks of the Ripoll River, although not in the level of development that could be expected for a regular situation without anthropic activity. Overall, the results indicated an improvement respect the previous work on 2002 by

Prat *et al.* Then, although the area has suffered from a high anthropic pressure, the restoration project seems to have benefited the phreatophytic communities, and MAR did not have a negative effect on them. It was also very interesting to discover that there was a strong demographic increase of bird populations in the reed beds by the Ripoll River. Among the identified birds, the presence of the dabbling duck, grey heron, cattle egret, little egret and common moorhen could be highlighted. These species are tolerant to degraded areas, but other species less tolerant and that started to be found in the area were the common coot, little grebe, different species of ducks (e.g. diving ducks and dabbling ducks) and waders. In addition, the restoration of the Ripoll River in the recent years enabled the emergence of fish in it, including the catfish, the common barbel, common carp, gambusia and largemouth bass (Sabadell Town Hall, 2010).

Considering the information available, the restoration project seems to have had a positive effect on the riparian and terrestrial phreatophytic vegetation. As part of the whole project to restore the area, the volume of water susceptible of being recharged increased, thus contributing to maintain groundwater levels (see section 5.5.9), necessary to support the groundwater-dependent ecosystems. In addition, the Ripoll River flow was augmented, thus supporting also the phreatophytic communities and enabling the development of fauna in it, which is as another positive effect.

Then, for groundwater-dependent ecosystems, we can consider that the MAR practice does not have a negative impact and does not pose a risk at RISMAR scheme, and that it has had a positive effect in some of the dependent ecosystems evaluated.

5.5.13. Energy and greenhouse gases considerations

Although this is not properly a hazard itself, when deciding to establish a MAR project it is important to take into account energy requirements in relation to alternative supply systems, as well as greenhouse gases considerations (NRMMC–EPHC–NHMRC, 2009). Then, all energy use in the MAR system must be considered and evaluated, and the maximum energy efficiency should be pursued. To account for all energy use the following points should be considered:

- Construction techniques, materials and equipment with low embedded energy.
- Gravity flows rather than pumping, and if pumps are used should be energy-efficient.
- Passive treatment systems rather than energy-consuming treatments, wherever interchangeable.
- Fail-safe data acquisition and control systems to minimise unnecessary use of vehicles.
- Renewable energy sources such as solar-powered.
- Optimal recharge pressures to maximise energy efficiency (in case the recharge is done by injection).
- Optimal unclogging processes for wells and basins.

In the case of RISMAR scheme the energy cost of recovered water that has undergone subsurface treatment and post-treatments should be compared to the energy cost of other alternative sources of water available. Other alternative sources of water in Sabadell could be treated wastewater or Ripoll River water. However, using treated wastewater or Ripoll River water is not recommended for the uses found in Sabadell, because the quality of these waters would not be enough. Then, the energy cost of the final treated water can be only compared with the use of potable mains water. To start with, the energy cost of treating wastewater in the Ripoll River WWTP should not be considered, as this process would take place as per legislation requirements, independently of the desire to reuse this alternative water source. Then, treated wastewater is the starting point for assessment. As a reference, the energy cost of the treatment performed at the Ripoll River WWTP was on average of 0.60 kW.h/m^3 on 2006 and of 0.69 kW.h/m^3 on 2007. This treated wastewater is sent upstream the Ripoll River, where water infiltrates. To estimate the energy cost of this process it has been considered that all the treated wastewater (6 hm^3 during the year 2007) is sent by gravity to Molí Torrella (which was not probably the case, as part of the water was sent by gravity to Sant Oleguer area, close to the WWTP), and half of the water is pumped upstream from the Molí Torrella area to the Torrent Colobrers area. The energy cost of this process was estimated to be of 21,292 kW.h for the whole year 2007. After this, the water is recovered in the mine, and the pumping energy consumption was estimated to be of 0.4 kW.h/m^3, considering a pumping rate of 0.004 kW.h/(m^3.m) (given in Plappally and Lienhard, 2012) and pumping the water at 100 m deep. After this, the water follows a double disinfection step (UV and chlorination) and filtration through a small sand filter. These three treatments are estimated to consume around 550 kW.h for the 25,000 m^3 of water recovered, considering the rates of consumption for each treatment given in Plappally and Lienhard (2012). Adding up all these energy consumptions, a final value of 1.27 kW.h/m^3 for the final treated water at RISMAR scheme during 2007 is obtained. Comparing this value to the reported average energy consumption to produce the potable water and distribute it on 2007, which was 0.23 kW.h/m^3 according to ATLL data (ATLL, 2008), it is clearly much higher for the final treated water. This value accounts for the distribution of water to all municipalities connected including Barcelona and Sabadell. However, treatments were updated at the ATLL company, and a reverse electrodialysis was introduced, increasing the average consumption value to 0.82 kW.h/m^3, on 2009 (ATLL, 2010). More recently, a desalination plant was constructed in el Prat de Llobregat, and the energy cost for this potable water was of 3.67 kW.h/m^3 on 2010 (ATLL, 2012). Bearing this in mind, although the energy consumption was high at RISMAR scheme, using potable water can be even higher than for final treated water if desalinated water is used. Besides, it must be considered that in 2007 only 25,000 m^3 were recovered from the mine, but this value was probably higher in later years, thus decreasing the energy cost per m^3, because the highest estimated energy consumption is for pumping the treated wastewater upstream the Ripoll River. As post-treatments applied are not highly energy consuming, only the pumping of treated wastewater upstream the Ripoll River and the recovery of the water would impact the energy consumption. If a recovery of 100,000 m^3 is simulated, the energy cost would be of 0.77 kW.h/m^3, which is in the same range or even lower than the energy cost for potable water in the recent years. In any case, the energy consumption for the final treated water at RISMAR scheme should be taken cautiously and re-evaluated with actual electrical consumption data of CASSA and EDS.

Another point to consider in the comparison of energy consumption between potable water and final treated water is the embodied energy of the construction implemented. It is very difficult to evaluate this cost in the case of the potable water, as ATLL has many different installations to treat and deliver the water to the consumers, and this evaluation is out of the scope of the present work. At RISMAR scheme, the embodied energy of the piping system to discharge the treated wastewater upstream the Ripoll River should be considered, but not for the constructed mine, as this was an old installation that has been recovered, thus reducing the cost of the infrastructure for the MAR system. Besides, as the water is not stored in a lagoon, tank or any other installations, but in the aquifer, this also reduces the embodied energy cost. So, although an estimated number for embodied energy is not given in the present work, it can be said that RISMAR scheme has probably a much lower embodied energy than the potable mains system.

Regarding greenhouse gases, they are generated due to energy consumption, and as subproduct of the wastewater treatment. A point to be considered is that in the Ripoll River WWTP there exists a cogeneration system, which uses biogas to produce energy, thus reducing the greenhouse gases production due to the wastewater treatment process.

A Life Cycle Assessment analysis considering all inputs and outputs should be performed, but this is out of the scope of the present work.

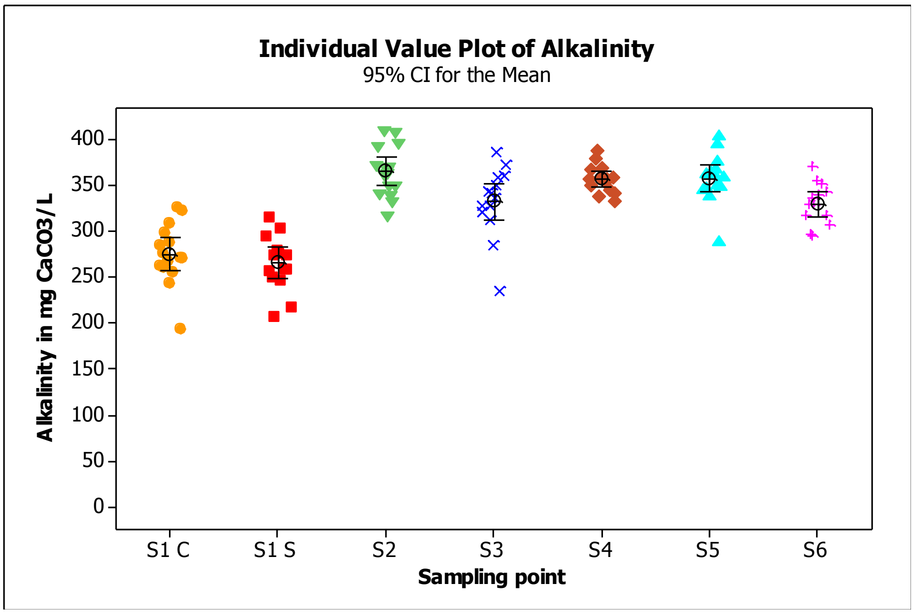
To sum up, the risks posed by energy consumption and greenhouse gases are low, but more investigation on the real energy consumption at the different steps of the process should be developed. However, this system uses less energy than alternative options (e.g. desalination, constructing lagoons or tanks for storage) and part of the water treatment relies on energy generated by biogas.

5.5.14. Other parameters measured

Several parameters were measured and selected in order to understand and have a "quick" glance at the quality of the water along the process.

Although these parameters are not hazards themselves, they are helpful in understanding the whole recycling process, to track any change in the wastewater and are commonly used in a daily basis in WWTP facilities or recycled water schemes. Temperature, pH and redox potential are commonly measured as part of daily monitoring programs. Besides, guideline values in the Spanish regulations exist for them.

Figure 42 Individual value plot of alkalinity in the different sampling points.



5.5.14.1. Alkalinity

Alkalinity indicates the capacity of the water to neutralize pH changes, and it results from the presence of hydroxides, carbonates and bicarbonates. Alkalinity in wastewater is important where chemical and biological treatment is to be used, in biological nutrient removal and where ammonia is to be removed by air stripping (Metcalf and Eddy, 2003). Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes and makes water less vulnerable to acid rain, protecting a major source of human consumption.

Alkalinity was always lower in the treated wastewater than in the river water and the recovered water, as can be appreciated in Figure 42.

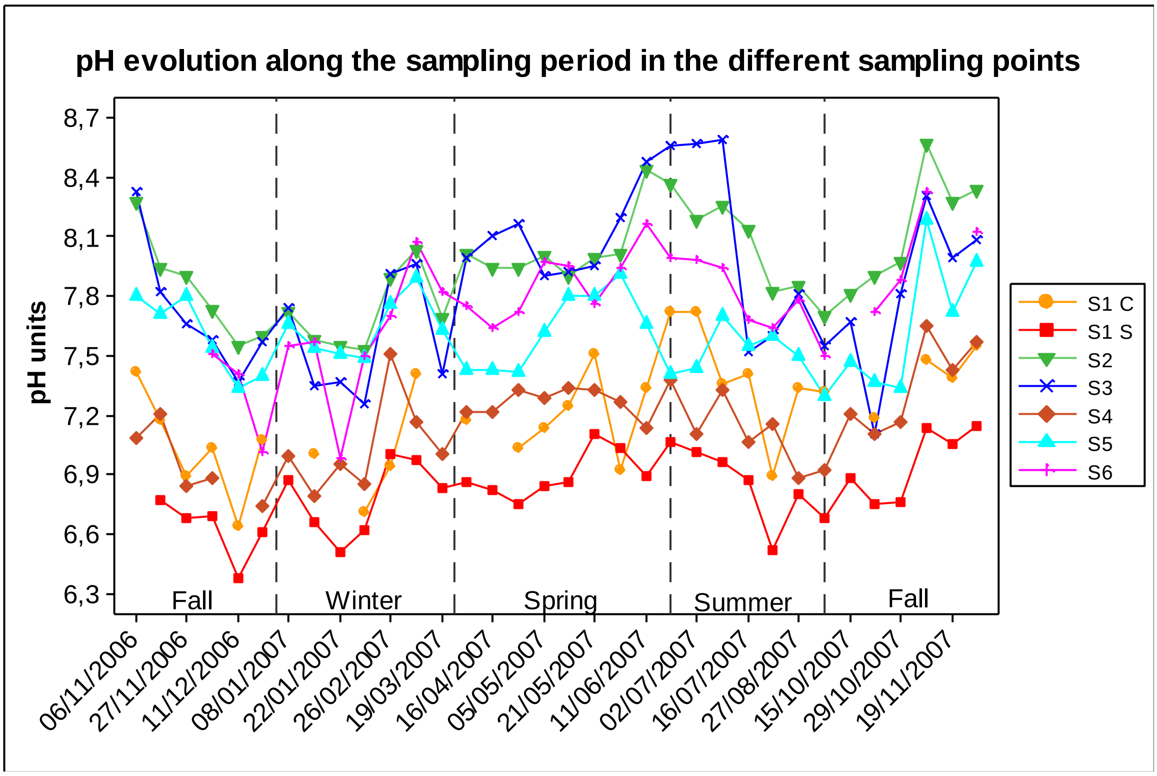
No guideline values exist for alkalinity.

5.5.14.2. pH

Although pH usually has no direct impact on consumers, it is one of the most widely used operational water quality parameters. It expresses the negative logarithm of the hydrogen-ion concentration. The concentration range suitable for the existence of most biological life is quite narrow, typically 6-9 (Metcalf and Eddy, 2003). One of the major objectives in controlling pH is to minimise corrosion and scaling in pipes and fittings. Corrosion can be reduced by the formation of a protective layer of calcium carbonate on the inside of the pipe or fitting, and the formation of this layer is affected by pH, among others. Under some conditions, particularly in the presence of strong oxidising agents such as chlorine, water with a pH between 6.5 and 7 can be quite corrosive. Chlorine disinfection efficiency is impaired above pH 8.0, although the optimum pH for monochloramine disinfectant formation is between 8.0 and 8.4. The guideline values are regularly based on minimising corrosion and scaling of plumbing fittings and pipes, but they are not health related (NHMRC-NRMMC, 2011; WHO, 2011a).

Comparing the average values for the different sampling points, it can be observed that the lowest values correspond to the treated wastewater, followed by the aquifer water. The river water presents in general higher pH values, indicative of the biological activity of algae and other organisms and contact with air. The final treated water presents higher pH values than the recovered water from the aquifer, due to the chlorine dosed for disinfection, which oxidizes and thus increases the pH.

Figure 43 pH evolution along the sampling period.



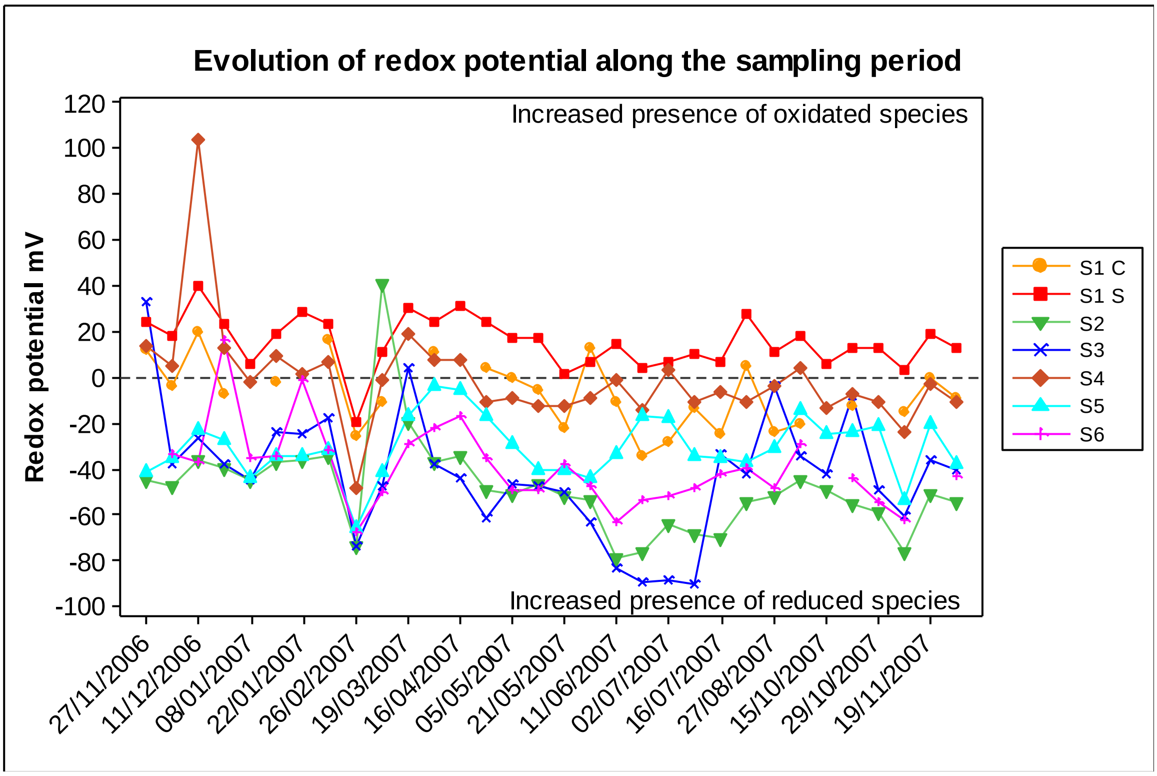
pH suffers variations along the year (see Figure 43). The river water after the discharges is the one that suffers stronger pH variations (S3, pH 7.1 – 8.6; S6, pH 7.0 – 8.3). This is explained by variations already occurring in the river water (S2, pH 7.5 – 8.6) plus the treated effluent discharges (S1 S, pH 6.4 – 7.1). In Figure 43 the different seasons have been separated with dashed lines. Different seasons show pH changes, due to the different level of activity of organisms in the waters. Then, the clearest example is the river water; when temperature and radiation increase in spring and summer, the metabolic activity of the living organisms and microorganisms also increase, thus increasing the pH. In winter, pH decreases, as is the period with the lowest metabolic activity. These changes also influence the treated wastewater pH, as the microorganisms of activated sludge also suffer the temperature changes. However, the seasonal change is more marked in the river water. The aquifer water (S4) does not suffer such strong seasonal fluctuations, but the pH also varies along the year.

pH guideline values set in the Spanish water reuse RD 1620/2007 and the Spanish drinking water RD 140/2003 are fulfilled for all sampling points. For the swimming pools RD 742/2013, the final treated water would fulfil the guideline values set (7.2-8) but for the maximum value measured (8.2). The other sampling points would not fulfil the swimming pools RD. Other guidelines considered (see Appendix E) would be also fulfilled.

5.5.14.3. Redox potential

Redox potential gives an idea of the oxygen present in the water and the reactions associated to oxidation and reduction processes. It is an intensity parameter of the overall redox reaction potential in the system, not the capacity of the system for specific oxidation or reduction reactions. Positive values for redox potential indicate that oxidation processes will be enhanced in the system, but does not exclude that reduction processes take place at the same time. Conversely, negative values indicate that reduction processes will be enhanced in the system, but does not exclude that oxidation processes take place too. Redox potential measurement can also be used in the operational monitoring of disinfection efficacy (WHO, 2011a).

Figure 44 Redox potential evolution along the sampling period.



Treated wastewater tends to present positive redox potentials, at least for the grab sample (S1 S). Composite sample (S1 C) is not a good representative of the treated wastewater redox status, and a grab sample is preferred regarding this parameter. River water presents negative redox potentials, while the aquifer water moves between positive and negative potentials, being close to 0 redox potential most of the time.

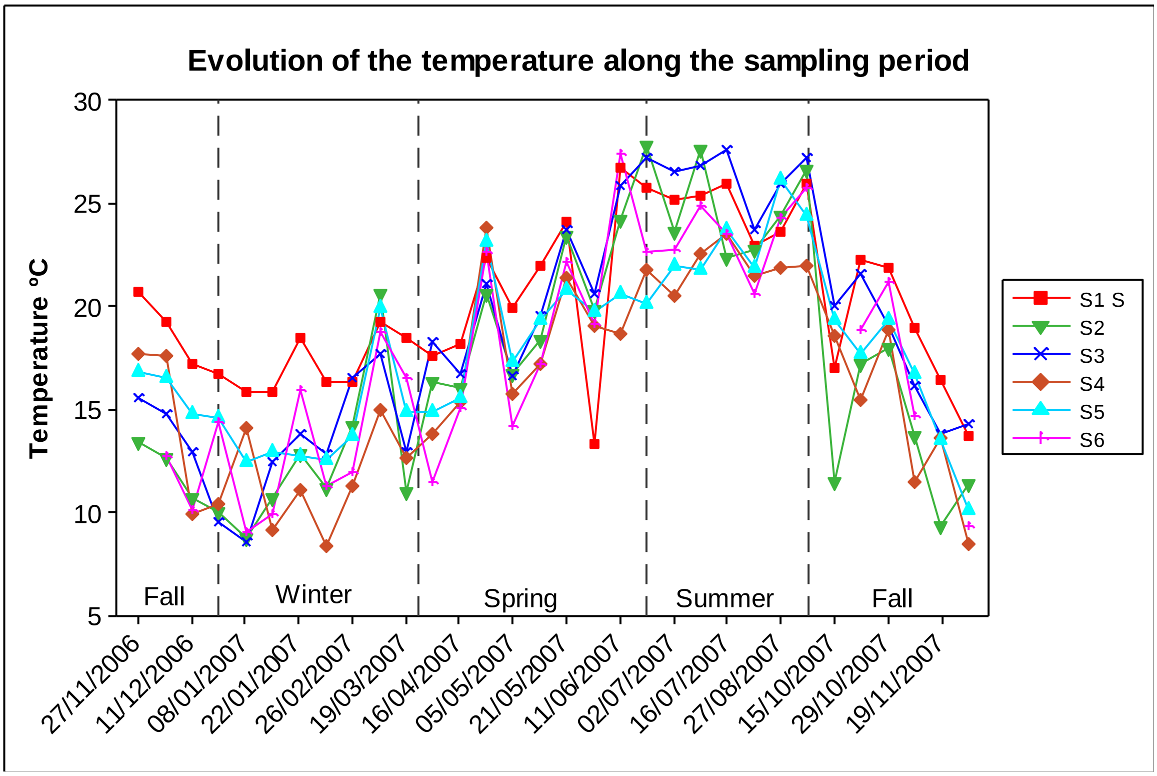
Iron and manganese reactions take place at potentials from 0 to +100 mV, thus explaining the presence of increased manganese concentrations in the aquifer water.

The swimming pools RD sets a redox potential between 250 and 900 mV, which is not achieved for any of the sampling points. However, in the RD it is said that "Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates." As chlorine is the disinfectant used for the final treated water, and probably, when the water is used to fill in the summer swimming pool additional chlorine is added (thus increasing the redox potential to positive values and getting to the minimum 250 mV requested), the guideline value would be fulfilled.

5.5.15. Temperature

Water temperature is important for the metabolic rate of the organisms living in it, which is increased with higher temperatures. Similarly, chemical reaction rates also increase with temperature, and this can lead to greater corrosion of pipes and fittings in closed systems. Disinfection processes are also more effective at higher temperatures. Low water temperatures tend to decrease the efficiency of water treatment processes by, for instance, affecting floc formation rates and sedimentation efficiency. Increased temperatures can also promote the growth of taste and odour producing organisms in lakes and impoundments, and in distribution systems. However, the effect of temperature in the different microorganisms is not the same, as some can withstand high temperatures while others need low ones to develop. Scale formation in hard waters will also be greater at higher temperatures. When water is discharged into a river, the temperature should not increase more than 3º C as per the Spanish water reuse RD. Increasing temperatures in a river will decrease the dissolved oxygen in it, thus posing a risk for the organisms living there (NHMRC-NRMMC, 2011; WHO, 2011a).

Figure 45 Temperature evolution along the sampling period.



Note: in this figure the temperature of the S1 C was not represented as the samples were kept refrigerated and the value was not real.

Strong fluctuations of water temperature occurred during the whole sampling period, and according to the season when the samples were taken, as it can be observed in Figure 45. It is interesting to note that the aquifer water also suffered those strong fluctuations, comparing to other aquifers where the water temperature is more constant along the year. As this is a riverbed filtration system, and the aquifer is connected to the river water in different points, the temperature of the aquifer is governed in part by the temperature of the river water. In most of the samples taken, the aquifer temperature was a bit lower than in other sampling points.

The difference in temperature between the treated wastewater and the river water was not big; on average, the temperature of the treated wastewater was 3 ºC higher than the river water temperature before the discharges (S2), and this was translated into an average increase in the river water temperature after the discharges of 1.6 ºC at S3 and of 0.4 ºC at S6. Although this water temperature increase can affect the ecosystems living in the river, it is to say that the presence of fish and birds increased in the recent years, and it does not seem that temperature change has been a problem.

During fall and winter, the lowest temperatures registered are for the river water before the discharges (S2) and the aquifer water (S4). During spring differences seem to be smaller and some lower peaks appear in the treated wastewater and the river water after the discharges (S6). In summer, the lowest values are for the aquifer water, and the river water presents the highest temperatures of the year, before and after the discharges of the treated effluent. This is due to the solar irradiation, which contributes to warm the river water. In addition, as the river is not deep, the water can be much more affected by the solar irradiation.

As the river water temperature does not increase more than 3ºC after the treated wastewater discharges, the Spanish water reuse RD guideline values are fulfilled, and it does not pose a risk for the organisms living in the Ripoll River. Regarding the swimming pools Spanish RD, the temperature range given is to be abided only for heated pool, so it does not apply to the final treated water at RISMAR scheme. In any case, the swimming pool is outdoors and it will be subjected to natural temperature fluctuations during the day, and it is only used during summertime.

5.5.16. Summary of risk assessments

The results of the risk assessments of the preceding sections are summarised in Table 16 (maximal risk assessment) and Table 17 (residual risk assessment). In these tables the end points are listed at the top of each column, and the twelve hazards are considered in each row. Where the risk has been determined to be high (H) the box has been shaded red, and where the risk is low (L) the box has been shaded green. A blank box means that the hazard does not apply to that particular end point.

In the maximal risk assessment the risk if treated wastewater was used for the different reuse options and end points is evaluated, whereas in the residual risk assessment the same is done with the final treated water. However, there are two exceptions for the residual risk assessment: the Ripoll River and the aquifer. Considering the RISMAR scheme and for the purposes of the risk assessment, the Ripoll River receives treated wastewater, so the residual risk of receiving final treated water cannot be assessed in this case, because this will not happen. Then, for the Ripoll River, there is only the maximal risk assessment, which considers the risk of receiving the treated wastewater comparing to not receiving it, and this end point does not appear in Table 17 for the residual risk assessment. For the aquifer, something similar occurs, as this end point will receive infiltrated water which is a mixture from the Ripoll River water and the treated wastewater, but it will not receive final treated water. The aquifer has been evaluated in the residual risk assessment regarding the difference between receiving only treated wastewater (maximal risk assessment) versus receiving a mixture from the Ripoll River and the treated wastewater, which is the reality. Thus, in the residual risk assessment the aquifer has been considered to receive the mixture of Ripoll River water and the treated wastewater.

Table 16 shows that for the maximal risk assessment most of the hazards need to be reduced if the risks are to be acceptable. In Table 17, corresponding to the residual risk assessment, a good part of the risks have been assessed to be at acceptable level, but there are still some risks that would need to be reduced depending on the scenarios and end points considered. However, those risks that would need to be reduced will hardly be reduced due to constrictions of RISMAR scheme.

According to the residual risk assessment, the hazards that need to be considered and managed at RISMAR scheme are:

- Pathogens: the deterministic microbial risk assessment with the data that have been provided is not sufficient to conclude that the risk to human health is acceptable. With the results obtained, it could be ruled out that the final treated water would not be acceptable for drinking water, but for the other uses considered it would not be clear. A probabilistic microbial risk assessment using the given data and also data from the literature has been conducted (see section 6); pathogen mean risks were assessed to be acceptable ($<1\times10^{-6}$ DALYs) for all index pathogens, but for the case of ingestion of water as drinking water. Nevertheless, this use is not in place at RISMAR scheme and it is not expected to be in the near future, unless further post-treatments are applied.
- Inorganic compounds: this group of compounds can pose a risk if the water is to be used as drinking water. However, as it has been said above, this use is not in place at RISMAR scheme and it is not expected to be in the near future, unless further post-treatments are applied. Nickel is a special case, as it can reach the aquifer, and it is present in high concentrations in the Ripoll River. Besides, it can affect the living species in the river and the plants. There are other inorganic compounds that can still pose a risk for the Ripoll River, as their presence is randomly detected in the treated effluent. Then, for the environmental end points it is considered that there is still a risk regarding inorganic compounds, but it cannot be said it is a high risk, so it has been categorized as a medium risk.
- Salinity: the salinity of the final treated water and of all the waters at RISMAR scheme was higher than the recommended guideline values and could pose a risk for the crops and create problems for other uses. A detailed evaluation of the crops grown in the area has been undergone, and there is risk for the majority of the crops regarding a yield reduction, to a smaller or higher extent. However, for most of them the yield reduction would not be higher than than 30%. Foliar injury could affect some of the crops if sprinkler irrigation is used, otherwise the risk would be low. For other plants in the area, the risk is low as they are adapted to the Mediterranean climate, and most of them are not affected by the salinity. For turfgrass, the risk can be reduced by growing cultivars tolerant to salinity. The infiltration rate would not be affected by the final treated water, thus not posing a risk for the soils. Regarding drinking water, chloride and sodium concentrations are too high and would not fulfil the Spanish drinking water RD, but would not pose a risk for the human health. Again, this use is not in place at RISMAR scheme.
- Nutrients: nutrients are reduced along the treatment train, but the measured ammonia in the final treated water does not fulfil the Spanish drinking water RD. Again, this use is not in place at RISMAR scheme, and for ammonia, the guideline value is set to avoid corrosion of copper pipes and fittings, but it is not a health guideline value. Nutrients are diluted and decrease when mixing the treated wastewater with the river water, thus posing a lower risk to the aquifer comparing to infiltrating directly treated wastewater. For the river, the risk posed by nutrients is increased by the treated wastewater discharges, but the average nutrients concentration is only a bit higher than the average nutrients concentration in the river water before the discharges, indicating that pollution is already present in the river.

- Organic compounds: the presence of different organic compounds in the treated wastewater introduces a source of them in the Ripoll River and the aquifer. The final treated water still presents phenols and other compounds that would not fulfil the Spanish drinking water RD. Again, this use is not in place at RISMAR scheme.

Regarding radionuclides, further investigations are required, but it is assumed with the data available that the risk posed is low.

Table 16 Maximal risk assessment regarding the hazards identified in the Managed Aquifer Recharge Guidelines.

MAR hazards	Human end points				Environmental end points				
	Crop consumption	Ingestion of aerosols	Ingestion of water while swimming	Drinking water	Crop	Soil	Trees, bushes	Ripoll River	Aquifer
1. Pathogens	H	H	H	H	H	L	L	L	L
2. Inorganic chemicals	H	L	L	H	M	M	M	M	H
3. Salinity, SAR and infiltration problems	L	L	L	M	M	L	L	L	L
4. Nutrients	L	L	L	H	L	L	L	M	H
5. Organic chemicals	H	L	M	H	M	M	M	M	H
6. Turbidity and particulates	L	L	L	H	M	H	M	L	L
7. Radionuclides	L	L	L	L					L
8. Pressure, flow rates, volumes and groundwater levels									L
9. Contaminant migration in fractured rock and karstic aquifers	L	L	L	L	L	L	L		L
10. Aquifer dissolution and stability of well and aquitard									H
11. Aquifer and groundwater-dependent ecosystems							L		L
12. Energy and greenhouse gas considerations (*)									

(*) This hazard does not apply exactly to any of the end points considered.

H: high risk; M: medium risk; L: low risk. Cells in white: the hazard does not apply to the end point.

Table 17 Residual risk assessment regarding the hazards identified in the Managed Aquifer Recharge Guidelines.

MAR hazards	Human end points				Environmental end points			
	Crop consumption	Ingestion of aerosols	Ingestion of water while swimming	Drinking water	Crop	Soil	Trees, bushes	Aquifer (**)
1. Pathogens	L	L	L	H	L	L	L	L
2. Inorganic chemicals	L	L	L	H	L	L	L	M
3. Salinity, SAR and infiltration problems	L	L	L	M	M	L	L	L
4. Nutrients	L	L	L	M	L	L	L	M
5. Organic chemicals	L	L	L	M	L	L	L	L
6. Turbidity and particulates	L	L	L	L	L	L	L	L
7. Radionuclides	L	L	L	L				L
8. Pressure, flow rates, volumes and groundwater levels								L
9. Contaminant migration in fractured rock and karstic aquifers	L	L	L	L	L	L	L	L
10. Aquifer dissolution and stability of well and aquitard								L
11. Aquifer and groundwater-dependent ecosystems							L	L
12. Energy and greenhouse gas considerations (*)								

(*) This hazard does not apply exactly to any of the end points considered.

(**) For the residual risk assessment of the aquifer, it has been considered that it receives the mixture of Ripoll River water and treated wastewater, not final treated water as in the other end points, because it would not be realistic.

H: high risk; M: medium risk; L: low risk. Cells in white: the hazard does not apply to the end point.

6. QUANTITATIVE MICROBIAL RISK ASSESSMENT (QMRA) AND SENSITIVITY ANALYSIS OF RISMAR SCHEME (SABADELL)

In section 5.5.2.1 the human health risk due to the presence of human pathogens in the treated wastewater and how the risk was reduced along the treatment train was evaluated. However, with the evaluation of the data it was concluded that it was not possible to quantitatively determine the risks to human health by solely assessing the reduction of all of the different pathogens along the treatment train. Therefore, a probabilistic quantitative microbial risk assessment (QMRA) has been performed to address this hazard, which is the object of the present section.

6.1. Objectives of the QMRA

The QMRA performed aims to:

1. Assess the suitability of the treatment train to reduce the pathogens load in case the final treated water is used:
    a. For urban purposes, including: urban irrigation, filling one of a dual network system and street cleaning.
    b. For crop irrigation purposes.
    c. For industrial uses.
    d. For recreational uses (e.g. fill in a summer swimming pool).
    e. For potable reuse (e.g. direct connection to water distribution network).

Emphasis is put in uses that are currently in place at RISMAR scheme, but it is also interesting to evaluate other possible uses that may be put in place in the future and the risk that they could entail for the population.

2. Compare the risks reduction by the treatment train applied:
    a. The risk reduction that the treatment train could achieve if all treatments had an optimal performance or similar to what it has been published in the literature. This risk reduction comparison could be considered to be done from a “theoretical point of view”, although it also uses data gathered in the site.
    b. The risk reduction that the treatment train achieves considering the pathogens’ data and the indicators’ data available at the site. This risk reduction comparison could be considered to be done from an “empirical point of view”, although it also uses data from the literature.
3. Assess the suitability of the RBF and subsurface treatment as an extra barrier to reduce the risks in the recycled water scheme. In this assessment, the subsurface treatment is considered from both a theoretical point of view and an empirical point of view, as it has been defined above.
4. Assess the efficacy of the other treatments considering the pathogens’ data and the indicators’ data available. In this assessment, the efficacy of the treatments is considered from both a theoretical point of view and an empirical point of view (for those cases where empirical data are available), as it has been defined above.

Part of the QMRA results given in this section (the ones that we defined as calculated from a “theoretical point of view”) have been published in Ayuso-Gabella *et al.* (2011). In this paper, only the risks attributed to water recycling for crop irrigation purposes were calculated, and other possible reuse scenarios were not evaluated. Besides, RISMAR scheme was not the only

MAR site evaluated, but other MAR sites (part of the RECLAIM WATER project) were evaluated too in this publication.

6.2. Hazards: selected pathogens

The illness most widely linked to polluted water consumption is gastroenteritis. Other respiratory or dermal illnesses can also be acquired by contact with the water, e.g. in a swimming pool. To a lesser extent, by the fecal-oral via illnesses like typhoid fever, hepatitis, arthritis, myocarditis, meningoencephalitis o Guillain-Barré syndrome can be transmitted too. Pathogens that are used as models for risk assessment considering gastrointestinal illness as recommended by the WHO (WHO, 2006b; WHO, 2011a), Australian Guidelines (NRMMC–EPHC–AHMC, 2006; NRMMC–EPHC–AHMC, 2011), US EPA (US EPA, 2010), Petterson *et al.* (2006), Haas *et al.* (1999), Havelaar and Melse (2003) and which were used in Ayuso-Gabella *et al.* (2011) are:

- *Campylobacter*, representing bacteria, because it is by far the most common cause of bacterial gastroenteritis. Besides, several complications have been reported in the literature caused by *Campylobacter*, of which Guillain-Barré syndrome and reactive arthritis are the most important from a public health point of view.
- Rotavirus, representing the viruses, as they are a very common cause of diarrhoea in many developed countries, they have a relatively high infectivity compared with other waterborne viruses and a dose-response model has been established.
- *Cryptosporidium*, for the protozoa, because it is reasonably infective, is resistant to chlorination and is one of the most important waterborne human pathogens in developed countries. In immunocompromised persons, particularly in AIDS patients, infection can persist until death.

These pathogens were selected as they are known to be present in wastewater and contribute to the greatest population health burden in terms of DALYs (WHO, 2006b; NRMMC–EPHC–AHMC, 2006). Besides, outbreaks as well as many reported cases in Spain and Catalonia due to the ingestion of these microorganisms support the use of these pathogens for the QMRA development.

Campylobacter is one of the most important pathogens for gastroenteritis caused by a notified microbiological agent in Spain. Eight outbreaks were reported in 2009 in Spain, being one due to water (CNE, 2011). In Catalonia, 3578 cases were reported in 2009 and 2926 in 2010, being the vast majority identified as *Campylobacter jejuni. Campylobacter* accounted for 45% of the gastroenteritis cases caused by a notified microbiological agent in 2009 and 47% in 2010 (CHD, 2010d). In addition, 4 outbreaks were identified during 2007 and 2008 (CHD, 2010a).

Rotavirus is the major cause of gastroenteritis worldwide and the third cause of gastroenteritis caused by a notified microbiological agent in Catalonia. It is well-known that attack rates for this pathogen are higher in children. In 2009, 1536 cases were reported, accounting for 20% of the gastroenteritis caused by a notifiable microbiological agent, while in 2010 the reported cases descended to 1363, accounting for 22% of the gastroenteritis cases caused by a notifiable microbiological agent (CHD, 2010d).

In Spain cryptosporidiosis is not subject to monitoring, although some autonomous communities report it together with the notifiable diseases, and in the future, is expected to be reported nationwide, following guidelines of the European Union. *Cryptosporidium* reported cases increased in Spain in the recent years. In 2009, 307 cases were reported, in front of 98 in 2008 and 136 in 2007 (CNE, 2011). This protozoan is not a notifiable microorganism in Catalonia, so no data are available from the Catalan Health Department (CHD). However, its presence in wastewater (Montemayor, 2005) confirms the highly possible infection in the population, and some of the outbreaks where the aetiological agent was not determined could have been caused by *Cryptosporidium*.

6.3. Dose-response

The dose-response models used in this QMRA are the same as described in NRMMC–EPHC-AHMC (2006). These dose response models and the rationale for them have been explained in section 4.3.2.2. In Table 18, the pathogens, dose-response models and constants used are given.

Table 18 Dose-response curves and constants used for each pathogen as per NRMMC–EPHC–AHMC (2006)

	Model	Formula	Constants
Campylobacter	β-Poisson	$Pi = 1-(1+d/\beta)^{-\alpha}$	$\alpha = 0.145$ $\beta = 7.58$
Cryptosporidium	exponential	$Pi = 1-e^{(-rd)}$	$r = 0.059$
Rotavirus	β-Poisson	$Pi = 1-(1+d/\beta)^{-\alpha}$	$\alpha = 0.253$ $\beta = 0.426$

Constants used in the dose-response models can be modified to adapt to specific illness or temporal situations, as can be the immunocompromised population, babies or hospitalized people. Gerba *et al.* (1996) considered that sensitive populations that potentially could be at a greater risk of serious illness and mortality from water and foodborne enteric microorganisms would include the very young and neonates, the elderly, pregnant women and the immunocompromised. The immunocompromised group included AIDS patients, cancer patients and organ transplanted patients.

In the present work, we have considered that any person that is hospitalized can be an immunocompromised, and that may suffer a higher risk than the rest of the population. For this purpose, different constants from the ones described in Table 18 have been used for the immunocompromised population scenario (see section 6.4 for a description of the scenarios), and are summarized in Table 19.

Table 19 Dose-response curves and constants used for each pathogen in the immunocompromised scenario, considering Cummins *et al.* (2010) for *Cryptosporidium* and calculating rotavirus and *Campylobacter*.

	Model	Formula	Constants
Campylobacter	β-Poisson	$Pi = 1-(1+d/\beta)^{-\alpha}$	$\alpha = 0.145$ $\beta = 1.26$
Cryptosporidium	exponential	$Pi = 1-e^{(-rd)}$	$r = 0.354$
Rotavirus	β-Poisson	$Pi = 1-(1+d/\beta)^{-\alpha}$	$\alpha = 0.253$ $\beta = 0.071$

Makri *et al.* (2004) used a constant 3 times higher than the regular one (see Table 19) for *Cryptosporidium*, while Cummins *et al.* (2010) used a constant 6 times higher. The rationale behind increasing this constant relies on the fact that less pathogen units are necessary to develop an illness caused by this protozoan in the immunocompromised population, thus the ID_{50} (pathogen dose at which 50% of the population develops a disease) is reduced. Considering the formula from Teunis *et al.* (1996):

$$ID_{50} = \frac{\ln 2}{r} \ ;$$

when the constant r increases, ID_{50} decreases. In our work, we have used the same constant used by Cummins *et al.* (2010) for *Cryptosporidium* in the immunocompromised population scenario.

For rotavirus and *Campylobacter*, no literature was found to guide the decision on which constant to use, so it was decided to calculate it, in order to reduce the ID_{50} also by 6 times to resemble the case of *Cryptosporidium*. Then, in the β-Poisson model, considering the formula from Teunis *et al.* (1996):

$$ID_{50} = \beta\left(2^{1/\alpha} - 1\right);$$

when the constant β decreases, ID_{50} decreases.

Calculating from the equation above and the regular constants for "normal" non-immunocompromised population set in Table 18, the ID_{50} for rotavirus and *Campylobacter* is:

ID_{50} for rotavirus = 6.17

ID_{50} for *Campylobacter* = 896

Then, isolating β from the formula, we obtain:

$$\beta = \frac{ID_{50}}{2^{1/\alpha} - 1}$$

and considering an $ID_{50}/6$, the calculated new β for the pathogens is:

β for rotavirus = 0.071

β for *Campylobacter* = 1.26

The summarized values of the constants used for the immunocompromised population are given in Table 19.

6.4. Exposure

To calculate the exposure to the final treated water it is necessary to know:

- The pathogen concentration in the final treated water.
- The water uses and the routes of exposure.
- The amount of water ingested by the population.
- The number of exposures to the final treated water per year.

The way in which the water comes into contact with the population, or the route of exposure, is very important for the exposure measurement. The routes of exposure have been identified according to the identified end points and the uses given to the final treated water (see section 5.3.6).

For exposure it is also very important to know the pathogen concentration in the final treated water. In order to do so, the approach that has been taken is to create a PDF with literature data adapted to RISMAR scheme for the pathogen concentration in the untreated wastewater. Then, from this initial concentration, the pathogen concentration in the final treated water for reuse has been obtained considering different removals for each barrier in the treatment train.

6.4.1. Scenarios and routes of exposure

Four main routes of exposure are considered, and according to these routes, different scenarios have been created for the QMRA. A summary of the probability distribution functions used for all the exposure scenarios is given in Table 20. For the present work, and considering the information available at the moment, the risk of water ingestion has been evaluated. The routes of exposure considered in the present risk assessment are recommended to be evaluated when running a water reuse scheme in the Australian and WHO Guidelines (NRMMC–EPHC–AHMC, 2006; WHO, 2006b).

6.4.1.1. Crop consumption (PDF-C)

This is the most typical and well-known route of exposure. By this route, vegetables irrigated with recycled water get to the consumer. Depending on the processing level and cooking of the vegetables, the risk for the human health is evaluated (WHO, 2006b).

In this study lettuce has been taken as a model, as it entails the highest theoretical risk. Lettuce retains and can trap a much higher amount of water than other vegetables, and pathogens (especially viruses) can hide in the leaves (Hamilton *et al.*, 2006; Petterson *et al.*, 2001a, b; Shuval *et al.*, 1997). Then, to measure the exposure, it is necessary not only to calculate the pathogen concentration in the recycled water but the amount of water retained or trapped between the lettuce leaves, which will give the actual dose of the pathogen per each crop ingestion. This amount of water retained and trapped between the lettuce leaves is cited in Shuval *et al.* (1997) and Hamilton *et al.* (2006) (see Table 20).

The amount of lettuce consumed has been estimated using data from the Spanish Ministry of Agriculture, Food and Environment (MAGRAMA, 2006). The data given in MAGRAMA (2006) are for the sum of lettuce, endive and escarole (curly endive) consumption. For the purposes of the risk assessment, the data of consumption of the three vegetables together have been used, and it has not been performed any correction to account only for lettuce consumption.

The number of exposures per year for this is scenario is of 365 (as many days as a year has), as the consumption values used were given as a daily average consumption.

Besides all these considerations, in this scenario it is important to account for the decay rate of the pathogens after post-harvest and the effect of the post-treatments applied. The post-harvest time has been considered to be ranging from 1 day to 1 week, as a longer time to get to be sold and consumed could damage the lettuce aspect and quality. The pathogen decay rate can vary considerably among the different pathogen groups and their desiccation response, and it is also dependant on the kind of lettuce, the leaf age and pathogen desiccation response. Values used for each pathogen have been adapted from different sources: Petterson and Ashbolt (2003); NRMMC–EPHC–AHMC (2006); and WHO (2006), and are given in Table 20. Finally, post-treatments applied can range from simply washing with water to cooking the vegetables at high temperatures, thus reducing considerably the pathogen load in the vegetable. For the purposes of this risk assessment, we have only considered as a post-treatment the washing of the vegetables, as it is highly possible to occur for lettuce, while cooking it would happen seldom. A fixed 1 $\log_{10}$ removal has been used (NRMMC–EPHC–AHMC, 2006; WHO, 2006b).

6.4.1.2. Accidental ingestion of aerosols

This route of exposure is recommended to be evaluated in WHO (2006) and NRMMC–EPHC–AHMC (2006). For this, four different scenarios have been considered: accidental ingestion of aerosols by agricultural workers (growers/irrigators), accidental ingestion of aerosols by inhabitants of local communities, accidental ingestion of aerosols by factory workers and accidental ingestion of aerosols by immunocompromised population.

Table 20 Exposure related probability distribution functions (PDFs) for the different scenarios evaluated in the risk assessment.

Scenarios and PDFs used	Volume ingested (L)	Lettuce ingested per day (g)	Water retained in the lettuce (mL/g)	Post-harvest time (days)	Post-harvest decay rate (log$_{10}$/day)	Washing of crop removal (log$_{10}$)	Exposures per year
Accidental ingestion of aerosols by agricultural workers (PDF-A)	U (10^{-3}, 10^{-4})[a]						U (183, 365)
Crop consumption (PDF-C)		N (21.3927, 0.8433)[b]	N (0.108, 0.019)[c]	T (1, 3, 7)	*Campylobacter*: U (0.5, 1) *Cryptosporidium*: U (0, 0.5) rotavirus: U (0.3, 0.8)[d]	1[a]	365[e]
Accidental ingestion of aerosols by inhabitants of local communities (PDF-L)	U (10^{-3}, 10^{-4})[a]						T (10, 52, 245)
Use of the recycled water as drinking water (PDF-D)	EV (0.48052; 0.40135) truncated at (0)[f]						365[e]
Accidental ingestion of aerosols by factory workers (PDF-F)	U (10^{-3}, 10^{-4})[a]						N (245, 20)
Accidental ingestion of a high volume of water while swimming or developing aquatic activities (PDF-S)	LN (1.85×10^{-1}, 6.28×10^{-4})[g]						T (2, 10, 75)
Cross-connection of dual network systems (PDF-CC)	EV (0.48052; 0.40135) truncated at (0)[f]						T (0.25, 1, 3)
Accidental ingestion of aerosols by the immunocompromised population (PDF-I)	U (10^{-3}, 10^{-4})[a]						T (2, 7, 30)

EV: external value PDF; N: normal PDF, PDF: Probability Distribution Function; T: triangular PDF, U: uniform PDF.

[a] Adapted from NRMMC–EPHC–AHMC (2006) and WHO (2006).

[b] Adapted consumption of leaf vegetables in Spain (Spanish Ministry of Agriculture, Fisheries and Food, 2006).

[c] Cited in Hamilton *et al.* (2006) and Shuval *et al.* (1997)

[d] Adapted from different sources: NRMMC–EPHC–AHMC (2006); Petterson and Ashbolt (2003); WHO (2006). Range of values depend on the kind of lettuce, the leaf age and pathogen desiccation response.

[e] Values were given as mean consumption per day, then the exposure has to be per one year (365 days).

[f] PDF created adjusting data given in Mons *et al.* (2005).

[g] PDF used in US EPA (2010).

6.4.1.2.1. Accidental ingestion of aerosols by agricultural workers (growers/irrigators) (PDF-A)

Growers/irrigators are a collective that can easily be affected by the quality of the water, as they are likely to be close to the irrigation sites. However, in this case, the few growers that use the final treated water at RISMAR scheme apply it in a way that entails a lower risk level, which is drip irrigation or flood irrigation. Using these irrigation methods the accidental ingestion of aerosols is much less probable, but for the purposes of the risk assessment, a worst case scenario has been considered, which irrigation by sprinklers is. On the other hand, growers/irrigators may develop immunity, by this water for irrigation. This immunity development has also not been considered in the risk assessment, thus a worst case has been preferred.

For the present risk assessment, it has been considered that growers/irrigators can be exposed between 183 and 365 times per year (see Table 20). This is a conservative assumption too, but it is well-known that many of them can work every day in the field and might be irrigating different parcels every day (e.g. different fields, different crops). Then, this scenario considers that irrigation can occur between every two days and daily. Although in some cases irrigators may only go weekly or even less often to the field due to a reduced crop extension (e.g. only one field to irrigate), growing crops not very much water demanding or water shortages, the most conservative assumption has been used.

The amount of water that can be ingested has been expressed as a uniform PDF, given the reported values of accidental spray ingestion during garden irrigation (between 0.001 L and 0.0001 L) in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006).

6.4.1.2.2. Accidental ingestion of aerosols by inhabitants of local communities (PDF-L)

Local communities can come into contact with the aerosols generated during irrigation of the park or sports area, and also during street cleaning. They can also come into contact with the aerosols if they pass by fields that are being irrigated. For local communities to come into contact with aerosols, the irrigation time during the day is very important to reduce the risk. It is always recommended to irrigate public spaces with reclaimed water at night or during times when access to the affected areas is reduced, but this is not always possible. Field irrigation usually occurs early in the morning or late in the evening, to reduce evapotranspiration losses and not to damage the crops (avoiding solar light to impact in the leaves after being irrigated). Street cleaning may occur during the day, but in some cities occurs at night, which would be also the recommended time.

A special case of accidental ingestion of aerosols by inhabitants of local communities is the immunocompromised people that go to or are in treatment at the Taulí Hospital, located by the Taulí Park. This group receives a special focus in the risk assessment and has been calculated separately (see section 6.4.1.2.4).

Local communities are likely to have less contact with the aerosols than the growers/irrigators, thus exposure considers:

- Occasional crossing of/passing by the field/park, considered as 10 times per year.
- During weekends, 1 day per week, which equals to 52 times per year.
- Every working day, e.g. a person working in the hospital or the area surrounding, which equals to 245 exposures per year.

These scenarios/possibilities have been translated to a triangular PDF (see Table 20).

The amount of water that can be ingested has been expressed as a uniform PDF, given the reported values of accidental spray ingestion during garden irrigation (between 0.001 L and 0.0001 L) in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006).

6.4.1.2.3. Accidental ingestion of aerosols by factory workers (PDF-F)

This case is similar to the one of growers/irrigators; exposure is low, but repeated.

In a study by Westrell *et al.* (2004), WWTP workers exposure to aerosols at the aeration basins and sludge dewatering was considered to be 0.001 to and 0.005 L per exposure, respectively. However, the contact with the recycled or untreated water is much more direct in a WWTP than in a factory, where workers may have much less contact to the recycled water. As there is no more data available regarding this case scenario, it can be considered that it is similar to the growers/irrigators and the local communities ones, with an accidental ingestion ranging from 0.001 L to 0.0001 L per exposure (NRMMC–EPHC–AHMC, 2006).

The number of exposures considers regular working days in factories. The PDF used is centred in 245 days as an average, and varying 20 days depending on the calendar set for each factory, and it has been expressed as a normal PDF (see Table 20).

6.4.1.2.4. Accidental ingestion of aerosols by the immunocompromised population (PDF-I)

Accidental ingestion of aerosols by immunocompromised population requires an especial attention in the risk assessment calculation. The volume of water ingested is the same for all accidental ingestion of aerosols scenarios, but in this case the number of exposures and the dose-response used is different.

The dose-response and constants used for this scenario have been explained in section 6.3 and Table 19. The different dose-response has an important impact in the model, as it assumes that with a lower dose of pathogens the immunocompromised population can develop a disease.

The number of exposures has been calculated considering the average stay in Taulí Hospital (that is located by the Taulí Park, which is being irrigated) during the last years and different durations of stays depending on the treatment received. Then, a triangular PDF has been constructed, considering:

- The average stay in the Taulí Hospital, which has been of 7 days in the last years.
- A shorter stay for minor surgeries of 2 days.
- A very long stay of one month (30 days) for more complicated surgeries or diseases. In this case, even longer stays can occur in the hospital, thus increasing the risk, but then it has been considered that the patient would not go outside the hospital every day, as the health situation would be more complicated.

The PDF assumes that these patients go for a walk in the Taulí Park every day during their stay in the Taulí Hospital, which is probably a conservative assumption as not all of them would like or be able to go outside. However, as the hospital is located by the park, the aerosols could also arrive to their rooms and be inhaled if irrigation occurred during the day.

6.4.1.3. Accidental ingestion of a high volume of water

A high volume of water (comparing to the aerosols ingestion) can be ingested while swimming or developing any kind of aquatic activities in the swimming pool, especially children. Another possibility for an accidental ingestion of a high volume of water can be a cross-connection of dual network systems, when the piping systems for drinking water and recycled water are located very close.

Accidental ingestion of a high volume of water can also occur during irrigation. In the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) it is considered that an accidental ingestion of 100mL once per year can occur. This risk has not been evaluated in the present risk assessment, as this route of exposure is not likely to occur. It is very difficult to ingest a higher volume of water unintentionally during irrigation. A possibility would be that the water would be ingested intentionally, e.g. the grower has run out of potable water, is thirsty and consumes final treated water. In any case, the risk of accidentally consuming a large volume of water has been evaluated for swimmers and cross-connection of dual network systems, so it has been addressed.

6.4.1.3.1. Accidental ingestion of a high volume of water while swimming or developing aquatic activities (PDF-S)

The volume of water ingested while swimming or developing any kind of aquatic activities in the swimming pool that has been considered is based on the published PDF by US EPA (2010). The PDF was obtained adjusting published data on ingestion of water while swimming. The original study (Dufour *et al.*, 2006) included adults and non-adults, and consumption was statistically significative higher for non-adults. However, a unique PDF with all data compiled was created, not differentiating between both groups. The PDF used for exposure is given in Table 20.

The number of exposures considered take into account that the swimming pool is occasionally filled in with recycled water, and it is only in use during the summer period, from middle June to end of August (Sabadell Town Hall, 2012). Exposures can vary between daily (especially for children) to once per week or even twice during the whole summer period. Then, a triangular PDF was constructed, considering these possibilities [Triangular (2, 10, 75)]. For the purposes of the QMRA, it has been considered that the swimming pool is always filled in with recycled water, which is not the case. Besides, swimming pools undergo chlorination in each cycle of use. This has not been included in the model, and only chlorination of the final treated water has been considered. Then, regarding this scenario, a probably too conservative estimation has been done and it should be taken into consideration for future risk assessments.

6.4.1.3.2. Cross-connection of dual network systems (PDF-CC)

Cross-connection is a possibility that could occur at RISMAR scheme, as for any dual network system, but that in reality, the chances are very low (see section 5.3.6.1). However, this scenario has also been considered for the risk assessment.

In case a cross-connection occurred, the worst case is that the population could drink the recycled water without boiling or any other in-house treatment (e.g. filters in the tap). Then, the cold tap water consumption has been estimated thanks to the mean values reported in a thorough review of many studies for different countries, published in Mons *et al.* (2005). Using the mean daily values reported for the different studies gathered in this report, a PDF was adjusted (see Table 20).

When a cross-connection occurs, duration ranges from hours to several days (US EPA, 2001). Westrell *et al.* (2003) considered an average time of 3 days. Godoy *et al.* (2011) reported an outbreak in Catalonia where the cause was a cross-connection of untreated wastewater in the potable water network, which also included a failure in the chlorine dosage which prompted a longer duration of the outbreak. The duration of the cross-connection was of around 1 day. In order to take into account different possibilities, the PDF constructed considers that the exposure can be a minimum of 6 hours, a most probable of 1 day and a maximum of 3 days [Triangular (0.25, 1, 3)], so it considers the values given in the cited studies. At RISMAR scheme, the population exposed would be reduced; it would not affect the whole Sabadell city but a small part of it, the part that is close to the RISMAR scheme.

6.4.1.4. Use of the recycled water as drinking water (PDF-D)

This use is not in place neither envisaged at RISMAR scheme. However, it is interesting to consider what could happen if in the future the water shortages increase and this possibility was evaluated to supply the population of Sabadell.

The cold tap water consumption has been estimated in the same way as for the cross-connection of dual network system scenario (see 6.4.1.3.2). The number of exposures in this case would be of 365, as many as days in the year, as the values reported in Mons *et al.* (2005) were mean daily values of cold tap water consumption.

6.4.2. Estimation of pathogen concentration in the final treated water

The conceptual model considers every treatment performed in the recycled water scheme as an independent barrier, so the pathogens are reduced through the different barriers. For every treatment/barrier, a PDF has been adjusted considering actual data gathered at RISMAR scheme and literature data. The PDFs selected are described in Table 21. In this way, the risks reduction by the treatment train applied can be compared.

The risk characterization has been developed for each scenario in two ways. In section 6.1 it has been pointed out that one of the objectives of the QMRA was to compare the risks reduction by the treatment train applied, and it has been evaluated in the following two ways:

1) The risk reduction that the treatment train could achieve if all treatments performed optimally or similarly to what it has been published in the literature. In Table 21 this has been cited as “theoretical risk characterization”, although it also uses actual data gathered in the site. In the theoretical risk characterization:
    - The aquifer treatment considers a decay rate for each pathogen and an estimated residence time. In the current study the decay rate of each of the reference pathogens has been considered constant as a function of time. However some studies have indicated that a biphasic decay should be used, especially for viruses (Petterson *et al.*, 2001). The decay rate for each pathogen was taken or adapted from literature data, while the residence time was estimated indirectly. For RISMAR scheme, several pollution events and the time that took to detect the microorganisms increase in the aquifer was of between one and two weeks. On the other hand, a hydrogeological study from Franch (2007) indicated that the permeability of the aquifer was high, and considering the depth of the riverbed, the result would be between one day and one week. Considering the pollution event and the hydrogeological study, the PDF for the residence time in the aquifer was created.
    - For the disinfection applied, each type (UV and chlorination) are considered separately, taking data from literature.
    - The sand filter performance also uses literature data for the PDF construction.
2) The risk reduction that the treatment train achieves considering the pathogens data and the indicators data available at RISMAR scheme. In Table 21 this is called “empirical risk characterization”, although it also uses data from the literature. In the empirical risk characterization:
    - The aquifer treatment PDF uses indicators removal data for the PDF construction, as well as the results obtained for the pathogens’ measurements done. Then, removal of several indicators was calculated and the minimum, most likely and maximum values were used to create a triangular PDF for each kind of pathogen, and compared with the actual pathogens data gathered. Bacterial fecal indicators (*E. coli*, Total bacteria at 27º and enterococci) were used for *Campylobacter*, *Clostridium* spores for *Cryptosporidium* and bacteriophages for rotavirus.

- The disinfection PDF includes UV, chlorination and the sand filter treatments in one PDF. This was not separated per treatment because indicators' and pathogens' samples were taken after these three treatments together. Then, indicators' removal data have been also used for the PDF construction, and it has been also compared with the actual pathogens' data gathered. As the same indicators were used along the treatment train, similarly to the aquifer treatment bacterial fecal indicators (*E. coli*, Total bacteria at 27º and enterococci) were used for *Campylobacter*, *Clostridium* spores for *Cryptosporidium* and bacteriophages for rotavirus.

The other PDFs constructed for the model are common for both risk characterizations, which are:

- Pathogens concentration in the raw wastewater: literature data have been used to construct the PDFs. In the case of *Campylobacter*, the reported data were highly variable, and it was not possible to adjust a lognormal PDF as it was done for the other two pathogens. Then, a uniform PDF was chosen. For rotavirus, data from Sedmark *et al.* (2005) were used to create a PDF. For *Cryptosporidium*, data from Montemayor *et al.* (2005) were used, which in this case are data from raw wastewater entering different WWTPs around Barcelona, which may be very similar to possible values in the raw wastewater entering the Ripoll River WWTP.
- WWTP removal: reported removals in the literature for primary and secondary treatment have been used to construct the PDFs for each pathogen. Data on the performance of the WWTP treatments was not available, but the quality of the secondary treated water (the discharged water) regarding indicators and pathogens was available and compared with literature data to create and estimation of the treatments performance.
- Mixture/dilution with Ripoll River removal: the secondary treated water is sent to the Ripoll River thanks to an emissary, is discharged to the Ripoll River and there it mixes with the river water and infiltrates into the aquifer. During this mixing, a dilution occurs. Then, a PDF has been constructed to account for this dilution. In this case, indicators removal (the same that has been explained above for the aquifer treatment and disinfection) has been considered to account for the dilution in the river water. In several sampling campaigns it was observed not a dilution but an increase in indicators concentration which occurred while mixing with the river water. This especially happened when the Ripoll River carried less quantity of water, a lower flow, so the discharges from WWPTs upstream the river had a bigger impact. This increase in indicators concentration has been taken into consideration in PDFs for *Campylobacter* and rotavirus, as corresponding bacterial and viral indicators data showed concentrations higher in the Ripoll River water after the discharges of the Ripoll River WWTP (S3) than in the secondary treated wastewater itself (S1). This was not the case for *Cryptosporidium*, as *Clostridium* spores (its corresponding indicator) were always reduced in number from the secondary treated wastewater (S1) to the river water after the discharges (S3).

6.5. Risk characterization

In the risk characterization all the previous information is integrated and a final risk result is obtained. For the present work, the risk of developing a disease has been calculated, and the result is given in DALYs.

Table 21 Probability distribution functions (PDFs) used for the pathogens concentration and the treatment train.

Risk characterization	**Theoretical risk characterization**			**Empirical risk characterization**		
Pathogen	***Campylobacter***	***Cryptosporidium***	**rotavirus**	***Campylobacter***	***Cryptosporidium***	**rotavirus**
Pathogen concentration in raw wastewater (n/L)	U (1000, 100000)[a]	LN (226, 84) truncated at (0; 1000)[b]	LN (1342; 6330) truncated at (0; 100000)[c]	U (1000, 100000)[a]	LN (226, 84) truncated at (0; 1000)[b]	LN (1342; 6330) truncated at (0; 100000)[c]
Primary + Secondary WWTP removal ($\log_{10}$)	T (1.0, 2.0, 3.5)[d]	T (0.5, 1.0, 1.5)[d]	T (0.5, 1.0, 2.1)[d]	T (1.0, 2.0, 3.5)[d]	T (0.5, 1.0, 1.5)[d]	T (0.5, 1.0, 2.1)[d]
Mixture/dilution with Ripoll River removal ($\log_{10}$)	LL (-1.6, 1.9, 4.4) truncated at (3.0)[e]	T (0.24, 0.87, 2.2)[e]	T (-1.0, 0.0, 2.0)[e]	LL (-1.6, 1.9, 4.4) truncated at (3.0)[e]	T (0.24, 0.87, 2.2)[e]	T (-1.0, 0.0, 2.0)[e]
Aquifer storage (days)	T (1.0, 7.0, 14)[f]	T (1.0, 7.0, 14)[f]	T (1.0, 7.0, 14)[f]			
Aquifer pathogen decay rate ($\log_{10}$/day)	T (0.020, 0.080, 1.5)[g]	N (0.012, 0.0030)[h]	T (0.012, 0.16, 0.83)[i]			
Aquifer removal (empirical) ($\log_{10}$)				T (1.7, 4.6, 5.9)[e]	T (1.6, 3.1, 3.9)[e]	T (1.6, 4.4, 6.0)[e]
UV removal ($\log_{10}$)	T (2.0, 3.0, 4.0)[a]	T (2.0, 3.0, 3.5)[a]	T (1.0, 2.0, 3.5)[a]			
Chlorination removal ($\log_{10}$)	T (2.0, 3.0, 4.0)[d]	T (0.0, 0.0, 0.5)[d]	T (1.0, 1.5, 3.0)[d]			
Rapid sand filtration ($\log_{10}$)	T (0.0, 0.0, 0.5)[d]	T (0.0, 0.0, 0.5)[d]	T (0.0, 0.0, 0.5)[d]			
Combined disinfection and sand filtration (empirical) ($\log_{10}$)				T (0.0, 1.5, 3.2) [e]	T (0.0, 0.53, 2.0) [e]	T (0.0, 0.87, 2.7) [e]

LL: loglogistic PDF; LN: lognormal PDF; N: normal PDF; T: triangular PDF; U: uniform PDF.

[a] Adapted from NRMMC–EPHC–AHMC (2006) and Westrell (2004).

[b] Adapted from Montemayor *et al.* (2005).

[c] Adapted from Sedmark *et al.* (2005).

[d] Adapted from NRMMC–EPHC–AHMC (2006).

[e] Data from RISMAR scheme on indicators were used to construct the PDFs (Böckelmann *et al.*, 2009; Levantesi *et al.*, 2010; La Mantia *et al.*, 2008a, b).

[f] Adapted from Franch (2007) and unpublished data on pollution events at RISMAR scheme.

[g] Adapted from John and Rose (2005).

[h] From Toze *et al.* (2009).

[i] Adapted from Pedley *et al.* (2006).

6.5.1. Probabilities of infection and disease, disease burdens and DALYs

The probability of infection has been calculated as the product of the exposure to the recovered water (by any of the previous routes and scenarios explained previously) and the probability that the exposure to one organism would result in infection. The annual risk of infection has been calculated in order to afterwards calculate DALYs, as per the methodology explained in section 4.3.2.4. The final probability of developing a waterborne disease given that an infection has occurred (after contact with the final treated water) is calculated from known ratios disease/infection, disease burdens and susceptibilities for the different pathogens, rendering a result in terms of DALYs. In Table 22 the ratios disease/infection, disease burdens and susceptibilities for the different pathogens and considering regular and immunocompromised populations are given.

Susceptibility for *Campylobacter* and *Cryptosporidium* has been considered to be equal to 1.0, which means that the whole population can be affected by these pathogens. This is a conservative assumption, which considers that the whole population is susceptible to illness. For rotavirus is not the same case, as gastroenteritis caused by this pathogen, which is severe enough to require hospitalisation, occurs most frequently in children below 24 months (Havelaar and Melse, 2003), and the vast majority of cases affect children under five years old. Then, a susceptibility fraction of 6% for rotavirus has been used, based on the fact that infection is common in very young children, causing illness and also providing subsequent immunity. The 6% equates to the percentage of the population aged less than five years in developed countries, which is the same for Sabadell and the area around per published data of 2009, 2010 and 2011 (INE, 2013). Rotavirus gastroenteritis in adults is unusual, since most infections occur subclinically.

Table 22 Ratios disease/infection, disease burdens and susceptibilities for the different pathogens (from Havelaar and Melse, 2003; NRMMC–EPHC–AHMC, 2006).

	Campylobacter	*Cryptosporidium*	rotavirus
Ratio disease-infection: probability of developing a disease given infection (regular population)	0.33	0.71	0.88
Ratio disease-infection: probability of developing a disease given infection (immunocompromised population)	1.0	1.0	1.0
Disease burden: DALYs per disease case (regular and immunocompromised population)	4.6×10^{-3}	1.5×10^{-3}	1.3×10^{-2}
Susceptibility: fraction of the population susceptible of suffering the disease (regular population)	1.0	1.0	0.06
Susceptibility: fraction of the population susceptible of suffering the disease (immunocompromised population)	1.0	1.0	1.0

For the immunocompromised population, we have assumed that the ratio disease/infection is equal to 1.0 in all pathogens, as in this population the susceptibility to developing a disease given infection can be much higher. The immunocompromised population does not have an immune system strong enough to fight against the pathogens and respond to an infection. Besides, the susceptibility fraction has also been considered to be of 1.0 for rotavirus. For immunocompromised adults rotaviruses pose a threat in causing severe gastroenteritis, although it does not appear to play an important role in diarrhoea occurring in adults infected with HIV (Havelaar and Melse, 2003). Nevertheless, a conservative assumption has been preferred and the susceptibility fraction has been considered to be of 1.0.

6.5.2. Monte Carlo simulations

When all the model inputs have been set, then it is the moment to run the Monte Carlo simulations.

For the Monte Carlo simulations, ten thousand iterations were performed for each simulation, using Latin Hypercube sampling, with @RISK Industrial v6.0 and v6.0 BETA (Palisade, Newfield, NY) and Microsoft Excel (Microsoft Corp., CA) software. The output is a PDF of risk expressed as DALYs.

An example of the QMRA calculation for rotavirus in the empirical risk calculation for the accidental ingestion of aerosols by growers/irrigators scenario and an example for *Cryptosporidium* in the theoretical risk calculation for the crop consumption scenario are given in Table C-1 and Table C-2 respectively. Each example represents one of the 10,000 hypothetical scenarios/combinations generated during the Monte Carlo simulations.

6.6. QMRA results

6.6.1. Risk of developing a disease measured in DALYs

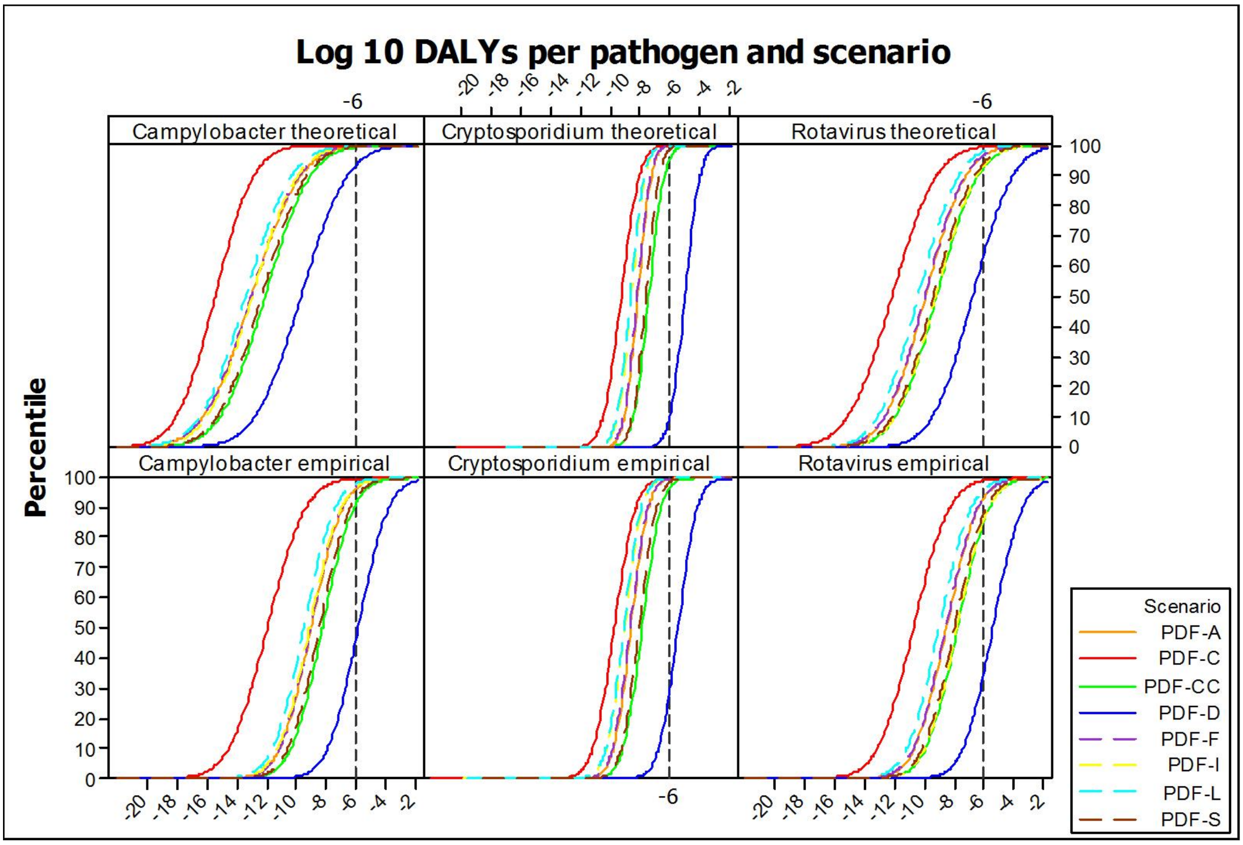
A summary of the QMRA risk results for each of the reference pathogens is shown in Table 22 (median, mean and 95th percentile results), and the resulting PDFs have been represented in Figure 47. For each of the pathogens, the risk was calculated considering the different scenarios set for water reuse and the theoretical and empirical risk characterization (see sections 6.4.1 and 6.4.2). Both in Table 23 and Figure 46 the represented PDFs correspond to the following scenarios:

- PDF-A: PDF results for accidental ingestion of aerosols by agricultural workers (growers / irrigators).
- PDF-C: PDF results for crop consumption.
- PDF-L: PDF results for accidental ingestion of aerosols by inhabitants of local communities.
- PDF-D: PDF results for use of the recycled water as drinking water.
- PDF-F: PDF results for accidental ingestion of aerosols by factory workers.
- PDF-S: PDF results for accidental ingestion of a high volume of water while swimming or developing aquatic activities.
- PDF-CC: PDF results for cross-connection of dual network systems.
- PDF-I: PDF results for accidental ingestion of aerosols by immunocompromised population.

The calculated median risks for each pathogen studied, as well as for the theoretical and empirical risk characterization were generally acceptable (median risk $<1.0\times10^{-6}$ DALYs), thus the final treated water is considered suitable for the different reuse scenarios, with the exception of the use as drinking water scenario. For the drinking water scenario, the median results fail for the three pathogens evaluated considering the empirical risk characterization (median results range from 1.7×10^{-6} to 4.3×10^{-6} DALYs), while the median fails for *Cryptosporidium* in the theoretical risk characterization (1.3×10^{-5} DALYs).

The calculated mean and 95th percentile are acceptable (mean or 95th percentile risk $<1.0\times10^{-6}$ DALYs) in the case of the theoretical risk characterization, but for the drinking water scenario, similar to the results obtained for the median. For the theoretical risk characterization and the drinking water scenario, rotavirus and *Cryptosporidium* fail for the mean and for the 95th percentile (values ranging from 1.4×10^{-4} to 3.6×10^{-5} DALYs). In the case of the empirical risk characterization, the calculated mean and 95th percentile are in most of the cases acceptable (mean or 95th percentile risk $<1.0\times10^{-6}$ DALYs), but, again, for the drinking water scenario, which fails for the three pathogens (values ranging from 1.1×10^{-4} to 8.1×10^{-5} DALYs). The difference is that in the case of the empirical risk characterization the median and the 95th percentile results are slightly higher than the reference value for some scenarios, which are: for rotavirus, the mean and 95th percentile results in the swimming scenario (1.6×10^{-6} and 3.1×10^{-6} DALYs, respectively), the cross-connection scenario (2.2×10^{-6} and 5.5×10^{-6} DALYs, respectively) and the immunocompromised scenario (2.9×10^{-6} and 4.5×10^{-6} DALYs, respectively); and for *Campylobacter*, the 95th percentile results in the swimming scenario (1.0×10^{-6} DALYs) and the cross-connection scenario (1.8×10^{-6} DALYs). In these cases, the calculated risk was slightly higher than the guideline value, thus the risk can be considered to be low.

Figure 46 Risk of developing a disease: resulting PDFs (PDF curves given are $\log_{10}$DALYs).



Note: The program used to create this figure did not allow using italics in headers. *Campylobacter* and *Cryptosporidium* should appear in italics.

Table 23 Risk of developing a disease: summary of the results of each PDF calculated in DALYs. [Note: those values highlighted in red are $\geq 1.0\times10^{-6}$ DALYs, which is the benchmark value set in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) and the WHO guidelines for water reuse (WHO, 2006b)].

PDF results calculated in DALYs			PDF-A	PDF-C	PDF-L	PDF-D	PDF-F	PDF-S	PDF-CC	PDF-I
rotavirus	Empirical risk characterization	Median	2.6×10^{-9}	1.8×10^{-11}	8.9×10^{-10}	**4.3×10^{-6}**	2.4×10^{-9}	9.3×10^{-9}	1.5×10^{-8}	1.3×10^{-8}
		Mean	5.5×10^{-7}	1.3×10^{-8}	2.2×10^{-7}	**8.1×10^{-5}**	5.2×10^{-7}	**1.6×10^{-6}**	**2.2×10^{-6}**	**2.9×10^{-6}**
		95th percentile	8.7×10^{-7}	1.2×10^{-8}	3.2×10^{-7}	**6.2×10^{-4}**	8.5×10^{-7}	**3.1×10^{-6}**	**5.5×10^{-6}**	**4.5×10^{-6}**
	Theoretical risk characterization	Median	1.6×10^{-10}	1.0×10^{-12}	5.4×10^{-11}	2.7×10^{-7}	1.5×10^{-10}	6.0×10^{-10}	9.3×10^{-10}	7.9×10^{-10}
		Mean	8.6×10^{-8}	1.8×10^{-9}	3.1×10^{-8}	**2.9×10^{-5}**	7.1×10^{-8}	2.6×10^{-7}	4.7×10^{-7}	5.3×10^{-7}
		95th percentile	1.2×10^{-7}	1.5×10^{-9}	3.7×10^{-8}	**1.7×10^{-4}**	1.0×10^{-7}	3.9×10^{-7}	8.0×10^{-7}	6.0×10^{-7}
Cryptosporidium	Empirical risk characterization	Median	2.7×10^{-9}	2.3×10^{-10}	8.6×10^{-10}	**4.3×10^{-6}**	2.4×10^{-9}	9.3×10^{-9}	1.6×10^{-8}	9.7×10^{-10}
		Mean	1.5×10^{-8}	2.2×10^{-9}	5.4×10^{-9}	**2.3×10^{-5}**	1.3×10^{-8}	5.3×10^{-8}	9.8×10^{-8}	6.0×10^{-9}
		95th percentile	6.1×10^{-8}	9.2×10^{-9}	2.2×10^{-8}	**1.1×10^{-4}**	5.7×10^{-8}	2.2×10^{-7}	4.0×10^{-7}	2.4×10^{-8}
	Theoretical risk characterization	Median	8.0×10^{-9}	6.8×10^{-10}	2.5×10^{-9}	**1.3×10^{-5}**	7.1×10^{-9}	2.7×10^{-8}	4.6×10^{-8}	2.8×10^{-9}
		Mean	2.2×10^{-8}	3.1×10^{-9}	7.7×10^{-9}	**3.6×10^{-5}**	1.9×10^{-8}	7.7×10^{-8}	1.5×10^{-7}	8.9×10^{-9}
		95th percentile	8.9×10^{-8}	1.3×10^{-8}	3.2×10^{-8}	**1.4×10^{-4}**	7.7×10^{-8}	3.1×10^{-7}	6.3×10^{-7}	3.5×10^{-8}
Campylobacter	Empirical risk characterization	Median	1.1×10^{-9}	1.4×10^{-12}	3.5×10^{-10}	**1.7×10^{-6}**	9.6×10^{-10}	3.7×10^{-9}	6.3×10^{-9}	8.0×10^{-10}
		Mean	1.5×10^{-7}	9.1×10^{-10}	5.2×10^{-8}	**7.1×10^{-5}**	1.2×10^{-7}	5.1×10^{-7}	7.8×10^{-7}	1.3×10^{-7}
		95th percentile	2.8×10^{-7}	1.0×10^{-9}	9.7×10^{-8}	**4.3×10^{-4}**	2.7×10^{-7}	**1.0×10^{-6}**	**1.8×10^{-6}**	2.4×10^{-7}
	Theoretical risk characterization	Median	1.7×10^{-13}	$<1.0\times10^{-17}$	5.2×10^{-14}	2.6×10^{-10}	1.5×10^{-13}	5.7×10^{-13}	9.5×10^{-13}	1.2×10^{-13}
		Mean	3.0×10^{-10}	2.3×10^{-12}	8.7×10^{-11}	4.8×10^{-7}	2.3×10^{-10}	9.3×10^{-10}	2.0×10^{-9}	3.2×10^{-10}
		95th percentile	5.5×10^{-10}	1.5×10^{-12}	1.6×10^{-10}	9.2×10^{-7}	4.9×10^{-10}	1.9×10^{-9}	3.4×10^{-9}	4.7×10^{-10}

Scenarios: A: accidental ingestion of aerosols by agricultural workers (growers / irrigators), C: crop consumption, L: accidental ingestion of aerosols by inhabitants of local communities, D: use of the recycled water as drinking water, F: accidental ingestion of aerosols by factory workers, S: Accidental ingestion of a high volume of water while swimming or developing aquatic activities, CC: cross-connection of dual network systems, I: accidental ingestion of aerosols by immunocompromised population.

Globally analysing the results obtained, the trend followed is that the drinking water, the cross-connection and the immunocompromised scenarios are the ones that potentially pose the highest risks whereas the crop consumption and the accidental ingestion of aerosols the lowest. A ranking of the risks posed by the different scenarios, pathogens, risk characterization type and statistics used to compare them is given in Table 24. Currently, the use of the recycled water as drinking water is not in place at RISMAR scheme, and is not planned for the future either. As said before (see 6.4.1.3.2), a cross-connection will be difficult to occur at RISMAR scheme, but it cannot be excluded to happen. However, the immunocompromised population is present as it is represented by the patients staying in the Taulí Hospital, by the Taulí Park. Then, this case should be taken a bit more cautiously, although as it has been pointed out before, the highest calculated risks for this scenario were in the same order of magnitude of the recommended guideline value of 10^{-6} DALYs, thus unlikely to pose a high risk, and the median results are below the guideline value. Then, considering the results obtained, all scenarios but drinking water could be considered to be acceptable in risk terms, and some attention should be paid for the swimming, cross-connection and immunocompromised scenarios as can be easily the focus of problems in the future if the empirical risk characterization is considered. Regarding the swimming scenario, the results should be taken cautiously, as a very conservative risk assessment has been developed.

Comparing the results obtained for each of the scenarios, risks characterizations and statistics calculated, for the different pathogens, rotavirus was the pathogen posing the highest risks whereas *Campylobacter* the lowest, but the differences between the pathogens were not important.

6.6.2. Risks reduction by the treatment train applied

The risks were calculated from a "theoretical point of view" and from an "empirical point of view", as it has been explained above. The difference between them is the risk reduction through the different treatments applied. In the theoretical risk characterization, the risk has been calculated considering that all treatments applied performed optimally and according to the general published data in the literature for treatment performance. In the empirical risk characterization, by the contrary, the risk has been calculated using data on real removals at the site as far as possible (for the WWTP treatments data from the literature were used as there were not empirical data). In both risk characterizations, the scenarios, dose-response models, disease burdens, pathogens concentration in the raw water and, in general, all input models but for the treatment train reduction are the same.

Table 24 Ranking of risks posed by the different scenarios, pathogens, risk characterization type and statistics used to compare them.

Risk	Statistics	rotavirus	*Cryptosporidium*	*Campylobacter*
Empirical	Median	D>CC>I>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>A>F>I>L>C
	Mean	D>I>CC>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>A>I>F>L>C
	95th perc.	D>CC>I>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>A>F>I>L>C
Theoretical	Median	D>CC>I>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>A>F>I>L>C
	Mean	D>I>CC>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>I>A>F>L>C
	95th perc.	D>CC>I>S>A>F>L>C	D>CC>S>A>F>I>L>C	D>CC>S>A>F>I>L>C

Scenarios: A: accidental ingestion of aerosols by agricultural workers (growers / irrigators), C: crop consumption, L: accidental ingestion of aerosols by inhabitants of local communities, D: use of the recycled water as drinking water, F: accidental ingestion of aerosols by factory workers, S: Accidental ingestion of a high volume of water while swimming or developing aquatic activities, CC: cross-connection of dual network systems, I: accidental ingestion of aerosols by immunocompromised population.

The minimum, average and maximum $\log_{10}$ pathogen removals have been calculated for each treatment in both risk characterizations and are summarized in Table 25. The total removal across the treatment train for both risk characterizations has been calculated considering the post-harvest decay (only applicable to the crop consumption scenario) and without the post-harvest decay. In all cases, but for *Cryptosporidium* average and maximum, the total $\log_{10}$ removals were higher for the theoretical risk characterization than for the empirical risk characterization. Only two treatments have different PDFs between the empirical and the theoretical case, which are the aquifer/subsurface treatment and the disinfection. For these treatments, data on indicators removal have been used for the empirical risk characterization, whereas literature data have been used in the theoretical risk characterization. For the other treatments, the PDFs and $\log_{10}$ removals used in the models are the same in the theoretical and the empirical risk characterizations. Thus, it is important to understand the differences between empirical and theoretical risk characterizations in the aquifer/subsurface and disinfection treatments in order to evaluate the risk reduction by the treatment train applied.

Regarding the aquifer/subsurface treatment performance, in the empirical case the $\log_{10}$ removals are higher than for the theoretical case. For all pathogens, the minimum and average $\log_{10}$ removals are higher in the empirical risk characterization than in the theoretical one, whereas the maximum is the same for rotavirus and *Campylobacter* (5.9 – 6.0 $\log_{10}$ removals). The maximum value could be even higher in some cases for the theoretical risk characterization, but it has been capped for all treatments to a maximum of 6.0 $\log_{10}$ removals, consistent with the reported maximum values validated for engineered treatments to ensure a conservative approach for protection of human health (NRMMC-EPHC–NHMRC, 2006). For *Cryptosporidium*, the minimum, the average and the maximum $\log_{10}$ removals are higher in the empirical risk characterization than in the theoretical, ranging from 1.6 to 3.9 $\log_{10}$ removals in the empirical and 0.00 to 0.25 $\log_{10}$ removals in the theoretical risk characterizations. This is due to the fact that in the theoretical risk characterization a decay rate and a residence time in the aquifer are used to calculate the $\log_{10}$ removals for the aquifer, and decay rates available in the literature are very low and the residence time at RISMAR scheme is considered to be short. In contraposition, in the empirical case, the removal achieved of indicators (*Clostridium* spores) is considered, and although the residence time may be short, the infiltration through the riverbed retains a good quantity of microorganisms. This retention through the infiltration process is not considered in the theoretical model, and it is very important for all pathogens removal, but especially for *Cryptosporidium*, where the decay rate in the aquifer/subsurface is very low. To support this empirical higher removal for *Cryptosporidium*, the results obtained for the few measurements done for this pathogen in the framework of the RECLAIM WATER project can be compared. Calculated $\log_{10}$ removals for this pathogen ranged from 0.63 to 1.04, and could have been much higher if a higher amount of water would have been filtered, as in most of the cases the pathogen could not be detected in the recovered water. Similarly, for *Giardia* $\log_{10}$ removals ranged from 1.60 to 1.95. These removals were much higher than the ones that could have been obtained just by considering only the decay in the aquifer. According to the results obtained for the aquifer/subsurface $\log_{10}$ removals, it has been made clear that the aquifer/subsurface treatment is a very important barrier to reduce the risks at RISMAR scheme. In order to better understand the importance of the aquifer/subsurface treatment as part of the whole treatment train, a sensitivity analysis has been performed (see section 6.7), and the results have been summarized in section 6.8. For rotavirus and *Campylobacter*, the differences between the empirical and the theoretical risk characterizations are smaller.

In contraposition to what happens with the aquifer/subsurface treatment, for the disinfection treatment the $\log_{10}$ removals are higher in the theoretical risk characterization than in the empirical risk characterization. In order to compare the disinfection $\log_{10}$ removals in the theoretical and empirical cases, the removal performed by the sand filter needs to be included. Although this is a physical treatment to remove particles, it needs to be considered together as for the empirical risk characterization it cannot be separated. This is due to the fact that the samples were measured from the recovered water and after the disinfection plus the sand filter, as the sand filter worked in continuous in the tank that stored the final treated water. Then, indicator values were obtained before the disinfection (recovered water) and after the disinfection and sand filtration, and the $\log_{10}$ removals were calculated between these two sampling points. For the theoretical risk characterization, the maximum $\log_{10}$ removals were 8.5 for *Campylobacter* and 7.0 for rotavirus, and for the empirical risk characterization were much lower (3.2 and 2.7 $\log_{10}$ removals, respectively). The minimum removals were also very different in the theoretical risk characterization respects to the empirical one: whereas in the theoretical risk characterization a minimum of 2.0 $\log_{10}$ removals were acknowledged for *Cryptosporidium* and rotavirus and 4.0 $\log_{10}$ removals for *Campylobacter*, in the empirical risk characterization all of them were close to 0. This is due to events of low performance of the chlorination treatment at RISMAR scheme and in general to the low performance of the UV treatment installed at the moment of performing the samplings. To sum up, although the theoretical disinfection applied in the treatment train should be enough at RISMAR scheme, the actual performance of the combined disinfection and sand filtration treatments during the sampling period when this work was developed was much lower than expected.

6.7. Sensitivity analysis

There are different ways in which a sensitivity analysis can be performed, depending on the evaluation that needs to be done. As explained in section 4.3.3, the methodology used has been previously described by Vose (1996), Frey and Patil (2002) and Zwietering and van Gerwen (2000). In our case, sensitivity analysis was performed in order to identify the factors/treatments that most affect the final risk. Then, the QMRA input parameters (factors/treatments) were assessed one by one by performing Monte Carlo simulations, removing each factor/treatment one at a time. In practice, the value of the factor/treatment of interest is held at zero, while leaving the pathogen concentration in raw water, dose-response, disease burdens and the other treatments unchanged. The change in the risk output is then taken as an indicator of the sensitivity of the evaluated treatment to the variability.

In order to evaluate the change in the risk output, the factor sensitivity (FS) was calculated by dividing the median risk estimate without the barrier considered (in DALYs) by the median risk estimate with all the barriers present (also in DALYs), with a $\log_{10}$ transformation:

$$\text{FS} = \log_{10}\text{ (median risk without the barrier / median risk with all the barriers)}$$

6.8. Sensitivity analysis results

A summary of the sensitivity analysis results for the different treatments applied and each of the reference pathogens, scenarios and risk characterizations is shown in Table 26. In this table, the FS value has been calculated using the median PDF results. The FS has also been calculated using the average and the 95th percentile values for reference. The FS results obtained using these statistics are given in Table D-3 and Table D-4 of Appendix D. Examples of the calculations are also given in Appendix D (Table D-1 and Table D-2).

Overall, the results obtained for the same treatment and pathogen in the different scenarios are equal, as the importance of each treatment in the framework of the whole treatment train must be the same. However, there are some differences for the drinking water scenario in some cases, with lower FS values but maintaining the same ranking/importance for the treatments in each pathogen and risk characterization.

Table 25 Log10 removals achieved by each treatment considering the empirical and the theoretical risk characterizations.

EMPIRICAL RISK CHARACTERIZATION: LOG$_{10}$ REMOVALS PER TREATMENT AND PATHOGEN	rotavirus			*Cryptosporidium*			*Campylobacter*		
	min	mean	max	min	mean	max	min	mean	max
WWTP log$_{10}$ removal	0.50	1.2	2.1	0.50	1.0	1.5	1.0	2.2	3.5
Mixture with river water log$_{10}$ removal	-0.99	0.33	2.0	0.25	1.1	2.2	-1.4	0.35	3.0
Aquifer/subsurface treatment log$_{10}$ removal	1.6	4.0	6.0	1.6	2.9	3.9	1.7	4.1	5.9
Combined disinfection and sand filter log$_{10}$ removal	0.015	1.2	2.7	0.010	0.86	2.0	0.022	1.6	3.2
Total postharvest log$_{10}$ removal	1.4	3.0	6.0	1.0	1.9	4.4	1.6	3.7	6.0
Treatment train total log$_{10}$ removal without postharvest treatment	1.2	6.7	12.8	2.4	5.8	9.6	1.3	8.1	15.6
Treatment train total log$_{10}$ removal with postharvest treatment (only applicable to crop consumption scenario)	2.5	9.7	18.8	3.4	7.7	13.9	2.9	11.9	21.6
THEORETICAL RISK CHARACTERIZATION: LOG$_{10}$ REMOVALS PER TREATMENT AND PATHOGEN	rotavirus			*Cryptosporidium*			*Campylobacter*		
	min	mean	max	min	mean	max	min	mean	max
WWTP log$_{10}$ removal	0.50	1.2	2.1	0.50	1.0	1.5	1.0	2.2	3.5
Mixture with river water log$_{10}$ removal	-0.99	0.33	2.0	0.25	1.1	2.2	-1.4	0.35	3.0
Aquifer/subsurface treatment log$_{10}$ removal	0.055	2.4	6.0	0.00	0.086	0.25	0.073	3.3	6.0
UV disinfection log$_{10}$ removal	1.0	2.2	3.5	2.0	2.8	3.5	2.0	3.0	4.0
Chlorination disinfection log$_{10}$ removal	1.0	1.8	3.0	0.00	0.17	0.50	2.0	3.0	4.0
Sand filter log$_{10}$ removal	0.00	0.17	0.50	0.00	0.17	0.50	0.00	0.17	0.50
Combined disinfection and sand filter log$_{10}$ removal (UV disinfection + Chlorination disinfection + Sand filter)	2.0	4.2	7.0	2.0	3.2	4.5	4.0	6.2	8.5
Total postharvest log$_{10}$ removal	1.4	3.0	6.0	1.0	1.9	4.4	1.6	3.7	6.0
Treatment train total log$_{10}$ removal without postharvest treatment	1.6	8.1	17.1	2.8	5.3	8.4	3.7	12.0	21.0
Treatment train total log$_{10}$ removal with postharvest (only applicable to crop consumption scenario)	3.0	11.1	23.1	3.8	7.3	12.8	5.3	15.8	27.0

For rotavirus, the most important treatment is the aquifer/subsurface treatment in the empirical risk characterization case (FS = 3.9 – 4.0 for all scenarios but for drinking water, where FS = 2.2), followed by the total post-harvest treatment (FS = 3.0, only applicable to the crop consumption scenario) and the WWTP treatment and combined disinfection and sand filter (FS = 1.2 – 1.3). In the theoretical risk characterization case, the most important treatments are the total post-harvest treatment (FS = 3.0, only applicable to the crop consumption scenario), the aquifer/subsurface treatment and the UV disinfection (FS = 2.2 – 2.3), followed by the chlorination disinfection (FS = 1.8 – 1.9) and the WWTP treatment (FS = 1.2). This difference in the results obtained by the empirical risk characterization versus the theoretical risk characterization is explained by the different PDFs used for the disinfection. As it has been explained in 6.6.2, the theoretical disinfection level that could be achieved by the treatments applied is not as efficient as expected, as the empirical indicators data point out. This effect happens also for the other two pathogens evaluated, thus creating strong differences in the results obtained in the empirical risk characterization versus the theoretical one. In both risk characterizations, the total post-harvest treatment plays a very important role in the risk reduction for the crop consumption scenario, whereas the mixture/dilution with the Ripoll River treatment has a negligible effect.

In the case of *Cryptosporidium*, the most important treatment is the aquifer/subsurface treatment in the empirical risk characterization case (FS = 2.9 for all scenarios but for drinking water, where FS = 2.4), followed by the total post-harvest treatment (FS = 1.9, only applicable to the crop consumption scenario). The other three treatments, mixture/dilution with Ripoll River, WWTP treatment and combined disinfection and sand filtration, achieve very similar FS values (around 1.0). In the theoretical risk characterization case, the most important treatment is the UV disinfection (FS = 2.8 – 2.9 for all scenarios but for drinking water, where FS = 1.9), followed by the total post-harvest treatment (FS = 1.9, only applicable to the crop consumption scenario) and the WWTP treatment and mixture/dilution with Ripoll River (FS = 0.98 – 1.1). Interestingly, for *Cryptosporidium* the aquifer/subsurface treatment has a negligible effect in the risk reduction in the theoretical risk characterization while it is the most important treatment in the empirical case. This can be explained by the fact that the aquifer/subsurface treatment at RISMAR scheme has a double effect: while the decay in the aquifer can be negligible due to the very low decay rate of this pathogen and the short residence time at RISMAR scheme, the filtration process has an important effect. This filtration effect is not considered in the theoretical risk characterization (see section 6.6.2 for a more detailed explanation on this).

For *Campylobacter*, the most important treatment is the aquifer/subsurface treatment in the empirical risk characterization case (FS = 4.0 - 4.1 for all scenarios but for drinking water, where FS = 2.9), followed by the total post-harvest treatment (FS = 3.7, only applicable to the crop consumption scenario), the WWTP treatment (FS = 2.1 – 2.2) and combined disinfection and sand filter treatment (FS = 1.5 – 1.6). In the theoretical risk characterization case, the most important treatments are the aquifer/subsurface treatment and the disinfection processes (FS = 3.0 – 3.3), followed by the WWTP treatment (FS = 2.2). In this case, the FS could not be calculated for the crop consumption scenario, because the median risk was zero, thus the FS for the total post-harvest treatment is lacking too. However, mean and 95th percentile results (see Table D-3 and Table D-4) for the total post-harvest treatment indicate that it is also a very important treatment (FS = 2.9 and 3.3, respectively). In both risk characterizations, the total post-harvest treatment plays a very important role in the risk reduction for the crop consumption scenario, whereas the mixture/dilution with Ripoll River has a negligible effect.

Table 26 Factor sensitivity results for each treatment train, pathogen and scenario. Values given have been calculated using median results for the PDFs.

EMPIRICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.0	1.0	0.99	1.0	0.99	0.99	1.0	0.99	2.2	2.2	2.1	2.1	2.2	2.1	2.1	2.2
Mixture/dilution with Ripoll River treatment	0.34	0.33	0.32	0.33	0.32	0.33	0.34	0.32	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.30	0.31	0.30	0.30	0.32	0.31	0.31	0.32
Aquifer/subsurface treatment	4.0	4.0	4.0	2.2	4.0	4.0	3.9	4.0	2.9	2.9	2.9	2.4	2.9	2.9	2.9	2.9	4.1	4.1	4.1	2.9	4.1	4.1	4.0	4.1
Combined disinfection and sand filter treatment	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	0.85	0.84	0.85	0.86	0.84	0.84	0.85	0.85	1.6	1.5	1.5	1.5	1.6	1.6	1.6	1.6
Total postharvest treatment	–	3.0	–	–	–	–	–	–	–	1.9	–	–	–	–	–	–	–	3.7	–	–	–	–	–	–
THEORETICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.0	1.0	1.0	0.98	1.0	1.0	0.99	1.0	2.2	n.d.	2.2	2.2	2.2	2.2	2.2	2.2
Mixture/dilution with Ripoll River treatment	0.37	0.37	0.36	0.37	0.36	0.35	0.36	0.37	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	0.39	n.d.	0.40	0.40	0.41	0.40	0.41	0.40
Aquifer/subsurface treatment	2.2	2.3	2.2	2.2	2.2	2.2	2.3	2.2	0.087	0.087	0.085	0.083	0.086	0.088	0.083	0.084	3.3	n.d.	3.3	3.3	3.3	3.3	3.3	3.3
UV disinfection treatment	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.8	2.8	2.8	1.9	2.9	2.8	2.8	2.8	3.0	n.d.	3.0	3.0	3.0	3.0	3.0	3.0
Chlorination disinfection treatment	1.8	1.8	1.8	1.8	1.9	1.8	1.9	1.8	0.17	0.16	0.17	0.16	0.17	0.16	0.16	0.17	3.0	n.d.	3.0	3.0	3.0	3.0	3.0	3.0
Sand filter treatment	0.18	0.17	0.17	0.17	0.17	0.17	0.17	0.15	0.17	0.16	0.17	0.17	0.16	0.17	0.17	0.17	0.17	n.d.	0.18	0.16	0.17	0.19	0.16	0.18
Total postharvest treatment	–	3.0	–	–	–	–	–	–	–	1.9	–	–	–	–	–	–	–	n.d.	–	–	–	–	–	–

Scenarios: A: accidental ingestion of aerosols by agricultural workers (growers / irrigators), C: crop consumption, L: accidental ingestion of aerosols by inhabitants of local communities, D: use of the recycled water as drinking water, F: accidental ingestion of aerosols by factory workers, S: Accidental ingestion of a high volume of water while swimming or developing aquatic activities, CC: cross-connection of dual network systems, I: accidental ingestion of aerosols by immunocompromised population.
n.d.: not determined. The factor sensitivity could not be calculated for the crop consumption scenario in *Campylobacter* as the median risk was zero.

According to the sensitivity results obtained, the aquifer/subsurface treatment is a crucial barrier to reduce the risks in the empirical risk characterization, whereas in the theoretical risk characterization its effect varies depending on the pathogen investigated. In turn, the disinfection treatment is much more important in the theoretical risk characterization comparing to the empirical one. These results indicate the importance of obtaining empirical data of the recycled water scheme that it is being evaluated in order to perform a strong risk characterization and understand fully the treatment train performance, as literature data can be of help but sometimes can be far away from the real performance of the systems.

7. RISK MANAGEMENT: THE TWELVE ELEMENTS OF THE AUSTRALIAN GUIDELINES FOR WATER RECYCLING AND THE MANAGED AQUIFER RECHARGE GUIDELINES

To develop the present Risk Management plan, the framework presented in the MAR guidelines (NRMMC–EPHC–AHMC, 2009) has been selected. This framework involves the 12 fundamental elements adopted in the Phase 1 guidelines for water recycling (NRMMC–EPHC–AHMC, 2006), that are actually based on the Australian Drinking Water Guidelines (NHMRC–NRMMC, 2004; NHMRC–NRMMC, 2011). The Framework was originally developed to guide the design of a structured and systematic approach for the management of drinking water quality from catchment to consumer, to ensure its safety and reliability. The Framework incorporated a preventive risk management approach, including elements of HACCP, ISO 9001 and AS/NZS 4360:2004, but applying them in a drinking water supply context (NHMRC–NRMMC, 2004). This framework could be applied and adapted to a recycled water scheme, and in this case, including MAR.

The 12 elements are organised within four general areas, which are:

- Commitment to responsible use and management of recycled water: This requires the application of a preventive risk management approach to support this use. The commitment requires active participation of Senior Managers, and a supportive organisational philosophy within agencies responsible for operating and managing recycled water schemes.
- System analysis and management: This requires an understanding of the entire recycled water scheme, the hazards and events that can compromise recycled water quality, and the preventive measures and operational control necessary for assuring safe and reliable use of recycled water.
- Supporting requirements: These include basic elements of good practices, such as employee training, community involvement, research and development, validation of process efficacy, and systems for documentation and reporting.
- Review: This includes evaluation and audit processes to ensure that the management system is functioning satisfactorily. It also provides a basis for review and continuous improvement.

Although the elements are not necessarily sequential, they should all be followed to ensure that the risk management plan is comprehensive (NRMMC–EPHC–AHMC, 2006; NRMMC–EPHC–AHMC, 2009).

7.1. Element 1: Commitment to responsible use and management of recycled water quality

7.1.1. Responsible use of recycled water

The development of the recycled water and MAR system based on the Ripoll River in Sabadell (RISMAR scheme) has been possible through the involvement of different parties, with expertise in different fields:

- Departament de Sostenibilitat i Gestió d'Ecosistemes de l'Ajuntament de Sabadell - Environmental Department of Sabadell Municipality (EDS).
- Agència Catalana de l'Aigua - Catalonia Water Agency (ACA).
- Departament de Salut de la Generalitat de Catalunya - Catalan Health Department (CHD).

- Companyia d'Aigües de Sabadell S.A. – Sabadell Water company (CASSA).
- Comission of the European Union through RECLAIM WATER project (EU).
- Universitat de Barcelona - University of Barcelona (UB).

Other relevant stakeholders identified at RISMAR scheme are:

- Taulí Park users.
- Swimming pool (Sant Oleguer sports area) users.
- Local irrigators using the Ripoll River or the Monar canal water.
- General public.

The partners involved have the expertise necessary to develop and support the scheme. Areas of expertise required include:

- Recycled water schemes management.
- Wastewater treatment and disinfection.
- Garden and soil management.
- Riverbed filtration, groundwater and subsurface storage management.
- Microbiological, physical and chemical water quality, and water quality monitoring.
- Water supply system operation e.g. security, storage operation, mains flushing.
- Technical writing e.g. policy, specifications, standard operating procedures.
- Quality management systems.

CHD was the responsible agency for human health. ACA was the responsible agency for environmental requirements. They were consulted throughout the design, construction and commissioning phases of RISMAR scheme to ensure that health and environment requirements were met. However, RISMAR scheme nowadays is not understood as a formal MAR system by the Catalan authorities, but as a system that exploits a groundwater well and uses it for different purposes. See a further discussion on this in section 7.1.2.

EDS commissioned the construction of the pipeline and pumps to send treated wastewater upstream the Ripoll River and the recovery of groundwater in the old mine property of CASSA. The whole scheme is operated, managed and maintained by CASSA on behalf of EDS. The storage tank, where the water is kept before being sent to the Taulí Park, is also owned by CASSA, who is also responsible for its operation and management.

The storage tank located at the Taulí Park, which distributes the water to all the sprinklers in the park, and to another storage tank used for street cleaning, is owned and managed by EDS.

7.1.2. Regulatory and formal requirements

This has been widely explained in section 5.1.3.

7.1.3. Scheme roles and responsibilities

CASSA

CASSA operates the:

- Sewerage main trunks.
- Wastewater treatment at the Ripoll River WWTP.

- Discharge of the secondary effluent to the Ripoll River through a pipeline system (emissary) and pumping.
- Maintenance of the mine.
- Recovery and post-treatment of the water to reuse it for urban park irrigation and street cleaning.

It is responsible for the management and operation of these areas. It is also responsible for first response to incidents and emergencies (public health and the environment), and monitoring and reporting. Asset management is a joint undertaking between CASSA and EDS

CASSA has ultimate accountability for compliance with:

- CHD approval conditions for the recycled water scheme (only when the final treatd water is used to fill in the swimming pool).
- Compliance with ACA license for effluent discharge from the Ripoll River WWTP to the Ripoll River.
- Compliance with ACA license to recover and use water from the mine located under the River.

ACA

ACA is responsible of ensuring that the RISMAR scheme works properly and fulfils any applicable regulations.

EDS

It is responsible for the management of the areas that CASSA operates. It is also responsible for first response to incidents and emergencies (public health and the environment), and monitoring and reporting.

Besides, EDS develops a great effort for public communication and to involve Sabadell population into the project to recover the Ripoll River and the area surrounding it.

7.1.4. Partnerships and engagement of stakeholders

The restoration project was undertaken by EDS but no public consultation was undergone before its start. In this sense, communication of the use of the treated wastewater was done by putting signs in the park and other kinds of information in the website of Sabadell Town Hall, including leaflets with information on the project which can be downloaded in the website. In addition, campaigns to increase awareness have also been undertaken, including workshops in schools, creation of walking and cycling routes in the area, or even an educational game.

Stakeholders using or being in contact with the treated wastewater include the general public of the Taulí Park, the fluvial park created along the Ripoll River and the sports area of Sant Oleguer, as well as passers by these areas, and, in general, the inhabitants of Sabadell city, as they are all benefited from saving water by using the final treated water instead of mains water.

7.1.5. Recycled water policy

CASSA

At CASSA, the recycled water policy is integrated in the general quality and environment policy. This quality and environment policy can be consulted at CASSA website http://www.cassa.es/es/ (CASSA, 2013a).

ACA

At ACA, the recycled water policy is integrated in the general environment policy, which is summarized and presented in its yearly report. The last yearly report can be consulted at ACA website http://aca-web.gencat.cat/aca/appmanager/aca/aca/ (ACA, 2012).

EDS

EDS does not have a recycled water policy neither an environment policy, but in their website there is detailed information on all the activities and projects in these areas. Regarding recycled water and RISMAR scheme, specific and detailed information can be found in its water website http://ca.sabadell.cat/Aigua/p/aigua_cat.asp (EDS, 2013), where the vision of EDS on a sustainable water cycle, and its pursue of using alternative water resources and reducing the water consumption is presented.

7.2. Element 2: Assessment of the MAR system

This element has been widely developed and explained in section 5 of the present work. To assess the recycled water and MAR system is recommended to consider the following points:

- Identify the source of recycled water, intended uses, receiving environments and routes of exposure: this has been developed in section 5.3.
- Perform an analysis of the recycled water and MAR system: this has been developed in sections 5.1 and 5.3.
- Assessment of water quality data: this has been developed in sections 5.4 and 5.5.
- Hazard identification and risk assessment: this has been developed in section 5.5.

7.3. Element 3: Preventive measures for recycled water and MAR management.

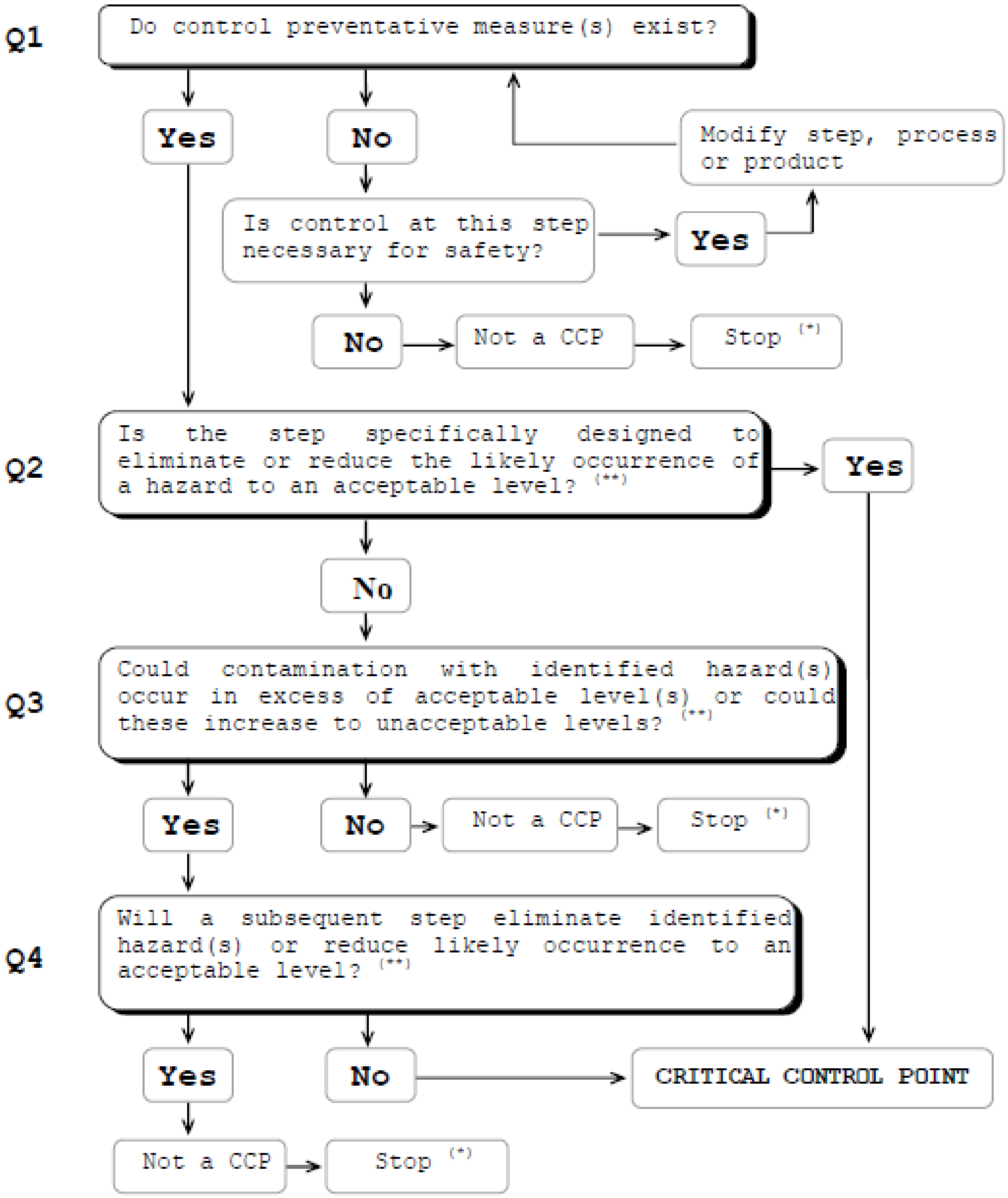
Prevention is an essential feature of effective management in any kind of process. Preventive measures are those actions, activities and processes used to prevent hazards from occurring or reduce them to acceptable levels. Hazards may occur or be introduced throughout the water system and preventive measures should be comprehensive, from catchment to end-users. Many preventive measures may control more than one hazard, while, as prescribed by the multiple-barrier approach, effective control of some hazards may require more than one preventive measure. The level of protection to control a hazard should be proportional to the associated risk (NHMRC–NRMMC, 2011).

All preventive measures are important and should be given on-going attention. However, some can prevent or reduce hazards that represent a significant risk and require elimination or reduction to assure supply of safe water for the uses required, and are amenable to greater operational control than others. These measures could be considered as critical control points (CCPs). A CCP is defined as an activity, procedure or process where control can be applied, and that is essential for preventing hazards that represent high risks or reducing them to acceptable levels (CAC, 2003; NRMMC–EPHC–AHMC, 2006; NHMRC–NRMMC, 2011). CCPs require:

- Operational parameters that can be measured, and for which critical limits (CLs) can be set to define effectiveness.
- Operational parameters that can be monitored frequently enough to reveal any failures in a timely manner.
- Procedures for corrective actions that can be implemented in response to deviation from critical limits.

In CAC (2003) a decision tree is given that can be used to identify critical control points. It has been reproduced in Figure 47. The questions included must be answered in a sequential way. It is interesting to note that in water recycling processes there might be many steps that could be identified as CCPs, but considering question 4, "Will a subsequent step eliminate identified hazard(s) or reduce likely occurrence to an acceptable level?", most of them will be only points of attention (POAs). If no subsequent operation is scheduled in the process to control this identified hazard, this particular process step becomes a CCP. If there is a subsequent operation or operations later in the process that will eliminate the identified hazard or reduce it to an acceptable level, this step is not a CCP. Then, in water recycling processes, that regularly include several treatment steps, probably the last treatment applied will be the only one that can be regarded as a CCP. The other treatment steps will be POAs. According to Dewettinck *et al.* (2001), POAs are to be seen as activities, places or factors that also need to be controlled but not in the same imperative way as CCPs. Nordic Sugar (2013) makes a clear distinction between CCPs and POAs in their HACCP plans. This has been summarized in Table 27.

Figure 47 Decision tree to identify CCPs (from CAC, 2003)



(*) Proceed to the next identified hazard in the described process.

(**)Acceptable and unacceptable levels need to be defined within the overall objectives in identifying the CCPs of HACCP plan.

Once CCPs and POAs have been identified, critical limits (CLs) and target criteria (TC) need to be set, which can be quantitative or qualitative. CLs are defined tolerances that distinguish acceptable from unacceptable performance. When a process that represents a CCP is operating within CLs, performance in terms of hazardous components removal is regarded as being acceptable. However, if the process deviates from its set CL, a loss of control has occurred, thus posing a risk. Corrective actions must be applied immediately to restore the process control. TC are performance goals more stringent than CLs, as they are designed to provide early warning that a CL is being approached, in order to apply corrective actions before an unacceptable risk occurs. Any deviation from established targets should be regarded as a trend towards loss of control of the process, and should result in appropriate actions being taken (NRMMC–EPHC–AHMC, 2006; NHMRC–NRMMC, 2011).

Table 27 Differences between CCPs and POAs (adapted from Nordic Sugar, 2013).

CCP	POA
• A high risk step, which is likely to get out of control. • Critical (and possible/applicable) control measures are needed in order to prevent, eliminate or reduce water safety hazards to an acceptable level. • If measures are out of control the corrective actions must include stop water production, stop water delivery, retesting, apply the same treatment again or divert the water. • The hazard is not eliminated or reduced to an acceptable level at a later stage in the process. • If not in control the end product consitutes a serious health risk.	• A moderate risk step. • Specific control measures essential to control the likelihood of introduction, contamination and/or proliferation of water safety hazards. • The hazard may be reduced at a later stage in the process. • If measures are out of control the corrective actions include reevaluating procedure and/or checking equipment.

Preventive measures and multiple barriers are present at RISMAR scheme, in order to reduce and prevent the risk posed by the treated wastewater recycling. Besides, CCPs and POAs were identified and evaluated, in order to properly implement the preventive measures.

7.3.1. Preventive measures and multiple-barrier approach

RISMAR scheme uses a multiple-barrier approach to minimise the risks to human health and to the environment. Different barriers were in place for RISMAR scheme during the development of the RECLAIM WATER project, namely:

- Source water protection.
- All the treatments performed to the source water and recycled water (the multiple-barrier approach).
- Separation of the piping system, tanks and connection to recycled water from the mains water system.

7.3.1.1. Source water protection

The source water is the secondary treated wastewater from the Ripoll River WWTP. To protect the human health and the environment, a system to control industrial wastewater and illegal disposals to the sewerage was implemented. Thanks to this system, the release of hazardous chemicals out of the levels permitted by the legislation is prevented and has been reduced for those compounds that cannot be avoided. Actually, in the recent years the number of factories running in the area has decreased, and those that release their process waters to the Ripoll River are a reduced number, closely monitored too.

The system to control industrial wastewater and illegal disposals to the sewerage works through a computerized system controlling wastewater discharges (SICARs, Sistema Informatitzat del Control d'Abocaments d'Aigües Residuals a Sabadell – Computerized system to control wastewater disposals in Sabadell), and it is sending continuous information to the EDS. This system enables recording and obtaining real-time information on parameters like pH, electrical conductivity, organic matter and suspended solids. This information can be visualized in panels present in EDS and both WWTPs in Sabadell (Ripoll River WWTP and Riu Sec WWTP), thus showing the quality of the wastewater circulating through the sewerage system. Different points of the sewerage system were selected and are controlled, so in case there is a pollution event this system will help in identifying its origin. Sensors were also located in the influent and effluent waters of both WWTPs, in order to control its performance and prevent uncontrolled disposals into the Ripoll River (EDS, 2013).

7.3.1.2. The multiple-barrier approach

The multiple-barrier approach, initially used in the management of drinking water quality, is also adopted in the management of recycled water schemes, and in our case, at RISMAR scheme. In this approach, multiple barriers or preventive measures are used to manage hazards, meaning that reduced performance of one barrier does not result in total loss of management. Importantly, it may be possible to temporarily increase the performance of the remaining barriers while remedial action is taken to restore function of the faulty barrier. In addition, as a combination, multiple barriers produce less variability in performance than single barriers (NRMMC–EPHC–AHMC, 2006).

At RISMAR scheme, the different barriers present in the system are:

- The system to control industrial wastewater and illegal disposals to the sewerage.
- Conventional treatments performed at the Ripoll River WWTP (primary and secondary treatments).
- Mixing and dilution with the Ripoll River water.
- Infiltration through the riverbed (RBF).
- Mixing and dilution with the groundwater.
- Disinfection by UV treatment.
- Disinfection by chlorination.
- Sand filtration to remove particles in the final treated water.

7.3.1.3. Design options and protections implemented in the multiple-barrier treatment

During the development of RISMAR scheme some specific protections and preventive measures in the treatment process were included, that at the time of developing the RECLAIM WATER project (finished in 2008) were the following ones:

- In the Ripoll River WWTP there is a by-pass to the river (downstream the recharge area) that can be used to divert water received at the WWTP and that cannot be treated at that moment, for instance if the flow is higher than usual due to a heavy rain period.
- Part of the restoration project in the Ripoll River area included the redistribution and update of the marginal vegetable gardens present in its banks. Sabadell Town Hall got the usufruct of a big part of them, thus ensuring a proper management and use of the area and the land, and this way avoiding uncontrolled disposals into the Ripoll River. This measure also helped in preventing and/or decreasing run-off of pesticides, nitrate and other compounds that were entering the river, as the land was closely controlled and vulnerable areas were not used for cultivation.
- Another action during the restoration project in the Ripoll River was to improve and reinforce the banks. During this work the riverbed was also dredged to enhance water recharge through it and to prevent clogging issues, as during the previous years the riverbed tended to be compacted, thus reducing the recharge rate.
- The chlorination system has a probe that continuously measures the chlorine concentration in the final treated water, which is kept in the tank located by the mine. This way, it is ensured that the 0.5 ppm chlorine concentration is kept constant all the time, and if the probe detects that the value is below, more chlorine is dosed.
- The tank that stores the final treated water is covered, which minimizes light entrance to restrict algal growth.

7.3.1.4. Restrictions on distribution system and application site

Preventive measures that involve restricting the distribution and use of recycled water are undertaken to avoid misuse of the final treated water and to better control possible incidents. At RISMAR scheme these include:

- In order to protect the mine installations, that had suffered from vandalism in the past, the area is restricted, and only personnel from CASSA and authorized persons can access it.
- The Taulí Park has specific signage to warn the public not to drink the sprinklers' water. Signage indicates that is reclaimed water (final treated water of the RISMAR scheme) for non-potable purposes.
- Irrigation of the Taulí Park occurs at night, whenever possible. This is a measure to avoid the public to have contact with the final treated water.

7.3.2. Operational issues at RISMAR scheme

The operation of the RISMAR scheme has experienced some failures/concerns during the development of the RECLAIM WATER project. These failures/concerns need to be regarded as opportunities for improvement and for gaining a better knowledge of the system. The most important ones are summarized below:

- Biofilm formation in the storage tank located by the mine: this was observed at the beginning of the project and again on spring 2007. The tank was cleansed yearly, but probably a disinfection failure permitted the creation of a new biofilm in it.
- March 2007: manganese concentration started to increase in the recovered water. The additional amount of manganese dissolved in the water reacted with the chlorine dosed for disinfection and a black precipitate appeared, which started to clog the chlorine probes and other small filters. The sand filter needed to be cleansed twice per week, instead of weekly.

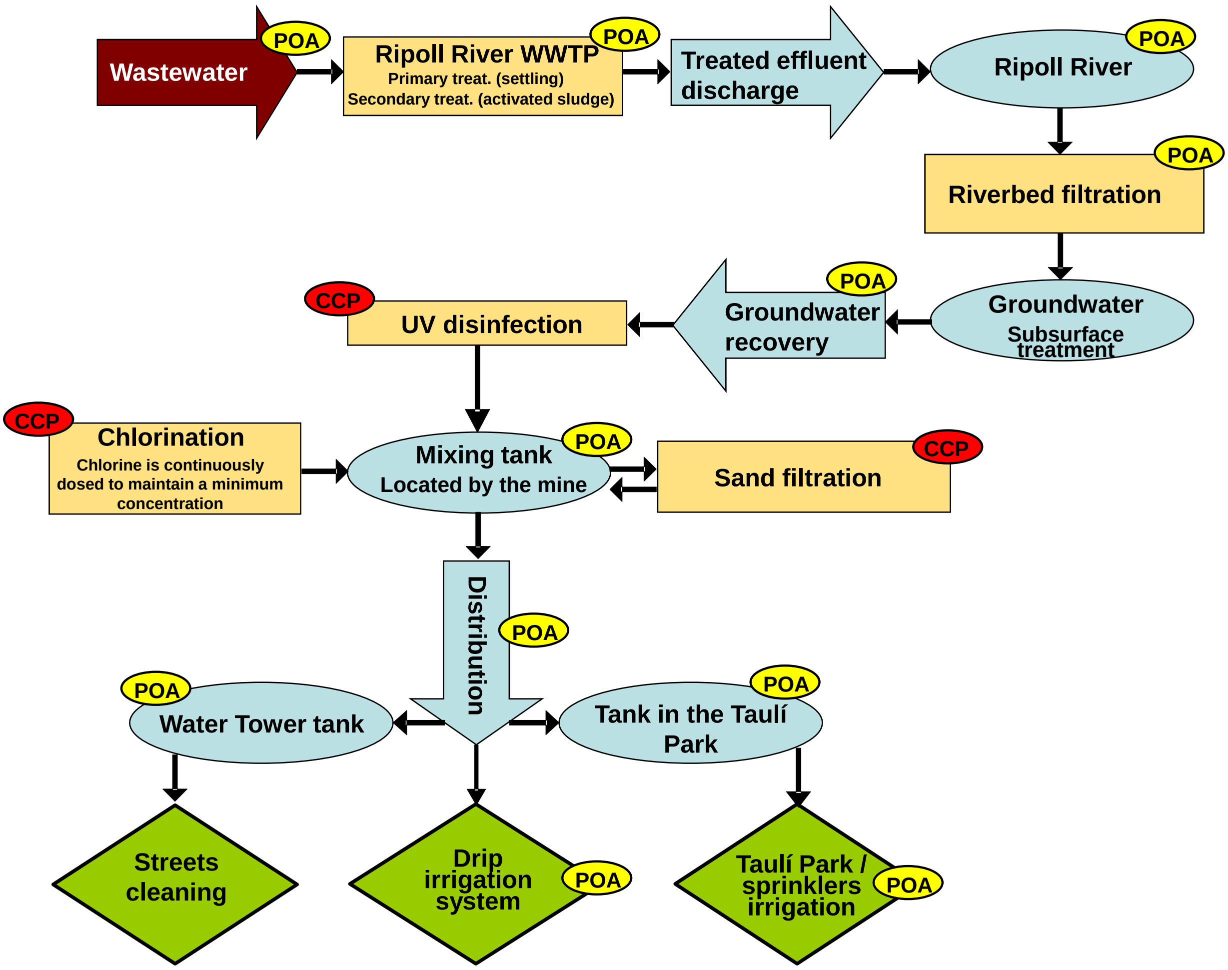
- July 2007: the pipe sending the treated effluent from the WWTP to the upper point of the river, the Torrent the Colobrers area, was broken down. The breakage was close to the mine area, so water was arriving mainly to one discharge point and not to both. This supposed an uneven distribution of the treated wastewater, but it did not pose a risk for RISMAR scheme.
- August 2007: heavy rain fell between the 13th and the 19th of August, and a breakage in the sewerage was detected on August 20th. As a consequence, untreated wastewater reached the river, close to the river mixture 1 sampling point (S3). That week, the mine showed higher microbiological values. However, due to the heavy rain, this wastewater was diluted, and the following week the results were not higher than usual.

These operational issues are considered in the next section, where CCPs and POAs are defined.

7.3.3. Critical control points (CCPs) and Points of Attention (POAs)

A summary of the critical control points (CCPs) and points of attention (POAs) identified for the RISMAR scheme is given in Figure 48.

Figure 48 Critical control points (CCPs) and points of attention (POAs) defined at RISMAR scheme.



Regarding the CCPs identified, it is important to note that mechanisms for operational control and possible corrective actions are in place at RISMAR scheme. These mechanisms for operational control involve probes measuring basic and/or operational parameters (e.g. pH, turbidity, conductivity), and a program of analyses including verification monitoring. The information obtained is recorded and evaluated by CASSA and EDS. For corrective actions, there are procedures in place to implement them. Below, a brief summary for each CCP and POA identified is given:

- Wastewater entering the Ripoll River WWTP (POA): wastewater contains many hazardous components that need to be reduced in order to reuse the water safely: pathogens, inorganic compounds, organic compounds, nutrients, salinity and particulates. Wastewater entering the Ripoll River WWTP needs to fulfil some requirements given in the Spanish regulations for untreated wastewater discharges. This is a way to control the possible illegal discharges from industries or other sources, and ensures that wastewater can be properly treated at the Ripoll River WWTP, considering its design parameters. In case wastewater received contains a peak of pollution it can be diverted to a pre-treatment where it can be further treated and controlled. Besides, as it has been explained before (see section 7.3.1.1), a system to control industrial wastewater and illegal disposals to the sewerage implemented by EDS to reduce likelihood of toxic chemical discharges is in place, and monitors the wastewater received in the sewerage system.

- Ripoll River WWTP conventional treatments (POA): secondary treated wastewater has undergone an important reduction on hazardous components concentrations, but they are still present in it. This treated wastewater, similarly to untreated wastewater, needs to fulfil Spanish regulations for treated wastewater discharges and, in this case, for discharges to the Ripoll River, that is sensitive to hazardous compounds concentrations. In case treated wastewater does not fulfil the critical limits (CLs) set it can be discharged downstream the Ripoll River to avoid infiltration in the mine area and reduce the spread of hazardous components, and, at the same time, corrective actions can be implemented in the WWTP to reduce the hazardous components concentrations. The treatments performed at the WWTP are a POA from a recycled water scheme point of view, but they are a CCP from the wastewater treatment point of view. This explains the frequency and monitoring program applied, that would be probably too extensive for a POA.

- Ripoll River (POA): the Ripoll River receives the secondary treated effluent discharges from the Ripoll River WWTP. The mixture of Ripoll River water and secondary treated effluent discharges infiltrates through the riverbed to the aquifer. Then, although the quality of the Ripoll River water cannot be directly controlled, and infiltration cannot be stopped in case a pollution peak is received, it is in fact a POA, as it is important to track any changes in it. The Ripoll River water is monitored by ACA and EDS, in different sampling campaigns and sampling points.

- Riverbed filtration (RBF) (POA): RBF is an important barrier for RISMAR scheme, which can strongly reduce hazardous components concentrations, especially pathogens, according to the results obtained during the sampling campaigns of the RECLAIM WATER project. Not only pathogens are reduced but other hazardous components (e.g. organic compounds). It is unknown to which extend the riverbed can develop clogging, and RBF is the POA for it. In the past, the riverbed was dredged in order to increase the recharge rate, and according to Sabadell Town Hall (1986), this was not properly performed. A decrease in infiltration rate can pose a risk for the sustainability of the system, and affect groundwater dependent ecosystems.

- Groundwater recovery (POA): during the subsurface treatment, dilution with native groundwater, decay of organic compounds and pathogens die-off occur. Recovered groundwater in the mine undergoes post-treatments (disinfection and chlorination) before its final use, then, the risk posed by pathogens is controlled in further barriers and it is not a CCP. Other hazardous substances to consider are inorganic compounds, which can be mobilised from the aquifer and increase in the recovered water, thus posing a risk. This process cannot be controlled at this point, it can only be monitored, for instance by means of pH and redox potential. In order to reduce inorganic compounds, further barriers need to be considered, thus it is not a CCP.

- UV disinfection (CCP): at RISMAR scheme, the final treated water that has undergone both UV disinfection and chlorination is controlled in different points. However, UV performance was not directly controlled, and, considering the failures detected in the disinfection treatment, it is recommended to control it. Besides, UV effectiveness is very important to reduce pathogens that are not sensitive to chlorination, as is the case of protozoa. Then, it is considered a CCP for this type of pathogens.
- Chlorination disinfection (CCP): chlorination is a typical CCP in all water treatment systems. Effectiveness of the chlorination system is monitored by taking different samples of the final treated water in different points, as verification monitoring of pathogens. At RISMAR scheme, the chlorination system has a probe to measure the residual chlorine in the water, and chlorine is dosed continuously in the tank located by the recovery area (mine). This is a CCP of the system, to reduce pathogens and protect the human health, and in case residual chlorine concentration in the water is below 0.5 ppm, more chlorine is dosed (e.g. corrective action). However, it must be taken into consideration that addition of chlorine to recycled water that contains nutrients can trigger the formation of disinfection by-products, which were monitored in the final treated water as verification monitoring.
- Sand filtration (CCP): a lamellar sand filter was coupled to the tank by the mine. The lamellar sand filter works in a continuous way together with the chlorination system, and it was implemented as a measure to reduce the presence of particles, the black precipitate created by oxidation of the dissolved manganese in the groundwater. This black precipitate was saturating the chlorine probes and causing malfunction of the chlorination system. The sand filter is a CCP, as it reduces the black precipitate in the final treated water, thus reducing the presence of particles. In case the black precipitate appears again, the performance of the sand filter needs to be evaluated and probably clean the filter.
- Mixing tank located by the mine (POA): the presence of pathogens is the most important hazard in the final treated water regarding the human health. Contamination, regrowth of opportunistic pathogens and biofilm formation can occur while storing the final treated water, as well as in the distribution network. In the case of the mixing tank, roofed and closed, chlorine is continuously dosed to prevent these problems. However, during the samplings performed in the framework of the RECLAIM WATER project, it was observed that there was a biofilm in the tank. This tank was yearly cleaned as per maintenance schedule of CASSA, and it was recommended to increase the cleaning frequency. Then, it is interesting to set the mixing tank as a POA, which can be visually controlled to detect and prevent the biofilm formation.
- Distribution network (POA): as in any distribution network, contamination, regrowth of opportunistic pathogens and biofilm formation can occur in there, posing a risk for the human health. Comparing to the tanks, in the distribution network is more difficult to implement corrective actions, as it is necessary to investigate and detect which part of the distribution network can be affected, isolate it from the rest and perform a cleaning process. At RISMAR scheme, the distribution network is controlled indirectly with the results obtained right after chlorination and the results obtained at the point of use (e.g. sprinklers' water). It should be also controlled at the sports area, which is another point of use. If there is a strong difference between them, the possibility of a regrowth event or a biofilm formation must be considered and controlled.

- Tank in the Taulí Park (POA): Similarly to the tank located by the mine, this tank can be affected by contamination, regrowth of opportunistic pathogens and biofilm formation. Then, it is a POA, and should be cleaned as per maintenance schedule, in this case by CASSA and EDS. For this tank, operational monitoring can be performed indirectly with the results obtained right after chlorination and the results obtained at the point of use (e.g. sprinklers water), similar to the distribution network. A visual control of it is also recommended.
- Water Tower tank (POA): again, this tank can potentially be affected by contamination, regrowth of opportunistic pathogens and biofilm formation. In this case, water samples are taken, especially to control the microbiological quality, although other parameters are also measured. Similarly to the tank in the Taulí Park, operational monitoring can be performed indirectly with the results from the samples obtained right after chlorination. In this case, the water is taken by the tankers and used for street cleaning. It would be good to, at some point, control this water. This tank is located by the Taulí Park, so not far away in the distribution network. A visual control of it is also recommended.
- Drip irrigation system (POA): drip irrigation system can be blocked by the presence of iron, particles, nutrients and microorganisms. It can also experiment contamination, regrowth of opportunistic pathogens and biofilm formation. Then, in order to prevent equipment malfunction and deterioration, this should be visually monitored regularly. It might not be necessary to take samples directly from the system, but only to regularly control it visually. If there is any malfunction, the area should be isolated and repaired.
- Sprinkler irrigation system (POA): the sprinkler irrigation system can suffer clogging due to soil particles coming from the irrigated area. It can also experiment contamination, regrowth of opportunistic pathogens and biofilm formation. It is controlled by taking samples of water directly from the sprinkler head. Samples were taken from different sprinklers every time a sampling campaign is performed, in order to cover the whole network. If one of the sprinklers suffers any problem, the area should be isolated and be repaired.

Critical limits (CLs) have been set for the CCPs and POAs. In Appendix F it is provided a summary of CCPs, POAs, potential hazardous events and compounds, CLs and TC, and monitoring and sampling frequency for RISMAR scheme. When the CCP or POA is already monitored by CASSA, EDS or ACA it is detailed in brackets. For those not monitored, a recommended monitoring is given.

7.4. Element 4: Operational procedures and process control

7.4.1. Operational management areas

A list of the operational management areas that apply to the RISMAR scheme is provided in Table 28.

7.4.2. Operational procedures

Within its Quality Assurance (QA) System, CASSA should have operational procedures to describe the activities associated with the RISMAR scheme. All CASSA employees should have access to last version of the procedures. As a minimum, procedures should cover:

- The Ripoll River WWTP: they should describe the process, operation, maintenance and monitoring activities related to all the treatments performed at the Ripoll River WWTP.
- RISMAR scheme process, operating and monitoring: they should describe the process, operation, maintenance and monitoring activities related to the RISMAR scheme.

- The collection of composite samples of the influent and effluent of the WWTP: they should detail the methods for the collection of 24 hour composite samples from the untreated wastewater and the treated effluent at the Ripoll River WWTP by the Process Operator on duty.
- How to take water samples along the system (excluding the collection of composite samples): they should detail the methods for collecting water samples in the different points of the RISMAR scheme.
- The maintenance and calibration of the equipments present at RISMAR scheme: they should ensure that the equipments are maintained and calibrated in a consistent manner. These procedures should be followed at Ripoll River WWTP and mine installations, as well as for the distribution network and point of use locations, and carried out by the Process Operator and/or the Laboratory assistant.
- Irrigation and street cleaning: they should be followed by Operators using the final treated water. For the Taulí Park, EDS may have their own procedures.

Table 28 RISMAR scheme operational management areas.

Operational management area	Organisational representation		
	CASSA	EDS	ACA and other
Treatment in Ripoll River WWTP	Operations committee, including Production and QA Managers; WWTP Supervisor; RISMAR scheme Supervisor		ACA representative, meeting once per year (recommended)
From treated wastewater discharge to the mine where water is recovered: Review water and wastewater treatment, water networks, recycled water networks, water and wastewater quality issues	Operations committee, including Production and QA Managers; RISMAR scheme Supervisor	EDS representatives dedicated to RISMAR scheme	ACA representative, meeting once per year (recommended)
Recovery in the mine: Check water recovery, volumes and quality issues	Operations committee, including Production and QA Managers; RISMAR scheme Supervisor	EDS representatives dedicated to RISMAR scheme	ACA representative, meeting once per year (recommended)
From the mine to the recycled water network, including Taulí Park irrigation and street cleaning: Review recycled water quality, recycled water networks, point of use problems	Operations committee, including Production and QA Managers; RISMAR scheme Supervisor	EDS representatives dedicated to RISMAR scheme	EDS representative

- To analyse data: a huge quantity of information is measured and registered in the RISMAR scheme. This information should be reviewed and contrasted in a timely manner, by the Operations committee, including Production and QA Managers, WWTP Supervisor and Recycled water Supervisor, and shared with EDS representatives.
- Corrective actions and preventive actions: they should be implemented in response to deviation from critical limits.

Besides, forms to record quality of the water samples taken along the system should be available and used by the Operators to introduce all the data generated for the RISMAR scheme as well as to register any changes or problems in the system.

As EDS monitors continuously through a SCADA system the influent and effluent of the Ripoll River WWTP, as well as other points in the sewerage system, results obtained should be reviewed in a timely manner and contrasted with CASSA. Then, EDS should also have procedures for:

- Maintenance and calibration of the SCADA equipments: they should ensure that equipments are maintained and calibrated in a consistent manner.
- To analyse data: a huge quantity of information is measured and registered at RISMAR scheme. This information should be reviewed and contrasted in a timely manner by EDS, and shared with CASSA representatives.

7.4.3. Operational monitoring and corrective and preventive actions

Operational monitoring is undertaken to confirm that processes are under control and is based on the use of parameters which provide an advanced warning that systems may be deviating to a point where control will be lost.

Current operational monitoring at RISMAR scheme entails monitoring the CCPs and POAs identified. CCPs and POAs are detailed in section 7.3.3 and summarized in Appendix F, along with the operational monitoring, critical limits, target criteria and corrective and preventive actions.

The results of the analyses performed should be periodically reviewed and discussed in internal meetings held at CASSA. Reporting procedures, responsibilities and periodicity should be decided by the Operations Committee.

7.4.4. Operational responsibilities, record keeping, data collection and reporting

Specific positions should be implemented to develop the different tasks.

CASSA Operators should be responsible for:

- Carrying out plant and equipment checkings.
- Sampling of the different water points.
- Performing the set analyses and recording the results obtained.
- Measuring groundwater levels and recording the results obtained.
- Running the different equipment.
- Performing the preventive maintenance and calibrations required.
- Reporting any problem with the equipment to the appropriate Supervisor.
- Recording any event in the Ripoll River WWTP and/or RISMAR scheme forms and files.

CASSA Supervisors (Ripoll River WWTP, RISMAR scheme) should be responsible for:

- Data collection and upload in a shared folder.
- Ensuring that Operators follow the appropriate procedures.
- Ensuring information is recorded in the appropriate forms and files.
- Recording any incident.

- Training of the Operators.
- Reporting to the appropriate Manager and taking actions on the system.
- Reviewing monthly operations and produce a monthly report.
- Discussing with EDS representative the results obtained and continuous improvement of the system.

EDS representative should be responsible for:

- Performing a SCADA trend review on a daily or weekly basis, depending on what is decided and the resources available.
- Recording the results in an appropriate form or report.
- Discussing with CASSA Supervisors the results obtained and continuous improvement of the system.

7.4.5. Equipment capability and maintenance

All equipment used either directly or indirectly for maintaining water quality should be included on an asset management system, that can be SAP, Blue Mountain Regulatory Asset Management, MAXIMO or similar. These programs are usually used to record both preventive and breakdown maintenance, as well as to schedule preventive maintenance tasks. SAP is one of the most widely used work management systems, and it is integrated with a number of functions enabling the storage of data, operational tasks and activities.

Equipment must be regularly checked and calibrated to ensure a good performance. Specific procedures should be applied to perform these tasks. These procedures should also set the frequency of calibration for all the equipments:

- Quality instruments measuring electrical conductivity, pH, redox potential, turbidity, temperature and pipeline pressure can be calibrated daily or every 1-6 months, depending on the instrument requirements (e.g. pH daily, pipeline pressure every 6 months).
- Pressure transducers in the wells should be calibrated every 6 months.
- Pipelines, pumps and valves can be checked monthly.

7.4.6. Materials and chemicals

Quality of chemicals used should be established with the suppliers and agreed on the contracts and the buying specifications. For some raw materials, an incoming inspection is recommended. Quality assurance for materials and chemicals is applied to ensure that they do not introduce contaminants into the recycled water scheme.

Procedures to evaluate the suppliers, to audit them and to verify chemicals and raw materials used should be available.

7.5. Element 5: Verification of recycled water quality and environmental performance

7.5.1. Recycled water quality monitoring

The purpose of the monitoring program is to provide a method for responding to system failures, ensuring that health and environmental performance targets are being achieved and to provide eventual trend analysis to avert potential problems or hazards. The Spanish water reuse RD 1620/2007 specifies the recycled water characteristics to be monitored and the guideline values to fulfil according to its final use, whereas the RD 509/1996 focusses on the treated wastewater quality requirements (see Table 4 and Table 5).

Operational monitoring has been discussed in section 7.4.3. Verification monitoring is intended to assess the overall performance of the treatment system, the ultimate quality of recycled water being supplied or discharged, and the quality of the receiving environments (NRMMC–EPHC–AHMC, 2006). Verification monitoring provides:

- Confidence for all stakeholders of recycled water, including users and regulators, in the quality of the water supplied and the functionality of the system as a whole.
- Confidence that environmental targets are being achieved.
- An indication of problems and a trigger for any immediate short-term corrective actions, or incident and emergency responses.

Verification monitoring differs from operational monitoring in that parameters used do not need to be readily measured in the water. Usually verification monitoring is performed in the final treated water, whereas operational monitoring targets the water undergoing the different treatments (what is called in-process inspections in QA programs). Another difference is that parameters required per regulations often are part of the verification monitoring, as few of them can be operational. Verification monitoring should be regarded as the final overall check that preventive measures are working effectively and that the target criteria or critical limits set from relevant guidelines are appropriate.

Current verification monitoring at RISMAR scheme entails monitoring the final treated water, as well as some of the CCPs and POAs identified (including receiving environments). Although CCPs are intended to be monitored for operational parameters, in order to have a real-time result and implement quick corrective actions in case a problem/hazard is detected, verification monitoring is also necessary for CCPs, in order to have more specific information of the recycled water scheme performance and to fulfil the Spanish legislation. CCPs and POAs are detailed in section 7.3.3, but regarding verification monitoring, not all of them need to be monitored. Appendix B summarizes the analyses and sampling points for RISMAR scheme verification monitoring. Analyses performed include those characteristics per the Spanish legislation as well as the ones recommended in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006). In the same table, critical limits, target criteria and corrective and preventive actions are summarized.

CASSA is responsible for verification monitoring. Besides, EDS and ACA perform additional samplings of the recycled water scheme, focussing in different points depending on their interest. The results of the analyses performed by CASSA and the other agencies should be periodically reviewed and discussed in internal meetings held at CASSA. Reporting procedures, responsibilities and periodicity should be decided by the Operations committee.

7.5.2. Application site and receiving environment monitoring

At the moment of developing the RECLAIM WATER project, the receiving environments were the ones described in section 5.3.5 (p. 78).

First of all, the Taulí Park and the trees along the Ripoll River banks needed to be considered. No monitoring of the trees neither the Taulí Park soils, grass and trees was performed, only visual checkings of them. A basic monitoring of the soils was performed as part of the RECLAIM WATER project, indicating that they were prone to salinization due to the use of the treated recycled water, but still on the limit of being in danger of losing the structure and properties (Ayuso-Gabella *et al.*, 2009).

Crops irrigated in the area need to be considered too. These crops can be irrigated with final treated water, Ripoll River water or groundwater, being the risks highly different. For the purposes of the risk assessment, only the final treated water was considered. The use of the other water sources is uncontrolled, and growers do it at their own risk. The situation in the area is that the crops are regularly grown for local consumption, and in many cases, for the families and friends of the irrigators. Selling of the produce occurs in limited occasions, and it is difficult to quantify. However, it would be strongly recommended to perform monitoring of the produce, at least once, to understand the possible pollution of the crops and the influence of the different water sources in the quality of the produce.

Other receiving environments included in the RISMAR scheme are the Ripoll River and the groundwater, already considered as POAs and monitored (see section 7.3.3 and Appendix F). These receiving environments are regularly controlled by EDS, and recommendations regarding the monitoring program, including operational as well as verification monitoring, have been included in Appendix F.

Finally, as the final treated water is used to fill in the swimming pool and to irrigate the sports area, the soils, grass and vegetation in the sports area should be monitored too. The characteristics to be checked, as well as the frequency, for the sports area and Taulí Park monitoring need to be set. It is recommended an annual checking, including soil chemistry and physical properties (e.g. salinization, dispersion, structural stability) and visual checking of the grass, trees and vegetation, as salinization effects are easily detectable in the plants and soil (e.g. yellowing, whitening or browning of leaves, or ponding effects).

7.5.3. Documentation and reliability

At CASSA, the data record is separated according to the sampling points, so for each sampling point that CASSA monitors the data are kept together in a separate excel file. Then, data from untreated wastewater and treated wastewater at the Ripoll River WWTP are kept together in one excel file, and data from the water recovery in the mine and sprinkler irrigation are kept together in another excel file too. Ripoll River data are gathered by EDS, and they are filed and kept together by EDS also in an excel file. However, a general monitoring plan covering the whole RISMAR scheme would be necessary and strongly recommended in order to have a global idea of the performance of the system. In the framework of the RECLAIM WATER project all the data gathered (from all sampling points) were filed together. ACA data consulted on Ripoll River and groundwater quality are available online (ACA, 2013). ACA reports all the water quality results in its website.

Procedures that should be available for operational monitoring (e.g. collection of composite samples, measurement of groundwater levels) should be the same for verification monitoring. One of these procedures should be devoted to reporting results of water quality, including operational and verification monitoring.

7.5.4. Satisfaction of users of recycled water

Currently the users of the recycled water at RISMAR scheme are EDS and CASSA. Then, as the users of the recycled water are the same ones that manage the system, satisfaction is supposed to be guaranteed.

Stakeholders that are in contact with the final treated water are the people crossing the Taulí Park and walking by the Ripoll River, users of the swimming pool and sports area and, globally, inhabitants of Sabadell city, as the final treated water is used for street cleaning. At the very beginning of the Ripoll River area restoration project, that included the RISMAR scheme, EDS started a campaign for public communication of the project and to involve the population in all the actions undertaken to improve the Ripoll River water quality. Part of it was to include a good amount of information in EDS website, and also developing activities in schools and games for children (EDS, 2013). However, this is not enough, as all these actions are part of the strategy of public communication, but at no point are gathered the views of the users and stakeholders. Implementing a system to receive, track and respond to customers comments and complaints would be a very useful tool for improvement, as complaints can be a source of valuable information on issues that may have not been identified by the monitoring program in place at RISMAR scheme.

Later on in the project, the final treated water started to be used to fill in a swimming pool and for irrigation of the sports area. Then, it would be good to also monitor the views, comments and complaints of the bathers and to develop a procedure and system to track customer enquiries, as well as to respond to users concerns. CASSA already has a system in place to track customer enquiries, but it is devoted to potable water mains supply. Then, it would only be necessary to open this system to receive enquiries regarding the final treated water.

7.5.5. Short-term evaluation of results

CASSA should have a procedure for short-term evaluation of results, which could be shared and also followed by EDS, as EDS is also responsible for performing part of the monitoring at RISMAR scheme. In this procedure, the frequency for the short-term evaluation of results, which is recommended to be of one month as a maximum, the way to analyse the data (e.g. statistics, graphics, reporting, etc.) and the partners and organizations to whom a report would be delivered should be established, as well as the way to discuss the results internally in the company. Results obtained should be compared with previous results and with historical data, to track tendencies and prevent losses of control in the system, and should be contrasted with established guideline values, and any regulatory requirements or agreed levels of service.

This procedure for short-term evaluation of results should be directly linked with a separate procedure in which the sampling points, monitored parameters and frequency for performing the monitoring should be established, as per recommendations in Appendix F. In order to have all the data accessible, an internal database recording all the results or any other way of data recording should be available, which also needs to be set in a procedure.

Exceedances of set guideline values (guideline values set in the Spanish legislation, as a minimum) should be reported immediately to EDS, and depending on the type and magnitude of the exceedance, to the ACA and CHD. Exceedances evaluation and reporting should follow an agreed incident protocol between CASSA, EDS, ACA and CHD.

7.5.6. Corrective responses

If non-conformances are detected, an investigation must be initiated. The way to register and document the non-conformance should be detailed in a specific procedure. For non-conformances recording, it is recommended to document the investigation and the actions taken to correct the problem and prevent its recurrence. If control measures were already in place, their failure should be deeply investigated. Corrective responses may be also required to respond to customer complaints, and these need to be also gathered in a procedure, that is recommended to be a separate one.

Corrective responses depend on the exceedance. As a minimum, the response involves investigation of plant performance records to confirm normal operation, and additional testing (in case there are available samples), first to confirm the exceedance and then to identify the root-cause for the non-conformance. Corrective responses are frequently set after evaluating operational results. However, results of the verification monitoring can also trigger a corrective response. In most of the cases, the response may involve the shut down of water recovery from the mine and the shut down of the final treated water distribution. These are rather quick responses to the operational or verification monitoring, but in some other cases the response may come in the long-term. For instance, soils in the Taulí Park have suffered from an increase in the salinity, although by now the overall risk is low. This problem may also be developing in the local orchards irrigated with the Ripoll River water or recovered groundwater in several natural and artificial wells. To minimize problems related with the salinity of the soils, that can decrease crop production and affect trees, bushes and vegetation in the Taulí Park, careful management is recommended and different approaches could be undertaken (ANZECC and ARMCANZ, 2000):

- Changing the frequency, duration and method of irrigation.
- Judicious timing of leaching irrigations.
- Mixing of irrigation water supplies.
- Implementing soil amendments.

In any case, it is important to respond immediately to non-conformances, that can be indicative of significant system failures, involving a risk for public health or the environment, or adversely affecting water quality for an extended period. Depending on the exceedance, it should be immediately reported to the relevant health or environment authority (see more information in section 7.6).

7.6. Element 6: Management of incidents and emergencies.

According to the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006), an incident notification and communication protocol incorporates:

- Emergency contact lists.
- Criteria for defining incidents.
- Notification requirements, including timeframes.
- Media and general communication protocols.

7.6.1. Communication

A public and media communication strategy should be developed before any incident or emergency situation occurs. In the case of RISMAR scheme, public communication should be managed by EDS, with CASSA communicating previously to EDS the incidents. This should be procedimented by CASSA and by EDS. However, procedures for internal communication should be also in place at CASSA, in order to make all associates aware of the incident or problem. Protocols for internal and external communication of incidents and emergencies should include a contact list of key people, agencies and businesses, detailed notification forms, procedures for internal and external notification, and definitions of responsibilities and authorities. Contact lists should be updated regularly (e.g. annually) to ensure they are accurate. Some companies enclose all the cited documents in an emergency management manual.

7.6.2. Incident and emergency response protocols

In order to be prepared to respond to incidents and emergency situations, the potential hazardous events at RISMAR scheme, their likelihood, consequences, corrective actions and response plans have to be defined. In the present work, this has been undertaken in different sections (see Table 16, Table 17 and Appendix F), and it was preliminarily prepared in Ayuso-Gabella *et al.* (2009). Key areas to be addressed in incident and emergency response plans, which should be clearly specified and defined for RISMAR scheme by CASSA and EDS, should include per Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) the following points:

- Response actions, including increased monitoring.

- Defined and clear responsibilities for the personnel, in order to respond to the incidents in a quick and effective way.
- Predetermined agreements on leading agencies for decisions on potential health or environmental impacts.
- Plans for alternative water supplies.
- Communication protocols and strategies, including notification procedures (internal, regulatory bodies, media and public).
- Mechanisms for increased health or environmental surveillance.

All employees involved with RISMAR scheme, including CASSA and EDS personnel, should receive a specific training regarding the different steps of the recycling process, possible incidents, corrective actions and proper communication pathways. Emergency response plans should be regularly reviewed and practised.

Following any incident or emergency situation, an investigation should be undertaken involving people from CASSA and EDS. The results of the investigation, as well as the description of the incident, actions taken and a plan to prevent similar incidents in the future, should be recorded and documented. A procedure for reporting incidents or emergency situations should be in place at CASSA and EDS regarding RISMAR scheme. For both partners, this procedure could be a general procedure to respond to incidents or emergency situations, which does not necessarily need to be a specific one for RISMAR scheme.

7.7. Elements 7 and 8: Operator, contractor and end user awareness and training. Community involvement and awareness.

Operators, contractors and end users need to be aware of the potential consequences of system failure, and of how decisions can affect public and environmental health. Consultation with users of recycled water, stakeholders and the general community is usually an essential component of the development of recycled water schemes, as public and stakeholder concerns can be very powerful. In the case of RISMAR scheme, as the restoration project entailed the recovery of the Ripoll River area and to avoid stopping irrigation of the Taulí Park during water shortages, the community received positively the project, although a formal consultation process was not developed.

Awareness and involvement of different stakeholders for RISMAR scheme has been developed mainly by EDS. EDS has developed an effective public communication program through their website, where a lot of information regarding RISMAR scheme and the restoration project is available. Community involvement and awareness has been undertaken by promoting initiatives to recover the quality of the Ripoll River. Several campaigns have been undertaken to clean the Ripoll River banks and the riverbed.

Regarding the use of the final treated water for park irrigation, EDS put sign-posts and metal plaques in the Taulí Park to make people aware that the water used for irrigation is recycled water, and that it is not potable water for drinking purposes. The same should be applied to the sports area, to avoid people drinking the water.

CASSA, on their side, has undertaken training and different measures to make all the Operators aware of the RISMAR scheme and how to handle the equipment, the different kinds of water and the facilities. Also punctual trainings may need to be undertaken for contractors and external suppliers. Main training areas for Operators of the RISMAR scheme should include and focus in:

- Wastewater, recovered water and final treated water distribution.

- Wastewater, recovered water and final treated water quality.
- Groundwater and river water quality and environment protection.
- Wastewater treatment and disinfection.

In the case of using the final treated water or Ripoll River water for crop irrigation, it would be recommended to prepare a brochure with guidelines for recycled water use. Irrigators and growers of recycled water should be issued with an information package explaining the proper use of the recycled water, and, if possible, it would be good to prepare a training course on best irrigation practices for them. This should be undertaken by EDS.

Training records should be maintained by the QA department in CASSA, as well as in EDS. A training procedure should be developed, including the necessary training/awareness sessions for new employees and for concepts refreshing of current employees.

7.8. Element 9: Validation, research and development.

According to 21 CFR 820.75 (US Government, 2002) and WHO (2006b), where the results of a process cannot be fully verified (100% of the product inspection) by subsequent inspection and testing, the process shall be validated with a high degree of assurance and approved according to established procedures. It is by design and validation that a manufacturer can establish confidence that the manufactured products will consistently meet their product specifications. Applying this concept to water recycling, validation of the process is necessary to ensure that the water quality meets the specifications set for the intended uses, and of course, it is not possible to verify 100% of the recycled water.

In the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) validation is viewed as a process that ensures effective operation and control of the recycled water scheme. To undertake the validation of a recycled water scheme the requirements cannot be as restrictive as are for drugs or medical devices (the field areas where validation started). Then, for a recycled water scheme including or not MAR, it may involve:

- Evaluating available scientific and technical information (including historical data and operational experience), as well as gathering new data in areas where are lacking.
- Undertaking simulations or developing pilot studies to design the multiple-barrier system to achieve a previously set final treated water quality.
- Undertaking investigations to validate the different barriers and treatments.
- Verifying critical limits and target criteria set for the system (design verification process).
- Updating operational procedures, in-process inspections, calibration, preventive maintenance and any other ancillary systems that may need to be created or reviewed after the validation process is finished.

7.8.1. Validation of processes

According to The Global Harmonization Task Force (GHTF, 2004), process validation lies in establishing by objective evidence that a process consistently produces a result or product complying with its predetermined requirements. Moving to the water recycling area, process validation is a powerful tool to ensure effective operation and control of the recycled water scheme, not only at the moment of executing the validation but also in the future. In the framework of water treatment, validation monitoring involves identifying the operational requirements that should be used to ensure that processes reduce risk to an acceptable level on an on-going basis (NHMRC–NRMMC, 2011). The more critical is the end use of the recycled water (e.g. drinking water), the more important is to validate the process.

Processes should be re-validated when variations occur, as might be:

- A progressive decrease in the process performance.
- The process window (limits for the equipment parameters, necessary to run the equipment and obtain a product complying with its predetermined requirements) needs to be modified according to changes in: new equipment, different source water, new end use, etc.
- A new treatment step is included in the treatment train, thus modifying the water quality for the subsequent treatment step.
- A treatment needs to be upgraded.
- Initial validation did not consider the different seasons of the year, and the impact of seasonility is high in the process.

For processes that are currently working, a retrospective validation can be executed; a desktop assessment based on existing evidence might be enough. In other cases, objective empirical evidence obtained from validation monitoring is needed. Validation is also important in "old" processes in order to ensure that the final quality is maintained and not decreased, and to have a better control of the process as well.

Minimum steps that a validation process needs to include are as follows:

- Installation Qualification (IQ): establishing by objective evidence that all key aspects and functions of the process equipment and ancillary system installation adhere to the manufacturer's approved specification and that the recommendations of the supplier of the equipment are suitably considered.
- Operational Qualification (OQ): establishing by objective evidence that the process, at the extremes of the operating window (worst case), produces a product which meets all predetermined requirements.
- Performance Qualification (PQ): establishing by objective evidence that the process, under anticipated conditions, consistently produces a product which meets all predetermined requirements.

At RISMAR scheme, a proper full process validation has not been developed, and it would be difficult to find a recycled water scheme in which it has. However, specific studies on the process performance have been executed, as part of the RECLAIM WATER project, and historical data have been gathered, so the validation can be considered under way. Key needs and projects have been identified in order to have a full process validation.

7.8.1.1. Wastewater treatment process

A validation of the treatments performed at the WWTP has not been executed; however, historical data are available and a retrospective validation, linking the quality data with the operational parameters used to operate the plant, could render easily a good OQ window and possibly set the process parameters window without difficulty. However, in this validation the impact of seasonality would be high, and different process windows for the different year's seasons should be considered.

Data are available for nutrients, electrical conductivity and gross organic matter indices, that can be used to perform a retrospective process validation. However, it is also very important to understand the real pathogens removal, for which a desktop approach has been developed, which is in fact the QMRA study (section 6). This approach would be good to be underpinned by empirical data on pathogens content in the untreated wastewater, as literature data have been used.

Regarding the SCADA system, at least a software validation should be developed. The system failed systematically in the data transference to the EDS, and this probably could be repaired or improved by validating the software appropriately. In any case, a good conservation and isolation, avoiding public access to the areas where the probes are located, is crucial for a good performance of the system. When this is ensured, software validation can be undertaken.

7.8.1.2. Ripoll River dilution

Direct process validation for the Ripoll River dilution is not possible, as external variables that cannot be controlled have a high impact in it. However, a close control of the volumes of water discharged into the Ripoll River is on-going in the Ripoll River WWTP. This control is important in order to prevent possible overloads in the river when heavy rain periods occur, but this was not the case at the moment of developing the RECLAIM WATER project.

7.8.1.3. Infiltration through the riverbed and subsurface treatment

Validation of the RBF and subsurface treatment processes is a difficult task, as infiltration cannot be directly modified as it can be in an engineered treatment, and the decay rate of organic compounds or die-off of microorganisms in the aquifer cannot be modified either. For clarification, there is not a process window to be controlled in order to infiltrate more or less water in the aquifer, as infiltration occurs naturally, neither there is a process window to be controlled in order to increase or decrease the decay rate of organic compounds or die-off of microorganisms. However, a good understanding of the infiltration rates, the fluctuations in the Ripoll River quality and the decay in the aquifer is important in order to operate the system, and this would be part of the research necessary at RISMAR. For instance, as dredging practices could be performed at RISMAR scheme in order to increase the infiltration rate, a minimum and maximum scrapping in order to control on-going infiltration rates at the riverbed could be validated.

Apart from the data generated in the framework of the RECLAIM WATER project, historical data are available for inorganic and organic compounds, nutrients, salinity and some more water related parameters, which can be used to perform a retrospective process validation. However, it is also very important to understand the real pathogens removal, for which a desktop approach has been developed, which is in fact the QMRA study (section 6). Potential subsurface removal has been compared to real removals calculated thanks to the results obtained from the RECLAIM WATER project monitoring. So, this could be considered as a validation monitoring, part of a future process validation. Regarding organic compounds, the data gathered can give a preliminary idea on the effect of the infiltration and subsurface decay processes in their removal. However, the mechanisms underlying this decay are not completely clear, so more research should be conducted on this area.

Regarding hydrochemistry, in the framework of the RECLAIM WATER project, and in order to understand the progression of redox processes in the RBF process using an infiltration water rich in organic matter and nutrients, some investigations were undertaken. This is very important in order to properly operate the system. Results obtained indicated that there was manganese dissolution, and although arsenic was not measured, its possible presence could be important (see sections 5.5.3.3 and 5.5.3.14). At the moment that CASSA installed a sand filter to treat the recovered water and remove the black precipitates it was unknown that the precipitates were oxidized manganese. With this information in mind, the sand filter could be better operated and a validation of it is possible.

7.8.1.4. Disinfection treatments

A formal validation of the disinfection treatments has not been performed at RISMAR scheme, but the process parameters to operate the UV and the chlorination system are controlled by CASSA. For UV, the intensity of the lamp and the water flow are very important process parameters. Then, it would be easy to develop a validation in this sense, setting the maximum and minimum values for the process parameters in order to maximize the disinfection process. Variables to be controlled could include enterococci (as they are indicators very resistant to disinfection treatments) and transmittance. Similarly to UV, chlorination could be validated. Regular measurements are performed by CASSA in order to know the residual chlorine present in the final treated water, and the probes are regularly checked. For chlorination process parameters, dose and contact time are also controlled, thus having all the information required to develop a validation.

7.8.1.5. Sand filtration post-treatment

Similarly to the disinfection treatments, a formal validation of the sand filtration post-treatment has not been performed at RISMAR scheme, but the process parameters to operate the sand filtration process are controlled by CASSA, and preventive maintenance of the filters is applied. Then, it would be easy to develop a validation in this sense, setting the maximum and minimum values for the process parameters in order to maximize the particle removal. Variables to be controlled could include turbidity and suspended solids.

Analogously for the filter to remove manganese, process parameters to operate the system are controlled by CASSA, and manganese concentrations could be measured in order to validate the treatment.

7.8.2. Design of equipment

When implementing a recycling water project or any other kind of water-related project, it is very important to consider the equipment that will be necessary. Depending on the required quality of the final treated water, resources available, volume of water to treat, etc. a different treatment train should be applied. When it comes to recycled water schemes already functioning, engineering studies should be undertaken when designing new equipment and infrastructure, or when implementing design changes to improve the treatment train performance and ancillary control systems. Regularly, new technologies require pilot-scale research and evaluation before full-scale implementation. In any case, design specifications should be established in advance to ensure that new equipment is able to meet the intended requirements and provide necessary process flexibility and controllability (NHMRC–NRMMC, 2011).

7.8.2.1. Wastewater treatment process

At the moment of designing the Ripoll River WWTP, the quantity and quality of the wastewater that would be received was considered. This prompted the construction of a WWTP with the capacities explained in Table 7.

Nowadays, the volume of water received is less than the expected, thus enabling a better performance of the WWTP.

SCADA equipment owned by EDS was designed and installed in order to have a real-time monitoring of possible spills into the sewerage system and to track the Ripoll River WWTP effluent quality. This is a powerful system that should be taken advantage of.

7.8.2.2. Ripoll River dilution

The discharge of the treated wastewater into the Ripoll River can be considered as a dilution of the treated wastewater, although sometimes it is not. In this case, when RISMAR scheme was conceived, the riverbed was already considered as a means of infiltration to recharge the aquifer with the secondary treated effluent, and the possible dilution of the treated wastewater was also taken into account. When designing the system, the volumes of water that would be discharged were also considered, and it was deemed important to distribute the discharges into different areas (see Figure 10, p. 86). To achieve this, a water emissary was constructed, as well as a pumping station. This way, the treated wastewater could be sent upstream the Ripoll River and reach two discharge areas, arriving to the one further away by pumping. The third discharge area was close to the WWTP, and water arrives there by gravity. This last discharge area is used only when there are surpluses in the Ripoll River WWTP that cannot be fully treated (e.g. during heavy rain periods).

7.8.2.3. Infiltration through the riverbed and subsurface treatment

When the restoration project was prepared, treated wastewater infiltration through the riverbed, thus an induced RBF, was considered to be the best option at RISMAR scheme. In a second step, the water needed to be recovered from the aquifer. To do so, an old mine installation present in the area was evaluated. Two wells were identified, one had been closed some years ago due to fecal pollution and the other one was considered to be acceptable for water recovery. This way, the cost for the installations was also lower than would have been if a fully new infrastructure had to be constructed. Overall, the RISMAR scheme takes advantage of old infrastructures and the natural infiltration through the riverbed, thus being a cheaper solution to implement MAR in Sabadell.

7.8.2.4. Disinfection treatments

When designing the treatments to be performed in the recovered water it was decided that disinfection, even though no recent pathogens neither indicators data were available, should be applied to the recovered water. This was due to the yet indicated presence of fecal pollution in another well close to the one used to recover the water. As the recovered water from the aquifer did not present many suspended solids and had a low turbidity, it was decided that a UV treatment could be used. Besides, in order to maintain the disinfection levels in time and prevent contamination along the pipeline or in the storage tanks, a chlorination treatment was decided to be applied too.

Recently the UV treatment was replaced by a newer one including a more potent lamp, in order to improve its performance. This was an improvement undertaken after the results obtained in the framework of the RECLAIM WATER project, which indicated that the performance of the UV was not as good as it should be.

7.8.2.5. Sand filtration post-treatment

A sand filtration post-treatment was implemented by CASSA in order to remove the black precipitates present in the final treated water. Thanks to the RECLAIM WATER project, it was known that these precipitates were manganese oxides, coming from the increased manganese dissolution from the aquifer and the oxidation by chlorination treatment. Besides, results obtained indicated that there was possibly arsenic too. According to these results and other studies fostered by EDS, a specific filter to remove arsenic was implemented as a post-treatment of the recovered water, as well as a better sand filtration system to remove particles (most of them created by the manganese dissolution and posterior precipitation after the chlorination treatment).

7.8.3. Research

Research is essential before, during and after the implementation of a water recycling system. In general, it is necessary to have a good understanding of the recycled water scheme to identify and characterise potential hazards and to fill gaps in knowledge, and it is also important from a continuous improvement perspective. Examples of research studies are given in the Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011), and here we detail the ones that could apply to RISMAR scheme as well as few more that would be specific for this system:

- Source water monitoring to understand the temporal and spatial variability of water quality parameters; and as in RISMAR scheme the source water is wastewater, assessing waste agreements to identify chemical contaminants that may be discharged into it.
- Development of early-warning systems to improve the management of poor water quality.
- Event-based monitoring to determine the magnitude of impacts (duration and maximum concentrations).
- Study the movement of water in the alluvial and Miocene aquifers, to determine its real residence time.
- Examine seasonal or outbreak impacts on microbiological quality of wastewater and final treated water.
- Study the biofilm creation in the storage tanks and recycled water pipeline.
- Evaluate the performance of the new UV system and its capacity to meet the required disinfection targets.

These are few examples to evidence the necessity for research at RISMAR scheme, seeking always to continuously improve.

7.8.3.1. Wastewater treatment process

Regarding the wastewater treatment process, research should be focused on identifying the real performance of the system for pathogens removal. As part of the RECLAIM WATER project, a microbiological monitoring of RISMAR scheme was performed, which has been explained in section 5.5.2. The vast majority of the measurements were done in the secondary effluent, not in the influent. Only two samplings included additional determinations for the influent water (data not shown). Removals for indicators ranged from 0.45 $\log_{10}$ units for *Clostridium* spores to 2.6 $\log_{10}$ units for bacteriophages. For *E. coli* this removal was of 2.2 $\log_{10}$ units. These results are in accordance to those indicated in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006). Then, pathogens presence in the influent water would be an interesting area to develop, in order to better understand pathogen loads received and to evaluate if the current treatments in place are enough for pathogens removal in the Ripoll River WWTP. Sampling during different seasons of the year would be recommended, to investigate differences in performance. Besides, in case there are enough resources, challenge tests would be recommended. Something similar to the work developed by Keegan (2009) could be done. In Keegan's work, the challenge tests were performed adding selected microorganisms to the water that was tertiary treated. The selected microorganisms were not harmful and had a similar size, thus a similar removal, to their corresponding pathogens. The microorganisms used were: MS2 phage as a surrogate for rotavirus, a yeast as a surrogate for *Cryptosporidium* and *Bacillus* spores as a surrogate for *Campylobacter*. The results of the challenge tests underpinned the expected capability of removal by the tertiary treatment, and, for RISMAR scheme, could be applied to the WWTP performance.

7.8.3.2. Ripoll River dilution

The Ripoll River receives waters from different sources, many of them being treated wastewater. Then, a close monitoring of the river in different areas and seasons would be good, in addition to the data gathered by ACA, EDS, and the data generated in the framework of the RECLAIM WATER project. This would help in better setting the expected efficiency of the infiltration process and to understand the probability of introducing in the aquifer harmful substances travelling in the river.

7.8.3.3. Infiltration and subsurface treatment

RBF and subsurface treatment is a key piece of the RISMAR scheme. Infiltration through the riverbed and decay in the aquifer are very important to reduce the risk and make the water suitable for its intended uses. However, for both the RBF and the subsurface treatment (especially for the latter one), there is in general a much less knowledge on its capability to inactivate pathogens and to reduce contaminants than for other engineered treatments. Then, an in-depth understanding of the processes underlying this risk reduction is the basis for a good operation of the system.

For a MAR system it is crucial to know the residence time of the recharged water in the aquifer, the mixing of native water with the infiltrated water and the flows inside the subsurface. For RISMAR scheme, a basic hydrogeological study is available, which indicates that the residence time might be short and that the Ripoll River water has a strong influence in the aquifer (Franch, 2007). Nevertheless, this information is not enough if a proper monitoring and control of the MAR system is desired. Then, first and foremost, an in-depth hydrogeological study of the RISMAR scheme is necessary. A tracer test would be strongly recommended also.

Regarding hydrochemistry, it has been explained above that in the framework of the RECLAIM WATER project some investigations were undertaken, and results obtained indicated that there was manganese dissolution and possibly arsenic too (see sections 5.5.3.3 and 5.5.3.14). According to these results and other studies fostered by EDS, a specific filter to remove arsenic was implemented as a post-treatment of the recovered water, as well as a better sand filtration system to remove particles (most of them created by the manganese dissolution and posterior precipitation after the chlorination treatment). Some more hydrochemical studies, in order to understand the current redox status of the aquifer and its progression after a long period of enhanced recharge, would be interesting and would help in its operation and validation. Besides, measurements of inorganic compounds for which there was not data available, would be necessary too.

Moving to pathogens removal, the QMRA study has been performed mainly considering microbiological indicators removal and data from the literature, and few pathogens' data available thanks to the RECLAIM WATER project. Then, in the future it would be recommended to develop a study to understand the real effect of the RBF process and the die-off of pathogens in the subsurface of RISMAR scheme. For RBF, direct measurement of pathogens in the river water, groundwater and riverbed would be necessary. Even though pathogens were measured in the river water and the recovered water in the framework of the RECLAIM WATER project, more samplings and analysis would be necessary, and they should include the riverbed materials. Regarding the decay rate of pathogens in the subsurface, it would be interesting to develop a pathogen decay chamber study. In this kind of study, a predetermined number of pathogens suspended in either filtered or non-filtered groundwater is introduced in chambers especially designed and then these chambers are deployed in the aquifer. The chambers are recovered with a certain periodicity and the amount of pathogens still present is measured. Field studies on pathogen survival in aquifers have already been developed in MAR sites in Australia (Martin and Dillon, 2005; Toze *et al.*, 2009). It would be useful to study the die-off rate of *Campylobacter*, *Cryptosporidium* and rotavirus, that are the pathogens recommended to be monitored in the Australian Guidelines for Water Recycling and the MAR guidelines and that were used for the QMRA study.

Clogging prediction studies would be interesting to prevent a future decrease in the infiltration rate. For MAR systems involving RBF, it is typical to perform dredging activities in the riverbed to avoid clogging and to enhance infiltration; a good example is the Llobregat River (IGME, 2006; ACA, 2010; Ortuño, 2011). At RISMAR scheme, dredging had been performed in the past, and according to Sabadell Town Hall (1986), this was not properly performed. Regarding clogging, it would be recommended to perform a similar work to the one done by Martin and

Dillon (2005), in which investigations were undertaken using laboratory columns packed with aquifer material collected from the MAR study site. This work enabled evaluation of clogging within the columns prior to the start of a full scale MAR scheme, thus being a baseline monitoring.

Behaviour of trace contaminants in the aquifer is another area on which to gather more knowledge. As part of the RECLAIM WATER project, and also in the framework of research performed by CASSA and EDS, a good quantity of trace chemicals was evaluated (see sections 5.5.6.3 and 5.5.6.4). According to the results obtained, there seemed to be a good removal of most of the trace contaminants investigated, but for the ones known to be more persistent and that are regularly used as tracers in hydrogeological studies. The concern is that only few samplings could be undertaken, due to project restrictions, and more research is needed to understand to which extent the detected and the non detected compounds can be removed.. Other trace contaminants different from the ones studied could be also evaluated.

7.8.3.4. Disinfection treatments

Disinfection is a key treatment that the recovered water requires, as it still has presence of microorganisms according to the results obtained in the framework of the RECLAIM WATER project. As it has been explained above (see section 7.8.2.4), the UV treatment was replaced by a newer one including a more potent lamp, in order to improve its performance. Then, this reflects the importance to monitor not only the final treated water but also the water after the UV treatment (before the chlorination process). This would be good in order to track the efficiency of the system, and it has been included in Appendix F.

Additionally for disinfection, although there is a lot of literature data regarding the effect of the different disinfection treatments on the different pathogenic groups, it would be necessary to monitor the pathogens presence in the final treated water in selected samplings, in order to corroborate that the modified disinfection treatments have been effective.

7.8.3.5. Sand filtration post-treatment

Sand filtration was performed to remove the black precipitates, and an additional filter to remove arsenic was implemented too. In order to understand the effectivity of these filtration processes, regular samplings of the final treated water for the presence of arsenic and manganese are recommended. These samplings could include other wells present in the area that tap the same aquifer, and end up in a wider study to understand the behaviour of these compounds in the system. This would help to control an increase in releases of these compounds or any other involved inorganic compounds that could be released from the aquifer, which could pose a risk at RISMAR scheme.

7.9. Element 10: Documentation and reporting.

7.9.1. Management of documentation and records

Management of documentation and records relating to RISMAR scheme should include but not be limited to:

- Operational and incident/emergency reporting.
- Customer complaints.
- Operational procedures.
- Monitoring results: spreadsheets and daily summaries.
- Monthly and other reports.
- Outcomes and minutes of the regular meetings.

CASSA has several certifications:

- ISO 9001:2008 for management of potable water distribution and management of WWTPs.
- ISO 14001:2004 for management of potable water distribution.
- OSHAS 18001:2007 for health and security at work.

Then, considering that CASSA is ISO 9001:2008 certified for management of potable water distribution and management of WWTPs, the next step, probably already in the company's strategy, is to certify in ISO 9001:2008 for RISMAR scheme.

According to the Australian Guidelines for Water Recycling and to ISO 9001:2008, CASSA should have specific and generic operational procedures designed to describe the activities associated with RISMAR scheme (see section 7.4.2). All employees should have access to current procedures, by means of specific training, an intranet or any other means of dissemination. All employees should be trained regarding forms, spreadsheets, procedures and any kind of documentation associated with RISMAR scheme.

CASSA procedures for the management of documentation and records should include but not be limited to:

- CASSA Quality Policy: this is available in their website (CASSA, 2013a).
- Management Review: how the review process which ensures on-going effectiveness and continual improvement of the Business System is executed. A key outcome is communication both internal and external.
- Performance Improvement: It is used to improve performance using various means.
- Documentation Management: how all company documentation under the Business System is managed.
- Compliance: CASSA is required to comply with legislation, standards, contracts and licenses. This document should establish and maintain a system to identify and access legal and other requirements which are directly applicable to the organisation.

Other procedures for operational monitoring, verification monitoring, emergencies and incidents have been cited in their corresponding sections (see sections 7.4, 7.5 and 7.6).

7.9.2. Reporting

Regulatory reporting obligations include:

- Heath-based reporting: this reporting is only related to the use of the final treated to fill in the swimming pool, and it is required by CHD.
- Environment-based reporting: this reporting is set by EDS and is mostly developed through regular meetings between the company and EDS, and required data by EDS are sent by CASSA through email channel.

The available reporting formats for RISMAR scheme should cover water quality, water quantity, operations, incidents and emergencies. In general, data are provided on a weekly, monthly and yearly basis. Abnormal events are reported in accordance with CHD notification and communication protocols. Possible data formats are shown in Table 29.

A monthly summary sheet is already compiled by CASSA and forwarded to Senior Management and EDS. EDS reviews this data and CASSA and EDS distribute the information to the appropriate agencies. RISMAR scheme results should be annually summarized in a report, similarly to what is done with the potable water that CASSA distributes in Sabadell and other municipalities. The annual report should include recovered water uses and volumes extracted, as well as a summary of the water quality and works done in the system.

7.10. Element 11: Evaluation and audit.

7.10.1. Long-term evaluation of results

Long-term evaluation of the results is performed at RISMAR scheme in different ways:

- CASSA performs an evaluation of the results for each part of the scheme. WWTP results should be reviewed on a daily basis, whereas final treated water should be reviewed bimonthly or monthly as a minimum. All the results should be put together in a file, and graphics and other visual tools should be used to give a snapshot of the global trending in the scheme.
- EDS also performs a regular evaluation of the results, reviewing the data sent by CASSA and proposing actions to improve the system.
- An annual report gathering the results of RISMAR scheme is recommended. This report should be produced by CASSA, as it has been explained in previous section 7.9.2. The annual report should contain the results obtained for wastewater as well as for the final treated water during the whole year.
- In the present PhD, a global analysis of the data obtained in the framework of the RECLAIM WATER project, as well as data from CASSA, EDS and ACA, has been done. Then, a trending analysis has been developed, which has proved to be also useful to set the basis for the CLs, TC, corrective and preventive actions, etc. Then, a similar analysis should be performed annually, in order to review the performance of the system and set the improvement goals.

Results of special monitoring programs should be assessed against the results of baseline monitoring.

Table 29 Possible data formats for RISMAR scheme.

Data source	Frequency	Format	Purpose
Event notifier email	As necessary	Email	This email captures abnormal issues across CASSA operations of RISMAR scheme
WWTP results	Monthly	Excel file sent by email	A database system for results evaluation and as a reporting tool.
RISMAR scheme results	Monthly	Excel file or results of the analyses performed by an external laboratory sent by email	A database system for results evaluation and as a reporting tool
Final treated water results	Monthly	Online database	Results from final treated water analyses are introduced in an online database run by the Ministry of Health
	Monthly	Excel file or results of the analyses performed by an external laboratory sent by email	A database system for results evaluation and as a reporting tool
RISMAR scheme results	Annually	Hard copy report	This report should be produced by CASSA and be used to satisfy the reporting requirements of the various regulatory agencies.

7.10.2. Audit of recycled water quality management

CASSA should have a procedure for internal and external auditing, detailing how the internal auditing activities will be performed and how the results and action items will be documented (for both internal and external auditing).

Internal audits should be performed at least yearly, and it is preferred to split the audit in different days to focus in different areas of the system. Internal audits will involve trained staff, and should include review of the management system and associated operational procedures and monitoring programs.

External audits need to be executed by qualified agencies. In the case of CASSA, external audits need to ensure that the system meets the requirements of ISO 9001:2008, ISO 14001:2004 and OSHAS 18001:2007 in the areas for which it has been certified. These audits are performed annually and are set by CASSA and the external agencies selected (e.g. AENOR for ISO 9001:2008).

The results of the audits must be documented and communicated to senior management and personnel responsible. Any non-conformances and actions to improve the system need to be implemented in a timely manner and documented, as in the subsequent audit they will be reviewed and followed-up.

7.11. Element 12: Review and continuous improvement.

7.11.1. Review by Senior Managers

CASSA and EDS representatives have regular meetings to discuss improvements to implement in the system and review the results of the monitoring. Besides, CASSA senior management should establish an operations committee that meet on a monthly basis as a minimum. This would be a forum where issues and concerns arising from, or impacting on, the RISMAR scheme can be discussed. Issues raised at this committee are those that are unable to be dealt with on a day to day basis.

CASSA senior management is committed to supplying recycled water fulfilling the required regulations, while maintaining the highest standards of quality of service. Different supporting systems should be in place to achieve the continuous improvement objectives: external and internal auditing processes, research and development, training, etc. On the other hand, CASSA participates in different European and Spanish projects, in conjunction with EDS, and collaborates with different universities through agreements and common projects to develop and in-depth understanding and improve the knowledge on RISMAR scheme. One of the first projects in which CASSA and EDS took place and help to build a stronger understanding of the recycling process was the RECLAIM WATER project, which is the leitmotiv of this PhD work.

7.11.2. Recycled water quality management improvement plan

CASSA has in place a program to improve different areas of the RISMAR scheme, as well as other projects. The most relevant projects, which can be applied to RISMAR scheme or to other sites and schemes, include (CASSA, 2013b):

- Project SENSOTUBO: develop a tube that will send intelligent signals. This will aid in detecting water leakages and cracks in the pipeline system, by controlling real-time pressure and flow.
- Project DEMOWARE: develop systems to measure and control the biofilm formation in the pipeline systems.

In order to improve the RISMAR scheme, several improvement topics could be:

- Consolidate the critical limits and target criteria for the aquifer that have been developed in the present work.
- Consolidate the aesthetic critical limits and target criteria for the final treated water. This would need to also review those parameters that could be attributed to the physical appearance of final treated water and/or arising from customers complaints received. This will be important for the water used in the sports area.
- Develop all of the research studies set in section 7.8.3, which will help to implement actions to improve the scheme.

8. DISCUSSION

8.1. Risk assessment

In the present section, only those hazardous components for which a residual risk was identified will be discussed. The other ones, as the risk was reduced along the treatment train to a low level, will not be discussed.

8.1.1. Pathogens, indicators and antibiotic resistance genes.

Detailed discussions on the analytical results obtained for pathogens, indicators and antibiotic resistance genes were already published in Levantesi *et al.* (2010) and Böckelmann *et al.* (2009). In the present section, the most interesting or important results are discussed, as well as other results not discussed in the cited publications.

The first concern regarding pathogens detection at RISMAR scheme is the presence of gene copies for *Salmonella*. In this case, it is especially important to consider the method used to detect this pathogen, which was quantitative PCR. By this method, DNA of viable and non-viable cells, as well as the remains of extracellular DNA can be detected and give a positive result for *Salmonella*. However, this does not exactly mean that there are viable cells in the water. In a study by Dupray *et al.* (1997) the degradation rates of DNA, both free and from dead *Salmonella typhimurium*, were evaluated in natural seawaters. The DNA of dead *S. typhimurium* was detected for up to 55 days and free DNA for up to eight days post-inoculation. This persistence could increase the risk of quantitative PCR false positives; therefore, ambient background levels of extracellular or dead cell DNA should be taken into account when conducting these studies. In any case, this positive amplification of *Salmonella* genes in all sampling points indicates that the pathogen has, at least, been present in the system recently and that it was present in the source water and the Ripoll River water before the discharges. Gene copies values obtained for the treated wastewater and the Ripoll River mixture 1 were similar to the ones obtained by Wéry *et al.* (2008) in a French WWTP and Levantesi *et al.* (2010) in an Italian WWTP (Nardò). If *Salmonella* had been cultured and grown by traditional methods, more reliable results on the presence of viable cells at RISMAR scheme would have been obtained. On the other hand, *Salmonella* is a typical pathogen causing many of the food outbreaks detected in Catalonia. Then, *Salmonella* is excreted in the faeces of infected individuals, arrives to the WWTP and is spread to the Ripoll River and can even reach the aquifer, which explains the detection of *Salmonella* gene copies at RISMAR scheme. However, it is interesting to point out that this pathogen was also present in the Ripoll River water before the discharges, thus indicating that its presence is widespread. At RISMAR scheme, sources of *Salmonella* before the Ripoll River WWTP treated wastewater discharges can be originated by discharges of other WWTPs upstream the Ripoll River or pollution by birds in the area, as it has been already explained in section 5.5.2.1.1.

Pathogenic viruses were only investigated in groundwater and final treated water, and were not detected. However, their presence at RISMAR scheme is highly possible, at least in the treated wastewater. Presence of pathogenic viruses (enterovirus, norovirus, rotavirus, hepatitis A virus, adenovirus) in wastewater, secondary treated wastewater, tertiary treated wastewater, seawater, groundwater and river water of Catalonia has been widely reported (Costán-Longares, 2008; Villena *et al.*, 2003; Pintó *et al.*, 2007; Lucena *et al.*, 1982; Lucena *et al.*, 1985, Pérez-Sautu *et al.*, 2012; Bofill-Mas *et al.*, 2011). Then, their presence at RISMAR scheme is highly possible, and should be further investigated, in order to support the data used for the QMRA and to better understand their presence, removal and risk posed for the different end points and uses considered.

Protozoa could pose a risk as they were still present in groundwater, although never detected in the final treated water. This is interesting, considering that there are studies reporting the presence of protozoa in the inlet and outlet of drinking water treatment plants in Galicia, Spain (Castro-Hermida *et al.*, 2010). MAR treatment, in this case, plays a role in reducing the (oo)cysts concentration in the infiltration water, thus enabling a better post-treatment. On the other hand, concentrations of *Cryptosporidium* oocysts in the treated wastewater and in the river water were similar to the ones reported by Montemayor *et al.* (2005), which used samples from the Llobregat River and WWTPs in Catalonia. This supported the use of the data presented in Montemayor *et al.* (2005) regarding *Cryptosporidium* oocysts in untreated wastewater to develop the corresponding PDF for the QMRA analysis. The results obtained for the treated wastewater and the river water regarding *Giardia* cysts and *Cryptosporidium* oocysts were in the low range of results reported in the literature (Tandoi *et al.*, 2012).

As explained previously in section 5.5.2.2, the microbiological indicators measured were still detected in the final treated water, and would not meet the Spanish water reuse RD (BOE, 2007b) for all the uses contemplated at RISMAR scheme, neither the Spanish drinking water RD (BOE, 2003) nor the swimming pools RD (BOE, 2013). Regarding these results, it is important to consider that we were more restrictive doing the measurements as we were using a higher volume of water for them than it is done in the regular practice. Then, while the legislation may ask for absence of *E. coli* in 100 mL, or a certain amount of *E. coli* in 100 mL, we were using up to 300 mL, 500 mL or even 1 L depending on the sample (some samples would clog the filter with 300 mL, other would not clog it even with 1 L), thus increasing the probability of detecting the bacterium. This was done because this is a research study. The effectivity of increasing the filtered volume of water to enhance the detection of *E. coli* or other indicators was demonstrated when, with the same sample, in one plaque 100 mL was filtered and the result was zero, while in other plaques 300 mL, 500 mL or even 1 L were filtered and the result was not zero. The same approach was used for the other indicators included in the Spanish drinking water RD, and if we had used only 100 mL, probably a higher proportion of the positive samples would have been negative. Analyses performed by external laboratories commissioned by CASSA and EDS did also detect the presence of microbiological indicators in the final treated water, although in a lower proportion of samples. Another point to consider is that in our work the samples for the microbiological indicators were treated, filtered and put in Petri dishes the same day that the sampling was performed, while for external laboratories, analyses start, as a minimum, a day after the sample is taken, and the quantity of microbiological indicators can decrease by up to one order of magnitude. This was observed in an initial sampling, where treated effluent composite and grab samples were measured for microbiological indicators; the composite sample was taken during the previous 24 hours, and for each indicator investigated, the results were between 0.5 to 0.9 $\log_{10}$ units lower in the composite sample comparing to the grab sample.

Leaving apart methodological discussions on the volume of water used for the measurements and the quickness to perform them, when trying to explain the microbiological indicators results in the final treated water it seems clear that their concentrations were highly impacted by the low performance of the disinfection treatment. The whole disinfection treatment (UV + chlorination) was able to reduce between 0.30 and 2.00 $\log_{10}$ units on average the indicators still present in the recovered water. Although there were few samples in which these removals were difficult to calculate, the removals obtained are very low comparing to the values published in the literature, which were indeed used to develop the theoretical risk assessment. This lower performance of the disinfection treatment was one of the reasons to include an empirical risk assessment in the present work. To support this low performance of the disinfection, the results for enterococci are very helpful: enterococci suffered the lowest reduction by the disinfection process, and their concentration was higher in the final treated water than in the groundwater in 47%of the samples. Enterococci are well-known indicators of the efficacy of the disinfection systems, as they are very resistant to them. Then, these results support the idea of a bad performance of the disinfection post-treatments. On the other hand, thanks to data gathered in few sampling campaigns, it seems that the problem was in fact a not very effective UV treatment and contamination in the storage tank located by the mine. Regarding the UV treatment, results from four samplings (data not shown) indicated removals between 0.04 and 1.6 $\log_{10}$ units for total coliforms, and 0.6 to 2.6 $\log_{10}$ units for *E. coli*, while in the Australian Guidelines for Water Recycling (NRMMC–EPHC–AHMC, 2006) it is acknowledged a minimum reduction of 2.0 $\log_{10}$ units for bacterial pathogens and *E. coli*. Values of 0.04 and 0.6 $\log_{10}$ units reduction are indicative of a low performance or failure of the treatment, and in two out of the four samplings the removal was low for both indicators. Regrowth in the storage tank located by the mine may have occurred with a high probability, as biofilm and microbial contamination was found in it during one of the sampling campaigns. This storage tank by the mine was not regularly sampled neither inspected visually by our group, although CASSA did regularly perform visual inspections. After the detection of the biofilm and microbial contamination, the storage tank was cleaned, and it was decided to increase the cleaning frequency, from yearly to twice per year or even more in case contamination was detected again. Additional samples were taken from the tank on the day that the contamination was detected (October 29, 2007), and total coliforms and bacteriophages were measured in a higher concentration than after the UV treatment, indicating a possible contamination. Pathogens could not be investigated in those samples. Bacterial regrowth seemed to have happened in the tank, and it would have been interesting to investigate the possible presence of opportunistic pathogens. Jjemba *et al.* (2010) investigated four water reclamation plants in USA, including the distribution networks and reservoirs. They demonstrated that although all of the treatment systems effectively reduced the levels of bacteria in the effluent, bacteria regrew in reservoirs and distribution systems because of the loss of residual disinfectant and high organic carbon levels. Contamination or regrowth in the distribution pipeline at RISMAR scheme cannot be supported by data, as the pipeline could not be sampled. Regarding the sprinklers, as there was contamination in the tank since an uncertain period of time, and the results obtained from the water coming out of the sprinklers were not much different than the ones obtained for the water in the tank or after both disinfection treatments, it cannot be completely ruled out that contamination also occurred in the sprinkler irrigation system.

Regarding ARGs, the results obtained for RISMAR scheme were widely discussed in Böckelmann *et al.* (2009). Interestingly, there was some correlation between the abundance of enterococci and the concentration of tetracycline and erythromycin resistance genes in the final treated water. This was in agreement with results from Martins da Costa *et al.* (2006), Łuczkiewicz *et al.* (2010), Ferreira da Silva *et al.* (2006) and Servais and Passerat (2009). Martins da Costa *et al.* (2006) work involved a Portuguese WWTP where *Enterococcus* isolates carried tetracycline and erythromycin resistance genes, while Ferreira da Silva and co-workers (2006) showed that tetracycline-resistant enterococci were not eliminated during wastewater treatment consisting of primary and secondary activated sludge processes. Łuczkiewicz *et al.* (2010) found also resistance to erythromycin and tetracycline among enterococci, and resistance to ampicillin, tetracycline and extended spectrum b-lactamase among *Escherichia coli* isolates in a WWTP in Poland. While these three works cited involved the investigation of WWTP effluents, Servais and Passerat (2009) investigated the presence of ARGs in Seine River. Among *E. coli* isolates, they could detect resistance to amoxicillin, tetracycline and clavulamic acid (extended spectrum b-lactamase), and among enterococci, resistances to erythromycin, tetracycline and ampicillin. So, in the cited studies, the same resistances that were detected at RISMAR scheme could be detected, in treated effluents and in river water. The presence of ARGs in the recycled water scheme is a risk for the human health that needs to be taken into consideration. If a pathogen carries one or more ARGs, it will be much more difficult to treat the infected people. Then, models for dose-response on ARGs are necessary, in order to properly evaluate the risks and develop a QMRA for them in the future. Some studies have considered that one gene copy of an

ARG can be considered as a one pathogen, but this assimilation may not be realistic and it is not based in actual data. Recently, different networks were developed to monitor ARGs, as the European Antimicrobial Resistance Surveillance System and the National Antimicrobial Resistance Monitoring System in the USA. However, these networks usually focus only on ARGs in human clinical isolates, and the presence of ARGs in aquatic systems has received much less attention. Although ARGs in recycled water schemes pose a risk, it must be considered to which extent they might be spread through water reuse. A good disinfection of the recycled water would kill the bacteria incorporating these resistances, thus would prevent their transfer to human or animals. In managing and preventing the risks posed by ARGs in the environment, controlling and reducing the consumption of antibiotics is a key measure. Nowadays, the consumption of antibiotics by humans and animals is being more and more controlled in order to reduce antibiotics releases to the environment and prevent the occurrence of antimicrobial resistances. On the other hand, it is also very important to ensure a good performance of the disinfection systems in place in order to reduce the risk posed by ARGs.

In the recent time, and in view of the poor performance of the disinfection treatments, a new UV treatment was installed at RISMAR scheme. In addition, in order to improve the performance of the chlorination system and to avoid clogging of the chlorine probes, a bigger sand filter was installed. After implementing these measures, CASSA and EDS commissioned analyses to external laboratories, and the results were satisfactory regarding the microbiological indicators. Then, our work helped to improve the post-treatments at RISMAR scheme.

Finally, and in view of the results obtained, regulations should not only focus on setting guideline values for *E. coli* or fecal coliforms. Other indicators, as *Clostridium* spores, bacteriophages and enterococci would be necessary in order to properly evaluate the performance of the recycled water schemes, drinking water, MAR or any other related water treatment trains. Enterococci are good indicators of the performance of the disinfection treatments, as they are rather resistant to them. *Clostridium* spores are a much more suited indicator of the possible presence of *Cryptosporidium* than *E. coli*, as demonstrated by Levantesi *et al.* (2010) and Costán-Longares *et al.* (2008). Bacteriophages are much more suited indicators for viral pathogens that the other indicators considered (Havelaar *et al.*, 1993; Costán-Longares *et al.*, 2008). The current water reuse RD (BOE, 2007b) sets guideline values for *E. coli* and helminth eggs. This latter group it is not recommended in any other guidelines elsewhere, as they are more typical of underdeveloped countries. Then, the requirement to measure helminth eggs and in a high frequency does not make sense. In addition, this measurement requires high volumes of water, which would be much better used to identify *Cryptosporidium* or other pathogens of interest. As it is difficult, time-consuming and expensive to measure pathogens in recycled water schemes including or not MAR, it is recommended to include different indicators in the regulations and try to adapt to what it really makes sense in the region or country.

8.1.2. Inorganic compounds and its mobilization from the aquifer

A good quantity of inorganic compounds was monitored in the framework of the RECLAIM WATER project. Here only the ones that could pose a risk or have a special relevance are going to be discussed.

Among the inorganic compounds that would not meet the drinking water Spanish legislation and could pose a risk if the water is used as drinking water there are nickel, chromium, arsenic and manganese.

Regarding manganese, the final treated water would not meet the guideline value set in the drinking water Spanish legislation, but this would not pose a risk for the human health. As discussed in section 5.5.3.14, the guideline value is more restrictive than the one set in other regulations, and it might have probably been set for aesthetic considerations. Manganese concentration was much higher in the recovered water than in the recharged water, as there was mobilization from the aquifer, as explained in section 5.5.3.14. This manganese mobilization has been widely described for RBF sites (Bourg and Bertin, 1993; Petrunic *et al.*, 2005; Oren *et al.*, 2007; de Vet *et al.*, 2010; Cikurel *et al.*, 2012), being one of them Shafdan, in Israel (Oren *et al.*, 2007; Cikurel *et al.*, 2012), which was also one of the RECLAIM WATER project sites. Manganese mobilization from the aquifer occurs by reductive dissolution of manganese oxides. Manganese oxides reductive dissolution is generally thought to occur concurrently with the reductive dissolution of iron oxides, and it is difficult to differentiate between microbial mediated and iron mediated reductive dissolution of manganese oxides (Petrunic *et al.*, 2005). In any case, this indicates a certain degree of anaerobiosis in the aquifer, and an overall evaluation of the redox status of the aquifer using a tool developed by Jurgens *et al.* (2009) indicates that in the aquifer there are mixed oxic-anoxic conditions. Manganese mobilization created a collateral problem, which was clogging of the chlorine probes due to the oxidation of the dissolved manganese (Mn^{2+}) when it came into contact with the chlorine dosed for disinfection. Then, in order to remove the black precipitates formed and to reduce clogging problems of the chlorine probes, a sand filter was installed for the final treated water. This was a temporary solution, and a bigger filter was installed later on. However, the real solution is to control the manganese dissolution from the aquifer, by controlling the DOC concentration in the infiltration water.

For arsenic, although it was not monitored during the RECLAIM WATER project, it was determined by CASSA, EDS and ACA, and its presence in wells close to the one where the water is pumped out indicates that it would be highly possible to find arsenic in the recovered water. During the development of the present work, the conditions of the aquifer did not seem to favour arsenic release to groundwater. There appear to be two distinct triggers that can lead to release of arsenic: one is the development of high pH (>8.5) and oxidising conditions in semi-arid or arid environments as a result of the combined effects of mineral weathering and high evaporation, and the high pH leads either to desorption of arsenic from metal oxides, or to prevention of arsenic from being adsorbed; the other one requires strong reducing conditions at near neutral pH, typically found in young alluvial aquifers, with very small sulphate concentrations (typically 1 µg/L or less), and arsenic is mobilised by reductive dissolution of iron and manganese oxides (van Helvoort *et al.*, 2006). Then, as in the aquifer there was never a pH higher than 8.5 (maximum measured pH value was 8.2), and sulphate concentrations were very high (average of 172 mg/L), it seems that arsenic release was not enhanced. CASSA and EDS, in view of the presence of arsenic in wells close to the one where water is recovered, and in order to use the final treated water to fill in the swimming pool and be prepared in case it was used for drinking water in the future, installed a specific filter to remove arsenic in the final treated water (a post-treatment). This was executed two years after the samplings were performed.

Nickel is a different case. Nickel concentration in the final treated water not only would be unacceptable for drinking water but it could also pose a risk in case peak values increased in frequency and magnitude. At the moment of developing the present work, only one sample out of 16 slightly exceeded the guideline value, posing a very low risk for the considered end points. The risk arises in the river water, where the guideline value was exceed by 46% of the samples measured. This definitely could pose a risk for the species living in it. Nickel sources at RISMAR scheme are the discharges of the Ripoll River WWTP and other WWTPs upstream, as well as diffuse pollution that can get to the river. A very high peak of nickel was detected in river water after the discharges (river mixture 2), and higher values than the guideline value were usual in the treated effluent discharges. Besides, river sediments were analysed (data not shown) and important concentrations of nickel were detected (ranging between 28-33 mg/kg), thus indicating a deposition/absorption of nickel in them. Then, in order to prevent build-up of pollution in the aquifer and accumulation in the river sediments (that could lead in a later desorption and release to the aquifer), and to decrease the risk posed to the living species in the river, the discharges of the WWTP should be controlled, as well as other possible discharges upstream the river.

For chromium, the concentrations measured in the final treated water do not pose a risk for the end points considered, neither for the human health even if it is used as drinking water. The risk arises from the peaks detected in the WWTP effluent, which could reach the aquifer and pose a risk if they increase. These peaks did not influence the river water chromium concentration, which was kept similar before and after the discharges (but for a peak in river mixture 2, not coinciding with the peaks in the treated wastewater). However, build-up of chromium may have occurred in the river sediments, where concentrations ranging from 46-58 mg/kg were measured (data not shown). Then, similarly to nickel, in order to prevent a higher accumulation in the river sediments, that could lead in a later desorption and release to the aquifer, the discharges of the WWTP should be controlled, as well as other possible discharges upstream the river.

Apart from chromium and nickel, there are other inorganic compounds whose concentrations were affected by the treated effluent discharges, which are cadmium and molybdenum, and to a lesser extent, copper and iron. Regarding cadmium and molybdenum, peaks in the treated wastewater were not subsequently detected in the river water neither the groundwater. However, as the peaks are much higher than the guideline values set, attention should be paid in order to prevent its presence in the treated wastewater, similarly to chromium and nickel. For copper and iron, even if their concentrations in the treated wastewater were a bit higher than in the river water or the groundwater, they would still meet the guideline values set in the Spanish legislation, as their concentrations are in general very small at RISMAR scheme. They are also diluted with the river water.

As pointed out before, discharges from WWTPs upstream the river can also affect the quality of the river water and the groundwater. Lead, for instance, was always below the guideline values set in the Spanish legislation at all sampling points, but for one measured value in the river water before the discharges. Then, it must be considered that not only treated wastewater discharges can affect the river water and groundwater quality, but also the river itself can carry discharges from WWTPs upstream that can affect the quality.

For aluminium and mercury, data from CASSA, EDS and ACA were used to perform the risk assessment, as they were not measured in the framework of the RECLAIM WATER project. According to the data consulted, they did not pose a risk for any of the end points considered. However, it would be interesting to monitor at some point the whole RISMAR scheme for these inorganic compounds, in order to completely rule out that they do not pose a risk for human health. Even more important would be to monitor the whole RISMAR scheme for beryllium, vanadium and tin, as they also have guideline values set in the Spanish legislation and they were not controlled in the framework of the RECLAIM WATER project neither by CASSA, EDS nor ACA. For these inorganic compounds no information at all is available.

It is also important to discuss at this point that the Spanish legislation, as well as other regulations, set guideline values in which there can be mistakes or incongruences that need to be considered. For cadmium, the Spanish water reuse RD 1620/2007 (BOE, 2007b) asks to follow RD 849/1986 (BOE, 1986) and the RD 907/2007 (BOE, 2007a) for pollutants. However, for guideline values, the RD 907/2007 requests to follow the environmental quality rules, which were previously regulated on RD 995/2000 (BOE, 2000) and are currently consolidated and set in the RD 60/2011 (BOE, 2011). Considering all these regulations, requested to be followed “inside” the Spanish water reuse RD, the guideline value for cadmium is 0.25 μg/L as annual average, with a maximum of 1.5 μg/L. Apart, the Spanish drinking water RD 140/2003 sets a guideline value of 5 μg/L. As a result, the Spanish water reuse RD is more restrictive than the Spanish drinking water RD. The guideline value set in the Spanish drinking water RD is similar to the drinking water guideline value set by the US EPA, and it is an incongruence to request higher water quality for park irrigation than for drinking water regarding cadmium. Another case is selenium, for which the guideline value is of 1 µg/L, and a guideline value of 10 µg/L is set in the Spanish drinking water RD. For selenium, it seems to be a typographic mistake in RD 995/2000, repeated in the RD 60/2011, as the RD 995/2000 recommends to use ICP as a reference method and sets a limit of detection for this method of 10 µg/L, which is in contradiction of setting a guideline value of 1 µg/L. These mistakes and/or incongruences need to be carefully evaluated by legislators, as there are many implications for a water reuse system or drinking water treatment plants. Besides, it was very difficult to gather all the guideline values that would apply for water reuse, as in the RD 1620/2007 it is asked to consult specific sections of other regulations, that might set or not a guideline value, and these regulations also ask to consult other regulations for the guideline values, as it has been explained above. So, in the end, to gather the guideline values applicable for the water reuse scheme it was necessary to check and integrate the values set in at least 4 different RDs, and in case two different guideline values were set for the same compound in the different regulations, the most restrictive one was followed for the purposes of the present work. This is misleading and time-consuming for facilities and companies operating water reuse systems, and also for researchers.

8.1.3. Salinity

Salinity could pose a risk for the crops grown in the area. Sodium and chloride can trigger foliar injury if sprinkler irrigation is used, and, overall, the salinity can reduce the yield of the crops. Turfgrass present in the Taulí Park could also be affected by the salinity, if the species/varieties used are not adapted to salinity. In order to reduce the salinity in the final treated water, there are only three possibilities: to add a post-treatment, like reverse osmosis or electrodyalisis reversal; to mix the final treated water with mains water; or to implement a program to reduce the salts entering the wastewater, similar to what Israel established (WHO, 2006b). At RISMAR scheme, the calculated consumption of energy per cubic meter of water recovered is rather high, as explained in section 5.5.13. As this is intended to be a low-cost system, it would not be appropriate to install advanced post-treatments to reduce the salinity content, as energy consumption would be much higher. Besides, the disposal of the brine formed, which is highly saline, creates another problem to solve. Regarding mixing with mains water, it would neither make sense at RISMAR scheme, as one of the goals of the system was to reduce the use of potable water for uses where it is not necessary. It would be interesting to try to apply a similar strategy to the one applied in Israel, which would also help to prevent other hazardous compounds ingress to wastewater, like inorganic and organic compounds. Measures that could be applied to RISMAR scheme, taking as a reference the case of Israel (WHO, 2006b) could be:

- Requirement to use potassium salts instead of sodium in ion exchangers in certain industries and regulation on the quantity of salts used for ion exchangers regeneration.
- Guidelines for controlling salt discharges from slaughterhouses (which in RISMAR scheme would be applied to textile industries).
- Limitations on industrial brine discharges to the sewer.
- Public education on the use of salts in dishwashers and the use of cleaning products.
- Limits on the concentration of salts in all industrial effluents.

Apart from reducing the salts content in the source water (wastewater), other strategies can also be followed in order to cope with the salinity of the final treated water, which include adapting the irrigation method, leaching practices, crop selection and blending water supplies (FAO, 1985; NRMMC–EPHC–AHMC, 2006).

The irrigation method plays an important role in salinity impact, as chloride and sodium injury (in sensitive species) can result from direct leaf absorption during overhead sprinkler irrigation.

Then, using drip irrigation, subsurface irrigation and furrow irrigation is recommended. In case overhead sprinkler irrigation needs to be used, certain management practices have been successful to counter it (FAO, 1985):

- Irrigate at night: night sprinkling is quite effective in reducing or eliminating both sodium and chloride toxicity due to foliar absorption and has also reduced the problem of foliar deposits. As humidity generally rises at night and winds decrease, the rate of evaporation and concentration is reduced.
- Avoid periods of high wind: hot, dry winds are a major factor in the concentration, absorption and deposition. Avoiding these periods for overhead sprinkling minimizes the problem.
- Control sprinkler drift: in hot, windy areas, the downwind drift from sprinkler irrigation presents a risk. To avoid drift during high risk periods requires sprinkling during early morning, late evening and night hours. Mist nozzles or high pressure impact sprinklers should be avoided in windy areas where drift is likely to be a problem.
- Increase sprinkler rotation speeds: slowly rotating sprinklers allow appreciable drying on the leaves between sprinkler rotations. More frequent or continuous wetting of foliage allows less drying of leaves and less absorption than intermittent wetting and drying.
- Increase rate of application: a higher rate of application may reduce damage by reducing the total period of crop wetting.
- Increase droplet size: sprinkler heads that apply a larger droplet size will result in less absorption as small droplets are more subject to evaporation and wind drift. While increasing droplet size may reduce the effect from foliar absorption, a further assessment needs to be made of the effect of droplet size on soil dispersion, which could cause greater runoff.
- Plant during cooler seasons: crops planted in the cooler season have a better chance to mature before the sodium or chloride can accumulate to high enough concentrations to cause toxicity damage.

Leaching can be used either to prevent a salinity problem or to correct the problem after it has been recognized from plant symptoms or damage to the crop. Salts can be leached by applying more water than that needed by the crop during the growing season. This extra water moves at least a portion of the salts below the root zone by deep percolation (leaching). However, the soil must have good drainage properties, to ensure salts can move downwards from the upper root zone through the lower root zone (FAO, 1985; NRMMC–EPHC–AHMC, 2006).

Dealing with the crops and plants grown, they can be selected in order to withstand the salinity of the water. As explained before, the plants grown in the Taulí Park, but for the grass, are tolerant to salinity. And even for the grass, it can be easy to select species or cultivars resistant to salinity. Regarding the crops grown in the area, there are crops that could be susceptible to salinity (e.g. bean and chickpea), and experience a reduced growth due to it. Then, if different crops need to be grown in the area and the final treated water is used for irrigation, it would be wise to select crops tolerant to salinity. On the other hand, there are periods in which the plants and crops are more severely affected by salinity, like germination. In these stituations, blending is recommended. For RISMAR scheme, this would mean to mix the final treated water with potable water or groundwater or use directly these kinds of water during germination and juvenile plant growth (FAO, 1985; NRMMC–EPHC–AHMC, 2006).

8.1.4. Nutrients

Most plants require nitrogen in greater quantity than any other soil nutrient. Nitrogen is generally found in high concentrations in treated wastewater, and at RISMAR scheme, treated wastewater and river water presented higher nitrogen concentrations than the recovered water. The final treated water presented an average nitrogen concentration of 4.2 mg/L. Sensitive crops may be affected by nitrogen concentrations above 5 mg/L, and yield or quality can be reduced. Most other crops are relatively unaffected until nitrogen exceeds 30 mg/L (FAO, 1985). On the other hand, the sensitivity of crops varies with the growth stage. Nitrogen requirements are high during early growth stages, while at flowering and fruiting stages it should be considered if the nitrogen present is excessive for the crop. Among sensitive crops there is grape, which is grown in Sabadell. Yields are often reduced and grapes may be late in maturing and present lower sugar contents with high nitrogen concentrations. At RISMAR, the average final treated water nitrogen concentration is lower than 5 mg/L, and 22% of the samples would present a higher nitrogen concentration, with a maximum of 11 mg/L. However, these higher nitrogen concentrations do not coincide with the fruiting period (end of summer and beginning of autumn), so table grape would not be affected.

Phosphorus is a major nutrient required for plant growth but can cause eutrophication in aquatic ecosystems. At RISMAR, treated wastewater discharges present concentrations of phosphorus that can enhance algal growth in the Ripoll River, and eutrophication has indeed occurred there. Eutrophication poses a risk for the fauna living in the river, as a higher phosphorus concentration triggers algal blooms, with the subsequent oxygen depletion. Cyanotoxins have not been measured in the framework of the RECLAIM WATER project neither by ACA, CASSA nor EDS. However, as the blooms detected in the river water are of macrophytes, the risk of having cyanobacterial blooms is very low, as macrophytes inhibit the growth of cyanobacteria by consuming phosphorus and competing for light (He *et al.*, 2014; Seto *et al.*, 2013; Wang *et al.*, 2012). In case there were cyanobacterial blooms, they could pose a risk for the humans and animals. So in the future it would be interesting to monitor cyanotoxins, especially if the final treated water was to be used as drinking water. CASSA and EDS were working to improve the performance of the secondary treatment at the Ripoll River WWTP, in order to reduce the concentration of phosphorus in the treated wastewater discharges. Besides, the construction of wetlands that would be treating around 8-10% of the Ripoll River water is a project undertaken by EDS and that is currently in place, as wetlands are functioning. Wetlands may have helped in reducing the nutrients concentration in the river water.

Potassium is also a major nutrient for plant growth. Considering its average concentration in the final treated water (15 mg/L), it would probably need to be added. WHO guidelines for water reuse in irrigation (WHO, 2006b) indicate that approximately 185 kg of potassium per hectare are required. Assuming an application rate of 5000 m^3/ha.year of final treated water, 75 kg of potassium per hectare would be applied, thus being much lower than the required. Then, potassium would need to be added to the crops.

8.1.5. Organic compounds

Organic matter was present at RISMAR scheme in the different sampling points. Several indices were used to characterize the gross organic matter, and of them, dissolved organic carbon (DOC) was a very important one. DOC plays an important role in MAR, as it can trigger the mobilization of metals from the aquifer, stimulate microbial growth and pollute the aquifer. Around 50% of DOC present in the river water was removed through riverbed filtration process. However, DOC was still present in the recovered water, and its presence in the aquifer can pose a risk. The only way to prevent aquifer pollution is to reduce the organic matter content in the infiltration water, as its concentration is very high in it. Typical wastewater gross organic matter indices are BOD_5 and COD. For these indices, a reduction along the treatment train was also observed, although in the recovered water they could still be measured, especially COD, thus indicating the presence of organic matter that could not degraded or is difficult to degrade.

Micropollutants are gaining more and more importance in the recent years when dealing with RBF, MAR, recycled water schemes and any other water related schemes. There is a huge amount of works devoted to them and their presence in MAR and in RBF (e.g. Heberer *et al.*, 2008; Maeng *et al.*, 2011; Schmidt *et al.*, 2007; Hoppe-Jones *et al.*, 2010, Massman *et al.*, 2006). In the framework of the RECLAIM WATER project, pharmaceutically active compounds (PhACs), disinfection by-products (DBPs), complexing agents and the EDC BPA were measured. CASSA and EDS measured other groups of organic compounds, including VOCs, pesticides and DBPs. For VOCs and pesticides, the very few compounds that could be detected in the recovered water or the final treated water were present at very low concentrations, which would not pose a risk for the human health neither for the environmental end points considered. Then, the only groups that will be considered in the present discussion are PhACs, DBPs, complexing agents and BPA.

Regarding the presence of PhACs in drinking water, WHO (2011b) devoted a specific monographic on them. The main conclusion was that adverse human health impacts are very unlikely from exposure to the trace concentrations of PhACs that could potentially be found in drinking water. According to WHO (2011b), concentrations of PhACs in surface water and groundwater sources impacted by wastewater discharges were typically less than 0.1 µg/L (or 100 ng/L) and detection in drinking-water was rare (well below 0.05 µg/L). Then, for those substances that had been detected, the concentrations were more than 1000-fold less than the lowest therapeutic dose, so the risk posed to the human health would be very low. Comparing these reported values to the ones obtained at RISMAR scheme for the recovered water, we can only find three PhACs with concentrations higher than 0.1 µg/L: carbamazepine, diatrizoate and iopromide. For all of them, calculated RQ values were equal or inferior to 1.8×10^{-3}, thus indicating that the risk for the human health was extremely low.

Different is the case of DBPs. In the framework of the RECLAIM WATER project, nitrosamines were investigated in one sampling campaign, and the measured concentrations could pose a risk for the human health. Similarly, CASSA and EDS measured THMs in the final treated water, and the measured concentrations could also pose a risk for the human health. In both cases, there are concerns regarding the guideline values set and used, as they differ between different regulations and guidelines or they lack (see sections 5.5.6.3 and 5.5.6.4). This makes difficult to completely evaluate the risk posed by these groups of compounds. In any case, although there are discrepancies on the increased risk of cancer due to ingestion of these compounds, what it is true is that THMs are inhaled while swimming, and a study by Kogevinas *et al.* (2010) indicated that THMs concentration in exhaled breath was seven times higher after swimming than before, thus indicating a concentration factor in the body after swimming. THMs were investigated in the final treated water by CASSA and EDS, and in the river water and the groundwater (in different wells of the area) by ACA (data not shown). THMs concentration in the final treated water is high, but they are not detected or detected in very low concentrations in the river water and the groundwater. This is explained by the presence of organic matter in the recovered water and the posterior disinfection by chlorination, which enhances their formation in the final treated water. For nitrosamines, NDMA was detected in the treated wastewater and the river water and NMOR in all sampling points. This ubiquitous presence was also reported by different authors. Wang *et al.* (2011) detected nitrosamines in source water and in drinking water. Van Huy *et al.* (2011) detected nitrosamines in river water and groundwater samples. And in a review by Nawrocki and Andrzejewski (2011), measured concentrations of different nitrosamines in wastewater and drinking water are gathered. At RISMAR scheme, nitrosamines should be investigated in more detail, in order to understand their probable concentrations in the final treated water and the risk posed by them.

Complexing agents benzotriazole and its derivatives tolyltriazoles are an interesting case to discuss. This group of compounds did not pose a risk at RISMAR scheme, considering the results of the only sampling campaign performed. However, there is controversy regarding the guideline values set for drinking water and/or for human health. The guideline value used to calculate the RQ values is set in a report by the DME EPA (2013), in which they gather a wide range of toxicological studies results and end up issuing a guideline value of 20 μg/L, derived from a LOAEL (Lowest Observed Adverse Effect Level) of 335 mg/kg body weight per day, which was considered the worst case from the studies evaluated. This LOAEL is similar to the one reported as a worst case in DECOS (2000), of 295 mg/kg body weight per day. However, in DECOS (2000) it is explained that although the data evaluated was inconclusive, there is the chance that these compounds are carcinogenic, and taking this possibility into consideration, they propose a NOAEL (No Observed Adverse Effect Level) of 9.8×10^{-4} mg/kg body weight/day, which the Australian Guidelines for Augmentation of drinking water supplies (NRMMC–EPHC–NHMRC, 2008) use to derive a drinking water guideline value of 7 ng/L. If this guideline value is considered, the calculated RQ values for these compounds in the final treated water would range between 41 and 346, extremely high and indicating a very high risk for the population. On the other hand, reported measured concentrations for these complexing agents in the literature are regularly in the μg/L range. Janna *et al.* (2011) measurements ranged from 0.84 to 3.6 μg/L for benzotriazole and 2.7 to 5.7 μg/L for tolyltriazoles in the effluents of WWTPs in the United Kingdom, and from 0.6 to 79.4 ng/L and <0.5 to 69.8 ng/L, respectively, in drinking water for the same country. Loos *et al.* (2010a) sampled groundwater from 164 different locations in Europe, and benzotriazole and tolyltriazoles were detected in more than 50% of them, up to 1.03 and 0.52 μg/L, respectively. Giger *et al.* (2006) sampled rivers and lakes from Switzerland, and measured benzotriazole concentrations ranging from 0.16 to 6.3 μg/L, while tolyltriazole concentrations ranged from 0.01 to 0.91 μg/L. Loos *et al.* (2010b) sampled the Danube River and maximum concentrations detected were 0.38 μg/L for benzotriazole and 0.13 μg/L for tolyltriazoles. Weiss and Reemtsma (2005) sampled different waters in Berlin, and the treated WWTP effluents average concentrations were of 9.6 μg/L for benzotriazole and 2.0 μg/L for tolyltriazole, while in Lake Tegel were 0.9 and 0.2 μg/L respectively, and under the limit of detection in groundwater. Measured concentrations at RISMAR scheme are in accordance to the literature. Then, if the guideline value of 7 ng/L (set taking into consideration the possible carcinogenicity of these compounds) is considered, then the risk is high in Europe and everywhere. In addition, it is interesting to note that Janna *et al.* (2011) in their study also point out that these complexing agents are part of dishwashers, in powder as well as in tablets, and the amounts present in them are in the range of 0.5 to 60 mg per 20 g of powder/tablet. These high concentrations were estimated to account for 30% of the inputs in the WWTPs, and as such, increase their concentration in the effluent. To sum up, complexing agents deserve a more in-depth study in order to have a clearer idea of their concentrations at RISMAR scheme, as only one sampling campaign was performed, and even more important is to understand their toxicity and possible carcinogenicity, in order to set proper guideline values in the regulations.

Bisphenol A (BPA) is one of the chemicals produced in highest volume worldwide, thus its presence in water is widespread. In light of uncertainties about the possibility of adverse human health effects at low doses of BPA, WHO (2011c) jointly with FAO held an expert meeting on this compound, to assess the safety of BPA. The main conclusions were that BPA has a low acute toxicity, it is not likely to be genotoxic and information is not sufficient to rule out its carcinogenicity. Controversy still lies on its reproductive and developmental toxicity, as well as neurotoxic and neuroendocrine effects. Maximum detected concentrations in drinking water, according to WHO (2011c), were of 1 μg/L, and comparing to the intake of bisphenol in food and its migration from cans, jars and bottles, the amounts ingested through drinking water can be considered too low to pose a risk for the human health. Reported average and maximum concentrations in European groundwaters were of 0.079 μg/L and 2.3 μg/L, respectively (Loos *et al.*, 2010a), while in European rivers were of 0.025 µg/L and 0.32 µg/L, respectively (Loos *et al.*, 2010b). The maximum value measured in the recovered water at RISMAR scheme was of 0.054 µg/L, thus in the lower range of the reported values for European groundwaters. However, the maximum value measured in river water was 0.71 µg/L, more than double the reported maximum value for European rivers. In contrast, a study by Kaspryk-Holden *et al.* (2009) reported concentration of BPA in river waters in England ranging from 6 to 68 µg/L, so two orders of magnitude higher than in the study by Loos *et al.* (2010b). These strong differences in results obtained at different locations for surface waters were also identified in a review by Flint *et al.* (2012). In any case, the values measured at RISMAR scheme would not pose a risk for the human health, with the current knowledge on BPA.

Micropollutant effects in aquatic organisms, vertebrates and wildlife have been also extensively evaluated. Regarding the effect of PhACs in aquatic organisms, Quinn *et al.* (2008) used a cnidarian to test the toxicity of different PhACs. However, the concentrations at which acute toxicity was developed were of mg/L, while the concentrations measured in surface water and groundwater are at least 3 orders of magnitude lower. This also applies to RISMAR scheme aquatic organisms, because concentrations measured at the river water before and after the treated wastewater discharges were 3 orders of magnitude lower. A thorough review by Fent *et al.* (2006) compiled a huge amount of information regarding acute and chronic toxicity of different PhACs for humans and animals. Comparing environmental measured concentrations and concentrations causing ecotoxicological effects, the overall results indicated that acute toxicity would be unlikely, but under certain circumstances, adverse effects can occur, like the case of vultures in the Indian continent exposed to diclofenac (Fent *et al.*, 2006). For chronic toxicity, there is a general lack of data on pharmaceuticals, in particular in fish. Comparison of available chronic toxicity data with environmental concentrations indicate that, for most of the investigated pharmaceuticals, the measured concentrations are too low in aquatic systems to induce chronic effects on traditional laboratory organisms, such as inhibition of algal growth and reproduction in *Daphnia*. For diclofenac, measured concentrations are closer to the ones inducing an effect in fish, ranging from 1-5 µg/L in different studies (Fent *et al.*, 2006). At RISMAR scheme, diclofenac concentration at the river water ranged from 63 to 336 ng/L, always lower than the lowest dose at which chronic effects were detected. Another important group to consider is hormones in water-related ecosystems, which have oestrogenic effects at extremely low and environmentally relevant concentrations, thus posing a risk for aquatic organisms. At RISMAR scheme, oestrone E1 was detected in the Ripoll River water at concentrations ranging from 13.5 to 36.5 ng/L, while Camacho-Muñoz *et al.* (2010) estimated the predicted no effect concentration for oestrone E1 to be of 100 ng/L, taking a safety factor 1000 times lower than the toxic concentration reported for the most sensitive species tested. Then, it can be considered that the risk posed by oestrone E1 at RISMAR scheme is very low. Regarding BPA, Flint *et al.* (2012) reviewed its effects in a wide range of species. For most of them, effects of BPA were observed at exposures equal or higher than 1 µg/L, but there were some groups for which effects could be detected at lower concentrations, as for instance developmental inhibition in marine copepods and oestrogen synthesis inhibition in longchin goby at a concentration of 0.1 µg/L. At RISMAR scheme, BPA could not be detected in the final treated water, and the maximum concentration measured in the recovered water was of 0.054 µg/L, low enough for not posing a risk. However, in the river water the maximum concentration measured was of 0.71 µg/L, which could pose a risk for invertebrates.

Another important point to investigate is the combined effects of pharmaceutical mixtures, because some studies point out their synergies: while the individual compounds had not adverse effect at the tested environmental concentrations, their addition did in some cases (Fent *et al.*, 2006; Escher *et al.*, 2011; Kümmerer, 2009). The majority of studies regarding pharmaceutical mixtures were devoted to oestrogenic chemicals, with few exceptions on other classes of pharmaceuticals, and they generally confirmed synergies for pharmaceuticals from the same therapeutic class (Escher *et al.*, 2011). In the same line, the combined effects of pharmaceutical mixtures belonging to other groups of compounds as well as mixtures between groups should be also investigated.

Apart from the effects to the humans and animals, there is growing concern regarding the accumulation of organic compounds in crops and plants. Uptake of PhACs has been reported for carbamazepine in ryegrass, cucumber and soybean (Winker *et al.*, 2010; Shenker *et al.*, 2010; Wu *et al.*, 2010); ibuprofen, naproxen and clofibric acid in lettuce and spath (Calderón-Preciado *et al.*, 2012); antibiotics in lettuce, spinach, carrots and barley (Jones-Lepp *et al.*, 2010; Migliore *et al.*, 1996). When reviewing the results of these works in detail, all these studies but for Calderón-Preciado *et al.* (2012) tested concentrations higher than the ones present in final treated water at RISMAR scheme, reaching values of mg/L, and the compounds accumulated in the leaves and roots of the plant, not in harvestable parts of the crop. In the work by Calderón-Preciado *et al.* (2012) concentrations tested were very low, and compounds accumulated in the lettuce leaves, which is the harvestable part of the crop. In fact, the final treated water at RISMAR scheme would present concentrations higher than the ones tested in this work. However, experiments were developed not in real field/soil conditions, but in culture media, thus increasing the availability of the organic compounds and facilitating their accumulation in the plants. There are studies indicating the accumulation of PhACs in soils irrigated with reclaimed wastewater (Kinney *et al.*, 2006) and their biodegradation in them (Al-Rajab *et al.*, 2010), thus reducing the risk of being incorporated into the crops. In addition, a study by Migliore *et al.* (1996) applying sulfadimethoxine to barley indicated that the bioaccumulation rate was much higher on synthetic medium than in soil. Nevertheless, there is a need to clarify to which extent PhACs and other micropollutants bioaccumulate in crops in real field conditions and at concentrations found in final treated waters, and also to which extent they can be ingested later on by humans and animals. Other micropollutants for which studies have been found are complexing agents and BPA. In the work by Castro *et al.* (2001) benzotriazole uptake by sunflower grown in hydroponic culture was investigated. Results indicated that at concentrations equal or below 75 mg/L of benzotriazole the plants did not show a negative physiological effect, but when concentrations of benzotriazole were increased in the water, the growth and water uptake by the plant was decreased. However, from the agronomical point of view, it should be understood in which parts of the plant they are accumulated. In any case, the threshold concentration at which effects were observed was much higher than the concentrations measured at RISMAR scheme (four orders of magnitude higher). For BPA, again, tested concentrations in soybean by Qiu *et al.* (2013); in broad bean, tomato, durum wheat and lettuce by Ferrara *et al.* (2006) and in kiwi by Speranza *et al.* (2011) were much higher than the concentrations measured at RISMAR scheme (between three and four orders of magnitude higher), which would not pose a risk for the crops. Different responses were observed: increased/decreased growth (depending on the concentration tested), morphological changes, increase in stress responses, decrease in chlorophyll and photosynthesis. In any case, the effects of organic compounds should be tested at “real” concentrations and considering mixtures, in order to understand if they really pose a risk for the plants or not, and to which extent they accumulate in those parts of the plants that are eaten.

8.2. QMRA

QMRA has proven to be very useful in better understanding the risk posed by pathogens at RISMAR scheme. The creation of the different exposure scenarios, adapted to the uses of the final treated water, is very important in order to properly evaluate the risks, as well as a good knowledge of the treatment performance and the pathogens usually circulating among the population. A discussion of different aspects of the QMRA work, as well as comparing with other studies found in the literature is given below.

It is interesting to consider here the pathogens selected for the QMRA. In the present work, the pathogens selected were the ones recommended in the WHO and Australian guidelines. Each of them represents a group of pathogens, they account for a great proportion of the gastrointestinal disease in the population and there are have been outbreaks as well as many reported cases in Spain and Catalonia due to the ingestion of these microorganisms. However, apart from the pathogens selected (*Campylobacter*, rotavirus and *Cryptosporidium*), there are other pathogens that have caused outbreaks in Spain and Catalonia, and for which there are many reported cases of illness. Some of these pathogens have been also selected for QMRA purposes in other works, together with the pathogens selected in the current work (Westrell *et al.*, 2004; Armstrong and Haas, 2007; Mara and Sleigh, 2010a,b; Navarro *et al.*, 2009; Schönning *et al.*, 2007; Ashbolt *et al.*, 2005; Howard *et al.*, 2006; Ahmed *et al.*, 2010). Selecting other pathogens to develop the QMRA is always possible and makes sense as long as a dose-response curve is available and their incidence in the population has been reported. One of these pathogens is *Salmonella* non-typhoid causing. For this pathogen, 2441 cases were reported in 2009 and 1693 in 2010 only in Catalonia (CHD, 2010d), accounting for 31% and 27% of the gastroenteritis caused by a notifiable microbiological agent, respectively. Data from Spain indicate that the most abundant detected *Salmonella* was *Salmonella enteritidis*, and that 39% of the cases affected children under 5 years old. Another interesting pathogen to consider is Enterotoxigenic *Escherichia coli*. This pathogen is not often detected, but in Catalonia it has increased recently, with 8 cases detected in 2010 respect to 1 case in 2009 (CHD, 2010d), being 4 out of the 8 cases *Escherichia coli* O157:H7. Incidence of this pathogen in Catalonia was of 0.054 per 100,000 inhabitants in 2010, while in Europe was of 1.2 per 100,000 inhabitants in 2007 (CHD, 2010c). Although prevalence seems to be much smaller in Spain and in Catalonia, it is also interesting to be considered in QMRA. In 2009, 223 cases of shigellosis were notified in Spain (CNE, 2011), of which 96 were detected in Catalonia. The number of cases decreased in 2010 to 80 in Catalonia too. Then, *Shigella* seems to be another pathogen to track. Norovirus is an emergent pathogen in Catalonia. Fifteen declared outbreaks related to gastrointestinal illness due to this pathogen were identified in 2008 (CHD, 2010d). Gastroenteritis caused by adenovirus accounted for 189 cases in Catalonia in 2010, and respiratory illness caused by adenovirus accounted for 205 cases (CHD, 2010d). Overall, it is interesting to consider that gastrointestinal illness attack rate in the Catalan population was nearly 3% in 2009 (CHD, 2010b), while gastrointestinal illness caused by notifiable microorganisms represented only 3.5% of the gastrointestinal illness cases reported. This is due to the fact that only in few cases of gastrointestinal illness a detailed investigation of the etiological agent is conducted. Finally, *Legionella* has been a pathogen of concern in the recent years in Spain, and even the RD for water reuse (BOE, 2007b) considers specifically its determination for some water reuse cases. In Catalonia, 270 cases were reported in 2010 (CHD, 2010d), being *Legionella pneumophila* the most commonly detected. To sum up, there are other pathogens of concern that could be used in the future to develop and update the QMRA performed in the present work.

Overall, comparing the results obtained for the three pathogens evaluated, rotavirus was the pathogen posing the highest risks, followed by *Cryptosporidium* and *Campylobacter*, being the latter the one posing the lowest risk. This is in agreement with other published works on QMRA (Alcalde, 2012; Ayuso-Gabella *et al.*, 2010; Page *et al.*, 2010; Toze *et al.*, 2009; Westrell *et al.*, 2004). These results regularly obey to the different resistance to disinfection treatments by the groups of pathogens. Then, viruses (e.g. rotavirus) are regularly more resistant to disinfection treatments than protozoa (e.g. *Cryptosporidium*), and both groups are much more resistant to disinfection treatments than bacteria (e.g. *Campylobacter*). For MAR, the trend followed is the same (Ayuso-Gabella *et al.*, 2010; Page *et al.*, 2010; Toze *et al.*, 2009). In any case, it is important for a QMRA study to include at least one representative for each of the pathogen groups, in order to have a better understanding of the risks posed by the different groups.

Dose-response models exist nowadays for most of the pathogens of interest, thus enabling to perform the QMRAs. These models have been created using data from animal or human feeding trials or with outbreak data, being the latter, in general, better fitted to reality. Although many models exist nowadays to represent the dose-response for different pathogens, these models usually consider the general population. Subpopulations at risk, as might be the immunocompromised, do not have, in general, well fitted models. For the present work, constants used by Makri *et al.* (2004) and Cummins *et al.* (2010) were considered, in order to better reflect the dose-response in the immunocompromised population. However, these "adapted" constants for the models are not available for all the pathogens. These works were devoted to *Cryptosporidium* only. For the other pathogens, considering the relationship between the constant used for the regular population and the constant used for the immunocompromised population, an extrapolation was done for the other pathogens evaluated, as there was no data available in the literature. This could have been an overestimation of the risks posed by the other pathogens in the immunocompromised population. It has been well studied in persons with AIDS that infection with *Cryptosporidium* leads to gastroenteritis in virtually all cases, and cryptosporidial diarrhoea is often severe, persistent, and profoundly debilitating, being life-threatening for most of them (Havelaar and Melse, 2003; Perz *et al.*, 1998). However, the same may not be applicable to rotavirus, *Campylobacter* or other pathogens. Then, although a higher sensitivity to pathogens in immunocompromised populations is expected, it is not clear to which extent this affects the dose-response curves for all the pathogens.

Regarding exposure, the present work has considered many different scenarios, which is not the case in most of the literature consulted. QMRA is regularly performed for drinking water, with some exceptions devoted to water recycling and/or MAR (Jolis *et al.*, 1999; Westrell *et al.*, 2004; Page *et al.*, 2010; Toze *et al.*, 2010; Ayuso-Gabella *et al.*, 2011) or recreational water (Diallo *et al.*, 2008; Baron, *et al.*, 1982; Pintal *et al.*, 2010; Rijal *et al.*, 2011). Regarding wastewater, treated wastewater or reclaimed water reuse for agriculture, most of the QMRA publications available only focus on the crop consumption scenario (Bastos *et al.*, 2008; Forslund *et al.*, 2010; Hamilton *et al.*, 2006; Mara *et al.*, 2007; Shuval *et al.*, 1997; Van Ginneken and Oron; 2000). The results obtained for the QMRA indicate that not only the crop consumption scenario needs to be evaluated but the aerosols ingestion, as the risk was indeed higher for the aerosols ingestion than for the crop consumption. Then, when using wastewater, treated wastewater or reclaimed water for irrigation, developing a QMRA considering only the crop consumption scenario would underestimate the risk posed by the practice. Cross-connection in dual network systems is another scenario to be considered, and that it may pose a high risk too. Another point to consider regarding the exposure are the assumptions taken for the ingestion dose and frequency. As far as possible, literature data have been used in the present work, but in some cases assumptions need to be done, and need to be the closer to the reality as possible. However, when there is a high uncertainty it is recommended to always follow a conservative approach for the QMRA calculations.

For the final risk characterization, it is necessary to have a good knowledge of the treatment effectiveness. Results obtained by the empirical risk characterization versus the theoretical risk characterization are rather different, and the difference between both characterizations only lies in the considered efficiency for the treatment train. A good knowledge of the real performance of the system is very important, and literature data should be only used in those cases where no information is available or a recycled water scheme including or not MAR is being designed. The risk results obtained for the different MAR sites evaluated in Page *et al.* (2010) and Ayuso-Gabella *et al.* (2011) are rather different depending on the type of MAR, pre-treatments and post-treatments used. In general, in both works the aquifer subsurface passage is very important, and it is valued as another barrier part of the treatment train.

QMRA can end in the risk of infection calculation or go a bit further by calculating the risk of developing a disease. The second option has been preferred in the present work, as not all infections end up in developing a disease. To do so, DALYs have been used, and disease burdens (DALYs per disease case) and ratios disease-infection were necessary for the calculations. The drawback is that these ratios and disease burdens are difficult to be found in the literature, especially for non-typical pathogens. Then, these burdens of disease and ratios disease-infection should be included in the published guidelines not only for the typical pathogens but for others too, in order to help in developing the QMRA studies.

Another point of discussion is the statistical index used to evaluate the risk. The 95^{th} percentile can be used as a measure of the robustness of the mean human health risk assessment. Where both the mean and the 95th percentile DALYs results are acceptable considering the risk benchmark value ($<1.0\times10^{-6}$ DALYs) it can be determined that the risk assessment is reasonably robust (Page *et al.*, 2010). The median value is widely used in QMRA works; however, using it as a reference for the risk evaluation, only ensures that 50% of the time the risk will be lower than the reference risk level. Then, it is more conservative to calculate and use the mean and the 95th percentile values for risk assessment discussions. Then, this should be also taken into consideration when issuing guidelines for QMRA.

8.3. Suitability of MAR as an additional barrier to water treatment

MAR by means of RBF has proven to be an additional barrier for water treatment, and credit should be given as an engineered treatment more. Different authors have been requesting to give credit to MAR and put it to the level of any other engineered treatment, considering it for regulations and guidelines (Hiscock and Grischek, 2002; Page *et al.*, 2010; Dillon, 2005; Dillon *et al.*, 2010; NRMMC-EPHC–NHMRC, 2009). The results obtained in many different works as well as the ones obtained in the present work support this request. The MAR guidelines (NRMMC-EPHC–NHMRC, 2009) are also a first approach to aid in using MAR and consider it as another treatment.

Regarding pathogens removal, the RBF had an important effect, being in fact the most important barrier at RISMAR scheme, as shown by QMRA and sensitivity analysis results, because disinfection did not work properly at the moment of developing the sampling campaigns and studies. Removal rates obtained for pathogens and microbiological indicators were similar to other RBF sites. In a RBF site in New Delhi, India, Sprenger *et al.* (2009) investigated the presence of adenovirus, norovirus, hepatitis A and E viruses, and all of them could be detected in the river water while they could not be detected in the recovered water. This is in concordance with the no detections of the investigated viral pathogens in the recovered water of RISMAR scheme, although for RISMAR scheme the river water was not investigated. In any case, the presence of viral pathogens in treated wastewater and river water at RISMAR scheme can be acknowledged, considering that these are typical pathogens reported by health authorities and that the WWTP that sends the treated wastewater to the river receives the wastewater from a hospital. Regarding protozoa, Weiss *et al.* (2005) obtained similar removals for both *Cryptosporidium* oocysts and *Giardia* cysts in three RBF sites across the US. The average *Cryptosporidium* oocysts removal thanks to the RBF process across the US sites ranged from 0.9 to 1.5 $\log_{10}$ units, while at RISMAR scheme the average removal for the three sampling campaigns was of 0.9 $\log_{10}$ units. For *Giardia* cysts, average removal in the US sites ranged from 1.3 to 1.9 $\log_{10}$ units, while at RISMAR scheme the average removal for the three sampling campaigns was of 1.8 $\log_{10}$ units.

For indicators, RBF had an important effect too, with very high removals in general for all of the indicators investigated. Weiss *et al.* (2005) measured different indicators for three RBF sites in the US, obtaining similar results to the ones obtained at RISMAR scheme. Total coliforms were monitored only in one of the three sites, and removal ranged from 5.5 to 6.1 $\log_{10}$ units depending on the well used, while at RISMAR scheme average and maximum removals were of 3.4 and 6.1 $\log_{10}$ units. For *Clostridium* spores, Weiss *et al.* (2005) obtained 4.5 to more than 4.9 $\log_{10}$ units removal in two of the RBF sites, while in the other one the removal ranged from 0.4 to 2.3 $\log_{10}$ units. At RISMAR scheme, average removal was of 2.5 $\log_{10}$ units, with a maximum of 3.5, similar to one of the sites investigated by Weiss *et al.* (2005). Bacteriophages removal was also similar to RISMAR scheme in the three RBF sites in US, ranging from 3.2 to more than 4.4 $\log_{10}$ units (Weiss *et al.*, 2005), and being on average of 3.4 $\log_{10}$ units at RISMAR scheme, with a maximum of 5.1 $\log_{10}$ units. This is also in accordance to the results obtained by Sprenger *et al.* (2009), ranging from 3.3 to 4.8 $\log_{10}$ units removal in an Indian case study.

Inorganic compounds did not suffer reductions due to RBF, but for iron, that seemed to be diluted while mixing with groundwater or being deposited in the river sediments. In contrast, barium and manganese increased in the recovered water. For barium, the increase could be due to releases from the sediments, as the recovered water had similar concentrations that the river water before the discharges, and the river water after the discharges presented a lower concentration due to dilution with the treated wastewater, in which barium concentration was very low. The case of manganese has been widely discussed previously in section 8.1.2, and it is a typical case of inorganic compounds mobilization from the aquifer due to the RBF process. Then, for RBF a reduction in inorganic compounds cannot be acknowledged, but it must be considered instead the possibility of inorganic compounds mobilization from the aquifer, which is one of the drawbacks of this technology (Hiscock and Grischek, 2002).

Salinity remained unchanged after RBF. In case the recovered water had a higher proportion of the initial "pristine" water of the Miocene aquifer, salinity could be lower. Nevertheless, the recovered water is from the alluvial aquifer, that is fed by the Ripoll River and the RBF process cannot do anything to reduce the salinity levels. It has been reported that among the undesirable effects of RBF there could be increases in hardness (Hiscock and Grischek, 2002), but this has not been the case at RISMAR scheme.

For nutrients there is an important reduction thanks to the RBF. For nitrogen, there are different pathways. Nitrite is regularly quickly oxidized to nitrate; nitrate can be diluted with the groundwater or reduced through denitrification, and ammonia can be assimilated by bacteria and algae living in the river sediments, transformed to nitrate under aerobic conditions in the aquifer or diluted with groundwater. Whichever is the pathway followed, nitrogen suffers globally a strong reduction thanks to the RBF process. Median reductions at RISMAR scheme thanks to RBF were of 69% for nitrite, 35% for nitrate and 74% for ammonia, while maximum removals obtained were of 89%, 75% and 88% respectively. Grischek *et al.* (1998) studied the denitrification in a RBF site in the River Elbe in Saxony (Germany), and according to their results, nitrate decrease thanks to RBF could range between 18 and 48% depending on the well monitored and the distance from the riverbed. Wang *et al.* (2007) studied the removal of nitrate and ammonia thanks to RBF in a highly polluted river in China. Their results indicated that a removal of around 51% was obtained for ammonia and from 23.5 to 25.5% for nitrate. Then, similarly to RISMAR scheme, ammonia was much more eliminated than nitrate. It has been reported that among the undesirable effects of RBF there could be increases in ammonia (Hiscock and Grischek, 2002), but this has not been the case at RISMAR scheme, as in fact, it has been reduced considerably. For phosphorus, its removal thanks to RBF is related to phosphate precipitation in the form of calcium, iron or aluminium phosphate in the ground. Phosphate removal occurred at RISMAR scheme, with a median removal of 49% and a maximum removal of 79%. De Vet *et al.* (2010) also observed orthophosphate reduction in a RBF in the Netherlands, and attributed this reduction to adsorption on iron (oxy)hydroxides present in the aquifer.

Organic matter was also reduced thanks to RBF. Around 50% of DOC present in the river water was removed through RBF. This removal is in accordance to published removals for riverbed filtration (Maeng *et al.*, 2011; Hoppe-Jones *et al.*, 2010; Singh *et al.*, 2010). Regarding SUVA, similar results to the ones obtained at RISMAR scheme were obtained at other RBF sites, as reported by Maeng *et al.* (2011). In most RBF sites SUVA increases after soil passage, suggesting a preferential removal of aliphatic organic matter during soil passage (Grünheid *et al.*, 2005).

Most of the trace organic compounds investigated were removed by RBF, except for some specific cases that will be discussed. In general, PhACs were strongly reduced thanks to RBF. For antibiotics, different studies on MAR sites reported strong removals (Heberer *et al.*, 2008; Maeng *et al.*, 2011) but for sulfamethoxazole. However, when MAR was performed through RBF, sulfamethoxazole removals seemed to be higher than with other types of MAR according to the results obtained by Grunheid *et al.* (2005) at Lake Tegel. At the same site, natural RBF and MAR by infiltration basins is present, and the removals were much higher for the RBF (80%) than for the infiltration basin (53%). At RISMAR scheme, sulfamethoxazole removals ranged from 67% to 88% in the two sampling campaigns performed, being in the same range to the removals reported for the RBF site by Grunheid *et al.* (2005). Clarithromycin exhibited a strong removal at RISMAR scheme, ranging from 89% to 95% in the two sampling campaigns performed, and in accordance to results obtained by Schmidt *et al.* (2007) in European RBF sites. In general, all antibiotics investigated were reduced by RBF at RISMAR scheme, and a good part of them could not be detected in the recovered water. Investigated anticonvulsants at RISMAR scheme were carbamazepine and primidone. Both of them could be detected in the recovered water and were poorly reduced by the RBF treatment. Similar results were obtained by Hoppe-Jones *et al.* (2010) and Massman *et al.* (2006) at other RBF sites, and were also reported in the reviews by Maeng *et al.* (2011) and Verstraeten *et al.* (2002). As it was indicated in section 5.5.6.3, anticonvulsant drugs are very persistent trace compounds (Rauch-Williams *et al.*, 2010), and this explains their presence in the recovered water and their poor removal. In field and column studies, carbamazepine has been found to be very persistent, with travel times (Drewes *et al.*, 2003) and reduction half-times (Löffler *et al.*, 2005) of more than one year. Anti-inflammatories investigated included diclofenac, ibuprofen and naproxen. Ibuprofen could not be detected in any of the sampling points, whereas diclofenac and naproxen underwent strong reduction by RBF at RISMAR scheme (up to 95%). Hoppe-Jones *et al.* (2010) could not detect diclofenac in the recovered water, and for ibuprofen and naproxen the reductions through RBF were also strong. Lipid regulators were removed during RBF at RISMAR scheme, being clofibric acid not detected in the recovered water and bezafibrate was reduced between 64% to 89%, depending on the sampling campaign. This is in accordance with reported removals by Maeng *et al.* (2011). Iopromide, one of the X-ray contrast media investigated, presented a very high removal after RBF, higher than 95% for the three sampling campaigns. Similar results were obtained by Grunheid *et al.* (2005) at Lake Tegel. In general, X-ray contrast media are compounds that RBF can easily remove, with published removals higher than 80% (Maeng *et al.*, 2011). This is in accordance to results obtained at RISMAR scheme for the investigated compounds, being two of them not detected in the recovered water. However, diatrizoate showed an irregular presence at RISMAR scheme, and removal cannot be acknowledged for RBF. For hormones, results obtained at the only sampling campaign performed at RISMAR scheme were nearly identical to the ones obtained by Zuehlke *et al.* (2004): 17-estradiol (E2) and 17-ethinylestradiol (EE2) were not detected in the river water, and oestrone (E1) was removed over 80% in their work and 99% in our sampling campaign at RISMAR scheme. Maeng *et al.* (2011) report several works in which different hormones are investigated and removals are high for MAR processes, being in most of the cases completely removed. The endocrine disruptor BPA seemed to be also removed by RBF, in different degree in the sampling campaigns when it was measured at RISMAR scheme. Hoppe-Jones *et al.* (2010) and Verstraeten *et al.* (2002) also reported removals for this compound during RBF.

Moving to other groups of organic compounds investigated, complexing agents did not follow a clear pattern at RISMAR scheme, as concentrations in the river water were higher than in the treated effluent discharges, and in the recovered water they seemed to be only slightly reduced.

In a work by Weiss and Reemtsma (2005) in Berlin, benzotriazole was detected at 0.2 µg/L in the bank filtrate, while tolyltriazoles were under the LOD (0.01 µg/L). At RISMAR scheme, values were much higher, being benzotriazole detected in the recovered water at a concentration of 1.9 µg/L and tolyltriazoles ranged from 0.2 to 2.0 µg/L. Again, these are results of only one sampling campaign; more analyses should be performed in order to state their concentrations in the recovered water and the extent to which RBF can remove them at RISMAR scheme. Regarding nitrosamines, Patterson *et al.* (2011) examined the fate of trace organic compounds, including NDMA and NMOR, in columns packed with aquifer materials from a MAR site. NDMA and NMOR did not degrade under either aerobic or anaerobic conditions, but it must be taken into consideration that these results were not from a real MAR site neither from a RBF one. In contraposition, Zhou *et al.* (2009) observed the fate of NDMA that had been discharged with water reclamation plant effluents to a MAR system by infiltrating water over 7 years, and found that in situ biodegradation of NDMA occurred in the groundwater. Around 80% of NDMA mass discharged with the effluents was biodegraded under anaerobic conditions. At RISMAR scheme, only NMOR could be detected in the recovered water, and the concentration was lower than in the infiltration water. NDMA, detected in the river water, was not detected in the recovered water at RISMAR scheme. These results are in accordance to results by Zhou *et al.* (2009), but they correspond to only one sampling campaign, so more sampling campaigns should be undertaken to understand the fate of nitrosamines during RBF at RISMAR scheme.

RBF had an important effect in removing suspended solids and in reducing turbidity of the river water. Average removals were higher than 80% for suspended solids, and the recovered water turbidity was always below 1 NTU. These results are much better than the ones obtained by Singh *et al.* (2010) in a RBF site in India.

Removal of pathogens, organic matter and different compounds in the subsurface could be increased with a longer residence time in the aquifer. Although the residence time in the aquifer is unknown, it was estimated to be of a maximum of 14 days, considering the results obtained after a microbiological pollution event occurred in the Ripoll River, which in less than 2 weeks was already detected in the recovered water from the aquifer. Then, when performing the QMRA from the theoretical point of view, the aquifer performance was modelled as a function of the decay rates of each pathogen and the residence time. The PDF constructed for the residence time considered a short one, thus having a high impact in the results. Then, first of all would be necessary to clearly determine the residence time in the aquifer, and in the future, it would be interesting to find other wells further away of the recharge area that could ensure a higher residence time in the aquifer and from which the water could be recovered. However, the cost of using these different wells and developing the project should be carefully assessed, as for RISMAR scheme the idea is to maintain a low-cost system. Another possibility in order to improve the RBF and to avoid future clogging of the riverbed would be reducing the microbiological load, organic matter and pollutants in the Ripoll River water and the Ripoll River WWTP effluent. Regarding the Ripoll River WWTP, the treatments performed are pretty well suited to fulfil the Spanish legislation on wastewater treatment and discharges to the environment. However, the secondary treatment performance regarding phosphorus removal was below expectations and could be improved. Since the development of the RECLAIM WATER project, the results could have been improved considerably. For the Ripoll River, two areas of work can be defined. On one hand, the construction of wetlands that would be treating around 8-10% of the Ripoll River water is a project undertaken by EDS and that is currently (2013) in place, as wetlands are functioning. In any case, in order to strongly reduce the microbiological load, organic matter and pollutants in the Ripoll River wetlands should treat a higher percentage of water. Another area for work is to improve the performance of the WWTPs upstream the Ripoll River, as the river water already carries on the pollutants before the Ripoll River WWTP effluent discharges. Although an agreement between the municipalities that the Ripoll River crosses was already achieved in order to protect the river and the ecosystems dependant on it, and that there are many initiatives and associations working in order to keep the river values, it is still an area of concern to improve the quality of the effluent discharges by WWTPs upstream the Ripoll River.

In any case, the suitability of MAR, in this case by RBF, as an additional barrier for water treatment has been widely demonstrated in the present work, as well as in the cited works in other RBF sites.

8.4. Risk management

Risk management has been widely applied and included in drinking water systems, and recently it has been applied to water recycling systems, including or not MAR. In the literature, risk management in water recycling systems has mainly been devoted to set CCPs and to apply the HACCP tool (Dewettinck *et al.*, 2001; Westrell *et al.*, 2004; Fournier, 2006; Ayuso-Gabella *et al.*, 2008; Alcalde, 2012). There are few works in which a whole risk management plan is detailed, and those that are available, are related to drinking water. Then, to our knowledge, the risk management plan developed in the present work, that goes further than setting CCPs and applying the HACCP tool, and applies the frameworks given in the Australian Guidelines for Water Recycling and MAR guidelines, is one of the few available research works related to recycled water schemes including MAR. However, this does not necessarily mean that recycling water facilities do not have their own risk management plan, but the contents are not regularly published, as they are usually considered “sensitive information”. This was the case of the work by Ayuso-Gabella *et al.* (unpublished draft) on Bolivar ASR site in Australia.

In the risk management the results of the risk assessment and QMRA, if it has been developed, are “put into practice” in the day-to-day work of the water recycling plants. It is important to develop a risk management plan in order to control those steps in the process that are key to reduce risks. Although QMRA it is not requested to be performed in the Australian Guidelines for Water Recycling or MAR guidelines, when developing a risk management plan questions of quantitative nature arise, which QMRA can prove useful in addressing (Signor, 2007). Those questions are related to:

- What is the health target?
- Which are the priority hazards?
- What is the significance of hazardous events?
- Is the overall treatment in place appropriate to produce reclaimed water which meets the health and environmental targets for its final uses?
- Which are the appropriate critical limits and target criteria?
- How much monitoring is necessary?
- Which level of corrective and preventive actions is needed?

To answer these questions, not only QMRA but some other tools are available. First of all, it is necessary to have clear and reliable guideline values and health targets in order to properly manage the risk. In case regulations and/or guidelines are available in the country where the risk management plan is being developed, those must be followed, and sometimes, the administration may ask for additional controls and reports on the results obtained. This implies that regulations and/or guidelines need to be based in sound science results and need to be carefully set, otherwise they are misleading and useless. Health targets could be a tolerable disease burden or be translated into water quality targets and/or performance targets. Setting the health target is the responsibility of the regulator and the target set for drinking or reclaimed water is the starting point for risk management by the water supplier (Medema and

Smeets, 2004). It has been discussed in previous sections the mistakes found in Spanish regulations and that they sometimes include parameters/indicators that do not give "interesting" information. Thus, the guideline values used for the development of a risk management plan sometimes are difficult to set, and require searching in the scientific literature and in regulations and/or guidelines from other countries. This has been the case in the present work. Once health targets and guideline values are defined, it is the turn to evaluate if the system complies with them, and QMRA can also be very helpful for this, although a deterministic risk assessment (as it has been done for chemicals) may be enough most of the times.

Guideline values and health targets need to be translated into critical limits and target criteria. This has been done in the present work; in this case, well-known guideline values for basic parameters have become the critical limits for the system, and at some points, target criteria have been set too, considering a value that could be considered as signal or alarm to more closely evaluate the performance of the system. However, setting of critical limits is complex and may have a significant impact on safety and costs, and arriving at the optimal limits will need several iterations, using practical experience and on-going scientific insights to further improve the operation of the water system (Medema and Smeets, 2004). They require that the people in charge of setting them have a strong expertise on the recycled water scheme including MAR. Practical experience is required too. Then, the critical limits set in the present work can be considered as a basis on which to build the future optimal critical limits for RISMAR scheme.

In case guideline values and health targets are exceeded, corrective and preventive actions must be implemented. In the present work, corrective and preventive actions have been proposed, some of them already in place at RISMAR scheme. It is important that as part of the risk management plan these corrective and preventive actions are set, in order to quickly solve the problems and/or prevent their occurrence. An example can be the implementation of new UV treatment at RISMAR scheme. It was initially installed as a corrective action, because it was observed that the UV equipment previously used was not working properly. But at the same time, this proved to be a good preventive action, avoiding water of becoming unsafe under rainfall events. Under regular conditions, infiltration through the riverbed reduces pathogens concentration. During rainfall events, the situation is different, as pathogens transport (especially viruses) is quick; they are desorbed and they are not retained as efficiently as in the riverbed (Cardús, 1991), so the groundwater may become contaminated. It is not possible to correct the efficacy of the soil passage during these events, but it is possible to enhance the UV or to increase the chlorine concentration dosed. The level of enhancement of UV treatment and/or chlorination can be tailored to the level of contamination found in the groundwater under such conditions.

One of the biggest challenges that a risk management plan needs to face is to anticipate hazardous events. Then, this means that to prevent their occurrence, an evaluation of "what can go wrong" should be done. Reported outbreaks in the literature are regularly related to hazardous events, which were directly linked either to periods of poorer source water quality, failures in water treatment plant performance or pollutants entrance into the system downstream of the major points of treatment, together with deficiencies in the water quality monitoring and response protocol (Signor, 2007). Besides, the human error is always possible. In the work by Wu *et al.* (2009) it is included a good review of drinking water incident cases and their corresponding human errors, that may serve as a basis and to be prepared to "what can go wrong" in drinking water treatment facilities as well as in water recycling ones. The importance of hazardous events and human errors is something that does not only apply to the water treatment area, but in general, to any kind of industry. As Paté-Cornell (2012) points out in her work, some industries seem to wait for an accident to take risk management measures, and regulators appear to have the same attitude. The excuse is often that these events are so rare as to be unimaginable, but signals can be observed, suddenly or gradually. In any case, those hazardous events need to be accounted for in the framework of risk management plans, in order to prevent them and apply quick corrective actions in case they occur. QMRA can assist in ranking these events, investing resources in those that may pose a really significant risk, and comparing the risk of different hazardous agents and hazardous events in alternative scenarios (Medema and Smeets, 2004). In the present work, hazardous events, like the pollution found in the aquifer after a strong rain event and the contamination found in the water tank located by the mine have been evaluated, integrated in the QMRA and addressed in the risk management plan, by means of setting critical limits and corrective and preventive actions. In the future, this should be enlarged with other potential hazardous events, that might have been captured in the literature or that may be envisaged by the Operators or other people working at RISMAR scheme. Although we cannot anticipate all the hazardous events that may happen, we can learn from the ones that have already happened and implement corrective and preventive measures. Brainstorming to "imagine" the events that may happen is recommended, and it requires the presence of different representatives from the company.

Monitoring programs are also an important point of the risk management systems. It is often very difficult to define which analyses, where and when to be performed, and at the same time, ensure that the costs are not too high that prevent to invest in other areas to improve the system. In the present work, the CCPs and POAs to control have been defined, and also the recommended monitoring program and frequency of sampling. Again, this is a first approach that needs to be re-evaluated in the future and put into an economic and resources perspective, yet it is recommended to implement it first and refine it later. The results of the monitoring program are the basis for the re-evaluation of the critical limits and target criteria, as well as important information for the QMRA and the risk assessment, that are recommended to be reviewed and updated after a certain period of time. One of the recommendations regarding the monitoring program is that in the future the aquifer should be continuously controlled by probes reaching different levels in it, and this could also be applied to the distribution system. The data sent are real-time data, which enables to take quick action in case hazardous events occur in the system. Besides, the location of probes in the aquifer would help in understanding the evolution of the groundwater and the effects of the recharge in it. However, data needs to be analysed in a timely manner and it does not preclude to keep the regular monitoring, as in general, online continuous monitoring data analysis should only complement traditional water sampling, rather than replace it (Nilsson *et al.*, 2007).

Overall, developing a risk management plan is a powerful tool for the water companies in order to better control their recycled water schemes including or not MAR.

9. CONCLUSIONS

The conclusions obtained from the present work are directly linked to the previous objectives set:

Objective 1: Evaluate the risk associated to the recycled water scheme including MAR.

- A recycled water scheme including riverbed filtration (RBF) can be an effective low-cost system for water reclamation and reuse. RBF, which is a type of Managed Aquifer Recharge (MAR), proved to be crucial to reduce the risk posed by most of the detected hazards.
- According to the overall results of the risk assessment, the risk posed by the different hazards is acceptable for the uses in place, but it would not be acceptable for drinking water and further investigations and post-treatments would be necessary for this use.
- The guidelines used as a basis to develop the risk assessment (Australian Guidelines for Water Recyling and Managed Aquifer Recharge Guidelines) are a useful tool to systematically evaluate the risk posed by the different hazards in a recycled water scheme including MAR.
- For pathogens, a probabilistic risk assessment (Quantitative Microbial Risk Assessment, QMRA) is preferred in front of a deterministic one to evaluate a recycled water scheme including or not MAR. The deterministic risk assessment proved to be insufficient to conclude that the risk to human health was or not acceptable.
- Not only human pathogens but plant pathogens should be considered when performing risk assessments in recycled water schemes including or not MAR, especially if the water is further used for crop or park irrigation.
- Antibiotic resistance genes (ARGs), although are not pathogens, should be also considered in future risk assessments in recycled water schemes including or not MAR, as they can pose a risk for the human health. Then, models for dose-response on ARGs are necessary.
- For a recycled water scheme including MAR, inorganic compounds must be evaluated carefully, especially if the final treated water is to be used as drinking water. During subsurface treatment, inorganic compounds can be mobilized from the aquifer and reach the recovered water, as for instance manganese. Then, it is necessary to evaluate which inorganic compounds are mobilized and if their concentrations are high enough to pose a risk for the human health, the environment or the equipment.
- Salinity is a hazard that could pose a risk for the crops and soils in case the water needs to be reused for irrigation. However, not only the irrigation water but the soil status, leaching fraction, irrigation practices, crops cultivated, infiltration rate and other factors play an important role for this use.
- Organic compounds are an area of concern nowadays, and their presence in the treated wastewater introduces a source of them in the recycled water scheme. However, most of them suffer a strong reduction through RBF and subsurface treatment, thus not posing a risk for the human health or the environment.
- DBPs are reduced along the recycled water scheme, but they can also appear if chlorination is used to disinfect the final treated water. Although RBF strongly reduces the organic matter present in the infiltration water, it can be still present in the final treated water in quantities enough to trigger the formation of DBPs.
- Although organic compounds are reduced through a recycled water scheme including or not MAR, the synergies of different groups of organic compounds in the final treated water should be investigated.

- According to the literature, crops can uptake and accumulate PhACs in experimental conditions, but it is not clear if this effect could happen at environmental concentrations, and in which parts of the crop would accumulate. Then, their effect should be tested at real concentrations and using reclaimed waters.
- RBF strongly reduces turbidity and particulates, as well as pathogens, nutrients and organic matter. These hazards are progressively reduced along the treatment train, thanks to the multiple barrier approach, in which RBF plays an important role. This supports the request by many authors of treating MAR as an additional treatment.
- Overall, when using treated wastewater to increase the infiltration in a RBF system it is crucial to know the river water quality before and after the discharges of treated wastewater, as pollution may already be present in the river and it must not be attributed to the treated wastewater discharges.
- In a recycled water scheme including MAR there are specific hazards related to the MAR practice, which need to be evaluated, namely: radionuclides; pressure, flow rates, volumes and groundwater levels; contaminant migration in fractured rock and karstic aquifers; aquifer dissolution and stability of wells; and aquifer and groundwater-dependent ecosystems. These hazards would not be evaluated in a recycled water scheme not including MAR. The risk posed by these hazards was evaluated, and it was acceptable. However, attention should be paid at manganese dissolution, and to the potential mobilization of other inorganic compounds like arsenic.
- For the hazard energy and greenhouse gases considerations, this is not directly a hazardous component for any of the end points considered; however, it is important for recycled water projects including or not MAR to evaluate the energy consumption and compare with other options before undertaking them. This hazard was only included in the MAR guidelines, and not present in any other guidelines consulted and used. A further discussion and agreement should be taken on this hazard, as it would not only apply to MAR schemes but to any recycled water scheme.
- To properly develop a risk assessment, it is crucial to have robust and reliable guideline values, as, in general, the current regulations are not enough. Besides, guideline values must be contrasted and selected according to a scientific basis, as mistakes have been found in the current Spanish regulations, and some guideline values are too restrictive or loose comparing to guideline values in other countries. Guideline values are necessary for all the compounds potentially found in water and need to be adapted to the type of water and uses of it. Discrepancies between different regulations and guidelines and even the lack of a guideline value in many compounds make the risk assessment difficult or even impossible.

Objective 2: Application of a probabilistic quantitative microbial risk assessment (QMRA) to the recycled water scheme including MAR, in order to better understand the risks posed by pathogens in the system.

- QMRA proved to be a useful tool to clarify the risk posed by pathogens in different uses of the final treated water.
- The RBF is a very important barrier to reduce the risk posed by pathogens in a recycled water scheme including RBF.
- Poor performance of disinfection treatments can be detected by analyzing different indicators and using higher volumes of water, as far as possible. QMRA can also help to unravel low performance of disinfection treatments.

- The other treatments of the recycled water scheme were more or less important depending on the pathogen selected. It is important to consider the post-harvest decay for the crop consumption scenario, as it also was important to reduce the risk.
- The drinking water scenario poses the highest risk, while cross-connection, swimming and the immunocompromised population would be the following ones.
- When developing a QMRA for a recycled water scheme including or not MAR, if the final treated water is used for irrigation not only the crop consumption scenario needs to be evaluated but the aerosols ingestion, as the risk is indeed higher for the aerosols ingestion than for the crop consumption.
- The immunocompromised population should be considered in risk assessments, and more data would be necessary in order to set dose-response constants for them.
- Empirical versus theoretical risk characterizations render slightly different results, and this should be taken into consideration in future QMRAs. Although in most cases real data from the system are lacking, it is important to use as much as possible data from the site, in order to have a more realistic result.
- Rotavirus was the pathogen posing the highest risks, followed by *Cryptosporidium* and *Campylobacter*.
- It is important for a QMRA study to include at least one representative for each of the pathogen groups, in order to have a better understanding of the risks posed by the different groups.
- Burdens of disease and ratios disease-infection should be included in the published guidelines not only for the typical pathogens (*Campylobacter*, *Cryptosporidium* and rotavirus) but for others too, in order to help in developing the QMRA studies.
- Mean and 95th percentile should be calculated in the risk characterization and should be used in risk assessment discussions, as a conservative approach. The median value is widely used in QMRA works; however, using it as a reference for the risk evaluation, it only ensures that 50% of the time the risk will be lower than the reference risk level. Then, this should be also taken into consideration when issuing guidelines for QMRA.

Objective 3: Develop a risk management plan for the recycled water scheme including MAR.

- To develop a risk management plan for a recycled water scheme including MAR it is fundamental to develop a thorough risk assessment before. The results obtained from the risk assessment must be integrated in the risk management plan, in the form of defined monitoring points, targets and critical limits for the hazardous compounds, in order to properly control the system.
- Setting critical limits and target criteria is a complex process that needs to include experts in the area. Critical limits and target criteria may need to be often reevaluated, using practical experience.
- Corrective and preventive actions must be set and identified in a recycled water scheme including MAR. Preventive measures regularly include each of the treatments applied in the multiple barrier system, as well as other ones like source water protection, design options adopted in the system and restrictions on the distribution system.
- Validation of processes is an important part of the risk management plan, as it ensures that the treatments implemented will consistently produce water of the expected

quality. Validation is common area in the medical industry, but it is not as common in the water one.

- When developing a risk management plan, especially if it is done outside the organizations running the recycled water scheme including MAR, sensitive data may have not been facilitated and some of the real practices may be unknown. However, a risk management plan can still be developed, including recommendations for those elements for which information is lacking.
- Hazardous events may be difficult to be anticipated, but literature on this area and practical experience from the recycled water scheme can be used to implement corrective and preventive actions to avoid them.

To sum up the key conclusions obtained for this work:

- Hazard and risk-related analysis are not only tools that should be used in drinking water schemes but also in recycled water ones, including or not MAR.
- MAR needs to be considered as a further barrier to treat water in the framework of a recycled water scheme.
- For pathogens risk assessment, QMRA studies (probabilistic risk assessments) should be developed as far as possible, instead of deterministic risk assessments.
- A thorough risk assessment is the basis to develop risk management plans, applied to a recycled water scheme or not.
- Risk management plans need to be developed in conjunction with different stakeholders, and including experts in the area.

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APPENDIX A: ENTRY LEVEL ASSESSMENT FOR MAR AT RISMAR SCHEME

Table A-1Entry-level risk assessment — Part 1: viability.

Attribute	Answer
1 Intended water use	
Is there an on-going local demand or clearly defined environmental benefit for recovered water that is compatible with local water management plans?	✓ Recovered water intended uses are park irrigation and street cleaning, marginally used for crop irrigation. In the future, other urban uses are contemplated.
2 Source water availability and right of access	
Is adequate source water available, and is harvesting this volume compatible with catchment water management plans?	✓ An adequate volume of treated wastewater is available; the treated wastewater is discharged to the Ripoll River on a regular basis, and riverbed filtration is maximized by discharging the water in different points.
3 Hydrogeological assessment	
Is there at least one aquifer at the proposed managed aquifer recharge site capable of storing additional water?	✓ The alluvial aquifer and the underlying Miocene aquifer are capable of storing additional water. Recharge of the alluvial aquifer will contribute to recharge the Miocene underlying aquifer. In addition, the enhanced recharge process will contribute to recover the aquifers levels, as both aquifers had been depleted due to previous high exploitation in the area.
Is the project compatible with groundwater management plans?	✓ The project is compatible with groundwater management plans.
4 space for water capture and treatment	
Is there sufficient land available for capture and treatment of the water?	✓ The Ripoll River WWTP was constructed to treat the wastewaters coming from the industrial area around and to restore the area. This WWTP is already treating the wastewater in order to discharge it to the Ripoll River. Sufficient land is available for capture and treatment of the water.
5 capability to design, construct and operate	
Is there a capability to design, construct and operate a managed aquifer recharge project?	✓ Capability exists between project partners to design, construct and operate the project. → Go to Part 2

Table A-2 Entry-level risk assessment — Part 2: degree of difficulty.

Question	Possible answers	RISMAR scheme answers	Difficulty
1 Source water quality with respect to groundwater environmental values			
Does source water quality meet the requirements for the environmental values of ambient groundwater?	If Yes — low risk of pollution is expected. If No — high maximal risk is likely. Expect Stage 2 investigations to assess preventive measures to reduce risk of groundwater contamination beyond attenuation zone (and size of attenuation zone).	No – environmental value of ambient groundwater is low, but the possibility to pollute it again with organic matter, faecal microorganisms, heavy metals and other micropollutants is high. It is necessary to assess the source water quality and the hydrogeology of the aquifer.	Moderate
2 Source water quality with respect to recovered water end use environmental values			
Does source water quality meet the requirements for the environmental values of intended end uses of water on recovery?	If Yes — low risk of pollution of recovered water is expected. However, this is not a sufficient condition for low risk due to aquifer reactions. If No — high maximal risk is likely. Expect Stage 2 investigations to assess this risk.	No – wastewater does not meet urban park irrigation, street cleaning and swimming pool water standards. Also, the risk posed to the Ripoll River and the aquifer needs to be evaluated. Require Stage 2 investigations to assess this risk.	Moderate
3 Source water quality with respect to clogging			
Is source water of low quality, for example: total suspended solids >10 mg/L, total organic carbon >10 mg/L, total nitrogen >10 mg/L? And is soil or aquifer free of macropores?	If Yes — high risk of clogging of infiltration facilities or recharge wells. Pre-treatment will need consideration regardless of answers to Q1 and Q2. If No — lower risk of clogging is expected. However, this is not a sufficient condition for low risk, due to dependence of clogging on aquifer characteristics that would be revealed by stage 2 investigations.	Yes – source water is of low quality, and could lead to a medium rate of clogging in the target sandy aquifer. Require Stage 2 investigations to assess this risk.	Moderate
4 Groundwater quality with respect to recovered water end use environmental values			
Does ambient groundwater meet the water quality requirements for the environmental values of intended end uses of water on recovery?	If Yes — low risk of inadequate recovery efficiency is expected. If No — some risk of inadequate recovery efficiency is expected.	No – ambient groundwater is not of quality enough the end used considered. Post-treatments (disinfection) are required. Human health risk due to pathogens must be addressed as part of stage 2 investigations.	Low

Question	Possible answers	RISMAR scheme answers	Difficulty
5 Groundwater and drinking water quality			
Is either drinking water supply, or protection of aquatic ecosystems with high conservation or ecological values, an environmental value of the target aquifer?	If Yes — high risk of groundwater pollution if recharged by water if answer to Q2 is No. If No — low risk of groundwater pollution is expected.	No – target aquifer is too saline for use as drinking water supply, and the presence of microorganisms and heavy metals could compromise the human health. Besides, the target aquifer does not support aquatic ecosystems with high conservation value, although it does support aquatic ecosystems.	Low
6 Groundwater salinity and recovery efficiency			
Does the salinity of native groundwater exceed: (a) 10000 mg/L, or (b) the salinity criterion for uses of recovered water?	If Yes to both — high risk of achieving only low recovery efficiency. Aquifer hydraulic characteristics, especially layering within the aquifer will need careful examination in Stage 2. If Yes to only (b) — moderate risk of low recovery efficiency is expected. If No to both — low risk of low recovery efficiency.	No – ambient groundwater salinity is high but appropriate for park irrigation and street cleaning, as well as for swimming pool water.	Low
7 Reactions between source water and aquifer			
Is redox status, pH, temperature, nutrient status and ionic strength of groundwater similar to that of source water?	If Yes — low risk of adverse reactions between source water and aquifer is expected. If No — high risk of adverse reactions between source water and the aquifer is possible, and will warrant geochemical modelling in Stage 2.	No – redox status, nutrient status, and ionic strength of source water is different to that of groundwater. Require Stage 2 investigations to assess this risk.	Moderate
8 Proximity of nearest existing groundwater users, connected ecosystems and property boundaries			
Are there other groundwater users, groundwater–connected ecosystems or a property boundary near (within 100–1000 m) the MAR site?	If Yes — high risk of impacts on users or ecosystems is possible, and this will warrant attention in Stage 2. If No — low risk of impacts on users or ecosystems is likely.	Yes – wells currently used by factories in the area, and targeting the same alluvial aquifer and the Miocene aquifer. However, both aquifers are unusable for drinking water. Require Stage 2 investigations to assess this risk.	High

Question	Possible answers	RISMAR scheme answers	Difficulty
9 Aquifer capacity and groundwater levels			
Is the aquifer confined and not artesian? or is it unconfined, with a watertable deeper than 4 m in rural areas or 8 m in urban areas?	If Yes — low risk of water logging or excessive groundwater mound height is expected. If No — high risk of water logging or excessive groundwater mound height is expected.	No – target aquifer is unconfined, with a watertable deeper than 8 m, located in an urban area and not artesian. Require Stage 2 investigations to assess this risk.	Moderate
10 Protection of water quality in unconfined aquifers			
Is the aquifer unconfined, with an intended use of recovered water that includes drinking water supplies?	If Yes — high risk of groundwater contamination from land and waste management. If No — lower risk of groundwater contamination from land and waste management.	No – target aquifer is unconfined, but uses of recovered water do not include drinking water supplies.	Low
11 Fractured rock, karstic or reactive aquifers			
Is the aquifer composed of fractured rock or karstic media, or known to contain reactive minerals?	If Yes — high risk of migration of recharge water is expected. There is a need for an enlarged attenuation zone, beyond which pre-existing environmental values of the aquifer are to be met. Dissolution of aquifer matrix and potential for mobilisation of metals warrant investigation in Stage 2. If No — low risk of the above is expected.	No – the target aquifer is not composed of fractured rock but contains reactive minerals. Mobilisation of metals has also happened (manganese). Require Stage 2 investigations to assess this risk.	Moderate
12 Similarity to successful projects			
Has another project in the same aquifer with similar source water been operating successfully for at least 12 months?	If Yes — take validation and verification data from the existing project(s) into account when designing the current project and the Stage 2 investigations and subsequent risk assessments. If No — expect that all uncertainties will need to be addressed in the Stage 2 investigations.	No – all uncertainties will need to be addressed in Stage 2 investigations.	Moderate

Question	Possible answers	RISMAR scheme answers	Difficulty
13 Management capability			
Does the proponent have experience with operating MAR sites with the same or higher degree of difficulty, or with water treatment or water supply operations involving a structured approach to water quality risk management?	If Yes — low risk of water quality failure due to Operator experience. If No — high risk of water quality failure due to Operator inexperience. The proponent is recommended to gain instruction in operating such systems (e.g. a MAR Operator's course or aquifer storage and recovery course) or engage a suitable Manager committed to effective risk management in parallel with Stage 2, to reduce precommissioning residual risks to low.	No – proponents have no experience with similar MAR operations. However, proponents have experience in water supply operations involving a structured approach to water quality risk management. Managers from the representatives of the different parties implicated have been involved in Stage 2 investigations, to reduce precommissioning residual risks to low.	Moderate
14 Planning and related requirements			
Does the proposed project require development approval; is it in a built up area; built on public, flood-prone or steep land; close to a property boundary; contain open water storages or engineering structures; likely to cause public health or safety issues, nuisance from noise, dust, odour or insects, or adverse environmental impacts?	If Yes – Development approval process will require that each potential issue is assessed and managed. This may require additional information and steps in design. If No – Process for development approval, if required, is likely to be considerably simpler.	Yes – project requires development approval. Require Stage 2 investigations to provide additional information.	Moderate

APPENDIX B: DATA TABLES FOR THE RISMAR SCHEME

The data summarised in the tables are from the RECLAIM WATER project. The data analysis includes:

- n: number of samples
- min: minimum value of the samples
- median: median value of the samples
- mean: mean value of the samples
- max: maximum value of the samples
- 95^{th}: 95^{th} percentile value of the samples

When a value is under the LOD, it is reported as inferior (<) to the LOD. The reference values used to compare are the ones set in the Spanish regulations, and detailed in section 4.2. These guideline values are also included in different columns of the tables.

Besides, there are two additional columns in which the risk is shaded in a different colour. In one column it is evaluated if the mean value of the samples is inferior to the guideline value, and in the other one, if the 95^{th} percentile value of the samples is inferior to the guideline value. For those columns, the colour coding is as follows:

- Green: the mean or 95^{th} percentile value of the samples for a determined parameter measured is below all the guideline values set in the Spanish legislation for the different reuse options.
- Orange: the mean or 95^{th} percentile value of the samples for a determined parameter slightly exceeds one of the guideline values set in the Spanish legislation for the different reuse options; then, they do not fulfil one of the reuse options but they fulfil the other ones. Further explanations are given in the risk assessment section (section 5.5).
- Red: the mean or 95^{th} percentile value of the samples for a determined parameter exceed more than one of the guideline values set in the Spanish legislation for the different reuse options. If there is only one guideline value set for that parameter and it is exceeded, then the risk is also shaded in red.
- Blank: no guideline value is given for that parameter in the Spanish legislation.

Table B-1 Data for composite treated wastewater sampling point (S1 C).

Parameter	**Units**	**n**	**min**	**median**	**mean**	**95th**	**max**	**SD**	**RD 1620/ 2007 UUR**	**RD 1620/ 2007 ARFC**	**RD 1620/ 2007 IR**	**RD 1620/ 2007 MAR**	**RD 140/ 2003 DW**	**RD 742/2013 BWSP**	**mean <GV**	**max <GV**
Alkalinity	CaCO$_3$ mg/L	15	194	271	276	324	327	33								
Bacteriophages	pfu/100mL	NA	NA	NA	NA	NA	NA	NA								
Barium	µg/L	14	10	18	19	28	30	7,0	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	15	236	330	336	395	398	40								
BOD Total	O$_2$ mg /L	12	3,0	5,5	6,2	12	15	3,2	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	14	249	289	300	360	401	37	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	14	< 0,10	< 0,10	0,19	0,58	0,75	0,19	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	14	65	74	77	91	96	9,2								
Carbonate	mg/L	15	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA								
Chloride	mg/L	15	161	323	342	506	513	91	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟧	🟧
Chromium	µg/L	14	< 10	12	33	127	202	53	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟥
Clostridium spores	cfu/100mL	NA	NA	NA	NA	NA	NA	NA					0 (3)		NA	NA
Cobalt	µg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O$_2$ mg /L	26	21	46	46	74	94	16								
COD Total	O$_2$ mg /L	26	27	55	60	101	111	21	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	14	4,8	8,9	8,6	13	13	2,8	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	12	< 10	< 10	< 10	< 10	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	14	< 0,20	0,37	0,39	0,68	0,79	0,16	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O$_2$ mg /L	14	10	14	14	17	18	2,4								
Electrical conductivity	dS/m	28	1,0	1,9	1,9	2,3	2,4	0,32		3			2.5		🟩	🟩
Enterococci	cfu/100mL	NA	NA	NA	NA	NA	NA	NA					0		NA	NA
Escherichia coli	cfu/100mL	NA	NA	NA	NA	NA	NA	NA	200	100	0-10000 (5)	1000	0	0	NA	NA
Fluoride	mg/L	14	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	NA	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 ºC)	cfu/100mL	NA	NA	NA	NA	NA	NA	NA					10000		NA	NA
Heterotrophic Bacteria (37 ºC)	cfu/100mL	NA	NA	NA	NA	NA	NA	NA								
Iron	µg/L	14	56	104	113	166	171	39	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	14	0,42	0,78	0,90	2,2	3,1	0,71	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	14	15	19	20	25	27	3,8								
Manganese	µg/L	14	16	31	32	46	46	9,2	2000 (1)	200	2000 (1)	2000 (1)	50		🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-2 Data for composite treated wastewater sampling point (S1 C) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	13	1,1	1,9	19	91	214	59		10					🟥	🟥
N-Ammonia	mg/L	26	< 0,50	1,7	3,1	11	15	3,7	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟥
N-Kjeldahl	mg/L	24	2,3	3,8	5,9	14	21	4,6								
N-Nitrate	mg/L	25	0,71	3,2	3,2	5,6	6,2	1,5				5.6 (7)	11.3		🟩	🟨
N-Nitrite	mg/L	12	< 0,080	0,21	0,26	0,57	0,66	0,17	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟨	🟨
N-Total	mg/L	23	4,6	8,6	9,4	17	25	4,4				10			🟩	🟥
Nickel	µg/L	13	33	55	119	417	886	231	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟥	🟥
pH	pH units	28	6,6	7,2	7,2	7,7	7,7	0,28	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟩	🟩
Phenols	mg/L	14	0,63	1,1	1,1	1,4	1,4	0,23	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟥	🟥
Potassium	mg/L	14	21	37	38	52	63	10								
P-Phosphate	mg/L	22	1,2	3,1	3,4	5,3	6,7	1,3	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	26	-34	-8,0	-7,2	15	20	15						250-900 (13)	🟥	🟥
SAR	SAR units	14	3,6	7,2	7,0	8,3	8,3	1,3		6					🟥	🟥
Selenium	µg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	14	122	268	266	341	351	57					200		🟥	🟥
Sulfate	mg/L	15	100	166	167	210	223	28	2000	2000			250		🟩	🟩
Suspended Solids	mg/L	27	< 1,0	7,4	7,4	15	15	3,9	20	20	5-35 (10)	35			🟨	🟨
SUVA	L/(mg.m)	13	2,0	2,9	2,8	3,4	3,4	0,46								
Temperature	ºC	25	4,3	11	12	20	24	5,1	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	NA	NA	NA	NA	NA	NA	NA					0		NA	NA
Transmittance (254 nm)	%	27	30	41	41	53	63	7,7								
Turbidity	NTU	28	< 0,50	3,2	3,8	8,8	12	2,7	10	10	1-15 (10)		1-5 (8)	5 (15)	🟥	🟥
Zinc	µg/L	14	39	73	70	96	97	18	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-3 Data for simple (grab sample) treated wastewater sampling point (S1 S).

Parameter	**Units**	**n**	**min**	**median**	**mean**	**95th**	**max**	**SD**	**RD 1620/ 2007 UUR**	**RD 1620/ 2007 ARFC**	**RD 1620/ 2007 IR**	**RD 1620/ 2007 MAR**	**RD 140/ 2003 DW**	**RD 742/2013 BWSP**	**mean <GV**	**max <GV**
Alkalinity	$CaCO_3$ mg/L	14	208	267	266	309	316	30								
Bacteriophages	pfu/100mL	18	2,0E+02	1,3E+04	1,5E+04	4,0E+04	5,0E+04	1,4E+04								
Barium	µg/L	17	8,8	15	17	26	34	7,1	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	14	254	326	324	377	386	37								
BOD Total	O_2 mg /L	7	6,0	7,0	11	18	19	5,6	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	17	245	297	296	357	375	39	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	17	< 0,10	< 0,10	0,19	0,46	1,4	0,30	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	17	55	70	73	90	99	11								
Carbonate	mg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA								
Chloride	mg/L	18	162	281	307	491	687	116	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟨	🟨
Chromium	µg/L	17	< 10	< 10	18	53	53	14	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟥
Clostridium spores	cfu/100mL	17	171	597	998	2159	2775	751					0 (3)		🟥	🟥
Cobalt	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	29	20	42	41	58	62	11								
COD Total	O_2 mg /L	29	22	50	57	103	142	25	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	17	3,9	6,4	6,7	11	12	2,2	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	2	< 10	NA	NA	NA	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	6	0,27	0,31	0,38	0,60	0,66	0,14	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O_2 mg /L	15	8,9	13	13	16	18	2,3								
Electrical conductivity	dS/m	33	0,74	1,7	1,7	2,2	2,3	0,32		3			2.5		🟩	🟩
Enterococci	cfu/100mL	15	6,0E+03	9,9E+03	1,2E+04	2,2E+04	3,1E+04	6,7E+03					0		🟥	🟥
Escherichia coli	cfu/100mL	33	9,0E+03	5,1E+04	9,2E+04	3,4E+05	4,6E+05	1,1E+05	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	16	< 0,50	< 0,50	< 0,50	0,70	1,3	0,20	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 °C)	cfu/100mL	15	9,5E+05	4,2E+06	2,7E+07	1,2E+08	3,0E+08	7,6E+07					10000		🟥	🟥
Heterotrophic Bacteria (37 °C)	cfu/100mL	15	1,4E+05	4,0E+05	6,2E+05	1,6E+06	1,7E+06	5,3E+05								
Iron	µg/L	16	48	97	96	134	142	27	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	17	0,44	0,70	0,80	1,5	1,7	0,35	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	17	14	18	19	27	28	4,1								
Manganese	µg/L	17	15	35	35	50	50	9,4	2000 (1)	200	2000 (1)	2000 (1)	50		🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-4 Data for simple (grab sample) treated wastewater sampling point (S1 S) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	16	0,86	1,8	11	66	72	23		10					🟥	🟥
N-Ammonia	mg/L	30	< 0,50	2,4	3,5	10	14	3,3	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟥
N-Kjeldahl	mg/L	26	2,0	6,5	7,9	20	22	5,3								
N-Nitrate	mg/L	32	0,38	2,8	3,0	5,8	8,2	1,6				5.6 (7)	11.3		🟩	🟨
N-Nitrite	mg/L	2	0,38	NA	0,49	NA	0,60	NA	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟨	🟨
N-Total	mg/L	26	5,1	9,4	11	22	25	5,1				10			🟥	🟥
Nickel	µg/L	16	14	47	74	256	265	76	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟥	🟥
pH	pH units	33	6,4	6,8	6,8	7,1	7,1	0,19	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟨	🟨
Phenols	mg/L	17	0,68	1,1	1,0	1,3	1,3	0,21	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟥	🟥
Potassium	mg/L	17	21	33	35	49	59	9,4								
P-Phosphate	mg/L	28	1,1	3,5	3,6	5,4	7,0	1,3	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	32	-19	16	15	30	40	11						250-900 (13)	🟥	🟥
SAR	SAR units	17	3,7	6,2	6,1	7,3	7,3	0,91		6					🟥	🟥
Selenium	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	17	124	229	227	305	318	46					200		🟥	🟥
Sulfate	mg/L	18	95	147	154	204	282	40	2000	2000			250		🟩	🟨
Suspended Solids	mg/L	32	3,0	7,4	10	22	50	8,9	20	20	5-35 (10)	35			🟨	🟥
SUVA	L/(mg.m)	15	1,9	2,8	2,8	3,2	3,4	0,40								
Temperature	ºC	32	13	19	20	26	27	3,9	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	33	3,0E+05	1,1E+06	1,8E+06	6,8E+06	9,2E+06	2,1E+06					0		🟥	🟥
Transmittance (254 nm)	%	33	37	46	45	53	67	5,7								
Turbidity	NTU	32	1,7	3,4	4,4	10	17	3,2	10	10	1-15 (10)		1-5 (8)	5 (15)	🟥	🟥
Zinc	µg/L	17	42	62	67	97	115	19	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-5 Data for Ripoll River reference sampling point (S2).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Alkalinity	$CaCO_3$ mg/L	15	318	364	365	409	410	28								
Bacteriophages	pfu/100mL	18	1,7E+02	7,0E+03	1,1E+04	2,9E+04	3,5E+04	1,2E+04								
Barium	µg/L	17	83	114	115	142	147	18	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	15	338	405	411	489	498	51								
BOD Total	O_2 mg /L	12	1,0	2,5	4,9	15	20	5,8	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	17	120	263	271	428	500	100	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	17	< 0,10	< 0,10	< 0,10	0,12	0,12	0,01	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	17	67	109	114	149	159	22								
Carbonate	mg/L	15	< 5,0	16	19	39	47	14								
Chloride	mg/L	18	166	358	355	535	579	119	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟨	🟨
Chromium	µg/L	17	< 10	< 10	15	34	40	8,9	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟩
Clostridium spores	cfu/100mL	17	7,0E+00	3,4E+01	7,1E+01	2,0E+02	4,1E+02	9,6E+01					0 (3)		🟥	🟥
Cobalt	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	30	< 10	22	23	38	44	8,2								
COD Total	O_2 mg /L	30	< 10	27	29	45	61	11	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	17	3,4	6,9	6,8	8,3	8,7	1,3	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	12	< 10	< 10	< 10	< 10	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	15	< 0,20	0,31	0,35	0,57	0,61	0,15	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O_2 mg /L	16	4,7	6,8	7,1	10	11	1,8								
Electrical conductivity	dS/m	34	1,0	2,0	2,0	2,8	2,9	0,55		3			2.5		🟩	🟨
Enterococci	cfu/100mL	15	2,7E+02	9,9E+02	1,3E+03	2,8E+03	3,4E+03	8,7E+02					0		🟥	🟥
Escherichia coli	cfu/100mL	33	1,0E+02	5,4E+03	1,4E+04	5,3E+04	1,5E+05	2,8E+04	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	16	< 0,50	< 0,50	0,53	0,65	0,75	0,069	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 ºC)	cfu/100mL	15	4,7E+04	5,6E+05	2,5E+06	1,0E+07	> 30000000	7,6E+06					10000		🟥	🟥
Heterotrophic Bacteria (37 ºC)	cfu/100mL	15	1,2E+04	4,6E+04	7,2E+04	1,5E+05	1,8E+05	5,2E+04								
Iron	µg/L	17	11	39	40	69	71	16	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	17	0,25	0,70	1,2	3,8	7,4	1,7	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟨
Magnesium	mg/L	17	21	34	35	45	47	6,4								
Manganese	µg/L	17	15	32	37	68	96	19	2000 (1)	200	2000 (1)	2000 (1)	50		🟩	🟨

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-6 Data for Ripoll River reference sampling point (S2) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	16	1,2	2,2	3,4	8,2	18	3,9		10					🟩	🟥
N-Ammonia	mg/L	31	< 0,50	1,2	2,1	5,4	10	2,1	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟨
N-Kjeldahl	mg/L	29	0,87	2,7	3,8	10	14	3,2								
N-Nitrate	mg/L	32	2,0	3,3	3,5	4,9	6,6	0,89				5.6 (7)	11.3		🟩	🟨
N-Nitrite	mg/L	13	< 0,080	0,12	0,28	0,79	1,2	0,32	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟨	🟨
N-Total	mg/L	28	3,0	6,6	7,4	14	17	3,1				10			🟩	🟥
Nickel	µg/L	16	< 10	11	17	37	49	11	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟩	🟥
pH	pH units	34	7,5	7,9	8,0	8,4	8,6	0,27	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟩	🟨
Phenols	mg/L	17	0,26	0,69	0,67	0,93	1,1	0,21	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟥	🟥
Potassium	mg/L	17	10	17	17	26	32	5,8								
P-Phosphate	mg/L	27	0,61	1,5	1,5	2,8	3,1	0,64	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	32	-79	-50	-48	-27	41	22						250-900 (13)	🟥	🟥
SAR	SAR units	17	3,0	5,9	5,7	7,9	8,0	1,6		6					🟩	🟥
Selenium	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	17	126	282	275	405	411	97					200		🟥	🟥
Sulfate	mg/L	18	94	182	182	270	286	54	2000	2000			250		🟩	🟨
Suspended Solids	mg/L	33	< 1,0	5,2	6,8	15	28	5,4	20	20	5-35 (10)	35			🟨	🟥
SUVA	L/(mg.m)	16	2,0	3,0	2,9	3,6	4,0	0,55								
Temperature	ºC	32	8,8	17	17	27	28	5,9	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	33	5,6E+04	1,9E+05	4,0E+05	8,7E+05	4,3E+06	7,4E+05					0		🟥	🟥
Transmittance (254 nm)	%	34	49	62	63	77	78	7,8								
Turbidity	NTU	34	< 0,50	4,2	5,0	12	23	4,2	10	10	1-15 (10)		1-5 (8)	5 (15)	🟥	🟥
Zinc	µg/L	17	15	29	31	51	58	11	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-7 Data for Ripoll River mixture 1 (after discharges) sampling point (S3).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Alkalinity	$CaCO_3$ mg/L	15	235	336	332	377	386	37								
Bacteriophages	pfu/100mL	18	1,2E+02	7,3E+03	2,1E+04	9,9E+04	1,1E+05	3,3E+04								
Barium	µg/L	17	21	93	88	120	140	27	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	15	282	377	373	439	441	54								
BOD Total	O_2 mg /L	12	2,0	4,0	4,5	8,5	9,0	2,3	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	17	133	263	275	448	449	90	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	17	< 0,10	< 0,10	0,12	0,16	0,41	0,076	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	17	68	96	102	127	128	16								
Carbonate	mg/L	15	< 5,0	7,8	18	55	93	23								
Chloride	mg/L	18	156	324	332	489	491	101	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟨	🟨
Chromium	µg/L	17	< 10	< 10	14	32	45	9,3	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟩
Clostridium spores	cfu/100mL	17	4,0E+00	1,1E+02	2,4E+02	8,7E+02	8,8E+02	2,7E+02					0 (3)		🟥	🟥
Cobalt	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	30	< 10	27	27	47	56	11								
COD Total	O_2 mg /L	30	16	38	38	66	75	15	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	17	4,7	6,7	6,7	8,4	9,6	1,2	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	12	< 10	< 10	< 10	< 10	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	15	< 0,20	0,40	0,39	0,63	0,77	0,17	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O_2 mg /L	16	6,0	8,5	9,4	14	14	2,6								
Electrical conductivity	dS/m	34	1,1	1,9	1,8	2,5	2,6	0,42		3			2.5		🟩	🟨
Enterococci	cfu/100mL	14	1,4E+02	6,7E+03	9,5E+03	2,9E+04	3,8E+04	1,0E+04					0		🟥	🟥
Escherichia coli	cfu/100mL	33	< 10	3,6E+04	5,7E+04	1,9E+05	2,7E+05	6,6E+04	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	16	< 0,50	< 0,50	0,55	0,75	1,1	0,15	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 ºC)	cfu/100mL	15	7,0E+04	2,3E+06	2,4E+07	1,0E+08	> 3,0E+08	7,6E+07					10000		🟥	🟥
Heterotrophic Bacteria (37 ºC)	cfu/100mL	15	3,0E+03	2,2E+05	4,3E+05	1,5E+06	2,6E+06	6,6E+05								
Iron	µg/L	17	29	53	57	95	123	25	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	17	0,32	0,51	0,80	2,5	3,2	0,79	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	17	18	30	30	39	40	5,4								
Manganese	µg/L	17	7,2	33	37	72	79	18	2000 (1)	200	2000 (1)	2000 (1)	50		🟩	🟨

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell. 50,6331701

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-8 Data for Ripoll River mixture (after discharges) sampling point (S3) (continued).

Parameter	**Units**	**n**	**min**	**median**	**mean**	**95th**	**max**	**SD**	**RD 1620/ 2007 UUR**	**RD 1620/ 2007 ARFC**	**RD 1620/ 2007 IR**	**RD 1620/ 2007 MAR**	**RD 140/ 2003 DW**	**RD 742/2013 BWSP**	**mean <GV**	**max <GV**
Molybdenum	µg/L	16	1,4	2,2	3,5	9,4	17	3,9		10					🟩	🟥
N-Ammonia	mg/L	31	< 0,50	2,2	2,3	4,7	5,2	1,3	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟨
N-Kjeldahl	mg/L	29	0,64	4,5	4,7	9,4	12	2,7								
N-Nitrate	mg/L	32	1,8	3,3	3,4	5,3	6,4	0,99				5.6 (7)	11.3		🟩	🟨
N-Nitrite	mg/L	13	< 0,080	0,26	0,30	0,63	0,73	0,20	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟨	🟨
N-Total	mg/L	28	3,9	8,2	8,3	13	16	2,8				10			🟩	🟥
Nickel	µg/L	16	< 10	22	21	34	43	9,2	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟥	🟥
pH	pH units	34	7,1	7,9	7,9	8,6	8,6	0,40	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟩	🟨
Phenols	mg/L	17	0,40	0,72	0,74	1,0	1,1	0,21	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟥	🟥
Potassium	mg/L	17	11	21	22	33	35	6,7								
P-Phosphate	mg/L	27	0,76	1,9	2,0	3,7	4,4	0,94	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	32	-90	-42	-42	-0,40	33	27						250-900 (13)	🟥	🟥
SAR	SAR units	17	3,2	5,5	5,5	7,3	7,6	1,4		6					🟩	🟥
Selenium	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	17	134	234	248	367	375	77					200		🟥	🟥
Sulfate	mg/L	18	97	170	175	247	269	48	2000	2000			250		🟩	🟨
Suspended Solids	mg/L	33	1,2	7,2	8,3	15	27	4,9	20	20	5-35 (10)	35			🟨	🟥
SUVA	L/(mg.m)	16	1,3	2,6	2,6	3,3	3,4	0,59								
Temperature	ºC	32	8,6	18	19	27	28	5,6	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	33	5,3E+04	6,4E+05	1,3E+06	5,1E+06	6,3E+06	1,6E+06					0		🟥	🟥
Transmittance (254 nm)	%	34	40	57	59	71	80	8,3								
Turbidity	NTU	34	< 0,50	5,3	6,6	16	34	6,1	10	10	1-15 (10)		1-5 (8)	5 (15)	🟥	🟥
Zinc	µg/L	17	21	35	38	58	67	13	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-9 Data for aquifer recovered water (mine) sampling point (S4).

Parameter	**Units**	**n**	**min**	**median**	**mean**	**95th**	**max**	**SD**	**RD 1620/ 2007 UUR**	**RD 1620/ 2007 ARFC**	**RD 1620/ 2007 IR**	**RD 1620/ 2007 MAR**	**RD 140/ 2003 DW**	**RD 742/2013 BWSP**	**mean <GV**	**max <GV**
Alkalinity	$CaCO_3$ mg/L	14	334	357	357	383	388	15								
Bacteriophages	pfu/100mL	18	< 0,1	1,6E+00	1,6E+01	7,1E+01	1,9E+02	4,4E+01								
Barium	µg/L	17	115	130	130	144	146	9,1	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	14	407	435	436	467	474	19								
BOD Total	O_2 mg /L	12	< 1,0	1,0	1,3	2,5	3,0	0,6	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	17	236	288	287	318	346	25	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	17	< 0,10	< 0,10	0,11	0,14	0,17	0,018	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	17	103	121	119	129	134	8,3								
Carbonate	mg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA								
Chloride	mg/L	18	169	324	309	375	384	51	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟨	🟨
Chromium	µg/L	17	< 10	< 10	13	28	35	7,0	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟩
Clostridium spores	cfu/100mL	18	< 0,1	1,9E-01	1,9E+00	9,3E+00	1,1E+01	3,3E+00					0 (3)		🟥	🟥
Cobalt	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	30	< 10	12	16	33	50	9,1								
COD Total	O_2 mg /L	30	< 10	15	19	40	61	12	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	16	4,2	5,5	5,5	6,7	6,8	0,79	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	12	< 10	< 10	< 10	< 10	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	15	< 0,20	0,25	0,29	0,47	0,56	0,11	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O_2 mg /L	16	2,9	4,4	4,7	6,9	8,6	1,3								
Electrical conductivity	dS/m	34	1,7	2,0	2,0	2,2	2,4	0,17		3			2.5		🟩	🟩
Enterococci	cfu/100mL	15	2,7E-01	3,0E+00	1,3E+01	6,0E+01	6,1E+01	2,0E+01					0		🟥	🟥
Escherichia coli	cfu/100mL	33	2,0E-01	2,5E+01	6,5E+01	2,8E+02	3,1E+02	9,3E+01	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	16	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	NA	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 °C)	cfu/100mL	15	4,1E+01	1,2E+02	5,2E+03	2,4E+04	3,3E+04	9,2E+03					10000		🟩	🟥
Heterotrophic Bacteria (37 °C)	cfu/100mL	15	1,4E+01	3,0E+02	1,2E+03	6,5E+03	8,1E+03	2,4E+03								
Iron	µg/L	17	< 10	23	26	37	45	8,6	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	16	0,20	0,38	0,47	0,93	1,6	0,35	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	17	31	37	37	41	41	3,0								
Manganese	µg/L	17	141	364	318	422	427	109	2000 (1)	200	2000 (1)	2000 (1)	50		🟥	🟥

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-10 Data for aquifer recovered water (mine) sampling point (S4) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	16	2,1	2,3	2,7	5,1	5,5	1,0		10					🟩	🟩
N-Ammonia	mg/L	31	< 0,50	0,50	0,63	0,93	1,7	0,3	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟨
N-Kjeldahl	mg/L	28	< 0,50	1,2	1,8	5,3	6,6	1,6								
N-Nitrate	mg/L	31	1,2	2,2	2,3	3,1	3,5	0,54				5.6 (7)	11.3		🟩	🟩
N-Nitrite	mg/L	13	< 0,080	< 0,080	0,081	0,086	0,093	0,0037	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟩	🟩
N-Total	mg/L	26	1,9	3,7	4,1	7,8	9,2	1,7				10			🟩	🟩
Nickel	µg/L	16	< 10	< 10	14	31	33	7,3	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟩	🟥
pH	pH units	33	6,7	7,2	7,1	7,5	7,7	0,23	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟨	🟩
Phenols	mg/L	17	< 0,25	0,45	0,45	0,64	0,65	0,13	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟩	🟥
Potassium	mg/L	17	12	15	15	17	18	1,8								
P-Phosphate	mg/L	24	0,65	1,0	1,0	1,2	1,3	0,17	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	32	-48	-3,5	-0,75	16	104	23						250-900 (13)	🟥	🟥
SAR	SAR units	17	4,6	5,2	5,2	5,8	6,0	0,39		6					🟩	🟩
Selenium	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	17	217	256	256	292	308	24					200		🟥	🟥
Sulfate	mg/L	18	119	175	177	212	239	28	2000	2000			250		🟩	🟩
Suspended Solids	mg/L	33	< 1,0	< 1,0	1,1	1,2	2,2	0,22	20	20	5-35 (10)	35			🟩	🟩
SUVA	L/(mg.m)	16	1,5	3,4	3,2	4,2	4,6	0,72								
Temperature	ºC	32	8,4	17	16	23	24	4,8	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	33	4,0E+00	4,2E+02	1,1E+03	4,4E+03	6,2E+03	1,6E+03					0		🟥	🟥
Transmittance (254 nm)	%	34	63	71	72	80	81	4,8								
Turbidity	NTU	34	< 0,50	< 0,50	< 0,50	< 0,50	0,74	0,041	10	10	1-15 (10)		1-5 (8)	5 (15)	🟩	🟩
Zinc	µg/L	17	13	30	85	346	373	115	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.
(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.
(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.
(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.
(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.
(9) Guideline values are given for Total Phosphorous, not P-Phosphate.
(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).
(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.
(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.
(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.
(14) Temperature range to be abided only for heated pools.
(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-11 Data for the final treated water (Sprinklers) sampling point (S5).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Alkalinity	$CaCO_3$ mg/L	15	289	362	358	398	405	26								
Bacteriophages	pfu/100mL	18	< 0,1	< 0,1	1,0E+01	2,7E+01	1,8E+02	4,1E+01								
Barium	µg/L	17	95	120	119	139	146	13	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	15	352	430	429	485	494	37								
BOD Total	O_2 mg /L	12	< 1,0	1,0	1,7	3,5	4,0	1,0	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	17	213	275	284	339	362	37	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	17	< 0,10	< 0,10	0,11	0,13	0,27	0,040	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟩
Calcium	mg/L	17	102	116	116	125	126	7,9								
Carbonate	mg/L	15	< 5,0	< 5,0	7,5	18	25	5,5								
Chloride	mg/L	18	213	334	317	360	362	41	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟧	🟧
Chromium	µg/L	17	< 10	< 10	14	36	37	8,7	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟩	🟩
Clostridium spores	cfu/100mL	18	< 0,1	< 0,1	2,1E-01	1,0E+00	1,0E+00	2,9E-01					0 (3)		🟥	🟥
Cobalt	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	30	< 10	< 10	15	35	79	14								
COD Total	O_2 mg /L	30	< 10	12	17	49	85	16	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	17	3,7	5,9	5,7	6,7	6,8	0,89	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	12	< 10	< 10	< 10	< 10	< 10	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		🟩	🟩
Detergents	mg/L	15	< 0,20	0,25	0,26	0,38	0,41	0,068	2 (1)	2 (1)	2 (1)	2 (1)			🟩	🟩
DOC	O_2 mg /L	16	3,0	4,6	4,5	5,6	5,8	0,74								
Electrical conductivity	dS/m	34	1,6	2,0	2,0	2,3	2,6	0,19		3			2.5		🟩	🟧
Enterococci	cfu/100mL	15	2,5E-01	1,0E+00	7,6E+00	3,1E+01	4,9E+01	1,4E+01					0		🟥	🟥
Escherichia coli	cfu/100mL	33	< 0,2	3,3E-01	3,5E+00	5,8E+00	9,4E+01	1,6E+01	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	16	< 0,50	< 0,50	< 0,50	< 0,50	< 0,50	NA	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 ºC)	cfu/100mL	15	3,3E-01	4,6E+01	1,4E+02	5,8E+02	8,2E+02	2,3E+02					10000		🟩	🟩
Heterotrophic Bacteria (37 ºC)	cfu/100mL	15	5,0E-01	9,0E+00	4,7E+02	2,0E+03	5,0E+03	1,3E+03								
Iron	µg/L	17	< 10	24	30	57	152	33	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟩
Lead	µg/L	17	0,13	0,23	0,35	0,77	1,1	0,26	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	17	30	36	36	39	39	2,7								
Manganese	µg/L	17	1,8	53	74	261	272	87	2000 (1)	200	2000 (1)	2000 (1)	50		🟧	🟥

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-12 Data for the final treated water (Sprinklers) sampling point (S5) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	16	1,7	2,2	2,7	5,4	6,6	1,3		10					🟩	🟩
N-Ammonia	mg/L	31	< 0,50	< 0,50	0,67	1,3	1,5	0,30	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟨
N-Kjeldahl	mg/L	28	< 0,50	1,5	2,1	5,4	7,9	1,8								
N-Nitrate	mg/L	32	1,2	2,1	2,2	3,0	3,4	0,53				5.6 (7)	11.3		🟩	🟩
N-Nitrite	mg/L	13	< 0,080	< 0,080	< 0,080	< 0,080	< 0,080	NA	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟩	🟩
N-Total	mg/L	27	2,0	3,7	4,2	7,4	11	2,0				10			🟩	🟩
Nickel	µg/L	16	< 10	< 10	12	21	29	5,2	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟩	🟥
pH	pH units	34	7,3	7,6	7,6	7,9	8,2	0,21	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟩	🟨
Phenols	mg/L	17	< 0,25	0,45	0,40	0,51	0,57	0,10	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟩	🟥
Potassium	mg/L	17	13	15	15	17	17	1,6								
P-Phosphate	mg/L	25	0,72	0,88	0,91	1,3	1,5	0,18	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	32	-66	-33	-30	-10	-4,0	13						250-900 (13)	🟥	🟥
SAR	SAR units	17	4,7	5,5	5,4	5,8	5,8	0,31		6					🟩	🟩
Selenium	µg/L	17	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	17	232	260	258	281	286	18					200		🟥	🟥
Sulfate	mg/L	18	79	177	172	199	211	29	2000	2000			250		🟩	🟩
Suspended Solids	mg/L	33	< 1,0	< 1,0	1,0	1,2	1,7	0,13	20	20	5-35 (10)	35			🟩	🟩
SUVA	L/(mg.m)	16	1,4	3,0	2,9	3,9	4,3	0,77								
Temperature	ºC	32	10	18	18	24	26	4,1	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	33	< 0,1	1,0E+00	4,9E+01	2,5E+02	4,1E+02	1,0E+02					0		🟥	🟥
Transmittance (254 nm)	%	34	64	75	75	86	90	6,3								
Turbidity	NTU	34	< 0,50	< 0,50	0,55	0,62	1,8	0,22	10	10	1-15 (10)		1-5 (8)	5 (15)	🟩	🟨
Zinc	µg/L	17	15	23	27	44	49	10	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

Table B-13 Data for Ripoll River mixture 2 (after discharges) sampling point (S6).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Alkalinity	$CaCO_3$ mg/L	13	295	330	330	362	370	23								
Bacteriophages	pfu/100mL	14	6,2E+02	1,4E+04	3,7E+04	1,4E+05	3,1E+05	8,1E+04								
Barium	µg/L	14	12	66	67	94	97	21	20000 (1)	20000 (1)	20000 (1)	20000 (1)			🟩	🟩
Bicarbonate	mg/L	13	319	392	385	432	452	39								
BOD Total	O_2 mg /L	3	3,0	5,0	4,7	5,9	6,0	1,5	40 (1)	40 (1)	40 (1)	40 (1)			🟩	🟩
Boron	µg/L	14	202	298	291	358	394	47	2000 (1)	500	2000 (1)	2000 (1)	1000		🟩	🟩
Cadmium	µg/L	14	< 0,10	< 0,10	0,24	0,78	2,0	0,50	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	0.25/1.5 (2, 4)	5		🟩	🟥
Calcium	mg/L	14	63	102	101	117	118	14								
Carbonate	mg/L	13	< 5,0	12	11	20	20	5,8								
Chloride	mg/L	14	213	317	324	460	489	80	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250		🟨	🟨
Chromium	µg/L	14	< 10	12	64	269	725	190	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	5/NA (2, 6) 50/NA (2)	50		🟥	🟥
Clostridium spores	cfu/100mL	14	1,1E+01	1,1E+02	1,5E+02	3,5E+02	4,4E+02	1,3E+02					0 (3)		🟥	🟥
Cobalt	µg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA		50					🟩	🟩
COD Soluble	O_2 mg /L	26	12	30	29	39	45	8,7								
COD Total	O_2 mg /L	26	18	35	40	73	99	17	160 (1)	160 (1)	160 (1)	160 (1)			🟩	🟩
Copper	µg/L	14	5,5	6,7	7,1	9,2	10	1,3	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	120/NA (2, 4)	2000		🟩	🟩
Cyanide	µg/L	1	NA	< 10	NA	NA	NA	NA	40/NA (2)	40/NA (2)	40/NA (2)	40/NA (2)	50		NA	NA
Detergents	mg/L	2	0,47	NA	NA	NA	0,52	NA	2 (1)	2 (1)	2 (1)	2 (1)			NA	NA
DOC	O_2 mg /L	11	7,0	9,4	10	18	23	4,5								
Electrical conductivity	dS/m	28	1,1	2,0	1,9	2,2	2,3	0,30		3			2.5		🟩	🟩
Enterococci	cfu/100mL	13	1,6E+03	5,0E+03	7,7E+03	2,2E+04	4,0E+04	1,0E+04					0		🟥	🟥
Escherichia coli	cfu/100mL	28	5,0E+03	3,0E+04	1,3E+05	3,3E+05	2,1E+06	3,9E+05	200	100	0-10000 (5)	1000	0	0	🟥	🟥
Fluoride	mg/L	9	< 0,50	< 0,50	0,56	0,81	0,92	0,14	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.7/NA (2)	1.5		🟩	🟩
Heterotrophic Bacteria (22 ºC)	cfu/100mL	13	3,5E+05	1,8E+06	2,8E+07	1,4E+08	30000000	8,2E+07					10000		🟥	🟥
Heterotrophic Bacteria (37 ºC)	cfu/100mL	13	3,1E+04	2,1E+05	7,9E+05	3,4E+06	6,7E+06	1,8E+06								
Iron	µg/L	14	28	70	77	140	235	48	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200		🟩	🟨
Lead	µg/L	14	0,34	0,69	0,75	1,4	1,4	0,35	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	7.2/NA (2)	25		🟩	🟩
Magnesium	mg/L	14	16	29	29	33	34	4,4								
Manganese	µg/L	14	25	75	73	106	108	24	2000 (1)	200	2000 (1)	2000 (1)	50		🟨	🟨

ARFC: Agricultural Reuse - Food Crops; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; COD: Chemical Oxygen Demand; DOC: Dissolved Organic Carbon; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; pfu: plaque forming units; RD: Royal Decree; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(3) RD 140/2003 requires de measurement of *Clostridium perfringens* including spores, but *Clostridium* spores were measured instead. When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity to also measure *Cryptosporidium* or other microorganisms and parasites.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(5) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(6) Value given for chromium VI, not for total chromium.

Table B-14 Data for Ripoll River mixture 2 (after discharges) sampling point (S6) (continued).

Parameter	Units	n	min	median	mean	95th	max	SD	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/2013 BWSP	mean <GV	max <GV
Molybdenum	µg/L	14	1,6	2,3	68	326	896	238		10					🟥	🟥
N-Ammonia	mg/L	27	0,57	1,4	2,3	4,8	18	3,3	12 (1, 7)	12 (1, 7)	12 (1, 7)	12 (1, 7)	0.4		🟨	🟥
N-Kjeldahl	mg/L	24	1,7	4,3	5,7	14	28	5,7								
N-Nitrate	mg/L	28	1,8	3,0	3,2	4,7	8,5	1,2				5.6 (7)	11.3		🟩	🟨
N-Nitrite	mg/L	2	0,23	NA	0,27	NA	0,30	NA	3 (1, 7)	3 (1, 7)	3 (1, 7)	3 (1, 7)	0.03-0.15 (8)		🟨	🟨
N-Total	mg/L	24	4,7	7,3	8,7	17	33	5,9				10			🟩	🟥
Nickel	µg/L	14	< 10	27	255	1173	3190	845	20/NA (2)	20/NA (2)	20/NA (2)	20/NA (2)	20		🟥	🟥
pH	pH units	29	7,0	7,8	7,7	8,1	8,3	0,30	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (12)	7.2-8 (12)	🟩	🟨
Phenols	mg/L	14	0,39	0,70	0,69	0,91	0,95	0,17	0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)			🟥	🟥
Potassium	mg/L	14	16	23	24	29	30	4,3								
P-Phosphate	mg/L	24	1,15	2,0	2,0	2,9	3,5	0,59	10 (1, 9)	10 (1, 9)	10 (1, 9)	10 (1, 9)			🟩	🟩
Redox Potential	mV	29	-68	-42	-39	-7,4	16	18						250-900 (13)	🟥	🟥
SAR	SAR units	14	3,6	5,8	5,6	6,6	6,7	0,91		6					🟩	🟥
Selenium	µg/L	14	< 5,0	< 5,0	< 5,0	< 5,0	< 5,0	NA	1/NA (2)	1/NA (2)	1/NA (2)	1/NA (2)	10		🟥	🟥
Sodium	mg/L	14	152	257	247	311	318	49					200		🟥	🟥
Sulfate	mg/L	14	114	168	177	247	269	41	2000	2000			250		🟩	🟨
Suspended Solids	mg/L	29	3,0	8,6	15	29	110	20	20	20	5-35 (10)	35			🟨	🟥
SUVA	L/(mg.m)	11	0,82	3,0	2,7	3,5	3,6	0,81								
Temperature	ºC	29	9,1	17	18	25	28	5,5	Δ3 (11)	Δ3 (11)	Δ3 (11)	Δ3 (11)		24-30 (14)	🟩	🟩
Total Coliforms	cfu/100mL	28	1,6E+05	9,7E+05	2,2E+06	6,6E+06	2,4E+07	4,6E+06					0		🟥	🟥
Transmittance (254 nm)	%	29	44	55	55	64	65	6,0								
Turbidity	NTU	28	1,6	7,4	12	14	131	24	10	10	1-15 (10)		1-5 (8)	5 (15)	🟥	🟥
Zinc	µg/L	14	16	33	38	64	67	17	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)	500/NA (2, 4)			🟩	🟩

ARFC: Agricultural Reuse - Food Crops; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; GV: Guideline Value; IR: Industrial Reuse; n: number of samples; NA: Not Applicable; NTU: Nefelometric Turbidity Unit; RD: Royal Decree; SAR: Sodium Absorption Ratio; SUVA: Specific Ultraviolet Absorption; UUR: Unrestricted Urban Reuse.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(4) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(7) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(8) Lower value applies when measured in the treatment plant outlet; upper value when measured in the distribution network.

(9) Guideline values are given for Total Phosphorous, not P-Phosphate.

(10) Guideline values range depends on the industrial use (the lowest and most restrictive value is for cooling towers, the highest value corresponds to other industrial uses).

(11) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(12) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

(13) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

(14) Temperature range to be abided only for heated pools.

(15) For values higher than 20 NTU the swimming pool will be closed until normalization.

APPENDIX C: EXAMPLES OF DRAWN VALUES FROM THE PDF DISTRIBUTIONS AND SIMULATIONS DONE

An example of the QMRA calculation for rotavirus in the empirical risk calculation for the accidental ingestion of aerosols by growers/irrigators scenario and an example for *Cryptosporidium* in the theoretical risk calculation for the crop consumption scenario are given in Table C-1 and Table C-2. Each table represents one of the 10,000 hypothetical scenarios/combinations generated during the Monte Carlo simulations.

Table C-1 Sample example for rotavirus in the empirical risk calculation for the accidental ingestion of aerosols by growers/irrigators scenario.

Parameter	Value	Comment
Rotavirus concentration in raw wastewater (rotavirus/L) [A]	*91*	*Sampled from PDF LN (1342, 6330)*
Primary + Secondary WWTP treatment removal ($\log_{10}$) [B]	1.3	Sampled from PDF T (0.5, 1.0, 2.1)
Rotavirus concentration in secondary effluent (rotavirus/L) [C]	4.9	Calculated from $A/10^B$
Mixture/dilution with Ripoll River removal ($\log_{10}$) [D]	0.53	Sampled from PDF T (-1.0, 0.0, 2.0)
Rotavirus concentration in infiltration water: Ripoll River + secondary effluent (rotavirus/L) [E]	1.4	Calculated from $C/10^D$
Aquifer/subsurface removal ($\log_{10}$) [F]	4.7	Sampled from PDF T (1.6, 4.4, 6.0)
Rotavirus concentration in recovered water (rotavirus/L) [G]	3.2×10^{-5}	Calculated from $E/10^F$
Disinfection + rapid sand filtration total removal (log10) [H]	0.47	Sampled from PDF T (0.0, 0.87, 2.7)
Rotavirus concentration in sprinklers/final irrigation water (rotavirus/L) [I]	1.1×10^{-5}	Sampled from PDF T (0.0, 0.87, 2.7)
Dose of water ingested during irrigation (L) [J]	6.5×10^{-4}	Sampled from PDF U (10^{-4}, 10^{-3})
Rotavirus dose per day (rotavirus) [K]	7.1×10^{-9}	Calculated from I×J
Dose-response: Daily probability of infection given ingestion of the lettuce [L]	4.2×10^{-9}	Calculated from $1-(1+K/0.426)^{-0.253}$
Number of exposures per year [M]	234	Sampled from PDF U (183, 365)
Yearly risk of infection [N]	9.8×10^{-7}	Calculated from $1-(1-X)^M$
Ratio disease/infection: probability of developing a disease given infection [O]	0.88	Fixed value
Disease burden: DALYs per disease case [P]	1.3×10^{-2}	Fixed value
Susceptibility: fraction of the population susceptible of suffering the disease [Q]	0.06	Fixed value
Calculated DALYs (pppy)	6.7×10^{-10}	Calculated from N×O×P×Q

Table C-2 Sample example for *Cryptosporidium* in the theoretical risk calculation for the crop consumption scenario.

Parameter	Value	Comment
Cryptosporidium concentration in raw wastewater (*Cryptosporidium*/L) [A]	222	Sampled from PDF LN (226, 84)
Primary + Secondary WWTP treatment removal ($\log_{10}$) [B]	0.94	Sampled from PDF T (0.5, 1.0, 1.5)
Cryptosporidium concentration in secondary effluent (*Cryptosporidium*/L) [C]	25	Calculated from $A/10^B$
Mixture/dilution with Ripoll River removal ($\log_{10}$) [D]	0.78	Sampled from PDF T (0.24, 0.87, 2.2)
Cryptosporidium concentration in infiltration water: Ripoll River + secondary effluent (*Cryptosporidium*/L) [E]	4.2	Calculated from $C/10^D$
Aquifer/subsurface storage (days) [F]	7.6	Sampled from PDF T (1.0, 7.0, 14)
Aquifer/subsurface *Cryptosporidium* decay rate ($\log_{10}$/day) [G]	0.011	Sampled from PDF N (0.012, 0.0030)
Aquifer/subsurface removal ($\log_{10}$) [H]	0.085	Calculated from F×G
Cryptosporidium concentration in recovered water (*Cryptosporidium*/L) [I]	3.5	Calculated from $E/10^H$
UV treatment removal ($\log_{10}$) [J]	2.7	Sampled from PDF T (2.0, 3.0, 3.5)
Chlorination treatment removal ($\log_{10}$) [K]	0.28	Sampled from PDF T (0.0, 0.0, 0.5)
Rapid sand filtration ($\log_{10}$) [L]	0.20	Sampled from PDF T (0.0, 0.0, 0.5)
Disinfection + rapid sand filtration total removal (log10) [M]	3.2	Calculated from J+K+L
Cryptosporidium concentration in sprinklers/final irrigation water (*Cryptosporidium*/L) [N]	2.3×10^{-3}	Calculated from $I/10^M$
Lettuce ingested per day (g) [O]	21	Sampled from PDF N (21, 0.84)
Water retained in the lettuce (mL/g) [P]	0.11	Sampled from PDF N (0.11, 0.019)
Dose of water ingested per lettuce ingested (L) [Q]	2.3×10^{-3}	Calculated from O×P/1000
Post-harvest time (days) [R]	5.7	Sampled from PDF T (1.0, 3.0, 7.0)
Post-harvest decay rate ($\log_{10}$/day) [S]	0.26	Sampled from PDF U (0.0, 0.5)
Washing removal ($\log_{10}$) [T]	1.0	Fixed value
Post-harvest + washing removal ($\log_{10}$) [U]	2.5	Calculated from R×S+T
Cryptosporidium dose per day (*Cryptosporidium*) [W]	1.9×10^{-8}	Calculated from $(N\times Q)/10^U$
Dose-response: Daily probability of infection given ingestion of the lettuce [X]	1.1×10^{-9}	Calculated from $1-\exp(-0.059\times W)$
Number of exposures per year [Y]	365	The number of exposures needs to be as many as days in a year, as the lettuce ingested is given per day
Yearly risk of infection [Z]	4.0×10^{-7}	Calculated from $1-(1-X)^Y$

Parameter	Value	Comment
Ratio disease/infection: probability of developing a disease given infection [AA]	0.71	Fixed value
Disease burden: DALYs per disease case [AB]	1.5×10^{-3}	Fixed value
Susceptibility: fraction of the population susceptible of suffering the disease [AC]	1.0	Fixed value
Calculated DALYs (pppy)	4.3×10^{-10}	Calculated from Z×AA×AB×AC

APPENDIX D: SAMPLE CALCULATION AND RESULTS FROM THE SENSITIVIY ANALYSIS (AVERAGE AND 95TH PERCENTILE RESULTS)

Sensitivity analysis is performed to identify which are the most or less important factors in a risk model, impacting the final risk result. In our case, sensitivity analysis is performed to identify the most effective treatments to reduce the risk for each pathogen and scenario considered. For sensitivity analysis, simulations are repeated eliminating one barrier each time. So, considering the example given in appendix C, 10,000 simulations would be performed replacing primary + secondary WWTP treatment removal PDF by zero; then, 10,000 simulations would be performed replacing mixture/dilution with Ripoll River treatment removal PDF by zero; and these calculations would be successively repeated for each treatment. When all simulations eliminating one treatment barrier each time are finished, then the factor sensitivity (FS) is calculated using the formula given in section 6.7.

Then, using the same examples given in appendix C, the FS calculations would be as follows:

Table D-1 Sample example of median FS calculation for rotavirus in the empirical risk characterization for the accidental ingestion of aerosols by growers/irrigators scenario.

Parameter	FS	Comment
Primary + Secondary WWTP treatment	1.2	Calculated from: FS = $\log_{10}(4.2\times10^{-8}/2.6\times10^{-9})$
Mixture/dilution with Ripoll River treatment	0.34	Calculated from: FS = $\log_{10}(5.8\times10^{-9}/2.6\times10^{-9})$
Aquifer/subsurface treatment	4.0	Calculated from: FS = $\log_{10}(2.8\times10^{-5}/2.6\times10^{-9})$
Combined disinfection and sand filter treatment	1.2	Calculated from: FS = $\log_{10}(4.3\times10^{-8}/2.6\times10^{-9})$

Table D-2 Sample example of median FS calculation for *Cryptosporidium* in the theoretical risk characterization for the crop consumption scenario.

Parameter	FS	Comment
Primary + Secondary WWTP treatment	1.0	Calculated from: FS = $\log_{10}(6.9\times10^{-9}/6.8\times10^{-10})$
Mixture/dilution with Ripoll River treatment	1.1	Calculated from: FS = $\log_{10}(8.9\times10^{-9}/6.8\times10^{-10})$
Aquifer/subsurface treatment	0.087	Calculated from: FS = $\log_{10}(8.3\times10^{-10}/6.8\times10^{-10})$
UV disinfection treatment	2.8	Calculated from: FS = $\log_{10}(4.7\times10^{-7}/6.8\times10^{-10})$
Chlorination disinfection treatment	0.16	Calculated from: FS = $\log_{10}(1.0\times10^{-9}/6.8\times10^{-10})$
Sand filter treatment	0.16	Calculated from: FS = $\log_{10}(9.9\times10^{-10}/6.8\times10^{-10})$
Total postharvest treatment	1.9	Calculated from: FS = $\log_{10}(5.0\times10^{-8}/6.8\times10^{-10})$

Sensitivity analysis results have been explained in section 6.8. In Table 26 the results for the median factor sensitivity (FS) have been summarized. However, it is also interesting to show the average and 95th percentile FS results, although not discussed. In this appendix, a summary of the average and 95th percentile FS results for each treatment, pathogen and scenario is given.

Table D-3 Factor sensitivity results for each treatment, pathogen and scenario. Values given have been calculated using average results for the PDFs.

EMPIRICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	0.95	1.1	0.98	0.49	0.94	0.87	0.76	1.0	0.94	0.95	0.95	0.90	0.95	0.95	0.95	0.95	1.8	1.9	1.8	0.95	1.8	1.7	1.5	1.8
Mixture/dilution with Ripoll River treatment	0.028	0.027	-0.029	0.18	0.023	0.041	0.067	0.035	0.93	0.93	0.93	0.92	0.93	0.93	0.95	0.93	-0.11	0.025	-0.078	0.18	-0.066	-0.098	-0.020	-0.11
Aquifer/subsurface treatment	2.4	2.9	2.5	0.90	2.4	2.1	1.9	2.6	2.6	2.6	2.6	1.6	2.6	2.6	2.6	2.6	2.9	3.2	3.0	1.3	3.0	2.7	2.4	3.0
Combined disinfection and sand filter treatment	0.85	0.87	0.89	0.48	0.82	0.77	0.69	0.93	0.68	0.68	0.69	0.75	0.68	0.69	0.69	0.69	1.2	1.2	1.2	0.75	1.2	1.1	1.0	1.2
Total postharvest treatment	–	2.3	–	–	–	–	–	–	–	1.6	–	–	–	–	–	–	–	2.9	–	–	–	–	–	–
THEORETICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	1.0	1.0	1.0	0.62	1.0	0.98	0.85	1.0	0.96	0.95	0.96	0.93	0.96	0.95	0.95	0.95	1.9	1.9	2.0	1.8	1.9	1.9	1.9	1.8
Mixture/dilution with Ripoll River treatment	-0.070	-0.044	-0.023	0.18	-0.056	-0.065	-0.036	-0.057	0.94	0.94	0.95	0.95	0.95	0.94	0.93	0.94	-0.13	-0.14	-0.041	0.11	-0.064	-0.085	-0.10	-0.13
Aquifer/subsurface treatment	1.1	1.1	1.2	0.86	1.2	1.1	1.1	1.2	0.084	0.085	0.084	0.26	0.084	0.085	0.084	0.084	1.2	1.2	1.3	1.4	1.3	1.3	1.3	1.2
UV disinfection treatment	1.8	1.9	1.8	0.90	1.8	1.6	1.4	1.8	2.7	2.7	2.7	1.5	2.7	2.7	2.7	2.7	2.9	2.9	2.8	2.3	2.8	2.9	2.8	2.8
Chlorination disinfection treatment	1.5	1.6	1.5	0.81	1.5	1.4	1.2	1.6	0.15	0.15	0.15	0.32	0.15	0.15	0.15	0.15	2.7	2.7	2.8	2.3	2.8	2.8	2.7	2.7
Sand filter treatment	0.17	0.15	0.18	0.19	0.17	0.16	0.14	0.16	0.15	0.15	0.16	0.32	0.16	0.15	0.15	0.15	0.14	0.11	0.17	0.35	0.16	0.16	0.15	0.13
Total postharvest treatment	–	2.4	–	–	–	–	–	–	–	1.6	–	–	–	–	–	–	–	2.9	–	–	–	–	–	–

A: accidental ingestion of aerosols by agricultural workers (growers / irrigators) scenario, C: crop consumption scenario, L: accidental ingestion of aerosols by inhabitants of local communities scenario, D: use of the recycled water as drinking water scenario, F: accidental ingestion of aerosols by factory workers scenario, S: Accidental ingestion of a high volume of water while swimming or developing aquatic activities scenario, CC: cross-connection of dual network systems scenario, I: accidental ingestion of aerosols by immunocompromised population scenario.

Table D-4 Factor sensitivity results for each treatment, pathogen and scenario. Values given have been calculated using 95th percentile results for the PDFs.

EMPIRICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	1.2	1.2	1.1	0.044	1.1	1.2	1.1	1.1	0.97	0.95	0.96	0.90	0.95	0.96	0.97	0.96	2.0	2.0	2.0	0.54	2.0	2.0	1.9	2.0
Mixture/dilution with Ripoll River treatment	0.14	0.15	0.11	0.040	0.12	0.14	0.15	0.14	0.94	0.94	0.96	0.89	0.94	0.95	0.95	0.95	0.12	0.096	-0.089	0.22	0.10	0.079	0.11	0.094
Aquifer/subsurface treatment	2.9	3.5	3.2	0.044	2.9	2.4	2.0	3.2	2.6	2.6	2.6	1.0	2.6	2.6	2.6	2.6	3.4	3.6	3.5	0.54	3.4	3.1	2.6	3.5
Combined disinfection and sand filter treatment	1.0	1.0	1.0	0.044	1.0	1.0	1.0	1.0	0.68	0.67	0.68	0.76	0.66	0.68	0.71	0.70	1.3	1.3	1.3	0.54	1.3	1.3	1.3	1.3
Total postharvest treatment	–	2.7	–	–	–	–	–	–	–	1.6	–	–	–	–	–	–	–	3.2	–	–	–	–	–	–
THEORETICAL RISK CHARACTERIZATION	rotavirus								*Cryptosporidium*								*Campylobacter*							
	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I	A	C	L	D	F	S	CC	I
Primary+ Secondary WWTP treatment	1.2	1.1	1.2	0.60	1.2	1.2	1.1	1.2	0.93	0.95	0.93	0.82	0.94	0.94	0.94	0.95	2.0	2.1	2.0	2.2	2.0	2.0	2.1	2..1
Mixture/dilution with Ripoll River treatment	0.074	0.13	0.12	0.25	0.10	0.14	0.10	0.10	0.89	0.93	0.90	0.80	0.89	0.89	0.89	0.91	0.079	0.13	0.11	0.26	0.070	0.045	0.13	0.070
Aquifer/subsurface treatment	1.5	1.5	1.5	0.60	1.5	1.5	1.4	1.5	0.090	0.079	0.085	0.27	0.084	0.072	0.079	0.081	1.6	1.8	1.6	1.8	1.6	1.6	1.6	1.6
UV disinfection treatment	2.0	2.0	2.1	0.60	2.0	2.0	1.9	2.0	2.7	2.7	2.7	0.87	2.7	2.7	2.6	2.7	2.9	3.0	3.0	3.0	2.9	2.9	2.9	2.9
Chlorination disinfection treatment	1.7	1.7	1.8	0.60	1.7	1.7	1.7	1.7	0.14	0.16	0.14	0.32	0.15	0.14	0.15	0.15	2.9	2.9	2.9	2.9	2.9	2.9	2.9	2.9
Sand filter treatment	0.16	0.16	0.18	0.30	0.18	0.17	0.16	0.17	0.15	0.14	0.13	0.32	0.15	0.14	0.14	0.14	0.17	0.18	0.17	0.39	0.16	0.15	0.17	0.15
Total postharvest treatment	–	2.7	–	–	–	–	–	–	–	1.6	–	–	–	–	–	–	–	3.3	–	–	–	–	–	–

A: accidental ingestion of aerosols by agricultural workers (growers / irrigators) scenario, C: crop consumption scenario, L: accidental ingestion of aerosols by inhabitants of local communities scenario, D: use of the recycled water as drinking water scenario, F: accidental ingestion of aerosols by factory workers scenario, S: Accidental ingestion of a high volume of water while swimming or developing aquatic activities scenario, CC: cross-connection of dual network systems scenario, I: accidental ingestion of aerosols by immunocompromised population scenario.

APPENDIX E: SUMMARY OF GUIDELINE VALUES USED FOR THE RISK ASSESSMENT

In section 4.2 it has been explained which the guideline values used for the risk assessment are. Primarily, the Spanish regulations (Royal Decrees) have been used, but also guidelines from WHO, Australia and US EPA have been considered for reference and comparison.

Guideline values have been selected according to the possible uses of the recycled water at RISMAR scheme. Current uses in place and possible future uses have been considered. Then, the corresponding guidelines for each use have been considered.

In the tables below the guideline values are given. Abbreviations for the regulations are detailed in the footnotes of the tables, as well as other comments. However, it is worthwhile detailing the guidelines and regulations used:

- Au DW G: Australian Drinking Water Guidelines (NHMRC–NRMMC, 2011).
- Au IW G: Australian Irrigation Water Guidelines (ANZECC and ARMCANZ, 2000).
- Au RW G: Australian Recreational Water Guidelines (NHMRC, 2008).
- Au AEW G: Australian Aquatic Ecosystems Water Guidelines (ANZECC and ARMCANZ, 2000).
- WHO DW G: World Health Organization Drinking Water Guidelines (WHO, 2011a).
- WHO IW G: World Health Organization Irrigation Water Guidelines (WHO, 2006b).
- WHO RW G: World Health Organization Recreational Water Guidelines (WHO, 2003a).
- US EPA several uses (UUR; ARFC; URR; IR; MAR; IPR; ER) guidelines: United States Environmental Protection Agency Guidelines for Water Reuse (US EPA, 2012). In these water reuse guidelines there are recommended guideline values, but there are also included regulations set in different states. Then, in the table, it is stated R or G, depending on if it is a value part of a regulation of any of the states that have regulations for reuse or a guideline value recommended by the US EPA in case there is no regulation set.
- RD 1620/2007 several uses (UUR; ARFC; IR; MAR) regulation: Royal Decree (Spanish regulation) for Water Reuse (BOE, 2007b). The Spanish government issued this law to regulate different uses accepted for the recycled water. At no point was contemplated the possibility of using the recycled water as drinking water, recreational water or any indirect potable reuse. In fact, these uses are prohibited in this regulation. Other regulations apply for drinking water and bathing water (swimming pools) that are also included in the table and cited below.
- RD 140/2003 DW: Royal Decree (Spanish regulation) for Drinking Water (BOE, 2003).
- RD 743/2013BWSP: Royal Decree (Spanish regulation) for Bathing Waters - Swimming Pools (BOE, 2013). The Spanish government issued this law to regulate the quality of the air and water in the swimming pools.

Table E-1 Summary of guideline values used for the risk assessment (1).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Acrilamide	µg/L	0.2		2		0.5		5								0.5					0.1	
Alachlor	µg/L					20		200								2	0.3/0.7 (5)	0.3/0.7 (5)	0.3/0.7 (5)	0.3/0.7 (5)		
Aldehyde	mg/L																1 (1)	1 (1)	1 (1)	1 (1)		
Aldrin	µg/L																				0.03	
Aldrin + dieldrin	µg/L	0.3		3		0.03		0.3									0.01/NA (2, 5)	0.01/NA (2, 5)	0.01/NA (2, 5)	0.01/NA (2, 5)		
Aluminium	mg/L	0.2 (3)	5 LTV, 20 STV		0.15	0.9	5	9		5 G						0.05-0.2	1 (1)	1 (1)	1 (1)	1 (1)	0.2	
Aniline	mg/L				4.8																	
Anthracene	µg/L																0.1/0.4 (5)	0.1/0.4 (5)	0.1/0.4 (5)	0.1/0.4 (5)		
Antimony	µg/L	3	100 LTV, 2000 STV	30		20		200								6					5	
Arsenic	µg/L	10		100	140-360 (4)	10	100	100		100 G						10	50/NA (5)	50/NA (5)	50/NA (5)	50/NA (5)	10	
Atrazine	µg/L	20		200	150	100		1000								3	0.6/2 (5)	0.6/2 (5)	0.6/2 (5)	0.6/2 (5)		
Bacteriophages	pfu/100mL	0							5 mean, 25 max R													
Barium	µg/L	2000		20000		700		7000								2000	20000 (1)	20000 (1)	20000 (1)	20000 (1)		
Benzene	µg/L	1		10	2000	10		100								5	10/50 (5)	10/50 (5)	10/50 (5)	10/50 (5)	1	
Benzofluoranthene	µg/L																0.03/NA (5)	0.03/NA (5)	0.03/NA (5)	0.03/NA (5)	10 (30)	

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; pfu: plaque forming units; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(2) The guideline value is given for the sum of aldrin, dieldrin, endrin and isodrin.

(3) This is not a health guideline value, but related to aesthetic considerations.

(4) First value applies to arsenic V and second value to arsenic III.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

Table E-2 Summary of guideline values used for the risk assessment (2).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Benzoperylene + indenopyrene	ng/L																2/NA (5)	2/NA (5)	2/NA (5)	2/NA (5)	10 (30)	
Benzopyrene	µg/L	0.01		0.1		0.7		7								0.2	0.05/0.1 (5)	0.05/0.1 (5)	0.05/0.1 (5)	0.05/0.1 (5)	0.01	
Beryllium	µg/L	60	100 LTV, 500 STV	600		12	100	120		100 G						4		100				
Bicarbonate	mg/L						90-500 (28)															
BOD Total	mg/L								5-60 R; 10 G	5-60 R; 10 G	5-30 R; 10 G	10-60 R; 30 G	5-60 R	5-60 R	5-30 R; 30 G		40 (1)	40 (1)	40 (1)	40 (1)		
Boron	µg/L	4000	500 (6)	40000	1300	2400	700	24000		750 G							2000 (1)	500	2000 (1)	2000 (1)	1000	
Bromate	µg/L	20		200		10		100								10					10	
Bromide	mg/L					6		60														2-5
Brominated diphenyl ethers	ng/L																0.5/NA (5)	0.5/NA (5)	0.5/NA (5)	0.5/NA (5)		
Bromodichloromethane	µg/L					60		600														
Bromoform	µg/L					100		1000														
Cadmium	µg/L	2	10 LTV, 50 STV	20	0.8	3	10	30		10 G						5	0.25/1.5 (5, 14)	0.25/1.5 (5, 14)	0.25/1.5 (5, 14)	0.25/1.5 (5, 14)	5	
Carbon tetrachloride	µg/L	3		30												5	12/NA (5)	12/NA (5)	12/NA (5)	12/NA (5)		
Chlordane	µg/L	2		20		0.2										2					0.10	
Chlorfenvinphos	µg/L	2															0.1/0.3 (5)	0.1/0.3 (5)	0.1/0.3 (5)	0.1/0.3 (5)		

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BOD: Biological Oxygen Demand; BWSP; Bathing Waters - Swimming Pools; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(14) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(28) Range according to slight to moderate restriction in use of the recycled water for irrigation and to a electrical conductivity between 0.7-3.0 dS/m.

(30) Guideline value set for the sum of benzofluoranthene, benzoperylene and indenopyrene.

Table E-3 Summary of guideline values used for the risk assessment (3).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Chloride	mg/L	250 (3)	175 (8); 350 (9)			250 (7)	142-355 (28)									250	2000 (1)	2000 (1)	2000 (1)	2000 (1)	250	
Chlorine residual combined	mg/L																				2	0.6
Chlorine residual free	mg/L	5		50	13	5	1	50	>1 to >5 R; >1 G	>1 to >5 R; >1 G	>1 R; >1 G	>1 to >5 R; >1 G	>0.5 to >1 R	>1 R; >1 G	>0.5 to >1 R; >1 G	4					1	0.5-2
Chloroalkanes	µg/L																0.4/1.4 (5)	0.4/1.4 (5)	0.4/1.4 (5)	0.4/1.4 (5)		
Chlorobenzene	µg/L	300		3000	1220 (11)											100	20/NA (5)	20/NA (5)	20/NA (5)	20/NA (5)		
Chloroform	µg/L					300		3000														
Chlorpyrifos	µg/L	10		100	1.2	30		300									0.03/0.1 (5)	0.03/0.1 (5)	0.03/0.1 (5)	0.03/0.1 (5)		
Chromium	µg/L	50	100 LTV, 1000 STV (12)	500	40 (12)	50	100	500		100 G						100	5/NA (5, 12) 50/NA (5)	5/NA (5, 12) 50/NA (5)	5/NA (5, 12) 50/NA (5)	5/NA (5, 12) 50/NA (5)	50	
Clostridium perfringens	cfu/100mL									5 mean, 25 max R (35)											0 (13)	
Cobalt	µg/L		50 LTV, 100 STV				50			50 G								50				

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

(3) This is not a health guideline value, but related to aesthetic considerations.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(8) A value superior to the referred one can cause foliar damage in sensitive crops.

(9) A value superior to the referred one can increase the uptake of cadmium from soil by plants.

(11) Guideline value given for the sum of different compounds included in the group.

(12) Guideline value given for chromium VI, not for total chromium.

(13) When measured values are higher than 0 cfu/100mL, health authorities will determine the necessity of measuring also *Cryptosporidium* or other microorganisms and parasites.

(28) Range according to slight to moderate restriction in use of the recycled water for irrigation and to a electrical conductivity between 0.7-3.0 dS/m.

(35) Guideline value given for *Clostridium* in general, not especifically *Clostridium perfringens* .

Table E-4 Summary of guideline values used for the risk assessment (4).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
COD Total	mg/L																160 (1)	160 (1)	160 (1)	160 (1)		
Colour	mg/L Pt/Co															15					15	
Copper	µg/L	2000	200 LTV, 5000 STV	20000	2.5	2000	200	20000		200 G						1300	120/NA (5, 14)	120/NA (5, 14)	120/NA (5, 14)	120/NA (5, 14)	2000	
Cryptosporidium	% removal															99 (19)						
Cyanide	µg/L	80		800	18	500		5000								200	40/NA (5)	40/NA (5)	40/NA (5)	40/NA (5)	50	
Detergents	mg/L				2.6											0.5	2 (1)	2 (1)	2 (1)	2 (1)		
DDT	µg/L	9		90	0.04	1		10									0.025/ NA (5)	0.025/ NA (5)	0.025/ NA (5)	0.025/ NA (5)		
DEHP	µg/L					8		80								6	1.3/NA (5)	1.3/NA (5)	1.3/NA (5)	1.3/NA (5)		
Dibromochloromethane	µg/L					100		1000														
1,2-Dichloroethane	µg/L	3		30		30		300								5	10/NA (5)	10/NA (5)	10/NA (5)	10/NA (5)	3	
Dichlorobenzene	µg/L	40		400	100	300		3000									20/NA (5)	20/NA (5)	20/NA (5)	20/NA (5)		
Dichloromethane	µg/L	4		40		20		200								5	20/NA (5)	20/NA (5)	20/NA (5)	20/NA (5)		
Dieldrin	µg/L																				0.03	
2,4-Dinitrophenol	µg/L				140																	
Diuron	µg/L	20	2	200													0.2/1.8 (5)	0.2/1.8 (5)	0.2/1.8 (5)	0.2/1.8 (5)		

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; COD: Chemical Oxygen Demand; cfu: colony forming units; DDT: (1,1,1-trichloro-di-(4-chlorophenyl) ethane); DEHP: Di(2-ethylhexyl)phthalate; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(14) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(19) Unfiltered systems are required to include *Cryptosporidium* in their existing watershed control provisions.

Table E-5 Summary of guideline values used for the risk assessment (5).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
DOC	mg/L													0.5-3 mean, 5 max R; 2 G (15)								
Electrical conductivity	dS/m	1 (7)	0.65 (16)	10		1.56 (7)	0.7-3.0 (36)									0.75		3			2.5	
Endosulfan	µg/L	20		200	1.8	20		200									0.005/ 0.01 (5)	0.005/ 0.01 (5)	0.005/ 0.01 (5)	0.005/ 0.01 (5)		
Endrin	µg/L				0.06	0.6		6								2						
Epichlorohydrin	µg/L	0.5		5		0.4		4								2					0.1	
Enterococci	cfu/100mL	0		40				35	4 mean, 9 max R	11 mean, 24 max R	4-11 mean, 9-24 max R	35 mean, 89-104 max R		4 mean, 9 max R							0	
Escherichia coli	cfu/100mL	0							0-20 mean, 14-200 max R; 0 mean,14 max G (17)	0-20 mean, 23-200 max; 0 mean, 14 max G (17)	0-20 mean, 23-75 max; 0 mean, 14 max G (17)	2.2-200 mean, 25-800 max R; 200 mean, 800 max (17)	200 mean, 800 max R (17)	20-200 mean, 75-400 max R (17)	14-200 mean, 25-200 max R; 200 mean, 800 max G (17)	0	200	100	0-10000 (18)	1000	0	0
Ethanol	mg/L				4																	
Ethylbenzene	µg/L	3		30		300		3000								700	30/NA (5)	30/NA (5)	30/NA (5)	30/NA (5)		

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DOC: Dissolved Organic Carbon; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; max: maximum; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(15) Regulations are given for TOC, not for DOC in USEPA guidelines.

(16) For sensitive crops; moderately sensitive 0.65-1.3, moderately tolerant 1.3-2.9. See ANZECC-ARMCANZ guidelines for a detailed tolerance of different crops.

(17) Regulations and guidelines are given for fecal coliforms, not for *E. coli* in US EPA guidelines (US EPA, 2012).

(18) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(36) Range according to slight to moderate restriction in use of the recycled water for irrigation regarding only the salinity of the water; <0.7 no restriction in use; ; > 3.0 for a severe restriction.

Table E-6 Summary of guideline values used for the risk assessment (6).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Fluoranthene	µg/L																0.1/1 (5)	0.1/1 (5)	0.1/1 (5)	0.1/1 (5)		
Fluoride	mg/L	1.5	1 LTV, 2 STV	15		1.5	1	15		1 G						4	1.7/NA (5)	1.7/NA (5)	1.7/NA (5)	1.7/NA (5)	1.5	
Giardia lamblia	% removal															99.9						
Hardness	mg/L $CaCO_3$	60-200 (23)				100-200 (23)																
Helminth eggs	eggs/L																0.1	0.1	0.1			
Heptachlor	µg/L	0.3		3	0.7	0.03		0.3								0.4					0.03	
Heptachlor epoxide	µg/L	0.3		3		0.03		0.3								0.2					0.03	
Heterotrophic Bacteria (22 °C)	cfu/100mL															50000					10000	
Hexachlorobenzene	µg/L					1		10								1	0.01/ 0.05 (5)	0.01/ 0.05 (5)	0.01/ 0.05 (5)	0.01/ 0.05 (5)		
Hexachlorobutadiene	µg/L	0.7		7		0.6		6									0.1/0.6 (5)	0.1/0.6 (5)	0.1/0.6 (5)	0.1/0.6 (5)		
Hexachlorocyclohexane	µg/L																0.02/ 0.04 (5)	0.02/ 0.04 (5)	0.02/ 0.04 (5)	0.02/ 0.04 (5)		
Hexachloroethane	µg/L				500																	
Iron	µg/L	300 (3)	200 LTV, 10000 STV			2000 (7)	5000			5000 G						300	2000 (1)	2000 (1)	2000 (1)	2000 (1)	200	
Isocyanate	mg/L																					75
Isoproturon	µg/L					9		90									0.3/1 (5)	0.3/1 (5)	0.3/1 (5)	0.3/1 (5)		
Lead	µg/L	10	2000 LTV, 5000 STV	100	9.4	10	5000	100		5000 G						15	7.2/NA (5)	7.2/NA (5)	7.2/NA (5)	7.2/NA (5)	25	

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(3) This is not a health guideline value, but related to aesthetic considerations.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(23) This is not a health guideline value, but related to reduce fouling, corrosion, scaling, equipment blocking and encrustration in pipes and fittings.

Table E-7 Summary of guideline values used for the risk assessment (7).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Legionella	cfu/L																100	1000	0-100 (18)			100
Manganese	µg/L	500	200 LTV, 10000 STV	5000	3600	400 (7)	100 (23); 200			200 G						50	2000 (1)	200	2000 (1)	2000 (1)	50	
Mercury	µg/L	1	2 LTV, 2 STV	10	5.4	6		60								2	0.05/ 0.07 (5)	0.05/ 0.07 (5)	0.05/ 0.07 (5)	0.05/ 0.07 (5)	1	
Metholachlor	µg/L	300		3000		10		100									1/NA (5)	1/NA (5)	1/NA (5)	1/NA (5)		
Microcystin	µg/L	1.3		10		1		10													1	
Molybdenum	µg/L	50	10 LTV, 50 STV	500		70	10	700		10 G								10				
N-Ammonia	mg/L	0.4 (3, 21)			1.9				4 mean, 6 max R	1-4 mean, 2-6 max R					2-4 mean, 4-6 max R		12 (1, 21)	12 (1, 21)	12 (1, 21)	12 (1, 21)	0.4 (21)	
N-Nitrate	mg/L	11 (21)		110 (21)	17	11		110					2.6 R (21)			10				5.6 (21)	11	
N-Nitrite	mg/L	0.9 (21)		9 (21)		0.9		9								1	3 (1, 21)	3 (1, 21)	3 (1, 21)	3 (1, 21)	0.03-0.15 (22)	
N-Total	mg/L		5 LTV, 25-125 STV				5		10 R (10)	10 R (10)		10 R (10)	10 R	10 R	3-6 R					10		
Naphthalene	µg/L				85												2.4/NA (5)	2.4/NA (5)	2.4/NA (5)	2.4/NA (5)		

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(3) This is not a health guideline value, but related to aesthetic considerations.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(10) In this case the guideline value given is not for total nitrogen but for the sum of N-ammonia and N-nitrate.

(18) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(21) Guideline values are given for nitrate, nitrite and ammonia. Then, the original set values given have been transformed to N-Nitrate, N-Nitrite and N-Ammonia.

(22) Lower value applies when measured in the treatment plant outlet; upper value when mesaured in the distribution network.

(23) This is not a health guideline value, but related to reduce fouling, corrosion, scaling, equipment blocking and encrustration in pipes and fittings.

Table E-8 Summary of guideline values used for the risk assessment (8).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Nickel	µg/L	20	200 LTV, 2000 STV	200	17	70	200	700		200 G							20/NA (5)	20/NA (5)	20/NA (5)	20/NA (5)	20	
Nitrobenzene	µg/L				1300																	
Nitrotoluene	µg/L				460 (11)																	
4-Nonylphenol	µg/L																0.3/2 (5)	0.3/2 (5)	0.3/2 (5)	0.3/2 (5)		
Nonylphenol	µg/L																0.3/2 (5)	0.3/2 (5)	0.3/2 (5)	0.3/2 (5)		
Octylphenol	µg/L																0.1/NA (5)	0.1/NA (5)	0.1/NA (5)	0.1/NA (5)		
Odour	Dilution index															3					3 at 25ºC	
Oil and grease	mg/L																20 (1)	20 (1)	20 (1)	20 (1)		
Oxidability to permanganate	mg/L																				5	
Pentachlorobenzene	ng/L																7/NA (5)	7/NA (5)	7/NA (5)	7/NA (5)		
Pentachlorophenol	µg/L	10		100		9		90								1	0.4/1 (5)	0.4/1 (5)	0.4/1 (5)	0.4/1 (5)		
Pesticides total	µg/L																50 (1)	50 (1)	50 (1)	50 (1)	0.50	
pH	pH units	6.5-8.5 (23)	6.0-8.5 (23)	6.5-8.5		6.5-8.5 (23)	6.5-8.0		6-9 G	6-9 G	6-9 G	6-9 G		6.5-8.5 G		6.5-8.5	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	5.5-9.5 (1)	6.5-9.5 (31)	7.2-8 (31)
Phenols	mg/L				1.2												0.5 (1)	0.5 (1)	0.5 (1)	0.5 (1)		
Phthalates	mg/L				6.5 (11)																	
Polycyclic aromatic hydrocarbons	µg/L																				0.1	

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(11) Guideline value given for the sum of different compounds included in the group.

(23) This is not a health guideline value, but related to reduce fouling, corrosion, scaling, equipment blocking and encrustration in pipes and fittings.

(31) When pH is found out of the recommended range, Langelier index must be measured and found in the range -0,5 to +0,5.

Table E-9 Summary of guideline values used for the risk assessment (9).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
P-Phosphate	mg/L		0.05 LTV (24), 0.8-12 STV (25)												1-2 R (25)		10 (1, 25)	10 (1, 25)	10 (1, 25)	10 (1, 25)		
Pseudomonas aeruginosa	cfu/100mL																					0
Redox Potential	mV																					250-900 (32)
SAR	SAR units		NA (29)				NA (29)											6				
Selenium	µg/L	10	20 LTV, 50 STV	100	34	40	20	400		20 G						50	1/NA (5)	1/NA (5)	1/NA (5)	1/NA (5)	10	
Simazine	µg/L	20		200	35	2		20								4	1/4 (5)	1/4 (5)	1/4 (5)	1/4 (5)		
Sodium	mg/L	180 (7)	115 (8)			200 (7)	92-207 (28)	2000 (7)													200	
Sulfate	mg/L	500		5000		500		5000								250	2000	2000			250	
Sulphide	µg/L	50 (3)					500 (26)	2.6 (26)									1000 (1)	1000 (1)	1000 (1)	1000 (1)		
Sulphite	µg/L																1000 (1)	1000 (1)	1000 (1)	1000 (1)		
Suspended Solids	mg/L						50		5-60 R	5-60 R	30 R	5-60 R; 30 G	5-60 R	5-30 R	5-30 R; 30 G		20	20	5-35 (18)	35		
Taste	Dilution index																				3	

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; SAR: Sodium Absorption Ratio; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(3) This is not a health guideline value, but related to aesthetic considerations.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(8) A value superior to the referred one can cause foliar damage in sensitive crops.

(24) To avoid bioclogging in irrigation equipment.

(25) Guideline values are given for Total Phosphorous, not P-Phosphate.

(26) Value for hydrogen sulfide.

(28) Range according to slight to moderate restriction in use of the recycled water for irrigation and to a electrical conductivity between 0.7-3.0 dS/m.

(29) SAR is given as a range according to the elecrical conductivity of the water. See the guidelines for more information.

(32) Redox potential will be measured when disinfectants used are different than chlorine, bromide or their derivates.

Table E-10 Summary of guideline values used for the risk assessment (10).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	RD 742/ 2013 BWSP
Temperature	ºC			15													Δ3 (27)	Δ3 (27)	Δ3 (27)	Δ3 (27)		24-30 (33)
Terbuthylazine	µg/L	10		100		7		70									1/NA (5)	1/NA (5)	1/NA (5)	1/NA (5)		
Tetrachloroethene	µg/L	50		500		40		400									10/NA (5)	10/NA (5)	10/NA (5)	10/NA (5)		
Tin	mg/L																10 (1)	10 (1)	10 (1)	10 (1)		
Toluene	µg/L	4		40		7		70								1000	50/NA (5)	50/NA (5)	50/NA (5)	50/NA (5)		
Total Coliforms	cfu/100mL								2.2 mean, 23-240 max R	2.2 mean, 23-240 max R	2.2 mean, 23-240 max R	2.2 mean, 23-240 max R	2.2 mean, 23 max R	1-2.2 mean, 0-4-240 max R; 0 mean, 14 max G	2.2 mean, 23 max R	0					0	
Tributyltin	ng/L																0.2/1.5 (5)	0.2/1.5 (5)	0.2/1.5 (5)	0.2/1.5 (5)		
Trichlorobenzene	µg/L	30		300	30	20		200								70	0.4/NA (5)	0.4/NA (5)	0.4/NA (5)	0.4/NA (5)		
1,1,1-Trichloroethane	µg/L					2000		20000								200	100/NA (5)	100/NA (5)	100/NA (5)	100/NA (5)		
1,1,2-Trichloroethane	µg/L				8400											5						
Trichloroethylene	µg/L					20		200								5	10/NA (5)	10/NA (5)	10/NA (5)	10/NA (5)		
Trichloroethene + tetrachloroethene	µg/L					20		200													10	
Trichloromethane	µg/L																2.5/NA (5)	2.5/NA (5)	2.5/NA (5)	2.5/NA (5)		
Trifluralin	µg/L	90		900	9	20		200									0.03/NA (5)	0.03/NA (5)	0.03/NA (5)	0.03/NA (5)		
Trihalomethanes total	µg/L	250		2500												80					100	

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; cfu: colony forming units; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; max: maximum; NA: Not Applicable; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(1) Guideline values given in annex IV of RD 849/1986, for the most restrictive values on industrial discharges.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(18) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(27) For discharges in rivers, the water temperature increase after the discharge should not be higher than 3ºC.

(33) Temperature range to be abided only for heated pools.

Table E-11 Summary of guideline values used for the risk assessment (11).

Parameter	Units	Au DW G	Au IW G	Au RW G	Au AEW G	WHO DW G	WHO IW G	WHO RW G	US EPA UUR	US EPA ARFC	US EPA URR	US EPA IR	US EPA MAR	US EPA IPR	US EPA ER	US EPA DW R	RD 1620/ 2007 UUR	RD 1620/ 2007 ARFC	RD 1620/ 2007 IR	RD 1620/ 2007 MAR	RD 140/ 2003 DW	P RD BWSP
Turbidity	NTU	5 (3)							0.2-2 mean, 0.5-10 max R; 2 G	0.2-2 mean, 0.5-10 max R; 2 G	0.2-2 mean, 0.5-10 max R; 2 G	0.2-2 mean, 0.5-10 max R	2 mean, 5 max G	0.1-2 mean, 0.5-10 max R; 2 G		0.3-5 (20)	10	10	1-15 (18)		1-5 (22)	5 (34)
Uranium	µg/L	17	10 LTV, 100 STV	170		30										30						
Vanadium	µg/L		10 LTV, 50 STV				100			100 G								100				
Vinyl chloride	µg/L	0.3		3		0.3		3								2					0.5	
Viruses	% removal															99.99						
Xylene	µg/L	20		200	980 (11)	0.3		3								10000	30/NA (5)	30/NA (5)	30/NA (5)	30/NA (5)		
Zinc	µg/L	3000 (7)	2000 LTV, 5000 STV		31	3000 (7)	2000			2000 G						5000	500/NA (5, 14)	500/NA (5, 14)	500/NA (5, 14)	500/NA (5, 14)		

AEW: Aquatic Ecosystems Water; ARFC: Agricultural Reuse - Food Crops; Au: Australian; BWSP; Bathing Waters - Swimming Pools; DW: Drinking Water; ER: Environmental Reuse; G: Guidelines; IPR: Indirect Potable Reuse; IR: Industrial Reuse; IW: Irrigation Water; LTV: Long-term Value; MAR: Managed Aquifer Recharge; max: maximum; NA: Not Applicable; NTU: Nefelometric Turbidity Units; R: Regulation; RD: Royal Decree (Spanish Regulation); RW: Recreational Water; STV: Short-term Value; URR: Unrestricted Recreational Reuse; US EPA: United States Environmental Protection Agency; UUR: Unrestricted Urban Reuse; WHO: World Health Organization.

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(3) This is not a health guideline value, but related to aesthetic considerations.

(5) Guideline values given in RD 63/2011, that abolishes former RD 995/2000. The first value corresponds to the annual average, and the second value to the maximum concentration permitted.

(7) This is not a health guideline value, but related to taste.

(11) Guideline value given for the sum of different compounds included in the group.

(14) Guideline value depends on the water hardness. Value given is according to high water hardness, as it is the case in Sabadell.

(18) Guideline values range depends on the industrial use (the most restrictive is for cooling towers).

(20) For systems that use conventional or direct filtration, maximum turbidity should be < 1 NTU, and turbidity should be ≤ 0.3 NTU in 95% of the samples. For systems that use filtration other than conventional or direct filtration maximum turbidity should be < 5 NTU.

(22) Lower value applies when measured in the treatment plant outlet; upper value when mesaured in the distribution network.

(34) For values higher than 20 NTU the swimming pool will be closed until normalization.

APPENDIX F: SUMMARY OF CRITICAL CONTROL POINTS (CCPS) AND POINTS OF ATTENTION (POAS), POTENTIAL HAZARDOUS EVENTS AND COMPOUNDS, OPERATIONAL AND VERIFICATION MONITORING, CRITICAL LIMITS (CL) AND TARGET CRITERIA (TC), MONITORING AND SAMPLING FREQUENCY, CORRECTIVE ACTIONS AND PREVENTIVE ACTIONS FOR RISMAR SCHEME

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
Wastewater entering the Ripoll River WWTP (POA)	- Illegal discharges or industrial discharges not fulfilling the requirements set in the RD 849/1986 - Malfunction of industries in the area	- Pathogens - Inorganic compounds - Organic compounds - Salinity - Nutrients - Turbidity and particulates - Radionuclides	- Operational monitoring (by EDS, continuous): pH, temperature, electrical conductivity, organic matter, turbidity, flow - Verification monitoring (by CASSA): flow, suspended solids, COD, BOD_5, total nitrogen, ammonia, nitrate and total phosphorus	- Operational monitoring (by EDS, continuous): * pH: 5.5 – 9.5 TC * electrical conductivity: ≤ 3 dS/m TC - Verification monitoring (by CASSA): * Flow: ≤ 30000 m^3/day * COD ≤ 1300 mg/L CL * BOD_5 ≤ 440 mg/L CL * Suspended solids ≤ 630 mg/L CL * Total nitrogen ≤ 79 mg/L CL * Total phosphorus ≤ 15 mg/L CL	- Operational monitoring (by CASSA): * Daily: flow, suspended solids * Three days/week: COD and BOD_5 * Two days/week: total nitrogen, ammonia, nitrate and total phosphorus - Operational monitoring (waste control system, by EDS): * Continuous monitoring of pH, temperature, electrical conductivity, organic matter, turbidity, flow	- Divert influent to a detention tank - Divert influent to an additional pre-treatment - Additional conventional treatments	- Waste control system for early detection of pollution peaks in the sewerage system
Ripoll River WWTP conventional	- Malfunction of WWTP (e.g. nutrient	- Pathogens - Inorganic compounds	- Operational monitoring (by EDS, continuous): pH,	- Operational monitoring (by EDS, continuous): * pH: 5.5 – 9.5 TC	- Operational monitoring (by CASSA):	- Discharge of the water downstream of	- Waste control system for early detection of

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
treatments (POA)	removal) - Strong rain events, when wastewater can be discharged to the Ripoll River without being treated (but diluted)	- Organic compounds - Salinity - Nutrients - Turbidity and particulates - Radionuclides	temperature, electrical conductivity, organic matter, turbidity, dissolved oxygen, nitrate, ammonia, orthophosphate, flow - Verification monitoring (by CASSA): flow, suspended solids, COD, BOD_5, total nitrogen, ammonia, nitrate and total phosphorus	* electrical conductivity: ≤ 3 dS/m TC - Verification monitoring (by CASSA): * COD ≤ 125 mg/L or reduction ≥ 75% CL, ≤ 100 mg/L TC * BOD_5 ≤ 25 mg/L or reduction ≥ 70% CL, ≤ 20 mg/L TC * Suspended solids ≤ 35 mg/L or a reduction ≥ 90% CL, ≤ 30 mg/L TC * Total nitrogen ≤ 10 mg/L or a reduction ≥ 70% CL * Total phosphorus ≤ 1 mg/L or a reduction ≥ 80% TC	* Daily: flow, suspended solids * Three days/week: COD and BOD_5 * Two days/week: total nitrogen, ammonia, nitrate and total phosphorus - Operational monitoring (waste control system, by EDS): * Continuous monitoring of pH, temperature, electrical conductivity, organic matter, turbidity, dissolved oxygen, nitrate, ammonia, orthophosphate, flow	the infiltration area - Use chemical coagulation for primary treatment (optional step) - Add pre-treatment - Increase aeration in secondary treatment	pollution peaks in the sewerage system - Ensure a proper functioning of the WWTP and control the results of the analyses in a timely manner - Upgrade the applied treatments (CASSA)
Ripoll River water (POA)	- Pollution of the Ripoll River by effluents of WWTPs upstream -Discharges or run-off from unsewered settlements upstream - Sewerage system breakages	- Pathogens - Inorganic compounds - Organic compounds - Salinity - Nutrients - Turbidity and particulates	- Verification monitoring (by EDS): specific samplings commissioned to UB ecology group to define the ecological status of the Ripoll River, including several ecological indicators, flow, pH, temperature, electrical conductivity, dissolved oxygen,	- No TC/CL defined, but several proposals to restore the Ripoll River ecological status, including riparian fauna and vegetation	- Verification monitoring (by EDS): * Ecological sampling campaigns: 2 per year (spring and summer) on 2001, 2002, 2005, 2006 and 2007 * Ripoll River and its affluents: used to be performed 4 times per year (one each season)	- Stop pumping if there has been a pollution peak/toxic spill in the Ripoll River - Long and deep restoration project, which improved the riverbed and the banks	- Management plan jointly developed with the municipalities upstream the Ripoll River to prevent illegal discharges and to improve the quality of the WWTP effluents

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
	or spills - Illegal discharges by neighbouring factories - City farmers discharges (leakages) and run-off (non-point pollution) - Pollution by birds - Clogging of the riverbed		nitrate, ammonia, colour, odour, turbidity, nitrite, nitrate, sulphate, orthophosphate, chloride, COD, suspended solids - Verification monitoring (by EDS): monitoring of the Ripoll River and its affluents: temperature, pH, electrical conductivity, turbidity, ammonia, total coliforms, *E. coli*, flow - Verification monitoring (by ACA): many basic parameters, inorganic compounds, organic compounds, nutrients, salinity and particulates		- Verification monitoring (by ACA): samplings: yearly	- Construction of a tertiary treatment by-passing part of the Ripoll River water, in order to reduce nutrients concentration	discharged - Monitoring of the river in different points by EDS
Riverbed filtration (POA)	- Pollution of the Ripoll River by effluents of WWTPs upstream - Discharges/ run-off from unsewered settlements upstream - Sewerage	- Pathogens - Inorganic compounds - Organic compounds - Salinity - Nutrients - Turbidity and particulates - Infiltration rate	- Verification monitoring (recommended): check infiltration rate and that it does not decrease; a decrease could indicate clogging of the riverbed	- A CL and/or TC will be set when a wider study of the infiltration rate is available	- Infiltration rate: it is recommended at least a yearly study. Depending on the results obtained, frequency can be increased to have a snapshot of seasonal changes.	- Construction of a tertiary treatment treating part of the Ripoll River water (a by-pass of around 10%), in order to reduce nutrients concentration - Dredging of	- Management plan jointly developed with the municipalities upstream the Ripoll River to prevent illegal discharges and to improve the quality of the

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
	system breakages or spills - Illegal discharges by neighbouring factories - City farmers discharges (leakages) and run-off - Pollution by birds - Clogging of the riverbed					the riverbed in case the clogging is strong	WWTP effluents discharged - Monitoring of the river in different points by EDS
Groundwater recovery (POA)	- Hard rain enhancing release of retained hazardous components in the soil, subsoil or vadose zone to the aquifer - Depletion of groundwater levels - Pollution plumes related to pollution events in the Ripoll River - Sewerage system breakages	- Pathogens - Inorganic compounds - Organic compounds - Salinity - Nutrients - Turbidity and particulates - Radionuclides - Volumes infiltrated and groundwater levels - Aquifer and groundwater-dependent ecosystems	- Operational monitoring (recommended): pH, electrical conductivity, turbidity, redox potential and check piezometric levels of both aquifers (for the alluvial aquifer, different wells located in Sabadell municipality should be selected) - Verification monitoring (recommended): *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22ºC and bacteriophages	- Operational monitoring (recommended): * pH: 6.0 – 8.0 CL, 6.2 – 7.8 TC * electrical conductivity: ≤ 3.0 dS/m CL, ≤ 2.6 dS/m TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC * redox potential: if it suffers a strong change, perform additional monitoring of inorganic compounds and TOC * Piezometric levels of Miocene aquifer: QLSub – Sabadell - 1: 113 MASL CL, 118 MASL TC QLSub – Sabadell - 2: 102	- Operational monitoring (recommended): In the future, it is recommended to install probes in the mine, in a depth close to where water is pumped, for continuous monitoring of: pH, electrical conductivity, turbidity, redox potential. Besides, checking of piezometric levels monthly - Verification	- Stop sending the Ripoll River WWTP effluent to the Ripoll River in the area close to where the mine is located - Check illegal disposals in the area - Stop pumping of groundwater	- Monitoring of groundwater quality in different points, including natural wells and private wells owned by factories in the area (lower frequency) - It is recommended to install other piezometers tapping the alluvial aquifer close to the area where the mine

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
	or spills		- Verification monitoring (by EDS): monitoring of natural wells in the area: temperature, pH, electrical conductivity, turbidity, ammonia, total coliforms, *E. coli*, flow - Verification monitoring (by CASSA): monitoring of the groundwater (specific sampling) for arsenic, manganese, organic compounds - Verification monitoring (by ACA): many basic parameters, inorganic compounds, organic compounds, nutrients, salinity and particulates	MASL TC, 107 MASL CL QLSub – Sabadell - 1: 108 MASL TC, 113 MASL CL * For the piezometric levels of the alluvial aquifer no CL and TC can be set, after a period of monitoring they will be set - Verification monitoring (recommended): no CL/TC set, just check the microbiological status of the aquifer in order to understand the performance of the system	monitoring (recommended): every three months (one sampling in each season) - Verification monitoring (by EDS): monitoring of natural wells in the area: used to be performed 4 times per year (one each season) - Verification monitoring (by CASSA): monitoring of the groundwater: specific sampling on 2004 for organic compounds before starting to recover groundwater, and on 2009 for arsenic and manganese to determine the possibility to use the water for other purposes - Verification monitoring (by ACA): yearly		is located - Review meteorological records for rain events that can be a source of hazardous components - Track any other potentially harmful events occurred in the Ripoll River or the effluent of the WWTP (e.g. sewerage system breakage or spill, malfunction of WWTP, etc.) and check if those may have affected the groundwater quality
UV disinfection (CCP)	- Malfunction/ failure of UV lamp	- Pathogens - Organic compounds	- Operational monitoring (recommended): pH	- Operational monitoring (recommended): * pH: 6.0 – 8.0 CL, 6.2 –	- Operational monitoring (recommended): In	- Stop pumping of groundwater - Replace UV	- Perform preventive maintenance of

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
	- High presence of particulates that decrease treatment performance	- Turbidity and particulates	and turbidity - Verification monitoring (recommended): *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22ºC and bacteriophages	7.8 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC - Verification monitoring (recommended): * *E. coli* ≤ 1 ufc/100 mL CL * *Clostridium* spores ≤ 1 ufc/100 mL CL * Enterococci ≤ 1 ufc/100 mL CL * total bacteria at 22ºC ≤ 10000 ufc/100 mL CL * bacteriophages ≤ 1 pfu/100 mL CL	the future, it is recommended to install probes right after the UV treatment and before the chlorination system for continuous monitoring of pH and turbidity - Verification monitoring (recommended): it is recommended to be performed monthly at the beginning, and if after 2 years results are satisfactory, can be reduced to every two or three months	lamp - Clean UV lamp - Modify time and/or dosage of UV irradiation - Perform additional filtration of pumped groundwater before the UV treatment - Modify UV equipment	the UV lamp - Cleaning of UV lamps monthly
Chlorination disinfection (CCP)	- Malfunction/ failure in the chlorination system, including chlorine probes (under dosing and overdosing) - Clogging of the chlorine probes	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Operational monitoring (by CASSA): residual chlorine - Operational monitoring (recommended): residual chlorine, pH, turbidity - Verification monitoring (by EDS): total bacteria at 22º, total coliforms, *E. coli*,	- Operational monitoring (recommended): * Residual chlorine 0.5-2 ppm CL, 0.6-1.8 ppm TC * pH: 6.5 – 8.5 CL, 6.7 – 8.3 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC - Verification monitoring (recommended): * *E. coli* 0 ufc/100 mL CL	- Operational monitoring (by CASSA): residual chlorine is monitored continuously. During the study, probes controlling chlorine dosage where additionally checked using a kit the same day that the sprinklers monitoring was performed by	- Increase of chlorine dosage when microorganisms appear in the water - Stop pumping of groundwater - Investigate chlorination failure and decide whether to increase UV	- Check chlorination probes bimonthly, when the residual chlorine is measured additionally with a kit - Microbiological monitoring of

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
			Clostridium perfringens, enterococci, residual chlorine, temperature, pH, electrical conductivity, colour, ammonia, nitrate, turbidity, chloride, sulphate, sodium, fluoride, inorganic compounds, organic compounds (see applicable sections of the present work for more information on the last three groups of compounds measured) - Verification monitoring (recommended): *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22º, bacteriophages	* *Clostridium* spores 0 ufc/100 mL CL * Enterococci 0 ufc/100 mL CL * total bacteria at 22º ≤ 100 ufc/100 mL CL * bacteriophages 0 pfu/100 mL	CASSA (bimonthly) - Operational monitoring (recommended): It is recommended to monitor in a continuous way: residual chlorine, pH and turbidity - Verification monitoring (by EDS): specific monitoring on 2008 to determine the possibility to use the water for other purposes, twice per month - Verification monitoring (recommended): monthly	treatment or dose more chlorine - Repair any possible breakage and perform an additional sampling to ensure that the problem has been solved	samples after UV and after chlorination
Sand filtration (CCP)	- Malfunction /failure in the sand filtration - Lamellar filter clogged, decreasing flow and rate	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- As chlorination and sand filtration are performed continuously in the water contained in the mixing tank, the sampling point to control both chlorination and sand filtration is the same, and is located in the	- As chlorination and sand filtration are performed continuously in the water contained in the mixing tank, the sampling point to control both chlorination and sand filtration is the same, and is located in the pipeline close to the	- As chlorination and sand filtration are performed continuously in the water contained in the mixing tank, the sampling point to control both chlorination and sand filtration is the same,	- Stop pumping of groundwater - Stop filtering and perform an additional cleaning and purging of the sand filter - Replace lamellar filter	- Regular cleaning and purging of the sand filter

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
			pipeline close to the chlorine probes. Then, operational and verification monitoring is the same as for chlorination CCP	chlorine probes. Then, CLs and TC are the same as for chlorination CCP	and is located in the pipeline close to the chlorine probes. Then, sampling frequency is the same as for chlorination CCP	- If the filter is clogged by black particles, check for an overdose of chlorine or malfunction in the chlorine probes. If this is not the case, perform a thorough investigation of the groundwater, for the possible increase of dissolved manganese and iron, released from the aquifer	
Mixing tank located by the mine (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Cracks in the tank, allowing light in it	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Verification monitoring (recommended): residual chlorine, pH, turbidity, *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22°, bacteriophages	- Verification monitoring (recommended): * residual chlorine 0.5-2 ppm CL, 0.6-1.8 ppm TC * pH: 6.5 – 8.5 CL, 6.7 – 8.3 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC * *E. coli* 0 ufc/100 mL CL * *Clostridium* spores 0 ufc/100 mL CL	- Verification monitoring (recommended): twice per year. In the same sampling, visually inspect the interior of the tank, to detect biofilm formation or odour, which can indicate bacterial regrowth. Sampling for the tank	- Stop delivering water from the mixing tank and perform additional cleaning of it - Temporarily increase chlorine dosage and/or UV treatment - Cracks repair	- Cleaning of the tank by an external vendor yearly. This was performed during the study, but it is recommended to perform the cleaning twice per year and perform the

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
				* Enterococci 0 ufc/100 mL CL * total bacteria at 22º ≤ 100 ufc/100 mL CL * bacteriophages: 0 pfu/100 mL	should be the same day as the sampling for UV and chlorination	- Cleaning of the tank	verification monitoring sampling the same day, taking samples before and after the cleaning
Distribution network (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Cracks in the pipeline, or any other damage	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Operational monitoring (recommended): pressure and flow changes	- Operational monitoring (recommended): CL and TC to be determined for pressure and flow changes	- Operational monitoring (recommended): continuous monitoring of pressure and flow changes	- Stop distribution of water and purge the system - Repair pipeline - Isolate part of the system	- Properly adjust pressure and flow - Ensure a good disinfection and chlorine residual
Tank in the Taulí Park (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Cracks in the tank, allowing light to enter into it	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Verification monitoring (recommended): residual chlorine, pH, turbidity, *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22º, bacteriophages	- Verification monitoring (recommended): * residual chlorine 0.5-2 ppm CL, 0.6-1.8 ppm TC * pH: 6.5 – 8.5 CL, 6.7 – 8.3 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC * *E. coli* 0 ufc/100 mL CL * *Clostridium* spores 0 ufc/100 mL CL * enterococci 0 ufc/100 mL CL * total bacteria at 22º ≤ 100 ufc/100 mL CL * bacteriophages: 0	- Verification monitoring (recommended): yearly. Visually inspect the interior of the tank, to detect biofilm formation or odour, which can indicate bacterial regrowth. Sampling for the tank should be performed the same day as the sampling for UV and chlorination	- Stop delivering water from the tank and perform additional cleaning of it - Temporarily increase chlorine dosage and/or UV treatment - Cracks repair - Cleaning of the tank	- Cleaning of the tank by an external vendor yearly

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
				pfu/100 mL			
Water Tower tank (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Cracks in the tank, allowing light in it	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Verification monitoring (by CASSA): total bacteria at 22°, total bacteria at 37°, total coliforms, *E. coli*, *Clostridium* spores, *Clostridium perfringens*, enterococci, Fecal streptococci, *Legionella*, pH, electrical conductivity, colour, taste, ammonia, nitrate, nitrite, temperature, turbidity, alkalinity, hardness, salinity related parameters, inorganic compounds, organic compounds (see applicable sections of the present work for more information on the last three groups of compounds measured) - Verification monitoring (recommended): residual chlorine, pH, turbidity, *E. coli*, *Clostridium* spores, enterococci, total bacteria at 22°, bacteriophages	- Verification monitoring (by CASSA): it was expected for all microbiological parameters to be under the LOD - Verification monitoring (recommended): * Residual chlorine 0.5-2 ppm CL, 0.6-1.8 ppm TC * pH: 6.5 – 8.5 CL, 6.7 – 8.3 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC * *E. coli* 0 ufc/100 mL CL * *Clostridium* spores 0 ufc/100 mL CL * enterococci 0 ufc/100 mL CL * total bacteria at 22° ≤ 100 ufc/100 mL CL * bacteriophages: 0 pfu/100 mL	- Verification monitoring (by CASSA): specific samplings on 2008 to determine the possibility to use the water for other purposes - Verification monitoring (recommended): yearly. In the same sampling, visually inspect the interior of the tank, to detect biofilm formation or odour, which can indicate bacterial regrowth. Sampling for the tank should be the same day as the sampling for UV and chlorination	- Stop delivering water from the tank and perform additional cleaning of it - Temporarily increase chlorine dosage and/or UV treatment - Cracks repair - Cleaning of the tank	- Cleaning of the tank by an external vendor yearly

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
Drip irrigation system (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Clogging of the equipment (e.g. iron, nutrients)	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Verification monitoring (recommended): visually inspect for clogging of the equipment	- Verification monitoring (recommended): no clogging of the equipment CL, no black spots present TC	- Verification monitoring (recommended): monthly	- Stop distribution of water and purge the system - Repair pipeline - Isolate part of the system	- Properly adjust pressure and flow - Ensure a good disinfection and chlorine residual
Sprinkler irrigation system (POA)	- Biofilm formation - Contamination - Regrowth of opportunistic pathogens - Irregular distribution of the water in the soil (puddling) - Clogging of the equipment (e.g. soil particles) - Malfunction/ failure of a sprinkler	- Pathogens - Inorganic compounds - Organic compounds - Turbidity and particulates - Nutrients	- Verification monitoring (by CASSA): total bacteria at 22^{o}, total bacteria at 32^{o}, total coliforms, *E. coli*, *Clostridium* spores, *Clostridium perfringens*, enterococci, Fecal streptococci, *Legionella*, electrical conductivity, pH, bicarbonate, calcium, chloride, magnesium, sodium, sulphate, boron, potassium, total nitrogen, nitrate, phosphorus - Verification monitoring (recommended): residual chlorine, pH, turbidity, *E. coli*, *Clostridium* spores, enterococci, total	- Verification monitoring (by CASSA): it was expected for all microbiological parameters to be under the LOD - Verification monitoring (recommended): * Residual chlorine 0.5-2 ppm CL, 0.6-1.8 ppm TC * pH: 6.5 – 8.5 CL, 6.7 – 8.3 TC * turbidity: ≤ 2.0 NTU CL, ≤ 1.5 NTU TC * *E. coli* 0 ufc/100 mL CL * *Clostridium* spores 0 ufc/100 mL CL * enterococci 0 ufc/100 mL CL * total bacteria at 22^{o} ≤ 100 ufc/100 mL CL * bacteriophages: 0	- Verification monitoring (by CASSA): microbiological parameters twice per month; the other parameters, twice per year - Verification monitoring (recommended): monthly	- Stop distribution of water and purge the system - Repair pipelines - Isolate part of the system - Repair the sprinklers - Irrigate only with sprinklers not affected (select the area for irrigation) or irrigate in a different time if repair takes longer	- Preventive maintenance of the sprinkler irrigation system

Critical Control Point (CCP) / Point Of Attention (POA)	Potential hazardous events	Potential hazardous components	Operational and verification monitoring	Critical limits (CL) / Target Criteria (TC)	Monitoring and sampling frequency	Corrective actions	Preventive actions
			bacteria at 22º, bacteriophages, *Legionella*.	pfu/100 mL * *Legionella*: < 50 ufc/100 mL CL (try to update the method to have a lower LOD)			

APPENDIX G: SUMMARY IN SPANISH

Resumen

La regeneración de aiguas es una práctica cada vez más generalizada, que puede incluir o no la recarga artificial de acuíferos (MAR: Managed Aquifer Recharge), y que requiere una evaluación de los riesgos en sistemas reales en uso.

El estudio actual se desarrolló en Sabadell, España. En este caso de estudio de MAR la recarga del acuífero se realiza a través del lecho del río Ripoll y se utiliza el efluente secundario de una depuradora. El agua que posteriormente se extrae del acuífero pasa por un tratamiento ultravioleta cloración y filtro de arena, y se utiliza para el riego de parques y limpieza de calles. Este sistema formó parte del proyecto europeo RECLAIM WATER, dedicado al MAR, y en el que participaban diferentes países. En el presente trabajo se ha desarrollado una evaluación y gestión del riesgo. Además, se ha realizado un estudio del riesgo probabilístico, cosa habitual en agua de bebida pero no en aguas regeneradas o en MAR.

Les datos utilizados para la evaluación del riesgo se generaron en el marco del proyecto RECLAIM WATER. Otros datos se obtuvieron de instituciones públicas y otros estudios.

La evaluación del riesgo para los usos considerados del agua recuperada y tratada indica que este es bajo y en algunos casos moderado, con la excepción del uso como agua de bebida, que no se prevee implementar en Sabadell. Los riesgos residuales que se deben considerar y gestionar tienen como protagonistas los compuestos inorgánicos, los compuestos orgánicos y la salinidad.

Otro resultado importante a tener en cuenta es que la recarga a través del lecho del río es un tratamiento efectivo para reduir los riesgos derivados de patógenos, nutrientes, compuestos orgánicos y partícules. Este resultado da soporte a la demanda de muchos autores de considerar el MAR como un tratamiento más.

Finalmente, se ha desarrollado un plan de gestión del riesgo, integrando los resultados de la evaluación del riesgo. En este plan no solo se han identificado los puntos de control critico sinó que también se han evaluado los doce elementos de las Guías Australianas para la gestión del riesgo en MAR, haciendo mucho más robusto el estudio. El énfasis se ha puesto en las acciones correctives y preventives, la definición de los puntos de control critico, la monitorización del sistema y los puntos de muestreo.

Introducción

El agua es una de las necesidades humanas esenciales. En nuestro mundo cambiante y densamente poblado, que en la actualidad ha llegado a siete mil millones de habitantes, el agua se está convirtiendo en una joya preciosa, distribuida de manera desigual y cada vez más escasa, y las proyecciones futuras son aún peores. En este difícil contexto, las fuentes alternativas de agua están ganando importancia, como parte de una solución global.

La reutilización del agua a nivel mundial es impulsada principalmente por dos motivos: primero, como una respuesta a una creciente demanda de agua y las limitaciones en la disponibilidad de agua dulce; y segundo, la reutilización del agua es impulsada por el deseo de aprovechar los beneficios económicos de las aguas residuales (US EPA, 2012).

Al agua regenerada se le pueden dar muchos usos diferentes, que se pueden clasificar en:

- Usos urbanos
- Uso agricultural (riego)
- Uso industrial
- Uso de recreo
- Uso ambiental
- Recarga artificial de acuíferos (MAR)

Nos centraremos en concreto en la recarga artificial de acuíferos (MAR).

Los motivos de implementar un sistema MAR utilizando agua reutilizada pueden ser: (1) Establecer barreras de intrusión salina en los acuíferos costeros.

(2) Proporcionar un tratamiento adicional para su reutilización futura.

(3) Aumentar los acuíferos potables o no potables, recuperar los niveles de agua y mantener los ecosistemas dependientes de las aguas subterráneas.

(4) Proporcionar almacenamiento de agua regenerada para su posterior recuperación y reutilización.

(5) Control o prevención del hundimiento del suelo.

(6) Diluir acuíferos salinizados o contaminados.

(7) Se usa como medio para mover el agua de un área a otra.

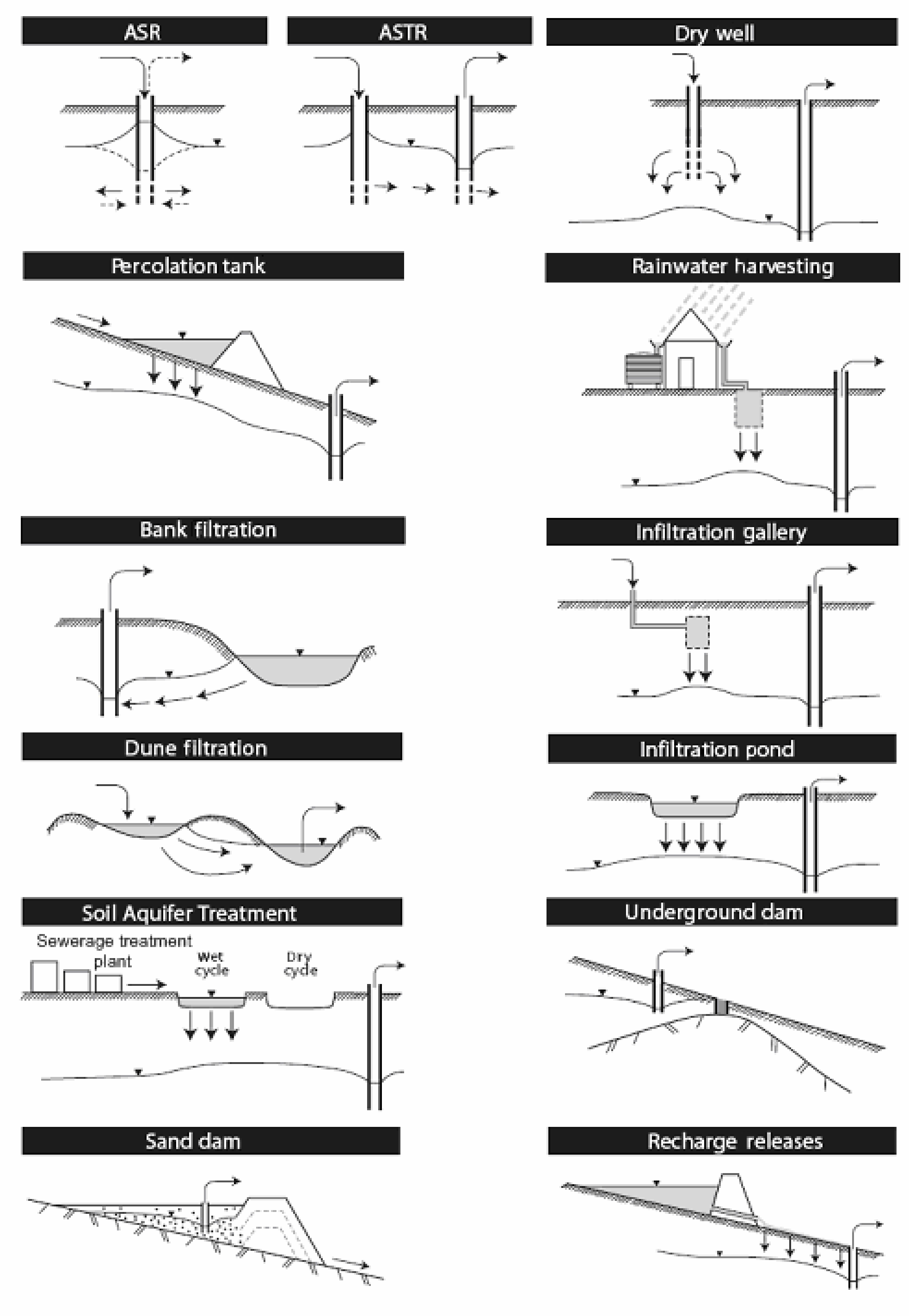
(8) Garantizar el suministro de agua.

En el caso de que el MAR se utilice como sistema de almacenamiento, transporte y / o medio para mejorar la calidad, al agua recuperada se puede dar cualquiera de los usos resumidos anteriormente, incluyendo el uso potable.

MAR ha ido ganando cada vez más importancia en los últimos años; prueba de ello son los proyectos financiados por la Comisión Europea "RECLAIM WATER" y "GABARDINE". El presente trabajo se ha desarrollado en el marco del proyecto RECLAIM WATER, y el caso de estudio de Sabadell formaba parte de él. En Sabadell, el sistema de agua reutilizada utiliza filtración a través del cauce del río como medio para recargar el acuífero aluvial bajo el río Ripoll.

MAR se puede realizar por dos medios: la infiltración / percolación a través del suelo o la inyección directa en el acuífero (por pozos construidos). Los diferentes tipos de MAR pueden diferenciarse en función del sistema utilizado para la recarga. Los tipos de MAR, según Dillon (2005) y NRMMC-EPHC-NHMRC (2009), se resumen en la siguiente figura.

Diferentes tipos de MAR dependiendo de los medios utilizados para hacer la recarga (extraído de NRMMC-EPHC–NHMRC, 2009).



En todo sistema de reutilización debe evaluarse el riesgo asociada a la práctica. El agua residual tratada puede contener aún diferentes microorganismos patógenos y sustancias que pueden causar un daño a la salud o al medio ambiente. NRC (1983) define la evaluación de riesgos de la siguiente manera:

> "Usamos la evaluación del riesgo para la caracterización de los posibles efectos adversos para la salud humana en virtud de las exposiciones dadas a los peligros ambientales. La evaluación de riesgos incluye varios elementos: descripción de los posibles efectos sobre la salud en base a una evaluación de los resultados epidemiológicos, clínicos, toxicológicos, y la investigación del medio ambiente; extrapolación de estos resultados para predecir el tipo y estimar la magnitud de los efectos para la salud humana bajo ciertas condiciones dadas de exposición; juicios en cuanto al número y las características de las personas expuestas a diversas intensidades y duraciones; y juicios sobre la existencia y la magnitud global del problema de salud pública. La evaluación de riesgos también incluye la caracterización de las incertidumbres inherentes en el proceso de inferir de riesgo".

Más en relación con la regeneración de aguas residuales y la reutilización, Asano *et al.* (2007) definen la evaluación de riesgos como "la caracterización y la estimación de los posibles efectos adversos para la salud asociados con la exposición de las personas o las poblaciones a los materiales y situaciones de riesgo cualitativo o cuantitativo".

Para la evaluación del riesgo es necesaria la definición de los posibles peligros, los escenarios, las rutas de exposición, las dosis y los límites aceptables, y con todo esto, hacer una caracterización del riesgo:

1. Identificación de peligros - la identificación de los agentes patógenos y la carga de enfermedad asociada a la salud humana; este paso también incluye la consideración de la variabilidad en las concentraciones de patógenos.

2. Dosis-respuesta - la relación entre la dosis del agente patógeno y la probabilidad de desarrollar una enfermedad.

3. Evaluación de la exposición - determinación del tamaño y la naturaleza de la población expuesta al riesgo, y la ruta, el volumen y la duración de la exposición.

4. Caracterización del Riesgo - la integración de los datos sobre la presencia de riesgos, dosis-respuesta y la exposición, obtenidos en los tres primeros pasos.

La evaluación del riesgo puede llevarse a cabo des de un punto de vista determinístico o probabilístico. En una evaluación de riesgos determinística, todas las entradas en el modelo son estimaciones puntuales, por ejemplo, media o percentil 95. Sin embargo, los datos pueden presentar una amplia gama de valores que no se tienen en cuenta cuando se trata de una estimación puntual. Esto conduce a una alta incertidumbre en el resultado de salida, que será también una estimación puntual. Para reducir esta incertidumbre asociada con el uso de las estimaciones puntuales, debe llevarse a cabo una evaluación de riesgos probabilística. Hoy en día, las evaluaciones de riesgos probabilísticos son cada vez más utilizadas, aunque su uso conlleva dificultades: es más complejo y requiere más datos y para ajustar los datos a una distribución. En cualquier caso, se prefiere un enfoque probabilístico al realizar evaluaciones de riesgos microbianos, y estos casos se denomina comúnmente como QMRA (estimación probabilística del riesgo microbiológico).

La evaluación de riesgos, ya sea determinística o probabilística, será útil siempre y cuando se integre en un plan de gestión del riesgo. Un plan de gestión del riesgo consiste en la identificación y gestión de los riesgos de una manera proactiva, en lugar de simplemente reaccionar cuando surgen problemas. En la aplicación de este enfoque para el reciclaje del agua, el primer paso es el desarrollo de una evaluación del riesgo, para identificar aquellos peligros que representan riesgos significativos para el uso final propuesto. El siguiente paso es identificar las medidas preventivas para controlar esos riesgos, y establecer programas de monitorización, para asegurar que las medidas de prevención funcionan con eficacia. El último paso es verificar que el sistema de gestión proporciona constantemente agua reciclada de una calidad que es apta para el uso previsto (NRMMC-EPHC-AHMC, 2006).

Objetivos

El presente trabajo se desarrolló en el marco del proyecto europeu RECLAIM WATER. El proyecto fue financiado por el sexto Programa Marco de la Unión Europea, bajo la temática "Cambio global y ecosistemas" (Unión Europea, 2006). Este proyecto se dedicó a proporcionar tecnologías eficaces que permitan controlar y mitigar los riesgos que plantean los contaminantes emergentes y patógenos en aguas residuales regeneradas y otras fuentes de agua utilizadas para MAR. La datos necesarios se generaron a partir de un conjunto de casos de estudio, siendo uno de ellos ubicado en Sabadell, llamado «RISMAR" en el presente trabajo. Uno de los sub-objetivos del proyecto fue:

> "... relacionar directamente los conocimientos obtenidos sobre los nuevos procesos de tratamiento y el comportamiento de los contaminantes con el riesgo asociado al uso indicado. Los estudios de riesgo cubren los pasos de la toma de agua, el tratamiento, el almacenamiento y la distribución, herramientas de análisis, sistemas de vigilancia y control y los procedimientos operativos, así como los procedimientos de comunicación. Una aplicación coherente de estos elementos en una serie de casos de estudio, que cubren las prácticas de reutilización más importantes, dará lugar a recomendaciones hasta el nivel del usuario final, donde la gestión de riesgos tiene que ser practicada a diario."

Las actividades de evaluación de riesgos y gestión de riesgos fueron coordinadas por el Grupo de Hidrología de la Unidad de Ciencias del Suelo de la Facultad de Farmacia de la Universidad de Barcelona, que fue socio implicado y contratado en el proyecto RECLAIM WATER. Una de las principales actividades llevadas a cabo por el Grupo de Hidrología en el marco del proyecto RECLAIM WATER era recopilar información, supervisar y evaluar el sistema de agua reutilizada que incluye MAR con base en el río Ripoll en Sabadell, des del punto de vista de evaluación y gestión del riesgo. Gracias al proyecto RECLAIM WATER se ha conseguido una mejor comprensión de la filtración a través del lecho del río (RBF) y el posterior tratamiento del agua recuperada. El conocimiento generado se ha incluído en el presente trabajo y se resume en varias publicaciones (véase la lista de publicaciones, sección 1).

El desarrollo de una evaluación de riesgos y un sistema de gestión de riesgos en un esquema de MAR es un reto que debe llevarse a cabo bajo diferentes perspectivas y adoptar una serie de medidas. La necesidad de indicadores fiables con el fin de validar el sistema, así como un conjunto de análisis para la monitorización tuvieron que ser adecuados al MAR. Una evaluación probabilística del riesgo también puede ayudar en el desarrollo del sistema de gestión de riesgos, reduciendo la cantidad de los análisis a realizar y también ganando un gran conocimiento sobre el sistema de agua reutilizada.

Los objetivos de la presente tesis son:

1. Evaluar el riesgo asociado al sistema de agua reutilizada que incluye MAR. RISMAR es un sistema RBF, basado en el río Ripoll, que cruza el municipio de Sabadell. Los sub-objetivos de esta evaluación de riesgos son:
    a. Evaluar la idoneidad de los tratamientos implementados en RISMAR para los diferentes usos del agua reutilizada con respecto a todos los peligros y los usuarios y matrices receptoras considerados.
    b. Identificar los peligros que todavía suponen un riesgo después de aplicar todo el proceso de tratamiento y que deben ser abordados en un plan de gestión de riesgos y/o en posteriores investigaciones.

2. La aplicación de una evaluación de riesgos microbiológicos probabilística (QMRA) para el sistema de agua reutilizada que incluye MAR, con el fin de comprender mejor los riesgos que plantean los patógenos en el sistema. Los sub-objetivos para el QMRA son:
    a. Evaluar la idoneidad de los tratamientos implementados en el sistema de agua reutilizada RISMAR para los diferentes usos del agua reutilizada con respecto a los microorganismos patógenos.
    b. Comparar la reducción del riesgo en los tratamientos aplicados.
    c. Evaluar la idoneidad del tratamiento RBF y el tratamiento en el subsuelo como una barrera adicional para reducir los riesgos en el sistema de agua reutilizada.
    d. Evaluar la eficacia de los otros tratamientos considernado los datos de patógenos e indicadores disponibles.
3. Desarrollar un plan de gestión del riesgo para el sistema de agua reutilizada que incluye MAR. Para estel plan de gestión de riesgos es importante integrar adecuadamente los resultados obtenidos de la evaluación del riesgo, que son información clave para la definición de los puntos de control, límites críticos y límietes de alerta para los riesgos, con el fin de controlar adecuadamente el sistema.

Métodos

En Sabadell se encuentra el caso de estudio del que es objeto el presente trabajo (RISMAR). Este sitio fue seleccionado por diferentes razones:

- Fue parte del proyecto RECLAIM WATER.
- Los datos relacionados con la calidad del agua y el funcionamiento del sistema se reunieron en el marco del proyecto RECLAIM WATER.
- Su proximidad a la Facultad de Farmacia (donde se encuentra el Grupo de Hidrología) en Barcelona, donde se está desarrollando el programa de doctorado, lo que facilita los muestreos y visitas al mismo.
- Es un sitio donde se realiza MAR utilizando una tecnología de bajo coste, ya que el agua se infiltra a través de un lecho del río en lugar de otras tecnologías de MAR de mayor coste, como por ejemplo, inyección en el acuífero.
- Todas las infraestructuras estaban disponibles para el Grupo de Hidrología, a fin de realizar las investigaciones, gracias al apoyo dado por CASSA y EDS.

Las evaluaciones de riesgo se realizaron de acuerdo con los procedimientos recomendados en las Guías Australianas de MAR (NRMMC-EPHC-NHMRC, 2009) y Guías Australianas para la Reutilización de Agua (NRMMC-EPHC-AHMC, 2006). Ambas guías recomiendan primero una evaluación del riesgo máximo y luego una evaluación del riesgo residual (pre-puesta en marcha y funcionamiento). La evaluación del riesgo máximo se realiza considerando que no hubiera barreras presentes en el sistema de reutilización, y que el agua residual se utilizara directamente sin tratamientos. Las evaluaciones de los riesgos residuales consideran los riesgos después de aplicar las barreras, que pueden ser los tratamientos aplicados, las medidas de protección a la captación, etc. En nuestro caso, entendemos como barreras los tratamientos aplicados y el MAR. Se recomienda realizar las evaluaciones del riesgo residual durante la pre-puesta en marcha y las fases operacionales (ver sección 5.2).

Al evaluar el riesgo para la salud humana y el medio ambiente debido a la reutilización de agua para los diferentes usos, se necesitan valores guía de calidad del agua, a fin de comparar los datos de calidad del agua con una norma establecida. Los valores de referencia utilizados fueron obtenidos de diferentes leyes españolas y guías publicadas por organismos como la OMS, la US EPA y el gobierno australiano.

Para la evaluación del riesgo microbiológico de tipo probabilística (QMRA) se ha utilizado el enfoque descrito en las Guías Australianas para la Reutilización de Agua (NRMMC-EPHC-AHMC, 2006) y las Guías de la OMS para la Reutilización de Agua (OMS, 2006b). El QMRA se realiza de acuerdo a los siguientes pasos (NRMMC-EPHC-AHMC, 2006; WHO, 2006b):

1. Identificación de peligros - la identificación de los agentes patógenos y la carga de enfermedad asociada a la salud humana; este paso también incluye la consideración de la variabilidad en las concentraciones de patógenos.

2. Dosis-respuesta - la relación entre la dosis del agente patógeno y la probabilidad de desarrollar una enfermedad.

3. Evaluación de la exposición - determinación del tamaño y la naturaleza de la población expuesta al riesgo, y la ruta, el volumen y la duración de la exposición.

4. Caracterización del Riesgo - la integración de los datos sobre la presencia de riesgos, dosis-respuesta y la exposición, obtenidos en los tres primeros pasos.

Las Guías Australianas para la Reutilización de Agua (NRMMC-EPHC-AHMC, 2006) y las Guías de la OMS para la Reutilización de agua (OMS, 2006b) definen un nivel de riesgo tolerable inferior a 10^{-6} DALYs o 1 microDALY (años de vida ajustados por discapacidad) por persona por año (pppy).

Para la evaluación del riesgo de microcontaminantes, el enfoque seleccionado en el presente trabajo se basa en las Guías de la EPA para la evaluación del riesgo químico (US EPA, 1987, 1998, 2002), también adoptadas por las Guías Australianas (NRMMC-EPHC -NHMRC, 2008). La metodología se basa en la comparación de la cantidad de un compuesto químico determinado con un valor de referencia o la ingesta de dosis diaria reportadas. Una forma de comparar las concentraciones de microcontaminantes medidas con un valor de referencia es con los cocientes de riesgo (RQ). El método de cocientes de riesgo (CR) es el método más utilizado para evaluar el riesgo de microcontaminantes, y consiste en una relación entre las concentraciones de microcontaminantes medidos a un valor de referencia. Si la relación es superior a uno, indica que el microcontaminante puede suponer un riesgo para la salud humana.

La gestión del riesgo está siendo ampliamente implementada y adoptada en muchas organizaciones diferentes, y en la actualidad se está aplicando en el sector del agua. Sistemas de gestión de riesgos son vistos como la forma más efectiva para asegurar la calidad adecuada de agua.

Muchas metodologías y sistemas se pueden seguir para desarrollar y aplicar un plan de Gestión de Riesgos. Algunas metodologías conocidas son la Evaluación de Peligros y Puntos Críticos de Control (APPCC), ISO 9001 y los Planes de Seguridad del Agua (OMS, 2011a).

Tomando como base los principios establecidos en HACCP e ISO 9001, el gobierno australiano ha desarrollado una serie de Guías, centrándose en el agua potable, la reutilización del agua, MAR, etc. En todas ests Guías, se establecen un total de doce elementos a desarrollar para la gestión del riesgo. Además, en las diferentes Guías desarrolladas para los tipos concretos de agua o procesos se dan diferentes detalles específicos a tener en cuenta. Ya que estas Guías son en general más detalladas y bien adaptadas a la disciplina del agua, se han seleccionado para el desarrollo de la gestión de riesgos en el presente estudio. En concreto, se han utilizado las Guías MAR (NRMMC-EPHC-NHMRC, 2009) y las Guías Australianas para la Reutilización de Agua Fase 1 (NRMMC-EPHC-AHMC, 2006).

Evaluación del riesgo en RISMAR (Sabadell)

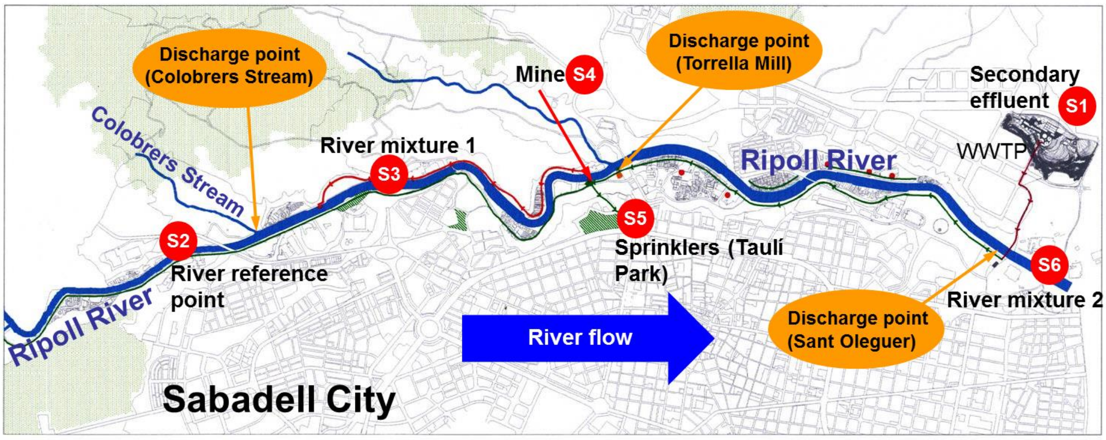
RISMAR es un caso de MAR donde la recarga se realiza por filtración a través del cauce del río. Así pues, el efluente secundario de la EDAR del Río Ripoll es vertido en el Río Ripoll en 3 puntos diferentes, y des del lecho del río se infiltra al acuífero. Posteriormente, en unas antiguas instalaciones para la recuperación de agua (denominadas "Mina"), se abstrae el agua del acuífero, se desinfecta con UV, cloración y se recircula el agua en continuo en un filtro de arena, para eliminar las partículas. El agua tratada se almacena en un depósito al lado de la Mina, y de allí se bombea al Parque Taulí para utilizarse como agua de riego. Hay tomas también para llenar los camiones cisterna y limpiar las calles con esta agua.

Se realizó una evaluación de riesgos inicial del esquema de RISMAR durante el desarrollo del proyecto RECLAIM WATER, que se resumió en diferentes informes del proyecto (Ayuso-Gabella, MN et al., 2006, 2007, 2008a y 2008b). Esta evaluación de riesgos se realizó inicialmente en forma cualitativa (Ayuso-Gabella, MN et al., 2007 y 2008b). Más tarde, se realizó una evaluación cuantitativa de riesgos preliminar (Ayuso-Gabella, MN et al., 2008a), que ya considera algunos de los peligros relacionados con un sistema MAR, pero otros seguían faltando y estaba incompleta.

En el presente trabajo, la evaluación del riesgo se ha desarrollado siguiendo las Guías Australianas para MAR (NRMMC-EPHC-NHMRC, 2009) y las Guías Australianas para la Reutilización de Aguas (NRMMC-EPHC-AHMC, 2006).

Para realizar la evaluación del riesgo, se tomaron muestras de agua y se analizaron para diferentes componentes, como parte del proyecto RECLAIM WATER. Los puntos de muestreo se detallan en la siguiente figura.

EDAR del Río Ripoll, puntos de muestreo, zonas de descarga de agua tratada y recuperación en el pozo para RISMAR.



Los compuestos peligrosos, características y circunstancias para la salud humana y/o el medio ambiente considerados para los fines de la evaluación del riesgo y que se enumeran y explican en las Guías Australianas para MAR (NRMMC-EPHC-NHMRC, 2009) son los siguientes:

1. Patógenos

2. Compuestos inorgánicos

3. Salinidad, SAR y problemas de infiltración

4. Nutrientes

5. Compuestos orgánicos

6. Turbidez y partículas
7. Compuestos con actividad radioactiva
8. Presión, caudal, volúmenes y niveles de agua subterránea
9. Migración de contaminantes en la roca fracturada y acuíferos kársticos
10. Disolución del acuífero y estabilidad de los pozos
11. Ecosistemas dependientes del agua subterránea
12. Generación de gases de efecto invernadero y el consumo de energía

Para todos ellos se ha realizado una evaluación del riesgo determinística, con la excepción de los patógenos, para los que se ha realizado una evaluación del riesgo probabilística aparte.

Los resultados de las evaluaciones de riesgo se resumen en las siguientes tablas. En estas tablas los criterios de valoración se indican en la parte superior de cada columna, y los doce peligros se consideran en cada fila. Cuando el riesgo se ha determinado que es alto (A) el recuadro se ha sombreado en rojo, y donde el riesgo es bajo (B) el recuadro se ha sombreado en verde. Un cuadro en blanco significa que el peligro no aplica a ese punto final particular.

La tabla para la evaluación del riesgo máximo muestra como en este caso la mayoría de los peligros deben ser reducidos para que el riesgo sea acceptable. En la tabla para la evaluación del riesgo residual se muestra como una buena parte de los riesgos han sido reducidos a un nivel aceptable, pero todavía hay algunos riesgos que tendrían que reducirse en función de los escenarios y puntos finales considerados. Sin embargo, los riesgos que tendrían que ser reducidos apenas se podrán reducir debido a restricciones del sistema RISMAR.

De acuerdo con la evaluación del riesgo residual, los peligros que deben tenerse en cuenta y gestionar en el sistema de reutilización de agua RISMAR son:

- Patógenos: la evaluación del riesgo microbiológica determinística con los datos que se han proporcionado no es suficiente para concluir que el riesgo para la salud humana es aceptable. Con los resultados obtenidos, se puede decir que el agua final tratada no sería aceptable como agua potable, pero para los demás usos considerados no estaría claro. Una evaluación del riesgo microbiológica probabilística utilizando los datos obtenidos y también datos de la literatura se ha llevado a cabo (ver sección 6); los riesgos medios fueron evaluados como aceptables ($<1\times10^{-6}$ DALYs) para todos los patógenos considerados, pero no en el caso de la ingestión de agua usada como agua potable. Sin embargo, este uso no está implementado en Sabadell y no se espera que lo sea en un futuro próximo, a menos que se apliquen otros tratamientos posteriores.
- Compuestos inorgánicos: este grupo de compuestos puede suponer un riesgo si el agua se va a utilizar como agua potable. Sin embargo, como se ha dicho anteriormente, este uso no está implementado en Sabadell y no se espera que lo sea en un futuro próximo,, a menos que se apliquen otros tratamientos posteriores. El níquel es un caso especial, ya que puede alcanzar el acuífero, y está presente en altas concentraciones en el río Ripoll. Además, puede afectar a las especies que viven en el río y las plantas. Hay otros compuestos inorgánicos que todavía pueden representar un riesgo para el río Ripoll, ya que su presencia se detecta de forma aleatoria en el efluente tratado. Entonces, para las ambientales se considera que todavía existe un riesgo con respecto a los compuestos inorgánicos, pero no se puede decir que es un riesgo alto, por lo que ha sido clasificado como un riesgo moderado.
- Salinidad: la salinidad del agua final tratada y de todas las aguas en el sistema RISMAR fue superior a los valores de referencia recomendados y podría suponer un riesgo para

los cultivos y crear problemas para otros usos. Se ha realizado una evaluación detallada de los cultivos de la zona, y no hay riesgo para la mayoría de los cultivos con respecto a una reducción del rendimiento. Para la mayoría de ellos la reducción del rendimiento no sería mayor que de 30%. El daño foliar podría afectar a algunos de los cultivos, si se utiliza el riego por aspersión, de lo contrario el riesgo sería bajo. Para otras plantas de la zona, el riesgo es bajo, ya que están adaptadas al clima mediterráneo, y la mayoría de ellas no se ven afectadas por la salinidad. Para el césped, el riesgo puede ser reducido utilizando cultivares tolerantes a la salinidad. La tasa de infiltración no se vería afectada, por lo tanto no supondría un riesgo para los suelos. En cuanto al escenario de reutilizar el agua como agua potable, las concentraciones de cloro y sodio serían demasiado altas y no cumplirían con el RD de agua potable español, pero no suponen un riesgo para la salud humana. Una vez más, este uso no está implementado en Sabadell y no se espera que lo sea en un futuro próximo.

- Nutrients: nutrients are reduced along the treatment train, but the measured ammonia in the final treated water does not fulfil the Spanish drinking water RD. Again, this use is not in place at RISMAR scheme, and for ammonia, the guideline value is set to avoid corrosion of copper pipes and fittings, but it is not a health guideline value. Nutrients are diluted and decrease when mixing the treated wastewater with the river water, thus posing a lower risk to the aquifer comparing to infiltrating directly treated wastewater. For the river, the risk posed by nutrients is increased by the treated wastewater discharges, but the average nutrients concentration is only a bit higher than the average nutrients concentration in the river water before the discharges, indicating that pollution is already present in the river.

- Los nutrientes: los nutrientes se reducen a lo largo del tratamiento, pero la concentración de amoníaco en el agua final tratada no cumple el RD de agua potable español. Una vez más, este uso no está implementado en Sabadell y no se espera que lo sea en un futuro próximo, y para el amoníaco, el valor de referencia se fija para evitar la corrosión de las tuberías de cobre y accesorios, pero no es un valor de referencia para la salud. Los nutrientes se diluyen y su concentración disminuye cuando se mezclan las aguas residuales tratadas con el agua del río, por lo tanto suponiendo un menor riesgo para el acuífero en comparación con la infiltración de las aguas residuales tratadas directamente. Para el río, el riesgo que plantean los nutrientes se incrementa por las descargas de aguas residuales tratadas, pero la concentración de nutrientes promedio sólo es un poco más alta que la concentración de nutrientes promedio en el agua del río antes de las descargas, lo que indica que la contaminación ya está presente en el río.

- Organic compounds: the presence of different organic compounds in the treated wastewater introduces a source of them in the Ripoll River and the aquifer. The final treated water still presents phenols and other compounds that would not fulfil the Spanish drinking water RD. Again, this use is not in place at RISMAR scheme.

- Compuestos orgánicos: la presencia de diferentes compuestos orgánicos en el agua residual tratada supone una fuente de entrada de los mismos al río Ripoll y al acuífero. El agua final tratada aún presenta fenoles y otros compuestos que no cumplirían con el RD de agua potable español. Una vez más, este uso no está implementado en Sabadell y no se espera que lo sea en un futuro próximo.

En cuanto a los compuestos con actividad radiológica, se necesitan más investigaciones, pero se asume con los datos disponibles que el riesgo que suponen es bajo.

Evaluación del riesgo máximo teniendo en cuenta los peligros identificados en las Guías de MAR.

Peligros en MAR	Rutas de ingestión (riesgo para la salud humana)				Matrices ambientales				
	Consumo de cultivos	Ingestión de aerosoles	Ingestión de agua durante el nado	Agua de bebida	Cultivo	Suelo	Árboles, arbustos	Río Ripoll	Acuífero
1. Patógenos	A	A	A	A	A	B	B	B	B
2. Compuestos inorgánicos	A	B	B	A	M	M	M	M	A
3. Salinidad, SAR y problemas de infiltración	B	B	B	M	M	B	B	B	B
4. Nutrientes	B	B	B	A	B	B	B	M	A
5. Compuestos orgánicos	A	B	M	A	M	M	M	M	A
6. Turbidez y partículas	B	B	B	A	M	A	M	B	B
7. Compuestos con actividad radioactiva	B	B	B	B					B
8. Presión, caudal, volúmenes y niveles de agua subterránea									B
9. Migración de contaminantes en la roca fracturada y acuíferos kársticos	B	B	B	B	B	B	B		B
10. Disolución del acuífero y estabilidad de los pozos									A
11. Ecosistemas dependientes del agua subterránea							B		B
12. Generación de gases de efecto invernadero y el consumo de energía (*)									

(*) Este peligro no aplica directamente a ninguna de las matrices ambientales o usuarios considerados.

A: riesgo alto; M: riesgo moderado; L: riesgo bajo. Celdas en blanco: el peligro no aplica a ninguna de las matrices o rutas de ingestión considerados.

Evaluación del riesgo residual teniendo en cuenta los peligros identificados en las Guías de MAR.

Peligros en MAR	Rutas de ingestión (riesgo para la salud humana)				Matrices ambientales			
	Consumo de cultivos	Ingestión de aerosoles	Ingestión de agua durante el nado	Agua de bebida	Cultivo	Suelo	Árboles, arbustos	Acuífero (**)
1. Patógenos	B	B	B	A	B	B	B	B
2. Compuestos inorgánicos	B	B	B	A	B	B	B	M
3. Salinidad, SAR y problemas de infiltración	B	B	B	M	M	B	B	B
4. Nutrientes	B	B	B	M	B	B	B	M
5. Compuestos orgánicos	B	B	B	M	B	B	B	B
6. Turbidez y partículas	B	B	B	B	B	B	B	B
7. Compuestos con actividad radioactiva	B	B	B	B				B
8. Presión, caudal, volúmenes y niveles de agua subterránea								B
9. Migración de contaminantes en la roca fracturada y acuíferos kársticos	B	B	B	B	B	B	B	B
10. Disolución del acuífero y estabilidad de los pozos								B
11. Ecosistemas dependientes del agua subterránea							B	B
12. Generación de gases de efecto invernadero y el consumo de energía (*)								

(*) Este peligro no aplica directamente a ninguna de las matrices ambientales o usuarios considerados.

(**) Para el riesgo residual en el acuífero, se ha considerado que recibe la mezcla de agua del Río Ripoll con el agua residual tratada, no el agua final tratada como se ha hecho en el resto de matrices ambientales, pues no sería realista.

A: riesgo alto; M: riesgo moderado; L: riesgo bajo. Celdas en blanco: el peligro no aplica a ninguna de las matrices o rutas de ingestión considerados.

QMRA (evaluación cuantitativa del riesgo microbiológico) y análisis de sensibilidad en RISMAR (Sabadell)

La enfermedad más ampliamente vinculada al consumo de agua contaminada es la gastroenteritis. Otras enfermedades respiratorias o cutáneas también pueden ser adquiridas por contacto con el agua, por ejemplo, en una piscina. En menor medida, por la vía fecal-oral también se pueden transmitir enfermedades como la fiebre tifoidea, hepatitis, artritis, miocarditis, meningoencefalitis síndrome de Guillain-Barré. Los patógenos que se utilizan como modelos para la evaluación de riesgos teniendo en cuenta las enfermedades gastrointestinales como recomienda la OMS (WHO, 2006b; WHO, 2011a), las Guías Australianas (NRMMC-EPHC-AHMC, 2006; NRMMC-EPHC-AHMC, 2011), la US EPA (US EPA, 2010), Petterson et al. (2006), Haas et al. (1999), Havelaar y Melse (2003) y que se utilizaron en también en Ayuso-Gabella et al. (2011) son:

- *Campylobacter*, representando a las bacterias, ya que es con diferencia la causa más común de gastroenteritis bacteriana. Además, varias complicaciones causadas por *Campylobacter* se han reportado en la literatura, de las cuales el síndrome de Guillain-Barré y la artritis reactiva son las más importantes desde el punto de vista de la salud pública.
- Rotavirus, en representación de los virus, ya que es una causa muy común de diarrea en muchos países desarrollados; tiene una infectividad relativamente alta en comparación con otros virus transmitidos por el agua y se ha establecido un modelo dosis-respuesta.
- *Cryptosporidium*, representando a los protozoos, porque es razonablemente infeccioso, es resistente a la cloración y es uno de los más importantes patógenos humanos transmitidos por el agua en los países desarrollados. En las personas inmunodeprimidas, particularmente en pacientes con SIDA, la infección puede persistir hasta la muerte.

Estos patógenos fueron seleccionados pues están presentes en las aguas residuales y contribuyen a la mayor carga de enfermedad de la población en términos de DALYs (WHO, 2006b; NRMMC-EPHC-AHMC, 2006). Además, brotes reportados en España y Cataluña apoyan el uso de estos patógenos para el desarrollo del QMRA.

Los modelos de dosis-respuesta utilizados en este QMRA son los mismos que se describen en NRMMC-EPHC-AHMC (2006).

Para calcular la exposición al agua final tratada es necesario saber:

- La concentración de patógenos en el agua final tratada.
- Los usos del agua y las vías de exposición.
- La cantidad de agua ingerida por la población.
- El número de exposiciones al agua final tratada por año.

La manera en la que el agua entra en contacto con la población, o la vía de exposición, es muy importante para la medición de la exposición. Las vías de exposición se han identificado de acuerdo a los criterios de valoración identificados y los usos dados al agua final tratada (ver sección 5.3.6).

Para la exposición también es muy importante conocer la concentración de patógenos en el agua final tratada. Para ello, el enfoque que se ha tomado es el de crear una función de distribución de la probabilidad (PDF) con datos de la literatura adaptados a RISMAR para la concentración de patógenos en las aguas residuales sin tratar. Luego, a partir de esta concentración inicial, la concentración de patógenos en el agua final tratada para su reutilización se ha obtenido considerando diferentes capacidades de eliminación para cada barrera en el tren de tratamiento.

Los escenarios que han sido considerados y sus correspondientes PDFs son los siguientes:

- PDF-A: resultados de la PDF para la ingestión accidental de aerosoles por agricultores.
- PDF-C: resultados de la PDF para el consumo de vegetales.
- PDF-L: resultados de la PDF para la ingestión accidental de aerosoles por habitants de las comunidades locales.
- PDF-D: resultados de la PDF para el uso como agua potable.
- PDF-F: resultados de la PDF para la ingestión accidental de aerosoles por trabajadores de fábricas.
- PDF-S: resultados de la PDF para la ingestión accidental de un volumen considerable de agua durante el nado o el desarrollo de actividades en el agua.
- PDF-CC: resultados de la PDF para interconexión de los sistemas de red duales.
- PDF-I: PDF resultados de la PDF para la ingestión accidental de aerosoles por la población inmunodeprimida.

La caracterización del riesgo se ha desarrollado para cada escenario de dos maneras:

1) La reducción del riesgo que los tratamientos podrían alcanzar si todos los tratamientos trabajarn con un rendimiento óptimo o de manera similar a lo que se ha publicado en la literatura. En la siguiente tabla esto ha sido denominado como "caracterización del riesgo teórico", aunque también utiliza datos reales recogidos en RISMAR.
2) La reducción del riesgo que los tratamientos logran teniendo en cuenta los datos de los agentes patógenos y los datos de los indicadores microbiológicos disponibles en el sistema RISMAR. En la siguiente tabla esto ha sido denominado como "caracterización del riesgo empírico", aunque también utiliza datos de la literatura.

En la siguiente tabla se muestran las PDFs utilizadas para los tratamientos, las concentraciones de patógenos y los dos tipos de caracterización del riesgo.

Funciones de distribución de la probabilidad (PDFs) utilizadas para la concentración de patógenos y para los tratamientos.

Caracterización del riesgo	Caracterización del riesgo teórica			Caracterización del riesgo empírica		
Patógeno	***Campylobacter***	***Cryptosporidium***	**rotavirus**	***Campylobacter***	***Cryptosporidium***	**rotavirus**
Concentración del patógeno en el agua residual (n/L)	U (1000, 100000)[a]	LN (226, 84) truncated at (0; 1000)[b]	LN (1342; 6330) truncated at (0; 100000)[c]	U (1000, 100000)[a]	LN (226, 84) truncated at (0; 1000)[b]	LN (1342; 6330) truncated at (0; 100000)[c]
Eliminación por tratamiento primario + secundario ($\log_{10}$)	T (1.0, 2.0, 3.5)[d]	T (0.5, 1.0, 1.5)[d]	T (0.5, 1.0, 2.1)[d]	T (1.0, 2.0, 3.5)[d]	T (0.5, 1.0, 1.5)[d]	T (0.5, 1.0, 2.1)[d]
Eliminación por mezcla/dilución con el agua del Río Ripoll ($\log_{10}$)	LL (-1.6, 1.9, 4.4) truncated at (3.0)[e]	T (0.24, 0.87, 2.2)[e]	T (-1.0, 0.0, 2.0)[e]	LL (-1.6, 1.9, 4.4) truncated at (3.0)[e]	T (0.24, 0.87, 2.2)[e]	T (-1.0, 0.0, 2.0)[e]
Tiempo de residencia en el acuífero (days)	T (1.0, 7.0, 14)[f]	T (1.0, 7.0, 14)[f]	T (1.0, 7.0, 14)[f]			
Eliminación (decay) en el acuífero ($\log_{10}$/day)	T (0.020, 0.080, 1.5)[g]	N (0.012, 0.0030)[h]	T (0.012, 0.16, 0.83)[i]			
Eliminación en el acuífero (empírica) ($\log_{10}$)				T (1.7, 4.6, 5.9)[e]	T (1.6, 3.1, 3.9)[e]	T (1.6, 4.4, 6.0)[e]
Eliminación por UV ($\log_{10}$)	T (2.0, 3.0, 4.0)[a]	T (2.0, 3.0, 3.5)[a]	T (1.0, 2.0, 3.5)[a]			
Eliminación por cloración ($\log_{10}$)	T (2.0, 3.0, 4.0)[d]	T (0.0, 0.0, 0.5)[d]	T (1.0, 1.5, 3.0)[d]			
Eliminación por filtro de arena ($\log_{10}$)	T (0.0, 0.0, 0.5)[d]	T (0.0, 0.0, 0.5)[d]	T (0.0, 0.0, 0.5)[d]			
Eliminación combinada desinfección + filtro de arena (empírica) ($\log_{10}$)				T (0.0, 1.5, 3.2) [e]	T (0.0, 0.53, 2.0) [e]	T (0.0, 0.87, 2.7) [e]

LL: loglogistic PDF; LN: lognormal PDF; N: normal PDF; T: triangular PDF; U: uniform PDF.

[a] Adaptado de NRMMC–EPHC–AHMC (2006) y Westrell (2004). [b] Adaptado de Montemayor *et al.* (2005). [c] Adaptado de Sedmark *et al.* (2005). [d] Adaptado de NRMMC–EPHC–AHMC (2006). [e] Datos de RISMAR de indicadores microbiológicos fueron utilizados (Böckelmann *et al.*, 2009; Levantesi *et al.*, 2010; La Mantia *et al.*, 2008a, b). [f] Adaptado de Franch (2007) y datos no publicados de RISMAR. [g] Adaptado de John and Rose (2005). [h] De Toze *et al.* (2009). [i] Adaptado de Pedley *et al.* (2006).

La probabilidad de infección se ha calculado como el producto de la exposición al agua recuperada (por cualquiera de las rutas y escenarios explicados previamente) y la probabilidad de que la exposición a un organismo daría lugar a infección. El riesgo anual de infección se ha calculado con el fin de calcular los DALYs después, según la metodología explicada en el apartado 4.3.2.4. La probabilidad final de desarrollar una enfermedad transmitida por el agua, dado que se ha producido una infección (después del contacto con el agua final tratada) se calcula a partir de las proporciones conocidas enfermedad/infección, cargas de enfermedad y la susceptibilidad a los diferentes agentes patógenos, lo que da un resultado en términos de DALYs.

Un resumen de los resultados del QMRA para cada uno de los agentes patógenos de referencia se muestra en la siguiente tabla (mediana, media y resultados percentil 95). Para cada uno de los agentes patógenos, se calculó el riesgo teniendo en cuenta los diferentes escenarios establecidos para la reutilización del agua y la caracterización teórica y empírica del riesgo.

La mediana para los riesgos calculados para cada patógeno estudiado, así como para la caracterización teórica y empírica del riesgo era generalmente aceptable (mediana $<1.0\times10^{-6}$ DALYs), así el agua final tratada se considera adecuada para los diferentes escenarios de reutilización, con la excepción del uso como agua potable. Para el escenario de agua potable, la mediana para los riesgos calculados falla para los tres patógenos evaluados teniendo en cuenta la caracterización del riesgo empírica (la mediana oscila entre 1.7×10^{-6} a 4.3×10^{-6} DALYs), mientras que la mediana falla para *Cryptosporidium* en la caracterización teórica del riesgo ($1.3\text{x}10^{-5}$ DALYs).

Riesgo de desarrollar una enfermedad: resumen de los resultados para cada una de las PDFs calculados en DALYs. [Nota: aquellos valores resaltadod en rojo son ≥1.0×10^{-6} DALYs, que es el valor de referencia dado en las Guías Australianas para la reutilización de aguas (NRMMC–EPHC–AHMC, 2006) y en las Guías de la OMS para la reutilización de aguas (WHO, 2006b)].

PDF resultados calculados en DALYs			PDF-A	PDF-C	PDF-L	PDF-D	PDF-F	PDF-S	PDF-CC	PDF-I
rotavirus	Caracterización del riesgo empírica	Mediana	2.6×10^{-9}	1.8×10^{-11}	8.9×10^{-10}	**4.3×10^{-6}**	2.4×10^{-9}	9.3×10^{-9}	1.5×10^{-8}	1.3×10^{-8}
		Media	5.5×10^{-7}	1.3×10^{-8}	2.2×10^{-7}	**8.1×10^{-5}**	5.2×10^{-7}	**1.6×10^{-6}**	**2.2×10^{-6}**	**2.9×10^{-6}**
		Percentil 95	8.7×10^{-7}	1.2×10^{-8}	3.2×10^{-7}	**6.2×10^{-4}**	8.5×10^{-7}	**3.1×10^{-6}**	**5.5×10^{-6}**	**4.5×10^{-6}**
	Caracterización del riesgo teórica	Mediana	1.6×10^{-10}	1.0×10^{-12}	5.4×10^{-11}	2.7×10^{-7}	1.5×10^{-10}	6.0×10^{-10}	9.3×10^{-10}	7.9×10^{-10}
		Media	8.6×10^{-8}	1.8×10^{-9}	3.1×10^{-8}	**2.9×10^{-5}**	7.1×10^{-8}	2.6×10^{-7}	4.7×10^{-7}	5.3×10^{-7}
		Percentil 95	1.2×10^{-7}	1.5×10^{-9}	3.7×10^{-8}	**1.7×10^{-4}**	1.0×10^{-7}	3.9×10^{-7}	8.0×10^{-7}	6.0×10^{-7}
Cryptosporidium	Caracterización del riesgo empírica	Mediana	2.7×10^{-9}	2.3×10^{-10}	8.6×10^{-10}	**4.3×10^{-6}**	2.4×10^{-9}	9.3×10^{-9}	1.6×10^{-8}	9.7×10^{-10}
		Media	1.5×10^{-8}	2.2×10^{-9}	5.4×10^{-9}	**2.3×10^{-5}**	1.3×10^{-8}	5.3×10^{-8}	9.8×10^{-8}	6.0×10^{-9}
		Percentil 95	6.1×10^{-8}	9.2×10^{-9}	2.2×10^{-8}	**1.1×10^{-4}**	5.7×10^{-8}	2.2×10^{-7}	4.0×10^{-7}	2.4×10^{-8}
	Caracterización del riesgo teórica	Mediana	8.0×10^{-9}	6.8×10^{-10}	2.5×10^{-9}	**1.3×10^{-5}**	7.1×10^{-9}	2.7×10^{-8}	4.6×10^{-8}	2.8×10^{-9}
		Media	2.2×10^{-8}	3.1×10^{-9}	7.7×10^{-9}	**3.6×10^{-5}**	1.9×10^{-8}	7.7×10^{-8}	1.5×10^{-7}	8.9×10^{-9}
		Percentil 95	8.9×10^{-8}	1.3×10^{-8}	3.2×10^{-8}	**1.4×10^{-4}**	7.7×10^{-8}	3.1×10^{-7}	6.3×10^{-7}	3.5×10^{-8}
Campylobacter	Caracterización del riesgo empírica	Mediana	1.1×10^{-9}	1.4×10^{-12}	3.5×10^{-10}	**1.7×10^{-6}**	9.6×10^{-10}	3.7×10^{-9}	6.3×10^{-9}	8.0×10^{-10}
		Media	1.5×10^{-7}	9.1×10^{-10}	5.2×10^{-8}	**7.1×10^{-5}**	1.2×10^{-7}	5.1×10^{-7}	7.8×10^{-7}	1.3×10^{-7}
		Percentil 95	2.8×10^{-7}	1.0×10^{-9}	9.7×10^{-8}	**4.3×10^{-4}**	2.7×10^{-7}	**1.0×10^{-6}**	**1.8×10^{-6}**	2.4×10^{-7}
	Caracterización del riesgo teórica	Mediana	1.7×10^{-13}	$<1.0\times10^{-17}$	5.2×10^{-14}	2.6×10^{-10}	1.5×10^{-13}	5.7×10^{-13}	9.5×10^{-13}	1.2×10^{-13}
		Media	3.0×10^{-10}	2.3×10^{-12}	8.7×10^{-11}	4.8×10^{-7}	2.3×10^{-10}	9.3×10^{-10}	2.0×10^{-9}	3.2×10^{-10}
		Percentil 95	5.5×10^{-10}	1.5×10^{-12}	1.6×10^{-10}	9.2×10^{-7}	4.9×10^{-10}	1.9×10^{-9}	3.4×10^{-9}	4.7×10^{-10}

Por otro lado, se realizó un análisis de sensibilidad para identificar los factores/tratamientos que más afectan al riesgo final. Entonces, los parámetros de entrada QMRA (factores / tratamientos) fueron evaluados de uno en uno mediante la realización de simulaciones de Monte Carlo, eliminando cada factor/tratamiento de uno en uno. En la práctica, el valor del factor/tratamiento de interés se mantiene a cero, mientras que se deja la concentración de patógenos en el agua residual sin tratar, la dosis-respuesta, las cargas de enfermedad y los otros tratamientos sin cambios.

En general, los resultados obtenidos para el mismo tratamiento y patógeno en los diferentes escenarios son iguales, ya que la importancia de cada tratamiento en el marco de todo el tren de tratamiento debe ser la misma. Sin embargo, hay algunas diferencias para el escenario de agua potable en algunos casos, pero manteniendo la misma clasificación / importancia para los tratamientos en cada patógeno y caracterización del riesgo.

De acuerdo con los resultados obtenidos, el tratamiento acuífero/subsuelo es una barrera crucial para reducir los riesgos en la caracterización del riesgo empírica, mientras que en la caracterización del riesgo teórica su efecto varía en función del agente patógeno investigado. A su vez, el tratamiento de desinfección es mucho más importante en la caracterización del riesgo teórico en comparación con el empírico. Estos resultados indican la importancia de obtener datos empíricos del sistema de agua reutilizada que se está evaluando con el fin de realizar una robusta caracterización del riesgo y comprender plenamente el rendimiento de los tratamientos, ya que los datos de la literatura pueden ser de ayuda, pero a veces pueden estar muy lejos del rendimiento real de los sistemas.

Gestión del riesgo: los doce elementos de las Guías Australianas para la reutilización de aguas y para MAR

Para el desarrollo del presente Plan de Gestión de Riesgos, se ha seleccionado la metodología presentada en las Guías Australianas de MAR (NRMMC-EPHC-AHMC, 2009). Esta metodología fue desarrollada originalmente para la gestión de la calidad del agua potable desde la captación hasta el consumidor, garantizando su seguridad y fiabilidad. Esta metodología puede ser aplicada y adaptada para un sistema de reutilización, y en este caso, incluyendo MAR.

Los 12 elementos que incluye la metodología no son necesariamente secuenciales, pero todos ellos deben ser seguidos para asegurar que el plan de gestión de riesgos sea integral (NRMMC-EPHC-AHMC, 2006; NRMMC-EPHC-AHMC, 2009).

1. Compromiso de uso y gestión responsable de la calidad del agua reciclada

Se deben identificar los responsables y las agencias implicadas en asegurar la calidad del agua, y en qué partes del sistema actúan o toman partido. Se deben dejar claros los roles.

En el caso de RISMAR, el departamento de medio ambiente del Ayuntamiento de Sabadell, CASSA (la compañía de aguas explotadora del sistema de reutilización), la Agencia Catalana del Agua y el Departamento de Salud son las agencias y organizaciones implicadas.

2. Evaluación del sistema MAR

Esto se ha realizado en diferentes secciones del documento, especialmente en la sección de evaluación del riesgo.

3. Las medidas preventivas para el agua reutilizada y gestión del MAR

La prevención es una característica esencial de una gestión eficaz en cualquier tipo de proceso. Las medidas preventivas son aquellas acciones, actividades y procesos utilizados para prevenir los riesgos que se produzcan o reducirlos a niveles aceptables. Los peligros pueden ocurrir o ser introducidos en todo el sistema de agua y las medidas preventivas deben ser integrales, desde la captación hasta los usuarios finales. En el caso de RISMAR, encontramos diferentes medidas preventivas:

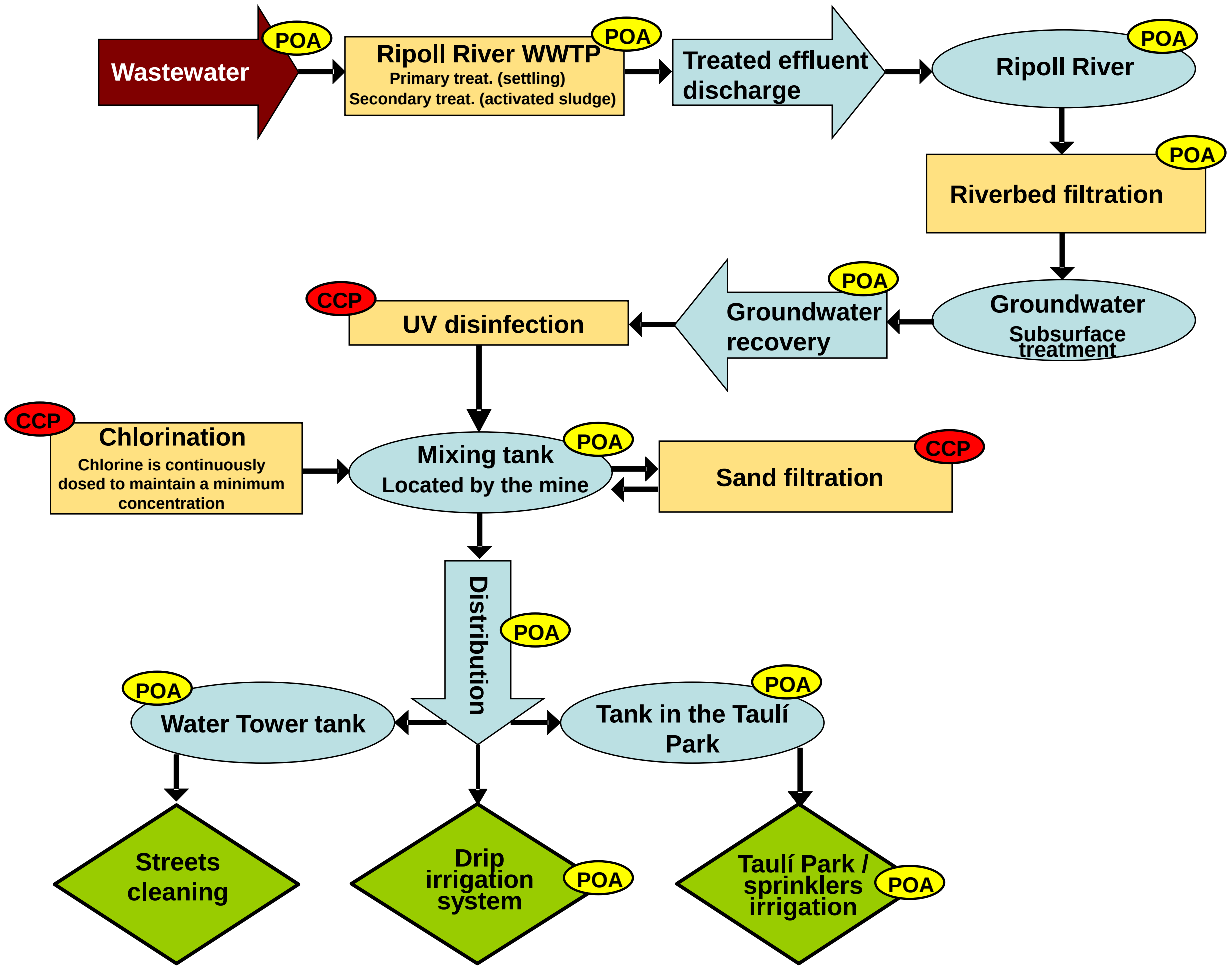
- Protección del agua residual: para proteger la salud humana y el medio ambiente, se implementó en el alcantarillado un sistema para el control de aguas residuales y descargas ilegales. Gracias a este sistema, se previene la liberación de productos químicos peligrosos fuera de los niveles permitidos por la legislación y se ha reducido para aquellos compuestos que no se pueden evitar. En realidad, en los últimos años el número de fábricas que funcionan en la zona ha disminuido, y las que liberan sus aguas de proceso hasta el río Ripoll son un número reducido, estrechamente vigilado también.
- Todos los tratamientos realizados al agua residual y al agua reutilizada (el enfoque de barreras múltiples): en RISMAR, las diferentes barreras presentes en el sistema son incluyen:
    - Los tratamientos convencionales realizados en la depuradora (tratamientos primario y secundario).
    - Mezcla y dilución con el agua del río Ripoll.
    - La infiltración a través del lecho del río (RBF).

  - Mezcla y dilución con el agua subterránea.
  - Desinfección mediante tratamiento UV.
  - Desinfección por cloración.
  - Filtro de arena para eliminar las partículas en el agua final tratada.
  - Separación del sistema de tuberías, tanques y la conexión a agua reutilizada respecto a la red de agua potable

Todas las medidas preventivas son importantes y se les debe prestar atención. Sin embargo, algunas pueden prevenir o reducir los peligros que representan un riesgo significativo y que requieren la eliminación o reducción del peligro para asegurar el suministro seguro de agua para los usos requeridos, y son susceptibles de un mayor control operacional que otras. Estas medidas podrían ser consideradas como puntos críticos de control (CCP). Los CCP se definen como una actividad, procedimiento o proceso en el que se puede aplicar control y que es esencial para la prevención de los peligros que representan altos riesgos o reducirlos a niveles aceptables (CAC, 2003; NRMMC-EPHC-AHMC, 2006; NHMRC-NRMMC , 2011).

En cuanto a la CCP identificados en RISMAR, es importante señalar que los mecanismos de control operacional y las posibles acciones correctivas están implementados en el sistema RISMAR. Estos mecanismos de control operativo incluyen sondas que miden parámetros básicos y/o operacionales (por ejemplo, pH, turbidez, conductividad), y un programa de análisis incluyendo una monitorización de verificación. La información obtenida es registrada y evaluada por CASSA y el departamento de medio ambiente del Ayuntamiento de Sabadell. Para las acciones correctivas, existen procedimientos para aplicarlas. Un resumen de los puntos críticos de control (PCC) y puntos de atención (POAs) identificados para a RISMAR se da en la siguiente figura.

Puntos críticos de control (PCC) y puntos de atención (POAs) para RISMAR.



4. Procedimientos de operación y control de procesos

Dentro de su sistema de Garantía de Calidad (QA), CASSA debe tener procedimientos operacionales para describir las actividades asociadas con RISMAR. Todos los empleados CASSA deben tener acceso a la última versión de los procedimientos. Como mínimo, los procedimientos deben cubrir:

- La EDAR del río Ripoll: deben describir el proceso, operación, mantenimiento y actividades de supervisión relacionadas con todos los tratamientos realizados la EDAR.
- Esquema del proceso RISMAR, funcionamiento y seguimiento: se deben describir las actividades del proceso, operación, mantenimiento y vigilancia relacionadas con RISMAR.
- La recolección de muestras compuestas del afluente y del efluente de la EDAR: se deben detallar los métodos para la recogida de muestras compuestas de 24 horas de las aguas residuales sin tratar y del efluente tratado en la EDAR por el operario de proceso.
- Cómo tomar muestras de agua a lo largo del sistema (excluyendo la recolección de muestras compuestas): se debe detallar los métodos de recogida de muestras de agua en los diferentes puntos de RISMAR.
- El mantenimiento y calibración de los equipos presentes en RISMAR: debe asegurarse que los equipos se mantienen calibrados de manera consistente. Estos procedimientos

se deben seguir en la EDAR y en las instalaciones de la mina, así como en la red de distribución y punto de lugares de uso, y se llevarán a cabo por el operario de procesos y/o el técnico de laboratorio.

- Riego y limpieza de calles: las instrucciones deben ser seguidas por operarios que utilizan el agua final tratada. Para el Parque Taulí, el departamento de medio ambiente del Ayuntamiento de Sabadell puede tener sus propios procedimientos.
- Análisis de datos: una enorme cantidad de información se genera y se registra en RISMAR. Esta información debe ser revisada y contrastada en el momento oportuno, por el comité de operaciones, incluyendo la producción y los gerentes de control de calidad, supervisor de laEDAR y supervisor agua reutilizada, y compartirlo con los representantes del departamento de medio ambiente del Ayuntamiento de Sabadell.
- Las acciones correctivas y acciones preventivas: deben ser implementadas en respuesta a la desviación de los límites críticos.

Además, los formatos para registrar la calidad de las muestras de agua tomadas a lo largo del sistema deben estar disponibles y ser utilizados por los operarios para introducir todos los datos generados por el sistema RISMAR así como para registrar los cambios o problemas en el sistema.

El control operacional se lleva a cabo para confirmar que los procesos están bajo control y se basa en el uso de parámetros que proporcionan una advertencia avanzada de que los sistemas se pueden estar desviando hasta un punto que puede comportar la pérdida del control. La monitorización operativa actual del sistema RISMAR implica el seguimiento de los PCC y POAs identificados. PCC y POAs se han detallado en la figura anterior y se resumen en el Apéndice F, junto con la monitorización operacional, los límites críticos, los límites de alerta y las acciones correctivas y preventivas.

5. La verificación de la calidad del agua reutilizada y el desempeño ambiental

La monitorización de verificación difiere de control operacional en que los parámetros utilizados no necesitan medirse rápidamente en el agua. Por lo general, la monitorización de verificación se realiza en el agua final tratada, mientras que el control operacional se dirige a las aguas de proceso (lo que se llama las inspecciones en proceso en los programas de control de calidad). Otra diferencia es que los parámetros exigidos por la normativa a menudo forman parte de la monitorización de verificación. La monitorización de verificación debe ser considerada como el chequeo general final que las medidas preventivas son eficaces y que los límites críticos o de alerta establecidos son los adecuados.

La monitorización de verificación actual para RISMAR implica el seguimiento del agua final tratada, así como algunos de los PCC y POAs identificados. Aunque los PCC están más relacionados con la monitorización de los parámetros operativos, con el fin de tener un resultado en tiempo real e implementar acciones correctivas rápidas en caso de que se detecte un problema / peligro, la monitorización de verificación también evalúa los PCC, con el fin de contar con información más específica del desempeño del sistema de agua reutilizada y para cumplir con la legislación española.

CASSA debe tener un procedimiento para la evaluación a corto plazo de los resultados, que podría ser compartida y seguida por el departamento de medio ambiente del Ayuntamiento de Sabadell. En este procedimiento, la frecuencia de la evaluación a corto plazo de los resultados, que se recomienda que sea de un mes, como máximo, la forma de analizar los datos (por ejemplo, estadísticas, gráficos, informes, etc.) y los socios y organizaciones para quien un informe sería entregado debe establecerse, así como la manera de tratar los resultados internamente en la empresa. Los resultados obtenidos se deben comparar con los resultados anteriores, y con los datos históricos, para hacer un seguimiento de las tendencias y prevenir la pérdida de control en el sistema, y deben ser contrastados con los valores guía establecidos, así como los requisitos reglamentarios o niveles acordados de servicio.

Las acciones correctivas dependen de cuánto se exceden los límites establecidos. En la mayoría de los casos, la respuesta puede implicar dejar de recuperar agua del pozo y el cierre de la distribución de agua final tratada. Estas acciones correctivas son más bien respuestas rápidas, pero en otros casos la respuesta puede venir a largo plazo. Por ejemplo, los suelos del Parque Taulí han sufrido un aumento de la salinidad, aunque por ahora el riesgo es bajo. Este problema también se puede estar desarrollando en los huertos regados con el agua del río Ripoll o agua subterránea recuperada en varios pozos naturales y artificiales. Para minimizar los problemas relacionados con la salinidad de los suelos, que pueden disminuir la producción de cultivos y afectar a árboles, arbustos y vegetación en el Parque Taulí, se recomienda:

- Cambio de la frecuencia, la duración y el método de riego.
- Revisar o establecer los riegos de lixiviación.Mezcla de los suministros de agua de
- riego con agua de red.
- La implementación de enmiendas en el suelo.

6. Gestión de incidentes y emergencias

Con el fin de estar preparados para responder a los incidentes y situaciones de emergencia, los posibles eventos peligrosos en el sistema RISMAR, su probabilidad, consecuencias, acciones correctivas y planes de respuesta han de ser definidos. Las principales áreas que se abordarán en los planes de gestión de incidentes y emergencias deben ser especificados y definidos para el sistema RISMAR por CASSA y departamento de medio ambiente del Ayuntamiento de Sabadell, incluyendo:

- Las acciones de respuesta, p.ej. el aumento de la vigilancia.
- Definición y responsabilidades claras para el personal, con el fin de responder a los incidentes de una manera rápida y eficaz.
- Acuerdos predeterminados con las agencias más importantes para las decisiones sobre los potenciales impactos en la salud o el medio ambiente.
- Los planes para los suministros de agua alternativos.
- Protocolos y estrategias de comunicación, incluidos los procedimientos de notificación (internos, organismos reguladores, medios de comunicación y público).
- Mecanismos para aumentar la salud o la vigilancia del medio ambiente.

Todos los empleados involucrados en el RISMAR, incluido el personal de CASSA y el departamento de medio ambiente del Ayuntamiento de Sabadell, deben recibir una formación específica sobre los diferentes pasos del proceso de reutilización, posibles incidencias, acciones correctivas y las vías de comunicación adecuadas. Los planes de respuesta de emergencia deben ser revisados y practicados con regularidad.

7 y 8. Operario, contratista y sensibilización de los usuarios finales. Participación de la comunidad y concienciación.

Los operarios, contratistas y usuarios finales tienen que ser conscientes de las posibles consecuencias de un fallo del sistema, y de cómo las decisiones pueden afectar a la salud pública y al medio ambiente. La consulta con los usuarios del agua reutilizada, las partes interesadas y la comunidad en general suele ser un componente esencial del desarrollo de los sistemas de agua reutilizada. En el caso de RISMAR, como el proyecto de restauración implicó la recuperación de la zona del río Ripoll y evitar dejar de regar el Parque Taulí durante la escasez de agua, la comunidad recibió positivamente el proyecto, a pesar de que un proceso de consulta formal no se desarrolló.

La sensibilización y participación de los diferentes grupos de interés para el sistema RISMAR se ha desarrollado principalmente por el departamento de medio ambiente del Ayuntamiento de Sabadell, a través de un programa de comunicación pública a través de su página web, donde se dispone de una gran cantidad de información sobre RISMAR y el proyecto de restauración. La implicación y la sensibilización de la comunidad se han llevado a cabo mediante la promoción de iniciativas para recuperar la calidad del río Ripoll. Se han realizado varias campañas para limpiar las orillas del río Ripoll y el lecho del río.

9. Validación, investigación y desarrollo

De acuerdo con 21 CFR 820.75 (US Government, 2002) y la OMS (WHO, 2006b), donde los resultados de un proceso no pueden ser totalmente verificados (100% de la inspección del producto) mediante inspección y pruebas, el proceso deberá ser validado con un alto grado de aseguramiento y aprobado de acuerdo con los procedimientos establecidos. Es por diseño y validación que un fabricante puede establecer la confianza de que los productos manufacturados cumplirán constantemente las especificaciones de los productos. Aplicando este concepto a la reutilización de aguas, la validación del proceso es necesaria para garantizar que la calidad del agua cumple con las especificaciones establecidas para los usos previstos, ya que no es posible verificar el 100% del agua reutilizada.

Para llevar a cabo la validación de un sistema de agua reciclada los requisitos no pueden ser tan restrictivos como lo son para los medicamentos o productos sanitarios (campo donde se inició la validación de procesos). Entonces, para un esquema de agua reutilizada que incluya o no MAR, la validación puede incluir:

- La evaluación de la información científica y técnica disponible (incluyendo los datos históricos y la experiencia operacional), así como la recopilación de nuevos datos en áreas donde se carece de los mismos.
- Estudios piloto para diseñar el sistema de barreras múltiples para conseguir un nivel de calidad de agua predeterminado.
- Llevar a cabo las investigaciones para validar las diferentes barreras y tratamientos.
- Verificación de los límites críticos y de alerta establecidos para el sistema (proceso de verificación del diseño).
- Actualización de los procedimientos operativos, en el proceso de inspección, calibración, mantenimiento preventivo y cualesquiera otros sistemas auxiliares que pueden necesitar ser creados o revisados después de que el proceso de validación haya terminado.

En el caso de RISMAR, esta validación no se ha realizado de manera formal, pero sí que se ha generado mucha de la información necesaria para que pueda ser realizada de forma retrospectiva. Los datos obtenidos en el proyecto RECLAIM WATER, la evaluación del riesgo, la monitorización del sistema por CASSA, etc. son entradas esenciales para el proceso de validación.

10. Documentación e informes

La gestión de la documentación y registros del sistema RISMAR debe incluir como mínimo:

- La notificación de incidentes / emergencias.
- Quejas de clientes.
- Procedimientos operacionales.
- Los resultados de la monitorización: hojas de cálculo y los resúmenes diarios.
- Informes mensuales y de otros tipos.
- Resultados y actas de las reuniones regulares.

Las obligaciones de información incluyen:

- Informes para el departamento de salud: este informe sólo está relacionado con el uso del agua final tratada para llenar la piscina, y es requerido por el departamento catalán de salud.
- Informes basados en el medio ambiente: este informe se desarrolla principalmente a través de reuniones periódicas entre CASSA y el departamento de medio ambiente del Ayuntamiento de Sabadell, y los datos los suele mandar CASSA por email.

11. Evaluación y auditorías

La evaluación a largo plazo de los resultados en RISMAR se realiza de diferentes maneras:

- CASSA lleva a cabo una evaluación de los resultados para cada parte del sistema. Los resultados de la EDAR deben ser revisados a diario, mientras que el agua final tratada debe ser revisada cada dos meses o mensualmente como mínimo.
- El departamento de medio ambiente del Ayuntamiento de Sabadell también realiza una evaluación periódica de los resultados, la revisión de los datos enviados por CASSA y propone acciones para mejorar el sistema.
- Se recomienda un informe anual de recopilación de los resultados del sistema RISMAR. Este informe debe ser producido por CASSA. El informe anual deberá contener los resultados obtenidos para las aguas residuales, así como para el agua final tratada durante todo el año.
- En el presente trabajo se ha hecho un análisis global de los datos obtenidos en el marco del proyecto RECLAIM WATER, así como datos de CASSA, el departamento de medio ambiente del Ayuntamiento de Sabadell y la Agencia Catalana del Agua. Un análisis similar se debería realizar anualmente, con el fin de revisar el desempeño del sistema y establecer los objetivos de mejora.

CASSA debe tener un procedimiento para auditorías internas y externas, que detalle cómo se llevarán a cabo las actividades y cómo se documentarán los resultados y puntos de acción.

Las auditorías internas deben realizarse por lo menos cada año, y se prefiere dividir la auditoría en diferentes días para centrarse en diferentes áreas del sistema.

Las auditorías externas deben ser ejecutadas por los organismos cualificados. En el caso de CASSA, las auditorías externas deben asegurarse de que el sistema cumple los requisitos de la norma ISO 9001: 2008, ISO 14001: 2004 y OSHAS 18001: 2007 en las áreas para las que ha sido certificado.

12. Revisión y mejora continua

CASSA y el departamento de medio ambiente del Ayuntamiento de Sabadell tienen reuniones regulares para discutir mejoras a implementar en el sistema y revisar los resultados de la vigilancia. Además, CASSA participa activamente en diversos proyectos europeos para la mejora de las tecnologías utilizadas.

Con el fin de mejorar el sistema RISMAR, varios proyectos de mejora podrían ser:

- Consolidar los límites críticos y de alerta para el acuífero.
- Consolidar los límites críticos estéticos y de alerta para el agua final tratada. Se tendrían que revisar también los parámetros que podrían atribuirse a la apariencia física del agua final tratada y/o derivados de las quejas de los clientes recibidas.
- Desarrollar todos los estudios de investigación establecidas en la sección 7.8.3, lo que ayudará a implementar acciones para mejorar el sistema.

Conclusiones

Las conclusions obtenidas en el presente trabajo se relacionan directamente con los objetivos previamente fijados:

Objetivo 1: Evaluación del riesgo asociado al sistema de reutilización que incluye MAR

- Un sistema reutilización incluyendo filtración a través del lecho del río (RBF) puede ser un eficaz sistema de bajo coste para la regeneración y reutilización del agua. RBF, que es un tipo de recarga de acuíferos (MAR), demostró ser crucial para reducir el riesgo que representan la mayor parte de los peligros detectados.
- De acuerdo con los resultados generales de la evaluación del riesgo, el riesgo que representan los diferentes peligros es aceptable para los usos implementados, pero no sería aceptable para el agua potable y nuevas investigaciones y tratamientos posteriores serían necesarios para este uso.
- Las directrices utilizadas como base para desarrollar la evaluación de riesgos (Guías Australianas para la Reutilización de Aguas y para el MAR) son una herramienta útil para evaluar sistemáticamente el riesgo planteado por los diferentes peligros en un sistema de reutilización incluyendo MAR.
- Para los patógenos, se prefiere una evaluación del riesgo probabilística (evaluación cuantitativa del riesgo microbiológico, QMRA) en lugar de una evaluación determinística para evaluar sistema de reutilización incluyendo MAR. La evaluación evaluación del riesgo determinística resultó ser insuficiente para concluir que el riesgo para la salud humana era o no aceptable.
- No sólo los patógenos humanos, sino patógenos de las plantas deben ser considerados al realizar la evaluación de riesgos en los sistemas de reutilización incluyendo o no MAR, especialmente si el agua se utiliza para el riego de cultivos o parques.
- Los genes de resistencia a antibióticos (ARG), aunque no son patógenos, deben ser también considerados en las futuras evaluaciones de riesgos en los sistemas de reutilización que incluyan o no MAR, ya que pueden suponer un riesgo para la salud humana. Para ello, modelos de dosis-respuesta en ARGs son necesarios.
- Para un sistema de reutilización que incluya MAR, los compuestos inorgánicos deben ser evaluados con cuidado, especialmente si el agua final es tratada para ser utilizada como agua potable. Durante el tratamiento en el subsuelo, diferentes compuestos inorgánicos pueden ser movilizados desde los sedimentos del acuífero y llegar al agua recuperada, como por ejemplo el manganeso. Entonces, es necesario evaluar qué compuestos inorgánicos se movilizan y si sus concentraciones son suficientemente altas como para suponer un riesgo para la salud humana, el medio ambiente o los equipos.
- La salinidad es un peligro que podría suponer un riesgo para los cultivos y los suelos en caso de que el agua sea reutilizada para el riego. Sin embargo, no sólo el agua de riego, pero el estado del suelo, la fracción de lixiviación, las prácticas de riego, los cultivos, la tasa de infiltración y otros factores juegan un papel importante el uso como agua de riego.
- Los compuestos orgánicos son un motivo de preocupación en la actualidad, y su presencia en las aguas residuales tratadas supone una fuente de los mismos en el agua regenerada. Sin embargo, la mayoría de ellos sufren una fuerte reducción a través del

RBF y el tratamiento en el subsuelo, por lo que no representan un riesgo para la salud humana o el medio ambiente.

- Los subproductos de desinfección (DBPs) se reducen a lo largo del sistema de reutilización, pero también pueden crearse si la cloración se usa para desinfectar el agua final tratada. Aunque el RBF reduce fuertemente la materia orgánica presente en el agua de infiltración, aún puede estar presente en el agua final tratada en cantidades suficientes para provocar la formación de DBPs.
- A pesar de que los compuestos orgánicos se reducen a través de un sistema de reutilización que incluya o no MAR, las sinergias de los diferentes grupos de compuestos orgánicos en el agua final tratada deberían ser investigadas.
- De acuerdo con la literatura, los cultivos pueden absorber y acumular compuestos farmacéuticos activos (PhACs) en condiciones experimentales, pero no está claro si este efecto podría ocurrir en concentraciones ambientales, y en qué partes del cultivo se acumularían. Entonces, su efecto debería ser probado a concentraciones reales y usando aguas reutilizadas.
- El RBF reduce fuertemente la turbidez y las partículas, así como patógenos, nutrientes y materia orgánica. Estos peligros se reducen progresivamente a lo largo del tren de tratamiento, gracias al enfoque de barreras múltiples, en el que RBF juega un papel importante. Esto apoya la petición de muchos autores de considerar al MAR como un tratamiento adicional.
- En general, cuando se utilizan aguas residuales tratadas para aumentar la infiltración en un sistema RBF es crucial conocer la calidad del agua del río antes y después de los vertidos de aguas residuales tratadas, ya que la contaminación puede estar ya presente en el río y no hay que atribuirla a la descargas de aguas residuales tratadas.
- En un sistema de reutilización que incluya MAR existen riesgos específicos relacionados con la práctica MAR, que deben ser evaluados, a saber: los compuestos con actividad radioactiva; presión, caudales, volúmenes y niveles de agua subterránea; migración de contaminantes en la roca fracturada y acuíferos kársticos; disolución del acuífero y estabilidad de los pozos; y los ecosistemas dependientes del agua subterránea y del acuífero. Estos peligros no serían evaluados en un sistema de reutilización que no incluyera MAR. Se evaluó el riesgo planteado por estos peligros, y era aceptable. Sin embargo, se debe prestar atención a la disolución de manganeso, y a la potencial movilización de otros compuestos inorgánicos como el arsénico.
- Para el peligro que considera la generación de gases de efecto invernadero y el consumo de energía, hay que decir que no es directamente un peligro para los recipientes considerados; sin embargo, es importante para los proyectos de reutilización de aguas que incluyan o no MAR evaluar el consumo de energía y comparar con otras opciones antes de llevarlos a cabo. Este peligro sólo estaba incluído en las Guías Australianas de MAR, y no está presente en ningunas otras guías consultadas y usadas. Para este peligro se debe discutir y llegar a un acuerdo, ya que no sólo se aplicaría a los sistemas de MAR sino a cualquier esquema de agua reutilizada.
- Para desarrollar correctamente una evaluación de riesgos, es fundamental contar con valores de referencia sólidos y fiables, ya que, en general, las regulaciones actuales no son suficientes. Además, los valores de referencia deben ser contrastadas y seleccionados de acuerdo con una base científica, ya que se han encontrado errores en la normativa española vigente, y algunos valores de referencia son poco o demasiado restrictivos en comparación con los valores de referencia en otros países. Los valores de referencia son necesarios para todos los compuestos potencialmente presentes en el

agua y deben adaptarse al tipo de agua y usos de la misma. Las discrepancias entre diferentes regulaciones y guías e incluso la falta de un valor de referencia en muchos compuestos hacen que la evaluación del riesgo sea difícil o incluso imposible.

Objetivo 2: La aplicación de una evaluación cuantitativa del riesgo microbiológico (QMRA) al sistema de reutilización incluyendo MAR, con el fin de comprender mejor los riesgos que plantean los patógenos en el sistema.

- El QMRA demostró ser una herramienta útil para discernir el riesgo que plantean los patógenos en los diferentes usos del agua final tratada.
- El RBF es una barrera muy importante para reducir el riesgo que representan los agentes patógenos en un esquema de agua reutilizada incluyendo RBF.
- Un bajo rendimiento de los tratamientos de desinfección se puede detectar mediante el análisis de diferentes indicadores y el uso de mayores volúmenes de agua para su análisis, en la medida de lo posible. El QMRA también puede ayudar a desentrañar un bajo rendimiento de los tratamientos de desinfección.
- Los otros tratamientos del sistema de regeneración fueron más o menos importantes dependiendo del patógeno seleccionado. Es importante tener en cuenta el deterioro post-cosecha de los microorganismos patógenos para el escenario de consumo de cultivos, ya que juega un papel importante para reducir el riesgo.
- El escenario de agua potable plantea el riesgo más alto, mientras que la conexión transversal, la natación y la población inmunodeficiente serían los siguientes.
- Cuando se desarrolla un QMRA para un sistema de agua reutilizada que incluya o no MAR, si el agua final tratada se utiliza para el riego no sólo el escenario de consumo de los cultivos debe ser evaluado, sino también la ingestión aerosoles, ya que el riesgo es de hecho más alto para la ingestión de aerosoles que para el consumo de cultivos regados con agua reutilizada.
- La población inmunodeprimida se debe considerar en la evaluación de riesgos, y más información sería necesaria para poder establecer las constantes dosis-respuesta para ellos.
- Las caracterizaciones de riesgo empíricas dan resultados ligeramente diferentes que las caracterizaciones de riesgo teóricas, y esto debe ser tenido en cuenta en futuros QMRAs. Aunque en la mayoría de los casos se carece de datos reales del sistema, es importante utilizar tanto como sea posible datos del caso de estudio en cuestión, con el fin de obtener un resultado más real.
- Rotavirus fue el patógeno que presentaba los mayores riesgos, seguido por *Cryptosporidium* y *Campylobacter*.
- Es importante en los estudios de QMRA incluir al menos un representante de cada uno de los grupos de patógenos, con el fin de entender mejor los riesgos planteados por los diferentes grupos.
- Las cargas de enfermedad y las relaciones enfermedad-infección deben ser incluídas en las guías publicadas no sólo para los patógenos típicos (*Campylobacter*, *Cryptosporidium* y rotavirus), sino para otros también, con el fin de ayudar en el desarrollo de los estudios QMRA.
- La media y el percentil 95 se deben calcular en la caracterización del riesgo y deben ser utilizados en las discusiones de evaluación de riesgos, como un enfoque conservador. La mediana es ampliamente utilizada en estudios de QMRA; sin embargo, su uso como una referencia para la evaluación del riesgo, sólo asegura que

el 50% de las veces el riesgo será más bajo que el nivel de riesgo de referencia. Entonces, esto se debe tener en cuenta también a la hora de emitir directrices para los estudios de QMRA.

Objetivo 3: Desarrollar un plan de gestión de riesgos para el sistema de reutilización que incluye MAR.

- Para desarrollar un plan de gestión de riesgos para un sistema de reutilización que incluye MAR es fundamental desarrollar antes una evaluación de riesgos exhaustiva. Los resultados obtenidos de la evaluación del riesgo deben integrarse en el plan de gestión de riesgos, en forma de puntos de control definidos, límites de alerta y límites críticos para los compuestos peligrosos, con el fin de controlar adecuadamente el sistema.
- Establecer límites críticos y límites de alerta es un proceso complejo que debe incluir a expertos en el área. Los límites críticos y límites de alerta pueden necesitar ser reevaluados a menudo, utilizando la experiencia práctica.
- Las acciones correctivas y preventivas se deben establecer e identificar en un sistema de reutilización que incluya MAR. Las medidas preventivas incluyen regularmente cada uno de los tratamientos aplicados en el sistema de barreras múltiples, así como otros como la protección de las fuentes de agua, las opciones de diseño adoptadas en el sistema y restricciones en el sistema de distribución.
- La validación de los procesos es una parte importante del plan de gestión de riesgos, ya que garantiza que los tratamientos implementados producirán consistentemente agua de la calidad esperada. La validación es un área común en la industria médica, pero no es tan común en la del agua.
- Cuando se desarrolla un plan de gestión de riesgos, sobre todo si se hace fuera de las organizaciones que explotan el sistema de reutilización que incluye MAR, la información sensible puede que no se facilite y algunas de las prácticas reales pueden ser desconocidas. Sin embargo, un plan de gestión de riesgos todavía se puede desarrollar, incluso incluyendo recomendaciones para aquellos elementos para los que se carece de información.
- Los eventos peligrosos pueden ser difíciles de prever, pero la literatura en esta área y la experiencia práctica sobre el sistema de reutilización se pueden usar para implementar acciones correctivas y preventivas para evitarlos.

El resumen de las principales conclusiones obtenidas para este trabajo es:

- Los análisis de peligros y de sus riesgos relacionados no son sólo herramientas que se deben utilizar en sistemas de aguas potables, sino también en los de aguas reutilizadas, incluyendo o no MAR.
- El MAR debe ser considerado como una barrera más para el tratamiento de agua en el marco de un sistema de agua reutilizada.
- Para la evaluación del riesgo de patógenos, estudios de tipo QMRA (evaluaciones de riesgo probabilísticas) deberían desarrollarse en la medida de lo posible, en lugar de las evaluaciones de riesgos determinísticas.
- Una evaluación exhaustiva de los riesgos es la base para desarrollar los planes de gestión de riesgos, aplicada o no a un sistema de agua reutilizada.

- Los planes de gestión de riesgos deben ser desarrollados en conjunto con las diferentes partes interesadas, e incluyendo expertos en el área.