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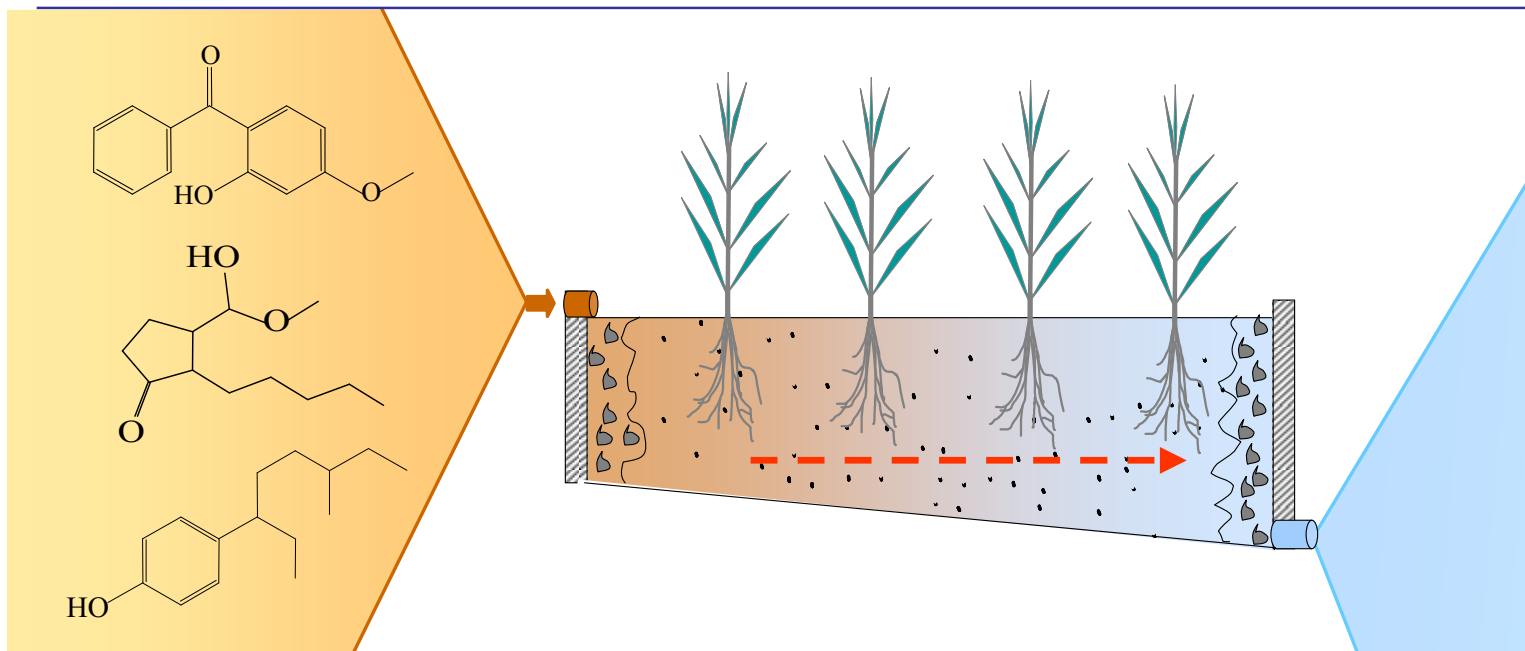


Universitat de Barcelona
Facultat de Química
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COMPORTAMENT DE CONTAMINANTS ORGÀNICS EN AIGUAMOLLS CONSTRUÏTS

I

FORMACIÓ DE SUBPRODUCTES DE DESINFECCIÓ DURANT EL PROCÉS DE REGENERACIÓ D'AIGÜES RESIDUALS



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Octubre del 2007

CAPÍTOL 3: Avaluació de la Formació de Subproductes de Desinfecció durant la Regeneració d'Aigües Residuals

.....
Les tres erres: Reduir, Reciclar i Reutilitzar
.....

3.1. Introducció

Donat que disposar d'un abastament d'aigua de forma estable durant tot l'any és una necessitat ineludible, l'ús d'aigües residuals depurades mitjançant un procés de regeneració, ja sigui per a un ús agrícola, municipal, recàrrega d'aqüífers o per refrigeració industrial, entre d'altres, és un pas cabdal per tal d'assolir una gestió sostenible d'aquest recurs.

La regeneració es defineix com el tractament que es du a terme a un aigua residual ja depurada per tal de fer-la segura per a la seva reutilització. La reutilització al mateix temps es defineix com l'ús beneficiari que es té d'una aigua tractada, essent possible tant la reutilització directa com indirecta. Mentre la primera fa esment a l'ús directe de l'aigua tractada, la segona fa referència a la barreja d'aquesta amb aigües de diferents orígens (Levine i Asano, 2004).

El tipus de tractament que es realitza a una aigua residual prèviament depurada depèn del seu ús, i inclou des d'una aplicació directa de l'efluent secundari, quan aquesta aigua està destinada a boscos i zones verdes no públiques, fins a l'osmosi inversa quan aquesta està destinada a aigua de beguda (exemple: Namíbia) (Delgado, 2003).

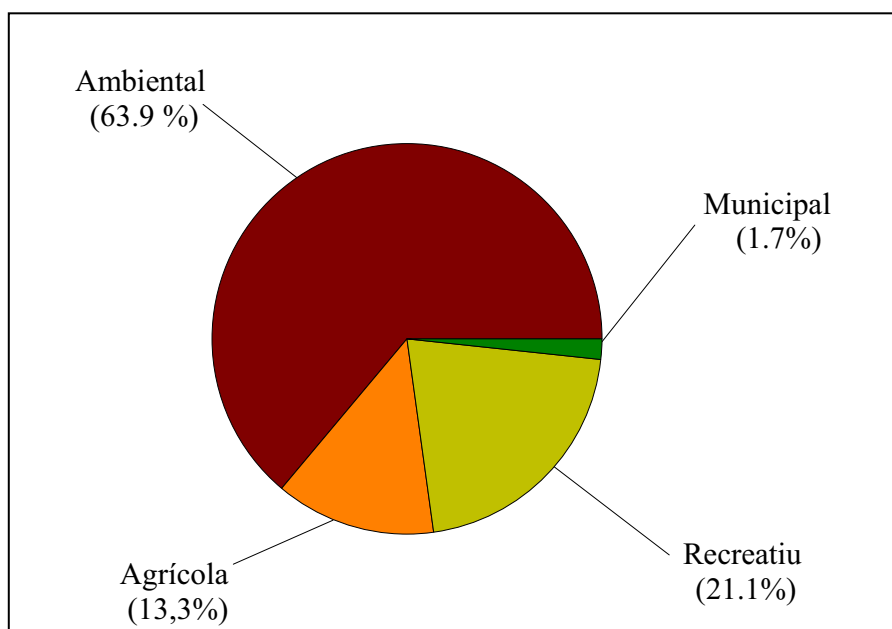


Figura 3.1. Distribució d'usos de l'aigua regenerada durant l'any 2005 a Catalunya (ACA, 2007).

Tal i com queda palès a la Figura 3.1, dels 22.3 hm³ d'aigua regenerada produïda a Catalunya (3% del total d'aigua depurada), l'ús ambiental sembla ser el predominant, mentre l'industrial encara no hi és present (0%). Concretament, l'aigua regenerada provinent de les EDARs (Platja d'Aro i Lloret de Mar) amb les que s'ha treballat en aquesta Tesi presenta una aplicació agrícola i ambiental, tot i que principalment s'empra per a un ús recreatiu (reg de camps de golf). En canvi, la regeneració duta a terme en l'EDAR de Mataró té una component purament experimental d'una explotació a escala pilot amb finalitat agrícola.

Totes les EDARs estudiades tenen la característica d'emprar hipoclorit sòdic com a etapa final de desinfecció, com s'ha comentat adés (secció 1.1.2) aquest desencadena la formació d'un gran ventall de subproductes de desinfecció, molts d'ells carcinògens. Així doncs, la tasca més important en la regeneració de l'aigua és arribar a un compromís entre la minimització del risc sanitari associat a la presència de microorganismes patògens i la minimització de la formació de DBPs. Això significa, l'aplicació de la mínima dosi de desinfectant per obtenir la màxima seguretat sanitària (Figura 3.2).

Les mesures reguladores han de tenir en consideració la disminució d'ambdós riscos, ja que quan s'incrementen els nivells de desinfecció al mateix temps també s'incrementa el risc d'augmentar el nivell de DBPs formats (Zwiener, 2006).

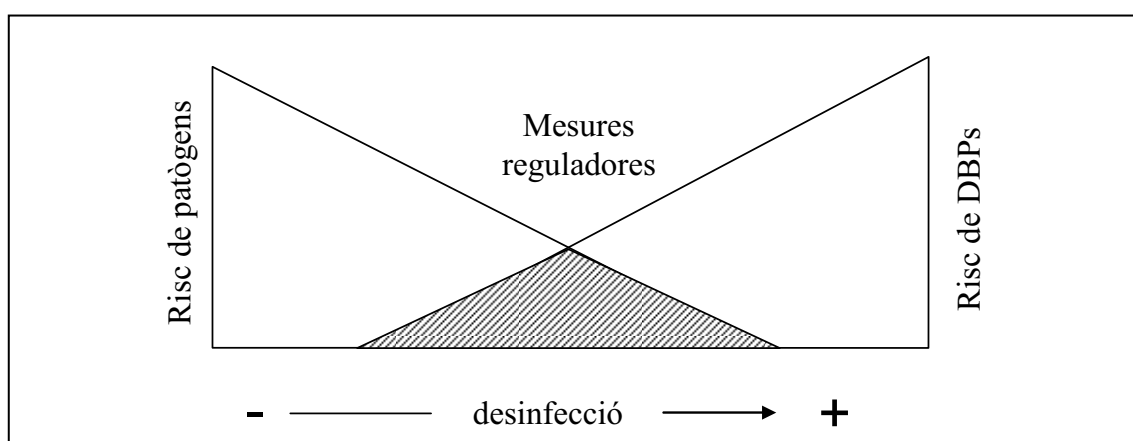


Figura 3.2. Relació entre increment de la desinfecció, el risc d'existència de patògens i la formació de DBPs (adaptat de Zwiener et al, 2006).

Tant la USEPA com la OMS han publicat unes directrius i manuals per tal de garantir la qualitat de l'aigua regenerada segons els diferents usos (USEPA, 1992; WHO, 2006). A nivell de l'Estat Espanyol, existeix un projecte de Reial Decret que regularà la qualitat

de les aigües en funció de l'ús a que es destinin (accessible a través de la pàgina web: http://www.crana.org/archivos/agua/el_agua_en_navarra/normativa/21_03_2006/ProyectoRDReutilizacion_20060522.pdf), incloent paràmetres analítics com ara els contaminants orgànics específics que figuren a la Directiva Marc de l'Aigua (2000/60/CE).

De tota manera, fins ara, l'article 272 del Reial Decret 849/1986 deixava a criteri propi del govern la qualitat de les aigües destinades a reutilització. Així doncs, els únics requeriments per tal d'explotar l'aigua regenerada eren els microbiològics (bacteris i paràsits) i els fisicoquímics (sòlids suspesos, turbolesa i metalls).

En aquest context normatiu i amb la intenció d'emplenar aquest buit legal, el maig del 2003 l'àrea de planificació de l'Agència Catalana de l'Aigua (ACA) va redactar el document "Criteris de qualitat de l'aigua regenerada segons diferents usos" (ACA, 2003). Aquest té en compte criteris com ara les concentracions de diferents plaguicides i detergents entra d'altres contaminants, però deixa de banda l'estudi de gran part dels contaminants emergents, dintre dels quals s'inclouen tant els subproductes de desinfecció (com a exemple; trihaloacètics i nitrosoamines (amb l'excepció dels trihalometans, que si que queden inclosos)) com els PPCPs.

3.2. Estructura del capítol

El plantejament del capítol es basa amb el fet que durant el procés de regeneració normalment s'empra l'hipoclorit sòdic com a agent desinfectant, generant-se tota una sèrie de subproductes de desinfecció, entre ells els THMs classificats com a possibles carcinògens.

Així doncs, tot i que l'estudi dels diferents factors que afecten la formació de THMs ha estat àmpliament descrit en aigües de beguda, en el cas de les aigües residuals aquests factors no han estat encara suficientment analitzats. En aquest sentit, és el primer cop que es du a terme un estudi d'aquestes característiques, tant per la durada del període de mostreig com tipus d'aigües analitzades (efluents secundaris i terciaris).

En l'article 7, "*Trihalomethane occurrence in chlorinated reclaimed water at full-scale wastewater treatment plants in NE Spain*", es realitza un estudi al llarg de dos anys que analitza la formació de THMs en aigües regenerades obtingudes a partir d'efluents

secundaris i terciaris mitjançant un procés de cloració i/o desinfecció amb UV. En aquest treball s'estudien les variables que poden afectar a la formació dels THMs durant el procés de regeneració (dosis de clor, radiació UV, nitrogen amoniacal, pH, bromur, demanda química d'oxigen (COD) i carboni orgànic total (TOC)).

3.3. Article 7: Trihalomethane occurrence in chlorinated reclaimed water at full-scale wastewater treatment plants in NE Spain

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Trihalomethane occurrence in chlorinated reclaimed water at full-scale wastewater treatment plants in NE Spain

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ABSTRACT

Total trihalomethane (TTHM) concentrations were determined in three chlorinated effluents (i.e. secondary and tertiary) from full-scale wastewater treatment plants (WWTP) in NE Spain over a 2-year monitoring period (May 2003–February 2005). Low TTHM concentrations (2–30 µg L⁻¹), according to international standards for drinking water (80–150 µg L⁻¹), were obtained in all samples analysed. The effects of (a) ammonia nitrogen and bromide concentrations, (b) UV light exposure, (c) tank storage, and (d) water temperature were evaluated. Two chlorination strategies were adopted: low chlorine dosages (2–5 mg Cl₂ L⁻¹) and a high-chlorine dosage (16 mg Cl₂ L⁻¹). The effects of storing chlorinated reclaimed water and of UV light exposure before chlorination were also evaluated. Samples collected over the 2-year monitoring period offered the possibility to assess the numerous variables affecting THM formation. A statistical evaluation of Platja d'Aro WWTP data set shows a low TTHM formation in the presence of high ammonia nitrogen concentration ($p < 0.05$). That result can be attributed to the formation of chloramines by reaction with added chlorine, at doses below breakpoint chlorination. An increase in TTHM concentration in the presence of bromide (0–1 mg L⁻¹) was also recorded ($p < 0.05$). In contrast to published reports, TOC had a negative effect on TTHM formation. COD and turbidity had no statistical significance on TTHM formation. As expected, chlorination promoted TTHM formation in the three water reclamation plants monitored. Nevertheless, no statistical difference was observed when chlorinated effluents were kept in storage tanks. Exposure to UV light did not affect either formation or removal of TTHM. The relative production of TTHM during warm and cold seasons was also evaluated. TTHM production decreased with higher temperatures, but that could be attributed to the increase of ammonia nitrogen concentration observed during the warm summer seasons.

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1. Introduction

Chlorine disinfection of treated wastewater commonly leads to the formation of disinfection by-products (DBPs), as a result of the oxidative breakdown of numerous organic substances present in treated effluents. DBPs are produced

by reaction of chlorine with humic substances present in water (Nikolaou and Lekkas, 2001). Trihalomethanes (THMs) constitute a major class of DBPs, including chloroform (CHCl₃), bromodichloromethane (CHCl₂Br), chlorodibromomethane (CHClBr₂) and bromoform (CHBr₃). THM were discovered in drinking water (Bellar et al., 1974; Rook, 1974),

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and their carcinogenic effects were observed in laboratory animals a few years later (NCI, 1976).

More recently, THM were classified as possible human carcinogens (Category 2B) by the International Agency for Research on Cancer (IARC, 1999). Furthermore, it has been shown that skin absorption and lung inhalation are potentially significant routes of exposure to some DBPs in water (Gordon et al., 1998; Fantuzzi et al., 2001; Xu and Weisel, 2005). Therefore, the use of chlorinated reclaimed water for agricultural applications, with the subsequent human consumption of crop foods irrigated with reclaimed water, could be a route of exposure to DBPs (Levine and Asano, 2004). Suspected THM toxicity has led to adoption of specific regulations for the control of total THM (TTHM) in drinking water. Such regulations or guidelines have been established by the World Health Organization (WHO) ($200\mu\text{g L}^{-1}$ only for chloroform), the US Environmental Protection Agency (US EPA) ($80\mu\text{g L}^{-1}$), and the European Union (EU) ($100\mu\text{g L}^{-1}$ by 2009) (Richardson, 2003). However, specific standards are not available for reclaimed water used for agricultural irrigation, except those included in the WHO guidelines for the maximum permissible chloroform concentration (0.47 mg kg^{-1}) in soils receiving untreated municipal wastewater (WHO, 1996).

Agricultural and landscape irrigation with reclaimed water is an alternative commonly adopted to overcome water shortages in arid and semiarid regions (Levine and Asano, 2004). Chlorination of treated effluents has been shown as the most cost effective technique for pathogen inactivation before agricultural irrigation. However, limited information is available on THM formation during chlorination of treated effluents (Wistrom et al., 1996; Koukouraki and Diamandopoulos, 2003; Yang et al., 2005), particularly at full-scale wastewater treatment plants (WWTP) under the effects of seasonal variations of effluent quality. Furthermore, limited information has been reported on the potential of UV light exposure for formation or removal of TTHM in association to chlorine addition, as a combined disinfection strategy becoming increasingly adopted (Perrot and Baron, 1995).

The main objective of this study was to determine the potential of chlorine disinfection and UV light exposure for

THM formation, during water reclamation for agricultural and landscape irrigation at three full-scale WWTP. TTHM concentrations in chlorinated reclaimed waters were monitored for 2 years, either in conjunction or independently of UV light exposure. Several water quality parameters, such as pH, ammonia nitrogen, bromide, electrical conductivity, COD, and turbidity were also studied to determine their possible correlation with TTHM formation. The seasonal variability of TTHM was assessed on the basis of water temperature.

2. Material and methods

2.1. Chemicals

Suprasolv[®] grade methanol was obtained from Merck (Darmstadt, Germany). Analytical grade chloroform, bromodichloromethane, chlorodibromomethane, bromoform, 2-bromochloropropane, and ascorbic acid were purchased from Sigma-Aldrich (Steinheim, Germany).

2.2. Reclamation plants description

The three WWTP studied are located in NE Spain. Fig. 1 shows a flow diagram of the three WWTP monitored. Reclamation processes include chlorination as the main disinfection process in all cases, and reclaimed effluents are used for agricultural and landscape irrigation. The WWTP located in Mataró (MT) is a demonstration plant that receives a portion of the secondary effluent from a treatment facility serving 205,000 equivalent inhabitants. The water reclamation process includes coagulation–flocculation, settling, and rapid sand filtration using a multilayer filter (Cilt-Filtomat, Barcelona, Spain). After physico-chemical treatment, treated water flows into two different disinfection channels. The first channel receives a flow of $0.7\text{ m}^3\text{ h}^{-1}$, that is exposed to UV light generated by two inline multi-wavelength UV lamps (Berson 400, Berson-UV-Techniek, the Netherlands), with a theoretical intensity of $200\text{--}400\text{ mJ cm}^{-2}$, before chlorine addition. The second channel receives the flow balance of $0.6\text{ m}^3\text{ h}^{-1}$, which is chlorinated before entering a disinfection

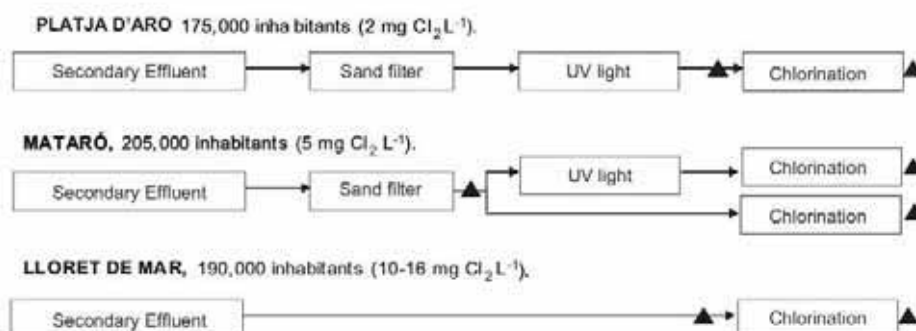


Fig. 1 - Flow diagram of the three WWTP studied, with indication of the populations served and the chlorine doses applied. Sampling points are designated with a solid triangle.

plug flow reactor, with a theoretical mean residence time of 90 min. Disinfected effluents are stored in separate glass-fiber tanks, with a capacity of 20 m³ each.

The second water reclamation plant is located in Platja d'Aro (PA) and receives treated effluent from a WWTP serving mostly a residential area with ca. 175,000 equivalent inhabitants. A portion of secondary effluent is diverted to a set of Hydroclear (USFilter) sand filters, and then disinfected by exposure to UV light produced by two Berson-inline 5000 NW 300. A chlorine dose of 5 mgL⁻¹ is also added to provide a residual disinfectant before the water enters the storage tank.

The third reclamation plant receives secondary effluent from Lloret de Mar (LM) WWTP. Lloret de Mar is a tourist resort, which reaches a peak population of 190,000 inhabitants during the summer. Secondary treatment includes a nitrification/denitrification reactor with high effluent recirculation that results in low ammonium concentrations. Secondary effluent from LM WWTP was chlorinated with a dose of 16 mgL⁻¹ in July 2003, and of 14 mgL⁻¹ in August 2004. The Lloret de Mar reclamation process includes only chlorine disinfection, while the reclamation processes at Platja d'Aro and Mataró include an advanced or tertiary treatment before disinfection.

2.3. Sampling strategy

Sampling periods, covering daily and seasonal variations, were established from May 2003 to February 2005. Seven 5-day sampling periods were adopted at PA WWTP, to collect water samples both before and after the chlorination step. Sampling at LM WWTP was conducted only during two weeks, as chlorination is limited to summer periods. The role of UV light exposure at MT WWTP was assessed during eight 5-day sampling periods, using chlorinated water with and without previous UV light exposure. The first four sampling periods were focused on the quality of the water stored in the tanks of MT WWTP, while the subsequent four sampling periods were directed to determine immediate changes in water quality due to chlorination, without considering the changes taking place during tank storage.

2.4. Analytical methodology

COD, ammonia nitrogen, bromide, electrical conductivity and turbidity analysis were determined following the APHA Standard Methods (APHA-AWWA-WPCF, 1995).

Water samples for THM analysis were collected in 40 mL glass vials containing 100 mg of ascorbic acid, to remove residual chlorine in water samples. Vials were filled to the top (headspace free) and kept refrigerated during transport to the laboratory, where they were stored at 4 °C until they were analysed. The total sample holding time was less than 48 h.

THM were analysed by headspace solid-phase microextraction (HS-SPME) combined with gas chromatography coupled to an electron capture detector (GC-ECD), as described by Cho et al. (2003). A sample portion of 1 mL was placed in a 40-mL vial. The vial was then sealed with a PTFE-lined septum screw cap, and spiked with 12.5 ng of the internal standard (i.e. 2-bromochloropropane) dissolved in methanol, by injection through the septum. Extraction was performed from the headspace during 30 min, under magnetic stirring, using

divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 50/30 µm fiber. The extraction temperature was set at 30 °C. Fiber desorption was carried out at 250 °C for 3 min in the injector port of a HP 5890 Series II GC (Palo Alto, CA, USA). A Rtx-VGC (60 m × 0.32 ID 1.8 µm film thickness) analytical column from Restek (Bellefonte, PA, USA) was used. Oven temperature was programmed to increase by 3 °C min⁻¹ from 30 °C (10 min) to 110 °C, and then by 10 °C min⁻¹ to 230 °C. Temperature was kept at 230 °C for 10 min. The carrier gas and make up gas were helium 4.6 (1.5 mL min⁻¹ at 70 °C) and nitrogen 5.0 (85 mL min⁻¹), respectively.

2.5. Statistical analysis

Experimental results were statistically evaluated using the SPSS 13 package (Chicago, IL, US). Adjustment of data sets to a normal distribution was always verified as to ensure that parametric statistics were applicable. Normal distributions were obtained by the Kolmogorov-Smirnov test after outliers were excluded from data sets. The comparison of means was conducted by the paired samples t-test, when THM concentrations were day-dependent (e.g. the chlorination effect in the PA WWTP), and by the independent samples t-test, when no dependence was observed (e.g. the effect of tank storage at MA WWTP).

3. Results and discussion

3.1. THM concentrations

Table 1 shows reclaimed water quality parameters (i.e. ammonia nitrogen, COD, pH, electrical conductivity, and turbidity), as determined at the different WWTP. High ammonia nitrogen concentrations were found in PA and MA WWTP effluents, while a low ammonia nitrogen concentration was found in LM WWTP effluent. Reclaimed water from MA WWTP showed an electrical conductivity, a bromide concentration and turbidity levels higher than those of the other two effluents, mainly due to industrial wastewater contributions reaching the MA WWTP.

Chloroform was the most abundant compound in chlorinated reclaimed water at the three WWTP studied, as previously reported for chlorine-disinfected drinking water (García-Villanova et al., 1997) and wastewater (Koukouraki and Diamandopoulos, 2003; Yang et al., 2005). Wastewater chlorination is an important determining factor of the chloroform concentrations actually observed. Fig. 2 shows that bromoform and chlorodibromomethane were often under the limit of detection and the limit of quantification, respectively, and that only chloroform and bromodichloromethane could be always quantified. TTHM concentrations (2–30 µg L⁻¹; Table 1) were always below drinking water quality standards, and often lower than one-tenth of the established limits.

3.2. TTHM formation after the chlorination step

Fig. 3 shows the relative increase of TTHM after the chlorination step. The concentration increase observed at

Table 1 – Quality parameters and total trihalomethane (TTHM) concentrations of reclaimed water produced at the three WWTP studied

Quality parameter	Platja D'Aro (PA)	Mataró (MA)	Mataró (MA-t) (Storage tank)	Lloret de Mar (LM) ^{a,b}
pH	7.69 ± 0.31	7.58 ± 0.18	7.83 ± 0.39	7.69 ± 0.33
Conductivity ($\mu\text{S cm}^{-1}$)	1181 ± 271.7	2616 ± 327.1	2917 ± 447	1076 ± 3.53
COD ($\text{mg O}_2 \text{ L}^{-1}$)	33.04 ± 11.85	76.95 ± 32.32	104.1 ± 21.92	33.5 ± 3.54
TOC (mg L^{-1})	13.06 ± 5.72	31.45 ± 10.07	24.56 ± 13.01	—
Ammonia nitrogen (mg L^{-1})	17.55 ± 16.18	25.90 ± 9.64	28.96 ± 6.81	7.0 ± 0.0/0.18 ± 0.03
Bromide (mg L^{-1})	0.56 ± 0.63	0.97 ± 0.47	1.10 ± 0.36	—
Turbidity (NTU)	2.96 ± 2.74	9.75 ± 9.27	6.49 ± 4.14	—
Cl ₂ /NH ₃ N ratio	0.76 ± 1.9	0.11 ± 0.04	0.09 ± 0.03	2.0 ± 0.0/93.3 ± 18.9
TTHMs ($\mu\text{g L}^{-1}$)	6.15 ± 4.68	6.02 ± 4.99	4.25 ± 3.61	9.7 ± 4.8/54.5 ± 28.0

^a Campaign 2003.
^b Campaign 2004.

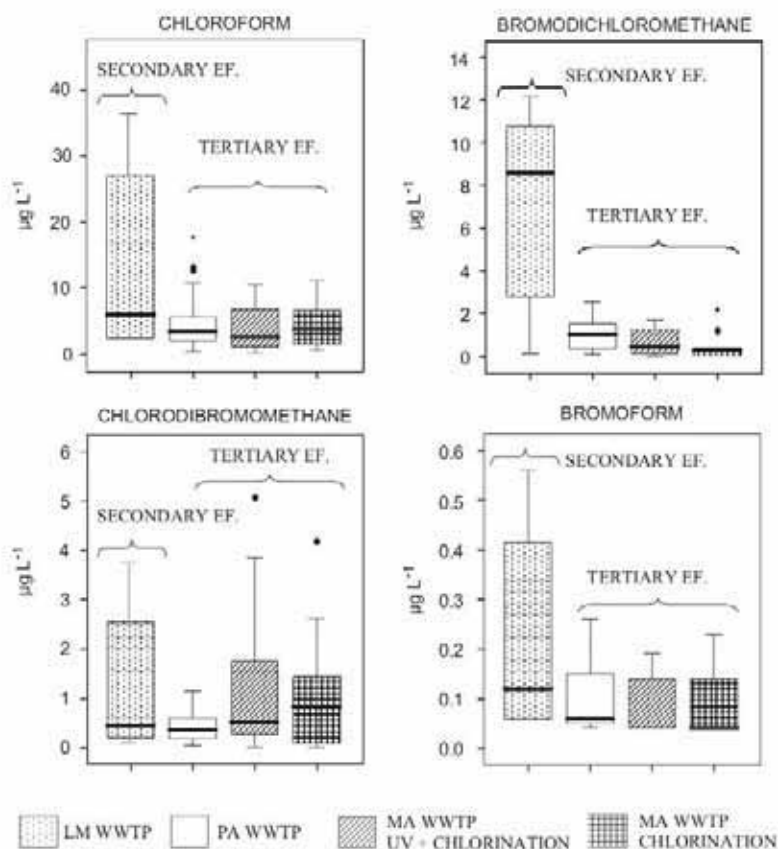


Fig. 2 – THM concentrations after chlorination at the three WWTP studied, classified as secondary and tertiary effluents. The box plots indicate the median, and the 25th and 75th percentiles for each compound. Outliers are indicated by black dots.

LM WWTP, using a chlorine dose of about $16 \text{ mg Cl}_2 \text{ L}^{-1}$, was 10 times higher than that observed at the other two WWTP, where lower chlorine doses (5 and $2 \text{ mg Cl}_2 \text{ L}^{-1}$) were applied to tertiary effluents. TTHM concentrations were generally

very low, because chlorine doses were below the breakpoint, as reported for similar effluents with high ammonia nitrogen concentration (Yang et al., 2005). Nevertheless, reclaimed water from LM WWTP, with a low ammonia nitrogen

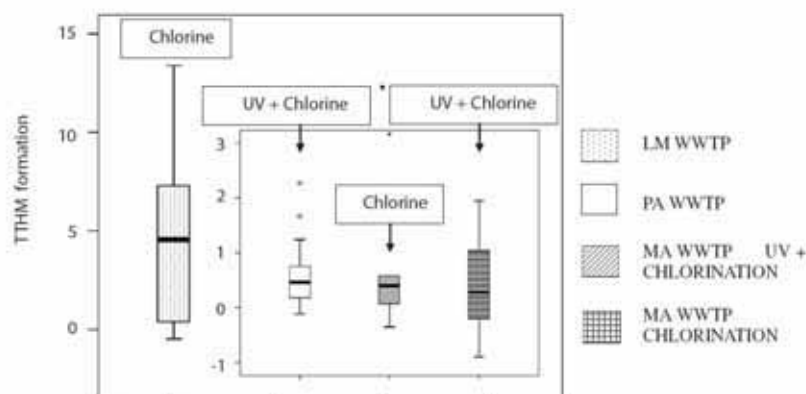


Fig. 3 – Box plots of the relative increases of TTHM formation ($(C_{out} - C_{in})/C_{in}$) at the three WWTP studied where C_{in} and C_{out} correspond to the TTHM levels before and after chlorination, respectively. Different scales have been used for Platja d'Aro (PA) and Mataró (MA) WWTP, due to the lower degree of TTHM formation at these two plants. All data values are presented.

concentration and a high chlorine dose, showed the highest TTHM concentrations, reaching nearly $70 \mu\text{g L}^{-1}$. To reach breakpoint chlorination, a chlorine dose close to 10 mg L^{-1} as active chlorine (Cl_2) is normally required for each 1.0 mg L^{-1} of ammonia-nitrogen ($\text{NH}_3\text{-N}$) (White, 1999). The chlorination processes at MT and the PA WWTP were operating at the far left side of the breakpoint curve, while that at the LM WWTP did operate at both above and below the breakpoint (Table 1). LM WWTP results were grouped in two different data sets: the 2003 campaign with low $\text{Cl}_2/\text{NH}_3\text{-N}$ ratio (i.e. 2.0), where the breakpoint was not reached and the TTHM levels observed were similar to those of the other two WWTP studied; and the 2004 campaign, where the breakpoint ratio was exceeded (i.e. 93) leading to formation of high TTHM levels. All these results are in accordance with those of a previous study, where well nitrified effluents resulted in high TTHM concentrations and poorly nitrified effluents generally inhibited TTHM formation (de Leer et al., 1990).

Table 2 summarises the statistical analysis of TTHM concentrations, before and after chlorination, at the three WWTP studied. There is a statistical significant difference as a function of chlorine dose at the three WWTP, indicating the potential of high chlorine doses for promoting the formation of TTHM. However, no significant differences were observed among chlorinated effluents after tank storage. This could be explained by the long residence time (several days) of reclaimed water in the tanks.

3.3. Correlation among TTHM formation and chlorination process at PA WWTP

Changes on TTHM concentrations at PA WWTP were not directly dependant on chlorination, as the plant operated under a constant chlorine dose. Table 3 shows the Pearson's correlation coefficients between water quality parameters reported in Table 1 and TTHM formation. Turbidity and COD have no statistically significant effect on TTHM formation.

However, ammonia nitrogen and bromide are directly involved in TTHM formation. An increase in ammonia nitrogen results in a TTHM decrease (Amy et al., 1984; Wistrom et al., 1996; Koukouraki and Diamandopoulos, 2003) due to chloramines formation (Fayyad and Al-Sheikh, 2001). The presence of bromide promotes an increase of TTHM concentration (Amy et al., 1984; Nikolaou and Lekkas, 2001). In fact, chloramines formation during chlorination of waters containing ammonia nitrogen and organic matter is faster than TTHM formation. Only when chloramines formation is completed, does haloform formation take place (Luong et al., 1982). Moreover, the slopes in Table 3 indicate that the potential of bromide for increasing TTHM concentrations is higher than the potential of ammonia nitrogen to prevent their formation. In contrast to results already published about the positive impact of TOC on THM formation in drinking water (Uyak et al., 2005), the statistical analysis showed a negative impact of TOC during chlorination of reclaimed effluents (Table 3). Although numerous factors can account for the different effect of TOC on TTHM formation potential, it is obvious that the differences in type and concentrations of the TOC present in drinking and reclaimed wastewater may explain the varying degree of chlorine reactivity with organic matter.

3.4. Effect of UV light exposure on TTHM formation

The effect of UV light exposure on TTHM formation was studied at the MA WWTP, as there was a possibility for UV light application in one of the two disinfection channels. A comparative statistical analysis of TTHM formation in the two channels was conducted. Fig. 4 shows TTHM concentrations found in reclaimed water, with and without UV light exposure. A matched-pair test indicates that there is no significant difference between water samples exposed to UV light and those not exposed to UV light, with a 95% probability ($p = 0.91$). Similar results were obtained in drinking water exposed to sunlight (Gallard and von Gunten, 2002) and when

Table 2 – Statistical analysis by the pair-sample t-test of the effect of chlorination on TTHM formation at the three WWTP studied (effects of tank storage and UV light exposure were also considered in Mataró WWTP)

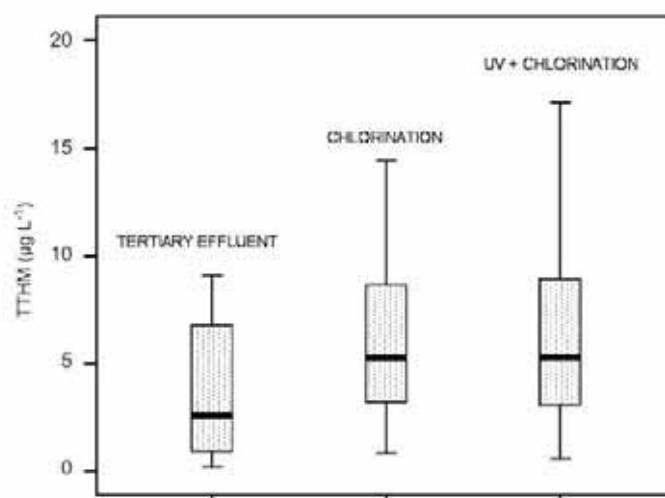
Statistical parameter	Platja d'Aro (PA)	Mataró (MA)				Lloret de Mar (LM)
		Before tank storage		After tank storage		
		Chlorination	UV+Chlorination	Chlorination	UV+Chlorination	
df	57	13	13	19	19	7
t-test	-4.377	-2.674	-3.781	-0.554	-1.662	-3.354
p-value	0.000 ^a	0.019 ^a	0.002 ^a	0.586 ^b	0.113 ^b	0.017 ^a

df: degree of freedom.
^a Significant difference at $p = 0.05$.
^b No significant difference at $p = 0.05$.

Table 3 – Pearson's correlation coefficients between water quality parameters and TTHM formation in chlorinated effluents at Platja d'Aro (PA) WWTP

Parameter	COD	TOC	Ammonia nitrogen	Bromide	Turbidity	pH
Slope ^a	0.001	-0.056	-0.022	0.045	-0.036	0.091
Pearson's correlation coefficient	0.196	-0.439	-0.381	0.464	-0.332	0.039
p-value	0.309	0.022 ^b	0.042 ^b	0.034 ^b	0.079	0.842

^a Related to a lineal regression.
^b Significant difference at $p = 0.05$.

**Fig. 4 – Box-plot of UV light exposure effects on TTHM formation in MT WWTP.**

examining the efficiency of UV exposure ($0-3500 \text{ mJcm}^{-2}$) for decreasing TTHM concentration (Boor and Mohseni, 2006). Nevertheless, Table 2 indicates that chlorination of UV light exposed reclaimed water results in a considerable decrease of the statistical significance level ($p = 0.002$), in comparison to that of reclaimed water not exposed to UV light ($p = 0.019$).

3.5. Seasonal variability of THM formation

Seasonal differences in THM formation as a function of water temperature were studied over a 2-year period at the PA WWTP, considering that increases in drinking water temperature are known to increase THM formation (García-Villanova et al., 1997; Uyak et al., 2005). Fig. 5 indicates

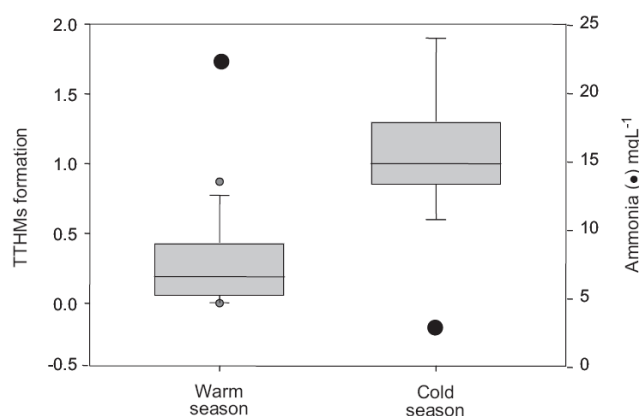


Fig. 5 – Seasonal variability of ammonia (●) and relative increase of TTHM formation (boxes) after a disinfection process using UV light exposure and chlorination, during a 2-year study period at PA WWTP. Bromide concentrations during the warm and cold seasons were 0.32 ± 0.27 and $0.91 \pm 0.82 \text{ mg L}^{-1}$, respectively.

that there is a seasonal variability of TTHM formation over the 2-year study period. A statistically significant difference was found between TTHM formation during cold (October to January) and warm (April to September) periods, with a probability higher than 95% ($p = 0.005$). Recent studies of TTHM formation in drinking water have shown that seasonal differences are correlated with water quality and temperature (Toroz and Uyak, 2005). Seasonal differences in water quality at the PA WWTP, serving an important tourist population during the spring and summer seasons, could explain the higher levels of TTHM formation during the cold season, most likely due to the lower ammonia nitrogen concentrations observed. Ammonia nitrogen concentrations were significantly higher during the warm season, as compared to the cold season ($p = 0.000$), resulting in a relatively lower TTHM formation.

4. Conclusions

Chlorination of non-nitrified secondary and tertiary treated wastewater, during water reclamation for agricultural and landscape irrigation, results in low TTHM formation. Chloroform was the most abundant DBP at the three water reclamation plants studied. TTHM concentrations observed during the 2-year study period never exceeded quality standards applicable to drinking water. Similar observations on the low TTHM formation in wastewater effluent have been reported in other studies, but have not been demonstrated in full-scale WWTP during periods of 2 years. Ammonia nitrogen present in wastewater effluents was a key factor in achieving breakpoint chlorination (White, 1999), as its reaction with chlorine (Jolley and Carpenter, 1983; Wistrom et al., 1996; Koukouraki and Diamandopoulos, 2003) results in other by-products such as chloramines (Fayyad and Al-Sheikh, 2001). Furthermore, chlorine could react with organic compounds present in wastewater, such as amino acids from

complex organic matter (Conyers and Scully, 1993; McCormick et al., 1993), leading to low TTHM formation. TTHM formation showed a positive correlation with bromide concentration and a negative correlation with initial ammonia nitrogen concentration and TOC. Moreover, no significant effect of UV light exposure on TTHM formation could be shown, in accordance with literature results (Gallard and von Gunten, 2002; Toor and Mohseni, 2006). A negative correlation was observed between seasonal changes of TTHM formation and water temperatures during warm tourist seasons, most likely due to the higher ammonia nitrogen concentrations recorded during those periods. In summary, this study supports that chlorine disinfection of reclaimed water used for agricultural and landscape irrigation results in lower TTHM concentrations than those observed in conventional drinking water supplies. The presence of significant concentrations of ammonia nitrogen (in the absence of nitrification processes) ensures that the risk of TTHM formation is significantly prevented.

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3.4. Discussió de les metodologies analítiques

La determinació de THMs es va dur a terme mitjançant la tècnica HS-SPME-GC-ECD. Per a aquesta finalitat es va seguir una adaptació de la metodologia desenvolupada per Cho *et al.* (2003). Tanmateix, en la present Tesi es va escollir la fibra de divinilbenzè / carboxè / polidimetilsiloxà (DVB/CAR/PDMS) ja que proporcionava una resposta suficient per tal de detectar els nivells presents en aigües regenerades.

El cromatograma obtingut emprant la metodologia descrita a l'article 7 (Figura 3.3) mostra una adequada separació cromatogràfica. La presència de pocs pics pertanyents a altres substàncies en l'interval de temps que elueixen els THMs és fruit de l'elevada selectivitat que s'obté d'aplicar un detector de captura d'electrons.

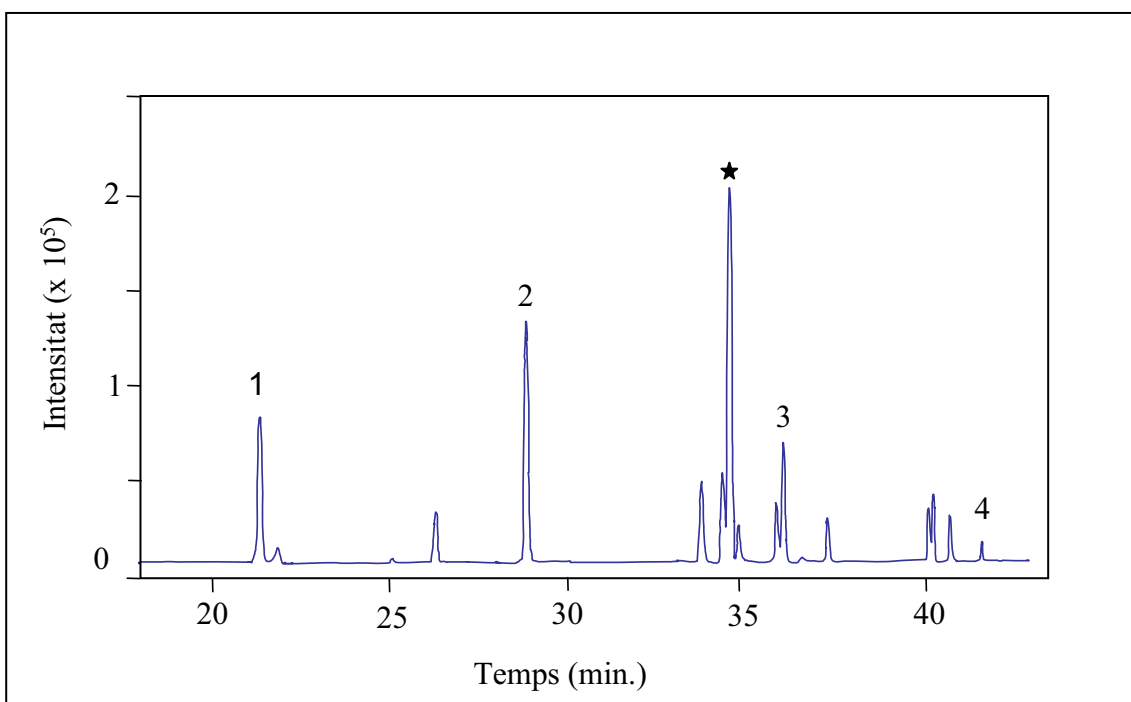


Figura 3.3. Cromatograma obtingut d'una mostra després del procés de cloració a l'EDAR de Platja d'Aro. Identificació dels compostos: (1) cloroform, (2) bromodiolometà, (3) dibromodiolometà, (4) bromoform, (*) 2-bromodiolopropà (*patró intern*).

Paràmetres de qualitat analítica

L'anàlisi per triplicat d'una mateixa mostra d'aigua durant un mateix dia va permetre calcular la repetibilitat del mètode. Pel que fa als LODs i LOQs, aquests es van realitzar emprant aigua de qualitat HPLC i mesurant l'àrea del blanc més tres o deu cops la seva desviació estàndard, segons si es tractés del LOD o el LOQ ($n=3$).

Tal i com es mostra a la Taula 3.1, els límits de linealitat, tant per al cloroform com per al bromoform van ser més elevats que els corresponents al bromodiclorometà i dibromoclorometà. Aquest fet diferencial es deu possiblement a l'existència de limitacions en l'equilibri gas-fibra en el cas del cloroform i a limitacions en l'equilibri aigua-gas en el cas del bromoform. Tots els coeficients de linealitat van ser superiors a 0.99.

Taula 3.1. Linealitat, repetibilitat, LODs i LOQs de la metodologia establerta en aquesta Tesi.

	Linealitat ($\mu\text{g L}^{-1}$)	Rep. (%)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)
Cloroform	0.25-100	3.1	0.09	0.25
Bromodiclorometà	0.08-25.0	2.7	0.02	0.08
Dibromoclorometà	0.05-12.5	2.6	0.02	0.05
Bromoform	0.14-100	3.4	0.04	0.14

Rep. Repetibilitat.

Atès a que el cloroform és el compost més volàtil i el que semblaria tenir menys afinitat per la fibra de tots els THMs, els seus LODs i LOQs van ser molt més elevats que no pas els corresponents a la resta de compostos. Tanmateix, els LODs van ser similars als obtinguts prèviament per HS-SPME-GC-ECD (Cho et al., 2003).

3.5. Discussió general dels resultats

Amb els resultats obtinguts arrel d'aquest treball, es pot preveure la concentració de THMs en una determinada aigua residual, almenys en el cas de les EDARs d'estudi, avaluant la concentració d'amoni, bromur i clor dosificat en cada moment.

Tot i que la dosis de clor afegida a l'aigua és el paràmetre més important per a la formació de THMs en aigua de beguda, en l'aigua residual regenerada, la presència o no d'amoni va resultar ser el paràmetre clau, ja que la presència d'aquest compost provoca la formació de cloramines. Així doncs, per tal d'excedir el punt de ruptura i accelerar la formació de THMs, es requereix d'una major dosi d'hipoclorit sòdic (veure secció 1.1.3.). En aquest sentit, eliminar completament l'amoni present en l'aigua residual semblaria ser una contradicció, almenys si el procés de desinfecció es realitza mitjançant clor.

Tanmateix, el fet que no es formin THMs no significa que no es formin d'altres subproductes de desinfecció. Així, la presència de monocloramina pot iniciar la formació de nitrosoamines (Mitch i Sedlak, 2002). De fet, la concentració màxima recomanada de nitrosodimetilamina (NDMA) (compost carcinogen) en aigües de beguda en l'estat de Califòrnia, per sobre de la qual s'ha de deixar d'abastir la població, és de 100 ng L^{-1} (CDHS, 2007), un miler de cops per sota del llindar establert per als THMs. A més de les nitrosamines, es poden formar una gran varietat d'altres subproductes de cloració, com ara els trihaloacètics o els trihalometans iodats. Finalment, tot i que l'ús d'altres agents desinfectants, com ara el diòxid de clor o l'ozó, redueix la formació de THMs (Rand et al., 2007), aquests no impedeixen que es formin d'altres subproductes, que poden ser igual o més perillosos que els THMs.

Molts cops la idoneïtat d'una aigua residual regenerada no radica només en la seva natura com a aigua. L'aportació de nutrients d'aquesta pot ser tant d'interès agrícola, doncs actua com a fertilitzant, com d'interès per a l'empresa explotadora de l'aigua regenerada, que no requereix d'un procés de regeneració tant eficient. Malgrat això, l'elevada conductivitat i la presència d'ions fitotòxics com el sodi o el bor en l'aigua regenerada poden afectar a la productivitat de certs conreus sensibles.

D'altra banda, si l'ús que se li dona és industrial, s'hauran de buscar sistemes de regeneració molt més adients, sovint més costosos. En aquest cas, els aigüamolls construïts descrits en el capítol 2 poden ser molt escaients, tot dissenyant-los per a les eficiències requerides en cada moment. Pel que fa a la qualitat microbiològica, l'aigüamoll de flux superficial de Can Cabanes assoleix els valors guia descrits per l'OMS per a l'ús agrícola.

Les possibilitats d'explotació de l'aigua residual són molt elevades. Pel que fa a Catalunya anualment s'aboquen al medi 713 hm^3 d'aigua residual depurada de les quals només un 3 % són reutilitzades (ACA, 2007). Tanmateix, la major part d'aquesta aigua tractada té els seus orígens prop de grans ciutats, i lluny de les àrees agrícoles. En aquest sentit, l'ús industrial, la recàrrega d'aqüífers així com el reg de parcs i jardins, en poden ser els usos més estratègics.

Així doncs, si s'aconsegueix un tractament i distribució de l'aigua regenerada fins als consumidors, tot garantint unes qualitats sanitàries adequades, la regeneració pot facilitar el subministrament d'aigua en el futur durant totes les èpoques de l'any.