



Sources of Contaminants of Emerging Concern in Groundwater of Barcelona Urban Area

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Abstract. Groundwater is a vital resource for the development of urban areas, where the problem focuses on the quantity and on the quality of this freshwater resource. Barcelona is a good example as because currently groundwater is used for irrigation of parks and gardens and street cleaning due to its poor quality as drinking water source. Among the pollutants found in groundwater, of special interest are contaminants of emerging concern (CEC), as they pose a high risk to the aquatic environment and human health. The behaviour, spatial distribution and processes that control them in the aquatic environment are still uncertain and most of them are unregulated. In this paper we study the inputs and processes controlling the hydrochemistry of Barcelona urban groundwater with special emphasis on the CEC. We selected 29 CEC that were detected at high concentrations of up to $1 \mu\text{g L}^{-1}$ (e.g. gemfibrozil, benzotriazole, among others). Towards the higher zones we identify groundwater with relative low mineralization more proximate to the natural recharge composition, while towards the urban area the anthropic inputs are evident (e.g. nitrate concentrations range from 50 to 200 mg L^{-1}). Near the Besòs river there is a clear contribution from this superficial water highly polluted, mostly from wastewater treatment plant (WWTP) discharges, and reducing conditions. The main contributor of CEC pollution in groundwater was the river-aquifer interaction (Besòs river), while towards the urban area it might come from sewage seepage and probably a minor input from urban runoff. The

redox state of these waters seems to control the fate and occurrence of several of these CEC. The limitations of this study are restricted to a single sampling campaign, therefore these results should be corroborated with other sampling campaigns, including the seasonal variations, which would allow establishing more robust conclusions.

1 Introduction

The availability of water resources is becoming increasingly scarce, at the same time that its demand is increasing, particularly in densely populated cities (e.g. Barcelona), where the water resource for supply comes mostly from surface sources (Howard et al., 2002). The use of groundwater can reduce pressure on conventional water supply sources and can be an essential resource in emergency situations, such as drought periods. Despite the poor quality of these waters, which are not suitable for human consumption, they can be used for other secondary uses (Vázquez-Suñe et al., 2005).

The contaminating sources in these areas are multiple; sewage seepage, septic tanks, urban runoff, landfills, urban and industrial discharges, contaminated soils or anthropic materials used as fill, contributions from polluted rivers, marine intrusion, fertilizers, pesticides, leaching due to rising levels, among others (Vázquez-Suñe et al., 2010). Therefore,

different groups of emerging organic contaminants (CEC) have been detected in urban aquifers.

The presence and evolution of these contaminants in aquifers depends on several factors as the lithology, hydraulic and textural properties of the soil, temperature, microbial environment (e.g. biochemical processes), redox state (e.g. chemical processes) and physicochemical properties of the specific compound (e.g. transport mechanisms) (Barbieri et al., 2011). Therefore, a correct assessment of groundwater quality requires the evaluation of all the processes that affect these contaminants (Jurado, 2013). These types of contaminants have been detected in various water matrices; wastewater, distribution network, surface water, sea, among others and are of particular interest given the potential damage they can generate to the aquatic environment and human health (Reungoat et al., 2010). In addition, due to the fact that the knowledge of these contaminants is much lower than that of traditional ones and most of these compounds do not present any regulation (Jurado, 2013).

This paper investigates the abundance and fate of the CEC in urban groundwater. The specific objectives were to (i) investigate the hydrochemistry and processes that were affecting the composition of these waters and (ii) characterize the distribution of CEC and the inputs/processes that were controlling them. We propose, for the first time in the urban aquifers of Barcelona, that some specific CECs can be used as indicators of different sources recharging the groundwaters.

2 Methods

2.1 Study site

Barcelona is located NE of the Iberian Peninsula (Spain), between the Collserola mountain range and the Mediterranean Sea, both limits have an NNE-SSW orientation. The other boundaries correspond to the Besòs river to the NE and the Llobregat river to the SW. It is a highly populated city, with 1 664 182 inhabitants in the Barcelona district (2020) and a surface of 101.35 km². Currently its main economic activity is tourism and services, with some industrial zones located towards the Port and Besòs river areas (IDESCAT, 2020), in addition to the construction sector. The climate is typically Mediterranean, with average rainfall of 600 mm yr⁻¹, but presents a high variability in the year, about 20 % of the total annual precipitation can occur in some months (Jurado et al., 2021), typical of Mediterranean climates.

At present Barcelona's groundwater, due to its bad quality, is used for secondary uses as street cleaning, garden irrigation and ornamental water fountains. But it can be considered as an alternative tap water since there are several aquifers below the city (Fig. 1a). The Paleozoic aquifer crops out at the NW at high elevations and is composed of shales and granites. Quaternary aquifers can be found in the rest of the city.

To the N and S in the low topographic areas, they are constituted by the alluvial and deltaic sediments of the Llobregat and Besòs rivers. In intermediate areas, they are made up of piedmont cones to the NW (towards the Collserola) and coarse alluvial sediments with calcareous materials in lower areas (Jurado et al., 2012). In addition, a series of superficial anthropic deposits have been identified locally (construction waste, old landfills, filling of anthropic materials). The main direction flow is from the Collserola towards the sea to the SE (Fig. 1a). Eight sources of recharge have been identified in the aquifers of Barcelona (Vázquez-Suñé et al., 2010): (1) inputs from the Besòs river, (2) rainfall to the N in non-urbanized areas, (3) seepage from the Ter river drinking water distribution network, (4) seepage from the Llobregat drinking water distribution network, (5) seepage from Ter wastewater, (6) seepage from Llobregat wastewater, (7) urban runoff, and (8) marine intrusion. The seepage from the pipes network can be considered one of the most important.

2.2 Sampling and analytical methods

A total of 32 water samples were collected: 31 from groundwater (Fig. 1b) and one from the Besòs river. Sampling was carried out during the dry season (July 2020), were solutes are probably more concentrated, around the city of Barcelona.

The analytical results of inorganic and the CEC were performed at CSIC – IDAEA. Cations and traces were analyzed by ICP-MS and anions by ion chromatography. The CEC analyses were performed by solid phase extraction and a multilayer mixed bed cartridge with four different specific sorbents, such as weak anion and cation exchangers (WAX and WCX), Oasis HLB commonly used for wide range screening, Bond Elut PPL to retain even the most polar analytes. Separation was performed using a Waters Acquity UPLC HSS T3 column (2.1 × 100 mm, 1.8 μm). The LC flow rate was 0.2 mL min⁻¹ with a column temperature of 40 °C and the LC run time was 19 min. More than 160 active pharmaceutical compounds with a wide range of polarity and various physicochemical characteristics were analyzed by liquid chromatography, high resolution mass spectrometry, Q-Exactive system, Orbitrap and independent data acquisition.

3 Results and Discussions

3.1 Inorganic Hydrochemistry

According to the proximity of the samples, population density, hydrogeochemical and hydrogeological similarity of the study area (proximity to the river, districts, hydrogeological formations, geology, etc.), the samples were grouped into 3 groups: Besòs, Barcelona Plain (B.P) and High Zone (H.Z.). Figure 1b shows these 3 groups and the Stiff diagrams of the samples. The Besòs group is located towards the Besòs

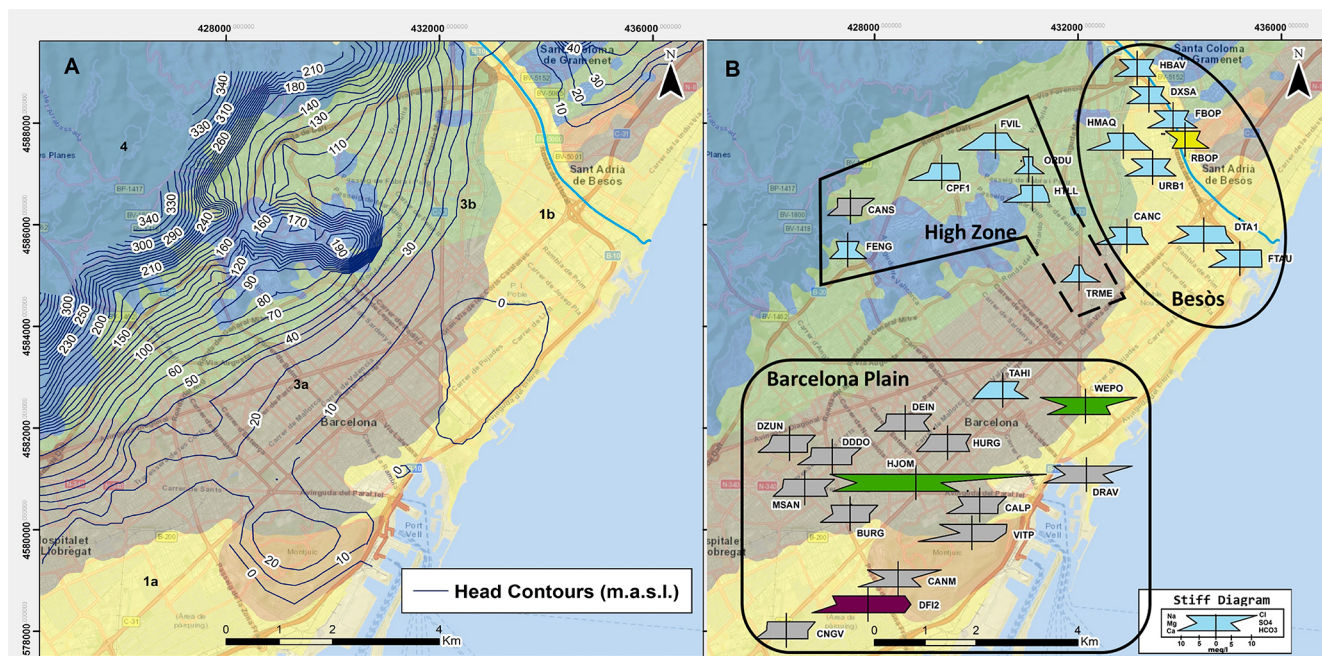


Figure 1. (a) Schematic description of the hydrogeology of Barcelona: (1a) Llobregat Delta made up of gravels, sands, silts and clays (Holocene, Quaternary), (1b) Besòs Delta composed of gravels, sands, silts and clays (Holocene, Quaternary), (2) Barcelona Plain (Montjuïc) made up of marls, sandstones and sands (Tertiary), (3a) Barcelona Plain consisting of alluvial deposits of carbonated clays (Pleistocene, Quaternary), (3b) Barcelona Plain (high zone) consisting of colluvial (foothill) deposits gravel, sand and silt, (4) Collserola Range consisting of shale and granites (Paleozoic). Head contours intervals are 10 m. Modified from ICGC (2017) and Bulboa (2021). (b) Samples location, stiff diagrams (blue: bicarbonate calcium, grey: chlorinated calcium, green: chlorinated sodium, purple: sulfated calcium, yellow: bicarbonate sodium) and 3 groups of water identified.

river with an absolute composition mostly bicarbonate calcium, relative low NO_3^- concentration ($<25 \text{ mg L}^{-1}$), reducing conditions and probably there is an influence of surface waters (Besòs river) in these samples. The H.Z are waters with lower mineralization close to the natural recharge zone with absolute composition mostly bicarbonate calcium with aerobic conditions. The B.P are waters located towards highly populated areas with longer residence time, so probably they had an important anthropic contribution, coherent with higher mineralization and NO_3^- concentration ($50\text{--}200 \text{ mg L}^{-1}$). They presented an absolute composition mostly chlorinated calcium and mainly aerobic conditions, particularly samples (TRME, CNGV and DFI2) presented higher content of iron ($1\text{--}2 \text{ mg L}^{-1}$) and/or manganese ($0.1\text{--}0.5 \text{ mg L}^{-1}$), so they would be in local reducing conditions. The dominance of calcium and bicarbonate was due to natural inputs and processes like water-rock interaction, coherent with abundance of carbonate materials with calcite, and the fact that the H.Z samples have this composition that can be considered the closest to the natural recharge. In the B.P samples the dominance of chlorinated facies can be attributed in some samples to a marine input (towards the coast) but mostly due to the longer residence time and anthropic inputs, coherent with higher nitrate concentrations. The redox state

of these waters is consistent with the statements of other authors (Jurado et al., 2021, 2013).

The study of some trace elements can contribute to elucidate some hydrochemical processes or point pollution events, higher levels of these are associated with anthropogenic activities such as and agricultural industry, hospital wastewater, and electronic waste (Yadav et al., 2018). The heavy metals (As, Sb, Pb) concentrations were within the standards of drinking water, nevertheless higher concentrations were observed in specific samples (e.g. TRME, CNGV, DFI2, DXSA, WEPO). Some of them are located in industrial areas (Port and Besòs Industrial zone), which can be attributed to contamination from this source. The sample DFI2 also presented higher concentration of sulfate (486 mg L^{-1}) which in some cases can be attributed to sewage seepage. Other processes as urban runoff infiltration can be considered the source of these higher concentrations, for instance the leaching of vehicle waste (Carrera, 1997). Most of these samples present reducing conditions (e.g. NO_3^- : $<25 \text{ mg L}^{-1}$, Fe^{+2} : $1\text{--}2 \text{ mg L}^{-1}$, Mn^{+2} : $0.05\text{--}0.5 \text{ mg L}^{-1}$), which is coherent with a point source pollution event (e.g. industrial).

3.2 Abundance and spatial distribution of CEC

A total of 29 CEC have been chosen; pharmaceuticals, personal care products, industrial products, food additives, drugs of abuse and lifestyle products. Table 1 shows the CEC analyzed along with their concentrations (mean, standard deviation and maximum) and frequency of detection in groundwater and in the river Besòs. For the groundwater, it was observed that most of the compounds presented an important positive asymmetry which occurs due to a series of anomalous values of higher concentrations. For example, gemfibrozil that presented the maximum concentration of 1359 ng L^{-1} , corresponds to an isolated sample (TRME) since the concentration of most of the samples is one to two orders of magnitude lower. Similar trend occurred with specific CEC at given locations/samples for instance to the industrial port area sample CNGV (e.g. bisphenol A, benzoylecgonine), DFI2 (e.g. ketoprofen), the upper zone of Besòs sample DXSA (diclofenac, diazepam), among others. This high asymmetry in the concentrations of the compounds might indicate that the sources or origin of these compounds are quite heterogeneous in the aquifer, and may be due to local conditions. In general, sewage seepage in the city has been considered as a source of diffuse contamination (Vázquez-Suñe et al., 2010), but it could be assimilated to point source pollution for some compounds.

In spite of the differences in resident time of the surface and groundwater samples, for most of the CEC, the concentration in the river was higher than the mean concentration in groundwater, however, with respect to the maximum concentrations, it was observed that half of the compounds presented higher concentrations in the aquifer, probably related to this anomalous samples. Considering that the river flows comes mostly from WWTP discharges in summer, which have a high CEC load, the fact that some compounds present lower concentrations in the river than in the aquifer, particularly in the Besòs area, may be due to (i) the properties of the compound, for example that it degrades faster in aerobic conditions (river) or presents a high persistency in the aquifer, (ii) higher removal efficiency in the WWTP and (iii) desorption of these compounds under specific conditions in the aquifer. Further investigation is required to clarify these observations.

The maximum concentration was for gemfibrozil, with 1359 ng L^{-1} and 90 % detection in groundwater and about 5 times higher in the river (6119 ng L^{-1}), however the Besòs samples presented low concentrations ($1\text{--}10 \text{ ng L}^{-1}$) indicating natural attenuation/degradation for this compound in this environment. Despite having the maximum concentration, this corresponds to an isolated sample (TRME: 1359 ng L^{-1}), the rest of the study area presented low concentrations ($<50 \text{ ng L}^{-1}$). The lowest concentrations are located towards the H.Z ($<1 \text{ ng L}^{-1}$). Saccharin follows with a maximum concentration of 610 ng L^{-1} and a 60 % frequency of detection, the river has a lower concentration of

215 ng L^{-1} . This compound follows the same trend as for gemfibrozil, an isolated anomalous sample (TRME) with higher concentration but most of the samples presented lower concentration ($<15 \text{ ng L}^{-1}$). Benzotriazole was found at maximum concentration of 355 ng L^{-1} and a detection frequency of 50 %, in the river the concentration was 4 times higher (1429 ng L^{-1}), the highest concentrations are distributed towards the Besòs ($150\text{--}355 \text{ ng L}^{-1}$), coherent with the river having the higher concentration (1429 ng L^{-1}), indicating that this industrial product is not effectively removed in the WWTP and probably is not affected by natural attenuation process or degradation. This observation is support by Mizukawa et al. (2017) as the authors found that this compound presents a high solubility, low biodegradation rate and high persistence in the aquatic environment, probably the discharge of effluent into the river is the main source of contamination of this compound. Also 3 samples; CPF1, TRME, DFI2, far away from the Besòs presented relative high concentrations, the latter two were in reducing conditions as well as the Besòs samples, so probably this compound might be favoured in this redox environment. Of the 32 samples analyzed, the compounds found in all samples (100 % of F.D) were benzoylecgonine (metabolite of cocaine), cotinine (metabolite of nicotine) and diclofenac (anti-inflammatory), indicating that they are commonly used by the inhabitants of Barcelona.

Figure 2a shows the frequency of detection of the CEC detected in the samples (i.e. the number/percentage of CEC found in the sample out of a total of 29). The samples with the highest percentage of detection were located towards the Besòs river and its surroundings, which is consistent with the fact that its flow is practically the WWTP discharge water, indicating that most of the analyzed compounds are not effectively removed by the treatments carried out at the WWTP. On the other hand samples belonging to the same aquifer but more distant from the river ($>1 \text{ km}$) presented a lower percentage probably due to natural attenuation processes and/or degradation of some compounds in their trajectory. There are also 2 particular samples with a high percentage of CEC, which is probably due to local conditions, for instance one located towards the high zone of the basin (CPF1) that could be due to the presence of nearby health centers (Vall d'Hebron Hospital $\sim 1 \text{ km}$ upstream). This hypothesis is enhanced by the high concentrations of human antibiotics (sulfadiazine and sulfapyridine) in this sample. According to Garcia-Gil et al. (2018), large hospitals might act as a point source of antibiotic contamination. The rest of the samples presented between 32 % and 60 % frequency of detection. Figure 2b shows the total CEC sum in each sample, the river sample presented the highest sum ($13\,148 \text{ ng L}^{-1}$), consistent with discharge waters from the WWTP, the sum in most of the groundwater samples were one to two orders of magnitude lower than the river, probably due to different sources and/or degradation process occurring in the aquifer, particularly in the Besòs area. The groundwater samples with the

Table 1. Concentration of CEC (ng L^{-1}) and frequency of detection (%) in groundwater and river.

Group	Compound	Concentration [ng L^{-1}]			Detection Frequency (%)	River [ng L^{-1}]
		Mean	Est. Desv.	Max.		
Antiinflammatory, Analgesic and TP	Acetaminophen	3	13	73	52	17
	Diclofenac	28	8	54	100	375
	Ketoprofen	1	4	16	6	< d.l.
	NO2-Diclofenac	0.1	0.2	1.3	45	1154
	4-Hydroxiclofenac	0.7	1.9	7.8	13	< d.l.
	Propyphenazone	0.8	1.8	7.8	84	2
Antibiotics	Sulfapyridine	3	15	81	45	2
	Sulfadiazine	1	3	12	65	8
	Sulfamethazine	2	3	12	68	< d.l.
Psychiatric Drugs	Phenytoin	13	37	196	55	408
	Odesmethylvelafaxine	1	4	23	87	837
	Venlafaxine	0.1	0.2	1.2	55	320
	Sertraline	3	14	79	10	151
	Diazepam	1	2	9	65	15
	Pentobarbital	3	7	37	45	< d.l.
Lipid Regulator	Gemfibrozil	47	244	1359	90	6119
	Bezafibrate	1	4	19	55	43
Cardiovascular Drugs and TP	Valsartan	2	4	20	52	< d.l.
	Valsartan acid	2	6	20	13	1252
Hormones	Estriolo	1	2	12	74	2
Industrial	Bisphenol-A	3	5	21	74	129
	Benzotriazole	48	93	355	52	1429
Personal Care Products	Climbazole	< d.l.	0.1	0.2	16	38
	BP4	0.4	1.0	4.5	32	610
Sweetener	Saccharin	23	110	610	58	215
Drugs of abuse and TP	Cocaine	0.4	1.3	7.2	90	< d.l.
	Benzeilecgonina	4	6	26	100	53
	Cocaetyleno	0.1	0.2	1.1	39	< d.l.
Life Style Compounds	Cotinine	11	26	151	100	134

highest concentrations were located towards the Besòs river, indicating an important contribution of surface water to the aquifer, in addition to a sample in the B.P with an anomalous high sum (TRME: 2372 ng L^{-1}), this sample showed high CEC sum but a relatively low mineralization ($673 \mu\text{S cm}^{-1}$), which is unexpected considering that when there are contributions of seepage pipes these usually carry a high load of ions such as sulfate, chloride, nitrate, sodium and others that would increase their mineralization. Additionally this sample showed clear signs of reducing conditions, of up to sulfate reduction which may favour the accumulation of some metals and CEC, indicating the potential contribution from multiple sources, particularly it showed anomalous high concentrations of cocaine, saccharin, sertraline, diazepam, cotinine and acetaminophen. These compounds can be associ-

ated with detoxification centres; cocaine is administered in controlled doses, saccharin is used in large quantities with water to attenuate withdrawal symptoms, as well as psychiatric drugs such as sertraline and diazepam. A detoxification center is located about 800 m west of the sample, which could be one of the sources of the high concentrations found. The lowest sums ($<50 \text{ ng L}^{-1}$) are mostly located towards the H.Z with the exception of the sample near Vall d'Hebron Hospital (CPF1), which is consistent with the fact that these waters have a short residence time and are located towards less populated areas. It is important to note that the sample HJOM, which presented an anomalous high electrical conductivity, does not showed high sum of CEC.

The high detection frequencies and total CEC sum observed relative to other sites (Wolf et al., 2006), is probably

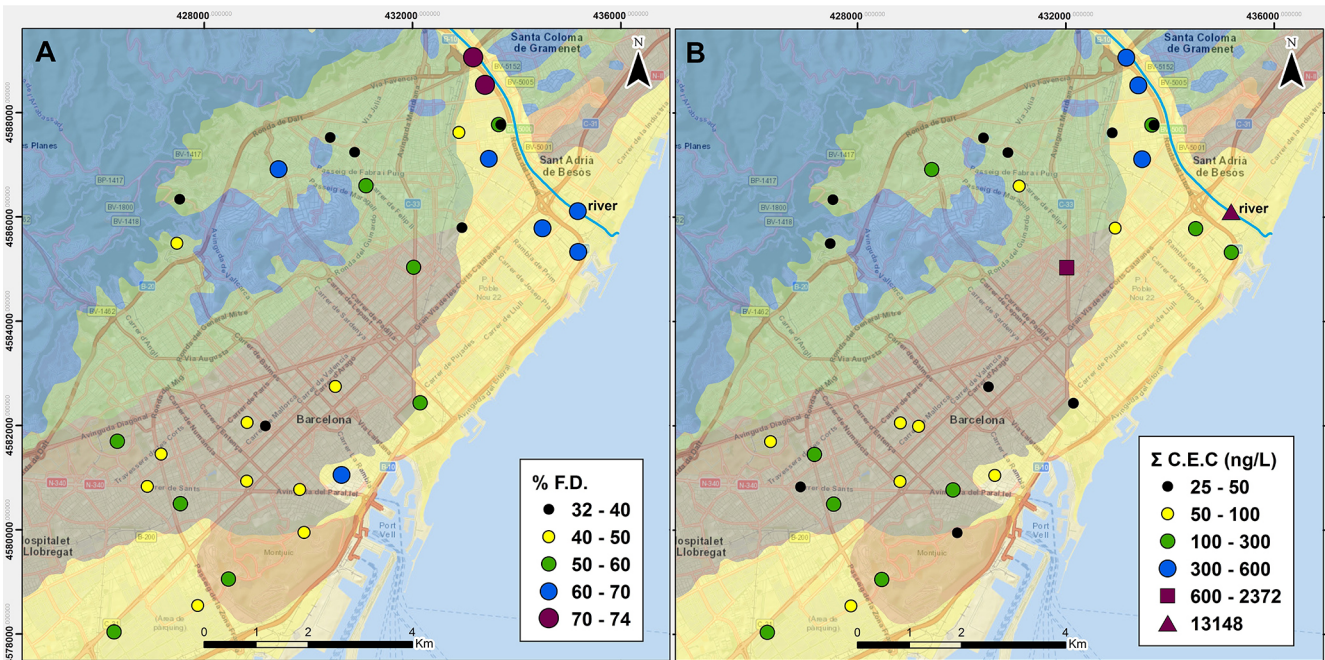


Figure 2. (a) Frequency of detection of CEC in the samples. (b) Spatial distribution of the sum of CEC in the samples.

due to the high population density in Barcelona as well as its lifestyle. For example, Sorensen et al. (2015), analyzed CEC in Africa (Kabwe, Zambia), where they mostly found products of agricultural origin and a generalized absence of pharmaceuticals, personal care products and lifestyle products, which in developed countries are commonly found. This could be attributable to natural attenuation of these compounds in the subsoil but mostly to the limited use of these products due to an unavailability and unaffordability.

3.3 Sources of CECs to groundwater

In order to ascertain the main processes/contributions controlling the hydrochemistry of these waters a Principal Component Analysis/Factor Analysis (FA) was performed (Fig. 3) considering 30 groundwater samples and the CEC that present at least a 50 % of detection in the samples, for this analysis the TRME sample was not considered due to its high anomaly detected. The XLSTAT 2021 software was used for this purpose. Varimax rotation was applied, which minimizes the number of variables with high loadings on each factor and simplifies the interpretation of the observed variables. The analysis was statistically valid due the KMO index obtained is 0.80, Cronbach's Alpha is 0.87 and the Bartlett's test for sphericity P -value is <0.05 .

From the FA, 2 main factors were extracted with eigenvalues greater than 1, which in total explain 73 % of the total variance, which is sufficient to give a good idea of the structure of the data. Variables with scores close to 1 form the factor indicating their similarity, while those close to 0

do not form the factor. Factor 1 (F1) explains 58 % of the variance, being the most relevant factor in the contribution of CEC to the aquifer. The variables with high factor loadings are acetaminophen, benzotriazole, diazepam, sulfadiazine, sulfamethazine and Σ CEC (Fig. 3a). These variables in general are those that presented the highest concentrations towards the Besòs, the contribution of CEC from the river to the aquifer can be considered the most important and of greater magnitude (Jurado et al., 2012), which is consistent with the fact that the variable Σ CEC is forming this factor, therefore F1 can be associated with contributions of CEC from the Besòs river to the aquifer (river aquifer interaction). Factor 2 (F2), which accumulated 20 % of the total variance, is saturated by the variables benzoylecgonine, bisphenol-A and cotinine, these variables in general presented a relative homogenous distribution around the whole territory indicating that their origin could be due to diffuse contamination, such as sewage seepage. In particular, bisphenol A has also been associated with recharge from urban runoff events (Os-enbrück et al., 2007).

Once the common factors have been estimated, it is important to calculate their scores in each sample, that is, the intensity with which the factor acts on each sample. Figure 3b shows the factor scores obtained for F1 and F2. The samples of the Besòs group are located mostly on the positive axis for F1. According to the results obtained, these samples would be those that had a greater contribution of CEC from the Besòs river. Particularly HBAV and DXSA presented the higher factor score and are located upstream, closer to the WWTP. Probably downstream the contribution would be

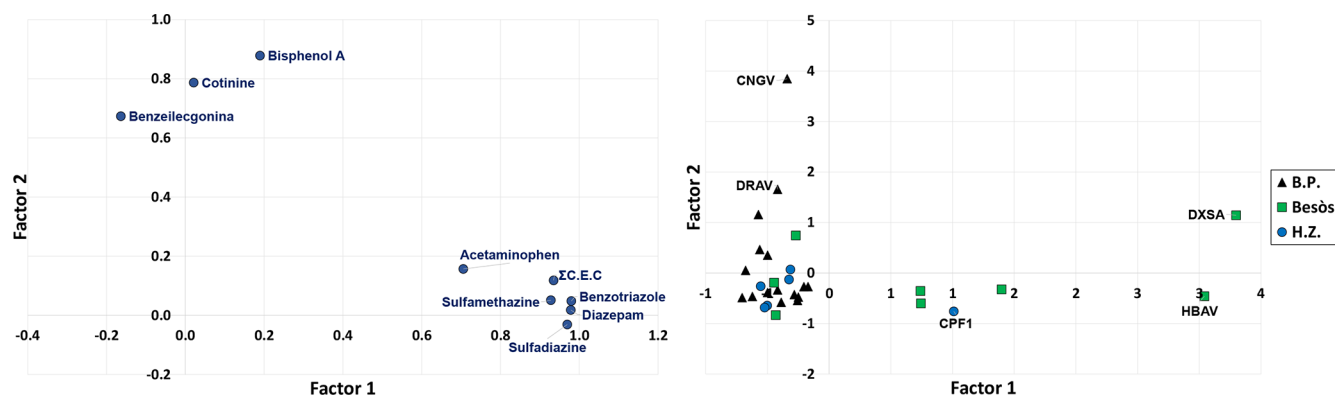


Figure 3. Graphics of F1 vs F2 and B: Factor scores of F1 vs F2.

lower since the CEC could be degraded in its path along the river. The samples from B.P and H.Z are located towards the negative axis of F1, indicating that this factor would not act in these samples, with the exception of CPF1, in which a probable focus of punctual contamination was identified (Hospital Vall d'Hebron), that would have similar characteristics to the contribution of the Besòs river.

For the F2, the samples of the H.Z presented negative values, indicating that the contributions by diffuse filtrations would not have an important intensity in these waters, this is coherent with the fact that these samples are located towards higher elevations where they have had a shorter residence time and there is a lower population density, also the frequency of detection and Σ CEC were lower. The samples that presented positive scores for F2 correspond to the B.P group located towards highly populated areas including some old city spots where the sewage system is quite old probably with lot of leakages, also these waters has longer residence time, which is coherent with a greater input of CEC through sewage seepage. Due to the presence of green infrastructure (parks, gardens and SUDs) in this area, an input of CEC from urban runoff could not be discarded. The highest factor score was observed for CNGV which is located towards an industrial area (Port) and DRAV in the Rambla del Raval, where a series of “narco apartments” are located. There are also a series of samples from B.P that are also located towards the negative axis of this factor, which is not consistent with the Σ CEC in these samples, probably the contribution is lower or this factor is indicating mainly contributions from industrial compounds and drugs of abuse. The DXSA sample showed positive factor scores for both factors, which is consistent with the fact that it is located near the Besòs and in an industrial area. In particular, the H.Z presented negative values for both factors with the exception of a particular sample (CPF1 near Hospital Vall d'Hebron), which would indicate that these samples have not had a significant contribution of CEC associated with these factors, which is consistent with the fact that these samples present low values of Σ CEC,

shorter residence time, located near the natural recharge area and in less populated districts.

4 Conclusions

The Complex hydrogeochemistry of Barcelona's urban groundwater is a result of the multiple inputs (recharge) and processes in the underground system; from natural (rain water input, rock-water interaction, etc.) to anthropic (sewage seepage, point source pollution, etc.). The distribution of the CEC along with the F.A indicates that the main input and of greater magnitude is the river-aquifer interaction towards the Besòs river, followed by sewage seepage across the urban area. Probably there's a minor input from urban runoff (e.g. SUDs). The redox conditions seem to be a first order control on the behaviour of the CEC, areas with reducing conditions showed generally higher concentrations and also higher concentrations of some heavy metals. Considering the limitations of this study, due to a single sampling campaign, these results should be contrasted with more sampling campaigns, enhancing the spatial and temporal data, allowing to address the seasonal variations and establishing more robust conclusions.

Code availability. The code can be provided by the corresponding authors upon request.

Data availability. All raw data can be provided by the corresponding authors.

Author contributions. LS, MT and RC are planned and executed the field campaign; EVS and LS supervised all the work related with the URBANWAT and UNBIASED project; SB and ME facilitated access to sampling points and reviewed the manuscript. DS, LS, MT, EV, RC, AJ and DP wrote the manuscript draft and reviewed and edited the manuscript.

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