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Occurrence and fate of emerging contaminants in urban groundwater. A case study: Barcelona

PhD Thesis

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Barcelona, July 2013

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I. Abstract

Ensuring good water quality is becoming a major challenge in urban areas. Urban aquifers may suffer pollution from different recharge sources such as water leakage from sewer and septic systems, seepage from rivers, seawater intrusion, and losses from water supply network among others. As a result, a wide range of organic pollutants are found in urban aquifers. Since these pollutants enter the groundwater environment through the aforementioned sources, their occurrence depends on the transport mechanisms as well as the chemical and biochemical processes that occurred simultaneously. Thus, a proper assessment of groundwater quality requires an understanding of all the processes that affect these pollutants. However, the quantification of these processes is not an easy task. The aims of this thesis are to investigate the occurrence of emerging organic contaminants (EOCs) and the processes that affect them in an urban aquifer.

An extensive review including the occurrence and fate of EOCs in Spanish groundwater and the evaluation of potential sources of contamination was carried out. Among organic contaminants found in groundwater, we have analysed pharmaceutically active compounds (PhACs), drugs of abuse (DAs) and personal care products in urban groundwater of Barcelona. The main sources of pollution of EOCs in urban areas are sewer leakage loss and infiltration from waste water treatment plants.

Once these contaminants enter the aquifer, their concentrations are affected by numerous processes, including dilution, adsorption and degradation. Many EOCs are removed from water by transformation or degradation, especially if the water has undergone a broad range of redox states. Therefore, identifying and quantifying the redox processes along a flow line is a key issue.

In order to quantify such processes, we have proposed an approach using mixing ratios. The application of environmental isotopes coupled with hydrochemistry data using mixing ratios has provided the isotopic quantification of groundwater recharge sources and the occurrence of redox processes such as sulphate reduction, aerobic respiration and denitrification. The approach enabled us: (1) to quantify the mixing ratios into groundwater (2) to evaluate redox processes.

II. Resumen

Garantizar una buena calidad del agua se está convirtiendo en un gran problema en zonas urbanas. Los acuíferos urbanos pueden sufrir contaminación a través de diversas fuentes de recarga, como fugas de agua de alcantarillado y fosas sépticas, las filtraciones desde los ríos contaminados, intrusión marina, y pérdidas de la red de abastecimiento de agua, entre otros. Por ello, en los acuíferos urbanos se encuentran numerosos contaminantes orgánicos. La presencia y evolución de estos contaminantes en los acuíferos depende de los mecanismos de transporte, así como de los procesos químicos y bioquímicos. Por lo tanto, una correcta evaluación de la calidad del agua subterránea requiere la evaluación de todos los procesos que afectan a estos contaminantes. Sin embargo, la cuantificación de estos procesos no es una tarea fácil. Los objetivos de la presente tesis son determinar la presencia de contaminantes orgánicos emergentes (COEs) y los procesos que los afectan en un acuífero urbano.

Se ha llevado a cabo una extensa revisión bibliográfica de la presencia de COEs en las aguas subterráneas de España y la identificación de posibles fuentes de contaminación. Entre los contaminantes orgánicos que se encuentran en las aguas subterráneas, se han analizado numerosos fármacos, drogas de abuso y productos de cuidado personal en las aguas subterráneas urbanas de Barcelona. Las principales fuentes de contaminación de los COEs en zonas urbanas suelen ser las pérdidas de las redes de alcantarillado y los efluentes de las estaciones depuradoras de aguas residuales.

Una vez que estos contaminantes están presentes en el acuífero, sus concentraciones se ven afectadas por numerosos procesos, incluyendo dilución, adsorción y degradación. Muchos COEs pueden ser eliminados del agua subterránea por procesos de transformación o degradación, especialmente si en el acuífero ha pasado por diferentes estados redox. Por ello, la identificación y cuantificación de los procesos redox en el acuífero es una cuestión clave.

Para cuantificar estos procesos, se ha propuesto un método que utiliza las proporciones de mezcla. La aplicación de los isótopos ambientales junto con los datos hidroquímicos ha proporcionado la cuantificación isotópica de fuentes de recarga de agua subterránea y la ocurrencia de procesos redox, como la sulfato reducción, la respiración aeróbica y desnitrificación. El uso de estas metodologías ha permitido: (1) cuantificar las proporciones de mezcla en el agua subterránea y (2) evaluar los procesos redox.

III. Resum

Garantir una bona qualitat de l'aigua s'està convertint en un seriós problema en les zones urbanes. Els aqüífers urbans poden patir contaminació de diverses fonts de recàrrega, com fuites d'aigua de clavegueram i fosses sèptiques, filtracions des dels rius contaminats, intrusió marina, i pèrdues de la xarxa de proveïment d'aigua, entre d'altres. Per això, en els aqüífers urbans es troben diversos contaminants orgànics. La presència i evolució d'aquests contaminants als aqüífers depèn dels mecanismes de transport, així com dels processos químics i bioquímics. Per tant, una correcta avaluació de la qualitat de l'aigua subterrània requereix un enteniment de tots els processos que afecten aquests contaminants. No obstant això, la quantificació d'aquests processos no és una tasca fàcil. Els objectius d'aquesta tesi són investigar la presència de contaminants orgànics emergents (COEs) i els processos que els afecten en un aqüífer urbà.

S'ha dut a terme una extensa revisió bibliogràfica de la presència de COEs en les aigües subterrànies d'Espanya, juntament amb l'avaluació de possibles fonts de contaminació. Entre els contaminants orgànics que es troben en les aigües subterrànies, s'han analitzat nombrosos fàrmacs, drogues d'abús i productes de cura personal en l'aigua subterrània urbana de Barcelona. Les principals fonts de contaminació dels COEs en zones urbanes són la pèrdua de les xarxes de clavegueram i els efluents de les estacions depuradores d'aigües residuals.

Una vegada que aquests contaminants són presents a l'aqüífer, les seves concentracions es veuen afectades per nombrosos processos, incloent dilució, adsorció i degradació. Molts COEs poden ser eliminats de l'aigua subterrània per processos de transformació o degradació, especialment si l'aqüífer ha passat per diferents estats redox. Per això, la identificació i quantificació dels processos redox a l'aqüífer és una qüestió clau.

Per quantificar aquests processos, s'ha proposat un mètode que utilitza les proporcions de mescla. L'aplicació dels isòtops ambientals juntament amb les dades hidroquímiques ha proporcionat la quantificació isotòpica de fonts de recàrrega d'aigua subterrània i l'ocurrència de processos redox, com la sulfato reducció, la respiració aeròbica i desnitrificació. L'ús d'aquestes metodologies ha permès: (1) quantificar les proporcions de barreja en l'aigua subterrània i (2) avaluar els processos redox.

IV. Acknowledgments

First of all, I would like to express my most sincere gratitude to my advisors Enric Vázquez-Suñé and Jesús Carrera, for giving me the opportunity to join the Hydrogeology Group. I really appreciate the confidence they had in me and their support and orientation during my PhD.

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I am grateful to all of my colleagues of the Hydrogeology Group. I was very lucky to have the opportunity to work in a group that gathers people from several countries; we were so many and so colourful! I especially thanked Estanis, Violeta, Silvia D, Francy, Marco B, Victor V, Dani P, and Laura C for their support and experiences shared along these last years. I do not want to forget also the "old" ones, Jordi F, Pablo G and Edu C. Some of you were an energy source in difficult moments. I also would like to thank to my geology peers Anna C and Núria A for their unconditional friendship and who did a good job raising my self-esteem when I was down.

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Vila site. The screen depths of the pumping wells and the piezometers are represented.

Figure 5.3. Comparison between the average concentration at the Besòs River and the average concentration in the aquifer for a several number of species as major and minor ions, metals, redox indicators, pesticides drugs of abuse (DAs, Jurado et al., 2012) and pharmaceutical active compounds (PhACs, López-Serna et al., 2013). The river data set is collected monthly by the Catalan Water Agency (ACA) 2 Km upstream of the study zone and it can be downloaded from http://www.gencat.cat/.

Figure 5.4. Plots of measured vs. estimated concentrations of all species at three end-members and observation points not including the geochemical processes. Notice that chloride and electrical conductivity behave conservative while dissolved oxygen, total organic carbon, nitrate did no (end-members concentration need to be dramatically reduce). This figure was modified from Tubau et al. (submitted).

Figure 5.5. Plots of measured vs. estimated concentrations of all species at all end-member and sampled points including the geochemical processes. Notice the better fit of the reactive species calcium, total nitrate, ammonium, dissolved oxygen, total organic carbon and nitrate.

Figure 5.6. Schematic cross-plot sections of concentration, x (mmol/l), at each observation point for the species that take part in the reactions accounting for the 4 campaigns. The reactions are: (R_1) calcite dissolution, (R_2) magnesite dissolution, (R3) Denitrification, (R4) Aerobic respiration, (R_5) Nitrification.

Figure 6.1. On the left, 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), (1c) Barcelona Plain consisting of carbonated clays (Pleistocene, Quaternary), (2) Barcelona Plain made up of marls, sandstones and sands (Tertiary) and (3) Collserola Range consisting of shale and granites (Palaeozoic). On the right, a piezometric map of the study area, which is divided into two distinct zones: Poble Sec (PS) and Besòs River Delta (BRD). The contour intervals are 2 m (continuous green line), for heads ranging from 5 to below 25 m (continuous blue line) and 25 m above (continuous orange line). At the bottom, observation points in each zone, including the depth of the screen: (u) upper, (m) middle, (l) lower and (a) totally screened.

Figure 6.2. Plot of $\delta^{18}O_{H2O}$-δD_{H2O} accounting for the recharge sources (and standard deviation) and groundwater samples collected in both zones: Poble Sec (PS, rhombus) and Besòs River Delta (BRD, rounds). Note that the different field campaigns are represented by the shade of grey: c2 is light grey, c3 is grey and c4 is dark grey. The local meteoric line (LML) represents the monthly isotopic composition of a long-term sampling period (1985-1992) at the monitoring station of Barcelona.

Figure 6.3. Plot of $\delta^{34}S_{SO4}$-$\delta^{18}O_{SO4}$ accounting for the recharge sources (and standard deviation) and groundwater samples collected in both zones: Poble Sec (PS, rhombus) and Besòs River Delta (BRD, rounds). Note that the different field campaigns are represented by the shade of grey: c2 is light grey, c3 is grey and c4 is dark grey.

Figure 6.4. Plots of measured and computed concentrations and isotopic compositions. Note that measured concentrations of the recharge sources fail to envelope the measured concentrations in several samples in both Poble Sec and Besòs River Delta

VII. List of tables

1. Introduction

1.1 Motivation and objectives

High population growth coupled to industrial and agricultural activities may result in both an increasing demand for water and the generation of wastewater. Groundwater is an alternative resource for water supply, especially during drought periods in semi-arid regions such as Spain. But groundwater may suffer pollution from different sources, including water leakage from sewer and septic systems, seepage from rivers and application of fertilizers and agrochemicals, among others (Foster; 2001; Vàzquez-Suñé et al., 2010). As a result, a wide range of organic pollutants can be found in aquifers posing a risk to groundwater quality (Wolf *et al.,* 2004). Thus, a proper assessment of groundwater quality requires the identification of the aforementioned pollutants and also the understanding of all the processes that affect them.

Among organic pollutants, emerging organic contaminants (EOCs) are of particular concern for several reasons. First, different classes of EOCs such as pharmaceuticals, drugs of abuse, surfactants and personal care products have been detected in waste water treatment plants (WWTPs) effluents (Petrovic et al., 2003; Radjenovic et al., 2007; Boleda et al., 2009; Martinez Bueno et al., 2012). Consequently, WWTP effluents may be the main source of pollution to groundwater due to the continuous entrance of EOCs into the aquatic environment. In addition, research has provided growing evidence that many EOCs are endocrine disrupting compounds (EDCs) (Liu *et al.,* 2009). Another cause for concern is that EOCs may be toxic and persistent. Despite their low concentrations, they may produce potentially harmful effects on ecosystems and human health (Jones-Lepp et al., 2004; Postigo et al., 2008; Reungoat et al., 2010), not to mention that the degradation products (DP) of some compounds such as alkylphenols are even more toxic than the parent product (Soares et al., 2008).

The concentration of EOCs in aquifers is affected by numerous processes, including concentration at the source, dilution, adsorption and degradation. Moreover, the aforementioned processes are linked. Some common sources of EOCs in urban aquifers areas are sewer leakage loss and infiltration from waste water treatment plants. These sources provide organic carbon to the water and may promote biodegradation reactions of a variety of EOCs. In addition to the tendency to sorb onto both organic and inorganic solids, many EOCs are removed from water by transformation (e.g. Barbieri *et al.,* 2012) or degradation, especially if the water has undergone a broad range of redox states (e.g. Christensen *et al.,* 2001; Barbieri *et al.,* 2011). Biodegradation processes are related to the redox state of water. Therefore, identifying the redox evolution along a flow line is a key issue.

In order to quantify such processes, modelling tools providing extensive biogeochemical capabilities are needed (Prommer *et al*., 2000). Reactive transport models describe the spatial and temporal evolution of a set of chemical species subject to transport phenomena and chemical reactions. But there are hard to build because a reliable flow and conservative transport model is required, involving the management of much information to characterize in great detail the study zone. Hence, simpler approaches are needed.

Assuming that transport can be thought as mixing of different water types along a groundwater flow path in an aquifer, mixing calculations are an alternative to reactive transport models. Mixing calculations include: (1) End Member Mixing Analysis (EMMA) (Hooper et al., 1990; Christophersen et al., 1990; Christophersen and Hooper, 1992; Hooper, 2003) and also (2) mixing ratios which are defined as the proportion of each of the mixing waters in a sample (Schemel et al., 2006). Mixing ratios are useful because they can be quantified from conservative chemical species even when the end-members are uncertain (Carrera *et al.,* 2004; Ruedi *et al.,* 2005). Their application is simpler than reactive transport modeling because only chemical data and a previous conceptual model of the study zone are needed. The concentration of the conservative solutes in a mixture is obtained by linear combination of the recharge sources. However, when deviations from perfect mixed exist; they may be due to the chemical processes.

The aims of this thesis are to assess the fate of selected EOCs in urban groundwater and to quantify the redox processes that may contribute to removal of EOCs from urban aquifers. Specific objectives have been:

(1) Review the state of art of the studies concerning EOCs in urban groundwater in Spain.

(2) Assess the fate of selected EOCs such as DAs and PhACs in an urban aquifer.

(3) Quantify the hydrogeochemical processes that might affect EOCs.

This thesis has been developed in several aquifers of the city of Barcelona.

1.2. Thesis outline

The thesis consists of 5 chapters plus introduction, conclusions and the references list. The body of the thesis is based on papers that have already been published, accepted or submitted to international journals. The references to the papers are contained in a footnote at the beginning of each chapter.

Chapter 2 reviews the presence of emerging organic contaminants (EOCs) that have been found in the groundwater in Spain in both rural and urban areas. The list of compounds includes pesticides, pharmaceutical active compounds (PhACs), selected industrial compounds, drugs of abuse (DAs), estrogens, personal care products and life-style compounds. The main sources of pollution and possible pathways have been summarised in this review. EOCs are likely to enter to the aquifer mainly through waste water treatment plants (WWTPs) effluents. They are present in groundwater at concentrations of ng/L to μg/L. The most studied compounds in Spanish groundwater were pesticides followed by industrial compounds and PhACs. It is important to mention that compared to other water bodies, such as rivers, groundwater is considerably less contaminated, which may be indicative of the natural attenuation capacity of aquifers. However, some EOCs have sometimes been detected at higher concentration levels in aquifers than in rivers, indicating the need for further research to understand their behaviour in the aquifers. For a wide array of compounds, their maximum concentrations show values above the European groundwater quality standard for individual pesticides (0.1 μg/L). Therefore, to preserve groundwater quality against deterioration it is necessary to define thresholds for the non-regulated compounds.

Chapter 3 is concerned with drugs of abuse (DAs) and their metabolites in urban groundwater at field scale in relation to (1) the spatial distribution of the groundwater samples, (2) the depth of the groundwater sample, (3) the presence of DAs in recharge sources, and (4) the identification of processes affecting the fate of DAs in groundwater. To this end, urban groundwater samples were collected in the city of Barcelona and a total of 21 drugs were analyzed including cocainics, amphetamine-like compounds, opioids, lysergics and cannabinoids and the prescribed drugs benzodiazepines. Overall, the highest groundwater concentrations and the largest number of detected DAs were found in zones basically recharged by a river that receives large amounts of effluents from waste water treatment plants (WWTPs). In contrast, urbanized areas yielded not only lower concentrations but also a much smaller number of drugs, which suggests a local origin. In fact, cocaine and its metabolite were dominant in more prosperous neighbourhoods, whereas the cheaper (MDMA) was the dominant DA in poorer districts. Concentrations of DAs estimated mainly from the waste water fraction in groundwater samples were consistently higher than the measured ones, suggesting that DAs undergo removal processes in both reducing and oxidizing conditions.

Chapter 4 presents the fate of carbamazepine (CBZ) and five of its metabolites in Barcelona's groundwater at a field scale under different redox conditions in connection with (1) the physicho-chemical properties of the target compounds, (2) the occurrence of common contaminants in urban groundwater of Barcelona and (3) the groundwater redox conditions. To this end, groundwater samples were collected in two distinct zones of Barcelona city: (1) Poble Sec and (2) Besòs River Delta in May 2010. Overall, the highest concentrations and the largest number of detected target compounds were found in Besòs River Delta, which is basically recharged by a river that receives large amounts of effluents from waste water treatments plants (WWTPs). Conversely, Poble Sec presented not only lower concentrations but also a smaller number of compounds. The results of this study show that CBZ was more susceptible to be removed under the oxidizing conditions of Poble Sec aquifers than the reducing conditions of Besòs River Delta. In the latter, the metabolites 2-hydroxycarbamazepine (2OH CBZ) and 3-hydroxycarbamazepine (3OH CBZ) and acridone (ACRON) were found to be highly persistent whilst 10,11-epoxy carbamazepine (CBZ-EP) and acridine (ACRIN) did not.

Chapter 5 presents a methodology to quantify chemical reactions using mixing ratios. This chapter is motivated by the understanding of geochemical processes that affect emerging organic contaminants in an urban aquifer. When such contaminants entered the groundwater environment through different sources, such as water leakage from sewer or septic systems, seepage from rivers, seawater intrusion, and losses from water supply networks among others, the identification of processes is highly uncertain. In order to estimate such processes we propose the use of mixing calculations. The concentration of a conservative solute in a mixture is obtained by linear combination of the end-members. If deviations from perfect mixed solutions exist; they may be due to the chemical processes. We propose an easy methodology to quantify such processes that consist of the following steps: (1) End-member mixing analysis to identify the recharge sources, (2) Identification of the chemical processes at the study area and selection of the non-conservative species to be considered in the analysis and (3) Evaluation of the mixing ratios including the chemical processes.

Chapter 6 investigated the different recharge sources and their mixing ratios in water samples from an urban aquifer. The application of environmental isotopes coupled with hydrochemistry provided the necessary information to isotopically quantify groundwater recharge sources and evaluate the occurrence of redox processes. In Besòs River Delta, a decrease in dissolved sulphate concentration and an increase in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values were observed in groundwater samples, both indicating sulphate reduction. Moreover, other chemical indicators supported a reducing environment, such as low or null levels of dissolved oxygen and nitrate, the presence of ammonium and an increase in dissolved iron and arsenic. The reducing conditions were probably induced by the organic carbon dissolved in water infiltrating from the River Besòs. In Poble Sec, the relationship between $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ presented a strong influence of sewage water infiltration into the aquifer. However, the aquifer is oxic and there is no influence of sulphate reduction.

Chapter 7 summarizes the main conclusions of the thesis.

There are three annexes that summarized the following information:

Annex I: Supplementary material of the chapters

Annex II: Scientific papers accepted in international journals

Annex III: Impact on the media

1.3. Articles and reports related to the development of the thesis

This thesis is the result of two complementary aspects: Scientific articles and technical reports. The list of scientific articles and technical reports related to the thesis are listed below.

1.3.1. Scientific articles

Jurado, A., Mastroianni, N., Vàzquez-Suñé, E., Carrera, J., Tubau, I., Pujades, E., Postigo, C., López de Alda, M., Barceló, D., (2012a). Drugs of abuse in urban groundwater. A case study: Barcelona. Sci. Total Environ. 424, 280-288. Doi: 10.1016/j.scitotenv.2012.02.074.

Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., (2012b). Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context. Science of the Total Environment 440, 82-94.

Jurado, A., Vàzquez-Suñé, E., Soler, A., Tubau, I., Carrera, J, Pujades, E., Anson, I., (2013). Application of multi-isotope data (O, D, C and S) to quantify redox processes in urban groundwater. Applied Geochemistry 34, 114-125. http://dx.doi.org/10.1016/j.apgeochem.2013.02.018.

López-Serna, R., **Jurado, A.,** Vàzquez-Suñé, E., Carrera, J., Petrovic, M., Barceló, D., (2013). Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain. Environmental Pollution 174, 305-315.

Jurado, A., López-Serna, R., Vázquez-Suñé, E., Carrera, J., Pujades, E., Petrovic, M., Barceló, D., 2012. Occurrence and fate of carbamazepine and 5 metabolites in an urban aquifer under different redox conditions. *Submitted HESS.*

Jurado, A., Tubau, I., Vàzquez-Suñé, E., Carrera, J., Pujades, E., (Submitted). Using mixing ratios to quantify chemical reactions. Submitted to Science of the Total Environment.

1.3.2. Technical reports

GHS-(UPC-CSIC), 2009a. *Avaluació i seguiment d'un pla de drenatge del freàtic a l'entorn de la Plaça de la Vila de Sant Adrià del Besòs (III)"* (GHS-(UPC-CSIC), 2009a). Grup d'Hidrologia Subterrània (UPC-CSIC), Ajuntament de Sant Adrià de Besòs.

GHS-(UPC-CSIC), 2009b. *Model hidrogeològic al pla de Barcelona i delta del Besòs per a l'obtenció d'alternatives d'aprofitament per a la producció d'aigua de consum.2a part: Caracterització de les zones pilot.* Grup d'Hidrologia Subterrània (UPC-CSIC), Agència Catalana de l'Aigua, Aigües Ter Llobregat, Entitat Metropolitana de Sanejament.

GHS-(UPC-CSIC), 2013. *Avaluació i seguiment d'un pla de drenatge del freàtic a l'entorn de la Plaça de la Vila de Sant Adrià del Besòs (IV)"* (GHS-(UPC-CSIC), 2013). Grup d'Hidrologia Subterrània (UPC-CSIC), Ajuntament de Sant Adrià de Besòs.

1.4. Participation in congresses

Event: Asociación Internacional de Hidrogeólos: Desafíos de la gestión para el siglo XXI 2011, Zaragoza, Spain, September 2011
Title: Drogas de abuso en las aguas subterráneas urbanas de la ciudad de Barcelona. Poster presentation
Authors: **A. Jurado,** E. Vazquez-Suñé, J. Carrera, I. Tubau, E Pujades, N. Mastroianni, C. Postigo, M. López De Alda, D. Barceló

Event: General Assembly 2012, Viena, April 2012
Title: Drugs of abuse in urban groundwater. A case study: Barcelona. Poster presentation
Authors: **A. Jurado,** N. Mastroianni, E. Vàzquez-Suñé, J. Carrera, I. Tubau, E. Pujades, C. Postigo, M. López De Alda, D. Barceló

Event: 3rd International conference on industrial and hazardous waste management 2012, Crete, Greece, September 2012
Title: Organic contaminants of emerging concern in agricultural and urban groundwaters. Catalonia and Barcelona (Spain) case studies. Oral presentation
Authors: D. Barceló, M. Petrovic, C. Postigo, R. López-Serna, M. Köck-Schulmeyer, N. Mastroianni, M. López de Alda, M.S. Díaz-Cruz, M.J. García-Galán, A. Ginebreda, **A. Jurado**, E. Vàzquez-Suñé, J. Carrera

Event: International conference. Pharmaceutical Products in the Environment: Is there a problem?, June 2013, Nîmes, France
Title: Occurrence and fate of carbamazepine and 5 metabolites in an urban aquifer under different redox conditions. Poster presentation
Authors: **A. Jurado,** R. López-Serna, E. Vàzquez-Suñé, J. Carrera, E. Pujades, M. Petrovic, D. Barceló

Event: 23 Goldschmidt, August 2013, Florence, Italy
Title: Modeling the Fate of the Pharmaceuticals in an Urban Aquifer. Besòs River Delta Case Study (Barcelona, Spain). Oral presentation.
Authors: **A. Jurado,** Vàzquez-Suñé, J. Carrera, E. Pujades, M. Petrovic, D. Barceló

Event: 246th ACS National Meeting, September 2013Indianapolis, Indiana, EEUU.
Title: Occurrence and fate of carbamazepine and 5 metabolites in an urban aquifer under different redox conditions. Oral presentation
Authors: D. Barceló, **A. Jurado,** R. López-Serna, E. Vàzquez-Suñé, J. Carrera, E. Pujades, M. Petrovic

2. Emerging organic contaminants in Groundwater in Spain: A review of sources, recent occurred and fate in a European context

2.1. Introduction

High population growth coupled with industrial and agricultural activities may result in both an increased demand for water and the generation of wastewater. According to directive 2006/118/EC, groundwater is the largest body of fresh water in the European Union. But it is also the most sensitive. Groundwater may suffer pollution from many sources, including water leakage from sewer and septic systems, seepage from rivers and application of fertilizers and agrochemicals, among others (Foster; 2001; Vàzquez-Suñé *et al.,* 2010). As a result, a wide range of organic pollutants can be found in aquifers posing a risk to groundwater quality (Wolf *et al.,* 2004). Thus, a proper assessment of groundwater quality requires the identification of such pollutants.

Among the different organic pollutants, emerging organic contaminants (EOCs) are of particular concern for several reasons. First, different classes of EOCs such as pharmaceuticals, drugs of abuse, surfactants and personal care products have been detected in waste water treatment plants (WWTPs) effluents (Petrovic *et al.,* 2003; Radjenovic *et al.,* 2007; Boleda *et al.,* 2009; Martinez Bueno *et al.,* 2012). Consequently, WWTP effluents may be the main source of pollution for groundwater due to the continuous entrance of EOCs into the aquatic environment. Second, research has provided growing evidence that many EOCs are endocrine disruptor compounds (EDCs) (Liu *et al.,* 2009). EDCs are found in a wide range of products, including plastic bottles, detergents, flame retardants, food, toys, cosmetics, pesticides, etc. and are thought to have adverse developmental and reproductive effects in both humans and wildlife (Campbell et al., 2006). Third, EOCs may be toxic and persistent and, despite being detected in low concentrations, may produce potentially harmful effects on ecosystems and human health (Jones-Lepp *et al.*, 2004; Postigo *et al.,* 2008a; Reungoat *et al.,* 2010), not to mention that the degradation products (DP) of some compounds such as alkylphenols are even more toxic than the parent products (Soares *et al.*, 2008).

To tackle the aforementioned problems it is necessary to define groundwater quality standards. To date, legislation on groundwater contamination by organic

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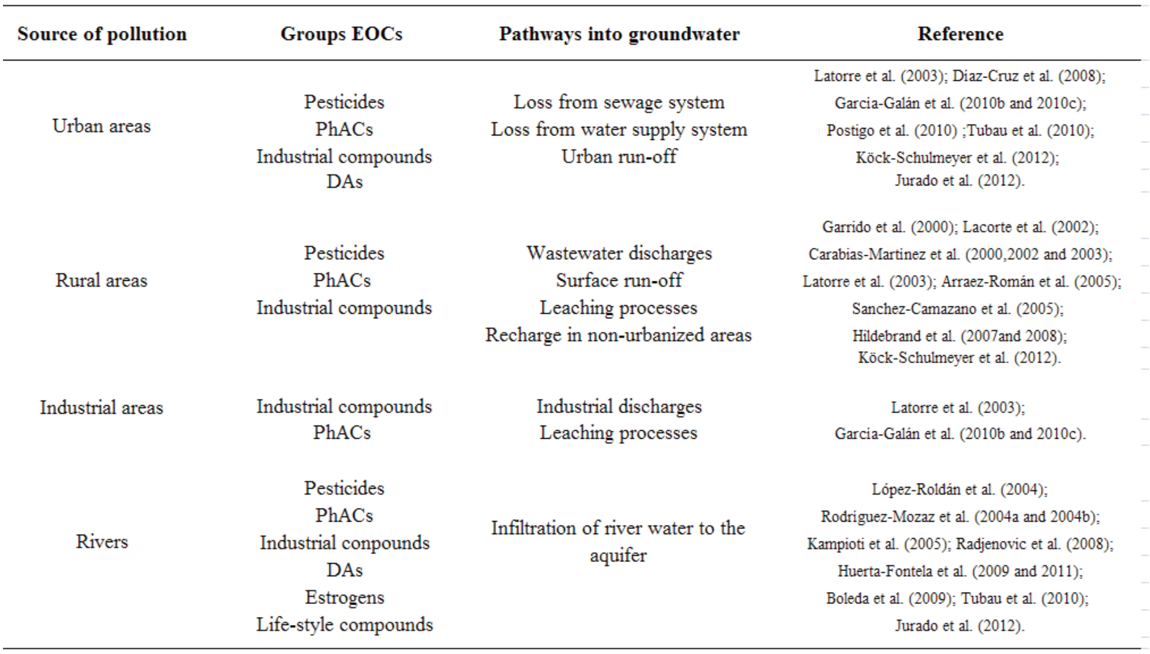
contaminants has only affected pesticides. The environmental quality standards for both individual substances, including their relevant metabolites and degradation and reaction products (0.1 µg/L) and for the sum (0.5 µg/L), have been established (European Parliament and Council of the European Union, 2006).

Most EOCs research has focused on both surface and waste waters. Groundwater has been much less studied. In the last decade, there have been some reviews on the occurrence and/or fate of specific EOCs such as pharmaceuticals in aquatic environments (Herberer, 2002; Mompelat *et al.,* 2009) and EDCs (Campbell *et al.,* 2006; Liu *et al.,* 2009; Silva *et al.,* 2012). Similarly, recent reviews have included a vast array of EOCs in freshwater sources (Murray *et al.,* 2010; Pal *et al.,* 2010), such as the Llobregat River Basin (Gonzalez *et al.,* 2012) and in waste waters (Bolong *et al.,* 2009; Muñoz *et al.,* 2009). Díaz-Cruz and Barceló (2008) reviewed priority and emerging organic micropollutants in different water resources intended for aquifer artificial recharge. But there is a lack of comprehensive reviews concerning a wide range of EOCs in groundwater. Only Stuart *et al.* (2012) reviewed the risk of emerging contaminants in the UK groundwater and Lapworth *et al*. (2012) summarised the sources, fate and occurrence of EOCs in the groundwater of Europe, the Middle East, North America and Asia. Here, we have extended the work of Lapworth *et al.* (2012) to other studies that have reported the occurrence of EOCs in Spanish groundwater.

In this paper, we review the presence of EOCs in the groundwater of Spain and evaluate the potential sources of contamination, the occurrence and the fate of such EOCs. Among the organic contaminants found in groundwater, we analyse pharmaceutically active compounds (PhACs), selected industrial compounds, drugs of abuse (DAs), estrogens, personal care products and life-style compounds. We have also addressed pesticides trying to focus on the more polar ones and transformation products. Special attention has been paid to the most frequently detected compounds and they have been compared with other studies carried out across Europe.

2.2. Identification of the potential sources of contamination

Groundwater pollution can be classified as point and non-point (or diffuse) source pollution. Point source pollution refers to contamination from discrete locations that can be easily identified with a single discharge source. Examples include municipal sewage treatment plant discharges, industrial discharges, accidental spills and landfills, among others (Lerner, 2008). In contrast, non-point source pollution is caused by pollution over a broad area and often cannot be easily identified as coming from a single or definite source. Agriculture is the main non-point polluter of groundwater in irrigated areas where fertilizers and other agrochemicals are applied (Chowdary *et al.*, 2005). Similarly, runoff from urban and agricultural areas and leakage from urban sewage systems are non-point sources of pollution (Trauth and Xanthopoulos, 1997; Vàzquez-Suñé et al., 2007a). Since non-point source compounds are usually applied over large areas, they may have a larger impact on the groundwater quality than point sources. Table 2.1 summarises the different sources of pollution and pathways into groundwater. It is necessary to identify the different pollution pathways to assess and reduce the introduction of contaminants into groundwater. Upon identification, effective reduction measures can be adopted to prevent the contamination of groundwater by EOCs.



Source of pollution	Groups EOCs	Pathways into groundwater	Reference
Urban areas	Pesticides PhACs Industrial compounds DAs	Loss from sewage system Loss from water supply system Urban run-off	Latorre et al. (2003); Diaz-Cruz et al. (2008); Garcia-Galán et al. (2010b and 2010c); Postigo et al. (2010) ;Tubau et al. (2010); Köck-Schulmeyer et al. (2012); Jurado et al. (2012).
Rural areas	Pesticides PhACs Industrial compounds	Wastewater discharges Surface run-off Leaching processes Recharge in non-urbanized areas	Garrido et al. (2000); Lacorte et al. (2002); Carabias-Martinez et al. (2000,2002 and 2003); Latorre et al. (2003); Arraez-Román et al. (2005); Sanchez-Camazano et al. (2005); Hildebrand et al. (2007and 2008); Köck-Schulmeyer et al. (2012).
Industrial areas	Industrial compounds PhACs	Industrial discharges Leaching processes	Latorre et al. (2003); Garcia-Galán et al. (2010b and 2010c).
Rivers	Pesticides PhACs Industrial compounds DAs Estrogens Life-style compounds	Infiltration of river water to the aquifer	López-Roldán et al. (2004); Rodriguez-Mozaz et al. (2004a and 2004b); Kampioti et al. (2005); Radjenovic et al. (2008); Huerta-Fontela et al. (2009 and 2011); Boleda et al. (2009); Tubau et al. (2010); Jurado et al. (2012).

Table 2.1. Sources and possible pathways of EOCs in the Spanish groundwater.

2.3. Occurrence and concentrations of EOCs in the groundwater of Spain

Research on EOCs in Spanish groundwater is reviewed in this section. A total of 33 studies have been included as a part of this review and their spatial extent is shown in Figure 2.1. Table S1 summarised the reported EOCs including the number of studies and the maximum concentrations found in the cited sources for each compound (see supplementary information Table S1 in Annex I for details).

Water Catchment Agencies are responsible for monitoring groundwater quality and specifically EOCs. But, to the author's knowledge, information about EOCs is not published. In some cases the information can be found in their web services but data are not compiled and interpreted in a public report. Yet, some of the data have been published in scientific journals and have been included in this review.

Figure 2.1. Spanish map with the spatial distribution of the EOCs studies included in this review. Note that the studies of Hildebrandt *et al.* (2007 and 2008) have been located in the Aragón region (n=2) but they spatial extent also includes Castilla León, Galicia, Navarra, la Rioja and Catalonia regions (*).

2.3.1. Pesticides

Pesticides are substances or mixtures of substances intended for preventing, destroying, repelling or mitigating pests. Pesticides are often categorised into four main classes according to the type of pest they control: herbicides; fungicides; insecticides and bactericides. We have addressed pesticides trying to focus on the more polar ones and transformation products. Note that less studied pesticides have also been summarised in Table S1 (supplementary material Annex I).

Studies

Garrido *et al.* (2000) carried out a survey to study the quality status of 13 different hydrological units and analysed 19 organophosphorous and 7 triazine herbicides. Similarly, 10 years later, Postigo *et al.* (2010a) and Köck-Schulmeyer *et al.* (2012) studied the occurrence of 22 pesticides in different aquifers of Catalonia where agricultural practices are significant. The presence of pesticides in groundwater of the Llobregat area has also been widely studied (Quintana *et al.,* 2001; López-Roldán *et al*., 2004; Rodriguez-Mozaz *et al.,* 2004a; Kampioti *et al.,* 2005; Teijon *et al.,* 2010) in 2000, 2002, 2003 and 2007-2008, respectively. Triazine herbicides, phenylureas and organophosphorous herbicides have been the most studied pesticides in the Llobregat basin. García-Galan *et al.* (2010a) analysed 9 triazine herbicides in groundwater samples collected in the province of Barcelona in March 2007.

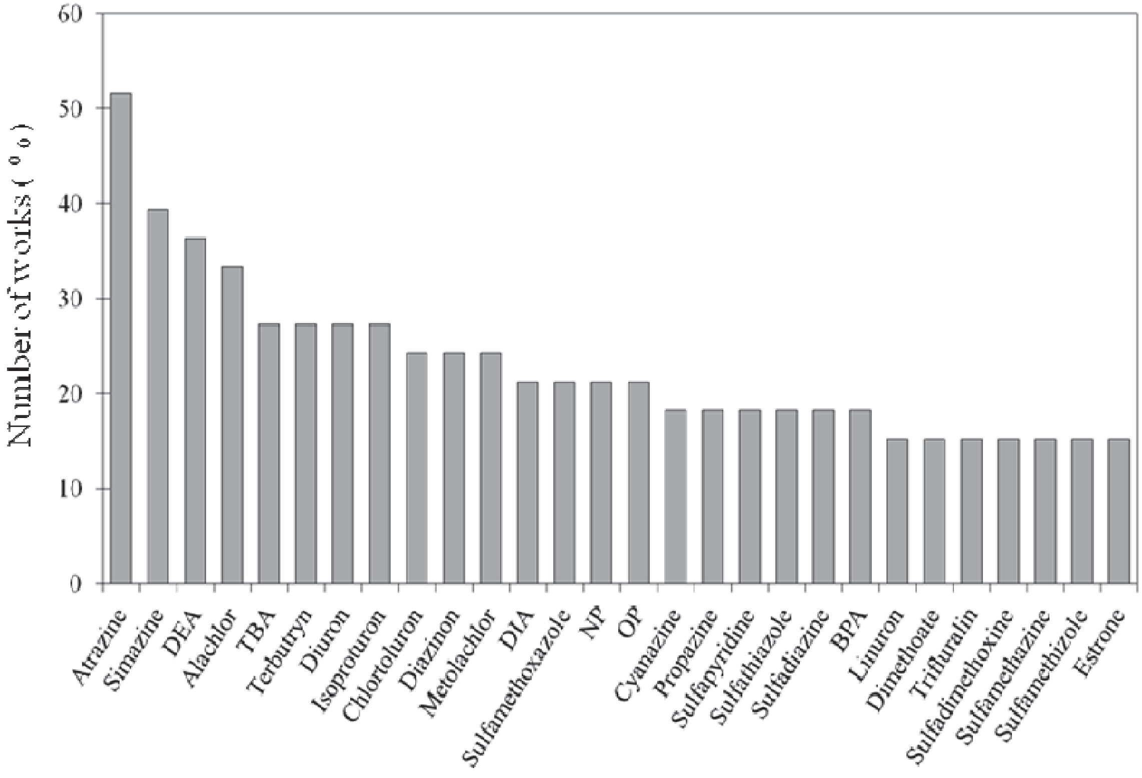


Figure 2.2. Most studied EOCs in the groundwater of Spain (%). The number of studies (n) performed was 33 and pesticides are by far the most reported compounds, followed by industrial compounds, PhACs and estrogens. Note that are represented the compounds reported in n≥ 5 (15%).

In some regions of Spain, the occurrence of specific pesticides has been studied according to the crops that are present in the agricultural areas. Sanchez-Camazano *et al.* (2005) analysed atrazine and alachlor in the Castilla León region, where corn crops are concentrated in four provinces (Salamanca, Avila, Zamora and Valladolid). Besides, in the area of Salamanca and Zamora in the same Castilla-León region, Carabias-Martínez *et al.* (2000 and 2003) studied the pollution due to currently used herbicides (ureas, triazines, amides) in the Guareña and Almar River basins. The main crops in the area are cereals followed by sunflower. Hildebrandt *et al.* (2007 and 2008) investigated the impact of atrazines, anilides and organosphosphorous herbicides in the aquifers of the Duero (in Castilla León region), the Ebro (in la Rioja, Navarra, Aragón and Catalonia regions) and the Miño (in Galicia region) River basins (Figure 2.1), where there are extensive areas of vineyards even though corn crops dominate. Finally, Arráez-Román *et al.* (2004) found carbamate insecticides used for agriculture in greenhouses in Almería (Andalucía region, SE Spain). The occurrence of pesticides has been recently studied in the Canary Islands (Gran Canaria) by Estévez *et al.* (2012). They screened the occurrence of several pesticides, including atrazines, organophosphorous insecticides, ureas and anilides, among others, in groundwater used for both irrigation and water supply purposes. In the same line, Bono-Blay *et al.* (2012) evaluated the presence of pesticides on groundwater intended for bottling.

The study of Belmonte *et al,* (2005) has not been included in this review because they analysed different compounds in both groundwater and surface bodies but results did not differentiate between matrices.

Concentrations and spatial distribution

In the aforementioned studies performed across Spain, the most ubiquitous compounds were: the triazine herbicides atrazine, simazine, the atrazine transformation product desethylatrazine (DEA), terbuthylazine (TBA) and terbutryn, the phenylureas isoproturon and diuron and the anilide alachlor (Figure 2.2). The maximum individual concentrations have been observed for the anilides alachlor (9.95 µg/L) and metolachlor (5.37 µg/L), malathion (3.5 µg/L), atrazine (3.45 µg/L), chlorfenvinphos (2.5 µg/L), dimethoate (2.3 µg/L), DEA (1.98 µg/L), chlortoluron (1.7 µg/L), simazine (1.69 µg/L); parathion-methyl (1.5 µg/L), TBA (1.27 µg/L) and linuron (1.01 µg/L). Many others, such as prometryn, the atrazine transformation product desisopropylatrazine (DIA), azinphos-ethyl, chlorpyrifos, fenitrothion and tributyl phosphate presented concentrations higher than 0.5 µg/L. Consequently, the environmental quality standard of 0.1 µg/L set for individual pesticides in groundwater by the EU directive 2006/118/EC was surpassed in several cases. The studies carried out in groundwater bodies from Catalonia showed high concentrations for some of these pesticides. Garrido *et al.* (2000) found high concentrations (exceeding 0.1 µg/L) of organophosphorous (malathion, parathion-methyl, fenitrothion, chlorfenvinphos, diazinon and dimethoate) and triazines (atrazine, prometryn and simazine) in groundwater samples collected from Catalonia between 1997 and 1998. Fenitrothion, diazinon and dimethoate, were found at lower concentrations 10 years later but atrazine and simanize, were found at similar concentrations (Postigo *et al.,* 2010a). This might indicate that: (1) organophosphorous insecticides are currently less applied but atrazine is still used despite being banned in the European Union in 2007 (Köck-Schulmeyer *et al.,* 2012) or (2) atrazine is more persistent than organophosphorous insecticides in the aquifer. Postigo *et al.* (2010a) also reported considerably high concentrations of the ureas linuron, diuron and chlortoluron. It is important to mention that the triazines atrazine, simazine and TBA presented decreasing concentrations over time in groundwater of the River Llobregat. As an example, atrazine concentrations in groundwater samples collected near the Sant Joan Despí waterworks were 0.025 µg/L in 2000, from 0.007 µg/L to 0.014 µg/L in 2002 and, 0.0023 µg/L in 2003. In the Ebro River catchment (NE-Spain), pesticide concentrations in groundwater were much higher than in the River Llobregat area but triazines also decreased in concentration over time. Hildebrandt *et al.* (2007 and 2008) reported high concentrations of some triazines in groundwater (1.42 µg/L, 1.25 µg/L, 0.79 µg/L and 0.54 µg/L for atrazine, DEA, DIA and simazine, respectively) and metolachor (0.26 µg/L) from samples collected in 2000-2001. However, in 2004 triazines concentrations decreased dramatically while metolachlor presented higher concentrations with a maximum concentration of 5.37 µg/L. The latter was detected at very low concentrations (0.0033 µg/L) in the River Llobregat area (Kampioti *et al.,* 2005). In central Spain (Castilla León region), triazine concentrations did not display a clear trend. Sánchez-Camazano *et al.* (2005) evaluated the inputs of atrazine in groundwater in 1997-1998 and reported concentrations from 0.04 µg/L to 3.45 µg/L while, in the same period, Carabias Martínez *et al.* (2000) found lower concentrations, ranging from 0.02 to 0.22 µg/L in 1998 and 0.16 µg/L in 1999 but found high concentrations of chlortoluron (0.4 to 1.7 µg/L). One year later (2000-2001), atrazine concentrations increased significantly, varying from 0.76 to 1.67 µg/L. These observations are related to the land use. High concentrations of atrazine were reported when corn was the main crop whereas high concentrations of chlortoluron were found when other cereal crops dominate. In the NW of Spain (the River Miño basin) only high concentrations of DEA and metalaxil were reported. In contrast, Canary Islands presented very low values of triazines (< 0.01 µg/L) and only chlorpyrifos-ethyl exceeded the 0.1 µg/L (up to 0.29 µg/L). Another group of pesticides found in groundwater in the South of Spain are carbamates but concentrations reported were always below the prescribed concentration established for individual pesticides in groundwater by the Directive 2006/118/EC.

To sum up, a wide range of pesticides has been studied in the groundwater of Spain over the last 10 years. The most studied pesticides have been triazines (atrazine>simazine> DEA>TBA=terbutryn>DIA) followed by phenyl urea herbicides (diuron=isoproturon>chlortoluron>linuron), anilides (alachlor>methachlor) and organophosphorous herbicides (diazinon>dimethoate). Out of the 80 pesticides that have been studied, 61 were reported in less than four studies and 30 were not detected in any groundwater sample (see Table S1 in Annex I).

2.3.2 Pharmaceuticals

The PhACs found in groundwater have been divided in the following therapeutic groups: Analgesic and anti-inflammatories, lipid regulators and cholesterol lowering statin drugs, psychiatric drugs, histamine receptor antagonists, tetracyclines, macrolides, fluoroquinolines, β-lactams, sulfonamides and other antibiotics, β-blockers, β and α agonist, barbiturates, diuretics, antidiabetics, anti-cancer, cardiac agents, contrast media agents, angiotestin agents, antifungals, dyspepsia drugs , anaesthetics, anthelmintics and antiseptics (see Table S1 in Annex I) .

Studies

Sulfonamide antibiotics (SAs) and their degradation products have been the most frequently reported group of PhACs in groundwater from Catalonia (Díaz-Cruz *et al.*, 2008; García-Galán *et al.,* 2010b, 2010c and 2011), mainly in the rural area but also in urban areas. Radjenovic *et al.* (2008) studied pharmaceuticals detected in the groundwater of the River Besòs aquifers (NE Spain) which are used as inflow to a drinking water treatment plant. The compounds analysed were analgesics and anti-inflammatory drugs such as ketoprofen, diclofenac, acetaminophen, mefenamic acid and propyphenazone, β-blockers such as sotalol and metoprolol, the antiepileptic drug carbamazepine, the antibiotic sulfamethoxazole, the lipid regulator gemfibrozil, the diuretic hydrochlorothiazide and the antidiabetic glibenclamide. Similarly, Huerta-Fontela *et al.* (2011) studied the occurrence of 48 PhACs in the raw water intended for drinking water production in the Llobregat area (South of Barcelona city), where groundwater is combined with treated surface water to improve the quality of the finished water. Jurado *et al.* (2012a) studied the psychiatric drugs alprazolam, lorazepam and diazepam in the aquifers of the Besòs River Delta and Barcelona Plain. Finally, Teijon *et al.* (2010) and Estévez *et al.* (2012) investigated the occurrence of a wide variety of PhACs (around 80 in both studies) in groundwater from the area of Llobregat and from the Canary Islands, respectively, including analgesics and anti-inflamatories, psychiatric drugs and SAs, among others (Table S1 in Annex I).

Concentrations and spatial distribution

In general, PhACs have been detected in lower concentrations than pesticides. Out of 161 PhACs investigated, 84 have never been detected (see Table S1 in Annex I).The most studied compounds (n≥4) have been in descending order sulfamethaxole>sulfapyridine=sulfadiazine=sulfathiazole>sulfadimethoxine=sulfamethizole=sulfamethazine>sulfamethoxypyridazine=sulfisoxazole=sulfamerazine=N4-acetylsulfamethazine=carbamazepine. The maximum individual concentrations have been for sulfacetamide (3461 ng/L), hydrochlorothiazide (2548 ng/L), sulfamerazine (744.7 ng/L), iopromide (687 ng/L), gemfibrozil (574 ng/L), sulfanitran (568.8 ng/L), diclofenac (477 ng/L) and sulfamethazine (446 ng/L). Several compounds such as iopamidol, codeine, ibuprofen, ketoprofen, mepivicaine, naproxen, propyphenazone, carbamazepine, nifuroxazide, furosemide, sulfamethoxazole, sulfapyridine, sulfaquinoxaline, benzalkonium chloride, N-acetyl-4-amino-antipiryne (4-AAA), N-formyl-4-amino-antipiryne (4-FAA), venlafaxime and atenolol have also been detected at concentrations above the reference threshold of 100 ng/L. We have chosen this reference threshold because it is the quality standard set for individual pesticides in groundwater by the EU directive 2006/118/EC.

As commented before, SAs have been widely studied in Catalonian aquifers over the last five years. The occurrence of some of these compounds seems to follow similar pattern. Sulfadimethoxine, sulfamethazine and sulfamethoxazole were repeatedly present in groundwater. In contrast, sulfamethiazole was infrequently detected. Livestock waste in rural areas could contribute to the occurrence of sulfadimethoxine and sulfamethazine because these two SAs are generally used in veterinary practices. In contrast, sulfamethoxazole, which is mainly used in humans, was found more often than expected in groundwater from rural areas (García-Galán *et al.,* 2010c) and presented the highest concentrations and detection frequencies in urban aquifers (Díaz-Cruz *et al.,* 2008; García-Galán *et al.,* 2010c). Sulfamethoxazole was also present in groundwater samples from the Llobregat River Delta area. Its high occurrence could be attributed to contamination from both point sources (WWTPs discharges into the rivers) and a diffuse source (losses from sewage systems) in densely populated areas. Apart from SAs, X-ray contrast media (iopamidol and iopromide), psychiatric drugs (carbamazepine, phenytoin and velafaxine), cardiac agents (hydrochlorothiazide and diltiazem), analgesics (4-AAA, 4-FAA, ibuprofen, codeine and diclofenac), fluoroquinolone antibiotics (ofloxacyn), β-blockers(acebutolol, atenolol, metoprolol, propanol and sotalol), angiotensin agents (ibesartan and valsartan) and antihistaminics (salbutamol) were also detected in groundwater of the Llobregat area (Boleda *et al.,* 2009; Teijon *et al.,* 2010; Huerta-Fontela *et al.,* 2011). Comparatively, fewer compounds were detected in the Besòs aquifers (North of Barcelona city), including analgesics (acetaminophen, ketoprofen, propyphenazone, mefenamic acid and diclofenac), cholesterol lowering statin drugs (gemfibrozil), psychiatric drug (carbamazepine), β-blockers (metoprolol and sotalol) and antidiabetics (glibenclamide) (Radjenovic *et al.*, 2008).

2.3.3. Industrial compounds

This category includes surfactants such as alkylphenol polyethoxylates (APEOs), which are used in a variety of industrial and domestic products (cleaning products, degreasers and detergents) and bisphenol A (BPA) and phthalates, mainly used to make plastics.

Studies

These compounds have been detected in rural groundwater as a result of agronomic practices and also in urban aquifers. Lacorte *et al.* (2002) and Latorre *et al.* (2003) reported the presence of the APEOs degradation products (DPs) nonylphenol (NP) and octylphenol (OP) and of BPA in agricultural areas of Catalonia. These agricultural areas are located near large cities with heavy industrial activity. At Sant Joan Despí waterworks, located in the Llobregat River area (South of Barcelona), López-Roldán *et al.* (2004) studied the presence of the bis (2-ethylhexyl) phthalate (DEHP), NP, OP and phenols such as 2,4 dichlorophenol, 4-chloro-3-mehylphenol, 4-chloro-2-methylphenol and 4-tert-butylphenol in groundwater. In the same area, BPA was monitored by Rodriguez-Mozaz *et al.* (2004a). Tubau *et al.* (2010) investigated the occurrence of surfactants, including linear alkylbenzene sulfonates (LAS) and APEOs DPs in Barcelona's urban groundwater. Sánchez-Avila *et al.* (2009) found that groundwater from the Maresme area (North of Barcelona) was contaminated by the phthalate dimethyl phthalate (DMP), the APEO DP nonylphenol monoethoxylate (NP_1EO) and BPA due to a wastewater leak. In the rest of Spain, there was little research about the industrial compounds. Bono-Blay *et al.* (2012) panneresented a study that evaluated the presence of phthalates, alkylphenols and BPA in groundwater resources intended for bottling and Hildebrandt *et al.* (2007) evaluated the presence of BPA, NP and OP in agricultural areas of the Ebro Basin.

Concentrations and spatial distribution

In general, industrial compounds have seldom been studied in groundwater samples. The most studied compounds have been NP, OP and BPA. The highest maximum individual concentrations have been observed for nonylphenol dicarboxylate (NP_2EC, 11.24 µg/L), DEHP (5.67 µg/L), NP (5.28 µg/L), LAS (5.06 µg/L), nonylphenol monocarboxylate (NP_1EC, 2.46 µg/L), OP (1.8 µg/L), BPA (1.5 µg/L) and diethyl phthalate (DEP, 1.12 µg/L). The maximum concentrations of APEOs DPs and LAS have been found in the aquifers of Barcelona, which reflects not only the industrial part of the city, but also a high sampling density. In this area, LAS are the surfactants most used at present and APEOs, which were banned in the 1990s, have also been detected in WWTPs (Gonzalez *et al.,* 2004) and in the River Besòs (Tubau *et al.,* 2010). In the Maresme area (North of Barcelona), only NP_1EO (0.45 µg/L) was detected whereas NP and OP were not detected (Sánchez-Avila *et al.,* 2009). Among the 6 phthalates analysed only DMP was detected and BPA was found at concentrations of 0.12 µg/L and 0.78 µg/L, respectively. In Llobregat River Delta aquifers, NP and OP were detected at considerably high concentrations (1.61 µg/L and 0.37 µg/L, respectively), but the highest concentration corresponded to the phthalate DEHP (5.67 µg/L). In contrast, BPA was detected at very low concentrations in Llobregat groundwater (0.007 µg/L). Groundwater of the Ebro River basin was free of BPA and NP and OP was detected at low concentrations (0.15 µg/L) (Hildebrandt *et al.,* 2007).

2.3.4. Drugs of abuse

Drugs of abuse include a long list of chemicals that are used with non-therapeutic purposes.

Studies

Little research is available about the presence of DAs and their metabolites in groundwater. DAs have been studied in a well used for pumping at a Spanish drinking water treatment plant (DWTP) located in NE Spain (Boleda *et al.,* 2009; Huerta-Fontela *et al.,* 2008a). The first comprehensive study that has specifically addressed the contamination of aquifers by DAs was developed in the Barcelona aquifers by Jurado *et al.* (2012a). DAs have also been reported in the aquifers of Canary Islands (Estévez *et al.*, 2012).

Concentrations and distribution

Thirteen of the 23 DAs analysed in groundwater have not been detected either in Barcelona or in Canary the Islands (see Table S1 in Annex I). Cannabidiol and ethylamphetamine were detected at the Canary Islands aquifer but the frequency of detection and the concentrations of the DAs measured were not specified, so the following results are based on Barcelona studies. Only trace concentrations of methadone (0.5 ng/L) and EDDP (2.3 ng/L) were reported in the River Llobregat aquifers (Boleda *et al.,* 2009). In Barcelona urban groundwater, the most frequently detected DAs were methadone (86%) and ecstasy (or MDMA) (64%). The highest values of concentrations corresponded to methadone (68.3 ng/L), cocaine (60.2 ng/L) and MDMA (36.8 ng/L). The largest number of detected DAs (opiods, cocaininc compounds and amphetamines) were found in a zone recharged by the River Besòs, which receives large amounts of effluents from WWTPs (total concentrations of 200 ng/L in some sampling points). Whereas, the urbanised areas presented fewer DAs and at lower concentrations. It is interesting to note that identified DAs correlate with social class. Jurado *et al.* (2012a) found cheap DAs (e.g. ecstasy) in groundwater from working class quarters, whereas cocaine was found in the groundwater of more affluent neighbourhoods.

2.3.5. Life-style compounds

A few studies reported the presence of nicotine and its metabolite cotininine and caffeine and its metabolites methylxanthine, paraxanthine, theophylline and theobromine and also caffeine c13. They were studied in Llobregat delta area (Huerta-Fontela *et al.,* 2008a; Teijon *et al.,* 2010) and in Canary Islands (Estévez *et al.,* 2012). Caffeine and Nicotine were frequently detected in aquifers of Gran Canaria (both 100 %) and also in Llobregat River Delta (77.4 % and 71.7%, respectively). However, in the same area, neither nicotine nor caffeine were detected in groundwater intended to improve raw water quality in a DWTP. Other compounds detected, at lower percentages, were theobromine and theophylline (50% each in Canary Islands) and paraxanthine (6% in Llobregat area). Neither caffeine c13 nor methylxanthine and cotinine were detected in groundwater. The maximum concentrations were for caffeine (505.5 ng/L), theobromine (252.5 ng/L), paraxanthine (147 ng/L) and nicotine (144 ng/L).

2.3.6. Estrogens and related compounds

Estrogens are a group of steroid compounds named for their importance in the estrous cycle and function as the primary female sex hormone. Some of the studies related to estrogens were developed in the River Llobregat aquifers in the municipality of Sant Joan Despí (Rodriguez-Mozaz *et al*., 2004a and 2004b; Farre *et al.,* 2007; Huerta Fontela *et al*., 2011). Farre *et al*. (2007) have also studied 3 isoflavones. Regarding the rest of Spain, only Estévez *et al*. (2012) studied the presence of the estrone in groundwater. The most studied compounds were the three major naturally occurring estrogens estrone (E1), estradiol (E2) and estriol (E3) and the synthetic estrogen Ethynyl Estradiol (EE). However, none of the compounds reported in the aforementioned studies were detected in the groundwater samples.

2.3.7. Personal care products

Personal care products are mainly used for beautification and in personal hygiene. These compounds were only reported by Teijon *et al.* (2010) in the groundwater of the Llobregat aquifers where polycyclic musks (galaxolide and tonalide), sunscreens (ethylhexyl methoxycinnamate), bacteriocide and antifungal agents (triclosan), among other compounds were found (see table S1 in Annex I). Only 3 of them were reported in groundwater at significantly high detection frequencies. The most detected was galaxolide (98%), followed by the antioxidant BHT (92.3%), and the sunscreen ethylhexyl methoxycinnamate (50%). The maximum concentrations were for BHT and galaxolide, 455 ng/L and 359 ng/L, respectively.

2.4. Assessment of the fate of EOCs in Spanish aquifers

Many EOCs have been found in Spanish groundwater at concentrations higher than 100 ng/L (Figure 2.3), highlighting the need to understand their fate in aquifers. The fate of EOCs in groundwater depends both on the physico-chemical properties of the contaminant and on the aquifer, notably the redox potential. The former tends to control mobility, the latter degradability (Christensen *et al.,* 2001; Barbieri *et al.,* 2011).

2.4.1. Physico-chemical properties of EOCs

Among contaminants properties, the octanol-water partition coefficient (K_{ow}) and the water solubility (S_w) are valuable parameters. The octanol-water partition coefficient is usually expressed as log K_{ow}. It measures how hydrophilic (log $K_{ow} < 4$) or hydrophobic (log $K_{ow} > 4$) an EOC is. Hydrophobic EOCs tend to bioaccumulate and usually have a high adsorption capacity especially onto organic matter (Choi *et al.,* 2005a; Jones-Lepp and Stevens, 2007). Conversely, EOCs with low log K_{ow} values tend to have high S_w and both lower bioaccumulation potential and soil/sediment adsorption coefficients (Silva *et al.,* 2012). However, care must be taken because log K_{ow} does not always correlate with adsorption capacity onto mineral sediments (de Ridder *et al.*, 2010).

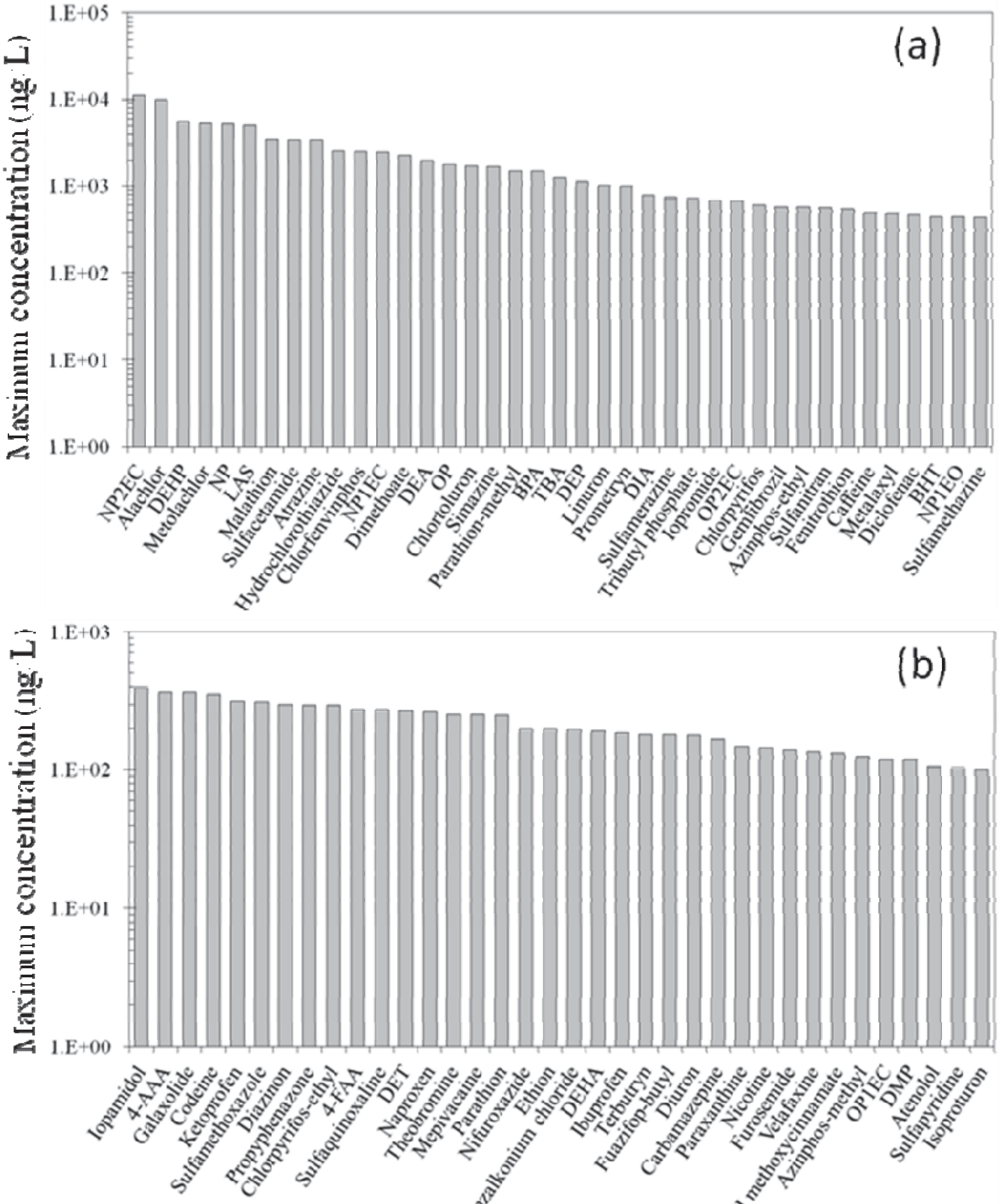
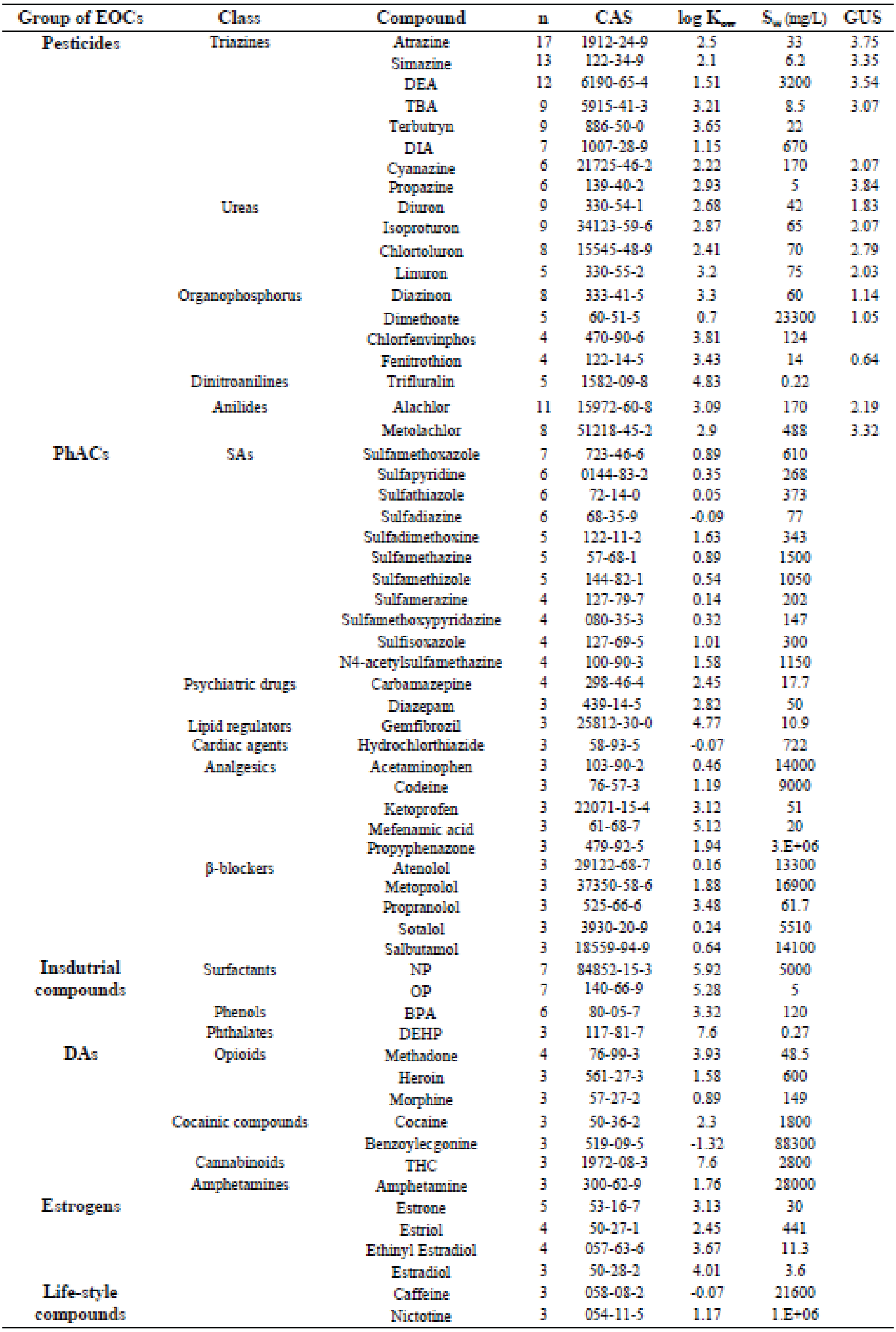


Figure 2.3. Maximum EOCs concentrations in the groundwater of Spain (ng/L). (a) Concentrations are higher than 400 ng/L and (b) Concentrations range from 100 ng/L to 400 ng/L.



Group of EOCs	Class	Compound	n	CAS	log K_{ow}	S_w (mg/L)	GUS
Pesticides	Triazines	Atrazine	17	1912-24-9	2.5	33	3.75
		Simazine	13	122-34-9	2.1	6.2	3.35
		DEA	12	6190-65-4	1.51	3200	3.54
		TBA	9	5915-41-3	3.21	8.5	3.07
		Terbutryn	9	886-50-0	3.65	22	
		DIA	7	1007-28-9	1.15	670	
		Cyanazine	6	21725-46-2	2.22	170	2.07
		Propazine	6	139-40-2	2.93	5	3.84
	Ureas	Diuron	9	330-54-1	2.68	42	1.83
		Isoproturon	9	34123-59-6	2.87	65	2.07
		Chlortoluron	8	15545-48-9	2.41	70	2.79
		Linuron	5	330-55-2	3.2	75	2.03
	Organophosphorus	Diazinon	8	333-41-5	3.3	60	1.14
		Dimethoate	5	60-51-5	0.7	23300	1.05
		Chlorfenvinphos	4	470-90-6	3.81	124	
		Fenitrothion	4	122-14-5	3.43	14	0.64
	Dinitroanilines	Trifluralin	5	1582-09-8	4.83	0.22	
	Anilides	Alachlor	11	15972-60-8	3.09	170	2.19
		Metolachlor	8	51218-45-2	2.9	488	3.32
PhACs	SAs	Sulfamethoxazole	7	723-46-6	0.89	610	
		Sulfapyridine	6	0144-83-2	0.35	268	
		Sulfathiazole	6	72-14-0	0.05	373	
		Sulfadiazine	6	68-35-9	-0.09	77	
		Sulfadimethoxine	5	122-11-2	1.63	343	
		Sulfamethazine	5	57-68-1	0.89	1500	
		Sulfamethizole	5	144-82-1	0.54	1050	
		Sulfamerazine	4	127-79-7	0.14	202	
		Sulfamethoxypyridazine	4	080-35-3	0.32	147	
		Sulfisoxazole	4	127-69-5	1.01	300	
		N4-acetylsulfamethazine	4	100-90-3	1.58	1150	
	Psychiatric drugs	Carbamazepine	4	298-46-4	2.45	17.7	
		Diazepam	3	439-14-5	2.82	50	
	Lipid regulators	Gemfibrozil	3	25812-30-0	4.77	10.9	
	Cardiac agents	Hydrochlorthiazide	3	58-93-5	-0.07	722	
	Analgesics	Acetaminophen	3	103-90-2	0.46	14000	
		Codeine	3	76-57-3	1.19	9000	
		Ketoprofen	3	22071-15-4	3.12	51	
		Mefenamic acid	3	61-68-7	5.12	20	
		Propyphenazone	3	479-92-5	1.94	3.E+06	
	β-blockers	Atenolol	3	29122-68-7	0.16	13300	
		Metoprolol	3	37350-58-6	1.88	16900	
		Propranolol	3	525-66-6	3.48	61.7	
		Sotalol	3	3930-20-9	0.24	5510	
		Salbutamol	3	18559-94-9	0.64	14100	
Insdutrial compounds	Surfactants	NP	7	84852-15-3	5.92	5000	
		OP	7	140-66-9	5.28	5	
	Phenols	BPA	6	80-05-7	3.32	120	
	Phthalates	DEHP	3	117-81-7	7.6	0.27	
DAs	Opioids	Methadone	4	76-99-3	3.93	48.5	
		Heroin	3	561-27-3	1.58	600	
		Morphine	3	57-27-2	0.89	149	
	Cocainic compounds	Cocaine	3	50-36-2	2.3	1800	
		Benzoylecgonine	3	519-09-5	-1.32	88300	
	Cannabinoids	THC	3	1972-08-3	7.6	2800	
	Amphetamines	Amphetamine	3	300-62-9	1.76	28000	
Estrogens		Estrone	5	53-16-7	3.13	30	
		Estriol	4	50-27-1	2.45	441	
		Ethinyl Estradiol	4	057-63-6	3.67	11.3	
		Estradiol	3	50-28-2	4.01	3.6	
Life-style compounds		Caffeine	3	058-08-2	-0.07	21600	
		Nictotine	3	054-11-5	1.17	1.E+06	

Table 2.2. Physicochemical properties and CAS number of the most reported EOCs. Values of water solubility S_w and log K_{ow} were extracted from http://www.syrres.com/what-we-do/databaseforms.aspx?id=386.

Concerning pesticides, another relevant parameter used in many studies (Hildebrandt *et al.,* 2007; Postigo *et al.,* 2010a; Bono-Blay *et al.,* 2012; Köck-Schulmeyer *et al.,* 2012) is the Groundwater Ubiquity Score (GUS) index (Gustafson, 1993). The GUS index is used to assess the leachability capacity of a pesticide indicating its intrinsic mobility. If GUS is higher than 2.8, the pesticide will likely be a "leacher".If GUS is less than 1.8, the pesticide will be a "non-leacher". Table 2.2 summarizes the GUS index for pesticides and the physico-chemical properties (log K_{ow} and S_w) of most of the EOCs plotted in Figure 2.2. Note that some PhACs, DAs, industrial compounds and life-style compounds ($n \geq 3$) are also included (Table 2.2). The pesticides' profile is dominated by the presence of triazines. Despite being fairly hydrophobic some of them were widely detected in groundwater samples (e.g. 80 %, 64%, 56% and 56% for simazine, atrazine, DEA and diuron, respectively in the study developed by Köck-Schulmeyer *et al.* (2012) and 89% and 87% for alachor and atrazine in the study performed by Sánchez-Camazano *et al.* (2005)). In contrast, the other triazines, phenylureas, organophosphorous and anilide pesticides were less frequently or not detected at all. For instance, cyanazine and fenitrothion were detected in less than 5% of the samples (Postigo *et al.,* 2010a). Linuron, chlortoluron and dimethoate were not detected in groundwater samples from the Llobregat area (Kampioti *et al.,* 2005). These frequencies of detection are more in accordance with the GUS index than the physico-chemical properties of the pesticides. Most of the frequently detected compounds (mainly triazines) have GUS indexes higher than 3. Conversely, fenitrothion, dimethoate and cyanazine are non-leacher pesticides (GUS index < 1.8, Table 2.2).

With regards to PhACs and DAs, few compounds are expected to present hydrophobic behaviour (log $K_{ow} > 4$ and low solubility). These compounds are the β-blocker propanolol, the analgesics ketoprofen and mefenamic acid, the lipid regulator gembifrozil and the cannabinoid THC. The remaining PhACs and DAs, according to their physico-chemical properties (Table 2.2), should present more hydrophilic behaviour being more frequently detected in the aquatic environment. In fact, some PhACs and in particular carbamazepine, have been qualified as suitable markers for anthropogenic influence in the aquatic environment (Clara *et al*., 2004; Gasser *et al.,* 2012; Muller *et al.,* 2012) since it is highly recalcitrant towards elimination in water/sediment (Löffler *et al.,* 2005).

Industrial compounds (NP, OP and DEHP) as well as both natural and synthetic estrogens have moderately low S_w and high log K_{ow} values and hence can be considered moderately hydrophobic compounds (Table 2.2). Estrogens have also been found to sorb in aquifer sediments. According to Ying *et al.* (2005) their soil sorption coefficients, expressed as log K_{oc}, range from 3.3 to 3.7. Therefore, it is not surprising that they have not been detected in groundwater in Spain. Finally, caffeine and nicotine showed hydrophilic behaviour with considerably high water solubility (Table 2.2).

2.4.2. Transformation and degradation processes

The concentration of EOCs in aquifers is affected by numerous processes, including concentration at the source, dilution, adsorption and degradation. Most studies are motivated by testing of pollution hypotheses. Therefore, they provide a biased picture of the actual state of groundwater bodies. In addition to the tendency to sorb onto both organic and inorganic solids, many EOCs are removed from water by transformation (e.g. Barbieri *et al.,* 2012) or degradation, especially if the water has undergone a broad range of redox states (e.g. Christensen *et al.*, 2001; Barbieri *et al.,* 2011). This, together the long residence time of water in aquifers, suggests that the most EOCs will tend to disappear. Unfortunately most studies do not reflect the redox state of water or its age. Old groundwaters are indeed free of EOCs (e.g. Teijon *et al.*, 2010), but this may reflect that EOCs had not been in use at the time of recharge. It is therefore clear that (1) EOCs analyses should be associated to groundwater studies in order to understand the representatively of observations, and (2) further research on degradation and transformation processes is needed to assess the long term fate of EOCs in groundwater.

2.4.3. River-groundwater interaction

Rivers are usually heavily polluted because of the effluents of WWTPs, industries and agriculture runoff. Understanding the interactions between groundwater and surface water is a key issue to assess the fate of EOCs in the aquifers, especially in heavily pumped aquifers, where rivers are the main source of groundwater recharge. This is certainly the case at the River Llobregat (Vàzquez-Suñé *et al.,* 2007b). There are some studies where the concentrations of some EOCs in the river (Llobregat and Besòs) can be compared with those of the aquifers (Quintana *et al.,* 2001; López-Róldan *et al.,* 2004; Rodríguez-Mozaz *et al.,* 2004a; Kampioti *et al.*, 2005; Tubau *et al.,* 2010; Huerta-Fontela *et al.,* 2011; Jurado *et al.,* 2012a). In general, the concentrations in the surface waters were higher than in the aquifers accounting for a wide array of pesticides, PhACs, DAs and selected industrial compounds (Figure 2.4). These should indicate natural attenuation capacity in the aquifer due to physical processes, such as sorption and dilution and biochemical processes. However, some compounds presented higher maximum concentration in the aquifer, such as the pesticides simazine, isoproturon, metolachlor, DEA, propanil, cyanazine, TBA and molinate, the industrial compounds NP, OP, NP_2EC and DEHP and the DAs methadone (METH) and ecstasy (MDMA). Note that none of the PhACs presented higher concentration in the aquifer than in the river. This fact suggests that further research is needed to understand the behaviour of the EOCs in the aquifers.

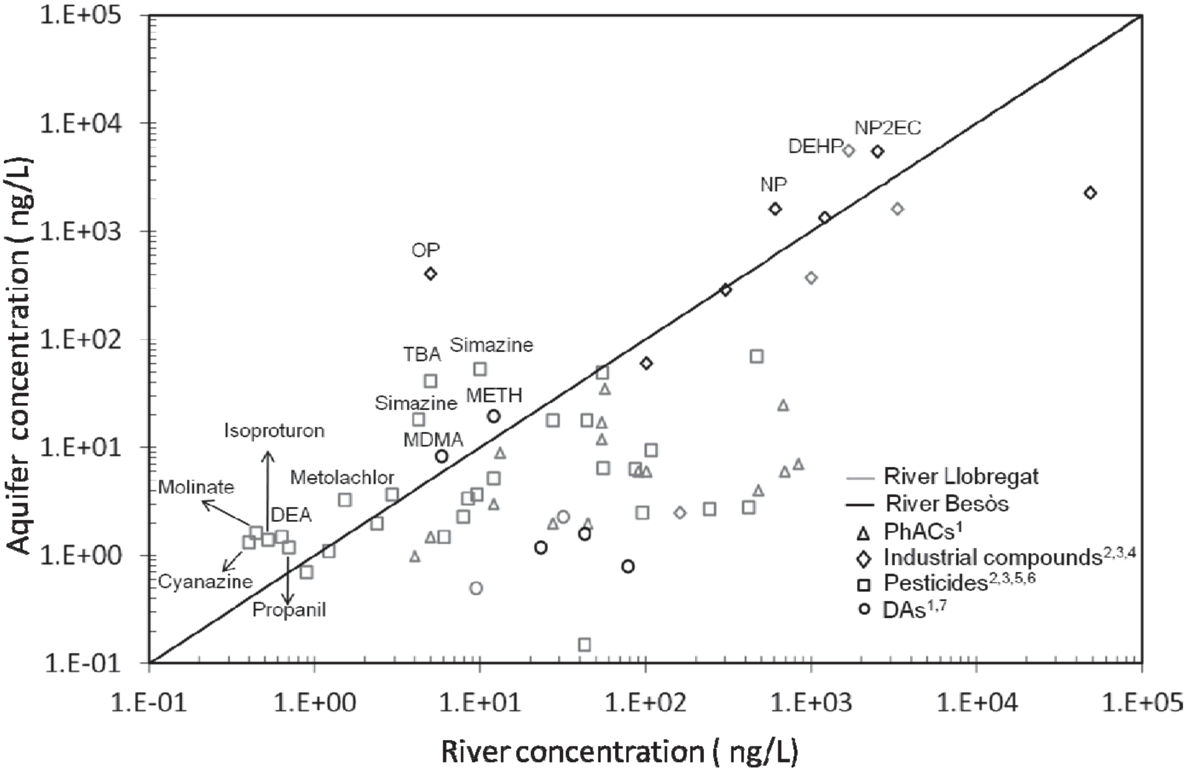


Figure 2.4. Measured concentrations of some EOCs in the Rivers Llobregat (grey) and Besòs (black) versus the concentrations reported in the aquifers of Barcelona. Note that aquifer concentrations are consistently much lower than surface waters for a wide array of compounds, suggesting the natural attenuation capacity of the aquifer. [1] Boleda *et al.* (2009) ,[2] López-Roldán *et al.* (2004),[3] Rodríguez-Mozaz *et al.* (2004a),[4] Tubau *et al.* (2010),[5] Quintana *et al.* (2001),[6] Kampioti *et al.* (2005) and [7] Jurado *et al.* (2012a).

2.5. Spain - European groundwater EOCs concentrations

It is not easy to establish criteria to compare the occurrence of EOCs in Spanish groundwater with the rest of European groundwater. There are several studies concerning EOCs all over Europe but each of them have analysed different compounds. We decided to establish a comparison of the maximum concentrations detected and taking into account the most recent works performed in European countries. We used the study performed of Loos *et al.* (2010) to compare the maximum concentrations of EOCs because it is the unique representative work that has monitored polar organic pollutants in European groundwater. In total, 59 selected organic compounds (PhAcs, pesticides, steroids, life-style compounds and industrial compounds) were analysed in 164 samples from 23 European countries. Out of the 59 organic compounds analysed in their survey, 33 have been included in this review. The maximum concentrations detected in the groundwater of Spain and in the Pan-European survey for selected pesticides, PhACs, industrial compounds and life-style compounds are plotted in Figure 2.5.

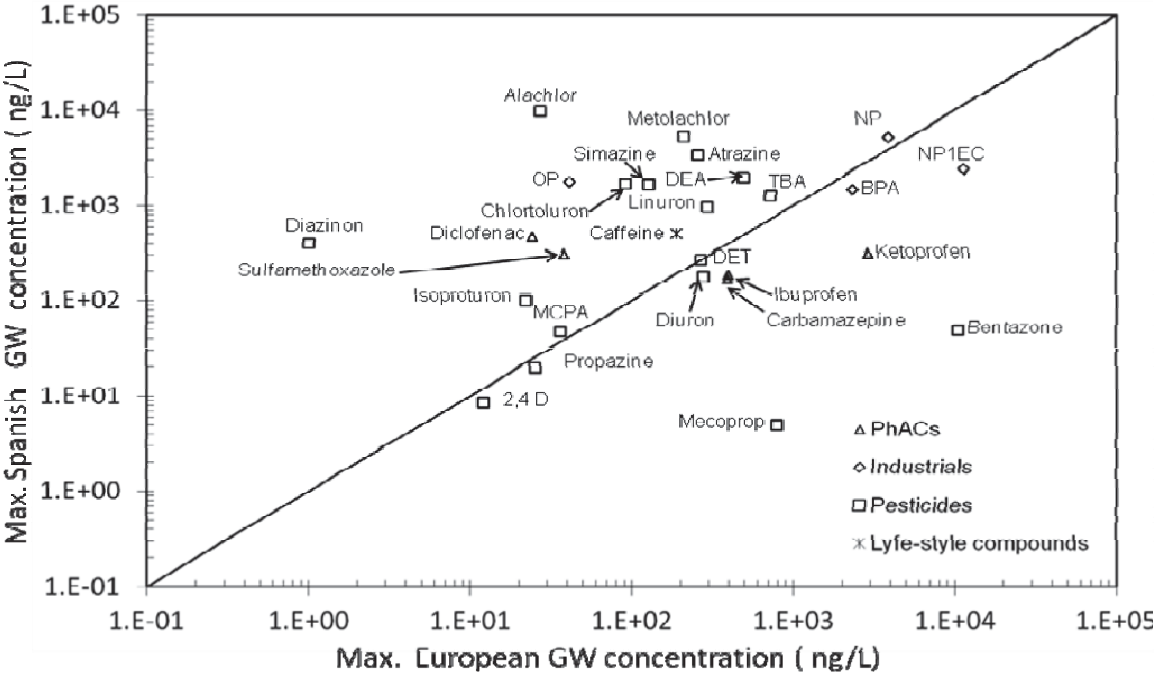


Figure 2.5. Maximum concentration of some EOCs in the groundwater (GW) of Spain versus the maximum concentration reported in the study of Loos *et al.* (2010). The EOCs include PhACs, pesticides, industrial compounds and life-style compounds.

In general, Spanish groundwater presents higher maximum concentrations than the Pan-European groundwater survey. The highest concentrations detected in the European survey were for NP_1EC (11316 ng/L), bentazone (10550 ng/L), NP (3850 ng/L), ketoprofen (2886 ng/L) and BPA (2299 ng/L). The profile of groundwater contamination seems to be dominated by industrial compounds (the APEOs DPs NP and OP and BPA) because they show high maximum concentrations in Spain and the European countries' aquifers. Pesticides (mainly atrazine and its metabolite DEA, simazine and TBA and its transformation product desethylterbuthylazine (DET)) also contribute to groundwater contamination.

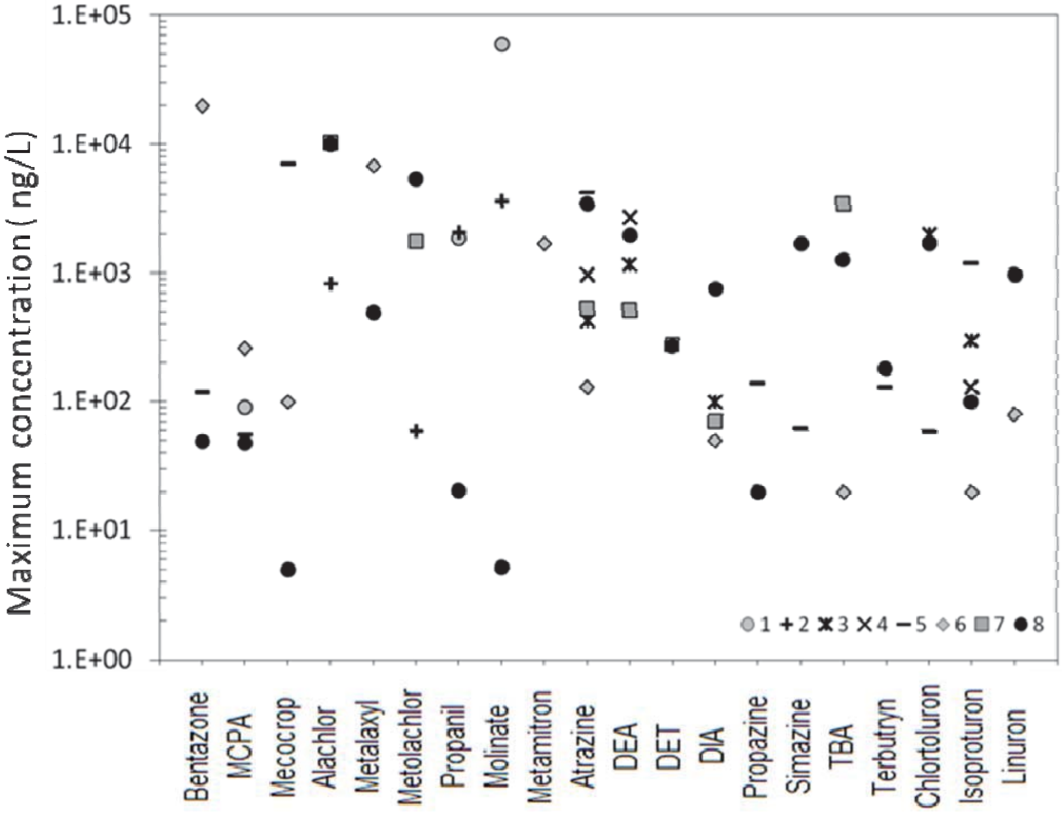


Figure 2.6. Maximum Spanish groundwater concentrations versus maximum European groundwater concentrations for some pesticides. References: [1]Silva *et al.* (2006),[2] Andrade and Stitger (2009),[3] Morvan *et al.* (2006),[4] Baran *et al.* (2007),[5] Lapworth *et al.* (2006),[6] Haarstad and Ludvigsen, (2007) and [7] Guzzela *et al.* (2005). Note that black dots (8) are the maximum Spanish groundwater concentrations of pesticides summarised in Table S1(Annex I).

There are some comprehensive monitoring surveys of individual EOCs in Europe. Pesticide compounds have recently been studied in groundwater in Portugal (Silva *et al.*, 2006, Andrade and Stigter, 2009), France (Morvan *et al.*, 2006; Baran *et al.*, 2007), the UK (Lapworth *et al.*, 2006), Italy (Guzzella *et al.*, 2005), Norway (Haarstad and Ludvigsen, 2007) and the Netherlands (ter Lak *et al.*, 2012). The presence of PhACs in European groundwater has been reported in Germany (Osenbrück *et al.*, 2007; Ternes *et al.*, 2007; Strauch et al., 2008; Reinstorf *et al.*, 2008; Wolf *et al.*, 2012), France (Rabiet *et al*, 2006; Vulliet and Cren-Olivé, 2011) and the UK (Stuart *et al.*, 2012). Hormones and industrial compounds have been less studied than pesticides and PhACs. Hormones and industrial compounds have been reported in Austria (Hohenblum *et al.*, 2004) and the latter also in Germany (Osenbrück *et al.,* 2007; Strauch *et al*., 2008; Reinstorf *et al.,* 2008) and the UK (Stuart *et al.,* 2012; Lapworth *et al.,* 2012). Personal care products and life-style compounds have been reported in Germany (Osenbrück *et al.,* 2007; Ternes *et al.,* 2007; Strauch *et al.,* 2008; Reinstorf *et al.,* 2008) and the UK (Stuart *et al.,* 2012; Lapworth *et al.,* 2012). The life-style compound caffeine has also been found in France (Rabiet *et al,* 2006). DAs, to the author's knowledge, have only been studied in the aquifers of Spain (Boleda *et al.,* 2009; Huerta-Fontela *et al.,* 2008a; Estévez *et al.,* 2012; Jurado *et al.,* 2012a). A comparison of the maximum concentrations reported in all the aforementioned studies allows us to distinguish between Spain and other European countries. This is shown in figure 2.6 for pesticides (only medium to polar compounds) and in figure 2.7 for the remaining EOCs reviewed.

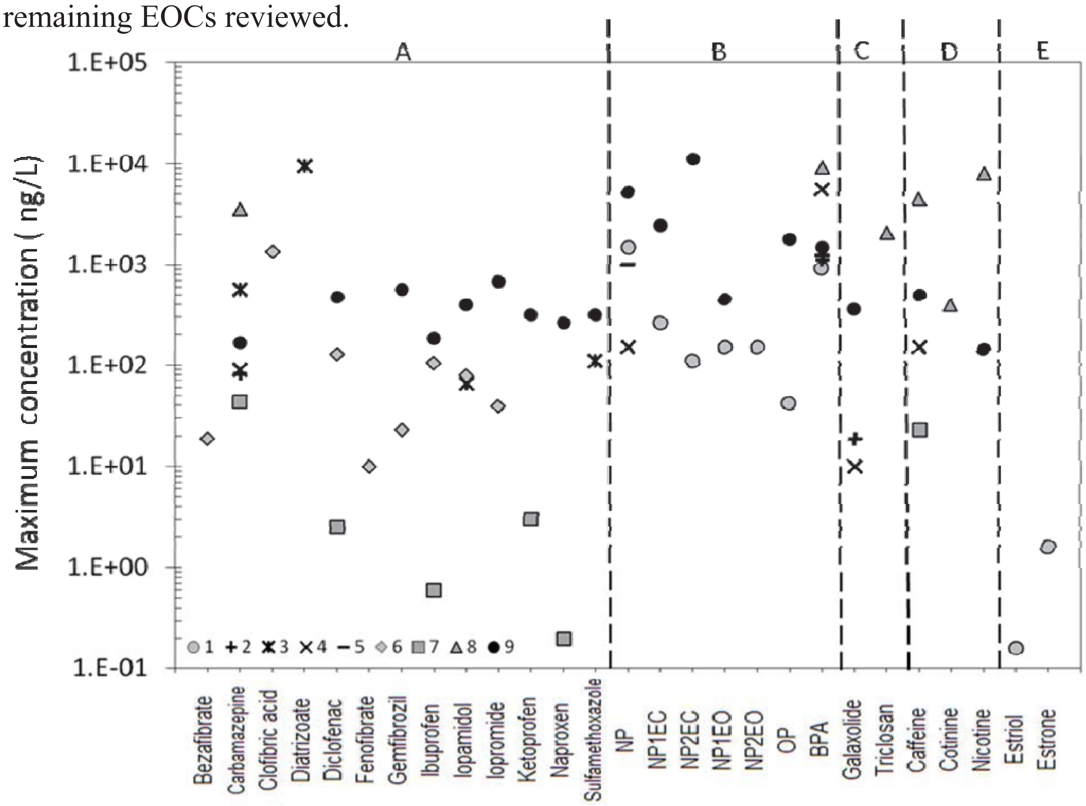


Figure 2.7. Maximum Spanish groundwater concentrations versus maximum European groundwater concentrations for (A) PhACs, (B) Industrial compounds, (C) Personal care products, (D) Life-style compounds and (E) Estrogens. References: [1] Hohenblum *et al.* (2007),[2] Osenbrück *et al.* (2007),[3] Ternes *et al.* (2007),[4] Strauch *et al.* (2008),[5] Reinstorf *et al.* (2008),[6] Wolf et al. (2012),[7] Rabiet *et al.* (2006) and [8] Stuart et al. (2012). Note that black dots (9) are the maximum Spanish groundwater concentrations of the aforementioned EOCs summarised in Table S1 (Annex I).

The lowest maximum pesticide concentrations were for mecocrop and molinate (both in Spain, at concentrations of 5 ng/L) whilst the highest maximum concentration were for molinate (Portugal, 59.46 µg/L) and bentazone (Norway, 20 µg/L). It must be noted that the maximum concentrations for most of these pesticides were higher in European than in Spanish groundwater. With regards the remaining EOCs, plotted in figure 2.7, maximum concentrations for PhACs were difficult to compare since the studies carried out in each country addressed different compounds. For instance, carbamazepine has been widely studied in Germany but, in general, studies covering a wide variety of PhACs in European countries are scarce and some of the compounds studied have not been detected in Spanish groundwater. For example, diatrizoate, clofibric acid and fenofibrate have not been reported in any groundwater sample in Spain but they have been measured in German (Wolf *et al.,* 2012) and French groundwater (Vulliet and Cren-Olivé, 2011). Meanwhile, the highest maximum groundwater concentrations for industrial compounds have mainly been detected in Spain. There are two exceptions, nonylphenol diethoxylated (NP_2EO), which has been not detected, and BPA, which highest maximum concentration has been found in the UK (Stuart *et al.,* 2012; Lapworth *et al.,* 2012). The personal care product galaxolide has presented its maximum concentration in Spain (Teijon *et al.,* 2010). As regards to life-style compounds, the highest maximum concentrations of caffeine (4.5 µg/L) and nicotine (8.07 µg/L) have been found in the UK aquifers (Stuart *et al.,* 2012; Lapworth *et al.,* 2012). None of the studied estrogens have been found in Spanish aquifers but some of them have been detected in groundwater from the rest of Europe at low concentrations (up to 10 ng/L).

In summary, it is interesting to note that most EOCs are usually detected at low ng/L concentrations or not detected at all in groundwater throughout Europe. While an increasing number of individual compounds are found at µg/L concentrations.

2.6. Conclusions

This work has reviewed the occurrence of various EOCs reported in Spain's groundwater. These include pesticides, PhACs, industrial compounds, DAs, estrogens, life-style compounds and personal care products. The major point source of pollution of these EOCs in groundwater corresponded to the effluents of WWTPs, which is largely a consequence of the motivation of the studies. The contamination profile seems to be dominated by industrial compounds, followed by pesticides and PhACs. The most relevant compounds contributing to Spanish groundwater contamination with individual concentration higher than 1000 ng/L are, in descending order, NP_2EC, alachlor, DEHP, metolachlor, NP, LAS, malathion, sulfacetamide, atrazine, hydrochlorothiazide, chlorfenvinphos, NP_1EC, dimethoate, DEA, OP, chlortoluron, simazine, parathion-methyl, BPA, TBA, DEP and linuron. Moreover, another 53 EOCs have been reported at concentrations between 100 and 1000 ng/L. Nevertheless, it is important to mention that compared to surface water bodies, such as rivers, groundwater is considerably less contaminated, indicating the natural attenuation capacity of the aquifers. However, some EOCs, namely, simazine, TBA, isoproturon, metolachlor, DEA, propanil, cyanazine, molinate, OP, NP, NP_2EC, DEHP, methadone and ecstasy, have sometimes been detected at higher concentrations in the aquifer than in the corresponding river. This might reflect the persistence of some organic compounds that were banned long ago, which is the case of industrial surfactants, and indicates the need for further research to understand their behaviour in the aquifers. The presence of some of these EOCs in groundwater from other European countries has also been reported with an increasing number showing individual concentration in the μg/L range. Consequently, proper assessment of groundwater quality against deterioration requires the investigation of a wide variety of compounds, of the processes they undergo in groundwater and perhaps the establishment of environmental quality criteria for a large number of contaminants such as PhACs, estrogens, DAs and life-style compounds.

3. Occurrence of drugs of abuse in urban groundwater. A case study: Barcelona

3.1 Introduction

In recent years, drugs of abuse (DAs) and their metabolites have been recognized as environmental contaminants. These compounds have become a major cause for concern because of their occurrence and because their toxicity and persistence are not well known. Despite being detected in low concentrations, DAs may produce potentially harmful effects on ecosystems and human health (Jones-Lepp *et al.*, 2004, Postigo *et al.,* 2008a). Moreover, the incomplete removal of some DAs during conventional waste water treatment represents the main source in surface and ground waters. Since both surface and ground waters can be used for water supply purposes, DAs and their metabolites have become a matter of considerable concern.

Numerous studies have reported the occurrence of DAs in the environment. The first comprehensive work was carried out by Zuccato *et al.,* (2005) in Italy. These authors described the presence of the illicit drug cocaine and its metabolite benzoylecgonine in wastewaters and surface waters. They applied at a local level the sewage epidemiological approach (Daughton, 2001) employing the measurements of benzoylecgonine in sewage water to estimate collective cocaine usage. Since then, a number of research groups have applied this methodology all around Europe, e.g. in Belgium (Van Nuijs *et al.,* 2011), France (Karolak *et al.,* 2010), Ireland (Bones et al., 2007),Croatia (Terzic *et al.,* 2010), Italy (Mari *et al.,* 2009, Zuccato *et al.,* 2008 and 2011; Castiglioni *et al.,* 2011), Spain (Postigo *et al.,* 2008a, 2008b, 2010b and 2011; Huerta-Fontela *et al.,* 2008b; Boleda *et al.,* 2009), Switzerland (Zuccato *et al.,* 2008; Berset *et al.,* 2010) and the United Kingdom (Kasprzyk-Hordern *et al.,* 2009; Zuccato *et al.,* 2008), and also in the USA(Bartelt-Hunt et al., 2009; Chiaia et al., 2008), Australia (Irvine *et al.,* 2011) and Canada (Metcalfe *et al.,* 2010). Trace levels of DAs and their metabolites have also been reported in drinking water (Huerta-Fontela *et al.,* 2008a; Boleda et al., 2009, 2011a and 2011b). However, the occurrence of DAs and their metabolites in groundwater has only been studied in a well water body used as source for abstraction of tap water at a Spanish drinking water treatment plant (DWTP) (Huerta-Fontela *et al.,* 2008a; Boleda et al., 2009, 2011a and 2011b). Hence, to our

This chapter is based on the paper: Jurado, A., Mastroianni, N., Vázquez-Suñé, E., Carrera, J., Tubau, I., Pujades, E., Postigo, C., de Alda, M.L., Barceló, D., (2012a). Drugs of abuse in urban groundwater. A case study: Barcelona. Science of the Total Environment 424, 280-288.

knowledge, this is the first comprehensive study to specifically address the contamination of aquifers by DAs.

The objective of this study was to investigate the occurrence of illicit drugs in an urban aquifer in relation to (1) the spatial distribution of DAs in Barcelona's groundwater, (2) the depth of the groundwater sample, (3) the presence of DAs in recharge sources, and (4) the assessment of the fate of DAs in Barcelona aquifers.

To this end, illicit drugs and metabolites belonging to 5 different chemical classes (cocainics, amphetamine-like compounds, opioids, lysergics and cannabinoids) and the prescribed drugs benzodiazepines were analyzed in groundwater samples collected at three sites in the city of Barcelona in May and December 2010.

3.2 Site description

The study area includes Barcelona and part of its metropolitan area in north-eastern Spain. The area is located between the Serra de Collserola (Catalan coastal ranges) and the Mediterranean Sea (Figure 3.1), both boundaries running approximately NNE–SSW. Other boundaries are constituted by two rivers, the Llobregat (SW) and the Besòs (NE). The climate is typically Mediterranean with an average rainfall of 600 mm per year.

Currently, groundwater is used for secondary uses such as streets cleaning and to water plants and public gardens. But it can be considered as an alternative tap water resource since there are several aquifers, characterized by their geological age, below the city (Figure 3.1). The Palaeozoic aquifer crops out at topographic highs to the NW, which consist of shales and granites. Quaternary aquifers can be found in the rest of the city. In 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 and coarse alluvial sediments.

3.3 Materials and methods

3.3.1 Sampling

Thirty-seven water samples were collected during two field campaigns in May 2010 (27 samples) and December 2010 (10 samples). One sample was obtained from the River Besòs and thirty-six samples were collected from groundwater: 27 from observation piezometers and 9 from pumping wells. The location of the wells and the

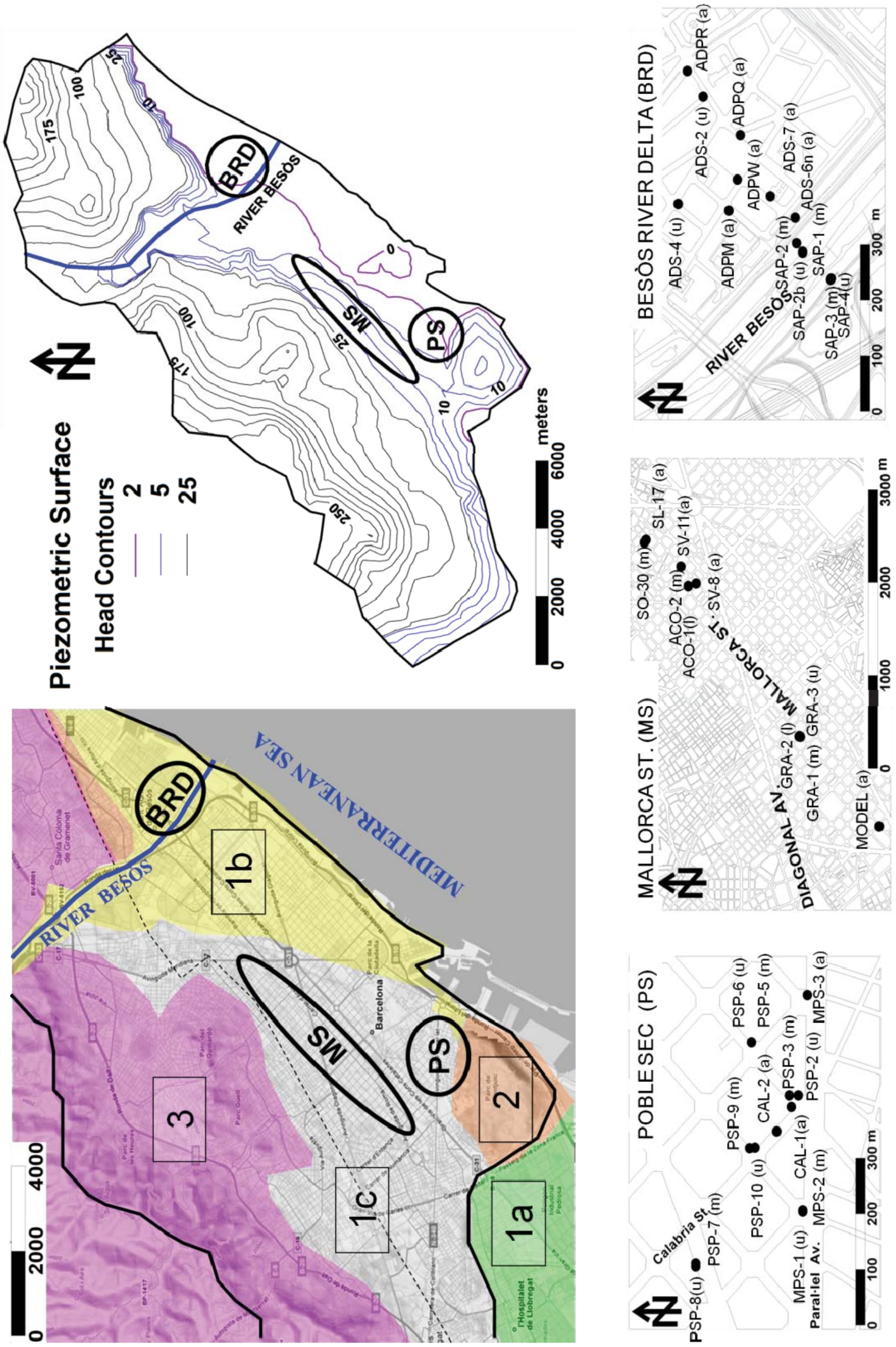


Figure 3.1. On the left, schematic description of the hydrogeology of Barcelona: (1a) Llobregat Delta made up of gravels, sands, silts and clays (Holocene, Quaternary), (1b) Besòs Delta composed of gravels, sands, silts and clays (Holocene, Quaternary), (1c) Barcelona Plain consisting of carbonated clays (Pleistocene, Quaternary), (2) Barcelona Plain made up of marls, sandstones and sands (Tertiary) and (3) Collserola Range consisting of shale and granites (Palaeozoic). On the right, a piezometric map of the study zone, which is divided into

three zones: (Z1) MS, (Z2) PS and (Z3) BRD. The contour intervals are 2 m (continuous purple line), for heads ranging from 5 to below 25 m (continuous blue line) and 25 m above (continuous black line). At the bottom, observation points on each zone, including the depth of the screen :(u) upper, (m) middle, (l) lower and (a) totally screened.

piezometers and the screen depths are displayed in Figure 3.1. Samples were collected in three different zones of the study area: (1) along Mallorca Street (MS) midway between the Collserola Range and the sea (a prosperous part of the city); (2) Poble Sec (PS), on the hillslope of Montjuich representing a less prosperous neighbourhood; and (3) Besòs River Delta (BRD), where groundwater comes mainly from the river. All the groundwater samples were obtained after pumping a volume of at least three times that of the piezometer. Field parameters measured in situ included electric conductivity, pH, temperature, Eh (also called redox potential) and dissolved oxygen. Water samples for drug analysis were measured continuously using a flow cell to avoid contact with the air. The instruments were calibrated daily by means of standard solutions. Samples were collected after stabilization of field parameters and were not filtered in the field. Instead, they were stored in a field refrigerator and taken to the laboratory at the end of the sampling day. Drug samples were stored in polyethylene terephthalate (PET) containers that were amber in colour to avoid photo degradation.

3.3.2 Target drug analytes

A total of 21 drugs and metabolites were analyzed. They belong to 6 different chemical classes: cocainics, cannabinoids, opioids, amphetamine-like compounds, lysergic compounds and benzodiazepines (Table 3.1). The investigated cocainic compounds were cocaine (CO), its major metabolite benzoylecgonine (BE), and cocaethylene (CE), a product formed when cocaine and ethanol are consumed simultaneously. The target cannabinoids constituted the main psychoactive component of the cannabis plant, Δ^9-tetrahydrocannabinol (THC), cannabinol (CBN), cannabidiol (CBD), and the two metabolic by-products 11-nor-9-carboxy-Δ9-tetrahydrocannabinol (THC-COOH) and 11-hydroxy-Δ9-tetrahydrocannabinol (OH-THC). Opioids surveyed were morphine (MOR), heroin (HER), the heroin metabolic product 6-acetylmorphine (6ACM), the opioid-agonist methadone (METH), and its main excretion product 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP). The group of amphetamine-like compounds investigated included amphetamine (AM), methamphetamine (MA), 3,4-methylenedioxymethamphetamine (MDMA or ecstasy), and ephedrine (EPH). The lysergic compound studied was the most potent known hallucinogenic substance, lysergic acid diethylamide (LSD). Benzodiazepines included alprazolam (ALP), diazepam (DIA) and lorazepam (LOR).

3.3.3 Analytical methods

Water samples collected in May and December 2010 were analyzed for general physical-chemical parameters at the ATLL (Aigües Ter Llobregat) laboratory and at the AMB (Àrea Metropolitana de Barcelona) laboratory, respectively.

Analysis of the target drugs and metabolites in the collected groundwater samples was carried out by on-line solid-phase extraction (SPE)-liquid chromatography-electrospray-tandem mass spectrometry (SPE-LC-ESI-MS/MS) following a methodology previously described by the authors for analysis of wastewaters (Postigo *et al.*, 2008b and 2011), readily adapted and validated for the present study to the analysis of groundwater matrices. In this method, samples (spiked with deuterated surrogate standards), aqueous calibrations solutions and blanks are analysed in a fully automated way with the aid of a Symbiosis-Pico system (Spark Holland, Emmen, The Netherlands) coupled on-line with the LC-MS/MS system. Samples (5 mL) are preconcentrated onto previously conditioned polymeric PLRPs cartridges (Spark Holland), and after washing of the cartridges with HPLC water, the retained compounds are eluted to the LC-MS/MS system with the chromatographic mobile phase, which consists of gradient acetonitrile/water modified with ammonium formate/formic acid. Chromatographic separation is carried out in a Purospher Star RP-18 end-capped column (125 x 2 mm, particle size 5 µm) and detection is performed in positive ion (PI) mode recording two selected reaction monitoring (SRM) transitions per analyte. Quantitation, based on peak areas, is carried out by the isotope dilution method. This method allows the determination of the compounds at concentrations between 0.4-9.2 ng/L (i.e., the method quantitation limits) and 500 ng/L, with satisfactory precision (relative standard deviations lower than 15 %) and accuracy (absolute recoveries above 80%) for most compounds.

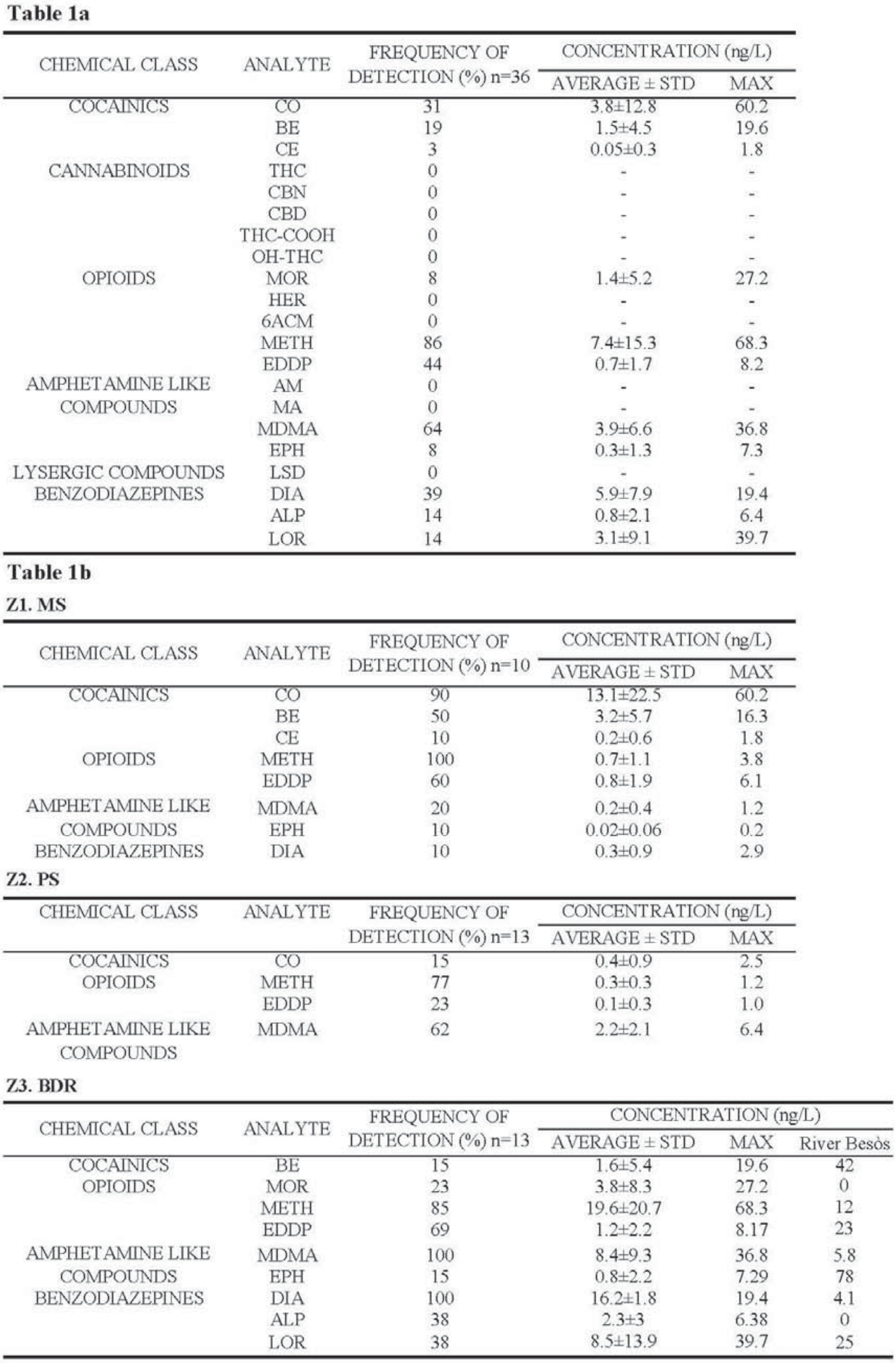


Table 1a

CHEMICAL CLASS	ANALYTE	FREQUENCY OF DETECTION (%) n=36	CONCENTRATION (ng/L)	
			AVERAGE ± STD	MAX
COCAINICS	CO	31	3.8±12.8	60.2
	BE	19	1.5±4.5	19.6
	CE	3	0.05±0.3	1.8
CANNABINOIDS	THC	0	-	-
	CBN	0	-	-
	CBD	0	-	-
	THC-COOH	0	-	-
	OH-THC	0	-	-
OPIOIDS	MOR	8	1.4±5.2	27.2
	HER	0	-	-
	6ACM	0	-	-
	METH	86	7.4±15.3	68.3
	EDDP	44	0.7±1.7	8.2
AMPHETAMINE LIKE COMPOUNDS	AM	0	-	-
	MA	0	-	-
	MDMA	64	3.9±6.6	36.8
	EPH	8	0.3±1.3	7.3
LYSERGIC COMPOUNDS	LSD	0	-	-
BENZODIAZEPINES	DIA	39	5.9±7.9	19.4
	ALP	14	0.8±2.1	6.4
	LOR	14	3.1±9.1	39.7

Table 1b

Z1. MS

CHEMICAL CLASS	ANALYTE	FREQUENCY OF DETECTION (%) n=10	CONCENTRATION (ng/L)	
			AVERAGE ± STD	MAX
COCAINICS	CO	90	13.1±22.5	60.2
	BE	50	3.2±5.7	16.3
	CE	10	0.2±0.6	1.8
OPIOIDS	METH	100	0.7±1.1	3.8
	EDDP	60	0.8±1.9	6.1
AMPHETAMINE LIKE COMPOUNDS	MDMA	20	0.2±0.4	1.2
	EPH	10	0.02±0.06	0.2
BENZODIAZEPINES	DIA	10	0.3±0.9	2.9

Z2. PS

CHEMICAL CLASS	ANALYTE	FREQUENCY OF DETECTION (%) n=13	CONCENTRATION (ng/L)	
			AVERAGE ± STD	MAX
COCAINICS	CO	15	0.4±0.9	2.5
OPIOIDS	METH	77	0.3±0.3	1.2
	EDDP	23	0.1±0.3	1.0
AMPHETAMINE LIKE COMPOUNDS	MDMA	62	2.2±2.1	6.4

Z3. BDR

CHEMICAL CLASS	ANALYTE	FREQUENCY OF DETECTION (%) n=13	CONCENTRATION (ng/L)		
			AVERAGE ± STD	MAX	River Besòs
COCAINICS	BE	15	1.6±5.4	19.6	42
OPIOIDS	MOR	23	3.8±8.3	27.2	0
	METH	85	19.6±20.7	68.3	12
	EDDP	69	1.2±2.2	8.17	23
AMPHETAMINE LIKE COMPOUNDS	MDMA	100	8.4±9.3	36.8	5.8
	EPH	15	0.8±2.2	7.29	78
BENZODIAZEPINES	DIA	100	16.2±1.8	19.4	4.1
	ALP	38	2.3±3	6.38	0
	LOR	38	8.5±13.9	39.7	25

Table 3.1. Frequency of detection (%) and average and maximum concentration (ng/L) of drugs and metabolites measured in **(1a)** Barcelona urban groundwater and **(1b)** detailed in each zone of the study area (MS, PS and BRD).

3.4 Results of Das in the urban groundwater of Barcelona

The average concentration and the maximum levels of the target drugs and metabolites measured in the groundwater samples and their detection frequency are summarized in Table 3.1a. Figure 3.2 shows the measured concentrations. No groundwater sample contained all the target compounds and no compound was present in all samples. Ten out of the 21 target compounds, namely, all 5 cannabinoids, LSD, HER, 6ACM, AM, and MA, were not detected in any sample. The most commonly detected drugs were METH, MDMA (or ecstasy) and EDDP (methadone metabolite), with detection frequencies of 86 %, 64 %, 45 %, respectively. DIA and CO were detected in between 30 % and 40 % of the samples; and the remaining compounds, namely, CE, MOR, EPH, and the benzodiazepines ALP and LOR, were detected in less than 20 % of the samples. The highest concentrations corresponded to METH (68.3 ng/L at SAP-4) and CO (60.2 ng/L at GRA-2).

The study area was divided into the three aforementioned zones (Zi). The DAs varied radically from one zone to another in terms of both concentrations and compounds detected (Table 3.1b). The results are given below.

Z1: MS

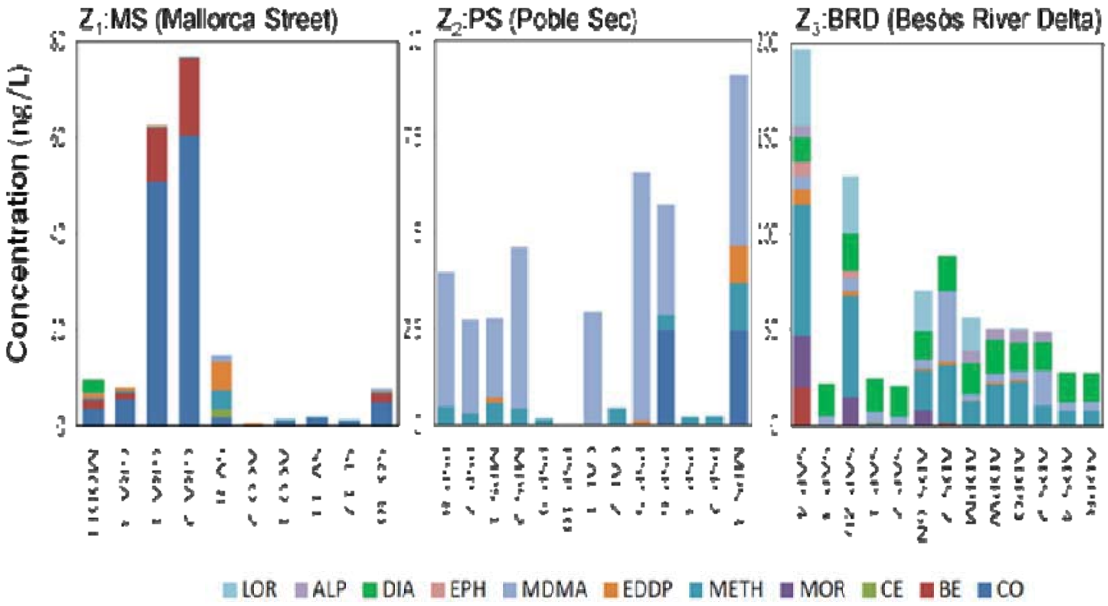


Figure 3.2. DAs (drugs of abuse) levels (ng/L) at the three sites: (Z1) MS, (Z2) PS and (Z3) BRD.

In the ten groundwater samples collected along MS (Z1), the compounds identified, ordered by decreasing frequency of detection, were METH>CO>EDDP>BE> MDMA>CE=EPH=DIA. Despite the fact that the ubiquity of METH was greater than that of cocainic compounds, it was present in groundwater at very low concentrations, on average 0.7 ng/L.

The highest levels were detected for two cocainic compounds, CO (ranging from 50 to 60 ng/L) and its major metabolite BE (ranging from 11 to 16 ng/L) at sampling points GRA-1 and GRA-2, respectively, where CO levels were higher than BE levels. This also occurred at sampling points GRA-3, MODEL, ACO-1, ACO-2 and SL-17 but at a lower concentration for both compounds (Figure 3.3). This finding contrasts with the concentrations reported in the literature where BE is higher than CO in surface and sewage waters (Table 3.2). CE, another metabolite of CO, was detected in one sample.

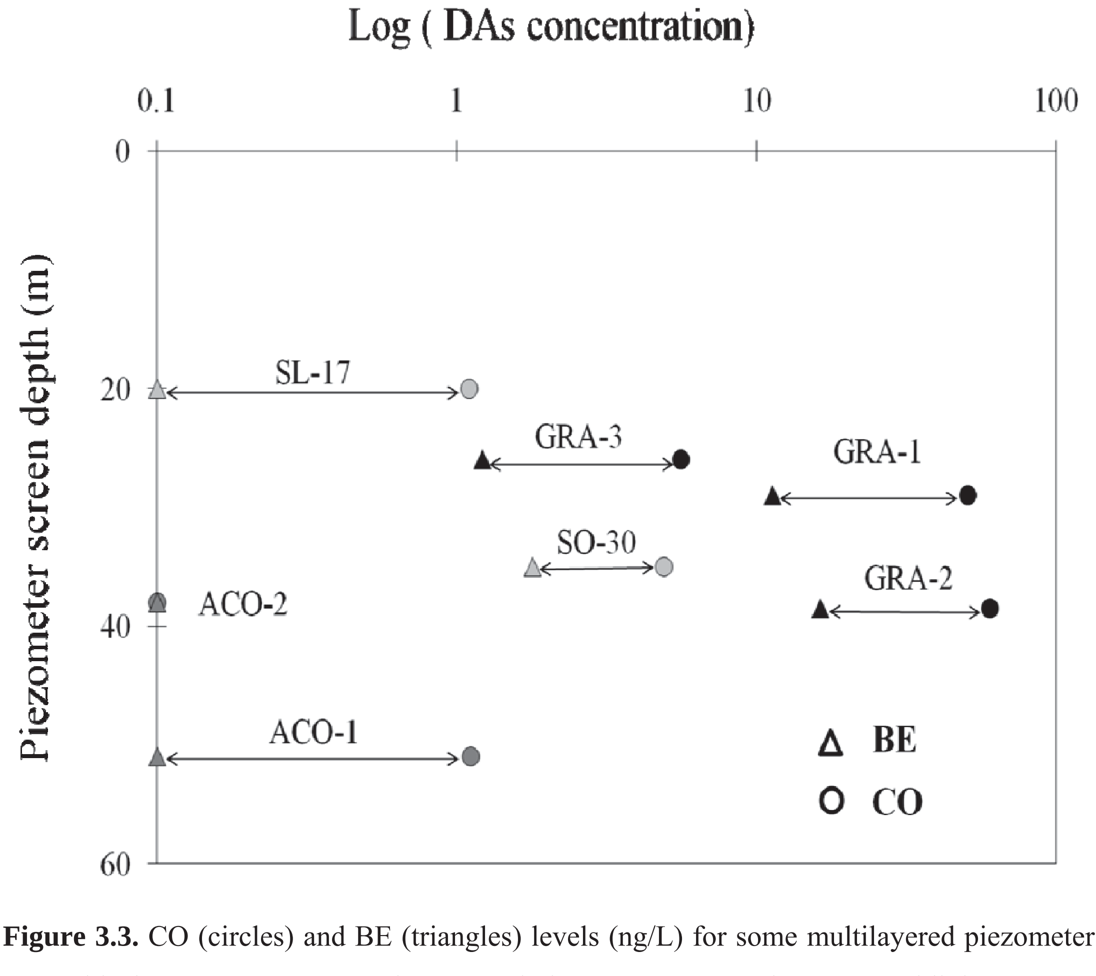


Figure 3.3. CO (circles) and BE (triangles) levels (ng/L) for some multilayered piezometers at Z1. In black: GRA-1, GRA 2 and GRA-3, dark grey: ACO-1 and ACO-2 and light grey: SO-30 and SL-17.

DRUGS OF ABUSE	TAP WATERS	WWTPs Influent	WWTPs Effluent	SURFACE WATERS
	Concentration (ng/L)	Concentration (ng/L)		Concentration (ng/L)
	Average/Range	Average/Range	Average/Range	Average/Range
COCAINICS				
CO	<LOD[1] 0.4[2]	79[6] 4-4700[7] 860.9±213.6[a,8]	17[6] 1-100[7] 6.2±3.7[a,8]	6[6] 0.1±0.0[a,3] 40±5[a,3] 9±2[a,3] 60±10[a,3] 10±4[a,3] 12.9±11.7[a,b,11] 4.6±1.2[a,c,11] 0.4-1.6[1]
BE	45[3] <LOD-1.5[1] 0.4[2]	810[6] 0.1-7500[7] 4225.7±1142.8[a,8]	216[6] 1-1500[7] 30.3±17.6[a,8]	77[6] 15±1[a,3] 70±25[a,3] 35±10[a,3] 150±60[a,3] 50±12[a,3] 36.7±13.9[a,b,11] 33.6±3.7[a,c,11] 14.6-20.1[1]
CE	0.2[2]	77.5±33.2[a,8]	1.7±1.2[a,8]	0.15±0.15[a]
OPIOIDS				
MOR		44±34.5[a,9] 162.9±20[a,8] 25.5-278[4]	22.5±33.6[a,9] 21.8±3.0[a,8] 12-81.1[4]	5.5±0.6[a,9] 1.5-12.2[4]
METH	0.17-0.85[4] 0.2[2]	12.7±8.9[a,9] 3.4-1531[4]	11.4±7.9[a,9] 3.4-732[4]	6.4±2.1[a,9] 1.9-9.4[4] 1.7-3[1]
EDDP	0.62-3.7[4] 0.4[2]	19.7±18.4[a,9] 3.3-1029[4]	22.4±23.6[a,9] 2.7-1150[4]	12.3±2.8[a,9] 5.2-31.4[4] 7.2-11.8[1]
6ACM		12.8±3.1[a,8]	3.6±0.5[a,8]	
AMPHETAMINES				
AM		15[6] 3-688[7] 41.1±9.1[a,8]	<LOQ[6] 4-210[7] 0.5±0.1[a,8]	0.94±1[a,9] 0.4±0.0[a,3] 50±5[a,3] 40±10[a,3] 9±3[a,3] 0.4±0.0[a,3]
MA		3-277[7] 18.2±5.8[a,8]	3-90[7] 6.3±0.6[a,8]	<0.2[3] 1±0.5[a,3] 1±0.1[a,3] 2±1[a,3] <0.2[3]
MDMA		49[6] 2-598[7] 133.6±29.8[a,8]	41[9] 2-267[7] 82.1±22.2[a,8]	3[9] 1.5±1[a,3] 25±10[a,3] 3±1[a] 40±5[a,3] 1±0.5[a,3] 0.7±1.2[a,b,11] 7.3±10.4[a,c,11] 0.4-1.3
EPH		591.9±62.3[a,8]	117.8±17.3[a,8]	15.2±5.6[a,b,11] 18.2±4.4[a,c,11]
CANNABINOIDS				
OH-THC		4.3±7.8[a,8]	8.4±3.8[a,8]	5.2±4.1[a,9]
THC		15.7±12.8[a,9] 11.3-127[4]	20.5[4]	<LOD-12[4]
YSERGIC COMPOUNDS				
LSD		2.8±1.2[a,8]	0.3±0.2[a,8]	
BENZODIAZEPINES				
DIA	<0.4[5]	n/d-49[10]	n/d[10]	3[6] 5[5] 1.2±0.0[a,b,11] 4.8±0.1[a,c,11]
ALP		n/d-4[10]	n/d-1[10]	
LOR		n/d-502[10]	n/d-532[10]	20.1±0.6[a,b,11] 31.5±4.4[a,c,11]

Table 3.2. Occurrence of DAs in tap water, influents and effluents of wastewater treatment plants (WWTP) and in surface waters (River Llobregat). LOD = limit of detection; LOQ = limit of quantification; n.d. = non detected; [a] Average concentration ± standard deviation; [b] Sample

collected at Molins de Rei; [c] Sample collected at St Joan d'Espí. References: [1] Boleda et al., 2011a; [2] Boleda et al., 2011b; [3] Huerta-Fontela et al., 2008a; [4] Boleda et al., 2009; [5] Huerta-Fontela et al., 2011; [6] Huerta-Fontela et al., 2007; [7] Huerta-Fontela et al., 2008b; [8] Postigo et al., 2008b; [9] Boleda et al.,2007 ; [10] Huerta-Fontela et al.,2010 and [11] Köck-Schulmeyer et al., 2011.

Z2: PS

Poble Sec was the area with the fewest drugs found in groundwater samples. The most commonly detected drug was METH (10 out of 13 samples) but the highest concentrations corresponded to the amphetamine-like compound MDMA (or ecstasy) detected at an average level of 2.2 ng/L. CO and EDDP were also found, but in less than 25% of the groundwater samples with an average concentration of 0.4 ng/L and 0.1 ng/L, respectively.

Z3: BRD

Since the River Besòs contains a large proportion of effluents from secondary WWTPs, a wide range of DAs were detected both in the river and in groundwater samples. The compounds identified in descending order were MDMA=DIA>METH> EDDP>ALP=LOR>MOR>EPH=BE. In contrast to Z1, cocainic compounds were absent (CO and CE) or found only in two samples (BE). MDMA was frequently detected at an average concentration of 8.4 ng/L but EPH was also found in 15% of the samples. DIA was present in all the samples collected and did not vary significantly in the aquifer, ranging from 12.9 to 19.4 ng/L. However, ALP and LOR were less common whereas ALP levels remained practically constant, 2.3 ng/L on average.LOR levels were significantly different, ranging from 1.6 to 39.7 ng/L.As in Z1 and Z2, METH and its metabolite EDDP, were commonly detected. METH levels were especially high in shallow piezometers near the river (between 53 and 68 ng/L) but were insignificant in the deep piezometers located at the same distance from the river.MOR was only found in 20 % of the samples near the river, with an average concentration of 3.8 ng/L.

3.5 Discussion

3.5.1 Spatial distribution of DAs in the groundwater samples

In view of the results of DAs in the three zones studied, it seems clear that drug consumption varies according to the district and is related to social status. CO is an expensive drug that was mainly detected in Z1, which is a more affluent district with several nightclubs. By contrast, Z2 is a less affluent area, in which the main drug detected was MDMA (or ecstasy), cheaper than CO which was detected in only two samples. In Z3, which is a popular area, a mixture of DAs was found because the main contribution to groundwater recharge is the river. As in Z2, the most commonly detected drug was MDMA. Although it would be interesting to define the relationship between drug consumption and affluence, our observations are restricted to the levels and zones in the study area.

3.5.2 DAs profile according to groundwater depth

The concentrations of most DAs decreased with the screen depth of the piezometer, which suggests either some kinetically controlled removal process, as residence time generally increases with depth, or an increasing proportion of water from the Collserola range. This trend was evident at the piezometers in the three zones. The most significant exception took place for cocainc compounds in Z1. As for CO and BE in Z1, the deeper the piezometer, the higher the concentration (Figure 3.3) for some multilayered piezometers (Figure 3.1), grouped as follows: (1) GRA-1, GRA-2 and GRA-3,(2) ACO-1 and ACO-2 and (3) SL-17 and SO-30. There is no easy explanation for these levels given that only a small percentage of a CO dose in humans is excreted in urine as the parent drug (5%), whereas a large amount is excreted as BE (45 %) (Baselt, 2004).Moreover, the high levels of CO and BE detected at piezometers GRA-1 and GRA-2 could indicate that an accidental or intentional disposal of CO occurred at a specific site (Zuccato et al., 2005). This is supported by the proximity of a high school and a police station to these sampling points.

3.5.3 DAs in recharge sources

3.5.3.1 Identification of the potential sources of recharge.

Several recharge sources have been identified in the aquifers of Barcelona (Vazquez-Suñe *et al.,* 2010). Direct rainfall recharge occurs in the non-urbanized areas in the Collserola Range. Seawater intrusion and water from the heavily polluted River Besòs must be considered potential recharge sources in low areas. Additional sources of groundwater recharge can be attributed to anthropogenic activities related to city development including loss from the water supply network. Barcelona is supplied with water from the Ter and Llobregat rivers. This gives rise to a division of the city into two zones with a different water quality and hence two different chemical compositions can be found in waste water. Finally, in paved areas, runoff water washes the road and atmospheric deposition, and recharges the aquifers through direct infiltration or sewer loss. To summarize, up to eight different recharge sources in Barcelona were identified: (1) River Besòs (RIV), (2) rainfall recharge in northern non urban area (R_R), (3) Ter river water supply (TER), (4) Llobregat river water supply (LLOB), (5) Ter river sewage water (SW_T), (6) Llobregat river sewage water (SW_LL), (7) City runoff (RUNOFF), and (8) Sea water intrusion (SEA).

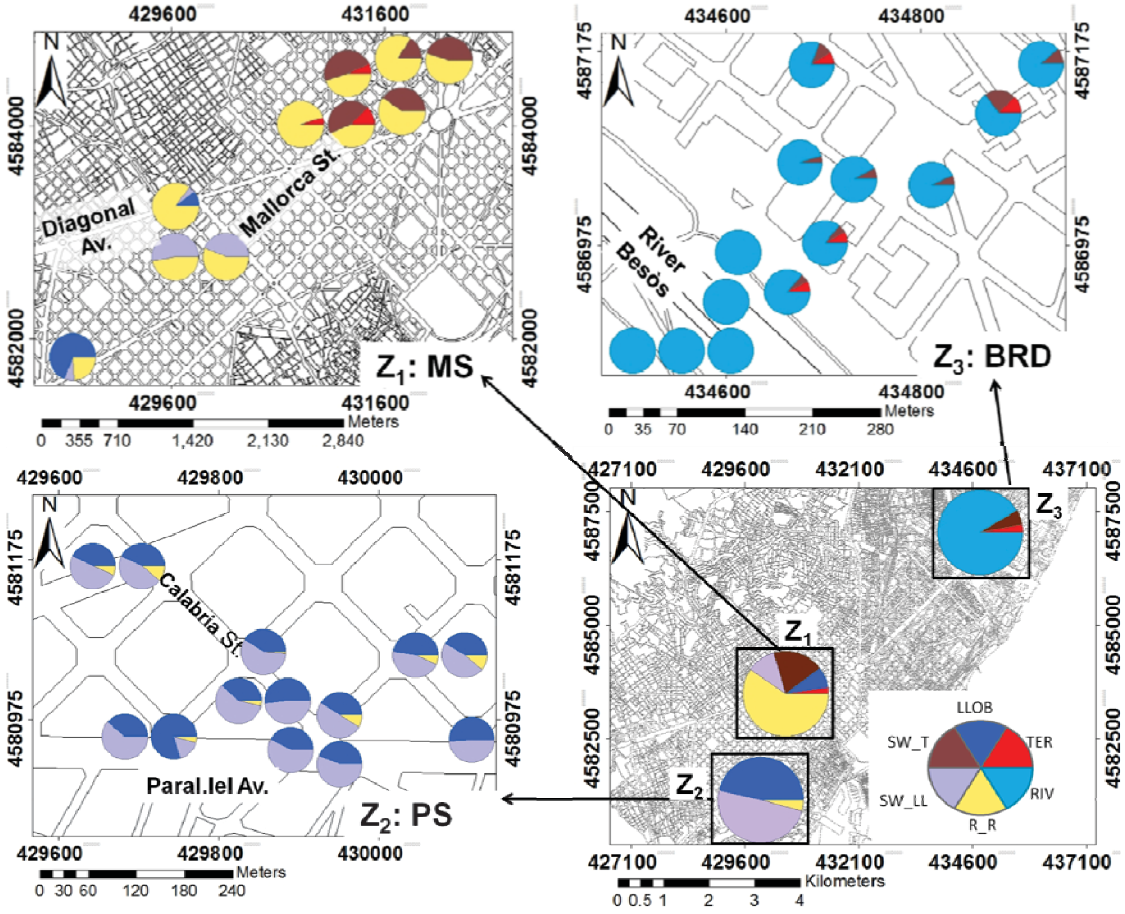


Figure 3.4. Mixing ratios evaluated at 36 wells accounting for 6 recharge sources. Note the average mixing ratios of each zone (Z1, Z2 and Z3) and the detailed scheme of each zone.

To compute the mixing ratios of these end-members in groundwater samples the approach of Carrera *et al.*, (2004) was used. This methodology identifies mixing ratios in the case of uncertain end-members using the concentration of mixed samples to reduce the uncertainty, assuming that the samples are a mixing of the end-members in an unknown proportion. The spatial distribution of the mixing ratios is illustrated in

Figure 3.4. According to the identified sources, in Z1 the main contributor to the total recharge was R_R (60%), especially in the deepest piezometers such as ACOPIO-1 and GRA-2, followed by the sewage network loss (31%) and water supply network loss (9%). In Z2, the main contributors were network sewage (SW_LL) and water supply loss (LL), accounting for 96 %. The remaining 4% corresponded to R_R. As for Z3, RIV (River Besòs) was by far the largest contributor to the total recharge, representing 91%. Other contributors to the recharge were network sewage (SW _T) and water supply loss (T). When considering the 3 zones as a whole, the average proportions of the contributors were the following: 21% from water supply network loss, 28% from sewage network loss, 18% due to infiltration in non-urbanized areas and 33% from the River Besòs.

3.5.3.2 DAs levels reported in recharge sources.

The occurrence of the DAs in some of the aforementioned recharge sources has been widely reported in the literature. Concentrations for NE Spain are summarized in Table 3.2.Cocainic compounds are the most ubiquitous and abundant compounds in the influents of the WWTP, especially BE, which reaches levels exceeding 7 µg/L. Some studies have also confirmed the ubiquity of the opioids MOR, METH and EDDP at relevant levels (ng/L range) in sewage influent. However, HER and 6ACM are seldom or not detected. Amphetamine-like compounds are found at comparatively lower concentrations than cocainics with maximum concentrations of 688 ng/L AM, 277 ng/L MA, 598 ng/L MDMA and 591.9 ng/L EPH. The other compounds such as lysergic, cannabinoids and benzodiazepines have been less studied and are found at relatively low concentrations.

Little research has been done on the occurrence of DAs in tap waters. Only the cocainics CO and BE and the opioids METH and EDDP have been detected in finished waters of a DWTP and at very low trace levels (Boleda *et al.,* 2011a, 2011b and 2009 and Huerta-Fontela *et al.,* 2008a) (table 3.2).

Another recharge source is the River Besòs, but, unfortunately, there are no data concerning DAs. We only have one sample from this river but we fear it may not be representative because the Besòs flow regime, like other Mediterranean rivers, is characterized by its variability, which is controlled by rainfall. However, the River Besòs shares some similarities with the River Llobregat, which has been the subject of many studies (Table 3.2). Both rivers undergo anthropogenic pressure, receiving extensive urban and industrial wastewater discharges. Consequently, the presence of the DAs can be expected at similar levels. The highest concentrations reported correspond to cocainic compounds, BE and CO, ranging from 15 to150 ng/L and from 0.4 to 60 ng/L, respectively. CE has been found at very low concentrations. The opioids present are MOR, METH and EDDP. METH is commonly present at lower levels than its metabolite EDDP. HER and 6ACM have not been detected. Amphetamine-like compounds have been frequently detected in the Llobregat. MA is present at concentrations lower than those of AM and MDMA, ranging from 0.4 to 50 ng/L. Levels of EPH have only been reported in one study at concentrations of up to 18 ng/L. Cannabinoids and lysergics are absent or found at very low concentrations. Benzodiazepine levels vary considerably between LOR and DIA, with maximum concentrations of 31.5 and 5 ng/L,respectively. ALP has not been detected in surface waters. Overall, as shown in Table 3.2, concentrations of DAs in surface waters are, on average, one or two orders of magnitude lower than in WWTP influents.

Given the high variability of flow rate and the water quality of the River Besòs and the relatively low residence time at the aquifer, it is not sufficient to consider only one end-member from the River Besòs. Instead, three were used to account for the temporal variability. To this end, since only one sample of the DAs in the River Besòs was available, we calculated the concentration of DAs in these river end-members with the river flow using a dilution factor (f) that is calculated as follows:

$$f= Q_s/Q_{em} \qquad (1)$$

where Q_s is the flow rate on the day of sampling and Q_{em} is the flow rate of the aforementioned end-members.

The adopted DAs concentrations for all sources are shown in table 3.3.

End-members		CO	BE	MOR	METH	EDDP	MDMA	EPH	DIA	LOR
Besòs River(RIV)	W1	-	21.4	2.6	6.4	11.8	3.0	40.2	2.1	13.0
	D1	-	131.9	15.8	39.4	72.9	18.3	225.0	12.9	80.1
	D2	-	172.1	20.6	51.5	95.1	23.8	319.0	16.8	104.6
Water Supply	TER LLOB	0.4	0.4	-	0.4	2.5	0	-	-	-
Sewage water	SW_TER SW_LLOB	50	500	-	7.5	12	50	-	-	50
Rainfall recharge non-urban	R_R	0	0	0	0	0	0	0	0	0

Table 3.3. Levels of DAs in the recharge sources expressed in ng/L. "- ": Not included in the analysis. W1: wet period; D1 and D2: dry periods.

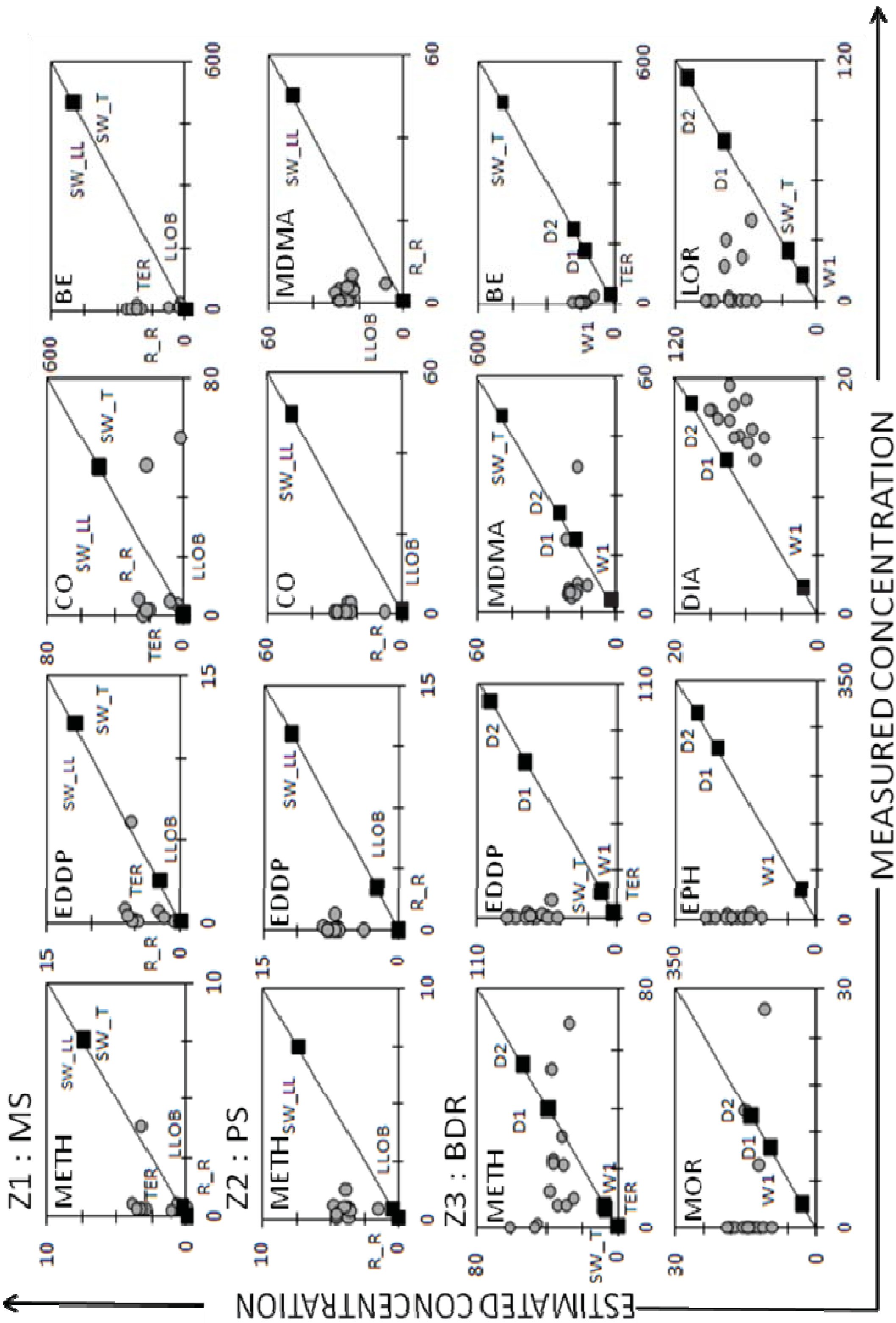


Figure 3.5. Measured concentrations of DAs in (Z1) MS, (Z2) PS and (Z3) BRD versus the concentration estimated from the end-members (squares) with the mixing ratios of figure 4.Note that measured concentrations are consistently much lower than expected. Note also that none of DAs behave conservatively and only the drugs that are representative of each zone are plotted.

3.5.4 Assessment of the fate of DAs in Barcelona aquifers.

Once the mixing ratios were assessed and the levels of DAs in the potential recharge source were determined, it was possible to assess the fate of DAs in the aquifer.

Z1: MS

Only the most commonly detected compounds along Mallorca Street are discussed in this study (CO, BE, METH and EDDP).These compounds behaved similarly (Figure 3.5). Estimated concentrations were higher than the measured ones, suggesting the occurrence of removal processes that depleted DAs in groundwater. The presence of species such as nitrate and the levels of dissolved oxygen indicate oxidizing conditions in this zone. Moreover, organic carbon is depleted, which indicates redox processes and suggests degradation of DAs. Regardless of the actual removal process, Figure 3.5 shows a dramatic reduction in the aquifer concentrations compared with that derived from simple mixing.

Z2: PS

As in Z1, only the most commonly detected compounds, which were METH, EDDP, MDMA and CO, are discussed. Sewage water is the main recharge source that contributed to the presence of DAs in the groundwater. But, again, the measured concentrations were much lower than the ones estimated from mixing ratios, which were the ones that should have been obtained from simple mixing (Figure 3.5). This observation lends support to the view that DAs are susceptible to chemical processes that result in their removal. As in Z1, oxidizing species and the absence of ammonium indicate oxidizing conditions.

Z3: BRD

Figure 3.5 plots the measured and estimated concentrations for BE, MOR, METH, EDDP, MDMA, EPH, DIA and LOR. All DAs, except DIA, behave in a similar way. They are significantly depleted in the aquifer, suggesting again removal processes. Biodegradation, adsorption and mixing processes can reduce DAs levels when river water infiltrates the aquifer. Only DIA levels fall close to the 1:1 line, indicating that DIA was less affected than the other DAs by removal processes and that concentration at the source may be higher than the assumed ones.

3.6 Conclusions

Groundwater in Barcelona aquifers contains DAs in low but measurable concentrations. The following conclusions may be drawn from this study:

(1) The most commonly detected drugs were CO, BE, METH, EDDP, MDMA, DIA, MOR, EPH, DIA and LOR, depending on the zone.

(2) The identified drugs appear to reflect distinct consumption patterns in the different areas and an intentional or accidental disposal of drugs in some cases. Cocainic compounds display higher concentrations in affluent districts whereas MDMA is the dominant drug in less prosperous neighbourhoods.

(3) Concentrations in the aquifer were generally much lower than those expected due to dilution, as calculated from the mixing ratios of the recharge sources. This suggests significant removal of DAs in the aquifer.

(4) These results, together with the limited sorption capacity of the sediments, suggest the degradation of DAs in the aquifer under different redox conditions: oxidizing conditions in Z1 and Z2 and reducing conditions in Z3.

4. Occurrence and fate of carbamazepine and 5 metabolites in an urban aquifer under different redox conditions

4.1 Introduction

Pharmaceutically active compounds (PhACs), including their metabolites, are a matter of growing concern because they might have a negative impact on ecosystems and human health. They may enter both surface and groundwater by many pathways, but mainly from raw sewer waters and from effluents of waste water treatment plants (WWTPs). As a result, a wide range of PhACs can be found in aquatic environments deteriorating groundwater quality. Consequently, PhACs are an emerging environmental issue.

Among a wide range of PhACs, carbamazepine (CBZ) is of high environmental relevance for several reasons. CBZ presents null or low removal during wastewater treatment. Effluent concentrations are often reduced by between 0-10% in most of WWTPs (Stamatelatou et al. 2003; Zhang et al., 2008). Moreover, some of its metabolites have been detected at higher concentrations in influents from WWTPs than CBZ (Gros et al., 2012) and also in finished waters from a drinking water treatment (Huerta-Fontela et al., 2011). CBZ has shown a persistent behavior in aquatic environments and is negligibly biodegraded (Patterson et al., 2011)

CBZ is a benzodiazepine commonly used as an anticonvulsant and mood stabilizing drug. After the oral administration of CBZ, 72% of the dose is excreted in the urine and 28% is eliminated in the faeces. Less than 3% of the drug is excreted unchanged in the urine (López-Serna et al., 2012a). CBZ is mainly metabolized in the liver through different pathways (Figure 4.1a). The main pathway corresponds to the formation of the major pharmacologically active metabolite, 10,11-epoxy carbamazepine (CBZ-EP), which comes from CBZ oxidation. Then CBZ-EP is hydrate to 10,11-dihydro-10,11-trans-dihydroxy carbamazepine. Lesser pathways include the formation of hydroxylated compounds such as 2-hydroxycarbamazepine (2OH CBZ) and 3-hydroxycarbamazepine (3OH CBZ) (Miao and Metcalfe, 2003), and the formation of iminostilbine. A minor pathway is the oxidation of CBZ into the leucocytes, ending in the formation of acridine (ACRIN) and acridone (ACRON) (Breton et al., 2005) (Figure 4.1b). But up to thirty-three metabolites have been indentified in urine (Lertratanangkonn and Horning, 1982).

This chapter is based on the paper: Jurado, A., López-Serna, R., Vázquez-Suñé, E., Carrera, J., Pujades, E., Petrovic, M., Barceló, D., 2012. Occurrence and fate of carbamazepine and 5 metabolites in an urban aquifer under different redox conditions. *Submitted to HESS.*

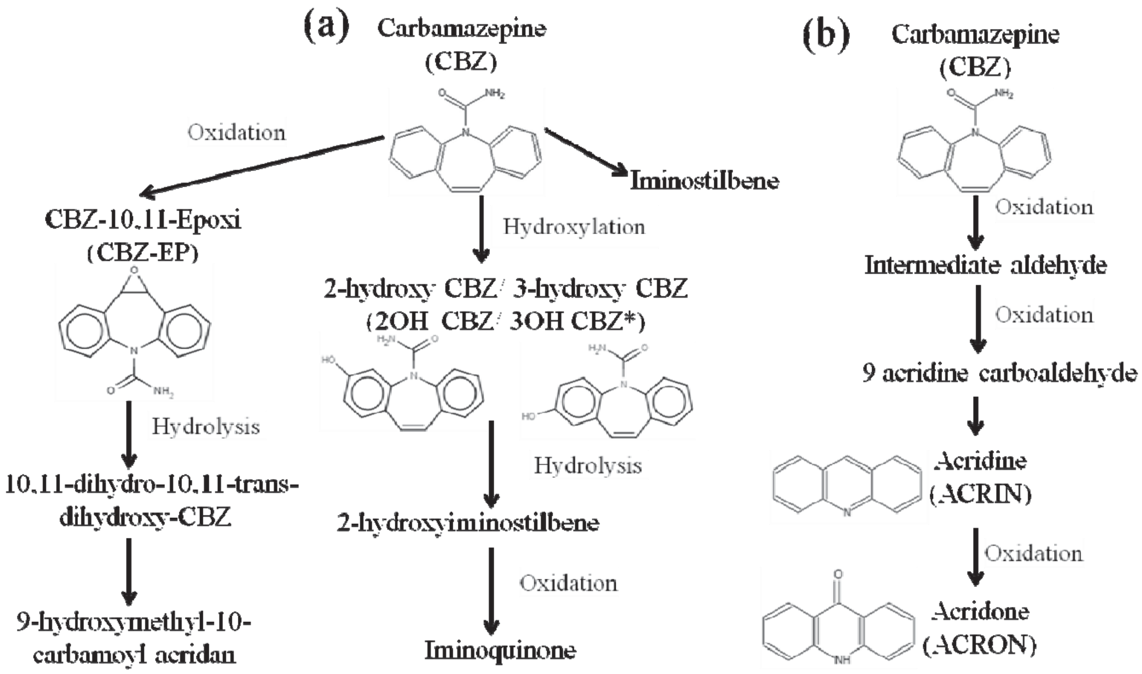


Figure 4.1. (a) Hepatic metabolism pathway of CBZ and **(b)** CBZ oxidation by leucocytes based on Breton et al. (2005). Note the chemical structures of the target compounds are included (CBZ, 3OH CBZ, 2OH CBZ, CBZ EP, ACRIN and ACRON). * The pathway of 3OH CBZ is not presented.

Most research into CBZ and its metabolites has been focused on wastewater. Researchers studied the most successful methods, such as UV irradiation, ozination and active sludge treatment, to remove them from wastewater influents and/or from raw waters used as source for abstraction of tap water (Kosjek et al., 2009; Lekkerkerker-Teunissen et al., 2012). High rates of removal have been observed by ozonation (Vieno et al., 2007; Hübner et al., 2012) and by UV/H_2O_2 induced photolytic degradation (Vogna et al., 2004) compared with the conventional biological wastewater treatment. However, these water treatment technologies may result in the formation of toxic by products such as acridine (ACRIN), which is as a mutagenic and carcinogenic compound (Chiron et al., 2006). CBZ levels have also been reported in surface waters (Vieno et al., 2006; Zhou et al., 2010; Nödler et al., 2011; Valcarcel et al., 2011). In groundwater, CBZ has been studied in bank filtration sites (Herberer et al., 2004; Massmann et al., 2008), artificial aquifer recharge (Drewes et al., 2003); and irrigated farms (Ternes et al., 2006; Chávez et al., 2011; Fenet et al., 2012), where river water receiving WWTPs effluents and large discharges of both treated or untreated waste water, has infiltrated the aquifer. CBZ is one of the most frequently detected pharmaceuticals in groundwater and at highest concentrations (Sacher et al., 2001;

Rabiet et al., 2006; Osenbrück et al., 2007; Loos et al., 2010; Chavez et al., 2011; Vulliet and Cren Ollivé, 2011; Fenet et al., 2012; Kuroda et al., 2012). Usually, measured CBZ concentrations in groundwater were of about 100 ng/L (Fenz et al., 2005; Teijon et al., 2010; Kuroda et al., 2012) although it has been detected at concentrations up to 2100 ng/L in an aquifer highly affected by sewage water discharge (Müller et al., 2012). In fact; several authors have proposed CBZ as an anthropogenic marker in aquatic environments because of its persistence (Clara et al., 2004; Kahle et al., 2009; Wolf et al., 2012). Little research has been done on the occurrence of CBZ metabolites in groundwater (Kahle *et al.,* 2009; Fenet *et al.,* 2012) and, specifically, there is a lack of works concerning the fate of CBZ metabolites in urban groundwater.

The objective of this study is to investigate the fate of CBZ and its metabolites in urban groundwater at a field scale under different redox conditions in connection with (1) the physicochemical properties of the target compounds, (2) the occurrence of common contaminants in urban groundwater of Barcelona and (3) the groundwater redox conditions. To this end, groundwater samples have been collected in two distinct zones of Barcelona city: (1) Poble Sec and (2) Besòs River Delta in May 2010

4.2 Materials and methods

4.2.1 Site description

The study area includes Barcelona and part of its metropolitan area in north-eastern Spain. The area is located between the Serra de Collserola (Catalan coastal ranges) and the Mediterranean Sea (Figure 4.2), both boundaries running approximately NNE–SSW. Other boundaries are constituted by two rivers, the Llobregat (SW) and the Besòs (NE). The climate is typically Mediterranean with an average rainfall of 600 mm per year. Currently, groundwater is used for secondary uses such as street cleaning and irrigation green areas. But it can be considered as an alternative tap water resource since there are several aquifers, characterized by their geological age, below the city (Figure 4.2). The Palaeozoic aquifer crops out at topographic highs to the NW, which consist of shales and granites. Quaternary and Tertiary aquifers can be found in the rest of the city. In 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 and coarse alluvial sediments. From the geological point of view, Poble Sec is located in the Barcelona Plain made up of carbonated clays. Below the Quaternary, the Tertiary (Miocene) is present. Miocene is made up of sandstones, marls and sandy

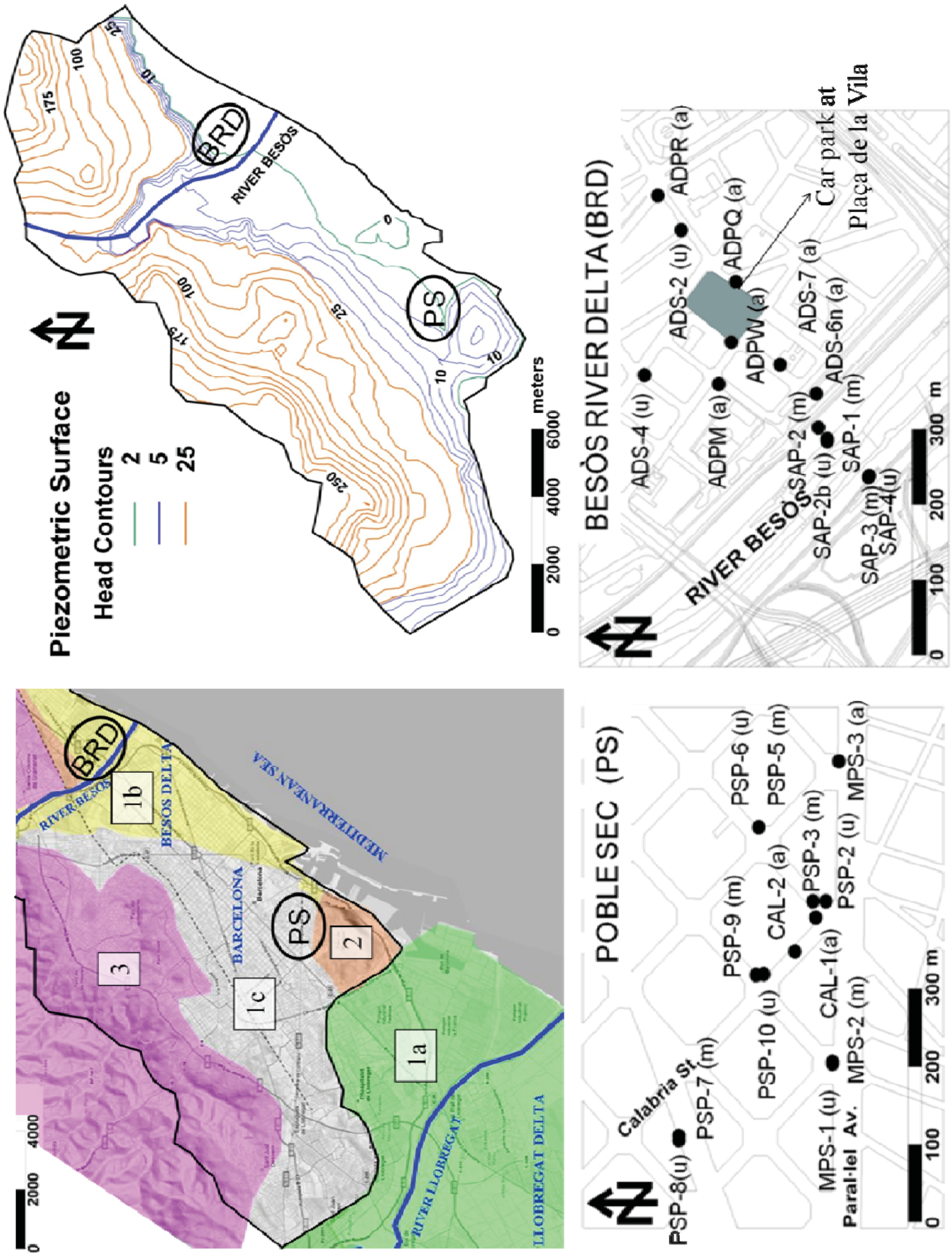


Figure 4.2. On the left, schematic description of the hydrogeology of Barcelona: (1a) Llobregat Delta made up of gravels, sands, silts and clays (Holocene, Quaternary), (1b) Besòs Delta composed of gravels, sands, silts and clays (Holocene, Quaternary), (1c) Barcelona Plain consisting of carbonated clays (Pleistocene, Quaternary), (2) Barcelona Plain made up of marls, sandstones and sands (Tertiary) and (3) Collserola Range consisting of shale and granites (Palaeozoic). On the right, a piezometric map of the study area, which is divided into two distinct zones: Poble Sec and Besòs River Delta. The contour intervals are 2 m (continuous green line), for heads ranging from 5 to below 25 m (continuous blue line) and 25 m above (continuous orange line). At the bottom, observation points on each zone, including the depth of the screen: (u) upper, (m) middle, (l) lower and (a) totally screened

gravels. The Besòs River Delta is located in the Quaternary Besòs Delta, which is bordered by the River Besòs and is close to the underground car park at the Plaça de la Vila site (Figure 4.2). The river flow is heavily dependent on seasonal rainfall. Groundwater flows generally from the River Besòs to the car park since there is a continuous pumping of about 150 l/s to avoid seepage problems. The basement is made of Palaeozoic granites and Cenozoic units, which consists of Miocene matrix-rich gravels and Pliocene grey marls. The fluvio-deltaic sediments of the Besòs Delta Complex are placed on the top of this basement, including 3 aquifers composed of sandy and gravelly bodies separated by lutitic units (Velasco *et al.,* 2012).

Several recharge sources have been identified in the aquifers of Barcelona (Vazquez-Suñe *et al.,* 2010): (1) River Besòs (RIV), (2) rainfall recharge in northern non urban area (REC), (3) Ter river water supply (TER), (4) Llobregat river water supply (LLOB), (5) Ter river sewage water (SW T), (6) Llobregat river sewage water (SW LL), (7) City runoff (RUNOFF), and (8) Sea water intrusion (SEA). Direct rainfall recharge occurs in the non-urbanized areas in the Collserola Range. Seawater intrusion and water from the heavily polluted River Besòs must be considered potential recharge sources in low areas. Additional sources of groundwater recharge can be attributed to anthropogenic activities related to city development including loss from the water supply network. Barcelona is supplied with water from the Rivers Ter and Llobregat. This gives rise to a division of the city into two zones with a different water quality and hence two different chemical compositions can be found in waste water. Finally, in paved areas, runoff water washes the road and atmospheric deposition, and recharges the aquifers through direct infiltration or sewer loss.

The aforementioned division of the water quality can be observed comparing some of the major and minor ions concentrations and some redox indicators in both Poble Sec and Besòs River Delta aquifers. Table 4.1 summarized the average concentrations (mg/L) and standard deviations of chloride, sulphate, bicarbonate, sodium, calcium, magnesium, nitrate, ammonium, dissolved oxygen and total organic carbon of the groundwater samples collected in May 2010. Overall, Besòs River Delta groundwater is less mineralised than Poble Sec since the average concentrations of chloride, sulphate, calcium, magnesium, nitrate and dissolved are much lower in (Table 4.1). Both zones presented neutral pHs. Some redox indicators such as the high levels of dissolved oxygen and nitrate (on average 4 mg/L, and 95.7 mg/L, respectively) and the low or null levels of ammonium (on average 0.03 mg/L), have evidenced the oxidizing conditions of the groundwater. Conversely, reducing conditions into groundwater have been suggested by the low levels of dissolved oxygen and nitrate (on average 1.5 mg/L, and 4.4 mg/L, respectively) and the presence of ammonium (4.3 mg/L, on average).

Average concentration± STD (mg/L)	**Poble Sec (n=13)**	**Besòs River Delta (n=13)**
Cl^-	296.8±23.3	195.8±17.7
SO_4^{2-}	277.9±23.6	147.9±12.8
HCO_3^-	349.1±23.5	402.8±19.5
Na^+	152.8±21.5	157.1±14
Ca^{2+}	208.3±10.3	125.8±8.9
Mg^{2+}	69±8.1	27.5±1.6
NO_3^-	95.7±19.7	3.3±7.7
NH_4^+	2.5E-2±3.3E-2	4.3±1.6
O_2	4±1.3	1.2±0.5
TOC	1±0.2	3.1±0.7
pH	7.2±0.1	7.4±0.2

Table 4.1. Average concentration (mg/L) and standard deviation of selected species measured in Poble Sec and Besòs River Delta aquifers in May 2010.

4.2.2 Sampling

Twenty-seven groundwater samples were collected in May 2010. One sample was obtained from the River Besòs and twenty-six samples were collected from groundwater: 17 from observation points and 9 from pumping wells. The location of the wells and the observation points and the screen depths are displayed in Figure 4.2 (Table S2, Supplementary material Annex I). Samples were collected in three different zones of the study area: (1) Poble Sec (PS) and (2) Besòs River Delta (BRD), where groundwater comes mainly from the river. All the groundwater samples were obtained after pumping a volume of at least three times that of the sampling point. Field parameters measured in situ included electric conductivity, pH, temperature, Eh and dissolved oxygen. They were measured continuously using a flow cell to avoid contact with the air. The instruments were calibrated daily by means of standard solutions. Samples were collected after stabilization of field parameters and were not filtered in the field. Instead, they were stored in a field refrigerator and taken to the laboratory at the end of the sampling day. Samples were stored in polyethylene terephthalate (PET) containers that were amber in colour to avoid photo degradation.

4.2.3 Target analytes

The selected target compounds are CBZ and 5 metabolites named as 2OH CBZ, 3OH CBZ, CBZ-EP, ACRON and ACRIN. Their chemical structures and the physicochemical properties are summarized in Figure 4.1 and Table 4.2, respectively. The chemical characteristics of the analyzed compounds were calculated using different software: Sparc on-line calculator version 4.6 (Sparc, 2011), ACD/I-Lab 2.0 software (ACD/Labs, 1996-2013) and ChemAxon Marvin Calulater Plug in (ChemAxon, 2007).

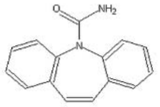
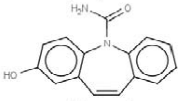
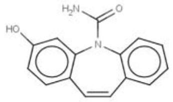
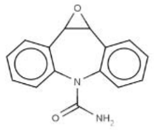
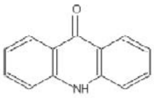
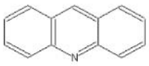
Pharmaceutical	CAS	Formula	Log K_{ow}	LogD_{ow} *	pK_a	Charge pH = 7	Charge pH = 8	Molecular structure
Carbamazepine (CBZ)	298-46-4	$C_{15}H_{12}N_2O$	3.64 ^{a} 2.67 ^{b} 2.77 ^{c}	3.64 ^{a} 2.67 ^{b} 2.77 ^{c}	n.e ^{a,c} pK_{a1} ^{b} = 0.1 pK_{a2} ^{b} =14.3	Neutral ^{a,b,c}	Neutral ^{a,b,c}	
3 OH carbamazepine (3OH CBZ)	68011-67-6	$C_{15}H_{12}N_2O_2$	3.45 ^{a} 2.46 ^{c}	3.37 ^{a} 2.46 ^{c}	8.2 ^{a} 9.19 ^{c}	Neutral ^{a,c}	Neu/Neg ^{a} (0.613/0.387) Neutral ^{c}	
2 OH carbamazepine (2OH CBZ)	68011-66-5	$C_{15}H_{12}N_2O_2$	3.45 ^{a} 2.46 ^{c}	3.42 ^{a} 2.46 ^{c}	8.69 ^{a} 9.15 ^{c}	Neutral ^{a,c}	Neu/Neg ^{a} (0.83/0.17) Neutral ^{c}	
10,11-epoxi carbamazepine (CBZ-EP)	36507-30-9	$C_{15}H_{12}N_2O_2$	2.61 ^{a} 1.97 ^{c}	2.61 ^{a} 1.97 ^{c}	n.e ^{a,c}	Neutral ^{a,c}	Neutral ^{a,c}	
Acridone (ACRON)	578-95-0	$C_{13}H_9NO$	2.79 ^{a} 2.57 ^{b} n.e ^{c}	2.79 ^{a} 2.57 ^{b} n.e ^{c}	n.e ^{a,c} pK_{a1} ^{b} = 0.8 pK_{a2} ^{b} =11.1	Neutral ^{a,b,c}	Neutral ^{a,b,c}	
Acridine (ACRIN)	260-94-6	$C_{13}H_9N$	3.3 ^{a} 3.42 ^{b} 3.51 ^{c}	3.30 ^{a} 3.42 ^{b} 3.49 ^{c}	4.93 ^{a} 5.6 ^{b} 6.15 ^{c}	Neutral ^{a,b} Neu/Pos ^{c} (0.88/0.12)	Neutral ^{a,b,c}	

Table 4.2. Physico-chemical properties of the target compounds analyzed in groundwater samples. “n.e.”: non evaluated and “*”: log D_{ow} calculated at pH=7.5.

^{a} Sparc predicted values (Sparc, 2011).

^{b} ACD/I-Lab predicted values calculated using Advanced Chemistry Development software (ACD/Labs, 1996-2013).

^{c} ChemAxon predicted values calculated using ChemAxon Marvin Calulater Plug in (ChemAxon, 2007).

4.2.4 Analytical methods

Analysis of the target compounds in the collected groundwater samples was carried out by on-online Solid Phase Extraction – Liquid Chromatography – electrospray – tandem Mass Spectrometry (SPE-LC-ESI-MS/MS) following a methodology previously described by the authors (López-Serna et al., 2010), readily adapted for the analysis of the metabolites (López-Serna et al., 2012b). In this method, samples (spiked with surrogate standards), aqueous calibration solutions are analyzed in a fully online automated way with the aid of a Symbiosis Pico system (Spark Holland, Emmen, The Netherlands) coupled with the LC-MS/MS system. The analytical procedure consisted of two sample injections, both of 2.5 mL in the positive and negative electrospray mode (ESI pos and ESI neg, respectively). In every injection, the sample is preconcentrated onto previously conditioned polymeric HySphere Resin GP cartridges from Spark Holland (Emmen, The Netherlands) and after washing of the cartridges with HPLC water, the retained compounds are eluted to the LC-MS/MS system with the chromatographic mobile phase, which consists of a gradient of ACN/0.1% (v/v) formic acid for ESI pos and a gradient of ACN:MeOH (1:1, v/v)/H_2O for ESI neg. Chromatographic separation is carried out in the end-capped analytical column Purospher Star RP-18 (125x2 mm. particle size 5 µm) from Merck (Darmstadt, Germany). Detection is performed in both modes recording two selected reaction monitoring (SRM) transitions per analyte and one SRM per surrogate by a 4000QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer equipped with a Turbo Ion Spray source from Applied Biosystems-Sciex (Foster City, California, USA). Quantitation, based on peak areas, is carried out by internal standard approach. This method allows the determination of compounds at concentrations of 0.3- 4.10 ng/L (i.e., the quantification limits) to 500 ng/L, with satisfactory precision and accuracy for all the compounds.

(a) Poble Sec

Compound	**Frequency of detection(%) n=13**	**Concentration (ng/L)**	
		Average±STD	Max
CBZ	92	7.1±7.1	17.8 (MPS-1)
3OH CBZ	0	-	-
2OH CBZ	0	-	-
CBZ-EP	8	0.11±0.39	1.4 (PSP-6)
ACRON	15	0.18±0.45	1.4 (PSP-2)
ACRIN	23	2.3±4.9	15.8 (PSP-3)

(b) Besòs River Delta

Compound	**Frequency of detection(%) n=13**	**Concentration (ng/L)**			
		Average±STD	Max	River Besòs	
				Wet	Dry*
CBZ	100	115.4±11.8	136 (ADS-7)	57.7	163.5
3OH CBZ	85	18.8±12.2	39.9 (SAP-2b)	17.3	49
2OH CBZ	92	27.8±14.4	47.9 (SAP-4)	27.1	76.8
CBZ-EP	69	2.9±2.9	8.4 (SAP-4)	13.9	39.4
ACRON	77	3±2.9	8.2 (ADS-7)	0	0
ACRIN	15	1.2±3.1	10.7 (SAP-4)	0	0

Table 4.3. Frequency of detection (%) and average and maximum concentrations (ng/L) of carbamazepine, metabolites and transformation products measured in urban groundwater of (3a) Poble Sec and (3b) Besòs River Delta. Note the River Besòs collected sample is also include. "*": expected concentrations.

4.3 Results

The average concentrations and the maximum levels of the target compounds measured in groundwater samples and their frequency of detection at each zone are summarized in Table 4.3. Figure 4.3 shows the measured concentrations for the parent compound CBZ and its metabolites (3OH CBZ, 2OH CBZ, CBZ-EP, ACRON and ACRIN). Note that concentrations at Besòs River Delta were, on average, one order of magnitude higher than Poble Sec ones (Figure 4.3). The most commonly detected drug was the parent compound CBZ in both zones. Despite the ubiquity of CBZ in both zones, it was present at lower concentrations in Poble Sec than Besòs River Delta aquifers (on average, 7.1 and 115.4 ng/L, respectively). Target compound concentrations of each zone are summarized in Table S3 (Annex I).

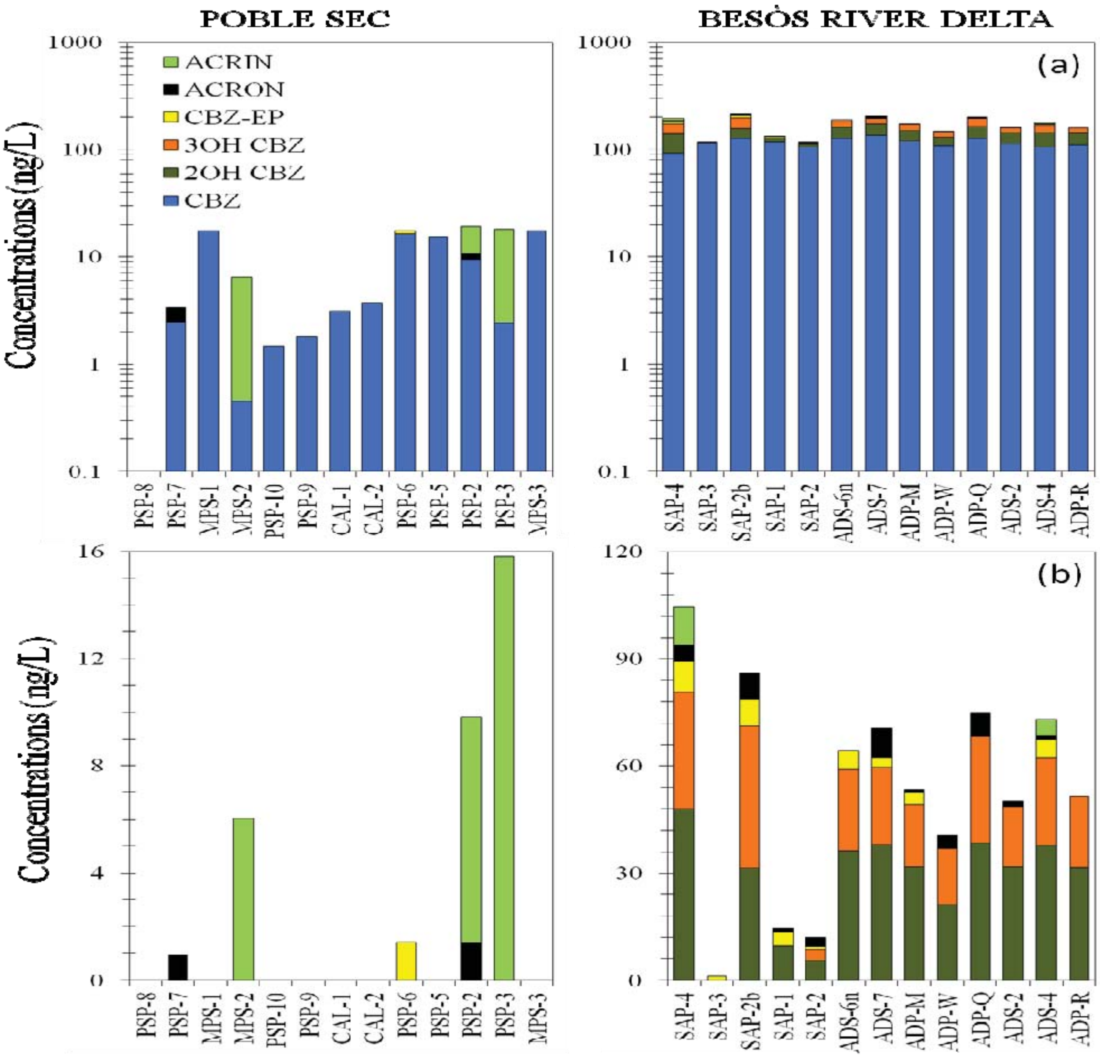


Figure 4.3. Concentrations (ng/L) of **(a)** carbamazepine (CBZ) and its metabolites (2OH CBZ, 3OH CBZ, CBZ-EP, ACRON and ACRIN) **(b)** only metabolites in Poble Sec (left) and Besòs River Delta (right) aquifers.

Poble Sec

No groundwater sample contained all the compounds. Two out of the 6 target compounds, namely 3OH CBZ and 2OH CBZ, were not detected in any sample. The most detected compound was CBZ with a detection frequency of 92%. The remaining compounds, CBZ-EP, ACRIN and ACRON, were detected in less than 25% of the samples. The highest concentrations corresponded to CBZ (17.8 ng/L at MPS-3) and ACRIN (15.8 ng/L at PSP-3).

Besòs River Delta

Since the River Besòs receives a large proportion of effluents from secondary WWTPs, all target compounds were identified at least in two groundwater samples. The compounds identified in descending order were: CBZ>2OH CBZ>3OH CBZ>ACRON>CBZ-EP>ACRIN (Table 4.3a). CBZ was present in all the samples collect and did not vary significantly in the aquifer, ranging from 92.2 to 136 ng/L. In contrast to Poble Sec, the metabolites 3OH CBZ, 2OH CBZ and CBZ-EP were widely detected (85%, 92% and 69% respectively). Both 3OH CBZ and 2OH CBZ were found at significant levels in the shallow part of the aquifer near the river (between 31.4 and 47.9 ng/L) but were null or insignificant in the deeper one (Figure 4.1). ACRON was found at lower levels and presented an average concentration of 3 ng/L. The highest concentrations corresponded to CBZ (136 ng/L at ADS-7), 2OH CBZ (47.9 ng/L at SAP-4) and 3OH CBZ (39.9 ng/L at SAP-2b).

4.4 Fate of CBZ and its metabolites in urban groundwater

The occurrence of the target compounds in aquifers is affected by their concentrations in the recharge sources and by the different processes that may occurre in the aquifers such as mixing, dilution, adsorption and/ or degradation. The widespread presence of CBZ in aquifers enhanced the need to understand its fate in groundwater. The fate of CBZ and its metabolites depend both on the physicochemical properties of the compound but also on the redox conditions of the aquifer. Mobility of a given compound tends to be controlled by the physicochemical properties and its degradability by the redox conditions of the aquifer.

4.4.1 Physicochemical properties of the target compounds

Among the chemical properties summarized in Table 4.2, the octanol-water coefficient (K_{ow}) is usually used to predict the behavior of the target compounds in the environment. It is usually expressed as log K_{ow} and it measures how hydrophobic (log K_{ow} >4) or hydrophilic (log K_{ow} <4) a compound is. Hydrophobic compounds usually have high adsorption capacity especially onto organic matter (Choi *et al.,* 2005a). However, in complex natural systems as aquifers, there are other relevant parameters, such as water pH, that control the proportion of ionized and nonionized forms for a given compound. Consequently, K_{ow} may not be the most suitable parameter to properly predict the fate of the target compounds in environmental conditions (Kwon and Armbrust, 2008). Wells, (2006) emphasised the need to considering chemical ionogenicity and proposed D_{ow} (the pH dependent octanol–water distribution ratio), which is a combination of K_{ow} and pK_a, as a more appropriate physicochemical parameter to understand the mobility of a compound in environmentally relevant pH conditions. In this work, log D_{ow} have been used to identify the ionizable functional groups of the target compounds at pH between 7 and 8 since all groundwater samples collected are in this range of pH (Table 4.1).

Based on the aforementioned properties it is possible to assess the mobility of the target compounds in the aquifer. CBZ is a moderate polar compound which has a pK_a of 14.3 related to the deprotonation of the NH_2 group and a pK_a<1 related to the protonation of the amino groups. This means CBZ is present in its neutral form in the groundwater environment because it does not contain ionizable functional groups at pHs between 7 and 8. As for carbamazepine metabolites, neutral molecules also dominate at groundwater pHs. Only low proportions of 2OH CBZ and 3OH CBZ might be present in their anionic form when their pK_a*s* are 8.69 and 8.2, respectively (Sparc, 2011) (Table 4.2). These anionic species correspond to the deprotonation of the hydroxyl group of the 2OH CBZ and 3OH CBZ and minor changes in *log* D_{ow} values can be observed with respect to *log* K_{ow}. Regarding ACRIN and ACRON, they both may exist as a neutral form at pHs of studied aquifers. According to Chemaxon (2007), the protonated specie of ACRIN might be present in groundwater at pH 7 when pK_a is 6.15.

To sum up, the investigated compounds can be mainly found in groundwater as neutral molecules. This might indicate that these compounds do not interact with the negative charged minerals in aquifer materials. Also their log K_{ow} values suggest a hydrophilic character and these compounds are not expected to be sorbed onto soils. However, their sorption behavior is highly dependent on factors such as the soil's organic matter content but several studies highlighted that CBZ is not extensively adsorbed onto soils (Clara et al., 2004; Yu et al., 2009; Calisto and Esteves, 2012).

These properties might indicate that CBZ and its metabolites can be highly persistent in aquifers.

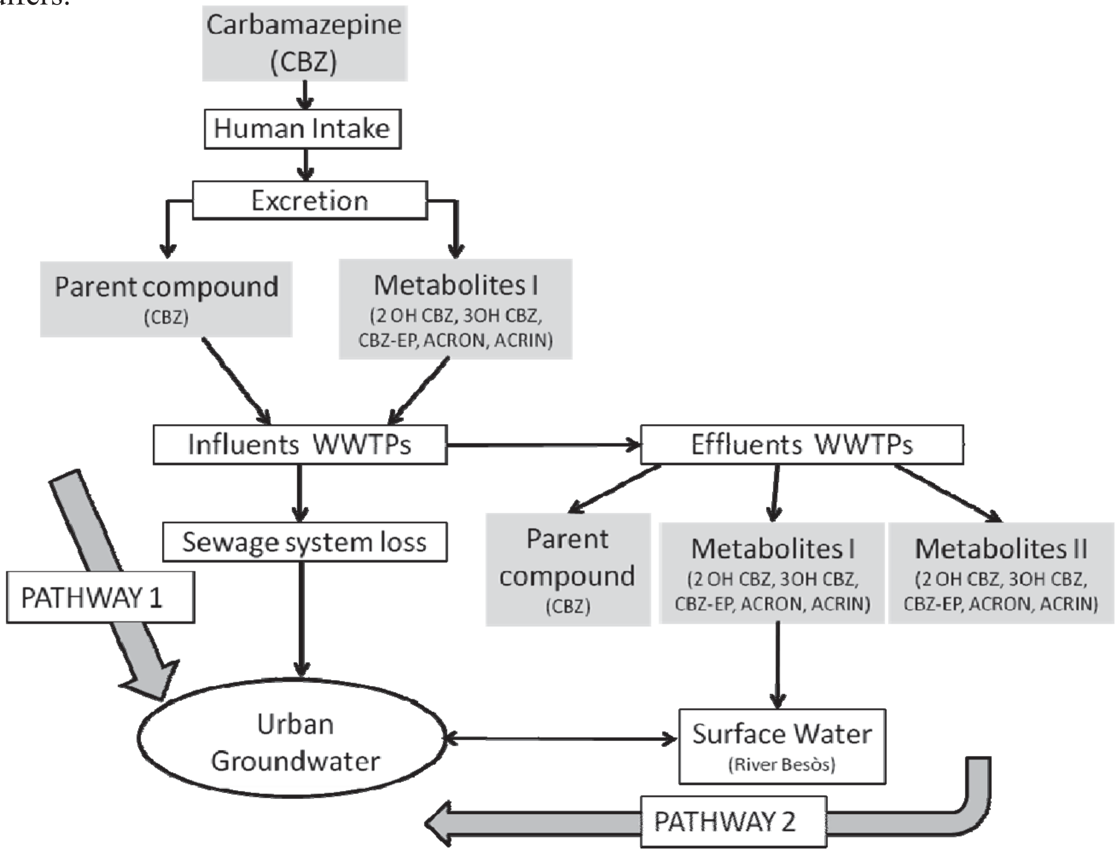
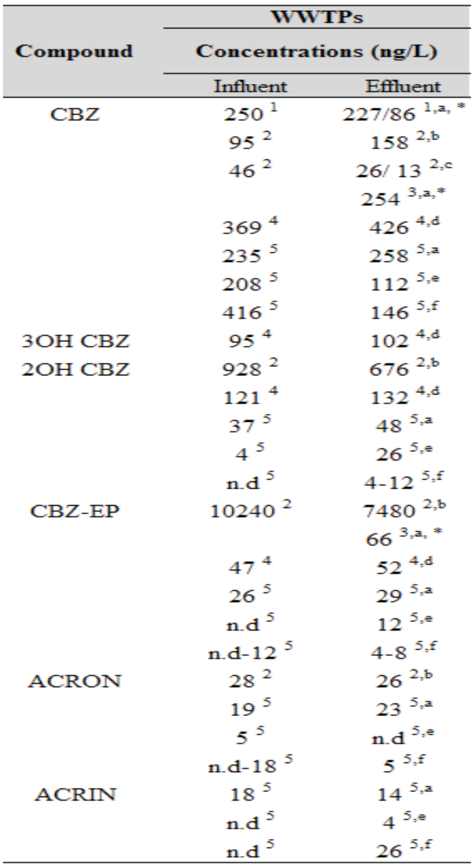


Figure 4.4. Main pathways of CBZ and its metabolites in the urban aquifers of Poble Sec (pathway 1) and Besòs River (pathway 2).

4.4.2 Occurrence of the target compounds related to generic pollution in Poble Sec and Besòs River Delta aquifers

The occurrence of the target compounds in aquifers depends on the concentrations in the recharge sources. A previous work performed by Jurado *et al.* (2012a) evaluated the proportion in which the aforementioned sources (see section 4.2.1) contributed to both Poble Sec and Besòs River Delta aquifers' recharge. In Poble Sec, the main contributor to the resident water was network sewage loss (50%, SW LL) followed by water supply loss (46%, LL). The remaining 4% corresponded to clean water recharge flowing from northern non urban area. Concerning the Besòs River Delta, River Besòs (RIV) was by far the largest contributor to the resident water, representing 91%. It is worth mentioning that River Besòs receives large amounts of effluents from WWTPs. Other contributors to the recharge were network sewage (6%, SW T) and water supply loss (3%, T). Figure 4.4 shows the potential sources of contamination of CBZ and its metabolites in the aquifers of Poble Sec (pathway 1,

Figure 4.4) and Besòs River Delta aquifers (pathway 2, Figure 4.4). In fact, the occurrence of CBZ and its metabolites have been widely reported in influents and effluents of WWTPs (Table 4.4). Levels detected are usually at low ng/L and only CBZ-EP has been detected at µg/L concentrations (Gros et al., 2012). Most of the target compounds are barely or not at all removed and the removal efficiency depends on the waste water treatment, being tertiary treatment combined with other technologies (UV disinfection) most effective (Lecquer et al., 2008; Teijon et al., 2010). It is interesting to note that some metabolites such as CBZ-EP and 2OH CBZ have been detected at higher concentrations than the parent compound CBZ (Miao and Metcalfe, 2003; Gros et al., 2012).



Compound	WWTPs	
	Concentrations (ng/L)	
	Influent	Effluent
CBZ	250 [1]	227/86 [1,a, *]
	95 [2]	158 [2,b]
	46 [2]	26/ 13 [2,c]
		254 [3,a,*]
	369 [4]	426 [4,d]
	235 [5]	258 [5,a]
	208 [5]	112 [5,e]
	416 [5]	146 [5,f]
3OH CBZ	95 [4]	102 [4,d]
2OH CBZ	928 [2]	676 [2,b]
	121 [4]	132 [4,d]
	37 [5]	48 [5,a]
	4 [5]	26 [5,e]
	n.d [5]	4-12 [5,f]
CBZ-EP	10240 [2]	7480 [2,b]
		66 [3,a, *]
	47 [4]	52 [4,d]
	26 [5]	29 [5,a]
	n.d [5]	12 [5,e]
	n.d-12 [5]	4-8 [5,f]
ACRON	28 [2]	26 [2,b]
	19 [5]	23 [5,a]
	5 [5]	n.d [5,e]
	n.d-18 [5]	5 [5,f]
ACRIN	18 [5]	14 [5,a]
	n.d [5]	4 [5,e]
	n.d [5]	26 [5,f]

Table 4.4. Average concentrations of CBZ and its metabolites in influents and effluents of wastewater treatment plants (WWTP).”n.d.”: non-detected and “*”: samples from the city of Barcelona. References: [1] Teijon et al. (2010); [2] Gros et al. (2012); [3] Martinez-Bueno et al. (2012); [4] Miao and Metcalfe (2003) and [5] Leclercq et al. (2008). Letter subscripts indicate the different WWTPs treatments: [a] Tertiary/Ultrafiltration+reverse osmosis+UV disinfection, [b] Secondary with conventional active sludge, [c] Secondary/Tertiary+UV disinfection, [d] Secondary+chlorine disinfection, [e] Trickling filter+posttertiary pond and [f] Waste stabilization ponds (depths 1.4-3.1 m).

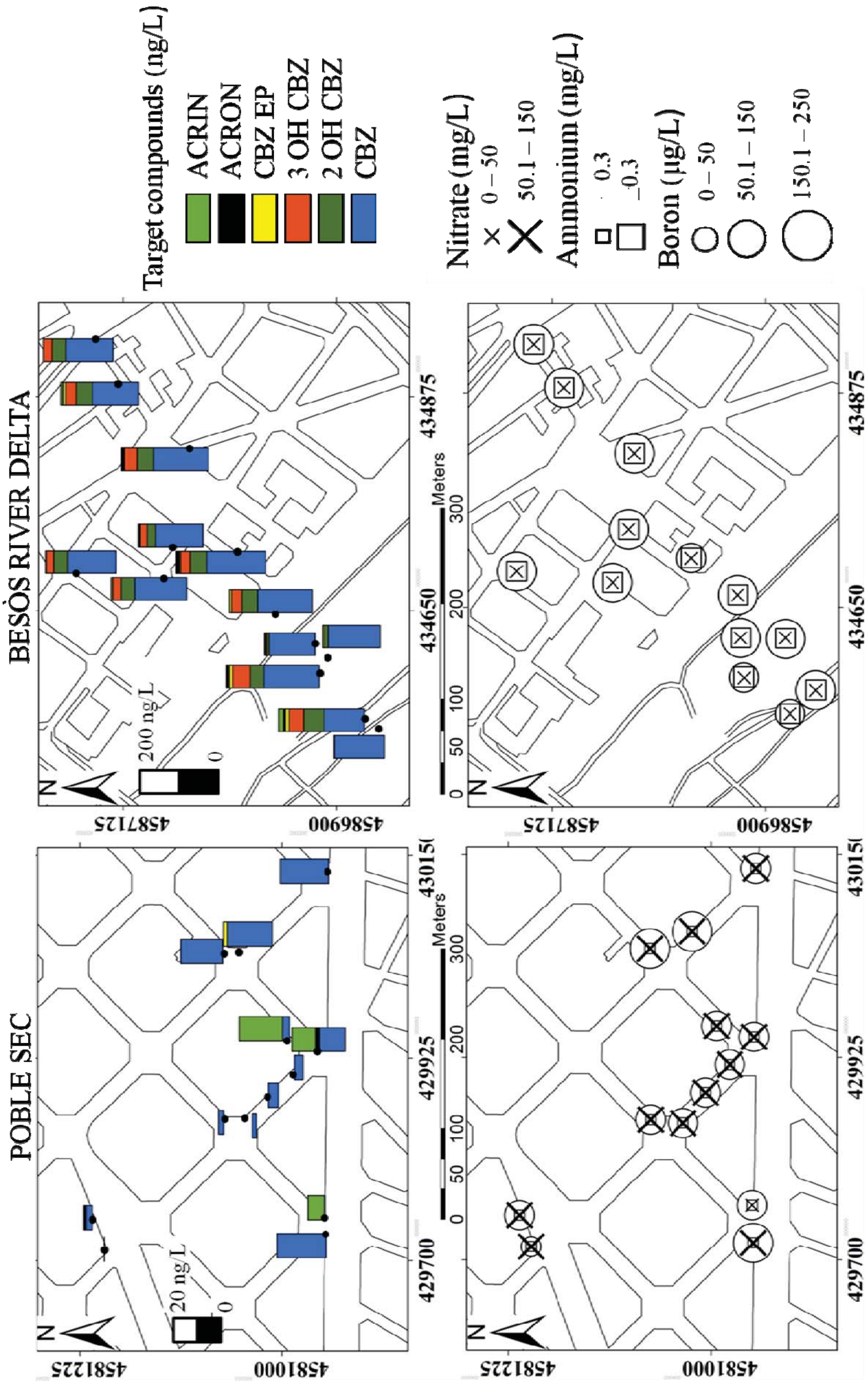


Figure 4.5. Spatial distribution of the six target compounds, ammonium, nitrate and boron in Poble Sec and Besòs River Delta aquifers.

The discussion of the occurrence of the target compounds in groundwater samples has been addressed with some of the main tracer species of waste water such as nitrate, ammonium and boron (Barrett et al., 1999; Rabiet et al., 2006; Trowsdale and Lerner 2006; Wolf *et al.,* 2012). The spatial distribution for selected generic contaminants and the target compounds is shown in Figure 4.5. Poble Sec groundwater has high levels of nitrate and low or null levels of ammonium. Twelve out of 13 samples have exceeded 50 mg/L of nitrate concentrations. Conversely, Besòs River Delta groundwater presented low nitrate levels and ammonium was present in significant concentrations. All groundwater samples exceed 1.5 mg/L of ammonium.

Overall, CBZ concentrations have been in good agreement with boron concentrations in Poble Sec groundwater (Figure 4.5). The highest boron concentrations have correlated with high CBZ concentrations. Therefore, the occurrence of CBZ and some of its metabolites in Poble Sec aquifers might be mainly related to network sewage loss since it has been detected in influents of WWTPs in Barcelona (Table 4.4). This trend has not been observed in Besòs River Delta (Figure 4.5). In this area, the highest concentrations and the largest number of detected target compounds can be attributed to their inefficient removal in WWTPs, whose effluents are directly discharged in the river. In both zones, groundwater concentrations of the target compounds were always lower than the reported values in WWTPs (Table 4.4), suggesting some removal processes that may occur in the aquifer.

4.4.3 Redox conditions of the aquifers

Usually, organic compounds may be naturally removed from groundwater, especially if this water has undergone a wide range of redox states (Christensen et al., 2001). However, CBZ and some of their metabolites seem to be highly persistent because it occurred in both, oxic and reducing conditions in Barcelona aquifers.

Poble Sec

As commented before, half of the groundwater recharge in the Poble Sec area comes from loss of raw sewage water networks (influents of WWTPs, Figure 4.6). Considering an average CBZ concentration of 200-250 ng/L from WWTPs influents (Teijon et al., 2010) (Table 4.4), expected concentrations of CBZ in the aquifer should be in the range of 100-125 ng/L. However, these expected concentrations are much higher than the measured values of CBZ in groundwater samples. This observation suggests that CBZ may be degraded due to removal processes (i.e. mixing and redox processes) that may have occurred: (1) in the unsaturated zone and/or under the oxic conditions of Poble Sec groundwater (Figure 4.6). Regarding CBZ metabolites, they did not contribute to groundwater contamination because they were poorly detected. Two observations can be made: (1) metabolites were present at groundwater but at concentrations below the limit of detection/quantification and (2) metabolites could be naturally removed in the aquifer and/or in the unsaturated zone. The discussion of the second observation would be better carried out having a sample from influents of Llobregat WWTPs. But these compounds have been reported in influents of WWTPs, on average, at low ng/L levels (Table 4.4). Therefore, this observation might support the view that CBZ metabolites are susceptible to chemical processes that result in their removal under oxic conditions. It is important to mention that ACRIN was found at high levels than the parent compound CBZ in two observation points (MSP-2 and PSP-3). Consequently, further research is needed to investigate the fate CBZ and its metabolites.

Besòs River Delta

Recharge in this area comes basically from the River Besòs (Figure 4.6). Therefore, understanding the interaction between river water and groundwater is a key point to assess the fate of the studied compounds in the aquifer. Natural attenuation capacity may occur in aquifers due to physical and biochemical processes (Jurado el al., 2012b). Groundwater in Besòs River Delta has a more reducing character than Poble Sec because redox processes such as aerobic respiration and denitrification could occur when river water infiltrates the aquifer. Nitrate and dissolved oxygen concentrations can reach, respectively, levels of 15 and 8 mg/L at River Besòs but measured concentrations are drastically reduced to null or low levels in the aquifer, supporting the occurrence of the aforementioned processes. However, average measured concentrations in the aquifer for CBZ, ACRIN and ACRON were higher than those measured in the river and similar for 2OH CBZ and 3OH CBZ. Only CBZ-EP presented lower concentrations in the aquifer than in the river (Table 4.3b). It is important to mention that the River Besòs sample was collected during abundant rainfall events (wet season) and a dilution of the target compounds could have occurred. River Besòs flow regime is characterized by its variability, which is mainly dependent on the rainfall. The dry season’s concentrations can be evaluated using a dilution factor (*f*) (Jurado et al., 2012a):

$$f = Q_s/Q_d \qquad (1)$$

where Q_s is the flow rate on the day of sampling (Q_s = 8.5 m^3/s) and $Q_{d,}$ is the average flow rate in dry seasons ($Q_{d,}$ = 3 m^3/s). Table 4.3b shows that expected levels of these contaminants are higher in dry seasons (D). Therefore, this suggests that levels of

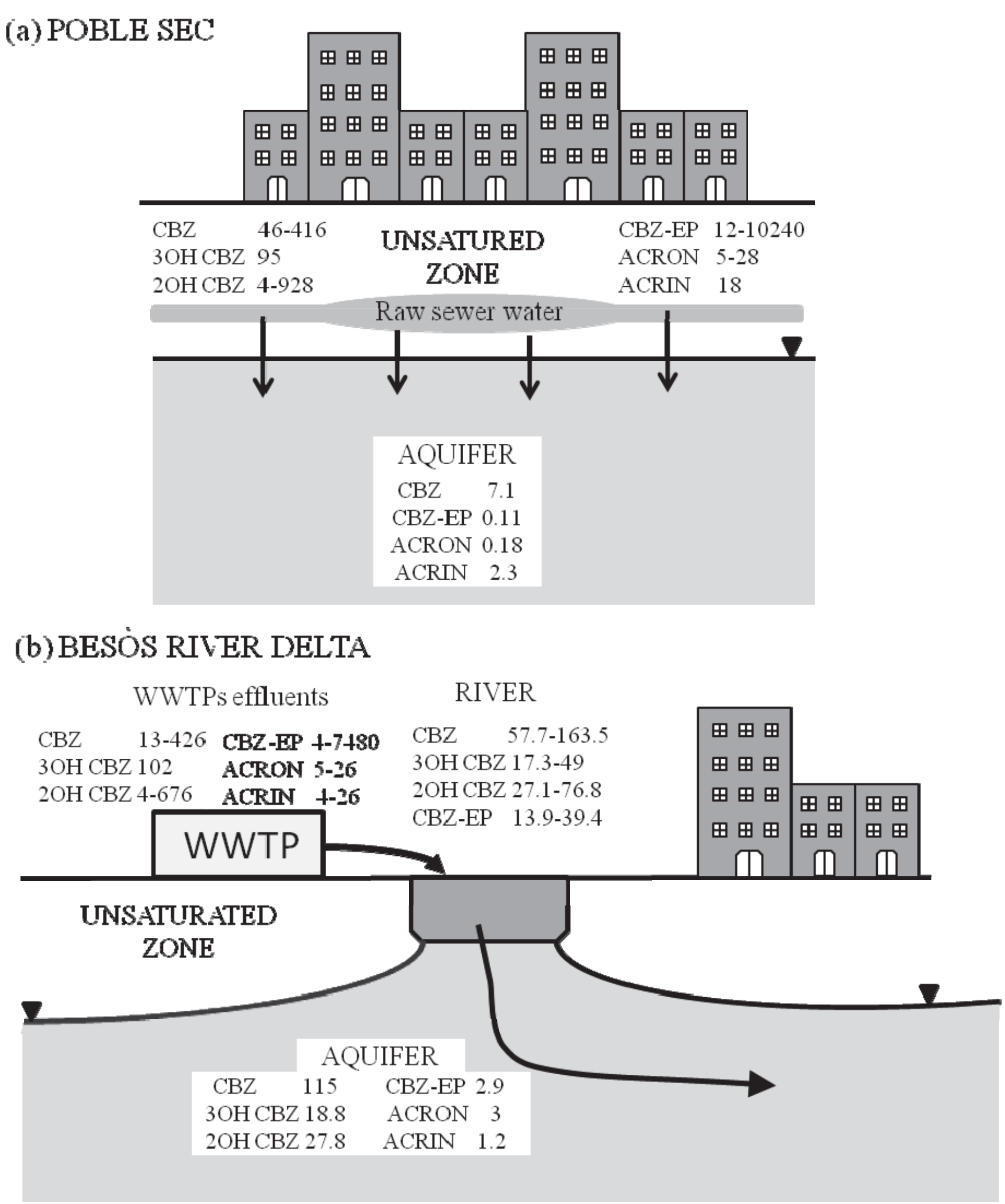


Figure 4.6. Concentrations of the target compounds (ng/L) in the recharge sources and in the aquifers of (a) Poble Sec and (b) Besòs River Delta.

CBZ and its metabolites in the aquifer might be higher than those measured in May 2010. In contrast to Poble Sec, CBZ seemed not to be degraded under the reducing conditions of Besòs River Delta groundwater because aquifer concentrations: (1) did not varied significantly in the observation points (ranging from 92 to 136 ng/L) and (2) presented similar values to those from the river (Figure 4.6). This trend was also observed for the metabolites 2OH CBZ and 3OH CBZ. Only the deepest observation points located near to the River Besòs, named as SAP-3, SAP-2 and SAP-1 (Figure 4.2), presented null or low levels of these metabolites (Figure 4.5). Also, the lowest levels of

TOC, oxygen and ammonium and, as the rest of observation points, null or low levels of nitrate were measured in these observation points in May 2010. This may suggest (1) long residence times in the deepest part of the aquifer and/or (2) that redox processes could remove 2OH CBZ and 3OH CBZ in the deepest observation points. Regarding CBZ-EP, the higher concentrations were detected in the observation points located near to the river and they progressively diminished following the flow lines to the pumping area. Therefore, CBZ-EP is found to be removed from groundwater. Although ACRIN and ACRON were not detected in the River Besòs, they have been reported in the effluents from WWTPs at concentrations of low ng/L. Therefore, they can be found in groundwater. Kosjek et al. (2009) found that ACRIN was susceptible to biological treatment with activated sludge (90% and 92% under anoxic and aerobic conditions, respectively) while ACRON was less efficiently removed (40 under aerobic comparing to 23% of anoxic removal. Whether these biological processes could be extrapolated to the environmental conditions of aquifer systems, this may indicate that ACRIN would be more easily biodegraded than ACRON. In fact, ACRIN and ACRON were detected in 15% and 77% of groundwater samples, respectively (4.3b).

To sum up, based on the data collected, CBZ, 2OH CBZ, 3OH CBZ and ACRON seem to be highly persistent in the redox conditions of Besòs River Delta groundwater. Only CBZ-EP seemed to be removed in the aquifer and also significant removal of 2OH CBZ and 3OH CBZ was found in the deepest observations points where the most strongly reducing conditions and the longest residence times occurred.

4.5 Conclusions

The following conclusions may be drawn from this study:

(1) The parent compound CBZ has been found in both Poble Sec and Besòs River Delta in high frequencies of detection but at Besòs River Delta the concentrations have been, on average, one order of magnitude higher.

(2) Metabolites of CBZ have been more widely detected and at higher concentrations in Besòs River Delta. This is due to the fact that the River Besòs receives large amounts of effluents from WWTPs that infiltrates the aquifer.

(3) CBZ and its metabolites are mainly present in its neutral form in Poble Sec and Besòs River Delta aquifers. This indicates that these compounds do not interact with the negatively charged minerals in aquifer materials and their log K_{ow} values suggest a

hydrophilic character. These properties might indicate that CBZ and its metabolites can be highly persistent in aquifers.

(4) CBZ seems to be more degraded under oxidizing conditions of Poble Sec because concentrations measured in groundwater have been lower than those expected from the recharge sources. Conversely, CBZ and the metabolites 3OH CBZ, 2OH CBZ and ACRON have been highly persistent under the reducing conditions of Besòs River Delta aquifers. Only CBZ-EP and ACRIN seemed to be removed into the aquifer.

(5) Concentrations of ACRIN have been found at higher concentrations than the parent compound CBZ in Poble Sec aquifers, highlighting that further research is needed to understand the fate of these compounds in the aquifers.

5. Using mixing ratios to quantify chemical reactions

5.1. Introduction

Ensuring good water quality is becoming a major challenge in urban areas. Urban aquifers may suffer pollution from different recharge sources such as water leakage from sewer and septic systems, seepage from rivers, seawater intrusion, and losses from water supply network among others. As a result, a wide range of organic pollutants are found in urban aquifers. Since these pollutants enter the groundwater environment through the aforementioned sources, their occurrence depends on the transport mechanisms as well as the chemical and biochemical processes that occurred simultaneously. Thus, a proper assessment of groundwater quality requires an understanding of all the processes that affects these pollutants, involving their quantification. However, the quantification of these processes is not an easy task.

In order to quantify such processes, modelling tools providing extensive biogeochemical capabilities are needed (Prommer *et al*., 2000). Reactive transport models describe the spatial and temporal evolution of a set of chemical species subject to transport phenomena and chemical reactions. In recent years, several numerical models have been suggested (Saaltink *et al*., 2004; Bea *et al*.,2009) and applied to leachate attenuation (Islam *et al*., 2001; Van Breukelen *et al*., 2004), pollution plumes (Brun and Engesgaard, 2002; Brun *et al*., 2002), microbially mediated reactions (Schäfer *et al*., 1998a and 1998b; Hunter *et al*., 1998; Tebes-Stevens *et al*., 1998; Wang and Papenguth., 2001), redox geochemistry (Keating and Bahr, 1998) and carbon cycle modelling cases (Greskowiak *et al*., 2005), among others. But their the performance demand previous hard work and effort since a reliable flow and conservative transport models are required, involving the management of much information to characterize in great detail the study zone. Hence, simpler approaches are needed.

Assuming that transport can be thought as mixing of different water types along a groundwater flow path in an aquifer, mixing calculations are an alternative to reactive transport models. Mixing calculations include: (1) End Member Mixing Analysis(EMMA) (Hooper et al., 1990; Christophersen et al., 1990; Christophersen and Hooper, 1992; Hooper, 2003) and also (2) mixing ratios which are defined as the proportion of each of the mixing waters in a sample (Schemel et al., 2006). Mixing ratios are useful because they can be quantified accounting for conservative chemical

This chapter is based on the paper: Jurado, A., Vàzquez-Suñé, E., Tubau, I., Carrera, J, Pujades, E. Using mixing ratios to quantify chemical reactions. Submitted to Science of the total environment.

species even when the end-members are uncertain (Carrera *et al.,* 2004; Rueedi *et al.,* 2005). Their application is simpler because only chemical data and a previous conceptual model of the study zone are needed. Mixing calculations are useful for a number hydrogeology tasks such as groundwater recharge sources in urban environments (Reeudi *et al*., 2009; Houhou *et al*., 2010; Vàzquez-Suñe *et al*., 2010). Other applications include the interaction between groundwater and surface water bodies (Plummer *et al*., 1998; Beyerle *et al*., 1999; Crandall *et al*., 1999; Lambs, 2003; Petita *et al*., 2010) and with aim of hydrograph separation (Subayongo et al., 2005; Ladouche *et al*., 2000). However, mixing calculations do not provide information about hydrogeochemical reactions.

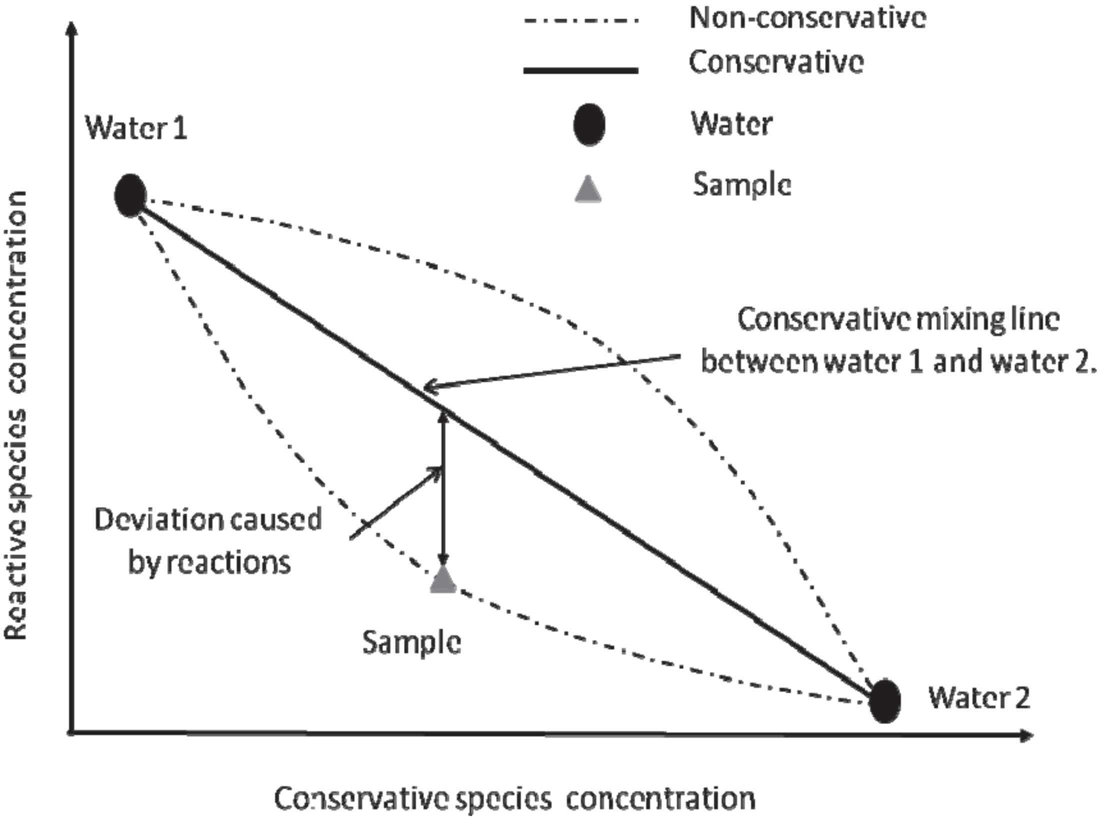


Figure 5.1. Plot of a conservative specie over a reactive specie considering two end-members. Note that the concentration of the conservative solutes in a mixture is obtained by linear combination of the end-members, represented by the black straight line, but when deviations from perfect mixed solutions exist; they may be due to the chemical processes controlling the system.

The concentration of the conservative solutes in a mixture is obtained by linear combination of the end-members. However, when deviations from perfect mixed exist; they may be due to the chemical processes (Figure 5.1). This concept has been often conjectured (Pitkanen et al., 1999; Laaksoharju *et al*., 1999; Balistrieri et al., 2003; Morell *et al*., 2007; Barros *et al*., 2008; Panagopoulos , 2008), but never formalized.

In summary, mixing models have been widely used in all branches of hydrology but they have never been applied to quantify chemical reactions. The objective of this work is to use mixing calculations to identify and quantify hydrogeochemical processes that occur when river water infiltrates an alluvial aquifer. This included the identification of the recharge sources and the identification and quantification of the geochemical processes undergone in each sampling point.

5.2. Materials and methods

5.2.1 Site description

The study area is located in north-eastern Barcelona, in the Besòs Delta River at the Sant Adrià del Besòs city. The area is bound by the River Besòs and is close to the underground car park at Plaça de la Vila site (Figure 5.2). Climate is typically Mediterranean with an average rainfall of 600 mm/year.

5.2.1.1 Previous works developed in Besòs River Delta aquifers

Vàzquez-Suñé *et al.* (2010) identified several recharge sources in the aquifers of Barcelona. These sources are the following: (1) River Besòs, (2) rainfall recharge in northern non-urban area, (3) River Ter water supply, (4) River Llobregat water supply, (5) River Ter sewage water, (6) River Llobregat sewage water, (7) City runoff and (8) Sea water intrusion. Among them, the River Besòs is the main contribution to resident groundwater recharge in the lower parts of the Besòs River catchment, where the samples of Besòs River Delta were collected (Ondiviela *et al*., 2005). In fact, the Vàzquez-Suñé *et al.* (2010) pointed out that groundwater composition in Besòs River area change significantly because the seasonal changes in river water quality. Consequently, it was necessary to characterize the variability of the River Besòs. This work was developed by Tubau *et al.* (submitted). The authors identified the minimum number of the river end-members to explain the variability several recharge sources in Besòs River Delta aquifers by means of end member mixing analysis (EMMA). Using a large hydrochemical database of the River Besòs, 3 different recharge sources were

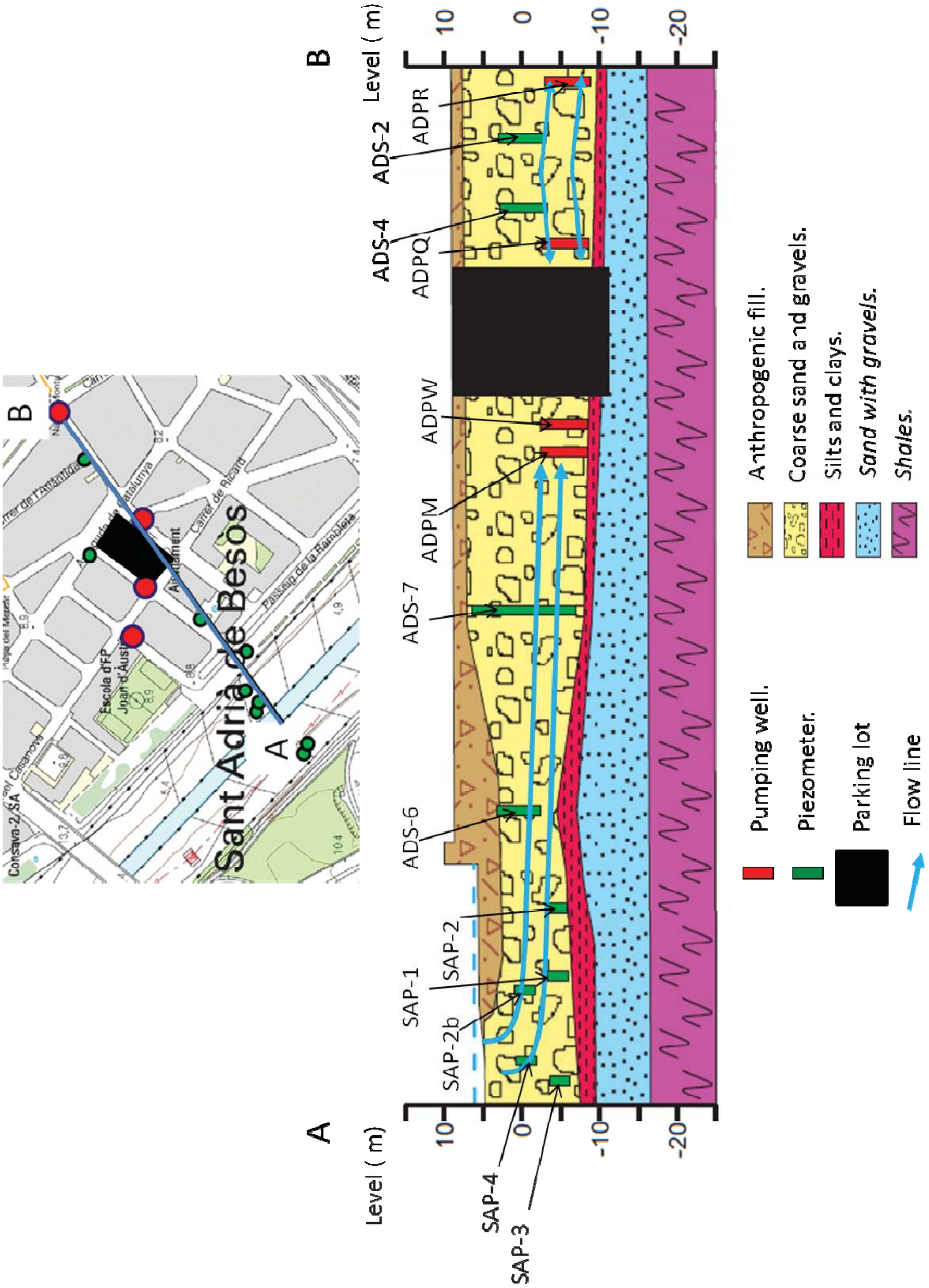


Figure 5.2. Schematic description of the hydrogeology of the study area. The study area is bound by the River Besòs and it is close to the underground car park at Plaça de la Vila site. The screen depths of the pumping wells and the piezometers are represented.

identified based on 11 tracers. These tracers were chloride (Cl^-), sulphate (SO_4^{2-}), sodium (Na^+), bicarbonate (HCO_3^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), nitrate (NO_3^-), ammonium (NH_4^+), total nitrogen (Ntot) and electrical conductivity (EC). Three end-members were identified to characterize the variability of the River Besòs were: 2 corresponding to dry season (D1 and D2) and one from the wet season (W1). Once end-members were selected according to the aforementioned 11 tracers, the concentrations of other less conservative species, such as fluoride (F^-), bromide (Br^-), boron (B), dissolved oxygen (O_2), total organic carbon (TOC), phosphate (PO_4^{3-}), phosphorous (P), iron (Fe), and arsenic (As) were also evaluated for the 3 river end-members using the MIX code (Carrera et al., 2004). The three river end-members selected have the following characteristics:

End-Member D1. This end-member presented the highest concentrations for all species, excepting for calcium, magnesium, nitrate, bromide, boron, oxygen, iron and arsenic. Oxygen and nitrate presented the lowest concentrations. This end-member might be representative for water coming from dry periods.

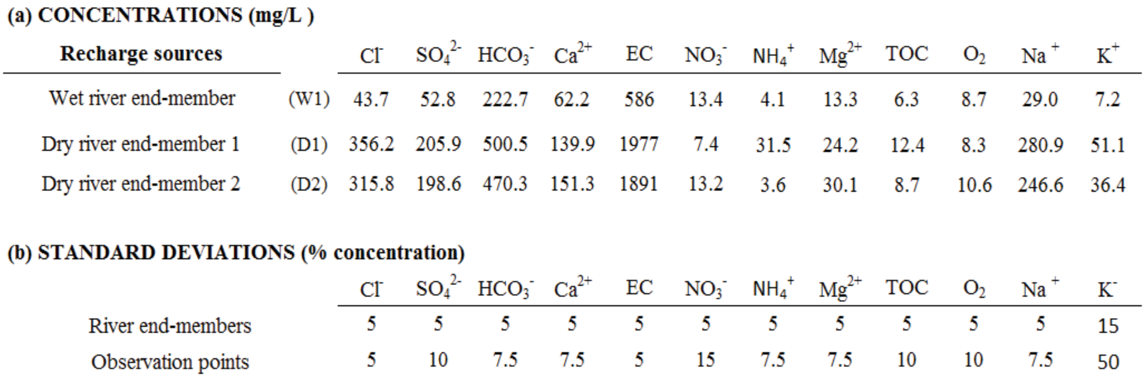
End-Member D2. Conversely to D1, this end-member presented the highest concentrations for oxygen, bromide, calcium, magnesium, boron and iron, and the lowest concentration for ammonium. This end-member also corresponded to dry periods but with higher concentration in dissolved oxygen than D1.

End-Member W1. This end-member presented the lowest concentration of all species excepting for nitrogen species concentrations. Nitrogen species were similar to end-member D2 but with lower concentrations for ammonium and total nitrogen. This end-member presented the highest concentration of nitrate and was attributed to wet periods, in which most of the river flow corresponds to rainwater, where nitrogen is in the nitrate form.

The concentrations of some of the aforementioned species are summarised in Table 5.1a. On average, the dry river end-members (D1 and D2) contributed more significantly to the total aquifer recharge than the wet end-member (W1), representing the percentages of 74% and 26 %, respectively. The river end-member D2 was the largest contributor to the total recharge, representing the 65% whilst D1 represented the remaining 9%.

Similarly, Jurado *et al.* (2013) also evaluated the total recharge in three different zones of the Barcelona metropolitan area, including the Besòs River Delta aquifers. In this work, apart from the River Besòs, two more recharge sources were included:

sewage water loss and runoff in paved areas. The tracers used were chloride, electrical conductivity, bicarbonate, sulphate, total nitrogen, $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$. As evaluated by previous works, River Besòs dry end-member was by far the largest contributor to the resident water of the aquifer, representing 88 % in total; 60% from dry conditions and 28 % from wet conditions. Other contributors to the recharge were network sewage loss (SW T) and runoff water in paved areas (RUNOFF) at low percentages, representing 6 % each. These end-members only contributed to groundwater recharge points located close to the parking site (ADPs, ADS2 and ADS4, Figure 5.2). Other studies developed in Besòs River Delta aquifers were concerned with the presence of organic micropollutants such as surfactants (Tubau *et al.,* 2010), drugs of abuse (Jurado et al., 2012a) and pharmaceutical active compounds (López-Serna *et al.,* 2013).



(a) CONCENTRATIONS (mg/L)

Recharge sources		Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	EC	NO_3^-	NH_4^+	Mg^{2+}	TOC	O_2	Na^+	K^+
Wet river end-member	(W1)	43.7	52.8	222.7	62.2	586	13.4	4.1	13.3	6.3	8.7	29.0	7.2
Dry river end-member 1	(D1)	356.2	205.9	500.5	139.9	1977	7.4	31.5	24.2	12.4	8.3	280.9	51.1
Dry river end-member 2	(D2)	315.8	198.6	470.3	151.3	1891	13.2	3.6	30.1	8.7	10.6	246.6	36.4

(b) STANDARD DEVIATIONS (% concentration)

	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	EC	NO_3^-	NH_4^+	Mg^{2+}	TOC	O_2	Na^+	K^-
River end-members	5	5	5	5	5	5	5	5	5	5	5	15
Observation points	5	10	7.5	7.5	5	15	7.5	7.5	10	10	7.5	50

Table 5.1 (a) River end-members initial concentrations of selected tracers for mixing ratios evaluation. The concentrations are expressed in mg/L and the electrical conductivity is expressed in µS/cm. **(b)** Standard deviations to be considered in MIX code for each tracer in the river end-members and groundwater samples expressed as a percentage of the concentration.

In the present work, we have extended the previous works carried out in Besòs River Delta aquifers. Only the work developed by Jurado et al. (2013), evaluate the possible occurrence of the sulphate reduction process at Besòs River Delta zone using the environmental isotopes such as $\delta^{34}S_{SO4}$- $\delta^{18}O_{SO4.}$ However, none of the previous works have formalised a methodology to quantify geochemical reactions that may occurred when river infiltrates the aquifer using mixing ratios.

5.2.1.2 Hydrogeology of the Besòs River Delta area

The hydrogeology of the Besòs River Delta area is highly dependent on the River Besòs flow regime. Like other Mediterranean rivers, it is characterized by its variability, which is controlled by rainfall. Groundwater flows generally from Besòs River to the parking since there is a continuous pumping of about 150 l/s to avoid seepage problems.

From the geological point of view, the study area is placed in the Quaternarian Besòs Delta. The bedrock is made of Palaeozoic granites and Tertiary clays (Velasco et al., 2012). On the top of this impervious base, are placed the fluvio-deltaic sediments of the Besòs Delta River that form two superposed aquifer strata, which constitute the two main aquifers. These aquifers are separated by a semiconfined unit make up of clays and silts (Figure 5.2).

5.2.2 Chemical reactions quantification

The methodology proposed to accomplish the objective consists of the following steps*:* (1) Identification of the recharge sources and selection of the appropriate tracers (2) Identification of the chemical processes at the study area and selection of the non-conservative species to be quantified in the analysis and (3) Evaluation of the mixing ratios including the chemical processes.

The first step is to identify the sources of recharge of the study area, which requires an accurate understanding of the system. The application of EMMA is used to summarize the information of the data set and to construct and ideal mixing model for a specific site. Afterwards, a preliminary choice has to be made to select the appropriate tracers that are used for EMMA. A necessary condition is that there are different in concentration between the end-members (Hooper et al., 1990). Vázquez-Suñé *et al.* (2010) formalize this requirement. Finally, the evaluation of mixing ratios derived from conservative species can be conducted. Mixing ratios describe the contribution to each end-member at each sample. To this end, MIX code was used (Carrera et al., 2004). This approach identifies mixing ratios in the case of uncertain end-members and it uses the concentration of mixed samples to reduce the uncertainty, assuming that the samples are a mixing of the end-members in an unknown proportion. This code was previously used to study evaluate mixing processes either in surface water such as rivers (Cánovas *et al.,* 2012a and 2012b; Galván *et al.,* 2012) and in groundwater (Vàzquez-Suñé *et al.,* 2010; Jiménez-Martínez *et al.,* 2011; Morales-Casique, 2012; Jurado *et al.,* 2012a and 2013).

The idea of this methodology is that *ni* conservative species coming from *ne* end-members mix in variable proportion in *nj* wells. The concentrations of the end-members are assumed highly uncertain because mixtures may vary over time. The purpose is to calculate mixing ratios taking into account that concentration data samples contain errors. Then the mixing equation of a mixture *j* at each observation point can be written as:

$$\hat{X}_{ij} = \sum_{e} \lambda_{ej} \hat{Y}_{ie}, \tag{1}$$

where $\hat{X}_{ij}$ and $\hat{Y}_{ie}$ are the concentrations of species *i* in sample *j* and end-member *e*, respectively, λ_{ej} is the proportion of end-member *e* in mixture *j*. The λ_{ej} must satisfy the constraints

$$0 \leq \lambda_{\mathrm{ej}} \leq 1 \quad , \tag{2}$$

$$\sum_{e} \lambda_{\mathrm{ej}} = 1 , \tag{3}$$

The concentrations of mixtures can be modified by adding the reactions. These can be treated as new end-members. Now, the mixing equation of a mixture j at each observation point can be written as,

$$X_{ij} = \sum_{e} \lambda_{ej} \hat{Y}_{ie} + R_{ij} \quad , \tag{4}$$

where R_{ij} is the concentration values of species *i* in a sample *j* due to the overall chemical reactions and it is defined as,

$$R_{ij} = \sum_{k} \delta_{ik} r_{kj} \quad , \tag{5}$$

where δ_{ik} is the stoichoimetric coefficient of the species *i* in a reaction *k* and r_{kj} is the reaction rate due to the reaction *k* in mixture *j*. Therefore, equation (5) can be expressed as follows:

$$X_{ij} = \sum_{e} \lambda_{ej} \hat{Y}_{ie} + \sum_{k} \delta_{ik} r_{kj} \quad , \tag{6}$$

Note that the stoichometric coefficient can be treated as a perfectly known end-member, while the reaction rates can be treated as unknown mixing ratio.

5.2.3 Sampling and analytical methods

Fifty-five water samples were collected from July 2007 to May 2010 during four different field campaigns on July 2007, February 2008, October 2008 and May 2010.

Four samples from the main recharge source of the aquifer, the River Besòs. Fifty-one samples were collected from the groundwater: 36 from observation piezometers and 15 from pumping wells. The wells and piezometers location as well as the screen depth of groundwater samples collected are illustrated on Figure 5.2. Note that the observation points were the same for each field campaign: 1 sample from the River Besòs, 9 from piezometers and 4 from the pumping wells except for the first campaign that were 3. All the groundwater samples were obtained by pumping until a volume that was at least three times that of the piezometer had been extracted. Field parameters measured in situ including electric conductivity, pH, temperature, Eh and dissolved oxygen. They were measured continuously using a flow cell to avoid contact with the air. The instruments were calibrated daily by means of standard solutions. Samples were collected after stabilization of field parameters and were not filtered in the field and they were stored in a field refrigerator and taken to the laboratory at the end of the sampling day. The discussion of the results of this study only addresses some of the major components such as chloride, sulphate, sodium, calcium, magnesium, and bicarbonate and the main tracer species of waste water such as nitrate, ammonium, and total organic carbon (TOC).

All the samples were analyzed at the laboratory of the ATLL (Aigües Ter Llobregat) in Barcelona. Chloride, sulphate and nitrate have been analyzed using ion chromatography (IC). Calcium and magnesium were analyzed by ICP-MS and prior to the analysis; the solution was acidified with 1% (v/v) HNO3 and centrifuged to 3500 rpm. Ammonium was analyzed by spectrophotometry (based on indophenol blue method) and a commercial reactive kit. The measuring range is 0.02 to 0.25 mg/L. Bicarbonate was analyzed manually by chemical evaluation with sulfuric acid, accounting for the pH of the sample. Both bicarbonate and ammonium must be analyzed within 24 hours of sample collection. TOC was analyzed using the 680 ºC combustion-infrared method with a platinum catalyst and using a Non-Dispersive Infra-Red (NDIR) detector. The amount organic carbon can be determined by the non-purgeable organic carbon (NPOC). It is based on the subtraction of inorganic carbon of the sample by purging the acidified sample, to a pH less than 2.0, with an inert gas. The TOC may be determined by means of TC measuring method. The sample is filtered through a 0.45 µm filter when turbidity exceeds 6 NTU.

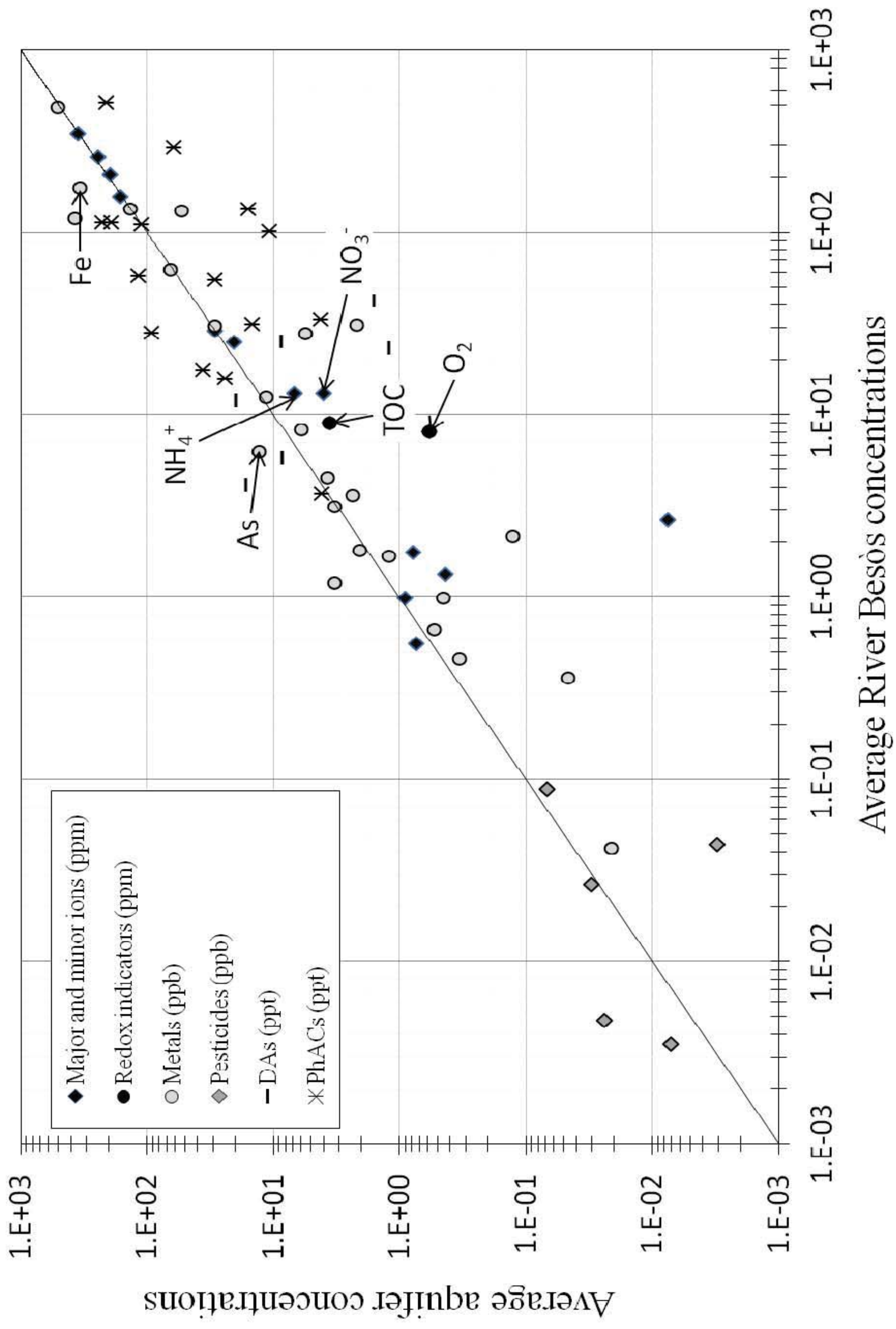


Figure 5.3. Comparison between the average concentration at the Besòs River and the average concentration in the aquifer for a several number of species as major and minor ions, metals, redox indicators, pesticides drugs of abuse (DAs, Jurado et al., 2012a) and pharmaceutical active compounds (PhACs, López-Serna et al., 2013). The river data set is collected monthly by the Catalan Water Agency (ACA) 2 Km upstream of the study zone and it can be downloaded from http://www.gencat.cat/.

5.3. Results and discussion

5.3.1 Identification of the biogeochemical processes and selection of the non-conservative species to be quantified in the analysis.

As mentioned before, the EMMA analysis in Besòs River Delta area was previously performed and three end-members from the river were needed to explain the variability of measured concentrations in groundwater (Tubau et al., submitted). The recharge sources, RUNOFF and SW T, were not taken into account because previous studies demonstrated their low contribution to groundwater recharge in the lower parts of the Besòs River catchment, (Jurado *et al.,* 2013). Consequently, in this work the three different end-members from the River were used to account for the temporal variability: wet conditions (W) and dry conditions (D1 and D2).

Prior inspection of the data suggested the occurrence of biogeochemical processes in Besòs River Delta aquifers. When River Besòs and aquifer average concentrations are compared for several tracers such as major and minor components, metals, pesticides, drugs of abuse (DAs) and pharmaceuticals active compounds (PhACs), it can observed that some species presented higher concentrations in the river than in the aquifer (Figure 5.3). As an example, oxidation and reduction processes can be deduced on Figure 5.3 where ammonium, nitrate and dissolved oxygen have lower concentrations in the aquifer than in the river. Nitrate concentrations at River Besòs can reach levels of 15 mg/L but measured concentrations at points located near the river (SAP's and ADS6n, Figure 5.2) are drastically reduced to null or very low levels (on average, 0.45 mg/L). This may be indicative that denitrification could occur when river water infiltrates the aquifer.

This fact is supported by the results obtained by Tubau *et al.* (submitted). In this work, only chloride, electrical conductivity, sodium and ammonium and total nitrogen behaved conservatively. However, calcium, bicarbonate, sulphate, magnesium, nitrate, TOC and dissolved oxygen did not (Figure 5.4). When measured and estimated concentrations were compared it could be observed that some samples fall away from the 1:1 line, particularly for the less conservative species. Measured concentrations for calcium, magnesium and bicarbonate were higher than the estimated ones. However, for TOC, nitrate and dissolved oxygen measured concentrations were lower than estimated ones. These might indicate that some processes, which depleted or released these species from groundwater, were occurring because they could

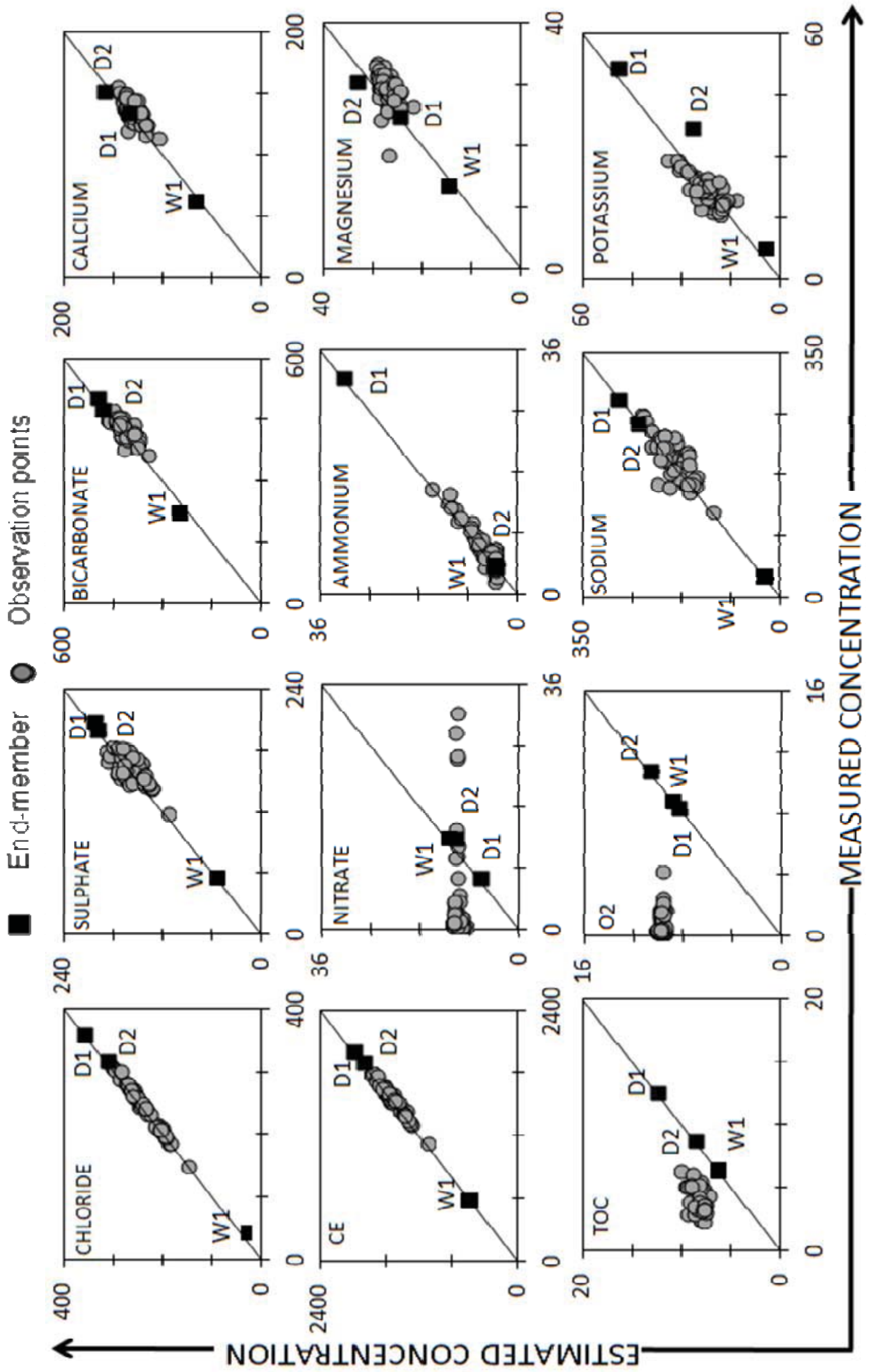


Figure 5.4. Plots of measured vs. estimated concentrations of all species at three end-members and observation points not including the geochemical processes. Notice that chloride and electrical conductivity behave conservative while dissolved oxygen, total organic carbon, nitrate did no (end-members concentration need to be dramatically reduce). This figure was modified from Tubau et al. (submitted).

not only be explained by pure mixing of Besòs River end-members D1, D2 and W1. These deviations may be due to the occurrence of biogeochemical processes that take place in the river-aquifer system, including oxidation and reduction processes (hereinafter redox processes) and dissolution/precipitation of minerals. The following processes were identified in Besòs River Delta aquifers:

$$(R_1)\quad CaCO_3\ (s) + H^+ \rightarrow HCO_3^- + Ca^{2+} \qquad \text{Calcite dissolution}$$

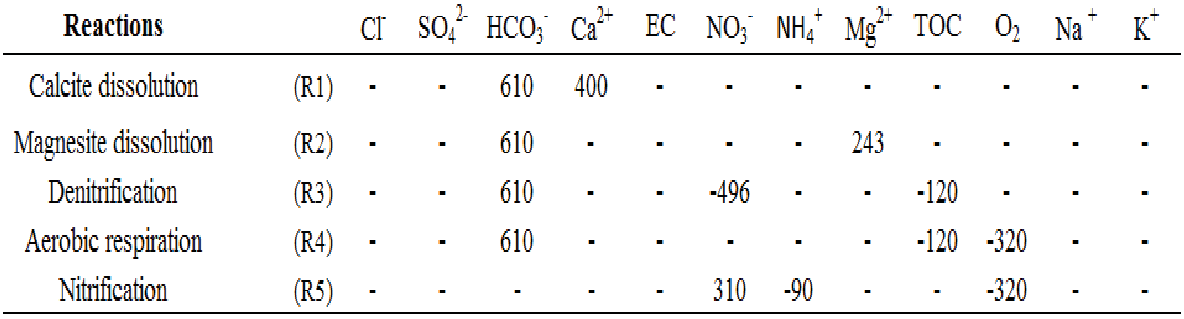
$$(R_2)\quad MgCO_3\ (s) + H^+ \rightarrow HCO_3^- + Mg^{2+} \qquad \text{Magnesite dissolution}$$

$$(R_3)\quad CH_2O + \frac{4}{5}NO_3^- \rightarrow \frac{2}{5}N_2 + HCO_3^- + \frac{1}{5}H^+ + \frac{2}{5}H_2O \qquad \text{Denitrification}$$

$$(R_4)\quad CH_2O + O_2 \rightarrow HCO_3^- + H^+ \qquad \text{Aerobic respiration}$$

$$(R_5)\quad \frac{1}{2}NH_4^+ + O_2 \rightarrow \frac{1}{2}NO_3^- + H^+ + \frac{1}{2}H_2O \qquad \text{Nitrification}$$

Based on the identified processes, the non-conservative species to be quantified in the analysis are calcium, bicarbonate, magnesium, total organic carbon (TOC), ammonium, nitrate, bicarbonate and dissolved oxygen.

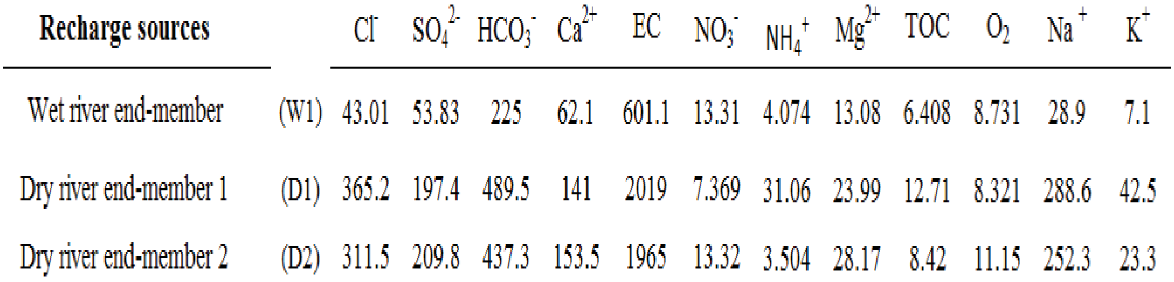


Reactions		Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	EC	NO_3^-	NH_4^+	Mg^{2+}	TOC	O_2	Na^+	K^+
Calcite dissolution	(R1)	-	-	610	400	-	-	-	-	-	-	-	-
Magnesite dissolution	(R2)	-	-	610	-	-	-	-	243	-	-	-	-
Denitrification	(R3)	-	-	610	-	-	-496	-	-	-120	-	-	-
Aerobic respiration	(R4)	-	-	610	-	-	-	-	-	-120	-320	-	-
Nitrification	(R5)	-	-	-	-	-	310	-90	-	-	-320	-	-

Table 5.2. Geochemical processes treated as end-members. Note that the geochemical processes can be included as a certain end-members because the stoichoimetric coefficients of the reactive species are known.

5.3.2 Evaluation of the mixing ratios including the geochemical processes.

Once geochemical processes were identified, the evaluation of mixing ratios including the geochemical processes could be done. The composition of all sampling points may be considered as a result of river water mixing (conservative) and groundwater-aquifer interactions (non-conservative). This evaluation was performed using the MIX code (Carrera *et al.*, 2004). This code allows us to incorporate uncertainty in both recharge sources and observation point measurements. Uncertainty is mainly related to sampling and analytical errors, lack of data and the occurrence of additional processes, such as geochemical reactions. Measurement uncertainty is quantified through covariance matrices. This code requires defining the reliability of measurements and the results depend on the assumed standard deviations. Consequently, standard deviations have to be selected carefully. Generally, standard deviations are selected depending on whether or not the tracers are conservative. For instance, some non-conservative species such as TOC and dissolved oxygen were expected to have assigned high standard deviations because they participate in geochemical processes. However, in this work, each reaction was included as a new end member (Table 5.2). For all the reactions considered, the selected value for the species involved in the reaction was its molecular weight times ten. As an example, in aerobic respiration reaction, organic matter (in terms of total organic carbon) and dissolved oxygen are transformed into bicarbonate and protons (not considered). The end-member's concentrations were -120 and -320 mg/L for TOC and dissolved oxygen, respectively, because they were depleted whilst bicarbonate was released to groundwater (610 mg/L). In general, the standard deviations assigned to both groundwater samples and recharge sources were significantly low for several reasons. First, recharge sources tracers were supposed to be accurately well know because they were previously evaluated (Tubau et al., submitted). Secondly, the uncertainty sharply decreased in the non-conservative tracers because chemical reactions were included as end-members. The standard deviations assigned were a percentage of the concentration for a specific tracer and they varied from 5 % to 15% in the recharge sources and 5 % to 50 % in the observation points (Table 5.1b).



Recharge sources		Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	EC	NO_3^-	NH_4^+	Mg^{2+}	TOC	O_2	Na^+	K^+
Wet river end-member	(W1)	43.01	53.83	225	62.1	601.1	13.31	4.074	13.08	6.408	8.731	28.9	7.1
Dry river end-member 1	(D1)	365.2	197.4	489.5	141	2019	7.369	31.06	23.99	12.71	8.321	288.6	42.5
Dry river end-member 2	(D2)	311.5	209.8	437.3	153.5	1965	13.32	3.504	28.17	8.42	11.15	252.3	23.3

Table 5.3. Computed concentrations in the end-members from the river for the selected tracers expressed in mg/L and in µS/cm for electrical conductivity.

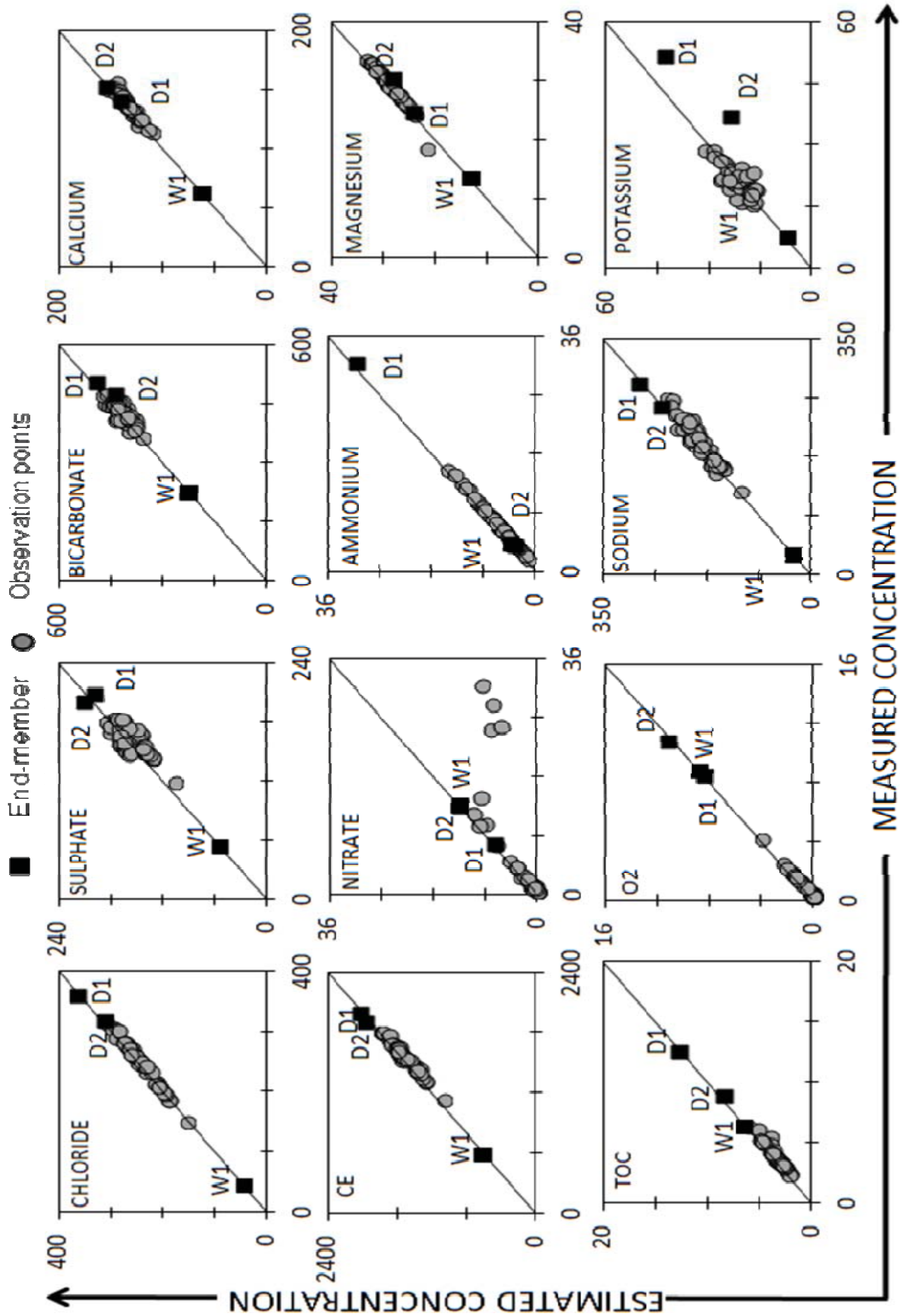


Figure 5.5. Plots of measured vs. estimated concentrations of all species at all end-member and sampled points including the geochemical processes. Notice the better fit of the reactive species calcium, total nitrate, ammonium, dissolved oxygen, total organic carbon and nitrate.

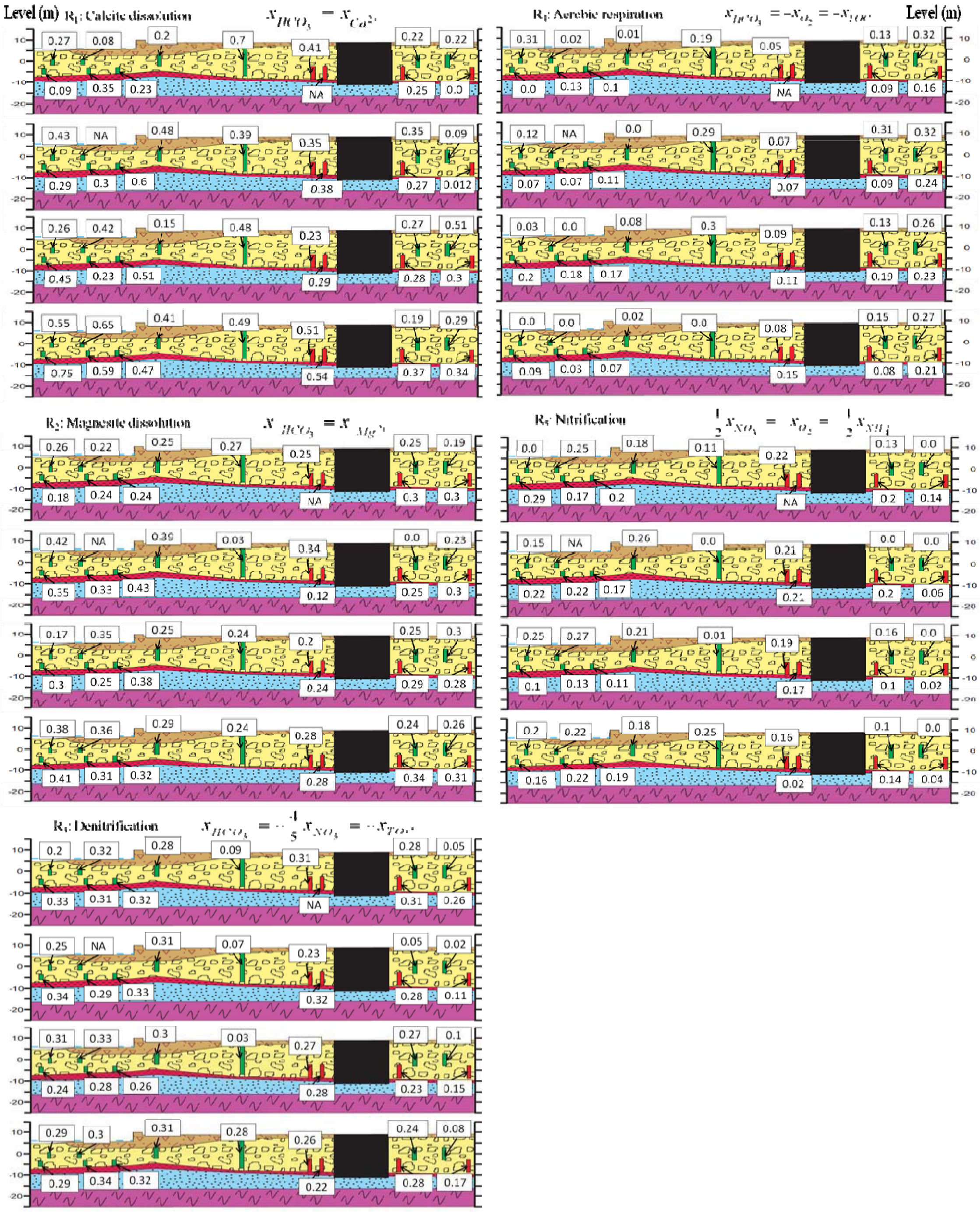


Figure 5.6. Schematic cross-plot sections of concentration, x (mmol/l), at each observation point for the species that take part in the reactions accounting for the 4 campaigns. The reactions are: (R_1) calcite dissolution, (R_2) magnesite dissolution, (R3) Denitrification, (R4) Aerobic respiration, (R_5) Nitrification.

Considering the reactions, the measured composition at a sampled point is the combination of River Besòs water mixing and chemical reactions for the less conservative species. River water mixing is the most relevant process since mixing ratios range from 82.8% (in sampling point SAP 3 in C3) to 93.4% (in sampling point ADS2 in C2). Generally, river water from dry periods dominates over wet period. The main river end-member contribution is D2 in most of the observation points. The contribution of wet end-member river water W1 was more significant in the last field campaign (C4) due to high precipitations occurred, which are directly related to River Besòs flow. In contrast, chemical reactions represent, on average, 11.4 % in the observation points. However, their contribution to the better fit of the reactive species was significantly important. The need to consider the reactions as end-members is illustrated in Figure 5.5. When measured and computed concentrations for all the tracers in recharge sources and observations points were compared (Figure 5.5), several observations could be made:

(1) Computed end-members concentrations from the river for all tracers considered were similar to measured ones in both zones, falling close to the 1:1 line. They were in line with the standard deviations assigned and, as expected, the computed values presented little variation (Table 5.3).

(2) Observation point concentrations for calcium, magnesium, dissolved oxygen, total organic carbon and nitrate close from the ideal mixing line, which supported the occurrence of the aforementioned processes. There were only some observation points, ADS-2 (C1, C3 and C4) and ADS-7 (C2), in which nitrate concentration cannot be explained by either mixing of river water and/or chemical reactions. This can be seen on Figure 5.5 because the aforementioned sampling points are below from the 1:1 line. Consequently, an unidentified end-member with a higher concentration of nitrate might be missing.

One of the most relevant results in this research was the quantification the aforementioned hydrogeochemical processes at each observation point for the non-conservative species. The quantification (mmol/L) of these processes and their spatial distribution can be observed in Figure 5.6. The significance of this process and its spatial distribution within the aquifer enabled the division of this study zone depending on the location of the points: (1) Points located near the river (SAP's and ADS-6n, Figure 5.2) and (2) points located closer to underground car park at Plaça de la Vila site (ADS-7, ADS-2, ADS-4 and ADP's, Figure 5.2). Generally, the significance of the hydrogeochemical processes was more important in points located near the river (SAP's and ADS-6n, Figure 5.2) for all reactions excepting for aerobic respiration. Besides, the occurrence of geochemical reactions was usually more significant in the deeper observations points (SAP-1, SAP-2 and SAP-3) than in the shallower ones. In the rest of observation points, clearly more affected by the continuous pumping of Plaça de la Vila site, no clear tendency was observed although the occurrence of geochemical processes also happened. The depleted (negative values) or released concentrations (positive values) of non-conservative species due to each reaction at each observation point accounting for the 4 different field campaigns are summarised in Tables S4 and S5 (see supplementary information Table S4 and S5 in Annex I for details).

5.4 Conclusions

The application of mixing ratios was a useful tool to quantify hydrogeochemical processes in a specific study area. The approach enables us to evaluate the occurrence of geochemical processes at each observation point. This methodology was validated in the Besòs River Delta study area and twelve tracers were used: chloride, sulphate, calcium, bicarbonate, electrical conductivity, ammonium, magnesium, dissolved oxygen, total organic carbon, nitrate, sodium and potassium. All except chloride, sodium, ammonium and electric conductivity, behaved in a non-conservative way when only River Besòs water mixing was considered. First, measured concentrations at sampling points of nitrate, total organic carbon and dissolved oxygen species were much lower than the recharge sources from the river, suggesting degradation processes. Second, measured concentrations in the observation points of calcite, bicarbonate and magnesium were generally higher than the computed ones, suggesting that a little amount of such concentrations may be released to groundwater. Consequently, these non-conservative tracers were affected by geochemical processes. When the identified reactions were included as end-members, the non-conservative species fall further close from the 1:1 line (ideal mixing line) supporting the occurrence of the hydrogeochemical processes when river water infiltrates the aquifer. The approach presented in this work can be used in any aquifer system not only to identify the recharge sources but also to quantify geochemical processes in a fast, simple and effective way.

6. Application of multi-isotope data (O, D, C and S) to quantify redox processes in urban groundwater

6.1 Introduction

Deterioration of groundwater quality in urban aquifers has become a matter of concern. In such areas, groundwater can be contaminated by a wide range of anthropogenic pollutants. Moreover, groundwater can be an alternative source of water supply in cities with an arid to semiarid climate (Tubau *et al.,* 2010). A proper assessment of groundwater quality requires the quantification of the total recharge and the composition of the various sources involved. These quantitative assessments enable to identify the origin and the fate of pollutants (from pollution to attenuation) and also evaluate management strategies.

However, evaluating the recharge in urban environments is essentially different from rural areas. This is mainly due to the high number of different sources, their variable composition, and the geochemical processes undergone by the mixtures. Thus, many traditional mixing ratio computations require that the concentrations of end-members to be different and accurately known. Currently, the concentrations of the different species in the end-members are not usually known with certainty. They can be highly variable in space and, especially, in time. This could be the reason why studies to identify and quantify sources and processes involved in the water quality of an urban aquifer are very scarce (see Vàzquez-Suñé *et al.,* 2010 and references therein, for a review).

Some common sources of groundwater in urban areas are sewer leakage and infiltration from waste water treatment plants. These sources provide organic carbon to the water and promote biodegradation reactions of a variety of pollutants (nitrate, sulphate, arsenic-bound to iron, organic micropollutants). Biodegradation processes are related to the redox state of water. Therefore, identifying the redox evolution along a flow line is a key issue.

Unlike physical processes such as dispersion, mixing and dilution; biodegradation implies a decrease in the total dissolved mass of a solute and may involve a variation of its isotopic proportions. This suggests that isotope studies can be

This chapter is based on the paper: Jurado, A., Vàzquez-Suñé, E., Soler, A., Tubau, I., Carrera, J, Pujades, E., Anson, I. (2013). Application of multi-isotope data (O, D, C and S) to quantify redox processes in urban groundwater. Applied Geochemistry 34, 114-125. http://dx.doi.org/10.1016/j.apgeochem.2013.02.018.

helpful to identify and quantify biodegradation processes. In fact, the application of environmental isotopes has been employed to characterise and assess different issues in urban groundwater recharge. Butler and Verhagen (1997) used water isotopes in the study of the city of Pretoria (South Africa) to differentiate between the local water recharge and water supply, which had a different isotopic composition. Choi *et al.* (2005b) complemented a hydrochemical study in the city of Seoul (South Korea) with isotopic data (water molecules and tritium) to determine the relationship between the uses of the soil and degradation of the groundwater quality. The isotopic composition of dissolved inorganic carbon has been used to quantify the recharge in Japan (Yasura *et al.,* 1999) and to identify old landfills (Clark and Fritz, 1997). Nitrate and sulphate isotopic compositions have been used to identify the different sources of contamination in urban aquifers and geochemical processes taking place in the aquifer (Fukada *et al.,* 2004; Bottrell *et al.,* 2008; Li *et al.,* 2010; Hosono *et al.,* 2011a). However, there are few multi-isotopic studies carried out in urban areas that not only identify the recharge sources but also quantify hydrochemical processes that may affect the pollutants (Osenbrück *et al*., 2007; Hosono *et al.,* 2009, 2010 and 2011b). To sum up, isotopes have been used successfully to identify and quantify the extent of redox processes, but in these approaches, the isotopic composition of the recharge sources was assumed constant. Furthermore, no degree of uncertainty was considered either in these sources or the observation points.

The main objective of this study was to investigate the occurrence of redox processes in an urban aquifer with environmental isotopes using mixing ratios accounting for the uncertainty of both the recharge sources and the observation points. This included the identification of the recharge sources and their isotopic composition, the evaluation of the mixing proportions for each sample, and the quantification of the geochemical processes undergone. To this end, $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$ coupled with hydrochemistry data were analyzed in groundwater samples collected at two different areas from the city of Barcelona from February 2007 to May 2010. Vàzquez-Suñé *et al. (*2010) previously determined the different sources of urban recharge in the aquifers of Barcelona. We used a multivariate statistical analysis method using the MIX code (Carrera *et al.,* 2004) to estimate the composition of the recharge sources and quantifying the proportions in which the different sources contribute to the total groundwater recharge in a given sample.

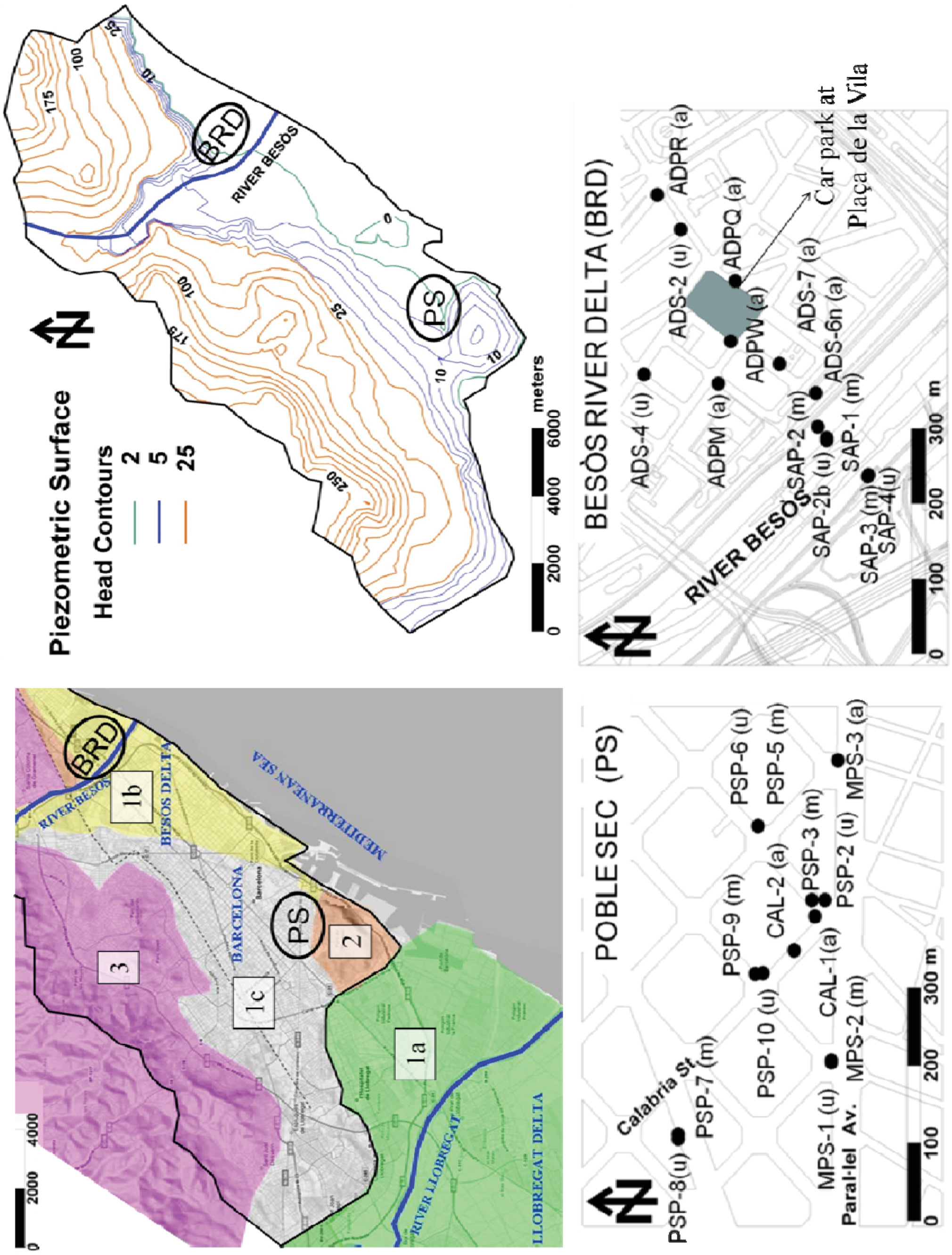


Figure 6.1. On the left, schematic description of the hydrogeology of Barcelona: (1a) Llobregat Delta made up of gravels, sands, silts and clays (Holocene, Quaternary), (1b) Besòs Delta composed of gravels, sands, silts and clays (Holocene, Quaternary), (1c) Barcelona Plain consisting of carbonated clays (Pleistocene, Quaternary), (2) Barcelona Plain made up of marls, sandstones and sands (Tertiary) and (3) Collserola Range consisting of shale and granites (Palaeozoic). On the right, a piezometric map of the study area, which is divided into two distinct zones: Poble Sec (PS) and Besòs River Delta (BRD). The contour intervals are 2 m (continuous green line), for heads ranging from 5 to below 25 m (continuous blue line) and 25 m above (continuous orange line). At the bottom, observation points in each zone, including the depth of the screen: (u) upper, (m) middle, (l) lower and (a) totally screened.

6.2. Materials and methods

6.2.1 Site description

The study area consists of two distinct zones: Poble Sec and Besòs River Delta, which are located in the Barcelona metropolitan area (NE Spain). Barcelona is bordered by the Mediterranean Sea, the Collserola range and the Rivers Besòs and LLobregat (Figure 6.1). Climate is typically Mediterranean with an average rainfall of 600 mm/year.

6.2.1.1 Previous works related to Barcelona urban groundwater

Vàzquez-Suñé *et al.* (2010) identified several recharge sources in the aquifers of Barcelona by means of end member mixing analysis. Using a large hydrochemical database, 8 different recharge sources could be identified based on 8 and 12 tracers. The recharge sources identified are the direct rainfall recharge which occurs in the non-urbanised areas in the Collserola Range. There are also three groundwater recharge sources from anthropogenic activities: (1) loss from water supply network (Barcelona is supplied with water from the Rivers Ter and Llobregat, which divide the city into two zones with a differing water quality), (2) loss from sewage water and (3) the runoff water in paved areas that washes the urban surface atmospheric deposition and recharges the aquifers through direct infiltration or sewer seepage. Finally, there are two inflows from surface water bodies: seawater intrusion and water from the heavily polluted River Besòs, which must be considered as a potential recharge sources in lower areas of the city. The latter contains a large proportion of effluents from waste water treatment plants. Tracers included chloride, sulphate, $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$, boron, fluoride, bromide, zinc, total nitrogen, residual alkalinity and EDTA. Some of the tracers used appear to be non-conservative and to address this uncertainty mixing ratios were computed considering and not considering the questionably conservative species. The authors concluded that the results using 8 (chloride, sulphate, $\delta^{34}S_{SO4}$, fluoride, bromide, $\delta^{18}O_{H2O}$, δD_{H2O} and total nitrogen) and 12 species were similar in terms of mixing ratios and suggested that the results obtained with 12 species were more realistic. According to Vàzquez-Suñé *et al.* (2010), 52% of the average total recharge in Barcelona aquifers was from loss in the water supply (22%) and sewage network (30%). Runoff water had a variable but locally major impact on the water resources representing, on average, 20 %, followed by rainfall recharge in non-urbanised area (17%) and the River Besòs (11%).

Similarly, Jurado *et al.* (2012a) evaluated the total recharge in three different zones of the Barcelona metropolitan area to investigate the occurrence of illicit drugs in an urban aquifer. This included the two pilot zones of Poble Sec and the Besòs River Delta. Overall, Poble Sec aquifers were mainly recharged from loss in sewage and water supply networks and the River Besòs was by far the largest contributor of the Besòs River Delta aquifers. In that work, the tracers used to evaluate the recharge sources were not specified. Other studies developed in Barcelona aquifers were concerned with the presence of organic micropollutants such as surfactants (Tubau *et al.,* 2010) and pharmaceutical active compounds (López-Serna *et al.,* 2013).

In the present work, we have extended the previous works carried out in Barcelona aquifers by the aforementioned authors in two aspects. Firstly, in contrast to Vàzquez-Suñé *et al.* (2010) who evaluated the total recharge at a regional scale, we have focused on two specific zones of the Barcelona metropolitan area: Poble Sec and Besòs River Delta. Secondly, although these two distinct zones were included in the study of Jurado *et al.* (2012a), they did not used environmental isotopes to evaluate the total recharge. Moreover, in both works, the evaluation of redox processes using environmental isotopes coupled with hydrochemistry has not been performed.

6.2.1.2 Hydrogeology of the pilot zones

Currently, groundwater in Poble Sec and Besòs River Delta areas is only used for secondary uses such as street-cleaning and to water public gardens. But it can be considered as an option as tap water resource, especially in periods of drought, since there are several aquifers with different lithologies, characterised by their geological age, under the city (Figure 6.1). The Paleozoic aquifer outcrops at the topographic heights located NW, which consists of shales and granites. Quaternary and Tertiary aquifers are found in the rest of the city. From the geological point of view, Poble Sec is located in the Barcelona Plain made up of carbonated clays. Below the Quaternary, the Tertiary (Miocene) is present. Miocene is made up of sandstones, marls and sandy gravels. Besòs River Delta is located in the Quaternary Besòs Delta, which is bordered by the River Besòs and is close to the underground car park at the Plaça de la Vila site (Figure 6.1). The river flow is heavily dependent on seasonal rainfall. The average flow of the river is 2.5 m^3/s, except for heavy rain events. Groundwater flows generally from the River Besòs to the car park since there is a continuous pumping of about 150 l/s to avoid seepage problems. The basement is made of Palaeozoic granites and Cenozoic units, which consists of Miocene matrix-rich gravels and Pliocene grey marls. The fluvio-deltaic sediments of the Besòs Delta Complex are placed on the top of this basement, including 3 aquifers composed of sandy and gravelly bodies separated by lutitic units (Velasco *et al.,* 2012).

6.2.2 Chemical reactions quantification

The methodology to evaluate the occurrence of redox processes consist of: (1) identification of the potential recharge sources and selection of the appropriate tracers, (2) evaluation of the mixing ratios in groundwater recharge and composition of the sources by means of multivariate statistical analysis and (3) assessment of the fate of environmental isotopes in groundwater samples.

We used the MIX code (Carrera *et al.,* 2004) to evaluate the occurrence of redox processes. The proposed algorithm consisted of the following steps: (1) Definition of initial mixing ratios by conventional least squares, assuming that the concentrations of end-members are known; (2) given the mixing ratios, maximise the likelihood function to estimate the expected values of mixture and end-member concentrations; (3) given the expected values of mixture and end-member concentrations, maximise the likelihood to obtain the mixing ratios; (4) repeat steps 2 and 3 until convergence. A detailed description of these steps and a derivation of the necessary equations can be found in Carrera *et al.* (2004).

The MIX code can evaluate mixing ratios in cases of uncertain end-members using the concentration of mixed samples to reduce the uncertainty. Uncertainty depends on several factors. Some of these factors are (1) sampling and analytical errors in both sources and measurement points (2) the number of measured samples to accurately characterise the recharge source composition, (3) the conservative behaviour of a given tracer and (4) the occurrence of unknown processes since recharge source water entered the aquifer until the mixture. As an example, flux averaged concentrations should be used when characterising aquifer discharges to perform salt balances in rivers. However, more proportion of diluted river water could inflow into aquifers during floods. Mixing ratios are evaluated assuming that the samples are a mixture of the recharge sources in an unknown proportion. The concentration of the conservative tracers in a mixture is obtained by a linear combination of the recharge sources. But, when deviations from perfect mixture exist they may be due to chemical processes. . This code was previously used to study evaluate mixing processes either in surface water such as rivers (Cánovas *et al.,* 2012a and 2012b; Galván *et al.,* 2012) and in groundwater (Vàzquez-Suñé *et al.,* 2010; Jiménez-Martínez *et al.,* 2011; Morales-Casique, 2012; Jurado *et al.,* 2012 and 2013).

6.2.3 Sampling

One hundred and six water samples were collected from July 2007 to May 2010 during four different field campaigns in July 2007 (c1), February 2008 (c2), October 2008 (c3) and May 2010 (c4). Four samples were from the River Besòs. One hundred and two samples were collected from groundwater: 67 from observation piezometers and 35 from pumping wells. Data of environmental isotopes $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ were available for c2 to c4 and $\delta^{13}C_{DIC}$ only for c4. The location of the wells and the piezometers and the screen depths are displayed in Figure 6.1. The specific depth of the observation points is shown in Table S2 (Annex I). All the groundwater samples were obtained by pumping until a volume that was at least three times what the piezometer was extracted. Field parameters measured in situ included electrical conductivity, pH, temperature and dissolved oxygen. They were measured continuously using a flow cell to avoid contact with the air. The instruments were calibrated daily by means of standard solutions. Samples were collected after stabilization of field parameters and were not filtered in the field. They were stored in a field refrigerator and taken to the laboratory at the end of the sampling day.

6.2.4 Analytical methods

Most species were analyzed at the laboratory of the ATLL (Aigües Ter Llobregat) in Barcelona. Chloride and sulphate were analyzed using ionic chromatography (IC). Basic cations and trace metals were analyzed by ICP-MS. For As and Fe prior to the analysis; the solution was acidified with 1% (v/v) HNO_3 and centrifuged to 3500 rpm. Ammonium was analyzed by spectrophotometry (based on indophenol blue method) and a commercial reactive kit. Bicarbonate was analyzed manually by chemical evaluation with sulphuric acid, accounting for the pH of the sample. Both bicarbonate and ammonium must be analyzed within 24 hours of the sample collection.

$\delta^{18}O$ and δD of water samples were analyzed based on Wavelength Scanned Cavity Ringdown Spectroscopy (WS-CRDS) for isotopic water measurements with a L2120-i Picarro® equipment from Malaga University (Spain). Six replicates for each sample were made, although the last three were selected for statistical treatment. Three water samples with known $\delta^{18}O$ and δD were used as Internal standards of NEU (-11.58,-79.48), SLAP (-6.55,-42.49) and MAR (-0.77, 0.43).

Dissolved sulphate isotopes were analyzed for $\delta^{34}S$ and $\delta^{18}O$ at the laboratory of "*Mineralogia Aplicada i Medi Ambient*" of the research group at the University of Barcelona (Spain). The water sample was acidified with HCl and a barium chloride solution was added in excess to variable sample volume for precipitating an expected amount of around 50 mg of $BaSO_4$. The precipitation was held at ~100°C in order to prevent $BaCO_3$ formation. The hot solution rested 1-3 days to settle the precipitate that was filtered through a 3 µm paper filter, dried at room temperature (7-10 days) and inserted into a Schott glass vial. $\delta^{34}S$ of dissolved sulphate was analyzed in a Carlo Erba Elemental Analyzer (EA) coupled in continuous flow to a Finnigan Delta C IRMS. $\delta^{18}O$ of dissolved sulphate^{-}was analyzed in duplicate using a ThermoQuest TC/EA unit (high temperature conversion elemental analyzer) with a Finnigan Matt Delta C IRMS. Isotope ratios were calculated using both international and internal laboratory standards. Dissolved inorganic carbon DIC measurements were carried out using a gas-bench system according to the use of the conventional H_3PO_4 method developed and described by Torres *et al.* (2005).

Notation was expressed in terms of delta (δ) per mil relative to the international standards (V-SMOW for δD, V-SMOW for $\delta^{18}O$, V-CDT for $\delta^{34}S$ and V-PDB for $\delta^{13}C$). Reproducibility of the samples was ±0.2 ‰ for $\delta^{34}S$, ±0.5 ‰ for $\delta^{18}O$ of SO_4^{-} , ±0.2 ‰ for $\delta^{13}C_{DIC}$; ±0.2 ‰ for $\delta^{18}O$ and ±0.3 ‰ for δD of water.

6.3. Results

6.3.1 General hydrochemistry

The average concentrations (mg/L) and standard deviations of chloride, sulphate, bicarbonate, sodium, calcium, magnesium, nitrate, ammonium and electrical conductivity (EC) of the groundwater samples collected at each zone are summarised in Table 6.1.

Poble Sec

Groundwater samples of the Poble Sec zone were Cl-(HCO_3/SO_4)-Ca-(Na) type and no significant differences were observed among the different field campaigns (Table 6.1b). Chloride and sulphate levels were usually above 290 mg/L and the average electrical conductivity (EC) was 1900 µS/cm. Some redox indicators such as the high levels of dissolved oxygen and nitrate (on average 3.5 mg/L, and 93 mg/L, respectively) and the low or null levels of ammonium (on average 0.03 mg/L), evidenced the oxidising conditions of the groundwater.

1a Barcelona urban groundwater

Zone	Cl^-	SO_4^{2-}	HCO_3^-	Na^-	Ca^{2+}	Mg^{2+}	NO_3^-	NH_4^+	EC
Poble Sec	306±30	291±49	302±35	163±33	196±26	70±14	93±29	3.2E-2±6.7E-2	1898±173
Besòs River Delta	244±35	161±14	349±31	196±29	134±9	28.5±2.5	4±7.6	6.7±3.2	1540±136

1b Detailed in both zones for each field campaign

Poble Sec

Field campaign	Cl^-	SO_4^{2-}	HCO_3^-	Na^-	Ca^{2+}	Mg^{2+}	NO_3^-	NH_4^+	EC
c1	306±32	291±57	305±35	178±39	194±26	71±9.8	91±25	6E-3±2E-2	1916±219
c2	308±22	293±37	304±20	151±33	201±40	74±22.8	90±24	6.5E-2±1E-1	1899±126
c3	312±42	301±70	314±54	170±33	180±13	66±9.1	96±44	3E-2±5E-2	1900±234
c4	297±23	278±24	286±19	153±21	208±10	69±8.1	96±20	2.5E-2±3E-2	1877±100

Besòs River Delta

Field campaign	Cl^-	SO_4^{2-}	HCO_3^-	Na^-	Ca^{2+}	Mg^{2+}	NO_3^-	NH_4^+	EC
c1	264±27	162±8	425±25	221±22	136±9	28.8±1.1	4.1±9.5	7.7±4.3	1612±110
c2	261±22	177±4	449±42	199±16	137±8	28.9±4.3	4.7±7.3	7.7±3	1619±83
c3	257±11	156±8	425±14	207±12	137±7	29±1.6	3.8±6.9	7.3±2.5	1580±40
c4	196±18	148±13	403±19	157±14	126±9	27.5±1.6	3.3±7.7	4.3±1.6	1356±87

Table 6.1. Average concentration (mg/L) and standard deviation of selected species measured in: (a) Poble Sec and Besòs River Delta and (b) detailed in both zones for each sampling campaign.

Besòs River Delta

Groundwater samples of Besòs River Delta were Cl-(HCO_3)-Na-(Ca) type. The average concentration of all the species presented little variation between field campaigns c1, c2 and c3 (Table 6.1b). In contrast, the last field campaign c4 presented, on average, lower concentrations than the first three campaigns for all species. Among them, chloride, sodium and ammonium were the species that presented the biggest differences (Table 6.1b). This could be related to the geochemistry of the River Besòs since it was also Cl-Na-(Ca)-(HCO_3) type accounting for c1, c2 and c3. However, river water of the last campaign was HCO_3-Ca-(Na) type because it was collected when rain events occurred and, consequently, presented lower concentrations due to the dilution effect.

Overall, Besòs River Delta groundwater was less mineralised than Poble Sec since the average concentration of chloride, sulphate, calcium, magnesium, nitrate and EC were much lower (Table 6.1a). In contrast to Poble Sec, reducing conditions into groundwater were suggested by the low levels of dissolved oxygen and nitrate (on average 0.6 mg/L, and 4 mg/L, respectively) and the presence of ammonium (6.7 mg/L, on average).

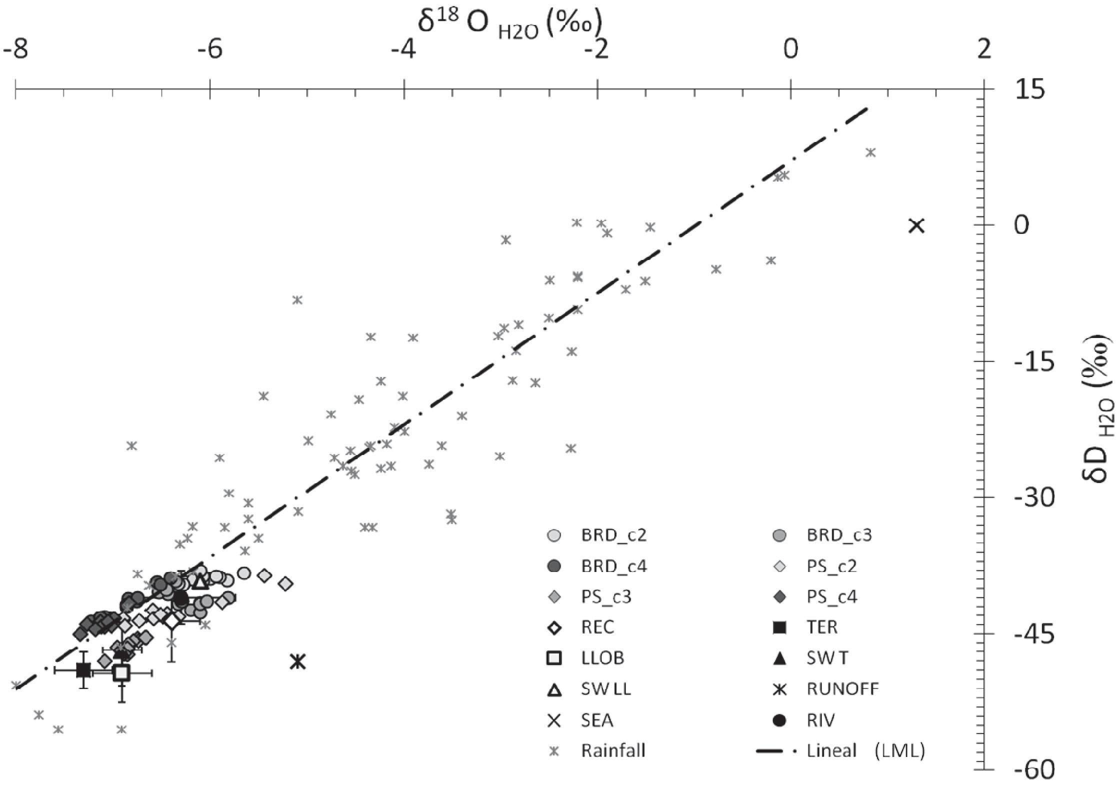


Figure 6.2. Plot of $\delta^{18}O_{H2O}$-δD_{H2O} accounting for the recharge sources (and standard deviation) and groundwater samples collected in both zones: Poble Sec (PS, rhombus) and Besòs River Delta (BRD, rounds). Note that the different field campaigns are represented by the shade of grey: c2 is light grey, c3 is grey and c4 is dark grey. The local meteoric line (LML) represents the monthly isotopic composition of a long-term sampling period (1985-1992) at the monitoring station of Barcelona.

6.3.2. Environmental isotopes

6.3.2.1 Environmental isotopes in the recharge sources

The isotopic composition of the recharge sources was evaluated using samples collected in different field campaigns. The isotopic composition of $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ of most of the recharge sources was first analyzed between 1998 and 1999. Later, between 2006-2007 and 2008-2010, more recharge source samples were collected, including $\delta^{13}C_{DIC}$. The average isotopic composition of available data and the standard deviations of the environmental isotopes $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4,}$ $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$ in the groundwater recharge sources are summarised in Table 6.2a. We have no data of the isotopic composition for the Llobregat sewage water (SW LL) so the values were taken from Otero *et al.* (2008). The isotopic composition of the water supply is slightly lighter than the sewage water for all the isotopes (Figure 6.2). Sewage waters have similar isotopic composition accounting for sulphur and oxygen isotopic values of dissolved sulphate but Ter sewage water (SW T) is lighter when considering water isotopes. Significant differences also existed between Ter and Llobregat water supply for the isotopic compositions of sulphur and oxygen isotopes of dissolved sulphate, the former being lighter (Figure 6.3).

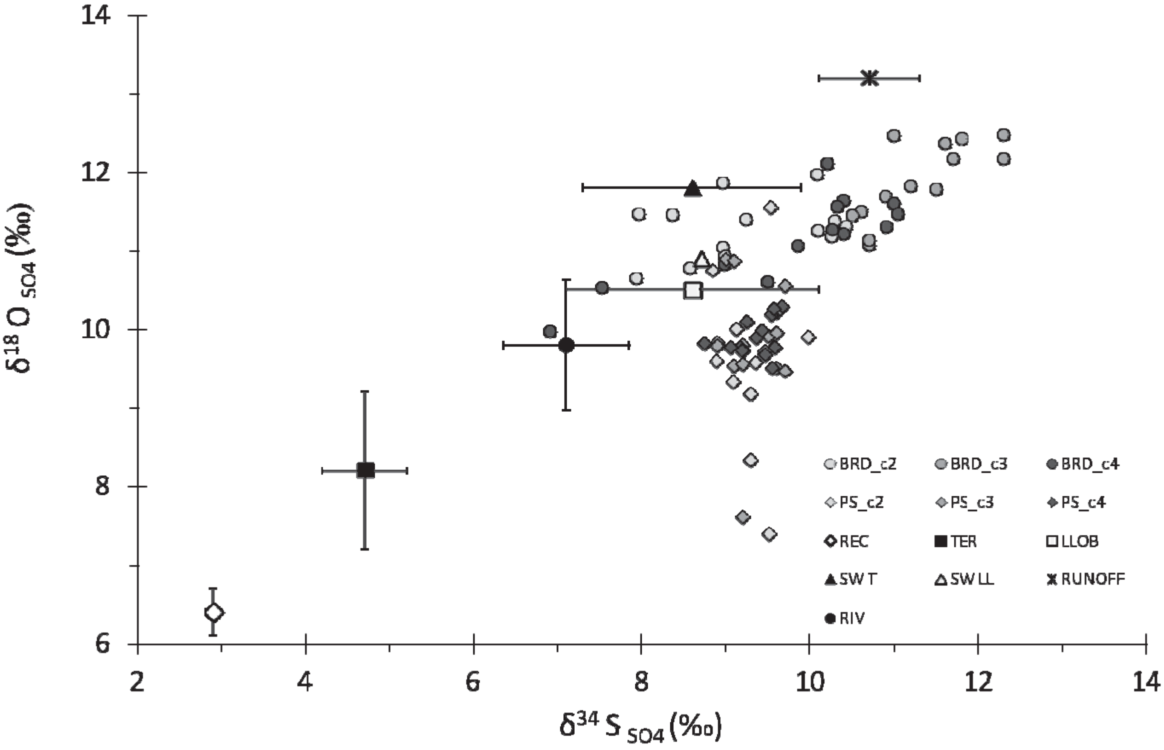
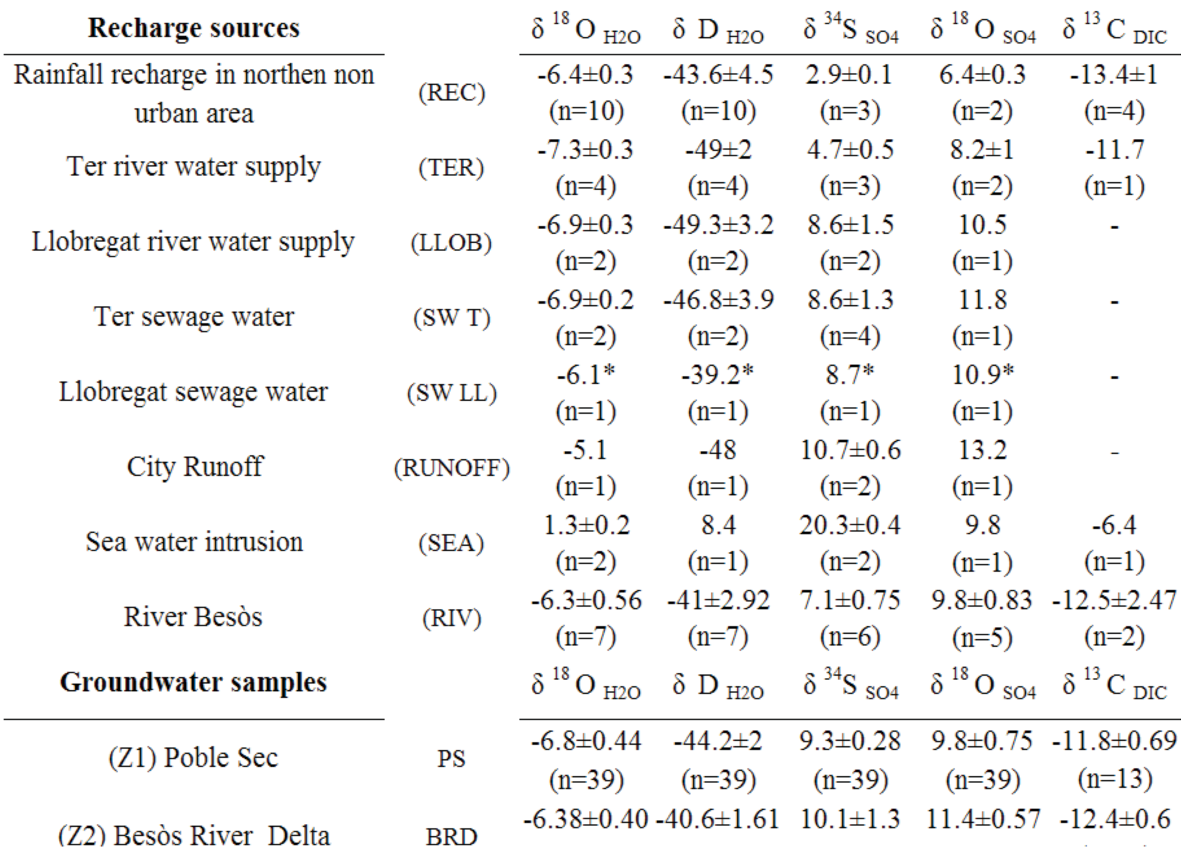


Figure 6.3. Plot of $\delta^{34}S_{SO4}$-$\delta^{18}O_{SO4}$ accounting for the recharge sources (and standard deviation) and groundwater samples collected in both zones: Poble Sec (PS, rhombus) and Besòs River Delta (BRD, rounds). Note that the different field campaigns are represented by the shade of grey: c2 is light grey, c3 is grey and c4 is dark grey.

6.3.2.2 Environmental isotopes in groundwater

Figure 6.2 and Figure 6.3 show the values $\delta^{18}O_{H2O}$ - δD_{H2O} and $\delta^{34}S_{SO4}$- $\delta^{18}O_{SO4}$ for the groundwater samples collected, respectively. Note that the isotopic composition of $\delta^{18}O_{H2O}$ and δD_{H2O} in c4 was lighter than those measured in c2 and also c3 in both zones (Figure 6.2). This could be explained by the rainfall events that occurred during the c4 field campaign. In Besòs River Delta zone, rain events caused a dilution effect in the Besòs flow regime, which directly affected groundwater composition. The average isotopic values and their standard deviation of the isotopes $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4,}$ $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$ measured in the groundwater samples are summarised in Table 6.2b for the two aforementioned zones. The results are given below.



Recharge sources		$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{13}C_{DIC}$
Rainfall recharge in northen non urban area	(REC)	-6.4±0.3 (n=10)	-43.6±4.5 (n=10)	2.9±0.1 (n=3)	6.4±0.3 (n=2)	-13.4±1 (n=4)
Ter river water supply	(TER)	-7.3±0.3 (n=4)	-49±2 (n=4)	4.7±0.5 (n=3)	8.2±1 (n=2)	-11.7 (n=1)
Llobregat river water supply	(LLOB)	-6.9±0.3 (n=2)	-49.3±3.2 (n=2)	8.6±1.5 (n=2)	10.5 (n=1)	-
Ter sewage water	(SW T)	-6.9±0.2 (n=2)	-46.8±3.9 (n=2)	8.6±1.3 (n=4)	11.8 (n=1)	-
Llobregat sewage water	(SW LL)	-6.1* (n=1)	-39.2* (n=1)	8.7* (n=1)	10.9* (n=1)	-
City Runoff	(RUNOFF)	-5.1 (n=1)	-48 (n=1)	10.7±0.6 (n=2)	13.2 (n=1)	-
Sea water intrusion	(SEA)	1.3±0.2 (n=2)	8.4 (n=1)	20.3±0.4 (n=2)	9.8 (n=1)	-6.4 (n=1)
River Besòs	(RIV)	-6.3±0.56 (n=7)	-41±2.92 (n=7)	7.1±0.75 (n=6)	9.8±0.83 (n=5)	-12.5±2.47 (n=2)
Groundwater samples		$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{13}C_{DIC}$
(Z1) Poble Sec	PS	-6.8±0.44 (n=39)	-44.2±2 (n=39)	9.3±0.28 (n=39)	9.8±0.75 (n=39)	-11.8±0.69 (n=13)
(Z2) Besòs River Delta	BRD	-6.38±0.40	-40.6±1.61	10.1±1.3	11.4±0.57	-12.4±0.6

Table 6.2. Average isotopic composition, standard deviation and number of samples of $\delta^{18}O_{H2O}$,δD_{H2O},$\delta^{34}S_{SO4}$,$\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$ in **(a)** recharge sources and **(b)** detailed in each zone of the study area.* Values from Otero *et al.* (2008).

Poble Sec

The water isotope values of the groundwater samples displayed compositional ranges between -7.3 ‰ and -5.2 ‰ for $\delta^{18}O_{H2O}$ and -48 ‰ and -38.5 ‰ for δD_{H2O}. Notably, most of the groundwater samples display a cluster and are in accordance to the local meteoric line. Sulphur and oxygen isotope values of sulphate in groundwater varied from +7.4 ‰ to +11.5 ‰ and +8.7 ‰ and +10 ‰, respectively. The average $\delta^{13}C_{DIC}$ is -11.8 ‰.

Besòs River Delta

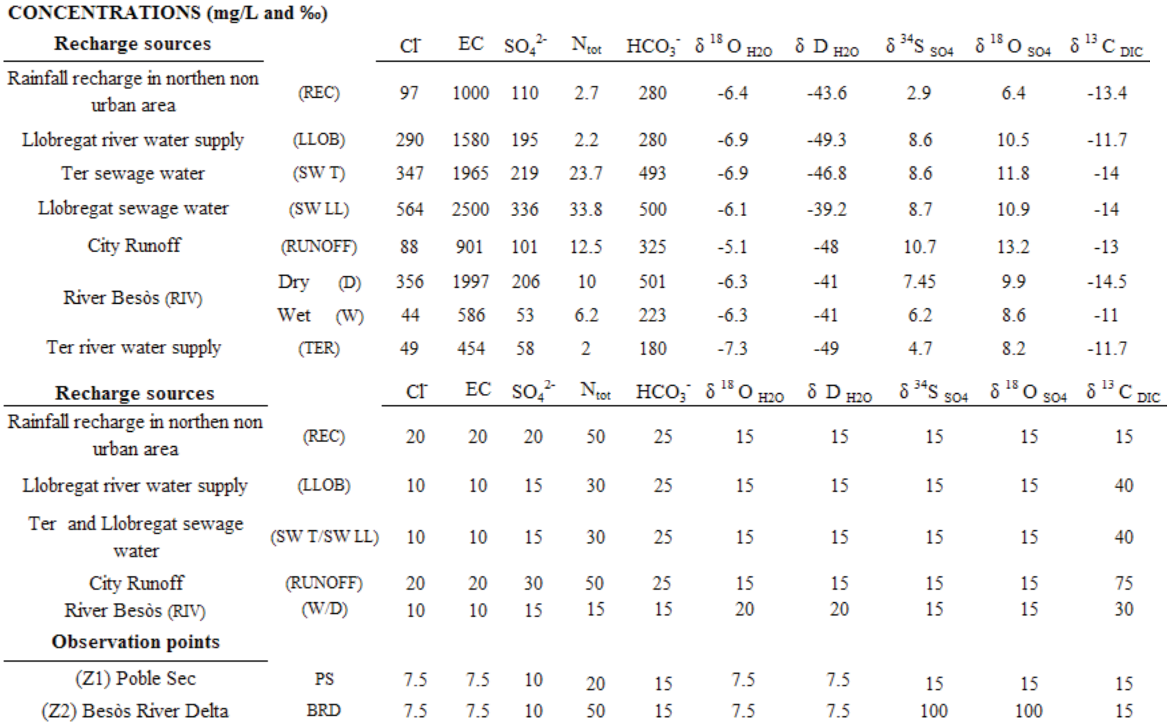
The isotopic composition of groundwater samples for $\delta^{18}O_{H2O}$ was similar to Poble Sec, ranging from -7.2 ‰ to -5.7 ‰ but the isotope values for δD_{H2O} varied in a narrow range between -43.6 ‰ and -38.1 ‰. Regarding dissolved sulphate isotope values: $\delta^{34}S_{SO4}$ ranged from +6.9 ‰ to +12.3 ‰ and $\delta^{18}O_{SO4}$ ranged from +10 ‰ to +12.5 ‰. At Besòs River Delta, the average $\delta^{13}C_{DIC}$ is similar to Poble Sec, being -12.4 ‰.

6.4. Discussion

6.4.1 Recharge sources identification and selection of the tracers in the pilot zones

As previously mentioned, up to eight different recharge sources were identified in Barcelona urban aquifers (Vàzquez-Suñé *et al.,* 2010): (1) rainfall recharge in the northern non urban area (REC), (2) river Ter water supply (TER), (3) river Llobregat water supply (LLOB) (4) river Ter sewage water (SW T), (5) river Llobregat sewage water (SW LL), (6) city runoff (RUNOFF), (7) sea water intrusion (SEA) and (8) river Besòs (RIV). Among these recharge sources, not all were considered in the pilot zones select for this study: Poble Sec and Besòs River Delta. SEA end-member was disregarded because neither Poble Sec nor Besòs River Delta were affected by sea water intrusion. Water supply in the pilot zones comes from two different rivers: Llobregat and Ter (LLOB and TER recharge sources). Poble Sec area is supplied by the River Llobregat and Besòs River Delta area is supplied by the River Ter. Consequently, two different compositions can also be found also in wastewater. Moreover, River Besòs (RIV) presents seasonal variations which reflected changes in water quality (Vàzquez-Suñé *et al.,* 2010). Therefore, it is not sufficient to consider only one end-member from the River Besòs because aquifer samples were collected at a local level during 4 different field campaigns from 2007 to 2010. Instead, two different end-members from this river were used to account for the temporal variability: wet conditions (W) and dry conditions (D). The former corresponded to diluted water related to wet periods or water supply inputs and the latter represented concentrated waters related to dry periods.

Selecting appropriate tracers is a critical step in mixing calculations (Morris *et al.,* 2006) because ideally, tracers should be conservative and their concentrations should vary widely from one source to another. Preliminary works developed for Barcelona aquifers suggested suitable tracers for differentiating the recharge sources adequately could be chloride, sulphate, total nitrogen, $\delta^{18}O_{H2O}$, δD_{H2O} and $\delta^{34}S_{SO4}$. In this study we also included electrical conductivity, bicarbonate, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$. We selected electrical conductivity because it behaves conservatively and the others because they may participate in the chemical reactions to be quantified. Their concentrations and isotopic compositions are detailed in Table 6.3a. As shown in Table 6.3a, tracer concentrations considering River Ter water supply and the River Besòs in wet season are similar. Consequently, we disregarded the water supply source (TER) because its contribution to the total recharge was much less significant than the River Besòs in the wet season (Jurado *et al.*, 2012a). Similarly, REC was not taken into account because previous studies demonstrated its null contribution to groundwater recharge in the lower parts of the Besòs River catchment, where the samples of Besòs River Delta were collected (Vàzquez-Suñé *et al.*, 2010).



CONCENTRATIONS (mg/L and ‰)

Recharge sources		Cl^-	EC	SO_4^{2-}	N_{tot}	HCO_3^-	$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{13}C_{DIC}$
Rainfall recharge in northen non urban area	(REC)	97	1000	110	2.7	280	-6.4	-43.6	2.9	6.4	-13.4
Llobregat river water supply	(LLOB)	290	1580	195	2.2	280	-6.9	-49.3	8.6	10.5	-11.7
Ter sewage water	(SW T)	347	1965	219	23.7	493	-6.9	-46.8	8.6	11.8	-14
Llobregat sewage water	(SW LL)	564	2500	336	33.8	500	-6.1	-39.2	8.7	10.9	-14
City Runoff	(RUNOFF)	88	901	101	12.5	325	-5.1	-48	10.7	13.2	-13
River Besòs (RIV)	Dry (D)	356	1997	206	10	501	-6.3	-41	7.45	9.9	-14.5
	Wet (W)	44	586	53	6.2	223	-6.3	-41	6.2	8.6	-11
Ter river water supply	(TER)	49	454	58	2	180	-7.3	-49	4.7	8.2	-11.7

Recharge sources		Cl^-	EC	SO_4^{2-}	N_{tot}	HCO_3^-	$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{13}C_{DIC}$
Rainfall recharge in northen non urban area	(REC)	20	20	20	50	25	15	15	15	15	15
Llobregat river water supply	(LLOB)	10	10	15	30	25	15	15	15	15	40
Ter and Llobregat sewage water	(SW T/SW LL)	10	10	15	30	25	15	15	15	15	40
City Runoff	(RUNOFF)	20	20	30	50	25	15	15	15	15	75
River Besòs (RIV)	(W/D)	10	10	15	15	15	20	20	15	15	30
Observation points											
(Z1) Poble Sec	PS	7.5	7.5	10	20	15	7.5	7.5	15	15	15
(Z2) Besòs River Delta	BRD	7.5	7.5	10	50	15	7.5	7.5	100	100	15

Table 6.3 (a) Initial concentrations of tracers selected for mixing ratios evaluation at each recharge source. The concentrations of the major ions and total nitrogen are expressed in mg/L, the electrical conductivity is expressed in µS/cm and the environmental isotopes in ‰. **(b)** Standard deviations to be considered in MIX code for each tracer in the recharge sources and groundwater samples expressed as a percentage of the concentration.

In summary, the recharge sources considered were LLOB, SW LL, REC and RUNOFF in Poble Sec zone and SW T, RUNOFF, RIV (W and T) in River Besòs Delta zone. The tracers selected were chloride, electrical conductivity, bicarbonate, sulphate, total nitrogen, $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$.

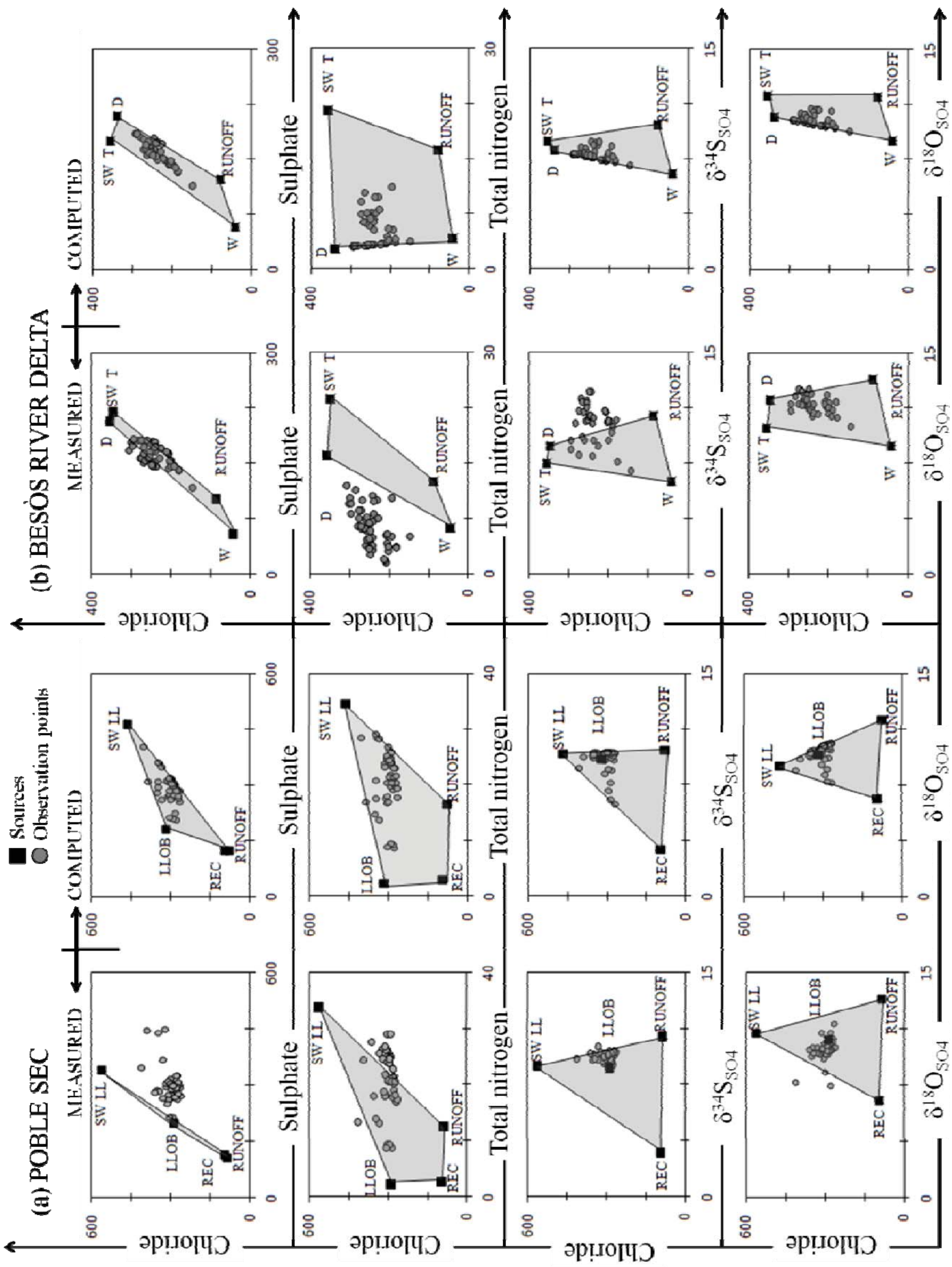


Figure 6.4. Plots of measured and computed concentrations and isotopic compositions. Note that measured concentrations of the recharge sources fail to envelope the measured concentrations in several samples in both Poble Sec and Besòs River Delta (Chloride versus sulphate, total nitrogen, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$). Conversely, computed recharge sources perfectly encircle the computed concentrations and isotopic compositions of considered tracers. Concentrations are in mg/L and isotopic composition in ‰.

6.4.2. Evaluation of the mixing ratios in groundwater recharge and composition of the sources

Mixing ratios in groundwater recharge were evaluated with MIX code (Carrera *et al.,* 2004). In this code, measurement uncertainty is quantified through covariance matrices. The need to consider uncertainty in recharge source concentrations is best illustrated in Figure 6.4 where measured end-member concentrations fail to envelop measurements of several observation points in plots such as chloride vs. sulphate, total nitrogen, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$. The code requires defining the reliability of measurements and the results depend on the assumed standard deviations. This suggests that standard deviations should be selected carefully. The standard deviations were selected depending on whether or not the tracers were conservative. The more conservative the tracer, the lower the assigned deviation. For instance, some environmental isotopes such as $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ could be non-conservative due to chemical processes. The standard deviations assigned to the recharge sources varied from 10 % to 75 % of the concentration for a specific tracer (Table 6.3). In general, the standard deviations assigned were lower in groundwater samples than those assigned to the recharge sources because recharge source composition was more uncertain (Table 6.3b).

Once standard deviations were assigned, chemical composition of the recharge sources and mixing ratios at each observation point could be evaluated. As shown in Figure 6.4, computed recharge source concentrations perfectly enveloped all the computed concentrations. However, it is important to analyse, the reliability of the computed chemical composition of recharge sources. When measured and computed concentrations for all the tracers in recharge sources and observations points were compared (Figure 6.5), several observations could be made:

(1) Computed recharge source concentrations for chloride, sulphate, bicarbonate and electrical conductivity were similar to measured ones in both zones, falling close to the 1:1 line. The same occurred with total nitrogen in Poble Sec. Also, computed and measured concentrations at the observation points for these species fell close to 1:1 line, especially for chloride and electrical conductivity.

(2)

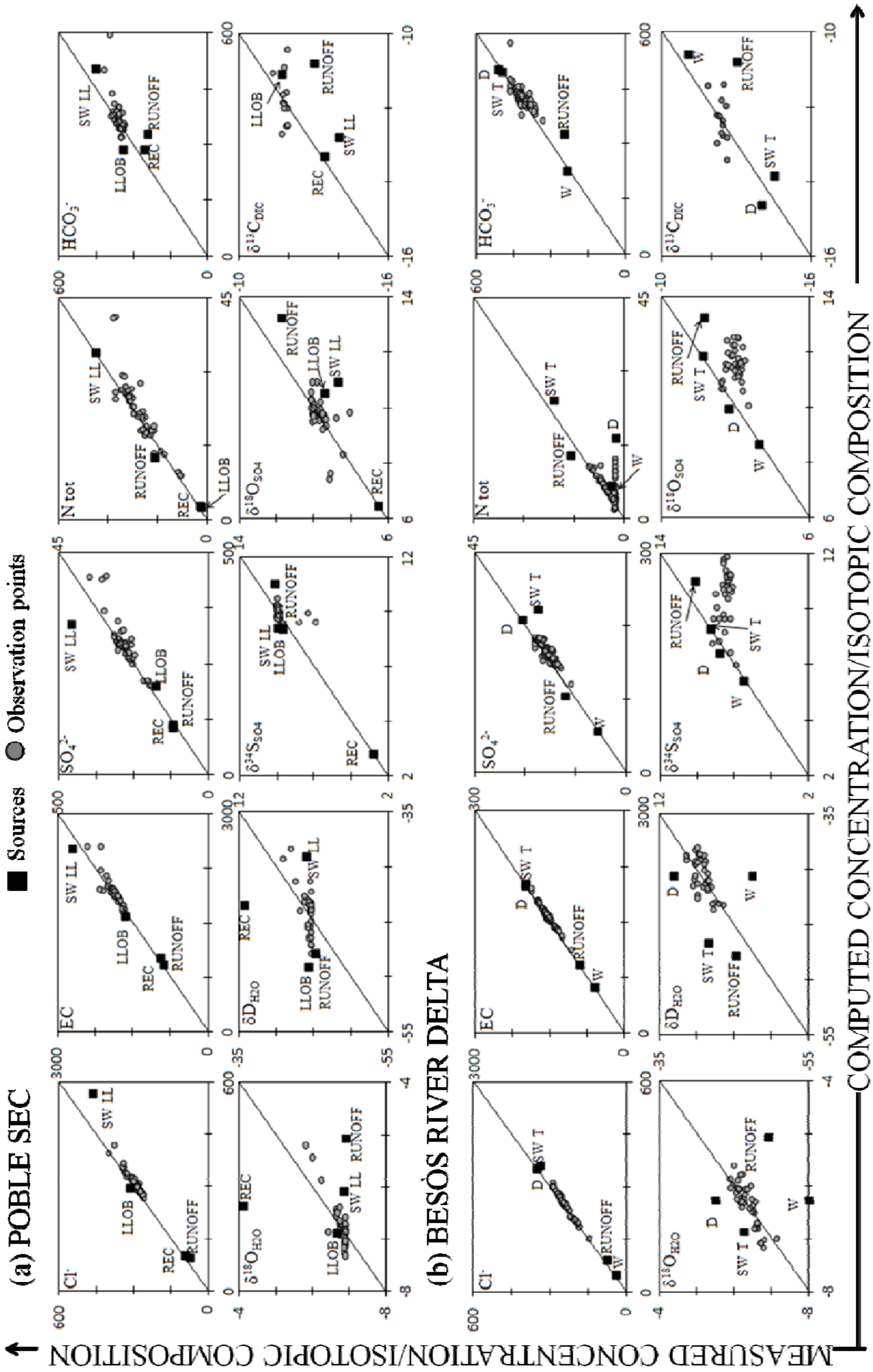
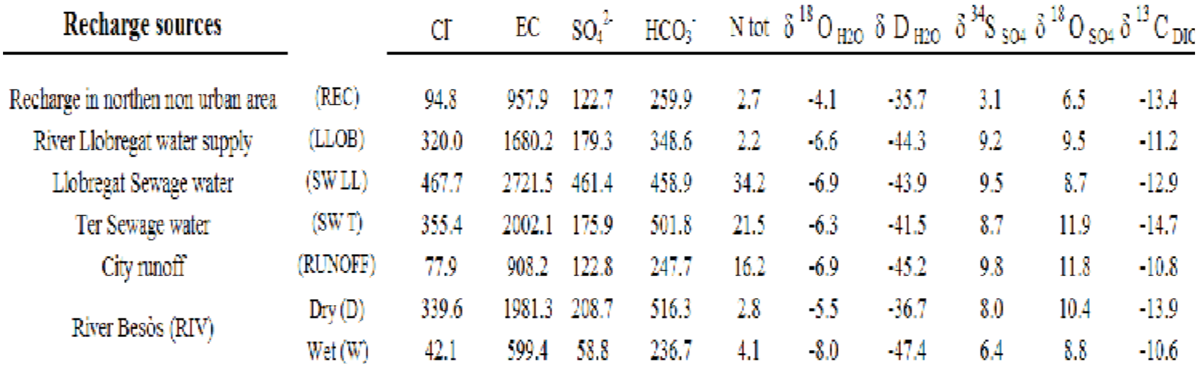


Figure 6.5. Computed versus measured concentrations and isotopic composition at all recharge sources and groundwater samples in Poble Sec (PS) and Besòs River Delta (BRD). Note that $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ isotopes of dissolved sulphate do not behaved conservatively at Besòs River Delta. Concentrations are in mg/L and isotopic composition in ‰.

(2) Computed concentration of total nitrogen at Besòs River Delta for dry end-member (D) was drastically reduced. Accordingly, measured concentrations for some observation points were lower than computed ones (Figure 6.5b). Nitrate concentrations at River Besòs can reach levels of 15 mg/L but measured concentrations at points located near the river (SAP's and ADS6n, Figure 6.1) are drastically reduced to null or very low levels (on average, 0.45 mg/L). This may be indicative that denitrification could occur when river water infiltrates the aquifer. Unfortunately, we did not analyse the environmental isotopes of dissolved nitrate in groundwater.

(3) Computed recharge concentrations were in line with the standard deviations assigned (Table 6.4). As observed with the general hydrochemistry, the separation of the city into two distinct water quality zones was supported by the computed recharge concentrations of SW T and SW LL. Overall, sewage waters were the more mineralised waters followed by dry end-member of the River Besòs. Among them, SW LL was the recharge source with the highest levels of chloride, electrical conductivity, sulphate and total nitrogen. Conversely, wet end-member from the River Besòs presented the lowest concentrations, except for total nitrogen. A more detailed discussion of the isotopic composition of the recharge sources and the assessment of the environmental isotopes in groundwater samples can be found in the following sections 6.4.3 and 6.4.4, respectively.



Recharge sources		Cl^-	EC	SO_4^{2-}	HCO_3^-	N tot	$\delta^{18}O_{H2O}$	δD_{H2O}	$\delta^{34}S_{SO4}$	$\delta^{18}O_{SO4}$	$\delta^{13}C_{DIC}$
Recharge in northen non urban area	(REC)	94.8	957.9	122.7	259.9	2.7	-4.1	-35.7	3.1	6.5	-13.4
River Llobregat water supply	(LLOB)	320.0	1680.2	179.3	348.6	2.2	-6.6	-44.3	9.2	9.5	-11.2
Llobregat Sewage water	(SW LL)	467.7	2721.5	461.4	458.9	34.2	-6.9	-43.9	9.5	8.7	-12.9
Ter Sewage water	(SW T)	355.4	2002.1	175.9	501.8	21.5	-6.3	-41.5	8.7	11.9	-14.7
City runoff	(RUNOFF)	77.9	908.2	122.8	247.7	16.2	-6.9	-45.2	9.8	11.8	-10.8
River Besòs (RIV)	Dry (D)	339.6	1981.3	208.7	516.3	2.8	-5.5	-36.7	8.0	10.4	-13.9
	Wet (W)	42.1	599.4	58.8	236.7	4.1	-8.0	-47.4	6.4	8.8	-10.6

Table 6.4. Computed concentrations and isotopic compositions in all the recharge sources for the selected tracers expressed in mg/L and ‰.

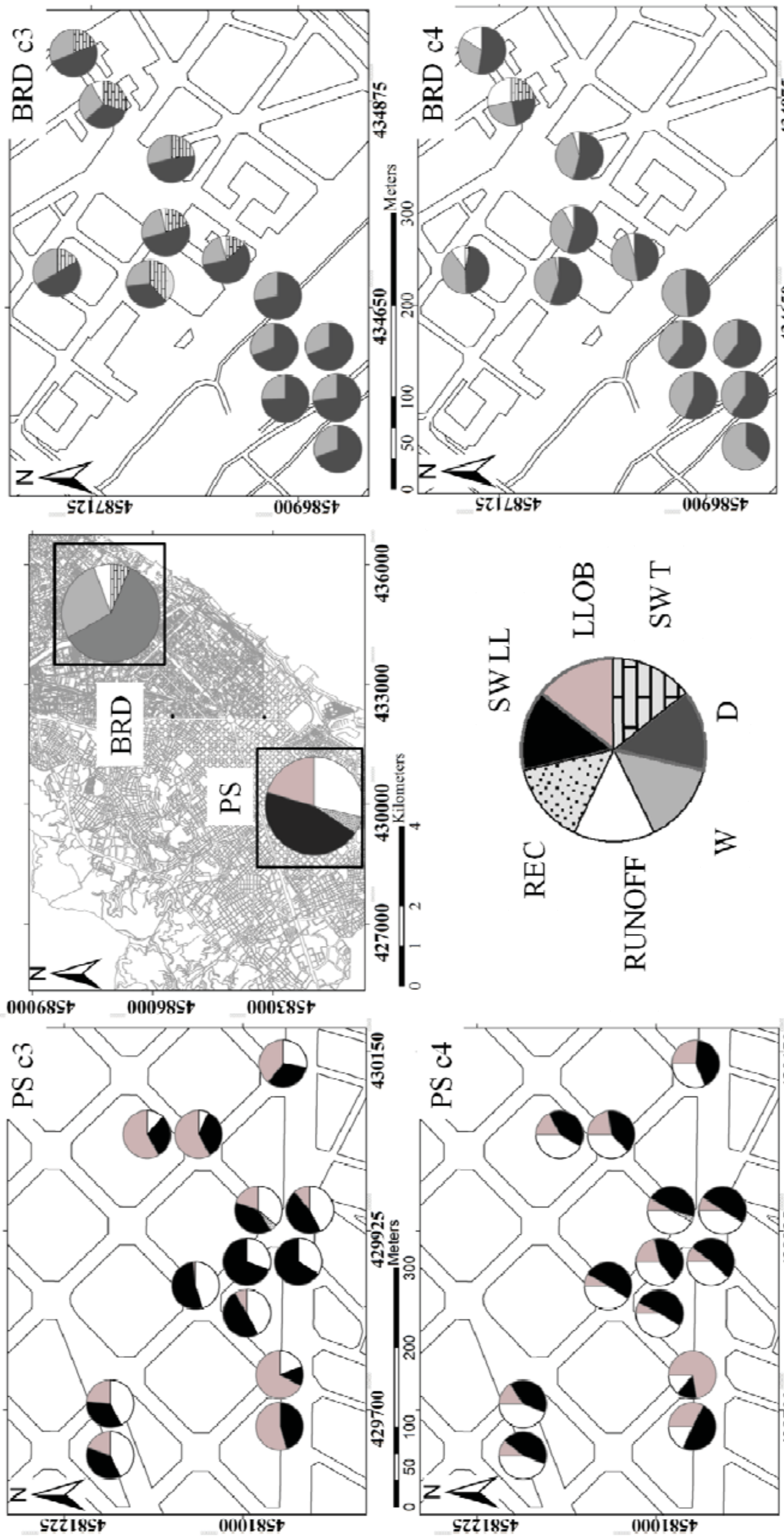


Figure 6.6. Spatial distribution of mixing ratios evaluated for c3 and c4 at both zones. Note the average mixing ratios considering all sampling campaigns of each zone (PS and BRD).

Computed mixing ratios help in deriving the mass balance of the study zones and directly depend on the composition of the recharge sources. Figure 6.6 shows the computed mixing ratios spatial distribution at each sampling point accounted for c3 and c4 in both zones. Also, it is shown the average mixing ratios for each recharge sources considering the four sampling campaigns in both zones. According to the identified sources, in Poble Sec the average main contributor to the total recharge was sewage network loss SW LL (46%) and no significant differences were observed among the different field campaigns. Runoff water in paved areas was highly variable, ranging from 24 % to 36 % in c1 and c4, respectively. Overall, it represented the 28 % of the resident water. The remaining 26 % corresponded to water supply network loss (20 %) and the recharge in non-urbanised areas (REC, 6%). As for Besòs River Delta, RIV (River Besòs) was by far the largest contributor to the total recharge, representing 88 % in total; 60% from dry conditions and 28 % from wet conditions. Seasonal variations of River Besòs dynamics were reflected in groundwater concentrations because wet conditions end-member was represented in c4, on average, 42 % of the total recharge. This could be explained because c4 samples were collected in a rainy period. In contrast, this end-member represented 25 %, 15 % and 29 % in the c1, c2 and c3, respectively. Table 6.4 shows the differences that existed between the end-members in wet and dry conditions, the latter being the one that presented high levels for all tracers, except for total nitrogen and $\delta^{13}C_{DIC}$. Other contributors to the recharge were network sewage loss (SW T) and runoff water in paved areas (RUNOFF) at low percentages, representing 6 % each. Note that both SW T and RUNOFF only contributed to groundwater recharge points located close to the parking site (Figure 6.6).

6.4.3. Isotopic composition of the recharge sources at the pilot zones

Table 6.4 summarises the computed isotopic composition of the environmental isotopes at all recharge sources.

6.4.3.1 Isotopic composition of $\delta^{18}O_{H2O}$ and δD_{H2O}

The computed isotopic composition of $\delta^{18}O_{H2O}$ and δD_{H2O} from REC presented the heaviest values among the other recharge sources. The isotopic composition of the water supply LLOB ($\delta^{18}O_{H2O}$= -6.6 ‰ and δD_{H2O}= -44.3 ‰) shows similar values to those from the River Llobregat ($\delta^{18}O_{H2O}$= -7 ‰. and δD_{H2O}= -45.5 ‰, Otero el *at.* (2008)). Both sewage waters (SW LL and SW T) presented similar isotopic composition. As regards to the end-members from the RIV, they presented distinct isotopic compositions. During dry conditions (D), values of $\delta^{18}O_{H2O}$ and δD_{H2O} were heavier than those in wet conditions (W), ranging from -5.5 ‰ to -8 ‰ for $\delta^{18}O_{H2O}$ and from -36.7 ‰ to -47.4 ‰ for δD_{H2O}, respectively. This could be explained taking into consideration the variability of the rainfall in the Besòs River Delta watershed, with higher values of $\delta^{18}O_{H2O}$ under warm temperatures (late spring and summer). All the computed values were in line with the standard deviations assigned.

6.4.3.2 Isotopic composition of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$

REC presented the lightest isotopic composition with values of $\delta^{34}S_{SO4}$=+3.1 ‰ and $\delta^{18}O_{SO4}$= +6.5 ‰. The values of $\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ for LLOB were in agreement with reported values of the River Llobregat (Otero *et al.,* 2008). Moreover, SW LL and SW T values were in the range of the isotopic composition measured in several sewage water treatment plants located along the River Llobregat and resulted in +7 ‰ to +14 ‰ for $\delta^{34}S_{SO4}$ and +8 ‰ to +12.5 % for $\delta^{18}O_{SO4}$ (Otero *et al.,* 2008). Since the River Besòs contains a large proportion of effluents from secondary waste water treatment plants, the isotopic composition of its dry end-member correspond to the values of sewage waters and treated sewage waters (Vitoria *et al.,* 2004 and Otero *et al.,* 2008). In contrast, wet end-member was 20% lighter than the dry end-member because of the River Besòs variability, which is controlled by rainfall.

6.4.3.3 Isotopic composition of $\delta^{13}C_{DIC}$

The computed values of $\delta^{13}C_{DIC}$ for all end-members were in complete agreement with the expected values of the $\delta^{13}C_{DIC}$ when the dissolved inorganic carbon of the groundwater was in equilibrium with the dioxide carbon of the soil/aquifer. These values ranged from -12 ‰ to -15 ‰ (Vogel and Ehhalt., 1963) and from -14 ‰ to -16 ‰ (Clark and Fritz, 1997).

6.4.4 Assessment of the fate of the environmental isotopes in groundwater samples

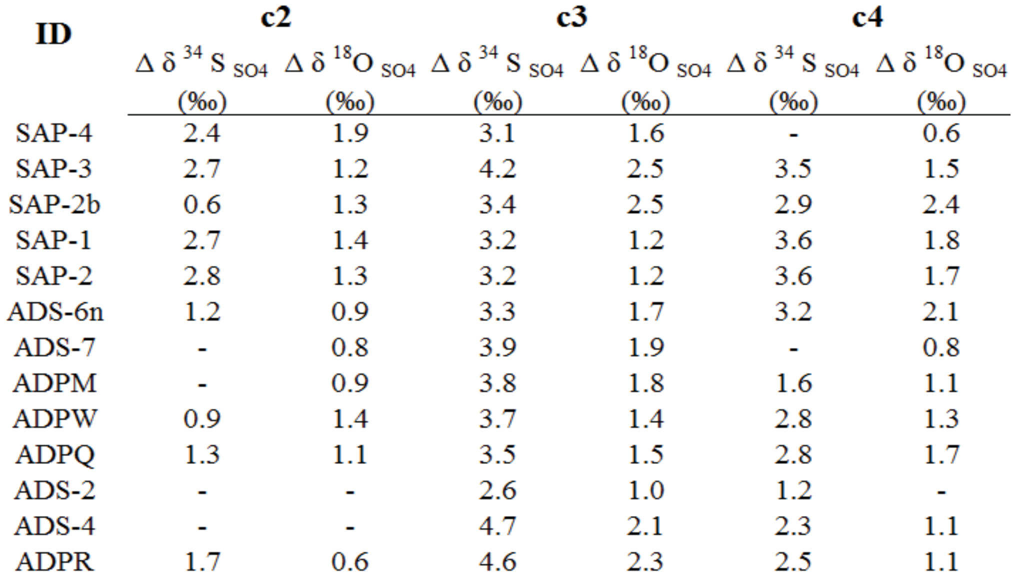
Once the mixing ratios were computed and the isotopic composition in the potential recharge sources determined, it was possible to assess the fate of these isotopes in the aquifer.

Poble Sec

Figure 6.5a shows the measured and computed isotopic composition of $\delta^{18}O_{H2O}$, δD_{H2O}, $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$ and $\delta^{13}C_{DIC}$ estimated from mixing ratios. When measured and estimated values were compared, it could be seen that a great number of samples fell relatively close to the 1:1 line (ideal mixing line). This fact indicated that the isotopic values for water and sulphate isotopes could be explained by a mixing of the different recharge sources considered (REC, RUNOFF, SW LL and LLOB).

Besòs River Delta

In contrast to Poble Sec, some environmental isotopes in groundwater samples of Besòs River Delta presented different behaviour (Figure 6.5b).Water isotopes and $\delta^{13}C_{DIC}$ isotopic composition could be explained by a mixing among the recharge sources (RUNOFF, W, D and SW T). However, this could not be applied to $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ because measured values were higher than the computed ones, suggesting the occurrence of geochemical processes that depleted sulphate in groundwater. Despite dissolved sulphate behaved conservatively, the environmental isotopes of sulphate did not (Figure 6.5b). Therefore, groundwater samples may have shifted from their original compositions. A general trend of increasing $\delta^{34}S_{SO4}$ with decreasing sulphate concentration was attributed to bacterial reduction (Grassi and Cortecci, 2005; Yamanaka and Kumagai, 2006). The maximum extent value was 4.7 ‰ for $\delta^{34}S_{SO4}$ and 2.5 ‰ for $\delta^{18}O_{SO4}$ (Table 6.5). The significance of this process and its distribution within the aquifer in terms of increments of $\delta^{34}S_{SO4}$ enabled the division of this study zone according to the location of the points: (1) Points located near the river (SAP's and ADS-6n, Figure 6.1) and (2) points located closer to underground car park at Plaça de la Vila site (ADS-7, ADS-2, ADS-4 and ADP's, Figure 6.1).



ID	c2		c3		c4	
	$\Delta\delta^{34}S_{SO4}$ (‰)	$\Delta\delta^{18}O_{SO4}$ (‰)	$\Delta\delta^{34}S_{SO4}$ (‰)	$\Delta\delta^{18}O_{SO4}$ (‰)	$\Delta\delta^{34}S_{SO4}$ (‰)	$\Delta\delta^{18}O_{SO4}$ (‰)
SAP-4	2.4	1.9	3.1	1.6	-	0.6
SAP-3	2.7	1.2	4.2	2.5	3.5	1.5
SAP-2b	0.6	1.3	3.4	2.5	2.9	2.4
SAP-1	2.7	1.4	3.2	1.2	3.6	1.8
SAP-2	2.8	1.3	3.2	1.2	3.6	1.7
ADS-6n	1.2	0.9	3.3	1.7	3.2	2.1
ADS-7	-	0.8	3.9	1.9	-	0.8
ADPM	-	0.9	3.8	1.8	1.6	1.1
ADPW	0.9	1.4	3.7	1.4	2.8	1.3
ADPQ	1.3	1.1	3.5	1.5	2.8	1.7
ADS-2	-	-	2.6	1.0	1.2	-
ADS-4	-	-	4.7	2.1	2.3	1.1
ADPR	1.7	0.6	4.6	2.3	2.5	1.1

Table 6.5. Quantification of sulphate reduction in terms of enrichment factors of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ (‰) at each observation point (ID) for sampling campaigns c2, c3 and c4.

The observation points located close to the river, presented constant increments of $\delta^{34}S_{SO4}$ during the different sampling periods (on average 2.7 ‰). But the average enrichment degree of $\delta^{34}S_{SO4}$ was more important in the deeper observations points (SAP-1, SAP-2 and SAP-3) than in the shallower ones, being 3.3 ‰ and 2.2 ‰, respectively. In the rest of observation points, clearly more affected by the continuous pumping of Plaça de la Vila site, no clear tendency was observed although sulphate reduction was also occurring but to a lower degree (on average 2.1 ‰).

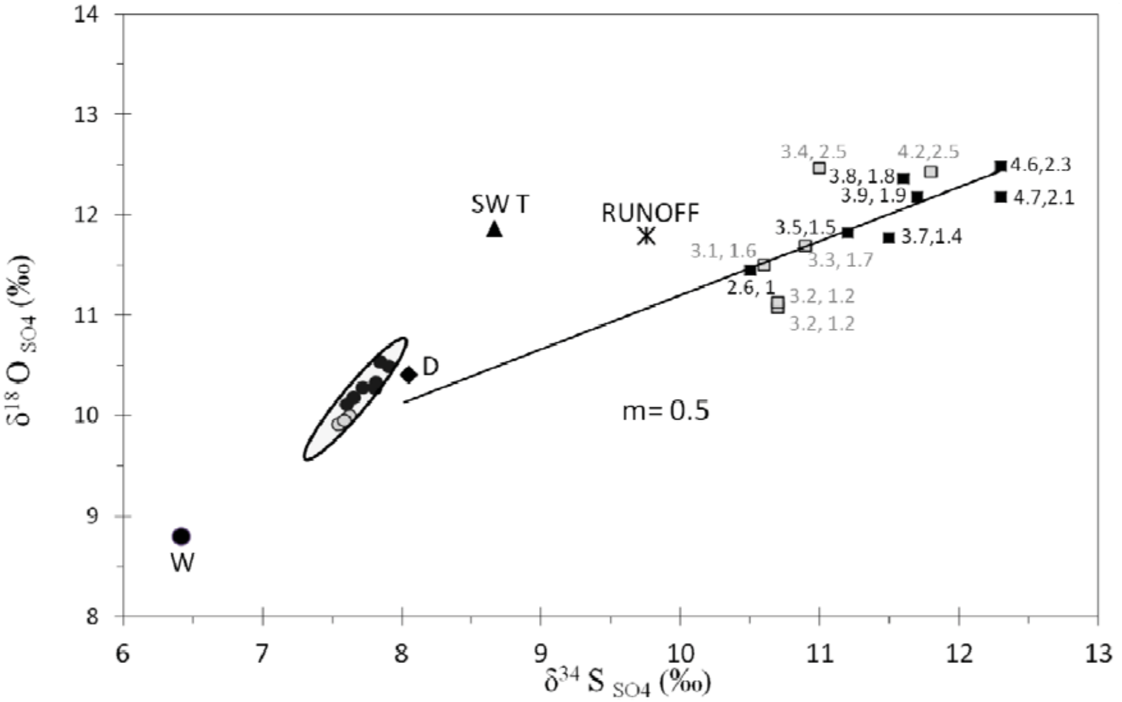
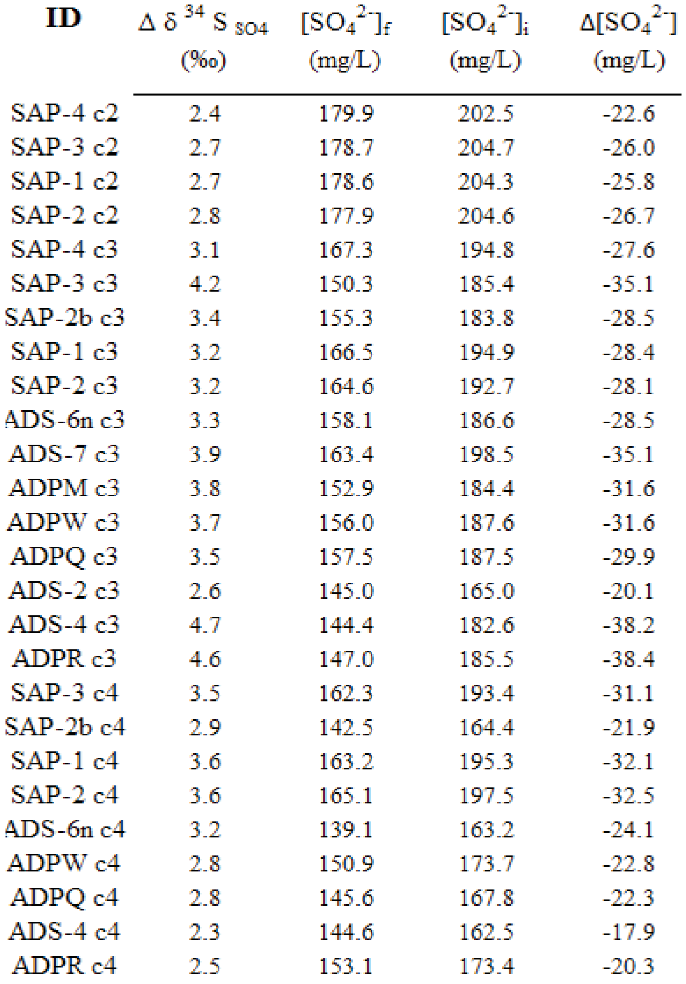


Figure 6.7. Relationship between $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in groundwater samples of the c3. Grey and black colours represented the observation points located near and far from the river, respectively. The encircled values are those expected by simple mixing of the recharge sources computed with MIX code. Note that the enrichment factor for $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ are detailed for each sampling point (‰).

One of the most relevant results in this research was the quantification of sulphate reduction at each observation point (Table 6.5). As an example, Figure 6.7 shows the expected isotopic composition of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ for c3 by simple mixing of the recharge sources (ranging between 7 ‰ and 8 ‰) and the quantification of sulphate reduction in terms of enrichment factors of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ at each sampling point. The enrichment ratio between $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ presented a slope (m) of 2 and it was much lower than those values obtained under experimental conditions, ranging from 2.5 to 4 (Mitzutani and Rafter, 1973). However, in application case studies the conditions are not as ideal as in lab experiments. The slope between $\varepsilon\ \delta^{34}S/\ \varepsilon\ \delta\ ^{18}O$ obtained by sulphate reduction in a sandy aquifer was close to 0.70 (Strebel *et al.*, 1990). Computed values of Table 6.5 allowed evaluating the depleted concentration of dissolved sulphate due to sulphate reduction process. It could be quantified according to the Rayleigh fractionation equation. The sulphur enrichment factors during sulphate reduction can vary from less than 0 ‰ to more than 45‰ (Aravena and Mayer, 2010). However, they range between 10 ‰ and 20 ‰ in hydrological settings (Strebel *et al.*, 1990; Dogramaci *et al.*, 2001; Spence *et al.*, 2001). Consequently, the initial dissolved sulphate concentration ($[SO_4^{2-}]_i$) was calculated according to a $\varepsilon^{34}S_{SO4}$= 20 ‰ in groundwater samples that presented increments of $\delta^{34}S$ higher than 2 delta units in Besòs River Delta. The use of $\varepsilon^{18}O_{SO4}$ was disregard because oxygen isotope ratios may approach to a constant value during bacterial sulphate reduction (Boettcher *et al.*, 2001).



ID	$\Delta\ \delta^{34}S_{SO4}$ (‰)	$[SO_4^{2-}]_f$ (mg/L)	$[SO_4^{2-}]_i$ (mg/L)	$\Delta[SO_4^{2-}]$ (mg/L)
SAP-4 c2	2.4	179.9	202.5	-22.6
SAP-3 c2	2.7	178.7	204.7	-26.0
SAP-1 c2	2.7	178.6	204.3	-25.8
SAP-2 c2	2.8	177.9	204.6	-26.7
SAP-4 c3	3.1	167.3	194.8	-27.6
SAP-3 c3	4.2	150.3	185.4	-35.1
SAP-2b c3	3.4	155.3	183.8	-28.5
SAP-1 c3	3.2	166.5	194.9	-28.4
SAP-2 c3	3.2	164.6	192.7	-28.1
ADS-6n c3	3.3	158.1	186.6	-28.5
ADS-7 c3	3.9	163.4	198.5	-35.1
ADPM c3	3.8	152.9	184.4	-31.6
ADPW c3	3.7	156.0	187.6	-31.6
ADPQ c3	3.5	157.5	187.5	-29.9
ADS-2 c3	2.6	145.0	165.0	-20.1
ADS-4 c3	4.7	144.4	182.6	-38.2
ADPR c3	4.6	147.0	185.5	-38.4
SAP-3 c4	3.5	162.3	193.4	-31.1
SAP-2b c4	2.9	142.5	164.4	-21.9
SAP-1 c4	3.6	163.2	195.3	-32.1
SAP-2 c4	3.6	165.1	197.5	-32.5
ADS-6n c4	3.2	139.1	163.2	-24.1
ADPW c4	2.8	150.9	173.7	-22.8
ADPQ c4	2.8	145.6	167.8	-22.3
ADS-4 c4	2.3	144.6	162.5	-17.9
ADPR c4	2.5	153.1	173.4	-20.3

Table 6.6. Evaluation of depleted dissolved sulphate due to the occurrence of sulphate reduction in selected groundwater samples for Besòs River Delta ($\varepsilon^{34}S_{SO4}$= -20 ‰.). Note that the

difference between residual and initial values of $\delta^{34}S_{SO4}$ is the $\Delta\ \delta^{34}S_{SO4}$ and $[SO_4^{2-}]_f$ and $[SO_4^{2-}]_i$ are the final and initial dissolved sulphate concentrations in groundwater samples.

The measured values of dissolved sulphate and the isotopic composition were used as final sulphate concentration ($[SO_4^{2-}]_f$) and residual value of $\delta^{34}S_{SO4}$, respectively. The initial composition of $\delta^{34}S_{SO4}$ was computed by the MIX code and this value represented a mixture among the different recharge sources. Note that the difference between residual and initial values of $\delta^{34}S_{SO4}$ is the $\Delta\ \delta^{34}S_{SO4}$ presented in Tables 6.5 and 6.6. Table 6.6 shows the evaluated initial sulphate concentration and the concentration depleted due to sulphate reduction in selected groundwater samples. Assuming that sulphate reduction occurred in the aquifer, dissolved sulphate was reduced, on average, 28 mg/L in Besòs River Delta. These concentrations were in agreement with the standard deviations assigned, representing 15% of the initial dissolved sulphate ($[SO_4^{2-}]_i$). The depleted sulphate concentration due to sulphate reduction was 18 mg/L when $\varepsilon^{34}S_{SO4}$= 30 ‰ (see Table S6 in Annex I).

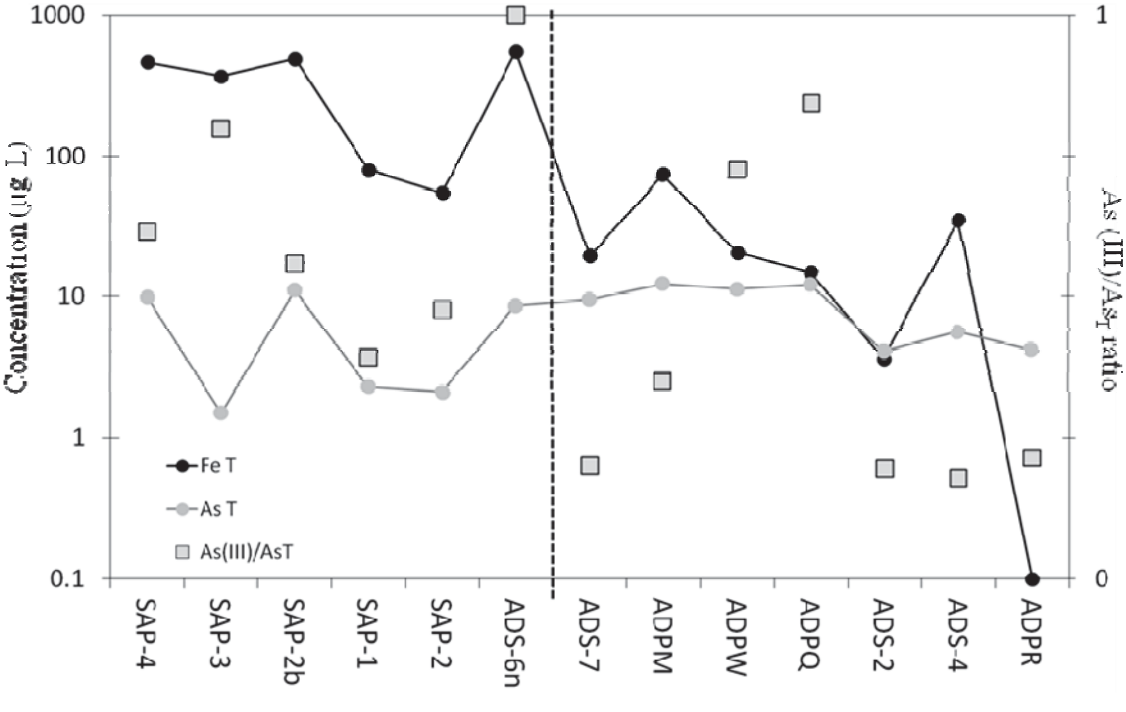


Figure 6.8. On the left axis, iron and arsenic concentrations in groundwater samples collected in c4. The ratio between As (III) and the total arsenic is plotted on the right axis. The black dashed line divided Besòs River Delta study zone considering the location of the sampling points (close or far to the river, Figure 6.1).

There were other chemical indicators that supported the occurrence of the sulphate reduction process at Besòs River Delta aquifers such as the presence of ammonium, the low concentrations of dissolved oxygen and the high levels of dissolved heavy metals like arsenic (As) and iron (Fe). As shown in Figure 6.8, As(III) /As_T concentration ratio demonstrated that arsenic reduced form (As(III)) was the predominant dissolved specie in the observation points located close to the river (SAP's and ADS-6n, see Figure 6.1) and in some points located near the park site (ADPQ and ADPW, Figure 6.1) supporting the reducing aquifer environment. According to Pierce and Moore (1981), arsenic tends to be adsorbed by amorphous iron hydroxide because it is ubiquitous in clays, soils and sediments and might be released in groundwater where sulphate reduction can occur (Plant *et al.*, 2005).

6.5 Conclusions

The application of environmental isotopes coupled with hydrochemistry data using mixing ratios has provided the isotopic quantification of groundwater recharge sources and the occurrence of redox processes such as sulphate reduction. The presented approach enabled: (1) to quantify the mixing ratios into groundwater considering a degree of uncertainty in both the recharge sources and the observation points and (2) to evaluate the occurrence of redox processes at each observation point. This application has been validated into two hydrochemically distinct zones. Poble Sec, where isotopic composition of recharge sources has shown a strong influence of sewage water infiltration into the aquifers and no sulphate reduction occurred in groundwater samples. In contrast, at Besòs River Delta, mainly recharge from river Besòs water, dissolved sulphate isotopes could not be explained by only simple mixing of the groundwater recharge sources because the measured compositions at the observation points were higher than the computed ones, suggesting the occurrence of sulphate reduction. The maximum extent value for $\delta^{34}S_{SO4}$ was 4.7 ‰. The approach taken in this study can be used in other aquifer systems to quantify not only groundwater recharge sources but to also quantify processes like nitrification, denitrification and sulphate reduction.

7. General conclusions

The following general results may be drawn from the elaboration of this thesis:

- An exhaustive review of the occurrence of various EOCs reported in Spain's groundwater was carried out. These include pesticides, PhACs, industrial compounds, DAs, estrogens, life-style compounds and personal care products. The major point source of pollution of these EOCs in groundwater corresponded to the effluents of WWTPs. The contamination profile seems to be dominated by industrial compounds, followed by pesticides and PhACs. Most EOCs are usually detected at low (ng/L) concentrations or not detected at all in groundwater throughout Europe. However, an increasing number of individual compounds are found at μg/L concentrations. Consequently, proper assessment of groundwater quality against deterioration requires the investigation of a wide variety of compounds, of the processes they undergo in groundwater and perhaps the establishment of environmental quality criteria.

- The occurrence of a wide range DAs was studied in the urban groundwater of Barcelona. DAs were present at low but measurable concentrations. Concentrations in the aquifer were generally much lower than those expected due to dilution, as calculated from the mixing ratios of the recharge sources. This suggests significant removal of DAs in the aquifer under different redox conditions: oxidizing conditions (Poble Sec and Mallorca Street) and reducing conditions (Sant Adrià).

- The occurrence and fate of CBZ and its metabolites in urban groundwater at a field scale under different redox conditions was investigated. The parent compound CBZ was found ubiquitously in both Poble Sec and Besòs River Delta. Metabolites of CBZ have been more widely detected and at higher concentrations in Besòs River Delta. This is due to the fact that the River Besòs receives large amounts of effluents from WWTPs that infiltrate into the aquifer. CBZ seems to be more degraded in Poble Sec aquifers because concentrations measured in groundwater have been lower than those expected from the recharge sources. Conversely, CBZ and the metabolites 3OH CBZ, 2OH CBZ and ACRON have not been degraded under the reducing conditions of Besòs River Delta aquifers possibly due to the short residence time in this aquifer. Only CBZ-EP and ACRIN seemed to be naturally removed into the aquifer.

- A methodology to quantify chemical reactions that may affect the emerging organic contaminants was presented using mixing ratios. This approach allows us to identify and quantify some of the geochemical processes undergone in each sampling point. These processes included aerobic respiration, nitrification and denitrification.

- The application of environmental isotopes coupled with hydrochemistry data using mixing ratios has provided the isotopic quantification of groundwater recharge sources and the occurrence of redox processes such as sulphate reduction. The approach presented can be used in aquifer systems to quantify not only groundwater recharge sources but also redox processes.

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ANNEXES

Annex I. Supplementary tables

Table S1 Summary for all EOCs studied in groundwater in Spain included in this review. Note that the maximum detected concentrations and references are detailed for each contaminant. n.d= not detected and “-“compounds detected by Estévez et al. (2012) but the frequency of detection and the concentrations were not specified.

Type of EOCS	Compound	Studies	Max (ng/L)	References
Pesticides				
Triazine herbicides	Ametryn	3	20	Garrido et al., 2000; Teijon et al., 2010; Estévez et al., 2012
	Atrazine	17	3450	Garrido et al., 2000 ; Quintana et al., 2001; Carabias-Martínez et al., 2000, 2002 and 2003; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Sánchez-Camazano et al., 2005; Hilderbrandt et al., 2007 and 2008; García-Galán et al., 2010a; Postigo et al., 2010; Teijon et al., 2010; Bono-Blay et al., 2012;Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Cyanazine	6	3.9	Quintana et al., 2001; Kampioti et al., 2005; García-Galán et al., 2010a; Postigo et al., 2010; Bono-Blay et al., 2012; Köck-Schulmeyer et al., 2012
	Desethylatrazine (DEA)	12	1980	Quintana et al., 2001; Carabias-Martínez et al., 2002; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Hilderbrandt et al., 2007 and 2008; García-Galán et al., 2010a; Postigo et al., 2010; Teijon et al., 2010; Bono-Blay et al., 2012; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Desethyldesisopropylatrazine (DEDIA)	1	n.d	Carabias-Martínez et al., 2002
	Desethylhydroxyatrazine (DEHA)	1	n.d	Carabias-Martínez et al., 2002
	Desethylterbuthylazine (DET)	2	270	Hildebrandt et al., 2008; García-Galán et al., 2010a
	Desisopropylatrazine (DIA)	7	790	Quintana et al., 2001; Kampioti et al., 2005; Hildebrandt et al., 2008; García-Galán et al., 2010a; Postigo et al., 2010; Bono-Blay et al 2012; Köck-Schumeyer et al., 2012
	Desisopropylhydroxyatrazine (DIHA)	1	n.d	Carabias-Martínez et al., 2002
	Hydroxyatrazine (HA)	1	n.d	Carabias-Martínez et al., 2002
	Hydroxyterbutylazine (HT)	1	n.d	Carabias-Martínez et al., 2002
	Prometon	2	10.6	Garrido et al., 2000; García-Galán et al.,2010a
	Prometryn	2	1000	Garrido et al., 2000; Bono-Blay et al., 2012
	Propazine	6	20	Garrido et al., 2000; Quintana et al., 2001; García-Galán et al.,2010a;Teijon et al., 2010; Bono-Blay et al., 2012; Estévez et al., 2012
	Sebuthylazine	2	n.d	García-Galán et al., 2010a; Bono-Blay et al., 2012
	Simazine	13	1690	Garrido et al., 2000 ; Quintana et al., 2001; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Hilderbrandt et al., 2007 and 2008; García-Galán et al., 2010a; Postigo et al., 2010; Teijon et al., 2010; Bono-Blay et al., 2012; Estévez et al., 2012; Köck-Schulmeyer et al., 2012

	Terbuthylazine (TBA)	9	1270	Quintana et al., 2001; Kampioti et al., 2005; Hilderbrandt et al., 2007 and 2008; Postigo et al., 2010; Teijon et al., 2010; Bono-Blay et al., 2012;Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Terbutryn	9	180	Garrido et al., 2000; Quintana et al., 2001; Carabias-Martínez et al., 2000, 2002 and 2003; Hildebrandt et al., 2007; Teijon et al., 2010; Bono-Blay et al., 2012; Estévez et al., 2012
Urea herbicides	Chlorsulfuron	2	n.d	Carabias-Martínez et al., 2000 and 2003
	Chlortoluron	8	1700	Carabias-Martínez et al., 2000, 2002, 2003; Kampioti et al., 2005; Postigo et al., 2010; Teijon et al., 2010; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	CMPU	1	n.d	Carabias-Martínez et al., 2002
	Diuron	9	178	Carabias-Martínez et al., 2000 and 2003; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Postigo et al., 2010; Teijon et al., 2010; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Isoproturon	9	100	Carabias-Martínez et al., 2000 and 2003; López-Roldán et al., 2004; Rodriguez-Mozaz et al., 2004a; Kampioti et al., 2005; Postigo et al., 2010; Teijon et al., 2010; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Linuron	5	1010	Carabias-Martínez et al., 2000 and 2003; Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Triasulfuron	1	n.d	Carabias-Martínez et al., 2000
Organophosphorous herbicides	Azinphos-ethyl	2	570	Garrido et al., 2000; Hildebrandt et al., 2007
	Azinphos-methyl	1	125	Garrido et al., 2000
	Bromophos-ethyl	1	n.d	Garrido et al., 2000
	Bromophos-methyl	1	n.d	Garrido et al., 2000
	Chlorfenvinphos	4	2500	Garrido et al., 2000; López-Roldán et al., 2004; Teijon et al., 2010; Estévez et al., 2012
	Chlorpyrifos-ethyl	3	294	Quintana et al., 2001; Teijon et al.,2010; Estévez et al., 2012
	Chlorpyrifos	2	600	Garrido et al.,2000; López-Roldán et al., 2004
	Chlorpyrifos-methyl	1	n.d	Teijon et al.,2010
	Coumaphos	1	n.d	Garrido et al., 2000
	Diazinon	8	300	Garrido et al., 2000; López-Roldán et al., 2004; Kampioti et al., 2005; Hildebrandt et al., 2007; Postigo et al., 2010; Teijon et al., 2010; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Dichlorfenthion	1	n.d	Garrido et al., 2000
	Dimethoate	5	2277	Quintana et al., 2001; López-Roldán et al., 2004; Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Ethion	3	200	Garrido et al., 2000; Teijon et al., 2010; Estévez et al., 2012
	Fenchlorphos	1	n.d	Garrido et al., 2000
	Fenitrothion	4	550	Garrido et al., 2000; Hildebrandt et al., 2007; Postigo et al.,2010; Köck-Schulmeyer et al., 2012
	Malathion	3	3500	Garrido et al., 2000; Postigo et al.,2010; Köck-Schulmeyer et al., 2012
	Methidathion	1	60	Garrido et al., 2000

	Parathion	2	250	Garrido et al., 2000; Estévez et al., 2012
	Parathion-methyl	3	1500	Garrido et al., 2000; Teijon et al., 2010; Estévez et al., 2012
	Parathion-ethyl	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Prathion-methyl	1	n.d	Estévez et al., 2012
	Phorate	1	10	Garrido et al., 2000
	Phosalone	1	n.d	Garrido et al., 2000
	Tetrachlorvinphos	1	n.d	Garrido et al., 2001
	Tributyl phosphate	1	730	Hildebrandt et al., 2007
Acid herbicides	2,4-D	3	8.6	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Bentazone	3	49.3	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Diclofop-methyl	1	n.d	Carabias-Martínez et al., 2003
	Fuazifop-butyl	2	180	Carabias-Martínez et al., 2000 and 2003
	MCPA	3	47.8	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Mecoprop	3	5	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
Anilides	Propanil	3	20.5	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
	Metalaxyl	1	490	Hildebrandt et al., 2008
	Alachlor	11	9950	Carabias-Martínez et al., 2000; Quintana et al., 2001; López-Roldán et al., 2004; Kampioti et al., 2005; Sánchez-Camazano et al., 2005; Hildebrandt et al., 2007; Postigo et al., 2010 ; Teijon et al., 2010; Bono-Blay et al., 2012; Estévez et al., 2012; Köck-Schulmeyer et al., 2012
	Metolachlor	8	5370	Quintana et al., 2001; Carabias-Martínez et al., 2003; Kampioti et al., 2005; Hildebrandt et al., 2007 and 2008; Postigo et al., 2010; Bono-Blay et al.,2012; Köck-Schulmeyer et al., 2012
Carbamate insecticides	3-hydroxy-carbofuran	1	29	Arráez-Román et al., 2004
	Aldicarb	1	27	Arráez-Román et al., 2004
	Aldicarb-sulfone	1	27.6	Arráez-Román et al., 2004
	Aldicarb-sulfoxide	1	23	Arráez-Román et al., 2004
	Carbofuran	1	24	Arráez-Román et al., 2004
	Molinate	3	5	Kampioti et al., 2005; Postigo et al., 2010; Köck-Schulmeyer et al., 2012
Dinitroaniline herbicides	Trifluralin	5	2.4	Quintana et al., 2001; Carabias-Martínez et al.,2003; López-Roldán et al., 2004; Teijon et al., 2010; Estévez et al., 2012
Pyridazinone herbicides	Chloridazon	2	n.d	Carabias-Martínez et al., 2000 and 2003
Uracil herbicides	Lenacil	2	n.d	Carabias-Martínez et al., 2000 and 2003
Triazinon herbicides	Metamitron	2	n.d	Carabias-Martínez et al., 2000 and 2003
	Metribuzin	3	n.d	Quintana et al., 2001; Carabias-Martínez et al., 2000 and 2003
Amide herbicides	Diflufenican	2	60	Carabias-Martínez et al., 2000 and 2003
Benzofuranyl sulfonate	Ethofumesate	2	n.d	Quintana et al., 2001; Carabias-Martínez et al., 2003
Thiazole fungicides	Thiabendazole	1	n.d	Estévez et al., 2012
Pyrethroid insecticides	Deltametrin	2	n.d	Teijon et al., 2010; Estévez et al., 2012

Quinoline fungicides	Ethoxyquin	1	n.d	Estévez et al., 2012
Imidazole fungicides	Iprodione	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Procymidone	2	-	Teijon et al., 2010; Estévez et al., 2012
Fumigant insecticides	Naftalene	1	n.d	Teijon et al., 2010
Diphenyl ether herbicides	Oxyfluorfen	1	12	Estévez et al., 2012
PhACs				
Therapeutic group				
Analgesics/anti-inflammatories	4-amino-antipiryne	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	4-dimethylaminoantipiryne	1	n.d	Teijon et al., 2010
	4-methylaminoantipyrine	1	n.d	Teijon et al., 2010
	Acetaminophen	3	34.7	Radjenovic et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Codeine	3	348.3	Boleda et al., 2009; Teijon et al., 2010; Estévez et al., 2012
	Diclofenac	2	477	Radjenovic et al., 2008; Teijon et al., 2010
	Fentanyl	1	n.d	Boleda et al., 2009
	Fenoprofen	1	n.d	Teijon et al., 2010
	Flufenamic acid	1	-	Estévez et al., 2012
	Ibuprofen	2	185	Teijon et al., 2010; Estévez et al., 2012
	Indomethacine	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Ketoprofen	3	314	Radjenovic et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Ketorolac	1	n.d	Teijon et al., 2010
	Meclofenamic acid	1	n.d	Estévez et al., 2012
	Mefenamic acid	3	32.5	Radjenovic et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Mepivacaine	1	252	Teijon et al., 2010
	Methylprednisolone 6α sodium	1	n.d	Teijon et al., 2010
	N-acetyl-4-amino-antipiryne (4-AAA)	1	362	Teijon et al., 2010
	Naproxen	2	263	Teijon et al., 2010; Estévez et al., 2012
	N-formyl-4-amino-antipiryne (4-FAA)	1	275	Estévez et al., 2012
	Norcodeine	1	n.d	Boleda et al., 2009
	Phenacetin	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Phenazone	2	-	Teijon et al., 2010; Estévez et al., 2012
	Phenylbutazone	1	n.d	Estévez et al., 2012
	Propyphenazone	3	296	Radjenovic et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Salicylic acid	1	n.d	Teijon et al., 2010
Lipid regulators and cholesterol lowering statin drugs	Bezafibrate	2	-	Teijon et al., 2010; Estévez et al., 2012
	Clofibric acid	1	n.d	Teijon et al., 2010
	Fenofibric acid	1	n.d	Teijon et al., 2010
	Fenofibrate	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Gemfibrozil	3	574	Radjenovic et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Mevastatin	2	n.d	Teijon et al., 2010; Estévez et al., 2012

	Pravastatin	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Simvastatin	1	n.d	Teijon et al., 2010
Psychiatric drugs	Amitriptyline	1	n.d	Teijon et al., 2010
	Alprazolam	1	6.4	Jurado et al., 2012
	Bromazepam	1	n.d	Huerta-Fontela et al., 2011
	Carbamazepine	4	167	Radjenovic et al., 2008; Teijon et al., 2010; Huerta-Fontela et al., 2011; Estévez et al., 2012
	Carbamaz epoxide	2	33	Teijon et al., 2010; Huerta-Fontela et al., 2011
	Citalopram	1	n.d	Teijon et al., 2010
	Chlordiazepoxide	1	n.d	Huerta-Fontela et al., 2011
	Chlorpromazine	1	n.d	Huerta-Fontela et al., 2011
	Clomipramine	1	n.d	Teijon et al., 2010
	Desmethylvenlafaxine	1	2	Huerta-Fontela et al., 2011
	Diazepam	3	19.4	Teijon et al., 2010; Estévez et al., 2012; Jurado et al., 2012
	Fluoxenthine	1	n.d	Teijon et al., 2010
	Lorazepam	1	39.7	Jurado et al., 2012
	Oxazepam	1	n.d	Huerta-Fontela et al., 2011
	Paroxethine	1	n.d	Teijon et al., 2010
	Phenytoin	1	78	Huerta-Fontela et al., 2011
	Primidone	2	n.d	Teijon et al., 2010; Huerta-Fontela et al., 2011
	Sertraline	1	n.d	Huerta-Fontela et al., 2011
	Velafaxine	2	134	Teijon et al., 2010; Huerta-Fontela et al., 2011
	Zolpidem	1	n.d	Huerta-Fontela et al., 2011
Histamine H2 receptor antagonists	Cimetidine	1	-	Estévez et al., 2012
	Famotidine	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Ranitidine	2	-	Teijon et al., 2010; Estévez et al., 2012
Histamine H1 receptor antagonists	Loratadine	1	n.d	Teijon et al., 2010
	Diphenhydramine	1	-	Estévez et al., 2012
Tetracycline antibiotics	Chlorotetracycline	1	n.d	Estévez et al., 2012
	Doxycycline	1	n.d	Estévez et al., 2012
	Demeclocycline	1	n.d	Estévez et al., 2012
	Minocycline	1	n.d	Estévez et al., 2012
	Oxytetracicline	1	n.d	Estévez et al., 2012
	Tetracycline	2	n.d	Teijon et al., 2010; Estévez et al., 2012
Macrolide antibiotics	Azithromycin	1	n.d	Teijon et al., 2010
	Clarithromycin	2	-	Teijon et al., 2010; Estévez et al., 2012
	Erythromycin	2	43	Teijon et al., 2010; Estévez et al., 2012
	Josamycin	1	n.d	Estévez et al., 2012
	Roxithromycin	1	n.d	Estévez et al., 2012

	Spiramycin	1	n.d	Estévez et al., 2012
	Tylosine	1	n.d	Estévez et al., 2012
Fluoroquinolone antibiotics	Ofloxacin	2	48	Teijon et al., 2010; Estévez et al., 2012
	Ciprofloxacin	1	n.d	Teijon et al., 2010
	Danofloxacin	1	-	Estévez et al., 2012
	Enoxacin	1	n.d	Estévez et al., 2012
	Enrofloxacin	1	n.d	Estévez et al., 2012
	Flumequine	1	n.d	Estévez et al., 2012
	Lomefloxacin	1	n.d	Estévez et al., 2012
	Oxolinic acid	1	n.d	Estévez et al., 2012
	Pipemidic acid	1	n.d	Estévez et al., 2012
	Norfloxacin	2	n.d	Teijon et al., 2010; Estévez et al., 2012
β-lactams	Amoxacillin	1	n.d	Teijon et al., 2010
	Cloxacillin	1	n.d	Estévez et al., 2012
	Dicloxacillin	1	n.d	Estévez et al., 2012
	Oxacillin	1	-	Estévez et al., 2012
	Lincomycin	2	-	Teijon et al., 2010; Estévez et al., 2012
Other antibiotics	Trimethoprim	2	-	Teijon et al., 2010; Estévez et al., 2012
	Metronidazole	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Nifuroxazide	1	~200	Estévez et al., 2012
	Benzothiazol	1	n.d	Estévez et al., 2012
	Carbadox	1	n.d	Estévez et al., 2012
	Cefotaxime	2	n.d	Teijon et al., 2010; Estévez et al., 2012
	Malachite green	1	-	Estévez et al., 2012
β-blockers	Acebutolol	1	8	Huerta-Fontela et al., 2011
	Atenolol	3	106	Teijon et al., 2010; Huerta-Fontela et al., 2011; Estévez et al., 2012
	Betaxolol	1	n.d	Huerta-Fontela et al., 2011
	Bisoprolol	1	n.d	Huerta-Fontela et al., 2011
	Doxazosin	1	n.d	Huerta-Fontela et al., 2011
	Labetalol	1	n.d	Huerta-Fontela et al., 2011
	Metoprolol	3	56.3	Radjenovic et al., 2008; Teijon et al., 2010; Huerta-Fontela et al., 2011
	Nadolol	1	n.d	Teijon et al., 2010
	Pindolol	1	n.d	Estévez et al., 2012
	Propranolol	3	62	Teijon et al., 2010; Huerta-Fontela et al., 2011; Estévez et al., 2012
	Sotalol	3	16	Radjenovic et al., 2008; Teijon et al., 2010; Huerta-Fontela et al., 2011
	Timolol	1	n.d	Estévez et al., 2012
β-agonists	Clembuterol	1	n.d	Estévez et al., 2012
	Salbutamol	3	9	Teijon et al., 2010; Huerta-Fontela et al., 2011; Estévez et al., 2012
	Terbutaline	1	n.d	Teijon et al., 2010

α-agonists	Phenylephrine	1	~10	Estévez et al., 2012
Diuretics	Furosemide	2	138	Teijon et al., 2010; Huerta-Fontela et al., 2011
	Bendroflumethiazide	1	n.d	Estévez et al., 2012
	Hydroflumethiazide	1	n.d	Estévez et al., 2012
Antidiabetics	Glibenclamide	1	27.6	Radjenovic et al., 2008
	Metformin	1	-	Estévez et al., 2012
Anti-cancer	Tamoxifen	2	n.d	Teijon et al., 2010; Huerta-Fontela et al., 2011
	Cyclophosphamido	1	n.d	Teijon et al., 2010
	Ifosfamide	1	n.d	Teijon et al., 2010
Angiotensin agents	Irbesartan	1	24	Huerta-Fontela et al., 2011
	Losartan	1	n.d	Huerta-Fontela et al., 2011
	Valsartan	1	26	Huerta-Fontela et al., 2011
Cardiac agents	Amlodipine	1	n.d	Huerta-Fontela et al., 2011
	Clopidogrel	1	n.d	Huerta-Fontela et al., 2011
	Diltiazem	2	2	Huerta-Fontela et al., 2011; Estévez et al., 2012
	Enalapril	1	n.d	Estévez et al., 2012
	Hydrochlorothiazide	3	2548	Radjenovic et al., 2008; Teijon et al., 2010; Huerta-Fontela et al., 2011
	Warfarin	2	n.d	Huerta-Fontela et al., 2011; Estévez et al., 2012
Contrast media	Iopamidol	1	396	Teijon et al., 2010
	Iopromide	1	687	Teijon et al., 2010
	Diatrizoate	1	n.d	Teijon et al., 2010
Sulfonamide antibiotics	Sulfamethoxazole	7	312.2	Díaz-Cruz et al., 2008; Radjenovic et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Teijon et al., 2010; Estévez et al., 2012
	Sulfadimethoxine	5	91.5	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Estévez et al., 2012
	N4-acetylsulfamerazine	1	18	García-Galán et al., 2011
	Sulfaquinoxaline	3	274	García-Galán et al., 2010b, 2010c and 2011
	N4-acetylsulfamethoxazole	1	5.5	García-Galán et al., 2011
	N4-acetylsulfapyridine	1	6	García-Galán et al., 2011
	Sulfapyridine	6	104	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Teijon et al., 2010; Estévez et al., 2012
	Sulfisomidin	3	64.4	García-Galán et al., 2010b, 2010c and 2011
	Sulfamethazine	5	446	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Teijon et al., 2010
	Sulfamerazine	4	744.7	García-Galán et al., 2010b, 2010c and 2011; Estévez et al., 2012
	Sulfamethoxypyridazine	4	68.7	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011
	Sulfisoxazole	4	17.1	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011
	Sulfabenzamide	3	10.3	García-Galán et al., 2010b, 2010c and 2011
	N4-acetylsulfamethazine	4	57	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011

	Sulfathiazole	6	16.8	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Teijon et al., 2010; Estévez et al., 2012
	Sulfadiazine	6	7	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Teijon et al., 2010; Estévez et al., 2012
	N4-acetylsulfadiazine	1	1	García-Galán et al., 2011
	Sulfamethizole	5	9.3	Díaz-Cruz et al., 2008; García-Galán et al., 2010b, 2010c and 2011; Estévez et al., 2012
	Sulfadoxine	3	53.6	García-Galán et al., 2010b, 2010c and 2011
	Succinyl-sulfathiazole	2	2.1	García-Galán et al., 2010c and 2011
	Sulfanitran	3	568.8	García-Galán et al., 2010b, 2010c and 2011
	Sulfaguanidine	2	91.8	García-Galán et al., 2010b and 2010c
	Sulfacetamide	2	3461	García-Galán et al., 2010b and 2010c
	Sulfachloropyridazine	1	n.d	Estévez et al., 2012
Antifungal medication	Clotrimazole	1	n.d	Teijon et al., 2010
	Miconazole	1	~1	Estévez et al., 2012
To treat dysepsia	Lansoprazole	1	n.d	Teijon et al., 2010
	Omeprazole	1	n.d	Teijon et al., 2010
Anthelmintics	Mebendazole	1	-	Estévez et al., 2012
Anaesthetics	Ketamine	1	n.d	Estévez et al., 2012
Antiseptics	Benzalkonium chloride	1	197.5	Estévez et al., 2012
Industrial compounds				
Surfactants	Linear alkylbenzene sulfonates (LAS)	1	5060	Tubau et al., 2010
	Nonylphenol dicarboxylate (NP2EC)	1	11240	Tubau et al., 2010
	Nonylphenol monocarboxylate (NP1EC)	1	2460	Tubau et al., 2010
	Nonylphenol dioethoxylate (NP2EO)	1	n.d	Sánchez-Avila et al., 2009
	Nonylphenol monoethoxylate (NP1EO)	1	450	Sánchez-Avila et al., 2009
	Nonylphenol (NP)	7	5280	Lacorte et al., 2002; Latorre et al., 2003; López-Roldán et al., 2004; Hildebrandt et al., 2007; Sánchez-Avila et al., 2009; Tubau et al., 2010; Bono-Blay et al., 2012
	Octylphenol dicarboxylate (OP2EC)	1	680	Tubau et al., 2010
	Octylphenol monocarboxylate (OP1EC)	1	120	Tubau et al., 2010
	Octylphenol (OP)	7	1800	Lacorte et al., 2002; Latorre et al., 2003; López-Roldán et al., 2004; Hildebrandt et al., 2007; Sánchez-Avila et al., 2009; Tubau et al., 2010; Bono-Blay et al., 2012
Phenols	4-chloro-3-methylphenol	1	n.d	López-Roldán et al., 2004
	4-chloro-2-methylphenol	1	n.d	López-Roldán et al., 2004
	2,4-dichlorophenol	1	n.d	López-Roldán et al., 2004
	4-tert-butylphenol	1	n.d	López-Roldán et al., 2004
	Bisphenol A (BPA)	6	1500	Lacorte et al., 2002; Latorre et al., 2003; Rodriguez-Mozaz et al., 2004a; Hildebrandt et al., 2007; Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
Phthalates	di(2-ethylhexyl) phthalate (DEHP)	3	5661	López-Roldán et al., 2004; Sánchez-Avila et al., 2009; Bono-Blay et al., 2012

	Dimethyl phthalate (DMP)	2	120	Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
	Diethyl phthalate (DEP)	2	1115	Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
	di-n-butyl phthalate (DBP)	2	n.d	Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
	Butyl benzyl phthalate (BBP)	2	n.d	Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
	Bis(2-ethylhexyl) adipate (DEHA)	2	192	Sánchez-Avila et al., 2009; Bono-Blay et al., 2012
DAs				
Chemical class				
Cocainics	Cocaine	3	60.2	Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012
	Benzoylecgonine	3	19.6	Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012
	Cocaethylene	1	1.8	Jurado et al., 2012
Cannabinoids	THC	3	n.d	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	Cannabinol	1	n.d	Jurado et al., 2012
	Cannabidiol	2	-	Estévez et al., 2012; Jurado et al., 2012
	THC-COOH	3	n.d	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	OH-THC	2	n.d	Estévez et al., 2012; Jurado et al., 2012
Opioids	Morphine	3	27.2	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	Ethylmorphine	1	n.d	Estévez et al., 2012
	Heroin	3	n.d	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	6-acetylmorphine	3	n.d	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	Methadone	4	68.3	Boleda et al., 2009; Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012
	EDDP	3	8.2	Boleda et al., 2009; Estévez et al., 2012; Jurado et al., 2012
	Normorphine	1	n.d	Boleda et al., 2009
Amphetamine like compounds	Amphetamine	3	n.d	Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012
	Ethylamphetamine	1	-	Estévez et al., 2012
	Metamphetamine	2	n.d	Estévez et al., 2012; Jurado et al., 2012
	MDA	2	n.d	Huerta-Fontela et al., 2008; Estévez et al., 2012
	MDEA	1	n.d	Estévez et al., 2012
	MDMA	3	36.8	Huerta-Fontela et al., 2008; Estévez et al., 2012; Jurado et al., 2012
	Ephedrine	2	7.3	Estévez et al., 2012; Jurado et al., 2012
Lysergic compounds	LSD	1	n.d	Jurado et al., 2012
Personal care products				
	2,7/2,8-dichloro-dibenzo-p-dioxin	1	n.d	Teijon et al., 2010
	3-(4-methylbenzylidene) camphor	1	n.d	Teijon et al., 2010
	Benzophenone-3	1	n.d	Teijon et al., 2010
	BHT	1	455	Teijon et al., 2010
	Biphenylol	1	n.d	Teijon et al., 2010
	Celestolide	1	n.d	Teijon et al., 2010
	Chlorophene	1	n.d	Teijon et al., 2010
	Ethylhexyl methoxycinnamate	1	132	Teijon et al., 2010

	Galaxolide	1	359	Teijon et al., 2010
	Musk ketone	1	n.d	Teijon et al., 2010
	Musk xylene	1	n.d	Teijon et al., 2010
	Octocrylene	1	n.d	Teijon et al., 2010
	Octyl-triazone	1	n.d	Teijon et al., 2010
	Phantolide	1	n.d	Teijon et al., 2010
	Tonalide	1	n.d	Teijon et al., 2010
	Traseolide	1	n.d	Teijon et al., 2010
	Triclosan	1	n.d	Teijon et al., 2010
Life-style compounds				
	Caffeine	3	505	Huerta-Fontela et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Nicotine	3	144	Huerta-Fontela et al., 2008; Teijon et al., 2010; Estévez et al., 2012
	Cotinine	2	n.d	Huerta-Fontela et al., 2008; Teijon et al., 2010
	Caffeine C13	1	n.d	Teijon et al., 2010
	Methylxanthine	1	n.d	Estévez et al., 2012
	Paraxanthine	2	147	Huerta-Fontela et al., 2008; Teijon et al., 2010
	Theobromine	1	252.5	Estévez et al., 2012
	Theophylline	1	35.2	Estévez et al., 2012
Estrogens				
	Estrone	5	n.d	Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2007; Huerta-Fontela et al., 2011; Estévez et al., 2012
	Estriol	4	n.d	Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2007; Huerta-Fontela et al., 2011
	Ethinyl Estradiol	4	n.d	Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2007; Huerta-Fontela et al., 2011
	Estradiol	3	n.d	Rodriguez-Mozaz et al., 2004a and 2004b; Farré et al., 2007
	Estradiol-17-glucuronide	2	n.d	Rodriguez-Mozaz et al., 2004a and 2004b
	Estrone-3-sulfate	2	n.d	Rodriguez-Mozaz et al., 2004a and 2004b
	Diethylstilbestrol	2	n.d	Rodriguez-Mozaz et al., 2004a and 2004b
	Estradiol diacetate	1	n.d	Rodriguez-Mozaz et al., 2004a
	Daidzein	1	n.d	Farré et al., 2007
	Genistein	1	n.d	Farré et al., 2007
	Biochanin A	1	n.d	Farré et al., 2007

Table S2. Screen depths of the observation points of Poble Sec and Besòs River Delta zones.

ZONE	SAMPLE	HEIGHT ABOVE SEA LEVEL (m)	SCREEN DEPTH (m)		LABEL*
			Upper screen depth	Lower screen depth	
Poble Sec (PS)	**PSP-8**	14	13	19	**u**
	PSP-7	14	23	27	**m**
	MPS-1	14.8	11.5	16	**u**
	MPS-2	14.7	25	32	**m**
	PSP-10	12.5	19	23	**u**
	PSP-9	12.2	24	26	**m**
	PSP-6	12	16	20	**u**
	PSP-5	12	21	25	**m**
	PSP-2	12.8	13	19	**u**
	PSP-3	13.1	23	27	**m**
	MPS-3	11.8	6	27	**a**
	CAL-1	13.1	-	-	**a**
	CAL-2	13	-	-	**a**
Besòs River Delta (BRD)	**SAP-4**	5	5.5	7.5	**u**
	SAP-3	5	10.5	12.5	**m**
	SAP-2b	5.25	4.5	6.5	**u**
	SAP-1	5.25	9.5	11.5	**m**
	SAP-2	5.25	9.5	11.5	**m**
	ADS-6n	8.4	3	15	**a**
	ADS-7	8.56	3	15	**a**
	ADPM	8.75	10.5	17.5	**a**
	ADPW	7.1	11	15	**a**
	ADPQ	8.05	10.5	17.4	**a**
	ADS-2	7.97	-	-	**u**
	ADS-4	8.9	-	-	**u**
	ADPR	8.2	9.5	16.5	**a**

***u:** upper screen depth; **m:** middle screen depth; **l:** lower screen depth; **a:** totally screened
"-": Screen depth not available

Table S3. Concentrations (ng/ L) for CBZ and its metabolites in Poble Sec and Besòs River Delta aquifers.

a) Poble Sec (PS)

SAMPLE	COMPOUND (ng/L)					
	CBZ	3OH CBZ	2OH CBZ	CBZ-EP	ACRON	ACRIN
PSP-8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
PSP-7	2.43	n.d.	n.d.	n.d.	0.941	n.d.
MPS-1	17.8	<LOQ	n.d.	<LOQ	n.d.	<LOQ
MPS-2	0.451	n.d.	n.d.	n.d.	n.d.	6.04
PSP-10	1.46	n.d.	n.d.	n.d.	n.d.	n.d.
PSP-9	1.83	n.d.	n.d.	n.d.	n.d.	n.d.
CAL-1	3.11	n.d.	n.d.	n.d.	n.d.	n.d.
CAL-2	3.72	n.d.	n.d.	n.d.	n.d.	n.d.
PSP-6	16.3	n.d.	n.d.	1.42	n.d.	n.d.
PSP-5	15.3	n.d.	n.d.	n.d.	<LOQ	<LOQ
PSP-2	9.39	n.d.	n.d.	n.d.	1.4	8.42
PSP-3	2.42	n.d.	n.d.	n.d.	n.d.	15.8
MPS-3	17.6	n.d.	n.d.	n.d.	n.d.	n.d.

b) Besòs River Delta (BRD)

Point ID	COMPOUND (ng/L)					
	CBZ	3OH CBZ	2OH CBZ	CBZ-EP	ACRON	ACRIN
SAP4	92.2	32.9	47.9	8.36	4.74	10.7
SAP3	116	<LOQ	<LOQ	1.14	n.d.	n.d.
SAP2BIS	127	39.9	31.4	7.45	7.17	n.d.
SAP1	118	<LOQ	9.65	3.66	1.24	n.d.
SAP2	105	2.98	5.51	1.07	2.52	n.d.
ADS6N	126	23	36.2	5.04	n.d.	n.d.
ADS7	136	21.7	38	2.73	8.2	n.d.
ADPM	120	17.5	31.6	3.35	1.07	n.d.
ADPW	108	15.5	21.3	n.d.	4.11	<LOQ
ADPQ	126	29.7	38.4	n.d.	6.85	n.d.
ADS2	112	16.9	31.6	<LOQ	1.84	n.d.
ADS4	105	24.4	37.9	4.99	1.18	4.45
ADPR	109	19.9	31.5	<LOQ	n.d.	n.d.

Table S4. Evaluation of the concentrations for the non-conservative tracers which take part in the identified geochemical processes. The negative symbol indicates that the specie is depleted from groundwater.

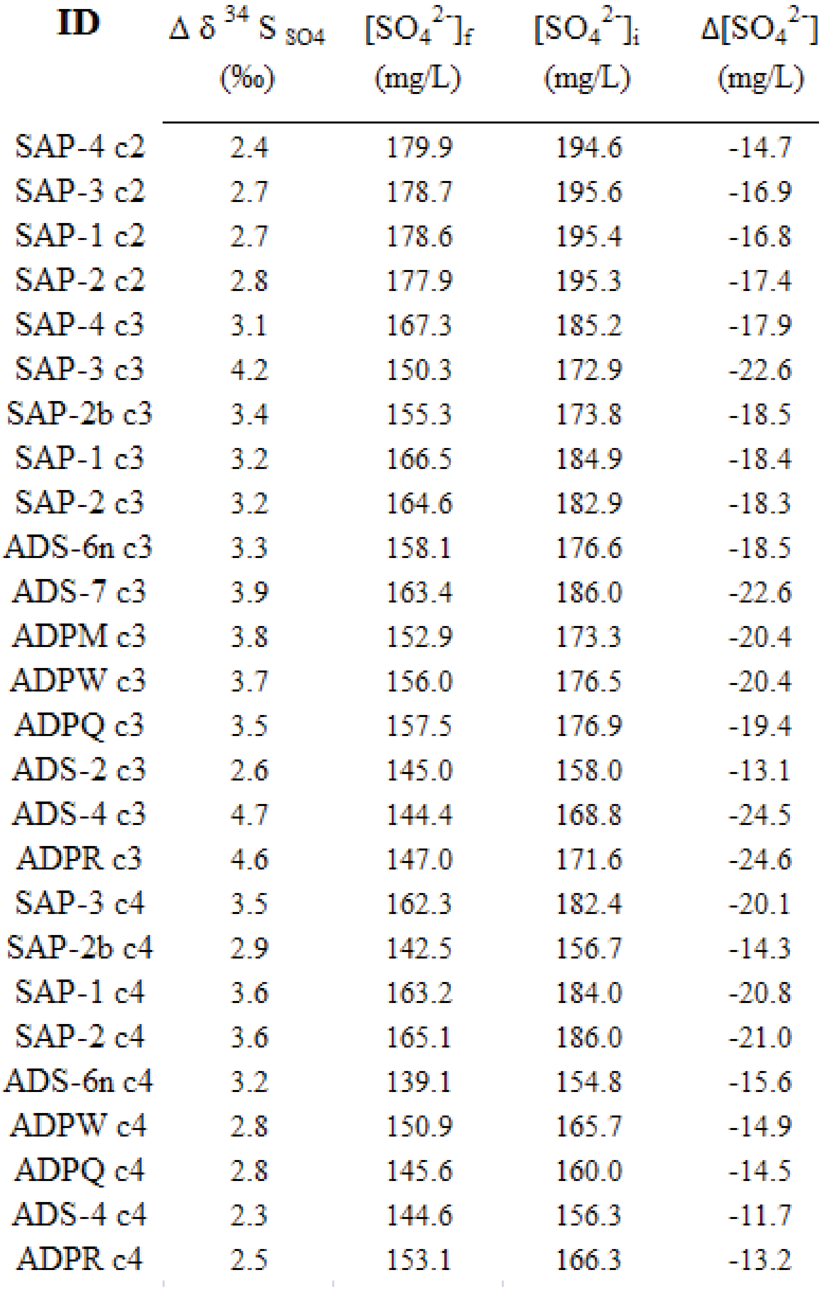
ID_POINT	Calcite dissolution		Magnesite dissolution		Denitrification			Aerobic respiration			Nitrification		
	HCO_3^- (mg/l)	Ca^{2+} (mg/l)	HCO_3^- (mg/l)	Mg^{2+} (mg/l)	HCO_3^- (mg/l)	TOC (mg/l)	NO_3^- (mg/l)	HCO_3^- (mg/l)	O_2 (mg/l)	TOC (mg/l)	NH_4^+ (mg/l)	O_2 (mg/l)	NO_3^- (mg/l)
SAP-4 C1	16.44	10.85	15.78	6.36	12.15	-2.26	-10.48	18.87	-9.12	-3.98	0.00	0.00	0.00
SAP-3 C1	5.48	3.62	10.93	4.40	20.05	-3.73	-17.29	0.00	0.00	0.00	-2.66	-9.38	8.68
SAP-2b C1	4.87	3.22	13.35	5.38	19.45	-3.62	-16.77	1.22	-0.59	-0.26	-2.30	-8.09	7.48
SAP-1 C1	21.31	14.07	14.57	5.87	18.84	-3.50	-16.24	7.91	-3.83	-1.67	-1.56	-5.50	5.09
SAP-2 C1	14.00	9.24	14.57	5.87	19.45	-3.62	-16.77	6.09	-2.94	-1.28	-1.84	-6.47	5.99
ADS-6 C1	12.18	8.04	15.18	6.11	17.02	-3.16	-14.67	6.09	-2.94	-1.28	-1.65	-5.83	5.39
ADS-7 C1	42.62	28.13	16.39	6.60	5.47	-1.02	-4.72	11.56	-5.59	-2.44	-1.01	-3.56	3.29
ADPM C1	24.96	16.48	15.18	6.11	18.84	-3.50	-16.24	3.04	-1.47	-0.64	-2.02	-7.12	6.59
ADPQ C1	15.22	10.05	18.21	7.34	18.84	-3.50	-16.24	5.48	-2.65	-1.16	-1.84	-6.47	5.99
ADS-4 C1	13.40	8.84	15.18	6.11	17.02	-3.16	-14.67	7.91	-3.83	-1.67	-1.19	-4.21	3.89
ADS-2 C1	13.40	8.84	11.53	4.65	3.04	-0.56	-2.62	19.47	-9.42	-4.11	0.00	0.00	0.00
ADPR C1	0.00	0.00	18.21	7.34	15.80	-2.94	-13.62	9.74	-4.71	-2.05	-1.29	-4.53	4.19
SAP-4 C2	26.18	17.28	25.49	10.27	15.19	-2.82	-13.10	7.30	-3.53	-1.54	-1.38	-4.85	4.49
SAP-3 C2	17.66	11.66	21.25	8.56	20.66	-3.84	-17.82	4.26	-2.06	-0.90	-2.02	-7.12	6.59
SAP-1 C2	18.27	12.06	20.03	8.07	20.05	-3.73	-17.29	4.26	-2.06	-0.90	-2.02	-7.12	6.59
SAP-2 C2	36.53	24.12	26.10	10.51	17.62	-3.28	-15.20	6.69	-3.24	-1.41	-1.56	-5.50	5.09
ADS-6 C2	29.23	19.29	23.67	9.54	18.84	-3.50	-16.24	0.00	0.00	0.00	-2.39	-8.41	7.78
ADS-7 C2	23.75	15.67	1.82	0.73	4.25	-0.79	-3.67	17.65	-8.54	-3.72	0.00	0.00	0.00
ADPM C2	21.31	14.07	20.64	8.31	13.98	-2.60	-12.05	4.26	-2.06	-0.90	-1.93	-6.80	6.29
ADPW C2	23.14	15.27	7.28	2.93	19.45	-3.62	-16.77	4.26	-2.06	-0.90	-1.93	-6.80	6.29
ADPQ C2	16.44	10.85	15.18	6.11	17.02	-3.16	-14.67	5.48	-2.65	-1.16	-1.84	-6.47	5.99
ADS-4 C2	21.31	14.07	0.00	0.00	3.04	-0.56	-2.62	18.87	-9.12	-3.98	0.00	0.00	0.00
ADS-2 C2	5.48	3.62	13.96	5.62	1.22	-0.23	-1.05	19.47	-9.42	-4.11	0.00	0.00	0.00
ADPR C2	7.31	4.82	18.21	7.34	6.68	-1.24	-5.76	14.61	-7.06	-3.08	-0.55	-1.94	1.80
SAP-4 C3	15.83	10.45	10.32	4.16	18.84	-3.50	-16.24	1.83	-0.88	-0.39	-2.30	-8.09	7.48
SAP-3 C3	27.40	18.09	18.21	7.34	14.58	-2.71	-12.58	12.17	-5.89	-2.57	-0.92	-3.24	2.99
SAP-2b C3	25.57	16.88	21.25	8.56	20.05	-3.73	-17.29	0.00	0.00	0.00	-2.48	-8.74	8.08
SAP-1 C3	14.00	9.24	15.18	6.11	17.02	-3.16	-14.67	10.95	-5.30	-2.31	-1.19	-4.21	3.89
SAP-2 C3	31.05	20.50	23.07	9.29	15.80	-2.94	-13.62	10.35	-5.00	-2.18	-1.01	-3.56	3.29

ID_POINT	Calcite dissolution		Magnesite dissolution		Denitrification			Aerobic respiration			Nitrification		
	HCO_3^- (mg/l)	Ca^{2+} (mg/l)	HCO_3^- (mg/l)	Mg^{2+} (mg/l)	HCO_3^- (mg/l)	TOC (mg/l)	NO_3^- (mg/l)	HCO_3^- (mg/l)	O_2 (mg/l)	TOC (mg/l)	NH_4^+ (mg/l)	O_2 (mg/l)	NO_3^- (mg/l)
ADS-6 C3	9.13	6.03	15.18	6.11	18.23	-3.39	-15.72	4.87	-2.35	-1.03	-1.93	-6.80	6.29
ADS-7 C3	29.23	19.29	14.57	5.87	1.82	-0.34	-1.57	18.26	-8.83	-3.85	-0.09	-0.32	0.30
ADPW C3	17.05	11.25	14.57	5.87	17.02	-3.16	-14.67	6.69	-3.24	-1.41	-1.56	-5.50	5.09
ADPM C3	14.00	9.24	12.14	4.89	16.41	-3.05	-14.15	5.48	-2.65	-1.16	-1.75	-6.15	5.69
ADPQ C3	17.05	11.25	17.60	7.09	13.98	-2.60	-12.05	11.56	-5.59	-2.44	-0.92	-3.24	2.99
ADS-4 C3	16.44	10.85	15.18	6.11	16.41	-3.05	-14.15	7.91	-3.83	-1.67	-1.47	-5.18	4.79
ADS-2 C3	31.05	20.50	18.82	7.58	6.08	-1.13	-5.24	15.82	-7.65	-3.34	0.00	0.00	0.00
ADPR C3	17.66	11.66	17.00	6.85	9.12	-1.69	-7.86	14.00	-6.77	-2.95	-0.18	-0.65	0.60
SAP-4 C4	33.49	22.11	23.07	9.29	17.62	-3.28	-15.20	0.00	0.00	0.00	-1.84	-6.47	5.99
SAP-3 C4	45.67	30.14	24.89	10.02	17.62	-3.28	-15.20	5.48	-2.65	-1.16	-1.47	-5.18	4.79
SAP-2b C4	39.58	26.12	21.85	8.80	18.23	-3.39	-15.72	0.00	0.00	0.00	-2.02	-7.12	6.59
SAP-1 C4	35.92	23.71	18.82	7.58	20.66	-3.84	-17.82	1.83	-0.88	-0.39	-2.02	-7.12	6.59
SAP-2 C4	28.62	18.89	19.42	7.82	19.45	-3.62	-16.77	4.26	-2.06	-0.90	-1.75	-6.15	5.69
ADS-6 C4	24.96	16.48	17.60	7.09	18.84	-3.50	-16.24	1.22	-0.59	-0.26	-1.65	-5.83	5.39
ADS-7 C4	29.83	19.69	14.57	5.87	17.02	-3.16	-14.67	0.00	0.00	0.00	-2.30	-8.09	7.48
ADPM C4	31.05	20.50	17.00	6.85	15.80	-2.94	-13.62	4.87	-2.35	-1.03	-1.47	-5.18	4.79
ADPW C4	32.88	21.70	17.00	6.85	13.37	-2.49	-11.53	9.13	-4.41	-1.93	-0.18	-0.65	0.60
ADPQ C4	22.53	14.87	20.64	8.31	17.02	-3.16	-14.67	4.87	-2.35	-1.03	-1.29	-4.53	4.19
ADS-4 C4	11.57	7.64	14.57	5.87	14.58	-2.71	-12.58	9.13	-4.41	-1.93	-0.92	-3.24	2.99
ADS-2 C4	17.66	11.66	15.78	6.36	4.86	-0.90	-4.19	16.43	-7.95	-3.47	0.00	0.00	0.00
ADPR C4	20.70	13.67	18.82	7.58	10.33	-1.92	-8.91	12.78	-6.18	-2.70	-0.37	-1.29	1.20

Table S5. Total released or depleted concentration for non-conservative tracers due to geochemical processes.

ID POINT	HCO_3^- (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	TOC (mg/l)	NO_3^- (mg/l)	O_2 (mg/l)	NH_4^+ (mg/l)
SAP-4 C1	63.2	10.85	6.36	-6.24	-10.48	-9.12	0.00
SAP-3 C1	36.5	3.62	4.40	-3.73	-8.61	-9.38	-2.66
SAP-2b C1	38.9	3.22	5.38	-3.87	-9.28	-8.68	-2.30
SAP-1 C1	62.6	14.07	5.87	-5.17	-11.15	-9.33	-1.56
SAP-2 C1	54.1	9.24	5.87	-4.90	-10.78	-9.42	-1.84
ADS-6 C1	50.5	8.04	6.11	-4.45	-9.28	-8.77	-1.65
ADS-7 C1	76.0	28.13	6.60	-3.46	-1.42	-9.15	-1.01
ADPM C1	62.0	16.48	6.11	-4.14	-9.66	-8.59	-2.02
ADPQ C1	57.7	10.05	7.34	-4.66	-10.26	-9.12	-1.84
ADS-4 C1	53.5	8.84	6.11	-4.83	-10.78	-8.03	-1.19
ADS-2 C1	47.4	8.84	4.65	-4.67	-2.62	-9.42	0.00
ADPR C1	43.7	0.00	7.34	-4.99	-9.43	-9.24	-1.29
SAP-4 C2	74.2	17.28	10.27	-4.36	-8.61	-8.39	-1.38
SAP-3 C2	63.8	11.66	8.56	-4.74	-11.23	-9.18	-2.02
SAP-1 C2	62.6	12.06	8.07	-4.63	-10.71	-9.18	-2.02
SAP-2 C2	87.0	24.12	10.51	-4.69	-10.11	-8.74	-1.56
ADS-6 C2	71.7	19.29	9.54	-3.50	-8.46	-8.41	-2.39
ADS-7 C2	47.5	15.67	0.73	-4.51	-3.67	-8.54	0.00
ADPM C2	60.2	14.07	8.31	-3.50	-5.77	-8.86	-1.93
ADPW C2	54.1	15.27	2.93	-4.51	-10.48	-8.86	-1.93
ADPQ C2	54.1	10.85	6.11	-4.32	-8.68	-9.12	-1.84
ADS-4 C2	43.2	14.07	0.00	-4.54	-2.62	-9.12	0.00
ADS-2 C2	40.1	3.62	5.62	-4.33	-1.05	-9.42	0.00
ADPR C2	46.8	4.82	7.34	-4.32	-3.97	-9.01	-0.55
SAP-4 C3	46.8	10.45	4.16	-3.89	-8.76	-8.97	-2.30
SAP-3 C3	72.4	18.09	7.34	-5.28	-9.58	-9.12	-0.92
SAP-2b C3	66.9	16.88	8.56	-3.73	-9.21	-8.74	-2.48
SAP-1 C3	57.1	9.24	6.11	-5.47	-10.78	-9.50	-1.19
SAP-2 C3	80.3	20.50	9.29	-5.12	-10.33	-8.56	-1.01
ADS-6 C3	47.4	6.03	6.11	-4.42	-9.43	-9.15	-1.93
ADS-7 C3	63.9	19.29	5.87	-4.19	-1.27	-9.15	-0.09
ADPW C3	55.3	11.25	5.87	-4.58	-9.58	-8.74	-1.56
ADPM C3	48.0	9.24	4.89	-4.21	-8.46	-8.80	-1.75
ADPQ C3	60.2	11.25	7.09	-5.04	-9.06	-8.83	-0.92
ADS-4 C3	55.9	10.85	6.11	-4.72	-9.36	-9.00	-1.47
ADS-2 C3	71.8	20.50	7.58	-4.47	-5.24	-7.65	0.00
ADPR C3	57.8	11.66	6.85	-4.65	-7.26	-7.42	-0.18
SAP-4 C4	74.2	22.11	9.29	-3.28	-9.21	-6.47	-1.84
SAP-3 C4	93.7	30.14	10.02	-4.43	-10.41	-7.83	-1.47
SAP-2b C4	79.7	26.12	8.80	-3.39	-9.13	-7.12	-2.02
SAP-1 C4	77.2	23.71	7.58	-4.23	-11.23	-8.00	-2.02
SAP-2 C4	71.7	18.89	7.82	-4.51	-11.08	-8.21	-1.75
ADS-6 C4	62.6	16.48	7.09	-3.76	-10.86	-6.41	-1.65
ADS-7 C4	61.4	19.69	5.87	-3.16	-7.19	-8.09	-2.30
ADPM C4	68.7	20.50	6.85	-3.96	-8.83	-7.53	-1.47
ADPW C4	72.4	21.70	6.85	-4.41	-10.93	-5.06	-0.18
ADPQ C4	65.1	14.87	8.31	-4.19	-10.48	-6.89	-1.29
ADS-4 C4	49.8	7.64	5.87	-4.64	-9.58	-7.65	-0.92
ADS-2 C4	54.7	11.66	6.36	-4.37	-4.19	-7.95	0.00
ADPR C4	62.6	13.67	7.58	-4.62	-7.71	-7.48	-0.37

Table S6. Evaluation of depleted dissolved sulphate due to the occurrence of sulphate reduction in selected groundwater samples for Besòs River Delta ($\varepsilon^{34}S_{SO4}$= -30 ‰.). Note that the difference between residual and initial values of $\delta^{34}S_{SO4}$ is the $\Delta\ \delta^{34}S_{SO4}$ and $[SO_4^{2-}]_f$ and $[SO_4^{2-}]_i$ are the final and initial dissolved sulphate concentrations in groundwater samples.



ID	$\Delta\ \delta^{34}S_{SO4}$ (‰)	$[SO_4^{2-}]_f$ (mg/L)	$[SO_4^{2-}]_i$ (mg/L)	$\Delta[SO_4^{2-}]$ (mg/L)
SAP-4 c2	2.4	179.9	194.6	-14.7
SAP-3 c2	2.7	178.7	195.6	-16.9
SAP-1 c2	2.7	178.6	195.4	-16.8
SAP-2 c2	2.8	177.9	195.3	-17.4
SAP-4 c3	3.1	167.3	185.2	-17.9
SAP-3 c3	4.2	150.3	172.9	-22.6
SAP-2b c3	3.4	155.3	173.8	-18.5
SAP-1 c3	3.2	166.5	184.9	-18.4
SAP-2 c3	3.2	164.6	182.9	-18.3
ADS-6n c3	3.3	158.1	176.6	-18.5
ADS-7 c3	3.9	163.4	186.0	-22.6
ADPM c3	3.8	152.9	173.3	-20.4
ADPW c3	3.7	156.0	176.5	-20.4
ADPQ c3	3.5	157.5	176.9	-19.4
ADS-2 c3	2.6	145.0	158.0	-13.1
ADS-4 c3	4.7	144.4	168.8	-24.5
ADPR c3	4.6	147.0	171.6	-24.6
SAP-3 c4	3.5	162.3	182.4	-20.1
SAP-2b c4	2.9	142.5	156.7	-14.3
SAP-1 c4	3.6	163.2	184.0	-20.8
SAP-2 c4	3.6	165.1	186.0	-21.0
ADS-6n c4	3.2	139.1	154.8	-15.6
ADPW c4	2.8	150.9	165.7	-14.9
ADPQ c4	2.8	145.6	160.0	-14.5
ADS-4 c4	2.3	144.6	156.3	-11.7
ADPR c4	2.5	153.1	166.3	-13.2

Annex II. Scientific papers accepted in international journals related with the elaboration of the thesis

ATTENTION ¡

Pages 149 to 193 of the thesis containing 4 articles are available at the editor’s web

- **Jurado, A., Vàzquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D.** *Emerging organic contaminants in groundwater in Spain: A review of sources, recent occurrence and fate in a European context.* Science of The Total Environment Volume 440, (2012) 82–94 doi:10.1016/j.scitotenv.2012.08.029.
  http://www.sciencedirect .com/article/pii/ S0048969712011138

- **Jurado, A., Mastroianni, N., Vàzquez-Suñé, E., Carrera, J., Tubau, I., Pujades, E., Postigo, C., López de Alda, M., Barceló, D.** *Drugs of abuse in urban groundwater. A case study: Barcelona* Science of the Total Environment 424 (2012) 280–288.
  doi:10.1016/j.scitotenv.2012.02.074
  http://www.sciencedirect.com/science/article/pii/S0048969712002860

- **Jurado, A., Vàzquez-Suñé, E., Solerc, A., Tubau, I., Carrera, J., Pujades, E., Anson, I.** *Application of multi-isotope data (O, D, C and S) to quantify redox processes in urban groundwater*. Applied Geochemistry 34 (2013) 114–125.
  doi:10.1016/j.apgeochem.2013.02.018
  http://www.sciencedirect .com/article/pii/ S0883292713000516

- **Rebeca López-Serna, R., Jurado, A., Vázquez-Suñé, E., Carrera, J., Petrovic, M., Barceló, D.** *Occurrence of 95 pharmaceuticals and transformation products in urban groundwaters underlying the metropolis of Barcelona, Spain*. Environmental Pollution 174 (2013) 305-315
  doi:10.1016/j.envpol.2012.11.022
  http://www.sciencedirect.com/science/article/pii/S0269749112005003

Annex III. Impact on the media

ATTENTION ¡

Pages 195 to 208 of the thesis containing 11

newspaper articles and notes from news agencies

1. **Madridejos, A**. *Les aigües freàtiques de Barcelona tenen rastres d'èxtasi.* El Periódico, 27 abril 201, p. 36
2. **Vila, I**. *La droga a la ciutat de Barcelona també va per barris*. El Punt/Avui. 27 abril 2012, p. 29
3. *Els aqüífers dibuixen un "mapa classista" del consum de drogues.* Regió 7, 27 abril 2012, p. 23
4. *Detectan restos de droga en las aguas del subsuelo de Barcelona*. El Mundo, 27 abril 2012
5. **Ferrado, M.I**. *Detecten restes de droga al aqüífers de Barcelona*. Ara, 27 abril 2012, p. "En breu" http://www.ara.cat/premium/societat/Detecten-restes-droga-aquifers-Barcelona_0_689931051.html
6. **Baquero, C.S**. *La cocaína flota en el subsuelo de Barcelona*. El Pais, Cataluña, 27 abril 2012 http://ccaa.elpais.com/ccaa/2012/04/27/catalunya/1335479742_129775.html
7. *Un estudi detecta importants nivells de cocaïna en pous de l'Eixample de Barcelona*. Ara.cat: http://www.ara.cat/societat/importants-nivells-cocaina-lEixample-Barcelona_0_689331229.html
8. *Un estudio detecta rastros de drogas en las aguas subterráneas de Barcelona*. La Vanguardia.com http://www.lavanguardia.com/salud/20120426/54285306978/un-estudio-detecta-rastros-drogas-enaguas-subterraneas-barcelona.html
9. *Cocaína en el Eixample, metadona en el Besòs*. El Mundo.es http://www.elmundo.es/elmundo/2012/04/26/barcelona/1335454834.htm
10. *Hallan rastros de drogas en aguas de Barcelona.* El Universal.com http://www.eluniversal.com.mx/articulos/70433.html
11. Agencia Catalana de Notícies. *Un estudi detecta importants nivells de cocaïna en pous del carrer Mallorca de Barcelona*. 26.04.2012 - 16.48 h http://www.acn.cat/acn/665892/Societat/text/cocaina-drogues-pous-aigues-subterranies-ICRA-carrer-Mallorca.html