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PhD Thesis

Assessment of groundwater recharge in urban areas

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I. Abstract

In the city of Barcelona and the townships situated in the deltaic area of the Besòs River, groundwater is recognized as an aspect of urban water cycle management. There is groundwater seepage into infrastructure and buildings that in turn require drainage, a part of which is introduced into sewage systems. Sensitized by this issue, city councils have had hydrologic studies carried out to analyze its causes and to plan alternative ways of using these resources while reducing treatment costs, and minimizing the impacts that groundwater and drainage have on infrastructure and vice versa. Based on these studies, and starting in 2000 some of this has been used for municipal practices (garden irrigation and street cleaning). Subsequently, due to a drought that affected the region between April 2007 and January 2009, the government entity in charge of Catalonian water sources (ACA) aims to get greater use out of urban groundwater in this area. This requires a comprehensive understanding of the hydrogeological characteristics of the environment, the availability and quality of these resources, and the appropriate tools for proper assessment and management. This has been the framework of this thesis.

Recharge is one of the most important aspects of water balance in aquifer systems in urban areas. Urbanization of the area alters the natural hydrological cycle and direct water recharge into aquifers by infiltration is reduced. In turn, evapotranspiration decreases and new recharge sources appear. This thesis presents, first, a methodology that allows for the quantifying of variability in space and time of the recharge in urban areas. Potential sources of recharge that have been considered are: (1) direct infiltration from rain and urban runoff, (2) losses from the sewer system, (3) losses from the water supply system, and (4) other specific sources of recharge (i.e. river infiltration, seawater intrusion, etc.). Recharge calculations are initially performed by applying analytical equations under various hypotheses. These results have been evaluated in the hydrogeological context through a numerical model of flow and transport in the whole area of study.

Secondly, and also throughout the study area, detection of some substances in groundwater has been analyzed. These substances and their degradation products, potentially present in recharging sources associated with urban environments, belong to so-called 'emerging organic pollutants'. These are organic chemical compounds used in the formulation of daily products for widespread use, such as pharmaceuticals, emulsions, care products and personal hygiene, household and industrial detergents, plastics, pesticides and herbicides, among others. There is relatively little known about these substances' introduction to and evolution in the aquifers.

Organic pollutants whose evolution and behavior in the groundwater is better understood can be degraded by natural processes controlled mainly by oxidation-reduction processes. Even in situ stimulation techniques have been developed which are able to accelerate these processes of natural attenuation of contaminated environments. Thirdly, in a preliminary way of attenuation processes detection, a methodology is presented using an end-member mixing analysis (EMMA) and MIX to compute mixing ratios and identify hydrochemical reactions. The methodology consists of (1) identifying the potential sources of recharge, (2) characterising recharge sources and mixed water samples using hydrogeochemistry, (3) selecting chemical species to be used in the analysis and (4) calculating mixing ratios and when departures from the mixing line exist, identifying hydrochemical processes. This approach has been applied in a pilot area in the Besòs River Delta.

II. Resumen

En la ciudad de Barcelona y municipios ubicados sobre los terrenos deltaicos del río Besòs, el agua subterránea es un factor que se tiene en cuenta en la gestión urbana del ciclo del agua. La filtración de aguas subterráneas en edificios e infraestructuras obliga el drenaje de estas aguas, parte de las cuáles son vertidas a la red de alcantarillado. Sensibilizados por esta problemática los ayuntamientos implicados encargaron estudios hidrogeológicos para analizar las causas y plantear alternativas para el aprovechamiento de estos recursos, reducir los costes del tratamiento, así como minimizar los impactos que las aguas subterráneas y drenajes puedan causar a las infraestructuras y viceversa. A raíz de estos estudios y desde el año 2000, parte de éstas se destinan a usos municipales (riego de jardines y limpieza de calles). Posteriormente y debido a un período de sequía que afectó desde abril de 2007 a enero de 2009, la entidad gestora de los recursos hídricos de Cataluña (Agència Catalana de l'Aigua, ACA) planteó un mayor aprovechamiento de los recursos de agua subterránea en este entorno urbano. Esto requiere un buen conocimiento de las características hidrogeológicas del medio, de la disponibilidad y calidad de estos recursos, así como de disponer de las herramientas adecuadas para su evaluación y correcta gestión. Esta tesis se enmarca en este contexto.

La recarga es uno de los aspectos más relevantes del balance hídrico en los sistemas acuíferos de zonas urbanas. La urbanización del territorio altera el ciclo hidrogeológico natural, la recarga directa de agua a los acuíferos por infiltración se reduce, disminuye la evapotranspiración y aparecen nuevas fuentes de recarga. En esta tesis se presenta, en primer lugar, una metodología para cuantificar la variabilidad espacial y temporal de la recarga en zona urbana. Las fuentes potenciales de recarga que se han considerado son: (1) infiltración directa de lluvia y de agua de escorrentía, (2) pérdidas del sistema de alcantarillado, (3) pérdidas de la red de abastecimiento y (4) otras fuentes específicas de recarga como la infiltración de agua de río o la intrusión marina, entre otras. El cálculo de la recarga se ha realizado inicialmente definiendo y aplicando ecuaciones analíticas bajo diversas hipótesis. Estos resultados se han evaluado en el contexto hidrogeológico mediante un modelo numérico de flujo y transporte en toda la zona de estudio.

En segundo lugar, también en toda la zona de estudio, se analiza la presencia en las aguas subterráneas de algunas sustancias potencialmente presentes en fuentes de recargas asociadas a entornos urbanos, y de las que se tiene relativo poco conocimiento de su introducción y evolución en los acuíferos. Estas substancias o sus productos de degradación pertenecen a los denominados 'contaminantes orgánicos emergentes'; se tratan de compuestos químicos orgánicos empleados en la formulación de productos de uso cotidiano y muy extendido, como son productos farmacéuticos, emulsiones, productos para el cuidado e higiene personal, detergentes domésticos e industriales, plásticos, pesticidas y herbicidas, entre otros.

Contaminantes orgánicos cuya evolución y comportamiento en las aguas subterráneas es más conocido pueden degradarse mediante procesos naturales controlados principalmente por procesos de oxidación-reducción. Incluso se han desarrollado técnicas de estimulación in-situ capaces de acelerar estos procesos de atenuación natural sobre medios contaminados. En una línea preliminar de detección de procesos de atenuación se presenta, en tercer lugar, una metodología para la evaluación de porcentajes de mezcla e identificación de procesos hidroquímicos Para ello se emplean procedimientos y herramientas estadísticas. Consiste en (1) identificación de las potenciales fuentes de recarga, (2) caracterización de las fuentes de recarga y las mezclas de agua usando especies químicas, (3) selección de las especies químicas que van a ser usadas en el análisis y (4) cálculo de los porcentajes de mezcla e identificación de procesos hidroquímicos cuando éstos se separan de la línea de mezcla. Esta metodología se ha aplicado a las aguas del río Besòs y las aguas subterráneas de una zona piloto en el Delta del Besòs.

III. Resum

En la ciutat de Barcelona i municipis ubicats sobre els terrenys deltaics del riu Besòs, l'aigua subterrània és un factor que es té en compte en la gestió urbana del cicle de l'aigua. La filtració d'aigües subterrànies en edificis i infraestructures obliguen el seu drenatge, una part de les quals s'aboquen a la xarxa de clavegueram. Sensibilitzats per aquesta problemàtica els ajuntaments implicats van encarregar estudis hidrogeològics per analitzar les causes i plantejar alternatives per l'aprofitament d'aquests recursos, reduir els costos del tractament, així com minimitzar els impactes que les aigües subterrànies i drenatges poden causar a les infraestructures i viceversa. A arrel d'aquest estudis i des de l'any 2000, part d'aquestes aigües es destinen a usos municipals (reg de jardins i neteja de carrers). Posteriorment i degut a un període de sequera que va afectar des de l'abril de 2007 fins gener de 2009, l'entitat gestora dels recursos hídrics de Catalunya (Agència Catalana de l'Aigua, ACA) va plantejar un major aprofitament d'aquests recursos d'aigua subterrània en aquest entorn urbà. Això requereix un bon coneixement del medi hidrogeològic, de la disponibilitat i qualitat, així com de les eines adequades per a la seva correcta avaluació i gestió. Aquest és el context en que emmarca aquesta tesis.

La recarrega és un dels aspectes més rellevants del balanç hídric en els sistemes aqüífers de zones urbanes. La urbanització del territori altera el cicle hidrogeològic natural, la recàrrega directa d'aigua als aqüífers per infiltració es redueix, disminueix l'evapotranspiració i apareixen noves fonts de recàrrega. En aquesta tesis es presenta, en primer lloc, una metodologia per a quantificar la variabilitat espaial i temporal de la recàrrega en zona urbana. Les fonts potencials de recàrrega que s'han considerat són: (1) infiltració directa de pluja i aigua d'escorrentia, (2) pèrdues del sistema de clavegueram, (3) pèrdues de la xarxa d'abastament i (4) altres fonts específiques de recàrrega com infiltració d'aigua del riu o intrusió marina, entre altres. El càlcul de la recàrrega s'ha realitzat inicialment definint i aplicant equacions analítiques sota diverses hipòtesis. Aquests resultats s'han avaluat en el context hidrogeològic mitjançant un model numèric de flux i transport en tota la zona d'estudi.

En segon lloc, també en tota la zona d'estudi, s'analitza la presència en les aigües subterrànies d'algunes substàncies potencialment presents en fonts de recàrrega associades a entorns urbans, i de les que es té relativament poc coneixement de la seva introducció i evolució en els aqüífers. Aquestes substàncies o els seus productes de degradació pertanyen als denominats 'contaminants orgànics emergents'; es tracten de compostos químics orgànics emprats en la formulació de productes d'ús quotidià i molt estès, com són productes farmacèutics, emulsions, productes per la cura e higiene personal, detergents domèstics i industrials, plàstics, pesticides y herbicides, entre altres.

Contaminants orgànics, l'evolució i comportament dels quals en les aigües subterrànies és més conegut, poden degradar-se mitjançant processos naturals controlats principalment per processos d'oxidació-reducció. Inclús s'han desenvolupat tècniques d'estimulació in-situ capaces d'accelerar aquests processos d'atenuació natural sobre medis contaminats. En una línea preliminar de detecció de processos d'atenuació es presenta, en tercer lloc, una metodologia que permet l'avaluació de percentatges de mescla e identificació de processos hidroquímics. Aquesta empra procediments i eines estadístiques. Consisteix en (1) identificació de las potencials fonts de recàrrega, (2) caracterització de les fonts de recàrrega i les mescles d'aigua emprant espècies químiques, (3) selecció de les especies químiques que van a ser emprades en l'anàlisi i (4) càlcul dels percentatges de mescla i identificació de processos hidroquímics d'aquells que es separen de la línea de mescla. Aquesta metodologia s'ha aplicat a les aigües del riu Besòs i les aigües subterrànies d'una zona pilot en el Delta del Besòs.

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1. Introduction

1.1. Background and objectives

The condition of water resources is an increasingly delicate situation. Especially in countries with arid and semi-arid climates, their future availability is decreasing and remains unfavorable or uncertain due to climate change. Increase in population and living standards also imply increases in demand for and pollution of these resources. To address this situation, various institutions, administrations, and managers are developing action plans that encourage efficient water use as well as the promotion of research for sustainable exploitation alternatives and the development of technology allowing for good comprehensive management of the entire water cycle (European Parliament and Council of the European Union, 2000). The great progress made in recent years in water purification techniques, pollutant analysis and management tools enables higher use of available water resources. Examples include seawater desalination, better reuse of treated wastewater, and improved artificial recharge techniques for aquifers.or secondary groundwater networks.

In the city of Barcelona and townships situated in the deltaic area in Besòs River there are groundwater seepage problems affecting infrastructure and buildings, which require the draining of this water. A major portion of this drainage is introduced into sewage system. Sensitized by this issue, city councils in charge have had hydrologic studies carried out to analyze its causes and to plan alternative ways to make use of these resources (Arandes, 2004), reduce treatment costs, and minimize the impacts that groundwater and drainage may have on infrastructure and vice versa. Based on these studies (some of which have been synthesized with a scientific approach by Vázquez-Suñé, E., 2003), some of this groundwater has been used since 2000 for municipal practices (garden irrigation and street cleaning). Since 2003 re-exploiting groundwater Besòs Delta for water supply, this operation was not performed since the 80s due to quality problems. In 2006 the consumption of underground water for municipal purposes reached 10% of the total. Subsequently, due to a drought that affected from April 2007 and January 2009, the government entity in charge of Catalonian water sources (ACA) has aimed to get greater use out of urban groundwater in this area. This requires a deep understanding of the hydrogeological characteristics of the environment, the availability and quality of these resources, and the appropriate tools for proper assessment and management. This has been the framework of this thesis.

This thesis is part of a collaboration agreement between the Polytechnic University of Catalonia (UPC) and other institutions, organizations and companies. It is a collaboration between UPC, the Metropolitan Water Services and Waste Treatment (EMSHTR), Aguas

Ter-Llobregat (ATLL) and the Catalan Water Agency (ACA) to develop a hydrogeologic numerical model of the Barcelona city and Besos River Delta to obtain alternative uses for the production of drinking water and for the study of degradation processes of pollutants in these aquifers. The other collaboration is between the UPC and Estacionaments Urbans of Sant Adria de Besos, S.A. (EUSAB) for the development and monitoring of the implementation of a plan to drain the water table in the vicinity of the Plaça de la Vila de Sant Adrià.

Groundwater management requires accurately determining the water balance. One of the most important aspects of understanding the groundwater balance in urban areas is the quantification of various contributions to the aquifer recharge. The urbanization of the territory alters the natural hydrological cycle by reducing the direct water recharge of aquifers by infiltration of precipitation while decreasing evapotranspiration and other sources of recharge appear as losses in the sewer system and losses in the supply network. Incorporation into surface and underground water systems of untreated sewage or other possible contributors specific to each case is another potential issue (Vázquez-Suñé et al., 2005 . In semi-arid areas the overall balance generally increases revenue from these resources. There is no universal method to asses recharge but some methods are more appropriate than others according to the specific needs of each case (Scanlon et al., 2002, Healy, 2010). In urban areas, a vast array of contaminants may be found because they are introduced into the aquifer through different recharge sources (Barber et al., 1988, Howard et al., 1996; Barrett et al., 1999; Pitt, 2001; Lerner, 2002; Morris et al., 2005; Vázquez-Suñé et al., 2005; Wakida & Lerner, 2005; Naik et al, 2008; Musolff, 2009). A number of organic compounds have been most recently detected in some refills sources (Ellis, 2006; Tubau et al., 2010; Jurado et al., 2012a and 2012b; Petrie et al., 2015) and there is little known about their introduction and evolution in the underground environment. Treated as so-called emerging contaminants, they are organic chemicals used in the formulation of widely used products, such as pharmaceuticals, emulsions, care products for personal hygiene, household and industrial detergents, plastics, pesticides and herbicides, among others. Some of these compounds or their degradation products have been identified as potentially linked to adverse health effects (EPA, 2001), and are subject to review for possible identification as priority substances or priority hazardous substances (European Parliament and Council of the European Union, 2008). Thus, the assessment of groundwater quality requires identifying not only a focus on contamination but also the processes that the pollutants undergo.

The objective of this thesis is to contribute to:

- Assessment of the groundwater recharge sources in urban areas.

- Analysis of the presence in urban groundwater of emerging contaminants in urban groundwater.
- Assessment to identify hydrochemical processes in groundwater.

These contributions have been applied in the groundwater under the city of Barcelona and Besòs River Delta area.

1.2. Thesis outline

This thesis consists of three chapters in addition to the introduction (Chapter 1), conclusions (Chapter 5) and references (Chapter 6). Each chapter focuses on one of the aforementioned objectives. The chapters are based on papers that have been published (2 accepted and 1 submitted) to international journals. The references to the papers are contained in footnote at the beginning of each chapter.

Chapter 2 presents a methodology to quantify the variability in space and time of the recharge into aquifers in urban areas. In this case, the considered potential sources of recharge are: (1) rain and urban runoff direct infiltration, (2) losses from the sewer system, (3) losses from water supply system, and (4) other specific sources of recharge (i.e. river infiltration, sea water intrusion, etc.). Recharge calculations are initially performed by defining and applying some analytical equations and validation has been assessed by groundwater flow and solute transport modelling. This approach has been applied in the aquifers under Barcelona city.

Chapter 3 investigates the fate of alkylphenol polyethoxylates (APEOs) degradation products (DPs) and the occurrence of linear alkylbenzene sulfonate (LAS) surfactants in urban groundwater at field scale. The occurrence of APEOs DPs in groundwater was studied in connection with: (1) sources of recharge or/and pollution containing these substances, (2) groundwater redox conditions, (3) occurrence of LAS, which are currently the domestic surfactants more used in the study area and (4) other common contaminants in urban groundwater in the city of Barcelona. The APEOs DPs analyzed included two nonylphenol carboxylates (NP2EC, NP1EC), two octylphenol carboxylates (OP2EC, OP1EC), nonylphenol (NP) and octylphenol (OP).

Chapter 4 presents a methodology using an end-member mixing analysis (EMMA) and MIX to compute .mixing ratios and identify hydrochemical processes in groundwater. This methodology are an alternative to complex models and can be used to estimate the relative importance of different sources of recharge. This approach has been applied in the Besòs River Delta area.

2. Quantification of Groundwater Recharge in Urban Environments.

This chapter is based on the paper Tubau I, Vázquez-Suñé E, Carrera J, Valhondo, C. Quantification of Groundwater Recharge in Urban Environments. Science of the Total Environment, submitted.

2.1. Introduction

Groundwater, with increasing frequency, is considered a key factor in the management of urban areas (Lerner, 1996; Chilton et al., 1997; Eyles, 1997; Chilton, 1999; Ellis, 1999; Howard & Israfilov, 2002; Custodio, 1997, 2004 and list of studies compiled by Naik et al., 2008). For one, some cities perform intensive pumping of groundwater for various uses (water supply, industry, etc.), which can produce a number of undesirable consequences such as ground subsidence or deterioration of the quality of water as a result of various particular causes (e.g. seawater intrusion). Moreover, the pumping of groundwater in many cities tends to be reduced or abandoned due to pollution and / or changes in land use (e.g. relocation of industries). In the latter case, the decline in groundwater extraction has caused a recovery of piezometric levels, generating floods and causing damage to underground infrastructure in many urban areas. Such is the case of Barcelona and its urban environment.

To control these structural problems it is usually necessary to pump groundwater in specific areas within the urban area (underground parking areas, building basements, tunnels, etc.). It is important to remember that groundwater extraction may be necessary or useful to cover various aspects of the growing demand for urban water. It is also due to become a strategic resource that can meet demand in moments when the usual supply sources may be suffering problems (drought, accidents, etc.). The latter consideration leads us to wonder whether urban groundwater can be used safely.

Urban aquifers can suffer from very diverse pollution sources, which include recharging from the losses of sewerage, polluted urban runoff, polluted rivers or other surface water, seawater intrusion, etc. As a result, a large number and variety of contaminants can be found in urban aquifers (Howard et al., 1996; Barrett et al., 1999; Pitt, 2001; Lerner, 2002; Morris et al., 2005; Vázquez-Suñé et al., 2005; Wakida & Lerner, 2005 ; Musolff, 2009). Besides "common" pollutants in the urban water environment, there are numerous organic pollutants of various origins, including a little understood and poorly legislated group know as *emerging organic contaminants* (EOCs), which are of particular concern for several reasons (Ellis, 2006; Tubau et al., 2010; Jurado et al., 2012a and 2012b; Petrie et al., 2015). To address these problems, we must understand the processes that determine the biological and chemical quality of urban groundwater, which in turn makes it necessary to quantify the groundwater balance and especially the recharge mechanisms (origin, quantity and quality).

Obviously, groundwater management in urban areas requires a detailed knowledge of the hydrogeological system as well as the adequate tools for predicting the amount and water quality evolution. In this sense, experience in urban groundwater is much lower than in natural areas. A key difference lies in recharge evaluation. A large number of studies have been published since the 90s that evaluate recharge in urban areas (see list of studies compiled by Naik et al., 2008), with no specific methodology. However, it is established that new urban groundwater recharge sources appear within supply network losses and sewer losses. Furthermore, evapotranspiration decreases due to the sealing surface. Therefore, there are generally higher rates of recharge in urban than in the natural settings (Lerner 2002, Vazquez-Suñe et al., 2005). Contribution evaluation of each recharge source has been addressed (Lerner et al., 2002). Given these uncertainties, mixing ratios can be used to better estimate the relative importance of different sources of recharge (Vazquez-suñe et al., 2010, Tubau et al., 2014). Furthermore, groundwater modeling may prove a good tool for total recharge evaluation (Vázquez-Suñé & Sánchez-Vila, 1999; Yang et al., 1999; Lerner, 2002 Hussein & Schwartz 2003, Dahan et al., 2004; Trowsdale & Lerner 2003 and 2007; Cox et al., 2007). However, this type of modeling requires a specific approach to identify the contribution of each particular source to the total recharge.

To address these specified uncertainties, a methodology is presented to perform groundwater modeling in urban areas that take into account flow and solute transport. However, application to real cases with numerous recharge sources, such as urban recharge, has been hindered by several issues. The first issue is associated with limited experience with the identification and selection of appropriate solutes. The second issue is the availability of long head and concentration records. Small and sparse records (in time and space) could cause the numerical solution to be non-identifiable or unstable.

The objective of this paper is to present a methodology to help overcome some of the issues above. This methodology will allow us to quantify the variability in space and time of the recharge into aquifers in urban areas. In this case, the considered potential sources of recharge are: (1) direct rain and urban runoff infiltration, (2) losses from the sewer system, (3) losses from the water supply system, and (4) other specific sources of recharge (i.e. river infiltration, seawater intrusion, etc.). Recharge calculations are initially performed by defining and applying some analytical equations and validation has been assessed based on groundwater flow and solute transport modeling. This allows urban groundwater management, by taking into account quantity and quality factors, to evaluate the relative contribution of different recharge sources by means of flow and solute transport modeling approach at a city scale. The methodology is applied to the assessment of recharge sources in the Barcelona city aquifers.

2.2. Methodology

The proposed method is applicable when groundwater data are sparse. This method can be considered a variation of the water-table fluctuation mass balance method (i.e. Healy and Cook, 2002; De Vries & Simmers, 2002). In essence, it is based on calibrating a large scale model while using appropriately parameterized areal recharge functions.

In practice, it consists of the following steps: 1) Conceptual model definition, 2) Implementation into a numerical model, 3) Parameterization of areal recharge, 4) Calibration and 5) Iteration. These steps are defined as follows.

1. Conceptual model Definition. This is achieved using conventional hydrogeological methods. It requires understanding geology, hydrogeology, meteorology, hydrology, soil uses, pumping rates, hydrochemistry, etc. Emphasis must be placed on evaluating not only total inputs and outputs, but also their evolution over time.

2. Implementation into a numerical model. Once a conceptual model has been defined, a numerical model is built. This requires specifying all parameters as well as the spatial and temporal discretization and boundary conditions (lateral inputs, recharge, pumping rates, etc).

3. Parameterization of areal recharge. Urban recharge is defined as a prescribed recharge inflow as follows:

$$r(x,t)=\sum_{i=1}^{Nf}\beta_i \; f_{Ri}(x,t) \qquad [1]$$

Where $r(x,t)$ is the recharge rate (here expressed per area unit and time unit), N_f is the number of terms, β_i are unknown urban recharge parameters to be estimated later and $f_{Ri}(x,t)$ are functions representing the time variation of recharge. Ideally, these functions represent different modes of urban recharge. The fact that they are left in terms of unknown factors β_i ought to simplify their definition, which must be prescribed by the modeler. As mentioned in the introduction, a detailed account of all processes involved can be quite difficult. Factors affecting these may include: (1) recharge sources (rainfall, water supply, sewage system); (2) percentage of urbanized area; (3) estimation of percentage of water distributed to losses for mains and sewers; (4) daily water consumption per person; (5) population density; among others. In the urban area all these factors can vary in time and space. Therefore, it is better to use simplified functions that capture the essence of the above, yet can be easily defined without the need for complex models. Some possible functions are defined below:

Recharge function $f_{Ri}(x,t)$ is implemented as a recharge rate in each recharge area, for a given time interval, as the sum of five recharge sources [2]:

$$[2] \qquad \mathrm{R}_{\mathrm{area}_{j,t}} = \mathrm{R}_{\mathrm{Pnu}} + \mathrm{R}_{\mathrm{Inu}} + \mathrm{R}_{\mathrm{Ss}} + \mathrm{R}_{\mathrm{Sww}} + \mathrm{R}_{\mathrm{Pww'}}$$

Disaggregated, they are:

$$[3] \qquad \mathrm{R}_{\mathrm{area}_{j,t}} = \begin{cases} \mathrm{R}_{\mathrm{Pnu}} & = \mathrm{f}_{\mathrm{nu}} \cdot \mathrm{WP} \cdot \left(1 - \mathrm{p}_{\mathrm{pav}}\right) + \\ \mathrm{R}_{\mathrm{Inu}} & = \mathrm{f}_{\mathrm{nu}} \cdot \mathrm{WI} \cdot \left(1 - \mathrm{p}_{\mathrm{pav}}\right) + \\ \mathrm{R}_{\mathrm{Sws}} & = \ \mathrm{f}_{\mathrm{ws}} \cdot \mathrm{WS} + \\ \mathrm{R}_{\mathrm{Sww}} & = \mathrm{f}_{\mathrm{ww}} \cdot [\mathrm{WS} \cdot (1 - \mathrm{f}_{\mathrm{ws}}) \cdot (1 - \mathrm{p}_{\mathrm{wsc}}) + \mathrm{WS}' \cdot (1 - \mathrm{p}_{\mathrm{wsc}'}) + \mathrm{WO}] \\ \mathrm{R}_{\mathrm{Pww}'} & = \mathrm{f}_{\mathrm{ww}'} \cdot \mathrm{WP} \cdot \mathrm{p}_{\mathrm{pav}} \cdot \mathrm{p}_{\mathrm{pww}} \end{cases}$$

Thus, concentration of a specific compound (Ci) which provides the recharging in each recharge area can be evaluated as [4]:

$$[4] \quad \mathrm{C}_{\mathrm{i},j,t} = \frac{\mathrm{C}_{\mathrm{i}_{\mathrm{Pnu}}} \cdot \mathrm{R}_{\mathrm{Pnu}} + \mathrm{C}_{\mathrm{i}_{\mathrm{Inu}}} \cdot \mathrm{R}_{\mathrm{Inu}} + \mathrm{C}_{\mathrm{i}_{\mathrm{Sws}}} \cdot \mathrm{R}_{\mathrm{Sws}} + \mathrm{C}_{\mathrm{i}_{\mathrm{Sww}}} \cdot \mathrm{R}_{\mathrm{Sww}} + \mathrm{C}_{\mathrm{i}_{\mathrm{Pww}'}} \cdot \mathrm{R}_{\mathrm{Pww}'}}{\mathrm{R}_{\mathrm{area}_{j,t}}}$$

Ci_{Pnu}, Ci_{Inu}, Ci_{Sws}, Ci_{Sww} and $Ci_{Pww'}$ are, respectively, the specific compound concentrations of each recharge source term.

In the following sections each of these variables will be defined.

Recharge sources conceptualization

The conceptual model to asses groundwater recharge in urban areas (Fig. 2.1 and Table 2.1) has been considered based on all available waters susceptible to being recharged in underground environments through elements that can only provide recharging. This particularly means potential waters from elements, both natural and artificial, that can also discharge groundwater have not been included, e.g. rivers, aquifer boundaries, sea borders, etc., with wastewater pipes below the water table being a special case. Here we have considered that the sewage system is unitary (both, pluvial and urban waste water is captured by the system).

Waters considered are classified into five types according to chemical characteristics, potential ways to enter ground, and origin. The rating values are:

(1) [WS] supply water flowing through the network;

(2) [WS'] supply water not flowing through the network, e.g. from pumping groundwater;

(3) [WP] rainwater;

(4) [WI] water infiltrated via the surface during periods of no precipitation, e.g. different water sources used for irrigation in areas not waterproofed; and

(5) [WO] other water discharged by the sewer system that is neither rainwater nor water supply, e.g. groundwater drains from basements.

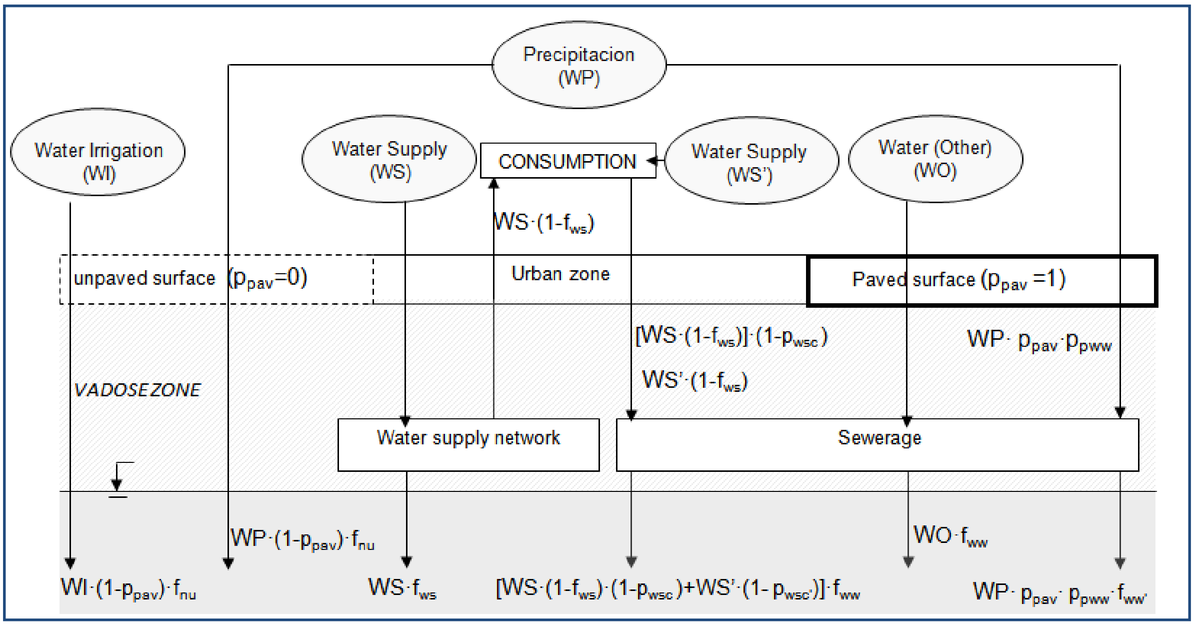


Figure 2-1 Conceptual model to asses groundwater recharge in urban areas (see also Table 1).

Table 2-1 Synthesis of terms and parameters of conceptual model to asses groundwater recharge in urban areas (see also Figure 1).

Group	**Parameter**	**Description**
Water volume entering to urban system	WS	water supply flowing through the supply network system
	WS'	water supply not flowing through the supply network
	WP	rainfall
	WI	water to irrigation
	WO	other water discharged by the sewer system
Groundwater recharge ratios (expressed as a decimal)	f_{ws}	percentage recharged from losses in the supply network
	f_{nu}	percentage recharged due to infiltration from surface
	f_{ww}	percentage recharged from sewer losses
	$f_{ww'}$	percentage recharged from sewer losses in rainy season
Factors adapted to spatial and temporal discretization	p_{pav}	paved area percentage
	p_{pww}	rainfall ratio flowing in the sewerage systems
	p_{wsc}	ratio of water supply (WS) consumed or retained and not returned to the sewer
	$p_{wsc'}$	ratio of water supply (WS') consumed or retained and not returned to the sewer

Nevertheless, only a percentage of total volume of these waters recharges aquifers. Percentages [f_{nu}, f_{ws}, f_{ww} and $f_{ww'}$] have been classified into three terms according to how potentially water can potentially enter the aquifer: (1) direct infiltration through unpaved areas [f_{nu}]; (2) losses of from supply mains [f_{ws}], where water flows under pressure; and (3) losses from sewer [f_{ww} and $f_{ww'}$], where water usually is not under pressure.

Urban paved surface is introduced as a percentage of paved area [p_{pav}]. This can change with time, p_{pww} is rainfall percentage captured by the urban drainage system or sewerage system, p_{wsc} and $p_{wsc'}$ are percentages of water supply consumed or retained, which therefore do not return to the sewer system.

One advantage of this kind of conceptual model is that it allows for balances with the global urban water cycle by taking into account contributions not specifically hydrogeological (also see: Eiswirth et al 2004; Thomas & Tellam; 2006; Morris et al., 2007; Vizintina at al. 2009, Freni et al. 2009).

Each of five recharge source terms is defined as follows (Fig. 2.1 and Table 2.1):

Rainfall recharge in non-urban area, R_{Pnu} [3.1]:

$$[3.1] \qquad \mathrm{R_{Pnu}} = \mathrm{f_{nu}} \cdot \mathrm{WP} \cdot \left(1 - \mathrm{p_{pav}}\right)$$

WP is rainfall total volume in an area for a given time interval; p_{pav} is unpaved area percentage (expressed as a decimal), which can be useful in areas where urbanized surface has changed over time, taking value 0 for natural area and 1 for urban; f_{nu} is the ratio of water that recharges aquifers due to surface infiltration. In short, R_{Pnu} corresponds to the natural recharge and therefore can be evaluated using common water balance calculations in the soil and taking into account parameters such as threshold runoff, evapotranspiration rate, unsaturated zone thickness, and soil moisture, among others.

Irrigation water in non-urban soil, R_{Inu} [3.2]:

$$[3.2] \qquad \mathrm{R_{Inu}} = \mathrm{f_{nu}} \cdot \mathrm{WI} \cdot \left(1 - \mathrm{p_{pav}}\right)$$

R_{Inu} is intended for agricultural areas included in an urban area, although it can also be considered irrigation of green areas in an urban context if this is assumed significant, either from a focus on quality or quantity. WI is irrigation water volume in an area for a given time interval, which could come from either previously recorded water volumes in the total balance of available water, e.g. from water supply (WS), or from new contributions to balance, e.g. pumping wells or rivers.

p_{pav} and f_{nu} are the same parameters described in [3.1]. In fact, although [3.1] and [3.2] have been separated, R_{Pnu} and R_{Inu} should be considered in conjunction with f_{nu} evaluation.

Rainfall recharge in urban surface, $R_{Pww'}$ [3.3]:

$$[3.3] \qquad \mathrm{R_{Pww'}} = \mathrm{f_{ww'}} \cdot \mathrm{WP} \cdot \mathrm{p_{pav}} \cdot \mathrm{p_{pww}}$$

WP and p_{pav} are described in [3.1]; p_{pww} is rainfall percentage captured by the urban drainage system or sewerage system in an area; f_{ww} is percentage recharged from losses from the sewer system in the rainy season.

Recharge from water supply network losses, R_{Sws} [3.4]:

$$[3.4] \qquad \mathrm{R_{Sws} = f_{ws} \cdot WS}$$

WS is volume of water supply flowing through the supply network in a given area and f_{ws} is the percentage (as a decimal) of this water reaching the aquifer from supply network losses. Several studies have estimated this percentage from the difference between water supply delivered, water billed and water disappointed and some works take data from network sectors in order to take into account fraud and losses from lattice defects (e.g.Valdés & Castelló, 2002).

Recharge from seepage losses, (R_{Sww}) [3.5]:

$$[3.5] \qquad \mathrm{R_{Sww} = f_{ww} \cdot [WS \cdot (1 - f_{ws}) \cdot (1 - p_{wsc}) + WS' \cdot (1 - p_{wsc'}) + WO]}$$

WS and f_{ws} are defined in [3.4]; WS' is water volume in an area for a given time interval for consumption that is not coming from the general supply network (i.e. from private wells or other sources of supply water), p_{wsc} and $p_{wsc'}$ are the respective percentages (expressed as decimals) of water supply (general or private) consumed or retained therefore does not return to the sewer system; WO is water volume intended for consumption (not from network supply) that is discharged into the sewer system - for instance water from groundwater drains to keep an underground structure such as a tunnel or building foundation dewatered; f_{ww} is a percentage (as decimal) of water reaching the aquifer from sewer losses. Chisala and Lerner (2008) explain case studies and approaches to quantify this parameter.

Parameters of this conceptual model do not explicitly take into account the processes of the non-saturated zone, an issue in urban areas that is addressed by Friedel (2006).

4. Calibration. Calibration consists of adjusting urban recharge parameters β_i together with the remaining model parameters, so as to fit observations while ensuring that both estimated parameters and the resulting model are consistent with prior information. The topic is very broad and a full description falls beyond the scope of this paper (see Carrera et al., 2005). The fact that recharge parameters are estimated does not require any special attention. The only issue is that, in practice, one needs to use inversion codes. Here we used the Maximum Likelihood Method (Carrera and Neuman, 1986) as implemented in VisualTRANSIN (GHS, 2004; Medina and Carrera, 1996), which leads to minimizing an objective function.

$$[5] \qquad F = \sum \lambda_h F_h + \sum \lambda_c F_c + \sum \lambda_p F_p$$

Where $F_h = (h - h^*)^t C_h^{-1} (h - h^*)$ is the head objective function, which penalizes departures between computed and measured heads (h and h*, respectively) with a weighting matrix C_h^{-1}. Similar definitions hold for F_c and F_p concentrations and model parameter objective functions, respectively. Appropriate weighting between these three terms can be obtained with the parameters λ_h, λ_c and λ_p.

5. Iteration The last two steps may be repeated using different recharge functions, or combinations of them, until a satisfactory fit is found.

2.3. Application to the Barcelona urban aquifers

2.3.1. Conceptual model Definition

Barcelona and its area of influence include the city and some municipalities in the metropolitan area (Fig. 2.2) with a population of over 3 million people. The area is bounded by the Collserola (north), the Mediterranean Sea and Besòs delta (north-east) and the Llobregat aquifers (southwest). The climate is Mediterranean, with an average rainfall of about 600 mm / year.

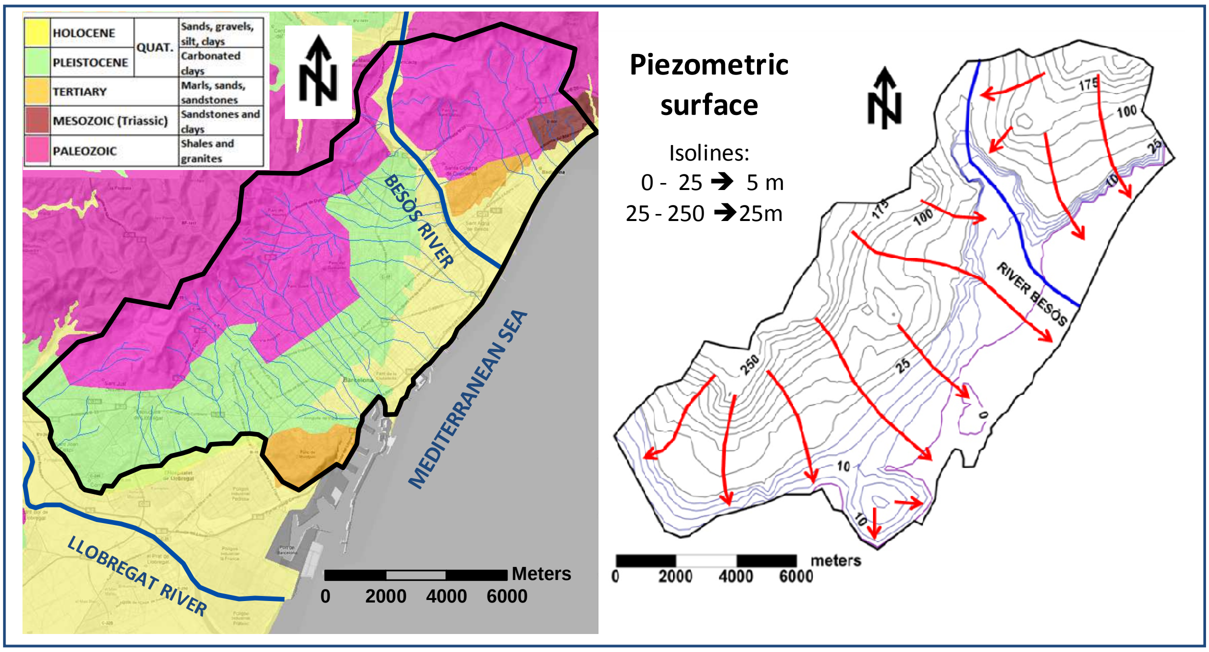


Figure 2-2 Schematic description of the hydrogeology of Barcelona. The left main hydrogeological units. Right piezometric map (For a better understanding have been represented as curves equidistance different level. The red lines represent flow lines.

Groundwater levels in Barcelona (Fig. 2.2) have been rising, which creates numerous problems for underground structures (subway, underground parking lots, basements, etc). In order to remediate this problem, Barcelona has developed the first phreatic water secondary distribution network in the world. Water from this secondary network is used for many purposes in garden irrigation and street cleaning. Recently, the Water authorities (Catalan Water agency, ACA) aim is to get greater use of urban groundwater in this area, even for water supply purposes. All of these possible uses are conditioned by processes controlling the water's quality. These processes must be understood for further development of the secondary network and possible supply uses. To this end, work will be performed throughout the whole city.

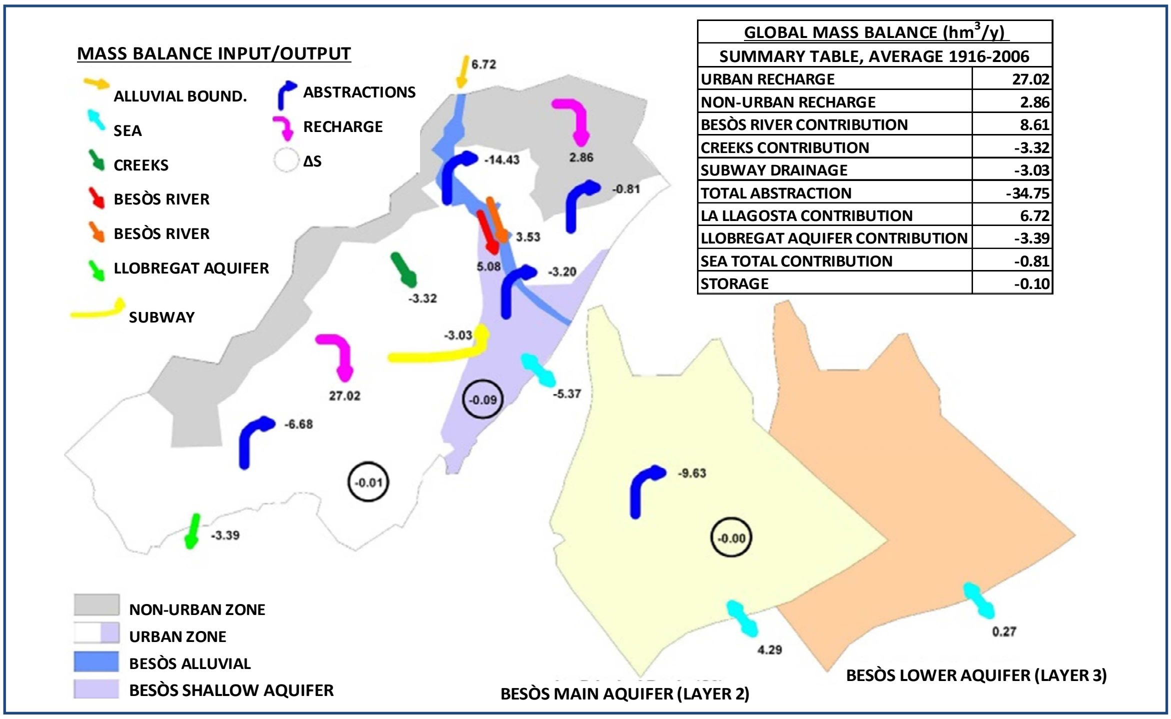
One of the key issues here is the evaluation of the different sources for recharge (Vazquez-Suñé et al., 2005, and 2010). These include: (1) The Besòs River, which largely contains water from secondary effluent WWTP (Wastewater Treatment Plants), especially during the summer; (2) the infiltration of rainfall in the highlands of the city that are not built on (considered in terms of natural water recharge as "clean"); (3) water supply network losses in the North-East area. This water is imported from the river Ter; (4) water supply network losses in the South-West area. This water is imported from the river Llobregat; (5) the wastewater generated in the North-East sector (from the river Ter); (6) wastewater sector South-West (from the river Llobregat); (7) urban runoff rainwater that leaches into much of the atmospheric deposition urban area (several kinds of "urban poles" emissions of vehicles and industries, etc.) and recharge aquifers through losses or direct infiltration of sewage; and (8) the intrusion of seawater. Each recharge source of groundwater in urban areas introduces specific compounds and contaminants into the soil and groundwater.

A city-wide geological model including flow and transports processes is already available. This will be refined at the pilot areas, which will be selected based on the availability of existing information. A complete Geological and Hydrogeological Database does this need to be capitalized (geology and previous hydraulic parameterization, groundwater heads evolution, groundwater hydrochemistry evolution, hydraulic test, pumping rates, etc.) has been used to build the model for these aquifers.

2.3.2. Flow and transport modeling

A huge numerical flow and solute transport model of the Barcelona aquifers has been conducted for water management purposes. The model is performed using finite element Visual Transin CODE (GHS, 2004). The model structure has been considered as consisting of three layers: the top layer represents the superficial aquifer systems of Barcelona, Badalona and Besòs Delta, the middle layer represents the Main Besòs Delta aquifer and the bottom layer represents the deepest Besòs Delta aquifer. This overlay network contains all available data (heads and chloride concentrations), limits and boundary conditions of the domain, hydraulic parameters of aquifers (i.e: conductivity, storage coefficient, porosity, etc.), groundwater extraction and recharge have also been included. The period covers modeling from 1916 to 2006.

In this model, calibration techniques have been used for an inverse problem. That is, all data entered have been compiled and the program returns hydraulic parameters consistent with the preliminary information available, which provide a better fit with the levels and concentrations measured. The adjustment is considered very good at the city scale. Another important aspect of the calibration consistency in the mass balance (conceptual model) is in regards to groundwater inflows and outflows in the whole system and their temporal variability. The model is considered to accurately reproduce the temporal evolution of inputs and outputs of the various elements of the system (Fig. 2.3). Until reaching the final calibration version of the model, quantification of recharge sources provide the most uncertain results. To assess a confident quantification of recharge sources the methodology described in the next section was applied.



GLOBAL MASS BALANCE (hm^3/y)	
SUMMARY TABLE, AVERAGE 1916-2006	
URBAN RECHARGE	27.02
NON-URBAN RECHARGE	2.86
BESÒS RIVER CONTRIBUTION	8.61
CREEKS CONTRIBUTION	-3.32
SUBWAY DRAINAGE	-3.03
TOTAL ABSTRACTION	-34.75
LA LLAGOSTA CONTRIBUTION	6.72
LLOBREGAT AQUIFER CONTRIBUTION	-3.39
SEA TOTAL CONTRIBUTION	-0.81
STORAGE	-0.10

Figure 2-3 Mass balance resulting of numerical model.

2.3.3. Simulation of urban recharge

Calculating with the recharge model created a function of time [Eq. 6] that brings together different types of recharge water depending on the type and source of the original water before infiltrating the ground, which are: (1) rainwater infiltration from the natural terrain (or land not build on), which qualifies as a "natural recharge", R_{Pnu}; (2) tap water from losses in the supply network, R_{Sws}, (3) sewer water from losses in the sewer system, R_{Sww} and R_{Pww}’ and (4) recharge from rivers or streams, which has been treated differently by another time function.

Substituting values into Eq.2:

$$[6] \qquad \mathrm{R}_{\mathrm{area}_{j,t}} = \begin{cases} \mathrm{R}_{\mathrm{Pnu}} & = \mathrm{f}_{\mathrm{nu}} \cdot \mathrm{WP} \cdot \left(1 - \mathrm{p}_{\mathrm{pav}}\right) + \\ \mathrm{R}_{\mathrm{Inu}} & = 0 + \\ \mathrm{R}_{\mathrm{Sws}} & = \ 0{,}12 \cdot \mathrm{WS} + \\ \mathrm{R}_{\mathrm{Sww}} & = 0{,}05 \cdot [\mathrm{WS} \cdot (1 - 0{,}12) \cdot (1 - 0{,}15) + 0 + 0] + \\ \mathrm{R}_{\mathrm{Pww'}} & = 0{,}10 \cdot \mathrm{WP} \cdot \mathrm{p}_{\mathrm{pav}} \cdot 1 \end{cases}$$

Simplifying:

$$[6.1] \qquad \mathrm{R}_{\mathrm{area}_{j,t}} = \left(\mathrm{f}_{\mathrm{nu}} \cdot \left(1 - \mathrm{p}_{\mathrm{pav}}\right) + 0{,}10 \cdot \mathrm{p}_{\mathrm{pav}}\right) \cdot \mathrm{WP} + 0{,}1574 \cdot \mathrm{WS}$$

Where WP, WS, f_{nu} and p_{pav} vary for each area j, and over time discretization (annually from 1916 to 1960 and monthly from 1960 to 2006). These are respectively: water volume from rainfall; water volume delivered to network; percentage of natural recharge of rainwater which was calculated by daily balance (subsequently integrated by the time interval discretized) of water in the ground; and p_{pav} representing land use, which takes value 0 for natural area and 1 for urban. Intermediate values are based on population density values depending on space and time.

Due to increased uncertainty of the other parameter it has been chosen to consider as constant both time and space, with the following values according to other works: (f_{ws}) the fraction of losses in the supply network that goes to recharge, value 0,12; (f_{ww}) the fraction of losses in the sewer system, value 0,05; ($f_{ww'}$) the fraction of losses in the sewers when it rains, value 0,10 and (p_{pww}), which represents the fraction of water supply used and retained, therefore not going into the sewer system, with value 0,15. All other terms omitted i.e. WI, WS', WO and $p_{wsc'}$ have not been taken into account because they are considered insignificant on the scale of work or do not have enough information.

Spatial distribution of groundwater recharge terms

The domain is divided into urban and non-urban area. This differentiation of current land use mapping has been made through land use maps. However, land use has not been constant over time. Therefore, the spatial and temporal evolution of land use has been made considering some available historical maps, but particularly through the distribution of population density.

The distribution of recharge losses in supply networks and sewage can be looked at in two ways: 1) a direct method based on mapping information networks supplemented by data flow circulates and / or age networks, etc. or 2) approximating the volume of water flowing through a given area to supply a certain number of people and assume a relationship between the volume of water losses and the network. The first method would currently be feasible due to the development of geographic information tools, but we do not have such information from the past. The second method, which has been used in this work, has the advantage of being simple while also supplying old series and continuous data population as well as water volumes. Therefore, in the model, the domain has been divided according to the data available from the evolution of population density. Usually the first division is made in terms of, but in the case of Barcelona subdivisions have been made for statistical areas of the City Council and for discrete neighborhoods in Badalona. In other municipalities domain subdivisions exist according to current land use (urban, non-urban and industrial).

With the aim of reducing the number of zones and by calculating according to the recharge time function in each zone, collections of neighboring areas have been grouped based on similar results concerning both time evolution and magnitude.

Furthermore, calculation of chloride concentrations provided for each recharge zone has also been performed with time functions for each of the recharge areas [Eq. 6]. These functions have been calculated taking into account the chloride contributions over time of each source of recharge (C_{Clnu}, $C_{ClPww'}$, C_{ClSsw} and C_{ClSww}).

$$[7] \quad C_{Cl,j,t} = \\ = \frac{\left(C_{Cl_{Pnu}} \cdot f_{nu} \cdot \left(1 - p_{pav}\right) + C_{Cl_{Pww'}} \cdot 0{,}10 \cdot p_{pav}\right) \cdot WP + \left(C_{Cl_{Ssw}} \cdot 0{,}12 + C_{Cl_{Sww}} \cdot 0{,}0374\right) \cdot WS}{\left(f_{nu} \cdot \left(1 - p_{pav}\right) + 0{,}10 \cdot p_{pav}\right) \cdot WP + 0{,}1574 \cdot WS}$$

Over time in the study area, there have been two types of water supply from different basins (Llobregat and Ter), which have different hydro chemical characteristics. Consequently concentrations of C_{ClSsw} and C_{ClSww} were applied in corresponding areas.

Calibration and iterative process

Initially, an adjustment was made for flow and transport parameter considering charging rates at 12% of water supply (f_{ws}=0,12) and 5% of water from sewer losses (f_{ww}=0,05). Having achieved an acceptable fit with this reference scenario, Rref (Fig. 2.3), it has been made different model calibrations have been made considering 7 different hypotheses of urban recharge (Table. 2.2).

These seven hypotheses have remained unchanged in small urbanized areas and those nearest river alluvium areas. The remaining recharge areas are those which have been varied in each of the 7 hypotheses. Assumptions recharge R1, R2, R3, R4 and R4' are variable over time. Hypothesis R5 has been considered constant over time, and each recharge zone is assigned a different value corresponding to the average calculated for each recharge function from Rref. Assumption recharge R6 has not been performed with a spatial discretization and is considered a unique area of urban recharge with a constant value over time. The difference between the scenarios with the assumption of lower recharge (R4 and R4') is the standard deviation assigned to recharge areas. R4 scenario, like the other scenarios, is assigned a standard deviation in the estimated initial recharging of 10%, while in the R4’ scenario it is 300%. Thus the R4’ scenario has greater freedom to modify the recharge zones corresponding (approximating) to the scenario considered that has greater estimated initial recharge (R1).

The other initial hydraulic parameters and deviations for calibration have remained the same in all scenarios. In summary, the hydraulic parameters that have been calibrated are: 33 recharge areas (recent alluvial not included); 50 transmissivity and permeability zones, in which all scenarios have an applied standard deviation of 0.3 orders of magnitude of the initial estimated; and 5 linear elements with mixed condition corresponding to a drip streams (recharge-discharge elements). In all scenarios, a standard deviation of 3 orders of magnitude of the initial estimated is applied. In addition to the standard deviations of each area, weights were added to each group of parameters that are 7, 3, and 1 for areas of transmissivity, recharge and elements with mixed condition respectively.

Table 2-2 Recharge scenario hypothesis.

	Recharge from losses in the supply network, f_{ws} [%]	Recharge from sewer losses, f_{ww} and $f_{ww'}$ [%]	Recharge term to flow calibration [%] , (1)	Standard deviation Recharge areas	Spatial discretization	Time varying	Time varying
Rref	12	5	15.7	0.1	Yes	Yes	Yes
R1	30	30	47.9	0.1	Yes	Yes	Yes
R2	30	1	30.6	0.1	Yes	Yes	Yes
R3	1	30	26.2	0.1	Yes	Yes	Yes
R4	1	1	1.8	0.1	Yes	Yes	Yes
R4'	1	1	1.8	3	Yes	Yes	Yes
R5	12	5	15.7	0.1	Yes	No	No
R6	12	5	15.7	0.1	No	No	No

(1)Eq. [6.1] to Rref scenario $R_{area_{i,t}} = \left(f_{nu} \cdot (1 - p_{pav}) + 0{,}10 \cdot p_{pav}\right) \cdot WP + 0{,}1574 \cdot WS$

In total there are 8730 head measurements spread over 1305 observation points and 652 measurements of chloride concentrations in 186 spread observation points. 65% and 59% of head measurements and concentration measurements respectively are concentrated between 1996 and 2006. Weight measures of head and chloride concentrations are 1 and 1E-9, respectively. Thus, measurements of chloride concentrations are hardly involved in these calibrations.

2.4. Results and discussion

Calibrations presented in this article enforce that the main contribution to the objective function is due to the adjustment of level measurements. (Fig. 2.4). Initially, the hypothesis that takes into account the highest recharge volumes is also the most divergent (R1), while the end of the calibration settings head is very similar in all scenarios, except for the hypothesis that takes into account lower recharge volumes and assumes a lower deviation (R4) and to a lesser extent the hypothesis of constant spatial and temporal recharge (R6). With regard to measures of chloride concentrations, which have been imposed with a low weight, adjusting them practically has not contributed to the calibration process (the initial and final objective functions they are nearly identical).In this case, the worst results are clearly the hypotheses of smaller recharges (R4 and R4 '). Low recharge within these scenarios causes water entry into aquifer systems through boundaries. Notable entries are in volume through the contours of the sea (Fig. 2.5).

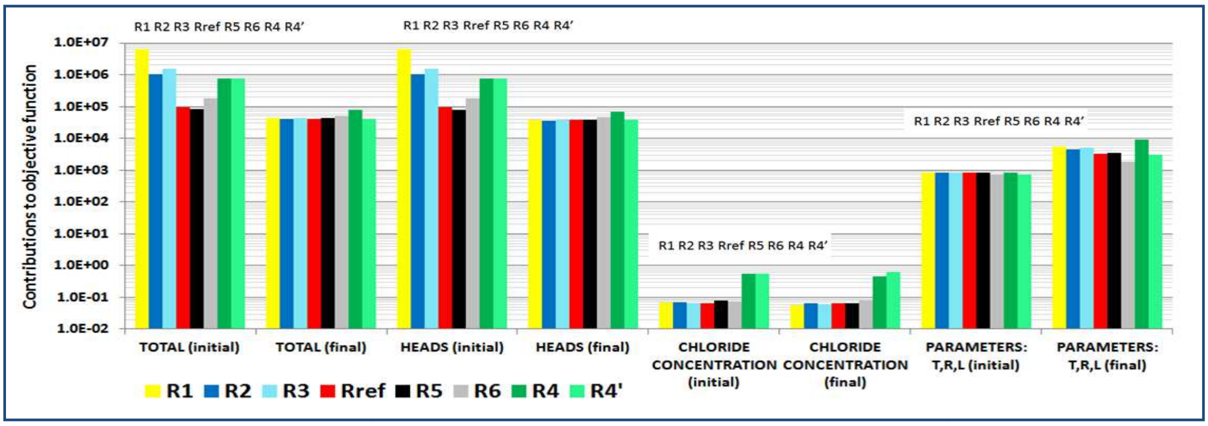


Figure 2-4 Initial and final contributions to objective function for each scenario. The ordinate axis is in log scale. Weights of groups of parameters are 7, 3 and 1 for transmissivity areas, recharge areas, and elements with mixed condition respectively. Weights measures of head and chloride concentrations are 1 and 1E-9, respectively.

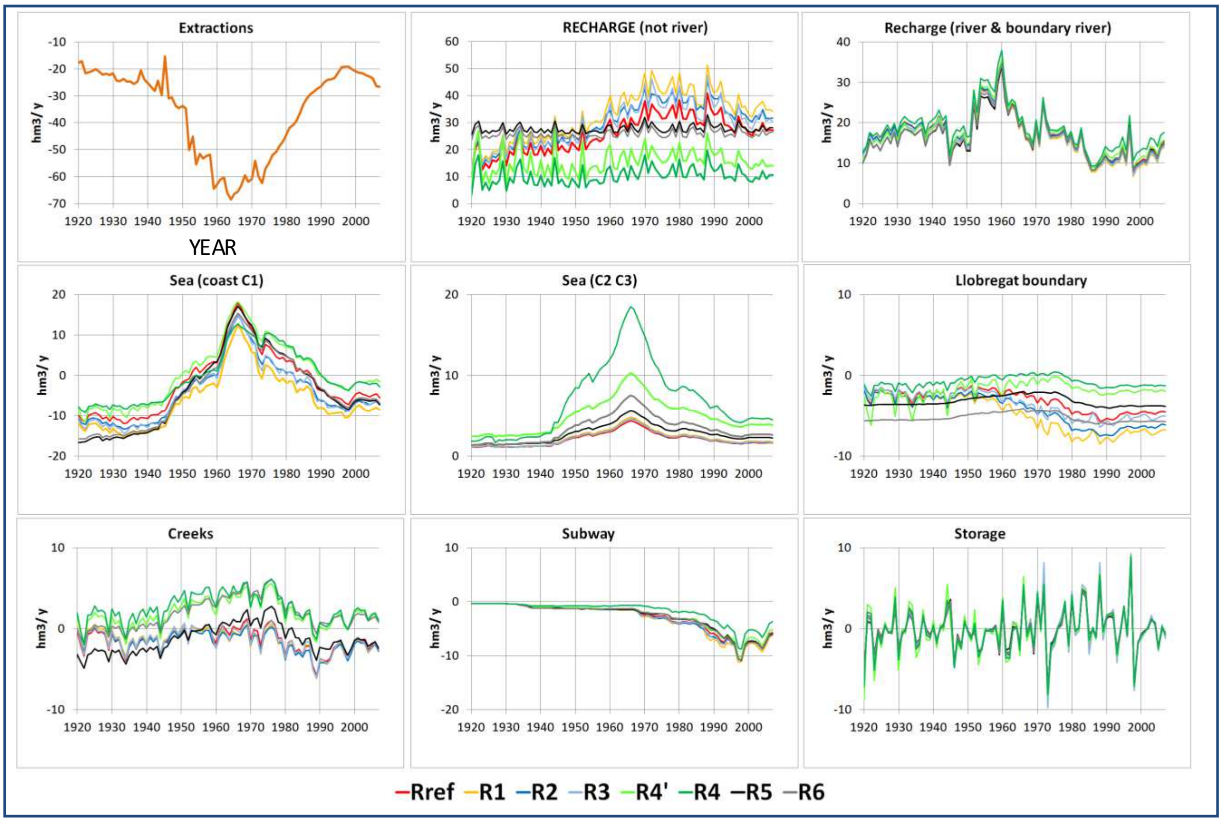


Figure 2-5 Simplified overall mass balance for each scenario.

For other assumptions, the terms of overall mass balance have been more limited. The total recharge calculated in urban area for the past 6 years (2000-2006, which is available as many observation points and measurements) has been bounded between 25 and 33 million m^3/year.

Measures of chloride concentrations (Fig. 2.6) clearly show that, due to heavy withdrawals, the deltaic aquifers have suffered saltwater intrusion problems during the 1960s and 70s. Today, virtually all aquifers have recovered from this pollution, with the exception of some located closer to the shore.

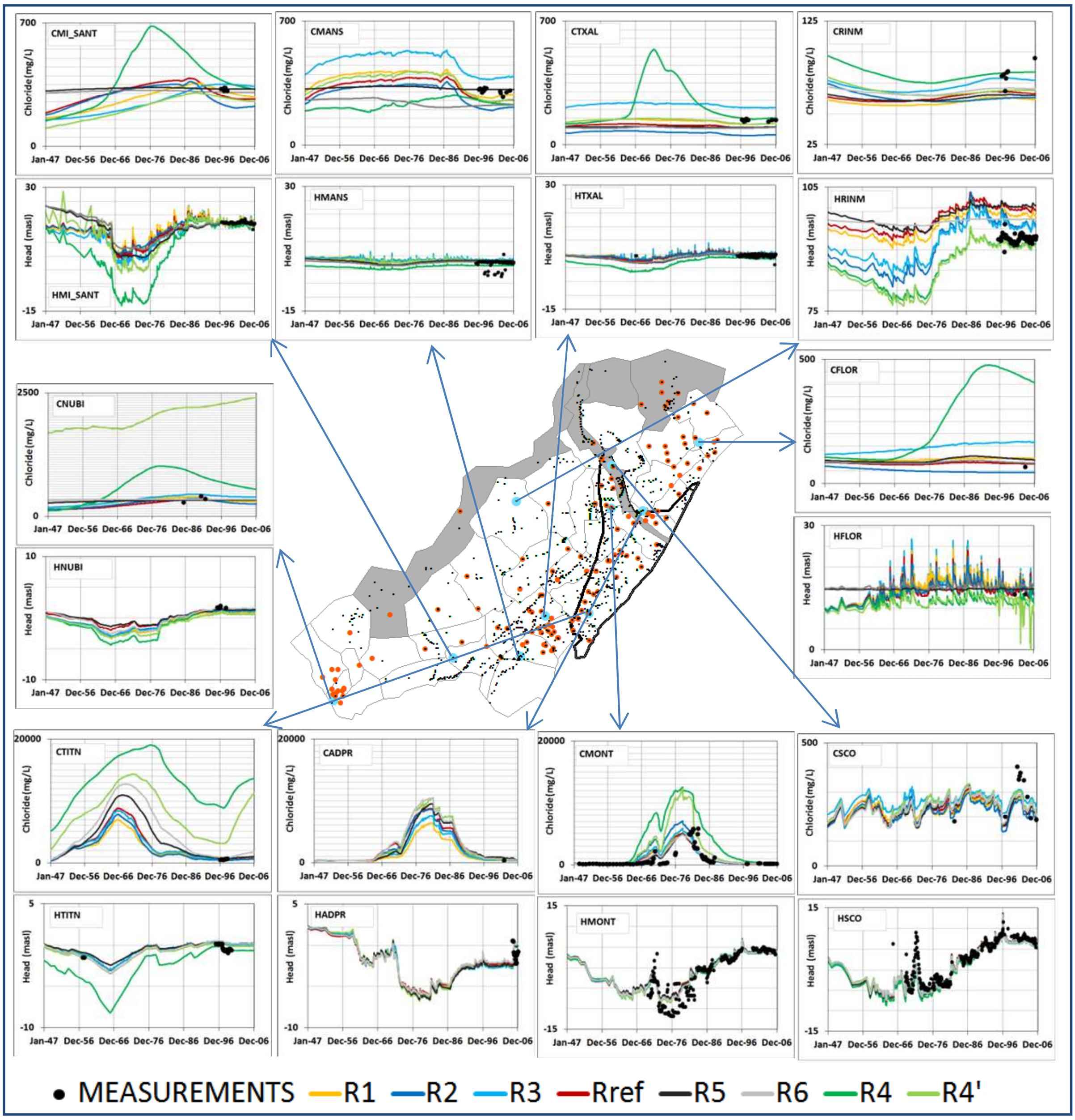
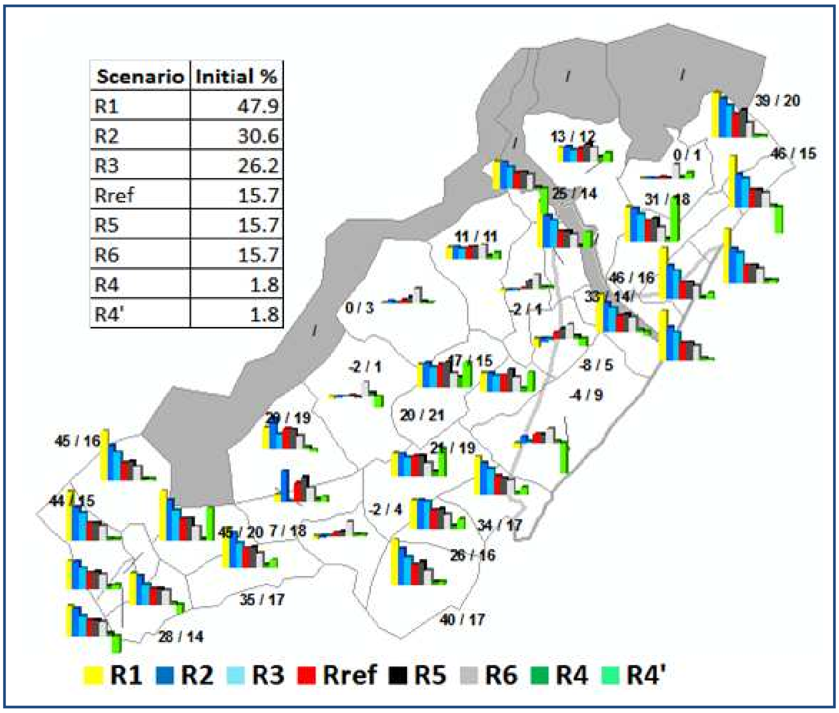


Figure 2-6 Examples of head and chloride concentration measured versus calculated. In map scheme, black points are observation points of head, orange points are observations of chloride concentration.

Therefore, although very good head settings are achieved with the hypothesis R4 'it is overrates seawater intrusion (Fig. 2.6) and thus the conceptual models of R4 and R4' hypothesis are neither valid throughout the delta area nor in areas influenced by other boundaries (Fig. 2.6, observation points MONT, ADPR, TITN NUBI and FLOR).

Considering both settings as head, in terms of chlorides concentrations as well as global modeling, the best-calibrated hypothesis for the delta area is that with the largest amount of recharging (R1). Nevertheless in urban areas the best fits are obtained with intermediate assumption, R2 in heads adjustment and Rref in chloride concentrations settings.

Regarding the temporal evolution of the recharge functions, it has been only slightly better with the form resulting from the reference scenario (Rref) with respect to the hypothesis of constant recharges over time (R5). So in a general assessment, the differences imposed in the form of the recharge function do not change the conceptual model nor generate significant difference settings. Nor was the amended conceptual model consistent with the hypothesis recharge constant in time and space (R6), although in this case the middle settings are significantly worse. Also, details were not established for the conceptual model of distribution of recharge from the rest of the contours and conditions (Fig. 2.7). These results are obviously determined by the spatial and temporal distribution of the measurements. In fact, these three hypotheses (Rref, R5 and R6) have quantified a similar recharge in the period 1996-2006 in which they have a greater number of observations (Fig. 2.5 and 2.6).



Scenario	Initial %
R1	47.9
R2	30.6
R3	26.2
Rref	15.7
R5	15.7
R6	15.7
R4	1.8
R4'	1.8

Figure 2-7 Recharge proportions calibrated for each scenario (proportions regarding to WS, see Table 2). Numbers in map are proportions of R1/ Rref scenarios.

2.5. Conclusions

Areal recharge may be the most important input in urban aquifer systems. Yet, accurate evaluation of this input is difficult. We presented a methodology to help estimate the areal recharge of urban aquifers. The proposed method is essentially similar to the water-table fluctuation mass balance method, applicable when groundwater head data are sparse, so that lack of spatial and temporal coverage is automatically interpolated by the model. It consists in (1) definition of the conceptual model; (2) implementation into a numerical model; (3) parameterization of urban recharge; (4) calibration and (5) iteration. The two last steps need to be repeated until finding the best fit is found or the range of uncertainty is narrowed. This methodology is applicable to complex systems by taking into account temporal variability of all water sources.

A transient (1916-2006) groundwater flow and solute transport model of the Barcelona urban aquifers was built as a tool for helping in defining the management program. This model was calibrated against heads and chloride concentration data obtaining very satisfactory fits for both variables. Mass balance and hydraulic parameters were also consistent with prior calculations.

This application reflects the importance of recharge evolution on the aquifers mass balance. They are one of the most important inputs. We believe that the situation found in the Barcelona urban aquifer may be typical of many urban aquifer systems. Areal recharge in urban areas may be a very significant portion of total inputs. Here it was the first.

Based on general criteria in the calibration process of recharge we provide that:

- Hypothesis to assess recharge in urban areas have been proposed based on percentages of water mains and sewer network susceptible to losses and recharge the groundwater scheme. These waters are classified according to their chemical properties, potential ways to enter the ground, and origin. For this particular study case, the spatial and temporal discretization recharge, in absence of more direct data, uses population density, per capita allocation, and land use.
- Calibration of various recharge scenarios requires that other parameters to be calibrated to have the minimum amount of deviation possible.
- A good head setting may not be sufficient to quantify recharge, especially in those areas influenced by boundaries; in which case hydrochemical measures are useful to validate or reject the resulting conceptual model.

3. Occurrence and fate of alkylphenol polyethoxylate degradation products and linear alkylbenzene sulfonate surfactants in urban groundwater: Barcelona case study.

This chapter is based on the paper Tubau I, Vázquez-Suñé E, Carrera J, González S, Petrovic M, López de Alda MJ, Barceló D. Occurrence and fate of alkylphenol polyethoxylate degradation products and linear alkylbenzene sulfonate surfactants in urban groundwater: Barcelona case study. Journal of Hydrology; 383(2010):102-110. doi:10.1016/j.hydrol.2009.11.030.

3.1. Introduction

High population growth increases the demand for water and the generation of wastewater. groundwater is an important resource of water supply in the world and aquifers in urban zones are vulnerable to contamination by a variety of contaminants due to urban activities. Approximately 90 % of the water for supply comes from imported surface water in the city of Barcelona, which is the study area. Since supply sources are subject to periodic droughts, the Catalan Water Agency (ACA) is seeking alternative water resources. There are a number of aquifers with varying lithologies and ages below the city (Váquez-Suñé et al., 2005). Therefore, groundwater must be considered as an option. The question is whether urban groundwater can be used safely. Urban aquifers may suffer pollution from different sources, including losses from water supply networks, leakage from sewers, seepage from rivers or other surface water bodies, seawater intrusion, etc. As a result, a large number and variety of contaminants may be found in urban aquifers (Howard et al., 1996; Barrett et al., 1999; Lerner, 2002; Morris et al., 2005; Váquez-Suñé et al., 2000; Wakida and Lerner, 2005; Naik et al., 2008). Some of these contaminants are subject to environmental quality standards (EQS) in drinking water (Council of the European Union, 1998), groundwater (European Parliament and Council of the European Union, 2006), and/or surface water (European Parliament and Council of the European Union, 2008). Other wastewater substances, also known as emerging contaminants, whose toxicity, occurrence and persistence are less well known, are subject to review for possible identification as priority substances or priority hazardous substances (European Parliament and Council of the European Union, 2008). The list of priority substances in the field of water policy, adopted for the first time in 2004 and revised in 2008, includes a total of 33 substances, some of which had never been subject to regulation in water before. This is the case of the alkylphenol polyethoxylates (APEOs) degradation products (DPs) nonylphenol (NP) and octylphenol (OP). APEOs are nonionic surfactants extensively used by industry, and in the past also in household products. Scientific evidence on the occurrence and toxicity in water of their degradation products motivated the identification of NP and OP as priority hazardous substances and the establishment of EQS for them in surface waters, which translated in annual average (AA) concentrations of 0.3 and 0.01-0.1 Ig/L for NP and OP, respectively, and a maximum allowable concentration (MAC) of 2 Ig/L for NP. These compounds as well as other APEOs DPs, such as alkylphenol carboxylates (APECs), are often found in surface waters, at concentrations sometimes surpassing the established EQS as evidenced, for instance, in a broad survey carried out at the European level in search for the occurrence of 35 selected compounds in river water samples from over 100 European rivers (Loos et al., 2009). Other studies, such as an extensive survey carried out in 2000 in the USA to evaluate the presence of 65 organic wastewater contaminants in 47 groundwater sites from 18 states, have evidenced also their presence in aquifers (Barnes et al., 2008). In fact, APEOs DPs were among the searched contaminants most abundant and most frequently detected in both of the above studies. In the study area, González et al. (2004) observed the presence of APEOs DPs and LAS at hundreds of Ig/L concentrations at the entry points of wastewater treatment plants (WWTPs). This study is focused on degradation products of nonionic surfactants APEOs and the ionic surfactants LAS. LAS and their degradation products (sulfophenyl carboxylates, SPC) are not regarded as priority substances although they are today the most common domestic surfactants in the area. Surfactants are used in a variety of industrial and domestic products such as cleaning products, degreasers and detergents. They are normally divided into four main groups: (1) anionics, (2) nonionics, (3) cationics and (4) amphoterics (Ying, 2006). Anionic and nonionic surfactants currently account for 90% (50% and 40% respectively) of the surfactant production in western Europe, i.e. 2.5 million tons in 2002. LAS account for 45% of the anionics, whereas fatty alcohol ethoxylates (AEs) and APEOs represent 60% and 10% of the nonionics, respectively (European Committee of Organic Surfactants and their Intermediates, 2007). The most widely studied APEOs are nonylphenol polyethoxylates (NPEOs) and octylphenol polyethoxylates (OPEOs), (see Fig. 3.1 for nomenclature).

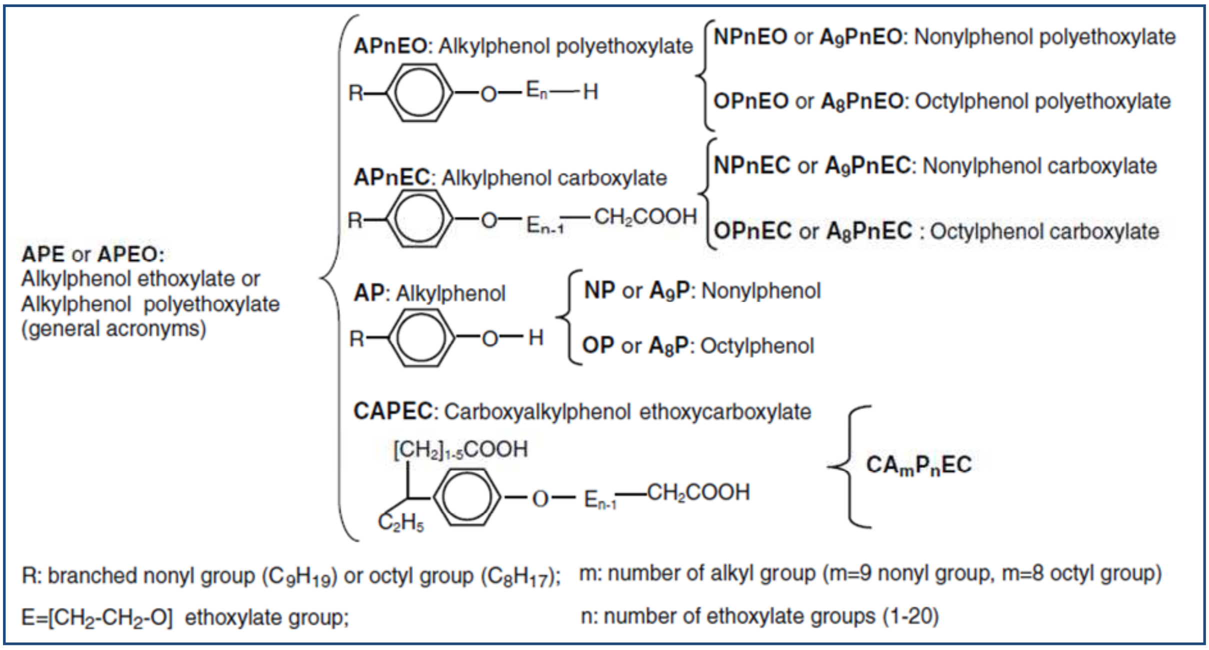


Figure 3-1 Acronyms and chemical structures of alkylphenol ethoxylates (APEOs) and some of their degradations products (DPs).

Commercially produced APEOs contain between 6 and 12 ethoxylate groups (APnEO, n = 6, …, 12). These undergo rapid primary biodegradation (Giger et al., 1984; Ahel et al.,1994a; Di Corcia et al., 1998; Jonkers et al., 2001). This initial biotransformation of APEOs produces degradation products with shortened ethoxy chains, mainly AP2Es and AP1Es (AP2EOs, AP1EOs and the more hydrophilic AP2ECs and AP1ECs), Fig. 3.2. Carboxylated ethoxy chains AP2ECs and AP1ECs have been observed in aerobic biodegradation (Ahel et al., 1994b; Lu et al., 2008) but not under anaerobic conditions (Lu et al., 2008). Anaerobically treated sewage sludge favors the formation of APs (Giger et al., 1984; Ahel et al., 1994a; Ejlertsson et al., 1999).

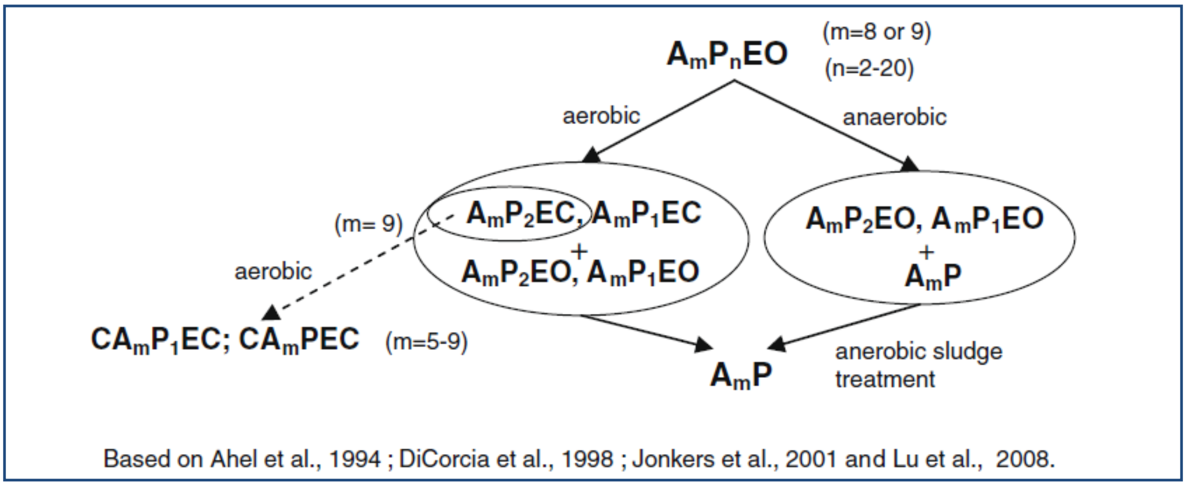


Figure 3-2 Biotransformation pathways of alkylphenol polyethoxylates.

The toxicity of APEOs is increased with decreasing ethoxylate chain length (Staples et al., 2004; Barber et al., 2007). Alkylphenol (AP) is their shortest chain and the most toxic (Environment Canada, 1999). Because of their toxicity and persistence, APEOs have been replaced by LAS and AEs since the mid 1960s. LAS and AEs are more biodegradable and their biodegradation products are less toxic (Kimerle and Swisher, 1977). LAS is aerobically well degraded and the formation of metabolites (mainly SPCs) well known (Yadav et al., 2001; Scheleheck et al., 2007) and display high levels of biodegradation in some WWTPs (Brunner et al., 1988; Schöberl and Marl, 1989; Thiele et al., 1997). However, LAS are believed not to degrade significantly under strictly anaerobic conditions in laboratory tests or anaerobic digester of sewage sludge (Berna et al., 2007). LAS, APEOs and their degradation products have been detected in the environment: estuarine and coastal zones (Vivian, 1986;

González et al., 2004; Zoller, 2006), rivers (Ahel et al., 1994b; Céspedes et al., 2005; Loos et al., 2009), groundwater with rapid infiltration of untreated and treated wastewater (Barber et al., 1988; Field et al., 1992; Leenheer et al., 2001; Latorre et al., 2003; Swartz et al., 2006). Moreover, the behavior of LAS and APEOs has been studied under laboratory conditions (Larson and Games, 1981; Manzano et al., 1998; Perales et al., 1999; Jonkers et al., 2001; Ying et al., 2008). Overall, it is not known to what extent do biodegradation pathways studied in the laboratory and wastewater plants explain what occurs in ppb concentration in the natural environment, especially in groundwater where the residence time is long and where water may undergo a sequence of redox conditions. In fact, Krueger et al. (1998) compared mass removal rates for LAS in laboratory column experiments and field tracer tests. Biodegradation was 2-3 times higher in the laboratory than in the field under similar concentrations of dissolved oxygen. Ying et al. (2008) compared the biodegradation of NPs and OPs under aerobic and anoxic conditions in the laboratory using water and soil from aquifers. There have been fewer studies on the fate of APEOs in urban groundwater, e.g. degradation of APEOs in groundwater near rivers (Ahel et al., 1996) and LAS in contamination plumes (Thurman et al., 1986; Barber et al., 1988; Larson et al., 1989). This study deals with the fate APEOs DPs and LAS surfactant in urban groundwater at field scale. To this end, the occurrence of APEOs DPs in groundwater was compared with: (1) sources of recharge or/and pollution containing these substances, (2) groundwater redox conditions, (3) occurrence of linear alkylbenzene sulfonate (LAS) which are nowadays the most common domestic surfactants in the area and (4) other common contaminants in urban groundwater in the city of Barcelona. The APEOs DPs analyzed were NP2EC, NP1EC, NP, OP2EC, OP1EC and OP. In this study, only the original LAS product was analyzed.

3.2.1. Site description

The study area occupies 136 km2 and includes Barcelona and some towns of the metropolitan area (Fig. 3.3), with a population of 2.2 million. Climate is Mediterranean with an average rainfall of some 600 mm/year. The area is bounded by the Collserola range (Catalan coastal ranges, maximum elevation 512 m.a.s.l.), the Mediterranean sea and Besòs delta (to the northeast) and the Llobregat delta (southwest). Aquifers with different lithologies and ages have been mapped under the city. groundwater flows generally seawards from the mountain range in all of them (Fig. 3.3). Several recharge sources in the aquifers of Barcelona have been identified (Váquez-Suñé et al., 2000). These include rainfall infiltration in the non-urbanized areas at the higher parts of the city (Fig. 3.3 and 3.4). They are regarded as ‘‘clean” natural recharge water. There are two potential inflows from surface water bodies: seawater intrusion and water from Besòs River.

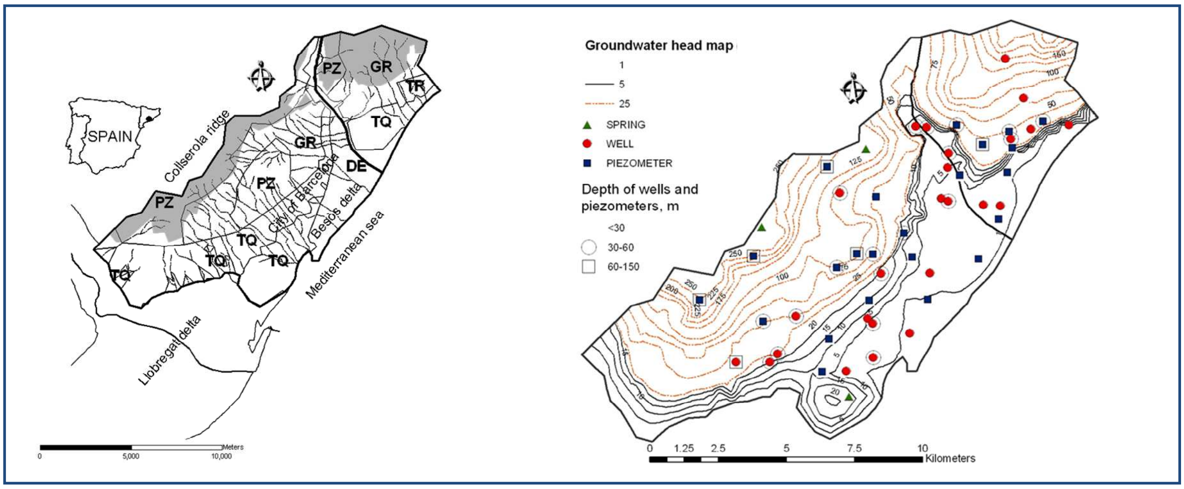
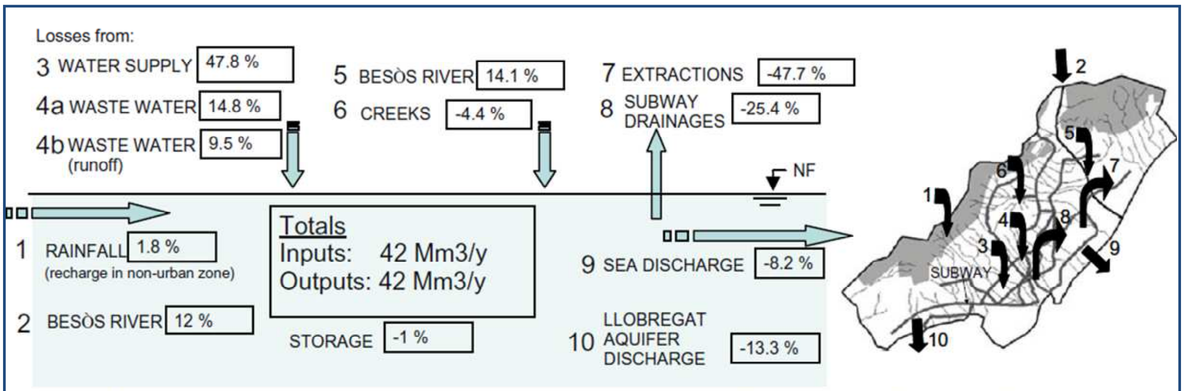


Figure 3-3 Schematic description of study area. Bottom, location and characteristics groundwater sampling points and piezometric map, note that contours interval are 5 m for heads below 25 m (continuous lines) and 25 m above (dashed). Note the change in gradient at the Paleozoic and Quaternary contacts.



(1): rainfall recharge in northern area; (2): inputs from aquifers out of boundary; (3): losses from water supply; (4): losses from wastewater, divided into (4a) waste water and (4b) waste water in rainfall events; (5): Besòs river recharge; (6): recharge from creeks; (7): groundwater extractions; (8): subway drainages; (9): sea discharge; (10): outputs to Llobregat aquifers.

Figure 3-4 Estimated annual average groundwater balance in the period 2000-2006 expressed as percentage of inputs (modified after Vázquez-Suñé et al., 2005).

The latter contains a large proportion of effluents from secondary WWTPs, especially during the summer. Additional sources of groundwater recharge attributable to anthropic activities include: (1) losses from the water supply network (supply water comes from the Llobregat River in southern quarters and from the Ter River in northern quarters), (2) in paved areas, runoff water, which washes away the urban surface atmospheric deposition and recharges the aquifers through direct infiltration or sewer seepage, and (3) losses from sewage water. Accordingly, we identified up to eight different recharge sources in the city of Barcelona: River Besòs, (2) rainfall recharge in northern non-urban area, Ter River water supply, (4) Llobregat River water supply, (5) Ter River sewage water, (6) Llobregat River sewage water, (7) City runoff and (8) Sea water intrusion.

2.3.4. Sampling

Fifty-three water samples were collected from September 2006 to January 2007 (Fig. 3.3). Two samples from possible recharge sources: one sample from River Besòs and one sample of drinking water from a public tap. Fifty-one samples were collected from groundwater: three samples from natural springs, 23 from observation piezometers and 25 from active wells belonging to private individuals and companies (i.e., currently pumped, not from disused wells). Piezometer and wells varied in depth (Fig. 3.3). Piezometer 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 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. Each water sample underwent chemical analysis in accordance with the Spanish guidelines for drinking water (Royal Decree 140/ 2003). These guidelines include 53 parameters (four radioactivity parameters were not analyzed). The discussion of the results of this study only addresses some of the main tracer species of waste water such as nitrate, ammonium, boron, Trichlorethene and Perchlorethene. Surfactant samples were stored in Polyethylene terephthalate (PET) containers that were amber in color to avoid photo-degradation. Containers were stored in a refrigerator at 4 °C until transport to the laboratory, where the samples were treated on a daily basis. Once in the laboratory, surfactants samples were filtered through 0.45 μm membrane filter and preconcentrated on LiChrolut C18 (Merck, Darmstadt, Germany) solid phase extraction (SPE) cartridges (IST, UK) within 24 h in order to avoid any degradation of target compounds and loss of sample integrity. All SPE experiments were performed using a Baker SPE 12 g apparatus (J.T. Baker, Deventer, Netherlands) connected to a vacuum system set at -15 psi for the dispensing of samples through the SPE cartridges. Disposable 3-mL cartridge columns packed with 500 mg of LiChrolut C18 sorbent from Merck (Darmstat, Germany) were activated and conditioned first with 7 mL of methanol and then with 3 mL of HPLC water at a flow rate of 1 mL/min. Samples were loaded at a flow rate of 5 mL/min. After preconcentration, the sorbents were completely dried (30 min) to avoid hydrolysis. After drying, the SPE cartridges were wrapped in aluminum foil and kept at -20 °C until analysis (max. 1 month). Cartridges were eluted with 2 x 4 mL of methanol. The eluates were evaporated to dryness with a gentle stream of nitrogen and reconstituted with methanol to a final volume of 1 mL. The complete SPE procedure is described by Petrovic et al. (2001).

2.3.5. Analytical methods

All solvents (water, acetonitrile and methanol) were high performance liquid chromatography (HPLC) grade and were purchased from Merck (Darmstadt, Germany). The standards used in this study were of the highest purity available. High purity (98%) 4-tert-OP and 4-NP were obtained from Aldrich (Milwaukee, WI, USA). OP1EC, OP2EC, NP1EC and NP2EC were synthesized according to the method described by Diaz et al. (2002). Commercial LAS with low dialkyltetralinsulfonate content (<0.5%) were supplied by Petroquimica Española S.A. in a single standard mixture with the proportional composition of the four homologs of: C10: 3.9%, C11: 37.4%, C12: 35.4%, C13: 23.1%. 4-n- NP-d8 used as the internal standard were obtained from Dr. S. Ehrenstorfer (Augsburg, Germany). Stock solutions (1 mg/mL) of individual standards and standard mixtures were prepared by dissolving precise amounts of pure standards in methanol. Standard working solutions were obtained by further dilution of stock solutions with methanol. Analyses were performed on a Waters 2690 series Alliance HPLC (Waters, Milford, MA) with a quaternary pump equipped with a 120 vial capacity sample management system. The analytes were separated on a 5 µlm, 125 x 2 mm i.d., C18 reversed-phase column (Purospher STAR RP-18), preceded by a guard column (4 x 4, 5 lm) of the same packing material, both supplied by Merck, Darmstadt, Germany. The sample injection volume was set at 10 µL. A binary mobile phase gradient with methanol (A) and water (B) was used for analyte separation at a flow rate of 200 µL/min. The elution gradient was linearly increased from 30% A to 80% A in 10 min, then increased to 95% A in 10 min and kept isocratic for 5 min. A benchtop triple quadrupole mass spectrometer Quattro liquid chromatography (LC) from Micromass (Manchester, UK) equipped with a pneumatically assisted electrospray probe and a Z-spray interface was used for this study. Capillary voltage was set at -2.8 kV, extractor lens at 7 V, and RF lens at 0.6 V. The source and desolvation temperatures were 150 and 350 °C, respectively. The nitrogen flows were optimized al 50 L/h for the in cone gas and 540 L/h for desolvation gas. For tandem mass spectrometry (MS-MS) experiments, the argon collision gas was maintained at the pressure of 5.8 x 10-3 mbar. The detection was performed under negative ionization (NI) by LC-MS-MS in multiple reactions monitoring (MRM) mode as described by Petrovic et al. (2003) and González et al. (2008).

3.2. Results and discussion

3.2.1. Generic pollution: ammonium, nitrate and perchlorethene

Results for generic contaminants are shown in Table 3.1 and Fig. 3.5. Based on the results of a statistical analysis of chemical data, groundwater samples collected in the study area were grouped into three categories (Z1, Z2 and Z3). Z1 are samples taken in non-urban zone and the remaining samples was divided according to the concentration of ammonium: samples with an ammonium concentration lower than 0.3 mg/L (Z2) and samples with a concentration higher than 0.3 mg/L (Z3). As it turns out, the samples in Z3 were collected in aquifers near River Besòs which flows over deltaic aquifers with high transmissivity and water levels close to the soil surface. As a result, most of the recharge comes from the river. Zone Z2 samples displayed fairly oxidizing conditions, mainly those located in the lower half of the city (Fig. 3.5). Reducing conditions are found in Z2 samples taken from deep piezometers with opening in schists (Fig. 3.3 and 3.5). Nitrate concentrations exceeding 50 mg/L were detected in 22 out of 33 samples and exceeded 50 lg/L of perchlorethene (PCE) in approximately one third of the samples. By contrast, reduced species such as ammonium prevailed in Z3 samples. Despite the fact that Z3 is in a predominantly industrial area, PCE and trichlorethene (TCE) concentrations were relatively lower (mean of 5.8 lg/L). Groundwater in the non-urban zone (Z1) was fairly diverse. Shallow samples were aerobic, while the deep ones were reducing. Nevertheless, total nitrogen, boron and PCE were low, indicating that pollution was much lower than in Z2 and Z3. Nitrate, ammonium and boron are used as tracers of waste water in urban groundwater (Wakida and Lerner, 2005; Barrett et al., 1999). High concentrations of boron (and ions such as chloride and sodium) were detected in samples from deltaic materials as a result of marine intrusion in the lower parts of the city. The results of one sample (“PEAR”, Fig. 3.5) are included in the study although they are not classified in zone Z2 because this sampleappears to come from an industrial pollution site and may not be representative of Z2 waters. Very high concentrations of total organic carbon were detected in this sample (186 mg/L, two orders of magnitude greater than the remaining samples), BTEX (benzene, toluene, ethylbenzene and xylenes) and low Eh.

Table 3-1 Generic contaminant average and maximum concentrations in the study area grouped according to the zones of Fig. 3.5.

	average (maximum)					
	Z1[a] (8 samples)		**Z2[a] (33 samples)**		**Z2[a] (33 samples)**	
Amonium (mg/L)	0.0	(0.24)	0.0	(0.07)	2.9	(8.6)
Nitrate (mg/L)	18.4	(49.94)	71.6	(280.74)	10.3	(24.15)
Boron (µg/L)	69.9	(154.94)	185.8	(753.53)	378.0	(700.47)
Tetraclorethene (µg/L)	1.0	(4.59)	53.9	(347.86)	5.8	(24)
Triclorethene (µg/L)	0.1	(0.53)	11.8	(119.6)	2.1	(5.3)

[a] Results are grouped as in Fig.3.5.

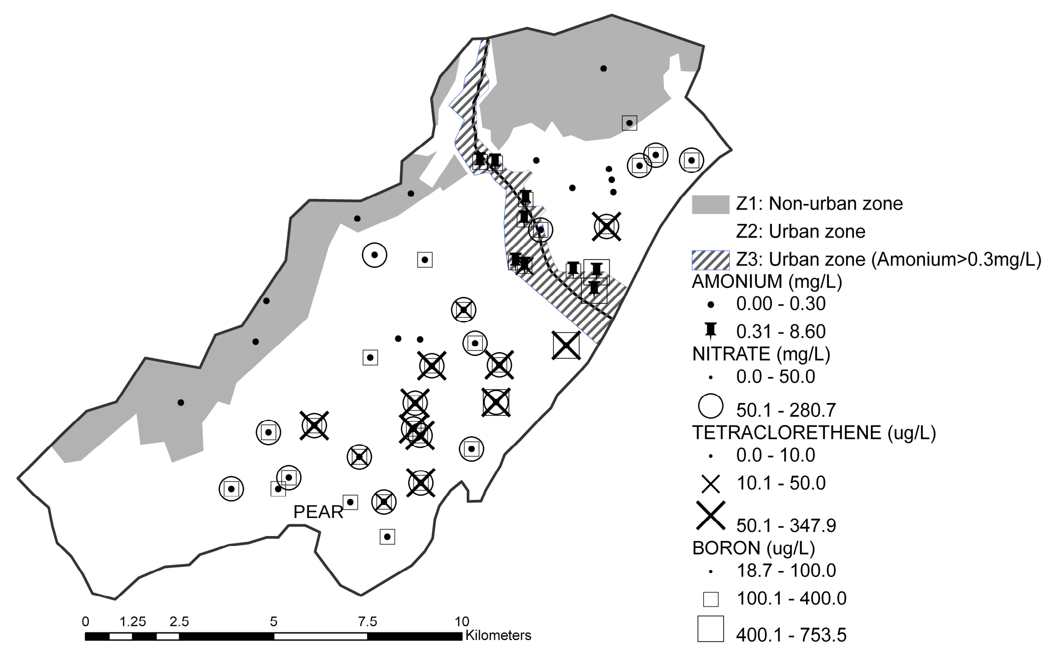


Figure 3-5 Spatial distribution of ammonium, nitrate, perchlorethene and boron.

3.2.1. Surfactants: LAS and APEOs degradation products

LAS was the surfactant with highest concentrations in potential recharge waters (Table 3.2). Despite the fact that alkylphenolic surfactants have been banned in domestic products in the study area since the 1990s, APEOs DPs were detected by González et al. (2004) in WWTPs and also in the river sample (Table 3.2). Notwithstanding, concentrations of APEOs DPs were much lower than LAS concentrations in recharge waters. This contrasts with aquifer samples from Z3 where higher concentrations of APEOs DPs than LAS were detected (Table 3.3 and Fig. 3.6). The highest concentrations of all the APEOs DPs were found in wells and piezometers located in Z3. Recharge in this area comes basically from the river. Nevertheless, measured concentrations in Z3 were higher than concentrations in the river, NP2EC being the maximum. Ahel et al. (1996)

also detected NP2EC as the degradation product with the highest concentrations in groundwater recharged from a river which contained.

Table 3-2 Concentrations of target compounds in potential recharge waters: WWTPs influent of site study, River Besòs and drinking tap water.

	Influent WWTP (1) Depurbaix	Influent WWTP (1) Besos	Tap water	Expected Z2 recharge 14.2 % WW	Besòs river Z3 recharge
LASs (µg/L)	307-1920 (910)	532-1635 (837)	1.0	98	48
NP2EC (µg/L)	--	--	0.1		2.5
NP1EC (µg/L)	182-450 (295)	108-478 (294)	0.1	33	1.2
NP (µg/L)	<lod-18 (4.5)	<lod-11 (2.6)	0.1	0.4	0.6
OP2EC	--	--	<lod		0.3
OP1EC (µg/L)	--	--	<lod		0.1
OP (µg/L)	<lod-14 (3.4)	<lod-11 (2.8)	<lod	0.3	<lod

n=6 expressed as maximum-minimum (mean values).(1) González et al., 2004.

Table 3-3 Statistics of measured concentrations of target compounds. Results are grouped according to the zones of Fig. 3.5 and 3.6.

	n>0.01/n			average [max; min], (µg/L)		
	Z1[a]	Z2[a]	Z3[a]	Z1[a]	Z2[a]	Z3[a]
LASs	8/8	33/33	9/9	0.41 [0.80; 0.13]	1.38 [5.06; 0.36]	2.28 [4.96; 0.68]
NP2EC	0/8	3/33	8/9	<lod	0.03 [0.58; <lod]	5.54 [11.24; <lod]
NP1EC	0/8	4/33	9/9	<lod	0.02 [0.22; <lod]	1.35 [2.46; 0.20]
NP	2/8	15/33	6/9	0.12 [0.12; <lod]	0.05 [0.22; <lod]	1.63 [5.28; <lod]
OP2EC	0/8	0/33	7/9	<lod	<lod	0.29 [0.68; <lod]
OP1EC	1/8	3/33	7/9	0.00 [0.01; <lod]	0.01 [0.06; <lod]	0.06 [0.12; <lod]
OP	0/8	0/33	3/9	<lod	<lod	0.41 [1.80; <lod]

(<lod): Limit of detection is 0.01 µg/L for all compounds. [a] Results are grouped as in Fig. 3.5 and 3.6.

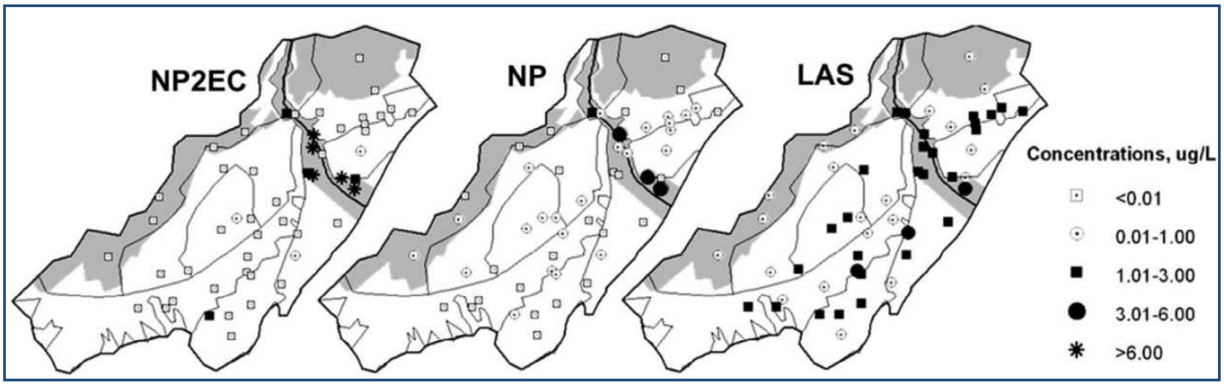


Figure 3-6 Spatial distribution of LAS surfactants and APEOs degradation products.

NP2EC correlates with the remaining carboxylated degradation products (Fig. 3.7), whereas it correlates less with NP and OP, which are more lipophilic and consequently have a greater tendency to remain adsorbed. Degradation products of nonylphenol group exceeded the octylphenol group as in the case of the Besòs River and the rivers of 27 European countries (Loos et al., 2009). By contrast, the octylphenol group was one order of magnitude higher than the nonylphenol group in groundwater samples of the United States (Barnes et al., 2008).

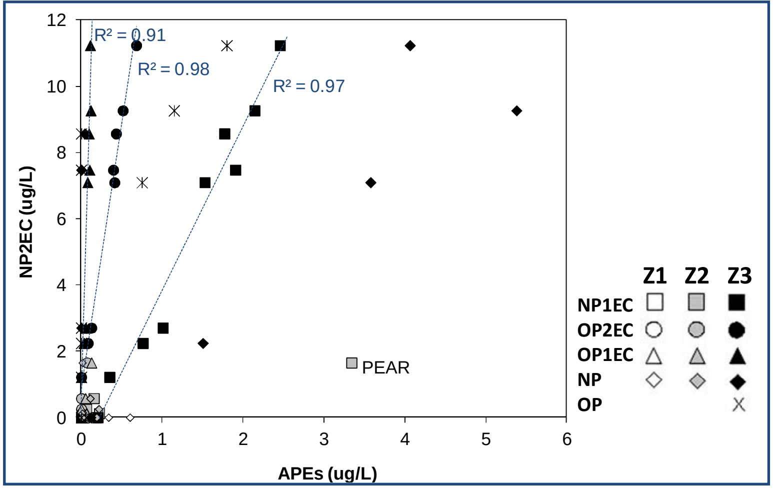


Figure 3-7 Relationship between NP2EC and the remaining APEOs degradation products.

Carboxylated degradation products of APEOs (NP2EC and NP1EC) were found in 14 samples in which ammonium was also detected. NP2EC concentrations in groundwater increased with increased ammonium in the samples with low dissolved oxygen treated waste water. (<3.2 mg/L). In fact, these concentrations correlate linearly with ammonium (Fig. 3.8). However, NP2EC concentrations were lower when dissolved oxygen was above the 2O2 : 1NHþ4 molar, (Fig. 3.8). NP2EC are carboxylates from the longer chains of APEOs that form in aerobic conditions (Fig. 1 and 2). Our results suggest that NP2EC and ammonium enter the saturated zone; NP2EC is degraded into small degradation products and ammonium is oxidized only when oxygen concentration is maintained at appropriate levels.

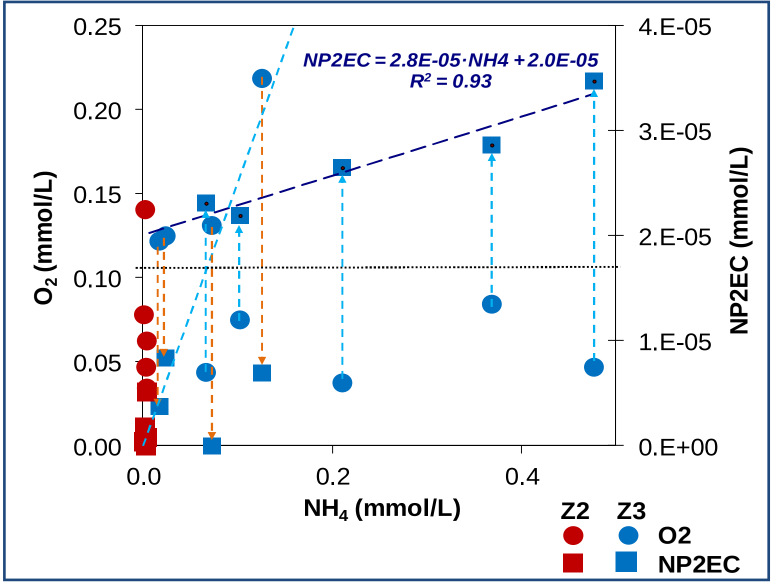


Figure 3-8 Relationship between ammonium, dissolved oxygen and NP2EC in Z2 and Z3 grounwater samples.

In the aquifers of this area (Z3), LAS was less than 10 % of LAS in the river sample, which indicates that LAS is being degraded. In the remaining portion of the urban zone (Z2), the maximum concentration of LAS resembled those in Z3 (5 µg/L) whereas in contrast to Z3, the concentrations of APEOs DPs were much lower. In this case, NP was the most widespread degradation product (15 out of 33 samples), reaching a maximum of 0.2 µg/L. The remaining DPs were detected in fewer than five samples, out of 33, with a maximum of 0.6 µg/L. In short, in the case of LAS as in the case of APEOs DPs, concentrations were much lower than expected taking into account the potential contribution of water recharge sources.

The maximum concentrations of LAS in groundwater accounted for about 0.6 % of waste water average concentrations (estimated at around 10-15 % of the average recharge concentration, Table 3.2). In this zone (Z2), oxidizing species indicative of oxidizing conditions such as nitrate and PCE were higher than in Z3. PCE showed a good correlation with potential redox in the field. Concentrations of PCE and TCE exceeding 20 µg/L were only detected in samples with Eh higher than 300 mV (Fig. 3.9).

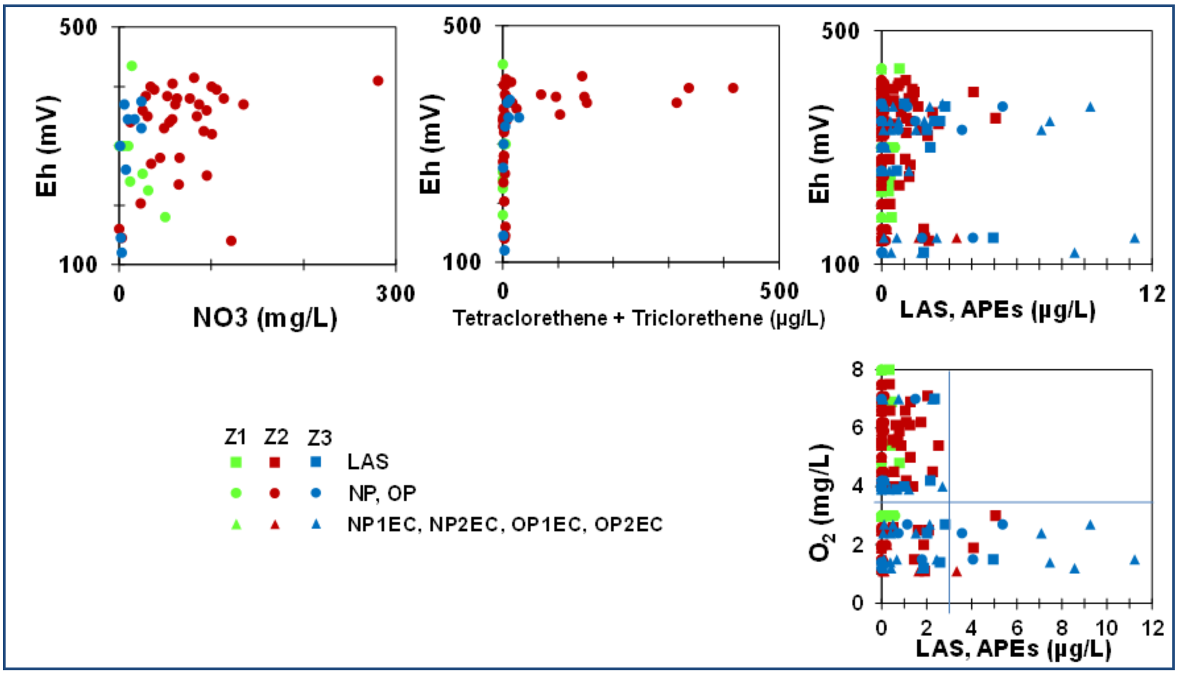


Figure 3-9 Relationship between redox potential, nitrate, PCE+TCE, dissolved oxygen, LAS and APEOs degradation products.

By contrast, Eh values measured in field did not correlate with LAS and APEOs DPs. Nevertheless, the concentration of these species depends on oxygen concentration in the two urban zones (Z2 and Z3). Whenever oxygen was higher than 4 mg/L, the concentration of LAS and APEOs DPs did not exceed 2.5 µg/L. This finding resembles the field and laboratory results of LAS of Krueger et al. (1998), in that surfactants and many degradation products are degraded under oxidizing conditions. In the non-urban zone (Z1) where samples were taken from aerobic and reducing groundwater, but where the level of pollution was lower than in Z2 and in Z3, concentrations of LAS and APEOs DPs were also lower than in the urban zones.

3.3. Conclusions

The following conclusions may be drawn from this study: Surfactants LAS and APEOs DPs were detected in urban groundwater. Concentrations of APEOs DPs were lower in the Besòs River than in aquifers recharged by river. NP2EC was detected in the highest concentrations. Although NP2EC is a degradation product from the longer chains of APEOs usually considered to form only under aerobic conditions (Ahel et al., 1994b; Lu et al., 2008), NP2EC concentrations in groundwater increased with increased ammonium in the samples with low dissolved oxygen. These results suggest that APEOs may degrade not only under aerobic conditions, but also under reducing condition. Some of the resulting degradation products degrade much slower (or do not degrade at all). As a result, their concentrations (notably those of NP2EC) build up in anoxic aquifers. Levels of APEOs DPs were lower than expected (between 10 and 1000 times) in portions of the zone where pollution was caused by sewage leakage, but oxidizing species prevail (high nitrate and PCE), indicating that APEOs are degraded or that they do not reach the saturated zone in oxidizing conditions. This conclusion is supported by the observation that the most widespread degradation product was NP (maximum of 0.2 µg/L), which is the ultimate degradation product of APEOs. Its moderate concentrations can be attributed to its tendency to sorb. The remaining degradation products were detected in fewer than five samples (maximum of 0.6 µg/L). _ LAS was the surfactant with highest concentrations in potential recharge waters and LAS was found in similar concentrations in both oxidizing and reducing aquifers, between 1 and 2 orders of magnitude less than the expected recharge, which suggests that the degradation processes of LAS may occur in diverse aquifer systems, even in reduced waters in which APEOs DPs are relatively more persistent. In all the cases, the concentrations of APEOs DPs and LAS seem to be limited by the concentration of dissolved oxygen measured in situ. Whenever oxygen was higher than 4 mg/L, the concentration of APEOs DPs and LAS did not exceed 2.5 µg/L. These results point to degradation of APEOs DPs in groundwater under different redox conditions and low concentrations. They should be useful for the design of both water purification plants and waste water treatment plants, as well as for complementing with artificial recharge projects.

4. Using EMMA and MIX analysis to asses mixing ratios and to identify hydrochemical reactions in groundwater

This chapter is based on the paper Tubau I, Vázquez-Suñé E, Jurado A, Carrera J. Using EMMA and MIX analysis to asses mixing ratios and to identify hydrochemical reactions in groundwater. Science of the Total Environment 470-471 (2014) 1120-1131. doi:10.1016/j.scitotenv.2013.10.121.

4.1. Introduction

The deterioration of groundwater quality has become a major issue in urban aquifers. In urban areas, a vast array of contaminants may be found because they are introduced into the aquifer through different recharge sources. Thus, the assessment of groundwater quality requires identifying not only the possible focus of contamination but also the processes that the pollutants undergo. In fact, this study is motivated by the assessment of groundwater quality at the Besòs River alluvial aquifer underneath Barcelona, Spain. Groundwater quality in this area is significantly better than river water quality, despite the fact that pumped groundwater is essentially recharged from the river.

A mass balance of chemical species is often used in hydrology and related sciences to aid in the evaluation of water balances. Its simplest form consists of measuring the concentrations of any conservative species occurring in inflowing and outflowing waters and, assuming continuity, establishing the mass balance of solute and water. However, the joint evaluation of recharge rates and quality can most likely be best achieved through flow and solute transport modelling when long head and concentration records are available. Because these models require the management of much information, simpler methodologies are necessary. Mixing calculations are an alternative to complex models and can be used to better estimate the relative importance of different sources of recharge.

Mixing calculations include (1) End-Member Mixing Analysis (EMMA) (Hooper et al., 1990; Hooper, 2003; Christophersen et al.,1990; Christophersen and Hooper, 1992; James and Roulet, 2006; Jones et al., 2006) and (2) mixing ratios (Schemel et al., 2006; McLaughlin et al., 2007; Bickle et al., 2007). An EMMA aims at identifying the minimum number of end-members required to explain the variability of measured concentrations and colinearity. An EMMA does not, however, allow us to compute mixing ratios. Thus, the application of other approaches is needed. Vàzquez-Suñé et al. (2010) present a methodology to compute mixing ratios and the composition of end-members using MIX (Carrera et al., 2004). This methodology consists of (1) the identification of potential recharge sources, (2) the selection of tracers, (3) the characterisation of the hydrochemical composition of potential recharge sources and mixed water samples and (4) the calculation of mixing ratios and the re-evaluation of end-members. This formulation may suffer from identifiability and colinearity.MIX aims to state whether mixing ratios can be computed from a priori defined end-members. Application to real cases with numerous potential end-members has been hindered due to several problems. The first relates to uncertainty in end-member definition caused by insufficiently documented spatial and temporal variability as well as conceptual problems. The second problem is the limited experience in selecting appropriate tracers, and the third is colinearity, which causes the solution to be unidentifiable or unstable.

The joint application of EMMA and MIX allows for the establishment of a methodology to select and evaluate the recharge sources and species in mixing calculations. It is possible to evaluate the entire system as a whole when setting up the system both to calculate and to evaluate the results. Moreover, the use of non-conservative species allows identification of chemical reactions. Whilst mixing analyses are essentially carried out with conservative tracers, they can also be used to identify reaction processes when departures from mixing lines (or planes) are identified (Skov et al., 1997; Pitkänen et al., 1999). As an example, Fig. 4.1 plots the average concentration at the Besòs River versus the average concentration in the aquifer for several species such as major and minor components, metals, polycyclic aromatic hydrocarbons (PAHs), pesticides and surfactants. Fig. 4.1 provides important information on the chemistry of the study area because it can be observed that the majority of the species have a higher concentration in the river than in the aquifer, suggesting hydrogeochemical processes. Consequently, distinguishing between mixing and chemical processes in groundwater is important in characterising the hydrochemical variation in both the recharge sources and the groundwater.

The objective of this study is to present an approach for using EMMA and MIX analyses jointly to assess mixing ratios and to identify hydrochemical reactions in groundwater. The methodology is applied to the assessment of river recharge waters in the Besòs Delta aquifers in Barcelona, Spain. The proposed approach consists of four steps: (1) identifying the potential sources of recharge, (2) characterising recharge sources and mixed water samples using hydrogeochemistry, (3) selecting chemical species (tracers) to be used in the analysis and (4) calculating mixing ratios and identification of hydrochemical reactions in groundwater.

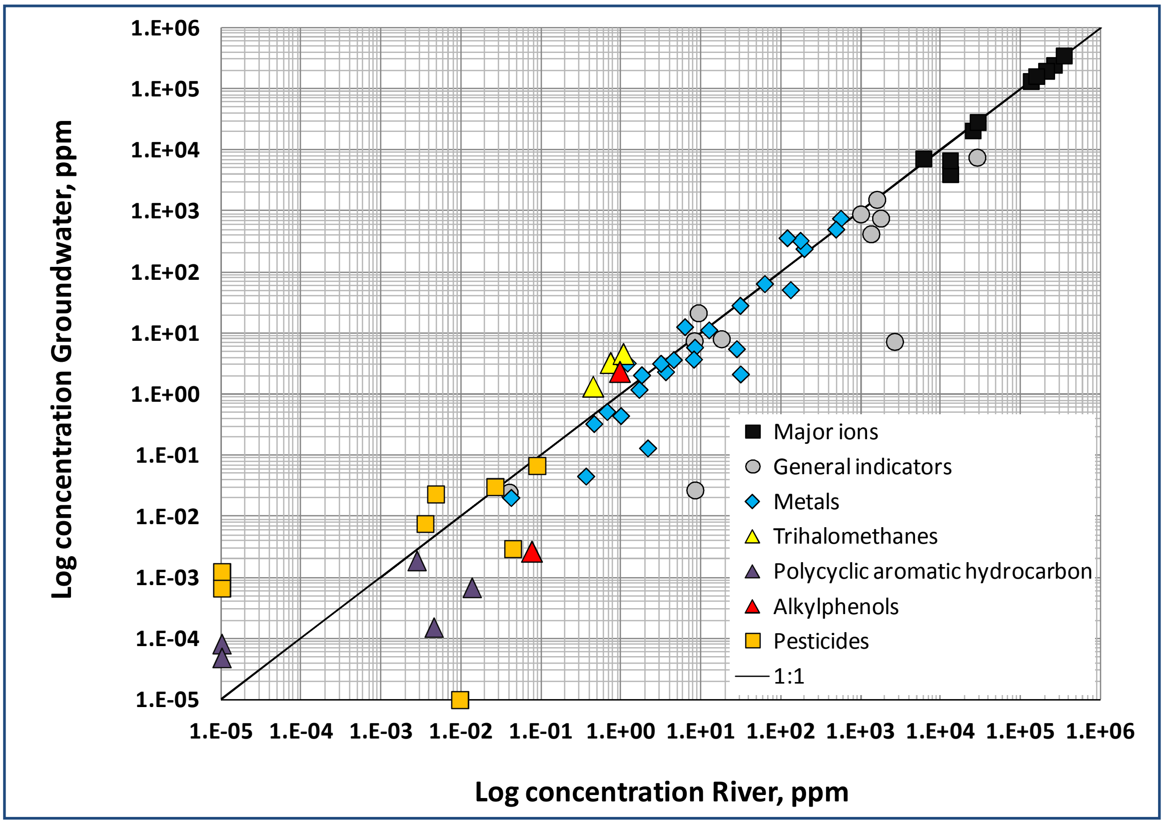


Figure 4-1 River versus groundwater average concentrations in the study area for several of species such as major and minor ions, metals, redox indicators, pesticides, among others. The river data set is collected monthly by the Catalan Water Agency (ACA) 2 km upstream of the study zone and it can be downloaded from http://www.gencat.cat.

4.2. Methodology and data treatment

4.2.1. Identify the sources of recharge

The identification of the recharge sources is specific in each study area and it requires an understanding of the system. Water balances and numerical models can help in disregarding potential sources or considering new ones. Anyway, a previous conceptual model is necessary in order to identify the potential end-members and to evaluate preliminary values for the overall groundwater balance. Flow rate and hydrochemistry of a recharge source can vary greatly over time. Therefore, it is wrong to consider a recharge source as a single component in the hydrochemical balance. The variability of the hydrochemical composition of a recharge source can be characterized by the integration of different end-members. In addition, the variability in the composition of a recharge source can be quantified from mixing calculations. The same could be applied to groundwater and its different recharge source contributions.

4.2.2. Characterization of the hydro chemical composition of potential recharge sources and mixed water samples

Qualitative analysis

Many of the hydrochemical species in the mixed waters can help in identifying the source waters, but a prior conceptual model is required both for an assessment of geochemical conditions and for selecting the tracer that might display the broadest range of concentration among the recharge sources. Most of the hydrochemical species considered cannot be used uncritically because their behavior might depend on local geochemical conditions (e.g., sulphate would not be conservative in reducing environments). Thus, the selection of the appropriate species is a critical step in mixing calculations (Barrett et al., 1999; Choi et al., 2005; Morris et al., 2006; Jurado et al., 2013). We have to take into account that their concentrations should also vary widely from one source to another. Again, it is necessary for a previous hydrochemical conceptual model to select the most helpful species.

Mixing calculations are representative of the analysed samples and incorporate some degree of uncertainty. These uncertainties are mainly related to sampling, handling and analytical errors; lack of data; and the occurrence of additional processes (reactions).

Multivariate analysis (EMMA) to select the end-members and the species in the mixing calculations

As stated above, an EMMA offers an approach where eigenvector and residual analysis of observed water chemistry estimates the number of contributing end-members. An EMMA aims at identifying the minimum number of end-members required to explain the variability of measured concentrations in time or space. An EMMA helps to manage the degree of uncertainty associated with the conceptual model. The explanation of the variance and the contribution of each species to the mixture are obtained from the analysis of information provided by the calculation of the eigenvalues. We propose the following methodological guidelines for the selection of end-members and species:

a) Initiate EMMA with all species and take further steps that will eliminate the species with the highest weight in the eigenvalue.
b) A common rule is to retain all eigenvectors associated with eigenvalues (n) greater or equal to 1, called the “rule of 1” (Hooper, 2003; Joreskog et al., 1976). This rule

consists of selecting the eigenvalues that explain variance greater than [1/number of specie].

c) Selection of species according to those eigenvalues that we want to explain. The number of end-members will be n + 1.

d) Projection of the observation points in the space defined by the eigenvectors associated with each eigenvalue. With this projection, it is possible to make a preliminary selection of end-members and an analysis of the points that fall outside the area defined by these end-members.

This type of graphic is a visual way to interpret the mixing of all the species involved and to assess the end-members. Hence, we can infer that source or a combination of source terms or processes may explain the mixing.

These steps may identify the species and/or combinations of species that better explain the end-members selected. In addition, we also have a pretty good idea of how far we can establish the system. The selected end-members and species considered in the EMMA analysis are those used for initiating the mixing calculations.

4.2.3. Compute mixing ratios and evaluation of the end-member composition

To study the influence of waters from different sources, the code MIX (Carrera et al., 2004) can be used. This software can be freely downloaded from http://www.h2ogeo.upc.es/software/MIX_PROGRAM/index.htm.

MIX is a maximum likelihood method for estimating mixing ratios whilst acknowledging uncertainty in end-member concentrations. Maximising the likelihood of concentration measurements with respect to both mixing ratios and end-member concentrations leads to a general constrained optimisation problem. The variables must satisfy some conditions to be suitable in mixing models: they must exhibit a conservative behavior and their values must be significantly different in the extreme components. This method also allows us to formulate a hypothesis about the geochemical reactions responsible for the non-conservative behavior in elements. MIX code allows the evaluation of mixing ratios in case of uncertain end members using the concentrations of mixed samples to reduce the uncertainty. In this approach measurement uncertainty is quantified through covariance matrices, which requires defining the reliability of measurements and the results depend on the assumed standard deviations. This code was previously used in several studies (Vàzquez-Suñé et al., 2010; Jiménez-Martínez et al., 2011; Morales-Casique, 2012; Cánovas et al., 2012a, 2012b; Galván et al., 2012; Jurado et al., 2012, 2013).

4.2.4. Site description

The Besòs River, located near Barcelona in the northeast of Spain, flows south-easterly and has a catchment area of 1038 km^2. The study area corresponds to the lower part of the catchment. It is located in north-eastern Barcelona, in the Besòs River Delta, at the town of Sant Adrià del Besòs, and it is close to the underground parking area at the Plaça de la Vila site (Fig. 4.2).

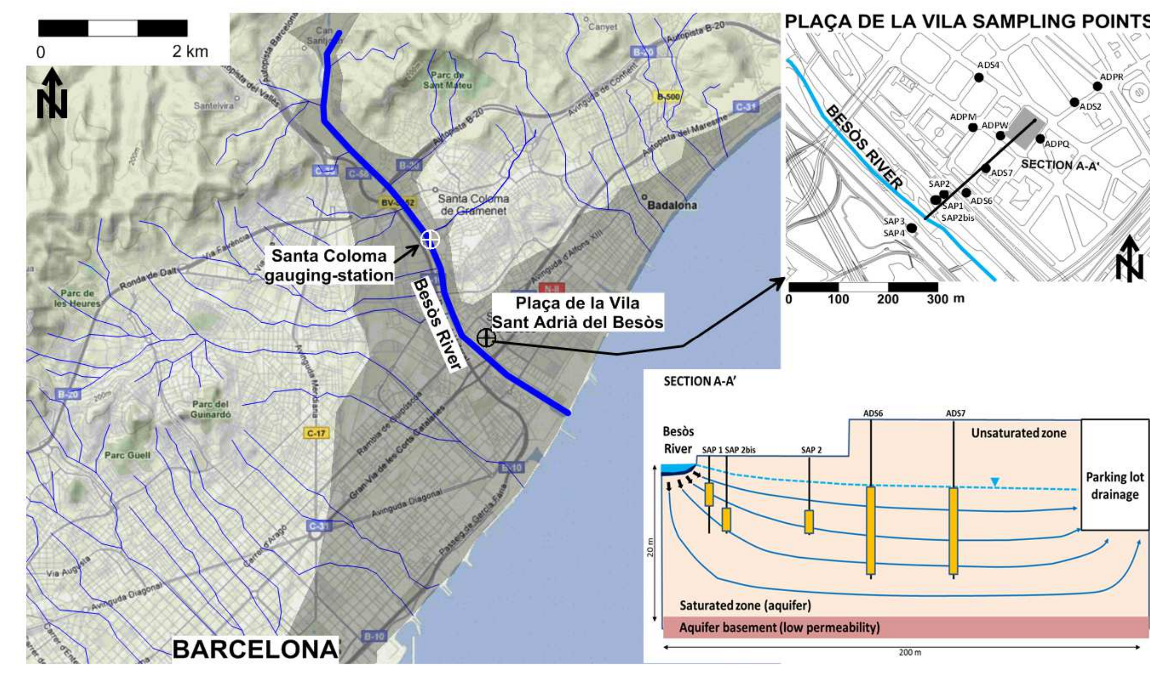


Figure 4-2 Location of the study area and hydrogeological conceptual model.

The climate is typically Mediterranean, with extreme temperatures in January and August and a yearly average temperature of 15 °C. Rainfall averages approximately 600 mm/year. Average stream flow is 4 m^3/s at the Santa Coloma gauging station (Fig. 4.2) belonging to the Catalan Water Agency (ACA). The gauging station is located approximately 2.5 km upstream from the Plaça de la Vila site and 4.5 km from the sea. River flow is measured daily, whilst river water quality samples are analysed monthly by the Catalan Water Agency (ACA).

The Besòs River is a good example of a Mediterranean fluvial system, with low baseflow (modal flow is 2 m^3/s), marked ebb flood, strong floods (more than 100 m^3/s) and very irregular flow patterns, which are mainly controlled by the rainfall events (Fig. 4.3). These events vary dramatically from year to year and within the year. River water quality depends on many factors. In the final part of the catchment (study area), river water could be considered to be a mix of water from different sources such as rainfall, raw sewer water, treated sewer water, waters from several parts of the catchment, etc.; furthermore, variation in time is very significant.

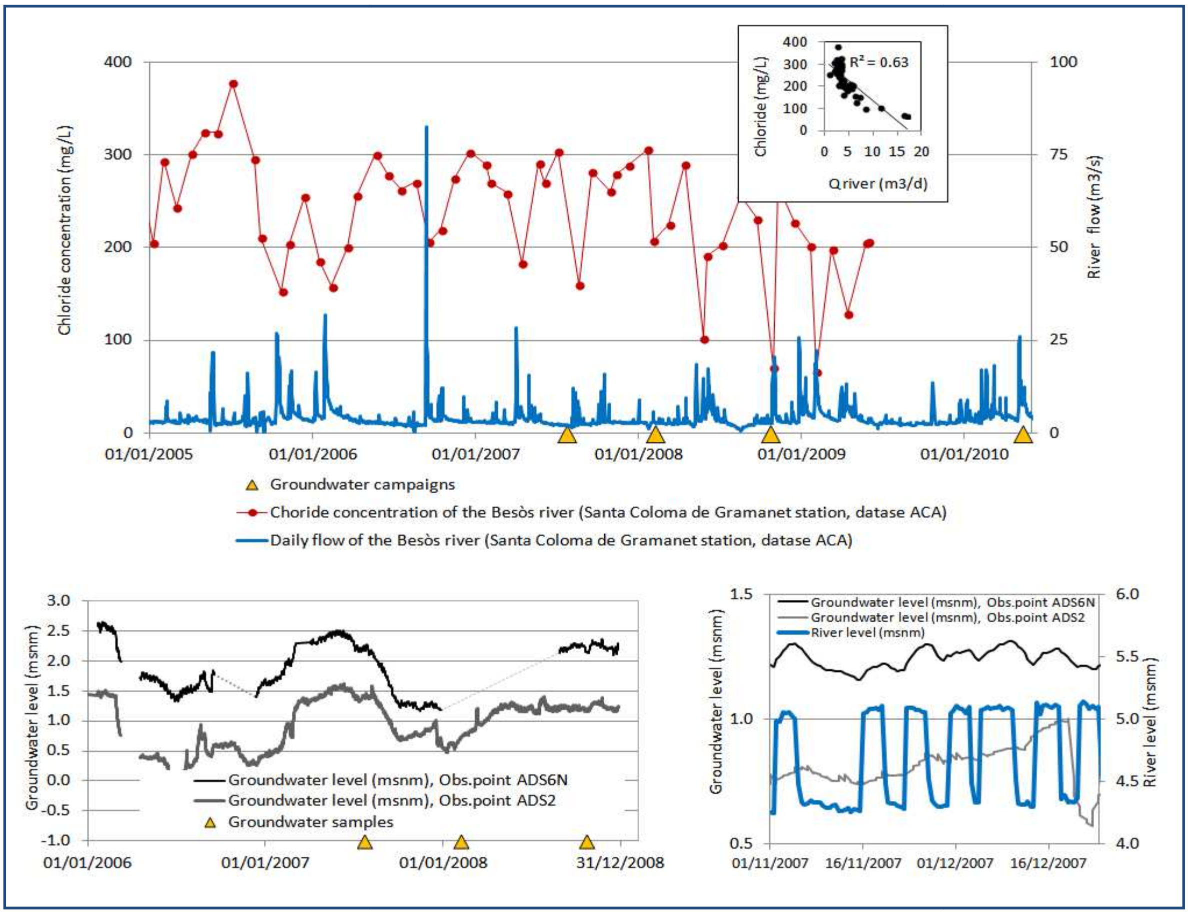


Figure 4-3 On the top, chloride concentrations and Besòs River flow from 2005 to 2010. At the bottom, evolution of groundwater versus river level. Note that the triangles represent the 4 groundwater sampling campaigns.

The geology of the study area was carried out by MOP (1966). We performed a thorough sedimentological study to update the geological model with new information obtained from civil work projects in the delta area. This allowed us to define in detail the three dimensional geological structure and to redefine aquifer units, their geometries, and the lateral connections both between units and the sea (Velasco et al., 2012).

The aquifers are formed within Quaternary sediments that rest discordantly on top of materials that range from Paleozoic to Pliocene. In the lower valley, there are typical fluvial aquifers, consisting of accumulations of alluvial sand and gravels. The delta itself begins at the end of the Lower Valley and consists of four deltaic sedimentary cycles. The youngest cycle displays wedge geometry with silts and clays separating two packages of sands and gravels. These geological bodies consist of three hydrogeological units: 1) Shallow Aquifer, which is an unconfined aquifer formed by sands; 2)Main Aquifer, which is made up of the deep aquifer at the Delta; and 3) Silt wedge (aquitard), which separates the shallow and deep aquifers.

The Besòs aquifers have suffered heavy water extraction since the end the 19th Century. Extraction produced large drawdowns, leading to seawater intrusion. Since the 1970s, urban pressures have caused many industries to migrate away from the city. This has resulted in a reduction of pumping and a progressive recovery of heads (Vàzquez-Suñé et al., 2005).

The river is hydraulically connected to the Shallow Aquifer at the Delta. The Besòs River's irregular flow pattern is reflected in the well hydrographs and the aquifers respond to river floods (Fig. 4.3).

Several recharge sources have been identified in the aquifers of the Besòs River Delta by Vàzquez-Suñé et al. (2010), including: (1) the Besòs River (RIV), (2) rainfall (REC), (3) the Ter River water supply (TER), (4) the Ter River sewage water (SW_T), and (5) city runoff (RUNOFF). Among these recharge sources, water from the polluted Besòs River may be considered the most important recharge source in the study area.

Groundwater generally flows from the Besòs River to the underground parking area at the Plaça de la Vila site because there is a continuous pumping of approximately 150-200 L/s to avoid seepage problems. Four drainage pumping wells and 16 piezometers were implemented to control the seepage problems in the parking area and to assess groundwater head variations in the surroundings areas (Fig. 4.2). Furthermore, this groundwater control network is periodically sampled for groundwater quality assessment. We assessed that almost all the groundwater extracted between the river and the parking drainage pumping is recharged from the river (Ondiviela et al., 2005).

4.2.5. Sampling and analysis

Water samples were collected from July 2007 to May 2010 in four different field campaigns in July 2007, February 2008, October 2008 and May 2010. Four samples from the Besòs River, considered the main recharge source of the aquifer, and 51 samples from the groundwater were collected. 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 were measured in situ including electrical conductivity (EC), 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 stabilisation 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. Each water sample underwent chemical analysis in accordance with the Spanish guidelines for drinking water (Royal Decree 140/2003). These guidelines include 53 parameters (four radioactivity parameters were not analysed).

All the samples were analysed at the ATLL (Aigües Ter Llobregat) laboratory in Barcelona. Chloride, sulphate and nitrate were analysed using ion chromatography (IC). Calcium, magnesium, iron and arsenic were analysed by ICP-MS and prior to the analysis, the solution was acidified with 1% (v/v) HNO3 and centrifuged to 3500 rpm. Ammonium was analysed by spectrophotometry (based on indophenol blue method) and using a commercial reactive kit. Bicarbonate was analysed manually by chemical evaluation with sulphuric acid, accounting for the pH of the sample. Total organic carbon (TOC) was analysed using the 680 °C combustion-infrared method with a platinum catalyst and using a Non-Dispersive Infra-Red (NDIR) detector. The amount of organic carbon can be determined by the non-purgeable organic carbon (NPOC). It is based on the removal of inorganic carbon from the sample by purging the acidified sample to a pH less than 2.0 with an inert gas. Total organic carbon (TOC) may be determined by means of TC measuring method.

Moreover, most of the above mentioned hydrochemical parameters of the Besòs River water have been measured monthly by the Catalan Water Agency (ACA, 2012) at the Santa Coloma gauging station (Fig. 4.3).

4.3. Results and discussion

4.3.1. Besòs River

4.3.1.1. Evaluation of the number of end-members and representative chemical species

Qualitative analysis

River water quality depends on many factors. In the final part of the catchment (study area), river water could be considered to be a mix of water from different sources, such as rainfall, raw sewer water, treated sewer water, waters from several parts of the catchment, etc.; furthermore, variation over time is very significant. As mentioned before, up to five different recharge sources have been identified in Besòs River Delta aquifers (RIV, REC, TER, SW_T and RUNOFF). However, previous studies have demonstrated that Besòs River is by far the largest contributor to groundwater recharge, representing the 90% (Jurado et al., 2013). Therefore, RIV has been the only recharge source that we have take into account. A more detailed discussion of the minimum number of end-members can be found in the following steps.

Multivariate analysis (EMMA) to select the end-members and species

As mentioned before, the Besòs River hydrochemistry data have been obtained from the surface water quality monitoring network of the Catalan Water Agency (ACA). The selected sampling period was from January 2005 to May 2009 and the samples have been collected on a monthly basis. The total number of species was 53, but not all of the species were analysed every time. Additionally, we collected four samples from the Besòs River during the four field groundwater campaigns in July 2007, February and October of 2008, and May 2010 (C1 to C4). In total, 56 samples from the Besòs River have been used to perform the EMMA.

The species selected in the EMMA were those with more data available in the ACA database and were mainly major species. The 11 selected species were chloride (Cl), sulphate (SO4), sodium (Na), bicarbonate (HCO3), calcium (Ca), magnesium (Mg), potassium (K), nitrate (NO3), ammonium (NH4), total nitrogen (Ntot) and electrical conductivity (EC).

River sample eigenvector evaluation was performed with the EMMA accounting for the aforementioned 11 species. Because we have selected 11 species in this analysis, an eigenvector must explain more than 9.1% (1/11) of the data variance using the rule of one. According to that rule, 3 eigenvectors should be retained and they explained the 90% of the total variance. Five different analyses were performed (Fig. 4.4).

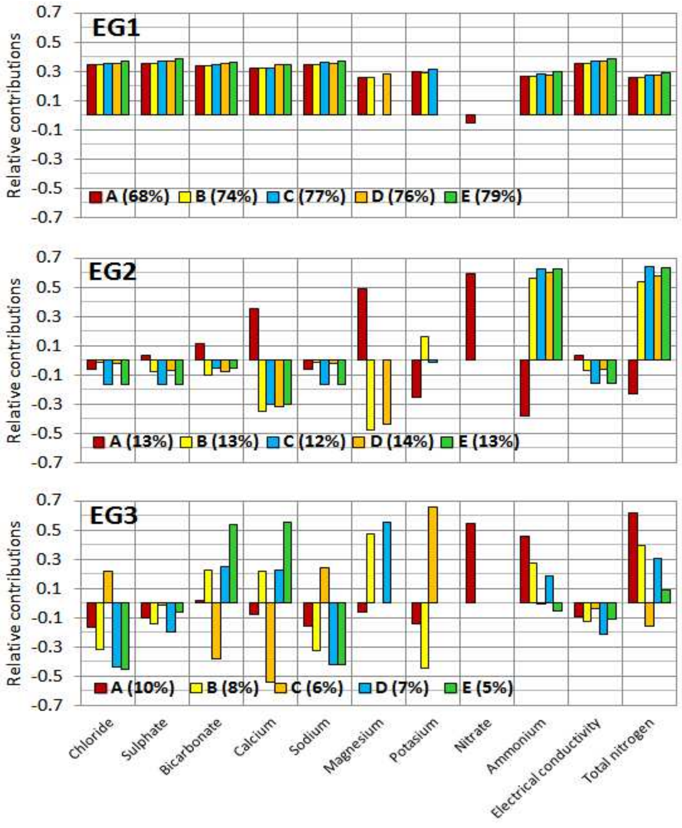


Figure 4-4 Eigenvectors 1, 2 and 3 resulting from processing the Besòs River data with EMMA. The analysis "A" includes the species chloride, sulphate, bicarbonate, calcium, sodium, magnesium, potassium, nitrate, ammonium, total nitrogen and electrical conductivity. The analysis "B" is equal to "A" but without nitrate; "C" is equal to "A" but without nitrate and magnesium; "D" is equal to "A" but without nitrate and potassium and "E" is equal to "A" but without nitrate, magnesium and potassium.

Analysis A

The first eigenvector explained 68% of the variance (Fig. 4.4, EG1 from analysis A). All the species except nitrate contribute significantly to that. The species that contributed most (relative weights ranging from 0.39 to 0.26) were, in descending order: EC, SO4, Na, Cl, HCO3, Ca, K, Mg, NH4, and Ntot. In contrast NO3, contributed less and with the opposite sign (−0.05). This first eigenvector was associated with two types of water from the River Besòs: (1) diluted water that corresponds to wet periods or water supply inputs and (2) concentrated waters related to dry periods. Nitrate concentration cannot be explained with these two end-members.

The second eigenvector additionally explained 13% of the total variance, which added to the total explained variance of 81%. The largest contribution was provided by NO3 (0.59), followed by Mg (0.49), NH4 (−0.38), Ca (0.36), K (−0.25) and Ntot (−0.23). It is important to mention that the species that contributed less to the second eigenvector (weights less than abs (0.1)) were the ones that contributed most to the first eigenvector.

The third eigenvector accounted for 10 % of the variance and was related to the concentrations of nitrogen species (weights were Ntot (0.62), NO3 (0.55), and NH4 (0.46)). The remaining species contributed with weights lower than 0.17.

Analysis B

When NO3 was not included in the EMMA (Fig. 4.4, analysis B), a total variance of 87 % was obtained with two eigenvectors. The first eigenvector corresponded to more or less diluted water and represented an increase from 68 % to 74 % of the total variance. The second eigenvector additionally explained 13 % of the total variance and was related to nitrogen species (weights of 0.56 for NH4 and 0.53 for Ntot). Mg and Ca species also contributed significantly but with the opposite sign (−0.48 and −0.35, respectively). As in the previous analysis, the remaining species contributed with weights lower than 0.17 The third eigenvector explained a variance lower than 10 % (100 % /10). The species that contributed most to this eigenvector were Mg (0.48) and K (−0.45) but with the opposite sign.

Analyses C, D and E

When NO3 and Mg (Fig. 4.4, analysis C), NO3 and K (Fig. 4.4, analysis D) NO3, Mg and K (Fig. 4.4, analysis E) were not included in the EMMA; the results were similar to the previous analysis B. The first two eigenvectors explained more than 85 % of the variance of the data in the three analyses. The first eigenvector distinguished between river water obtained during wet and dry periods, whilst the second eigenvector was related to the nitrogen concentrations (mainly ammonium concentration). Consequently, based on the results obtained, we decided to not explain the nitrate concentrations. The conceptual model to explain the 87 % of river composition corresponds to three end-members (n + 1 eigenvector): EM1 was an extreme low concentration associated to rainfall periods, EM2 and EM3 were more concentrated ends, distinguished mainly by high ammonium and low calcium and magnesium. The selection of the end members was performed by plotting the eigenvectors (Fig. 4.5).

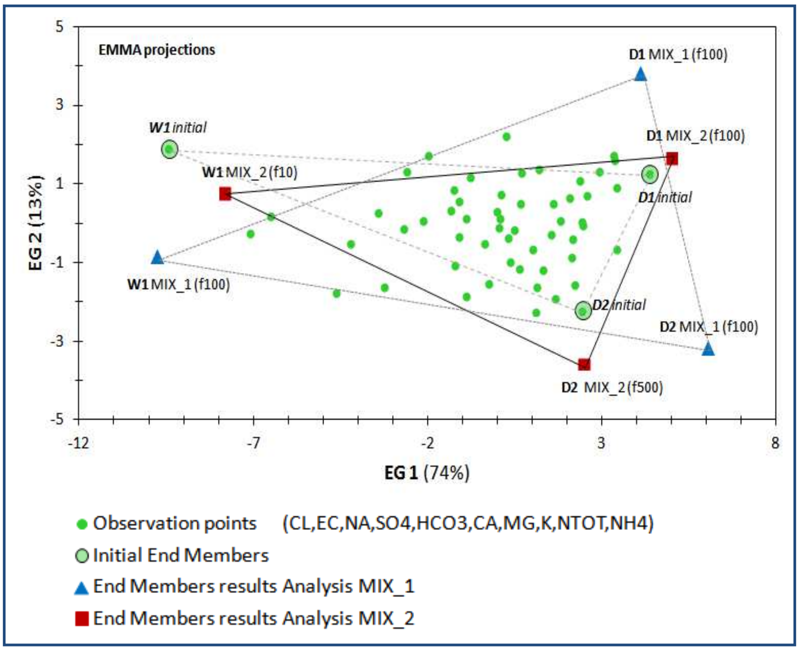


Figure 4-5 Projection of the eigenvectors 1 and 2 for the analysis “B”. Note that the resulting end-members in mixing calculations (MIX_1 and MIX_2, Table 4.1) evaluated with EMMA are also projected. The difference between the analysis and MIX_1 and MIX_2 is the variances assigned to the end-members. In the analysis MIX_1 the variances assigned to each species for the end-members are multiplied by a factor of 100, whereas in analysis MIX_2 they are multiplied by factors of 10, 500 and 100, respectively, for the End-MembersW1, D1 and D2.

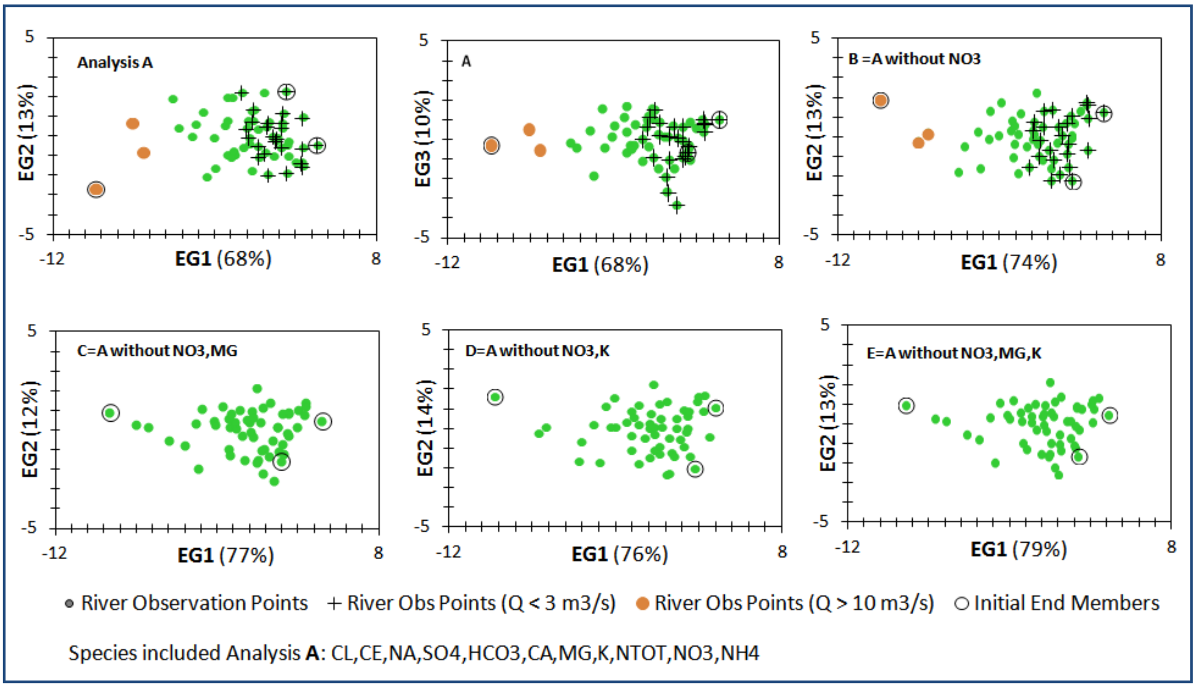


Figure 4-6 Projection of the eigenvectors 1, 2 and 3 for the analysis “A” to “E” (Fig. 4.4) resulting from processing the Besòs River data with EMMA.

4.3.1.2. Evaluation of end-members composition

In the projections (Fig. 4.6), the X axis in all cases corresponds to the first eigenvector, which ranged from approximately −10 (diluted river end-member) to +5 (concentrated river end-member). The amplitude of the Y axis with respect to X axis is less than half. Except for analysis A, the Y axis represents an eigenvector that explains the concentrations of NH4 and Ntot. In all the projections, the majority of the river water points lie in the interior of a triangle that described the mixture between 3 end-members.

The mixing analysis was performed with the end-members that resulted from the projection of the analysis B (Fig. 4.5). These river end-members corresponded to the river samples from days 29/10/2008 (W1, diluted end-member), 06/07/2005 and 23/07/2007 (D1 and D2, respectively, concentrated end-members).

4.3.1.3. Computation of river water mixing ratios and end-member composition re-evaluation

MIX analysis has allowed us to computing mixing ratios and the composition of the end-members. River water concentrations may fluctuate significantly, so that the average concentration may not be representative of river recharge to the aquifer. Evaluating the recharge coming from the different sources in river waters has been necessary. First, overall recharge may be best evaluated if the relative importance of each source is known. Second, pollution risk and geochemical processes depend on the chemical and biological signatures of the different recharged river waters.

To compute mixing ratios, we have used the same Besòs River hydrochemical data from the ACA as was used in the EMMA.

As explained before, the end-members selected from the EMMA were the river samples from days 29/10/2008 (W1, diluted end member), 06/07/2005 and 23/07/2007 (D1 and D2, respectively, concentrated end-members), Table 4.1. By assignment of standard deviation, a weight has been assigned to each end-member depending on their consistency during EMMA process. The eigenvector projections allow us to estimate the range of variance that covers the proportion that may be assigned to an unrecognised end-member or to a non-mixing process. For instance, we decided not to explain the nitrate concentrations because they can be affected by other processes apart from simple mixing. Therefore, the standard deviations of less conservative tracers in the observation points have been relatively high in order to obtain the theoretical composition but this does not affect the results.

Table 4-1 Results evaluated using MIX for River Besòs data (MIX_1 and MIX_2). The difference between the analysis and MIX_1 and MIX_2 are the variances assigned to the end-members. Fig. 4.5 shows the eigenvector projection evaluated by EMMA and the resulting end-members for both analysis. Initially, mixing calculations MIX_1 and MIX_2 were carried out using the species chloride, electrical conductivity, sodium, sulphate, bicarbonate, calcium, magnesium, potassium, total nitrogen, ammonium and nitrate. Once established that the computation satisfies the conceptual model (MIX_2); phosphorus, phosphate, fluoride, total organic carbon, arsenic, bromide, boron, dissolved oxygen and iron were added. The variances assigned to these species in the observation points were: (1) a factor of 10 when data are available and (1) a factor of 100 when there were no data that have been applied a factor of 100. The variances of the end-members for the species added were sufficiently large (factor of 1000) to not influence the evaluated results. “Ri: Average concentration in Besòs River observation points”.

	Inicial concentrations			**Applied standar deviation**					**End member results**					
Analysis	MIX_1 & MIX_2	MIX_1 & MIX_2	MIX_1 & MIX_2	MIX_1 & MIX_2	MIX_1	MIX_2	MIX_2	MIX_2	MIX_1	MIX_1	MIX_1	MIX_2	MIX_2	MIX_2
	EM1: W1	EM2:D1	EM3:D2	Observation points	EM: W1,D1 & D2	EM1:W1	EM2:D1	EM3:D2	EM1:W1	EM2:D1	EM3:D2	EM1:W1	EM2:D1	EM3:D2
Chloride	70.5	377.4	306.5	0.05·Ri	100·Ri	10·Ri	100·Ri	500·Ri	9.1	441.4	280.2	43.7	356.2	315.8
Electrical conductivity	439.0	1995.0	1782.0	0.07·Ri	100·Ri	10·Ri	100·Ri	500·Ri	431.6	2342.3	1750.5	585.6	1996.5	1891.5
Sodium	50.7	297.9	251.8	0.07·Ri	100·Ri	10·Ri	100·Ri	500·Ri	0.5	347.5	220.8	29.0	280.9	246.6
Sulphate	40.0	195.0	183.1	0.07·Ri	100·Ri	10·Ri	100·Ri	500·Ri	36.9	245.0	180.1	52.8	205.9	198.6
Bicarbonate	124.8	448.7	441.3	0.10·Ri	100·Ri	10·Ri	100·Ri	500·Ri	182.3	518.3	503.5	222.7	500.5	470.3
Calcium	36.1	128.9	148.1	0.07·Ri	100·Ri	10·Ri	100·Ri	500·Ri	59.1	163.6	123.0	62.2	133.9	151.3
Magnesium	5.2	22.7	30.4	0.24·Ri	100·Ri	10·Ri	100·Ri	500·Ri	13.4	30.2	23.1	13.2	24.2	30.1
Potasium	9.9	54.4	26.9	0.30·Ri	100·Ri	10·Ri	100·Ri	500·Ri	-0.4	54.1	44.7	7.2	51.1	36.4
Total nitrogen	2.9	23.4	13.0	0.15·Ri	100·Ri	10·Ri	100·Ri	500·Ri	-2.2	8.8	35.4	6.2	26.1	5.7
Nitrate	5.9	18.8	15.4	100·Ri	100·Ri	10·Ri	100·Ri	500·Ri	14.9	7.1	10.6	13.4	7.4	13.2
Ammonium	2.0	24.6	12.3	0.15·Ri	100·Ri	10·Ri	100·Ri	500·Ri	-7.1	9.3	42.4	4.1	31.5	3.6
Phosphorus	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	-0.034	2.305	2.012
Phosphate	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	1.904	3.818	3.177
Fluoride	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	0.187	1.244	0.374
Total organic carbon	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	6.3	12.4	8.7
Arsenic	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	0.003	0.006	0.008
Bromide	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	0.059	0.57	0.854
Boron	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	0.034	0.218	0.292
Dissolved oxygen	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	8.7	8.3	10.6
Iron	-	-	-	10·Ri or 100·Ri	-	1000·Ri	1000·Ri	1000·Ri	-	-	-	0.036	0.209	0.232

The end-member W1 was found to be more consistent whereas D2 was less consistent (Fig. 4.5). The concentrations of each river end member accounting for these species are shown in Table 4.1. Some of the analysed species appear to be non-conservative. For example, nitrogen species and measured potassium concentrations in the water coming from samples were different compared to those in end-members. This suggests that these species, coming mainly from the sewage system, might be affected by redox processes, adsorbed or degraded in the river, which is indeed the case for most water-borne organic pollutants. To address this uncertainty, mixing ratios were computed considering these “less” conservative species. In these cases, the standard deviations assigned were higher than the most conservative species (Table 4.1). The standard deviations were assigned taking into account the following: (1) sampling error, (2) analytical error, (3) others (i.e., mixing proportion that may represent non-included end-members, non-conservatives processes or incomplete data sets). Because the evaluation of the river end-member concentrations was performed using the concentration in the observation points, the standard deviations in the river end-members should be higher than those assigned to the observation points. The standard deviation of the river samples and the end-member accounting for the 11 species is shown in Table 4.1.

The concentrations of other less conservative species, such as fluoride (F), bromide (Br), boron (B), dissolved oxygen (O2), total organic carbon (TOC), phosphate (PO4), phosphorous (P), iron (Fe), and arsenic (As), have also been evaluated in this analysis for the 3 river end-members. However, a complete data register is not available for the afore mentioned species. Consequently, their expected concentrations have been evaluated considering: (1) the end-member concentrations computed in the previous Section 3.1.2 and (2) the river samples available for these species on specific days. The standard deviations assigned to these species (Table 4.1) were chosen to modify as little as possible the river end-member concentration previously evaluated and also bearing in mind that the concentrations of the less conservative species do not dramatically change the previous results. Notably, the standard deviations assigned to these new species in the river samples have been slightly lower when data are available. The results of this run are shown in Fig. 4.7 and Table 4.1.

The three river end-members retained have the following characteristics: End-Member W1: River water that presented the lowest concentration of all species excepting nitrogen species concentrations. Nitrogen species are similar to End-Member D2, with low concentrations for ammonium and total nitrogen, and the highest concentration is for nitrate among the three end-members. This end-member was attributed to wet periods, in which most of the river flow corresponds to rainwater and where nitrogen is in the nitrate form. Species of End-Member W1 with estimated concentrations greater than measured are magnesium, calcium, bicarbonate and nitrate (Fig. 4.7). This may indicate that some dissolution of carbonates and oxidation of nitrogen species occur in the river apart from simple mixing in wet periods. End-Member D1: River water that generally 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 may be attributed to water coming from dry periods. End-Member D2: This 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.

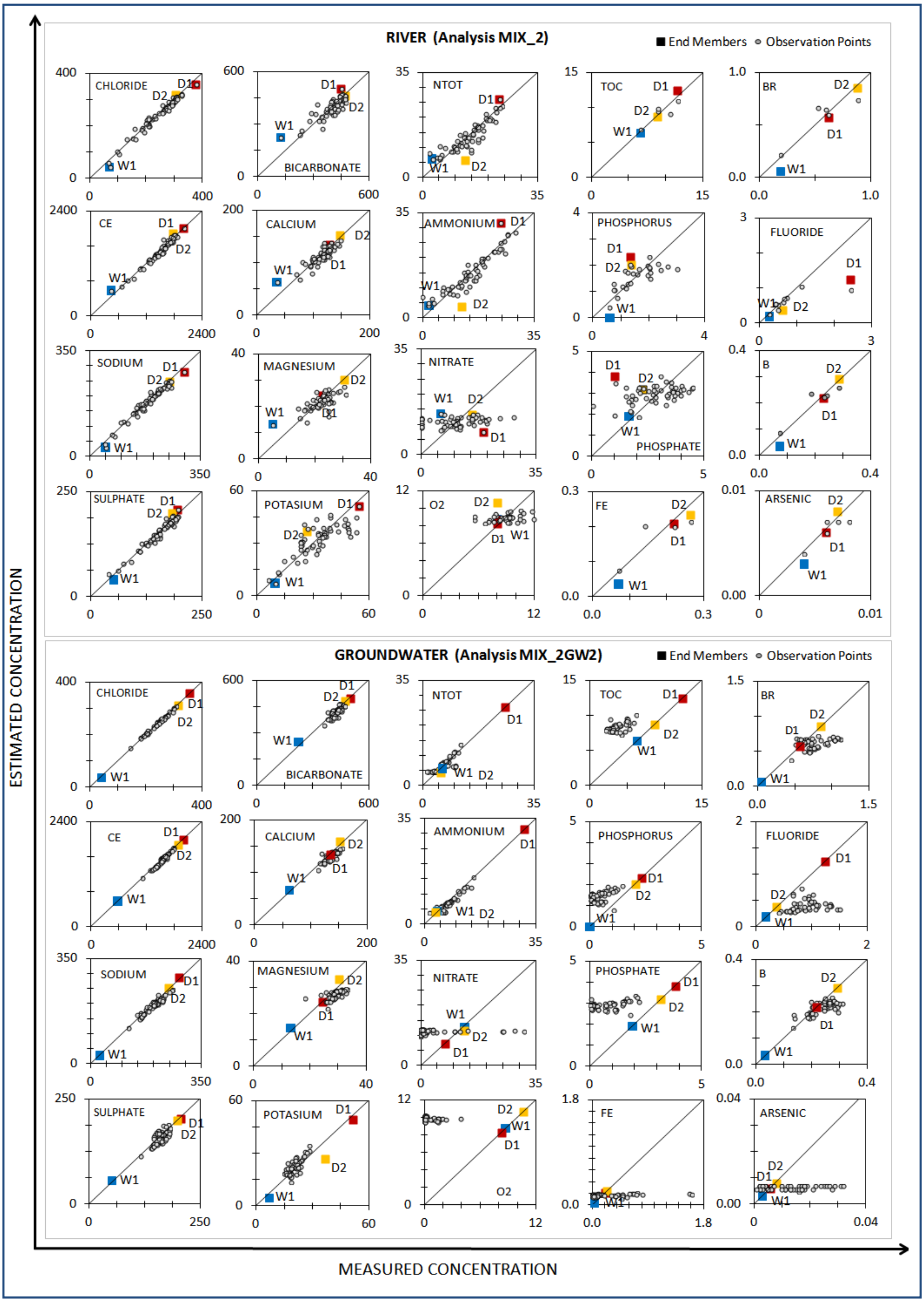


Figure 4-7 Measured concentrations versus estimated concentrations in the Besòs River (upper plots) and in groundwater (lower plots). Data and the assigned variances can be seen in Table 4.1 (MIX_2 analysis) to the river and in Table 4.2 (analysis MIX_2GW2) for groundwater.

4.3.2. Groundwater

4.3.2.1. Evaluation of the number of end-members and representative chemical species

Qualitative analysis

We have identified up to five different potential recharge sources for groundwater in the whole of Barcelona (Vàzquez-Suñé et al., 2010). De Buen (2009) assessed that up to 95 % the groundwater between the river and the parking drainage pumping is recharged from the Besòs River.

Multivariate analysis (EMMA) to select the end-members and species

Fifty-one groundwater samples were collected from July 2007 to May 2010 during four different field campaigns in July 2007, February 2008, October 2008 and May 2010. The species analysed included major and minor ions, heavy metals, pesticides and polycyclic aromatic hydrocarbons, among other. Out of 122 species analysed in groundwater samples, the following 19 have been used to compute groundwater EMMA: chloride (Cl), sulphate (SO4), sodium (Na), bicarbonate (HCO3), calcium (Ca), magnesium (Mg), potassium (K), ammonium(NH4), total nitrogen (Ntot), electrical conductivity (EC), fluoride (F), bromide (Br), boron (B), dissolved oxygen (O2), total organic carbon (TOC), phosphate (PO4), phosphorous (P), iron (Fe), and arsenic (As).

The first step was performance of the EMMA. The EMMA aims to identify the minimum number of end-members required. As we have selected 19 species in this analysis, an eigenvector must explain more than 5 % (1/19) of the data variance using the rule of one.

The groundwater eigenvectors in an analogous analysis from the river were similar, resulting in two eigenvectors (analysis B Groundwater, Fig. 4.8). In the analysis B groundwater, the first eigenvector, in which all species made significant contributions in the same direction, the weights ranged from 0.18 to 0.40. The second eigenvector made an important contribution of total nitrogen, ammonium and potassium as well as of magnesium, sulphate and calcium but with opposite sign. The species chloride, bicarbonate, sodium and electrical conductivity contributed less. When considering only ten species (analysis B), two eigenvectors (contribution clearly N5) were necessary, resulting in 3 end-members that explained 79% of the total variance (Fig. 4.8). When considering the 19 species (analysis F groundwater, Fig. 4.8) three eigenvectors were necessary (contribution clearly N5), resulting in four end members that explained 73% of the total variance. As in the river, the first eigenvector (Fig. 4.8) allowed us to distinguish between concentrated and diluted river waters. All the species, except bromide, made significant contributions with a positive sign. Only dissolved oxygen contributed with an opposite sign. The highest weights were for chloride, EC and sodium. Relative weights in the second eigenvector were significantly different. In that case, the largest contributions were not nitrogen species, but sulphate in the opposite sign, followed by boron, fluoride and bromide; in the other sign, these were phosphate, phosphorous and arsenic. Fig. 4.9 shows the eigenvector projection for the analysis groundwater resulting from processing groundwater data with EMMA.

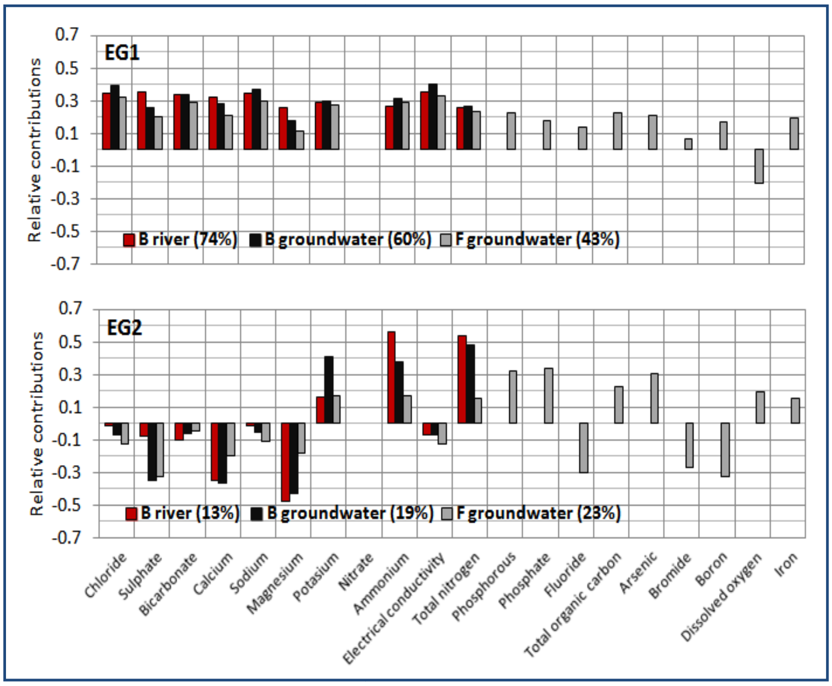


Figure 4-8 Eigenvectors 1 and 2 and resulting from processing both River Besòs (analysis "B river", Fig. 4.4) and the groundwater data (analysis "B groundwater" and "F groundwater") with EMMA. Note that the analyses "B" include the following species: chloride, sulphate, bicarbonate, calcium, sodium, magnesium, potassium, ammonium, total nitrogen and electrical conductivity. The analysis "F" includes the species phosphorous, phosphate, fluoride, total organic carbon, arsenic, boron, bromide dissolved oxygen and iron.

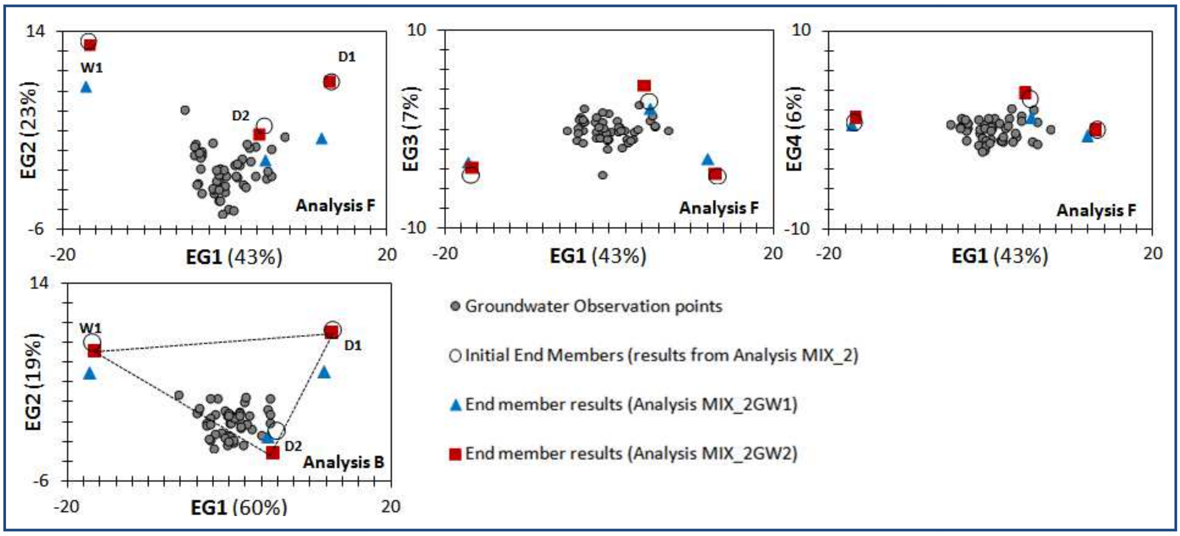


Figure 4-9 Projection of the eigenvectors for the analysis "B" and "F" (Fig. 4.4) resulting from processing groundwater data with EMMA.

4.3.2.1. Evaluation of end-members composition

The mixing analysis was performed with the end-members that resulted from the projection of the Analysis "MIX_2" from the river (Table 4.2). We have noted that the aquifer is mainly recharged by the river. Consequently, the three end-members retained in the EMMA of the river water have been used (W1, D1 and D2). It was necessary to assess whether groundwater concentrations can be explained by mixing processes of these end members and to quantify their proportions. The computed composition of the river recharged water for the 20 species is shown in Table 4.2 (Analysis "MIX_GW2"). Groundwater mixing ratio evaluation has been performed; therefore, it was intended that the concentrations of the observation points of groundwater would not change the previous adjustment determined in the river. Therefore, the standard deviations assigned to the observation points (Table 4.2) were higher than those assigned to the end-members. Moreover, the standard deviations at the groundwater observation points were selected depending on whether species were more or less conservative.

Table 4-2 Results evaluated using MIX for groundwater data (MIX_1GW1 andMIX_2GW2). Note that the river end-members were those evaluated in the analysisMIX_2, and the variances assigned to the river end-members are lower than those assigned to the observation points because we assumed that the aquifer is mainly recharged by the Besòs River. "Ri: Average concentration in Besòs River observation points" and "Gi: Average concentration at Groundwater observation points".

Analysis MIX_2GW2	**Inicial Concentrations**			**Applied standar deviation**			**End member results**		
	EM1:W1	EM2:D1	EM3:D2	Obs. points (expresed f(Ri))	Obs. points (expresed f(Gi))	EM: W1,D1 & D2	EM1:W1	EM2:D1	EM3:D2
Chloride (mg/L)	43.7	356.2	315.8	0.05·Ri	0.05·Gi	0.04·Ri	36.4	358.3	312.0
Electrical Conductivity (µS/cm)	585.6	1996.5	1891.5	0.07·Ri	0.07·Gi	0.03·Ri	586.4	1991.0	1867.8
Sodium (mg/L)	29.0	280.9	246.6	0.07·Ri	0.07·Gi	0.05·Ri	27.2	286.3	251.6
Sulphate (mg/L)	52.8	205.9	198.6	0.12·Ri	0.11·Gi	0.04·Ri	55.5	201.8	198.1
Bicarbonate (mg/L)	222.7	500.5	470.3	0.11·Ri	0.10·Gi	0.07·Ri	247.8	496.6	481.0
Calcium (mg/L)	62.2	133.9	151.3	0.19·Ri	0.16·Gi	0.06·Ri	65.9	134.0	158.4
Magnesium (mg/L)	13.2	24.2	30.1	0.37·Ri	0.28·Gi	0.10·Ri	14.5	24.5	33.0
Potasium (mg/L)	7.2	51.1	36.4	0.50·Ri	0.79·Gi	0.17·Ri	4.6	49.2	26.6
Total nitrogen (mg/L)	6.2	26.1	5.7	0.43·Ri	1·Gi	0.12·Ri	5.7	25.9	4.3
Nitrate (mg/L)	13.4	7.4	13.2	5.54·Ri	15·Gi	0.47·Ri	12.7	7.1	11.5
Ammonium (mg/L)	4.1	31.5	3.6	0.40·Ri	0.90·Gi	0.12·Ri	4.2	31.6	4.0
Phosphorus (mg/L)	0.000	2.305	2.012	7328·Ri	27756·Gi	0.48·Ri	0.000	2.305	2.012
Phosphate (mg/L)	1.904	3.818	3.177	29758·Ri	125434·Gi	0.70·Ri	1.904	3.818	3.177
Fluoride (mg/L)	0.187	1.244	0.374	14193·Ri	11342·Gi	0.57·Ri	0.187	1.244	0.374
Total organic carbon (mg/L)	6.323	12.427	8.663	3283·Ri	8652·Gi	0.21·Ri	6.323	12.427	8.663
Arsenic (mg/L)	0.003	0.006	0.008	4085·Ri	1970·Gi	0.31·Ri	0.003	0.006	0.008
Bromide (mg/L)	0.059	0.57	0.854	5729·Ri	4304·Gi	0.43·Ri	0.059	0.570	0.854
Boron (mg/L)	0.034	0.218	0.292	5466·Ri	4631·Gi	0.38·Ri	0.034	0.218	0.292
Dissolved oxygen (mg/L)	8.736	8.267	10.601	3998·Ri	59779·Gi	0.26·Ri	8.736	8.267	10.601
Iron (mg/L)	0.036	0.209	0.232	5788·Ri	3751·Gi	0.35·Ri	0.036	0.209	0.232

4.3.2.2. Compute groundwater mixing ratios

Among the three end-members considered, D2 was by far the largest contributor to the total recharge, representing the 65 %, followed by the wet river end-member (W1, 26 %). The remaining 9 % corresponded to D1. The contribution of W1 was more significant during the last field campaign (C4) because of the frequent rain events (Fig. 4.3), being the 41 % of the total recharge. Accounting for the other 3 campaigns, W1 represented, on average, only the 20 % of the total recharge. On average, the dry river end-members (D1 and D2) contributed more significantly to the total recharge than the wet end-member (W1), representing the percentages of 74 % and 26 %, respectively. These results are consistent with the rainfall events that occurred in the Besòs River Delta, which controlled the Besòs River flow dynamics. The wet end-member is related to short but intense rainfall events whilst the dry end-members are related to the null or low levels of rainfall that occur the rest of the year. This is especially dramatic in summer where River Besòs flow

4.3.3. Identification of hydro chemical processes in groundwater

The presented methodology could be useful to identify some hydrogeochemical processes. When comparing the average concentrations at the Besòs River with the average concentration in the aquifer for several species as major and minor components, metals, polycyclic aromatic hydrocarbons (PAHs), pesticides and surfactants, it can observed that the concentration of a number of the species is higher in the river than in the aquifer (Fig. 4.1). As an example, oxidation and reduction processes might be deduced from Fig. 4.1, where ammonium, nitrate and dissolved oxygen have lower concentrations in the aquifer. As shown in Fig. 4.7, some species did not behave conservatively because they diverged away from the ideal mixing line. These deviations could be attributed to hydrogeochemical processes that take place in the river aquifer system. On the one hand, estimated concentrations of tracers such as magnesium and, to a lesser extent, calcium have generally mainly comes from wastewater treatment plant effluents, which is represented by the river end-member D1. been lower than measured ones (Fig. 4.7). This fact might be indicative that some dissolution processes of carbonates can occur in the aquifer apart from simple mixing of river water. It is also estimated that groundwater has an excess of bromide, fluoride, arsenic, iron, and boron to a lesser extent than the theoretical mix of the river. On the other hand, potassium, dissolved oxygen, TOC, phosphates, phosphorous and nitrate presented higher estimated concentrations than measured ones. Consequently, hydrogeochemical processes might be depleting the aforementioned species from the aquifer. Dissolved oxygen, nitrate and TOC may undergo redox processes whilst potassium may be exchanged with other cations such as calcium or magnesium.

4.4. Conclusions

We have presented a methodology for assessing mixing ratios and identifying hydrochemical reactions in groundwater. In this approach, we use EMMA and MIX analysis jointly. The methodology is applied to the assessment of river recharge waters in the Besòs Delta aquifers in Barcelona, Spain. The application of this methodology in the case of study has allowed us to: identify the minimum number of the river end-members required to explain the variability of measured concentrations. Three end-members were finally selected: 2 corresponding to dry season (D1 and D2) and one from the wet season (W1).

The identification of end-members was used not only to evaluate the river recharge into the aquifer but also to compute the expected concentration of some species, such as phosphates, fluoride, boron, TOC and bromide.

River water mixing was the most representative recharge source into the aquifer. Overall, dry season end-members dominated over wet season end-member, in a proportion 4:1.

Some species did not properly fit the mixing line. This suggests the identification of some geochemical processes that may occur in the river-aquifer system such as redox processes, dissolution processes and ion exchange processes.

5. Conclusions

This chapter includes a summary of the main contributions of this thesis. The major findings respond to the overall aim of gaining a better understanding of the nature of groundwater in urban areas. This includes assessing the volume and quality of aquifer recharge as well as differentiating within the groundwater composition between concentrations of compounds from sources of recharge, and concentrations variations due to hydrochemical processes.

First, a methodology has been presented to help estimate the areal recharge in urban aquifers. It is based on calibrating a large scale model using appropriately parameterized areal recharge functions. These functions are considered percentages of water susceptible to recharging the aquifers. Waters are classified according to their chemical properties, potential ways to enter the ground, and origin. This approach allows groundwater management to be included in the management of other water cycle functions in the city.

A transient groundwater flow and solute transport model of the Barcelona urban aquifers was built as a tool to help in defining the management program. This application has shown the importance of recharge evolution on the aquifers mass balance.

Regarding possible introduction of substances or pollutants from potential sources of recharge, a campaign to collect groundwater samples throughout the study area has been conducted. Among other compounds, substances used in the formulation of industrial products and common domestic products were analyzed.

For one, ionic surfactants linear alkylbenzene sulfonate (LAS) have been analyzed. LAS and their degradation products (sulfophenyl carboxylates, SPC) are not regarded as priority substances although they are today the most common domestic surfactant in the area. LAS concentrations were detected more than one order of magnitude lower than expected based on recharge sources and in comparison with other substances such as nitrate, ammonium perchlorethene or trichlorethene, in all (oxidizing and reducing) aquifers, which suggests degradation of these substances under different redox conditions..

Secondly, nonionic surfactant extensively used by industry (and in the past also in household products) has been analyzed. Specifically, alkylphenol polyethoxylates (APEOs) and their degradation products (DPs) nonylphenol polyethoxylates (NP2EC, NP1EC), octylphenol polyethoxylates (OP2EC, OP1EC), nonylphenol (NP) and octylphenol (OP). The toxicity of APEOs is increased with decreasing ethoxylate chain length. NP and OP (their shortest chain) are considered hazardous substances.

The highest groundwater concentrations of APEOs and DPs were detected in aquifers whose major source of recharge is a river receiving large amounts of effluents from secondary waste water treatment plants (WWTPs). In fact, APEOs DPs concentrations were above those in the river. NP2EC was the compound detected at highest concentrations. These increase with ammonium in samples with low dissolved oxygen. These degradation products were virtually absent in oxidizing aquifers whose main source of recharge is not the river. In this case, only the ultimate degradation product (NP) was detected, which suggests that parent compounds have degraded.

A methodology to compute mixing ratios and to identify hydrochemical reactions in groundwater has also been presented. It is based on using an end-member mixing analysis (EMMA) and MIX. This approach has been applied in a Besòs River Delta pilot area.

Performed in the Besòs River the results showed that 3 end-members are required to explain its temporal variability, accounting for the selected species. Under the assumption that groundwater is a mix of river water, the results indicate that redox processes, carbonate dissolution/precipitation and ion exchange processes may occur in Besòs Delta aquifer. Also relative excesses and defaults of certain compounds have been quantified in groundwater (e.g. bromide, fluoride, boron, arsenic, and TOC, phosphorous, phosphate, respectively).

Other scientific papers published by international journals related to this thesis are:

- Vàzquez-Suñé E., Carrera J., Tubau I., Sánchez-Vila X., Soler A., 2010. An approach to identify urban groundwater recharge. Hydrology and Earth System Sciences 14 (2010) 2085-2097.

  http://dx.doi.org/10.5194/hess-14-2085-2010
- Velasco V., Cabello P., Vàzquez-Suñé E., López-Blanco M., Ramos E., Tubau I., 2012. A stratigraphic sequence based geological model for constraining hydrogeological modeling in the urbanized area of the Quaternary Besòs Delta (NW Mediterranean Coast, Spain). Geol Acta 2012;10(4):373–93. http://dx.doi.org/10.1344/105.000001757
- 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 (2013) 114-125.

  http://dx.doi.org/10.1016/j.apgeochem.2013.02.018
- Velasco V., Tubau, I., Vàzquez-Suñé E., Gogu R. Gaitanaru D.. Alcaraz M., Serrano-Juan A., Fernández-García D., Garrido, T., Fraile, J., Sánchez-Vila, X., 2014. GIS-based hydrogeochemical analysis tools(QUIMET). Computer & Geosciencies 70 (2014) 164-180.
- Jurado, A., Vázquez-Suñé, E., Carrera, J., Tubau, I, and Pujades, E. 2015. Quantifying chemical reactions by using mixing analysis. Science of the Total Environment 502 (2015) 448–456.
  http://dx.doi.org/10.1016/j.scitotenv.2014.09.036

The abstracts of these papers are attached at the end of this document, as well as papers in the chapters on which this thesis is based:

- Tubau I., Vázquez-Suñé E., Carrera J., González S., Petrovic M., López de Alda M.J., Barceló D., 2010. Occurrence and fate of alkylphenol polyethoxylate degradation products and linear alkylbenzene sulfonate surfactants in urban ground water: Barcelona case study. Journal of Hydrology 383 (2010) 102-110.
- Tubau I., Vázquez-Suñé E., Jurado A., Carrera J., 2014. Using EMMA and MIX analysis to asses mixing ratios and to identify hydrochemical reactions in groundwater. Science of The Total Environment 470-471 (2014) 1120-1131.
- *Tubau I, Vázquez-Suñé E, Carrera J, Valhondo, C. Quantification of Groundwater Recharge in Urban Environments. Science of the Total Environment (submitted).*

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Ahel M., Giger W., Schaffner C., **1994b**. Behaviour of alkykphenol polyethoxylate surfactants in the aquatic environment-II. Occurrence and transformation in rivers. Water Research 28 (5), 1143-1152.

Ahel M., Giger W., Schaffner C., **1996**. Behaviour of alkykphenol polyethoxylate surfactants in the aquatic environment-III. Occurrence and elimination of their persistent metabolites during infiltration of river water to ground water. Water Research 30 (1), 37–46.

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Annex: Abstracts of papers related to the development of this thesis

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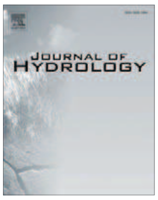

Occurrence and fate of alkylphenol polyethoxylate degradation products and linear alkylbenzene sulfonate surfactants in urban ground water: Barcelona case study

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SUMMARY

This study investigates the fate of alkylphenol polyethoxylates (APEOs) degradation products (DPs) and the occurrence of linear alkylbenzene sulfonate (LAS) surfactants in urban ground water at field scale. The occurrence of APEOs DPs in ground water was studied in connection with: (1) sources of recharge or/and pollution containing these substances, (2) ground water redox conditions, (3) occurrence of LAS, which are currently the domestic surfactants more used in the study area and (4) other common contaminants in urban ground water in the city of Barcelona. The APEOs DPs analyzed included two nonylphenol carboxylates (NP2EC, NP1EC), two octylphenol carboxylates (OP2EC, OP1EC), nonylphenol (NP) and octylphenol (OP). The highest groundwater concentrations of APEOs DPs were detected in aquifers whose major source of recharge is a river receiving large amounts of effluents from secondary waste water treatment plants (WWTPs). In fact, APEOs DPs concentrations were above those in the river. NP2EC was the compound detected at highest concentrations. These increase with ammonium in samples with low dissolved oxygen. These degradation products were virtually absent in oxidizing aquifers whose main source of recharge is not the river. In this case, only the ultimate degradation product (NP) was detected, which suggests that parent compounds have degraded. These results indicate that APEOs are persistent or less degraded in reducing conditions, whereas they are degraded when oxidizing conditions prevail. By contrast, LAS concentrations were more than one order of magnitude lower than expected based on recharge sources in all (oxidizing and reducing) aquifers.

Introduction

High population growth increases the demand for water and the generation of wastewater. Ground water is an important resource of water supply in the world and aquifers in urban zones are vulnerable to contamination by a variety of contaminants due to urban activities. Approximately 90% of the water for supply comes from imported surface water in the city of Barcelona, which is the study area. Since supply sources are subject to periodic droughts, the Catalan Water Agency (ACA) is seeking alternative water resources. There are a number of aquifers with varying lithologies and ages below the city (Váquez-Suñé et al., 2005). Therefore, ground water must be considered as an option. The question is whether urban ground water can be used safely.

Urban aquifers may suffer pollution from different sources, including losses from water supply networks, leakage from sewers, seepage from rivers or other surface water bodies, seawater intrusion, etc. As a result, a large number and variety of contaminants may be found in urban aquifers (Howard et al., 1996; Barrett et al., 1999; Lerner, 2002; Morris et al., 2005; Váquez-Suñé et al., 2000; Wakida and Lerner, 2005; Naik et al., 2008). Some of these contaminants are subject to environmental quality standards (EQS) in drinking water (Council of the European Union, 1998), groundwater (European Parliament and Council of the European Union, 2006), and/or surface water (European Parliament and Council of the European Union, 2008). Other wastewater substances, also known as emerging contaminants, whose toxicity, occurrence and persistence are less well known, are subject to review for possible identification as priority substances or priority hazardous substances (European Parliament and Council of the European Union, 2008).

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Using EMMA and MIX analysis to assess mixing ratios and to identify hydrochemical reactions in groundwater

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HIGHLIGHTS

- Approach using EMMA and MIX to asses mixing ratios in groundwater.
- Polluted river recharge in urban aquifers.
- Three end-members are retained to explain temporal variability of river water.
- Departures from mixing lines might represent the occurrence of processes.

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ABSTRACT

This study presents a methodology using an end-member mixing analysis (EMMA) and MIX to compute mixing ratios and to identify hydrochemical reactions in groundwater. The methodology consists of (1) identifying the potential sources of recharge, (2) characterising recharge sources and mixed water samples using hydrogeochemistry, (3) selecting chemical species to be used in the analysis and (4) calculating mixing ratios and identification of hydrochemical reactions in groundwater. This approach has been applied in the Besòs River Delta area, where we have collected 51 groundwater samples and a long data register of the hydrogeochemistry of the Besòs River created by the Catalan Water Agency is also available. The EMMA performed in the Besòs River suggests that 3 end-members are required to explain its temporal variability, accounting for the species chloride, sulphate, sodium, bicarbonate, calcium, magnesium, potassium, ammonium, total nitrogen, and electrical conductivity. One river end-member is from the wet periods (W1), and two are from dry periods (D1 and D2). These end-members have been used to compute mixing ratios in groundwater samples because the Besòs River is considered the main recharge source for the aquifer. Overall, dry season end-members dominated over the wet season end-member, in a proportion of 4:1. Moreover, when departures from the mixing line exist, geochemical processes might be identified. Redox processes, carbonate dissolution/precipitation and ion exchange processes may occur in Besòs Delta aquifer.

1. Introduction

The deterioration of groundwater quality has become a major issue in urban aquifers. In urban areas, a vast array of contaminants may be found because they are introduced into the aquifer through different recharge sources. Thus, the assessment of groundwater quality requires identifying not only the possible focus of contamination but also the processes that the pollutants undergo. In fact, this study is motivated by the assessment of groundwater quality at the Besòs River alluvial aquifer underneath Barcelona, Spain. Groundwater quality in this area is significantly better than river water quality, despite the fact that pumped groundwater is essentially recharged from the river.

A mass balance of chemical species is often used in hydrology and related sciences to aid in the evaluation of water balances. Its simplest form consists of measuring the concentrations of any conservative species occurring in inflowing and outflowing waters and, assuming continuity, establishing the mass balance of solute and water. However, the joint evaluation of recharge rates and quality can most likely be best achieved through flow and solute transport modelling when long head and concentration records are available. Because these models require the management of much information, simpler methodologies are necessary.

Mixing calculations are an alternative to complex models and can be used to better estimate the relative importance of different sources of recharge. Mixing calculations include (1) End-Member Mixing Analysis

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An approach to identify urban groundwater recharge

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Abstract. Evaluating the proportion in which waters from different origins are mixed in a given water sample is relevant for many hydrogeological problems, such as quantifying total recharge, assessing groundwater pollution risks, or managing water resources. Our work is motivated by urban hydrogeology, where waters with different chemical signature can be identified (losses from water supply and sewage networks, infiltration from surface runoff and other water bodies, lateral aquifers inflows, ...). The relative contribution of different sources to total recharge can be quantified by means of solute mass balances, but application is hindered by the large number of potential origins. Hence, the need to incorporate data from a large number of conservative species, the uncertainty in sources concentrations and measurement errors. We present a methodology to compute mixing ratios and end-members composition, which consists of (i) Identification of potential recharge sources, (ii) Selection of tracers, (iii) Characterization of the hydrochemical composition of potential recharge sources and mixed water samples, and (iv) Computation of mixing ratios and reevaluation of end-members. The analysis performed in a data set from samples of the Barcelona city aquifers suggests that the main contributors to total recharge are the water supply network losses (22%), the sewage network losses (30%), rainfall, concentrated in the non-urbanized areas (17%), from runoff infiltration (20%), and the Besòs River (11%). Regarding species, halogens (chloride, fluoride and bromide), sulfate, total nitrogen, and stable isotopes (^{18}O, ^{2}H, and ^{34}S) behaved quite conservatively. Boron, residual alkalinity, EDTA and Zn did not. Yet, including these species in the computations did not affect significantly the proportion estimations.

1 Introduction

Groundwater is increasingly recognized as a factor in urban management (see reviews by: Lerner, 1996; Chilton et al., 1997; Eyles, 1997; Chilton, 1999; Ellis, 1999; Llamas and Custodio, 2002; Howard and Israfilov, 2002; AIH_GE, 2004; Vázquez-Suñe et al., 2005a). On one hand, some cities still show overexploitation with a series of unwanted outcomes such as subsidence, or deterioration in water quality due to a number of causes including seawater pollution. On the other hand, groundwater pumping has been abandoned in many cities because of pollution and/or changes in land uses (notoriously relocation of industries). This has caused heads to rise, leading to flooding and potential structural damage to underground urban structures. Controlling heads rise may demand groundwater pumping in selected locations. Pumping may also be needed to address the increasing demand of water in a sustainable way. Amongst other things, this requires understanding the processes affecting water chemical and microbiological quality. A proper assessment of groundwater quality involves the quantification of overall recharge, as well as the quality assessment of the various sources involved.

Evaluating recharge in urban environments is essentially different from that in natural systems for two reasons: (1) recharge sources are radically different and (2) less experience is available. Surface infiltration is greatly reduced because a large portion of surface area is virtually impervious. Therefore, most rainfall becomes runoff, which is diverted to a drainage system. However, reductions in direct infiltration can be counterbalanced by reductions in evapotranspiration. Moreover, new sources of recharge may arise in cities, such as losses in the sewage system (Wolf et al., 2004; Blackwood et al., 2005) or in the water distribution system (world-wide losses exceed 50 L/person/day, but reported

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A sequence stratigraphic based geological model for constraining hydrogeological modeling in the urbanized area of the Quaternary Besòs delta (NW Mediterranean coast, Spain)

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ABSTRACT

The Quaternary Besòs delta is located on the Mediterranean coast in NE Spain. The Besòs Delta Complex includes 3 aquifers constituted by 3 sandy and gravelly bodies, separated by lutitic units. These aquifers supply water for domestic and industrial use in this area. Management of groundwater has been problematic in the Besòs delta since the 1960s, and continues to pose major problems for subsurface engineering works in this highly urbanized region. This study seeks to demonstrate the advantages of detailed geological characterization and modeling for designing and constructing a hydrogeological model.

Available information of the subsurface was compiled, integrated and homogenized in a geospatial database. The interpretation of these data enabled us to delimit geological units by means of a sequence stratigraphic subdivision. A three-dimensional facies belt-based model of the Besòs delta was built on the basis of this geological characterization. This model was used to constrain the distribution of hydraulic parameters and thus to obtain a consistent hydrogeological model of the delta, which was calibrated by data of water management and production over the last hundred years. The resulting hydrogeological model yielded new insights into water front displacements in the aquifer during the time-span considered, improving predictions in an attempt to optimize aquifer management.

KEYWORDS Groundwater. Delta. Sequence stratigraphy. Geological model. Hydrogeological model.

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

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ABSTRACT

The different recharge sources and their mixing ratios were investigated in water samples from an urban aquifer. Two distinct zones from Barcelona city were compared: (1) Poble Sec and (2) Besòs River Delta, which are located in a densely populated area with a strong industrial impact. In this study 106 water samples were collected from July 2007 to May 2010 for hydrochemical and isotopic characterisation. 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 the Besòs River Delta, a decrease in dissolved SO_4^{2-} concentration and an increase in $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values were observed in groundwater samples, both indicating SO_4^{2-} reduction. Moreover, other chemical indicators supported a reducing environment, such as low or null levels of dissolved O_2 and NO_3^-, the presence of NH_4^+ and an increase in dissolved Fe and As. The reducing conditions were probably induced by the organic C dissolved in water infiltrating from the River Besòs. In Poble Sec, the relationship between $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ showed a strong influence of sewage water infiltration into the aquifer. However, the aquifer is oxic and there is no influence of SO_4^{2-} reduction.

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 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 chemical compounds (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 large 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 C to the water and promote biodegradation reactions of a variety of pollutants (NO_3^-, SO_4^{2-}, As-bound to Fe, 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 helpful in identifying and quantifying 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. (2005) complemented a hydrochemical study in

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GIS-based hydrogeochemical analysis tools (QUIMET)

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ABSTRACT

A software platform (QUIMET) was developed to improve the sorting, analysis, calculations, visualizations, and interpretations of hydrogeochemical data in a GIS environment. QUIMET is composed of a geospatial database plus a set of tools specially designed for graphical and statistical analysis of hydrogeochemical data. The geospatial database has been designed to include organic and inorganic chemical records, as well as relevant physical parameters (temperature, Eh, electrical conductivity). The instruments for analysis cover a wide range of methodologies for querying, interpreting, and comparing groundwater quality data. They include, among others, chemical time-series analysis, ionic balance calculations, correlation of chemical parameters, and calculation of various common hydrogeochemical diagrams (Salinity, Schoeller–Berkaloff, Piper, and Stiff). The GIS platform allows the generation of maps of the spatial distribution of parameters and diagrams. Moreover, it allows performing a complete statistical analysis of the data including descriptive statistic univariate and bivariate analysis, the latter including generation of correlation matrices and graphics. Finally, QUIMET offers interoperability with other external platforms. The platform is illustrated with a geochemical data set from the city of Badalona, located on the Mediterranean coast in NE Spain.

1. Introduction

Water availability and accessibility must emphasize quality aspects, such as whether water complies to given standards required for any particular use (Barthel et al., 2008). In a given site the quality of groundwater may be adversely affected by factors such as industrialization, irrigation practices, or urbanization (Foster, 2001; Vázquez-Suñè et al., 2005b; Scanlon et al., 2005; Ketata et al., 2011). An accurate assessment of the negative impacts of these different activities is paramount for the protection of water bodies and ecosystems associated (Navarro-Ortega et al., 2012). In order to ensure compliance with standard regulatory guidelines (e.g., the European Water Frame Directive, WHO guidelines), continuous monitoring, evaluation, and interpretation of a large database involving many potential geochemical parameters is required. This includes: (a) determining the origin of groundwater and the processes controlling its chemical composition and the corresponding spatio-temporal distribution; (b) evaluating the current groundwater quality trend with reference to soil use, as well as geological and hydrogeological setup; and (c) establishing the regional background composition of groundwater (in Mendizabal and Stuyfzand, 2009).

Accomplishing these tasks is not straightforward. The major difficulties to be faced arise from: (i) the need to manipulate large data sets collected over many years; (ii) the integration of data stemming from diverse sources and gathered with different data access techniques and formats; (iii) the management of data with varying quality standards (and thus different associated errors) and temporal and spatial extent, with potential big gaps of information at the spatial or temporal scales in some areas; (iv) data-handling derived from both field data, analysis of water samples at the laboratory and groundwater models (also representative scales of data are quite different), and (v) the integration of groundwater quality information with other relevant information such as geological data.

Optimal data management of this vast amount of spatio-temporal information cannot be readily handled without the combination of a comprehensive geospatial database and a number of efficient technologies and methodologies capable of classifying, comparing, summarizing and interpreting huge data sets. Classic groundwater analysis

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Quantifying chemical reactions by using mixing analysis

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HIGHLIGHTS

- Urban aquifer is infiltrated by a polluted river that is the main recharge source.
- Three end-members are necessary to explain the temporal variability of river water.
- Departures from ideal mixing line are attributed to chemical processes.
- Mixing calculations are used to quantify chemical processes in urban groundwater.
- The processes quantified are redox processes and carbonate dissolution.

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ABSTRACT

This work is motivated by a sound understanding of the chemical processes that affect the organic pollutants in an urban aquifer. We propose an approach to quantify such processes using mixing calculations. The methodology consists of the following steps: (1) identification of the recharge sources (end-members) and selection of the species (conservative and non-conservative) to be used, (2) identification of the chemical processes and (3) evaluation of mixing ratios including the chemical processes. This methodology has been applied in the Besòs River Delta (NE Barcelona, Spain), where the River Besòs is the main aquifer recharge source. A total number of 51 groundwater samples were collected from July 2007 to May 2010 during four field campaigns. Three river end-members were necessary to explain the temporal variability of the River Besòs: one river end-member is from the wet periods (W1) and two are from dry periods (D1 and D2). This methodology has proved to be useful not only to compute the mixing ratios but also to quantify processes such as calcite and magnesite dissolution, aerobic respiration and denitrification undergone at each observation point.

1. Introduction

Ensuring good water quality is a major challenge in urban areas. Urban aquifers may suffer pollution from recharge sources such as water leakage from sewer and septic systems, seepage from rivers, seawater intrusion, and losses from water supply network etc. As a result, a wide range of organic pollutants are found in urban aquifers. Since these pollutants reach groundwater environment, their occurrence depends on simultaneous transport and biogeochemical processes. For a quantitative assessment of groundwater quality a sound understanding of all these processes affecting these pollutants is essential. However, the quantification of these processes is not an easy task.

In order to quantify such processes, modelling tools that provide extensive biogeochemical capabilities are necessary (Prommer et al., 2000). Reactive transport models quantify the spatial and temporal evolution of a number of chemical species subjected to transport phenomena and chemical reactions. Numerous codes have been developed in recent years. They have been applied to problems such as leachate attenuation (Islam et al., 2001; Van Breukelen et al., 2004), pollution plumes (Brun et al., 2002), microbially mediated reactions (Schäfer et al., 1998a,b; Hunter et al., 1998; Tebes-Stevens et al., 1999; Wang and Papenguth, 2001), carbon cycle modelling cases (Greskowiak et al., 2005) and the quantification of redox processes in aquifers (Keating and Bahr, 1998; McGuire et al., 2002; Massmann et al., 2004; Miotlinski, 2008) and in the hyporheic zone (Miller et al., 2006; Zarnetske et al., 2011). However, simpler approaches are required since these techniques are tedious and time consuming because of the need for a reliable flow and conservative transport models.

Mixing calculations constitute an alternative to reactive transport models. Mixing calculations typically involved: (1) End-Member Mixing Analysis (EMMA) (Hooper et al., 1990; Hooper, 2003) to find the minimum number of end-members required to explain a set of chemical analyses, and (2) mixing ratios defined as the proportion of

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