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Escola Tècnica Superior d'Enginyeria de Camins, Canals i Ports de Barcelona

Departament d'Enginyeria del Terreny, Cartogràfica i Geofísica

## DOCTORAL THESIS

# URBAN GROUNDWATER. BARCELONA CITY CASE STUDY

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# RESUMEN

Cuando se estudian las aguas subterráneas en zonas urbanas deben tenerse en cuenta una serie de cuestiones específicas. La urbanización del territorio afecta significativamente al ciclo del agua tanto en cantidad como en calidad, en particular a la parte relacionada con la recarga y descarga de los acuíferos. Además las aguas pueden afectar a las infraestructuras urbanas subterráneas como sótanos, parkings, túneles de Metro o ferrocarril, conducciones, etc. Por estos motivos el estudio de las aguas subterráneas en zonas urbanas emerge con fuerza dentro de la hidrogeología. Algunos de los temas específicos para su estudio son: 1) Variaciones del nivel freático causadas por cambios en los usos del suelo y del agua; 2) Contaminación de las aguas subterráneas por la presencia de focos contaminantes tanto puntuales como difusos; 3) Caracterización y cuantificación de los componentes del balance hidrogeológico; 4) especificidades en la modelación del flujo subterráneo y el transporte de contaminantes; y 5) Integración de los datos hidrogeológicos para su gestión. Algunos de estos temas se ilustran aquí sobre el ejemplo de la ciudad de Barcelona. En los últimos años, tanto desde el ámbito público como privado, se ha llevado a cabo un amplio estudio hidrogeológico de la ciudad. El ascenso del nivel freático se ha convertido en un serio problema para muchas estructuras subterráneas, principalmente parkings y la red del Metro. Este ascenso se ha debido básicamente a la disminución en la explotación de las aguas subterráneas por una reducción significativa del consumo de agua para usos industriales. Aquí se presenta una evaluación de los principales términos que afectan a la recarga cuyo resultado es la cuantificación del balance hidrogeológico en el periodo comprendido entre 1965 a 1995. Se ha cuantificado en unos 40 $hm^3/a$ la cantidad total de agua que debe bombearse de los acuíferos para mantener los niveles freáticos a las cotas actuales. Si se bombean cantidades menores los niveles freáticos seguirán ascendiendo y continuaran los problemas. Se han sugerido algunos usos alternativos para estas aguas.

Este caso puede considerarse un buen ejemplo de como la evolución de la urbanización en cualquier ciudad genera una serie de problemas respecto la disponibilidad y calidad de las aguas subterráneas con las implicaciones tanto sociales como económicas que esto comporta. Para un buen conocimiento de la hidrogeologia urbana es preciso un análisis cuantitativo del flujo de agua y de su calidad, para ello es preciso 1) identificar los procesos hidrogeológicos; 2) caracterización de acuíferos y modelación y 3) gestión de los recursos hídricos. Al aplicar esta metodología a Barcelona se ha obtenido, entre otras cosas, un modelo capaz de ser utilizado como herramienta de gestión. Estos modelos se podrán aplicar si las aguas subterráneas quedan contempladas como un elemento más a tener en cuenta por los gestores locales.

Un tema clave para el estudio de la hidrogeología urbana es la evaluación de los diversos términos que componen la recarga (agua de la red de abastecimiento, del alcantarillado, agua de escorrentía urbana, infiltración directa, etc.) Discriminar todos estos términos es importante para evaluar el balance, para conocer el riesgo de contaminación de los acuíferos y para plantear una correcta gestión. Es necesario conocer cuales son los diversos compuestos hidroquímicos e isotópicos presentes en las aguas de recarga. El objetivo es identificar, y si es posible cuantificar, las diversas fuentes de recarga y sus proporciones. Se ha revisado un buen número de experiencias y casos internacionales que listan en el uso de diversos tipos de trazadores aplicados a los estudios de aguas subterráneas.

La cuantificación de las diversas fuentes de recarga se puede establecer a partir de balances de solutos. El puntos críticos son: 1) la gran cantidad de fuentes de recarga existentes que implican tener que usar un gran número de especies conservativas; 2) la incertidumbre en las concentraciones de estas fuentes y 3) los errores de medida.

Teniendo en cuenta estas limitaciones se presenta un método basado en el análisis estadístico multivariado para el cálculo de las proporciones de mezcla de las fuentes de recarga en un gran número de puntos de mezcla. Este método está basado en la presunción que las medidas de las concentraciones contienen errores. Minimizando la función de verosimilitud respecto a las concentraciones de las fuentes y de las mezclas se llega a un problema de optimización. Para resolver este problema se presenta un algoritmo de aplicado a dos ejemplos sintéticos. Los resultados confirman la conjeturas de partida, es decir, las concentraciones de las mezclas contienen información sobre las concentraciones de las fuentes. Así pues, al haber consistencia entre ambos implica que una mejora en los cálculos de las mezclas y también en el conocimiento más preciso de las fuentes.

Esta metodología se ha aplicado a los acuíferos de Barcelona. El primer paso ha sido la identificación de las fuentes de recarga potenciales: agua de abastecimiento, con dos tipologías diferentes, aguas residuales y de escorrentía urbana, aguas de infiltración directa ,aguas de infiltración del río Besós y aguas de intrusión marina. Después de su estudio hidroquímico e isotópico se han determinado ocho especies químicas más o menos conservativas para identificar las posibles fuentes de recarga. La aplicación de este método estadístico ha permitido calcular las proporciones de mezcla de las diversas fuentes de recarga en las diversas zonas de los acuíferos de la ciudad.

# ABSTRACT

A number of specific issues must be considered when dealing with groundwater in urban areas. Urbanization significantly affects the natural water cycle, both in terms of quantity and quality. In particular, the main contributors to recharge and discharge clearly differ from those in natural systems. Moreover, water can affect underground city infrastructures, such as basements, public transport services (trains, subway, …), and conductions. As a result, urban groundwater is emerging as a distinct branch of hydrogeology. Topics that are specific to urban groundwater include: 1) Fluctuations in groundwater levels caused by changes in land and water uses; 2) Pollution problems caused by point or non-point sources in urban areas; 3) Characterization and quantification of the components contributing to groundwater balance; 4) Specific characteristics of groundwater flow and solute transport models in urban areas; and 5) Integration of data for sustainable urban water management. Some of these issues are illustrated here for the case of Barcelona, where both the public and the private sectors have carried out a comprehensive hydrogeological study during the last years. Rising of groundwater levels beneath the city of Barcelona has become a serious problem to urban structures, such as the subway and underground parking areas. This rise is mainly due to a decline in groundwater exploitation, following a reduction in high water-consuming industrial activity in the city. We present an evaluation of the main terms affecting recharge in the city. The outcome is a global groundwater balance for the period 1965-1995. It has been quantified that a total rate of 40 million $m^3$ per year should be pumped from the aquifers underneath the city in order to keep to the present groundwater levels. A lesser amount would lead to a rise in levels, and to continuing problems. Possible uses for this additional water are suggested.

This case can be considered an example of how urbanisation poses some threats to both availability and quality of groundwater resources in large cities worldwide, with their corresponding significant social, environmental and economic implications. A good knowledge of urban hydrology requires a detailed quantitative analysis of not only water fluxes, but also their quality. In any real case study one has to face at least three aspects: (1) process identification, (2) aquifer characterisation and modelling, and (3) water resources management. This three-fold methodology has been applied to the city of Barcelona. The outcome is a groundwater model which may, among other things, become a management tool. This is an important step towards considering groundwater as one of the topics to be taken into account in city planning.

One of the key issues in urban hydrogeology is the evaluation of the relative contribution of the different sources of recharge (water from mains and sewers, direct infiltration, runoff, etc.). Discriminating among recharge sources is important for the overall recharge evaluation, for assessing groundwater pollution risks and for groundwater management. To do so, it is necessary to know the different hydrochemical compounds and isotopes present in groundwater and recharge water. The objective is to identify, and if possible to quantify, the various recharge water types and their proportion. We have reviewed a large number of cases and international experiences illustrating the use of several tracers in urban groundwater studies.

Quantification of the contribution from the different recharge terms can be achieved by means of solute mass balances. The critical points in the process are: (1) the large amount of source terms, which leads to the necessity of a large number of conservative species to be used, (2) the uncertainty in the concentrations of sources, and (3) the measurement errors.

A method based on multivariate statistical analysis is presented for estimating the proportions in which a small number of end-member waters are mixed in a large number of samples. The method is based on assuming that errors affect all concentration measurements. Maximizing the likelihood of these with respect to both mixing ratios and end-member concentrations leads to a general constrained optimization problem. An algorithm for solving this problem is presented and applied to two synthetic problems. Results confirm the conjecture that motivates this work. That is, mixtures concentration measurements contain information about end-member concentrations. As a result, ensuring that the latter are consistent with the former leads to a significant improvement of not only end-member estimates, but also mixing ratio estimates.

This method has been applied to the city of Barcelona. In this city a number of potential sources were identified. These include: losses from the water supply network (with two different sources of water), losses from sewers, infiltration from the Besòs River, infiltration in unpaved areas, and seawater intrusion. After studying the results from the chemical and isotopical analyses, eight chemical species were found to be conservative and to provide a potential for source discrimination. The application of the statistical analyses allowed us to compute the proportions of each recharge source for a number of different locations in Barcelona.

## FIGURE INDEX

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# CHAPTER 0 FOREWORD

This chapter defines the history, motivation, aims and structure of the thesis. It also list those scientific articles and technical reports related to its development.

## 0.1 INTRODUCTION

In the mid 90's newspapers regularly displayed news about groundwater in the city of Barcelona (Figure 0.1). Most of them focused on the problems that the presence of phreatic waters causes on urban groundwaters. Statements such as **"The subway had to be closed… ", "Phreatic waters threatens...", "Groundwater rising causes floding"** are examples of the existing problem.

Many problems had been detected before the 90's (i.e. infiltrations of significant water volumes in underground stations, parking lots, basements, etc.). In most of the cases, they were isolated problems that were solved independently (UPC, 1992).

A progressive increase in infiltrated water volumes has been observed. Since them, new points are appearing where infiltrations take place. Therefore, it was only then that the problem of phreatic waters became obvious throughout the city and the local authorities sought an explanation to the confusion and claims of the citizens. This situation is translated, for instance, in a first inventory of the "problems related to water infiltrations" elaborated by the Barcelona Municipalities in the mid 90's.

In order to know the origin of the problem, its evolution and possible solutions, the local authorities consulted and later signed a cooperation agreement with the "Hydrogeology Group" of the UPC.

el Periódico Viernes, 14 de marzo de 1997

COSAS DE LA VIDA 27

GRAN BARCELONA

Mc

## El agua freática amenaza Sant Martí

El distrito es el más afectado por el aumento de los acuíferos del subsuelo

Un estudio advierte que el nivel subirá 3 metros en 10 años en la zona del Besòs

Algunos sótanos, 'parkings', galerías de servicios y túneles ya sufren filtraciones

MERCÈ CONESA
Barcelona

El nivel freático de las aguas subterráneas de Barcelona amenaza a buena parte del distrito de Sant Martí. De no adoptarse medidas, éste seguirá subiendo unos tres metros en los próximos diez años en la zona cercana al Besòs y entre uno y dos metros en la parte alta de la ciudad. El aumento en los barrios cercanos al río es especialmente preocupante, ya que en la zona en que confluyen las calles Lope de Vega y Pallars, el nivel freático está actualmente tres metros por debajo de la superficie, y en la de Lluís Companys con Pujades, a seis metros.

El Ayuntamiento de Barcelona está estudiando qué medidas deberían adoptarse para frenar esta subida, básicamente motivada por el cese de la actividad de pozos extractores que antaño utilizaban las indust

Las aguas s
de Barcelona

Línea de costa histórica

Terreno ganado al mar

Diez islas del

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34 LA VANGUARDIA

CIUDADES

VIERNES, 20 OCTUBRE 199

## El metro tuvo que ser cerrado por grietas en la zona donde más sube el agua subterránea

■ El Ayuntamiento de Barcelona confirma que la subida del acuífero

### Poblenou y l'Hospitalet

■ Lluís Gutiérrez, gerente de la empresa encargada del mantenimiento de los colectores de Barcelona, confirmó ayer la subida de los niveles de las aguas subterráneas de Barcelona, sobre todo en el barrio de Poblenou y en algunas zonas de l'Hospitalet cercanas al río Llobregat. Gutiérrez apunta que parte de estas aguas que se filtran pueden estar contaminadas a causa de procesos industriales, y contener elementos químicos que podrían afectar a las estructuras de los túneles del

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## La subida del nivel freático de las aguas del Besòs inunda varios aparcamientos

ESTER LÓPEZ
Santa Coloma de Gramenet

El nivel freático de las aguas
del Besòs en la zon
Coloma ha aument
dos últimos años
peligrosa y ha supe
7,5 metros de altur
blema, que experi
tendencia a aument
sionado ya en Santa
inundación de do
mientos, lo que ha
Ayuntamiento a ado
das urgentes. El niv
puede llegar hasta
metros.

En la calle de Sant Joaquim, un aparcamiento municipal

trada de agua. En estos momentos se están sacando 75 li-

---

Ciudades

14-enero-1997

## El nivel del agua subterránea crece a una velocidad inquietante en el área de Barcelona

■ Las lluvias de los últimos meses han activado este fenómeno en la zona del Besòs, lo que ha disparado las inundaciones de subterráneos

BARCELONA. – Las aguas subterráneas de Barcelona siguen subiendo de nivel, por lo que se multiplican las incidencias motivadas por las inundaciones achacables a este fenómeno en sótanos y aparcamientos. Los expertos que por encargo del Ayuntamiento de Barcelona elaboran un estudio al respecto han confirmado la recuperación natural de los acuíferos en la zona de Barcelona estos años y, además, han comprobado que en los últimos meses la velocidad de este proceso se ha acelerado en la cuenca del Besòs.

La situación en las dos cuencas hidrográficas del área de Barcelona parece ser diferente. En la zona del Llobregat (Zona Franca, plaza Espanya), la subida de las aguas es

### EL SUBSUELO DEL ÁREA METROPOLITANA

Las zonas más bajas del área metropolitana próximas a la desembocadura del Besòs y el delta del Llobregat son las más proclives a sufrir inundaciones por la subida del nivel del acuífero. En estas zonas, el suelo se asienta sobre capas de arcillas y limos negros impermeables donde el agua filtrada se va almacenando. En la superficie, hay una capa de terreno seco que, en caso de una gran acumulación de caudal, también puede quedar saturado de agua

TIPOS DE SUELO

- Gravas, arenas, limos y arcillas de llano aluvial y deltaico, más proclive a inundarse
- Arcillas, limos, gravas y roca
- Pizarras y rocas

INUNDACIONES RECIENTES

1. Edificio en construcción
2. Aparcamiento subterráneo
3. Sótanos
4. Aparcamiento subterráneo
5. Paso inferior
6. Túnel del metro

**Figure 0.1.** –Noticias en la prensa relacionadas con problemas producidos por las aguas subterráneas

## 0.2 MOTIVATION AND AIMS

During that time, only a few exhaustive hydrological studies focused on the urban area. Although there were already some articles and books (Hurst and Wilkinson, 1985; Lerner et al., 1990) where the most frequent problems regarding urban groundwater were exposed, experience on these cases was limited. In this context, the works planed to hydrologically characterize the city of Barcelona (or generally for any other urban area) lacked an specific methodology.

Thus, the following objectives were formulated:

- Firstly, to acquire some knowledge on the hydrological functioning of the city where we live, with whom we feel identified and where we have those pieces of information fragmented or blurred by tradition. It is a personal challenge to get to gather all this knowledge and define a conceptual model of the hydrological functioning, while relating it with the historical aspects of urban development.
- Secondly, it is essential that, the acquisition of this knowledge is followed by a series of ideas and solutions for the needs and problems posed, which will be provided to the management and public entities.
- Thirdly, specific methodologies should be learned, acquired and applied to satisfactorily deal with the study of urban groundwater.
- Finally, new methodologies should be improved and developed to study and quantify hydrogeological balances in urban areas. New perspectives will appear in a knowledge field recently developed and that, at medium or long term, will gain a determinant relevance. It should be noted that there are two very relevant fields for the future decades: the integral management of water and the increase in the population, specially in the cities.

The elaboration of this thesis should allow one to answer these concerns and to adequately respond to the aims considered.

## 0.3 METHODOLOGY

In order to cover all the aims, a work plan was established, including the following steps:

- An essential part was the search for the history and studies concerning urban groundwater in order to determine those specific hydrological aspects of urban areas.
- The common and more relevant aspects in most of the studies regarding urban groundwater were collected from the references consulted. Furthermore, the questions necessary in order to achieve a sustainable management of groundwater in urban areas were analysed.
- From the research carried out and, in cooperation with public management, the knowledge acquired in urban groundwater studies was applied to Barcelona,. The hydrogeological study in the city area allowed defining a conceptual model of how the interaction between aquifers works (water balance, water quality, etc.). This information allowed determining the origin of most of the existing problems and finding the solutions, not only at a local scale, but also in general, in a sustainable management context.
- In spite of all this, there are still a series of methodological lacks. That is why it was necessary to develop and apply new technologies. In this sense, an effort was made in the development of hydrological quantifying methodologies in urban areas.

  Special care was taken in the determination and quantification of the origin of groundwater in urban areas. This aspect was dealt with from the application of hydrological numerical models in the urban area, as well as from the identification and quantification of chemical species characteristic of the different sources reloading the aquifers, which allowed discriminating the possible sources and quantifying the relative input of each of them.
- All this helped to gather some knowledge and methodologies that allowed dealing, quite accurately, with the study of urban groundwater. These knowledge and methodologies were set as an example in its application to the hydrogeology of the city of Barcelona.

## 0.4 STRUCTURE

The structure of the thesis shows the methodological development above-mentioned in a progressive and coherent way.

It has been divided in 8 chapters, besides this foreward. The 7th and 8th correspond to the general conclusions and to the reference list, respectively. The rest belongs to the body of the thesis, which is structured as self-contained chapters. That is, each one of them is written as a scientific article, with its introduction, development and conclusions. Thus, it is possible to read each chapter independently. This format was chosen in order to reinforce the aspects exposed in each of them and to ease and rend coherent the reading. The only drawback is some redundancy.

The organisation of each chapter in the thesis as a whole allows a logical order in the general argumentation and in the progressive study in detail of urban groundwater.

The structure that results is summarised as follows:

**Chapter 0.-** Preamble:

Definition of the introduction, motivation, aims and structure of the current thesis. List of those scientific articles and technical reports related.

**Chapter 1.-** Introduction:

Review of the state-of-the-art of the studies concerning urban groundwater. Definition of the most relevant and characteristic aspects that should be taken into account. Some of them are illustrated, using Barcelona as an example.

**Chapter 2.-** Hydrogeological study of Barcelona:

Synthesis of the result of urban groundwater tests carried out in the city of Barcelona. Definition of the conceptual model for the general hydrogeological functioning.

**Chapter 3.-** Modelling and quantification of the hydrological balance in Barcelona:

Synthesis of the results of the numerical modelling of the aquifers from a previous conceptual model. Improvement of the hydrogeological balance quantification. Example of the use of these methodologies in the public management of groundwater in Barcelona.

**Chapter 4.-** Selection of tracers for the identification of the origin of groundwater in urban areas:

Review and state-of-the-art of the different chemical and isotopical compounds capable of discriminating the origin of groundwater in urban areas. These tracers can be applied not only to the identification, but also to the quantification of the different reloading sources.

**Chapter 5.-** Methodological development for the calculation of mixture proportions:

Explanation of the development of a new methodology based on the statistical multivariate analysis. This method allows quantifying the mixture proportions of the waters reloading the aquifer, as it improves the knowledge on the characteristics of extreme waters.

**Chapter 6.-** Application of the mixture calculation to Barcelona aquifers:

Application of the methodology based on the statistical multivariate analysis to Barcelona aquifers.

**Chapter 7.-** General conclusions.

Discussion of the results obtained.

**Chapter 8.-** Reference list.

## 0.5 ARTICLES AND REPORTS RELATED TO THE DEVELOPMENT OF THE THESIS

This thesis is characterised for being the result of the intersection of two complementary aspects:

1. Scientific: definition of new knowledge fields in the urban groundwater area and development of the methodologies necessary for its application.
2. Technical: application to the study of urban groundwater in the city of Barcelona. Cooperation with the public management when dealing with urban groundwater.

The development of this thesis was conditioned by this double viewpoint, which has enriched both aspects. As a result, many articles and technical reports were written on the subject. A list of them is shown below.

## 0.6 SCIENTIFIC ARTICLES:

**Vázquez-Suñé, E**., X. Sánchez-Vila, J. Carrera (1996) "Groundwater level rises in Barcelona". In: "Environment and Interaction". Proceedings of the International symposium held at the university of Porto, November 18-19, 1996. Paper 12, 6 pag.

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**Vázquez-Suñé, E**., E. Abarca, X. Sánchez-Vila, J. Carrera y M. Enrich (2001). "El modelo numérico del acuífero superficial del delta del Llobregat como herramienta de planificación. evaluación de impactos y medidas correctoras". VII Simposio de hidrogeología. T XXIII, pp: 43-59. AEH-IGME, 2001 (NIPO: 405-01-003-8).

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## 0.8 PARTICIPATION IN CONGRESSES AND SEMINARIES RELATED TO URBAN GROUNDWATER :

**La evaluación de la recarga a los acuíferos en la planificación hidrológica.** Seminario celebrado en Las Palmas de Gran Canaria, Enero 1997. AIH-GE/ITGE. Presentación Oral.

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**XXIII General Assembly of the European Union of Geophysical Society**. Niza, Francia 20-24 Abril 2000. Presentación Oral.

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# CHAPTER 1. URBAN GROUNDWATER, AN EMERGING BRANCH OF HYDROGEOLOGY : A REVIEW OF SPECIFIC ISSUES

## 1.1 INTRODUCTION

Groundwater beneath cities is becoming increasingly important, with links to scientific, economical, social, legal and political issues. The impacts of groundwater within a specific urban area depend both on its geographical location and the economic status of the city or even the country. African and southern Asia cities often face difficulties in supplying sufficient amounts of good-quality water. Their main interests are therefore water quantity and quality. In developed countries, however, urban groundwater is posed in economical and environmental terms. Using groundwater may reduce pressure upon conventional freshwater supply sources. On the other hand, not using this groundwater may lead to flooding and structural damage to underground structures (subway system, basements, underground parking areas, etc.)

While water is often scarce, water demand in cities is large and, in many cases, increasing with time. Many large cities rely mostly on surface water for supply purposes (see Howard and Gelo, 2002, for a compilation of the largest cities in world with respect to the use of surface or groundwater as primary source). As urban population grows, conjunctive use of surface and groundwater is likely to become increasingly common, and water management is to be enhanced (Gossell et al., 1999; Aldrick et al., 1999). Groundwater, even when its quality makes it unsuitable for drinking, can be used after treatment for several alternative purposes. This would reduce the need for high-quality water.

Fundamental flow and transport processes affecting urban groundwater are not essentially different from those affecting rural water, but the time and space scales involved are significantly different. The main space-time issues related to the changes in the quantity and quality of groundwater in urban areas are:

Groundwater cycle directly linked to the history of urbanization,

Fluctuations in groundwater levels related to anthropogenic activity

Strong groundwater pollution caused by human activities

The presence of underground structures either permanent or temporary (e.g., construction sites).

Quantification of groundwater fluxes and modeling become difficult tasks, mainly due to lack of data, lack of planning (actions usually respond to emergencies rather than planning), and difficulties in communication between the scientific community and city managers/policy makers.

As a result, urban groundwater has emerged in recent years as a specialized area of study within hydrogeology. While the basics of groundwater as a science are well established, the specific aspects of groundwater in urban environments have only recently been recognised. Testimony to the emergence of urban groundwater as an important area of study includes the establishment in 1993 of a “Commission on Groundwater in Urban Areas” by the International Association of Hydrogeologists (IAH), the publication of urban groundwater books (Lerner, 1996; Eyles 1997; Howard and Israfilov, 2002), and an increasing numbers of international congresses and workshops (Chilton et al., 1997; Ellis, 1999; and Tineo, 1999). These events have been motivated by the strong interaction between city growth and groundwater environmental impacts.

Most of the issues presented in this paper have been addressed in one way or another by different researchers (see the compiling works of Chilton et al., 1997 and 1999; Ellis, 1999; Howard and Gelo, 2002), although unfortunately seldom in a much needed integrated or unified framework for a given city case study. More importantly, the task remains to incorporate these findings in the urban planning process if we are going to avoid the errors of our not so distant past (Howard, 1997).

The purpose of this paper is to synthesize several topics that are significant in an urban groundwater study. These include both quantity and quality issues, and are illustrated with a case study in Barcelona.

## 1.2 SIGNIFICANT TOPICS IN URBAN GROUNDWATER STUDIES

In recent years several research groups have developed comprehensive methodologies for evaluating groundwater resources in urban areas. Two stages are necessary:

1) identifying the most significant factors in the urban hydrogeological cycle, and

2) developing and applying methodologies to quantify and control these factors

We address here the most significant elements regarding groundwater balance and solute transport in an urban environment

### Evaluation of recharge and water balance

Understanding any aquifer requires knowledge of water fluxes: their magnitude, relative importance, and dependence upon hydrological parameters. A conceptual /schematic view of the water cycle in urban environments is shown in Figure 1.1.

Changes in land use caused by urban development lead to disruption of the natural hydrogeological cycle. Recharge to the system is greatly modified; direct recharge due to infiltration of precipitation is often reduced, but so is evapotranspiration. Moreover, recharge is increased by losses in both the water supply and sewage systems. Estimation of all the various contributions to the urban water cycle is very difficult and has not yet been standardized (Lerner, 1997).

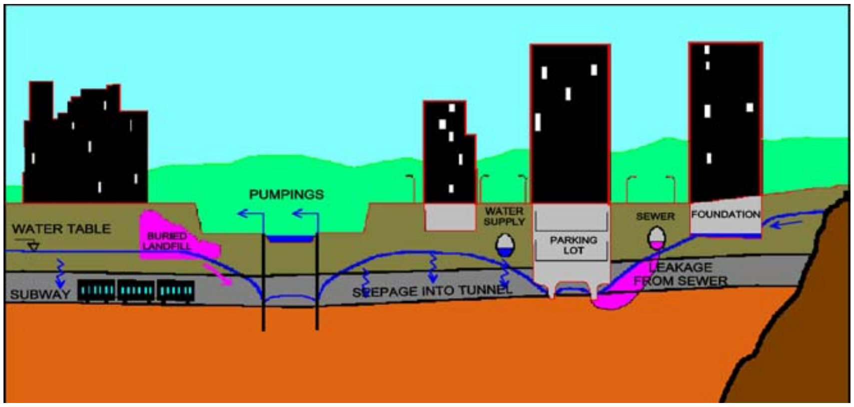

**Figure 1.1. -**The groundwater cycle in urban environments

Recharge is the most difficult term to evaluate in the water balance of most aquifers. For years, hydrogeologists have worked on methods to estimate it, and a large body of experience has been built up. Methods include: direct measurements (expensive, difficult to regionalize in space and extend in time), water balance at a soil column (often imprecise), hydrodynamic methods, including modelling (expensive, data intensive), mass balance of solutes (requires a good understanding, appropriate solutes not always found), and empirical methods (imprecise, require site specific validation). While a universal method does not exist, an approach suitable for each specific need can normally be found.

Evaluation of recharge in urban environments is essentially different from that in natural systems for two reasons: (1) less experience is available and (2) different processes (sources) are involved. Regarding the latter, it must be recognised that, direct infiltration is greatly reduced in paved cities because a large portion of the city surface area is virtually impervious, but this effect can be counterbalanced by increased indirect recharge via pluvial soakaways from roofs or paved surfaces. Importantly, extensive impervious surface causes radical reductions in evapotranspiration, and thus a net increase in available water. Moreover, new sources of recharge may arise in cities, either from water distribution mains (losses commonly exceed 15% of the water supply) or from sewage systems. While methods are available for evaluating these sources (see Lerner, 1997, for a review), validation is difficult. Certainly, experience in conducting such studies is much less than for recharge estimation in natural systems and studies must be purpose designed to meet the needs of each individual city.

The fact that recharge generally comes from at least three sources: rainfall, water supply and sewers (although other sources can be identified in specific cases) is both an added difficulty and a challenge. Discrimination among sources is important because of pollution risk (notably from sewers and infiltration of urban runoff) and the need to develop appropriate management strategies. Direct measurement of the contribution of a particular source has been possible in only a few cases, and the measurements still incorporate a large amount of uncertainty (Kim et al. 2001). Indirect, crude estimates can probably be obtained from the number of inhabitants, population density, history, type of urban development, type and age of the water supply and sewage systems, etc., but we are not aware of any good examples where this approach has been used.

Discriminating between sources of recharge can probably be best achieved using a mass balance computation involving chemical species associated with the known sources. Halogens (especially F and Br), boron, zinc and EDTA are good examples (Trauth and Xanthopoulus, 1997; Carrera, 1997; Gäbler and Barh, 1999; Robbins and Gilbert, 2000). Also, Rivers et al. (1996) and Barrett et al. (1999) suggest the use of a nitrogen isotope ($^{15}N$). When water supply is imported from long distances or from substantially different altitudes, it is likely to find a marked isotopic signature. In such cases environmental isotopes such as $^{18}O$ and D can be useful for discriminating between local rainfall recharge and imported water recharge (Butler and Verhagen, 1997).

Using multi-solute balance equations to quantify recharge is an alternative since the work in rural environments by Adar and Neuman (1988) and Adar et al. (1988). This methodology has been applied to quantify recharge in urban environments by Yang et al. (1999) and Lerner and Yang (2000) in the city of Nottingham. Suk and Lee (1999) use cluster and factor analyses to characterize groundwater hydrochemical system.

Castillo (2000) presented a methodology based on multivariate statistics analysis to estimate the contribution of the different sources to a given location in the aquifer using chemical species. The methodology involves 4 steps: 1) identification of the potential recharge sources in a given location of the aquifer; 2) identification of the conservative chemical species to be used in the mass balance equations; 3) determination of the mean and standard deviation of all chemical species for every source; and 4) application of the multivariate analysis methodology to find the most probable proportion of each source at each measured well. The advantage of a multivariate methodology is that it allows incorporating uncertainty in the measurements both at the sources and the sampling points. This methodology, applied to the city of Barcelona (Vázquez-Suñé, et al., 2000), allowed quantifying the relative importance of losses in mains and sewers, direct infiltration and inflows from the river, and the sea for different areas in the city.

Water flow and solute transport modelling

The components of the water balance can be quantified separately. Alternatively, inflows can be determined in an integrated way using modelling.

Modelling of urban problems is in a relatively early stage of development. While efforts have been made to evaluate and predict urban water level fluctuations (Vázquez-Suñé et al., 1997; Bonomi and Cavallin, 1997, among others), work remains to be done before modelling can be considered an effective tool for dealing with the full integration of urban groundwater issues. Models can play different roles. For the purpose of this discussion we consider three: (1) process identification, (2) hydrogeological integration and aquifer characterization, and (3) water resources management.

Urban models display specific features that make them different from models in non-urban aquifers. First, they need to take into account the historical evolution of the urban area including progressive changes in land use. Second, the recharge in any given area depends on factors that are directly related to population density (such as the water network density) and to the time period during which the area was developed (that is, the historical evolution of the city). Third, groundwater abstraction by individuals or industries is difficult to evaluate, and it is often underestimated, as many wells are undeclared or plainly illegal, or simply the country has no infrastructure that can handle a permanent data base for extractions. Finally, urban underground structures are singular features in a model whose interactions with the groundwater system may need to be addressed individually.

Perhaps one of the most significant aspects of a urban groundwater model is the immense amount of information that must be processed. Information is scattered along many sources (local authorities, local suppliers, private consumers, historical archives, etc.), and often comes available at different stages during the modelling process, requiring the conceptual model to be revised frequently.

In the framework of the Barcelona hydrogeological study construction of the groundwater flow model (Vázquez-Suñé and Sánchez-Vila, 1999) involved geological discrimination of aquifers, model conceptualisation, identification of recharge sources, establishment of boundary conditions and hydraulic parameterisation. The model was calibrated using piezometric data for the period 1900 – 1999 and explicitly includes railway and subway tunnels. An output of the model is the relative contribution of the various elements of the groundwater balance, Figure 1.2, and its evolution in time.

The most significant finding is the confirmation that most of the aquifer recharge is due to leakage from drinking water and sewage networks. Inflow from the sea was reversed just in 1997. Until that time seawater intrusion occurred in response to heavy pumping from the subway and local industry. Today these abstractions have virtually ceased and outflows along the coast have been restored. The study illustrates how groundwater flows can change rapidly in urban environments.

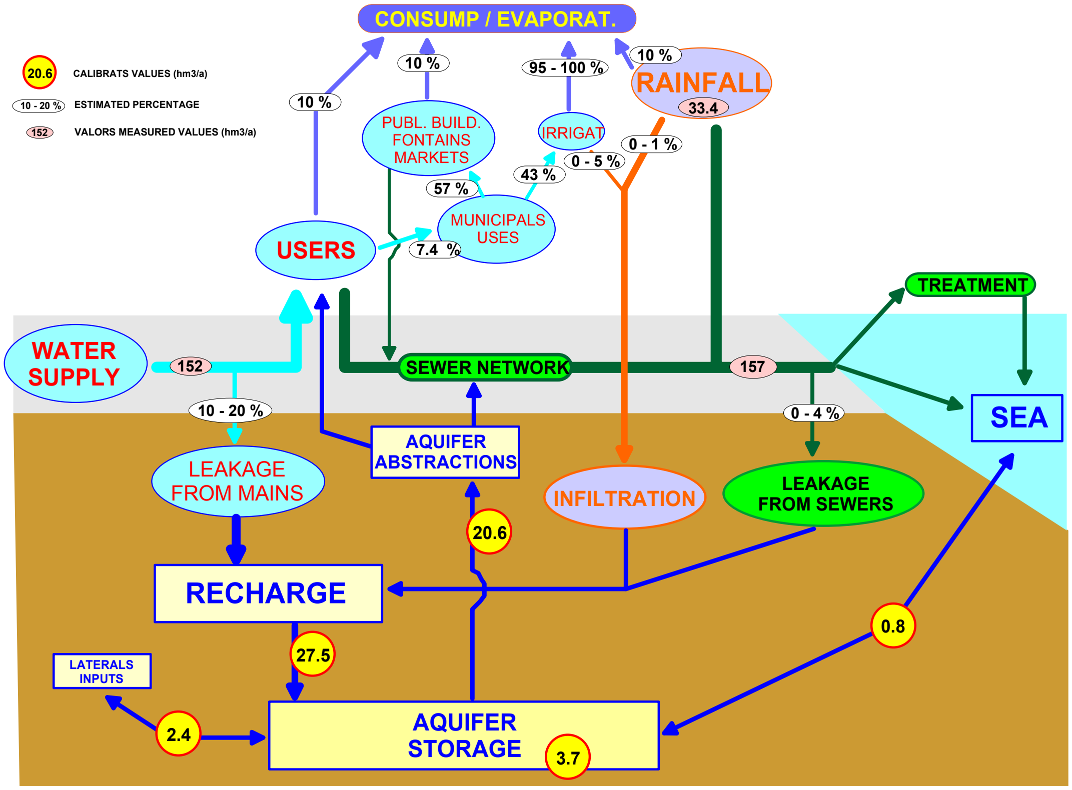

**Figure 1.2.-** Quantification of the terms involved in the urban groundwater balance in Barcelona

### Fluctuation of groundwater levels. Problems with underground structures.

In many European cities, early stages of urbanization were associated to an increase in industrial activity. Industry became an important water consumer, and the proliferation of factories commonly caused a significant decrease in water levels (groundwater mining). Additionally, industries became sources of pollution, due to leak and spills. Evaluating these problems, and developing appropriate methods of protection and remediation, is far from attaining a level of practicality and maturity (Lerner and Tellam, 1992; Harris, 1997; Hooker et al., 1999; Cheney et al., 1999).

Lowering of groundwater levels may produce local and large scale subsidence in recent, normally consolidated sediments. This effect can be caused not only by direct pumping, but also by the construction of underground structures which can act as drains or form barriers against natural flow; thereby decreasing (also increasing) levels locally (Marinos and Kavvadas, 1997). In such cases subsidence is local and can affect service pipes (water, electricity, gas,…) due to differential settlements. Predicting changes in groundwater levels caused by construction, and therefore the potential amount of subsidence, has proven to be a difficult task (Brassington, 1985, Dobie and Newman, 1985; Hurst and Wilkinson, 1985).

Subsidence can also be of regional extent, when it is caused by excess pumping (Larson et al. 2001). This type of subsidence may increase the risk of flooding during storms due to problems of drainage (e.g. Venice). In coastal areas this may also produce beach retreat, that can be mistaken for enhanced coastal erosion (Custodio, 1997). Compaction of relatively shallow formations threatens buildings resting on floating piles and produce differential settlement in buildings due to the inhomogeneity of the underlying soil. Subsidence is mostly irreversible.

Decreasing water levels can also threaten buildings founded with wooden piles. When areas of the surface of the piles, initially located in the saturated zone, get in contact with air due to dewatering, their degradation rate accelerates greatly, with subsequent building damage (Fookes et al. 1985). Lowering of groundwater level causes particular problems in coastal cities. Depleted water levels can lead to seawater intrusion which brings saline water rich in sulphate, into contact with concrete and metallic foundations and buried structures, thus accelerating corrosion rates.

Late stages of urban development and the decline of industries located in cities often lead to rising groundwater levels (see, for example, the Milan case study, Bonomi and Cavallin, 1997). These simply represent the recovery of head due to reduced pumping, but these rises can also be exacerbated by increases in recharge resulting from losses in the water supply systems, commonly for what has become a densely populated city. Water level rises affect urban structures that were designed in periods when water levels were depressed, and constructed without acknowledging that water levels could some day recover. Many European cities currently suffer this problem which affects subway tunnels, underground parking lots, domestic cellars, and entrenched parts of roads (Vázquez-Suñé et al., 1997; Lerner and Barrett, 1996; Riemann, 1997; among others). It is also important to note that, conversely, and as explained before, urban structures can themselves affect groundwater flow, by acting as impermeable barriers (Marinos and Kavvadas, 1997).

The main consequences of water level rise are the progressive flooding of underground spaces and excavations, the added costs to any new excavation (as inflow water must be pumped out of the excavation site), and the reduced capacity of drainage systems to deal with storms, as even in dry periods the drainage system has to be used in part to evacuate all the seepage water (Johnson, 1994). In addition, underground structures such as tunnels, cellars, parking lots, sewers and building foundations can also be seriously affected, mainly related to seepage problems and uplift on structures (Hurst and Wilkinson, 1985; Brassington and Rushton, 1987).

The literature reports several case studies concerning the interaction between tunnels and underground constructions and the surrounding environments. Regarding groundwater, however, these are related to inflows that cause technical construction problems (Marinos and Kavvadas, 1998; Kavvadas et al. 1996; Cesano and Olofsson, 1997). Tunnellers are well aware of these. Unfortunately the related environmental problems are not considered nearly as often.

Groundwater levels in Barcelona have followed the evolutionary trend typically expected in a mature industrial city. Abstraction of water for industrial use began in the early 20th century and increased to reach a maximum of 60 –70 millions m$^3$ per year by the early 1970's. Drawdowns in different parts of the city ranged from a few meters to more than 15 m in several areas. Pumping was severely reduced following the late

1970's due to groundwater contamination and the departure of industry. Today, water levels have, for the most part, almost recovered to levels recorded a century ago (Vázquez-Suñe et al., 1997).

An important portion of the subway system and many buildings were built during the period 1950 – 1975, coinciding with the period of maximum water level depletion. At that time, neither designers nor constructors were aware that groundwater levels could recover to the past levels. As a result, groundwater is causing severe problems at present. The subway system has to pump around 10 -15 million $m^3$ per year to drain the tunnels and, in addition, 5 million $m^3$ per year are pumped from railway tunnels. Underground parkings and buildings with deep foundations are similarly affected, although pumping rates are lower. The situation is not limited to a small area, but rather it is spread throughout the city, particularly near the coast (see Figure 1.3), where the topography is flat and the groundwater levels are close to the surface.

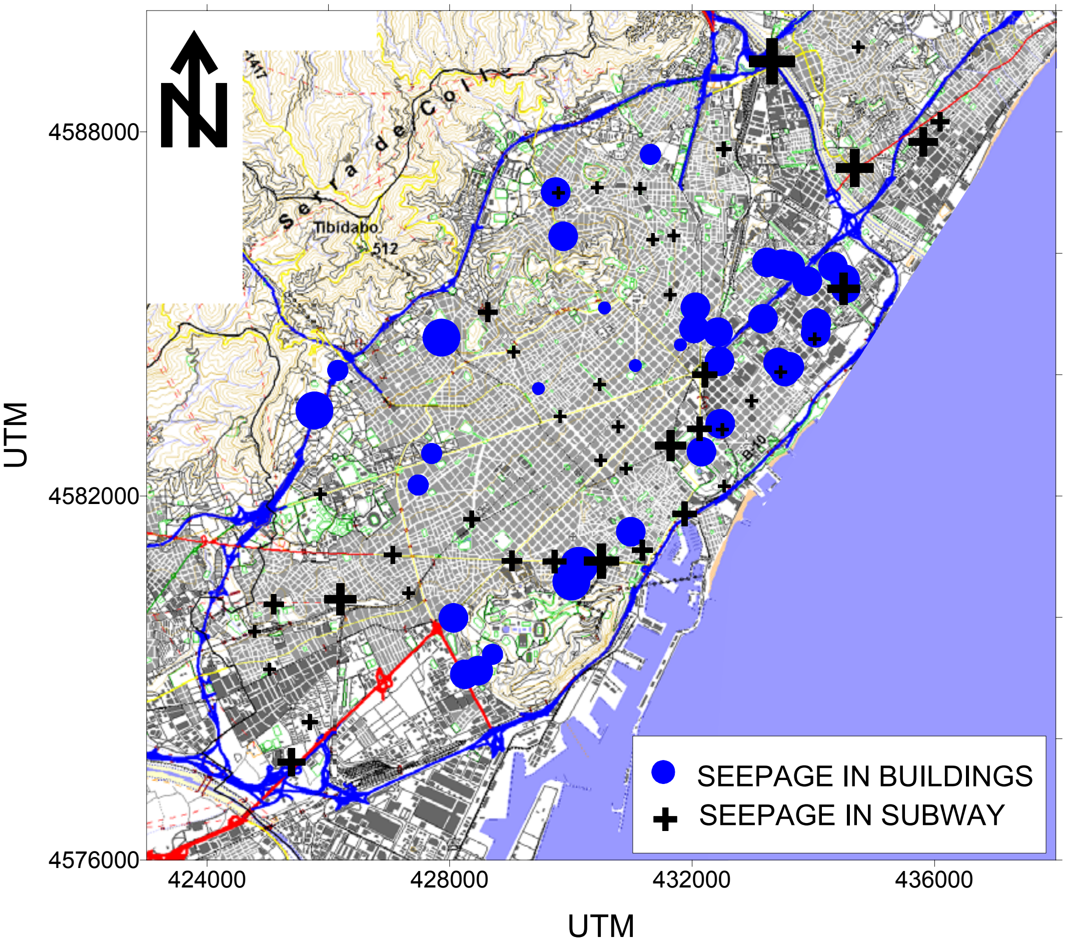

**Figure 1.3.-** Seepage problems in Barcelona city. Symbol size proportional to amount of seepage.

### Urban groundwater contamination

Groundwater contamination has been the focus of significant research efforts over the last two decades. As a result, pollution from point sources is relatively well understood and the same can be said for agricultural distributed sources. The fate of many pollutants is also well known. However, urban environments are unique for several reasons, the most important being the numerous potential sources. Direct sources include leakage from sewers, septic tanks, urban runoff, landfills, storage tanks, simply solid wastes and materials deposited on the ground, gasoline spills, seepage from contaminated rivers, seawater intrusion, fertilizers, pesticides, de-icing products, and lixiviation from rising groundwater levels (see Navarro et al. , 1992, for a case study), among others.

Direct contamination from the sewage system is common in many cities (Eiswirth and Hötzl, 1997, Lawrence et al. 2000, Pitt et al., 1999, Pokarajac, 1999). Figure 1.4 provides an example of sewage contamination beneath a large city in Thailand. Contaminants typically include different compounds of nitrogen, detergents, medical compounds and their metabolites (Heberer and Stan, 1997, Scheytt et al. 1998), caffeine (Seiler et al., 1999), DNA (Sabir et al., 2000), and EDTA (Alder et al., 1990), among others. Unfortunately, quantification of these processes and the estimation of sewage losses at the city scale remain difficult.

Apart from the direct sources, there are also indirect ones. Mixing sewage water (high organic load) with chlorinated supply water may lead to further pollution by toxic chlorinated and recalcitrant compounds. Moreover, changes in groundwater chemistry may also change the chemical conditions under which the pollutants were immobilized (Lawrence et al. 2000), thus mobilizing toxic compounds (typically, heavy metals). Only few results are available regarding the new contaminants that appear as a result of mixing and partial degradation (Hetterschijt et al., 2000).

On the other hand, significant improvements in water quality often occur as a consequence of organic matter oxidation. Much research has been done on understanding degradation processes (Eiswirth and Hötzl, 1997; Gooddy et al., 1997; Lerner et al., 1999; Whitehead et al., 1999; and Lerner and Yang, 2000). However, no safe predictions can yet be made. This is specially severe because organic pollutants degradation is the limiting factor for groundwater exploitation in many cities.

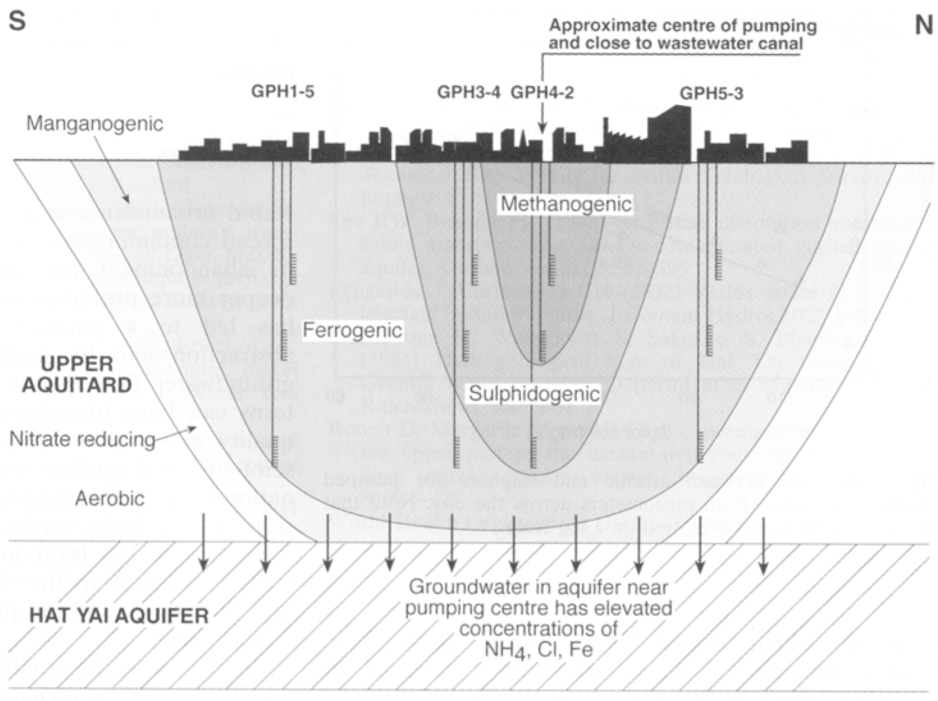

**Figure 1.4.-** Schematic north-south section trough the upper aquitard of Hat Yai, showing redox zones that have developed. (Lawrence et al. 2000).

The three main sources of pollution that have been identified in Barcelona are: losses from the sewer system, infiltration of urban runoff which mobilizes contaminants form the pavement, particularly in light rains or in the initial period of heavy rains, and seawater intrusion. Regarding seawater intrusion, its significance has been related to groundwater level change which, in turn, can be directly correlated with the industrial development of the city. In the eastern part of the city (Besós river delta) seawater intrusion was detected as far as 2 km inland during the 1970’s. The recovery of groundwater levels has reversed the direction of flow and some of the wells that were highly saline now exhibit values of electrical conductivity that are comparable to those found in the 1950’s (see Figure 1.5).

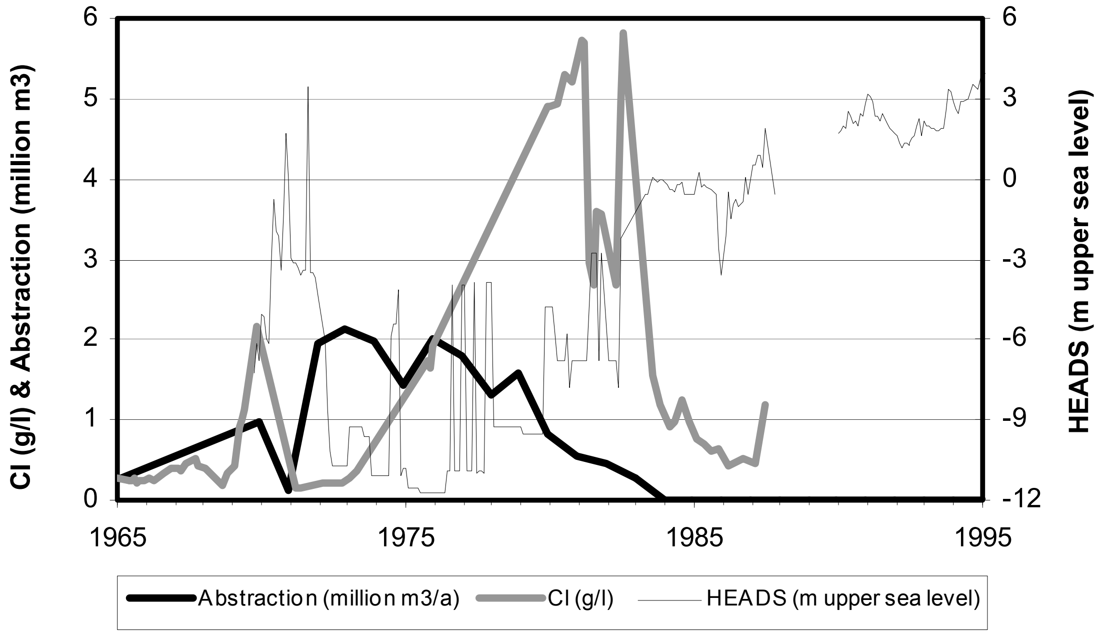

**Figure 1.5.-** Groundwater level and hydrochemical evolution related to abstraction in Montsolis well, Besós aquifer, Barcelona

## 1.3 DISCUSSION: SUSTAINABLE GROUNDWATER MANAGEMENT

As with other issues, groundwater management in urban areas is not essentially different from that in rural areas. It involves pumping permits, definition of allowed uses, delineation of protection areas, identification of polluters, monitoring, etc. Actual implementation of management strategies is very sensitive to the status of the country and the city sources of water. Traditionally, little attention has been paid to groundwater by city managers, unless it was used for supply.

This situation may be changing because of the emergence of sustainability as a concept for guiding decision making. Sustainable management calls for using resources in a manner that does not compromise their use by future generations. This applies both to water as a resource (one should protect water resources quantity and quality) and to the city as a unit (whenever possibly and sensible, one should rely on local resources). In practice, the concept has evolved towards sensible decision making. When analysing sustainability of the city, this implies recognizing groundwater as a resource that needs to be protected and that can be used.

Traditionally, a zero level groundwater management was applied in many cities, either because of lack of interest or because of practical difficulties. This was the case in cities where most of the extractions come from unregulated private wells, which is a common situation in major cities in southern Asia (Foster et al. 1999). An intermediate level of management would be to impose the restriction in activities using aquifer vulnerability concepts (Morris et al., 1997). Again, urban areas display particularities with respect to rural systems due the interactions between groundwater and anthropogenic activities (Scharp et al. 1997; Johansson et al., 1999; Aller et al., 1987; Zaporozec and Eaton, 1996).

A next step would be the creation of a full groundwater and solute transport model of the city. This type of models account for a full groundwater balance of the system, with the quantification of the main terms contributing to recharge and discharge from the system. These models can be used to test possible scenarios of aquifer exploitation and/or pollution related problems. In fact, the process of model building requires making an effort towards overall understanding, which may pay off in subsequent steps.

Sustainable groundwater management calls for understanding urban the water cycle by (someone close to) decision makers. This is needed for:

Restricting dangerous activities in sensitive areas

Protecting natural waters (e.g., deep aquifers), including actions oriented to prevent their mixing with contaminated water.

Promoting the use of lesser quality groundwater for secondary distribution network

In general, taking into account groundwater when dealing with underground issues (subway constructions, excavation permits, etc.).

Some of these objectives can be achieved through maps (e.g., areas where gas stations are forbidden) or even dynamic models (e.g., likely evolution of depth to groundwater in a given area). However, long-term effectiveness require a continued follow-up. In practice, large cities may require in-house expertise and a person responsible for groundwater related issues. Realistically, this can only be achieved if politicians become committed.

Sustainable management requires fully integrated model, incorporating integrated water management to city planning comprehensive models. Models should deal with water resources global optimisation criteria, looking for policies that would allow saving and reutilization of water or focus on the determination of certain bodies of water as new resources, while at the same time deal with the potential problems of using (subsidence, saltwater intrusion) or non using (floodings, seepage into buildings, …) groundwater as a resource. This should be posted in economical terms including social, political and environmental costs. The models described require a number of tools which are capable of storing, integrating and managing a huge volume of spatially referenced data, allowing for a fast treatment of all the information in the modelled area (e.g. Geographical Information System, Watkins et al., 1996). While such a fully integrated approach is as yet undefined, an example of where things may be heading is provided by Rotterdam (Figure 1.6).

In Barcelona, groundwater is becoming an issue governing decision making. Specific groundwater studies have been made for the new tunnels (road, subway and railways), a secondary distribution network is being developed (see Figure 1.7), etc. As part of these efforts, the groundwater model (Vázquez et al, 1997) continues to be used for evaluating the evolution of groundwater levels and the impact of pumping for the secondary network. In fact, the focus is shifting to a commercial issue: how to sell all the lesser-quality pumped water.

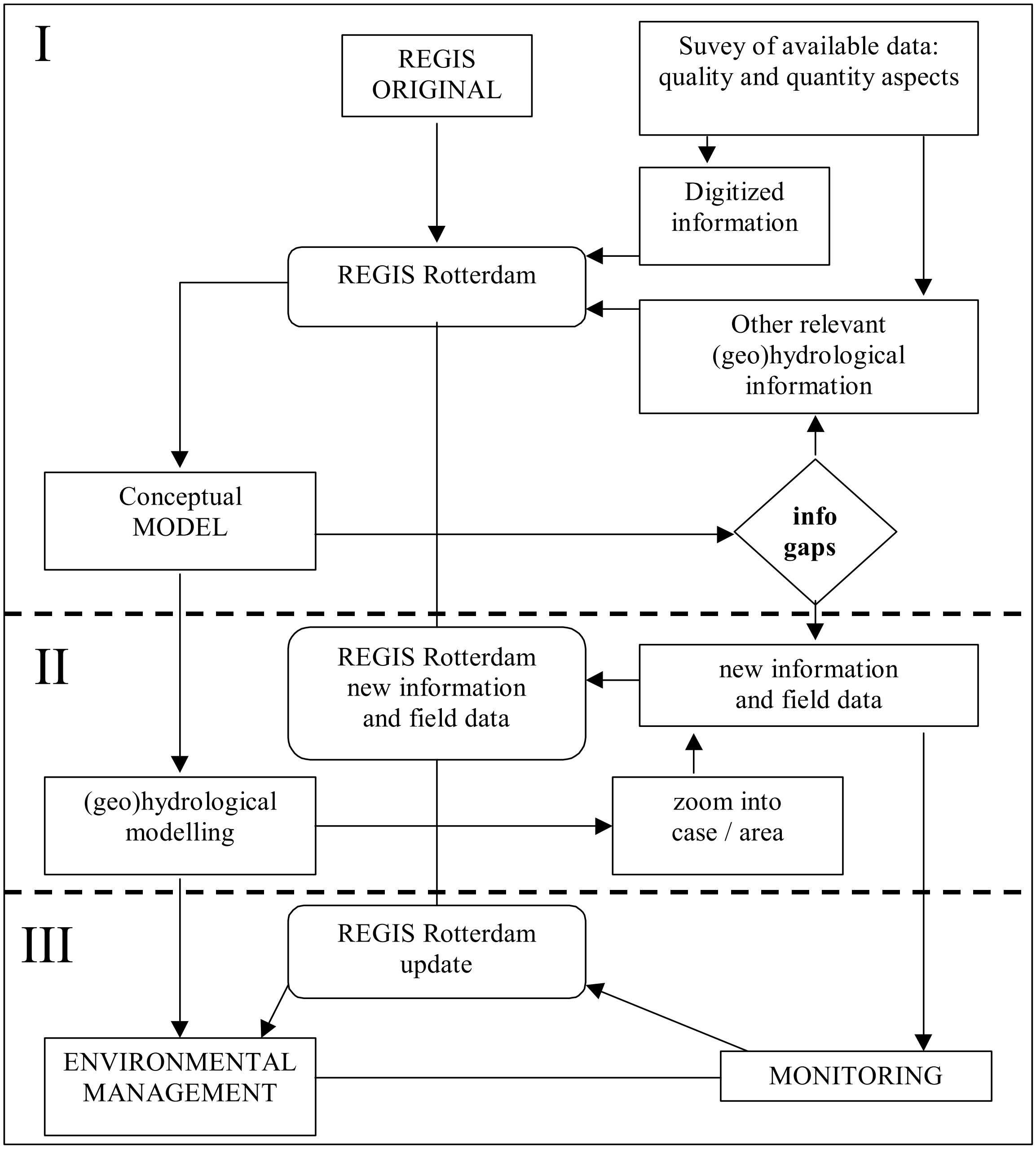

**Figure 1.6.-** Project management scheme in Rotterdam. (Molenaar et al., 1997).

**Figure 1.7.-** Groundwater use for park irrigation in Barcelona

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## 1.4 SUMMARY AND CONCLUSIONS

The high demand for water, the deterioration of drinking water quality, and the general hydrological problem of discrepancy in time and/or space between need and availability of water are common problems to most cities throughout the world. A more efficient and ecological use of the water resources is seriously needed.

Some important issues regarding groundwater flow in urban areas have been identified. Development in urban areas significantly changes the hydrogeological cycle. In turn these changes can cause serious social, economic and environmental impacts. Hence, urban groundwater has emerged in recent years as an important, specialised area within hydrogeology.

In this paper, the main issues of concern in an urban groundwater study have been reviewed. These include both quantity and quality issues.

Developing conceptual models for any aquifer requires a good understanding of water fluxes. This includes evaluating the most important components of recharge and discharge. Evaluating recharge in urban environments is methodologically different from that in natural systems for two reasons: first, less experience is available for estimating some of the components and second, different sources are involved. A full account of the whole water balance requires not only overall computations of recharge, but also direct measurements or indirect estimates of flux for each source component.

Flow and transport models can be used for data integration. Therefore, they help understanding urban groundwater. Moreover, they are quantitative and allow one to predict changes in groundwater levels and the resulting water quality implications. That is, they can help decision making.

A singular feature of groundwater in cities is the presence of underground structures that interact with groundwater. This relationship is two ways. On one hand, they disrupt the natural groundwater flow and affect quality. On the other, the structure can be damaged by seepage. In the latter case, the nature of damage may depend on groundwater quality and whether levels are rising or falling.

Groundwater contamination in urban environments is another major issue and is complicated by the large number of potential sources of contamination, and the numerous, distinct contaminants that can be found in a city. Groundwater protection is largely based on empirical rules and there is a need for early warning indicators of impeding contamination.

Urban groundwater protection requires an integrated framework that involves the use of groundwater models that could be understood by decision-makers. Management models must be based on specific criteria that would allow defining, characterising and quantifying the potential risk to aquifers and the natural systems associated with them, as well as on urban structures and the local population. In this sense there is a need to incorporate social and political factors into urban hydrology studies. This would encourage city managers to recognise groundwater as a key component in the city planning process.

Increasing social pressure on city managers to advance towards sustainability will help promoting the recognition of groundwater as an important resource in cities. Therefore, one should expect this field to continue growing.

# CHAPTER 2. RISING. GROUNDWATER LEVELS IN BARCELONA: EVOLUTION ON URBAN STRUCTURES

## 2.1 INTRODUCTION AND PRESENT GROUNDWATER SITUATION

Barcelona is located in north-eastern Spain, between a mountain range named Serra de Collcerola and the Mediterranean Sea (see Figure 2.1), both boundaries running approximately in the NNE-SSW direction. The other boundaries are two rivers, Llobregat and Besós, which form a simple rectangular shape with a slight slope going from the mountain range to the sea. Some hills break this slope, the main one being Montjuic, near the sea. Other hills are located near the mountain range, forming local steep slopes that give rise to some streams, although most of them are presently urbanised.

In the subsurface of Barcelona we can separate different aquifers which can be characterised by their geological age. A schematic representation of the aquifers can be seen in Figure 2.1.

The Palaeozoic aquifer is composed of shales and granites. Catchments in this aquifer are located in the topographic highs of the city and production is from both wells and mines. Quaternary aquifers can be found in the rest of the city; in topographic low areas, they correspond to the alluvial and deltaic sediments of the Llobregat and Besós rivers; in intermediate areas, they correspond to piedmont cones and to coarse alluvial sediments.

Since the middle of the XIXth Century, the aquifers underneath Barcelona have been supporting heavy water extraction, particularly the two deltaic aquifers, where production is highest due to the large transmissivity values associated with the alluvial material. Historically this extraction produced very large drawdowns, leading to groundwater levels below the sea at certain points, with the associated impacts on the chemical quality of the water due to seawater intrusion. Since the 1970's, urban pressures have caused many industries to migrate from the city to other areas. This resulted in a decrease in total extraction and a progressive recovery in the groundwater levels.

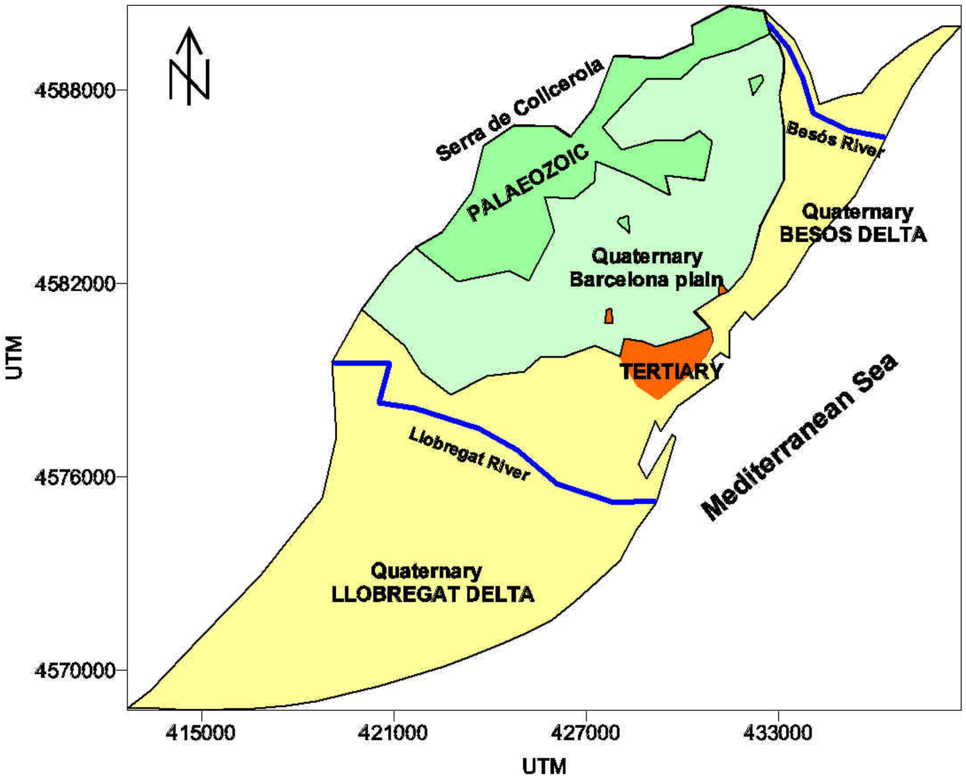


**Figure 2.1.-** Hydrogeological scheme of Barcelona area.

During the last few years, the continuous rise in the groundwater levels has become a serious threat to some underground urban structures. In the last 30 years, rises from 1 to 10 m in the water table have been observed in certain areas. Many urban structures were designed and constructed at times of minimum water levels, and the possibility of water reaching the structure level was never considered. The rise in groundwater levels has produced increasing seepage in into public and private structures, such as the metropolitan subway, sewage network, and underground parking areas. The total amount of water that is currently being pumped from the metropolitan subway is about 12 million m$^3$/year. The problem is not restricted to a few points, but is quite general (see Figure 2.2).

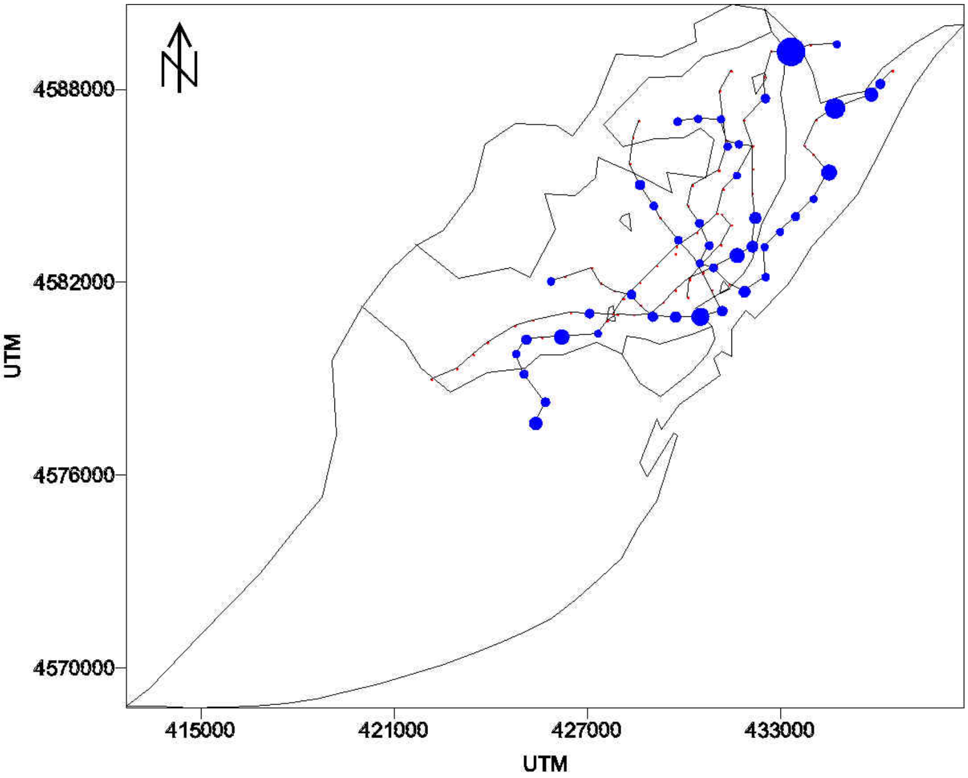


**Figure 2. 2.-** Location of seepage problems in the subway system. Size points are proportional to seepage.

The effects upon urban underground structures is also spread throughout the city. Figure 2.3 is a map of the depth from the surface to the water level. This map has been obtained by subtracting the piezometric map corresponding to December 1996 from the topography. The piezometric map was obtained by interpolation from more than 30 piezometer data values. We see that in a large area of the city, the depth to the water level is less than 6 m, which corresponds to two underground car park floors. This figure demonstrates the extent of the impact on underground structures throughout the city.

The economic impact of maintaining these structures under the new groundwater conditions is very high. To the need for drainage works, such as impermeabilisation, installation of pumps, and pipes for the seepage water, must be added the energy cost of continuously pumping rather high flows. It is important to further note that the use of the city sewage system for evacuating all the seepage water is not a very good solution, as it can affect the proper functioning of the system during periods of critical need, such as summer storms.

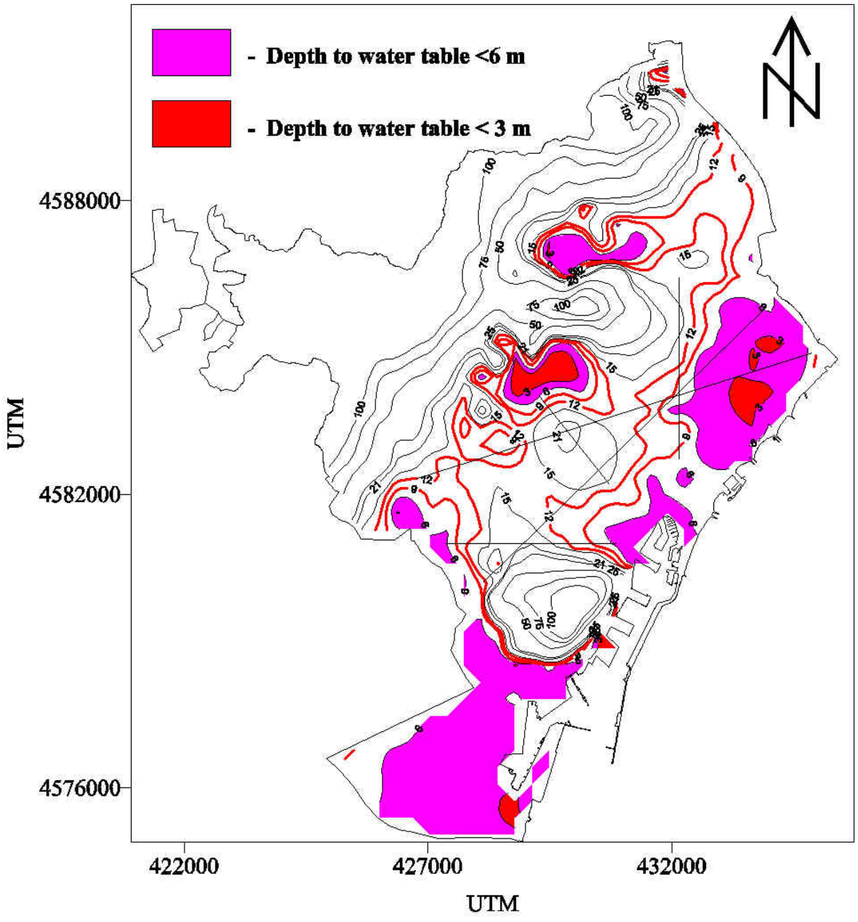


**Figure 2.3.-** Depth to groundwater table in December 1996 (in meters).

## 2.2 URBAN HYDROLOGICAL BALANCE

A good knowledge of urban hydrology requires a detailed analysis of the water flows: their magnitude, relative importance, and dependence upon hydrological parameters (Lerner, 1990). The analysis must consider both the quantity and the quality of the water, from the moment the water enters the system (by precipitation or by direct import from other zones), to when it leaves (by runoff, evaporation, extraction). To complete the full hydrological cycle a lot of data are needed, which includes climatology, flows in the supply and sewage system, and outflow to the sea. The conceptual scheme of the groundwater balance in Barcelona is shown in Figure 2.4.

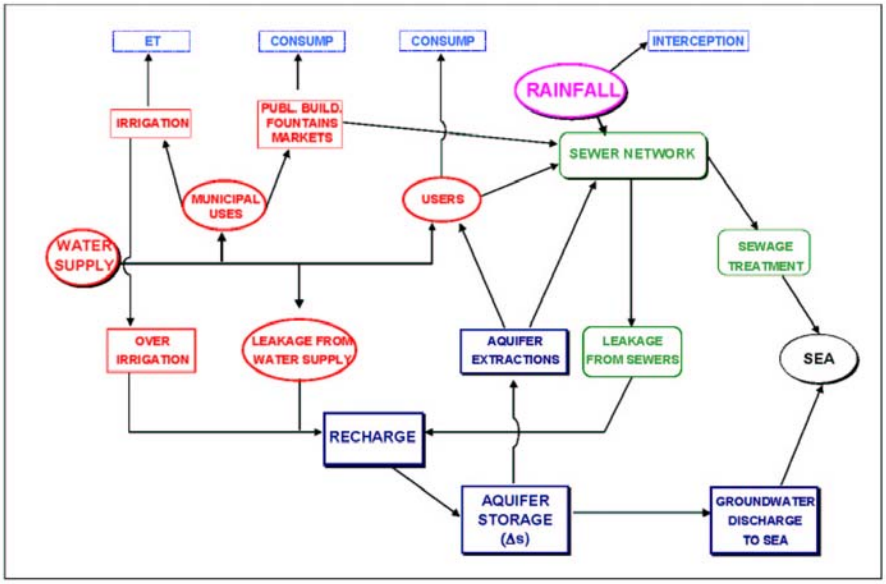


**Figure 2.4.-** Conceptualisation of urban hydrogeological cycle in Barcelona.

The overall balance is divided into two sub-balances. The first one corresponds to water in the supply plus sewage networks; the second is a proper groundwater balance. To evaluate the different terms in the balance we needed some historical data, provided by the local supply and sewage companies and the local authorities.

We have established an annual balance for the period 1965-95. Some of the missing data have been obtained by interpolations or extrapolations. This causes some uncertainty in the closure of the balance.

The different terms taking part in the balance are briefly described and quantified next:

### Water supply system

There are two basic numbers that are known with a very small error: The total volume of water supplied to the distribution system, and the amount of water actually used by the consumers. The difference are losses in the network, which are an input to the water balance system. During the period 1965-95, both the total supply volume and the computed factor of losses (ratio between losses and total supply) have been diminishing with time, mainly due to the progressive modernisation of the network. Figure 2.5 shows the evolution of the total water losses during the study period. This value is the most significant in quantitative terms of the full groundwater balance.

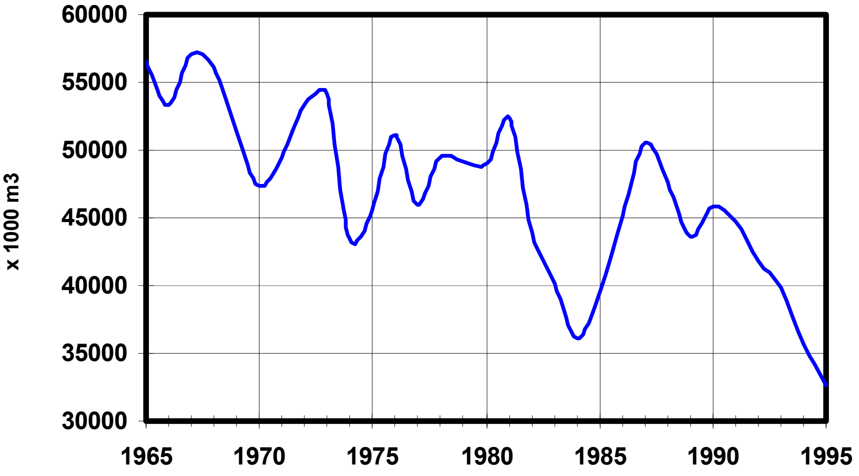


**Figure 2.5.-** Evolution of water losses pertaining to the supply system.

### Rainfall

We used data, from a representative point in the city, corresponding to instantaneous rainfall and outflow rates in the sewage system, measured ¨on line¨. It was found that 85-90% of the rainfall is directly diverted to the sewage system. The remaining 10-15%

can be divided into surface runoff (which is considered negligible for rains with a return period smaller than ten years), surface retention, and infiltration. Surface retention is evaluated from the response to single episodes of rainfall. It is found that rainfall below a threshold of 1 mm produces no changes in the sewage flow rates. This value is adopted as representative of surface retention, accounting for 10% of the total rainfall in an average year. Infiltration is then estimated between 0-5%, with a mean value of 2% (Vázquez-Suñé and Sánchez-Vila, 1997). We do not distinguish infiltration in non-urbanised zones, as urbanisation in the city is very intensive.

**Sewage water**

Water flowing into the sewage network comes from different sources: Rainfall, return from users, return from irrigation, and water coming from the subway or underground constructions. Parés et al. (1985) evaluate the return from users as 90% of the total water supplied to users. This value agrees with the data from Lerner (1990), who estimates a consumption of 20 l/hab/day, which turns out to be around 8% of the water supply in Barcelona. Losses from the sewage system, which is an input in the balance, are estimated about 5% of the total flowing water. The remaining water discharges to the sea.

**Return of irrigation**

This quantity is equal to the difference between the water supplied for irrigation and the actual evapotranspiration (ETR). Data about irrigation rates is supplied by the local authorities. The ETR is assumed equal to the ETP (1000 mm according to Hernández and Vázquez-Suñé, 1995).

**Water mines and subway**

There are a number of ancient water mines draining the Palaeozoic aquifer. The annual volume extracted from these mines is about 1.2 million $m^3$ .

The subway system drained 13.1 million $m^3$ during 1995. This value is difficult to extrapolate to the past, as it is known that seepage to the subway system has increased during the last years, but it is not known in what amount. The water coming from both mines and the subway system goes directly to the sewage system.

**Pumping wells for industrial and private supply purposes**

In the Lower Valley of the Besós River, the amount of groundwater pumped for industrial and private supply purposes during the 60's was as high as 60 million

$m^3$/year. Since the late 70's there has been an increase in urbanisation, and many heavy industries have moved out of the city. The total amount of the water extracted at present from the aquifers is about 5 million $m^3$/year.

**Groundwater discharge to sea**

This term can be computed from Darcy's law. During the study period this value ranged from 2 - 7 million $m^3$/year.

When all the previous values are input into the conceptual balance in Figure 2.4, the storage variation can be estimated. We consider the initial situation to correspond to 1965, although it was already a period where the groundwater levels were below the ones applicable to a steady state case.

In Figure 2.6 we see the evolution of Δs (change of aquifer storage) with time; this gives us an indication of the evolution of global groundwater levels with time. From 1965 to 1975 we see that the levels went down, as the aquifers were still being exploited above their recharge rates. At that time, and due to a world economic crisis, several industries shut down, extraction diminished, and levels started recovering. Around 1987, the late 80s, levels were again at the same situation as in 1965. Finally, during the last 10 years levels have progressively increased from 1 to 10 m depending on the zone.

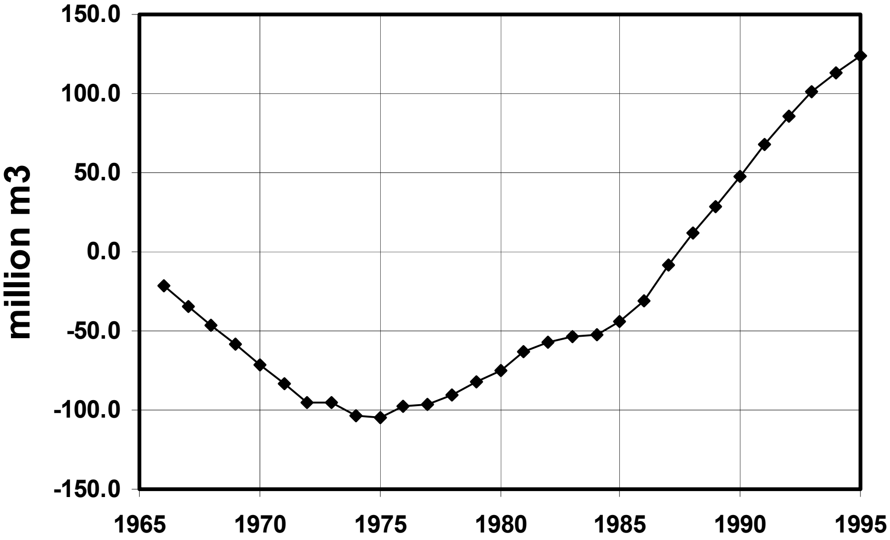


**Figure 2. 6.-** Evolution of water storage during the period 1965-95.

From the balance we conclude that a total of around 40 million $m^3$/year should pumped to keep the present groundwater levels. This figure includes present day rates of industrial pumping and seepage to the subway, in an amount of 20 million $m^3$. The remaining 20 million $m^3$ are causing groundwater levels to rise. Unless additional pumping takes place the situation would get worse in the future. The local authorities should either undertake pumping themselves or allow industries to increase their groundwater consumption by fiscal incentives.

## 2.3 GROUNDWATER QUALITY AND HYDROCHEMISTRY

The first quantitative information about the hydrochemical characteristics of the groundwater flow in Barcelona goes back to 1960. In addition, we have performed two new sampling rounds in 1996, with at least 50 control points from a few private wells and from water seepage into the subway tunnels.

Wells located in the northwest part of the city yield water with low quantities of Cl and Mg, as they are close to the highest recharge zone, where the aquifer comprises metamorphic rocks and granites.

Groundwater from the Barcelona plain shows a zonation, according to Piper classification, from sodium sulphate chloride, near the mountains, to magnesium calcium chloride, close to the sea. The increasing quantity of Ca and Mg is probably due to the interaction with the aquifer materials. Also, over this entire area, high concentrations of $NO_3$ are detected, with values around 100 ppm. We found low $NO_3$ concentrations in the old town area, probably due to two reasons: 1) In the middle of the 80's, a significant part of the sewage system was replaced, thus reducing seepage; 2) The aquifer in that area is less permeable, giving large renewal times, so that denitrification processes can take place.

Groundwater from the Llobregat delta area contains high Cl concentrations, and the relations rMg/rCa and $rCl/rHCO_3$ increase towards the sea, thus indicating seawater intrusion caused by both the high extraction rates, and the recent works that have enlarged the Barcelona Harbour.

In the Besós delta, east of the city, data available suggests that since the 60s there has been a significant seawater intrusion, as a consequence of intensive water extraction due to industrial activities (MOP, 1966; Custodio et al., 1976). In the Poble Nou area, the seawater front intruded as much as 1.5 km from the shore. Water in that area contained 15000 ppm Cl and 36400 μS/cm of Electrical Conductivity. The rMg/rCa ratio had risen up to 5, while the $rCl/rHCO_3$ ratio had surpassed 10.

During the 70's the progressive degradation of groundwater caused by seawater intrusion led to a significant reduction in industrial extraction, and in particular to the closure of some urban water supply wells located 3-4 km from sea. The migration of several industries to other areas outside the city, and the subsequent reduction in water extraction led to a slow recovery of the water quality and the retreat of this intrusion front.

At present, Cl concentrations in the city vary from 500 to 4000 ppm, the ratio rMg/rCl is around 1 - 2, $rCl/rHCO_3$ goes from 2 - 10, and $rSO_4/rCl$ is between 0.2 - 1. All these values confirm the progressive recuperation of groundwater levels and the increase in the amount of water flowing from the aquifers to the sea.

Figure 2.7 shows the evolution in quality, at one well located 3 km inland, related to the total extraction in that area. The well was originally used for supply to the city. We see that between 1970 and 1983 there was a great degradation in the quality, which led to the closure of the well for supply purposes. Since then, extraction in the area has fallen rapidly, and the quality in this and nearby wells has slowly recovered.

Table 2.1 Shows the evolution of Cl and some ionic ratios in another well in the same area and its significant decrease since 1966.

**Table 2. 1.-** Quality evolution in Besós delta aquifer

| "Frigo" well | rMg/rCa | $rCl/rHCO_3$ | Cl (ppm) |
|---|---|---|---|
| 1966 | 1.5 | 20 | 9000 |
| 1980 | 0.75 | 3.8 | 1079 |
| 1996 | 0.61 | 0.58 | 149 |

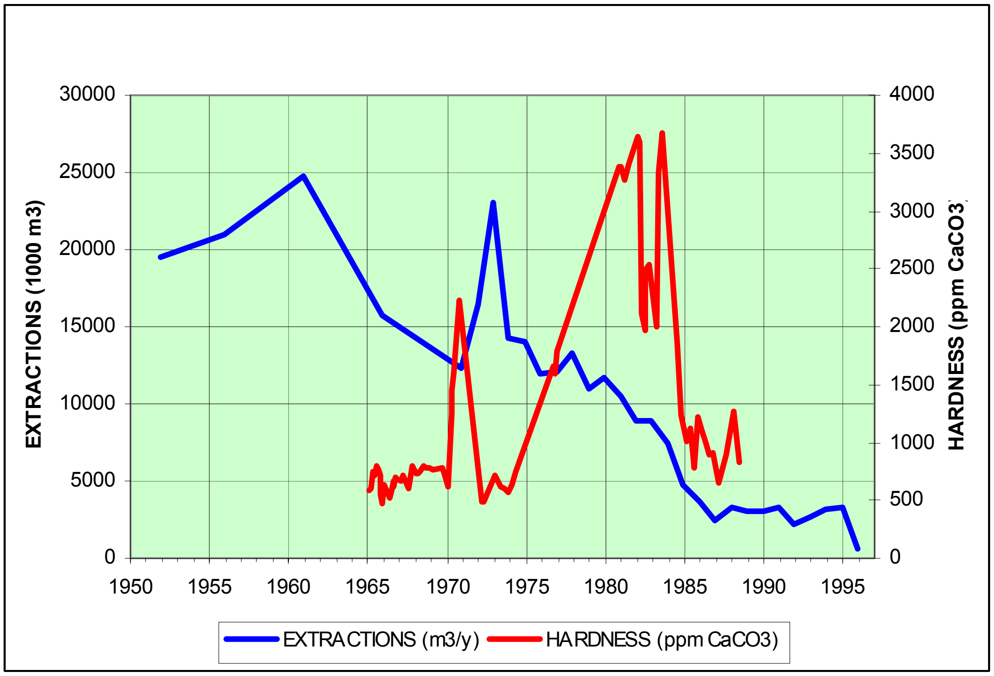


**Figure 2.7.-** Extraction and quality groundwater evolution.

## 2.4 POSSIBLE USES OF GROUNDWATER IN THE CITY

From the previous paragraphs it is clear that the actual rate of extraction is not enough to hold the water levels in their present position. Some additional water should be pumped from the aquifers. It has also been found that this water is, for many uses, of acceptable quality, although it cannot be used for drinking purposes.

The additional water should not be diverted into the sewage system, but could otherwise be put to a number of possible uses in what can be considered as an integrated and rational management of the total hydraulic resources. In this spirit, we consider two possible applications:

Substitute potable water by groundwater, whenever this is possible use within technical and economical constrains. The idea is to use groundwater in all the applications where we do not need to meet the standards of potable water; that is, garden watering, street cleaning, sewage network cleaning, among others. An idea that is currently under consideration is to suply the new areas under construction with a secondary water supply line, with lower quality water (and so, less expensive) to be used in toilets, refrigeration systems, and so on.

Regenerate the Besós river-bed, by supplying an ecologically beneficial, good-quality water, without having to further treat the water.

# CHAPTER 3. GROUNDWATER MODELLING IN URBAN AREAS AS A TOOL FOR LOCAL AUTHORITIES MANAGEMENT. BARCELONA CASE STUDY (SPAIN).

## 3.1 INTRODUCTION

The study of urban groundwater is motivated by the strong interaction between city socioeconomic development and groundwater environmental impacts. Urbanisation clearly affects both availability and quality of groundwater resources. This affection leads to significant social, environmental and economic implications. Problems caused by urbanisation are being faced by many cities worldwide, so that researchers and municipal managers have addressed them, although, in general, treating them separately and not in an integrated framework.

A good knowledge of urban hydrology requires a detailed analysis of water fluxes: their magnitude, relative importance, and dependence upon hydrological parameters. The analysis must consider both the quantity and the quality of water, from the moment it enters the system through rainfall infiltration, river water, or other sources, until it leaves through runoff, evaporation or withdrawal.

In this paper the real case study of Barcelona is addressed. We present first the motivation that has moved the local authorities to consider that a full groundwater study needed to be developed. The study faces three aspects: (1) process identification, including sink/sources characterisation (2) aquifer modelling, including hydrogeological data integration, and (3) water resources management. The work included different steps such as: geological study, hydrogeological conceptualisation, recharge sources, boundary conditions, and global water balance. The final outcome is a groundwater model. We present its main features and an application to city local water management.

## 3.2 GROUNDWATER IN BARCELONA

Barcelona is located in north-eastern Spain, between a mountain range named Serra de Collcerola and the Mediterranean Sea. The city is bounded by two rivers, Besós and Llobregat (Figure 3.1). In Barcelona there are different aquifers, characterised by their geological age. A schematic representation of these aquifers can also be seen in Figure 3.1 (city main streets are plotted for location purposes). The Palaeozoic aquifer is composed of shales and granites. Quaternary aquifers correspond to the alluvial and deltaic sediments of the Llobregat and Besós rivers; in intermediate areas, they correspond to piedmont cones and coarse alluvial sediments.

During the last few years a large increase in seepage into public and private underground structures (the metropolitan subway, sewage network, and underground parking areas) has been observed. As an example, the total amount of water that is currently being pumped from the metropolitan subway is about 12 million m$^3$/year. Furthermore, the seepage problem is not restricted to a few areas, but is quite a general problem throughout the city (see Figure 3.2).

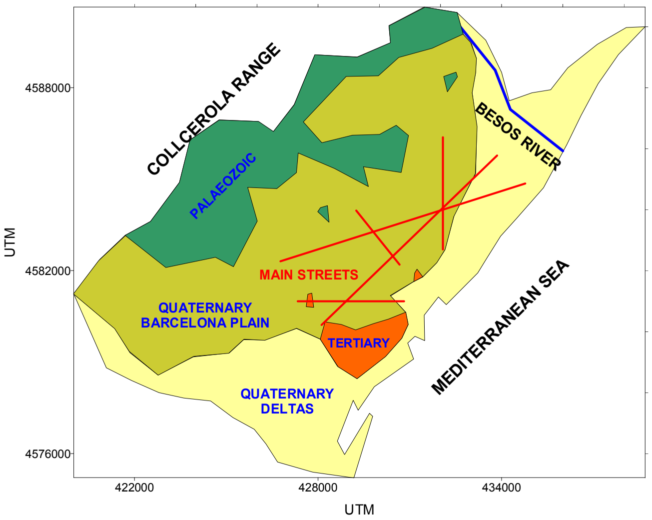


**Figure 3.1.-** Hydrogeological scheme of Barcelona area

On the present groundwater situation, the economic impact of reducing the seepage problems by maintaining groundwater below the structure foundation levels is very high. The impact of maintaining the levels high (no external actions) is also very significant: To the need for drainage works, such as impermeabilisation, pump installation, and water disposal, one must add the energy cost of continuously pumping the rather high flows that have to be evacuated. It is important to further note that the use of the city sewage system for evacuating all the seepage water is not a very good solution, as it can affect the proper functioning of the system during periods of critical need, such as summer storms.

The reason for the high phreatic levels can be understood by historical considerations. Since the middle of the XIXth Century, the aquifers underneath Barcelona have been supporting heavy water withdrawals. This produced very large drawdowns, leading to hydraulic head values below sea level at certain points, with the associated impacts on the chemical quality of the water due to seawater intrusion.

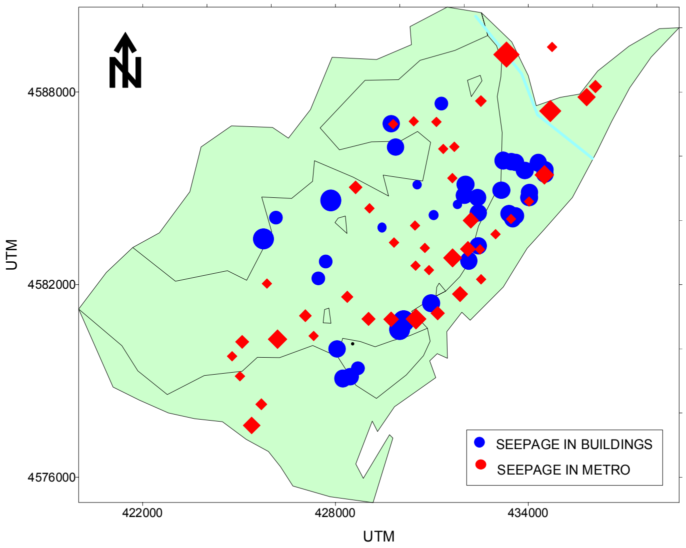


**Figure 3.2.-** Seepage problems in Barcelona. Point sizes are proportional to seepage

Already in this century, and since the 1970's, urban pressure has caused many industries to migrate from the city to other areas. This has resulted in a decrease in total withdrawal and a progressive recovery in the groundwater levels. As a consequence seepage has increased. During the last 30 years, rises from 1 to 10 m in the water table have been observed in certain areas (Figure 3.3).

The continuous rise in the groundwater levels has become a serious threat to some underground urban structures Many of them were designed and constructed at times of minimum water levels, and the possibility of water reaching the structure level was never considered.

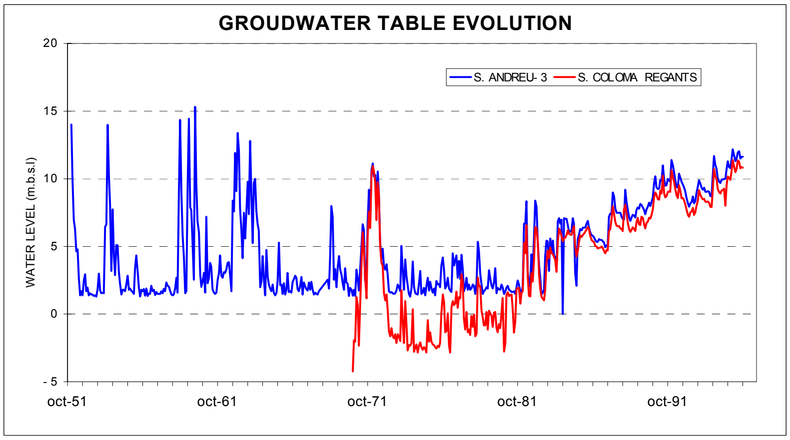


**Figure 3.3.-** Evolution of groundwater table in wells located near the Besós River

## 3.3 FACING THE PROBLEM

The municipal authorities were very interested in knowing the causes for the increasing seepage, what would be the evolution of the problem in the future, and possible solutions. The important volume of groundwater beneath Barcelona offers the possibility of its exploitation and management, which would help controlling the groundwater levels and would become an additional water resource for the city. This exploitation might be included into a global hydraulic resources planning in sustainable conditions. The main idea is the progressive substitution of high quality treated water by less quality water in many municipal uses, such as street cleaning, sewage system cleaning, municipal park and garden watering, and also in some industrial uses, whenever technically and economically possible.

In 1995 the local authorities started a huge plan of groundwater development which included: (1) Quantification of the total amount of groundwater that could be used in sustainable conditions; (2) possible uses for this water; (3) technical projects for new extraction wells; (4) financial viability studies; (5) groundwater management; and (6) development and installation of monitoring systems for hydraulic heads and flow rates.

In order to face these different points a groundwater model of the whole city was built. The model included the reinterpretation of geology in a hydrogeological context, the evolution of heads and extraction rates, a geochemical study, and a quantification of the water balance. This led to the definition of a sound conceptual model (Vázquez-Suñé et al. 1997).

## 3.4 THE GROUNDWATER MODEL

The conceptual model thus obtained was implemented in a numerical model with multiple purposes: integrating different historical data, accounting for the present situation, validating the conceptual model, quantifying groundwater flows (water balance), and finally, being able to predict the future evolution of the groundwater levels under different scenarios. Additionally the integration effort helps reducing uncertainty in the hydraulic parameters. The aim of the numerical model is to be included as a management tool for water decision making in the city of Barcelona.

The initial task in the modelling process was to build a data base which was fed with all available information, including geological, hydraulic head, hydraulic parameter, and quality data from more than 1000 wells and boreholes drilled along the present century.

The next step in the modelling process is discretisation. Spatially, it consists of defining a zonation of the hydraulic parameters based upon geological considerations and available data; a 2-D finite element mesh consisting on 1762 triangular elements is then superimposed. Temporally, the model starts in 1900, with observation times of one year, until 1960, and of three months from then on (until 1997).

An important point to make is the way underground structures are treated in the model. Water inflow is considered a linear relationship between the water level at the aquifer and the foundation level of the structures. In any case the inflow must be null until the time structures were constructed (independently of water level evolution).

Calibration was performed using TRANSIN_III (Galarza et al., 1996). This is a finite element code that allows automatic calibration of the non-linear hydraulic parameters. The calibration process accounted for 414 observation points (where head measures were available). The fit between computed and observed heads (Figure 3.4) is remarkable.

An important outcome of the model is the groundwater balance displayed in Table 3.1. Quantification of the different terms involved in the water balance are critical for two points: a) knowing which are the main points to be stressed when managing the groundwater resources, and b) suggesting corrective measures.

**Table 3.1**: Global water balance for different years (in hm$^3$/year)

| Year | Recharge | Outflow to sea | Lateral inflows | Extractions Wells+others | Extraction Subway | Water Storage |
|---|---|---|---|---|---|---|
| 1960 | 27.6 | -17.2 | 4.1 | 40.2 | 0.04 | 0.4 |
| 1970 | 35.7 | -17.8 | -4.0 | 56.3 | 1.3 | -0.1 |
| 1980 | 36.3 | -7.8 | -3.2 | 42.7 | 2.4 | 2.2 |
| 1990 | 34.6 | -4.2 | -5.2 | 36.4 | 6.0 | 1.7 |
| 1995 | 27.5 | 0.8 | 2.4 | 14.6 | 6.0 | 3.7 |
| 1996 | 27.5 | 2.2 | 4.6 | 9.6 | 7.1 | 3.9 |

Some considerations arise from the water balance presented. The model allows quantifying more precisely urban recharge (see Vàzquez-Suñé and Sánchez-Vila, 1997 for previous estimations). Recharge is conditioned by the losses in the water supply and sewage systems, which account for a very large part of the water entering the aquifers. Additional inflows are excess watering in green zones and direct infiltration of rainfall. Regarding this last one, it has been decreasing due to progressive urbanisation.

Water flowing from/to the sea is important as a potential source of pollution. The excess in groundwater extractions during the 1960's and the corresponding drawdown led to significant seawater intrusion, with loss in water quality. Table 3.1 reflects the relationship between total extractions and seawater intrusion, with a maximum close to 20 hm$^3$/year. From then on, a decrease in water inflow from the sea is observed; as a consequence water has recovered part of its initial chemical quality.

Regarding seepage to the subway system, it seems that some of the water entering the system does not correspond to groundwater seepage, but to leakage in water systems or to surface water infiltration. In any case the problem associated to seepage is still important and it is increasing in time.

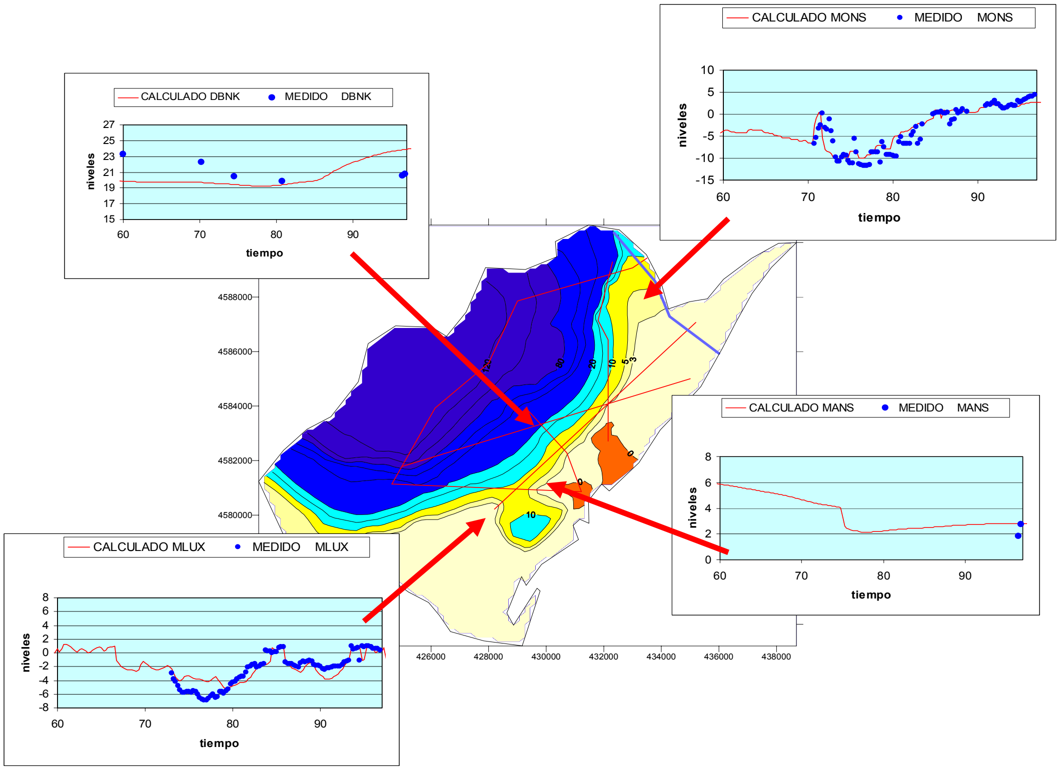


**Figure 3.4.-** Groundwater level fit obtained from calibration at selected locations

The final column in the table is water storage. It is clear that in recent years the net balance is positive, which corresponds to increasing phreatic levels. The minimum historical levels correspond to years 1960-80. This was a time of economic expansion in Barcelona, so that many buildings were built during these two decades. At that time few people could suspect that groundwater levels would ever recover their historical values so that many buildings were constructed without impermeabilisation measures. This is now the main reason for seepage. Notice that in such cases seepage could result in concrete or steel damage, leading to structural failure.

The economic considerations associated to groundwater levels should be included in a management context. The groundwater model can be integrated in this context. We have to distinguish between global and local management. In a global framework, a piezometric observation network has been defined. It consists in a total of 30 measuring points, distributed throughout the city, where heads are measured and water samples are taken for quality analysis periodically. The application of the model to this network helped defining the potential risk areas and, in particular, where to locate a system of wells that could optimally control water level rises if necessary.

In a local framework the model is used to define local actions that use groundwater as an additional resource in selected areas and, mainly, to predict the outcome of such exploitations. An example is presented in the next section.

## 3.5 THE MODEL AS A MANAGEMENT TOOL IN A REAL PROBLEM

The numerical model has recently been used as the managing tool it was designed for in a number of cases. We outline the particular motivation, the different parts involved, how the model was used, the main results, and the political decisions finally taken in one of such cases. The selected case is that of the new Fluvial Park that is being constructed at the Besós River.

Until recent times environmental issues were typically neglected in city planning. At present most big projects in large cities in Spain are trying to recover part of the urban space for the citizens. Following this idea, in Barcelona a project under construction aims at recovering the river-bed of one of the major rivers that marks the city limit. After recovering the chemical quality of the surface water, some grass areas will be planted both in the river-bed and in a nearby urban park. All these areas are planned for leisure purposes. The new area is called the Besós River Fluvial Park and its main importance is that it is located in an area with a large historical deficit in green zones.

We focus here in water management for this new area. A total amount close to 1 $hm^3$/year must be supplied to the area in order to maintain the green areas and an artificial lake. The first idea was to use water from the local drinking water supply system. An alternative is to use groundwater from wells located nearby. Using water from the river was discarded for quality reasons. The final decision was casted in a global management concept where the model presented previously was a key tool.

The different authorities and companies that gave some input to be used in the decision process were: (1) The contractor, who had to provide the installation for whatever alternative was selected; (2) the City Council, who wanted to include this action in the context of using groundwater for non-drinking purposes; (3) the Subway Managing

Company, who is having seepage problems in the subway line that under crosses the Besós River in an amount of 0.8 hm$^3$/year (it is significant to indicate that another alternative considered was to directly use the seepage water from the subway system); (4) the Water Supply Company, with a project for groundwater abstraction, up to 500 L/s, in the Sant Andreu wells; these wells were used for supplying purposes until 1980, and then abandoned due to the decrease in water quality; and (5) private people who are having problems with seepage in several underground parking areas in the zone.

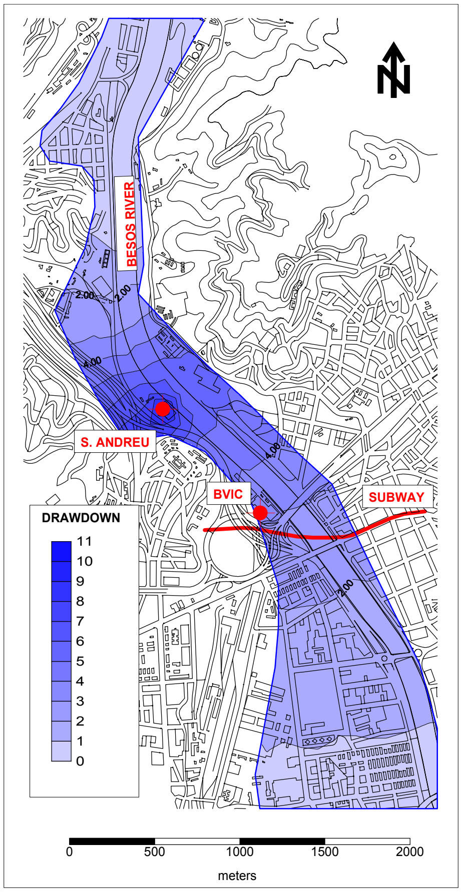


**Figure 3.5.-** Calculated drawdowns

The numerical model presented previously was used to analyse a number of pumping scenarios. The main scenario studied was the compatibility of pumping 15 hm$^3$/year in the Sant Andreu wells plus 1 hm$^3$/year in an abstraction well located beside the Baró de Viver (BVIC) subway station (see Figure 3.5). Compatibility is measured in terms of admissible drawdowns. As an outcome from the model we could further obtain the effect of pumping upon the groundwater levels along the subway line.

The effects on the groundwater levels can be seen in Figure 3.5, where equal drawdown lines are plotted. Maximum drawdowns are located near the Sant Andreu wells, as expected. The effects along the subway line are quite significant, as phreatic levels show a decrease around 2.9 m in the right margin and around 2.3 m in the left margin. This results in an important decrease in seepage which is now reduced to around 0.3 $hm^3$/year; furthermore, the length of the area affected by seepage gets reduced in 200 m.

These results helped in the decision making, as finally the City Council decided to implement the fully groundwater option, as it was technically feasible, economically competitive and was of some benefit to the Subway Managing Company and to the city in general, because the pressure on good quality water decreased.

This is not the only case the model has been applied for decision taking process. Recently there was another experience to use groundwater for watering the Botanic Garden, located in Montjuic (the Olympic Mountain). Water will be abstracted from the City Plain, carried inside the subway tunnels and pumped up to the mountain. The model was used in this case to evaluate the amount of water that could be abstracted with acceptable drawdowns.

## 3.6 DISCUSSION

The study of urban groundwater is motivated by the strong interaction between city socioeconomic development and groundwater environmental impacts. This interaction is generally neglected in real cases. A global analysis of the impact of groundwater in a city must include both aquifer characterisation (done by hydrogeologists), water resources management (public or private companies), and city planning (politics).

An integrated framework involves the use of groundwater models that could be understood by decision makers. Models of this type must be based on certain criteria that would allow defining, characterising and quantifying the potential risk of aquifers and natural systems associated to them, as well as on urban structures, with all the implications to the population. This should allow city managers to consider groundwater as one of the topics to be taken into account in city planning. In this context, water can be considered either as an alternative resource (for park irrigation, street cleaning, secondary distribution networks, water supply, etc.), or as a nuisance (protection of existing structures, precautions and/or permissions for future developments).

# CHAPTER 4. THE USE OF TRACERS IN URBAN HYDROGEOLOGY

## 4.1 INTRODUCTION

Hydrogeological studies in urban areas are motivated by the strong interaction between groundwater and the socio-economical development of the cities. In fact, groundwater problems have proven to be very similar in many cities all over the world (Chilton et al. 1997, 1999; Ellis, 1999). Progressive (and in some cases accelerated) urbanization affects not only availability of water, but also quality. While groundwater flow in urban areas is not essentially different from that elsewhere, abundance of water sources makes its study difficult. This is why it is so important to identify the different sources of recharge (Barrett et al. 1999, Yang et al. 1999).

The use of a single tracer makes it difficult to achieve conclusions on the water balance of an area. Usually several tracers need to be used in a combined way in order to avoid possible overlaps in its concentration in the potential recharge sources. The use of these tracers can ease the identification of different sources, only if their concentration or isotopic content are sufficiently characteristic. Only those chemical species, present in certain sources and whose concentration or relationship of two specific ions is characteristic, will be useful. For instance, the import of supply water to a city with isotopic and chemical characteristics different from local groundwater can allow identifying and quantifying recharge due to losses in the supply system.

Potential recharge sources common in many urban areas include urban surface run-off water, losses in the draining system, losses in the drinking water supply system, the interaction of aquifers with surface water masses such as rivers, lakes, the sea, etc. Selection of chemical species will be conditioned by potential sources of recharge.

Chemical species can be used to indicate the origin of the recharge water, but not to quantify it. Moreover degradation, sorption, fractioning or other mass transfer processes between solid and water often prevent their use as “conservative” tracers.

Some chemical species, documented as good indicators of the different recharge sources in urban areas are indicated below. Some of them can be used to quantify the contributions of the above sources.

The aim of this paper is to present a synthesis of worldwide experiences on the use of chemical and isotopic tracers to identify urban recharge sources. Several base cases, extracted from the references and in which these tracers have been or could be actually used in urban areas, are analysed. Special emphasis has been placed on the applied aspects and existing limitations, as wells as in the most significant aspects of their use.

## 4.2 MAJOR IONS

### Halogens

Chloride ($Cl^-$) is one of the major ions in the composition of groundwater. It is considered as an ideal tracer due to its abundance, high solubility, stability and because it almost does not interact with the soil.

Concentration of $Cl^-$ in freshwater ranges from 10 to 250 mg/L, while sea water ranges from 18000 to 21000 mg/L, depending on the site. This tracer facilitates identifying aquifers affected by sea water intrusion.

Chloride is also a good indicator of the presence of sewage because human activity increase Cl- concentration in approximately 200 mg/L. In many cases, increases in the concentrations of Cl, $SO_4$ and $NO_3$ are related to recharge caused by losses in sewage systems (Carrera, 1997).

Bromide ($Br^-$) and iodide ($I^-$), and to a lesser degree fluoride ($F^-$), have a similar behaviour to that of chloride; although they are found at much smaller concentrations. They show characteristic concentrations in sea water and sewage. They were used as ideal tracers in many cases, especially bromide (Davis et al., 1998, Laukonen et al., 2000). Sometimes, it is the ratio of one ion to another, rather than concentration itself, what allows best to identify the source of water. For example, as shown in table 4.1, the Cl- to Br- ratio can help in identifying the source of recharge (Davis et al., 1998; Venglosh and Pankratov 1998; Custodio and Herrera, 2000).

**Table 4.1:** Usual intervals in Cl/Br ratios, depending on the water origin (Carrera, 1997).

| Water origin | Cl/Br interval |
|---|---|
| Superficial run-off | 9-90 |
| Urban sewage | 250-520 |
| Halite brine | 2000-4000 |
| Non-altered granite water | 100-150 |
| Alluvial granite aquifer water | 90-180 |
| Rainwater | 30-200 |
| Sea water | 290 |

### Sulphate

Sulphate ($SO^{2-}_4$) is one of the most mobile anions in subsoil. It rarely suffers any sorption, but when anions can be sorbed (e.g., low pH) the order of preference in anion absorption is, as stated by (Beek et al., 1978), as follows:

$SO^{2-}_4 > NO^-_3 > Cl^-$

Sea water contains high concentrations of sulphates reaching values close to 3000 mg/L. Groundwater concentration in the areas where there are not many minerals containing sulphur, ranges 60-70 mg/L, (Härig, 1991, Kerndorff et al., 1985), mostly from atmospheric origin. In areas rich in gypsum or anhydrite, groundwater can contain up to 1500 mg/L of sulphate (Otero y Soler, 2002).

Concentration of sulphate in sewage normally ranges from 100 to 300 mg/L. In order to use sulphate as a sewage indicator the natural cycle of sulphur should be taken into account, as well as the variations due to anthropogenic effects.

**Table 4.2:** Sources of Sulphur in domestic sewage (Koppe & Stozek, 1993):

| Origin | Total sulphur [g · person$^{-1}$ · day$^{-1}$] | Increase in total sulphur [mg/L]* |
|---|---|---|
| Urine | 1,3 | 6,5 |
| Dregs | 0,2 | 1,0 |
| Washing machine | 3,5 | 17,5 |
| Cooking waste | 0,2 | 1,0 |
| TOTAL | 5,2 | 26,0 |

* Considering that the water use is of 200 L · person$^{-1}$ · day$^{-1}$.

Anthropogenic sources of sulphur are listed in Table 4.2. The fact that sulphur compounds tend to easily oxidate to sulphates implies an increase in the concentration of sulphates in some 78 mg/L, with respect to that of supply water.

Some local increases of sulphate in groundwater could be a consequence of often circumstances, such as the dissolution of gypsum in landfills, the use of sulphates for agriculture manure or of gypsum for the rehabilitation of salinised soils (exchange of soil-fixed sodium for calcium present in gypsum $CaSO_4 \cdot 2H_2O$).

The oxidation of pyrite ($FeS_2$) or other sulphides can also increase the concentration of sulphate in water. This process, in nitrate-polluted aquifers, could be due to the chemical denitrification in which sulphate is released (Kölle, 1988):

$$14\ NO_3^- + 5\ FeS_2 + 4\ H^+ \rightarrow 7N_2 + 10\ SO_4^{2-} + 5\ Fe^{2+} + 2\ H_2O$$

On the other hand, due to the antropic activity there is an imbalance regarding the natural cycle of sulphur which shows a net transfer of sulphur from shore to sea through the atmosphere (Stumm & Morgan, 1995). The release of $SO_2$ coming from the combustion of fossil combustibles causes sulphur to increase in the atmosphere and thus in the wet or dry atmospheric deposition, that is a widespread increase of sulphur. In polluted areas, the concentration of sulphate in rainwater is of 30-100 mg/L and reaches peak values of 450 mg/L. The mean concentration in rainwater in Central Europe is of 3 mg/L of sulphate (Kerndorff et al., 1985).

Under reducing conditions (for instance in sewage or landfill lixiviates) there could be a biological reduction in sulphate.

Furthermore, as discussed later, the isotopic geochemistry of sulphur and oxygen from dissolved sulphate allows determining if the sulphate dissolved in water comes from the oxidation of sulphurs (Toran & Harris, 1989; Manzano et al., 2001), as well as the existence of sulphate-reduction processes (Krouse, 1980 y Van Stempvoort, D.R. y Krouse, H.R. 1994).

### Nitrogen

Nitrogen in urban groundwater suggests the existence of domestic sewage recharge. Nitrate has traditionally been used as an indicator of human or animal pollution. However, a quantitative use is difficult because nitrate is not conservative. It is possible that sewage contain lots of nitrogen in an ammonium form, but it can be oxidized to become nitrate. On the other hand, nitrate concentrations can decrease due to reduction if water contains high concentration of dissolved organic carbon (DOC).

Nitrogen in water can appear in different compounds such as nitrates ($NO_3$), ammonium ($NH_4$) and nitrites ($NO_2$). The dominant species depends on redox conditions. The transformation processes of nitrogen compounds, such as denitrification and ammonium volatilization, cause nitrogen losses to gas form and thus the mass balance is not conservative. Still, this can be neglected, and total nitrogen is treated as a nearby conservative tracer

The isotopic geochemistry of nitrogen of $NH_4^+$, $NO_3^-$, $NO_2$ and of oxygen of $NO_3^-$ and $NO_2$ allows revealing and quantifying not only denitrification processes (Heaton, 1986) but also validating their conservative character (Vitoria et al., 2002).

## 4.3 OTHER IONS

### Boron

Natural concentration of boron in groundwater and rainwater usually ranges between 0,02 and 0,1 mg/L (Custodio y Llamas, 1983). Boron is used for manufacturing glass, porcelain, carpets, cosmetics, manures, photographic products, when treating leather and in metal soldering and tempering. It is massively employed as sodium perborate in detergents to whitewash. Thus Boron is widely used by human beings and it is eliminated through solid waste (nearly 1/3 of the total) and through sewage (2/3 approximately). That is why it is so abundant and becomes a good indicator of sewage (Dietz, 1975). An amount of up to 7000 mg/L of boron can be found in groundwater near landfills (Arneth et al., 1986). Boron is not only found in domestic waste, there can also be other local boron sources like ceramic enamel and asphalt fabric industries (Candela, 1984).

Concentration of boron in sewage ranges normally between 0,5 and 2 mg/L (Koppe & Stozek, 1993), which is 5 to 100 times greater than non-polluted natural water. Boron is partially retained in water treatment plants.

Boron in water solutions can be found as borate ion $B(OH)_4^-$, as a non-dissociated boric acid $B(OH)_3$ and as borates (Na, Ca, Mg)$B(OH)_4^+$. Speciation is controlled by pH, salinity and caption concentration. In the subsoil, boron is adsorbed by clayey minerals and depends on the speciation.

Not only is the total content of boron a good indicator of pollution but also the ratio B/Cl. This value is greater in sewage ($\approx$ 1-5x$10^{-3}$) than in non-polluted groundwater ($\approx$ 5x$10^{-4}$) or seawater ($\approx$ $10^{-4}$).

### Phosphates

Phosphates are an indicator of sewage as they are normally used in detergents. Although they are indicated as $PO_4^{3-}$, prevailing species can be $H_3PO_4$, $H_2PO_4^-$ y $HPO_4^{2-}$ depending on pH (Stumm y Morgan, 1995). They are believed to be poor tracers in groundwater because they adsorb or precipitate easily. Robertson & Harman, (1999) believe that the behaviour of phosphates is controlled by adsorption processes which are fast and reversible. In places where there has been no prior urban pollution, phosphate can be virtually immobilized trough sorption. However, if redox conditions return to oxidizing, desorption will occur and phosphate can become persistent.

### Heavy metals

If the draining system is unitary, sewage and surface run-off flow together. A good indicator of the latter would be Zn (Carrera, 1997), which is related to vehicle waste lixiviated. Generally most heavy metals, such as Fe, Al, Pb, etc., display a similar behaviour.

Most heavy metals tend to be retained by the soil except under low pH or reduced conditions. Therefore, they cannot be used as a tracer, even through they may be indicators of human activity. Regarding this aspect Müller (2000), in a series of tests in an aquifer in Baviera, classifies metals regarding their decreasing mobility (As > Se > Ni > Hg > Co > Cr >> Sb > Cu ≈ Cd ≈ Pb). The existence of organic ligants and, specially, ethylendiaminotetracetic acid (EDTA) could ease the mobilization through complication of some of these metals.

### EDTA and NTA

Ethylendiaminotetracetic acid (EDTA) was synthesized for the first time in 1931 and it is mostly used in industrial processes to avoid the presence of heavy metals in water dissolutions, as they catalyse decomposition reactions of the process constituents and can form metal salts, which precipitate. EDTA is also used as a preservative in cosmetics and foods, and as a medicine for the treatment of metal poisoning.

Generally EDTA is present in domestic and industrial cleaners and its concentration in sewage ranges from 10 to 500 μg/l (Trauth & Xanthopoulos, 1997). This concentration is 30 to 1600 times greater than the analytic threshold of 0,3 μg/l, which is the maximum concentration estimated for non-polluted natural water.

The only known way to significantly degrade chemically EDTA is the photolysis of the iron compound Fe(III)-EDTA (Kari, 1994), thus, it should be taken into account for sampling. Normally, biological degradation is lower than 5% for 115 days (Bolton et al., 1993). There is no record on the possibility that they may suffer significant sorption processes in sediments or suspended particles in groundwater (Nowack, 1996). Bolton et al. (1993) determined adsorption rates for EDTA over five types of sediments and obtained values ranging 0,1 to 5,6 L/kg for concentrations in dissolution of $10^{-5}$ M.

Given these properties it is not amazing that EDTA is not eliminated or retained in conventional water treatment plants (Adler et al., 1990). EDTA has been used as an indicator for sewage pollution in Karlsruhe, Germany (Trauth & Xanthopoulos, 1997).

Nitrilotriacetate (NTA) is normally used in detergents as a substitute for phosphates and in water treatment plants as a regulating agent for hardness when combined with Ca and Mg (Adler et al., 1990). NTA may be used as an indicator for sewage pollution but, opposite to EDTA, NTA quickly undergoes biodegradation processes (Adler et al., 1990).

### Gadolinium

Gadolinium (Gd) is an element that belongs to the Lanthanoid Group. Gadolinium appears in sewage originated as gadopenthetic acid, which is used in medicine as an assay agent in Magnetic Resonance Imaging (MRI). Gd(III) often forms stable complexes with organic ligants and are excreted form the human body very fast, becoming part of sewage. Water treatment plants cannot eliminate it, so it incorporates to surface or groundwater.

Its presence in the Berlin area has been reported in sewage at the exit of water treatment plants, in water from rivers (Knappe et al. 1999). A correlation might be observed between the increase in the concentration and the amount of sewage produced. They also studied aquifers artificially recharged with treated sewage, and observed how pumping wells showed significant concentrations of gadolinium.

## 4.4 ORGANIC COMPOUNDS

### MTBE

The methyl tertiary-butyl ether (MTBE) is a gasoline additive, that is used in some areas to reduce the emanations of carbon monoxide to the atmosphere. It is a volatile compound found in groundwater in several cities all over the USA. It is a very persistent and mobile compound that can pass from shallow to deep aquifers quite easily. In superficial aquifers, concentrations were measured ranging from 0,2 to 20 ng/L (Squillace, 1997).

As stated by Robbins and Gilbert (2000) it can be used as a conservative tracer, and it can also correlate with other hydrocarbons, such as benzene and toluene, in order to find the mass reloaded or biodegraded in them.

**Metabolites and pharmaceutical products**

Several metabolites and pharmaceutical products were detected in groundwater. Albaiges et al. (1986) recorded more than 50 organic compounds, including pharmaceutical products, in groundwater near waste landfills in Barcelona. Seiler et al., (1999) detected in some areas of the USA **chlorpropamide**, a product to treat diabetes, and **phensuximide** and **carbamazepine** to treat epilepsy and strokes. Their capacity of adsorption and/or degradation is still unknown, although it is thought to be high. The determination of these compounds can be very useful to identify the different sources of pollution, such as sewage and waste landfills.

As a result of some studies carried out near Berlin whose aim was to find weed-killer in aquifers artificially recharged with sewage water, concentrations of chlofibric acid and N-(fenilsulfonil)-sarcosine, at a range 4 ηg/l and 150 ηg/l respectively, were detected. Their presence was recorded in deep wells of up to 125 m (Heberer et al., 1996; Heberer & Stan, 1997). Concentrations of N-(fenilsulfonil)-sarcosine found in sewage used for artificial recharge were smaller than those found in underlying groundwater, which contributes to think of it being a metabolite (Heberer & Stan, 1997).

Chlofibric acid (2-(4)-chlorofenoxi-2-methyl-propionic acid) is a metabolite of chlofibrate, ethofyllinchlofibrate and ethofibrate, all substances administrated as medicines, because of their regulating effect on blood pressure. In 1970 maximum concentration of chlofibric acid was already found at a range 2 to 10 μg/L in sewage and in water coming from treatment plants (Garrison et al. 1976).

As stated by Heberer & Stan (1997) the origin of **N-(fenilsulfonil)-sarcosine** is uncertain. It seems to be a metabolite of N-(fenil-sulfonil)-capronic acid, which is used as an inhibitor for corrosion in metal treatment.

Both compounds are very persistent and seem to avoid to be eliminated in water treatment processes. They were found in the supply water for Berlin in chlofibric acid concentrations of 270 ηg/L and 105 η/L for N-(fenilsulfonil)-sarcosine. They were also found in superficial water in several German rivers, in the Danube and in Po river in

Italy, which proves that it is a generalized phenomenon in sewage. As stated by Scheytt et al. (1998) chlofibric acid probably is photodegradable and biodegradable.

### Caffeine

**Caffeine** is a chemical stimulant found in beverages such as coffee, soft drinks and some foods. It is clearly a domestic sewage tracer. Caffeine is detected in sewage at a concentration of 20 to 300 ηg/L (Barber et al.; 1995). Its concentration in the Mississippi river and its tributaries could be correlated with the contributions of the main urban centers that pour their sewage in them. Seiler et al. (1999) reported caffeine in groundwater near Reno, Nevada, with concentrations of up to 0,23 μg/L. It correlates with nitrate pollution and it is presumed to be a good indicator of groundwater pollution due to domestic sewage.

## 4.5 ENVIRONMENTAL ISOTOPES

### Water molecule stable isotopes: D and $^{18}$O

There are many examples of how to use these isotopes, which seem to be the most popular and most widely applied. The fact they are part of the water molecule makes them widely ideal tracers.

There is some experience in urban areas. Butler and Verhagen (1997) evaluate the percentage of supply water that infiltrates in the underlying aquifers in Mountain View (Pretoria, South Africa). They observed that the difference between the values for $\delta^{18}$O and δD in underground and supply water is quite significant. This allows them to establish the percentage of supply water present in aquifers, which ranges from 5 to 10 %.

Seiler and Alvarado (1999) present one example in city of Caracas. They try to identify the best aquifer levels for water supply. They searched for those areas where potential pollution was lowest. Establishing the corresponding mass balance, it can be observed that 41 % of the aquifer’s recharge consists of water coming from the supply and draining systems. This also helps validating the existent conceptual system, and thus allows establishing the exploitation and control criteria.

### $^{15}N$

Rivers et al. (1996), Barrett et al. (1997) and Barrett et al. (1999) used different tracers, and especially $^{15}N$, to characterize losses in the sewage system or other pollution sources affecting the aquifers under the city of Nottingham. Hiscock et al. (1997) applied this methodology to London, while Whitehead et al. (1999) applied it to Liverpool.

In all cases, the interpretation was difficult as the possible recharge sources displayed an isotopic compositions with significant overlaps among them (Figure 4.1). This is due in part to the isotopic fractionation mechanisms in the transformation processes of N, such as denitrification (Barrett et al., 1999) or volatilization of ammonium (Hiscock et al., 1997).

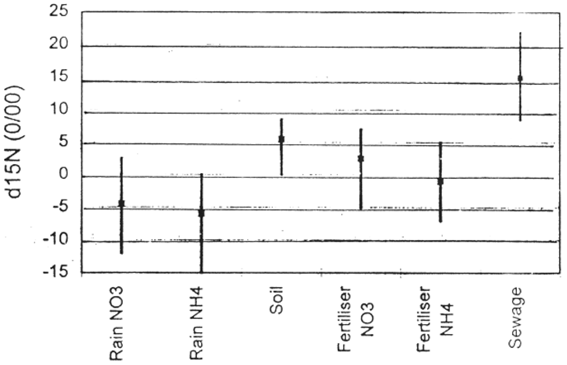


**Figure 4.1.-** Typical variation range for $\delta^{15}N$ for different Nitrogen sources (Barrett et al. 1999).

Not only in the aquifers containing Triassic sandstones (Nottingham and Liverpool), but also in those containing chalk in London, the recharge coming from the losses in the sewage system can be identified as it shows an isotopic content of $\delta^{15}N > 10$ ‰. Lower contents could belong to other sources, such as the use of fertilizers ($\delta^{15}N$ from -8 ‰ to 8 ‰), rainwater ($\delta^{15}N$ from -15 ‰ to 3 ‰), the presence of N in the soil ($\delta^{15}N$ from 0 ‰ to 8 ‰), or simply for being a mixture of the different sources.

Although the use of this isotope in rural areas could help, not only, to identify the origin but also to determine the quantity of the different nitrogen sources: fertilizers, cattle waste and septic tanks (Aravena & Robertson, 1998; Vitoria et al., 2001; 2002). In the case of urban areas, its use in combination with other tracers, did not allow quantifying recharge. This is due to the difficulty to isolate the possible sources from one another, and to characterize the possible chemical transformations of N throughout a seepage line which lead to isotopic fractionation. Although its use as an origin tracer to quantify recharge could be quite limited, its use as a process tracer allows determining the existence or nonexistence of nitrification or denitrification, and thus the conservative or non-conservative behaviour of nitrate, and other compounds related to these processes ($SO_4$, $HCO_3$, etc) for its possible use in quantifying recharge.

### $^{34}S$

The natural origin of sulphur (S) compounds usually comes from the dissolution of minerals such as sulphur, sulphates and sulphur compounds, such as dehydrated calcium sulphate (anhydrite), hydrated calcium sulphate (gypsum) and iron disulphide (pyrite) and at a minor degree, the possible contribution of sea aerosol. The antropic contribution of S compounds can derive in multiple sources, such as inorganic fertilizers, plaguicides, solid waste, detergents, liquid and atmospheric effluents, not only from an urban origin but also from industrial origin: tanning, dyeing, thermal power stations, fertilizer industries, mining, etc.(Barrett et al., 1999; Soler et al., 2002).

Hughes et al. (1999) used the isotopic composition of S and O of sulphate dissolved to the determination of the origin of pollution and the identification of recharge in urban areas in Triassic sandstone aquifer in Birmingham, Nottingham and Liverpool. These authors also analyse possible recharge sources. From the results in these three cities, it is deduced that the oxidation processes of sulphurs take place in the most superficial part of the aquifers, which is significant in the attenuation of other pollutants. There are no cases recorded on the reduction of sulphates in none of these aquifers (Figure 4.2). Isotopic data of groundwater did not help quantifying in detail the possible contributions of each of these sources, although they certainly allowed a clear identification of some of them. As stated by these authors, the main sources of $SO_4$ contribution are preindustrial precipitation, oxidation of the pyrite from the Quaternary sediments placed on aquifers, dissolution of evaporites in Triassic sediments and presence of industrial $H_2SO_4$. No contributions coming from sewage were identified. Generally, an enrichment of the isotopic content in urban areas takes place. It should be noted that the $\delta^{34}S$ content in the precipitation ranges from +2,1 to –7,1‰, and can be distinguished from that derived from local building materials, which ranges from +0,4 to –13,8‰. This difference could be used to quantify recharge in urban and non-urban areas.

Vázquez-Suñé et al. (2001) developed an application of $^{34}S_{SO4}$ in the aquifers of Barcelona. It was determined that the contents in $\delta^{34}S$ are characteristic of each of the sources recharge the aquifers (Table 4.2). Sewage always displays heavier $\delta^{34}S$ values than supply water. This is due to the contribution of domestic detergents and to the reduction processes of sulphates associated to water with a high content in organic matter.

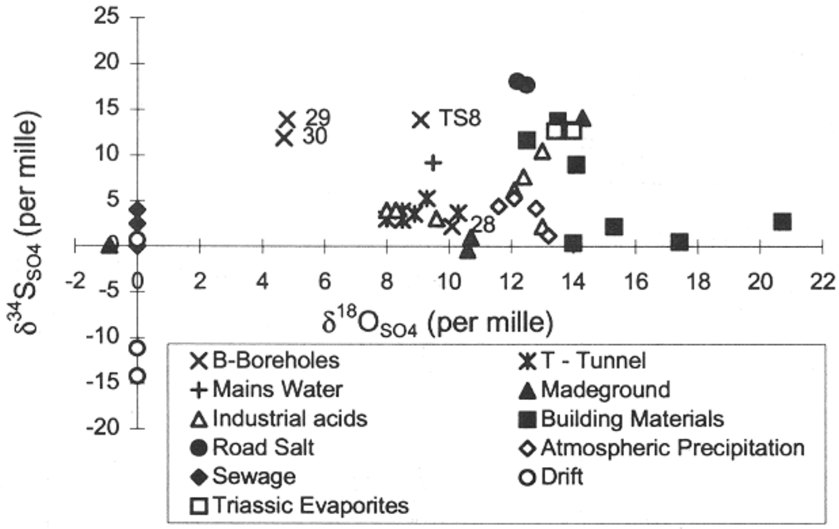


**Figure 4.2.-** $\delta^{34}S$ and $\delta^{18}O$ of $SO_4$ in the possible $SO_4$ and S sources (Hughes et al., 1999).

**Table 4.3** $\delta^{34}S_{SO4}$ values in water belonging to the potential sources of recharge to the aquifers.

| $\delta^{34}S_{SO4}$ (CDT, ponderate with $SO_4$ (mg/L) | RECHARGE SOURCE |
|---|---|
| >1 | Recharge sources in non-urbanized areas |
| 0.75 | Sewage water (from the Ter river) |
| 0.6 | Supply water (from the Llobregat river) |
| 0.5 | Water from the Besós river |
| 0.15 | City Runoff |
| 0.11 | Supply water (from the Ter river) |
| 0.1 | Sea water |

The contributions due to losses in the supply and sewage systems are about 80 % of the water contained in the aquifers underlying the city. This allows identifying which are the areas recharged by water coming from the Ter and Llobregat rivers, and quantifying the contributions of each recharge sources.

Soler et al. (2002) carried out the study of the origin of sulphate dissolved in water belonging to the Llobregat river. These authors characterize the different anthropic sources of sulphate (thermal power station, dyeing and tanning industries, potash mining, gypsum mining, chemical industries, galvanizing, etc.), and determine that anthropic sulphate plays an important role in the sulphur cycle of this river. This paper concludes that in order to use this tracer in the quantification of the different sulphate sources it is necessary to work in smaller areas, where the amount of sources is low enough to avoid the possible effects of the compositional overlap of $\delta^{34}S_{SO4}$. Otero & Soler (2002) applied this same technique to a reduced part of this same basin, distinguishing the application of $\delta^{34}S_{SO4}$ in the discrimination of the origin of water salinization from natural and antropic sources (potash mining and inorganic fertilizers).

### $^{13}$C

Yasuhara et al. (1999) use the content in $^{13}C$ to quantify recharge due to precipitation in Yamagata (Japan). The study focus on the relationship between rainwater recharge and infiltration from the Mamigasaki river. The authors estimate that the proportion of rainwater that infiltrates is significantly high.

Clark & Fritz (1997) stated that landfills can be identified because of their content in $\delta^{13}C$. Reducing conditions beneath landfills favour $CH_4$, $SH_2$, and even $H_2$. Under these conditions, there is a strong isotope fractionation affecting $\delta^{13}C$ and $\delta D$. Both isotopes suffer a strong enrichment, in which $\delta D$ can even reach a positive value.

The presence of $CH_4$ in groundwater cannot define in itself the existence of a landfill; on this account, $\delta^{13}C$ together with dissolved inorganic carbon (DIC) can be of great help. In many landfills with a high production of $CH_4$ there is also $CO_2$ or DIC enriched with $^{13}C$ (Figure 4.3).

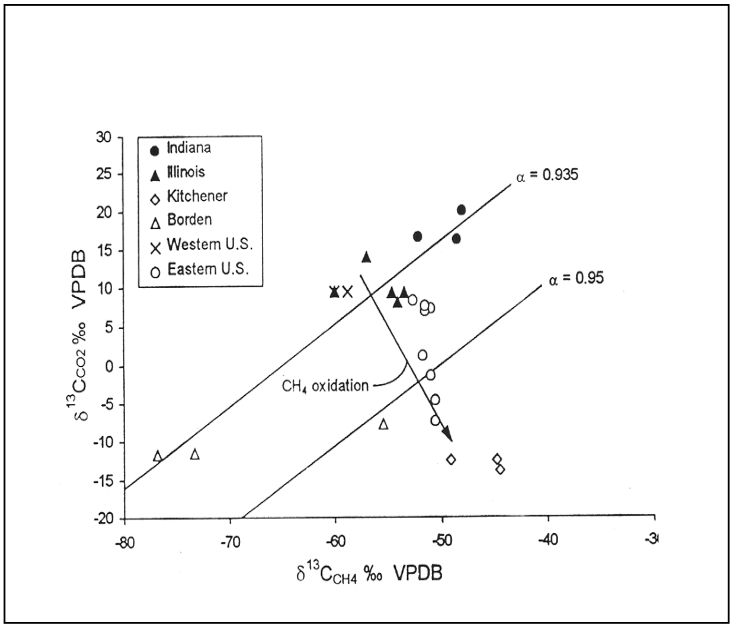


**Figure 4.3.-** Content in $\delta^{13}$C of $CH_4$ and $CO_2$ in the water of a landfill. The strong $\delta^{13}C_{CO2}$ enrichment suggests a $CH_4$ production due to $CO_2$ reduction. A general tendency to $CH_4$ oxidation is observed due to aerobic bacteria (Clark & Fritz, 1997).

### $^{11}$B

Boron has two isotopes, $^{11}$B and $^{10}$B, with a natural abundance of 80,1 % and 19,9 % respectively. Gäbel & Bahr (1999) analyse the isotopic content of boron ($^{11}$B) in order to identify the pollution due to urban effluents in groundwater. They stated that boron can be used as an indicator of pollution due to sewage because sodium perborate is used as whitewasher in detergents. The isotopic content of boron can also help to identify this. Thus, the isotopic content of B in a natural environment is of a $\delta^{11}$B between -30 and + 59 ‰, while the range in sodium perborate, habitually used in detergents, is of a $\delta^{11}$B between –4,8 ‰ and +3,1 ‰ . In sea water the isotopic content is located near a $\delta^{11}$B of +40 ‰.

The above study analyses a part of the Innerste river (Germany) in which the effluents of the urban water treatment plant of a nearby city are poured. Throughout the river and the alluvial aquifer there are several sampling points, not only in superficial water but also in groundwater. The objective is to identify pollution due to sewage poured in the adjacent aquifers.

Using the isotopic content $\delta^{11}$B, together with the concentration in B and Li, 3 kinds of water can be observed. The first one corresponds to that water present in the river and to 2 wells of the alluvial aquifer that show values of $\delta^{11}$B near 0 ‰. Another group is that formed of the wells with $\delta^{11}$B values of 16,4 to 20,0 ‰. Finally, a third group consists of other wells with values between –9 and –17,1 ‰. In the first group the content in $\delta^{11}$B has an anthropogenetic origin due to the infiltration into the aquifer of the polluted river water. In the other two groups, the content, in one of the cases very high and in the other one very low, suggests that the origin is probably geogenetic, with different rates for both cases, as the wells do not show indices of infiltration of water from the river.

In this case doubts on the geogenetic contribution or on the existing supply, regarding the content in $\delta^{11}$B, limits its application as a quantifier of river infiltration

Vengosh et al., (1994) used this difference in $\delta^{11}$B values to distinguish sea water intrusion from sewage pollution in an artificial recharge area with sewage affected by sea water in Israel.

### $^{87}$Sr/$^{86}$Sr

Sr isotopes have been widely used as tracers for natural sources of this element dissolved in water (Goldstein & Jacobsen, 1987; Palmer & Edmond, 1992, among others) being less used as tracers for pollutant sources (Martin & McCulloch, 1999; Böhlke & Horan, 2000, among others). The isotopic geochemistry of Sr determines the rate $^{87}$Sr/$^{86}$Sr and it is considered that, given the mass difference between the isotopes, there is no isotopic fractioning during the changes in temperature, Eh and pH in the environment.

In a study on the application of S and Sr isotopes as tracers of natural or antropic origin of the compounds dissolved in the superficial water of the Llobregat river. Soler et al. (2002) conclude that part of the strontium dissolved in the water of this river must be of antropic origin. Antich et al. (2000, 2001) observed that the Sr dissolved in the Cardener river could have a natural and antropic origin, and that the main contribution sources of antropic Sr to the water are inorganic fertilizers, domestic detergents present in urban sewage and the mining of evaporating materials, although in the latter case the isotopic composition coincides with the natural composition when manipulating natural materials.

### $^{137}$Cs and $^{90}$Sr

Shestopalov et al. (1997) and Goudzenko (1997) analyse the presence of $^{137}$Cs and $^{90}$Sr in groundwater near Chernobyl and Kiev. Due to the nuclear accident that took place in the nuclear power station of Chernobyl in 1986, two radioactive isotopes ($^{137}$Cs and $^{90}$Sr) can be observed in groundwater, which are the causes for pollution due to fission products.

During the years of study of the groundwater and the presence and behaviour of pollutants, a great difference between $^{137}$Cs and $^{90}$Sr was observed regarding their chemical properties, as well as those controlling the delay properties. The measures taken allow defining that most of the content in $^{139}$Cs is located in the first 100 meters of soil in Kiev's industrial area. Vertical preferred circulation areas, which allowed the incorporation of pollutants to inferior captive aquifers exploited for supply reasons, were recorded (Goudzenko 1997). Recharge could be evaluated thanks to the information supplied by these isotopes.

### $^{37}$Cl

Clark & Fritz (1997) comment the possibility of characterizing potential sources of contamination by chlorinated organic compounds by means of $\delta^{37}$Cl and $\delta^{13}$C. Those sources of contamination could be sewage, industrial spills and landfills. It seems that Cl-C bonds favour isotope $^{37}$Cl. The possible variations in the manufacturing of these compounds affect their isotopic content in $^{37}$Cl and $^{13}$C. This could be used to discriminate each manufacturer's product in order to determine where is the source for each contamination. Nevertheless, the natural biodegradation processes of these compounds, as well as evaporation, undertake a strong isotopic fractionation of $^{13}$C and $^{37}$Cl respectively (Hunkeler et al., 1999).

## 4.6 TRACERS FOR IDENTIFICATION AND DATING

There are many isotopic methods that could be used to quantify the age of groundwater. The most common techniques are based on radioactive dating. Urban groundwater dating is important to establish a correct conceptual model and to define possible recharge or lateral transfer sources of old as well as young water, preferred circulation paths, etc.

Given the strong development of cities in recent decades, it is usual to date young water using short-term isotopes ($^{3}$H, $^{32}$Si, $^{222}$Rn, $^{37}$Ar) or those produced by human activity ($^{3}$H, $^{14}$C, $^{36}$Cl, $^{85}$Kr), which yield information on the most recent recharge.

### $^{3}$H

$^{3}$H is one of the most widely used isotopes for recent recharge dating. It is used normally in combination with other isotopes, such as D and $^{18}$O. There are many examples of its application, including Seiler & Alvarado (1999), Yasuhara et al. (1999), Butler & Verhagen (1997), UPC (1998).

In the above studies, information is complemented with other isotopes or ions to establish the main recharge sources, while $^{3}$H is used to contrast results, establish circulation times consistent with the conceptual model (to determine the adequate mixing model), and determine potentially polluted aquifers. For example, Clark y Fritz (1997) show high values of $^{3}$H in landfills. These anomalous values could be due to the existence of waste containing luminescent painting and thus tritium hydrocarbon.

### $^{14}$C

Clark y Fritz (1997) describe how $^{14}$C can be used to identify landfills. It has been observed that in many landfills $^{14}$C activity can be quite high, not only because of $CH_4$ but also because of dissolved organic matter. The later may date from a period of time similar to that of thermonuclear tests.

### $^{3}$H/$^{3}$He

The advantage of using these isotopes as a whole is the possibility of determining the real ages regardless of the difficulties associated to the entry function of tritium or the presence of the thermonuclear peak. The disadvantage is the complexity of the analysis of $^{3}$He.

Tompson et al. (1999) and Dunkle et al. (1999) analysed the age of urban sewage, the first one in an artificial recharge area of urban sewage in California (USA), and the second one in a sewage tipping in the aquifer of a military resort in Massachusetts (USA).

### $SF_6$

Fulda & Kinzelbach (2000) used $SF_6$ to trace and date groundwater. $SF_6$ is an inert gas in most aquifers. Its entry function is well-known. Its concentration in air has increased over recent years. Its solubility in water depends on temperature. Once this data is known, the entry function can be established. This methodology was applied in the Stuttgard / Bad Cannstatt aquifer, which is one of the most important mineral-water aquifers in Germany. Applying a piston-flow model the age of recharge water was calculated regarding the distance of the wells to the recharge areas. The results obtained are coherent with previous flow models, thus validating the applicability of this methodology.

### CFC

As well as $SF_6$, CFC (chlorofuorcarbide) is a gas caused by the antropic activity that over the last 50 years has increased its concentration in the atmosphere. They are inert gases which behave as almost-ideal tracers in groundwater. They are conservative except under bacterial oxidant conditions, and could also undergo a delay due to the sorption processes. The evolution of CFC concentrations in air is well-known and an entry function could be defined in groundwater. (Fulda et al. (2000) made a sampling of $^{3}H$ and different types of CFC (CFC-11, CFC-12 and CFC-13) in an aquifer in Germany. By the use of a flow and transfer model, they validate the results obtained and the conceptual model. This application proves the usefulness of this kind of tracers, especially regarding $^{3}H$ and CFC-13.

The use of other isotopes ($^{36}Cl$, $^{32}Si$, $^{222}Rn$, $^{37}Ar$, $^{85}Kr$, etc.) to date current or medium-term groundwater flow in urban areas has the same objectives as those exposed here up to now, so that in fact, if there is an adequate analytical technique, a methodology, quite similar to any of these isotopes, could be applied.

## 4.7 CONCLUSIONS

It is important to identify the different sources of recharge in urban areas. The use of a single tracer makes it difficult to achieve conclusions on the water balance of an area.

The use of several tracers can ease the identification of different sources, only if their concentration or isotopic contents are sufficiently characteristic. Only those chemical species, present in certain sources and whose concentration or relationship is characteristic, will be useful.

There are many experiences worldwide on the use of chemical and isotope tracers to identify urban recharge sources.

In urban groundwater studies, it is first necessary to determine, or presume, potential tracers in recharge sources. More common tracers are major ions, as halogens (especially chloride and bromide), sulphate, and total nitrogen. Other possible tracers could be other ions as boron, phosphates and some heavy metals.

Its recommended the use of other tracers as organic compound and environmental (commonly D, $^{18}O$, and more recently used $^{15}N$, $^{34}S$, etc) and radioactive isotopes.

It is possible to perform mixing calculations after the analysis of the tracers in different sources of recharge and groundwater. Even with poor accuracy in some compounds and with overlapping could be possible to identify, and in some cases quantify different sources of recharge in urban groundwater.

# CHAPTER 5. A METHODOLOGY TO COMPUTE MIXING RATIOS WITH UNCERTAIN END MEMBERS

## 5.1 INTRODUCTION

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 in inflowing and outflowing waters and, assuming continuity, establishing the mass balance of solute and water as (see Figure 5.1):

$$Q_1 x_1 + Q_2 x_2 = Q_p y_p \qquad (1)$$

$$Q_1 + Q_2 = Q_p \qquad (2)$$

where $Q_1$ and $Q_2$ are the inflow rates, $x_1$ and $x_2$ are the corresponding concentrations (in this example only two end-members are considered) and $Q_p$ and $y_p$ are the outflow rate and concentration, respectively. Actually, flow rates can be eliminated from these equations. Dividing (1) and (2) by $Q_T$ leads to:

$$\delta_{p1} x_1 + \delta_{p2} x_2 = y_p \qquad (3)$$

$$\delta_{p1} + \delta_{p2} = 1 \qquad (4)$$

where $\delta_{p1}$ and $\delta_{p2}$ are the mixing ratios of end members 1 and 2 in sample p. If $x_1$ is not equal to $x_2$, then equations (3) and (4) can be easily solved for $\delta_{p1}$ and $\delta_{p2}$. In turn, measurement of any one of the flow rates allows deriving the others as $Q_1 = \delta_{p1} Q_p$ and $Q_2 = \delta_{p2} Q_p$. In short, mixing ratios help in deriving the mass balance of a water body.

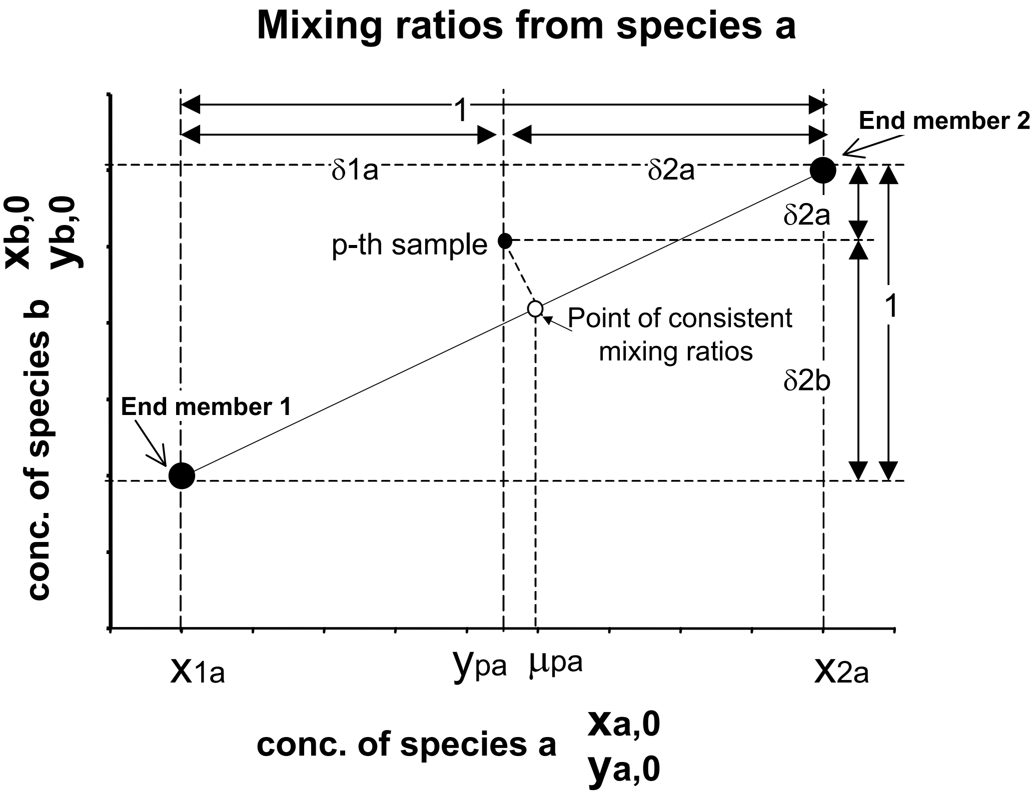


**Figure 5.1.-** Illustration of mixing calculations. Given the concentrations ($x_{1a}$ and $x_{2a}$) of a chemical species, *a*, in two source waters (end-members), it is possible to derive the mixing ratios in mixed sample, *p*, from its concentration $y_{pa}$. When the concentrations of two (*a* and *b*) or more species are available, measurement errors will lead to inconsistent mixing ratios. It is then possible to use least-squares, or a similar technique, to estimate consistent mixing ratios. Reversely, if these are known, one can estimate consistent concentrations.

These calculations are basic enough to be described in classical hydrogeology textbooks [*Custodio y Llamas*, 1983; *Zuber*, 1986 and many others]. We have included them here to introduce the basic notation. However, we wish to stress that they are used in all branches of hydrology. Recent applications include the evaluation of groundwater inflows to surface water bodies *Ojiambo et al*, [2001] or viceversa [*Plummer et al*, 1998; *Stute et al*, 1997]. They have also been used for the purpose of hydrograph separation [*Joerin et al*, 2002] or to evaluate the sources of recharge to groundwater

[*Pitkänen et al*, 1999]. In fact, our original motivation for this work stems from the identification of recharge to urban groundwater, where many end-members are possible [*Yang et al*, 1999; *Suk and Lee*, 1999; Vázquez-Suñé et al, 1997].

Mixing calculations are also used in other branches of earth sciences. For example, erosion rates can be determined from the composition of suspended and dissolved solids in rivers [*Allegre et al*, 1996; *Roy et al*, 1999]. Emission inventories into the atmosphere can also be obtained with the aid of mixing calculations [*Biesenthal* and *Shepson*, 1997]. These are also used to discriminate between mineral dissolution and atmospheric deposition as the origin of solutes in mountain rivers [*Johnson et al*, 2001; *Williams et al*, 2001].

Mixing analyses are essentially done with conservative tracers. However, they can also be used to identify reaction processes. In this case, departures from mixing lines (or planes) are attributed to chemical reactions [*Skov et al*, 1997; *Pitkänen et al*, 1999].

Most of the above examples require introducing some complexity in equations (1) and (2). For example, if more than one species is available, mixing ratios derived from each species may not be consistent. A least-squares approach may be required, then, to minimize what are often termed analytical errors. Actually, when concentration measurements from two species are known, one can derive the mixing ratios from three end-members, as illustrated in Figure 5.2. In fact, the methodology can be easily extended to any number of sources, $n_e$, provided that concentrations of, at least, $n_e$-1 conservative species are available.

The most immediate modification of the basic mixing model of Figure 5.1 is to transform it into a zero-th order compartment (cell or reactor) by taking into account storage. In such case, concentrations of the mixture and, possibly, inflows are time-dependent. Allowing several of these compartments to exchange water and solutes leads to the mixing cells model [*Campana and Simpson*, 1984]. This type of model has been generalized by Adar and coworkers. They use a suite of chemical and isotopic tracers to identify spatially varying recharge [*Adar and Nativ*, 2000; *Adar et al*, 1988, 1992].

In summary mixing models are widely used in all branches of hydrology and also in other sciences. Yet, they are consistently based on the assumption that the concentrations of end members are perfectly known, an assumption that is rarely met.

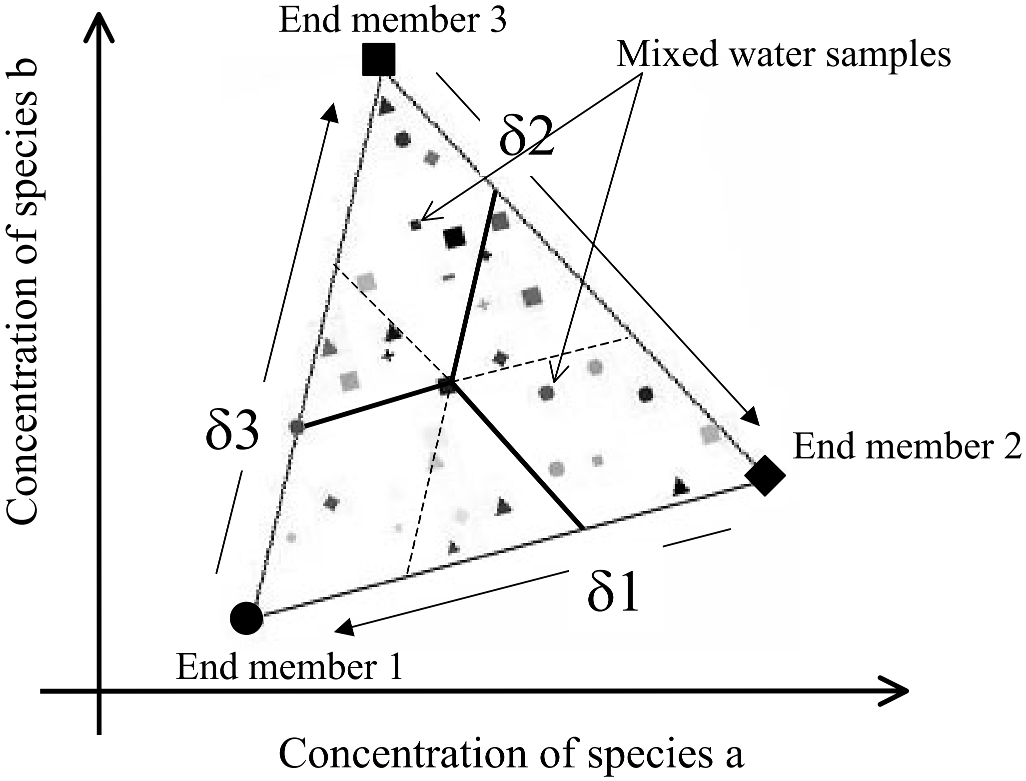


**Figure 5.2.-** Definition of mixing ratios in a problem with three end-members and two species.

Uncertainty in end-member concentrations is caused by analytical errors but, most importantly, by insufficiently documented spatial and temporal variability as well as conceptual problems. In the case of rainfall, one does not know when recharge does occur. As a result, it is difficult to characterize the portion of precipitation actually entering into soil and aquifer, even if the spatial and temporal variability of rainfall were exhaustively sampled. This is one of the main handicaps for the use of isotopes of H and O. A similar problem occurs with river inflows into aquifers, which may concentrate during floods. Reversely, flux averaged concentrations should be used when characterizing aquifer discharges to perform salt balances in rivers and lakes. However, conventional sampling yields resident concentrations. This, together with recharge variability makes the resulting mixing ratios highly uncertain [*Joerin et al*, 2002].

In short, accurate definition of the concentrations in the sources of any body of water is very difficult. Certainly, such definition can only be achieved after reaching a level of knowledge of the system far superior to what is expected from the salt balances described here, to begin with. Therefore, one must accept at the outset that the concentrations of end members are uncertain in many, if not most, mixing calculations. In fact, as illustrated in Figure 5.3, actual concentration data impose severe constraints on valid end-members concentrations. The concentrations of mixed samples are likely to be less uncertain than those of end members. One might argue that they are subjected only to analytical errors (much smaller than the sources of errors discussed for end members). Actually, the situation may be more complex because the mixing models of Figures 5.1 and 5.2 implicitly assume end-member concentrations to be the same for all mixed samples. This may not be the case, which can be interpreted as a source of errors, and thus uncertainty, in the concentration of mixed samples. Still, one would expect aquifer dilution mechanisms to filter out most temporal fluctuations in end-members. Therefore, even in these cases, mixed water concentrations should be less uncertain than those of end-members. Therefore using the former should help reduce uncertainty in the latter and, hence, in computed mixing ratios.

The objective of our work is to derive a methodology to identify mixing ratios in the case of uncertain end-members using the concentrations of mixed samples to reduce such uncertainty. The proposed approach is an extension of that by *Kent et al* [1990], who derived a methodology for fitting planes to uncertain data. Our extension is two-fold. First, we generalize it to the case of an arbitrary number of unknowns (the previous authors only estimated the two coefficients of the plane equation). Second, we apply it to mixing equations, which implies imposing constraints such as (4), plus non-negativity of mixing ratios.

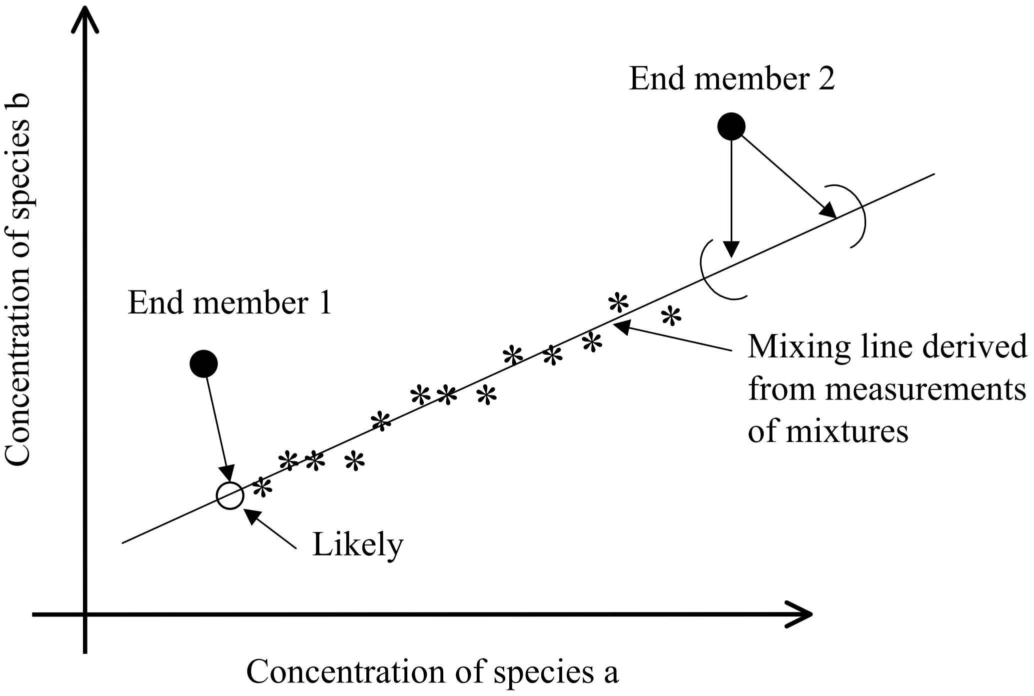


**Figure 5.3.-** Mixed water samples often define mixing lines more accurately than "noisy" end-member concentrations. In such case, taking mixing constraints into account may significantly reduce uncertainty in end-member concentrations by imposing consistency. Consistency is meant in two ways. First, end-members should fall in the mixing line. Second, mixed waters should fall within the interval defined by end-members. This second condition does not constrain the concentration of end-members 2, but reduces the uncertainty of end-member 1.

## 5.2 PROPOSED APPROACH

### Problem statement and solution steps

The problem is to find the proportions in which $ne$ end-member waters are mixed in $np$ samples. To this end, the concentrations of $ns$ species are measured in each of the mixtures. Measurements are also available for the concentrations of end members. That is a total of $nw = ne + np$ full analyses are available. Measurements uncertainty is quantified through covariance matrices.

The proposed algorithm consists of the following steps:

- Step 0: Initialisation. Definition of initial mixing ratios by conventional least-squares, assuming that the concentrations of end-members are known.

- Step 1: Given the mixing ratios, maximize the likelihood function to estimate the expected values of mixtures and end-members concentrations

- Step 2: Given the expected values of mixtures and end-member concentrations, maximize the likelihood to obtain the mixing ratios
- Repeat steps 1 and 2 until convergence.

Following is a description of each of these steps and a derivation of the necessary equations.

**Conventional least-squares for each sample assuming known end-members**

The mixing equation of each mixture *p* can be written as:

$$y_{ps} = \sum_{e=1}^{ne} \delta_{pe} x_{es} + \varepsilon_{ps} \qquad s = 1, \ \cdots, ns \tag{5}$$

where $y_{ps}$ and $x_{es}$ are the concentrations of species *s* in sample *p* and end-member *e*, respectively, $\delta_{pe}$ is the proportion of end member *e* in mixture *p,* and $\varepsilon_{ps}$ is an error. The latter is often termed measurement error, even though it may be caused not only by measurements, but also by conceptual errors (e.g., non-constant end-member concentration). Following previous work [Carrera and Newman, 1986; Medina and Carrera 1994] we formulate the estimation problem in a maximum likelihood framework. Assuming that the concentrations of end-members are known and that errors are normally distributed, the likelihood function is:

$$L_p = \exp\left[ -\frac{1}{2} (\mathbf{y}_p - \mathbf{F}\boldsymbol{\delta}_p)^t \mathbf{A}_p^{-1} (\mathbf{y}_p - \mathbf{F}\boldsymbol{\delta}_p) \right] \tag{6}$$

where $\mathbf{y}_p$ is the vector of all species measured at the *p-th* sample $\left[ \mathbf{y}_p^t = (y_{p1}, \ \cdots, y_{ps}, \cdots y_{pns}) \right]$, $\mathbf{A}_p$ is their covariance matrix, $\mathbf{F}$ is the $ns \times ne$ dimensional matrix of all chemical analyses of end members $\left[ \mathbf{F} = \ \{x_{es}\} \right]$ and $\boldsymbol{\delta}_p$ is the vector of mixing ratios $\left[ \boldsymbol{\delta}_p^t = (\delta_{p1}, \cdots \delta_{pe}, \cdots, \delta_{p\ ne}) \right]$. This latter vector must satisfy the constraint that mixing ratios add up to 1:

$$\boldsymbol{\delta}_p^t \mathbf{1}_{ne} = 1 \tag{7}$$

where $\mathbf{1}_{ne}$ is a *ne*- dimensional vector of 1's.

In order to maximize (6) subject to (7), we build the Lagrangian function

$$\mathrm{L}_p = -\ln L_p + \lambda_p \boldsymbol{\delta}_p^t \mathbf{1}_{ne} \tag{8}$$

where $\lambda_p$ is a Lagrangian multiplier.

Taking derivatives of (8) with respect to $\boldsymbol{\delta}_p$ and $\lambda_p$ leads to the well know linearly constrained least squares equations:

$$\begin{pmatrix} \mathbf{F}^t \mathbf{A}_p \mathbf{F} & \mathbf{1}_{ne} \\ \mathbf{1}_{ne}^t & 0 \end{pmatrix} \begin{pmatrix} \boldsymbol{\delta}_p \\ \lambda_p \end{pmatrix} = \begin{pmatrix} \mathbf{F}_p^t \mathbf{A}_p^{-1} \mathbf{y}_p \\ 1 \end{pmatrix} \tag{9}$$

It should be noticed that, if the same species are analysed for all samples and they have the same covariance matrix, then the coefficient matrix in (9) will also be the same for all samples. This, together with the fact that the dimension of the system (*ne*+1) is relatively small, makes it very easy to obtain the mixing ratios for each sample separately. The only difficult arises from the fact that mixing ratios must also satisfy the constraint

$$0 \le \delta_{pe} \le 1 \tag{10}$$

This, together with (7) defines the set of feasible solutions, which is a simplex set. Its vertices are obtained by setting each mixing ratio to one while letting the others be equal to zero. In general, this type of problems can be difficult (see, e.g., Gill, [1981], for a discussion). In our case, however, constraint (7) implies that it is sufficient to impose non-negativity (the condition $\delta_{ep} \le 1$ is satisfied automatically). In fact, since $\mathbf{A}_p$ is positive definite, the objective function is convex. As a result, it is sufficient to set to zero mixing ratios that are negative after the initial solution of (9), and solve again (9) for the remaining ratios.

### Formulation of the problem for known mixing ratios. The likelihood function

As stated, the objective is to find the most likely concentrations of samples and end members that jointly satisfy the mixing equations, provided that mixing ratios are known. To this end, we define the vector of all concentration data, $\mathbf{z}$, which consists of *ns* vectors $\mathbf{z}_s$ containing the analyses of each species *s* at all end-members and samples:

$$\mathbf{z}_s^t = (\mathbf{x}_s^t,\ \mathbf{y}_s^t) = \left[ x_{s1}, \ldots, x_{s\,ne}, y_{s1}, \ldots, y_{s\,np} \right] \qquad s = 1, \ldots, ns \tag{11}$$

Let $\boldsymbol{\mu}_s$ and $\boldsymbol{\mu}$ be the expected values of $\mathbf{z}_s$ and $\mathbf{z}$, respectively. Because we are working with all samples together, mixing ratios are best written as a matrix, rather than as a vector:

$$\boldsymbol{\Delta} = \begin{bmatrix} \boldsymbol{\delta}_1^t \\ \boldsymbol{\delta}_p^t \\ . \\ . \\ \boldsymbol{\delta}_{np}^t \end{bmatrix} = \begin{bmatrix} \delta_{11} & \delta_{1e} & . & . & \delta_{1\,ne} \\ \delta_{p1} & \delta_{pe} & . & . & \delta_{p\,ne} \\ . & . & . & . & . \\ . & . & . & . & . \\ \delta_{np1} & \delta_{npe} & . & . & \delta_{np\,ne} \end{bmatrix} \tag{12}$$

For compactly, it is convenient to define $\boldsymbol{\Gamma} = (\boldsymbol{\Delta}, -\mathbf{I}_{np\ x\ np})$, the extended mixing ratios matrix. This is used to define the constraints on mixing ratios, by writing (7) simultaneously for all species as:

$$\boldsymbol{\Gamma}\ \mathbf{1}_{ne+np} = \mathbf{0}_{np} \tag{13}$$

Similarly, constraints on the means are obtained by writing the mixing equations in matrix form assuming the errors are zero-mean:

$$\boldsymbol{\Gamma}\ \boldsymbol{\mu}_s = \mathbf{0}_{np} \qquad s = 1, \cdots, ns \tag{14}$$

which expresses the expected value of (5) for all samples. The normality assumption allows us to write the likelihood function as:

$$L = \exp\left[ -\frac{1}{2} (\mathbf{z} - \boldsymbol{\mu})^t \mathbf{A}^{-1} (\mathbf{z} - \boldsymbol{\mu}) \right] \tag{15}$$

where $\mathbf{A}$ is the covariance matrix of all chemical analyses taken as known. In our implementation we have assumed, for simplicity, but without loss of generality, that errors in one species are independent of errors in other species. However, for any species, they may well be correlated across samples. This implies that we will be able to filter out systematic errors caused by improper handling of one species. This assumption simplifies significantly the specification of $\mathbf{A}$. In any case, such simplification allows us to rewrite (15) as:

$$f = \ln L = \sum_{s=1}^{ns} \left[ -\frac{1}{2} (\mathbf{z}_s - \boldsymbol{\mu}_s)^t \mathbf{A}_s^{-1} (\mathbf{z}_s - \boldsymbol{\mu}_s) \right] \tag{16}$$

This function has to be maximized with respect to $\mathbf{\Delta}$ and $\boldsymbol{\mu}$, while ensuring that constraints (13) over $\mathbf{\Delta}$ and (14) over $\boldsymbol{\mu}$ are satisfied. We propose to do it in two stages: first, obtain $\boldsymbol{\mu}$ given $\mathbf{\Delta}$ and, second, obtain $\mathbf{\Delta}$ given $\boldsymbol{\mu}$. These steps are repeated until convergence.

**Estimation of $\boldsymbol{\mu}$, assuming $\mathbf{\Delta}$ fully known**

In order to maximize (16), subject to (14), we first build the Lagrangian:

$$\mathrm{L} = \sum_{s=1}^{ns} \left[ -\frac{1}{2} (\mathbf{z}_s - \boldsymbol{\mu}_s)^t \mathbf{A}_s^{-1} (\mathbf{z}_s - \boldsymbol{\mu}_s) \right] + \boldsymbol{\lambda}_s^t \mathbf{\Gamma} \boldsymbol{\mu}_s \tag{17}$$

where $\boldsymbol{\lambda}_s$ is the $np$ – dimension vector of Lagrange multipliers. Taking derivatives of $\mathrm{L}$ with respect to $\boldsymbol{\mu}_s$ and $\boldsymbol{\lambda}_s$ and setting them to zero leads to

$$\boldsymbol{\mu}_s = \mathbf{z}_s + \mathbf{A}_s \mathbf{\Gamma}^t \boldsymbol{\lambda}_s \tag{18}$$

where $\boldsymbol{\lambda}_s$ is obtained by multiplying this equation by $\mathbf{\Gamma}$ while bearing (13) in mind. This yields

$$\boldsymbol{\lambda}_s = -\mathbf{C}_s \mathbf{\Gamma} \mathbf{z}_s \tag{19}$$

where $\mathbf{C}_s = (\mathbf{\Gamma} \mathbf{A}_s \mathbf{\Gamma}^t)^{-1}$. Finally, substituting this vector back in (18) yields the solution we were seeking:

$$\boldsymbol{\mu}_s = \mathbf{z}_s - \mathbf{A}_s \mathbf{\Gamma}^t (\mathbf{\Gamma} \mathbf{A}_s \mathbf{\Gamma}^t)^{-1} \mathbf{\Gamma} \mathbf{z}_s \tag{20}$$

It is interesting to notice from (20) that $\boldsymbol{\mu}_s$ is simply the projection of data $\mathbf{z}_s$ on the mixing equations (5). The effect of projecting measurements of end-member concentrations into the mixing equation was illustrated in Figure 5.3.

**Derivation of the equations for $\mathbf{\Delta}$, assuming known $\boldsymbol{\mu}$**

The objective now is to find the mixing ratios $(\mathbf{\Delta})$ that maximize the likelihood, knowing that the expected values of concentrations are given by (20). Substituting (20) in (16) and applying (14) yields the updated objective function. In order to maximize it with respect to $\mathbf{\Delta}$ while imposing constraints (13), we build again a Lagrangian function:

$$\mathrm{L} = -\frac{1}{2}\sum_{s=1}^{ns}\mathbf{z}_s^t\boldsymbol{\Gamma}^t(\boldsymbol{\Gamma}\mathbf{A}_i\boldsymbol{\Gamma}^t)^{-1}\boldsymbol{\Gamma}\mathbf{z}_s + \boldsymbol{\beta}^t\boldsymbol{\Gamma}\,\mathbf{1} \qquad (21)$$

where $\boldsymbol{\beta}$ is the *np* dimensional vector of Lagrange multipliers. The condition of minimum requires deriving (21) with respect to $\boldsymbol{\Delta}$ and $\boldsymbol{\beta}$. This is somewhat complex, but facilitated by taking into account that:

$$\frac{\partial}{\partial\boldsymbol{\Delta}}(\mathbf{a}^t\boldsymbol{\Gamma}\,\mathbf{b}) = \mathbf{a}\mathbf{b}_{ne}^t \qquad (22)$$

where **a** and **b** are arbitrary constant vectors of dimensions *np* and *nw*, respectively, and $\mathbf{b}_{\mathrm{ne}}$ is a *ne*-dimensional vector equal to the first *ne* components of **b**. Equation (22) is easily derived by considering that $\partial\Gamma_{ij}/\partial\delta_{kl}$ equals 1 if *i*=*k* and *j*=*l*, and 0 otherwise.

Taking derivatives of (21) with respect to $\boldsymbol{\Delta}$ and $\boldsymbol{\beta}$ while bearing (22) in mind and making use of (19) and (20) leads to:

$$\partial\,\mathrm{L}/\partial\boldsymbol{\Delta} = \mathbf{F} = \sum_{s=1}^{ns}\boldsymbol{\lambda}_s\boldsymbol{\mu}_{sne}^t + \boldsymbol{\beta}\mathbf{1}_{ne}^t = \mathbf{0} \qquad (23a)$$

$$\partial\,\mathrm{L}/\partial\boldsymbol{\beta} = \mathbf{f} = \boldsymbol{\Gamma}\mathbf{1}_{nw} = \mathbf{0} \qquad \ldots\ldots\ldots \qquad (23b)$$

This is a non-linear system with $np \times ne + np$ equations and unknowns ($np \times ne$ mixing ratios, $\boldsymbol{\Delta}$, and *np* Lagrange multipliers, $\boldsymbol{\beta}$). We have solved it using the Newton-Raphson method, while imposing the non-negativity constraints discussed in Section 2.2. The solution method is outlined in the following section.

### Newton-Raphson solution of the minimum conditions

For solving the non-linear system (23), we have expanded **F** with respect to $\boldsymbol{\Delta}$:

$$\mathbf{F}^{k+1} \approx \mathbf{F}^k + \frac{\partial\,\mathbf{F}}{\partial\,\boldsymbol{\Delta}}\left(\boldsymbol{\Delta}^{k+1} - \boldsymbol{\Delta}^k\right) \qquad (24)$$

Using (24), (23) is approximated as:

$$\begin{pmatrix} \dfrac{\partial\mathbf{F}}{\partial\boldsymbol{\Delta}} & \mathbf{I}_{np\ np\ ne} \\ \mathbf{I}_{ne\ ne\ np}^t & \mathbf{0}_{ne\ np} \end{pmatrix} \begin{pmatrix} \mathbf{D} \\ \boldsymbol{\beta} \end{pmatrix} = \begin{pmatrix} \mathbf{F} \\ \mathbf{0}_{ne} \end{pmatrix} \qquad (25)$$

where $\mathbf{I}_{np\ np\ ne}$ is a *ne*-dimensional vector of *np* dimensional identity matrices. The components of $\partial \mathbf{F}/\partial \mathbf{\Delta}$ are derived in the Appendix. Ideally, **D** is equal to $\mathbf{\Delta}^{k+1}$ - $\mathbf{\Delta}^{k}$. However, the step may be reduced if $\mathbf{\Delta}^{k}$ + **D** leads to worsening the objective function (21). Therefore, $\mathbf{\Delta}$ is updated according to:

$$\mathbf{\Delta}^{k+1} = \mathbf{\Delta}^{k} + \alpha\,\mathbf{D} \tag{26}$$

where $\alpha$ is chosen, starting at 1, so that the updated mixing ratio matrix yields an improved objective function. Actually, a 1-D search is performed using the techniques described by Gill (1981) and Carrera and Newman (1986).

Only non-negativity lateral constraints need to be imposed to solve the optimisation problem, as discussed in section 2.1. To do so, when (26) yields a negative mixing ratio, $\delta_{pe}$, its value is fixed to zero (that is, the non-negativity constraint is activated). This constraint can be released (that is, $\delta_{pe}$ allowed to vary), when increasing $\delta_{pe}$ may improve the objective function (i.e., when $\partial \mathrm{L}/\partial\delta_{pe} \geq 0$). Therefore, at the minimum, the following conditions are satisfied:

$$\partial \mathrm{L}/\partial\delta_{pe} = 0 \qquad \text{if } \delta_{pe} > 0 \tag{27a}$$

$$\partial \mathrm{L}/\partial\delta_{pe} \leq 0 \qquad \text{if } \delta_{pe} = 0 \tag{27b}$$

These are termed Kuhn-Tucher conditions [Gill, 1981].

### Implementation

Actual implementation of the above method consists of the following steps.

- Step 0. Initialisation (*k* = 0). This can be done by defining a set of arbitrary initial mixing ratios, $\mathbf{\Delta}^{0}$, or by least squares. The latter implies solving equation (9) and imposing non-negativity constraints as discussed in section 2.1.
- Step 1. *k =k+1.*
- Step 2. Compute $\boldsymbol{\lambda}_s^{k+1}$ and $\boldsymbol{\mu}_s^{k+1}$ using equations (19) and (20), respectively. Substitute into (16) to obtain the objective function $f^{k+1}$ and into (23a) to compute $\partial \mathrm{L}/\partial\mathbf{\Delta}$.
- Step 3. Convergence test (only if *k*>0):

- If $\max_{ep}\left|\delta_{ep}^{k+1}-\delta_{ep}^{k}\right|$ < tolerance and $\left|f^{k+1}-f^{k}\right|$ < tolerance, then STOP

- If the objective function worsens or its improvement is not sufficient, then reduce $\alpha$, set $\mathbf{\Delta}^k=\mathbf{\Delta}^k+\alpha\,\mathbf{D}$, test constraints (that is, activate non-negativity constraints when $\partial f/\partial\delta<0$), and return to step 2.

- Otherwise, continue to step 4.

- Step 4. Update $\mathbf{\Delta}$. Solve (25) for **D**, compute $\mathbf{\Delta}^{k+1}$ according to (26) with $\alpha=1$. Test non negativity constraints and go to step 1.

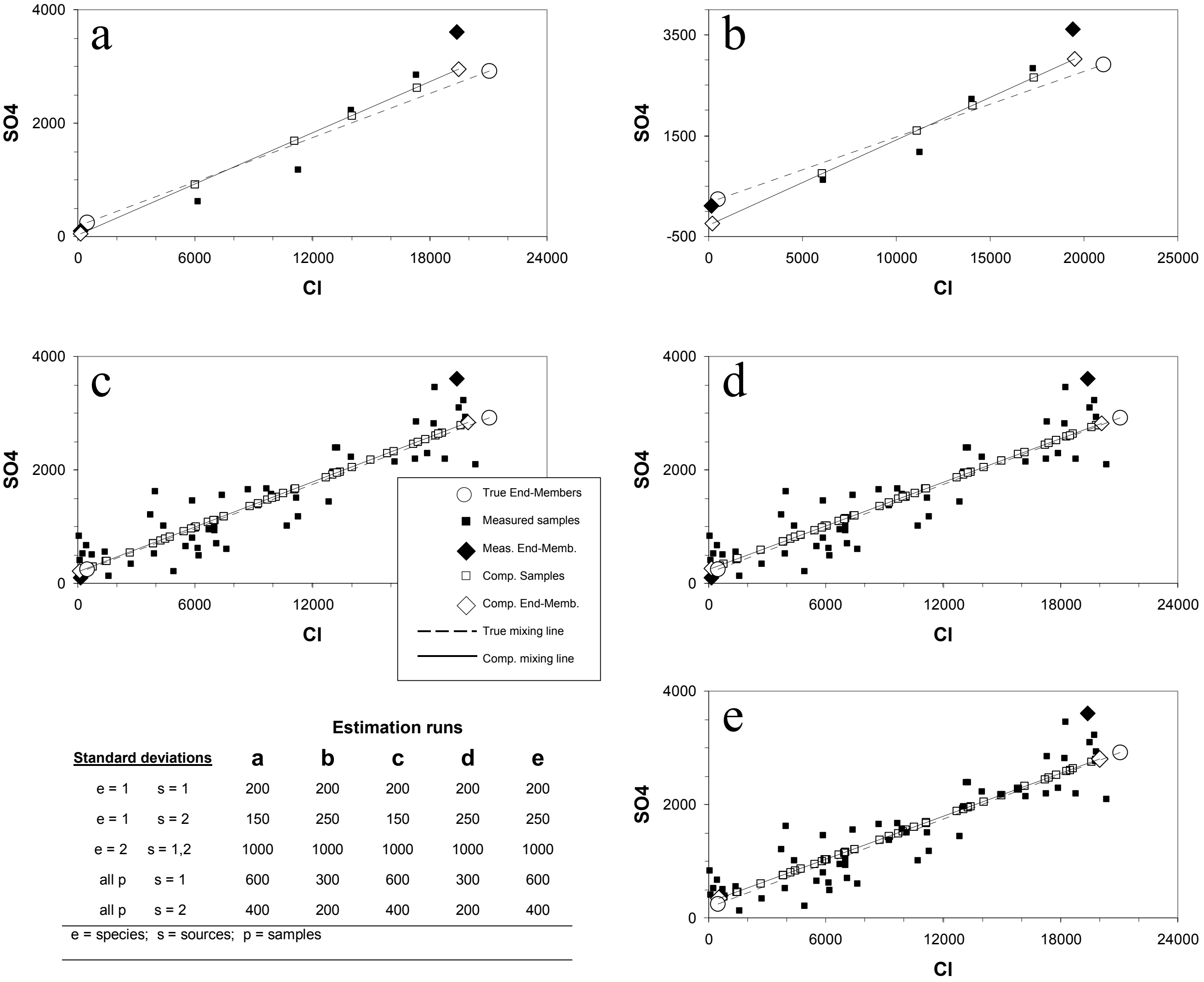
This algorithm was programmed in FORTRAN. Preliminary tests showed that sometimes it failed to converge, in the sense that trying different initial mixing ratios $\mathbf{\Delta}^0$ led to different minima. When testing synthetic examples, we observed that initialising with the least squares solution is a robust option when $\mathbf{x}_s$ is not far from $\boldsymbol{\mu}_{s\,ne}$ (i.e., when end-members are relatively well known). Otherwise, uniform mixing (i.e. $\delta_{se}=1/ne$) or random initialisation may be better. Since the cost of each trial is moderate, we have opted for trying several initial mixing ratios (least squares, uniform and around 10 random perturbations) and selecting the best as solution. This approach converges in virtually every case. The resulting code is available on request.

### APPLICATION 1. Two end-members.

This example is aimed at illustrating a case with two sources and two species. The example is inspired by Barcelona groundwater, with the two end-members being Besós River and Mediterranean sea water and the two species being chloride and sulphate. Other than that, the example is totally synthetic. Basic data are presented in Table 5.1. Data for the runs were obtained by randomly generating mixing ratios. These “true” ratios, together with the “true” end-member concentrations, are used to obtain the “true” concentrations of mixtures. Measurements are obtained by adding a random noise with the standard deviations of Table 5.1. These measurements will be used for all runs but e as shown in Table 5.1. Differences between runs are restricted to the number of mixtures (4 or 50) or the input standard deviations of both end members and mixed samples, also shown in Table 5.1.

The first two runs are aimed at illustrating the role of the assigned standard derivations when the number of samples is small. Hence, only four wells are used. In this case, the mixing line is poorly defined (Figure 5.5a). This reflects the noise in the measurements of mixtures. In fact, when the variance of end-members is increased and that of mixed samples is reduced without actually changing the concentrations (run b), the effect of noise in the latter is emphasized. As a result, concentration of species 1 in end-member 1 becomes negative (Figure 5.5b and Table 5.1).

It might be argued that concentrations should be constrained to be positive (the same as proportions). We have found, however, that negative concentrations are a very rare event, practically restricted to end-members and to situations where several parameters are inappropriate. In this case, the variance of the end member concentration was artificially increased, that of mixtures was artificially reduced and the number of mixtures is too small. When the variances are fixed (run a) or the number of samples increased to 50 (run d), or both (run c), the problem is fixed (Table 5.1 and Figure 5.4).



**Estimation runs**

| Standard deviations | | a | b | c | d | e |
|---|---|---|---|---|---|---|
| e = 1 | s = 1 | 200 | 200 | 200 | 200 | 200 |
| e = 1 | s = 2 | 150 | 250 | 150 | 250 | 250 |
| e = 2 | s = 1,2 | 1000 | 1000 | 1000 | 1000 | 1000 |
| all p | s = 1 | 600 | 300 | 600 | 300 | 600 |
| all p | s = 2 | 400 | 200 | 400 | 200 | 400 |

e = species; s = sources; p = samples

**Figure 5.4.-** Results of example 1. Only 4 samples are used in runs a and b. This leads to poor mixing lines and estimation of end-member concentrations. Moreover, results are quite sensitive to small variations on input standard derivations leading to negative concentrations in end-member 1 (run b). Mixing lines are much better and less sensitive to input statistics when 50 samples are used (runs c and d). In this example, computed end-member concentrations are slightly improved if input "measurements" are well within the interval of mixed samples measurements (run e).

Further examination of Table 5.1 makes it apparent that the concentration of species 1 is consistently underestimated. This reflects the very small value of the measurements of species 1 concentration in some mixed samples. Sometimes, it reflects the opposite (namely, that end-member measurements are far away from the interval of mixture measurements, recall Figure 5.3). In both cases, the problem is fixed by perturbing measurements of end-member concentrations forwards the center of gravity of all concentration measurements while keeping a relatively large variance. This is what motivates run e (Table 5.2), which indeed leads to improved estimates of end-members. In practical situations, however, it may not be easy to assess the validity of such concentrations.

**Table 5.1:** Data for the runs of Example 1. Concentration data for all runs (except for end-member 1 in rune) have been generated with the true standard deviations. However, input standard have been changed for each estimation run, leading to the end-member concentrations shown below.

| | | **True** | **Measured[1] (input)** | **Estimation Runs** | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | **a** | **b** | **c** | **d** | **e** |
| Number of samples (np) | | | | 4 | 4 | 50 | 50 | 50 |
| STANDARD DEVIATIONS | | | | | | | | |
| e = 1 | s = 1 | 200 | | 200 | 200 | 200 | 200 | 200 |
| e = 1 | s = 2 | 150 | | 150 | 250 | 150 | 250 | 250 |
| e = 2 | s = 1,2 | 1000 | | 1000 | 1000 | 1000 | 1000 | 1000 |
| all p | s = 1 | 600 | | 600 | 300 | 600 | 300 | 600 |
| all p | s = 2 | 400 | | 400 | 200 | 400 | 200 | 400 |
| CONCENTRATIONS OF END-MEMBERS | | | | | | | | |
| e = 1 | s = 1 | 478 | 143 (600) | 157 | 179 | 117 | 130 | 511 |
| e = 1 | s = 2 | 244 | 102 (400) | 49 | -237 | 210 | 264 | 337 |
| e = 2 | s = 1 | 21050 | 19405 | 19504 | 19503 | 19971 | 20097 | 19985 |
| E = 2 | s = 2 | 2910 | 3611 | 2946 | 3022 | 2837 | 2621 | 2804 |

[1] Measured values of end-member concentrations for all runs but e (values in parenthesis)

**Table 5.2.:** True end member concentrations and standard deviations of noise in example 2.

| | Species | | | | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 |
| True concentrations | | | | | |
| End-member 1 | 500 | 700 | 100 | 800 | 200 |
| End-member 2 | 100 | 100 | 400 | 200 | 700 |
| End-member 3 | 700 | 400 | 900 | 600 | 50 |
| Standard deviations (low variance noise) | | | | | |
| End-member 1 | 100 | 100 | 50 | 100 | 50 |
| End-member 2 | 50 | 50 | 100 | 50 | 100 |
| End-member 3 | 100 | 100 | 100 | 100 | 25 |
| Standard deviations (high variance noise) | | | | | |
| End-member 1 | 200 | 200 | 75 | 200 | 75 |
| End-member 2 | 75 | 75 | 200 | 75 | 200 |
| End-member 3 | 200 | 200 | 200 | 200 | 30 |

**APPLICATION example 2**

This example is aimed at illustrating the benefits of redundancy (large number of samples and species) upon the estimation of both end-members concentrations and mixing ratios. The formulation of the test is analogous to that of previous section.

1) Start with perfectly known concentrations of five hypothetical species at three end-member waters. These are shown in Table 5.2.

2) Generate 100 mixed samples from 100 uniformly distributed mixing ratios sets. These will be termed “true” mixing ratios.

3) Measured data are generated by adding a random noise with varying standard deviation (see Table 5.2) to both end-members and mixed samples. Notice that standard deviation is much larger for end-members waters than for mixed samples. Two sets of end members have been generated (low and high variance). All these data are shown in Figures 5.5a and 5.5b.

4) Results are evaluated in terms of several indices

- Mixing ratios average absolute error
- Correlation between true and computed mixing ratios.
- Improvement index for end-member concentrations, defined as

$$IM = \frac{1}{\sum_{s=1}^{ns}\sum_{e=1}^{ne}\frac{(x_{se}-\mu_{se})^2}{\sigma_{se}^2}}$$

This latter index measures the improvement caused by estimation (IM=2 implies that the mean square error of end-member concentrations has been reduced by a factor of two during estimation).

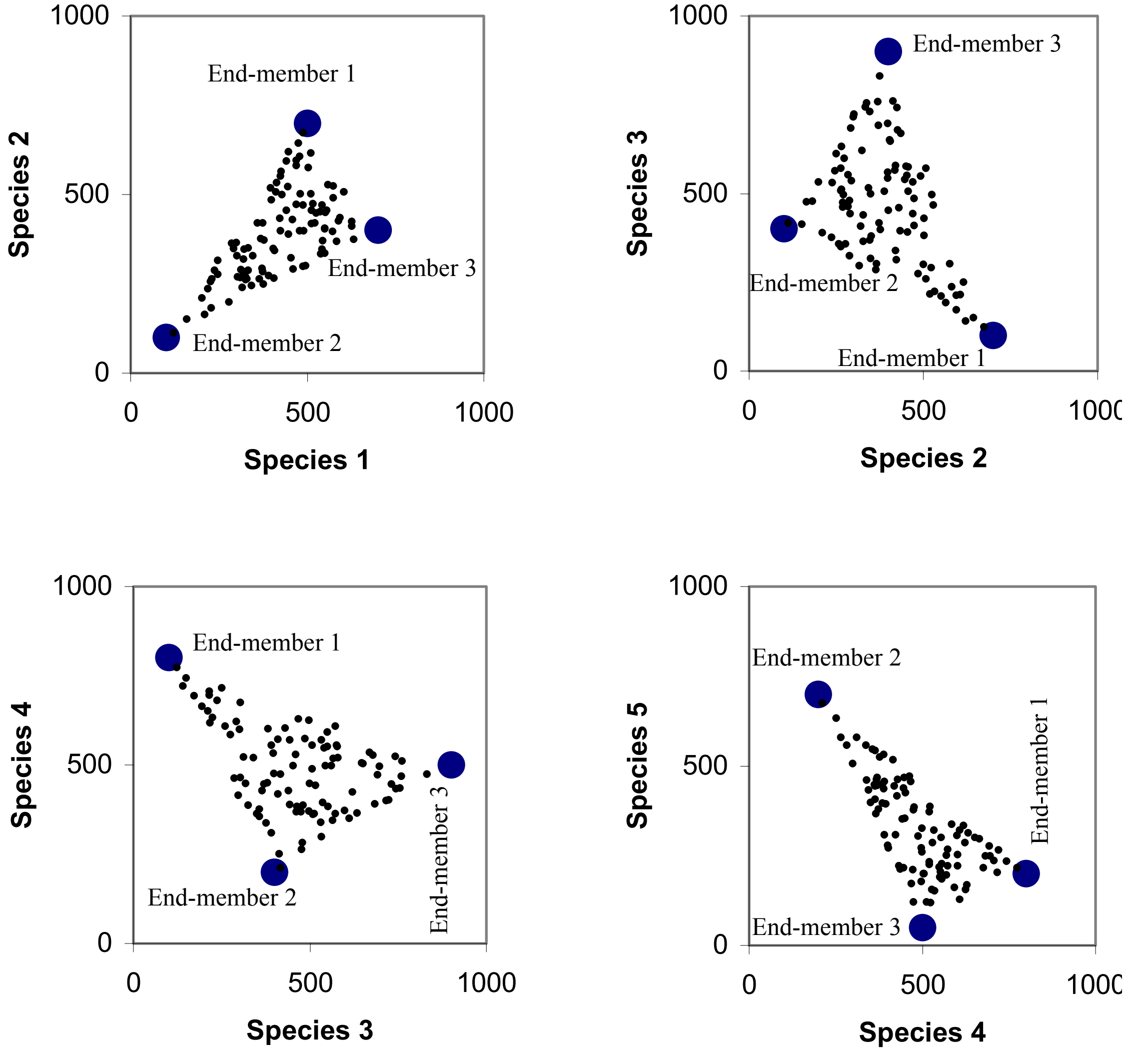


**Figure 5.5a.-** Relationships between species, end-members and mixing sample for example 2.

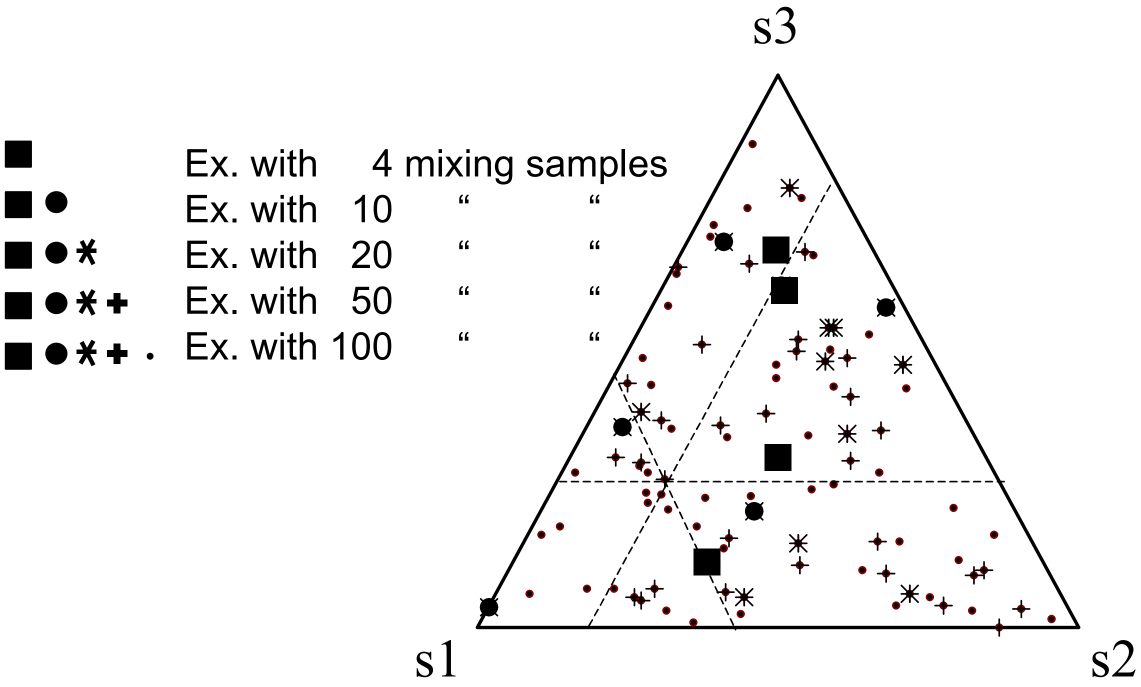


**Figure 5.5b**.- Proportions of "true mixing samples" ("measured data") from sources for example 2.

Figure 5.6 displays the evolution of correlation coefficients between true and estimated mixing ratios for varying number of samples. A number of issues deserve discussion. First, in general, correlation grows with the number of samples. This observation is consistent with the motivation of our work. That is, data from one sample help estimating the others. Obviously, this contrasts with least squares, where mixing ratios are estimated independently for each sample, so that they do not benefit from each other. Still, results are comparable for a small number of samples (actually, least squares slightly outperforms likelihood in the low noise case with only 4 samples). Second, the proposed method yields results that are significantly better than least squares except for the 4 samples case. Correlations for the likelihood method are consistently above 0.99 when more than 10 samples are used, and reach up to 0.998 for 100 samples. Least squares estimates, on the other hand, fluctuate between 0.97 and 0.98, when using small error end-member concentrations, or between 0.93 and 0.94 in the large error case. Finally, when the number of samples is moderate (more than 10), correlations exhibit negligible sensitivity to the size of errors in end-member concentrations. Again, this contrasts with least squares estimates, whose quality degrades significantly with increasing errors.

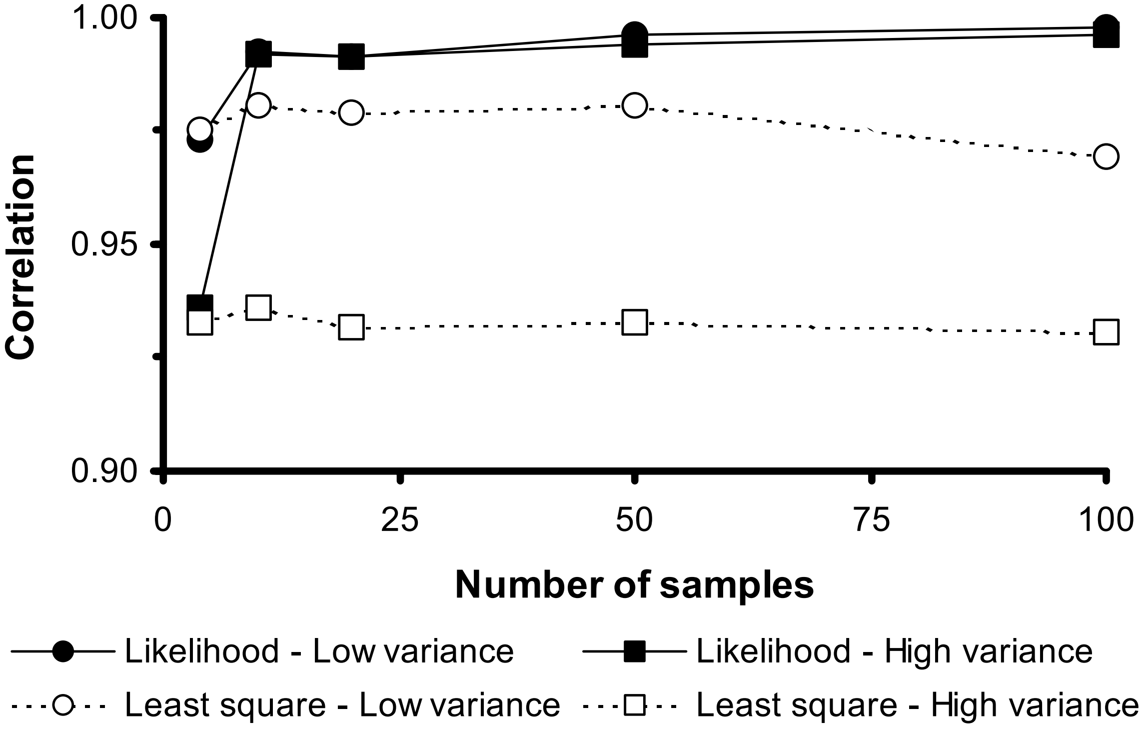


**Figure 5.6.-** Correlation between computed and true mixing ratios for example 2 as a function of the number of samples. Notice that correlation improves with increasing number of samples in the likelihood method, thus yielding much better results than conventional least squares, which does not depend on the number of samples. Notice also that, contrary to least squares, likelihood results display little sensitivity to the noise of end-member concentration measurements.

Similar results can be observed in terms of the average absolute error of estimated mixing ratios (Figure 5.7). The main difference is that, now, least-squares outperforms likelihood in the 4 samples case, both for small and large errors in input end-member concentrations. Obviously, this reflects a random fluctuation because the average error of least squares estimates, which is independent of the number of wells, is larger than that of the likelihood method. However, this observation stresses that the real benefit of the proposed method comes from increasing the number of wells, which causes errors in mixing ratios to drop to nearly 0.01, with little sensitivity to errors in end member concentrations.

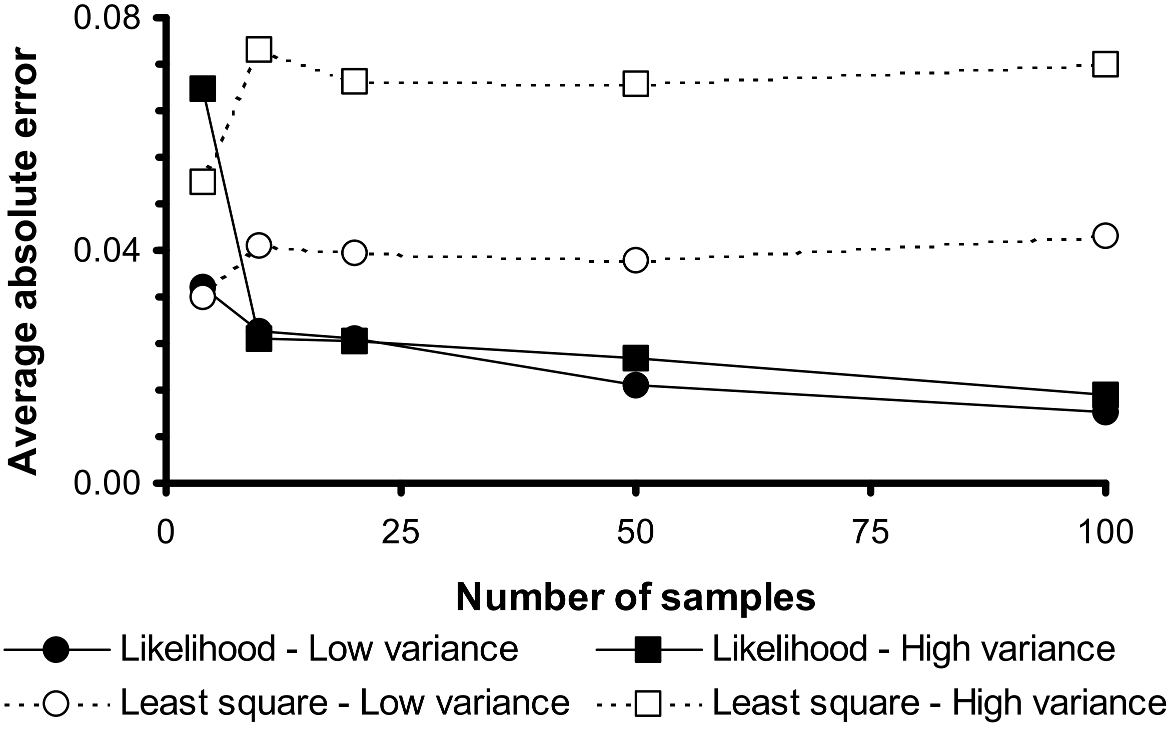


**Figure 5.7.-** Average absolute error in estimated mixing ratios versus number of samples for example 2. It is worth noticing that, with the likelihood method, errors are reduced when the number of wells is increased, while using least squares no improvement is observed.

Finally, the improvement index is shown in Figure 5.8. It is clear that estimated end-member concentrations are much better than their input counterparts. The improvement index grows from 3, in the case of 4 samples, to 8 for 100 samples. In fact, it is this improvement what caused the reduction in mixing ratios errors with increasing number of samples shown in Figure 5.6 and 5.7.

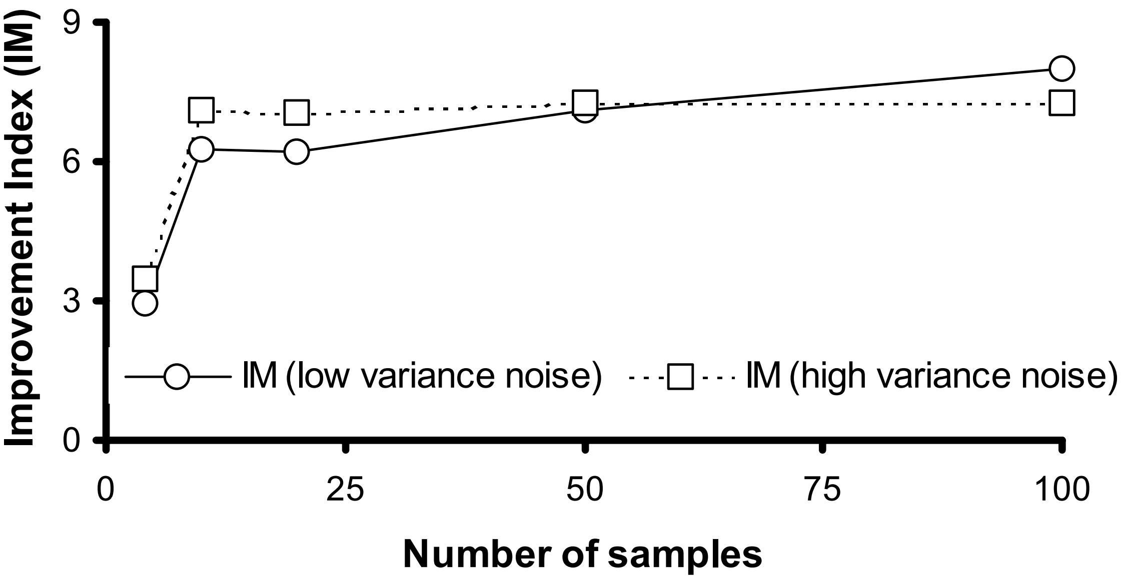


**Figure 5.8.-** Improvement (in estimated end-member concentration) index versus number of samples.

## 5.3 CONCLUSIONS

A method has been developed for estimating the proportions in which a few end-members are mixed in a possibly large number of water samples. The method is based on maximizing the likelihood of measured concentrations with respect to both mixing ratios and end-member concentrations. This leads to a general constrained optimisation problem. A solution method has been programmed and runs rather efficiently.

The method was based on the conjecture that the concentrations of mixtures contain information about the concentrations of end-members. Therefore, estimates of the latter can be improved from measurements of the former. This is further emphasized by the fact that spatial and temporal fluctuations of water and concentration inflows often leads to hard-to-estimate end member concentrations. Mixing, on the other hand, tends to dampen the effect of those fluctuations. Therefore, one may expect much lesser uncertainty on the concentrations of mixed samples than on those of end-members.

Two synthetic examples have been analysed. Results confirm that, indeed, simultaneous use of several mixed samples helps improving end-member concentrations. This improvement can be attributed to the fact that the proposed method forces end-members to be consistent with mixed waters. Consistency is meant in two ways. First, estimated end-member concentrations are forced to fall within the mixing line (plane or hyperplane, depending on the number of analysed species). When a large number of samples is available, this mixing line should be well characterized. Second, estimated sample concentrations are forced to fall within the interval defined by end-members. This also causes a favourable perturbation on estimated end-member concentrations whenever several mixed samples lack sizable proportions of one end-member.

As a result of the improvement in end-member concentrations, estimates of mixing ratios are also improved. More importantly, these are relatively robust, in the sense that they are not dramatically affected by small variations in input standard deviations, which is the only data that needs to be specified.

## APPENDIX. Computation of $\partial \mathbf{F} / \partial \boldsymbol{\Delta}$

Using equation (23a) for **F** and taking derivatives leads to:

$$\frac{\partial F_{ij}}{\partial \delta_{kl}} = \sum_{s=1}^{ns} \left( \frac{\partial \lambda_{si}}{\partial \delta_{kl}} \quad \mu_{sj} + \lambda_{si} \frac{\partial \mu_{sj}}{\partial \delta_{kl}} \right) \begin{matrix} i,k = 1,\cdots,np \\ j,l = 1,\cdots,ne \end{matrix} \qquad \text{(A1)}$$

We now substitute (19) into (A1) to simplify the first term of the right hand side. We use the fact that

$$\frac{\partial \boldsymbol{\lambda}_s}{\partial \boldsymbol{\Delta}} = \mathbf{C}_s \frac{\partial \boldsymbol{\Gamma}}{\partial \boldsymbol{\Delta}} \mathbf{b}_s \qquad \text{(A2)}$$

where $\mathbf{b}_s = 2\hat{\varepsilon}_s - \mathbf{z}_s$, and $\hat{\varepsilon}_s = \mathbf{z}_s - \boldsymbol{\mu}_s$ is the estimate of measurement errors. As $\partial \Gamma_{uv} / \partial \delta_{kl} = 1$, if *n=k* and *v=l* , the first summand in the right hand side of (A1) becomes:

$$\frac{\partial \lambda_{si}}{\partial \delta_{kl}} \mu_{sj} = C_{sik}\, b_{sl} \mu_{sj} \qquad \text{(A3)}$$

Similarly, the second summand is developed by first noting that we are just seeking the first *ne* components of $\boldsymbol{\mu}_s$ (20). These are given by:

$$\boldsymbol{\mu}_{sne} = \mathbf{x}_s - \mathbf{A}_{sne} \boldsymbol{\Gamma}^t \mathbf{C}_s \boldsymbol{\Gamma} z_s \qquad \text{(A4)}$$

where $\mathbf{A}_{sne}$ represents the top *ne* rows of $\mathbf{A}_s$ (i.e., those involving the covariances of end-member concentrations of species *s* among themselves and with those of sampling points). Taking derivatives of this expression yields:

$$\frac{\partial \boldsymbol{\mu}_{sne}^t}{\partial \boldsymbol{\Delta}} = \left( -\mathbf{z}_s^t \frac{\partial \boldsymbol{\Gamma}^t}{\partial \boldsymbol{\Delta}} \mathbf{C}_s \boldsymbol{\Gamma} - 2\boldsymbol{\lambda}_s^t \frac{\partial \boldsymbol{\Gamma}}{\partial \boldsymbol{\Delta}} \mathbf{A}_s \boldsymbol{\Gamma} + \boldsymbol{\lambda}_s^t \frac{\partial \boldsymbol{\Gamma}}{\partial \boldsymbol{\Delta}} \right) \mathbf{A}_{sne} \qquad \text{(A5)}$$

Here, we have made use of the expression of $\mathbf{C}_s$ and the rules for deriving the inverse of a matrix. We now define:

$$\mathbf{P} = \mathbf{C}_s \boldsymbol{\Gamma} \mathbf{A}_{sne} \quad ; \quad \mathbf{U} = \mathbf{A}_s \boldsymbol{\Gamma}^t \mathbf{P} \qquad \text{(A6)}$$

Using these definitions and (A5), the second term in the right hand side of (A1) can be expressed components-wise as:

$$\lambda_{si} \frac{\partial \mu_{sj}}{\partial \delta_{kl}} = x_{si} (-z_{sl} P_{kj} - 2\lambda_{sk} U_{lj} + \lambda_{sk} \mathbf{A}_{slj}) \qquad \text{(A7)}$$

Adding this to (A3) and summing up over all species yields $\partial F_{ij} / \partial \delta_{kl}$, which is what we were seeking.

# CHAPTER 6. MULTIVARIATE STATISTICAL ANALISYS METHODOLOGY FOR THE DISCRIMINATION AND QUANTIFICATION OF RECHARGE TERMS IN URBAN AREAS

## 6.1 INTRODUCTION

Groundwater is increasingly recognized as a factor in urban management. Because of pollution and changes in land uses, groundwater pumping is being abandoned in many cities with large industrial tradition. This has caused groundwater levels to rise, leading to flooding and potential damage to underground urban structures. Rising groundwater levels have been observed in several cities in Europe, such as Barcelona, Milan and London, among others. Moreover, sustainability calls for using local resources, including groundwater, which in most cases is chemically and microbiologically acceptable for many potential uses. As a result, understanding the processes affecting the quantity and quality of groundwater is becoming increasingly important.

Availability and quality of groundwater are direct consequences of the sources of groundwater recharge. Evaluation of recharge in urban environments is essentially different from that in natural systems for two reasons: (1) less experience is available, and (2) the recharge sources involved are radically different. Regarding the latter, one must bear in mind that surface infiltration is greatly reduced because a large portion of the city surface area is virtually impervious. Rainfall, then, becomes mostly runoff, which is mostly diverted to the sewage system. The reduction in direct infiltration can be counterbalanced by radical reductions in evapotranspiration. Moreover, new sources of recharge may arise in cities, either from losses in the water distribution system (in most cities world-wide losses exceed 50l per inhabitant and day, but this figure goes up to 180l/nih-day in Seoul-Kim et al; 2001) or from the sewage systems. The presence of a number of sources is both an added difficulty and a challenge. While methods are available for evaluating these sources (Lerner et al., 1990; Lerner, 1997; Trauth and Xanthopoulos, 1997; Barrett et al. 1999; Yang et al., 1999), validation and quantification are difficult. Certainly, experience is much shorter than with natural recharge.

As a consequence, regardless of the method, the joint evaluation should probably be tested through flow and solute transport modelling when long head and concentration records are available. Inverse modeling may prove a good tool for total recharge evaluation (Vázquez-Suñé et al. 1997, Yang et al. 1999). On the other hand, this type of modeling would not help discerning the contribution of each particular source to the total recharge.

Discrimination among sources is important for several reasons. First, evaluating the overall recharge may be best achieved if the relative importance of each source is known (because some of the sources may be easier to estimate than others). Second, pollution risk and geochemical processes are very sensitive to the chemical quality of the recharge water. Finally, proper groundwater management requires knowing the amount of water recharged in different city locations. Typical management decisions include where and how much to pump, whether or not to repair a sewer or a water distribution main, etc. These decisions can be best supported if the relative importance of each groundwater source is known.

Unfortunately, quantification of the different recharge sources of is not an easy task. Direct measurement is possible only in a few cases. Specific tests need to be performed to evaluate sewer losses and their reliability is uncertain (Lerner, 1990). Rainfall recharge in urban areas can only be measured in expensive pilot studies whose representativity is limited. The same caution note is applicable to the interaction between groundwater and urban surface water bodies (rivers, lakes,...) Water supply losses are easier to measure either by overall balance (supply minus use) or by minimum night flows. Yet, they are uncertain. Even if total losses are known, their spatial distribution is not.

Classical balance methods for evaluating recharge are based on equilibrium of conservative chemical species. Direct mass balance allows computing the proportions of mixing. As an example, assume a city with two sources of recharge. Source 1 contains 1000 mg/l of $Cl^-$. Source 2 contains 0 mg/l of $Cl^-$. A measurement of 400 mg/l implies that 40 % of the water in the sample is coming from source 1, while 60 % is coming from source 2. In practice, however, concentrations of the end-members sources are rarely as different as in the above example. Therefore a first challenge is to identify species that are markedly different in each source of recharge. The number of species that are needed to apply geochemical balance methods grows with the number of potential sources. Second, the concentrations of the different species at the end-members may not be known with certainty. They can be highly variable in space and, specially, time (consider, for example, the case of a sewer carrying both waste and runoff water which is quite common in the Mediterranean areas). Moreover, recharge may not be constant in time, so that the average concentration may not be representative of the recharge water. For example, in the case of the sewer, most recharge may occur during flood periods. In summary, mass balance methods require dealing with two issues: selection of tracers and proper evaluation of end-members (or, rather, accounting for the uncertainties in end-members when performing mixing calculations).

A critical step is selecting the appropriate tracers (Barrett et al; 1999; Yang et al; 1999). While not all methods used for the evaluation of recharge in natural systems can be extended to urban systems, the use of natural or artificial tracers and environmental isotopes is perhaps one of the best alternatives for both cases. Many authors compare solute concentrations in urban and rural areas (Barrett, et al 1997, 1999), yet experience does not suffice to ascertain which solutes may best be used as end points. Halogens (especially F and Br), Boron, Zinc and EDTA are sometimes suggested (Carrera, 1997, Trauth and Xanthopoulos, 1997). Rivers et al. (1996) and Barrett et al., (1999) suggest the use of nitrogen isotopes ($^{15}N$). Other possible tracers are organic compounds, metabolites, etc. When water used for supply is imported from long distance, chances of a marked isotopic signature do exist. This suggests using environmental isotopes for discriminating between local rainfall recharge and imported water recharge (Butler and Verhagen, 1997). For tracer selection this purposes, detailed analyses should be made of all the potential sources (or end-members). Groundwater samples must also be taken at a representative number of wells throughout the aquifer in order to get a spatial distribution of the contributions of each end-members.

The use of tracers to identify recharge sources is not new. Adar and Neuman (1988), Adar et al. (1988, 1992) and Adar and Nativ (2000) used multi-solute mass balances to quantify recharge to a rural aquifer. Yang et al. (1999) and Lerner and Yang (2000) applied that methodology to quantify recharge in the city of Nottingham. Suk and Lee (1999) used cluster and factor analyses to characterize a groundwater hydrochemical system of Gozan-Dong, a Korean residential and industrial area. All of them are based on the idea of using mixing equations to evaluate the fraction of water coming from the different sources in a given sample. However they all assume end-members concentrations to be accurately known. In this context, Carrera et al. (submitted) extended the method of Kent et al. (1990) so as to account for any number of dimensions (sources of water), to allow for estimates of the end-members, and to impose constrains to the solution, while keeping the concept of measurement errors.

The objective of this paper is to show a complete application of the methodology to evaluate the relative importance of the different sources of recharge in urban environments. We apply the methodology to the city of Barcelona where the recharge sources have been well identified in previous works (Vázquez-Suñé et al., 1997).

## 6.2 METHODOLOGY

**The full approach proposed consists of the following steps:**

A. Identify the sources of recharge. This requires understanding the hydrogeology of the system. Water balances and numerical models are very practical tools to help in this stage. In particular they can help in disregarding potential sources or accounting for new ones. In any case, a preliminary conceptual model is needed to identify potential end-members and to get preliminary values of the overall groundwater balance.

B. Select the chemical species to be included in the geochemical balances. These species should be conservative and their concentrations should vary widely from one source to another. Ideally, they should be non-expensive and easy (fast) to analyse with accuracy. Again, one needs a preliminary hydrochemical conceptual model to guess which species might be more helpful. Experience from other cities may also help. Some trial and error may be needed in any case.

C. Compute mixing ratios. Here, we propose using the approach of Carrera et al. (submitted), which is summarized below. This method allows improving the knowledge of end-member concentrations from data gathered from groundwater samples assuming these samples come from mixing of the end-members in an unknown proportion.

D. Synthesis of results. Mixing ratios derived in step C are representative of the water samples analysed and incorporate some degree of uncertainty requires a synthesis effort.

E. Possibly, iterate. The analysis of results may point out the need for including new sources of recharge or new tracer species. The conceptual model may need a revision so that steps A to D need to be repeated.

In the following section we will outline this method and data considerations. We then apply the above steps to the Barcelona aquifers.

## 6.3 MASS BALANCE EQUATIONS

The problem of determining the proportions from each source at any given location may be casted in a multivariate statistical framework. This framework allows accounting for a different number of equations and unknowns, and to include explicitly the uncertainties in the determination of the chemical concentrations in each source.

The method presented next is an extension of that proposed by Kent et al. (1990). In this paper we present some basic ideas; the full mathematical development can be found in Carrera et al (Submitted) and Chapter 5. While the method was initially developed in the context of mixing of waters, it could be applied to many others problems in nature.

The idea of the method is that *ns* conservative species coming from *ne* end-members (recharge sources) mix in variable proportion in *np* wells. The concentrations of the sources are assumed constant but highly uncertain, while those of the mixtures may change over time but are less uncertain. The objective is to evaluate mixing ratios acknowledging that concentration data contain errors. Then the concentration of each species at each particular well would satisfy the following mass balance equation

$$y_{ps} = \sum_{e=1}^{ne} \delta_{pe} \cdot x_{es} + \varepsilon_{ps} \qquad (1) \qquad \text{[eq. 5, Chapter 5]}$$

where,

$y_{ps}$ = Concentration of species $e$ in the well $p$.

$x_s$ = Concentration of species $e$ in the source $e$.

$\delta_{pe}$ = Percentage of water in well $p$ coming from source $e$

$ne$ = Number of sources (end–members)

$\varepsilon_{ps}$ = Error in the measurement

The vector of unknowns, $\delta_p^t = \left[\delta_{p1}, \delta_{pe}, ..., \delta_{ne}\right]$, must comply the following constrains:

$$0 \leq \delta_{pe} \leq 1 \qquad (2a) \qquad \text{[eq. 10, Chapter 5]}$$

$$\sum_{e=1}^{ne} \delta_{pe} = 1 \qquad (2b) \qquad \text{[eq. 7, Chapter 5]}$$

The sources are common to the $np$ wells, so we cannot consider them independently and we must work with all the wells at the same time. We start by defining the vector of variables $z_s$, one for each chemical species, ($s$ = $1,...,ns$), that includes the concentrations in sources and wells:

$$\mathbf{z}_s^t = (\mathbf{x}_s^t,\ \mathbf{y}_s^t) = \left[x_{s1}, ..., x_{s\,ne}, y_{s1}, ..., y_{s\,np}\right] \qquad s = 1,...,ns \ (3) \qquad \text{[eq. 7, Chapter 5]}$$

Each $z_s$ is considered independent and normally distributed with means $\mu_s$ and covariance matrix, $\mathbf{A}_s$, assumed known. The unknowns are a total of $np$ vectors $\delta_p$ each having $ne$ components, which correspond to the percentages of each source in each of the $np$ wells. The vectors are, of course, independent of the analysed species. These vectors can be written in matrix form, using a new matrix $\Delta$, of dimension MxN, given by the juxtaposition of the $\delta_p$ vectors $\Delta^T = (\delta_1, ..., \delta_M)$. We can further define $\Gamma$, matrix with dimensions $np\left(n_e + n_p\right)$, such that $\Gamma = (\Delta, -\mathbf{I})$. This matrix must verify

$$\Gamma \ \mu_s = \mathbf{0} \qquad (4)$$

$$\mathbf{\Gamma}\ \mathbf{1} = \mathbf{0} \qquad (5)$$

with **1** a unit vector of dimensions $N+M$. $\Delta$ is estimated by the maximum likelihood method. Since $\mu_s$ is constrained by (4) we introduce the Lagrange Multiplier $\lambda_s$ to built the overall Lagrangian:

$$\mathrm{L} = \sum_{s=1}^{ns}\left[-\frac{1}{2}(\mathbf{z}_s - \boldsymbol{\mu}_s)^t \mathbf{A}_s^{-1}(\mathbf{z}_s - \boldsymbol{\mu}_s)\right] + \boldsymbol{\lambda}_s^t \mathbf{\Gamma} \boldsymbol{\mu}_s \qquad (6) \qquad \text{[eq. 17, Chapter 5]}$$

The likelihood has to be maximized with respect to $\Delta$ and **$\mu$,** while ensuring that constrains (2) over $\Delta$ and (4) and (5) over $\mu$ are satisfied. This is achieved in two steps that are repeated iteratively. First, the likelihood is maximized with respect to $\mu$ given $\Delta$, which is estimates of the expected values of all concentrations are obtained. Second, the likelihood is maximized with respect to $\Delta$ given $\mu$. The first problem is linear. The second is non-linear, thus requiring the use of the Newton-Raphson method.

This methodology is implemented in a Fortran 77 code, "***MIX",*** compiled for PC [Castillo, (2000) and Carrera et al. (submitted)]. Due to the non-linearity of the system of equations it is necessary to provide an initial guess for the solution. We have found the best alternative for the initial guess to bean initial approximation calculated by Least Square, which corresponds to ignoring uncertainty. Best results regarding both convergence time and the actual solution are normally obtained when the initial approximation is close to the actual solution. It seems that the optimisation procedure has a number of local minimums that can be far away from the overall global minimum. When several solutions are obtained depending on the initial guess, we must develop a methodology for selecting the most appropriate. This methodology is three-step: 1) to compare the objective function; 2) check whether differences between measured and computed recharge sources composition are consistent; and 3) check whether computed proportion of recharge sources in wells are consistent with the conceptual model.

The knowledge of the full system must account for geology, geography, urban growth, demography, presence of subway and other underground structures, distribution and age of water mains and sewers, parks and irrigation areas, location of industries, industrial history, etc. All this knowledge must be taken into account when trying to explain the results in each particular well.

## 6.4 APPLICATION TO BARCELONA

### Sources

The geographical limits of Barcelona City are the Collserola Range (maximum elevation 512 m.a.s.l.), the Mediterranean Sea and rivers Besòs (to the northeast) and Llobregat (southwest). A number of aquifers, with different lithologies and ages, have been mapped below the city. Three out of the four geographical limits are potential inflow sources: seawater, direct recharge water (coming from the rainfall and directly infiltrated through the non-urbanized areas in the northern and topographical highs of the city), and water from the Besòs River, highly polluted. Additional sources of groundwater recharge can be attributed to antropic actions related to city development. The first one is supply water, which has two different origins (water coming from rivers Ter and Llobregat –the latter more saline-), leading to a separation of the city into two zones with distinct water quality. As a consequence of the two different origins in the supply water, we find also different chemical compositions in waste water. Finally, in paved areas, runoff water washes the urban surface and recharges the aquifers through direct infiltration or sewage losses. In summary, we have identified up to eight different recharge sources in the city:

1. Besós river
2. Direct recharge (rainfall infiltration)
3. Ter river water supply
4. Llobregat river water supply
5. Ter river sewage water
6. Llobregat river sewage water
7. City runoff
8. Sea water intrusion

## 6.5 TRACER AND WELL SELECTION

All the above sources have been sampled for chemical and isotopical analysis. These analyses include main ions, microbiologic indicators, halogens, heavy metals, EDTA, and isotopes $^{34}S$, $^{18}O$ and D. A historical record is available for some of these sources.

Moreover, up to 30 wells distributed throughout the city (Figure 6.1) have been analysed every three months in the last five years, so that a large chemical database is available.

From the analysed recharge water and groundwater and based on bibliographic research 12 chemical species were selected. These species were Cl, $SO_4$, $^{34}S$, B, F, Br, EDTA, Zn, $^{18}O$, D, N and Residual Alkalinity.

From simple data inspection some of these species had to be discarded because could not be determined well or simply because they are not conservative. For example, EDTA was discarded because measured concentrations in the water coming from wells were very low with respect to the values measured in water coming from end-members, (Figure 6.2) meaning that the behaviour was non-conservative. A similar situation is observed for B, Residual Alkalinity and Zn, but differences were not as dramatic as EDTA. In summary, EDTA, B, Residual Alkalinity and Zn were not included in the mass balance methodology.

Finally a total of 8 species were selected. These species discriminate quite well the major sources of recharge and have been found in preliminary analysis to be the most conservative. Table 6.1 contains the concentration of each species in sources and wells.

As is described above sources were considered chemically invariant with time. Measured variations have been associated to non-ideal sampling conditions, which render each value uncertain. Mean and standard deviation of measurements are considered as estimators of the expected value and the degree of uncertainty in the actual value of the source concentration.

Visual inspection of concentration data allowed us to detect some wells in which concentrations are not consistent with selected sources. Local contamination, damaged wells and local changes in geochemical conditions (red-ox processes) lead us to discard three of these wells (POLO, PUIG and TITN). At the end we consider 22 wells in the analysis.

We considered that the proportions coming from each source in the wells may change with time in response to changes in mixing ratios. That is, what we are seeking are the mixing ratios of each groundwater sample. Therefore, it would not be appropriate to average them. For the sake of consistency, we opted for restricting the study to a single campaign. For this application data used are from May-1999 campaign in 22 wells. Because in most cases species concentrations in wells are constant in time errors associated to a single species and well, are considered the sum of analytical, sampling and handling errors and was obtained from standard deviation in the measurements of each species in each well. For some of the species in certain wells there are very few data (i.e. F, $^{34}$S, Br) or the conceptual model is uncertain (i.e other point sources, contamination, red-ox processes, etc.). In these cases, the standard deviation is increased and the opposite if the conceptual model and concentrations are well knows. Table 6.1 displays the standard deviation of the concentration values for each species in sources and wells.

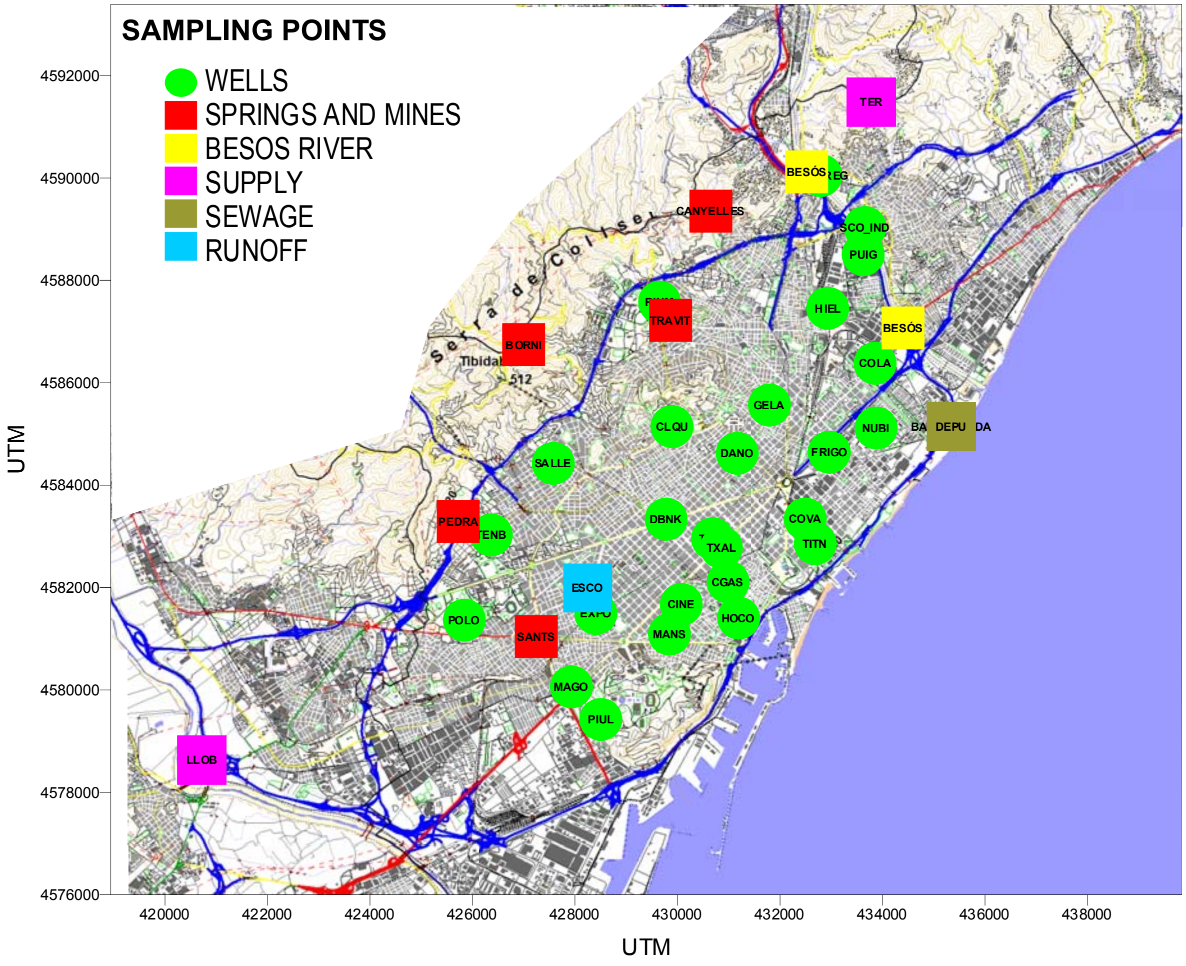


**Figure 6.1.-** Potential recharge water and groundwater. Regular sampling points

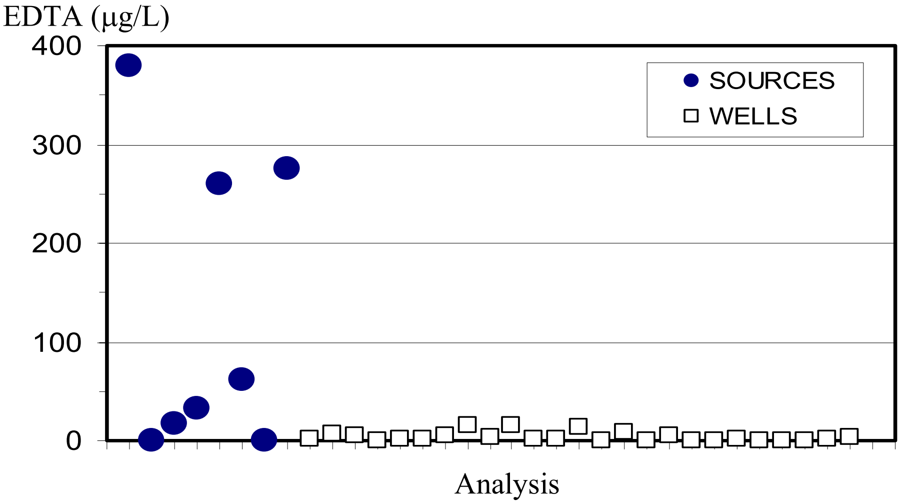


**Figure 6.2.-** EDTA concentrations measured in inflow sources at groundwater samples in Barcelona. It is clear that the latter are significantly smaller than the former, thus invalidating the use of EDTA as a conservative tracer

**Table 6.1.:** Concentrations and standard deviation of species in sources and wells

| **SOURCES** | **Concentrations in sources** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cl (mg/L)** | **SO4 (mg/L)** | **δ34S(*)** | **F (μg/L)** | **δ 18O** | **δ D** | **N (mg/L)** | **Br (mg/L)** |
| BESOS RIVER | 220.00 | 177.00 | 2.7 | 860.0 | -5.95 | -41.2 | 19.5 | 6.67 |
| DIRECT RECHARGE | 92.00 | 109.90 | 1.7 | 110.0 | -5.91 | -38.5 | 2.3 | 2.18 |
| SUPPLY (TER RIVER) | 72.95 | 78.23 | 1.2 | 150.0 | -7.38 | -49.9 | 2.2 | 0.98 |
| SUPPLY (LLOBREGAT RIVER) | 289.07 | 195.23 | 3.0 | 200.0 | -6.93 | -49.3 | 2.3 | 2.68 |
| SEWAGE (TER) | 347.30 | 218.76 | 3.3 | 340.0 | -6.91 | -46.8 | 33.7 | 8.90 |
| CITY RUNOFF | 89.70 | 101.05 | 1.5 | 550.0 | -4.57 | -26.1 | 12.6 | 3.09 |
| SEA INTRUSION | 21050.00 | 2910.00 | 44.5 | 1000.0 | 1.50 | 8.2 | 0.8 | 120.00 |
| SEWAGE (LLOBREGAT) | 563.42 | 335.76 | 5.1 | 390.0 | -6.45 | -46.1 | 33.7 | 10.61 |

| **WELLS** | **Concentrations in wells** | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cl (mg/L)** | **SO4 (mg/L)** | **δ 34S(*)** | **F (μg/L)** | **δ 18O** | **δ D** | **N (mg/L)** | **Br (mg/L)** |
| CINE | 157.0 | 178.3 | 2.70 | 355.0 | -6.70 | -44.0 | 25.5 | 2.53 |
| COLA | 205.0 | 238.6 | 3.61 | 216.0 | -6.20 | -41.0 | 12.0 | 2.66 |
| COVA | 243.0 | 301.9 | 4.57 | 253.0 | -6.80 | -48.0 | 20.6 | 2.56 |
| DANO | 109.0 | 202.3 | 3.07 | 315.0 | -7.00 | -45.0 | 25.1 | 1.27 |
| DBNK | 103.8 | 138.9 | 2.10 | 430.0 | -7.20 | -53.0 | 22.8 | 1.10 |
| EXPO | 296.0 | 255.8 | 3.87 | 385.0 | -6.90 | -47.0 | 22.1 | 2.84 |
| FRIG | 259.0 | 314.1 | 4.76 | 267.0 | -7.10 | -50.0 | 22.0 | 1.75 |
| GELA | 131.0 | 106.4 | 1.61 | 267.0 | -6.30 | -46.0 | 9.3 | 2.99 |
| HIEL | 175.0 | 196.1 | 2.97 | 369.0 | -6.80 | -50.0 | 19.7 | 1.69 |
| HOCO | 336.0 | 240.5 | 3.64 | 221.0 | -6.90 | -51.0 | 11.9 | 3.42 |
| MAGO | 329.0 | 242.0 | 3.67 | 300.0 | -6.80 | -48.0 | 21.7 | 3.16 |
| MANS | 308.0 | 277.5 | 4.20 | 217.0 | -6.80 | -49.0 | 36.8 | 3.29 |
| PIUL | 478.0 | 187.6 | 2.85 | 291.0 | -6.80 | -50.0 | 10.5 | 9.65 |
| RINM | 79.0 | 236.9 | 3.58 | 596.0 | -6.70 | -46.0 | 20.0 | 1.24 |
| SALL | 262.0 | 196.0 | 2.97 | 242.0 | -6.80 | -48.0 | 14.2 | 3.08 |
| TAIG | 153.0 | 205.9 | 3.11 | 380.0 | -6.10 | -46.0 | 16.6 | 1.57 |
| TENB | 417.0 | 263.0 | 3.98 | 383.0 | -6.80 | -48.0 | 13.0 | 4.23 |
| TXAL | 144.0 | 209.6 | 3.18 | 403.0 | -6.80 | -50.0 | 25.7 | 1.68 |
| REGA | 217.0 | 172.4 | 2.61 | 464.0 | -5.41 | -39.4 | 4.6 | 0.49 |
| SCO1 | 211.9 | 220.7 | 3.34 | 197.0 | -5.31 | -40.0 | 5.8 | 0.54 |
| SANT | 322.5 | 246.1 | 3.73 | 360.0 | -6.70 | -50.0 | 14.0 | 3.27 |
| PEDR | 289.0 | 211.8 | 3.21 | 407.0 | -7.00 | -48.0 | 4.5 | 2.65 |

| **SOURCES** | | | **Standart deviation in sources** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cl (mg/L)** | **SO4 (mg/L)** | **δ 34S(*)** | **F (μg/L)** | **δ 18O** | **δ D** | **N (mg/L)** | **Br (mg/L)** |
| BESOS RIVER | 84.0 | 56.0 | 0.81 | 450.1 | 0.45 | 4.2 | 11.0 | 2.68 |
| DIRECT RECHARGE | 3.7 | 6.1 | 0.20 | 43.2 | 0.02 | 2.1 | 1.0 | 1.00 |
| SUPPLY (TER RIVER) | 14.8 | 16.2 | 0.26 | 43.2 | 0.37 | 0.9 | 1.1 | 1.12 |
| SUPPLY (LLOBREGAT RIVER) | 63.9 | 40.5 | 0.63 | 27.3 | 0.33 | 3.2 | 1.0 | 1.16 |
| SEWAGE (TER) | 118.2 | 100.0 | 1.35 | 225.7 | 0.15 | 3.9 | 7.4 | 8.06 |
| CITY RUNOFF | 35.0 | 84.2 | 1.28 | 100.5 | 2.50 | 20.0 | 11.0 | 2.24 |
| SEA INTRUSION | 1.0 | 1.0 | 0.10 | 10.0 | 0.01 | 0.1 | 1.0 | 1.00 |
| SEWAGE (LLOBREGAT) | 118.2 | 100.0 | 1.35 | 225.7 | 0.15 | 3.9 | 7.4 | 8.06 |

| **WELLS** | | | **Standart deviation in wells** | | | | | |
|---|---|---|---|---|---|---|---|---|
| | **Cl (mg/L)** | **SO4 (mg/L)** | **δ 34S(*)** | **F (μg/L)** | **δ 18O** | **δ D** | **N (mg/L)** | **Br (mg/L)** |
| CINE | 100.0 | 32.7 | 2.75 | 200.0 | 0.05 | 2.5 | 9.2 | 0.10 |
| COLA | 10.0 | 19.0 | 2.00 | 500.0 | 0.08 | 1.8 | 8.0 | 3.00 |
| COVA | 10.0 | 40.6 | 2.00 | 500.0 | 0.42 | 5.0 | 2.1 | 3.00 |
| DANO | 21.5 | 37.8 | 3.22 | 64.8 | 0.08 | 2.5 | 4.8 | 0.10 |
| DBNK | 7.0 | 17.2 | 2.09 | 200.0 | 1.00 | 5.0 | 1.2 | 3.00 |
| EXPO | 13.3 | 22.8 | 3.87 | 200.0 | 0.22 | 0.7 | 6.1 | 0.10 |
| FRIG | 10.0 | 41.9 | 2.00 | 500.0 | 0.30 | 5.0 | 20.0 | 3.00 |
| GELA | 51.2 | 46.5 | 1.65 | 33.0 | 0.28 | 0.1 | 20.0 | 0.10 |
| HIEL | 67.7 | 46.2 | 2.95 | 200.0 | 0.11 | 3.0 | 1.7 | 3.00 |
| HOCO | 81.6 | 47.1 | 3.65 | 56.9 | 0.06 | 5.0 | 20.0 | 0.10 |
| MAGO | 22.1 | 30.3 | 3.66 | 19.0 | 0.08 | 1.6 | 0.7 | 0.10 |
| MANS | 9.5 | 25.1 | 4.24 | 34.5 | 0.12 | 1.8 | 20.0 | 3.00 |
| PIUL | 150.0 | 24.5 | 2.90 | 29.3 | 0.74 | 3.0 | 20.0 | 3.00 |
| RINM | 4.9 | 25.7 | 3.62 | 300.0 | 0.33 | 2.6 | 2.5 | 0.10 |
| SALL | 19.7 | 20.5 | 3.00 | 21.1 | 0.11 | 1.4 | 3.1 | 0.10 |
| TAIG | 11.4 | 26.0 | 3.14 | 200.0 | 0.92 | 2.9 | 20.0 | 3.00 |
| TENB | 150.0 | 100.0 | 5.00 | 200.0 | 0.34 | 2.8 | 1.5 | 3.00 |
| TXAL | 6.1 | 35.1 | 3.16 | 21.1 | 0.18 | 3.5 | 1.1 | 0.10 |
| REGA | 10.0 | 20.0 | 0.10 | 500.0 | 0.25 | 2.0 | 10.0 | 6.00 |
| SCO1 | 10.0 | 20.0 | 0.50 | 500.0 | 0.25 | 2.0 | 10.0 | 6.00 |
| SANT | 7.4 | 50.3 | 3.76 | 200.0 | 0.15 | 3.4 | 0.8 | 0.10 |
| PEDR | 31.9 | 100.0 | 5.00 | 200.0 | 0.28 | 2.7 | 20.0 | 0.08 |

(*) δ $^{34}$S DCT, weighted with $SO_4$ (mg/L)

## 6.6 DISCUSSION OF RESULTS

Results from the application of the maximum likelihood methodology include expected values of concentrations and mixing ratios. Here we discuss these by comparison with prior expectations and conceptual model. Computed composition of recharge sources is show in Table 6.3. Concentrations normally fall within the mean plus or minus one standard deviation. Chemical species considered for those calculations that show less deviation are, in order, Cl, $^{18}O$, $^{2}H$, $SO_4$ and $^{34}S$. Larger differences become apparent in F, N and Br (Figure 6.3), possibly reflecting non conservative behaviour of N and high uncertainties in F and Br analysis.

City runoff waters displays large differences between measured and computed composition. This may well reflect that temporal variations are very significant in this particular source, which motivated large standard deviations in the first place. Great isotopic variations of $^{18}O$ and D in rainfall and variable contents of $SO_4$ and N justify the computed differences.

Spatial distribution of the mixing proportions of the wells is shown in Figure 6.4, and Table 6.4. Groundwater composition of the wells is perfectly correlated with main sources of recharge present in this area. For example, the southern part of the city water supply comes from the Llobregat river and in northern part from the Ter river. This zonification is clearly show in groundwater, demonstrating that loss in mains is one of the important sources of recharge. The same is observed with sewer waters. Waters coming from high non-urbanized areas, flowing down to the sea, can be found in the whole system, but in low proportion. The city runoff waters can be found in the whole area, again in low proportions, except at some specific points. River water is located mainly in the vicinity wells.

The calculations agree with initial approximations done by other methodologies. The changes in mix proportions, even in wells close to each other, can be attributed to the heterogeneity of recharge mechanisms, depending on the proximity and quality of mains, sewer system, underground structures, etc, that could change local characteristics in the aquifers. There are some wells that display little proportions of sources not corresponding with its location. This reflects spurious behaviour of the methodology and specifically the fact that there are not restrictions of any source in any well.

The use of these results is not straight forwards. On one hand, they reflect resident water concentrations and mixing ratios. These values are important by themselves (they suggest how can water be exploited), but can not be used as indicators of the relative importance of the recharge sources. To do so, a flow model is needed. To illustrate this point, let us to consider a case where clean natural recharge water is infiltrated from the upstream edge of the aquifer while wastewater is recharged in the lowest part. A large percentage of natural recharge water over most of the area would simply reflect the most wastewater enters in the lowest portion of the city. That is, in order to evaluate overall recharge balance, one would need to evaluate mixing ratios of the outflowing waters and evaluate them. Here, we have approximated them by the wells located downstream (closest to the coastline), indicated in table 6.4. The average mixing ratios may indicate overall recharge ratios.

**Table 6.2.:** Computed concentrations in sources.

| SOURCES | Concentrations in sources | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cl (mg/L) | SO4 (mg/L) | δ34S(*) | F (μg/L) | δ 18O | δ D | N (mg/L) | Br (mg/L) |
| BESOS RIVER | 192.9 | 213.0 | 3.16 | 619.0 | -5.32 | -39.1 | 9.6 | 5.49 |
| DIRECT RECHARGE | 92.1 | 109.9 | 1.66 | 108.6 | -5.91 | -38.5 | 2.3 | 2.07 |
| SUPPLY (TER RIVER) | 70.4 | 75.8 | 1.18 | 149.2 | -7.15 | -50.2 | 2.4 | 1.98 |
| SUPPLY (LLOBREGAT RIVER) | 288.8 | 209.8 | 3.00 | 200.2 | -7.12 | -48.7 | 2.3 | 2.54 |
| SEWAGE (TER) | 61.5 | 300.7 | 3.79 | 299.9 | -6.99 | -46.8 | 23.2 | 0.41 |
| CITY RUNOFF | 70.9 | 89.7 | 1.61 | 520.6 | -7.03 | -47.8 | 25.6 | 1.19 |
| SEA INTRUSION | 21050.0 | 2910.0 | 44.52 | 1000.0 | 1.50 | 8.2 | 0.8 | 120.03 |
| SEWAGE (LLOBREGAT) | 546.9 | 382.3 | 5.45 | 205.5 | -6.46 | -48.6 | 34.8 | 5.69 |

(*) $\delta\ ^{34}S$ DCT, weighted with $SO_4$ (mg/L)

**Table 6.3.:** Computed mix proportions of sources in wells (%).

| SOURCES | DIRECT RECHARGE | BESOS RIVER | SUPPLY (TER) | SUPPLY (LLOBREGAT) | SEWAGE (TER) | CITY RUNOFF | SEA INTRUSION | SEWAGE (LLOBREGAT) |
|---|---|---|---|---|---|---|---|---|
| **WELLS** | | | | | | | | |
| CINE* | 15.9 | 1.3 | 0.0 | 0.0 | 9.6 | 55.5 | 0.4 | 17.4 |
| COLA | 5.2 | 45.6 | 0.0 | 23.7 | 20.0 | 0.0 | 0.0 | 5.5 |
| COVA* | 0.0 | 3.6 | 7.0 | 17.7 | 43.9 | 0.0 | 0.0 | 27.7 |
| DANO | 3.8 | 0.0 | 10.5 | 3.1 | 44.2 | 32.0 | 0.0 | 6.4 |
| DBNK | 0.0 | 0.0 | 16.6 | 0.0 | 15.1 | 60.7 | 0.0 | 7.6 |
| EXPO | 0.0 | 6.4 | 0.0 | 20.7 | 29.2 | 23.1 | 0.3 | 20.2 |
| FRIG** | 0.2 | 0.0 | 3.7 | 25.9 | 41.7 | 0.0 | 0.0 | 28.6 |
| GELA | 10.9 | 26.1 | 62.4 | 0.0 | 0.0 | 0.5 | 0.1 | 0.0 |
| HIEL | 0.0 | 7.5 | 28.3 | 0.0 | 21.7 | 21.3 | 0.0 | 21.2 |
| HOCO | 0.0 | 0.2 | 37.2 | 15.4 | 25.2 | 0.0 | 0.8 | 21.1 |
| MAGO* | 2.4 | 0.0 | 2.4 | 22.2 | 14.7 | 27.0 | 0.3 | 30.9 |
| MANS* | 0.2 | 0.0 | 25.4 | 1.5 | 31.3 | 0.1 | 0.2 | 41.3 |
| PIUL* | 0.0 | 3.7 | 49.3 | 0.8 | 0.0 | 26.3 | 1.7 | 18.2 |
| RINM | 0.0 | 12.6 | 0.0 | 0.0 | 64.3 | 23.1 | 0.0 | 0.0 |
| SALL | 0.0 | 6.2 | 50.0 | 0.0 | 20.3 | 5.4 | 0.5 | 17.6 |
| TAIG | 9.2 | 16.4 | 9.0 | 0.0 | 31.6 | 24.8 | 0.1 | 8.8 |
| TENB | 0.0 | 0.8 | 45.7 | 0.0 | 51.9 | 0.0 | 1.7 | 0.0 |
| TXAL* | 0.7 | 0.0 | 0.0 | 0.0 | 28.8 | 54.7 | 0.0 | 15.7 |
| REGA | 46.1 | 53.5 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 0.0 |
| SCO1 | 10.5 | 81.6 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 7.9 |
| SANT | 1.1 | 9.6 | 16.6 | 29.0 | 20.4 | 7.6 | 0.5 | 15.3 |
| PEDR | 0.0 | 6.1 | 16.7 | 34.8 | 24.5 | 17.2 | 0.7 | 0.0 |
| **Average** | **4.8** | **12.8** | **17.3** | **8.9** | **24.5** | **17.2** | **0.3** | **14.2** |
| **Downstream Average(*)** | **2.8** | **1.2** | **12.5** | **9.7** | **24.3** | **23.4** | **0.4** | **25.7** |

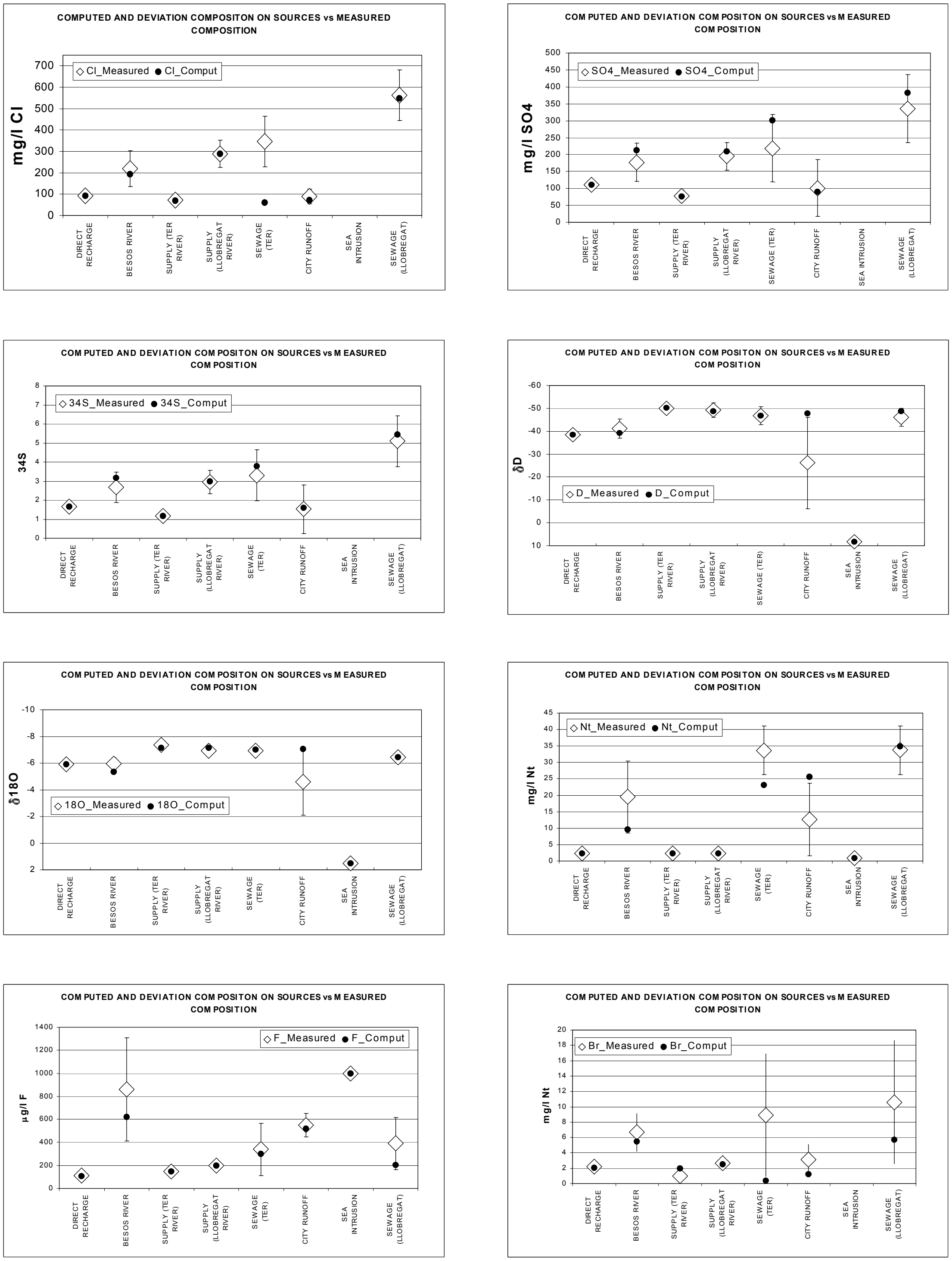


**Figure 6.3.-** Differences between calculated and measured parameters in recharge sources of Barcelona. Bars displays de deviation considered on measured parameters

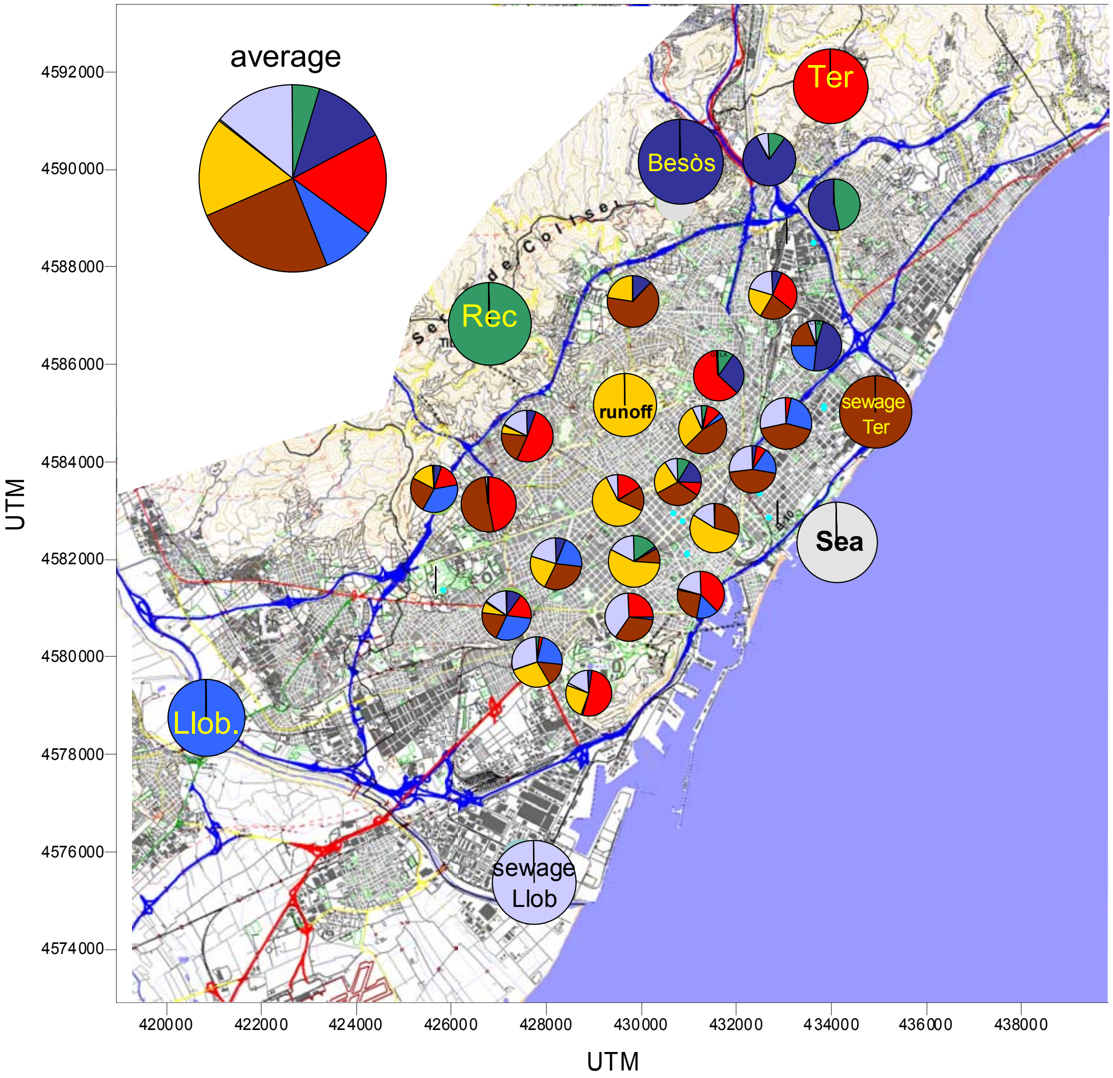


Figure 6.4.- **Recharge sources proportions calculated for wells in Barcelona aquifers**

## 6.7 CONCLUSIONS

Recharge is often the most difficult term to evaluate in the hydrogeological cycle on urban environments. In last years several authors have tried to compute it using different methodologies. Some of these methodologies are based on mass balance equations.

A general method based on multivariate statistical analysis has been developed for quantifying the percentage that each identified source contributes to resident water. The method accounts for measurement errors, and has been implemented in a computer code.

The method developed allowed us to compute the composition of recharge sources and the proportion of each source in groundwater in the urban area of Barcelona.

Eight chemical species have been identified as potentially useful for characterizing and quantifying the sources of groundwater recharge in the urban area of Barcelona The tracers used in recharge quantification are Cl, $^{18}O$, $^{2}H$, $SO_4$, $^{34}S$, F, N and Br. The first five behaved appropriately, the others did not, possibly due to non-conservative behaviour of N and high errors and variability of F and Br. Other species as EDTA, B, Residual Alkalinity and Zn are considered not conservative.

Mapping source proportion in wells gives us a view of the overall distribution of recharge sources. Computed mixing ratios are generally consistent with our conceptual model and resulting concentrations are rather close to measurements. This implies that results are satisfactory and that the methodology can be considered validated.

The methodology presented can be useful to quantify the origin of recharge in an urban area. However, the transfer from mixing ratios to recharge ratios is not straight forwards. In general, a flow model will be required to properly account for spatial and temporal variations. A preliminary analysis of one results, based on the ratios of downstream wells suggest that 50 % comes from wastewater, 22 % from the water supply network and 23 % from runoff infiltration, and other sources in less proportions. This has consequences in both the evaluation of groundwater balances and in identifying the potential quality of groundwater based upon the quality of water in the sources. This has important potential implications in groundwater management in urban areas.

# CHAPTER 7 GENERAL CONCLUSIONS.

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

- An exhaustive review of the references and recent advances in the field of urban groundwater was carried out. The main questions that should be taken into account were defined and collected in order to provide a general overview of any study related to urban groundwater, not only from the most conceptual aspects, but also from their application and management.

- A conceptual model of the hydrogeological functioning of the city was established. The interaction between groundwater and urban structures was analysed. The hydrological balance was established at a semiquantitative level.

- The application of numerical modelling methodologies to Barcelona aquifers allowed quantifying more accurately the hydrological balance and the relationship with underground urban structures. These tools were used as an aid to the management of groundwater by the local authorities and other implicated entities.

- An exhaustive literature review and compilation of the main chemical and isotopical compounds, was carried out in order to discriminate the possible sources reloading the aquifers in urban areas.

- A method based on the statistical multivariate analysis was developed to allow calculating the mixture proportions of waters recharged to the aquifer, as well as improving the knowledge on the characteristics of extreme waters.

- Several tracers were chosen from the waters recharging Barcelona aquifers and a multivariate statistical analysis method was applied. The mixture proportions of the different sources that contribute to the global recharge of aquifers was determined and their knowledge improved.

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