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10 Groundwater Baseline Composition and Geochemical Controls in the Doñana Aquifer System, SW Spain

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E. LOZANO

The geochemical controls of groundwater baseline chemistry of the Doñana aquifer system (DAS – SW Spain) have been characterised using major and minor inorganic components and environmental isotopes. In unconfined areas, groundwater baseline is controlled mainly by rainwater composition, which is of Na–Cl type, equilibrium with silica and dissolution of soil CO_2 , Na- and K-feldspars, and CaCO_3 where present. The resulting mineralisation ranges from very low to moderate. Groundwater baseline changes from the unconfined areas to the confined sector mostly by mixing with old marine water, Na/Ca–(Mg) cation exchange, sulphate reduction and calcite dissolution/precipitation. The resulting salinity ranges from 1 mS cm^{-1} up to 80 mS cm^{-1} .

In the shallower layers (<40 m) of the unconfined areas, groundwater baseline has been modified by different human activities, as shown by the presence of agrochemicals (nutrients, metals, pesticides) and of industry-derived airborne pollutants (mainly metals coming from the nearby Huelva industrial site and from open-pit mining sulphide

exploitation). This is supported by tritium based ages, which show residence times greater than 40 years for flow lines deeper than 35–40 m.

Groundwater composition in the confined areas is mostly naturally derived (baseline), as supported by ^{14}C ages ranging from 1 to more than 15 kyr. Agriculture-derived pollutants are present in groundwater below irrigation areas exploiting groundwater confined layers close to the northern boundary of the aquifer confined under the marshes, as well as the unconfined aquifer.

10.1 Introduction

The DAS is situated close to the southwestern Atlantic coast of Spain, between the Guadalquivir River and the Portuguese border, and covers an area of about 2700 km^2 . The area belongs to the provinces of Huelva, Sevilla and Cádiz. The main towns are Sevilla (1.6×10^6 inhabitants), some 100 km to the NE; Cádiz (0.2×10^6 inhabitants), some 60 km to the SE; and Huelva (0.05×10^6 inhabitants),

situated some 70 km to the West. However, most of the Doñana core area is uninhabited, except for people in charge of the environmental protection, some researchers, the occasional developers of some natural resources, and visitors.

Doñana is a Ramsar Convention protected area for wildlife and waterfowl. It comprises one of the largest valuable environmental zones in Spain: some 1100 km² are protected under the legal statutes of a National Park (human activities are severely restricted) and a Natural Park (some controlled farming and light tourism activities are allowed, such as pine cone collection, charcoal production and walking). (Fig. 10.1).

Outside the protected zones, large areas are used for irrigation, established late in the

1970s when a groundwater-based irrigation farming development plan started. It was sponsored by the United Nations Food and Agriculture Organization and the Spanish Government. Tourism is also an important economic activity. It is mainly beach-based and concentrated both seasonally (spring and summer) and spatially (Matalascañas and Mazagón coastal resorts with a capacity of around 300,000 people). A religious pilgrimage concentrates around 1 million people during one week at El Rocío village every year, close to the marshes and other fragile areas of the National Park. This causes a serious impact on the environment, mainly from the great number of vehicles and waste dumping.

The climate is Mediterranean sub-humid with Atlantic influence characterised by dry

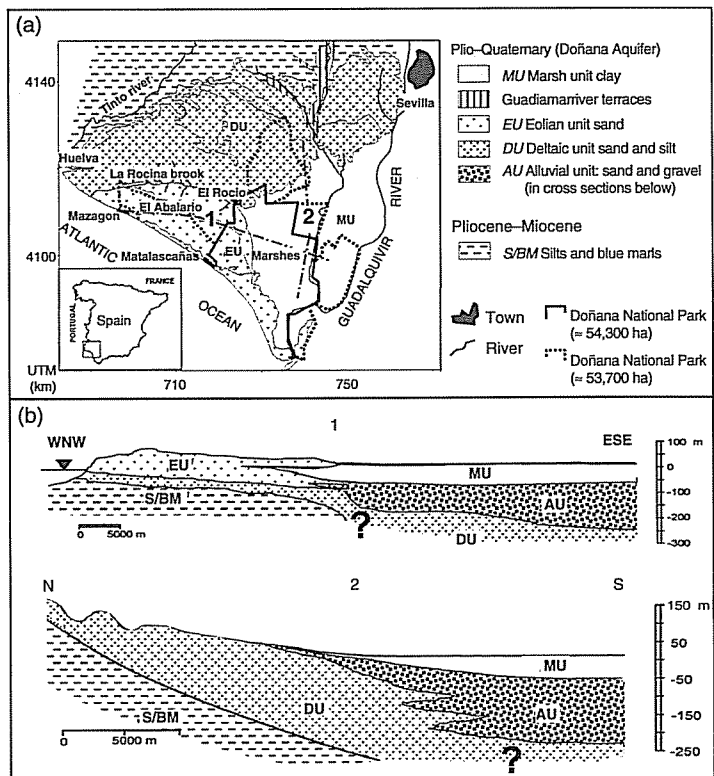


Fig. 10.1 Location, geology and geometry of the Doñana aquifer system. The aquifer limits coincide with those of the Plio-Quaternary sediments.

summers and wet winters. Mean rainfall, concentrated between October and March, is 500–600 mm, but has a very high inter-annual variability, from 1100 mm to 250 mm. Mean yearly temperature is around 17°C near the coast and 18°C in the centre of the area. Values above 35°C are often reached during July–August, while values under 0°C are seldom attained during December–January. Temperature shows very small inter-annual variation. The mean number of annual sun hours is close to 3000.

Two large rivers, the Tinto River to the NW, and the Guadalquivir River to the E, surround the aquifer area, but they do not contribute water to it. Surface water inside the territory is limited to a couple of small groundwater fed permanent rivers and some seasonal brooks, and to some permanent and many small temporal lagoons in small depressions in which the water-table crops out. Groundwater is the only permanent water source both for human and environmental uses.

Intensive groundwater exploitation since early in the 1980s, mostly for irrigation and to supply touristic areas, but also locally for some environmental uses, led to a groundwater level drawdown and to the development of conspicuous localised piezometric depression cones. The resulting water-table drawdown has reduced the aquifer's natural discharge through springs, streams and phreatic evapotranspiration, thus inducing slow vegetation changes and modifying the hydrological behaviour of wetlands (Coletto 2004; Manzano et al. 2005a).

Groundwater chemistry in most of the aquifer has been studied previously in several projects focusing on the aquifer behaviour characterisation. This information has been integrated with new studies carried out

in the framework of the EU project BaSeLiNe (2003), which focused on the natural (baseline) groundwater composition and its origin.

10.2 Geological and hydrogeological setting

The DAS comprises Plio–Quaternary, mostly unconsolidated, fine sediments deposited in fluvio-marine (alluvial, deltaic, aeolian, estuarine and marshy) environments, which overlie Pliocene and Miocene silts and marls. The Miocene to Quaternary sediments form a single multi-layered series between a few metres thick inland to more than 200 m thick at the coastline.

The aquifer system has a total surface area of around 2700 km², some 1800 km² of which comprises clay-rich marshland. The rest is mostly a sandy area, especially the coastal fringe, (some 70 km in length and a few to 30 km wide), going from the Guadalquivir river mouth to the Tinto river estuary, near the town of Huelva (Fig. 10.1).

The aquifer geometry and structure are shown in the cross sections of Fig. 10.1:

- From N to S: the lithology and thickness of the Quaternary units are variable. It consists of a thick Deltaic Unit of silts and sands (DU in Fig. 10.1), which is replaced near the northern border of the marshes by gravelly layers of the Alluvial Unit (AU in Fig. 10.1). This unit thickens to the south, has interlayers of clays and reaches the centre of the marshes. Further to the S, the gravels change gradually into sands, silts and clays, overlapping similar Miocene and Pliocene sediments (marls, silts and sandy silts), and giving way to a thick (50 to >300 m) sequence of very fine sediments (Salvany and Custodio 1995). The alluvial sediments are covered by

a sequence (50–70 m thick) of estuarine and marshy clays (Marsh Unit, MU in Fig. 10.1), nowadays separated from the sea by a recent littoral sand spit.

• From NW to SE: on top of the Miocene and Pliocene marine marls and silts there is a thin (<20 m) deltaic layer with gravels, which is covered by a thick (c.80 m) sand unit of Pleistocene to Recent age. This unit comprises fluvio-marine sediments overlain by alluvial and then aeolian sands. The aeolian layers have several interlayered clay bodies of lacustrine origin, sometimes with peat. In spite of its diverse origin, the whole sequence is named Aeolian Unit (EU in Fig. 10.1).

At the regional scale the surface of the aquifer system shows two lithologic domains: a clayey one in the marsh area, and a sandy one to the N and W of the marshes. The sandy domain roughly behaves as a water-table aquifer which in some places has two layers, a coarse one at depth and an overlying fine sand unit. Under the clayey domain a large volume of confined aquifer develops. Recharge to the aquifer occurs by rain infiltration in the sandy areas to the N and W of the marshes. There is also recharge through excess irrigation water in the agricultural areas, which however are irrigated with local groundwater and thus do not imply additional water.

Also at a regional scale, groundwater flows mostly to the S and SE – that is, to the area confined under the marshes –, to a main brook called La Rocina, and to the ocean. Under natural conditions, discharge takes place as seepage to the ocean, to the streams and to the many small phreatic wetlands situated on top of the aeolian sands, as phreatic evapotranspiration, as upward flows near the boundary (ecotone) between the sands and the clays, and perhaps through the Quaternary

clays in the confined area, although this is probably a minor term of the water balance. The SE sector of the confined aquifer (Alluvial Unit and Marsh Unit) contains almost immobile, old connate marine water which has not been flushed out on account of the low hydraulic head prevailing since the late Holocene sea level stabilisation some 6 ka BP (Manzano et al. 2001).

However, intensive groundwater abstraction has partially depleted natural discharge during the last three decades. Agricultural wells are concentrated near and along the contact between the sands and the clays, so that nowadays a large proportion of recharge water is pumped out from the unconfined area, largely in a zone close to the marshes (Custodio and Palancar 1995; Trick and Custodio 2004). Intensive and localised pumping has decreased phreatic evapotranspiration and natural seepage to springs and wetlands (Manzano et al. 2005a). Also, some local flow reversals between the Alluvial Unit confined under the clays and the overlying Quaternary clays, have been recognised to the NE of the marshes. They are contributing to the salinisation of formerly fresh groundwater irrigation wells.

The aquifer permeability ranges from moderate to low, with the most permeable materials (alluvial and aeolian sands with some thin interlayered gravel layers) cropping out to the west and north of the system.

10.3 Materials and methods used

This groundwater baseline study focuses on the western sector between La Rocina brook, the Atlantic Ocean and the centre of the marshes (see Fig. 10.1). Although less intensive, the study was also extended to a regional

groundwater flow path from the northern unconfined sector to the centre of the marshes.

Both historical and newly obtained chemical data were used to characterise the baseline composition of groundwater. Previous information on major components and environmental isotopes is abundant (Baonza et al. 1982; Poncela et al. 1992; Iglesias 1999; Delgado et al. 2001; Lozano et al. 2001, 2005; Manzano et al. 2001; Lozano 2004). For the purposes of the present study, about one hundred new samples were collected within the BaSeLiNe project during two campaigns (November 2000 and July 2001). They were analysed for major and some minor components, trace elements, and ^3H , $\delta^{18}\text{O}$, $\delta^2\text{H}$, $\delta^{13}\text{C}$ and ^{14}C . Most of the samples are from single-screen boreholes, a few are from multi-screened boreholes or open wells, and a few samples are lagoon waters.

The samples were collected in double-cap polyethylene bottles. Samples for trace elements were filtered with fibreglass 0.45 μm Millipore filters, acidified to pH less than 2 and kept refrigerated at around 4°C until analysis. The analyses were performed at the British Geological Survey (BGS, Wallingford, UK) and also at the Geological Survey of Spain (IGME, Tres Cantos laboratory in Madrid, Spain), using ICP-AES in both laboratories. Ten duplicates were used to check the coherence between both laboratories. In addition, 24 samples (fresh and brackish waters) were analysed for Br and Cl in the IGME by slow flow ion chromatography to characterise the origin of water salinity.

Tritium was analysed at the CEDEX (Centro de Experimentación de Obras Públicas) laboratory in Madrid (Spain); some analyses

of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were performed at the CSIC (Consejo Superior de Investigaciones Científicas) laboratory in Granada (Spain) and the rest were analysed at the CEDEX; $\delta^{13}\text{C}$ and ^{14}C were analysed at the University of Bern (Switzerland).

Time series data for Ca, Mg, Na, K, SO_4 , HCO_3 , pH, EC and groundwater levels from the water quality monitoring networks of the IGME and the IARA (Instituto Andaluz de Reforma Agraria, Andalusian Government) have also been used for the study of temporal and spatial chemical trends. The period covered is from 1973 to 2000. Measurement frequencies are variable: the decades between 1970 and 1980 are poorly represented, with few analyses, while the best-covered period (from 1990 to 2000) has monthly or even fortnightly measurements. Some 40 wells and boreholes have been studied, their datasets ranging from 100 to 400 measurements. These data are not shown in this paper, only the main conclusions from the studies.

Simple statistical treatment, classical hydrogeological graphs and hydrogeological cross sections have been used to identify and illustrate chemical water types, their spatial distribution and the existence of time/space chemical trends. The code SPSS8.0 (SPSS Inc. 1998) has been used for the statistical study of the most significant chemical variables (average, median, mode, standard deviation, variance, rank, maximum, minimum, and the 25, 50, 75 and 97.7 percentiles) and for principal component analysis (PCA).

The code PHREEQC-Version 2 (Parkhurst and Appelo 2002) has been used to check the hydrogeochemical conceptual model proposed for groundwater baseline evolution along flow paths.

10.4 Sources of chemical baseline levels in the Doñana aquifer

The primary sources of the chemical baseline levels groundwater chemistry are rainfall inputs and aquifer mineralogy. Both have been characterised in the study. As polluting sources and pollution processes are almost ubiquitous, potential pollution sources are also listed, and the presence of pollution indicators has been studied.

10.4.1 Rainfall and atmospheric fallout chemistry

Rainfall chemistry can be considered the minimum baseline concentrations in groundwater. The data available for the studied area come from three different sources and six different sites, randomly placed at different distances from the coast. Up to now, no attempt has been made to quantify the local landward chemical gradient of rainfall chemistry, although there is a recent study for chloride concentrations in the Iberian Peninsula rainfall (Alcalá and Custodio 2004).

Existing data were integrated and elaborated by Iglesias et al. (1996). Because of the different sampling places and sources, one of the most adequate ways of looking at the significant values is through simple statistical treatment. The 25, 50 and 75 percentile values of major elements, pH and electrical conductivity (EC) are shown in Table 10.1, which illustrates the characteristic compositions of the 34 samples available.

Local rainwater is of Na-Cl type. Most of the ionic ratios clearly show that the main solute source is of marine origin, both as wet

and dry deposition. The SO_4/Cl ratio, in equivalents, shows a sulphate excess ($\text{SO}_4/\text{Cl} = 0.2\text{--}0.9$) with respect to seawater ($\text{SO}_4/\text{Cl} = 0.1$). Using Cl mass balance between rain and phreatic water, only about 30% of S in rainwater can be accounted for from a marine origin. In areas without agricultural influence, the rest (70%) may be partly attributed to atmospheric supply of sulphide particles from the W of the aquifer recharge area (the dominant wind direction). The proposed original source for these particles is either open-pit mining activities in the numerous sulphide mines of the Portuguese-Spanish Pyrite Fringe, which crops out to the N and NW of Doñana, and/or industrial emissions from the Huelva industrial site, situated some 30 km to the NW. Part of the studied sector is under cultivation, so agrochemicals are also a local source of sulphur to groundwater, although atmospheric

Table 10.1 Characteristic composition of 34 rainwater samples taken at different places and periods over the western Doñana recharge area.

Component (mg L^{-1})	Percentiles		
	25%	50%	75%
HCO_3	6.1	8.54	16.46
SO_4	1.92	3.37	8.17
Cl	4.26	7.8	11.35
NO_3	0.06	0.12	0.62
Na	3	4.14	6.21
K	0.39	0.78	1.12
Ca	1.6	2.2	4.8
Mg	0.48	0.73	1.57
NH_4	0	0.18	0.54
CE $\mu\text{S cm}^{-1}$	37	50	69
pH	5.8	6.2	6.7

Note: Values incorporate dissolved dry deposition.

Source: After Iglesias et al. (1996).

input of sulphide particles has also to be considered.

10.4.2 *Aquifer mineralogy*

Aquifer mineralogy is dominated by amorphous silica, with some spatial differences due to the presence of K- and Na-feldspars (microcline and albite); illite, chlorite and kaolinite are minor components. Carbonate, mostly CaCO_3 , is present either as detrital grains or as shell remains, except in the upper sand layers of the western sector, where they have already been leached by rainfall infiltration.

10.4.3 *Pollution sources*

Although less accurately known, urban, agricultural and industrial water contamination sources are abundant in the aquifer recharge areas (Manzano et al. 2005b):

- Farming (agriculture and some animal farming) is widely developed on the aquifer outcrop area causing diffuse soil and both surface and groundwater contamination by nutrients, pesticides and heavy metals. Agrochemically derived SO_4 , NO_3 , Co, Cu, Br and Zn have been identified in shallow and intermediate depth groundwaters, according to previous and present studies;
- the highly contaminant agro-industry (mostly olive related) is concentrated around some villages on the northern outcrop of the aquifer. They generate a well-known surface water (rivers and streams) pollution problem by mostly difficult to degrade organic matter from olive oil production and also Na coming from olive treatment with NaOH;
- most of the sewer network has been developed in the last 15–20 yr, and some small villages and factories still dump untreated

waste water to the local streams and brooks and into infiltration areas;

- petroleum refining and pyrite burning, among other highly polluting activities, have been active since decades ago at the Huelva industrial site, some 30 km to the W of the recharge area.

Some pollution indicators have been studied and reported below. Though being a potential polluting source, up to now, marine intrusion has not been detected in the coastal area.

10.5 Hydrochemical characteristics of groundwater

10.5.1 *Water types*

A first approach to groundwater chemistry at a regional scale shows that water salinity ranges over three orders of magnitude. When plotting all the samples in logarithmic or similar plots (Fig. 10.2) it seems as if most of the waters were either the result of mixing or an evolution between two members:

- 1 A freshwater member, with EC (electrical conductivity) less than 1 mS cm^{-1} and mostly of Na–Cl type (locally Na–Ca–Cl– HCO_3);
- 2 A saline water member, with EC = $1\text{--}80 \text{ mS cm}^{-1}$ and mostly of Na–Ca–Cl– HCO_3 type.

The freshwater member corresponds to the most characteristic groundwater found in the western water-table area down to 40–50 m depth. The saline one is characteristic of the area confined under the marshes and also of some shallow layers in the Aeolian Unit around phreatic lagoons.

Though many samples are really the result of vertical mixing between fresh groundwater, flowing upward through or close to the marshy clays, and saline pore water, many others are mostly the result of local

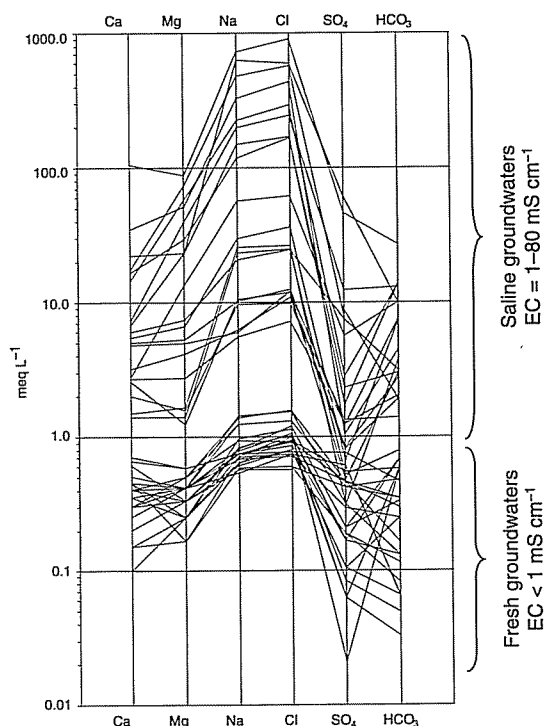


Fig. 10.2 Representative fresh and saline groundwaters from the Doñana area. Most of them have the same Na-Cl chemical facies, though locally some Na-Ca-Cl-HCO₃ waters may exist.

evaporative concentration in shallow lagoons, both directly or by dissolving previously deposited salts. Locally, water-table groundwater to the seaward side of the coastal dunes gets its moderate salinity mostly from marine spray.

Baseline composition ranges of fresh and saline waters were obtained through a basic statistical study. However the characteristic values and ranges are not described here, as the most relevant results arise from the interpretation of their regional evolution and changes with depth, as well as from the

study of the geochemical processes that control the calculated ranges.

10.5.2 Temporal and spatial groundwater chemistry evolution and causes

10.5.2.1 Evolution along main flow paths

Groundwater chemistry evolves along a flow path as shown in Fig. 10.3. Shallow and intermediate depth groundwater in the western water-table area is of Na-Cl type and has low mineralisation (EC less than 0.5 mS cm⁻¹). After previous and contemporary studies this water has been interpreted as the result of slightly evaporated rainwater, dissolving soil CO₂ and Na/K feldspars (Fig. 10.4). At greater depths (>50 m) groundwater mineralisation increases and water becomes of Ca-HCO₃ type as a result of calcite dissolution.

Flowing to the east, as groundwater approaches the marine and estuarine sediments it becomes brackish and saline mostly because of mixing with saline groundwater. A saline groundwater body (>40 mS cm⁻¹) is found in the coastal area, sometimes more concentrated than seawater. Recirculation of evaporated seawater when the marshes were open to the sea is a possible origin (Konikow and Rodríguez-Arévalo 1993).

A broad mixing zone develops from NW to SE under the marshes, but its geometry is not well known due to the difficulties of drilling adequate observation boreholes in the marsh area and of obtaining representative samples in a multi-layer aquifer. A number of baseline changes can however be identified at a local scale including: (1) increasing content of marine related water; (2) equilibrium with calcite; (3) sulphate reduction; (4) cation exchange between Na in solution and Ca/Mg in the solid phase.

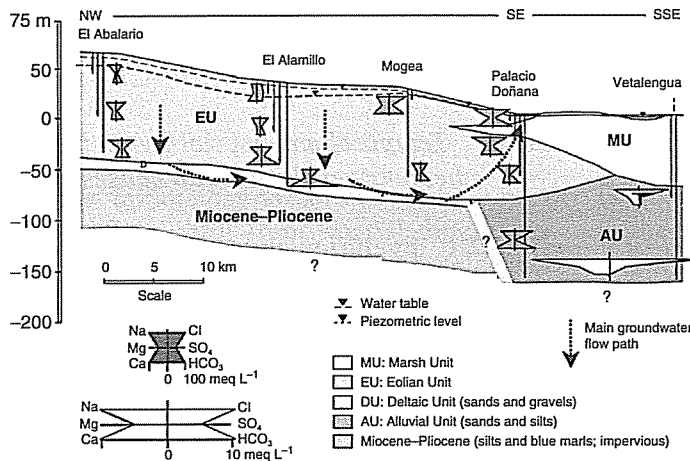


Fig. 10.3 Groundwater chemical evolution W-E along main flow paths. The section goes from El Abalarío, in the water-table western area, to the marshes (see Fig. 10.1).

A chromatographic spatial distribution is difficult to observe because of the few available sampling points southward, multi-screened boreholes and pumping wells in the marshes, which are not adequate to get samples following flow paths.

This chemical cross section is representative, in general terms, of groundwater evolution along flow at a wider scale. In the water-table area to the N of the marshes, where the aquifer is thin (<50 m) and consists of silts and siliceous and carbonate silty sands, groundwater is of the Ca-HCO₃ or Na-Ca-HCO₃-Cl type, but as it reaches the confined area groundwater evolves rapidly to a Na-Cl type and becomes brackish and finally salty.

10.5.2.2 Variations in depth and their causes

The evolution of major elements with depth in the western water-table area has already been introduced in Figs. 10.3 and 10.4. The combination of major elements with some minor and trace elements supports the hydrogeochemical model already proposed and adds new information.

Figure 10.5 summarises the statistical parameters for the elements whose concentrations vary significantly with depth. The term Upper Unit refers to the upper and central parts of the Aeolian Unit in cross section 1 of Fig. 10.1, where carbonates are absent. Lower Unit refers to the lower part of the Aeolian Unit plus the sediments of the Deltaic Unit, where carbonates exist. Almost all the components have a wider range of concentrations in the Upper Unit than in the Lower Unit. Very different situations can be observed for different elements when taking into account the median or the 75 percentile: •Ca, HCO₃, Ba, Sr and Mn are clearly more abundant in the Lower Unit. Except for Mn, all of them can be accounted for by the presence and dissolution of biogenic carbonate in this unit, while they are absent in the Upper Unit; •Na, Cl and Mg show very similar concentrations in both units, but they are slightly more abundant in the Upper Unit. This points to recharge water as the single common source. Mg evolution shows the apparent absence of dolomite in the Lower Unit, although Iglesias (1999) mentioned that this mineral is present in the northern part (see Fig. 10.4).

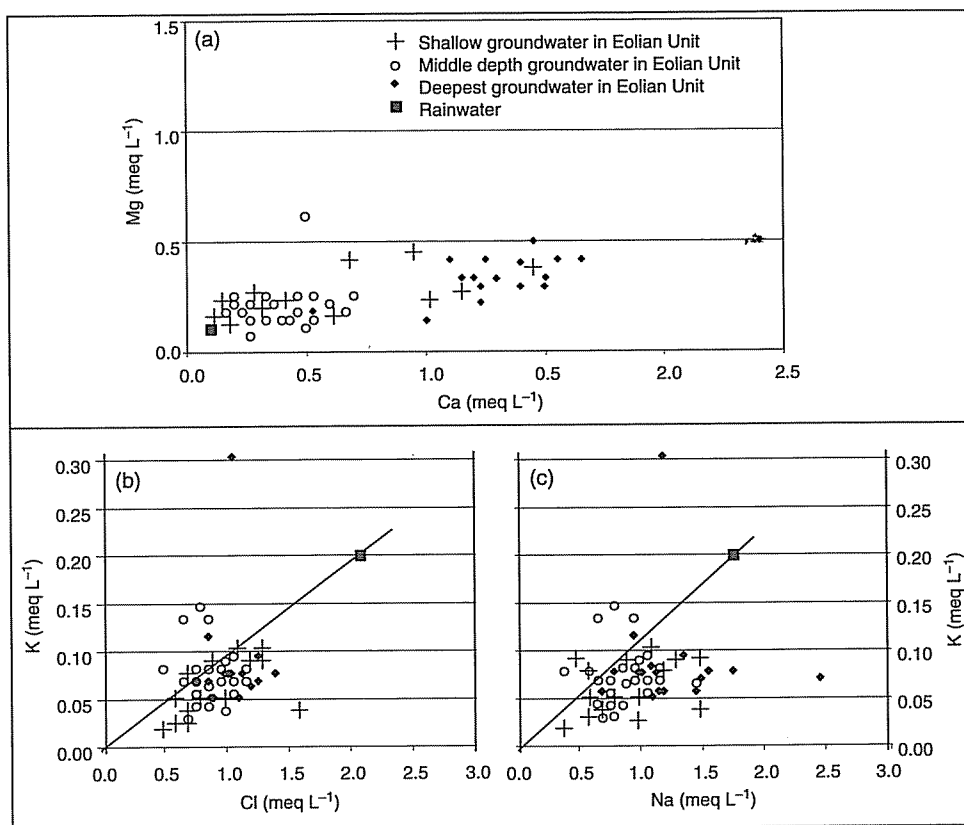


Fig. 10.4 (a) Mg versus Ca content in groundwater of the western water-table area as a function of depth. The aquifer is formed by siliceous sands and carbonate-containing sediments are present only in the deepest layers. The evolution of the Mg/Ca ratio suggests that there is only calcite, and dolomite is not present. (b) K versus Cl content in groundwater of the same area. The line separates the samples where Cl and K have a common origin (rainwater; samples along and below the line) and those including an additional source of K (samples above the line). (c) K versus Na content in the same groundwaters. The figure shows that there is a common source for K and Na in the groundwaters above the line, and this points to feldspar dissolution in the shallow and middle layers of the aquifer. Those processes have been checked by numerical modelling. (Redrawn after Iglesias 1999.)

•SO₄, NO₃, Co, Cu and Zn are clearly more abundant in the Upper Unit. The possible lithological sources (silicates) in both units are the same, so in the Upper Unit there is at least an additional source for these elements, which is considered to be recent, since they are not found yet in the Lower Unit. In the next section, two possible (anthropogenic)

sources are introduced to support these observations.

10.5.2.3 Temporal variations and their causes

After the combined study of chemical and groundwater level time series, and their

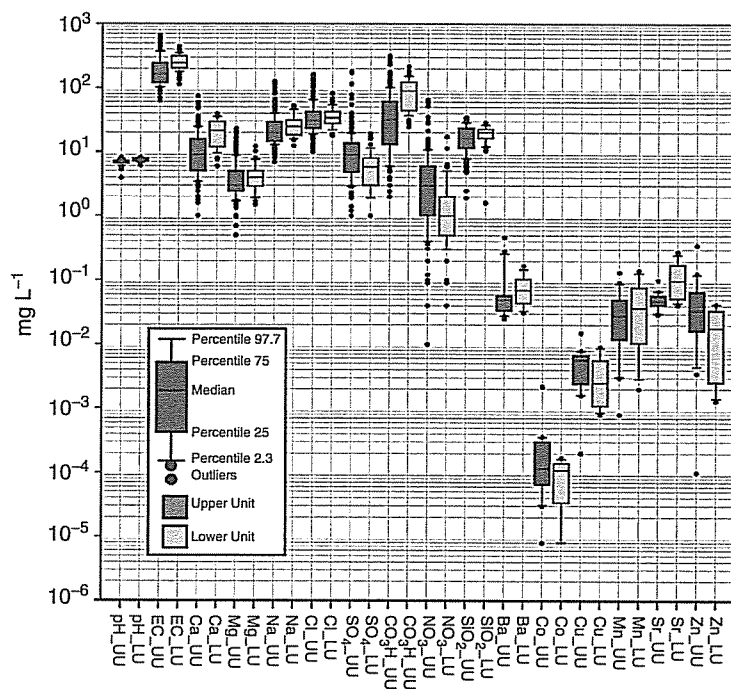


Fig. 10.5 Box plots of those elements with concentrations varying significantly with depth in the western recharge area. The Upper Unit is formed of siliceous aeolian sands without carbonates; the Lower Unit is formed by siliceous littoral sands and gravels with carbonates.

integration into the available knowledge about groundwater development and soil-use changes in different sectors, only a few out of the 40 analysed wells show visible temporal chemical variations. Changes are, however, very subtle, and there is not the same degree of certainty about the different proposed causes of evolution, so complementary work has to be done in some cases.

Two main types of evolution and proposed causes have been observed in two different zones (Fig. 10.6).

a) In the agricultural area to the NE of the marshes (the transition zone from the unconfined sands to the clays) groundwater development is intensive. A slight groundwater salinisation due to pumping-induced displacement of old saline water from the S towards the agricultural wells in the N is observed. Concentrations of Cl, Na, Mg and

SO₄ increase with time, because the saline water inflow fraction increases.

Most of the wells do not show permanent groundwater salinisation, but oscillating displacements of the mixing zone linked to seasonal pumping patterns seems to control groundwater chemistry. This cannot be observed with standard 'concentration versus time' plots, but it shows up when ion concentrations are plotted versus Cl (Fig. 10.6). When Cl increases because of saline water inflow to the well, Na increases in a lower proportion, Ca increases conspicuously and HCO₃ decreases significantly. This points to Na_{liquid}/Ca_{solid} exchange and to CaCO₃ precipitation as Ca activity increases. Numerical modelling with PHREEQC has validated the proposed geochemical model.

b) In the area to the NW of El Rocío, agriculture was abandoned early in the 1990s

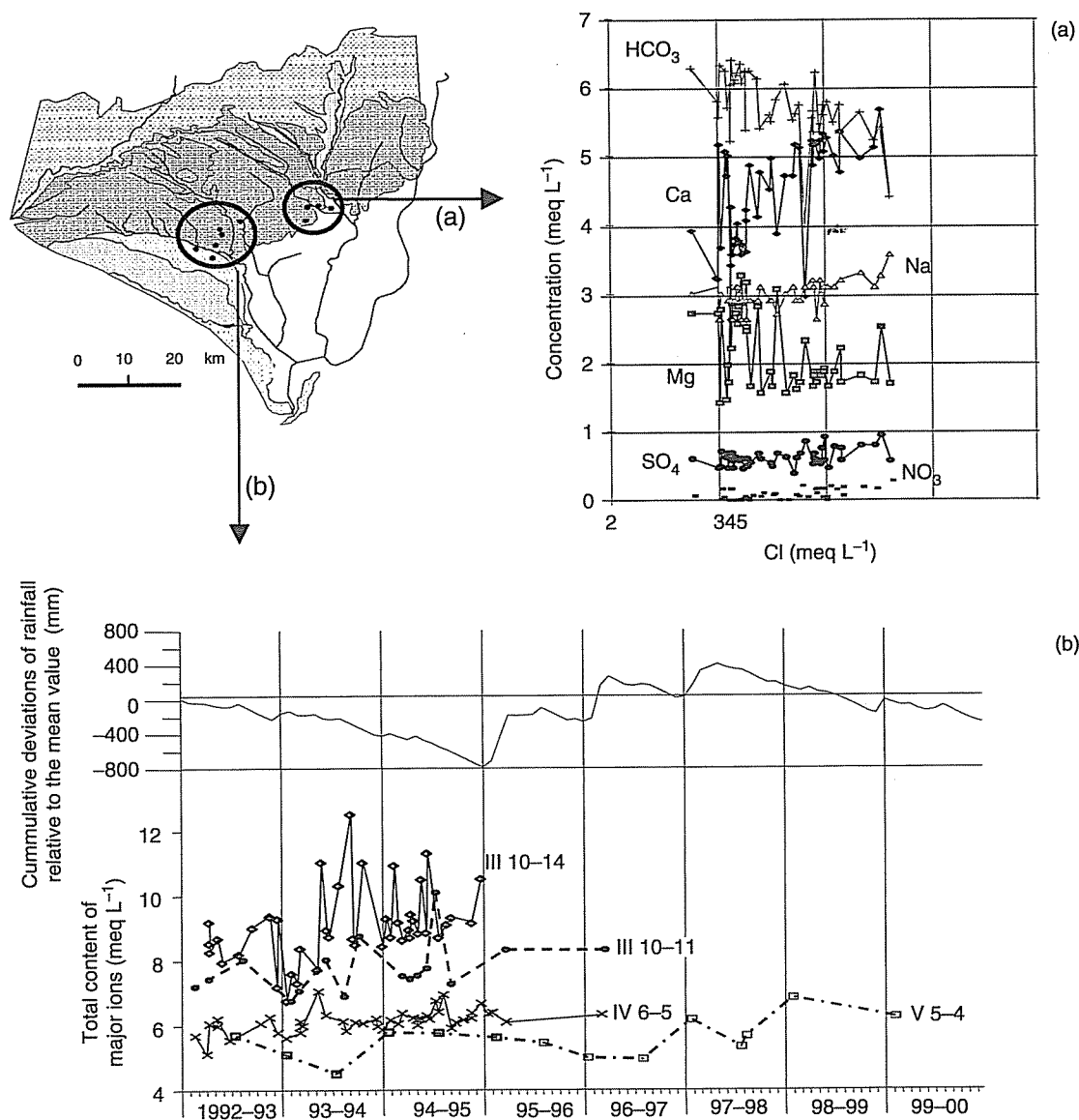


Fig. 10.6 Observed trends of groundwater chemistry temporal evolution: (a) Well in the agricultural area to the NE of the marshes: groundwater salinity increases due to pumping-induced displacement of old saline water from the south towards the agricultural wells in the north. Cl, Na, Mg and SO₄ increase due to growing saline water content; Ca increases due to Na_{liquid}/Ca_{solid} exchange, while HCO₃ decreases because of CaCO₃ precipitation as Ca activity increases. (b) Wells in a former agricultural area close to El Rocío. A slight groundwater salinisation that seems to follow a climatic pattern is observed. It is attributed to the input of salts remaining in the shallower part of the unsaturated zone transported by rainwater recharge.

(although re-established in the last few years), the data do not cover this period. A slight groundwater salinisation that seems to follow a climatic pattern is observed. It is primarily attributed to downward displacement by rainwater recharge of the salts remaining in the shallower part of the terrain since the times of active irrigated agriculture. This could be a very common polluting mechanism in the area during the coming years.

10.5.2.4 Pollution indicators and sources

In the upper part of the unconfined areas (less than 40 m depth), groundwater baseline composition has already been impacted by different human activities:

1 Agricultural pollution. In the agricultural areas, the presence of NO_3 (up to 65 mg L^{-1} in some shallow samples) denotes that baseline has already been modified by human activity. Besides the rain (with NO_3 concentrations $<1 \text{ mg L}^{-1}$), there are two nitrogen sources in the area: agrochemicals applied in agriculture (the principal one, but localised) and livestock farming (secondary but widespread until a few years ago).

In the westernmost, best-studied recharge area (El Abalario), SO_4 and NO_3 ranges and median concentrations are higher in the upper layers of the aquifers than in the lower ones. It is also the case for some trace components such as Zn, Co or Br (see Fig. 10.5). PCA calculations point to a common origin for Zn, Cr, Fe and Ni, which seems to be different to that of Cl, Na, Ca, Ba, Sr, Mn, pH and SiO_2 , assumed to be lithological. This suggests that SO_4 and NO_3 , Zn, Cr, Fe and nitrogen probably come from agrochemicals, and that they are still in transit to the deep layers of the aquifer.

In the confined areas, ^{14}C groundwater ages range from a few to more than 16 ka (dissolved inorganic carbon – DIC – content not evolves from the recharge areas to the confined aquifer). All the samples available are however admixtures of old and young components, as indicated by the presence of measurable tritium (Fig. 10.7) and NO_3 in most of them (Manzano et al. 2001). A few saline samples from the agricultural zone to the NE of the marshes contained NO_3 (between 0.3 and 100 mg L^{-1}), thus agriculture can account for this contamination. However, many others are from boreholes placed well inside the marshes and far from the farming areas (e.g. borehole 13 in Fig. 10.7). In these boreholes, NO_3 can be explained through (1) the existence of vertical flows along boreholes in the confined areas and (2) the presence of remnants of almost immobile drilling water in the formations surrounding the sampled boreholes.

2 Atmospheric pollution. Heavy metals have been found down to 25–30 m depth (Iglesias 1999; BaSeLiNe 2003). In the farming areas, they can also be derived from agrochemicals, but in the protected areas (free of agricultural activity) the increased concentrations of some industrially derived elements in the upper layers of the saturated zone reflect the atmospheric input of pollutants from the nearby Huelva industrial area. This is supported by the calculated tritium ages for the western water-table area, which show residence times (t_r) of a few years in the top 10 m, $t_r < 35$ years for groundwater shallower than 35–40 m and $t_r > 40$ years for groundwater deeper than 40 m. The ^{14}C ages indicate that even the oldest groundwaters in the water-table areas are less than a few centuries old.

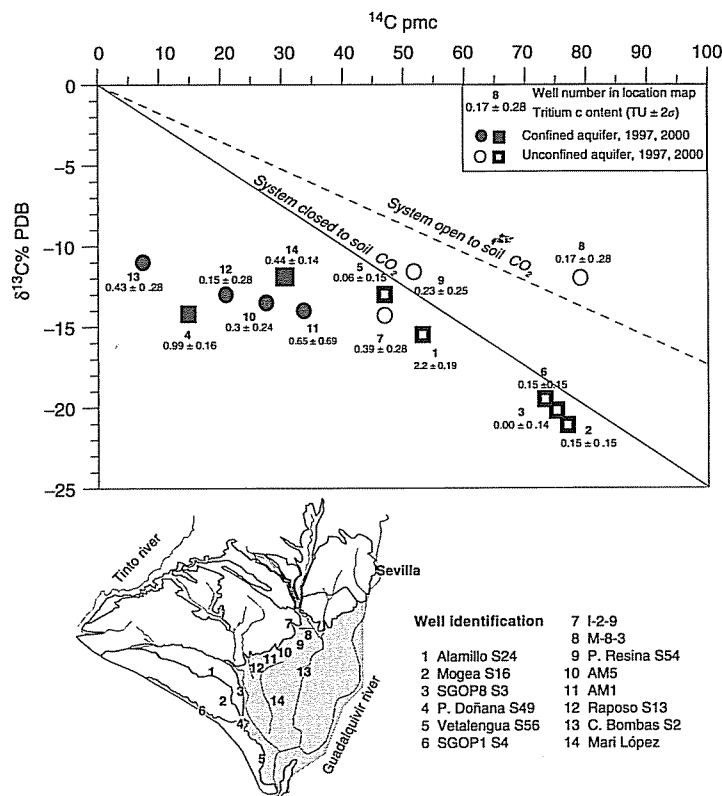


Fig. 10.7 Tritium, ¹³C and ¹⁴C contents in groundwater in the water-table aquifer and in the confined sector under the marshes.

Moreover, the observed SO₄ excess in local rainwater relative to marine airborne sources also points to additional sulphur sources in recharge water. Two sources can potentially be contributing: dust and gas emissions from the nearby Huelva industrial site to the W of Doñana, and pyrite-derived dust transported from the many open-pit mining activities in the Spanish-Portuguese Pyrite Fringe, to the N and NW of Doñana.

10.6 The geochemical model of groundwater baseline in the DAS

The studies to characterise groundwater baseline composition and evolution have

focused mainly in the western recharge area and, less intensively, in the northern one. The integration of previous studies and the new results have allowed the development of a geochemical model to explain groundwater baseline composition.

The geochemical model of groundwater baseline in the siliceous DAS can be established as a function of the unconfined or confined character of the aquifer as follows:

- 1 *Groundwater baseline in the unconfined areas of the aquifer.* The following main processes control geochemical evolution: (a) rainwater composition, which is of Na-Cl type, but with sulphate and other anthropogenically-derived components from the nearby Huelva industrial site;

- (b) equilibrium with silica;
- (c) dissolution of soil CO₂;
- (d) dissolution of Na/K feldspars;
- (e) dissolution of CaCO₃ (in the deepest layers of the western unconfined area and throughout the northern unconfined area).

The resulting mineralisation ranges from low to moderate (<0.2 to 1 mS cm⁻¹). In the upper part of the unconfined areas (c.<40 m deep), groundwater baseline has already been impacted by different human activities. In the agricultural areas, this is pointed out by the presence of agrochemically derived substances (Br, pesticides, SO₄, NO₃, heavy metals) down to depths of 25–35 m. In the protected areas, where agriculture has never been active, the higher concentrations of some industrially derived elements (mainly metals) in the upper layers of the saturated zone with respect to the deeper ones reflects the atmospheric input of pollutants from the nearby Huelva industrial site. This agrees with the calculated tritium-based ages for the western water-table area, which have residence times less than 35 years for flow paths shallower than 35–40 m, and more than 40 years for deeper flow paths. Radiocarbon-based ages show that even the oldest groundwaters in the water-table areas are younger than a few centuries.

2 Groundwater baseline evolution from the water-table to the confined areas. Following the main groundwater flow paths from the unconfined to the confined parts of the aquifer (from N to S and from W to SE), the main chemical change is that groundwater becomes increasingly saline because of mixing with the old marine water trapped both in the confined permeable layers and in the clays. A broad mixing zone develops from NW to SE under the marshes, but its geometry is not well known due to the difficulties

of drilling adequate observation boreholes and of obtaining representative samples in a multi-layered aquifer.

3 Groundwater baseline in the confined sector of the DAS. Baseline composition changes mostly due to the following processes:

- (a) mixing with modified old marine water;
- (b) equilibrium with calcite;
- (c) cation exchange [Na/Ca-(Mg)] in moving fresh-saline water fronts;
- (d) sulphate reduction (depletion with respect to conservative mixing with sea water);
- (e) probably C incorporation from sedimentary organic matter evolution, although the ¹³C studies did not confirm this.

The resulting salinities range from 1 mS cm⁻¹ up to 80 mS cm⁻¹. Although groundwater chemistry in the confined area is mostly naturally derived (baseline), in some agricultural wells exploiting confined layers close to the northern water-table area, groundwater baseline is already being modified by agricultural pollutants.

10.7 Conclusions

The DAS is a thick, detrital and mostly siliceous young system situated in an area that shares intensive groundwater use for agriculture and human supply with strictly protected natural habitats that depend on groundwater. Using the methodology proposed in Chapter 1 of this book, the natural water quality of the Doñana aquifer has been studied. This methodology is based on a geochemical approach, so that through the integrated use of statistics, chemical trends, time tracers and geochemical modelling it has been possible to establish the natural groundwater quality variations and the responsible processes, as well as to identify

the areas and potential sources of the pollution processes observed.

The groundwater quality of the DAS and its natural or altered nature may be summarised as follows:

- The unconfined part of the aquifer contains low mineralised freshwater that is of the Na-Cl type, with low hardness, and is slightly acidic in the upper part of the western area. It becomes harder and more alkaline where the terrain still contains remnants of calcite shells, and it is also slightly more saline due to decreasing recharge rate. Anthropogenic effects from airborne pollutants and agricultural activities are limited to the upper part of the aquifer.
- The confined part of the aquifer mostly contains brackish to connate saline water, emplaced in the past. There is a broad mixing zone with the freshwater of the unconfined aquifer that is currently altered to some extent by the effect of groundwater development.

Thus, the early protection of a large part of the territory since the 1980s has contributed to the preservation of groundwater baseline conditions, which still prevail in parts of the aquifer. However, and beyond the local disturbance of groundwater baseline by agricultural and/or industrial pollution, the natural baseline is currently also being modified in the shallower layers of the protected area due to atmospheric input of pollutants, incorporated into rainwater recharge to the aquifers.

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