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ORIGINAL ARTICLE

Water qualitiy and distribution of trace elements in the Doñana aquifer (SW Spain)

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Abstract The variations of groundwater quality in the unconfined zone of the Almonte-Marismas aquifer, upon which Doñana National Park is located, are analysed. Most sampled points are multiple piezometers, allowing for the vertical distribution study of the hydrogeochemical characteristics in the aquifer. Temperature, pH, electrical conductivity, dissolved oxygen and redox potential were determined in the field. A large number of parameters, including major ions and a large amount of minor and trace elements, were analysed. In the southern zone, where aeolian sands crop out, water composition in the shallower part of the aquifer is of the sodium chloride type, with low pH (5.5–6) and mineralization (<200 µS/cm) values. As water circulates through the aquifer, bicarbonate and calcium concentrations increase slightly. In agricultural or urban zones, nitrates and sulphates present their highest contents in the upper part of the aquifer. In zones with low pH levels (around 6), concentration of many trace metals (Al, Co, Cr, Cu, Ni, Zn, etc.) also shows a distribution similar to that of sulphates and nitrates, which indicates its fertilizer-linked origin. In zones with neutral or alkaline pH, regardless of high nitrate content, concentration of the above mentioned metals is very low due to its immobilisation by surface adsorption processes. The distribution of Br contents also shows the effects of agricultural pollution.

Keywords Groundwater · Pollution · Trace elements · Aquifer · Doñana

Introduction

Doñana National Park (DNP), with an extension of 760 km^2, is one of the most important wetlands in Europe as a wintering site for numerous waterfowl and as a key point in the migration route of other birds. The Park belongs to the RAMSAR Convention and the MAB Programme, and is considered a World Heritage site by UNESCO.

Many ecosystems of this large wetland depend on groundwater. DNP receives groundwater contribution from the Almonte-Marismas aquifer, with a much larger extension than the Park itself (Fig. 1). The water table is very close to the ground surface, where different plant communities can be distinguished depending on water depth (Custodio 1995; Muñoz Reinoso and García Novo 2005) and water quality (Manzano and Custodio 2006). In addition, the aquifer feeds a large number of seasonal and permanent lagoons and main streams, such as the Rocina Creek (Fig. 1), which forms a rich lush gallery forest.

From the 1970s, intense exploitation of groundwater in the DNP surrounding areas has been performed for: (1) agricultural use in the surrounding areas of the DNP, and (2) supply of Matalascañas tourist resort, which, although smaller than the former, are performed in a zone adjacent to the Park.

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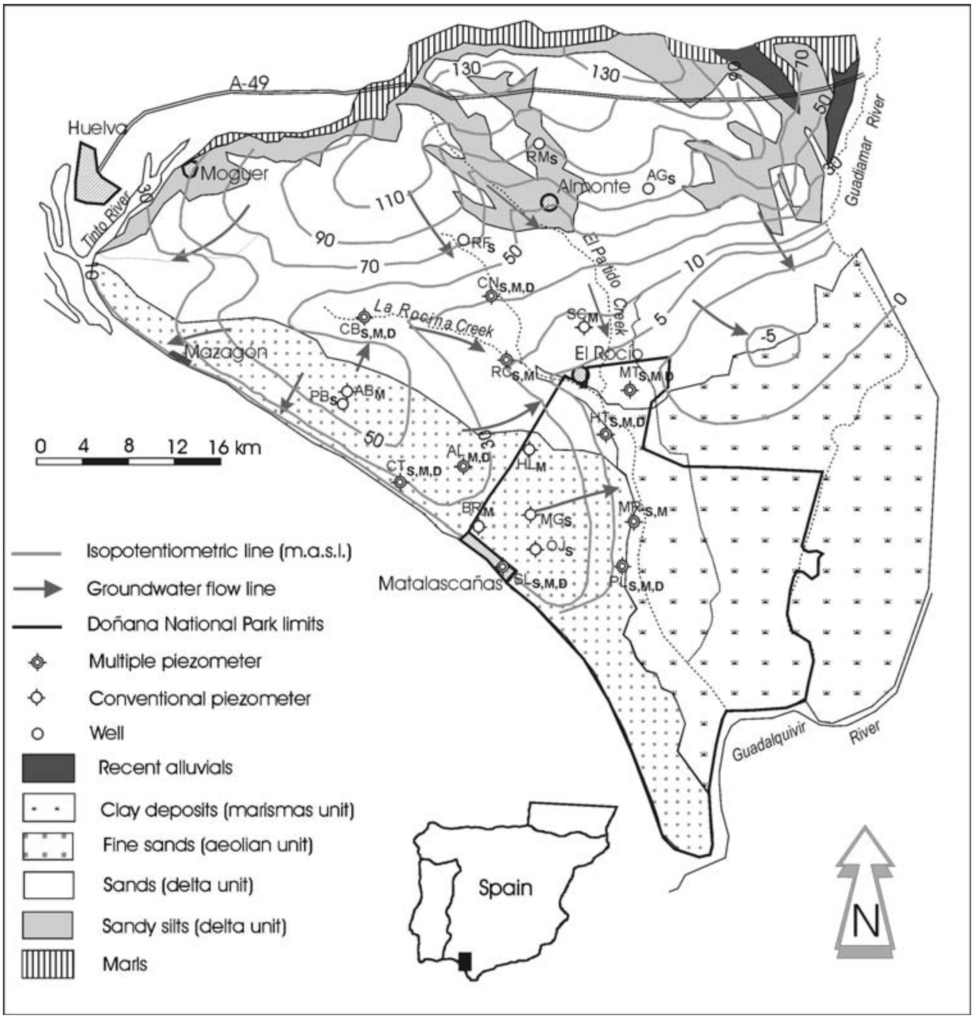


Fig. 1 Hydrogeological map of the Almonte-Marismas aquifer which shows the limits of Doñana National Park and the sampled points (isopotentiometric lines from Manzano and Custodio 2006). Subindexes indicate the sampling depth: *S* shallow, *M* intermediate and *D* deep

There are several works warning about the impact that groundwater withdrawals can have on DNP (Llamas 1988; Suso and Llamas 1993; Trick and Custodio 2004). The works by Serrano and Serrano (1996), Zunzunegui et al. (1998) and Muñoz Reinoso (2001) point out that a number of changes are already occurring in some ecosystems close to the zones where groundwater withdrawals are greater.

Groundwater quality variations may also have an impact on DNP ecosystems (Custodio 1995). The natural vegetation in Doñana has adapted to local groundwater chemistry (Manzano and Custodio 2006), thus any variation in groundwater quality can cause changes in the different ecosystems. However, research on the hydrochemistry and quality of groundwater in this system is scarce. Baonza et al. (1984) have done an extensive work focused on the distribution of water isotopes (^{18}O, ^{2}H and ^{3}H) in the aquifer. Other works analyse the hydrochemical characteristics of some specific sectors (Manzano et al. 1991; Delgado et al. 2001; Lozano et al. 2002). There are no works analysing the contents of trace elements in the aquifer.

The objectives of this work are, on the one hand, the hydrochemical characterisation of the unconfined part of the Almonte-Marismas aquifer in the DNP surrounding areas and to identify potential anthropogenic influences on groundwater quality.

Hydrogeological setting

The impermeable base of the aquifer is made up of Upper Tortonian-Lower Pliocene marls that crop out north of the system and go progressively deeper to the SE, so that the thickness of the aquifer increases in this direction.

According to Salvany and Custodio (1995), four plio-quaternary units are found on these loams: (1) deltaic unit, made up of sands, silts and gravels, (2) aeolian unit, developed mainly on the littoral strip and made up of very homogeneous fine sands, (3) alluvial unit, made up of gravels, sands, silts and clays which are mostly found under the current marshes, and (4) marsh unit, mainly made up of clays and silts, and overlying the alluvial unit. Grain size variations at a lower scale cause the aquifer to present a large heterogeneity, both vertically and horizontally.

In the marshes, the confined aquifer is overlain by clay deposits. In this zone, there are sectors with high salinity due to the presence of seawater of connate origin (ITGE 1992), trapped by the recent closure of the Guadalquivir River estuary (Ruiz et al. 2004). The aeolian unit, south of the Rocina Creek, has a low permeability and acts as an aquitard overlying the deepest layer (deltaic unit) of higher transmissivity (Custodio 1995; Trick and Custodio 2004).

The water table is very shallow (between 1 and 10 m), adapting itself to the topography. Groundwater natural flow direction is toward the sea in the coastal zone, toward the Tinto River in the western sector, toward the confined aquifer under the marsh in the SE, and toward the main streams of the sector (Fig. 1).

The aquifer thickness increases from 10 m in the northern part up to over 200 m to the South. Transmissivities range from some 10^{-4} m^2/s in the northern part of the aquifer to values near 10^{-2} m^2/s in the zones close to the northern boundary of the marsh. The storage coefficient ranges from 10^{-4} to 10^{-3} in the confined aquifer, and from 2 to 5% in the unconfined part (ITGE 1992).

The system's main source of recharge is direct infiltration from precipitation in the unconfined part of the aquifer. The aquifer resources are around 200 hm^3/year. Discharge occurs in different ways: drainage toward the main streams of the zone, flow to the sea in the coastal zone, evapotranspiration in zones with a shallow water table level, and slow flow through the clay layers of the marsh. Finally, by pumpage, which has been relevant since the mid 1970s and is currently estimated around 60 hm^3/year.

Materials and methods

To conduct the sampling, the piezometric control network which the Guadalquivir Hydrographic Confederation has in the Almonte-Marismas aquifer was used (Fig. 1). Most of these piezometers are multiple, i.e. are made up of several perforations at different depths. Depending on depth at each point, different piezometers have been distinguished: shallow, with an average depth of 17 m (subindex S); intermediate, with an average depth of 52 m (subindex M); and deep, with an average depth of 97 m (subindex D).

The piezometers are made of PVC, slotted in their final section and packed with 1–3 mm diameter silica gravel (Mantecón et al. 1995). Drillings with metal casing were not sampled to prevent potential contamination of trace elements. Some samples were also collected in excavated shallow wells, with maximum depth of 20 m (points PAB_S, HAT_S, ALG_S, REF_S and REM_S). The depth of control points is shown in Table 1.

The sampling was conducted in September 2004. Samples were obtained using a GRUNDFOSS 1.4401 DIN W.-Nr stainless steel pump activated by a generator set. Before measurement, the piezometer was pumped long enough to renovate the water inside and to allow for stabilisation of the water physical–chemical characteristics.

Temperature, electrical conductivity, pH, dissolved oxygen and redox potential were determined in situ using portable meters (HI 9025, HI 9033 and HI 9143). For the determination of the redox potential, a sampling probe with a platinum electrode and an Ag/AgCl reference electrode was used. The equipment was calibrated before the sampling. The redox potential was corrected to obtain the potential relative to the hydrogen electrode (Nordstrom and Wilde 1998).

A sample was collected at each point for the analysis of cations and another for anions. The samples were filtered (0.45 μm) in the field and cold stored in prewashed polyethylene bottles. The sample for the analysis of cations was acidified with Merck® suprapure HNO_3 to a pH of less than 2.

The analyses were performed at the University of Huelva R&D services. The determination of anions (Cl, SO_4, F, Br, NO_3, NO_2) was conducted by high performance liquid chromatography (HPLC) using a Dionex DX-120 ion chromatographer. The analyses of bicarbonates and carbonates were conducted in triplicate by volumetric measurement with HCl 0.01 N.

The determination of Ca, Mg, Na, K, Si, Al, Fe and Mn was performed with a Jobin Yvon (ICP-OES) optical spectrometer (JY Ultima 2), equipped with a cyclonic concentric nebulizer. Multielement calibration standards were prepared from individual certified standards (SCP SCIENCE).

The determination of trace elements (As, Ba, Be, Cd, Cd, Co, Cr, Cs, Cu, Li, Mo, Ni, Pb, Rb, Se, Sr, Th, Tl, U, V, W, Y and Zn) was performed by ICP-MS (HP4500). External calibration was done with SPEX® blank, 1, 10 and 50 μg/L multielement solution standards CLMS-1, CLMS-2 and CLMS-4. During determinations a monitor 10 μg/L solution was included to control the signal evolution during the sequence performance and, where needed, to correct equipment drift. The measurement accuracy was better than 5% RSD for most of the analysed elements.

The laboratory has a quality control plan. For each series of analyses a duplicate sample is included at random. A blank is introduced at the beginning of the series and then every ten samples. The calibration standards used are periodically analysed. Finally, analyses are verified by certified reference materials (SRM® NIST 1640 for trace elements). The error for electrical balance between anions and cations is lower than 5%, except for two samples with a very low salinity (129 and 205 μS/cm), which is of 8.9%.

The saturation index of the samples was analysed using the WATEQ4F programme (Ball and Nordstrom 1991).

Table 1 Field data and major ion concentrations

	Well depth (m)	Water depth (m)	Temperature (°C)	pH	EC (µS/cm)	Eh (mV)	DO (mg/L)	DO (%)	HCO_3 (mg/L)	CO_3 (mg/L)
AB_M	70.0	2.65	21.6	7.50	180	366	2.9	31.0	55.6	ND
AG_S	22.5	ND	20.5	7.48	1022	324	11.0	122.0	481.0	ND
AL_M	54.0	5.95	20.3	5.88	106	265	4.1	48.0	13.9	ND
AL_D	112.0	18.91	20.4	10.49	212	231	5.9	64.0	48.7	13.9
BR_M	48.0	ND	20.5	6.31	129	332	8.7	93.0	8.1	ND
CB_S	24.0	3.34	21.0	9.63	427	274	5.9	64.0	26.7	7.0
CB_M	40.0	2.85	22.4	8.14	1199	246	ND	ND	207.5	ND
CB_D	63.0	0.00	22.7	8.22	885	191	1.9	21.0	231.8	ND
CN_S	6.0	2.20	23.0	6.09	247	326	6.8	78.0	28.5	ND
CN_M	23.0	2.90	22.0	7.19	435	315	3.6	40.0	197.0	ND
CN_D	50.0	1.58	20.4	8.26	326	121	0.0	0.0	114.7	ND
CT_S	22.0	8.90	20.8	5.66	116	386	9.6	79.8	2.3	ND
CT_M	54.4	8.00	20.5	6.04	109	343	4.0	43.5	5.8	ND
CT_D	121.0	5.75	20.4	8.23	225	365	0.6	6.9	85.8	ND
HL_M	62.4	5.32	20.1	7.28	196	141	0.0	0.0	0.0	ND
HT_S	4.0	1.20	23.0	5.87	813	344	1.9	22.0	16.2	ND
HT_M	49.3	3.80	20.3	9.65	205	264	4.4	48.0	24.3	7.0
HT_D	63.3	3.65	20.4	8.20	256	331	5.1	54.0	105.5	ND
MG_S	14.0	2.13	20.3	6.51	224	356	6.9	74.0	24.3	ND
MR_S	15.2	0.30	21.5	6.64	172	212	3.1	34.0	0.0	ND
MR_M	24.5	Flowing	19.9	6.47	175	212	1.9	21.0	0.0	ND
MT_S	27.0	4.85	20.1	8.14	329	303	7.6	80.0	133.3	ND
MT_M	100.0	4.46	20.0	7.58	332	313	1.4	15.0	162.3	ND
MT_D	153.0	3.90	19.5	7.53	445	317	1.4	15.0	202.8	ND
OJ_S	18.0	2.72	19.6	7.13	136	347	7.4	78.0	29.0	ND
PB_S	5.0	3.62	24.0	7.18	341	321	4.2	48.0	233.0	ND
PL_S	9.0	0.50	21.5	7.96	265	224	6.2	68.0	92.7	ND
PL_M	28.0	Flowing	20.2	7.05	225	163	0.0	0.0	60.2	ND
PL_D	64.0	Flowing	20.1	6.85	170	323	2.5	27.0	48.7	ND
RC_S	9.7	2.15	22.5	5.88	251	318	7.6	87.0	7.0	ND
RC_M	25.8	0.32	19.6	7.83	283	134	4.9	52.5	100.4	ND
RF_S	9.7	1.60	21.5	6.46	405	344	5.3	59.0	29.0	ND
RM_S	15.3	6.50	21.2	7.96	428	322	7.5	83.0	179.6	ND
SC_M	44.0	18.92	20.9	6.29	575	331	8.7	95.0	27.8	ND
SL_S	45.6	12.45	20.5	6.43	409	291	8.1	87.0	66.1	ND
SL_M	103.0	12.50	20.5	5.46	128	325	5.0	59.1	13.9	ND
SL_D	150.0	14.90	20.2	6.83	162	152	0.0	0.0	29.4	ND
Mean	47.3	5.28	20.9	7.25	339	277	4.6	50	83.6	9.3
Median	40.0	3.64	20.5	7.18	251	317	4.7	50	48.7	7.0
Minimum	4.0	0.00	19.5	5.46	106	−121	0.0	0	0.0	0.0
Maximum	153.0	18.92	24.0	10.49	1199	386	11.0	122	481.0	13.9
SD	39.7	5.09	1.1	1.16	257	96	3.0	32	99.0	4.0

	SO_4 (mg/L)	Cl (mg/L)	F (mg/L)	Br (mg/L)	NO_2 (mg/L)	NO_3 (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SiO_2 (mg/L)
AB_M	3.4	24.0	<0.1	0.10	<0.1	4.7	14.0	3.5	15.0	9.6	23.6
AG_S	88.8	88.8	0.59	0.74	<0.1	74.8	47.0	32.0	217.0	1.0	79.3
AL_M	3.1	22.4	<0.1	0.12	<0.1	0.0	4.0	1.9	14.0	2.1	17.1

Table 1 continued

	SO_4 (mg/L)	Cl (mg/L)	F (mg/L)	Br (mg/L)	NO_2 (mg/L)	NO_3 (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	SiO_2 (mg/L)
$\mathrm{AL_D}$	7.0	28.4	<0.1	0.10	<0.1	4.7	5.0	2.3	23.0	24.0	17.1
$\mathrm{BR_M}$	9.8	22.0	<0.1	<0.1	<0.1	6.0	6.0	4.0	14.0	0.8	17.1
$\mathrm{CB_S}$	40.2	111.0	<0.1	0.43	<0.1	2.6	34.0	3.1	70.0	4.0	12.9
$\mathrm{CB_M}$	<0,1	376.0	0.30	2.22	<0.1	5.0	25.0	17.0	263.0	7.3	15.0
$\mathrm{CB_D}$	<0,1	229.0	0.18	1.29	<0.1	6.0	10.0	12.0	216.0	6.6	15.0
$\mathrm{CN_S}$	37.6	27.6	<0.1	0.18	<0.1	30.3	10.0	5.2	37.0	11.0	38.6
$\mathrm{CN_M}$	22.0	43.4	0.10	0.17	<0.1	17.7	48.0	12.0	51.0	3.6	21.4
$\mathrm{CN_D}$	3.5	44.8	<0.1	0.20	<0.1	3.1	17.0	6.4	36.0	1.8	17.1
$\mathrm{CT_S}$	4.4	29.2	<0.1	<0.1	<0.1	2.4	2.0	2.3	15.0	2.3	12.9
$\mathrm{CT_M}$	2.6	26.4	<0.1	<0.1	<0.1	6.0	4.0	1.6	13.0	3.0	15.0
$\mathrm{CT_D}$	9.6	31.4	<0.1	0.10	0.26	0.0	26.0	3.6	23.0	4.7	32.1
$\mathrm{HL_M}$	2.9	38.3	0.12	0.14	<0.1	1.2	11.0	2.6	24.0	4.1	18.4
$\mathrm{HT_S}$	124.0	208.0	0.19	0.60	<0.1	16.9	38.0	18.0	114.0	8.7	17.1
$\mathrm{HT_M}$	24.7	37.1	0.12	0.14	<0.1	0.7	13.0	0.8	24.0	3.4	10.9
$\mathrm{HT_D}$	5.2	30.8	<0.1	0.12	<0.1	0.3	31.0	3.2	20.0	3.1	21.0
$\mathrm{MG_S}$	21.2	41.1	<0.1	0.13	<0.1	8.1	14.0	7.2	23.0	1.4	17.1
$\mathrm{MR_S}$	4.9	32.3	<0.1	0.11	<0.1	1.8	8.0	2.1	22.0	2.4	27.9
$\mathrm{MR_M}$	4.7	34.7	<0.1	0.13	<0.1	<0.1	6.7	2.3	23.0	2.3	27.9
$\mathrm{MT_S}$	10.9	41.2	0.11	0.17	<0.1	7.0	25.0	8.4	35.0	5.7	17.1
$\mathrm{MT_M}$	8.8	36.0	<0.1	0.14	<0.1	<0.1	40.0	6.5	27.0	1.7	27.9
$\mathrm{MT_D}$	16.6	56.7	<0.1	0.20	<0.1	0.8	53.0	9.3	38.0	2.1	23.6
$\mathrm{OJ_S}$	10.8	18.9	<0.1	<0.1	<0.1	3.3	7.8	3.1	13.0	2.2	13.9
$\mathrm{PB_S}$	16.8	14.6	<0.1	<0.1	<0.1	20.7	68.0	7.4	11.0	9.7	6.4
$\mathrm{PL_S}$	5.5	43.9	<0.1	0.13	<0.1	2.1	27.0	4.0	32.0	2.1	27.9
$\mathrm{PL_M}$	5.3	42.2	<0.1	0.15	<0.1	<0.1	16.0	3.8	30.0	0.5	32.1
$\mathrm{PL_D}$	3.7	26.0	<0.1	<0.1	<0.1	1.1	11.0	3.0	21.0	1.8	38.6
$\mathrm{RC_S}$	14.3	52.2	<0.1	0.18	<0.1	15.7	6.7	5.6	33.0	2.2	14.8
$\mathrm{RC_M}$	4.7	39.4	<0.1	0.21	<0.1	1.7	21.0	4.6	38.0	2.8	23.6
$\mathrm{RF_S}$	56.7	82.7	<0.1	0.29	<0.1	5.5	31.0	15.0	34.0	6.1	7.7
$\mathrm{RM_S}$	21.5	18.0	0.37	0.30	<0.1	77.1	62.0	19.0	14.0	1.4	27.9
$\mathrm{SC_M}$	38.6	101.0	<0.1	1.32	<0.1	94.7	20.0	13.0	77.0	6.8	32.1
$\mathrm{SL_S}$	56.7	52.9	<0.1	0.18	<0.1	42.9	22.0	17.0	54.0	2.2	12.9
$\mathrm{SL_M}$	5.9	24.6	<0.1	<0.1	<0.1	4.2	4.0	1.8	19.0	1.6	34.3
$\mathrm{SL_D}$	2.1	30.0	<0.1	<0.1	<0.1	0.0	6.0	2.4	21.0	3.3	10.7
Mean	20.0	59.6	0.23	0.35	0.26	13.8	21.5	7.2	47.4	4.3	22.3
Median	9.6	37.1	0.18	0.17	0.26	4.7	16.0	4.0	24.0	2.8	17.1
Minimum	<0,1	14.6	<0.1	<0.1	<0.1	<0.1	2.0	0.8	11.0	0.5	6.4
Maximum	124.0	376.0	0.59	2.22	0.26	94.7	68.0	32.0	263.0	24.0	79.3
SD	26.5	70.7	0.16	0.48	–	23.6	17.3	6.7	59.6	4.29	12.75

(*T* temperature, *EC* electrical conductivity, *DO* dissolved oxygen, *ND* not determinated). Well depth and water depth from surface

Results

Physical–chemical parameters and major ions

Results are shown in Table 1. Values for pH range from slightly acid (5.46 in $\mathrm{SL_M}$) to very alkaline (10.49 in $\mathrm{AL_D}$). In general, in the shallow piezometers and wells of the southern zone pH values lower than 7 are obtained, while in deeper water and the northern part pH values increase (Table 1).

Redox potential values are higher in the shallow piezometers (close to 300 mV) due to the existence of dissolved oxygen coming from recharge water. In the deep piezometers, Eh and dissolved oxygen values decrease, in some cases reaching very reducing conditions (up to

−121 mV). Electrical conductivity ranges from very little saline samples (106 µS/cm in AL$_M$) to slightly saline (1,199 µS/cm in CB$_M$).

Major ions have been represented in the form of modified Stiff diagrams (Fig. 2). The following types of samples can be distinguished:

1. The prevalent facies is of the sodium chloride type. Within this group, a subdivision can be made according to electrical conductivity: (a) scarcely saline samples, with electrical conductivity lower than 260 µS/cm (AL$_M$, BR$_M$, CT$_S$, CT$_M$, HT$_M$, HL$_M$, MR$_S$, MR$_M$, MG$_S$, OJ$_S$, PL$_M$, PL$_D$, RC$_S$, SL$_M$, SL$_D$), (b) samples with electrical conductivity higher than 800 µS/cm (CB$_M$, CB$_S$, HT$_S$) and (c) a third group with intermediate values (SC$_M$, CB$_S$).
2. Calcium bicarbonate water (AB$_M$, MT$_M$, MT$_D$, PB$_S$, RM$_S$), with electrical conductivity intermediate values (from 332 to 445 µS/cm).
3. Sodium–calcium or calcium–sodium chloride–bicarbonate water (AL$_D$, AG$_S$, CN$_M$, CN$_D$, CT$_D$, HT$_D$, MT$_S$, PL$_S$, RC$_M$). These samples have an intermediate salinity (212–430 µS/cm), except for the AG$_S$ point, which presents a much higher electrical conductivity (1022 µS/cm).
4. Mixed water, where there is no predominant anion (CN$_S$, RF$_S$, SL$_S$), with electrical conductivity intermediate values (247 a 409 µS/cm).

Nitrate concentration ranges from <0.1 to 95 mg/L, with higher values (>30 mg/L) in the points SC$_M$, AG$_S$, RM$_S$ and CN$_S$ (located in the northern zone) and in the shallow piezometer located in the urban area of Matalascañas (SL$_S$). The high silica concentrations are also outstanding, with mean values of 22 mg/L and a maximum of 79 mg/L (Table 1).

Minor and trace elements

Taking median values into account (Table 2), the highest contents correspond to Sr (87 µg/L), Ba (38 µg/L), Fe (34 µg/L) and Al (19 µg/L). Mn and Zn show values close to 10 µg/L. Cu, Li and Rb are between 1 and 5 µg/L. The

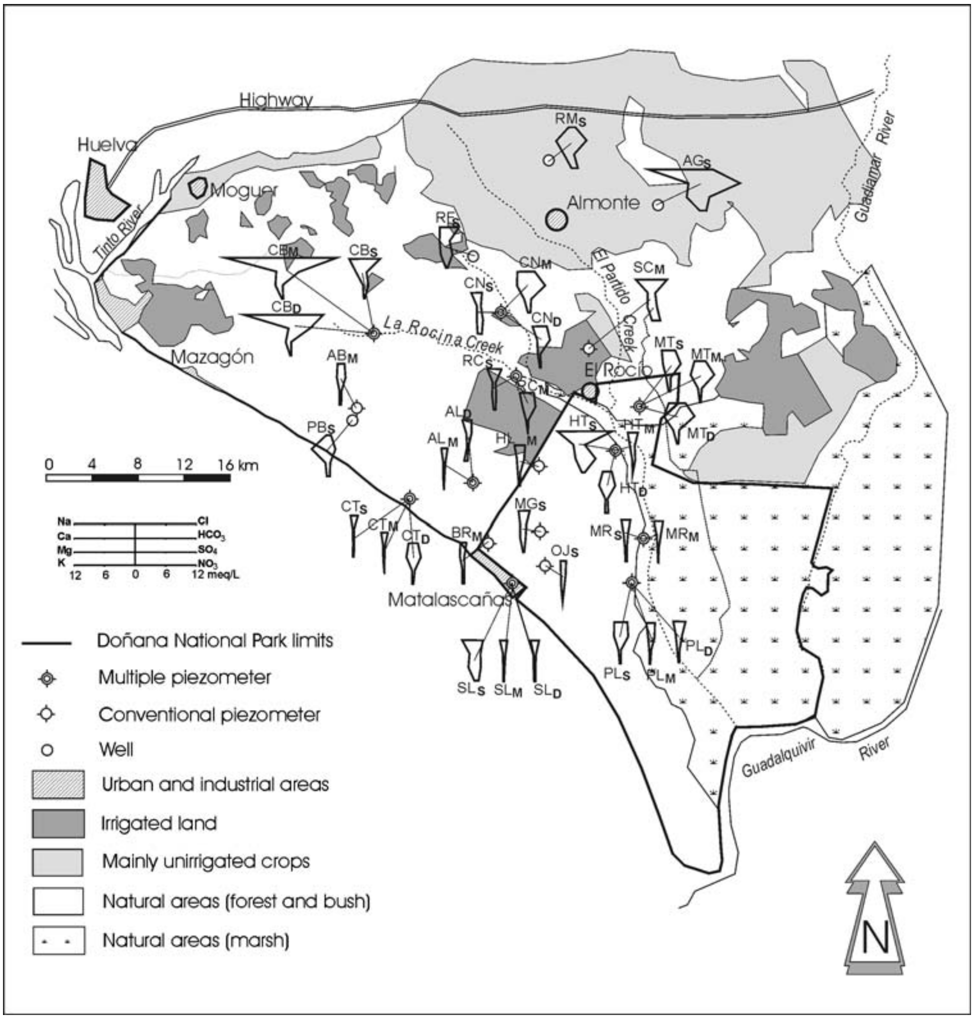


Fig. 2 Modified stiff diagrams of the sampled points (subindexes show the sampling depth: *S* shallow, *M* intermediate and *D* deep)

Table 2 Minor and trace element concentrations

	Al (μg/L)	As (μg/L)	Ba (μg/L)	Be (μg/L)	Cd (μg/L)	Co (μg/L)	Cr (μg/L)	Cs (μg/L)	Cu (μg/L)	Fe (μg/L)	Li (μg/L)	Mn (μg/L)
AB$_{M}$	42	0.32	75.1	<0.01	0.01	0.03	0.63	0.834	0.9	8	49.6	1
AG$_{S}$	<5	5.29	62.8	<0.01	<0.01	0.13	2.33	0.027	10.0	<5	9.3	<1
AL$_{M}$	13	0.08	30.4	<0.01	0.04	1.97	0.35	0.031	1.9	<5	0.8	91
AL$_{D}$	229	0.36	199.2	<0.01	0.03	0.08	0.55	2.243	2.5	24	177.6	2
BR$_{M}$	<5	0.06	13.9	<0.01	0.14	0.05	1.55	0.013	4.3	39	0.5	2
CB$_{S}$	370	0.67	68.2	<0.01	0.08	0.07	1.29	0.191	5.2	38	11.5	5
CB$_{M}$	33	1.47	47.2	<0.01	0.03	0.06	4.82	0.054	11.0	71	32.1	11
CB$_{D}$	14	0.83	29.0	<0.01	0.01	0.07	3.01	0.025	8.4	30	24.5	11
CN$_{S}$	7800	2.57	46.6	0.2	0.07	2.28	8.75	0.552	5.8	911	4.2	97
CN$_{M}$	13	2.07	58.7	<0.01	0.01	0.15	0.81	0.020	2.7	20	6.2	73
CN$_{D}$	38	0.15	20.2	<0.01	<0.01	0.04	0.87	0.026	2.5	25	9.8	10
CT$_{S}$	6	0.09	32.6	0.18	0.02	0.08	0.56	0.057	1.8	22	1.1	7
CT$_{M}$	<5	0.09	30.0	0.03	0.04	0.02	0.42	0.054	0.6	16	1.0	4
CT$_{D}$	26	4.32	40.6	<0.01	0.01	0.04	0.77	0.028	2.4	44	1.8	5
HL$_{M}$	107	0.29	49.0	0.01	0.06	0.14	1.49	0.026	3.6	336	1.7	8
HT$_{S}$	121	1.92	95.3	1.13	0.07	0.82	4.69	0.045	5.5	90	4.3	415
HT$_{M}$	57	1.97	22.5	<0.01	<0.01	0.05	1.49	0.049	1.3	11	3.9	1
HT$_{D}$	9	1.46	37.6	<0.01	0.03	0.03	0.91	0.017	1.5	25	2.5	2
MG$_{S}$	<5	0.21	56.4	<0.01	0.11	0.10	0.72	0.020	2.2	96	0.6	12
MR$_{S}$	8	0.93	17.4	<0.01	<0.01	0.21	1.21	0.006	1.2	580	0.6	33
MR$_{M}$	8	1.06	21.9	<0.01	<0.01	0.53	1.16	0.004	2.5	<5	0.7	28
MT$_{S}$	42	10.46	133.2	<0.01	0.04	0.05	0.47	0.130	3.9	12	22.0	<1
MT$_{M}$	6	1.43	38.6	<0.01	0.15	0.04	0.17	0.011	1.5	<5	3.8	1
MT$_{D}$	7	0.94	54.6	<0.01	0.02	0.08	0.23	0.019	2.3	6	3.8	10
OJ$_{S}$	28	0.72	13.0	<0.01	0.01	0.05	1.23	0.011	1.8	17	0.4	<1
PB$_{S}$	25	0.79	5.6	<0.01	<0.01	0.09	0.26	0.067	6.5	14	<0.1	4
PL$_{S}$	23	3.77	35.8	<0.01	<0.01	0.04	0.83	<0.001	6.6	58	3.4	129
PL$_{M}$	5	5.66	22.6	<0.01	0.06	0.18	0.82	<0.001	1.4	967	1.8	71
PL$_{D}$	10	0.12	14.1	<0.01	0.02	0.03	0.56	<0.001	1.3	30	1.3	2
RC$_{S}$	<5	0.43	46.9	0.12	<0.01	0.28	3.23	0.081	2.4	413	0.9	12
RC$_{M}$	24	2.22	79.2	<0.01	0.01	0.05	1.36	0.009	1.5	27	4.3	218
RF$_{S}$	9	1.25	87.8	0.06	<0.01	0.69	1.60	0.191	2.1	58	5.5	58
RM$_{S}$	5	0.50	26.9	<0.01	0.01	0.04	0.96	0.053	4.9	5	4.1	1
SC$_{M}$	50	0.77	51.8	<0.01	0.08	0.17	1.46	0.052	5.4	43	8.6	6
SL$_{S}$	<5	0.24	38.6	<0.01	0.04	0.04	3.20	0.017	3.3	389	0.4	4
SL$_{M}$	10	0.40	9.6	0.01	<0.01	0.03	0.32	0.027	1.4	25	1.0	3
SL$_{D}$	15	0.07	21.1	<0.01	0.03	0.07	0.25	0.013	1.2	9683	0.6	832
Mean	295	1.51	46.9	0.21	0.05	0.24	1.50	0.147	3.38	428	11.3	64
Median	23	0.79	38.6	0.09	0.03	0.07	0.91	0.028	2.39	30	3.6	9
Minimum	<5	0.06	5.6	<0.01	<0.01	0.02	0.17	<0.001	0.56	<5	<0.1	<1
Maximun	7800	10.46	199.2	1.13	0.15	2.28	8.75	2.243	11.04	9683	177.6	832
SD	1395	2.08	37.2	0.38	0.04	0.49	1.68	0.405	2.56	1680	30.3	158

	Mo (μg/L)	Ni (μg/L)	Pb (μg/L)	Rb (μg/L)	Se (μg/L)	Sr (μg/L)	Th (μg/L)	Tl (μg/L)	U (μg/L)	V (μg/L)	W (μg/L)	Y (μg/L)	Zn (μg/L)
AB$_{M}$	<0.1	0.59	0.22	26.2	0.37	109	0.005	0.056	0.054	1.48	0.05	0.02	2.6
AG$_{S}$	0.4	0.65	0.15	1.8	2.94	169	<0.001	0.021	1.493	8.90	<0.01	0.02	32.3
AL$_{M}$	<0.1	0.69	0.19	3.7	<0.01	22	0.016	0.054	0.027	0.23	<0.01	0.08	9.6

Table 2 continued

	Mo (μg/L)	Ni (μg/L)	Pb (μg/L)	Rb (μg/L)	Se (μg/L)	Sr (μg/L)	Th (μg/L)	Tl (μg/L)	U (μg/L)	V (μg/L)	W (μg/L)	Y (μg/L)	Zn (μg/L)
AL_D	1.6	4.36	0.38	74.6	<0.01	306	0.011	0.026	0.038	7.02	1.40	0.03	8.4
BR_M	<0.1	0.28	0.41	2.3	0.31	46	0.004	0.017	0.014	0.67	<0.01	0.13	4.5
CB_S	1.1	1.86	0.48	7.5	0.85	183	0.010	0.017	0.061	30.69	1.05	0.04	27.2
CB_M	<0.1	1.26	9.58	3.1	1.45	262	0.006	0.007	0.029	1.58	0.12	0.03	7.1
CB_D	<0.1	0.54	0.07	1.9	0.73	225	0.009	0.010	0.015	0.99	0.13	0.03	3.5
CN_S	<0.1	5.56	5.23	14.1	1.26	45	0.768	0.091	0.738	10.09	0.75	10.79	46.0
CN_M	0.1	1.20	0.10	3.1	0.22	133	0.003	0.021	0.386	0.57	0.81	0.07	9.2
CN_D	<0.1	0.45	0.03	2.2	0.37	112	0.002	0.006	0.024	0.45	0.01	0.10	2.5
CT_S	<0.1	0.38	1.39	6.5	<0.01	20	0.008	0.073	0.017	0.25	<0.01	0.04	8.6
CT_M	<0.1	0.33	0.14	7.5	<0.01	21	0.013	0.060	0.015	0.11	<0.01	0.02	3.6
CT_D	40.0	0.46	1.10	6.4	0.04	68	0.008	0.037	0.169	1.57	0.18	0.05	15.8
HL_M	0.4	1.40	3.27	7.4	<0.01	45	0.014	0.030	0.016	0.59	<0.01	0.27	28.8
HT_S	0.1	5.54	0.16	5.0	1.83	145	0.006	0.038	0.034	2.89	<0.01	7.63	18.9
HT_M	12.7	0.35	0.20	5.5	<0.01	87	0.008	0.040	0.013	0.64	0.11	0.02	2.3
HT_D	4.7	0.43	0.31	4.2	<0.01	87	0.004	0.038	0.073	0.34	<0.01	0.02	6.6
MG_S	<0.1	0.82	0.24	4.3	0.39	68	0.036	0.043	0.028	0.73	0.05	0.11	14.1
MR_S	<0.1	0.75	0.22	1.7	<0.01	35	<0.001	0.037	0.006	0.33	<0.01	0.07	7.8
MR_M	<0.1	0.49	0.24	1.5	<0.01	38	<0.001	0.033	0.009	0.37	<0.01	0.05	6.5
MT_S	7.7	0.76	0.26	12.2	0.83	107	0.027	0.043	1.907	1.67	2.36	0.05	5.2
MT_M	0.1	0.42	0.01	1.1	1.01	100	0.026	0.027	0.537	1.29	0.05	0.06	6.0
MT_D	0.3	0.54	0.18	1.1	0.82	119	0.024	0.029	1.130	1.01	0.05	0.05	4.1
OJ_S	0.3	1.50	3.69	4.0	<0.01	41	<0.001	0.032	0.012	5.39	0.29	0.07	13.5
PB_S	1.1	0.62	0.02	6.7	2.20	130	0.005	0.011	0.383	3.45	<0.01	0.03	4.1
PL_S	<0.1	0.59	0.10	0.2	<0.01	54	0.007	0.010	0.005	0.37	0.12	0.03	4.6
PL_M	<0.1	0.37	<0.01	0.6	<0.01	50	<0.001	0.013	0.007	0.33	<0.01	0.02	2.9
PL_D	<0.1	0.30	0.09	0.3	0.41	48	0.003	0.009	0.006	0.65	<0.01	0.02	2.0
RC_S	<0.1	1.08	1.23	3.4	<0.01	48	0.070	0.050	0.241	1.82	<0.01	3.16	20.8
RC_M	0.2	0.69	0.22	2.6	<0.01	91	<0.001	0.042	0.028	0.68	<0.01	0.07	4.1
RF_S	0.1	2.23	0.38	11.4	0.42	124	0.004	0.127	0.077	0.95	<0.01	0.18	4.7
RM_S	0.1	0.41	0.08	2.6	0.21	121	0.003	0.031	0.676	4.13	<0.01	0.01	7.2
SC_M	0.2	2.06	0.47	7.5	1.23	107	0.018	0.028	0.037	1.10	0.08	1.43	20.7
SL_S	<0.1	0.52	0.13	2.8	0.84	129	<0.001	0.020	0.020	1.27	<0.01	0.54	7.4
SL_M	<0.1	0.38	0.48	2.9	<0.01	27	0.040	0.043	0.024	0.71	<0.01	0.06	3.8
SL_D	<0.1	0.45	0.19	2.8	<0.01	33	0.021	0.036	0.016	0.08	<0.01	0.03	11.2
Mean	3.97	1.12	0.88	6.83	0.89	96	0.039	0.035	0.226	2.58	0.45	0.69	10.5
Median	0.35	0.59	0.22	3.45	0.82	87	0.009	0.032	0.028	0.95	0.12	0.05	7.06
Minimum	<0.1	0.28	<0.01	0.18	<0.01	20	<0.001	0.006	0.005	0.08	<0.01	0.01	2.0
Maximun	40.04	5.56	9.58	74.61	2.94	306	0.768	0.127	1.907	30.69	2.36	10.79	46.0
SD	9.61	1.32	1.87	12.44	0.73	67	0.138	0.02	0.439	5.32	0.64	2.17	9.9

rest of trace elements are below 1 μg/L. Al, Fe and Mn follow a lognormal distribution, with mean values much higher than those of the median, due to the existence of very high extreme values (Table 2; Fig. 3).

These values are within the range of those found in other sandstone and sandy aquifers (Table 3). Values by Edmunds and Smedley (2000) correspond to the median values in a UK sandstone aquifer. Data by Kilchmann et al. (2004) correspond to the range of mean values obtained in molasse aquifers in the Alps without anthropogenic influence. Data by Lee and Helsel (2005) come from a research on aquifers used for drinking water supply in the USA. Finally, data by Vissers et al. (2006) correspond to a sandy aquifer in Netherlands.

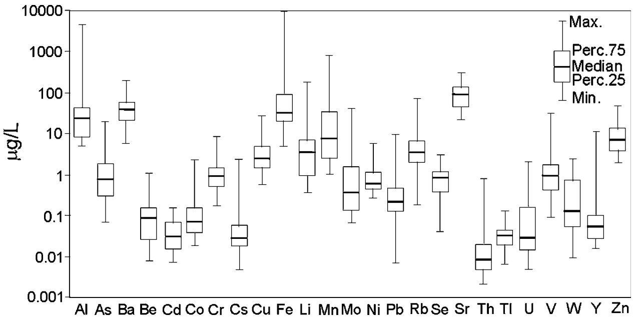


Fig. 3 Box and whisker diagrams for minor and trace elements (µg/L)

In the piezometer CN_S very high Al concentration (7,800 µg/L) is found. This sample was analysed again but the same value was obtained. High Al concentration probably corresponds to colloidal particles that pass the filter of 0.45 µm pore diameter (Langmuir 1997). This point also shows the maximum values of Co, Cr, Ni, Sc, Th, Y and Zn. In point AL_D maximum values of Ba, Cs, Rb, Sr (and also K) are found. Maximum values of Fe and Mn are observed in point SL_D.

Table 3 Comparison of the median values for minor and trace elements found in this study and those found in other previous works

	1	2	3	4	5
F (mg/L)	0.18	0.08	<0.2		
Br (mg/L)	0.17	0.09	0.003–0.022		
Al (µg/L)	23		0.9–8.2		2.4
As (µg/L)	0.8		<0.5	0.7	0.94
Ba (µg/L)	39	100	26–31	44	85
Cd (µg/L)	0.03		<0.2		0.005
Co (µg/L)	0.07		<0.2	0.13	0.08
Cr (µg/L)	0.91		0.2–0.8	1	0.45
Cs (µg/L)	0.03	0.3			0.004
Cu (µg/L)	2.4		<0.2–0.5	1.04	0.4
Fe (µg/L)	30		<2–11		2400
Li (µg/L)	3.6	15.6	2–8		2.0
Mn (µg/L)	9	5.1	0.5–5.5		260
Mo (µg/L)	0.35	0.62		0.74	0.13
Ni (µg/L)	0.59		0.5–1.0	0.68	0.66
Pb (µg/L)	0.22		<0.2–0.3	0.11	0.18
Rb (µg/L)	3.45	2.9	0.5–0.8		0.58
Se (µg/L)	0.82			0.2	0.4
Sr (µg/L)	87	297	215–368		290
U (µg/L)	0.03				0.01
V (µg/L)	0.95				0.22
Y (µg/L)	0.05				0.06
Zn (µg/L)	7.21		0.4–1.1	7.62	4.1

1: This study, 2: Edmunds and Smedley (2000), 3: Kilchman et al. (2004), 4: Lee and Helsel (2005) and 5: Vissers et al. (2006)

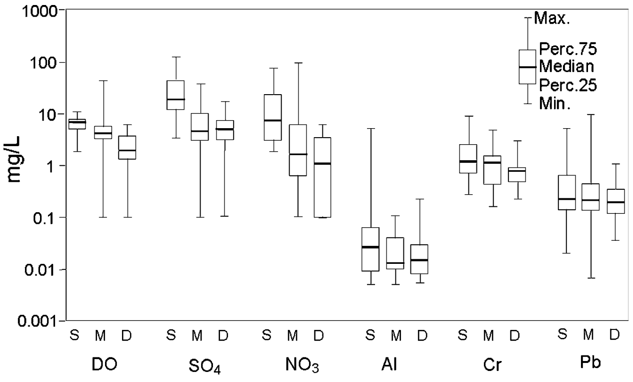


Fig. 4 Variation of some variables among shallow (*S*), intermediate (*M*) and deep (*D*) points (*DO* dissolved oxygen)

Variations with depth

Figure 4 shows the variation of some variables among the shallow (S), intermediate (M) and deep (D) wells and piezometers. Obviously, dissolved oxygen concentration decreases with depth. Nitrates decrease remarkably with depth as well, and, to a lower extent, also sulphates, aluminium and chrome do. In the case of aluminium there seems to be a minimum at intermediate depths and a new relative increase in deeper waters (Fig. 4). Lead also seems to show a trend to decrease with depth, although not as clear as that of Cr.

Other elements whose concentration decreases with depth are Mg, Co, Cu, Fe, Mn, Ni, Rb, Se, Th, Tl, U, Y and Zn. On the contrary, there are other variables that increase with depth, mainly pH, bicarbonates, K, Li and Mo. The rest of elements do not show a clear trend.

Discussion

Physical–chemical parameters and major elements

In the northern part of the aquifer, the main water type is calcium–bicarbonate due to the presence of carbonate minerals in the materials that make up the aquifer. pH values are higher than 7 and salinity of the samples is slightly higher (around 400 µS/cm) than at points in the southern zone.

In the southern zone, the predominant hydrochemical facies is of the sodium chloride type. In this zone, the materials that make up the aquifer are non-reactive silica sands, so that groundwater composition is conditioned by that of rain water, which in this zone shows the same composition as that of marine aerosols (Iglesias 1999; Manzano and Custodio 2006), concentrated by the effect of evaporation in the soil. In shallower waters, electrical conductivity is very low (<200 µS/cm), pH values tend to

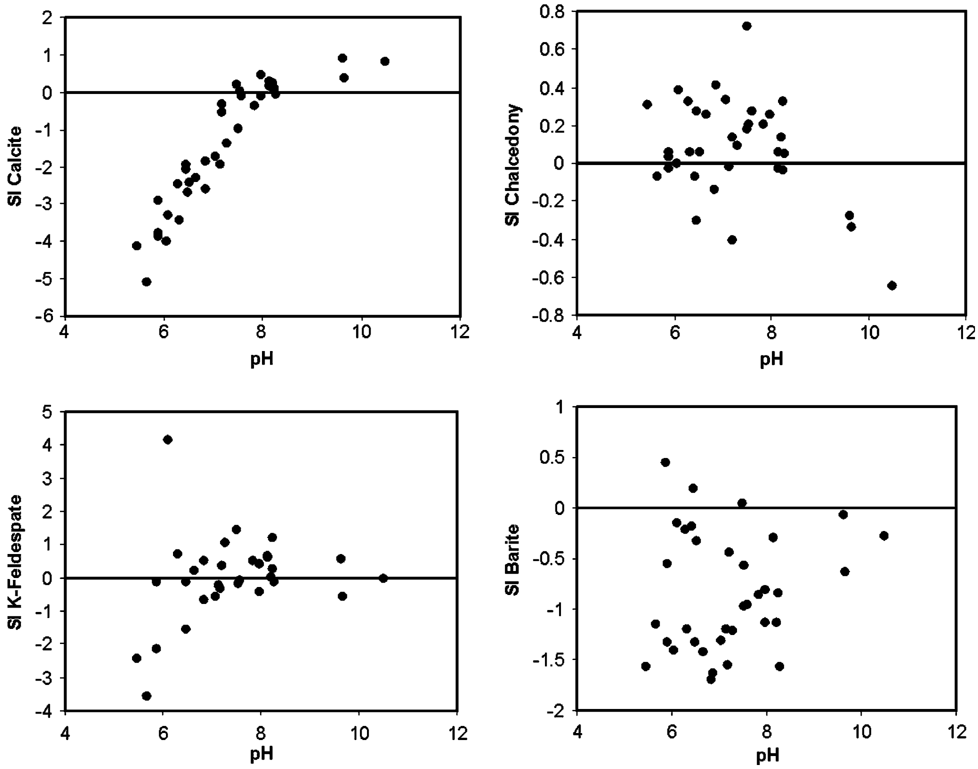


Fig. 5 Variation of saturation indices (*SI*) for some minerals with pH

be slightly acid (between 5.5 and 6) and dissolved oxygen concentration is high (as a result, high redox potential values are achieved).

As water flows through the aquifer, Ca and HCO$_3$ concentrations rise slightly, increasing pH (for example, point CT). This can be due to the dissolution of small concentrations of carbonate minerals or to the hydrolysis of silicates of the calcium plagioclase type, favoured by a longer contact of water with the aquifer materials. The facies tends to be of the sodium–calcium chloride–bicarbonate type and the salinity increases slightly (approximately 200–300 µS/cm). Figure 5 shows how the samples with pH lower than 7 are clearly undersaturated in calcite, those with pH close to 8 are at equilibrium, and those with pH higher than 9 are oversaturated.

There are some points (HT$_S$, CB$_M$, CB$_D$ and AG$_S$) of higher salinity (between 800 and 1,200 µS/cm). In the first case (HT$_S$), this may be the result of the influence of evaporation in the marsh, on whose clay deposits this well is located. In the zone of point CB there may be saline water of connate origin which is still unwashed probably because in this zone there are plenty of finer grain sized materials. Point AG$_S$ is located north, and has sodium bicarbonate facies and high nitrate and sulphate concentration.

On the other hand, there are some shallow points, located in the agricultural zones, with high concentrations of nitrates and sulphates (SC$_M$, RM$_S$, AG$_S$, CN$_S$, HT$_S$, RC$_S$) which indicate fertilizer pollution. Another point with high nitrate and sulphate concentrations is SL$_S$, but in this case, there may be an urban origin linked to leaks in the sewer system, since this piezometer is located within the town of Matalascañas. The high sulphate content in low saline waters of the southern zone of the aquifer causes the water to become of a mixed type (Fig. 2).

Silica concentration is high in the whole aquifer (median of 17.8 mg/L). Figure 5 shows that all samples are very close to saturation in chalcedony. This equilibrium is quickly reached due to a fast hydrolysis of silicate minerals or to the mobilisation of silica from soil complexes (Edmund and Smedley 2000).

Minor and trace elements

In the points where very alkaline pH is reached (such as AL$_D$), concentration of K (24 mg/L), Rb (75 µg/L) and other elements such as Ba, Cs, Sr, Li and Al increases drastically. The mineralogical composition of sands of aeolian origin is mainly made up of quartz (>95%) and, secondly, of feldspars (approximately 2%); the rest of minerals are found in smaller rates (Leyva et al. 1976). The high concentrations of these elements are probably due to the alteration of K-feldspar under such extreme pH conditions (Frapporti et al. 1996). The state of water saturation with respect to K-feldspar (Fig. 5) shows values near to

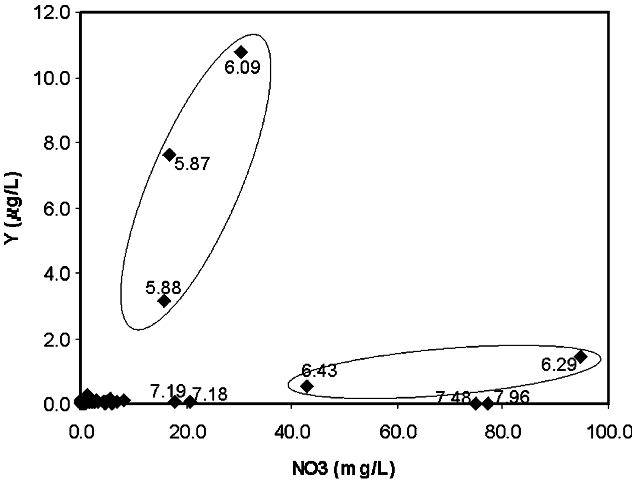


Fig. 6 Plot of NO_3 versus Y concentration (the figures shown indicate pH values of the samples)

equilibrium in a large number of samples, especially in those with pH values higher than 9.

Fe and Mn concentration in water increases with depth because conditions are more reducing, as dissolved oxygen runs out, and these elements are more soluble in their reduced form (Smedley and Edmunds 2002). In zones with very low Eh values the absence of sulphate and nitrates, due to the reductions of these compounds, is associated with high Fe and Mn concentrations.

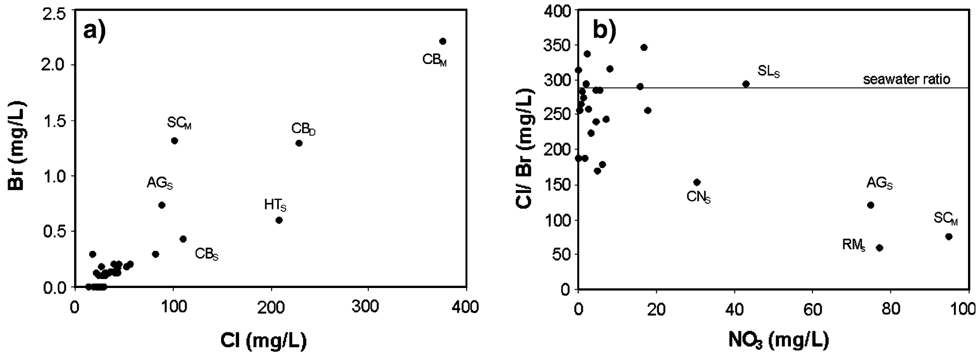
As can be observed in Fig. 4, Cr and Al metals (together with Be, Co, Cu, Cs, Ni, Pb, Rb, Tl, Y and Zn) show higher concentrations in the upper part of the aquifer, which seems to indicate that they are also linked to anthropogenic contamination. However, these elements do not present significant correlations with NO_3 and SO_4. This can be explained on the basis of the effect of pH on their mobility. Figure 6 shows that the points with a slightly acid pH (between 5.87 and 6.09), even with a relatively low nitrate content, have high concentrations of Y (along with other elements such as Al, Cu, Pb, etc.). With pH values close to 6.5, Y concentration is much lower than in the previous points, although it is still noticeable. With pH values higher than 7, concentration of these metals is very low, despite the high concentrations of nitrates.

This indicates that these metals have the same source as nitrates (fertilizers used in agriculture) but their behaviour is different depending on water pH. In more acidic conditions (pH around 6) metals are more mobile because surface adsorption processes decrease (Langmuir 1997), whereas with pH values higher than 7, metals are retained on the surface of solid particles and their concentration in water is very small, despite high nitrate concentrations.

Frapporti et al. (1996) find high concentration of metals (Al, Cd, Co, Cu, Ni, Y and Zn) in shallow sandy aquifers with a low neutralization capacity. They attribute this fact to the mobilisation caused to acidification processes by acid rain. However, we found that at those points with low pH values located in natural zones, without agricultural influence and therefore with very low nitrate and sulphate values (for example, CT_S, AL_M, BR_M), concentration of these metals is very low. This indicates that these elements do not come from the aquifer materials that are mobilised due to the low pH values, but rather from fertilizers, and they increase their mobility as pH decreases.

Br concentration has a distribution similar to that of Cl (Fig. 7a). Its maximum values are reached at points CB_M and CB_D, which seems to confirm the presence of more saline waters of connate origin in this zone. At the rest of the points bromine would come from slightly Br-enriched marine aerosols with respect to seawater (Davis et al. 1998; Edmunds and Smedley 2000). However, in Fig. 7a it can be checked that point SC_M, which presents the highest concentration of NO_3, has a higher Br content than would correspond to it on the basis of the Cl/Br ratio. This leads us to think about a potential contribution of bromide by agricultural activities. Methyl bromide is a fungicide that has been broadly used in this area for strawberry crop, until it has been recently forbidden due to its effect on the ozone layer. Figure 7b seems to confirm its origin; the points with the highest amounts of nitrates are the ones with a smaller Cl/Br ratio, due to Br contributions of agricultural origin (Sánchez-Martos et al. 2002). The SL_S sample does not

Fig. 7 Plots of **a** Cl versus Br and **b** NO_3 versus Cl/Br ratio



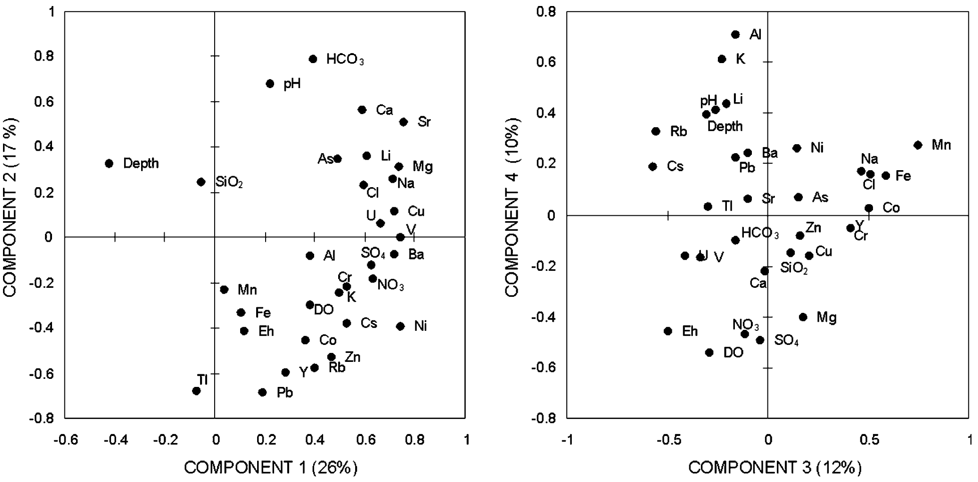


Fig. 8 PCA of variables (*T* temperature, *DO* dissolved oxygen)

follow this pattern, but in this case nitrates are of urban rather than agricultural origin.

Principal component analysis

Given the large number of determined variables, a Principal Component Analysis (PCA) was performed to help interpreting the results. Some variables (Be, Br, Cd, CO_3, F, NO_2, Mo, Se, Th and W) were not included, since they present many values below the detection limit. As many variables do not follow a normal distribution, the PCA starts from Spearman's rank correlation matrix (Davis 1986).

Figure 8 shows the factor loadings of variables in the first four components and Fig. 9 shows the scores of the samples. The first component explains 26% of the variance; the variables with the highest weight are Sr, Mg, Na, Ba, Ca, Cu, Ni, NO_3, SO_4 and V. The samples with the highest score in this component (Fig. 9) are the most saline: AG_S, CB_M, HT_S and CN_S. Obviously, this component is due to the sample salinity, which can increase because of (1) carbonate dissolution, (2) the existence of chloride salts and (3) the contamination caused by agricultural and urban activities. This component shows an inverse correlation with depth because pollution affects the upper part of the aquifer.

The second component explains 17% of the variance. In the positive pole we find HCO_3, pH, and, to a lesser extent, Ca and Sr. In the negative pole of the component we find metals such as Pb, Y, Rb and Zn, along with Eh and dissolved oxygen concentration. The samples with more positive scores are CB_D, AG_S and CN_D, whereas in the negative pole CN_S clearly stands out. This component is due to metals (Pb, Rb, Tl, Y, etc.) being more mobile at the points with a lower pH, especially those affected by pollution (CN_S, which also shows influence of component 1 due to high sulphate and nitrate concentration).

The third component explains 12% of the variance and is mainly due to the high Fe and Mn concentrations, which are higher in the SL_D sample (Figs. 8, 9). The fourth component (10% of the variance) is controlled in the

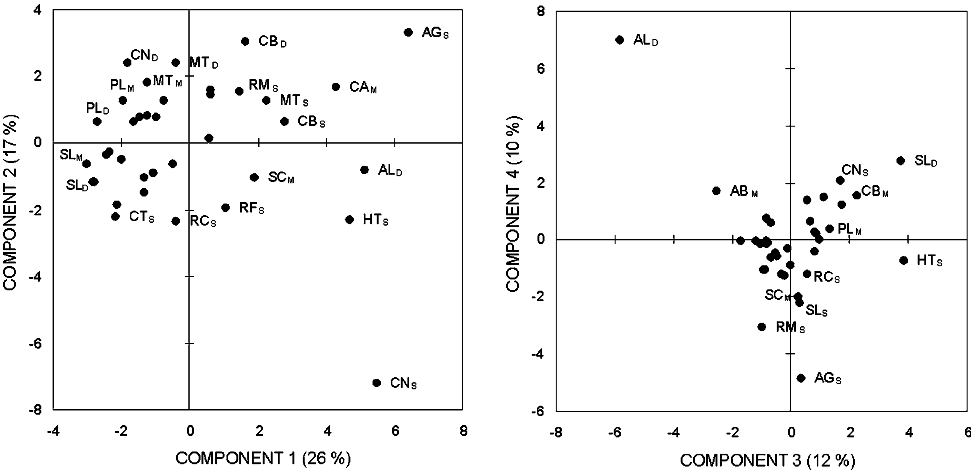


Fig. 9 PCA of samples (only the points with a high score in some of the components are identified)

positive pole by Al, K, Li and Rb coming from K-feldspar hydrolysis in the lower parts of the aquifer under very alkaline conditions. In the negative part we find Eh, SO_4, NO_3 and dissolved oxygen because their low values in deep zones.

Some trace elements do not have a clear behaviour. In the case of Ba, this can be explained because its concentration in some samples can be controlled by barite solubility. In Fig. 5 we can see how the $SI = 0$ line seems to be an upper boundary below which the samples are found.

Conclusions

Water quality in the Almonte-Marismas aquifer is conditioned by lithological factors, time of residence and pollution of agricultural and urban origin. The composition of recent water of the southern zone, where very unreactive silica sands are predominant, is similar to that of precipitation water (which presents itself great influence from marine aerosols), although more concentrated due to the effect of evapotranspiration in the soil. This water is of the sodium chloride type, has a very low electrical conductivity (<200 μS/cm) and a slightly acid pH (around 6).

Water circulation in the aquifer leads to dissolved oxygen decrease and dissolution of small amounts of carbonate minerals, which rises pH to values close to neutral and results in a slight salinity increase. Water tends to be of the sodium–calcium chloride–bicarbonate type. In the absence of carbonate minerals, K-feldspar hydrolysis can take place, resulting in scarcely saline waters with very alkaline pH and high concentrations of K and other trace elements such as Al, Ba, Cs, Li, Rb and Sr.

In agricultural and urban zones, sulphate and nitrate contributions cause the water to become of the mixed type. Pollution causes sulphate and nitrate concentration to show stratification in the aquifer, with the highest values in the shallower part. If pH values are slightly acid (around 6) and come along with nitrates and sulphates, we have high concentrations of trace metals such as Al, Be, Co, Cr, Cs, Cu, Ni, Pb, Rb, Tl, Y and Zn also come from fertilizers. If pH values are neutral or alkaline, concentration of these metals is very low, despite the fact that very high nitrate values may be reached because they are immobilised by surficial adsorption processes.

In the northern zone the greater abundance of carbonate minerals results in pH values between 7 and 8, and in a higher salinity of water, with facies predominantly of the bicarbonate–calcium type. In some points, there are also high concentrations of nitrates of agricultural origin.

Other zones have more saline water (close to 1,000 μS/cm), with sodium–chloride facies, which are due to the presence of salts of connate origin or to evaporation in the marsh. Br distribution is linked to the existence of these chloride salts, although an increase of their content (as related to chloride concentration) is also detected in agricultural zones due to the use of methyl bromide.

Although some actions with the objective of accomplishing a sustainable agriculture are being implemented (González-Delgado 2006), more efforts are needed to control the groundwater contamination.

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