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Origin of high ammonium, arsenic and boron concentrations in the proximity of a mine: Natural vs. anthropogenic processes

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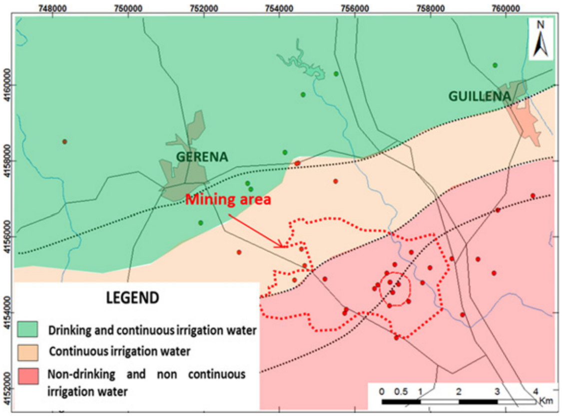
HIGHLIGHTS

- Differentiation between natural and anthropogenic sources of NH_4, As and B
- Assessment of hydrogeochemical processes that control the presence of NH_4, As and B in groundwater
- High NH_4, As and B concentrations in Niebla-Posadas aquifer
- Contribution to scientific-based aquifer management
- Aquifer zonation based on groundwater quality for its good management

GRAPHICAL ABSTRACT



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ABSTRACT

High ammonium (NH_4), arsenic (As) and boron (B) concentrations are found in aquifers worldwide and are often related to human activities. However, natural processes can also lead to groundwater quality problems. High NH_4, As and B concentrations have been identified in the confined, deep portion of the Niebla-Posadas aquifer, which is near the Cobre Las Cruces (CLC) mining complex. The mine has implemented a Drainage and Reinjection System comprising two rings of wells around the open pit mine, were the internal ring drains and the external ring is used for water reinjection into the aquifer. Differentiating geogenic and anthropogenic sources and processes is therefore crucial to ensuring good management of groundwater in this sensitive area where groundwater is extensively used for agriculture, industry, mining and human supply. No NH_4, As and B are found in the recharge area, but their concentrations increase with depth, salinity and residence time of water in the aquifer. The increased salinity down-flow is interpreted as the result of natural mixing between infiltrated meteoric water and the remains of connate waters (up to 8%) trapped within the pores.

Ammonium and boron are interpreted as the result of marine solid organic matter degradation by the sulfate dissolved in the recharge water. The light $\delta^{15}N_{NH4}$ values confirm that its origin is linked to marine organic matter.

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Dissolution FeOOH
Geogenic origin

High arsenic concentrations in groundwater are interpreted as being derived from reductive dissolution of As-bearing goethite by dissolved organic matter. The lack of correlation between dissolved Fe and As is explained by the massive precipitation of siderite, which is abundantly found in the mineralization. Therefore, the presence of high arsenic, ammonium and boron concentrations is attributed to natural processes. Ammonium, arsenic, boron and salinity define three zones of groundwater quality: the first zone is close to the recharge area and contains water of sufficient quality for human drinking; the second zone is downflow and contains groundwater suitable for continuous irrigation but not drinkable due to high ammonium concentrations; and the third zone contains groundwater of elevated salinity (up to 5940 μS cm^{-1}) and is not useable due to high ammonium, arsenic and boron concentrations.

1. Introduction

Increasing demand and conflicting water uses worldwide are leading to groundwater quality changes caused by variations in physical water management (e.g.: Currell et al., 2011 and 2013). The difficulty of managing groundwater lies in its sensitivity to (1) direct anthropogenic pollution (Belkin et al., 2000; Sapek, 2005), (2) indirect pollution due to abstraction induced chemical changes (Cendón et al., 2014; Harvey et al., 2003), and/or (3) geogenic causes related to water interaction with the host aquifer (both rocks and water) or along groundwater flows (Swartz et al., 2004; McArthur et al., 2001). Differentiating natural and anthropogenic sources is therefore crucial to ensure good management of groundwater. However, it can be very difficult in some instances to ascertain the source and/or processes associated with contamination (Sancha and Castro, 2001; Harms-Ringdahl, 2007; Williams et al., 1998).

Numerous aquifers worldwide have groundwater quality problems related to elevated concentrations of arsenic. High mining-related As concentrations (200–1700 μg L^{-1}), often associated to dewatering activities, have been identified in many parts of the world such as Thailand (Williams et al., 1996; Williams, 1997), Greece (Wilson and Hawkins, 1978), Ghana (Smedley, 1996), Alaska (Welch et al., 1988) and Canada (Azcue et al., 1994), among others. However, high arsenic concentrations can also be due to natural processes at many sites around the world. Thus, arsenic can be mobilized by weathering reactions (Manning and Goldberg, 1997b; Nicolli et al., 1989; Welch et al., 1988; Savage et al., 2000; Wang et al., 2006; Mukherjee and Fryar, 2008), geothermal processes (Yokoyama et al., 1993; Robinson et al., 1995; Ellis and Mahon, 1977; Criaud and Fouillac, 1989; Thompson and Demonge, 1996), or reductive dissolution of iron oxides (Nickson et al., 2000; Berg et al., 2001; Smedley and Kinniburgh, 2002; Halim et al., 2010).

Ammonium contamination is often described as being due to agricultural practices such as water irrigation returns and the use of fertilizers and manure (Kohl et al., 1971; Aravena et al., 1993; Chen et al., 2004; Tang et al., 2004, among many others). In some cases, however, ammonium concentrations as high as 390 mg L^{-1} have also been attributed to geogenic processes. In all cases, ammonium in pore water is related to high concentrations of organic matter in sediments (Ortega-Guerrero, 2003; Hinkle et al., 2007; Mastrocicco et al., 2013). In the Pearl River Delta, China, Jiao et al. (2010) observed concentrations as high as 290 mg L^{-1} in the aquifer, with a Holocene-Pleistocene aquitard being even richer in ammonium. In all cases, ammonium is attributed to the decomposition of organic matter under reducing geochemical conditions.

Anthropogenic boron contamination in aquifers has been attributed to leaking septic systems (Massmann et al., 2008) and borate mining in Turkey (Gemici et al., 2008). Unlike ammonium and arsenic, high boron concentrations of geogenic origin have been more rarely reported in the literature, and most of them are related to geothermal activity (Bernard et al., 2011; Grassi et al., 2014) and Na-Cl brines (Wunsch et al., 2013; Palmucci and Rusi, 2014). High boron concentrations have also been described in deep aquifers in Bangladesh and Michigan (Ravenscroft and McArthur, 2003; Halim et al., 2010), and they are associated with chloride and Ca/Na cation exchange and are attributed to the mixing of fresh water with displaced ancient seawater.

The Niebla-Posadas (NP) aquifer (S Spain) is an example where ammonium, arsenic and boron levels are high within the confined, deep portion of the aquifer. This aquifer is part of the Guadalquivir Basin and contributes part of the total resources for supply of drinking water and for agricultural, industrial and mining activities in a highly populated area of southern Spain. Concentrations of these three compounds locally exceed current World Health Organization guidelines for drinking water (WHO, 2008) and recommended values by the U.S. Environmental Protection Agency for continuous irrigation (USEPA, 2012). The Spanish regulations for drinking water (RD140/2003), according to the European Water Framework Directive (WFD), have values close to the WHO values, which are more restrictive for some compounds. High concentrations of these contaminants have alerted the public opinion and numerous environmental groups have drawn attention to the main anthropogenic activities in the zone, especially the mining exploitation of Cobre Las Cruces (CLC), as well as Aznalcollar past and projected activities.

The CLC complex is one of the largest open pit mining exploitations of copper in Europe, and it is located in the centre of the study area. The mining project has implemented a Drainage Reinjection System (DRS) for groundwater comprising two rings of wells around the mine perimeter, where the internal ring drains and the external ring is used for water reinjection. The main objective of this system is to prevent the decrease in the piezometric level in areas outside of the mining complex. The rate of pumping/reinjection is approximately 1.2 hm^3/year.

This paper presents a detailed hydrogeochemical and isotopic study suggesting the natural origin of high ammonium, arsenic and boron concentrations in the deeper sections of the aquifer. The aim of this research is to provide an assessment of a set of tools to differentiate the geogenic/anthropogenic sources and processes, with particular attention to processes controlling ammonium, arsenic and boron concentrations. To reach this objective, was necessary to: a) characterize the sources of solutes; b) investigate the spatial distributions of solutes in relation to sources, local geology and potential mobilization mechanisms; and c) identify the geochemical processes that control the presence of these solutes. This approach can be applied to other sites where elevated concentrations of ammonium, arsenic and boron are found and more generally to mine sites where water-rock interactions at a regional level are a concern.

2. Material and methods

2.1. Hydrogeological setting

The Guadalquivir Basin, with an area of 56.978 km^2, was formed during the Neogene and is part of a foreland basin developed between the Betic range (active margin) and the Iberian massif (passive margin) (Fig. 1A).

The study area is located approximately 20 km North of Seville, and it is limited by Sierra Morena (Iberian massif) to the north and by the Cortijuelos creek along the southern boundary. The western and eastern limits are defined by the Guadiamar and the Ribera de Huelva rivers, respectively. The Niebla-Posadas (NP) aquifer extends across the study area from N to S, with the Cobre Las Cruces (CLC) open pit mine located in the central part of the study area (Fig. 1B).

The climate is characterized as temperate-warm Mediterranean with influences from the Atlantic Ocean and the surrounding main relief units. Current average annual temperatures are 15–18 °C in the valley region, and the precipitation is characterized by both spatial and temporal irregularity, with an average annual precipitation of 500–600 mm/y and an annual average evapotranspiration of 991 mm/y (CHG, 2012).

The surface geology is mainly covered by Quaternary materials associated with river deposits. The underlying Cenozoic Gibraleón Formation (Fm) is composed of bluish marls. These marls are of marine origin and are rich in planktonic, benthic microfauna and organic matter. These form a wedge that thickens southwards from 0 m near the recharge zone to over 110 m close to the CLC mine and up to 800 m at 20 km south of the mine (Fig. 1C). These marls have been prospected for gas at ~15 km south of the studied area. Sandwiched between the bluish marls and the underlying Palaeozoic basement, the Niebla Formation hosts the main part of the NP aquifer, and it is formed by conglomerates, detrital limestone and sandstone with abundant marine micro and macrofauna. The Niebla Fm outcrops to the north in the recharge area and dips southward to where it is confined by the overlying

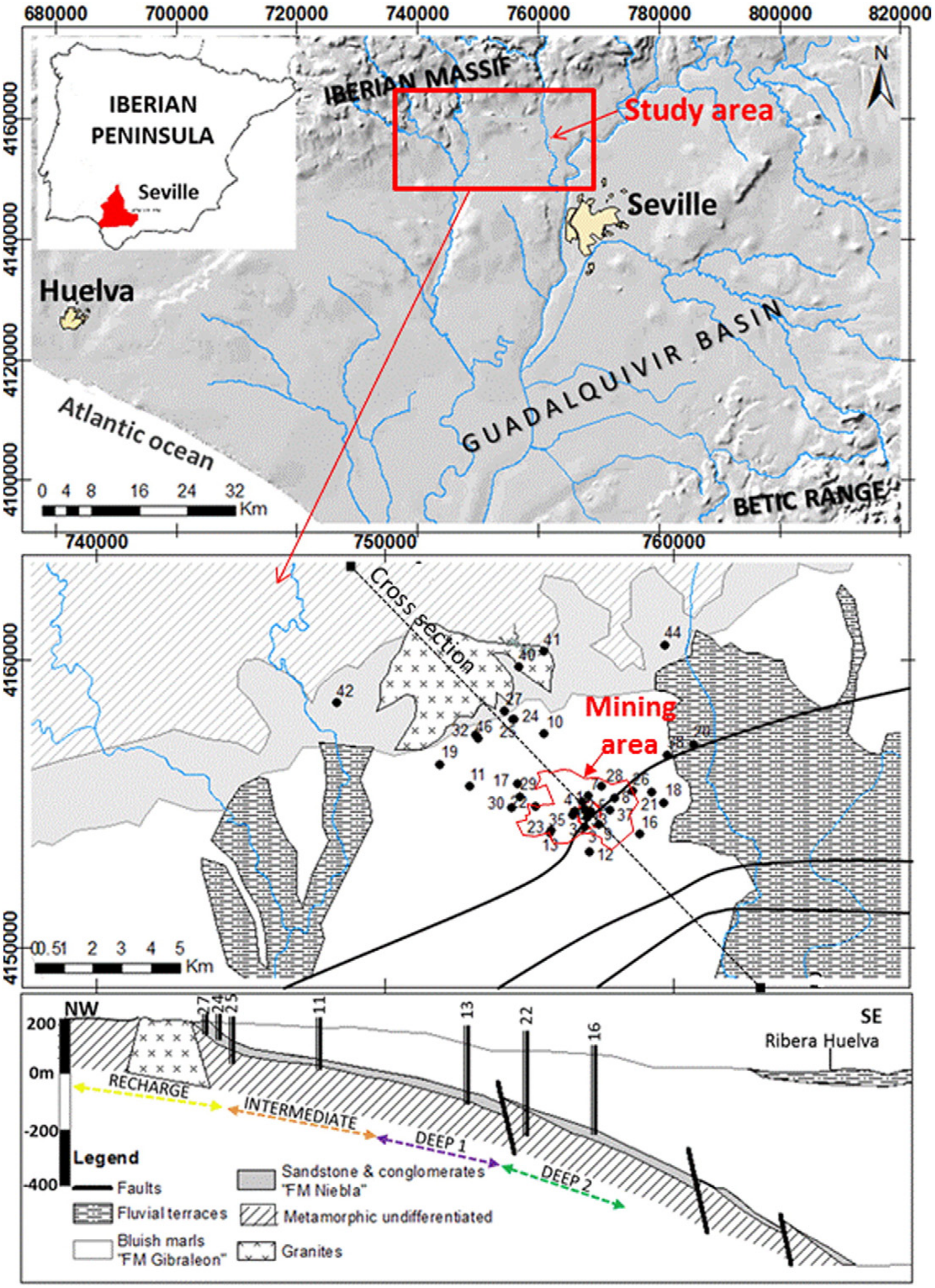

Fig. 1. A) Regional map and location of the studied area, B) geological map of the area and CLC location, and C) general cross section. ETRS_1989_UTM_Zone_29N.

blue marls. The Palaeozoic basement (Culm Fm) is made of quartzite, schists, granite and volcanogenic massive sulfide deposits (Blake, 2008; Capitán, 2006 and Fernández-Caliani and Galán, 1991). Major faults with a SW-NE orientation and secondary faults with a NW-SE orientation affect the basement materials (Fig. 1B and C).

The detrital strata of the Niebla Fm, together with the weathered portion of the upper Palaeozoic basement, form the NP aquifer. This heterogeneous aquifer is 10 to 30 m thick and gradually dips southward with a 4–6% slope. It is confined in close proximity to the recharge area by the low transmissivity (<5 m^2/d) marls. Transmissivity values of the NP aquifer range between 10 and 500 m^2/d, with storage coefficient values on the order of 10^{-2} within the unconfined zone and between 10^{-3} and 10^{-5} in the confined areas (CHG, 2012). Recharge of the aquifer is by rainwater infiltration in the outcropping area and from Palaeozoic materials and recharge from ephemeral streams also must be considered. The total estimated annual recharge is 32 hm^3 (25 mm/y) for an area of 1300 km^2 between the towns of Gerena and Posadas. The discharge is 34 hm^3/y and corresponds to agricultural and consumption extractions, without regard to the extractions for mining use (CHG, 2012; Navarro et al., 1993).

The Palaeozoic basement outcrops to the north of the recharge area coinciding with increased elevation (up to 500 m). Very little information exists on the groundwater potential of the Palaeozoic basement or weather a deeper regional system may be possible within the fractured interconnected Palaeozoic shales (Gómez de las Heras et al., 2001).

Based on groundwater residence times and hydrogeochemical indicators, four zones (Recharge, Intermediate, Deep 1 and Deep 2) have been proposed for the NP aquifer (Scheiber et al., 2015). Thus, residence times for each zone of <60 (Recharge), ~20,000 (Intermediate), ~30,000 (Deep 1) and >30,000 (Deep 2) years were obtained from ^{3}H, ^{14}C and ^{36}Cl analyses, respectively.

2.2. Groundwater sampling and analysis

Groundwater samples were collected from a total of 40 wells and piezometers, distributed throughout the study area but with a higher density of sampling points in the deep aquifer zone (Fig. 1B). Wells were sampled during two field campaigns carried out in February 2012 and September 2013. Wells were purged and samples collected after removing three well volumes or once field parameters had stabilized. The physico-chemical parameters such as temperature (°C), pH, specific conductance (SC, μS cm^{-1}), Eh and dissolved oxygen (DO, mg L^{-1}) were measured in situ inside a closed flow cell. Total alkalinity was determined in the field by acid–base titration using an Aquamerck Alkalinity kit.

Groundwater samples for general chemistry were collected in high-density polyethylene, 25 mL bottles for anions and 50 mL for cation-trace samples, previously filtered through a 0.22 μm nylon filter. Cation-tracer samples were acidified with 1 mL of 20% diluted nitric acid for sample preservation. Anions were analysed by High Performance Liquid Chromatography (HPLC) and cations by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The total trace elements concentrations were measured by inductively coupled plasma and mass spectrometry (ICP-MS). In order to differentiate arsenite (As (III)) from arsenate (As(V)) field speciation cartridges were used (Meng and Wang, 1998). Dissolved Organic Carbon (DOC) samples were collected in 30 mL glass bottles previously muffled. These samples were filtered through a 0.45 μm and acidified with 1 mL of HCl (2N). Bottles were sealed with Parafilm® to minimize any contact with air. DOC was analysed by the catalytic oxidation method at 680 °C using a Shimadzu TOC-V CSH instrument, with a detection limit of 0.05 mg L^{-1}. NH_4^+ and I^- concentrations were analysed with ion selective electrodes Orion 9512, with an error of ±2%.

Twelve samples for CH_4 and H_2S gas analysis were collected in 250 mL glass bottles, with septum cap and stored in an upside-down vertical position according with Capasso and Inguaggiato (1998). The CH_4 in the gas phase was determined using a Trace GC Ultra ThermoFisher Scientific chromatograph, with a detection limit of 0.58 mg L^{-1} and analytical error from ±0.001 to ±0.009 mg L^{-1}. The CH_4 dissolved in water was calculated by the liquid gas partition coefficient (Alberto et al., 2000). The H_2S content in the liquid phase was analysed by ionic chromatography with a DIONEX model IC5000, and with a variable wavelength detector with a detection limit of 0.005 mg L^{-1} S_2 and an analytical error of 5%.

The samples were collected in high-density polyethylene bottles of 250 mL capacity, previously filtered through a 0.22 μm nylon filter and preserved by adding H_2SO_4 (10%) to keep pH below 5.5. At the laboratory, over the water sample a filter-pack is placed by the ammonia trap. Filter-packs consist a 1 cm-diameter GF/D filter (WHATMAN) acidified with 30 μL of 8N H_2SO_4, sandwiched between two 2.5 cm diameter 10 μm pore-size Teflon membranes. Two mL of Na(OH) 5N solution was added in order to increase pH to a value above 12 pH units causing NH_4^+ to convert to NH_3. The bottle was quickly sealed and placed in an orbital shaker during 7 days at room temperature in order to favour the NH_3 diffusion into the headspace. NH_3 was then trapped into the filter and converted to $(NH_4^+)_2$ SO_4. After one week the filter-pack was placed in an acid-washed glass bottle and placed in a freezer-drier during 2 h to remove any water from the filter. Then the GF/D filter was removed, placed in a silver-cup and analysed immediately in an EA-IRMS. The $\delta^{15}N_{NH4+}$ were analysed by a diffusion method based on protocols by Sebilo et al. (2004) and Holmes et al. (1998).

Geochemical modelling of aqueous speciation and solubility calculation were performed with PHEEQC code (Parkhurst and Appelo, 2013) using the WATEQ4F thermodynamic database (Ball and Nordstrom, 2001). Additionally, the code was used to calculate solution charge balance as a Quality Assurance and Quality Control (QA/QC) measure for solution composition.

3. Results

Groundwater temperatures vary from 14.7 to 37.5 °C, with an average value of 25.5 °C. Cooler temperatures are found in the recharge zone, and temperatures increase towards the deeper zone. The pH values range between 6.8 and 10.6, with the highest pH values found in the deeper SE zones. Specific conductance (SC) values are between 388 and 5940 μS cm^{-1}, also increasing with depth. Eh values, while taken with caution, ranged between 177.7 mV in the recharge zone to −297 mV in the deeper areas (Table 1).

Major ion compositions (Fig. 2) differentiate four main compositional types. Groundwater in the recharge zone is of the Ca–HCO_3-type, and it transitions to Na–(Ca)–HCO_3 in the intermediate zone and to Na–HCO_3 in the Deep zone 1. Samples from the Deep zone 2 are of the Na–Cl-type and represent the most evolved compositions in the study area. In general, Na and Cl show a high correlation of $R^2 = 0.92$ (Table A1 of supplementary information), adapting to a seawater mixture line but with sodium excess.

Nitrate concentrations are only found close to agricultural and farm areas in the recharge zone, with concentrations ranging from 16.4 to 97.2 mg L^{-1}. Samples number 42, 40 and 41 (Fig. 1B) have nitrate concentrations that exceed or are close to the drinking water guidelines (WHO). Nitrite has not been detected, but high ammonium concentrations ranging from 0.04 to 12.8 mg L^{-1} are found in 70% of the wells (Table 1). Sulfate concentrations are generally low, ranging from 0.1 mg L^{-1} to 115 mg L^{-1} (Table 1). Concentrations of H_2S are 0.1 ± 0.01 mg L^{-1} and are only present at samples sites with the lowest sulfate concentrations and where a H_2S-smell was identified in the field. Methane concentrations were mostly below the detection limit (0.58 mg L^{-1}), except for one sample with a value of 1.09 mg L^{-1} (sample 5, located in the Deep zone 2).

Arsenic generally occurs as As (III), with concentrations ranging from below the limit of detection to 0.18 mg L^{-1}, with a mean value

Table 1
Groundwater parameters of the studied area (concentrations in mg L^{-1}). SD (standard deviation). Recommended limits for drinking water (WHO, 2008) and for frequent irrigation (USEPA, 2012).

	MIN.	MAX.	AVE	MEDIAN	SD	WHO (2008)	USEPA (2012)
pH	6.8	10.6	7.9	7.7	0.9	6.5–8.5	–
Eh (mV)	−297	177.7	−8.2	44.7	166.6	–	–
SC (uS·cm^{-1})	388.0	5940.0	1611.1	1189.2	1065.8	1500	4000
T (°C)	14.7	37.5	25.5	25.3	5.2	–	–
DOC	0.2	15.9	3.5	4.2	3.3	–	–
Cl^-	12.6	1581.3	276.4	149.9	315.5	250	–
NO_3^-	<0.1	97.2	11.0	0.1	24.8	50	–
SO_4^{-2}	<0.1	115.3	16.5	9.5	24.2	250	–
HCO_3^-	158.5	570.9	365.6	365.8	100.3	–	–
Ca	0.6	177.0	45.3	24.0	51.0	200	–
K	<0.1	43.4	5.5	4.1	6.5	30	–
Mg	<0.001	50.6	7.2	3.9	9.5	150	–
Na	14.6	1061.8	238.0	218.6	220.0	200	–
NH_4	0.04	12.8	2.6	2.3	2.7	0.2	–
I^-	<0.01	0.67	0.11	0.1	0.13	–	–
Br^-	0.09	5.25	0.90	0.5	1.15	–	–
Fe	<0.002	0.89	0.211	0.09	0.220	0.3	5
Mn	<0.001	0.43	0.03	0.01	0.07	0.5	0.2
B	0.02	3.48	0.94	0.63	0.94	0.5	0.75
As	<0.00003	0.18	0.006	0.002	0.03	0.01	0.1
F	0.15	6.79	2.46	1.64	2.12	1.5	–
$\delta^{18}O$	−5.1	−3.8	−4.7	−4.8	+0.26	–	–
δ^2H	−30.3	−20.4	−28.0	−28.4	+1.72	–	–
$\delta^{15}N_{NH4}$	−3.9	0.7	−1.4	−1.2	+1.6	–	–

of 0.006 mg L^{-1}. Of the 40 points measured, four have As (III) values >0.01 mg L^{-1} (above the WHO guideline), six points have As (III) concentrations between 5 and 0.01 mg L^{-1} and the remaining points have concentrations <0.0005 mg L^{-1}.

Boron concentrations in the study area range between 0.02 and 3.48 mg L^{-1}, with an average value of 0.94 mg L^{-1}. Approximately 55% of sampled points have boron concentrations that are above the WHO limit for drinking water, and ~50% of the points do not meet the USEPA recommendations for frequent irrigation water (Table 1). Similarly, ammonium concentrations vary between 0.04 and 12.82 mg L^{-1}, with an average value of 2.61 mg L^{-1}. This average value is above the guideline value set by the WHO (0.2 mg L^{-1}) for drinking water, and the standard limit is exceeded in 76% of the sampled points (Table 1).

Water stable isotope data from previous campaigns (Scheiber et al., 2015) have been complemented with new results (see Table A2 of supplementary information). Groundwater isotopic ratios range between −20.4 to −30.3‰ for δ^2H and between −3.8 to −5.1‰ for $\delta^{18}O$ (V-

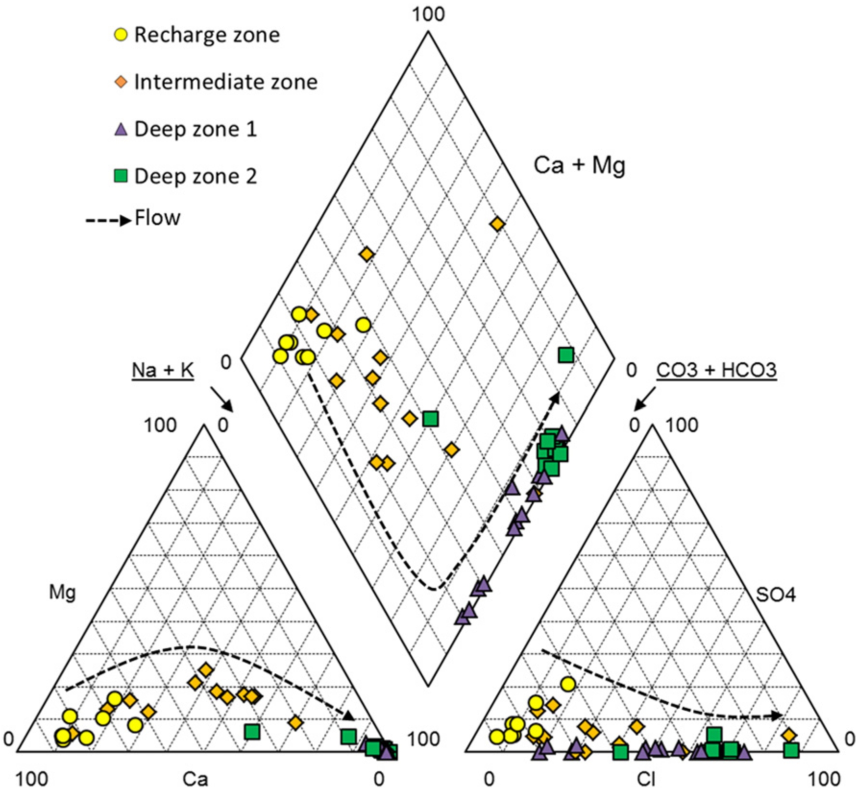

Fig. 2. Piper diagram showing major ion chemistry of the sampled points. The arrows follow the NW–SE flow direction.

SMOW). The deuterium excess, defined as D-excess = δ^2H–8 δ^{18}O (Dansgaard, 1964), has an average of 11.1 ± 1.6‰. These values are close to 10‰ and suggest a major Atlantic source for rainfall recharge when compared with the typical deuterium excess values of ~13.7‰ determined for modern western Mediterranean rainfall (Celle-Jeanton et al., 2001). Groundwater deuterium excess values are also consistent with other regional groundwater values from Doñana National Park (D-excess = 10.9 ± 3.1) (Iglesias, 1999; Jiménez and Custodio, 2008).

A limited number of samples (n = 8) have been analysed for δ^{15}N of dissolved ammonium to assess nitrogen sources. The $\delta^{15}N_{NH4}$ values range between −3.9 and +0.7‰, with an average value of −1.4‰.

4. Discussion

4.1. Origin of major solutes

The NP aquifer has a well-defined recharge area and an overlying confining layer of increasing thickness as the aquifer dips south along the flow direction. Groundwater salinity increases along the flow direction, with major ion compositions varying from Ca–HCO_3-type in the recharge area to Na–Cl-type in the deeper samples recovered. The increasing salinity could be due to: (1) dissolution of evaporites, (2) evapotranspiration processes in the recharge water or (3) mixing between meteoric water and connate marine water. There is no evidence of the existence of evaporites dispersed within the marls. Moreover, the dissolution of evaporites would lead to Cl/Br ratios much higher than those observed (Cendón et al., 2004). The low chloride concentrations found in wells located within the Palaeozoic recharge zone rule out evapotranspiration in the soil as a significant source of groundwater salinity. Finally, the Cl/Br ratio values approach those of seawater ($R_{Cl/Br}$ 600) in samples from the deepest zones suggesting mixing with a marine contribution. However, depleted water stable isotopes (Fig. 3) seem to constrain a significant mixing with seawater. Samples with higher chloride concentrations generally show the most depleted water isotopic values, with all groundwater samples plotting along the modern precipitation weighted least square regression lines PWLSR (Hughes and Crawford, 2012) for Seville and Gibraltar (Fig. 3). D-excess values in groundwater samples adjusts better with rainfall values derived from Atlantic fronts and are similar to those from Gibraltar. This could be due to the relatively limited rainfall water stable isotope data set available for Seville (six years). Similar isotopic ratios to those obtained in groundwater have been found in others regional studies, such as in Doñana (Manzano et al., 2001) and the southwest of Portugal (Fernandes and Carreira, 2008).

The depleted δ^2H/δ^{18}O values in the deepest groundwater are consistent with palaeo-recharge under different climatic conditions. Palaeoclimatic studies based on nobles gas recharge temperatures (Edmunds et al., 2004) and speleothems (Valsero and José, 2002 and Jiménez de Cisneros and Caballero, 2013) conclude that the Late Pleistocene recorded climatic periods with temperatures up to 5 °C colder than the current annual average temperature. This coincides with the findings of Scheiber et al., 2015, where the groundwater travel time from the recharge zone to the deepest zone was >30,000 years. These differences in associated groundwater recharge temperatures could explain the depleted δ^2H/δ^{18}O values in the deepest zones.

Cenozoic marine sediments overly the Palaeozoic substrate, and marine water is expected to have occupied the porosity. Once the marine conditions receded, continental fresh waters progressively pushed and displaced the relict marine waters (Abad de Los Santos, 2007). Considering that the salinity originated from mixing between meteoric and relict marine waters, and based on the Cl/Br ratios, a maximum seawater contribution of up to 8% would explain the salinity of the deepest zones. The small seawater contribution would not produce any significant displacement of water stable isotope ratios based on the δ^{18}O vs Cl relationship, which is not shown.

A relative increase in Na concentrations with respect to expected seawater ratios is observed from the intermediate zone and towards deeper portions of the aquifer (Fig. 4). This effect can be explained by a Na-Ca exchange process that takes place within dispersed clay layers in the aquifer or within the overlying formation (blue marls). The exchange of Ca for Na can also be observed in the Piper diagram, where Na increases and Ca decreases while the HCO_3 concentration remains constant (Fig. 2). This process has been identified in coastal aquifers when continental waters flush marine water (Appelo, 1994; Custodio and Llamas, 1976; Custodio and Bruggeman, 1987).

NO_3 is the only major solute detected that is of anthropogenic origin and it has concentrations reaching up to 102 mg L^{-1} in localized areas of the recharge zone, with an average concentration of 41.7 mg L^{-1} (n = 6). These local high NO_3 concentrations are due to agricultural practices and may be from sewage/septic tank leaks from the town of Gerena. Nitrate in the intermediate and deep zones is generally below the detection limit (Table A2 of supplementary information). This effect could be due to: (1) nitrate only originating from recent recharge that has not yet affected down-gradient concentrations, or (2) nitrate reduction.

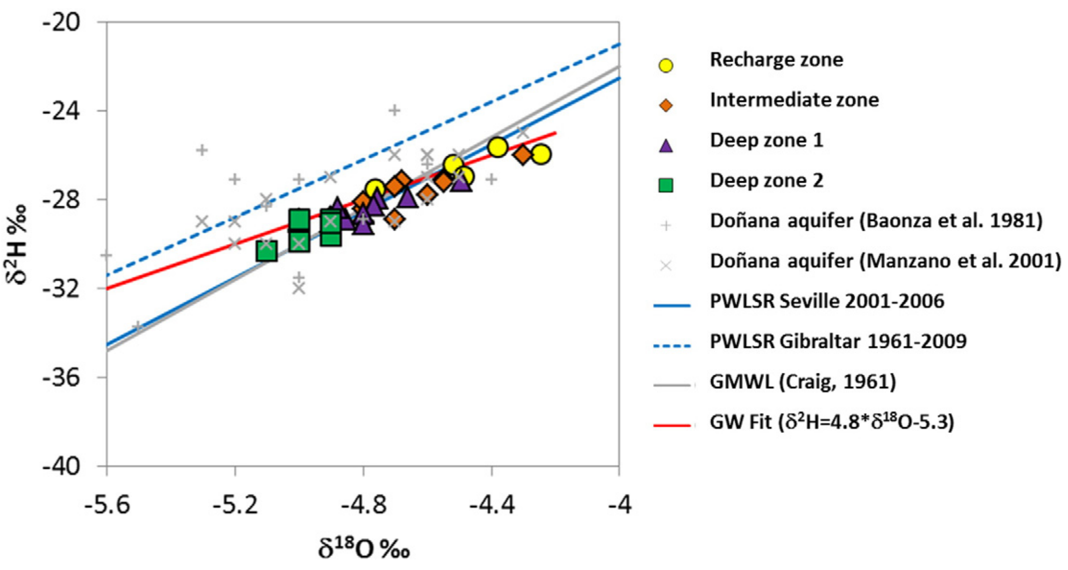

Fig. 3. δ^{18}O vs. δ^2H plot for groundwater samples.

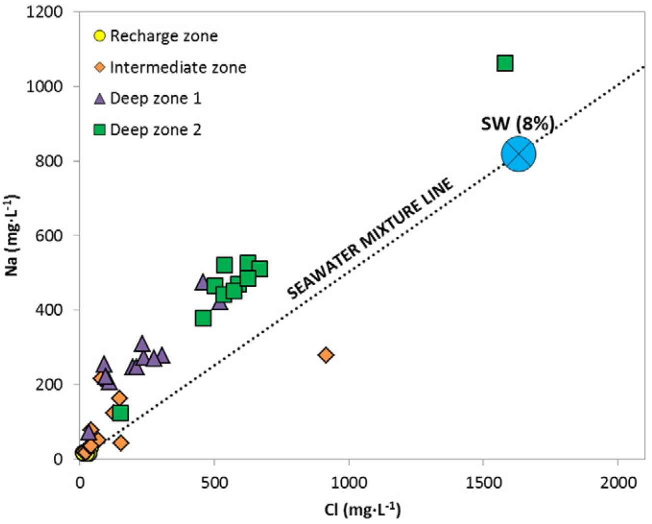

Fig. 4. Plot of Na vs. Cl in groundwater (concentration in mg L^{-1}). SW = Seawater 8%.

However, the absence of ^3H in intermediate groundwater suggests that the nitrate plume has not yet reached the deeper zones.

Sulfate in the recharge zone can be as high as 115 mg L^{-1}, but it decreases below the detection level (0.1 mg L^{-1}) in the intermediate and deep zones, with H_2S concentrations reaching up to 0.1 mg L^{-1} in some wells. The isotopes of the SO_4 molecule clearly confirm the existence of sulfate reducing processes, with remnant sulfate in groundwater from the intermediate and deep zones showing a distinct trend towards heavier $\delta^{18}O$ and $\delta^{34}S$ values (Scheiber et al., 2015). Although methane has only been detected in one sample, the possibility of reduction processes progressing up to the methanogenesis stage cannot be ruled out.

4.2. Origin of minor solutes (As, B and NH_4)

Of all minor and trace elements/compounds analysed in groundwater, only ammonium, arsenic and boron have anomalously high concentrations that are one order of magnitude higher than those commonly found in average surface water (Gaillardet et al., 2004). Ammonium concentrations of up to 12.8 mg L^{-1} have been found in the Deep zone 2, and concentrations of 0.18 mg L^{-1} for arsenic and 3.48 mg L^{-1} for boron have also been found within this zone. Several natural sources can explain the high ammonium, arsenic and boron concentrations observed in the groundwater. The natural origin is supported by the following: (1) the recharge zone of the aquifer has low ammonium, arsenic and boron concentrations, and high concentrations are only found in the deepest zones located to the SW of the study area; (2) the transit to deeper parts of the aquifer is confined by a thick marl layer (> 200 m) with low permeability, which seals the aquifer system (Fig. 1B and C); and (3) groundwater residence times >20 ky have been identified in groundwater containing the higher concentrations (Scheiber et al., 2015).

The arsenic mobilization is interpreted as related to the reductive dissolution of Fe-oxyhydroxides. This natural process is well-known and has been observed in reducing aquifers (Berg et al., 2001; McArthur et al., 2001; Ahmed et al., 2004; Halim et al., 2010). Generally, Fe-oxyhydroxides are characterized by a very high specific surface area of ± 300 m^2/g (Davis and Leckie, 1978) and a high adsorption capacity, which is capable of adsorbing large amounts of arsenic (van der Zee et al., 2003; Wang et al., 2012). Thus, the reductive dissolution of these minerals involves the release of any arsenic present in groundwater. Instead of mining operations, several observations indicate a geogenic origin in the case of the NP aquifer: 1) goethite gossan deposits are scattered on the surface of the Palaeozoic series below the NP strata, with the CLC ore deposit being the most representative; 2) goethite contains up to 0.8% As (CLC, unpublished data); 3) Dissolved Organic Carbon (DOC) concentrations are above the typical values in groundwater (>1 mg L^{-1}), indicating the important role of organic matter in the hydrogeochemical evolution of these waters; 4) arsenic is mostly As(III), which is characteristic of reducing environments; 5) the higher concentrations are scattered across the studied area, and are not directly linked to mining; and (6) historical data obtained before the mining activity show higher As and NH_4 concentrations of up to 0.1 and 5 mg L^{-1}, respectively (CLC, 2005).

In many studies where the reductive dissolution of FeOOH has been associated with high arsenic concentrations a moderate relationship between DOC, As and Fe is observed (Anawar et al., 2003; Ahmed et al., 2004; Halim et al., 2009). However, no correlation is found in the studied area (Table A1 of supplementary information). This has been explained in some instances as a non-simultaneous reduction of As and Fe (Islam et al., 2004), or as re-adsorption of As (Nickson et al., 2000). However, the lack of correlation in this case is attributed to massive precipitation of siderite in the NP aquifer. Thermodynamic calculations indicate that groundwater in the Deep zones 1 and 2 are supersaturated and very near to equilibrium with respect to siderite. Moreover, the goethite-made gossan is massively replaced by siderite (Yesares et al., 2014a; Yesares et al., 2014b). The siderites exhibit light $\delta^{13}C$ values (between −13.4 and −47.95‰) that are typical of C from organic origin (Capitán Suárez, 2006) and have been interpreted as the largest documented occurrence of a microbially derived ore assemblage (Tornos et al., 2014).

The strong correlation of B with NH_4 ($R^2 = 0.91$, Table A1 of supplementary information) suggests a common process controlling their concentrations in groundwater. Similarly, the weak correlation observed between As and B and between As and NH_4 indicates that these processes are at least in part different from those concentrating As. Indeed, NH_4 and B show a clear positive correlation with Cl (Fig. 5A and B).

Several samples have ammonium, boron, iodide and fluoride concentrations higher than seawater (Fig. 6A). Taking into account the modern seawater concentrations for NH_4, B, I and F, the expected contribution from a maximum of 8% of seawater mixing, and the concentrations found in groundwater samples, enrichment factors of 3200, 9, 140 and 85 are found (Table 2). This suggests that an extra source and additional processes are associated with these compounds.

Nitrogen is a fundamental nutrient and is a constituent of multiple organisms, so it is generally associated with organic matter in C:N proportions of 16:106 (Redfield, 1934). Iodine is also assimilated by marine organisms, and organic matter is an important source of iodine for this reason (Price and Calvert, 1973; Kennedy and Elderfield, 1987; Worden, 1996). Strong correlations of iodine with ammonium ($R^2 = 0.86$) and boron ($R^2 = 0.83$) (Table A1 of the Supplementary information) suggest organic matter degradation as the source for both species in groundwater (Fig. 6A and B). In the case of fluoride, the correlations are not so clear, but there is a strong correlation with boron ($R^2 = 0.82$) and weaker correlations with ammonium ($R^2 = 0.57$) and iodide ($R^2 = 0.39$).

This suggestion is confirmed by light $\delta^{13}C$ and $\delta^{15}N_{NH4}$ values found in the groundwater of the deepest zones. The light $\delta^{13}C$ values obtained in the deepest zones (from −6.63 to −11.43‰) suggest that the organic matter degradation has an important role in the groundwater chemistry (Table A2). A detailed and quantitative discussion of the chemical processes affecting the $\delta^{13}C$ values can be found in Scheiber et al. (2015). The nitrogen in the sedimentary rock is accumulated as organic matter during the sedimentation process and is incorporated during the diagenesis process as ammonium. It has been suggested that the $\delta^{15}N_{TOTAL}$ values of sedimentary rocks are representative of $\delta^{15}N_{NH4}$ values (Holloway and Dahlgren, 2002). Under reducing conditions, the organic matter degradation can release high ammonium concentrations (reaction 1). A weak correlation between NH_4 and HCO_3 is observed, but

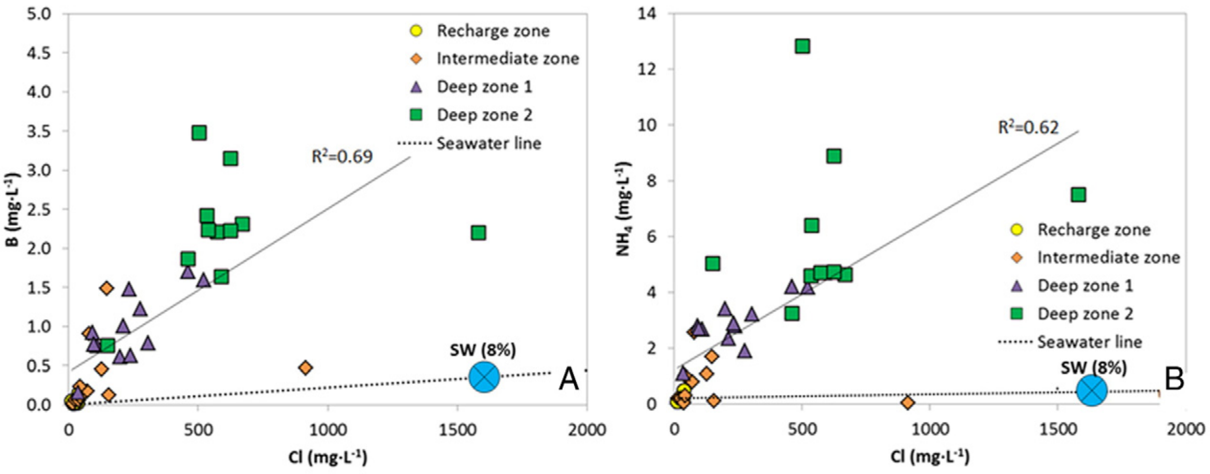

Fig. 5. Plots of A) boron and chloride and B) ammonium and chloride. SW = Seawater 8%.

this can be affected by siderite precipitation in the vicinity of the ore.

$$NO_3^- + H_2O + 2CH_2O \leftrightarrow NH_4^+ + 2HCO_3^- \quad (1)$$

The δ^{15}N fractionation under laboratory conditions between sedimentary organic matter and pore water ammonium has been investigated by Prokopenko et al., (2006). The results show that pore water $\delta^{15}N_{NH4}$ values (<0.7‰) are generally lighter than those of the sedimentary material (≈5‰) due to a small isotope fractionation associated with organic matter degradation ($\varepsilon = -0.7‰ \pm 0.2‰$). However, the $\delta^{15}N_{NH4}$ values of pore water and sedimentary material in some samples can be quite similar due to the low fractionation factor. There are several aspects that can vary the isotopic ratios, such as depth, N content, bacterial activity and degree of organic matter degradation (Prokopenko et al., 2006). The groundwater of the NP aquifer has $\delta^{15}N_{NH4}$ values between −3.9 and 0.7‰ (Fig. 7), which are similar to those of the marlstones recovered from North Atlantic cores (Rau et al., 1987), where a range between −2.7 and 2.3‰ is observed. Borowski and Paull (2000) reported heavier values of $\delta^{15}N_{NH4+}$ (+3.6 to +4.9‰) in pore water produced by microbial fermentation reactions in deeper marine sediments under sulfate reducing conditions. The similarity between the $\delta^{15}N_{NH4}$ values in groundwater and in marl organic matter found elsewhere suggests that high ammonium concentrations could be derived from organic matter degradation of the bluish marls in the "Gibraleon Fm".

High boron contents can be attributed to sorption–desorption processes where seawater B is sorbed onto the surfaces of sediments. Desorption and release to groundwater takes place during the freshening-up stage when fresh continental water displaces seawater in aquifers. The competitive action of HCO_3/CO_3 could drive desorption from mineral surfaces, producing a B/HCO_3 correlation as observed in aquifers in Bangladesh and Michigan (Ravenscroft and McArthur, 2003). However, no positive correlation between B and HCO_3 has been observed in the studied area, but HCO_3 concentrations are strongly buffered by the dissolution of calcite and precipitation of siderite in the deep zones of the NP aquifer. Therefore, B sorption–desorption cannot be ruled out.

An alternative, although similar, explanation for B origin is to assume sorption into solid marine organic matter. Thus, B sorption in the organic matter of soils has been demonstrated to be one order of magnitude more efficient than on mineral surfaces, such as clays and Fe-oxides (Goldberg, 1997). Moreover, oil reservoir brines are commonly enriched in B, so organic matter maturation seems to be a possible source of B during thermal maturation (Williams, 2000). The degradation of organic matter by SO_4 from recharge water would account for the release of B to the pore water of the NP aquifer (Fig. 8).

Defining groundwater quality for each defined zones is essential for good management of the NP aquifer. In addition to mining, the main consumption of the groundwater is for agriculture and drinking water associated with the surroundings villages. Moreover, the aquifer also

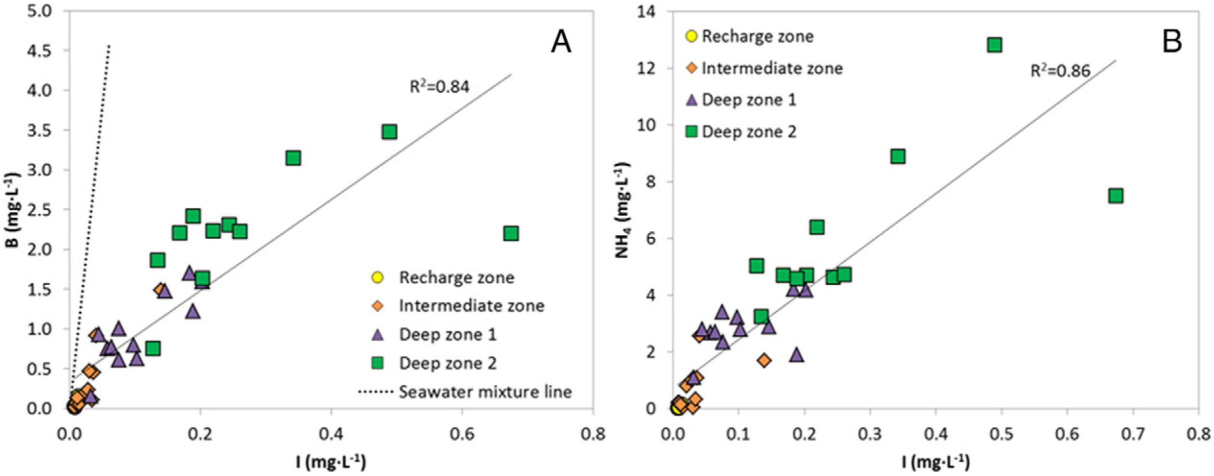

Fig. 6. Plots of A) boron and iodide, B) ammonium and iodide.

Table 2
NH_4, B, I and F concentrations in seawater, mixed water with an 8% contribution of seawater, and groundwater samples (mg L^{-1}). The enrichment factor is calculated under the assumption that groundwater mixes with a maximum of 8% of seawater. Seawater concentrations for NH_4 and B are from Yuan-Hui, 1991, those of I and F are from Truesdall et al., 2000 and Berner and Berner, 1987, respectively.

	NH_4	B	I	F
Seawater concentration	0.05	4.6	0.06	1
Concentration contribution from 8% of seawater	0.004	0.368	0.0048	0.08
GW samples maximum concentrations	12.8	3.48	0.67	6.79
Enrichment factor	3200	9	140	85

represents a drinkable water reserve for the city of Seville and its conurbation in severe drought events. Therefore, the guideline defined by the WHO (2008) for drinking water and the USEPA recommendations for irrigation have been used to assess the water quality of the aquifer based on ammonium, arsenic, boron and salinity. The groundwater of the studied area exhibits a clear increase in salinity and loss of quality from NW to SE. Recharge area: In general, the groundwater in this area has acceptable characteristics for drinking water (NH_4, As, B and salinity) and continuous irrigation, except in local cases where high nitrate concentrations related to agriculture has been detected. Intermediate zone: Drinking water and high water quality are found in the NW half of this zone. The intermediate SE half, however, has NH_4 concentrations above the drinking water standards. The salinity and B concentrations allow the use of the water for continuous irrigation of many types of crops. Deep zones 1 and 2: Groundwater from these zones has high concentrations of ammonium, arsenic, boron and salinity and is not suitable for drinking or for continuous irrigation use.

Based on the described water quality data, three different uses of groundwater can be established: drinking and continuous irrigation, irrigation only and none (Fig. 9). In this paper, only NH_4, As, B and salinity has considered for determining the groundwater quality. Other parameters or compounds not addressed here may affect the delineation of the drinking and continuous irrigation water zone.

Beyond the description of water quality and the classification of aquifer zones, correct management requires the definition of a methodology for discriminating anthropogenic from geogenic origins for the solutes that constrain the water quality, such as As, NH_4 and B. This is particularly necessary in an area of water scarcity and aquifer exploitation by various and often conflicting users. Here, we present evidence that, rather than mining operations, arsenic is related to the reductive dissolution of As-bearing goethite mineralization in a reducing environment, similar to the cases described for SW Asia (Smedley and Kinniburgh, 2002). Evidence of such a process includes the low redox potential, and the massive precipitation of siderite with light $\delta^{13}C$ values. Moreover, we also demonstrate that NH_4, B, I and F are also of geogenic origin and are correlated. Anomalous concentrations of all such elements have also been previously referred to in an aquitard from northern Mexico (Ortega-Guerrero, 2003), but the relationships among them are not mentioned. A strong correlation of all of these elements with salinity is also observed. However, unlike similar aquifers in Michigan and Bangladesh (Ravenscroft and McArthur, 2003; Halim et al., 2010), the concentrations of these elements in the NP aquifer cannot be explained by mixing with seawater, but they require another source. An origin of marine organic matter degradation under a reducing environment is postulated for NH_4, B, I and F. The evidence for organic matter degradation includes the light $\delta^{13}C$ and $\delta^{15}N$ values measured in groundwater. This is in agreement with the origin attributed by Jiao et al. (2010) for the NH_4 and I of pore water in the Pearl River Delta, China, although these authors did not supply direct evidence.

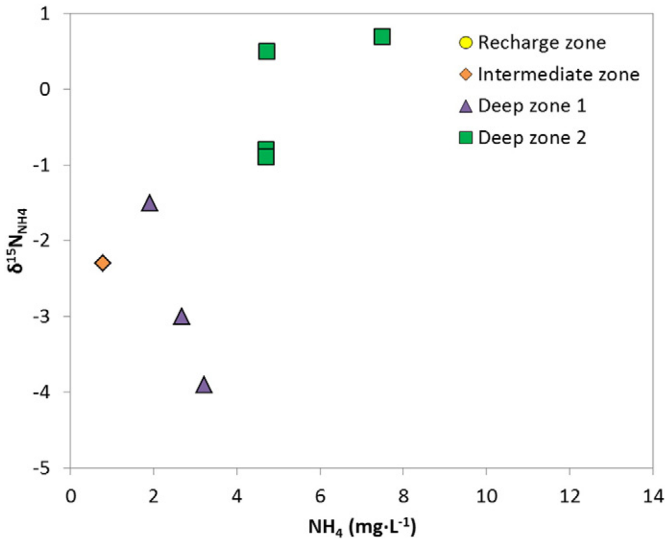

Fig. 7. Plot of $\delta^{15}N_{NH4}$ vs. NH_4.

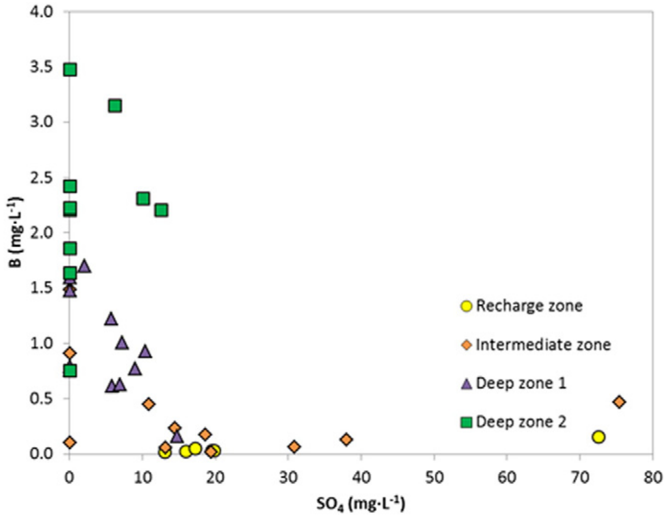

Fig. 8. Correlation between B and SO_4.

5. Conclusion

Groundwater flows from NW to SE evolving from Ca–HCO_3 to Na–HCO_3 and finally to Na–Cl type waters with increasing depth. In general, the increased salinity down-flow is a natural characteristic of this system, with two groundwater systems possibly being mixed in different proportions: A) a shallower, faster system associated with recharge in the Cenozoic portion of the NP aquifer, with slightly enriched water stable isotope values, lower Cl/Br ratios and an enrichment in Na due to ion-exchange processes; and B) a deeper, slower system associated with groundwater recharged at the coldest period during last 30 ky, with some remains of marine pore waters of up to 8% and Cl/Br ratios closer to marine-derived values.

High arsenic, ammonium and boron concentrations are found in the deeper zone of the NP aquifer. None of these solutes are found in the recharge area, but their concentrations increase with depth. They appear in zones already isolated from the surface by a thick sequence of low-permeability marls and in groundwater with residence times >30 ky. Therefore, the presence of high arsenic, ammonium and boron concentrations is attributed to geogenic processes.

The arsenic distribution follows a different pattern that is not strictly linked to salinity. Arsenic in groundwater is interpreted as originated from the reductive dissolution of As-bearing goethite by dissolved organic matter. Goethite was formed by the oxidation of original

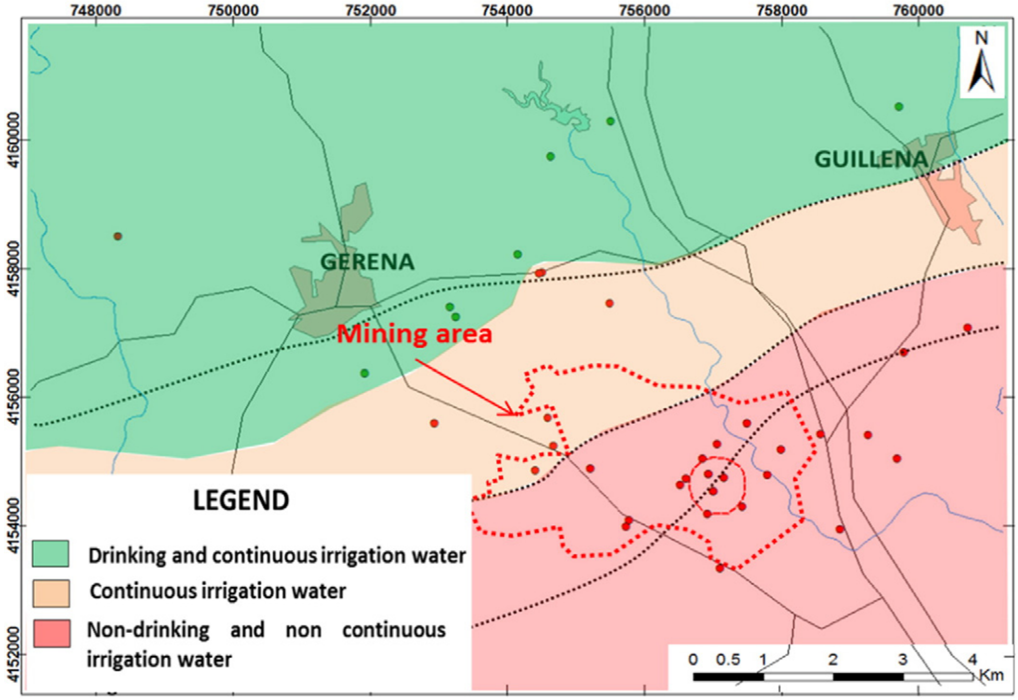

Fig. 9. Map of groundwater quality from ammonium, arsenic, boron and chloride concentrations. The dashed lines mark the four zones: Recharge, Intermediate, Deep 1 and Deep 2. ETRS_1989_UTM_Zone_29N.

Palaeozoic ore exposed to atmospheric conditions during the pre-Miocene age. Arsenic in groundwater depends, therefore, on the location of goethite mineralization. The lack of the expected correlation between Fe and As is explained by the massive precipitation of siderite.

Ammonium and boron, together with iodide and fluoride, clearly increase with chloride from NW to SE and are interpreted as being the result of degradation of marine solid organic matter by sulphate dissolved in the recharge water. The light $\delta^{15}N_{NH4}$ values confirm that its origin is linked to marine organic matter.

Related to management implications, three zones of groundwater quality were defined based on the ammonium, arsenic, boron and salinity data: the first zone, which is closer to the recharge area, contains water of human drinkable quality; the second zone downflow contains groundwater suitable for continuous irrigation but not for drinking, due to its high ammonium concentrations; and the third zone contains groundwater of elevated salinity (up to 5940 $\mu S\ cm^{-1}$) and high ammonium, arsenic and boron concentrations not being usable.

The accurate investigation of the interactions between water, organic matter and rock is indispensable for the correct determination of the origin of water quality in areas with high human pressure on aquifers.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2015.09.098.

References

Abad de Los Santos, M., 2007. La transgresión tortoniense en el margen pasivo de la cuenca del Guadalquivir: respuesta estratigráfica e implicaciones paleontológicas. Published PhD Thesis. Universidad de Huelva (527 pp.).

Ahmed, K.M., Bhattacharya, P., Hasan, M.A., Akhter, S.H., Alam, S.M.M., Bhuyian, M.A.H., Imam, M.B., Khan, A.A., Sracek, O., 2004. Arsenic enrichment in groundwater of the alluvial aquifers in Bangladesh: an overview. Appl. Geochem. 181–200.

Alberto, M.C.R., Arah, J.R.M., Neue, H.U., Wassmann, R., Lantin, R.S., Aduna, J.B., Bronson, K.F., 2000. A sampling technique for the determination of dissolved methane in soil solution. Chemosphere Global Change Sci. 2 (1), 57–63.

Anawar, H. M., Akai, J., Komaki, K., Terao, H., Yoshioka, T., Ishizuka, T., Safiullah, S., and Kato, K., (2003). Geochemical occurrence of arsenic in groundwater of Bangladesh: sources and mobilization processes, J. Geochem. Explor., v. 77, no. 2–3, p. 109–131.

Appelo, C.A.J., 1994. Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. Water Resour. Res. 30 (10), 2793–2805.

Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. Ground Water 31, 180–186.

Azcue, J.M., Murdoch, A., Rosa, F., Hall, G.E.M., 1994. Effects of abandoned gold mine tailings on the arsenic concentrations in water and sediments of Jack of Clubs Lake, BC. Environ. Technol. 15, 669–678.

Ball, J.M., Nordstrom, D.K., 2001. User's manual for WATEQ4F with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. U.S. Geological Survey Water Resources. Investigation Report 91–183.

Belkin, H.E., Zheng, B., Finkelman, R.B., 2000. Human health effects of domestic combustion of coal in rural China: a causal factor for arsenic and fluorine poisoning. 2nd World Chinese Conf. Geological Sciences, Extended Abstr., August 2000. Stanford Univ., pp. 522–524.

Berg, M., Tran, H. C., Nguyen, T. C., Pham, H. V., Schertenleib, R., and Giger, W., (2001). Arsenic contamination of groundwater and drinking water in Vietnam: A human health threat, Environ. Sci. Technol., v. 35, no. 13, p. 2621–2626.

Bernard, R., Taran, Y., Pennisi, M., Tello, E., Ramirez, A., 2011. Chloride and boron behavior in fluids of Los Humeros geothermal field (Mexico): a model based on the existence of deep acid brine. Appl. Geochem. 26 (12), 2064–2073.

Berner, E.K., Berner, R.A., 1987. The global water cycle: geochemistry and environment. Prentice-Hall.

Blake, C., 2008. The mineralogical characterisation and interpretation of a precious metal-bearing fossil gossan, Las Cruces, Spain: Published PhD Thesis. Cardiff University (207 pp.).

Borowski, W.S., Paull, C.K., 2000. Data report: nitrogen isotopic composition of pore-water ammonium, Blake ridge, site 9971. In: Paull, C.K., Matsumoto, R., Wallace, P.J., Dillon, W.P. (Eds.), Proceedings of the Ocean Drilling Program, Scientific Results. 164–171.

Capasso, G., Inguaggiato, S., 1998. A simple method for the determination of dissolved gases in natural waters. An application to thermal waters from Vulcano Island. Appl. Geochem. 13 (5), 631–642.

Capitán Suárez, M.A., 2006. Mineralogía y geoquímica de la alteración superficial de depósitos de sulfuros masivos en la faja pirítica ibèrica. Departamento de geología. Universidad de Huelva (UHU), p. 368.

Celle-Jeanton, H., Travi, Y., Blavoux, B., 2001. Isotopic typology of the precipitation in the Western Mediterranean region at three different time scales. Geophysical Research Letters 28 (7), 1215–1218.

Cendón, D.I., Peryt, T.M., Ayora, C., Pueyo, J.J., Taberner, C., 2004. The importance of recycling processes in the Middle Miocene Badenian evaporite basin (Carpathian foredeep): paleoenvironmental implications: Palaeogeography, Palaeoclimatology. Palaeoecology 212 (1–2), 141–158.

Cendón, D. I., Hankin, S. I., Williams, J. P., Van der Ley, M., Peterson, M., Hughes, C. E., Meredith, K., Graham, I. T., Hollins, S. E., Levchenko, V., and Chisari, R., 2014, Groundwater residence time in a dissected and weathered sandstone plateau: Kulnura–Mangrove Mountain aquifer, NSW Australia, Aust. J. Earth Sci., v. 61, no. 3, p. 475–499.

Chen, J.Y., Tang, C.Y., Shen, Y.J., Sakura, Y., Fukushima, Y., 2004. Nitrate pollution of groundwater in a wastewater irrigated field in Hebei Province China. Wastewater Re-Use and Groundwater Quality 285, 23–27.

CHG, 2012. Propuesta de proyecto de plan hidrológico de la demarcación hidrográfica del Guadalquivir. Sevilla.

CLC (2005). Valoración ambiental del estado pre-operacional EVA-0, Sevilla, Diciembre 2005, 77 pag. http://www.cobrelascruces.com/index.php/documentos-de-interes/.

Criaud, A., Fouillac, C., 1989. The distribution of arsenic(III) and arsenic(V) in geothermal waters: examples from the Massif Central of France, the Island of Dominica in the Leeward Islands of the Caribbean, the Valles Caldera of New Mexico, USA, and southwest Bulgaria. Chem. Geol. 76, 259–269.

Currell, M., Cartwright, I., Raveggi, M., Han, D., 2011. Controls on elevated fluoride and arsenic concentrations in groundwater from the Yuncheng Basin, China. Appl. Geochem. 26 (4), 540–552.

Currell, M., Cendón, D., Cheng, X., 2013. Analysis of environmental isotopes in groundwater to understand the response of a vulnerable coastal aquifer to pumping: Western Port Basin, south-eastern Australia. Hydrogeol. J. 21 (7), 1413–1427.

Custodio, E., Bruggeman, G.A., 1987. Groundwater problems in coastal areas. Studies & Reports in Hydrology. 45. UNESCO, Paris, pp. 1–576.

Custodio, E., Llamas, M.R., 1976. Hidrología Subterránea. Ediciones Omega, Barcelona, pp. 1–2350.

Dansgaard, W., 1964. Stable isotopes in precipitation. Tellus 16 (4), 436–468.

Davis, J.A., Leckie, J.O., 1978. Effect of adsorbed complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12 (12), 1309–1315.

Edmunds, W.M., Dodo, A., Djoret, D., Gaye, C.H., Goni, I.B., Travi, Y., Gasse, F., 2004. Groundwater as an Archive of Climatic and Environmental Change: Europe to Africa. In Past Climate Variability Through Europe and Africa (pp. 279–306) Springer, Netherlands.

Ellis, A.J., Mahon, W.A.J., 1977. Chemistry and Geothermal Systems. Academic Press, New York.

Fernandes, P.G., Carreira, P.M., 2008. Isotopic evidence of aquifer recharge during the last ice age in Portugal. J. Hydrol. 361 (3), 291–308.

Fernández-Caliani, J., Galán, E., 1991. Las pizarras de la faja piritica ibérica (zona sur-Portuguesa): geología, mineralogía y aplicaciones industriales. Estud. Geol. 47 (5–6), 295–303. http://dx.doi.org/10.3989/egeol.91475-6425.

Gaillardet, J., Viers, J. and Dupre, B. (2004). Trace elements in river waters. In: Treatise on Geochemistry. Holland, H.D. and Turekian, K.K. (editors), Elsevier, Amsterdam. 5: 225–272.

Gemici, Ü., Tarcan, G., Helvacı, C., Somay, A.M., 2008. High arsenic and boron concentrations in groundwaters related to mining activity in the bigadiç borate deposits (Western Turkey). Appl. Geochem. 23 (8), 2462–2476.

Goldberg, S., 1997. Reactions of boron with soils. Plant Soil 193 (1–2), 35–48.

Gómez de las Heras, J., López-Geta, J.A., Mediavilla, C., Sahuquillo, A., Custodio, E., 2001. Comportamiento hidráulico y modelación hidrogeológica de las formaciones paleozoicas y miocenas de la cuenca del río Guadiamar. Boletín Geológico y Minero, número especial, pp. 257–282.

Grassi, S., Amadori, M., Pennisi, M., Cortecci, G., 2014. Identifying sources of B and as contamination in surface water and groundwater downstream of the larderello geothermal–industrial area (Tuscany–central Italy). J. Hydrol. 509, 66–82.

Halim, M. A., Majumder, R. K., Nessa, S. A., Oda, K., Hiroshiro, Y., Saha, B. B., Hassain, S. M., Latif, S. A., Islam, M. A., and Jinno, K., (2009). Groundwater contamination with arsenic in Sherajdikhan Bangladesh: geochemical and hydrological implications, Environ. Geol., v. 58, no. 1, p. 73–84.

Halim, M. A., Majumder, R. K., Nessa, S. A., Hiroshiro, Y., Sasaki, K., Saha, B. B., Saepuloh, A., and Jinno, K., (2010). Evaluation of processes controlling the geochemical constituents in deep groundwater in Bangladesh: spatial variability on arsenic and boron enrichment, J. Hazard. Mater., v. 180, no. 1–3, p. 50–62.

Harms-Ringdahl, P., 2007. Identifying possible sources of ammonium ions and arsenic in groundwater in the Nam Du area, Vietnam. MS Thesis 82. Swedish Univ. Agric. Sci., Dept. Soil Sci.

Harvey, C., C. Swartz, A. Badruzzaman, N. Keon-Blute, W. Yu, M. Ali, J. Jay, R. Beckie, V. Niedan and D. Brabander (2003). Response to comments on arsenic mobility and groundwater extraction in Bangladesh. Science 300(5619): 584–584.

Hinkle, S.R., Böhlke, J.K., Duff, J.K., Morgan, D.S., Weick, R.J., 2007. Aquifer-scale controls on the distribution of nitrate and ammonium in ground water near La pine, Oregon, USA. J. Hydrol. 333, 486–503.

Holloway, J.M., Dahlgren, R.A., 2002. Nitrogen in rock: occurrences and biogeochemical implications. Glob. Biogeochem. Cycles 16 (4), 65–71.

Holmes, R.M., McClelland, J.W., Sigman, D.M., Fry, B., Peterson, B.J., 1998. Measuring 15N–NH$_4^+$ in marine, estuarine and fresh waters: an adaptation of the ammonia diffusion method. Mar. Chem. 60, 235–243.

Hughes, C.E., Crawford, J., 2012. A new precipitation weighted method for determining the meteoric water line for hydrological applications demonstrated using Australian and global GNIP data. J. Hydrol. 464–465, 344–351.

Iglesias, M., 1999. Hydrogeochemical Characterization of Groundwater Flow in El Abalario, Doñana, Huelva. PhD Thesis. Universidad Politécnica de Cataluña, Spain.

Islam, F.S., Gault, A.G., Boothman, C., Polya, D.A., Charnock, J.M., Chatterjee, D., Lloyd, J.R., 2004. Role of metal-reducing bacteria in arsenic release from Bengal delta sediments. Nature 430 (6995), 68–71.

Jiao, J. J., Wang, Y., Cherry, J. A., Wang, X. S., Zhi, B. F., Du, H. Y., and Wen, D.G., (2010). Abnormally high ammonium of natural origin in a coastal aquifer-aquitard system in the Pearl River Delta China, Environ. Sci. Technol., v. 44, no. 19, p. 7470–7475.

Jiménez, D., Custodio, E., 2008. El exceso de deuterio en la lluvia y en la recarga a los acuíferos en el área circum-mediterránea y en la costa mediterránea Española [deuterium excess in rain and recharge to the aquifers in the circum-mediterranean área and in the Spanish coastal area]. Boletín Geológico Minero. Madrid. 119, 21–32.

Jiménez de Cisneros, C., Caballero, E., 2013. Paleoclimate reconstruction during MIS5a based on a speleothem from Nerja Cave, Málaga, South Spain. Nat. Sci. 5, 533–540. http://dx.doi.org/10.4236/ns.2013.55067.

Kennedy, H.A., Elderfield, H., 1987. Iodine diagenesis in pelagic deep-sea sediments. Geochim. Cosmochim. Acta 51 (9), 2489–2504.

Kohl, D. H., Shearer, G. B., and Commoner, B., (1971). Fertilizer nitrogen-contribution to nitrate in surface water in a corn belt watershed: Science, v. 174, no. 4016, p. 1331.

Manning, B.A., Goldberg, S., 1997b. Adsorption and stability of arsenic (III) at the clay mineral-water interface. Environ. Sci. Technol. 31, 2005–2011.

Manzano, M., Soler, A., Carrera, J. y E. Custodio (2001). Composición isotópica (δ^{18}O, δ^{2}H y δ^{34}S) de las aguas del área afectada por el vertido minero de Aznalcóllar (SO España). En A. Medina, J. Carrera y L. Vives (Editores) Las Caras del Agua Subterránea. Serie Hidrogeología y Aguas Subterráneas, N° 1. IGME, Madrid, 477–487.

Massmann, G., Sültenfuß, J., Dünnbier, U., Knappe, A., Taute, T., Pekdeger, A., 2008. Investigation of groundwater residence times during bank filtration in berlin: a multi-tracer approach. Hydrol. Process. 22 (6), 788–801.

Mastrocicco, M., Giambastiani, B.M.S., Colombani, N., 2013. Ammonium occurrence in a salinized lowland coastal aquifer (Ferrara, Italy). Hydrol. Process. 27 (24), 3495–3501.

McArthur, J.M., Ravenscroft, P., Safiullah, S., Thirlwall, M.F., 2001. Arsenic in groundwater: testing pollution mechanisms for aquifers in Bangladesh. Water Resour. Res. 37, 109–117.

Meng, X., Wang, W., 1998, July. Speciation of arsenic by disposable cartridges. In book of posters of the third international conference on arsenic exposure and health effects. Society of Environmental Geochemistry and Health Denver, Colorado.

Mukherjee, A., Fryar, A.E., 2008. Deeper groundwater chemistry and geochemical modeling of the arsenic affected western Bengal basin, West Bengal, India. Appl. Geochem. 863–894.

Navarro, A., Fernández, A., Doblas, J.G., 1993. In: ME, I.G. (Ed.), Instituto Geológico y Minero de España, pp. 255–256.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl. Geochem. 403–413.

Nicolli, H.B., Suriano, J.M., Peral, M.A.G., Ferpozzi, L.H., Baleani, O.A., 1989. Groundwater contamination with arsenic and other trace-elements in an area of the Pampa, province of Cordoba, Argentina. Environ. Geol. Water Sci. 14, 3–16.

Ortega-Guerrero, A., (2003). Origin and geochemical evolution of groundwater in a closed-basin clayey aquitard Northern Mexico, J. Hydrol., v. 284, no. 1–4, p. 26–44.

Palmucci, W., Rusi, S., 2014. Boron-rich groundwater in Central Eastern Italy: a hydrogeochemical and statistical approach to define origin and distribution. Environmental Earth Sciences 72 (12), 5139–5157.

Parkhurst, D.L., and Appelo, C.A.J., (2013). Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, (book 6, chap. A43, 497 p.), available only at http://pubs.usgs.gov/tm/06/a43.

Price, N.B., Calvert, S.E., 1973. The geochemistry of iodine in oxidised and reduced recent marine sediments. Geochim. Cosmochim. Acta 37 (9), 2149–2158.

Prokopenko, M. G., Hammond, D. E., Stott, L. (2006). 9. Lack of Isotopic Fractionation of 15 N of Organic Matter during Long-Term Diagenesis in Marine Sediments, ODP Leg 202, Sites 1234 and 1235.

Rau, G.H., Arthur, M.A., Dean, W.E., 1987. N-15/N-14 variations in cretaceous Atlantic sedimentary sequences: implication for past changes in marine nitrogen biogeochemistry, earth planet. Sci. Lett. 82, 269–279.

Ravenscroft, P., McArthur, J.M., 2003. Mechanism of regional enrichment of groundwater by boron: the examples of Bangladesh and Michigan, USA. Appl. Geochem. 1413–1430.

Redfield, A.C., 1934. On the Proportions of Organic Derivatives in Sea Water and Their Relation to the Composition of Plankton. James Johnson Memorial Volume, Liverpool, In, pp. 177–192.

Robinson, B., Outred, H., Brooks, R., Kirkman, J., 1995. The distribution and fate of arsenic in the Waikato River System, North Island, New Zealand. Chem. Speciat. Bioavailab. 7, 89–96.

Sancha, A.M., Castro, M.L., 2001. Arsenic in Latin America: occurrence, exposure, health effects and remediation. In: Chapell, W.R., Abernathy, C.O., Calderon, R.L. (Eds.), Arsenic Exposure and Health Effects IV. Elsevier, Amsterdam , pp. 87–96, www.aulados.net (Temas Ambientales 2007 31).

Sapek, A., 2005. Agriculture activities as a source of nitrates in groundwater. In: Razowska-Jaworek, L., Sadurski, A. (Eds.), Nitrates in Groundwater. A.A. Balkema Publishers, Leiden.

Savage, K.S., Tingle, T.N., O'Day, P.A., Waychunas, G.A., Bird, D.K., 2000. Arsenic speciation in pyrite and secondary weathering phases, Mother Lode gold district, Tuolumne County, California. Appl. Geochem. 15 (8), 1219–1244.

Scheiber, L., Ayora, C., Vázquez-Suñé, E., Cendón, D. I., Soler, A., Custodio, E., and Baquero, J. C., (2015). Recent and old groundwater in the Niebla-Posadas regional aquifer (southern Spain): Implications for its management: J. Hydrol., v. 523, p. 624–635.

Sebilo, M., Mayer, B., Grably, M., Billiou, D., Mariotti, A., 2004. The use of the ammonium diffusion. Method for $\delta^{15}N_{NH4+}$ and $\delta^{15}N_{NO3}$ measurements: comparison with other techniques. Environ. Chem. 1 (2), 99–103.

Smedley, P.L., 1996. Arsenic in rural groundwater in Ghana. J. Afr. Earth Sci. 22, 459–470.

Smedley, P.L., Kinniburgh, D.G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Appl. Geochem. 17, 517–568.

Swartz, C.H., Blute, N.K., Badruzzman, B., Ali, A., Brabander, D., Jay, J., Besancon, J., Islam, S., Hemond, H.F., Harvey, C.F., 2004. Mobility of arsenic in a Bangladesh aquifer: inferences from geochemical profiles, leaching data, and mineralogical characterization. Geochim. Cosmochim. Acta 68 (22), 4539–4557.

Tang, C., Chen, J., Shindo, S., Sakura, Y., Zhang, W., and Shen, Y., (2004). Assessment of groundwater contamination by nitrates associated with wastewater irrigation: a case study in Shijiazhuang region China, Hydrol. Process., v. 18, no. 12, p. 2303–2312.

Thompson, J.M., Demonge, J.M., 1996. Chemical analyses of hot springs, pools, and geysers from Yellowstone National Park, Wyoming and vicinity, 1980–1993. US Geol. Surv. Open File Rep. 96–68.

Tornos, F., Velasco, F., Menor-Salván, C., Delgado, A., Slack, J.F., Escobar, J.M., 2014. Formation of recent Pb-Ag-Au mineralization by potential sub-surface microbial activity. Nat. Commun. 5 8 pp.

Truesdall, V.W., Bale, A.J., Woodward, M., (2000). The meridional distribution of dissolved iodine in near-surface waters of the Atlantic Ocean. Prog. Oceanogr. 45, 387–400.

USEPA (2012) Guidelines for water reuse. EPA/600/R-12/618, 643 pp.

USEPA, 2012. Guidelines for Water Reuse (EPA Publication EPA/600/R-12/618. September 2012) U.S. Environmental Protection Agency.

Valsero, D., José, J., 2002. Los sistemas kársticos de la provincia de Málaga y su evolución: contribución al conocimiento paleoclimático del Cuaternario en el Mediterráneo occidental. PhD Thesis. Complutense University of Madrid, Spain (404 pp.).

Van der Zee, C., Roberts, D.R., Rancourt, D.G., Slomp, C.P., 2003. Nanogoethite is the dominant reactive oxyhydroxide phase in lake and marine sediments. Geology 31 (11), 993–996.

Wang, Z.H., Ye, W.S., Shu, W.C., Li, M.H., Wong, C.Y., 2006. Land arsenic uptake and accumulation in fern species growing at arsenic-contaminated sites of southern China: field surveys. International Journal of Phytoremediation 1–11.

Wang Y, Jiao JJ, Cherry JA. (2012). Occurrence and geochemical behavior of arsenic in a coastal aquifer-aquitard system of the Pearl River Delta, China. Sci. Total Environ. (2012 Jun); 427–428 286–297. doi: http://dx.doi.org/10.1016/j.scitotenv.2012.04.006. PubMed PMID: 22554534.

Welch, A.H., Lico, M.S., Hughes, J.L., 1988. Arsenic in ground-water of the western United States. Ground Water 26, 333–347.

WHO, 2008. Guidelines for Drinking Water Quality. third ed. World Health Organization, Geneva, Switzerland (668 pp.).

Williams, M., 1997. Mining-related arsenic hazards: Thailand case-study. Summary report. Brit. Geol. Surv. Tech. Rep. (WC/97/49).

Williams, L.B., 2000. Boron Isotope Geochemistry During Burial Diagenesis. Ph.D. Thesis. University of Calgary, Calgary, Alberta (168 pp.).

Williams, M., Fordyce, F., Paijitprapapon, A., Charoenchaisri, P., 1996. Arsenic contamination in surface drainage and groundwater in part of the Southeast Asian tin belt, Nakhon Si Thammarat Province, southern Thailand. Environ. Geol. 27, 16–33.

Williams, A. E., Lund, L. J., Johnson, J. A., Kabala, Z. J. (1998). Natural and anthropogenic nitrate contamination of groundwater in a rural community, California, Environ. Sci. Technol., 32, 32–39, 1998.

Wilson, F.H., Hawkins, D.B., 1978. Arsenic in streams, stream sediments and ground water, Fairbanks area. Alaska. Environ. Geol. 2, 195–202.

Worden, R.H., 1996. Controls on halogen concentrations in sedimentary formation waters. Mineral. Mag. 60 (399), 259–274.

Wunsch, A., Navarre-Sitchler, A.K., McCray, J.E., 2013. Geochemical implications of brine leakage into freshwater aquifers. Groundwater 51 (6), 855–865.

Yesares, L., Sáez, R., Nieto, J.M., de Almodóvar, G.R., Cooper, S., 2014a. Supergene enrichment of precious metals by natural amalgamation in the Las cruces weathering profile (Iberian pyrite belt, SW Spain). Ore Geol. Rev. 58 (0), 14–26.

Yesares, L., Sáez, R., Nieto, J.M., Ruiz De Almodovar, G., Gómez, J.L., Escobar, J.M., 2014b. The Las Cruces deposit, Iberian pyrite belt, Spain. Ore Geol. Rev. 66 (2015), 25–46.

Yokoyama, T., Takahashi, Y., Tarutani, T., 1993. Simultaneous determination of arsenic and arsenious acids in geothermal water. Chem. Geol. 103, 103–111.

Yuan-Hui, L., 1991. Distribution patterns of the elements in the ocean: a synthesis. Geochim. Cosmochim. Acta 55 (11), 3223–3240.