Differentiating the source and origin of high ammonium, arsenic and boron concentrations in the proximity of a mine site

Laura Scheiber [a;*], Carlos Ayora [a], Enric Vázquez-Suñé [a], Dioni I. Cendón [b, c], Albert Soler [d]

[a] *Institute of Environmental Assessment and Water Research, CSIC, Jordi Girona 18. E-08034, Barcelona, Spain*
[b]*Australian Nuclear Science and Technology Organisation, Locked Bag 2001, Kirrawee DC, NSW 2232, Australia*
[c]*School of Biological, Earth and Environmental Sciences (BEES), University of New South Wales (UNSW), NSW 2052, Australia*
[d]*Departament de Cristal·lografia, Mineralogia i Dipòsits Minerals. Facultat de Geologia. Universitat de Barcelona. C/Martí Franquès, sn. Barcelona (Spain)*

ABSTRACT

High ammonium, arsenic and boron concentration affect in part the Niebla-Posadas (NP) aquifer with concentrations locally above drinking water guidelines (WHO) and even for water reuse (USEPA). These high concentrations are generally in proximity to mining activities but in this case these concentrations are due to natural process detected around the groundwater monitoring network but not in neighbouring areas as waters are not useful for watering purpose and no irrigation wells access the target aquifer. This oxyhydroxide has the capacity of arsenic absorb and under reducing conditions the FeOOH dissolves releasing arsenic to groundwater. This process is accompanied for marine organic matter decomposition rich in nitrogen and with high boron content. The strong boron and chlorine correlation allow to determine the marine origin of boron but its exceed respect the seawater indicate that there is another boron sources. The high sodium-boron correlation and the negative relation between boron and calcium confirms that absorption and desorption boron process is controlled by exchange processes in the

organic matter. Based on these results it can be differentiating two groundwater areas of different water quality.

1. INTRODUCTION

Groundwater is a major source for domestic, industrial and agricultural uses supplying a third of the world population (Ponce Montes de Leon, 2001). The difficulty of managing this resource 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 to (3) geogenic causes related to water interaction with the host aquifer or along groundwater flows (Swartz et al., 2003; McArthur et al., 2001). Differentiating natural and anthropogenic sources is therefore crucial to ensure a good management of groundwater. However, in some instances can be very difficult to ascertain the origin and cause of contamination as in Chile (Sancha and Castro, 2001), Vietnam (Harms-Ringdahl, 2007) and California (Williams et al., 1998).

Numerous aquifers worldwide have groundwater quality problems related to elevated concentration of ammonium, arsenic and/or boron. Often, many of these cases are directly related with human activities such as agriculture and mining, the last generally associated to dewatering processes. High groundwater arsenic concentrations related to mining operations has been identified in many parts of the world as Thailand (Williams et al., 1996; Williams, 1997), Greece (Wilson and Hawkins, 1978), Ghana (Smedly, 1996), Alaska (Welch et al., 1988) and Canada (Azcue et al., 1994) amongst others. In these examples arsenic concentration in the aquifers ranged from 200 $\mu g \cdot L^{-1}$ to 1700 $\mu g \cdot L^{-1}$, 20-170 times above WHO guideline levels for drinking water.

Ammonium and boron contamination is often related to agricultural practices such as: water irrigation returns and use of fertilizers (Kohl et al., 1971; Butterwick et al., 1989; Chen et al., 2004; Tang et al., 2004 and amongst many others).

However, high ammonium, arsenic and boron concentration can also be due to natural processes. Arsenic can be mobilized by weathering reactions (Manning and Goldberg, 1977b; Wang et al., 2006; Mukherjee et al., 2008; Halim et al., 2010), geothermal processes as reported in Argentina (Nicoli et al., 1989), Japan (Yokoyama et al., 1993), New Zealand (Robinson et al., 1995), Chile (Ellis and Mahon, 1977), France (Criaud and Fouillac, 1989) and the USA (Thompson and Demonge, 1996) or even related to biological activity (Benner, 2008).

High boron and ammonium natural concentrations have also been identified in many aquifers worldwide as USA (Roy et al., 2003; Hinkle et al., 2007; Glessner and Roy, 2009), Mexico (Ortega-Guerrero, 2003), Asia (Berg et al., 2001; Jiao et al., 2010), Australia (Linderfelt and Turner, 2001) and Europe (Deak et al., 1993; Lorite-Herrera et al., 2009). Natural high concentration in some instances may be the result of residual seawater or salt water intrusion (BGS, 2001; Hassan et al., 1998; Rahman et al., 2000), decomposition of organic matter (Schilling, 2002; Lorite-Herrera et al., 2009; Halim et al., 2010), cation exchange processes under anoxic conditions (Appelo, 2005; Kroeger et al., 2007), dissolution of evaporites (Ravenscroft et al., 2001), mineral weathering (McArthur et al., 2001; Ravenscroft et al. 2003), geothermal processes and adsorption/desorption processes on mineral surface (Goldberg et al. 1993).

The Niebla-Posadas (NP) aquifer (S Spain) constitutes an example where ammonium, arsenic and boron levels are high in the confined, deep portion of the aquifer. This aquifer is part of the Guadalquivir Basin, a highly populated area, and constitutes a vital resource for supply of drinking water as well as for the agricultural, industrial and mining activities in southern Spain. Concentrations of these three components exceed in some cases 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). High concentrations of these contaminants have alerted the public opinion and numerous environmental groups have placed the main anthropogenic activities of the zone under the spotlight, especially the mining explotation of Cobre Las Cruces (CLC) and, in near future, Aznalcollar and the (DRS) used around the mine.

The CLC complex is the largest copper mine, and one of the largest open pits in Europe. . The mining project has implemented a Drainage and Reinjection System (DRS) for groundwater comprising two rings of wells around the mine perimeter, the internal ring drains the NP aquifer, while the external is used for water reinjection to prevent the decrease of the piezometric.

This paper presents a detailed hydrogeochemical and isotopic study that aims to discriminate the origin of high ammonium, arsenic and boron concentrations in the NP aquifer. This will be achieved by: a) characterizing sources of solutes, specially ammonium, arsenic and boron, b) investigating their spatial distribution in relation to sources, local geology and potential mobilization mechanisms and c) identifying the geochemical processes that control the presence of these solutes. The overall research provides an assessment of tools to differentiate natural sources and processes for high concentrations of undesired solutes.

2. MATERIALS AND METHODS

2.1. Hydrogeological setting

The Guadalquivir Basin with an area of 56.978 km² was formed in a foreland basin developed between the Betic range (active margin) and the Iberian massif (passive margin) during the Neogene (Fig.1).The Niebla-Posadas (NP) aquifer occupies the Northern edge of the basin.

The area selected for studding is located about 20 km North of Seville, limited by Sierra Morena (Iberian massif) to the north and the Cortijuelos creek on the southern boundary. The west and east limits are defined by the Guadiamar river and the “Ribera de Huelva” respectively. The

Cobre Las Cruces (CLC) open pit mine is located in the central part of the study area (Fig. 1A, B).

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 9-10 °C in mountainous areas and 15-18 °C in the valley region. The precipitation is characterized by both spatial and temporal irregularity, being the average annual precipitation of 500-600 mm/y with an evapotranspiration annual average of 991 mm/y (CHG 2012).

The studied area is mainly covered by Quaternary materials associated with river deposits with underlying Cenozoic bluish marls of the Arcillas Gibraleón Formation (Fm). These marls are of marine origin, rich in planktonic, benthic microfauna and organic matter. These form a wedge that thickens southwards from ~50 m near the recharge zone to over 800 m in the south of the CLC mine (Fig.1). Sandwiched between the bluish marls and the underlying Paleozoic basement the, the Niebla Formation hosts the main part of the NP aquifer and is formed by conglomerates, detrital limestone and sandstone with abundant marine microfauna. The Niebla Fm outcrops to the north (recharge area) and dips southward as it is confined by the overlying blue marls.Some gas deposits have been prospected in this formation and in the marls one hundred kilometers South of the studied area.The Paleozoic basement (Culm Fm) is made of quartzite, schists, granite and volcanogenic massive sulfide deposits (Blake, 2008; Capitán Suarez, 2006 and Fernández-Caliani and Galán, 1991). Major faults with a SW-NE orientation and secondary faults with NW-SE orientation affect the basement materials (Fig.1C).

The detrital strata of the Niebla Fm jointly with the weathered portion of the upper Paleozoic basement form the NP aquifer. This 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 marls with a low transmissivity (<5 m^2/d). Transmissivity values of the NP aquifer range between 10 and 500 m^2/d and storage coefficient values are of the order of 10^{-2} in 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. Total estimated recharge is 9 hm^3/y and the pumping activity is the main discharge estimated at 40 hm^3/y (CHG, 2012).

The Paleozoic basement outcrops to the north of the recharge area coinciding with increased elevation (up to 500 m). No much information exists on the groundwater potential of the Paleozoic basement or weather a deeper regional system may be possible within the fractured interconnected Paleozoic shales (Gómez de las Heras et al., 2001).

Based on groundwater residence times and hydrogeochemical indicators four areas (Recharge, Intermediate, Deep 1 and Deep 2) have been proposed for the NP aquifer (Scheiber et al. 2015). Thus, residence times of xxx, xxx, xxx and xxx years have been obtained from ^{3}H, ^{14}C and ^{36}Cl dating.

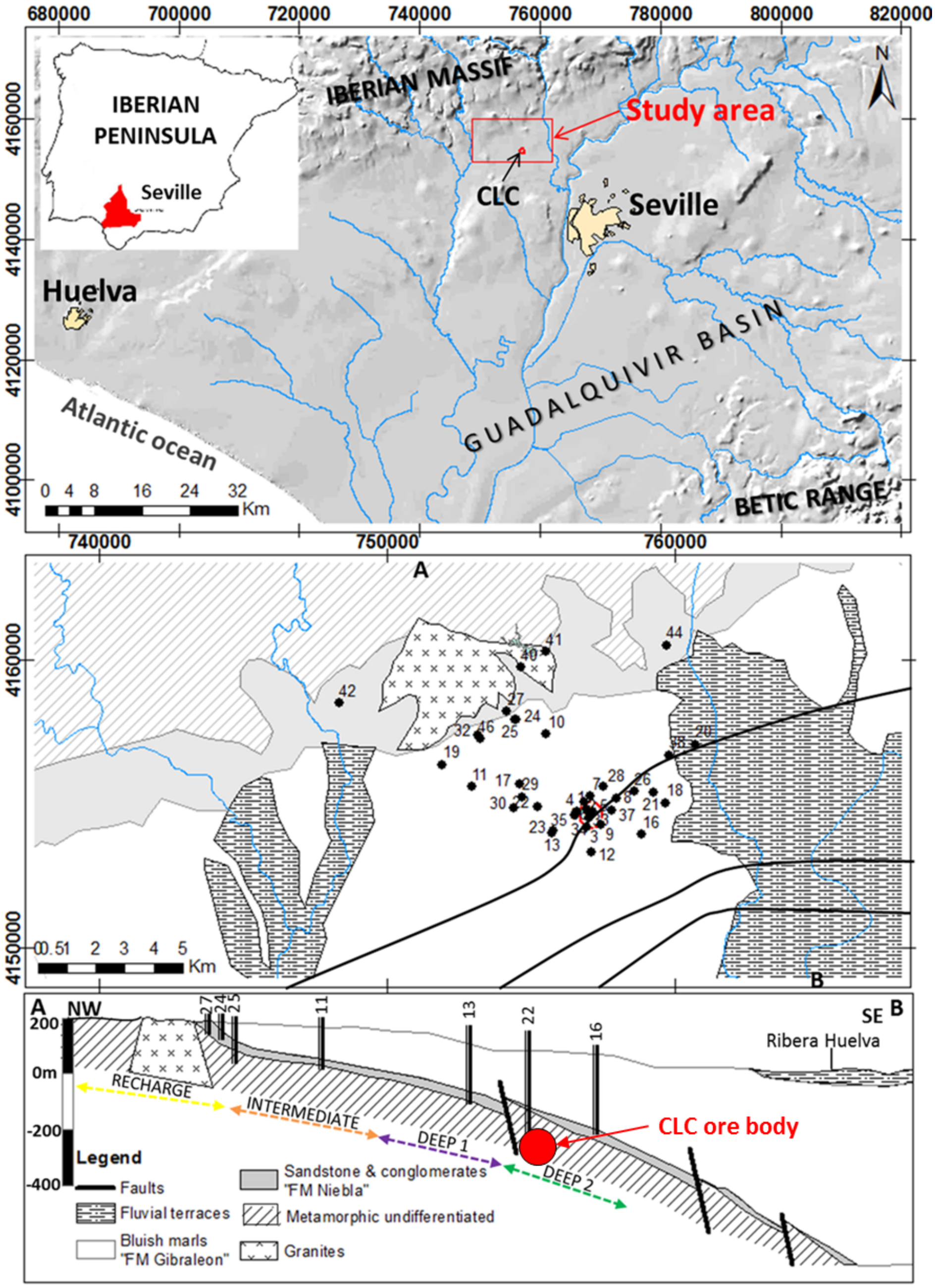

Fig. 1: A) Regional map and location of the studied area; B) Geological map of the area, location of the

2.2. Groundwater sampling and analysis

Groundwater samples were collected from a total of 40 wells and pizometres, 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 flied parameters had stabilized. The physico-chemical parameters such as temperature (ºC), pH, Electrical Conductivity (EC, $\mu S \cdot cm^{-1}$), Eh and dissolved oxygen (DO, $mg \cdot L^{-1}$) 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 tracer 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 et al., 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. NH_4^+ and I^- concentrations were analysed with a selective electrode 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 and analytical error from ±0.001 to ±0.009 mg·L. The CH_4 dissolved in water was calculated by the liquid gas partition coefficient. 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 S_2 and an analytical error of 5%.

The $\delta^{15}N_{NH4+}$ were analysed by a diffusion method based on protocols by Sebilo et al., (2004) and Holmes et al., (1998). 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. 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 $(NH_4^+)_2SO_4$. After one week the filter-pack was placed in an acid-washed glass bottle and placed in a freezer-drier during 2 hours to remove any water from the filter. Then the GF/D filter was removed and placed in a silver-cup to immediately analyze in an EA-IRMS.

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3. RESULTS

A summary of the main hydrochemical parameters measured is shown in Table 1.

	MIN.	MAX.	AVE	MEDIAN	SD	WHO (2008)	USEPA (2012)
pH	6.8	10.6	7.9	7.7	0.9	6.5-8.5	-
C.E. ($uS \cdot L^{-1}$)	388.0	5940.0	1624.9	1275.0	1074.4	1500	-
T (ºC)	14.7	37.5	25.5	25.1	5.2	-	-
Alk ($mg \cdot L^{-1}$ CaCO3)	130.0	468.2	296.9	300.0	81.4	-	-
DOC ($mg \cdot L^{-1}$)	0.2	15.9	3.5	3.7	3.4	-	-
Cl^- ($mg \cdot L^{-1}$)	12.6	1581.3	281.2	151.4	317.9	250	-
NO_3^- ($mg \cdot L^{-1}$)	0.1	102.3	11.2	0.1	24.1	50	-
SO_4^{-2} ($mg \cdot L^{-1}$)	0.1	115.3	16.9	10.1	24.4	250	-
HCO_3^- ($mg \cdot L^{-1}$)	158.5	570.9	361.3	365.8	100.3	-	-
Ca ($mg \cdot L^{-1}$)	0.6	177.0	46.3	29.0	51.0	200	-
K ($mg \cdot L^{-1}$)	0.1	43.4	5.5	4.1	6.6	30	-
Mg ($mg \cdot L^{-1}$)	0.001	50.6	7.3	4.0	9.6	150	-
Na ($mg \cdot L^{-1}$)	14.6	1061.8	238.5	221.1	222.7	200	-
NH_4 ($mg \cdot L^{-1}$)	0.04	12.8	2.6	2.1	2.8	0.2	-
I^- ($mg \cdot L^{-1}$)	0.007	0.67	0.11	0.06	0.14	-	-
Br^- ($mg \cdot L^{-1}$)	0.09	5.25	0.90	0.46	1.15	-	-
Fe ($mg \cdot L^{-1}$)	0.002	0.888	0.211	0.087	0.220	0.3	5
Mn (($mg \cdot L^{-1}$)	0.00	0.43	0.03	0.01	0.07	0.5	-
B (($mg \cdot L^{-1}$))	0.017	3.48	0.94	0.63	0.95	0.5	0.75
As (($mg \cdot L^{-1}$))	0.00003	0.18	6.9	1.5	27.1	0.01	0.01

Table 1. Groundwater parameters of the studied area (concentrations in mg/L) . Recommended limits for drinking water (WHO 2008) and for frequent irrigation (USEPA 2012).

Groundwater temperatures vary from 14.7 to 37.5 °C with an average value of 26.1 ºC. Cooler temperatures are in the recharge zone and increase towards the deeper zone. The pH values range between 6.8 and 10.6, with highest pH values found in the deeper SE zones. Specific conductance (SC) values are between 388 and 5940 $\mu S \cdot cm^{-1}$, also increasing with depth. Eh valuesranged between 177 mV in the recharge zone to -300 mV in the deeper ones

The major ions compositions (Fig.2) differentiate four main compositional types. Groundwater in the recharge zone is of Ca-HCO_3-type transitioning to Na-(Ca)-HCO_3 in the intermediate zone and Na-HCO_3 within the deep zone 1. The most evolved samples from the Deep zone 2 are of the Na-Cl-type. In general Na and Cl show a high correlation (R^2= 0.92) adapting to a seawater mixture line but with sodium excess. This excess has been interpreted as due to the replacement of Na initially present in the exchange complex by Ca-rich water from the recharge.

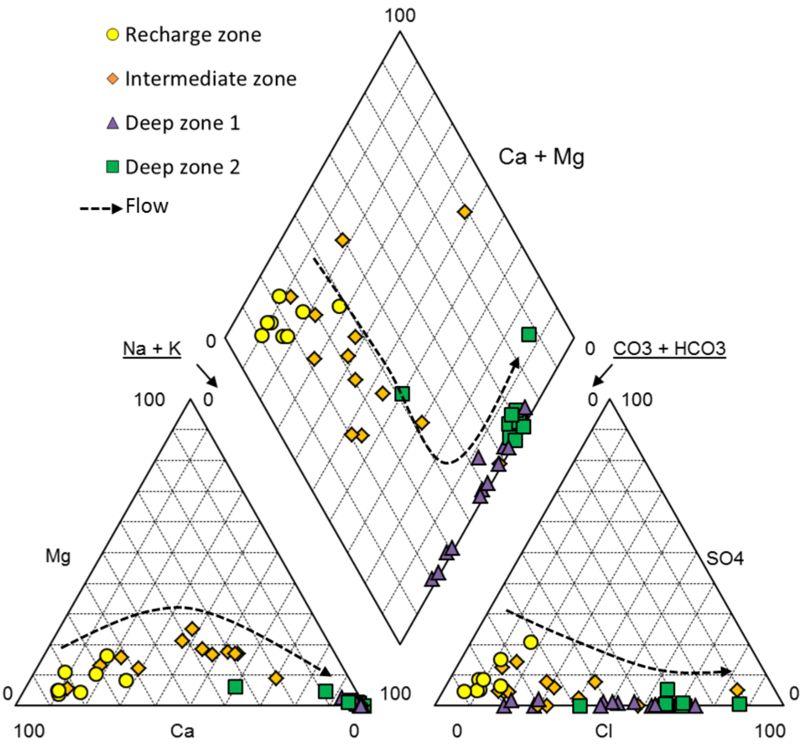

Fig.2. Piper diagram showing major ions chemistry of the sampled points. The arrows follow the NW-SE flow direction.

Nitrate concentrations are only found close to agricultural and farms areas in the recharge zone with concentrations ranging from 18 to 95 mg·L^{-1}. Nitrite has not been detected but high ammonium concentrations are found in 70% of the wells ranging from 0.043 to 12.8 mg·L^{-1} (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 range between 0.09 and 0.11 mg·L^{-1} and are higher at samples site with the lowest sulfate and where a H_2S-smell was identified in the field. Methane concentrations were mostly below detection limit (0.58 mg·L^{-1}) except for one sample with a value of 1.09 mg·L^{-1}.

Arsenic is generally found as As (III) with concentrations between 0.03 and 178.72 µg·L^{-1} and a mean value of 6.87 µg·L^{-1}. Of the 40 points measured, 4 provide As (III) values >10 µg·L^{-1} above the WHO guideline, 6 points have As (III) concentration between 5 and 10 µg·L^{-1} and the remaining points have concentrations <5 µg·L^{-1}. Boron concentrations in the study area range between 0.017 and 3.48 mg·L^{-1} with an average value of 0.944 mg·L^{-1}.. Approximately 55% of sampled points show boron concentrations above the WHO's standard limits of drinking water and ~50% 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 far above the guideline value set by WHO (0.2 mg·L^{-1}) for drinking water and the standard limit is exceeded in 76% of the sampled points (Table 1).

To better understand nitrogen sources a limited number of samples (n=8) has been analysed for $\delta^{15}N$ of dissolved ammonium. The $\delta^{15}N_{NH4}$ values range between -3.9 and 0.7 ‰ with an average value of -1.4 ‰.

4 DISCUSSION

4.1. Major elements hydrochemistry

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 ions varying from Ca-HCO_3-type in the recharge area to Na-Cl-type in the deeper samples recovered. The increasing salinity has been interpreted as the result of mixing with relict syndepositional marine water incorporation, with fluids trapped within the porosity during the transgressive Tortonian stage (Abad de los Santos, 2007). The marine origin is supported by Cl/Br ratios with values close to seawater ($R_{Cl/Br}$~ 600) in the deepest zones.. However, samples with higher chloride concentrations generally show more depleted ^2H and ^{18}O isotopic values, with all groundwater plotting along a line contained within the modern precipitation weighted least square regression lines PWLSR (Hughes and Crawford 2012) for Seville and Gibraltar (Fig.3A). Despite the short rainfall water data set available for Seville (6 years), deuterium excess in groundwater samples adjusts better to those expected from rainfall derived from Atlantic fronts and it is similar to that of Gibraltar. Similar deuterium excess values are also observed in groundwater samples with longer residence times either within the field area or in neighboring sites like Doñana (Manzano et al. 2001).

The depleted $\delta^2H/\delta^{18}O$ values in the deepest zones could be consistent with paleo-recharge under different climatic and/or topographic conditions. Thus, samples in the study area (Deep 1 and 2 zones) residence times, estimated at >30 ky (Scheiber et al. 2015) and generally correspond to the more depleted water stable isotopes values. Temperatures of paleo-recharge calculated in Doñana from nobles gases (Manzano et al., 2001) suggest no major climatic changes since the Pleistocene.

Two differentiated data clusters are illustrated by comparing water stable isotopes with Cl (Fig. 3B). The Cenozoic portion of the aquifer follows a slightly depleting trend with increasing salinity, probably due to the mixing with deeper Paleozoic groundwater. Consistently, deeper samples within the Paleozoic form a parallel group of samples with lighter isotopes, the scatter of the values suggesting some degree of mixing with shallower groundwater. The Paleozoic outcrops to the north reaching altitudes of up to 500 m. Therefore an altitude effect on rainfall could account for depleted water stable isotopes in the Paleozoic groundwater.

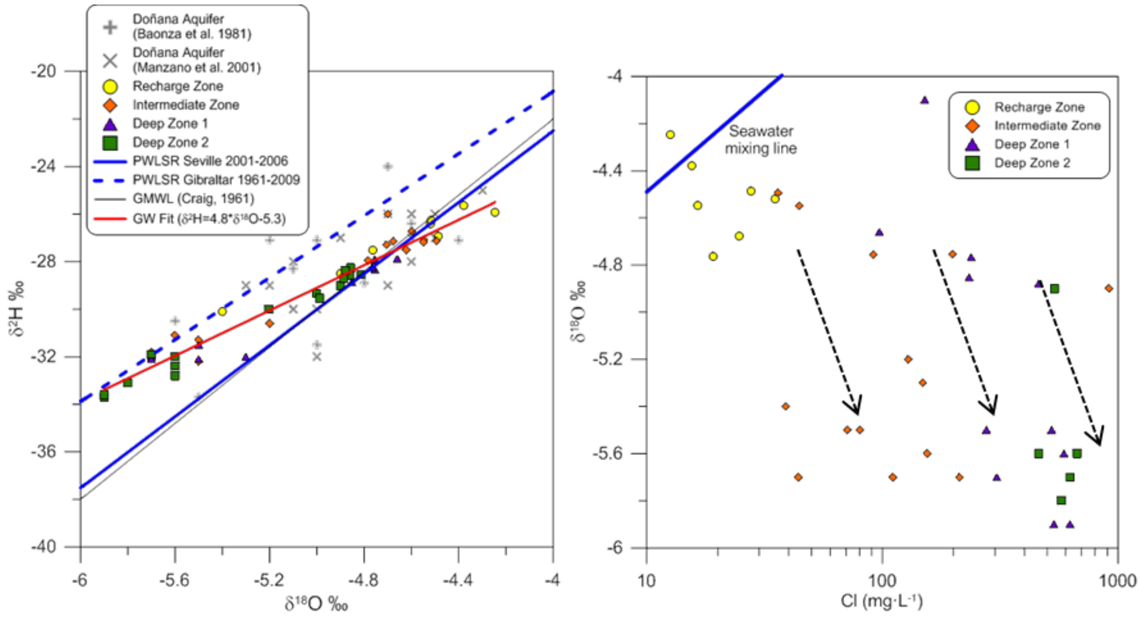

Fig.3. A) $\delta^{18}O$ vs. $\delta\ ^2H$ plot; and B) $\delta^{18}O$ vs. Cl^- plot of groundwater samples . **B)**

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 neighbouring formations (blue marls). The exchange of Ca for Na can be also 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 pore water (Appelo, 1994; Custodio and Bruggeman, 1980).

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The only major solute of anthropogenic origin detected is NO_3 with high concentration reaching up to 98 mg·L^{-1} in localized areas of the recharge. These local high NO_3 concentrations are due to agricultural practices and a sewage leak from the village. Nitrate in the intermediate and deep zones is generally below detection limit except for some values in close proximity to the recharge area (Table A1 of supplementary information).

Sulphate in the recharge zone can be as high a 115 mg/L, but decreases dramatically below detection level (0.1 mg/L) in the intermediate and deep zones. In some wells from these zones, H2S has been measured in concentrations up to 0.11 mg/L, The isotopes of the SO4 molecule clearly confirm the existence of sulphate-reducing conditions. Thus, the samples from the intermediate and deep zones show 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 a methanogenesis zone cannot be ruled out with the present data set.

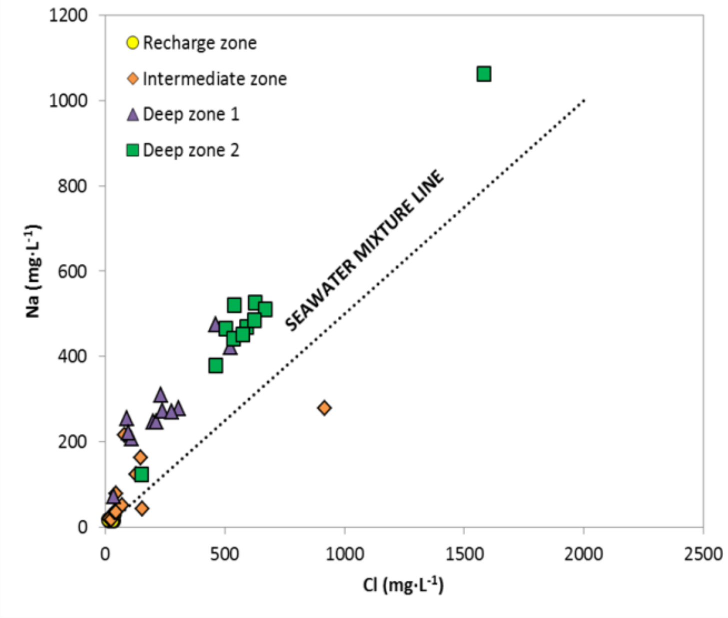

Fig.4. Plot of Na vs. Cl in groundwater (concentration in mg·L^{-1}).

5.2. The origin of As, B abd NH4 Of all analysed minor and trace elements/compounds in groundwater only ammonium, arsenic and boron have anomalously high concentrations and 1 order of magnitude higher than those found in surface water averages (Gaillardet et al., 2004). Thus, in the NP aquifer, ammonium concentrations of up to 12.8 mg·L^{-1} have been found in the Deep Zone 2, with concentrations of 0.18 mg·L^{-1} for arsenic and 3.48 mg·L^{-1} for boron also reaching higher levels in the deep zone 2.

Several sources can explain the high ammonium, arsenic and boron concentrations observed in the groundwater, all interpreted as from a natural origin. The natural origin for the high concentrations is supported by: (1) The recharge zone of the aquifer has low ammonium, arsenic and boron concentrations and high concentrations are 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.1); (3) groundwater residence times >20 ky have been identified in areas containing the higher concentrations (Scheiber et al., 2015).

The arsenic mobilization related to the reductive dissolution of Fe-oxyhydroxids is a well-known natural process observed in reducing aquifers (Berg et al., 2001; 2008; McArthur et al., 2001) . The Fe-oxyhydroxides are characterized by a very high specific surface area and high adsorption capacity capable of adsorbing large amount of arsenic (van der Zee et al., 2003; Wang et al., 2012). Thus, the reductive dissolution of these minerals involves the release of high arsenic concentrations to groundwater. Rather than to mining operations, several observations point to this geogenic origin in the NP aquifer: 1) Goethite gossan deposits are scattered in the surface of Paleozoic series below the NP strata, being the CLC ore deposit the most representative; 2) Goethite contains up to 0.8% As (CLC, unpublished data); 3) Dissolved Organic Carbon concentrations are above the typical values in groundwater (>1 $mg\cdot L^{-1}$) indicating the important role of organic matter in the hydrogeochemical evolution of these wàters 4) Arsenic is mostly As(III), characteristic of reducing environments,; 5) The higher concentrations are found scattered in the studied area, not directly linked to mining (Figure 5); and (6) Historical data obtained before mine activity show As concentrations of up to 0.063 $mg\cdot L^{-1}$ in a survey of local groundwater collected in 1998.

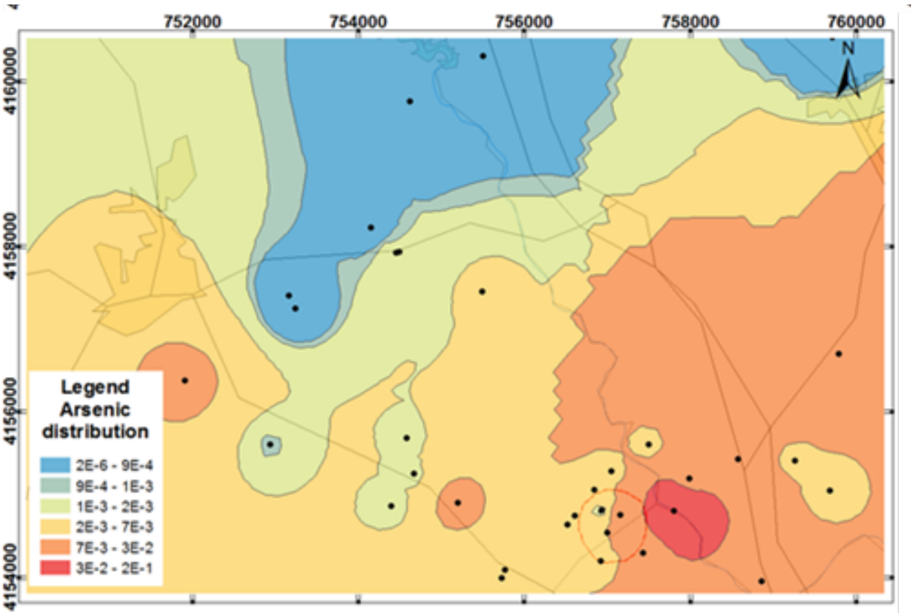

Fig.5. Result of Inverse Distance Weighting (IDW) interpolation of arsenic concentration (mg/L) The red cicle represents the CLC open pit (?)

In many studies where the reductive dissolution of FeOOH explains high arsenic concentration 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 2 of Supporting Information). Rather than to non simultaneous reduction of As and Fe (Islam et al.,2004), or to re-adsorption of As (Nickson et al.,2000), the reason for this lack of correlation is attributed to the massive precipitation of siderite in the NP aquifer. Indeed thermodynamic calculations with the software PHREEQC and the Wateq database (Appelo et al., 2005),indicates that groundwater in the deep zones 1 and 2 are supersaturated and very near to equilibrium in siderite Moreover, the goethite-made gossan is massively replaced by siderite ((Yesares et al. 2014). This siderite masses show very light δ^{13}C values typical of C from organic origin, and has been interpreted as largest documented occurrence of recent microbial activity producing an ore assemblage (Tonos al., 2014).

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The strong correlation B/NH$_4$ (0.91, Table 2 of Supporting Information) suggests a common process controlling their concentration in groundwater. Similarly, the weak correlation observed between As/B and As/NH$_4$ indicates that these processes are at least in part different from those concentrating As. Indeed, NH4 and B show a clear positive correlation with Cl (Figure 6A,B).

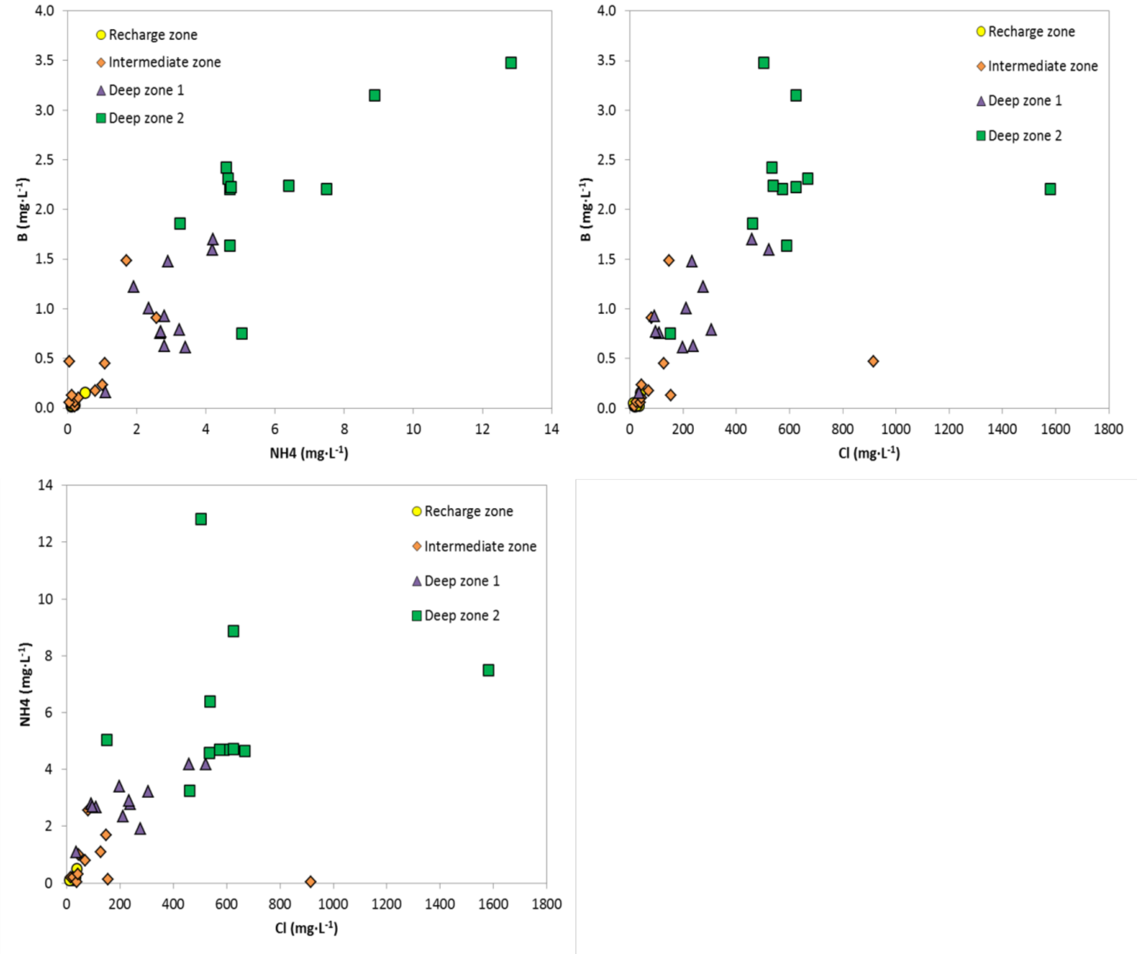

Fig.6. Plots of NH4 (a), B(B) and I (C) versus Cl concentrations

Several samples have boron and iodine concentration higher than seawater (i.e., B around 4.5 mg/L, Rakestraw and Mahncke, 1935, and I 0.6, Truesdall, 1995). Owing to groundwater from shows mixing with seawater less than 10%, there must be enrichment processes for these compounds other than seawater mixing.

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High Boron contents in Bangladesh and Michigan aqüífers have been attributed to a geogènic origin. Thus, seawater B would be sorbed onto mineral surfaces of sediments. Then, the competitive action of HCO_3/CO_3 as fresh continental water displaces saline pore wàter in aqüífers would drive its desorption from mineral surfaces. A positive B/HCO3 correlation is therefore observed (Ravenscroft and McArthur, 2003). No positive correlation between B, HCO_3 and ionic strenght has been observed in the studied area. The described process, however, cannot be ruled out because HCO3 concentration is strongly buffered by the dissolution of calcite and precipitation of siderite in the deep zones of the NP aquifer.

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 proved to be one order of magnitude more efficient than in mineral surfaces, such as clays and Fe-oxides (Goldberg, 1997). Moreover, oil reservoir brines are commonly enriched in B, and therefore, organic matter maturation is seen as a possible source for B in thermal maturation (Williams et al., 2000). The degradation of organic matter by SO4 from recharge water would account for the release of B to the pore water. of the NP aquifer.

A parallel geochemical path would be followed by NH4 and I. Nitrogen is a fundamental nutrient and constituent of multiple organisms, and forms an is an essential component of marine organic matter in a N:C proportion of 16:106 (Redfield, 1934).Iodine may also be highly assimilated by marine organisms and for this reason e organic matter is an important source of iodine (Price and Calvert, 1973; Kennedy and Elderfield, 1987a,b). The strong correlation of iodine with ammonium (R^2=0.86) and boron (R^2=0.83) (Table 2, Supplementary Information) links the organic matter and its degradation to an increase of the three components in NP groundwater concentrations . Iodine concentrations higher than seawater and strong correlation between NH4 and I has been described in the porewater of an aquitard in the coastal aquifer of Pearl River Delta, China (Jiao et al., 2010). These authors attributed the NH4 concentrations, as high as 390 mg/L to a geogenic origin without further precision.

The nitrogen in the sedimentary rock comes of organic matter accumulated during the sedimentation process. This nitrogen is incorporated during diagenesis process as ammonium in clay minerals and organic matter (Holloway and Dahlgren, 2002) and under reducing conditions the organic matter degradation release high ammonium concentration (reaction 2).

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

The $\delta^{15}N$ fractionation has been investigated by many authors and especially by Prokopenko et al., (2006) were focus in the sedimentary organic matter. Experimentally has obtained the $\delta^{15}N$ values of sedimentary organic matter and the pore water. As result, the pore water $\delta^{15}N$ values (<0.7 ‰) are lighter than the sedimentary material (≈5 ‰). This fact leads to the conclusion that there is an isotope fractionation associated with the organic matter degradation (Prokopenko et al., 2006). The fractionation factor can vary depend of depth, reservoir, N content, bacterial activity, organic matter degradation degree, etc. These factors, can explain the high ammonium concentration and the light $\delta^{15}N_{NH4}$ values detected in the deepest samples (Fig.9). The light $\delta^{15}N_{NH4}$ values obtained of the groundwater are compatible with those $\delta^{15}N$ values found in the study area sedimentary rocks. For example, Rau et al., (1987) determined in marlstones in North Atlantic $\delta^{15}N$ values between -2.68 and 2.27, range very similar than the NP aquifer ($\delta^{15}N_{NH4}$ between -3.9 and 0.7 ‰). This similarity suggests that the high ammonium concentration comes of the organic matter degradation presents in the bluish marls “FM Gibraleon”.

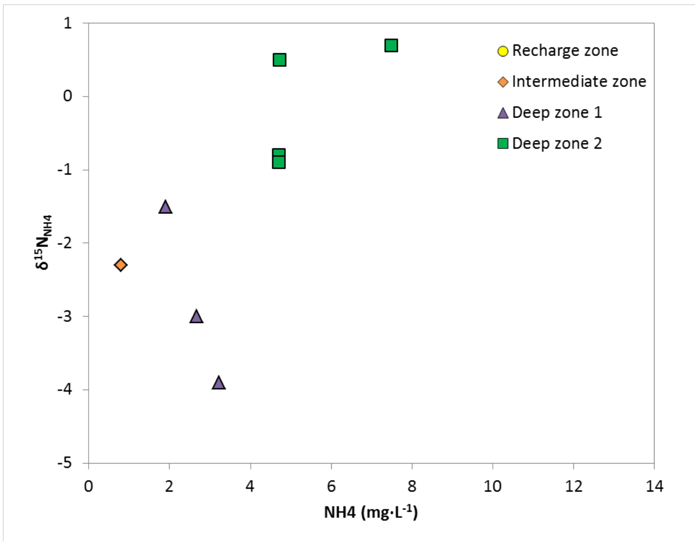

Fig.8. Correlation between $\delta^{15}N_{NH4}$ and NH_4.

5.1. IMPLICATIONS FOR THE MANAGEMENT OF AQUIFER

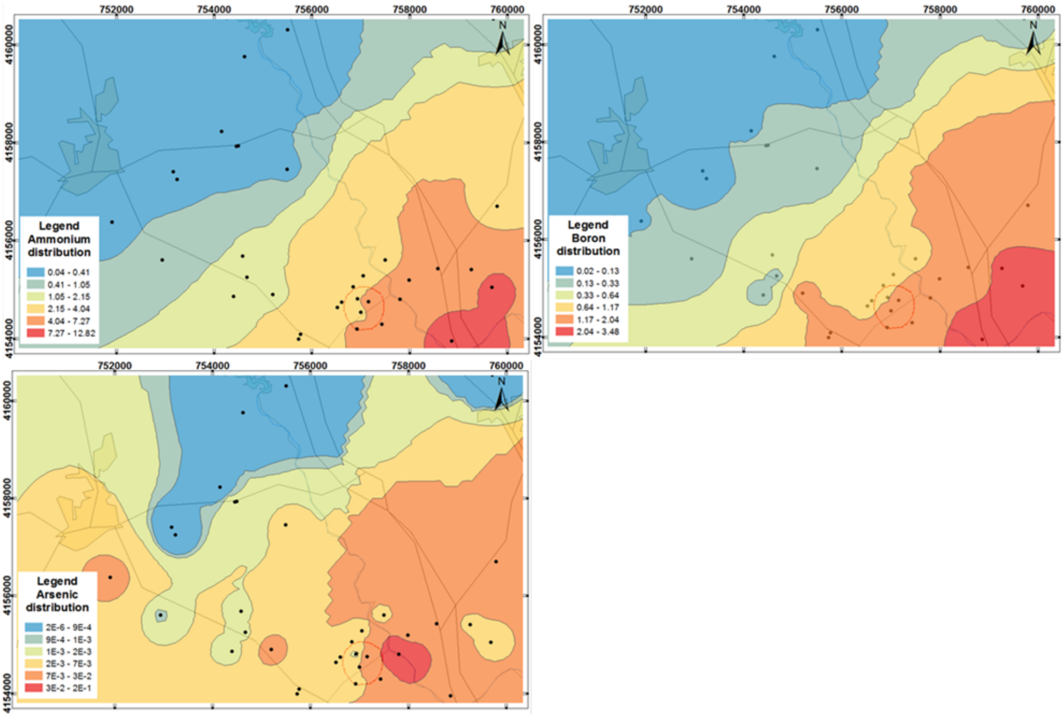

Fig.10. Result of Inverse Distance Weighting (IDW) interpolation of ammonium, arsenic and boron concentration.

Defining groundwater quality for each defined zones is essential for a good management of the NP aquifer. In addition to mining, the main consumption of the groundwater is for agriculture and drinking water of the villages of the surroundings. Moreover, the awuifer also represents a potable water reserve for the city of Sevilla and conurbation in severe drought events. Therefore, the guideline defined by WHO (2008) for drinking water, and the USEPA recommendations for irrigation have been used to assess the water quality of the aquifer. Groundwater of the studied area presents a clear increase in salinity and loss of quality from NW to SE (Fig .9A, B,C). Recharge area: In generally, the groundwater in this area presents acceptable characteristics for drinking water and irrigation, except in very local cases where has been detected high nitrate concentration related with agriculture. Intermediate zone: Drinking water and quality is found in the NW half of this zone. The deeper SE half, however, show NH4 concentrations above the drinking water standards. The salinity (Cl and Na) and B concentrations allow their use for irrigation of many types of crops. Deep zones 1 and 2: Groundwater from this zone contains high concentration of ammonium, arsenic, boron and salinity and for this raison is not suitable for drinking or for irrigation use.

Based on the described quality data three different uses of groundwater can be stablished: driking and irrigation, only irrigation and none (Figure 10)

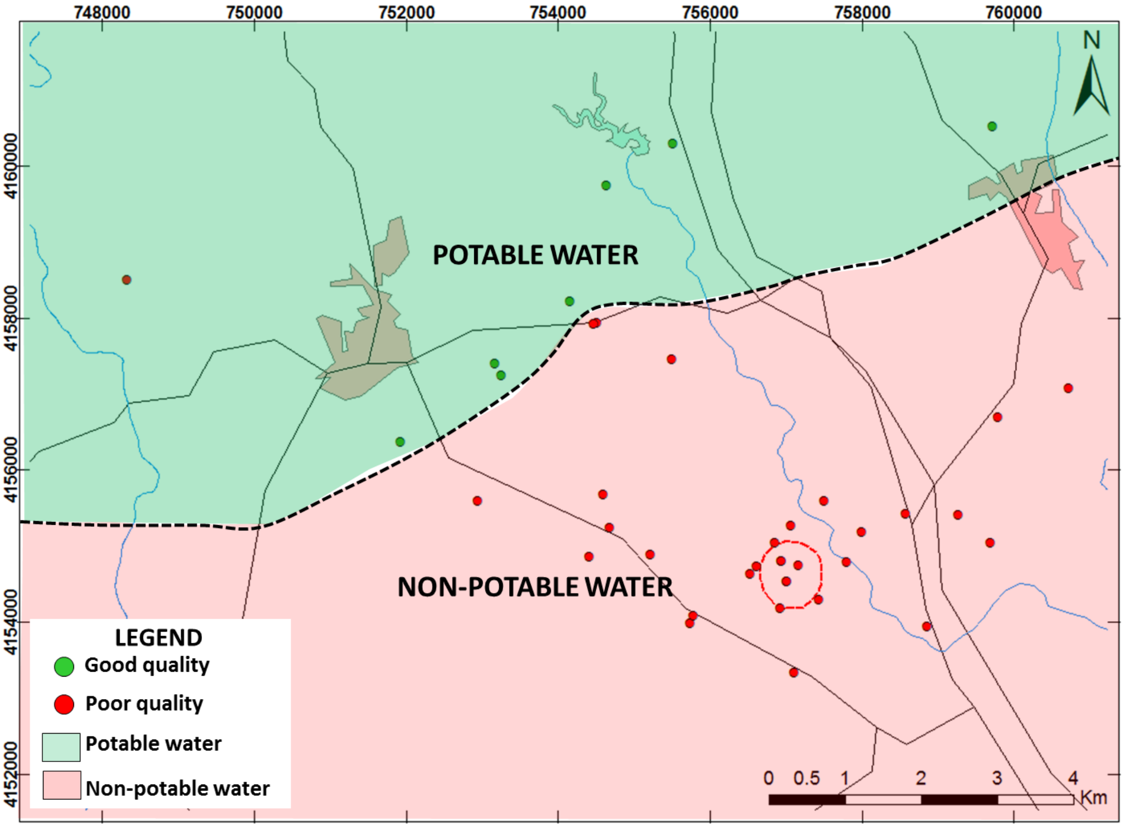

Fig.11. Map of possible uses of groundwater in the studied area. The triangles are the re-injection wells concentration.

What is the impact of the pumping and reinjection system on the hydrochemistry? The CLC open pit is located in the deep zone of the NP aquifer. Therefore, the pumped water contains high salinity and NH4 and B concentrations. When reinjected, this type of water would not affect the quality of the aquifer in the injection sectors 1 to 5, containing water of similar quality. However, the reinjection of the pumped water in reinjection sectors 6 and 7, may dramatically affect the drinking water reserves of the NW half of the intermediate zone, and should be conveniently treated for NH4, B and salinity before being reinjected.

6. CONCLUSION

The high arsenic, ammonium and boron concentration are found in the deeper zone of the NP aquifer. None of these solutes is found in the recharge are, but their concentration increases with depth and residence time of water in the aquifer. Thus, they appear in zones already isolated from surface by a thick sequence of low permeability marls, and with residence times of water in the aquifer longer than 20000 (?) years. Therefore, rather than anthropogenic, their presence in groundwater is attributed to natural processes.

Groundwater flows from NW to SE evolving in chemistry from Ca-HCO3 to Na- HCO3 and finally Na-Cl type. Salinity increases with residence time in the aquifer, by mixing up to 10% of marine water trapped within the porosity, as indicated by the clear marine Br/Cl ratio. Ammonium and boron, together with iodide, clearly increase with chloride from NW to SE, and are interpreted as result of the degradation of marine solid organic matter by the sulfate dissolved in the recharge water. The light $\delta^{15}N_{NH4}$ values confirm its origin linked to marine organic matter.

Arsenic distribution follows a different pattern, not strictly linked to salinity. Arsenic in groundwater is interpreted as originated from the reductive dissolution of the As-bearing goethite by dissolved organic matter. Goethite was formed by the oxidation of sulfides by the Miocene atmosphere and is located evenly on the Paleozoic paleosurface. Arsenic in groundwater depends, therefore, on the location of goethite mineralizations. The lack of the expected correlation between Fe and As is explained by the massive precipitation of siderite. The light $\delta^{13}C$ values of siderite confirms its origins from organic matter degradation.

The NP aquifer contains drinking water quality in the recharge zone and in the shallower zone of the confined aquifer to the NW of the studied zone. The concentration of NH4, B, and the salinity invalidates groundwater for potable and even for continued irrigation. use. The pumping and reinjection system of the CLC mine affects the deep aquifer. The NW sector of the reinjection system should ensure a drinking water quality in order to preserve the drinking water resources of the NP aquifer.

Finally, based on all the information obtained has been able to define two groundwater zones with different quality grades (Potable, non-potable). This conclusion is helpful for improve the management of this resource.

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	SAMPLE	pH	SC (uS/cm)	T (ºC)	DOC	Cl	NO3	SO4	HCO3	Ca	K	Mg	Na	NH4	I	Br-	Fe	Mn	B	As	15N	13C	δ2H (‰)	δ18O (‰)
RECHARGE ZONE	**44**	6.9	957	22.5	0.38	39.4	0.1	72.6	442.4	97.8	1.4	14.7	30.8	0.50	0.01	0.22	0.400	0.002	0.15	0.0001		-11.44	-26.3	
	42	6.9	922	19.8	0.63	15.5	97.2	16.0	381.3	109.0	0.1	3.8	14.8	0.10	0.01	0.14	0.400	0.002	0.03	0.0001		-11.90	-25.6	-4.4
	40	7.1	903	18.6	0.31	19.1	48.1	13.1	268.5	102.7	0.1	2.8	14.6	0.10	0.01	0.09	0.400	0.000	0.02	0.0001			-27.5	-4.8
	43	7.1	999	14.7	0.00	35.0	41.6	19.6	297.5	118.3	0.1	9.9	14.8	0.20	0.01	0.18	0.400	0.001	0.03	0.0001			-26.4	-4.5
	41	6.9	1028	19.6	0.54	27.7	47.1	19.9	427.1	120.2	0.1	4.3	15.8	0.10	0.01	0.14	0.400	0.001	0.03	0.0002			-26.9	-4.5
	27	7.4	607	20.4	0.74	12.6	16.4	17.3	213.6	68.6	1.9	2.3	16.3	0.10	0.01	0.12	0.400	0.001	0.05	0.0002		-10.73	-25.9	-4.2
INTERMEDIATE ZONE	**46**	7.2	629	21.2	0.66	16.4	24.3	19.4	236.4	68.0	2.9	6.0	19.3	0.20	0.01	0.11	0.400	0.002	0.02	0.0000		-10.02	-27.1	-4.5
	32	7.1	916	19.8	0.35	24.7	44.6	30.9	236.4	98.7	4.7	4.0	17.0	0.20	0.01	0.12	0.400	0.003	0.06	0.0005			-27.1	-4.7
	24	7.3	491	21.3	3.32	38.9	0.1	13.2	292.6	58.4	5.2	7.4	33.7	0.04	0.02	0.10	0.006	0.010	0.06	0.0008		-11.20	-30.1	-5.4
	1	8.4	1015	28.1	4.94	80.3	0.1	0.1	548.7	1.6	3.3	0.5	216.0	2.57	0.04	0.10	0.005	0.002	0.91	0.0000			-32.1	-5.5
	11	7.5	578	23.3	4.64	71.1	0.1	18.6	243.8	49.0	3.5	15.0	49.5	0.79	0.02	5.25	0.005	0.014	0.18	0.0009	-2.3	-10.09	-31.3	-5.5
	29	7.4	837	25.1	0.23	44.4	0.1	14.4	308.1	33.7	3.9	12.5	77.6	1.00	0.03	0.23	0.400	0.031	0.23	0.0015		-5.57	-27.2	-4.5
	17	7.7	812	24.3	4.50	128.6	0.1	10.9	317.0	32.0	5.4	8.2	122.7	1.08	0.04	0.38	0.002	0.035	0.45	0.0016		-11.05	-30.6	-5.2
	25	7.0	4200	21.7	4.73	915.6	13.4	75.4	201.5	177.0	4.1	50.6	279.3	0.04	0.03	0.10	0.006	0.003	0.47	0.0017		-10.08	-28.5	-4.9
	10	8.2	388	22.6	4.60	43.9	0.1	0.1	158.5	29.0	2.4	11.9	34.3	0.31	0.03	0.46	0.006	0.013	0.10	0.0025		-10.69	-31.8	-5.7
	19	8.0	989	21.7	4.44	155.0	9.2	38.0	317.0	144.7	5.1	16.5	43.3	0.12	0.01	0.10	0.004	0.012	0.13	0.0097			-31.1	-5.6
	22	10.3	943	23.5	7.56	148.4	0.1	0.1	182.9	0.9	3.4	0.0	163.1	1.70	0.14	0.35	0.005	0.000	1.49	0.0120			-32.0	-5.3
DEEP ZONE 1	**28**	8.7	1846	27	0.66	198.6	0.1	5.8	328.6	2.1	3.9	0.1	247.3	3.40	0.08	0.81	0.400	0.010	0.61	0.0005		-6.16	-27.9	-4.8
	4	8.6	1006	31.7	4.88	110.6	0.1	0.1	475.5	1.7	3.2	0.4	208.2	2.68	0.06	0.10	0.012	0.002	0.76	0.0005	-3	-8.09	-31.9	-5.7
	33	8.9	1441	21.8	0.32	91.4	0.1	10.4	570.9	1.0	3.4	0.1	255.7	2.80	0.04	0.42	0.400	0.003	0.93	0.0006			-27.9	-4.8
	13	8.3	1275	26.6	7.83	212.2	0.1	7.2	390.2	2.2	3.7	0.6	246.8	2.35	0.08	0.56	0.006	0.001	1.01	0.0006		-8.81	-32.1	-5.7
	30	7.4	834	25.6	0.36	36.0	0.1	14.7	308.1	35.9	3.9	12.5	71.3	1.10	0.03	0.20	0.400	0.049	0.16	0.0011		-3.80	-27.1	-4.5
	7	8.4	1491	29.2	4.16	305.8	0.1	0.1	317.0	4.0	4.5	0.9	277.7	3.23	0.10	0.93	0.006	0.006	0.79	0.0015	-3.9		-32.0	-5.7
	35	9.0	1397	27.8	0.79	97.1	0.1	9.0	401.2	1.0	3.3	0.1	221.1	2.70	0.06	0.45	0.888	0.003	0.77	0.0021		-7.57	-27.9	-4.7
	36	8.6	1889	28.2	0.26	238.0	0.1	6.9	305.1	2.6	4.0	0.1	273.1	2.80	0.10	0.86	0.400	0.005	0.63	0.0024		-7.44	-28.3	-4.8
	23	8.4	2360	24.4	7.14	522.6	0.1	0.1	304.8	7.6	7.0	1.7	422.4	4.18	0.20	1.51	0.009	0.036	1.59	0.0025			-31.5	-5.5
	20	8.0	1499	26	4.75	276.4	0.1	5.8	426.7	13.3	4.4	4.1	271.3	1.91	0.19	0.92	0.002	0.016	1.22	0.0060	-1.5	-10.81	-32.2	-5.5
	38	8.4	1973	26.7	0.26	233.1	0.1	0.1	442.4	2.4	4.4	0.1	310.8	2.90	0.15	0.94	0.400	0.005	1.48	0.0079			-28.9	-4.9
	34	8.3	2326	29.3	1.32	459.9	0.1	2.1	457.6	3.0	6.3	0.1	475.9	4.20	0.18	1.76	0.400	0.006	1.70	0.0083			-28.4	-4.9
DEEP ZONE 2	**26**	7.5	987	26.5	15.89	151.4	0.1	0.1	365.8	63.7	3.7	7.1	123.0	5.04	0.13	0.10	0.007	0.159	0.75	0.0011			-21.7	-4.1
	18	10.1	2750	27.5	9.76	625.3	8.4	6.3	548.7	1.0	7.2	0.1	525.2	8.88	0.34	0.40	0.025	0.000	3.15	0.0014			-33.7	-5.9
	3	8.3	2510	31.8	4.50	589.1	0.1	0.1	402.4	5.1	6.5	2.1	469.1	4.70	0.20	1.14	0.023	0.011	1.64	0.0016	-0.8	-9.27	-32.4	-5.6
	16	10.6	2420	25.5	7.83	503.3	0.1	0.1	353.6	0.6	5.6	0.0	464.4	12.82	0.49	0.69	0.035	0.000	3.48	0.0024				
	12	8.0	2390	32.5	2.86	534.6	0.1	0.1	487.7	5.1	5.6	1.9	442.2	4.58	0.19	0.82	0.020	0.005	2.42	0.0025		-7.58	-33.6	-5.9
	9	8.0	2400	32.5	5.58	574.2	0.1	0.1	414.5	5.5	6.1	2.2	451.7	4.70	0.17	0.63	0.036	0.007	2.21	0.0039	-0.9	-8.94	-33.1	-5.8
	21	7.9	2880	31.9	5.50	669.3	10.5	10.1	463.3	14.0	9.2	5.4	510.1	4.64	0.24	1.99		0.005	2.31	0.0050		-10.84	-32.8	-5.6
	2	7.8	2080	28.7	4.75	460.5	0.1	0.1	365.8	5.1	10.1	2.7	378.9	3.25	0.13	1.11	0.137	0.009	1.86	0.0052			-32.0	-5.6
	8	7.7	2670	35.3	5.45	624.6	0.1	0.1	524.3	12.8	8.7	5.1	484.1	4.72	0.26	1.35	0.016	0.012	2.22	0.0121	0.5	-10.71	-31.9	-5.7
	5	7.3	5940	37.5	4.57	1581.3	16.7	12.5	390.2	95.1	15.0	30.1	1061.8	7.49	0.67	4.95	0.005	0.112	2.20	0.0138	0.7		-31.9	-5.7
	37	7.5	2714	36.5	0.49	538.4	0.1	62.5	440.8	19.1	7.7	3.7	519.7	6.40	0.22	2.17	0.400	0.055	2.24	0.1787		-9.79	-29.0	-4.9