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

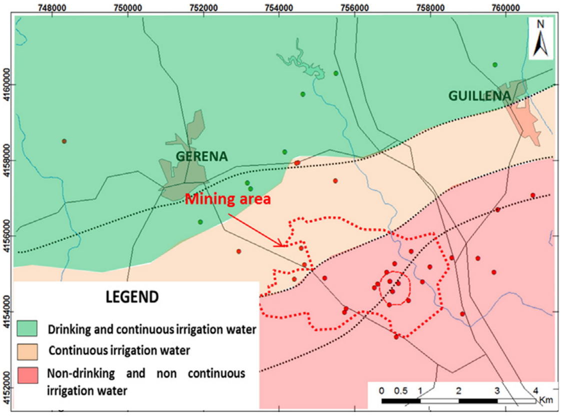
Laura Scheiber [a,*], Carlos Ayora [a], Enric Vázquez-Suñé [a], Dioni I. Cendón [b,c], Albert Soler [d], Juan Carlos Baquero [e]

[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*
[e] *Cobre Las Cruces S.A., Carretera SE-3410 km 4, 41860 Gerena, Sevilla, Spain*

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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* Corresponding author.
E-mail address: scheiber.ls@gmail.com (L. Scheiber).

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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,