



Tracking natural and anthropogenic origins of dissolved arsenic during surface and groundwater interaction in a post-closure mining context: Isotopic constraints



Mahmoud Khaska^{a,b,*}, Corinne Le Gal La Salle^{a,b}, Patrick Verdoux^a, René Boutin^c

^a Univ. Nimes, EA 7352 CHROME, rue du Dr Georges Salan, 30021 Nimes, France

^b Aix-Marseille Université, CNRS-IRD-Collège de France, UM 34 CEREGE, Technopôle de l'Arbois, BP80, 13545 Aix-en-Provence, France

^c LHyGeS Laboratory, UMR 7517, University of Strasbourg, Blessig street 1, Strasbourg cedex 67084, France

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ABSTRACT

Arsenic contamination of stream waters and groundwater is a real issue in Au–As mine environments. At the Salsigne Au–As mine, southern France, arsenic contamination persists after closure and remediation of the site. In this study, natural and anthropogenic arsenic inputs in surface water and groundwater are identified based on ⁸⁷Sr/⁸⁶Sr, and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ isotopic composition of water.

In the wet season, downstream of the remediated zone, the arsenic contents in stream water and alluvial aquifer groundwater are high, with values in the order of 36 $\mu\text{g/L}$ and 40 $\mu\text{g/L}$ respectively, while upstream natural background average concentrations are around 4 $\mu\text{g/L}$. Locally down-gradient of the reclaimed area, arsenic concentrations in stream water showed 2 peaks, one during an important rainy event (101 mm) in the wet season in May, and a longer one over the dry period, reaching 120 and 110 $\mu\text{g/L}$ respectively.

The temporal variations in arsenic content in stream water can be explained i) during the dry season, by release of arsenic stored in the alluvial sediments through increased contribution from base flow and decreased stream flow and ii) during major rainy events, by mobilization of arsenic associated with important surface runoff.

The ⁸⁷Sr/⁸⁶Sr ratios associated with increasing arsenic content in stream waters downstream of the reclaimed area are significantly lower than that of the natural Sr inherited from Variscan formations. These low ⁸⁷Sr/⁸⁶Sr ratios are likely to be associated with the decontaminating water treatment processes, used in the past and still at present, where CaO, produced from marine limestone and therefore showing a low ⁸⁷Sr/⁸⁶Sr ratios, is used to precipitate $\text{Ca}_3(\text{AsO}_4)_2$. The low Sr isotope signatures will then impact on the Sr isotope ratio of (1) the Ca-arsenate stored in tailing dams, (2) effluent currently produced by water treatment process and (3) groundwater draining from the overall site. Furthermore, $\Delta^2\text{H}$ shows that the low ⁸⁷Sr/⁸⁶Sr ratio, arsenic rich water is characterized by an evaporated signature suggesting a potential influence of water impacted by evaporation during storage in decantation lagoons.

This study shows the suitability of Sr and stable isotopes of water as tracers to differentiate natural and anthropogenic sources of arsenic release or other trace elements from mining context where CaO is used for water treatment.

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* Corresponding author at: Univ. Nimes, EA 7352 CHROME, rue du Dr Georges Salan, 30021 Nimes, France. Tel.: +33 466 709 971; fax: +33 466 709 989.
E-mail address: mahmoud.khaska@unimes.fr (M. Khaska).

1. Introduction

The environmental impacts of arsenic mining activities and their effects on ecosystems and human health are observed in stream waters and groundwater several decades after mine closure (Bates et al., 1992; Casiot et al., 2009; Daus et al., 2000; Mukherjee et al., 2008a; Wang and Mulligan, 2006; Williams, 2001; Wong et al., 1999). During mining activities, toxic elements such as arsenic are dispersed mainly by aerial transport of dusts, gas and fumes from the mine and extraction plants to the surrounding environment over distances of about 10 km or more. After mine closure, the waste rock dumps and tailing dams are impacted by mechanical and chemical weathering and generate acid mine drainages (AMD) due to oxidation of sulfur and As-bearing minerals by run-off waters and infiltrated rainwater. AMD commonly have an acidic pH and high contents of dissolved metalloids and anions such as SO_4 and AsO_4 (Sánchez-Rodas et al., 2005; Smedley et al., 1996). Significant amounts of As and metalloids are released by AMD into the environment (run-off and stream waters, groundwater, soils, sediments) and introduced into the food chain (Smedley and Kinniburgh, 2002; Smith et al., 2002; Vicente-Martorell et al., 2009). The As contents of AMD and stream waters impacted by AMD may reach 1 to 10 mg/L or more (Lottermoser, 2003; Smedley and Kinniburgh, 2002).

Adsorption and desorption are two of the major processes controlling arsenic mobility in soils, sediments and aquifers (Dousova et al., 2012; Morin and Calas, 2006; Mukherjee et al., 2008b; Peters, 2008; Polizzotto et al., 2008). Arsenic preferentially adsorbs on iron oxides, carbonates, clays and organic materials (Smedley and Kinniburgh, 2002). The sorption processes are controlled by prevailing physico-chemical parameters mainly the redox conditions, pH, and temperature (Handley et al., 2013; Sharif et al., 2008; Welch and Lico, 1998; Zheng et al., 2004). In addition, increasing ionic strength decreases the amount of adsorbed arsenic as a result of electrostatic interactions (Bauer and Blodau, 2006; Mohan and Pittman, 2007). Reductive dissolution of arsenic bearing oxides (iron, manganese, aluminum), promotes the release of arsenic adsorbed to their surface (Bose and Sharma, 2002; Handley et al., 2013; Nickson et al., 1998; Pedersen et al., 2006). These processes have been proposed as mechanisms for arsenic mobilization in Bangladesh, Vietnam and Cambodia (Smedley and Kinniburgh, 2002). Similarly, acidification of the environment, leading to the dissolution of oxides, induces an increase in arsenic concentrations (Masscheleyn et al., 1991).

The Salsigne mining district (Fig. 1a and b) located in the Orbiel River watershed (Aude, southern France) is typical of a contaminated site after mine decommissioning. The main mining activity at Salsigne began in the nineteenth century for iron, then in 1908, for gold and arsenic. The open pit and mine were closed in 1998 and 2004, respectively. Recurrent proof of arsenic contamination of stream waters, alluvial aquifers and vegetables in the Orbiel Valley, was obtained both before and after mine closure. Consequently, a large campaign of decontamination, confining and rehabilitation was carried out from 2001 to 2006, and focused on mill tailings disposal and processing plants. Nevertheless, since 2006, waters with high arsenic contents (commonly in the range of 1 to 80 mg/L) were discovered in the Orbiel Valley.

In such environments it is essential to differentiate between remnant anthropogenic pollution and the contribution of naturally contaminant rich surface water and groundwater. The aim of this paper is to test a suite of geochemical tracers to assess the origin of high metalloids concentrations in the vicinity of reclaimed mining sites. Common treatment processes used on mining sites are the addition of lime, both in ore and effluents treatment, and storage in decantation basins. Hence we propose to use a combination of tracers including stable isotopes of water and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is chosen as a tracer of groundwater origin, mixing processes, water–rock interaction, and anthropogenic contamination in environments with contrasting imprints, as presented in Faure (1986) and illustrated in recent studies (Aquilina et al., 2002; Cary et al., 2014; Deng et al., 2009; Khaska et al., 2013; Négrel and Petelet-Giraud, 2005; Petelet-Giraud et al., 2003; Pierson-Wickmann et al., 2009; Vengosh et al., 2013).

The stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$) provide information on the recharge processes and the origin of groundwater (Craig, 1961). Deviations from the Global Meteoric Water Line (GMWL) indicate modification of the groundwater by evaporation (Dansgaard, 1964; Faure, 1986). In this paper the As concentrations of surface water and groundwater are assessed first, both upstream and downstream of the ore processing site. Then information derived from the isotope tracers, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and ^{18}O and ^2H is investigated. Supporting observations are provided based on local alluvial sediments analyses (Section 2.1 in Supporting information). Finally, the origin and release processes of As into the stream water are discussed and a conceptual model is derived showing rough estimates of fluxes and highlighting the isotopic tracers approach. This study tracks the transport and fate of arsenic between surface and groundwater based on Sr isotopes.

2. Site overview

The Salsigne Au–As–Fe deposit (Aude, southern France) (Fig. 1a and b) occurs as stock works and lodes several meters wide (4–15 m) in the southern foothills of the Montagne Noire (S1, Supplemental Information). The ore is located in late Variscan NS normal faults that crosscut stacked and southward-recumbent nappes of low grade metasedimentary rocks. These formations are Paleozoic in age and include quartzites, schists, calc-schists and limestones (Berger et al., 1993; Demange et al., 2006). The major ore minerals of the Salsigne mining district comprise pyrite, arsenopyrite, pyrrhotite, chalcopyrite, and bismuthinite and the minor ones galena, sphalerite, scheelite and wolframite (Marcoux and Lescuyer, 1994). In the northern part of the study area, the Orbiel River crosscuts the Variscan metamorphic basement. The Orbiel Valley is therefore deeply embanked from site S1 to S5 (Fig. 1a and b) by metamorphic formations. More to the South, Paleocene and Eocene formations overlay the Paleozoic basement. There, the Orbiel Valley widens and recent alluvial deposits are increasingly abundant from site S5 to site S9 (Fig. 1a and b). The remediated zone is located at the limit of the northern and southern parts of the Orbiel Valley. The site history is complex and lime has been used throughout the ore process, fumes and effluent treatments, and as a result of this usage several lagoons, tailing dams and storage areas existed or still exist on site. The current study does not aim

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