



Contributions of natural arsenic sources to surface waters on a high grade arsenic-geochemical anomaly (French Massif Central)

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ARTICLE INFO

Article history:

Received 22 February 2012

Received in revised form 24 May 2012

Accepted 28 May 2012

Available online 27 June 2012

Keywords:

Dissolved arsenic

Flux

Runoff

Weathering

Soil

Box model

ABSTRACT

The subwatershed studied drains a non-exploited area of the St-Yrieix-la-Perche gold mining district (French Massif Central) and it is located on an arsenic (As) geochemical anomaly. In this context, it is important to know the geochemical processes involved in the transfer of As from solid environmental compartments to the aquatic system. The stream showed a temporal variation of dissolved As (As_d) content from $69.4 \mu\text{g.L}^{-1}$ in the low flow period to $7.5 \mu\text{g.L}^{-1}$ in the high flow period. Upstream, ground- and wetland waters had As_d concentrations up to 215 and $169 \mu\text{g.L}^{-1}$, respectively. The main representative As sources were determined at the subwatershed scale with *in-situ* monitoring of major and trace element contents in different waters and single extraction experiments. The As sources to stream water could be regrouped into two components: (i) one As-rich group (mainly in the low flow period) with groundwater, gallery exploration outlet waters and wetland waters, and (ii) one As-poor group (mainly in the high flow period) with rainwaters and soil solutions. In the soil profile, As_d showed a significant decrease from $52.4 \mu\text{g.L}^{-1}$ in the 0–5 cm superficial soil horizon to $14.4 \mu\text{g.L}^{-1}$ in the 135–165 cm deep soil horizon. This decrease may be related to pedogenic processes and suggests an evolution of As-bearing phase stability through the soil profile. Quantification of As_d fluxes at the subwatershed scale showed that groundwater was the major input (>80%) of As_d to surface water. Moreover, natural weathering of the As-rich solid phases showed an impact on the As release, mainly from superficial soil horizons with runoff contributing about 5% to As input in surface water.

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1. Introduction

Mining districts, known for their environmental impacts (Fergusson, 1990; Nriagu, 1994; Smedley and Kinniburgh, 2002), encompass geochemical anomalies, exploration and exploitation galleries and mine wastes (Cidu et al., 2001; Passariello et al., 2002; Courtin-Nomade et al., 2005). These different sources lead to widespread contamination in addition to runoff and metal-rich soil weathering (O'Neill, 1995; Sadiq, 1997; Bauer and Blodau, 2006). Specifically for gold-mining activities (Fergusson, 1990; Nriagu, 1994; Smedley and Kinniburgh, 2002), weathering of As-bearing phases in geochemical anomalies can be considered as a diffuse source of pollution into ground- and surface waters. Arsenic is initially present in sulfide deposits and As transfer to the aqueous reservoir may be influenced by the formation of secondary phases (sulfates, Fe-, Mn- and Al-oxyhydroxides) which do not trap all mobilized As from primary phase alteration and by the sorption on

oxyhydroxides and clay minerals (Cullen and Reimer, 1989; Sadiq, 1997; Lin and Puls, 2000; Goldberg, 2002; Morin and Calas, 2006; Cancès et al., 2008; Courtin-Nomade et al., 2010). All these phases are permanent or temporary sinks of As depending on their stability and their As-retention capacity (Craw et al., 2003; Paktunc et al., 2003).

Environmental conditions (redox, ionic strength and pH) and microbial activities (Masscheleyn et al., 1991; Bissen and Frimmel, 2003) influence the mobility and bioavailability of As when partial or complete solid phase dissolution or desorption is induced (Cullen and Reimer, 1989; Matera and Le Hécho, 2001; Wang and Mulligan, 2006a). Arsenic release can cause problems in drinking water supplies (Chen et al., 1995; Duxbury et al., 2003; Harvey et al., 2005; Hopenhayn, 2006). It also induces ecosystem modifications, depending on As concentrations, speciation and toxicity towards living organisms (Léonard, 1991; Eisler, 1994; Das et al., 2004; Casiot et al., 2009). In natural aqueous systems, As exists essentially in 4 oxidation states (−3, 0, +3, +5) (Smedley and Kinniburgh, 2002), but As(III) and As(V) are the most common forms encountered in the surface environment (Cullen and Reimer, 1989; Smedley and Kinniburgh, 2002). However, As(V) is usually less mobile and less toxic than As(III) in oxic environments (Ferguson and Gavis, 1972; Boyle and Jonasson, 1973; Yamauchi and Fowler, 1994).

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The study was carried out in the Saint-Yrieix-la-Perche gold mining district (Garonne basin, SW France; Fig. 1) where As sources in waters, soils and sediments are related to (i) a high grade As geochemical background, (ii) leaching of mining wastes, and (iii) As remobilization due to mining activities which increased surface contact between bedrock and groundwater. A subwatershed, located on a non-exploited area in this mining district, was chosen in order to understand As transfer from the weathering of natural geochemical anomalies and to compare with impacts of mining activities. This site has high total As concentrations in subsurface soil horizons (up to 1500 mg.kg^{-1} ; Bossy et al., 2010) which decrease in surface soil horizons. This decrease was related to As-bearing mineral phase evolution from arsenates (mostly Ba-rich pharmacosiderite) in bedrock and in the deepest soil horizon into less As-concentrated Fe-oxyhydroxides (*i.e.* ferrihydrite, goethite and hematite). In this context, As leaching from soil can be considered as a significant source of water contamination and the transfer mechanisms from solid phases to waters required more investigation. Therefore, the objectives of this study were to identify and quantify the potential As sources in the subwatershed during one hydrological cycle, focusing on As fate in the dissolved fraction ($<0.2 \mu\text{m}$ filtration). Several approaches were used to quantify As concentration in different types of waters and to assess As transfer at a subwatershed scale: (i) high-frequency sampling of rain-, stream, wetland, ground- and gallery exploration outlet waters, runoff and soil solutions to establish spatio-temporal variations of As inputs to surface waters, (ii) seasonal variations of As and Fe speciation in all the studied water compartments (except runoff and soil solutions) in order to identify processes controlling As mobility under different redox conditions and (iii) single chemical extractions of soil horizon samples to characterize As release during As-bearing phase weathering.

2. General description of the study site

The studied area is located in the Upper Isle basin, draining the Saint-Yrieix-la-Perche gold mining district (Fig. 1). Previous studies performed in this district showed large As transfer from mining waste

weathering (Roussel et al., 2000; Courtin-Nomade et al., 2003, 2005) and its impact on bed-sediment and suspended matter mineralogy (Grosbois et al., 2007, 2011). Indeed, spatial distribution of As bulk concentration in sediment showed 3 significant increases corresponding to the 3 drained mineralized veins and associated mine sites. Identified As-bearing phases in the solid fraction were primary sulfides (arsenopyrite and As-rich pyrite only in bed-sediment), (Fe, Mn)-oxyhydroxides and clay aggregates (Grosbois et al., 2007, 2011). These studies in the Isle basin showed that this area caused environmental problems due to elevated As concentrations in surface waters (average annual discharge-weighted As concentration = $14 \mu\text{g.L}^{-1}$; Grosbois et al., 2009) and its large transport as particulate forms (As annual flux in suspended matter was $2.6 \text{ kg.km}^{-2}.\text{yr}^{-1}$; Grosbois et al., 2009). Regarding As transfer and sources, monitoring of surface waters showed 3 main mechanisms controlling dissolved As concentrations: (i) As rich-soil, bedrock and sediment runoff *via* atmospheric inputs, (ii) mineralized vein alteration, whether exploited or not, *via* groundwater inputs and mining waste weathering, and (iii) As trapping by Fe (III)-oxyhydroxide formation in the aquifer (Grosbois et al., 2009).

In order to better identify and quantify all As inputs and outputs at a basin scale, a small subwatershed of 1.5 km^2 was chosen to allow intensive sampling of all possible sources. This subwatershed is located on an As geochemical anomaly without any mining activity. Consequently, in this study, the possible As contamination to ground- and surface waters mainly had a natural origin (only exploration galleries were excavated).

3. Sampling and analytical methodology

3.1. Water collection and analyses

Sampling campaigns of different waters (surface, rain, ground-, gallery exploration outlet, wetland waters, soil solutions and runoff waters) were performed during the 2007 and 2008 hydrological years. Their locations in the subwatershed are shown in Fig. 1 and their sampling methods are summarized in Table 1. All water sample

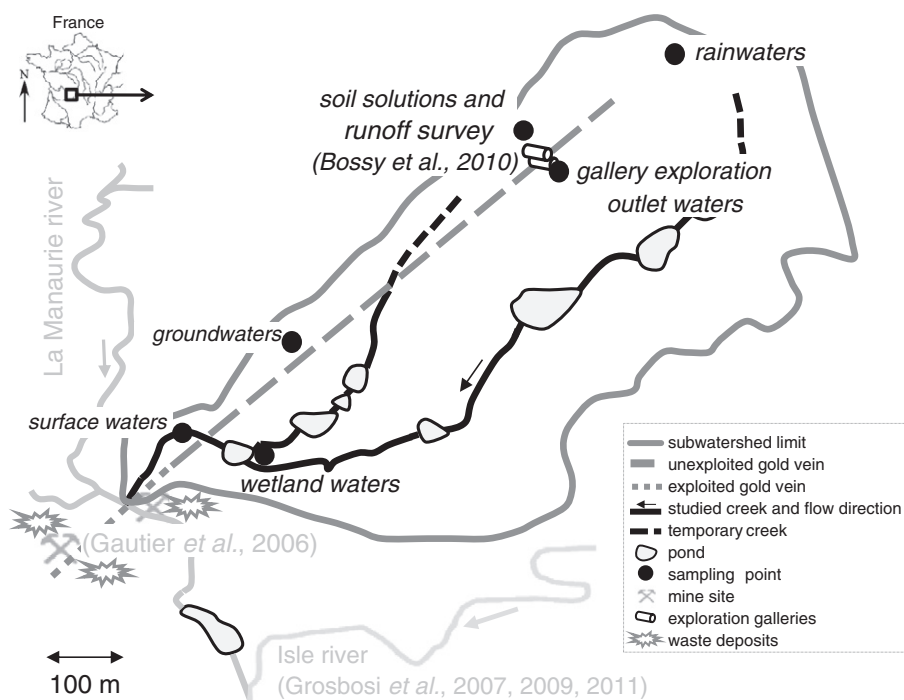


Fig. 1. Location of the studied subwatershed with sampling points in the Saint-Yrieix-la-Perche Au mining district located in the Upper Isle basin. Bossy et al. (2010) studied soil profile with As-bearing phase characterization; Gautier et al. (2006) studied ferrihydrite formation.

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