



Experimental simulation of arsenic desorption from Quaternary aquifer sediments following sea water intrusion

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ABSTRACT

Alluvial sediments from the coastal area in southern Tuscany (Italy) characterized by a significant As anomaly (As > 500 mg/kg) are subjected to seawater intrusion due to groundwater exploitation. Sequential extractions and kinetic experiments were carried out on Quaternary alluvial sediments to quantify the interaction between As oxianions (adsorbed on mineral surfaces) and Cl⁻ in solutions and to establish if this mechanism may contribute to the release of As in groundwater.

The natural water-rock interaction in the aquifer was simulated in two experiments by saturating the samples with four solutions with increasing chlorinity for different time.

Firstly, a rapid change in the aquifer salinity (e.g. fast seawater intrusion, groundwater over pumping) was simulated by an interaction sediment/solution of 24 h. Solutions with Cl⁻ ≤ 2000 mg/L extracted up to 76 µg/kg of As, while seawater (Sol 4₍₂₄₎: Cl⁻ ~ 18,500 mg/L) extracted up to 161 µg/kg of As.

In a second experiment, the ingression of water with increasing salinity in the aquifer, followed by the withdrawal of the water after progressively longer interaction times with the aquifer sediments, was simulated. The timing of the As-Cl reaction was constrained by saturating the samples with four solutions with increasing salinity (Sol1₍₈₄₎: Cl⁻ ~ 0 mg/L; Sol2₍₈₄₎: Cl⁻ = 250 mg/L; Sol3₍₈₄₎: Cl⁻ = 2000 mg/L; Sol4₍₈₄₎: Cl⁻ = 15,886 mg/L) that interacted with the sediment samples for longer saturation times (up to 21 days for each solution). After saturation with the previous three solutions up to 62 µg/kg of As were extracted by seawater, following a salinity increase from 2000 mg/L Cl to a chlorinity close to seawater, representing ~60% of the exchangeable As fraction in the sediments.

Our results constrained the timing of sediment/solution interaction of As desorption and showed that after a rapid intrusion of seawater or after a relatively long period of interaction with saline solutions an aquifer with similar geology releases in groundwater concentrations of As exceeding the 10 µg/L limit for drinking water. Also, this study estimated the potential effects caused by the ingression of seawater in lowland alluvial coastal areas induced by groundwaters exploitation or by extreme weather events. Such information is crucial for management authorities to mitigate and predict the effects of As hazard in groundwater driven by changes in the environmental aquifer conditions (e.g. seasonal fluctuations of the water table and/or changes in salinity of coastal aquifers), which are becoming increasingly frequent as consequence of climate change.

1. Introduction

Arsenic (As) is present in soils and groundwaters due to both natural sources and anthropogenic activities (e.g. Nicolli et al., 1989; Manning and Goldberg, 1997; Williams et al., 1998; Smedley and Kinniburgh, 2002; Scheiber et al., 2016). As described by Dixit and Hering (2003) several mechanisms (singly or in combination) explain As mobility

under different conditions which encompass inorganic and organic reactions (O'Neill, 1995; Pongratz, 1998; Smedley and Kinniburgh, 2002). In several parts of the world the presence of geogenic As anomaly in the soil is causing extensive As contamination of groundwaters used by millions of people as source of drinking water, resulting in persistent negative health effects on the local inhabitants (Yu et al., 2003; Argos et al., 2010; Joseph et al., 2015; Bhowmick et al., 2018). Concentrations

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of As higher than 50 µg/L have been found in groundwaters around the world including Bangladesh, India, Nepal, Thailand, China, Taiwan, Vietnam, Chile, Argentina, Hungary and parts of the USA (e.g. Smedley and Kinniburgh, 2002; McArthur et al., 2004; Hossain, 2006; Bhattacharya et al., 2007; Lu et al., 2010; Bhowmick et al., 2018).

The alluvial and deltaic aquifers of Bangladesh and West Bengal represent the most serious contaminated area identified globally with million people drinking water with arsenic concentrations above 10 µg/L and up to 50 µg/L (Das et al., 2009), causing about 20% of the death in the area (Argos et al., 2010). In general, these anomalous As-rich groundwaters are found in aquifers hosted by coastal Holocene/Quaternary alluvial and deltaic environments (Kippler et al., 2016). Alluvial and deltaic plains typically have a low elevation with respect to sea level and are extremely vulnerable to a number of natural hazards such as cyclones, tidal surges, salinity intrusion, riverbank erosion, and shoreline recession frequently as a consequence of climate changes such as in the case of Bangladesh (Baten et al., 2015). All these phenomena may cause an increase in salinity in aquifers in addition to groundwater over pumping. Arsenic is considered to be efficiently adsorbed onto iron oxide in many alluvial and deltaic environments. However, the sorption behavior of As is, in principle, also dependent by the competition with other anions such as those usually present in seawater. In particular, the role of chloride ion as a competitor for As adsorption onto Fe-oxyhydroxides is highly debated. For example, Zhang et al. (2004) stated that chloride may slightly enhance the As adsorption onto a mineral mixture where hematite was predominant. On the contrary, Keon et al. (2001), in a sequential extraction experiment in soils, proved that MgCl₂ brings into solution the exchangeable As fraction, allowing ionic exchange between Cl⁻ and oxyanions of As (AsO₄³⁻ and AsO₃⁻). Goh and Lim (2005) have quantitatively estimated the As extracted in artificially contaminated soils by solutions made by different salts (NaCl, Na₂SO₄, Na₂CO₃, Na₃PO₄) concluding that NaCl releases into solution the highest concentration of As in the first 30 min of reaction, independently on the salt concentration. Liu et al. (2003) have correlated the high As concentrations occurring in the groundwater of the coastal areas of Taiwan to the interaction of sediment/sea water favouring ionic exchange between Cl⁻ and As. Pansar-Kallio and Manninen (1997) stated that variations in the ionic strength and ionic exchange might induce an As mobilization.

Few studies have been published to estimate the extent of As mobilization under anion-rich or saline conditions (e.g. Wasay et al., 2000; Jackson and Miller, 2000; Alam et al., 2001; Keon et al., 2001; Cai et al., 2002; Goh and Lim, 2005; Raposo et al., 2006; Sun et al., 2015). To date there are not specific experiments that quantify the ionic exchange between As-oxyanions and Cl⁻ and the kinetic of this reaction in the natural aquifer environment, although this aspect is of relevance in groundwaters hosted by alluvial and deltaic plains that suffer a limited amount of flushing by freshwaters (cf. Smedley and Kinniburgh, 2002).

In this work a set of experiments was designed to simulate the natural interaction between groundwater and seawater in an aquifer, by saturating aquifer sediments rich in As with solutions at increasing chlorinity for different interval of time. The aims of this study were 1) to quantify the interaction between As oxyanions (adsorbed on mineral surfaces) and Cl⁻ in solutions, 2) to establish if this mechanism may contribute to the release of As in groundwater, and 3) to estimate the effects caused by the ingress of saline solutions in aquifers characterized by geogenic As anomaly.

The experiments were carried out on three alluvial samples from the Pecora River Valley Quaternary deposit in Southern Tuscany (Italy). This Quaternary sequence (Benvenuti et al., 2009) is characterized by a significant geogenic As anomaly (As > 1000 mg/kg; Protano et al., 1998; Costagliola et al., 2004, 2010) with an extension of about 25 km² reaching a depth of 90 m close to the coast (Rossato et al., 2011). In water wells of this Quaternary sequence, As contents may exceed the accepted drinking water standards (Rossato et al., 2011) and a

correlation between salinity and As concentration in rock wells has not yet been demonstrated. The Quaternary deposits of the Pecora River are thus a key area where to test the effects of seawater intrusion on As mobility and its release to groundwater, being coastal aquifers hosted by recent sediments one of the main cause of drinking water contamination in the world (Smedley and Kinniburgh, 2002).

2. Study area

2.1. Geological background and sampling area

The geology of the Pecora River Valley is described in detail in Benvenuti et al. (2009) and Costagliola et al. (2008). A concise description is outlined hereafter. The geology of Tuscany is related to the Northern Apennines tectonic chain formation (Bonini and Sani, 2002). During the late Miocene and Plio-Pleistocene post-collisional phases, regional metamorphism and the emplacement of magmatic bodies (Innocenti et al., 1992; Serri et al., 2001) triggered the formation of a suite of hydrothermal ore deposits (Lattanzi et al., 1994). In Southern Tuscany, those deposits are often found in veins along the late Apenninic tectonic structures, which reach the upper crustal levels of this district, making this region one of the largest mining district of Italy, exploited since Etruscan times (c. 700 BC; Chiarantini et al., 2009; Costagliola et al., 2010). During the post-orogenic structural evolution (Late Tortonian-Upper Messinian) several continental and shallow marine basins developed and were filled with clastic sediments (Martini and Sagri, 1993) and later superimposed by Quaternary alluvial/colluvial deposits. The Pecora River Valley is an example of those Neogene/Quaternary basins (Costagliola et al., 2008; Benvenuti et al., 2009).

The Neogene/Quaternary sequence of the Pecora River Valley was selected for this experiment because it is close to the Tyrrhenian Sea and it is characterized by a large As anomaly (Fig. 1b) and flushed by a groundwater flowing from inland to the sea under a gentle westward hydraulic gradient. Concentrations of As in the sedimentary sequence are up to 1000 mg/kg (Benvenuti et al., 2009; Costagliola et al., 2008, 2010), well above the regional background value of 7 mg/kg (Protano et al., 1998) and above the range of 4–39 mg/kg found in the local pre-Neogene bedrock and in the upper Messinian fluvial gravels (Benvenuti et al., 2009; Costagliola et al., 2010). The origin of this anomaly is mainly geogenic. Following Costagliola et al. (2010), the Neogene/Quaternary sequence of the Pecora River Valley is the results of the erosion, and subsequent re-deposition, of As-bearing minerals (mainly arsenian-pyrite) hosted in veins emplaced along the late Apenninic tectonic structures that cropped out in the paleo-catchment of the river. This Quaternary alluvial/colluvial deposits, bordering the sea coast in Southern Tuscany, host aquifers that are known to be exposed to episodic sea water intrusion caused by groundwater overexploitation (Grassi and Netti, 2000). Samples were collected at La Forra, north west of the village of Valpiana from the unit identified as “P2all”, part of the Palaeo Pecora 2 synthem (P2) (Middle Pleistocene?–Holocene, Benvenuti et al., 2009) (Fig. 1).

3. Methods

Three samples, labelled L01, L02 and L03, were selected as the most representative of the local aquifer lithology based on previous studies (Costagliola et al., 2010). After air-drying, each sample was sieved using a 2 mm brass sieve and quartered. The passing fraction was divided in two parts using a riffle splitter. One part was used for the desorption experiments, while the other half was ground with an agate mortar and used for XRD, XRF, total digestion and sequential extraction analyses.

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