Research article

Mobility and chemical fate of arsenic and antimony in water and sediments of Sarouq River catchment, Takab geothermal field, northwest Iran

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ABSTRACT

Arsenic (As) and antimony (Sb) concentrations in water and sediments were determined along flow paths in the Sarouq River, Zarshuran and Agh Darreh streams. The results indicate high As and Sb concentrations in water and sediment samples. Raman spectroscopy shows hematite (α-Fe_2O_3), goethite [α-FeO(OH)] and lepidocrocite [γ-FeO(OH)] in sediment samples. Calculated saturation indices (SI) indicate oversaturation with respect to amorphous $Fe(OH)_3$ for all samples, but undersaturation with respect to Al and Mn mineral and amorphous phases. Therefore, ferric oxides and hydroxides are assumed to be principal mineral phases for arsenic and antimony attenuation by adsorption/co-precipitation processes. The considerable difference between As and Sb concentration in sediment is due to strong adsorption of As(V) into the solid phase. Also, lower affinity of Sb(V) for mineral surfaces suggests a greater potential for aqueous transport. The adsorption of arsenic and antimony was examined using the Freundlich adsorption isotherm to determine their distribution model in water-sediment system and its compatibility with the existing theoretical model. The results showed that the adsorption behavior of both elements complies with the Freundlich adsorption isotherm.

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1. Introduction

Geogenic and anthropogenic arsenic (As) and antimony (Sb) occur widely throughout the environment. In general, the natural abundance of As and Sb in the Earth's upper continental crust is low (4.8 mg/kg and 0.4 mg/kg, respectively) (Rudnick and Gao, 2014). Baseline concentrations of As and Sb in river water are also low, although, elevated concentrations can be found near geothermal fields, mine districts and in areas contaminated by human activities (Wilson et al., 2012; Serafimovska et al., 2013; Ordonez et al., 2014; Bundschuh and Maity, 2015).

Arsenic and antimony can exist in a variety of oxidation states (-III, 0,III,V), however, they mainly occur in two oxidation states as As(III), Sb(III) and As(V), Sb(V) in environmental, biological and geochemical samples (Hem, 1992; Filella et al., 2002a, b; Smedley and Kinniburgh, 2002). Concern arises from As and Sb toxicity and their suspected human carcinogenic properties. Thus, arsenic, antimony and their compounds are considered to be priority pollutants by the US EPA and the EU (Filella et al., 2002).

The fate of arsenic and antimony in natural water is influenced by a variety of processes including secondary mineral precipitation, aqueous complexation, and sorption onto particles and colloids within the water column or streambed sediments. The concentration of As and Sb is mainly controlled by their sorption or co-precipitation to particulates and colloids of secondary phases such as amorphous ferric-hydroxide or ferrihydrite, $Fe(OH)_3$, or other high surface area materials.

The colloidal and fine-grained sorbents can be transported long distances before settling to the sediment, serving as a significant transport vector for As and Sb from the source regions (Plumlee et al., 1999; Smith, 1999). On the other hand, with changing the oxidation-reduction condition the metal(loid) remobilization from sediment to the overlying water may occur, which could increase the significance of the pollutant threat. Therefore, a key factor in considering the impact of these toxic elements on water quality is the extent to which the metal(loid) partition between solution and solid phases. The most widely used analytical isotherm for modeling adsorption of elements on sorbents is the Freundlich isotherm (Borgnino et al., 2012; Gautham et al., 2012; Xi et al.,

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2013). Generally, experimental data is fitted to the Freundlich adsorption isotherm models, and the best-fitted model is used to characterize equilibrium adsorption. As the appropriate adsorption model was selected, the adsorption parameters of the model were obtained and used to describe the adsorption characteristics. Freundlich-type adsorption is considered to be a multi-layer process in which the amount of adsorbed solute per unit adsorbent mass increases gradually.

The present study is an attempt to use the Freundlich parameters obtained with given values in the field to predict and compare the adsorption/desorption behavior of arsenic and antimony in river bed sediment. The obtained results may contribute to understanding the mobility and bioavailability of arsenic and antimony in contaminated river and surface water resources. Determination of As and Sb concentrations and their distribution between the solid and solution phases is part of the water-sediment system. The described models of the elements distribution in the water-sediment system provide an opportunity for understanding and predicting the risk assessment.

2. Study area

Takab geothermal field hosting the Agh Darreh and Zarshuran gold deposits is located in the northwest of Iran within the Urumieh—Dokhtar volcanic belt (Fig. 1). Epithermal systems and recent geothermal activity in the region have a close spatial and temporal relationship with Late Cenozoic to Quaternary, shallow-level magmatic activity. Arsenic-antimony-gold is the main type of ore occurrence in the Takab area with a mining history that goes back hundreds of years. The Agh Darreh deposit occurs in hydrothermally leached Miocene reefal limestone in the Takab geothermal field. The Agh Darreh deposit with 5.2 million tonnes of ore

(average grade of 4.68 g/t Au) (Klatt, 2000), is currently active and mine spoil with high metal and metalloids (As, Sb and Hg) content is dumped on the surface. At present, more than 850,000 tonnes of mine spoil containing As and Sb-bearing sulphide minerals is piled up. Gold mineralization at the Zarshuran (2.5 million tonnes grading 10 g/t Au) (Asadi et al., 1999), is hosted by Precambrian carbonate and black shale into which a weakly mineralized granitoid has intruded. The long history of mining in Zarshuran has also produced a large volume of waste dumped on the surface and exposed to weathering. The Zarshuran and Agh Darreh streams are two main tributaries of the Sarouq River catchment (Fig. 1). More than 80% of the run-off from the two mines discharges into the Sarouq River via the Agh Darreh and Zarshuran streams (Fig. 1). In addition, some metal(loid) contamination in the area is related to thermal and cold springs that are remnants of Quaternary volcanism, originated from circulation of meteoric water into the underlying layers and rises up towards the surface (Sharifi et al., 2016). Thus, the Sarouq River is expected to be highly contaminated by the wastewater from the mining sites and springs. Discharge rate of the springs varies from less than 1 L/s to a maximum of 100 L/s. The large number of springs and their low discharge value could be considered an indication of the effect of the faults on the groundwater circulation. The catchment area of the Sarouq River is mountainous and the general flow direction follows the topographic slope. The rock units in the Sarouq River bed are mostly impermeable marly formations (Sharifi et al., 2016). Minimum and maximum elevation in the study area is about 1785 and 2955, respectively, with an average of 2650 m above mean sea level. The mean annual precipitation in the Takab area is 300 mm. At high altitude, snow predominates and contributes to the recharge processes late in the spring. The average annual flow of the Sarouq has been reported to be 225 m^3 by the West Azerbaijan Regional Water
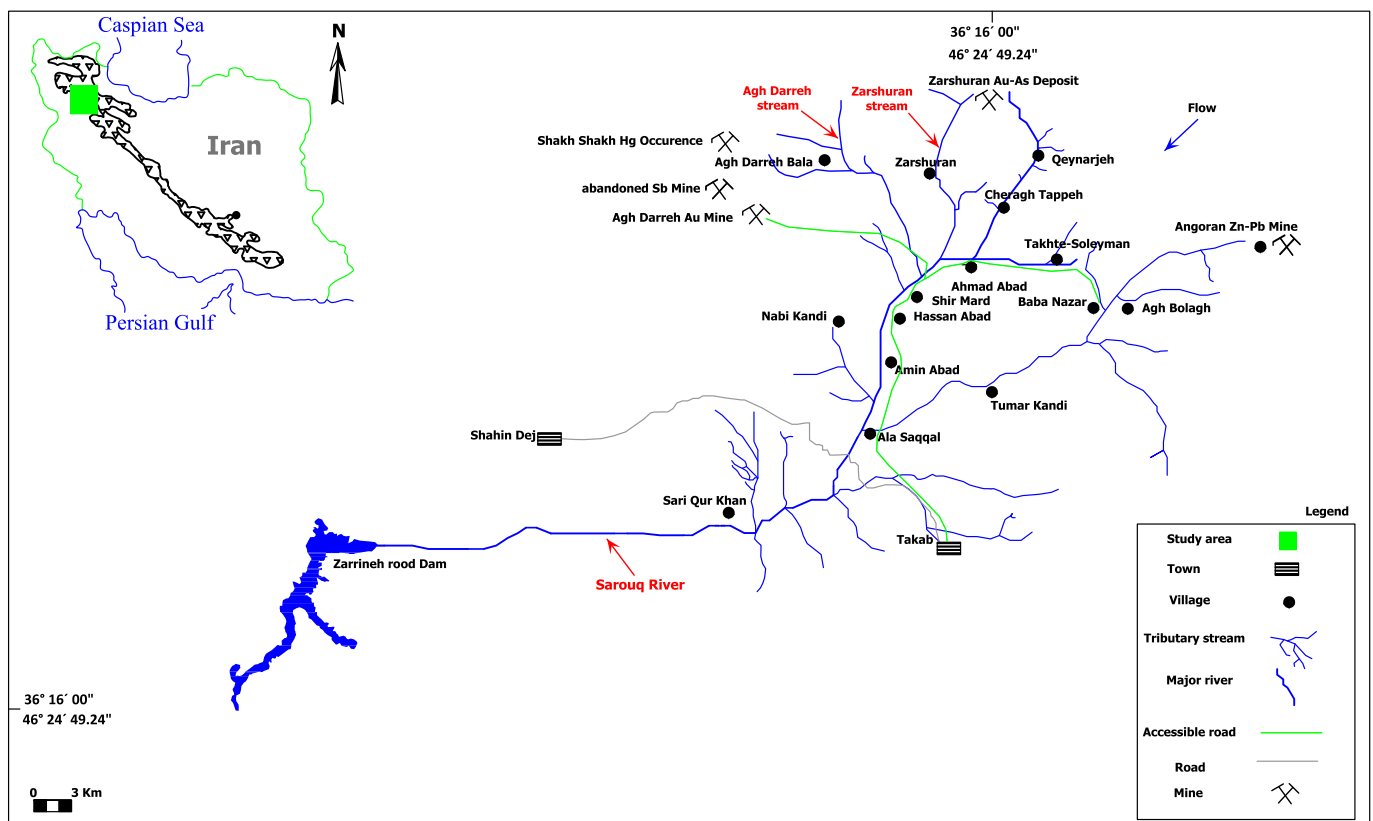

Fig. 1. Map showing the Sarouq River catchment.