

Speciation Dynamics of Arsenic in Tailing Heap Leachates at an Abandoned Uranium-mining Site

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Abstract

The fate and effect of arsenic in mine water is influenced by its interaction with other ions, the physicochemical conditions of the water and biological process involving macrophytes and micro-organisms, which determine the actual speciation of arsenic. In view of this, we investigated the migration and speciation of inorganic arsenic in mine water discharged from a spring of leachates from a uranium-tailing heap to a wetland pond in Zobes-Mechelgrün in south-west Saxony in Germany. The field studies were complimented with laboratory investigation of the role of co-existing cations, also the impact of micro-organisms in the speciation dynamics of arsenic in surface mine water has been considered. Therefore, this article reports the findings, which highlight the interchanging of speciation status of inorganic arsenic in the aquatic system. Further, it reveals that availability of oxygen alone is not enough for oxidation of As III to As V.

Key words: Arsenic speciation, arsenic resistant bacteria, Iron, phosphates, uranium-tailing heap, mine water

Introduction

Most uranium mining wastes contain a number of other toxic elements, which in are given less remediation attention compared to uranium during the restoration of former mining sites. One such toxic element is arsenic, which is in most instances either co-precipitated or adsorbed on pyrite minerals in the tailing dumps (Ahn *et al.*, 2005). Arsenic is readily released from the pyrite mineral in acidic conditions and through biological activities, and leached into either groundwater or may be discharged to surface water through springs (Fey and Desborough, 2004). The migration of arsenic from such springs to uncontaminated water bodies is a function of the arsenic speciation, which depends on geochemical and biological interactions under the specific physicochemical conditions of the milieu. One of the important interactions is the sorption of arsenic on ferric hydroxide complexes (Wiertz *et al.*, 2006) and the oxidation of arsenic from oxidation state three to five under oxic conditions (Barra *et al.*, 2000). Thus, more arsenate (As V) than arsenite (As III) is expected to dominate in the surface mine waters because they are mostly shallow and oxic. The As V readily adsorbs and co-precipitates with ferric hydroxide complexes. Logically, arsenic elimination from the water pathway should follow automatically. However, the actual scenario in most water of former uranium mines is totally the opposite – the water still contains high levels of arsenic. Therefore, there should be other explanations beyond the pure geochemical processes based on thermodynamic principles. In view of this, we investigated the arsenic migration with emphasis on its speciation dynamics in mine water discharged from a spring of leachates on a uranium-tailing heap to a wetland pond at an abandoned uranium-mining site in Zobes-Mechelgrün (Vogtland), south-west of Saxony in Germany. The field studies were complimented with laboratory investigation of the contribution of the interaction with the Fe ion and biological activity to the arsenic speciation dynamics in the mine water flowing from the spring into the wetland. Therefore, the current article reports on the studies and explains the processes that arsenic underwent in the leachates stream that feeds into a wetland before discharge again into a stream.

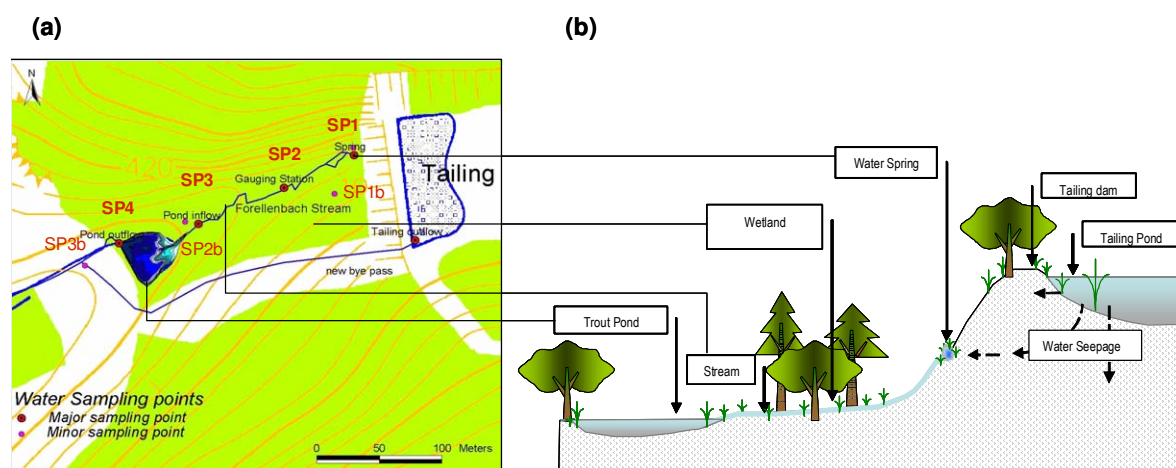
Material and Methods

Study site and sampling

The field studies were conducted at an abandoned uranium mine close to Neuensalz, Revier Zobes (Vogtland) in south-west Saxony in Germany. The water and sediment sampling points were located

along the gradient from the spring on the slopes of the tailing dam through a wetland to the outlet of the wetland pond. These are denoted SP1 to SP4 in Figure 1. Strains of arsenic resistant micro-organisms were isolated from the site, which were later used in laboratory investigation of the role of micro-organisms in the arsenic speciation of the surface mine water. The water and sediment samples were processed for determination of gradient variation in total arsenic content and distribution of inorganic arsenic species in the water (leachates).

Figure 1 (a) Map of the study site at a former uranium mining site of Revier Zobes, Vogtland haft 277) showing the sample points along a gradient from the spring at the foot of the tailing dam into the wetland and the pond; (b) is is the schematic profile of the site emphasising the difference in topographic gradient which facilitates mixing of the leachate with air. The steep sloop at the foot of the dam acts as a mixing cascade and dramatically increases the dissolved oxygen in the leachates



Laboratory experiments

(a) Role of dissolved Fe ion in oxidation of As III to As V

Oxidation of $500\mu\text{g L}^{-1}$ As III supplied as NaH_2AsO_3 were tested in aerobic and anaerobic conditions with or without Fe ion supplied as $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$. Anaerobic conditions were created by deoxygenating with nitrogen for 24 hours and conducting the experiments in an oxygen-free hood (Glove box). Samples were withdrawn periodically and analysed for As III and As V concentrations.

(b) Bio-reduction of As V to As III

A strain of arsenic resistant bacteria, isolated from the sediments at the study sites, was used in the experiment. Initial As V in the test media was $500\mu\text{g L}^{-1}$, and it was supplied as NaH_2AsO_4 . The experiment was conducted under anaerobic conditions in a deoxygenated glove box. The experiment ran for a week, the spent culture medium was collected and analysed for the As III and As V.

Analytical methods

Total dissolved arsenic concentration ($[\text{As}_{\text{tot}}]$) and total dissolved iron ($[\text{Fe}_{\text{tot}}]$) were determined with ICP-MS and AAS. The separation of arsenic into inorganic species of As III and As V concentrations was determined with ICP-MS coupled with ion chromatography.

Results and Discussion

Gradient concentration of arsenic and Fe ions

The concentration of arsenic in leachates was highest at the spring (SP1, $106.2 \pm 30.5 \mu\text{g L}^{-1}$ As). Lowest concentrations were measured at the outlet of the wetland pond (SP4, $42.3 \pm 12.4 \mu\text{g L}^{-1}$ As). Similarly, dissolved Fe ions were extremely high at SP1 ($\sim 500 \mu\text{g L}^{-1}$) but reduced significantly by 10-folds at SP2. Further, dissolved oxygen recorded 0% at SP1, but rapidly increased to almost 100 % at

SP2. This was facilitated with the fall of water down a slope of maximum gradient of 60% over a stretch of about 10-20 metres. The increase of dissolved oxygen content in the leachates was partially responsible for the oxidation of Fe II to Fe III. Consequently, Fe III hydroxides were precipitated. Possibly, a good amount of arsenic either co-precipitated with or adsorbed on the Fe III hydroxides. This explains the relationship of arsenic to iron content in sediments as was reported in Fritzsche et al. (2006). The sediments at the leachate spring of the had almost 6000 mg kg⁻¹ arsenic.

Gradient speciation changes of inorganic arsenic

The current results showed that the leachates contained more As III than As V species as they are discharged at the spring and a few meters after the rapid drop at the foot of the tailing dam. Samples in the pond and outlet had higher As V than As III species and less iron content (also see figure 2). However, As III species predominated in interstitial water extracted from the pond sediment cores. At the outlet, there were no significant differences in As III and As V species. Therefore, the flowing of the leachates down a steep gradient provides a good environment for mixing with air and drastically increases oxygen content. This results into oxidation of Fe II to Fe III, which co-precipitates with As V species leaving As III in the water. The As III later oxidised to As V in the pond. However, there should be more factors that maintain the balance between As III and As V as observed in the water sample at the pond outlet.

The role of Fe ions in oxidation of As III to As V

The complementary laboratory investigation revealed that oxidation of As III to As V does not proceed readily under oxic condition, unless oxidation accelerators are present. Figure 3 shows that there was significant low oxidation to As V in absence of the Fe ion in both aerobic and anaerobic experiments, while As V was measured in abundance only in the experiment conducted in oxygen-rich conditions in presence of Fe ions. The oxidation of As III occurs at high redox potential (Eh > 450 mV vs. Ag/AgCl). Thus, ferric ions participate as electron acceptors during the oxidation of As III to As V (Wiertz et al., 2006). Hence, once the Fe III oxidised and co-precipitated with As V species in the water, the non-oxidised AS III did not automatically transform to As V. This also explains partially why As III was measured down stream and at the pond outlet.

Figure 2 Gradient distribution of arsenic species in leachates from spring to the outlet of the wetland pond. Values are mean of several samples and bars are standard deviation, n=16

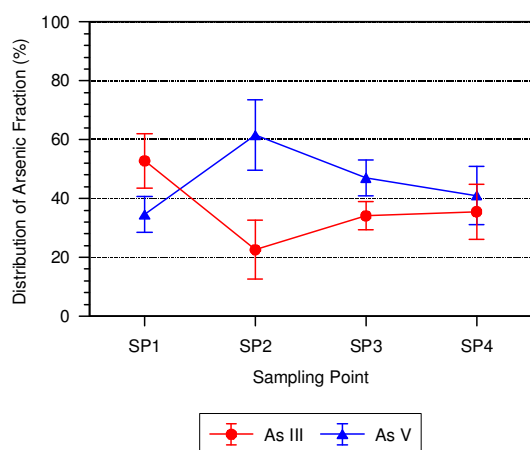
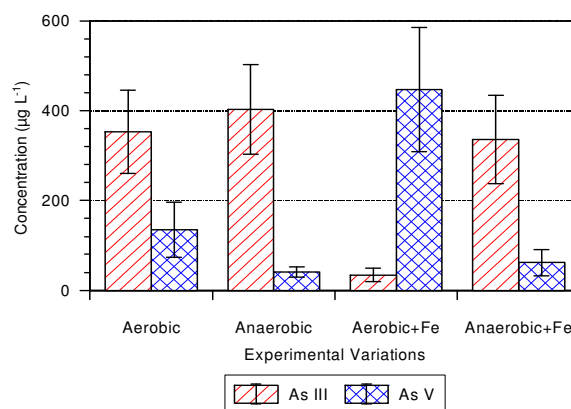


Figure 3 Concentrations of arsenic species at the end of 24 hours oxidation experiments. The initial As III concentration was 500 µg L⁻¹, and the values are means of four replications, and the bars are standard deviation



Role of microorganism in reduction of As V to As III

Analysis of spent medium used in a week of incubating resistant bacteria, strain MG 3, reveals that there was considerable reduction of As III to As V. The As III accounted for as high as 26.7±12.3% and 42.3±9.7% of the total arsenic concentration measured in the spent media in aerobic and anaerobic conditions, respectively. Considering that arsenic was exclusively supplied as As V, the presence of

As(III) testifies to the responsibility of the arsenic resistant bacteria culture in the transformation of As V to As III. Further, the lack of significant differences between aerobic and anaerobic culture suggests that the reduction of arsenic was not necessarily due to involvement of arsenic as an alternative energy acquisition source. This partially explains the dynamic changes in the arsenic speciation in the wetland in the study site. Presumably, the resistant microorganism in the contaminated water reduces the arsenic from oxidation state five to three as a counter toxic mechanism. Consequently, relatively high fractions of As III were measured down the stream, in the wetland and even at the pond outlet.

The mechanism in the overall arsenic speciation dynamics

As the leachate water flows downstream from the spring through the wetlands into the pond, there is mixing with oxygen that results in oxidation of As III to As V and also formation of Fe III oxides which co-precipitates with As V, while dissolved Fe ions catalyse oxidation of As III to As V. Consequently, the wetland pond had high As V species. However, the bio-reduction of As V to As III, which consequently remains in the As III form in the lower streams up to the pond outlet because there were less Fe ions as dissolved species.

Conclusion

The current results reveal that the speciation of inorganic arsenic as tailings water flows down stream through the wetland into the pond is very dynamic, oscillating between species of As III and As V. The complimentary laboratory result suggests that pure geochemical process are either compensated for or counteracted by biological processes. As a result, the actual processes in the field are far from equilibrium conditions. Hence, general thermodynamic rules are never or partially observed. However, the current laboratory results are not enough to explain the process behind the dynamics of inorganic arsenic speciation in mine leachates. To comprehensively explain the processes involved, there is a need to examine the impact under several ion interactions, biological processes, and different physicochemical conditions, and also in combination of all of the above mentioned parameters.

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