Environmental Pollution 158 (2010) 3439–3444

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Concentrations and speciation of arsenic in groundwater polluted by warfare agents

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The environmental fate and behavior of phenylarsenicals in groundwater are influenced by the geochemical environment.

ARTICLE INFO

Article history:
Received 16 March 2010
Received in revised form
17 June 2010
Accepted 18 June 2010

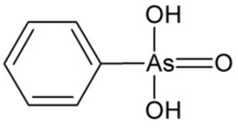
Keywords:
Phenylarsenicals
Arsenic species
Groundwater conditions

ABSTRACT

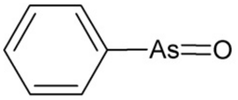
Groundwater polluted with phenylarsenicals from former warfare agent deposits and their metabolites was investigated with respect to the behavior of relevant arsenic species. Depth profiles at the estimated source and at about 1 km downgradient from the source zone were sampled. The source zone is characterized by high total arsenic concentrations up to 16 mg L^{-1} and is dominated by organic arsenic compounds. The concentrations in the downgradient region are much lower (up to 400 μg L^{-1}) and show a high proportion of inorganic arsenic species. Iron precipitation seems to be an effective mechanism to prevent dispersion of inorganic arsenic as well as phenylarsonic acid. Reductive conditions were observed in the deeper zone with predominant occurrence of trivalent arsenic species. The inorganic species are in redox equilibrium, whereas the phenylarsenic compounds have variable proportions. Methylphenylarsinic acid was identified in groundwater in traces which indicates microbial degradation activity.

1. Introduction

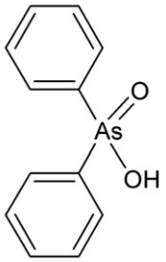
Besides geogenic arsenic contaminations in groundwater (e.g. Smedley and Kinniburgh, 2002; Mukherjee et al., 2006), anthropogenic arsenic compounds may pollute groundwater on a large scale. Phenylarsenic compounds (CLARK I and II, Pfiffikus) were produced extensively as chemical warfare agents during World War I and to a lesser extent also during World War II (Martinetz, 1996). They have been gaining in scientific interest in recent years. Phenylarsonic acid (pentavalent As, PAA), phenylarsine oxide (trivalent As, PAO) and diphenylarsinic acid (pentavalent As, DPAA) as hydrolysis products of the original compounds were found as typical contaminants in groundwater that had been in contact with deposits of these warfare agents (Daus et al., 2008):



phenylarsonic acid (PAA)



phenylarsine oxide (PAO)



diphenylarsinic acid (DPAA)

Little is known about the geochemical and microbiological processes taking place in such contaminated groundwater environments. From soil investigations it is known that bacteria degrade diphenyl- and triphenylarsenic compounds in contaminated soil with low rates, and PAA was identified as a degradation product from triphenylarsine oxide (PAO) (Köhler et al., 2001).

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doi:10.1016/j.envpol.2010.06.029

Nakamiya et al. (2007) demonstrated that DPAA was degraded into cis,cis-muconate and arsenic acid in contaminated soil from Kamisu City, Japan. It was also suggested that methyldiphenylarsine oxide (MDPAO) is one of the transformation products from DPAA by methylation. The conditions in the groundwater differ from investigations, which were accomplished in soils or plants, by many parameters (temperature, availability of oxygen or co-substrates, microbial community, microbial activity). However, there are some indications for microbial degradation also under anaerobic conditions in the groundwater (Hempel et al., 2009).

The toxicity of phenylarsenicals in groundwater attracted public attention in 2002. The inhabitants in the vicinity of the town Kamisu, Japan, exhibited uncommon clinical symptoms of the central nervous system (Ishii et al., 2004). In 2003, bis(diphenylarsine) oxide, DPAA, and PAA were detected in groundwater consumed by the inhabitants (Ishizaki et al., 2005; Kinoshita et al., 2005).

There are several sites in Germany where the groundwater is contaminated by warfare agents from the World Wars I and II (Martinetz, 1996). One of them is a former filling station for chemical warfare agents and it is located near the city of Dessau, Saxony-Anhalt, Germany. In 2005 source remediation by soil excavation was executed down to 3 m below surface. Nevertheless, high concentrations of arsenic are still being detected in the groundwater nowadays. The aim of this study was to analyze the arsenic species occurring in this contaminated aquifer as well as about 1 km downgradient of the source zone in cross-sections. The different geochemical and possibly microbial processes should be discussed with respect to their relevance to the fate of the phenylarsenicals in such an environment.

2. Materials and methods

2.1. Sampling site and groundwater sampling

Water samples were taken on the site of a former ammunition depot and filling station for chemical warfare agents in the supposed source zone and about 1 km downgradient from it (see Fig. 1).

For sampling, the direct push-technology with the Geoprobe®-System Sampling Point 16 with stainless steel filters was used (Dietrich and Leven, 2006). The water was pumped up by a peristaltic pump with HDPE tubes. An amount of 10 L were pumped to rinse the system before water sampling. The static groundwater level was about 3.0 m below the surface. The samples at the source zone (cross-section: SZ-01 up to SZ-06 over about 60 m) were taken every 1.2 m from the groundwater level down to 15 m below the surface which was estimated to be the most polluted depth zone. This first sampling campaign was done in June 2008.

The groundwater samples at the different downgradient sites (cross-section DG-01 up to DG-05 over about 400 m) were taken from the following depth-ranges: 4.8–5.8 m, 6.0–7.0 m, 7.2–8.2 m, 8.4–9.4 m, 10.8–11.8 m, 13.2–14.2 m, 16.8–17.8 m, 20.4–21.4 m and 24.0–25.0 m below surface. The investigations were done down to 25 m depth in this region to screen the whole upper aquifer. This second sampling campaign was done in November 2008.

Redox potential, conductivity, pH value and temperature were measured immediately during sampling in a flow-through-cell by the common sensors (WTW, Germany). Sub-samples of each of the aqueous samples were stored in completely filled 100 mL PE-bottles for anion analyses. For determination of arsenic species in parallel samples of 100 mL, 1 mL of phosphoric acid (1 mol L^{-1}) was added to preserve the species until analysis (Daus et al., 2008). All samples were stored at 6 °C in the dark.

2.2. Chemical analysis

Different organic and inorganic arsenic species were detected and quantified by a speciation method described by Daus et al. (2008) using high performance liquid chromatography (HPLC) with a RSpak NN-614 column (150 × 6 mm, Shodex Japan). The chromatographic system (System Gold, BECKMAN,) was coupled with an inductively coupled plasma mass spectrometry (ICP-MS, PQ ExCell, THERMO) for arsenic detection. For the quantification of arsenic species calibration samples were prepared from stock solutions of arsenite (As(III), 0.05 mol As L^{-1}, Merck), arsenate (As(V), 1000 mg L^{-1} As, Titrisol®, Merck), phenylarsonic acid (1000 mg L^{-1} As, Fluka Analytical) and phenylarsine oxide (1000 mg L^{-1} As, Sigma). Additionally, methylphenylarsinic acid (courtesy of Prof. Kaise, Tokyo University of Pharmacy and Life Sciences, Japan) was used to identify a peak in the chromatogram. The stock solutions were diluted to get the mixed standards with the appropriate concentrations. The calibration curves of all standard solutions resulted in similar parameters for arsenic. A calibration equation was used by calculating mean slopes and intercepts to estimate the concentrations of non-identified peaks and of DPAA, which was not available as a standard substance.

The total concentrations of arsenic, iron and calcium were determined by inductively coupled plasma – mass spectrometry (ICP-MS, ELAN-DRCe, Perkin Elmer) or by inductively coupled plasma – atomic emission spectrometry (ICP-AES; CIROS, Spectro Analytical Instruments GmbH & Co. KG) in dependence on the concentrations. In the non-acidified samples nitrate, chloride, and sulfate were determined using an ion-chromatograph DX 500 (Dionex) with an IonPack AS12A/AG12A column. Phosphate and ammonium were analyzed in these samples by UV–Vis spectrometry (EPOS Analyzer 5060, Eppendorf).

3. Results

3.1. The source zone of contamination

The site under investigation where warfare agents were handled in the 1940s, has a long and obvious history of groundwater contamination by arsenic. Almost nothing is known about the

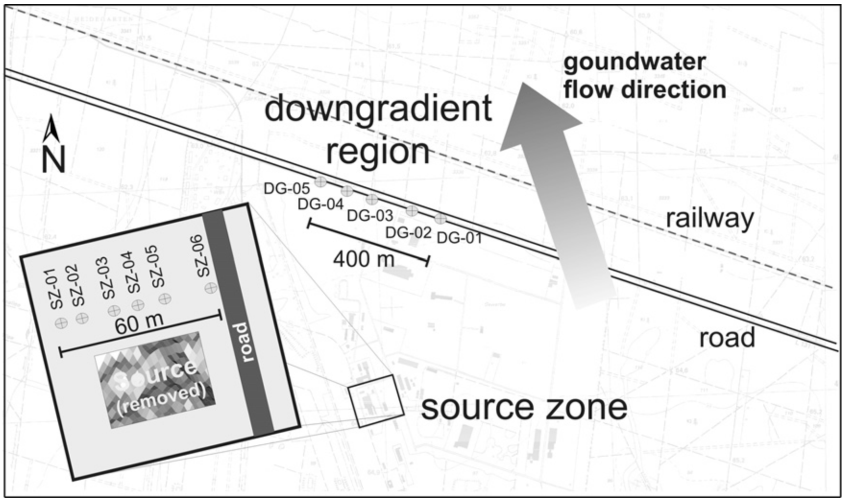

Fig. 1. Location of the sampling sites (SZ- source zone; DG-downgradient region).