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Redox-cycling of arsenic along the water pathways in sulfidic metasediment areas in northern Sweden

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ABSTRACT

Arsenic has emerged as a problem element in groundwater. The most common mechanism of mobilising As from the solid phase into water is through the reductive dissolution of ferric oxyhydroxides. This investigation was made in northern Sweden where metasediments containing pyrite, pyrrhotite and arsenopyrite underlay about 4000 km^2. The overlying till contains as much as up to 100 mg kg^{-1} As. Speciation of the dissolved As shows that arsenite dominates largely over arsenate. The Fe oxyhydroxides formed may contain up to 0.5% As. Sandy sediments may contain 100–500 mg kg^{-1}. Arsenic and Fe are closely correlated. The cycling of As in water, flora and fauna in wetlands has been studied. Ferric reduction occurs in wetlands and groundwater rich in Fe, and As is found to be discharging into ditches, brooks and streams. Wetland trees and plants show a moderately elevated content of As with a few species showing above 2 mg kg^{-1}, the permissible level in fodder for domestic animals. The only plants having a high content of As are *Equisetum* species showing up to 26 mg kg^{-1}. These plants make up a small fraction of the food of wild, grazing and browsing animals, for example moose and reindeer, and does not seem to constitute an environmental risk. However, the animals could be exposed to considerable amounts of As by drinking water from springs in wetlands. In the fauna, an elevated As content has so far been found in a limited number of benthic macroinvertebrate samples (1.23–42.1 mg kg^{-1} dry weight), in which inorganic As species (arsenate) predominate in the extractable fraction (62–82%) with lower amounts of arsenite, mono- and dimethylarsenic acid. Some samples also contained arsenobetaine, trimethylarsine oxide and tetramethylarsonium ion. To the authors' knowledge, this is the first report on As speciation in benthic macroinvertebrates. Fish species from polluted streams (pike and brown trout) had normal As levels (0.57–1.84 mg kg^{-1} dry weight), mainly present in a form of arsenobetaine (brown trout) or arsenobetaine and dimethylarsinic acid (pike). As both fish species also contained minor amounts of arsenite and arsenate, it is estimated that there is no serious health risk to potential consumers.

1. Introduction

Arsenic is an old poison that has gained renewed attention, especially in connection to its widespread occurrence at chronically toxic levels in groundwater, particularly in Bangladesh (Bhattacharya et al., 1997, 2007; Mukherjee et al., 2008). The As in the sediments under investigation in those studies is at a global background level or slightly elevated in places. Nevertheless, the concentrations in groundwater reach mg L^{-1} values at some places (Bhattacharya et al., 2002). Specific for As is the fact that toxic levels of dissolved species can be mobilised even from a low content in the geological strata under specific geochemical conditions. In the Bengal delta, the redox-conditions favour the reduction of ferric hydroxides onto which As is adsorbed, leading to a groundwater with high concentrations of Fe(II) and As. Another condition for mobilising As is a high pH (P. Bhattacharya et al., 2006).

In Västerbotten county in northern Sweden, considerably elevated concentrations of As have been detected in tills and sediments in connection with sulfide ores (A. Bhattacharya et al., 2006) and to sulfidic metasediments (Andersson and Lax, 2000). Even though As, with the exception of some accumulator species (Singh et al., 2010), is not generally easily taken up by plants, elevated contents in plants have been seen where the soil content is high (Meharg and Hartley-Whitaker, 2002). In view of the abundance of peatlands and other wetlands in the region studied here, there exist conditions for the reductive mobilisation of As and elevated concentrations in the groundwater and soil solution (Roden et al., 2010). The mobilisation is likely to be through microbial mediation (Routh et al., 2005, 2007; Routh and Hjelmquist, 2011).

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Metasediments of Proterozoic age cover about 3000 km^2 in the central part of Västerbotten county in northern Sweden. The metasediments are partly greyish and arenitic or blackish and phyllitic in nature. They belong to the Svecofennian suite of rocks, overlying the sub aqueous volcanic rocks that host a number of sulfide ore bodies (Kathol and Weihed, 2005). The phyllitic metasediments are often sulfidic, containing pyrite, pyrrhotite and minor amounts of arsenopyrite. Another salient feature is their content of graphite mirroring their formation in an anaerobic environment. The major minerals are quartz and plagioclase as larger grains in a groundmass of microcline, sericite and chlorite (Gavelin, 1939). Gavelin (1939) gives an analysis for a graphite rich phyllitic shist with a S content of as much as 10%. In total, 122 analyses of metasediments (phyllites) are published by Svensson (1970, 1980). A selection of these, from the area in which this investigation was performed, is presented in Table 1. The elements are present in skewed distributions while both mean and median contents are given. Dumas (1985) presents an analysis of nine samples from area B in Fig. 1 of the phyllitic rocks with S and Zn contents slightly lower than the values given in Table 1. The metasediments have been described by Kautsky (1957) from the central part of the area under investigation, and by Edelman (1969) from the western part. The most exhaustive investigation of the mineralogy and structure of the metasediments is given by Dumas (1985). She has called the fine-grained sediments (<0.06 mm) mudstones while the coarser ones (>0.06–0.63 mm) have been named siltstones. The soils in the area are uniformly podzolic. The As content of the metasediments is mirrored in an elevated content in the till above and in the glacial ice movement direction (Andersson and Lax, 2000; Lax and Selinus, 2005).

Inorganic As species are more toxic than organic ones (Vahter and Concha, 2001). Arsenate and arsenite are about 500 times more toxic than the organic species monometylarsonic acid (MMA), dimetylarsinic acid (DMA) and arsenobetaine and As sugar (Francesconi, 2005). Methylation is considered to be a way for organisms to detoxify inorganic As species (Vahter and Concha, 2001).

Evidence of redox-governed mobilisation and immobilisation of the As originating from the sulfidic metasediments can be found along the water pathways in the studied area. In the podzolic soils in upland areas arseniferous sulfides are oxidised and the mobilised As is largely found in the B-horizons of the podzolic soils (Gustafsson and Jacks, 1995). In discharge areas the As may be remobilised by reduction of Fe oxyhydroxides acting as adsorbents for the As. The groundwater levels in discharge areas are affected by seasonal short term reduction–oxidation cycling of the Fe and As (Mitchell and Branfireun, 2005) as well as by long term cycling in these boreal forest areas due to forest drainage and forest management such as clear cutting. In the studied areas forest drainage is likely to play an important role as both sink and source for As, with 400 km of drainage ditches per km^2 being dug in the 1980s. When these ditches are clogged over a forest generation, raising the groundwater level, a sizeable mobilisation of As through reduction of Fe oxyhydroxides will occur.

This investigation was aimed at investigating the cycling of As in soil, water, flora and fauna along the water pathways in areas with sulfidic metasediments. The ultimate aim has been to find out whether the elevated concentrations observed in soils may be an environmental threat to animals and humans.

Table 1
Selected elements in metasediments. Data from Svensson (1980).

Element	Number of samples	Mean value	Median value	Max value
S (%)	30	1.98	0.7	10.6
As (mg kg^{-1})	30	38	15	190
Zn (mg kg^{-1})	30	436	250	2300

2. Materials and methods

2.1. Study areas

The regional mapping of As in tills performed by the Swedish Geological Survey (Andersson and Lax, 2000) was used to identify sites with elevated As in the soil. Conditions for mobilising As were suspected to occur in wetlands under reducing conditions.

Three main areas have been studied, an area south of Malå (A), another area north of Norsjö (B) and a third area north of Skellefteå (C) (Fig. 1). The common feature of the areas is that they are predominantly underlain by argilitic metasediments. The precipitation in the region is around 600 mm and the mean annual temperature +1 °C. The studied areas are covered with a boreal forest on podzolic soils with spruce (*Picea abies*) and pine (*Pinus silvestris*) as the dominating tree species.

In area A, a forest ditch draining 0.078 km^2 (7.8 ha) is studied by sampling water and sediments. The ditch is surrounded by a peatland. The peat is thin, <0.5 m thick. As much as 4 km of drainage ditches per ha were dug in the area in the 1980s. Further downstream speciation was performed by filtering and dialysis, for a lake with an area of 1.5 ha.

Area B is the main study site. Water and sediment have been sampled along two 100 m long stretches of a brook with a catchment area of 10.7 km^2. About 30% of the area, around the stream, is peatland. Several groundwater seepages with Fe oxyhydroxide precipitates were found along edges of the stream. In addition two forest ditches, tributaries to the brook, have been studied, one of them in a transect from the upland to the ditch (Fig. 2). Most of the vegetation samples in the wetlands along the ditches were collected in area B as well as most fauna samples.

Area C was studied along a 200 m stretch of a brook draining 3.69 km^2. The brook extends into upland peat areas by forest ditches. The peat cover is generally thin, no more than 1 m thick. Some sediment samples were collected upstream in small tributaries of the brook.

A common feature of the areas is the presence of extensive lengths of drainage ditches. Forest drainage has been carried out in the region in campaigns whenever subsidies have been available and in the intervals between these campaigns the ditches have been clogged raising the groundwater levels. In an area surrounding site A, as much as 12 km of forest ditches per km^2 were dug in the 1980s. This promoted sulfide oxidation while the clogging of the ditches during the subsequent decades have resulted in raising groundwater levels causing reducing conditions in discharge areas. The common clear-cutting of forestry has a similar effect, raising groundwater levels and contributing to the mobilisation of As by reductive dissolution of Fe oxyhydroxides (Bhattacharya et al., 2007).

Four soil profiles were sampled from pits dug in podzolic soils (Table 2). Above ground portions of plants and trees were sampled and air-dried.

Drainage ditches, small creeks and two larger streams were investigated by sediment sampling and through the collection of samples from plants and trees. Furthermore, benthic macroinvertebrates and fish were caught from the creeks and streams using fish nets and a kick net for benthic macroinvertebrates.

In connection with wetlands, Fe oxyhydroxides were seen where reduced groundwater was discharging. The sandy sediments were commonly orange to reddish in colour, covered by Fe oxyhydroxides.