

Controls on the Mobility of Arsenic in Sediments of Milltown Reservoir, Montana, USA

James I. Drever (drever@uwyo.edu)¹ & Patricia J. S. Colberg (pczoo@uwyo.edu)²

¹ Dept. Geology & Geophysics, Univ. Wyoming, Laramie, WY 82071, USA

² Dept. Zoology & Physiology, Univ. Wyoming, Laramie, WY 82071, USA

Introduction

Milltown Reservoir, Montana, USA, is located approximately 100 km downstream from the large-scale mining activities of Butte and Anaconda. The reservoir is largely filled with fine-grained sediments containing high concentrations of Cu, Zn, Pb, Cd, and As. A plume of high arsenic concentrations extends from the base of the fine-grained reservoir sediments into the underlying coarse-grained alluvial aquifer. The purpose of this study was to investigate the controls, both inorganic and microbial, on the mobility of arsenic at this site.

Methods

Cores were obtained from the reservoir sediments and pore waters were extracted by squeezing under a nitrogen atmosphere. Solid phases were analysed by scanning electron microscopy and by a selective dissolution procedure. Various microbial enrichment experiments were performed using core material from the site.

Results and discussion

Background sulphate concentrations in the reservoir are around 200ppm. Some sulphide oxidation occurs in the upper part of the sediment, causing a decrease in pH from around 7.5 to 6.5–7 and an increase in dissolved sulphate concentration to about 700ppm. Elevated dissolved zinc and copper concentrations are associated with the sulphide oxidation. Sulphate concentrations decrease to less than 5ppm in the deeper parts of the sediment; pH values are close to 7.5.

The pore-waters in the sediments of the reservoir have dissolved arsenic concentrations of up to 17ppm. The highest concentrations are associated with anaerobic environments, where sulphate reduction is complete. High arsenic concentrations are not observed in the depth interval where bacterial iron reduction (but not sulphate reduction) is occurring, nor where active sulphate reduction is taking place.

Pore waters in all but the uppermost reservoir sediments are supersaturated with respect to siderite, but only very minor amounts of siderite are present in the sediments. It appears that hydrous ferric oxides are not completely reduced before sulphate reduction occurs and persist throughout the sediment.

According to equilibrium thermodynamics, as the environment became progressively more reducing, the following sequence should occur:

1. Ferrihydrite should be reduced (to dissolved ferrous iron or siderite). Any As adsorbed to ferrihydrite should be released.
2. As(V) should be reduced to As(III). As(III) is relatively weakly adsorbed, so adsorbed As should be released to solution.
3. Sulphate reduction should occur. Arsenic should precipitate (as arsenopyrite or an arsenic sulphide) so long as sulphide is available. When sulphide is depleted, arsenic should be soluble.

In the deeper sediments, solid-phase arsenic is about 80% in the form of a sulphide (detrital copper-iron-arsenic sulphides or arsenopyrite, FeAsS) and about 20% in a weakly adsorbed form. This weakly-adsorbed arsenic is presumably the source of dissolved arsenic in the groundwater. The "redox pumping" mechanism of Moore (1994) is not the only source of labile arsenic in the system.

Microbiological experiments using sediments from the site have shown that both sulphate- and iron-reducing bacteria are present throughout the sediment column. Sulphate reducers from the site were shown to precipitate arsenopyrite (Rittle et al., 1995). The presence of adsorbed copper inhibited reduction of ferrihydrite by bacteria from the site (Markwiese et al. 1998); we are investigating whether adsorbed arsenic causes a similar inhibition. We are also investigating the relative rates of sulphate reduction and ferrihydrite reduction in these sediments.

Conclusion

A simple thermodynamic model in which electron acceptors are reduced in succession and arsenic(V) is controlled by adsorption onto iron oxyhydroxides in oxidising environments does not match the field data. High dissolved arsenic concentrations do not occur until sulphate reduction is complete. It appears that the relative rates of microbial reduction of iron oxyhydroxides, As(V), and sulphate play a major role in determining the mobility of arsenic in this system.

Markwiese JT, Meyer JS & Colberg PJS, *Environ. Toxicol. & Chem.*, **17**, 675–678, (1998).

Moore JN, *Am. Chem. Soc. Adv. Chem. Ser.*, **237**, 451–471, (1994).

Rittle KA, Drever JI & Colberg PJS, *Geomicrobiol. J.*, **13**, 1–12, (1995).