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Diel changes in water chemistry in an arsenic-rich stream and treatment-pond system

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Abstract

Arsenic concentrations are elevated in surface waters of the Warm Springs Ponds Operable Unit (WSPOU), located at the head of the upper Clark Fork River Superfund site, Montana, USA. Arsenic is derived from historical deposition of smelter emissions (Mill and Willow Creeks) and historical mining and milling wastes (Silver Bow Creek). Although long-term monitoring has characterized the general seasonal and flow-related trends in As concentrations in these streams and the pond system used to treat Silver Bow Creek water, little is known about solubility controls and sorption processes that influence diel cycles in As concentrations.

Diel (24-h) sampling was conducted in July 2004 and August 2005 at the outlet of the treatment ponds, at two locations along a nearby reconstructed stream channel that diverts tributary water around the ponds, and at Silver Bow Creek 2 km below the ponds. Dissolved As concentration increased up to 51% during the day at most of the stream sites, whereas little or no diel change was displayed at the treatment-pond outlet. The strong cycle in streams is explained by pH- and temperature-dependent sorption of As onto hydrous metal oxides or biofilms on the streambed. Concentrations of dissolved Ca^{2+} and HCO_3^- at the stream sites showed a diel temporal pattern opposite to that of As, and geochemical modeling supports the hypothesis that the concentrations of Ca^{2+} and HCO_3^- were controlled by precipitation of calcite during the warm afternoon hours when pH rose above 9.0. Nightly increases in dissolved Mn and Fe(II) concentrations were out of phase with concentrations of other divalent cations and are more likely explained by redox phenomena.

Keywords: Geochemistry; Diel; Diurnal; Adsorption; Superfund; Clark Fork River; Montana; Manganese; Arsenic; Heavy metals

1. Introduction

A number of previous studies have documented the phenomenon of diel (diurnal or 24-h) variations in the concentrations of arsenic and heavy metals in rivers and streams (Fuller and Davis, 1989; Brick and Moore, 1996; Nimick et al., 1998, 2003, 2005; Kuwabara, 1992; Gammons et al., 2005; Shope et al., 2006; Parker et al., 2007a,b; Barringer et al., in press). In their pioneering study, Fuller and Davis (1989) found that dissolved As concentrations in Whitewood Creek, an alkaline stream

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draining abandoned mine lands in the Black Hills of South Dakota, increased up to 40% during the day and decreased a corresponding amount at night. Nimick et al. (1998) found similar diel fluctuations in dissolved As concentration of up to 20% in the Madison and upper Missouri Rivers of Montana, a watershed that receives large As loads from geothermal springs in Yellowstone National Park. More recently, Nimick et al. (2003, 2005) found diel variations in dissolved As concentration of up to 55% in High Ore Creek and Prickly Pear Creek, two small, alkaline streams draining abandoned mine lands of the Boulder Batholith in southwestern Montana. In all of these case studies, dissolved As concentrations reached a maximum in the late afternoon and a minimum in the early morning, near sunrise. Even larger diel variations in concentrations of heavy metals such as Cd, Cu, Fe, Mn, and Zn have been noted in pH-neutral to alkaline streams (Bourg and Bertin, 1996; Brick and Moore, 1996; Nimick et al., 2003, 2005; Gammons et al., 2005; Parker et al., 2007b). In most cases, these divalent cations show the opposite temporal pattern to that of anionic As species, with concentrations increasing at night and decreasing during the day (Nimick et al., 2003).

Many hypotheses have been invoked to explain diel metal cycling, including pH- and/or temperature-dependent adsorption onto secondary minerals and biofilms on the streambed (Fuller and Davis, 1989; Nimick et al., 2003; Jones et al., 2004; Gammons et al., 2005; Shope et al., 2006; Parker et al., 2007a; Barringer et al., in press), precipitation/dissolution of carbonates or other minerals containing metals (Nimick et al., 2003), diurnal changes in the flux of shallow ground water or hyporheic water into the stream (Brick and Moore, 1996), redox reactions involving secondary Mn and Fe oxyhydroxide minerals (Brick and Moore, 1996; Haack and Warren, 2003; Harrison et al., 2005), and biological uptake (Morris et al., 2005, 2006). Regardless of the exact mechanisms responsible for their existence, diel cycles in arsenic and heavy metals have important implications for planning and implementing water-quality sampling in rivers and streams. In many cases, the concentration information obtained will depend on what time of day the sample was collected. Nimick et al. (2005) presented an example in which dissolved Zn concentrations in samples collected from Prickly Pear Creek in the afternoon were less than the State of Montana's regulatory standard for protection of aquatic life, whereas concentrations in samples collected early in the morning exceeded this standard. Furthermore, Nimick et al. (2005) illustrated that the total range in dissolved Zn concentration in a single 24-h period can be nearly as much as the range in Zn concentrations during an entire year including periods of high flow during spring snowmelt and low flow during the summer and winter.

The purpose of the present study is to examine diel variations in arsenic and trace metals in a stream and treatment-pond system located near the headwaters of

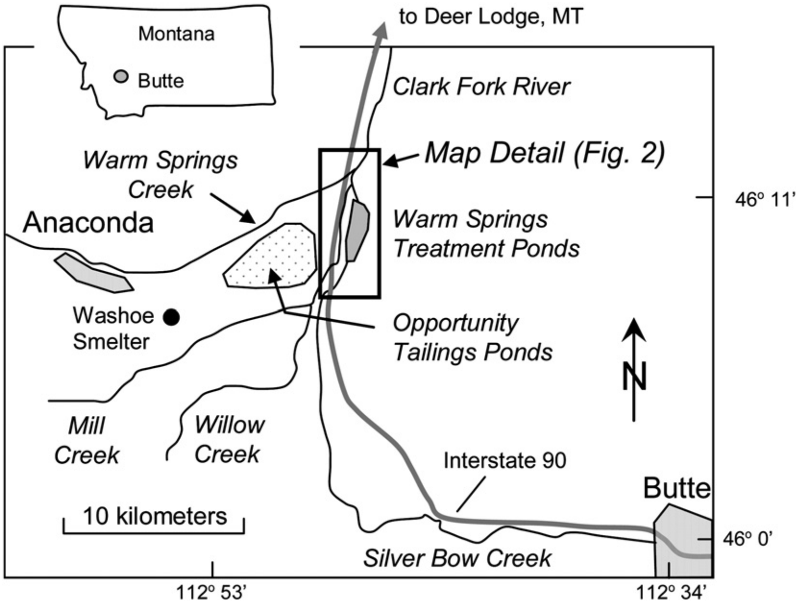

Fig. 1. Location of the study area. All of the streams eventually converge to the Clark Fork River, which flows off the north end of the map.