



Zinc, copper, nickel, and arsenic monitoring in natural streams using in-situ iron–manganese oxide coated stream pebbles

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ABSTRACT

Elements such as zinc, copper, nickel, and arsenic pose a concern for drinking water quality and ecosystem health and tracking these often nonpoint source contaminants in groundwater presents a significant challenge due to the heterogeneous spatial distribution of sources. Developing an approach to help locate the sources of zinc, copper, nickel, and arsenic in ground and surface water sources could potentially provide a rapid, repeatable, and inexpensive technique for environmental assessment. Iron–manganese oxide coated streambed pebbles have a surface affinity for metals and could serve as in-situ monitors. The analysis of pebble coatings and surface water sampled from Pennypack Creek and its tributaries, in southeastern Pennsylvania, USA, tests the ability of pebble coatings to reflect in-stream concentrations of zinc, copper, nickel, and arsenic and track the source of higher concentrations upstream and in tributary branches. Quartz pebbles, 5–7 cm in diameter, with brown-red coatings were sampled along the main stem and tributaries of the Pennypack Creek followed by leaching coatings with 4 M nitric acid with 0.03 M hydrochloric acid for 24 h. Quartz pebbles were selected to minimize elemental contamination from metal bearing minerals in the sample. All metals in the leachate are significantly correlated ($p < 0.15$) with iron on the coatings. Zinc, copper, and nickel show elevated concentrations on the pebble coatings near the middle of the watershed compared to concentrations on coatings at other sampling sites. To predict the arsenic source in the main stem, two segments of the Pennypack Creek were chosen for calculations of relative discharge and concentration. Arsenic concentrations (normalized to surface area) on pebbles in the main stems are 5.62 ng/cm² and 12.7 ng/cm² and the predicted values are 13.3 ng/cm² and 28.6 ng/cm² which satisfy mixing within the tributaries. Results suggest that iron–manganese coated stream pebbles are useful indicators of zinc, copper, nickel, and arsenic location within a watershed, but that the source of arsenic differs from that of the other metals of interest. Zinc, copper, and nickel data suggest a geochemical signal from nearby railroads or industrial point source contamination and arsenic data suggests a geogenic source or industrial point source contamination that is traced upstream from a main stem to tributaries using pebble coating concentrations and relative discharge.

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1. Introduction and background

1.1. Previous work with iron/manganese oxide coatings and metals

Metals such as zinc (Zn), copper (Cu), nickel (Ni), and arsenic (As) are harmful to humans, aquatic plants, and animals at elevated concentrations in water, soils, and rocks (Dangleben et al., 2013; Liu et al., 2009; Stasinos and Zabetakis, 2013; Wang et al., 2011). The maximum contaminant limit (MCL) for As is 10 µg/L and the maximum contaminant limit goal (MCLG) for Cu is 1.3 mg/L (Environmental Protection Agency, 2009). Zinc and Ni do not have MCL values for drinking water but have criteria maximum concentration values of 7400 µg/L and 470 µg/L respectively for acute exposure by aquatic communities in

freshwater systems (Environmental Protection Agency, 2014). Prolonged exposure to these metals can cause health problems such as cancer or immune deficiencies. These metals are often deposited in the environment from multiple geogenic and anthropogenic sources, therefore tracing when and where they enter the hydrologic system is challenging. Geogenic sources of metals on the Earth's surface include erosion or dissolution of crustal material or atmospheric deposition from dust (Callender, 2003; Smedley and Kinniburgh, 2002). Anthropogenic sources include mining, smokestack emissions, industrial runoff, fertilizers, and pesticides (Bissen and Frimmel, 2003; Callender, 2003; Thuy et al., 2007). Developing ways to locate the source(s) of these potential contaminants will help to improve assessment and remediation efforts as it is difficult to rectify environmental contamination if the source is unknown.

Rock coatings were first studied by Alexander von Humboldt in the early 1800s (Dorn et al., 2012; von Humboldt, 1812). Observations of black-brown crusts on stream pebbles were made along the Orinoco

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River between the missions of Carichana and Santa Barbara and it was deduced that these iron and manganese coatings were deposited from the river water. Since then, rock coatings have been used to find mineral deposits (Huelin et al., 2006; Robinson, 1983). Previous in-situ and laboratory experiments have successfully demonstrated the use of stream sediments, iron, and manganese oxide coated quartz pebbles, ceramic plates, or limonite chips as source location indicators of elements suitable for mining (Carpenter, 1975; Huelin et al., 2006; Tingley and Castor, 1999; Zumlot et al., 2009). These methods trace the location of mineralized deposits by analyzing the geochemistry of the substrate or pebble coatings in a stream and following the geochemical signal upstream. Fine-grained sediments record elemental concentrations within their crystal structure as well as elements sorbed to the crystal or amorphous surface. Sequential extraction is sometimes necessary to quantify which phase a metal is associated with or a total digestion to analyze the whole rock geochemistry (Dong et al., 2002; Soares et al., 1999; Tingley and Castor, 1999).

Whereas these sediment analysis techniques have proven useful in locating large ore bodies for mining; few similar studies have been performed to find lower concentration elements. Given the affinity of stream pebble iron–manganese oxide coatings to metals, we here propose and test a method for environmental monitoring that has previously been used for mineral exploration (Huelin et al., 2006). This technique is advantageous because researchers can use the natural accumulation of iron and manganese on pebbles to understand chemical interactions in watersheds; including groundwater–surface water interactions as well as environmental monitoring. In addition to studying in-situ pebbles, this technique can be further adapted by using glass beads or ceramic plates as substrates to measure accumulation rates. The research presented herein is a first-order approach to applying a mining exploration technique to environmental geochemical questions.

This study seeks to answer the question: can iron–manganese oxide coated stream pebbles behave as in-situ environmental monitors for zinc, copper, nickel, and arsenic? It is, however, important to note that because this study makes a significant transition between using stream sediments for identifying major ore bodies to identifying trace elements, the authors make some first order assumptions that are addressed in detail throughout the text. These assumptions include the homogeneity of oxide coatings on quartz pebbles and the stability of the pebbles on the stream channel bed.

In the 1970s and 1980s, a suite of literature was published that explored the efficacy of stream pebbles as geochemical tracers compared to stream sediments of sand and silt grain size. The stream pebbles captured a geochemical record of the stream and surrounding areas through metal sorption to iron and manganese oxide coatings (Carpenter, 1975; Carpenter and Hayes, 1980; Nowlan, 1976; Robinson, 1982; Whitney, 1975). The sorption of metals to these coatings is uniform as the pebbles are (mostly) in place and record the geochemical signal of the water flowing over them, in contrast to finer grained sediments that are transported as suspended sediment (Robinson, 1983). While the pebble remains in place in a stream, coatings will accumulate, and sorption of metals to the surface will come into equilibrium with the overlying stream chemistry.

Dissolved iron and manganese are readily found in groundwater and surface water and oxygenated surface waters create conditions for Fe and Mn oxides to precipitate on rock surfaces (Carpenter, 1975; Cornell and Schwertmann, 2003). Iron and manganese oxide coatings form on pebbles or ceramic plates as rapidly as a few weeks and will continue to accrete for as long as three years, or until an event causes erosion and degradation of the coatings (Carpenter and Hayes, 1980). The timing of oxide coating formation is thought to be related to groundwater–stream water interactions (Carpenter and Hayes, 1980), with groundwater contributing the dissolved iron and manganese.

Zinc, copper, nickel, and arsenic sorb to iron oxide minerals such as goethite, amorphous iron oxides, lepidocrocite, and hematite (Dixit and Hering, 2003; Miller et al., 2013). Sorption of arsenic to sediments

has been documented in the Inner Coastal Plain of New Jersey, USA (Barringer et al., 2010) and in cave streams of the Pautler Cave System in Southwest Illinois (Friedrich and Catalano, 2012) where arsenic sorbs to iron and manganese oxides. Zinc, copper, and nickel have been shown to sorb to iron oxides on stream pebbles and ceramic plates in experimental settings and in natural stream environments (Carpenter and Hayes, 1980; Nowlan, 1976). Metals can either co-sorb during formation of iron–manganese oxides or sorb once the coatings are established. In either case, research shows that metals such as Zn, Cu, Ni, and As adsorb to coatings within 36 h to 7 days (Miyata et al., 2007; Robinson, 1983) and rates of adsorption are relatively constant over a one year study (Carpenter and Hayes, 1980).

1.2. Sediment stability and discharge

The two main factors that control the stability of stream bedload are the slope of the water surface and discharge. Greater slopes and discharge generate higher bed shear stresses capable of entraining and transporting larger grain sizes. While both pebble-sized and sand-silt-sized grains have been successfully used as geochemical tracers (Huelin et al., 2006; Whitney, 1975), pebble and cobble-sized grains are stable at higher discharges, which allow precipitation of iron and manganese oxide coatings and metal sorption to continue for longer periods of time. One way to explore bedload stability is to estimate the critical shear stress needed to move a pebble, which can be estimated using the Shield's criterion (Parker et al., 2011) parameterized with channel metrics derived from Lidar data, and discharge characterized by USGS gaging stations. These calculations can identify that portion of the bedload grain size distribution that likely stay in place for long periods of time, more than minutes or days, and permit iron and manganese coatings to accumulate.

The flux of metals to a stream (J) are calculated using

$$J = Q * C \quad (1)$$

where Q is the discharge and C is the concentration (Audry et al., 2004). If discharge is not known, relative discharges can be calculated using conservative elements from each section of the stream of interest (Langmuir, 1997). An additional first order assumption about stream volume is to assume discharge is relatively proportional to stream order. For example, if there are two first order streams entering a second order stream, relative discharge can be approximated by assigning each first order stream 50% of the input to the second order stream. While this is an approximation, it provides a reasonable estimate if all other data are lacking. Carranza (2004) assessed the usefulness of stream order as a variable in geochemical anomalies and found that using stream order as a dilution factor of stream sediment geochemistry was useful for interpretations of reconnaissance of geochemical anomalies.

2. Methods

2.1. Location

Pennypack Creek drains a largely urbanized watershed, flowing south from Triassic–Jurassic Newark Basin sedimentary rocks through Precambrian–Ordovician igneous and metamorphic rocks (Fig. 1). The headwaters of the Pennypack Creek are located in Horsham, PA, a north-eastern suburb of Philadelphia, and flow 40 km (Philadelphia Water Department, 2009) south through Philadelphia to the Delaware River. The dominant land use of the Pennypack watershed is residential (52%) followed by wooded (14%), parking (5.6%), commercial (5.3%), agriculture (3.75%), and manufacturing (3.31%). Additional land use types include transportation, recreation, golf courses, and mining (Philadelphia Water Department, 2009). Newark Basin rocks have elevated levels of arsenic (Blake and Peters, 2015; Peters and Burkert,

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