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/cm^2 and 12.7 ng/cm^2 and the predicted values are 13.3 ng/cm^2 and 28.6 ng/cm^2 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 (Frierdich 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

$$J = Q * C \tag{1}$$

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 northeastern 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,
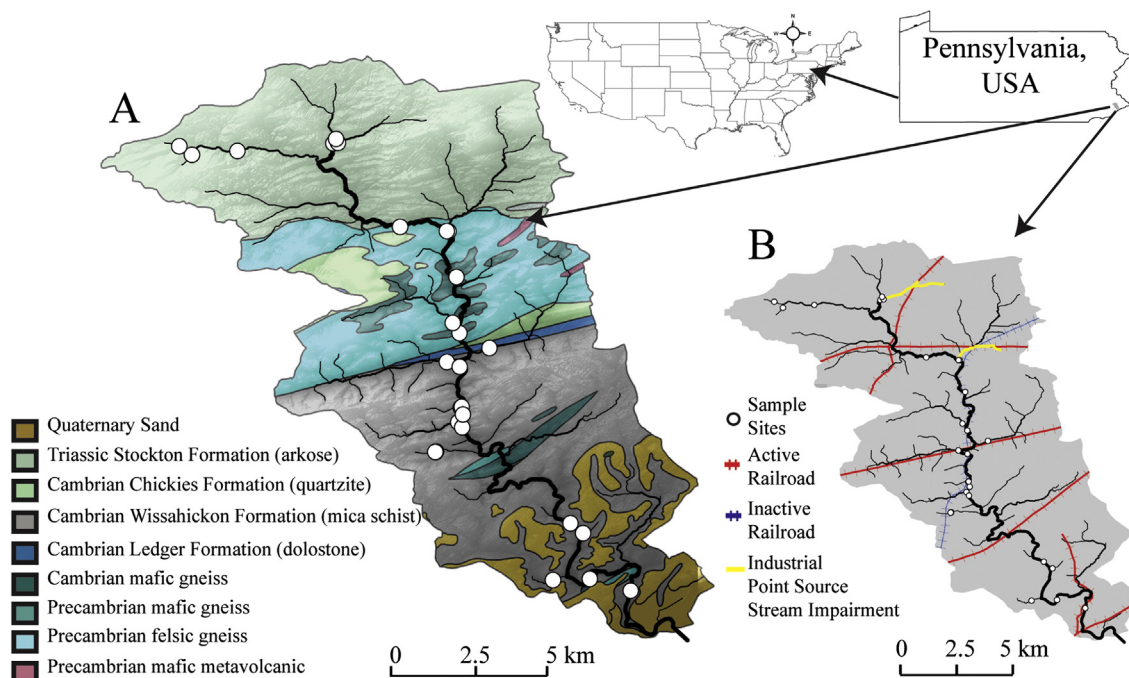
Fig. 1. Location of Pennypack Creek. A — Left watershed has topographic elevation indicated by geologic map draped over topography. Simplified bedrock geology indicated with a general northeast strike. B — watershed shows locations of active (red) and inactive rail lines (blue) as well as two tributaries that are impaired by industrial point source solution (yellow). Sampling locations are denoted by white circles in both watershed maps. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2008) and zinc, copper, and nickel are high in soils near industrial areas like those of Philadelphia (Environmental Protection Agency, 2013). The majority of stream impairment to the Pennypack Creek is from urban runoff, but there are two tributaries with industrial point source pollution, which includes organics, metals, nutrients, and flow variability (Philadelphia Water Department, 2009) (Fig. 1). Metals from railroads and emissions from smokestacks leave behind geochemical signatures in soils and waters (Kam et al., 2013; Liu et al., 2009; Lorenzo et al., 2006). The Philadelphia area has multiple train lines and industrial areas (Fig. 1). With the anthropogenic and geogenic geochemistry of the area, the Pennypack creek provides an ideal location to test the ability of stream pebbles to record surface water metal concentrations (Fig. 1).

2.2. Sampling and analysis

At each sample location, chosen for access and spatial distribution within the watershed, along the Pennypack Creek and its tributaries, a water sample and a selection of quartz pebbles between 5 cm and 7 cm along the major axis were collected (Fig. 2). Pebble and water samples were collected in the summertime at baseflow, from riffles, during three sampling dates approximately one week apart. Pebbles with a quartz composition were preferred to minimize metal contributions from the pebbles themselves and maximize contributions from the surface coatings during extraction. Pebbles were placed into 50 mL polypropylene centrifuge tubes (one pebble per tube) and the coatings leached using 4 M nitric acid with 0.03 M hydrochloric acid. In five locations, two pebbles were sampled to test reproducibility and results from duplicates were averaged for data analysis. Typically, 15 mL of mixed acid was added to each centrifuge tube to cover each pebble, and left to leach for 24 h. The leachate was then filtered through a 0.45 μm Whatman polypropylene filter and the pH raised from <1 to 3 using 5 mL 8 M NaOH to match the matrix of the calibration standards. For each pebble, the final volume of acids and base were recorded for use in final calculations of amount in the leachate. The majority of samples

had a final volume of 20 mL. To calculate the elemental concentration of the pebble surface, we used the following equation:

$$C_{surface} = \frac{C_{leachate} * V_{leachate}}{A_{pebble}} \qquad (2)$$

where:

$C_{surface}$ is the elemental concentration of the pebble surface (ng/cm^2)
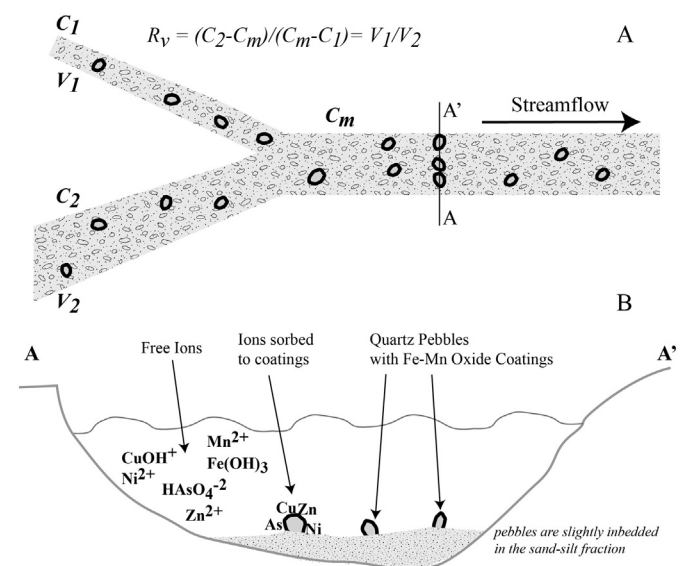$C_{leachate}$ is the elemental concentration of the leachate (ng/mL)

Fig. 2. Map view and cross section of stream. A — The map view shows direction of streamflow and locations of mixing equation variables. B — The cross section (A–A′) shows free ions, ions sorbed to coatings and quartz pebbles with Fe–Mn oxide coatings (thick black outline around gray pebbles). Pebbles sampled were slightly embedded in the sand–silt grain size of the stream bed.

$V_{leachate}$ is the final volume of the leachate (mL) after addition of the base to adjust pH

A_{pebble} is the estimated surface area of the pebble (cm^2) calculated by Eq. (3).

Grab samples of water were collected into acid precleaned low density polyethylene bottles and acidified to a pH of 2 with double distilled nitric acid for metals analysis. Temperature, pH, and specific conductance were measured with an Oakton Multi-Parameter PCSTEestr 35 probe in the field. Water and leachate samples were analyzed using an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Thermo Elemental X-Series, Winsford, UK). Elemental concentrations were measured using a six point standard calibration curve with an absolute accuracy of 5% and a precision better than 3%. Cations were measured using pneumatic nebulization with a spray chamber while arsenic concentrations were measured by hydride generation attached to the ICP-MS. Aqueous species and sorption quantities were calculated using PHREEQC to evaluate the dominant species of Zn, Cu, Ni, and As, and sorption patterns on hydrous ferrous oxides (Parkhurst and Appelo, 2013) (Fig. 2).

2.3. Calculations and assumptions

In order to compare results among samples, elemental concentrations are normalized to pebble surface area. Surface area was quantified by weighing dry pebbles and using the equation:

$$y = 373.13x^{0.6367} \qquad (3)$$

where y is the pebble surface area (cm^2) and x is the pebble mass in kilograms (Cooper and Testa, 2001). The relationship in Eq. (2) is derived by Cooper and Testa (2001) measuring the surface area of rocks by foil-wrapping and the weight of each rock. The relationship between surface area and rocks of the derived power equation is $r^2 = 0.9774$.

Spatial distributions of samples were plotted using latitude and longitude data in ArcGIS. Correlations and significance among iron and manganese versus zinc, nickel, copper, and arsenic were calculated with Pearson's product moment calculations.

Relative discharge values of tributary streams were calculated to enable mass balance of the metals between the tributary and main stem using the following equation:

$$R_v = (C_2 - C_m)/(C_m - C_1) = V_1/V_2 \qquad (4)$$

where R_v is the mixing ratio, C_1 is the concentration of the tracer, in this case conductivity or calcium, from input stream 1, C_2 is the concentration of conductivity or calcium from input stream 2, C_m is the concentration of conductivity or calcium of the main stem of the stream, V_1 is the relative volume (or discharge) of water entering the main stem from stream 1 and V_2 is the relative discharge entering the main stem from stream 2 (Langmuir, 1997) (Fig. 2). These discharge values assume that the two tributaries conservatively mix, with no loss or gain of water through subsurface flows. Relative discharge values (fraction of 1) were then multiplied by the arsenic concentrations measured on the pebbles to quantify the relative chemical flux (mass/time). To predict the amount of an element on a pebble in the main stem receiving elemental input from tributaries, the fluxes from the two tributaries are summed and termed the predicted value.

To assess the potential for pebble entrainment and subsequent loss of coatings, shear stress was calculated. The slope of the stream bed and the water height at bankfull were calculated using LiDAR digital elevation models and the ArcHydro tool in ArcGIS. Critical stress was calculated using the following equation:

$$\tau_c = \tau * (\rho_p - \rho_w)D_{50} \, g \qquad (5)$$

where τ_c is the critical shear stress, τ^* is shield's criterion, taken to be 0.045 for gravel, ρ_p is the density of the quartz pebble (2600 kg/m^3), ρ_w is the density of water (1000 kg/m^3), D_{50} is the intermediate axis grain size (5 cm) used for all sites, and g is the gravity (Parker et al., 2011).

3. Results and discussion

3.1. Water chemistry

The concentration of As, Zn, Cu, and Ni in water samples are below contaminant limits for both drinking water and stream water (Environmental Protection Agency, 2009) however, the water and pebble coating concentrations of As, Zn, Cu, and Ni are all above the detection limit for the analysis method. The dominant aqueous species (the species with the highest concentration), from the main stem of segment 1, of Zn and Ni, as modeled in the software PHREEQC (minteqV4 database), is Zn^{+2} and Ni^{+2} and of Cu is $CuOH^+$, while the dominant aqueous species of As is $HAsO_4^{-2}$. The free ions of both Zn and Ni have similar apparent cationic radii, which would suggest that the geochemical behavior of these two elements may be similar and the geochemical behavior of the arsenic and copper species may differ. Despite these differences, a PHREEQC sorption model of these aqueous species predicts nearly 100% sorption to iron oxides for As, Zn, Cu, and Ni at a pH of 8.6. The pH of the Pennypack Creek and tributaries ranges from 6.87 to 8.82. The Dzombak and Morel DDL surface complexation model was configured with hydrous ferric oxides as the adsorbent and the area of the site was 600 m^2/g and the mass was 0.09 g.

3.2. Fe and Mn coatings

The concentration of Zn, Cu, Ni, and As leached from pebble surfaces from all 34 samples were compared to both iron and manganese concentrations in the coatings to generally assess sorbate/sorbent relationship (Fig. 3). For easier visual comparison, the $\log_{10}$ values of $C_{surface}$ for the metals as well as Fe and Mn are plotted. All of the metals have positive significant correlations with iron ($p \leq 0.15$), however, only As has a significant relationship with manganese. Thermodynamic modeling using PHREEQC predicts that adsorption to iron is nearly 100%, for Zn, Cu, Ni, and As on iron oxide coatings. The lack of significant correlations between Mn and all metals except As suggest that the Mn-bearing oxide coatings may not be efficient in incorporating Zn, Cu, and Ni or that these elements have different source areas than Mn Both Fe-oxide and Mn-oxide coatings are able to incorporate arsenic and therefore may be able to assist in understanding arsenic distribution throughout the watershed.

3.3. Calculations of pebble stability

The long axis diameter of the pebbles sampled range from 5 to 7 cm and the intermediate axis diameter range from 4 to 6 cm. Three sampling locations in the creek were chosen for transport calculations, the headwaters, roughly the center of the watershed (mid), and near the mouth of the creek. The slope of the stream bed varies depending on location with the steepest slope near the headwaters, 0.010, the intermediate slope at the mouth, 0.0020, and the shallowest slope at mid, 0.00070. The average water height at bankfull are 0.90 m, 2.0 m, and 3.0 m for the headwaters, mid, and mouth of the creek respectively. The average height at baseflow was estimated at 0.30 m during field sampling. The D_{50} value for the diameter of the intermediate axis used is 0.05 m. The value used for Shield's Criterion is 0.045 (Barton, 2008).

Bed shear stress of 37 N/m^2, a first order estimate for the creek, suggests that pebbles at each location will not move at baseflow, but pebbles at the headwaters and mouth may be entrained at bankfull given a pebble size of 0.05 m (Table 1). These calculations suggest that pebbles will generally remain emplaced until a flooding event occurs. Historical crests on the Pennypack Creek in Philadelphia are reported
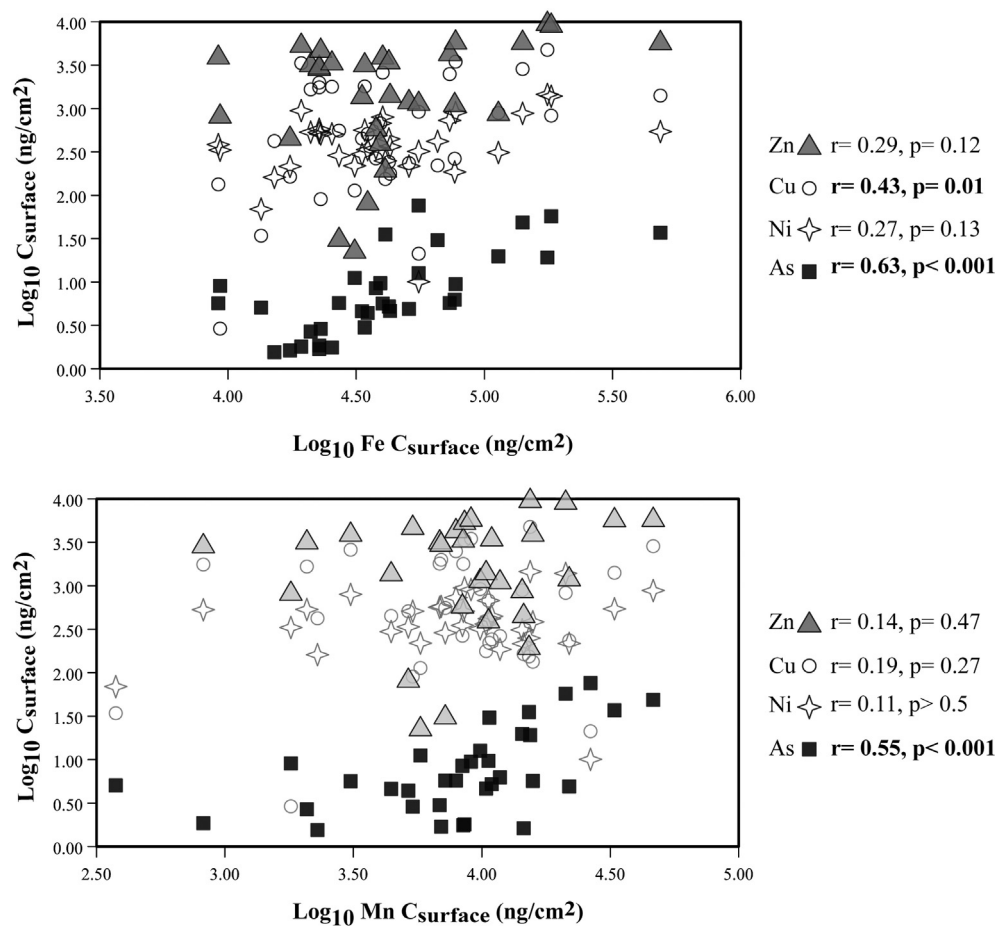
Fig. 3. $C_{surface}$ for metals as a function of iron and manganese $C_{surface}$. Both axes are the $\log_{10}$ values of $C_{surface}$. Zn, Cu, Ni, and As are significantly correlated to iron. Only As is also significantly correlated to manganese.

by the National Weather Service, with 17 major flooding events occurring over 45 years (National Weather Service, 2013) and discharge is at baseflow 60% of the time between 1965 and 2014 (United States Geological Survey, 2014). Given these data, we assume that pebbles in the Pennypack Creek are not regularly entrained in the stream. However, if pebbles are moved, it can be assumed that given the small size of the watershed (56 mi²), precipitation events would affect the discharge throughout the Pennypack Creek in a similar way and that all pebbles would move and therefore the pebbles as geochemical probes would be reset the same way. The friction among pebbles during a flood would likely result in abrasion of the coatings (Phillips, 2003) and remove the initial geochemical signal, which would allow for new signals to be deposited. Once the pebbles are emplaced after a flood, they would each begin to accumulate iron oxides and metals again. To ensure that pebbles have not moved, it is important to sample pebbles large enough that they will not be entrained by tau bankfull. This can be calculated by changing D_{50} in Eq. (4) to increase tau critical to be greater than tau bankfull. Using the equations for tau, we can predict that a D_{50} of Pennypack headwaters of 0.12 m will have a large tau critical to remain in place at bankfull and the D_{50} of the mouth should be 0.09 m to remain in place more consistently.

3.4. Zn, Cu, Ni, and As in the Pennypack Creek

The data used for the calculation of $C_{surface}$ for two stream segments are shown in Table 2. The concentrations of each metal, normalized to pebble surface area, are plotted on a map using ArcGIS (Fig. 4). The pattern of high and low concentrations is similar between Zn, Cu, and Ni, while As has a distinctively different pattern. Arsenic is highest at several point locations in the watershed, while Zn, Cu, and Ni are elevated in the center and headwaters of the watershed. Each data point shown in Fig. 4 is at a different location with the average concentration of duplicates plotted. These results could arise from a combination of: 1) Zinc, copper, and nickel originating from different sources than arsenic, 2) aqueous chemistry of arsenic differs from Zn, Ni, and Cu. Zinc, copper, and nickel may be more directly related to industry in the area, while arsenic may be more related to the bedrock chemistry and/or industry in the area. Predominantly found as an oxyanion, arsenic is redox and pH sensitive while Zn, Ni, and Cu are +2 ions that are not as greatly affected by redox and pH.

Two pebbles were collected at a subset of randomly chosen locations to assess reproducibility. Twelve of fifteen samples have Ni, Cu, and Zn reproducibilities less than 15% relative percent standard deviation

Table 1
Slope, water height, average grain size, and tau values for Pennypack Creek at its headwaters, mid, and mouth. A τ_0 value greater than $\tau_{critical}$ suggests that a pebble will become entrained.

LOCATION	Slope	avg $h_{bankfull}$ (m)	avg $h_{baseflow}$ (m)	D_{50} (m)	$\tau_{o\ bankfull}$ (N/m²)	$\tau_{o\ baseflow}$ (N/m²)	τ^* (Shield's criterion)	$\tau_{critical}$ (N/m2)
Pennypack Creek headwaters	0.010	0.90	0.30	0.05	88	29	0.045	37
Pennypack Creek mid	0.00070	2.0	0.30	0.05	14	2.1	0.045	37
Pennypack Creek mouth	0.0020	3.0	0.30	0.05	59	5.9	0.045	37

Table 2
Calculation of As $C_{surface}$ for segments 1 and 2. Surface area and $C_{surface}$ are calcuated using Eqs. (2) and (3).

Segment 1	Mass (kg)	Surface area (cm^2)	$V_{leachate}$ (mL)	As (ng/mL) $C_{leachate}$	As (ng/cm^2) $C_{surface}$
Tributary A	0.0184	29.3	20.0	54.1	36.9
Tributary B	0.0161	26.9	20.0	3.62	2.69
Main Stem	0.00765	16.8	20.0	4.71	5.61
Segment 2					
Tributary A	0.0107	20.8	20.0	6.51	6.26
Tributary B	0.0100	19.9	20.0	75.8	76.2
Main Stem	0.0066	15.3	20.0	9.66	12.7

(RSD). At the lowest concentrations, three samples have RSD percentages of 40, 50, and 65, but are still 2SD higher than the blank. Arsenic, which is closer to the detection limit, had reproducibility ranging from 32–100% RSD. Despite the high RSD, variance between most sites is about 10× this RSD and likely still provides a usable signal.

The magnitude and spatial distribution of As concentrations sorbed to pebble coatings differs from concentrations of Zn, Cu, and Ni. These differences are likely due to the locations of the sources of the elements in the watershed, whether geogenic or anthropogenic and the geochemical properties of the elements. The geochemical signature of Zn, Cu and Ni are likely explained by a legacy of industry or by modern pollutants in this urban environment (Philadelphia Water Department, 2009). Most of the areas of the elevated concentrations of Zn, Cu, and Ni are located near rail lines (Fig. 1). The association between higher metals concentrations and railroad lines has been observed in Sichuan, China, Juchhof near Zurich, Switzerland, Los Angeles, Ca, USA, among others (Kam et al., 2013; Liu et al., 2009; Lorenzo et al., 2006). Heavy metals may be emitted by fuel combustion in diesel-electric locomotives or cargo leakage along the tracks and are deposited onto plants and soils through dry and wet deposition (Wilkomirski et al., 2011). While rail lines are likely not the only source of these heavy metals on stream pebbles, the close proximity of the railroad suggests that it could be a source. Additionally, the Cambrian and Precambrian mafic rocks in the watershed contain heavy metals such as Zn, Cu, and Ni and therefore could be another explanation of source. The location of the high concentrations of Zn, Cu, and Ni is not far from the southern

tributary shown in Fig. 1 as impaired. Arsenic concentrations from stream sediments in New England have been found to have a strong positive correlation with bedrock arsenic concentrations and a weaker positive correlation with past agriculture use (Robinson and Ayotte, 2006). In the Pennypack Creek, two tributaries with high concentrations of arsenic join the main stem of the creek. Downstream of these two tributaries, higher concentrations of arsenic are recorded in the stream pebbles.

3.5. Testing pebble accuracy with mixing ratios

The mixing of waters from tributary streams to the main channel of the stream permits the evaluation of how changes in elemental concentration are recorded in the pebbles. Two stream locations with entering tributaries were selected to assess how arsenic sorption to the pebbles responds to inputs of water with different arsenic concentrations. The relative proportions of discharge from each tributary were estimated using electrical conductivity, [Ca] concentrations, and stream order. Discharge calculated using electrical conductivity agreed within 5% of the discharge calculated using [Ca], so the conductivity measurement will be used in further calculations since it is an easier parameter to measure in future studies.

The two segments were sampled on the same day; therefore temperature and redox were similar within each reach (Fig. 5). In segment 1, the upstream and tributary percent of total main stem discharge were 31% and 69% while the stream order fraction divides the discharge inputs equally between the tributaries. The arsenic concentrations on the pebbles from input tributaries in segment 1 are 36.9 ng/cm^2 and 2.69 ng/cm^2; and when the discharge fractions are multiplied by the arsenic concentrations, the flux from each tributary becomes 11.49 ng/cm^2 and 1.86 ng/cm^2 respectively. Therefore, the predicted value of arsenic on the pebble in the main stem is 13.3 ng/cm^2 (solid gray line), which is higher than the actual measured value of 5.62 ng/cm^2 (dashed line). The input streams show a distinct concentration difference, the higher arsenic concentration is more than 13 times the lower concentration, which shows that the primary arsenic flux is from the tributary stream, and accounts for 31% of discharge to the main stem.
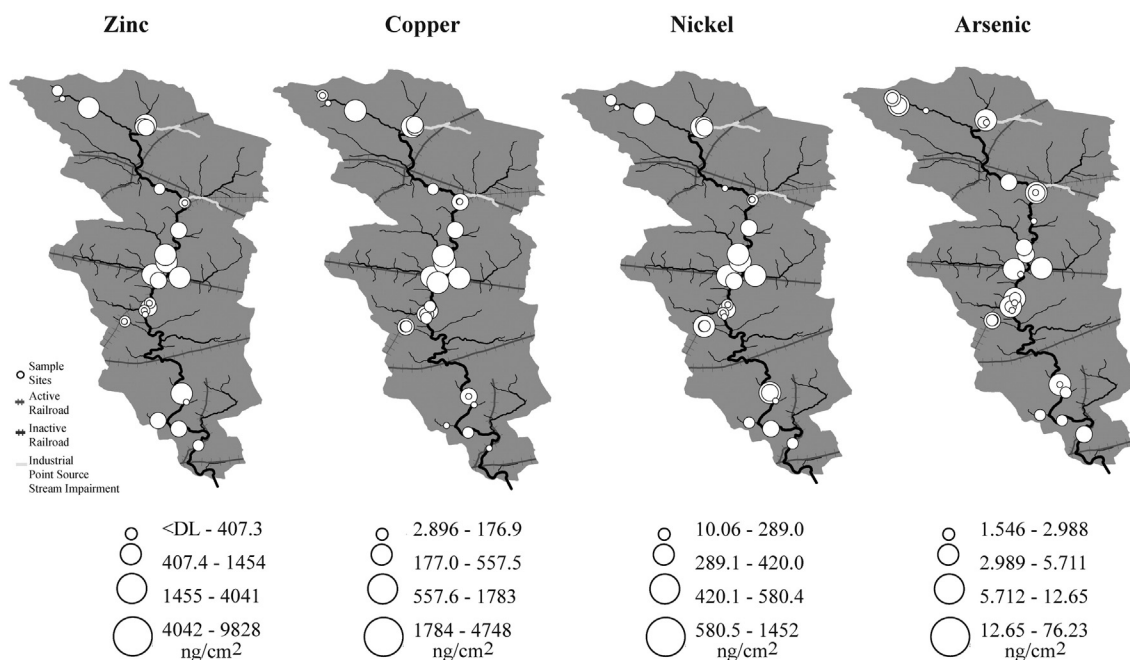

Fig. 4. Spatial and geochemical quantile distribution of, $C_{surface}$ of, zinc, copper, nickel, and arsenic in the Pennypack Creek watershed. Zn, Cu, and Ni display similar spatial and geochemical patterns while arsenic is different.
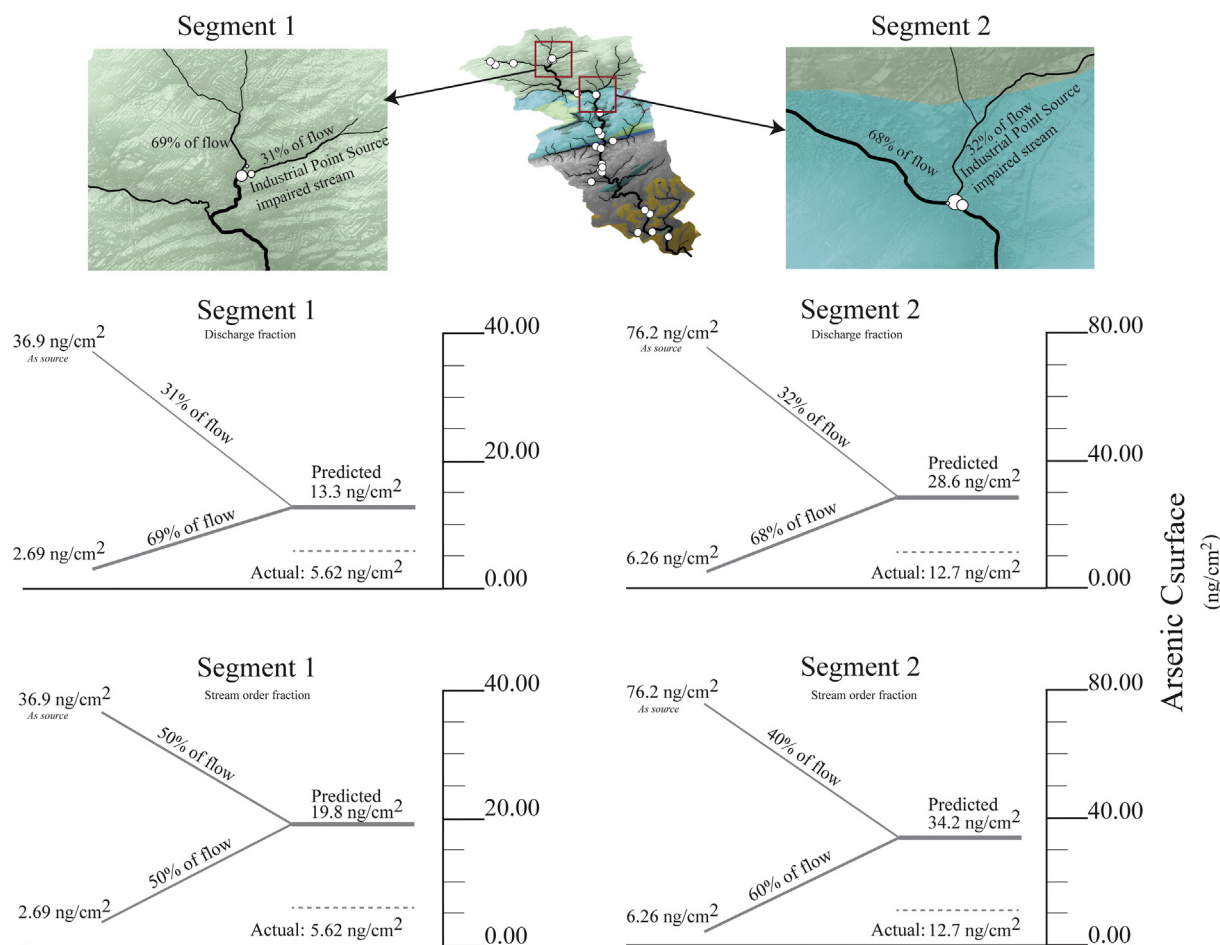
Fig. 5. Two stream segments showing fraction of flow to the main stem of the Pennypack Creek and the concentration of arsenic at each location. Predicted amounts are shown as well as actual measured amount.

Segment 2 results follow a similar overall trend as segment 1. In segment 2, the lower discharge has the higher arsenic concentration, 76.2 ng/cm^2 and 32% of the flow versus 6.26 ng/cm^2 and 68% of the flow for the other tributary. The predicted arsenic concentration in the main stem of 28.6 ng/cm^2 is greater than the actual measured value of 12.7 ng/cm^2.

Using stream order instead of discharge ratios for the mixing calculations results in less accurate results (Fig. 5). For segment 1, the predicted concentration would be 19.8 ng/cm^2 compared to the measured value of 5.62 ng/cm^2. For segment 2, the predicted concentration would be 34.2 ng/cm^2 compared to the measured value of 12.7 ng/cm^2.

In both example cases described above, the amount of predicted arsenic on a pebble on the main stream with two stream inputs appears to over predict the amount of measured arsenic in the main stem of the stream. Conservation of mass appears to be modestly well recorded, with measured values of the main stem samples recording concentrations between the inputs to the reach. Iron oxide coatings on quartz pebbles appear to at least record the spatial distribution of arsenic concentrations, with some degree of consistent over prediction downstream of mixing. The over prediction may be due to adsorption kinetics or heterogeneity of the sample, but further inquiry is necessary to fully understand this process on the iron oxide coatings. The concentration of arsenic on these pebbles is small, at the nanogram scale, but iron coated pebbles show promise of tracing the source of arsenic. This appears to work at these small concentrations, and will likely work at higher concentrations. Further investigation is necessary to explore elements at higher concentrations. The same mixing calculations were done

with data from Zn, Cu, and Ni (Table 3), with the predictions of main stem concentrations for segment 1 showing values within 61% to 102% of the actual value. Concentration predictions for segment 2 are not as promising with predicted values within 20% to 66% of the actual values. This is most likely because Zn, Cu, and Ni are easily desorbed and therefore the concentrations or 'signal' on stream pebbles do not faithfully record the watershed concentrations.

To further understand processes in segments 1 and 2, the mixing concentrations of Zn, Cu, Ni, and As in the surface water were calculated by multiplying the stream discharge fraction by the elemental concentration (Table 3). In segment 1, the tributary water accurately predicts the main stem water by $\pm 21\%$, however in segment 2, only the Ni and As concentrations are accurately predicted. While the water concentrations easily show mixing, they do not directly record the higher concentrations of metals that are found on the pebble leachate. For instance, the leachate concentrations for arsenic in segment 1 are 1080 ppb, 94.2 ppb, and 72.4 ppb for tributary A, tributary B, and the main stem. These values are between 200 and 4000 times larger than concentrations in the water, which suggests that the pebble oxide coatings are a better environmental tracer.

The two segments chosen for comparison each have an impaired stream, as presented by the Philadelphia Water Department (2009). In both segments, tributary A is the impaired stream, the lower discharge input, and the higher arsenic input. This suggests that the arsenic could be coming from the industrial point source locations and that the pebble successfully monitored the elements in these locations. However, we cannot exclude the possibility of a geogenic sources, but future studies could focus on this question.

Table 3
Pebble and water mixing data for segments 1 and 2 (as data shown in Fig. 5).

		Pebble				Water			
		Ni (ng/cm^2) ∗ Discharge fraction	Cu (ng/cm^2) ∗ Discharge fraction	Zn (ng/cm^2) ∗ Discharge fraction	As (ng/cm^2) ∗ Discharge fraction	Ni (ppb) ∗ Discharge fraction	Cu (ppb) ∗ Discharge fraction	Zn (ppb) ∗ Discharge fraction	As (ppb) ∗ Discharge fraction
Segment 1									
Trib A		169	438	1830	11.4	0.148	0.692	2.18	0.099
Trib B		370	1148	2278	1.85	0.646	1.40	5.33	0.214
Main stem	Actual	795	2596	4038	5.62	0.917	1.72	6.27	0.317
	Predicted	539	1586	4108	13.3	0.794	2.09	7.51	0.313
Segment 2									
Trib A		126	179	779	4.26	0.989	3.95	9.06	0.206
Trib B		3.22	6.76	<DL	24.4	0.301	0.380	1.804	0.050
Main stem	Actual	322	917	1183	12.7	1.42	10.8	15.7	0.276
	Predicted	129	186	779	28.7	1.29	4.33	10.9	0.256

4. Conclusion

The main objective of this study was to test the use of in-situ iron-manganese coated quartz pebbles to incorporate Zn, Cu, and Ni and As and then to begin to understand the distribution of concentrations in the watershed. Each of these elements had a significant relationship with the amount of iron coating the pebbles. The methods used in this study show initial promise in their usefulness for geochemical research though more studies on accumulation rates, substrate differences, reproducibility and leachate differences are necessary. The spatial distribution of Zn, Cu, and Ni differ from that of arsenic and we suggest this difference is due to elemental behavior and source. The source of arsenic in the Pennypack Creek is likely to be a mix of geogenic and anthropogenic dependent upon the location along the long axis of the stream. Concentrations of arsenic were sufficiently predicted by mixing of tributary streams with the main stem of the stream. Arsenic appears to be readily tracked using these coated pebbles and continued studies could further develop this method for other elements.

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