

**ARSENIC TRANSPORT IN GROUNDWATER, SURFACE WATER, AND THE
HYPORHEIC ZONE OF A MINE-INFLUENCED STREAM-AQUIFER SYSTEM**

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Abstract

We investigated the transport of dissolved arsenic in groundwater, surface water and the hyporheic zone in a stream-aquifer system influenced by an abandoned arsenopyrite mine. Mine tailing piles consisting of a host of arsenic-bearing minerals including arsenopyrite and scorodite remain adjacent to the stream and represent a continuous source of arsenic. Arsenic loads from the stream, springs, and groundwater were quantified at the study reach on nine dates from January to August 2005 and a mass-balance approach was used to determine hyporheic retention. Arsenic loading from the groundwater was the dominate source of arsenic to the stream, while loads from springs represented a substantial proportion of the total arsenic load during spring. Arsenic loads in surface and groundwater were significantly elevated during summer. Elevated temperatures during summer may lead to increased arsenic loading by increasing dissolution rate of arsenic source minerals and/or increases in microbially-mediated dissolution processes. The hyporheic zone was shown to be retaining arsenic in the upstream-most sub-reach. Retention most likely occurs through the sorption of dissolved arsenic onto hyporheic sediments. In downstream sub-reaches, hyporheic sediments are derived from mine-tailing piles which have high arsenic content. The hyporheic zone in these sub-reaches was shown to be releasing dissolved arsenic. The historic influence of mining activity has resulted in multiple sources of arsenic to the stream which has increased arsenic contamination of the surface waters.

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1. Introduction

Arsenic is a toxic trace element linked to numerous forms of skin, bladder, and lung cancer (NRC 1999). Because the primary source of human exposure is through contaminated drinking water (Smedley and Kinniburgh 2002), addressing transport and transformation of arsenic in stream-aquifer systems is vitally important to water quality concerns worldwide. In regions of India and Bangladesh, groundwater high in arsenic concentration results in exposure of millions of people to contaminated drinking water above the World Health Organization limit of $10 \mu\text{g L}^{-1}$ (Nickson et al. 2000). In the environment, naturally-occurring and anthropogenic sources of arsenic include geothermal regions (Moore et al. 1988, Welch et al. 1988, Nimick et al. 1998), arsenic-bearing sulfide deposits (Schreiber et al. 2000), poultry litter application (Garbarino et al. 2003, Brown et al. 2005), and industrial wastes (Spliethoff and Hemond 1996). Elevated arsenic concentrations in stream-aquifer systems are often associated with mining activity (Moore and Luoma 1990, Smedley and Kinniburgh 2002).

Arsenic mobility is strongly influenced by precipitation-dissolution, oxidation-reduction, and microbially-mediated reactions (Cullen and Reimer 1989, Nicholas et al. 2003). Previous work has shown high seasonality in arsenic concentrations in lentic (Aggett and O'Brien 1985, Anderson and Bruland 1991, Spliethoff et al. 1995) and lotic systems (McLaren and Kim 1995, Gault et al. 2003), and there is an apparent need for more research on seasonal shifts in arsenic concentration and transport (McLaren and Kim 1995).

It is estimated that more than 3,000 community water supplies will be in violation of the new EPA drinking water maximum contaminant level of $10 \mu\text{g L}^{-1}$ (Clifford and Ghurye 2002). Understanding the causes of arsenic contamination in both surface and groundwater requires evaluation of the hyporheic zone (Nagorski and Moore 1999), especially in anthropogenic aquifers where the conditions of the hyporheic zone may be altered (Hancock 2002). The hyporheic zone is widely recognized as a surface water – groundwater interface important to solute transport and transformation in stream-aquifer systems (Bencala 1993, Findlay 1995). Driven by channel morphology and head

gradients (Harvey and Bencala 1993), the hyporheic zone is defined as the subsurface volume beneath the streambed that contains greater than 10% recently advected surface water (Triska et al. 1989). The hyporheic zone is characterized by steep chemical gradients and can have pH and redox conditions not seen in the adjacent surface or groundwater. As nutrients and contaminants move through stream-aquifer systems, biogeochemical conditions in the hyporheic zone can influence chemical reactions that alter solute transport and transformation (Findlay et al. 1993, Valett 1993). Hyporheic processes have been shown to have a significant effect on the downstream transport of trace metals at the drainage basin scale (Harvey and Fuller 1998). Previous studies have shown the hyporheic zone to be both a source and sink of metals and metalloids (Benner et al. 1995, Harvey and Fuller 1998, Nagorski and Moore 1999). However, estimates of arsenic flux from the hyporheic zone have not been quantified, so while mechanisms of release have been elucidated, the effect of the hyporheic zone on reach-scale arsenic transport is still uncertain. One successful technique for quantifying reach-scale loads of dissolved organic matter (Wallis 1981), dissolved organic carbon (Fiebig 1995), and nitrate (Burns 1998) is the mass-balance approach. Although not previously applied to metals, this approach offers a useful technique for quantifying the transport of trace elements such as arsenic in surface water, groundwater, and the hyporheic zone. The goals of this research were to (1) quantify loads of dissolved arsenic entering and leaving a mine-influenced stream reach, (2) investigate the spatial and temporal variability in arsenic loading, and (3) use a mass balance approach to determine the role of the hyporheic zone in the transport and transformation of arsenic.

2. Study Site

The study site is a second-order headwater stream in Floyd County, VA adjacent to the abandoned Brinton Arsenic Mine (Figure 1). Arsenopyrite was mined for the production of arsenic, which included roasting the ore to generate arsenic trioxide. While the mine was in operation from 1903 to 1919, over 75 tons of arsenic trioxide were produced (Dietrich 1959). Heterogeneous mine tailing piles of roasted and unprocessed

ore remain at the site, adjacent to the stream. A host of arsenic-bearing minerals, including arsenopyrite and its weathering product scorodite, have been identified in the piles (Dove and Rimstidt 1985, Schreiber et al. 2004). Total arsenic concentrations in the surface soils range from 400 to over 70,000 ppm (Rocovich 1976).

The stream originates ca. 200 m upstream of the mine tailing piles where the catchment is forested with deciduous trees, and is relatively uninfluenced by the mine (Chaffin et al. 2005, Lottig 2005). Downstream in the mine-influenced reach, the stream flows adjacent to the tailing piles for approximately 45 m along which they form the northern bank of the stream. Further downstream of the piles, the stream flows through forested riparian zones. Mass wasting of the tailing piles during floods results in continuous scouring and replenishment of stream sediments. The stream has an average width of 0.74 m, an average depth of 4 cm, a slope of ca. 4%, and is characterized by sand and gravel sized sediment. There are very few pools and debris dams along the mine tailings area, which is devoid of vegetation. The stream discharges into Purgatory Creek ca. 1 km downstream of the mine and eventually flows into the Roanoke River.

Depth to water table in the unconfined alluvial aquifer varies from 0.1 m to 5 m. In the area of the mine tailings piles, the alluvial aquifer is shallow and is not insulated by soil or vegetation. Resistivity profiles indicate areas of high hydraulic conductivity associated with the mine tailings piles. Groundwater from the aquifer discharges to the stream, as shown by positive vertical hydraulic gradients (VHG) and dilution gauging. Three intermittent springs discharge to the stream along the study reach. Total spring discharge is usually less than 0.1 L/s and averages ca. 3% of stream flow.

Along the study reach, there is high spatial variability in arsenic concentrations both in surface and groundwater. Groundwater arsenic concentrations (200 to 18,000 $\mu\text{g L}^{-1}$) are orders of magnitude higher than stream water concentrations. Arsenic concentrations in surface water increase 50-fold along the study reach. Springs from the mine tailings piles typically have higher arsenic concentrations than groundwater. Subsurface arsenic concentrations can vary by an order of magnitude over a distance of 1 m in some locations.

3. Methods

3.1. Mass-balance Approach

The mass-balance approach requires quantification of surface water arsenic loads entering and leaving the study reach. In the absence of additional surface water inputs, the difference between these input and output loads is assumed to be the net groundwater load entering the stream. This net load incorporates arsenic load from both groundwater discharge and the hyporheic zone. Through the mass-balance approach, hyporheic influence is assessed by comparing net groundwater load to the gross groundwater load, which is derived from groundwater discharge and estimates of subsurface arsenic concentrations.

Arsenic loads were determined at a given boundary using the following equation:

$$L = [As] * Q \quad (1)$$

where [As] is arsenic concentration [$\mu\text{g L}^{-1}$] and Q is discharge [L s^{-1}]. All arsenic concentrations were measured directly from surface water and wells. Discharge was quantified by dilution gauging and flumes (See 3.2.2. Hydrologic Methods). Input loads to the study reach included upstream load, L_{up} , spring load, L_{spr} , and net groundwater load, L_{net} , which represented the combined groundwater and hyporheic zone loads (Figure 2). Because net groundwater load was based on direct measurements of surface water discharge and arsenic concentrations, this term had the highest accuracy and least variability and was used to compare spatial and temporal trends in groundwater arsenic loading. The output load from the study reach was the downstream load, L_{dwn} . Net groundwater load was calculated as the difference between surface output and input loads using equation 2:

$$L_{net} = L_{dwn} - L_{up} - L_{spr} \quad (2)$$

The overall mass balance equation is:

$$\Delta S = L_{gross} - L_{down} + L_{up} + L_{spr} \quad (3)$$

where ΔS is the hyporheic retention term, representing the change in mass of arsenic stored in the hyporheic zone over time, and L_{gross} , L_{down} , L_{up} and L_{spr} represent the gross groundwater load, stream load leaving the study reach, stream load entering the study reach and spring load entering the study reach, respectively (Figure 2). Gross groundwater load, L_{gross} , represents the input load of arsenic from the aquifer to the hyporheic zone. Although arsenic loads from the surface water to the hyporheic zone must also occur, the groundwater load was assumed to be the dominant load entering the hyporheic zone because groundwater arsenic concentrations were an order of magnitude larger than stream water counterparts. Gross groundwater load was determined using the following equation:

$$L_{gross} = [As_{gw}] * Q_{gw} \quad (4)$$

where $[As_{gw}]$ is the geometric mean of groundwater arsenic concentrations [$\mu\text{g L}^{-1}$] and Q_{gw} is groundwater discharge [L s^{-1}].

The load of arsenic either retained or released by the hyporheic zone was calculated using equation (5):

$$R = L_{gross} - L_{net} \quad (5)$$

where positive retention terms indicate net retention of arsenic from the hyporheic zone and negative retention terms indicate net release of arsenic in the hyporheic zone.

Hyporheic retention terms, R , were calculated individually for each sub-reach (see 3.3.1. Study Reach Division) and then summed to determine total hyporheic retention of the study reach.

This mass balance approach used to determine hyporheic retention assumed two conditions. The first assumption was that the hyporheic load that entered the stream did

not undergo biogeochemical transformations once it entered the water column and was transported conservatively downstream. Dissolved arsenic is unlikely to undergo sorption reactions in the water column as it has little interaction with solids. The second assumption was that all subsurface hyporheic flow had discharged to the stream by the end of the study reach.

Statistical analysis of the hyporheic retention term calculated from the mass-balance approach is not possible because gross and net groundwater loads contain multiple terms and are interrelated through the discharge term. Another quantitative method for examining the role of the hyporheic zone is through comparison of two independent measurements of groundwater arsenic concentrations: expected groundwater arsenic concentration based on net groundwater load and arsenic concentrations measured in groundwater wells. This approach is similar to that used by Kimball et al. (2002) who compared metal loads by comparing sampled inflow concentrations to concentrations derived from instream metal loads. Expected groundwater arsenic concentration was calculated using equation (6):

$$[As]_{net} = \frac{L_{net}}{Q_{gw}} \quad (6)$$

where $[As]_{net}$ represents the expected groundwater arsenic concentration of a given sub-reach and L_{net} and Q_{gw} represents the net groundwater load and groundwater discharge of that sub-reach. If the hyporheic zone does not affect arsenic transport, then measured mean groundwater arsenic concentration should match expected groundwater concentration ($[As]_{net}$). However, if observed and expected concentrations are vastly different, then either the hyporheic zone is influencing arsenic transport or there are substantial groundwater flows that were not accounted for. The role of the hyporheic zone in retaining or releasing arsenic was statistically analyzed by comparing the difference between natural log transformed data of mean groundwater arsenic concentration and expected groundwater arsenic concentrations within each sub-reach. This approach accounted for the largest source of variability in the mass balance which

was groundwater arsenic concentrations. If the measured and expected concentrations were significantly different within a sub-reach, then the hyporheic retention term of that sub-reach was assumed to be significant and was added to the reach-scale estimate. However, if there was no significant difference in concentrations within a sub-reach, then the hyporheic retention term was not included in the reach-scale estimate. The effects of hyporheic retention on the transport of arsenic were compared by calculating percent change of the gross groundwater load by dividing the hyporheic retention term by gross groundwater load within each sub-reach. Sub-reach estimates of net groundwater load (g d^{-1}) were converted to loads per meter stream length ($\text{g m}^{-1}\text{d}^{-1}$) by dividing net groundwater load by sub-reach length, which allowed for direct comparison of relative contributions among sub-reaches.

3.2. Hydrologic Characterization

3.2.1. Site Instrumentation

An arbitrary 0 m datum was established upstream of the mine by Chaffin et al. (2005). For this project, the study reach begins at a point of flow constriction 202 m downstream of the datum (Figure 1). The study reach ends at a flume located at 290 m. Along the 88 m study reach, the site is instrumented with over 60 wells installed to various depths below ground surface. The site was previously instrumented with 10 groundwater wells in the mine tailing piles and 10 shallow subsurface wells located in the stream channel and riparian zone (Schreiber et al. 2004). From July to October 2004, 20 additional wells were installed in the hillslope on both sides of the stream which were used to create water table maps. During the same time, 23 shallow subsurface wells were installed at depths varying from 0.2 to 0.7 m below the stream bed to delineate the depth of the hyporheic zone. Piezometers constructed of PVC pipes (1.3 cm OD) were installed to a depth of 30 cm below the stream bed at intervals of 5 m along the study reach to measure VHG (Valett 1993). All wells were surveyed in October 2004 and water level measurements from the stream and monitoring wells were used to create groundwater flow nets using Surfer[®] (Golden Software, Inc., Golden, Colorado).

A 1 ft H-flume (Tracom Inc., Alpharetta, GA) was installed downstream of the mine at 290 m. The flume was instrumented with a stilling well and Nomad data logger (Intech Instruments LTD., Auckland, New Zealand) to record stage every 15 min. In March 2005, a pressure transducer was installed in a monitoring well located in the mine tailings piles ca. 5 m from the stream channel. The pressure transducer recorded water level and temperature every 15 min. A temperature logger was installed below the water table at a depth of 0.55 below ground surface with a hand auger to compare the relationship between borehole temperature and groundwater temperature. This logger was installed ca. 1 m from the well with the pressure transducer and set to record temperature every 15 min from 27 August to 9 October 2005.

3.2.2. Hydrologic Methods

Under various discharge conditions, 15 preliminary tracer injections were conducted from March to December 2004, which were used to divide the study reach into hydrologically distinct sub-reaches (See 3.3.1. Study Reach Division). Initially chloride was used as a conservative tracer. However, high chloride concentrations in some wells prevented accurate assessments of percent surface water. A coinjection of Rhodamine WT (RWT; Kingscote Chemicals, Inc., Miamisburg, Ohio) and chloride was used to estimate stream discharge in July 2004. Estimates of stream discharge based on RWT and chloride were 1.52 and 1.46 respectively $L s^{-1}$, suggesting that errors due to RWT sorption are not a concern at the site. In all following injections, including those used to calculate loads, RWT was injected into the stream at a constant rate and allowed to reach plateau conditions along the study reach. Stream water and shallow subsurface wells were then sampled to delineate the hyporheic zone and to determine stream and groundwater discharge by dilution gauging. All samples were analyzed for RWT fluorescence in the laboratory on a Turner Designs model 10 AU field fluorometer (Turner Designs, Inc., Sunnyville, CA). Stream discharge at a given stream location was determined using the following equation:

$$Q_{str} = \frac{ABS_{inj} * Q_{pump}}{ABS_{str} - ABS_{bck}} \quad (7)$$

where ABS_{inj} is the absorbance of the injectate, Q_{pump} is the discharge of the pump [$L s^{-1}$], and ABS_{str} and ABS_{bck} represent the absorbance of the stream water under plateau conditions and background conditions, respectively, at a given point along the study reach. Groundwater discharge was determined by the dilution gauging method using the following equation:

$$Q_{gw} = Q_{dwn} - Q_{up} - Q_{spr} \quad (8)$$

where Q_{dwn} and Q_{up} represents stream discharge determined by dilution gauging at a given downstream and upstream point, respectively [$L s^{-1}$] and Q_{spr} represents spring discharge quantified volumetrically by measuring volume of water over time with a modified flume installed in the spring channel. Lateral inflow ($L m^{-1} s^{-1}$) was determined by dividing the groundwater discharge term by stream reach length.

Percent surface water was determined for each well sample using equation (9); any sample containing >10% surface water was considered hyporheic (Triska et al. 1989).

$$\%SW = \frac{ABS_{well} - ABS_{bck}}{ABS_{str} - ABS_{bck}} * (100) \quad (9)$$

where ABS_{well} and ABS_{str} represents the absorbance of the well sample and the absorbance of the surface water sample closest to the well under plateau conditions and, ABS_{bck} represents the background absorbance of water in the well or stream.

3.3. Application of the Mass-balance to the Study Reach

3.3.1. Study Reach Division

To apply the mass-balance approach, the study reach was divided into five sub-reaches based on hydrometric data (channel flow, lateral inflow, VHGs, water table maps) collected from March to December 2004 and subsurface arsenic concentrations measured in November 2004 (Table 1). Arsenic concentrations used in the division of the study reach were measured in existing shallow subsurface wells and in PVC (1.3 cm OD) piezometers installed at depths varying from 0.3 to 0.5 m below ground surface. Five meter sections with similar lateral inflow and VHGs were grouped together to form sub-reaches that also had similar groundwater flowpaths (Figure 3). Sub-reach divisions also grouped areas with similar subsurface arsenic concentrations and were positioned far enough downstream of springs to allow for complete mixing of the conservative tracer.

3.3.2. Mass-balance Instrumentation

Groundwater wells used in calculation of gross groundwater load were constructed of PVC (3.2 cm OD) and installed so that a 20 cm screened interval (slot size 254 μm) integrated depths varying from 0.35 to 0.75 m below stream-bed. Five preliminary, 24-hr injections of RWT were conducted (July – November 2004) under variable baseflow conditions, and tracer distributions in the subsurface were used to determine a maximum hyporheic zone depth of 0.35 m. Subsequent tracer injections were conducted to ensure that groundwater wells were placed outside of the hyporheic zone. A total of 34 paired wells was installed along the study reach with relatively consistent spacing within each sub-reach (Figure 3). Paired wells consisted of one well installed directly in the stream channel and one well installed no more than 0.5 m from the edge of the stream on the bank from which the dominate groundwater flow paths entered the stream. The number of wells apportioned to a sub-reach was proportional to the percentage of groundwater discharge received by that sub-reach with a minimum number of six wells per sub-reach. On 17 May 2005, seven additional wells were installed in sub-reach 4 to address additional groundwater flowpaths determined by groundwater flow nets and stream discharge profiles.

3.4. Sampling

Water samples for load calculations were sampled on 9 dates (ca. once a month) from January to August 2005 under baseflow conditions. Groundwater arsenic concentrations were determined for 6 – 13 groundwater wells in each sub-reach. During groundwater sampling, one well volume was purged (~140 mL) with a peristaltic pump and allowed to recharge. Then a hand pump was used to pump small volumes (<125 mL) into a trap; volumes were kept small to ensure sampling of proximate well water. A 10-mL syringe, purged with two syringe volumes, then was used to sample the trap. The remaining sample was used to determine percent surface water for each groundwater well sample; any sample containing >10% water recently advected from the surface channel (i.e., hyporheic water) was not used in the calculation of the gross groundwater load. Spring and stream water arsenic samples at each site were taken in duplicate with a 10-mL syringe. All stream water, groundwater, and spring water arsenic samples were filtered through a 0.45- μ m filter and acidified with trace-metal grade HNO₃ to pH < 2 in the field. Samples were analyzed in the laboratory for total dissolved arsenic using a Perkin Elmer Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) following EPA methods (EPA 1992).

3.5. Hyporheic Microcosms

Eighteen microcosms containing hyporheic sediments collected from the study reach during September 2005 were incubated with a mixture of surface water and groundwater to ascertain if sediments from the hyporheic zone would release or retain dissolved arsenic. Composite samples of sediment integrating depths 5 to 25 cm below the stream bed were collected from each sub-reach (n = 3/ sub-reach) plus a location upstream of the study reach, transported on ice and processed in the laboratory within 4 hours. Microcosms were constructed in 250-mL Erlenmeyer flasks with 200 g (150 cm³) of wet and drained sediment (sieved to <4.75 mm) and a 100-mL mixture of filtered (< 0.45 μ m) surface water (75 %) and groundwater (25 %) with a final arsenic concentration

of $885 \mu\text{g L}^{-1}$. Surface water was collected 10 m upstream of the study reach and groundwater was collected from a well installed in the alluvial aquifer adjacent to the stream. Initial dissolved oxygen (DO) and pH were recorded by direct measurement and initial dissolved arsenic concentration was measured in a water sample obtained by syringe. Flasks were capped with sponges to allow gas exchange and shaken at 100 rpm in a refrigerator (15°C). Microcosms were sampled for dissolved As, DO, and pH at 90 minutes and 24 hours. Samples were filtered through a $0.45\text{-}\mu\text{m}$ filter and acidified with trace-metal grade HNO_3 to $\text{pH} < 2$ and were analyzed in the laboratory for total arsenic using a Perkin Elmer Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS) following EPA methods (EPA 1992).

4. Results

4.1. Arsenic loads

4.1.1. Spatial variability of discharge and arsenic loading

Over the 9 sampling dates, stream discharge at the downstream boundary of the study reach varied from 1.1 to 3.6 L s^{-1} with a mean of $2.26 \pm 0.32 \text{ L s}^{-1}$ (mean \pm standard error; Figure 4a). Over the same period, upstream discharge varied from 0.6 to 2.7 L s^{-1} with a mean of $1.5 \pm 0.25 \text{ L s}^{-1}$. Mean spring discharge (sum of all three springs) was $0.07 \pm 0.02 \text{ L s}^{-1}$ which on average comprised only 3% of total discharge. Over the length of the reach, groundwater discharge represented 30% of total discharge inputs to the stream with a mean of $0.69 \pm 0.05 \text{ L s}^{-1}$. Within the reach, groundwater discharge was unevenly distributed among sub-reaches (Figure 5). On average, sub-reaches 2, 3, and 4 contributed 75% of total groundwater inputs to the study reach (Figure 5a). Mean groundwater discharge was highest in sub-reach 4 ($0.22 \pm 0.01 \text{ L s}^{-1}$). At the same time, sub-reach 5 contributed only 10% of total groundwater discharge. Mean groundwater discharge in sub-reach 1 was $0.11 \pm 0.02 \text{ L s}^{-1}$, 15% of total groundwater discharge.

Over the nine months of observation, the dominant arsenic source to the stream was the net groundwater load, which contributed $96 \pm 6.7 \text{ g d}^{-1}$ (Figure 4b). While the

study reach received 66% of its discharge from upstream, upstream load ($1.4 \pm 0.15 \text{ g d}^{-1}$) contributed only 1% of total arsenic inputs to the stream (Figure 6). Mean spring load was $16 \pm 3.0 \text{ g d}^{-1}$ (5 - 25% of total arsenic inputs). Downstream load leaving the study reach varied from 66 to 125 g d^{-1} . Mean downstream load was $113.4 \pm 6.40 \text{ g d}^{-1}$, representing a hundred-fold increase in arsenic load compared to upstream input.

Net groundwater load varied greatly among sub-reaches (Figure 7). Per unit stream length, net groundwater load of sub-reach 4 ($3.7 \pm 0.19 \text{ g m}^{-1} \text{ d}^{-1}$) was two-fold larger than sub-reach 3 and a hundred-fold larger than sub-reach 1 ($P < 0.0001$; Figure 7b). Sub-reaches 2 and 3 contributed 15 and 22% of total groundwater arsenic load (Figure 7a) and 22 and 21% of total groundwater discharge (Figure 5a), respectively. Sub-reach 4 contributed 57% of total groundwater arsenic load while contributing 31% of total groundwater discharge. The combined net groundwater load of sub-reaches 1 and 5 was 5.6 g d^{-1} which was less than 6% of total groundwater load. In May, an additional spring was noted to be discharging into the stream in sub-reach 4 at 254 m. Discharge could not be quantified at this spring because it was small and diffuse. Because of the elevated concentration of this source ($6000 \mu\text{g L}^{-1}$), discharges as small as 0.02 L s^{-1} could result in contributions of 10 g d^{-1} . Thus, it represented a potentially large load of arsenic to the stream. Because this load could not be quantified over time, it was incorporated into the mass balance as part of the net groundwater load.

4.1.2. Temporal variability of arsenic loading.

Average arsenic concentrations in groundwater, surface water, and springs increased two- to four-fold from winter to summer (Figure 8). Groundwater arsenic concentrations showed high variability in the summer compared to winter (coefficient of variation 0.89 and 1.1, respectively). On average, mean arsenic concentrations in springs were three times higher than groundwater and ten times higher than surface water concentrations.

Except for arsenic loads associated with springs, all loads were greater in summer than in winter, with loads increasing an average of 63% during this time (Figure 9).

From winter to summer, mean net groundwater load increased by 40 g d⁻¹ (P = 0.0123), and mean downstream load increased by 36 g d⁻¹ (P = 0.0155). While upstream load increased from winter to summer (P = 0.0064), it showed little seasonal variation over the course of the study with a range of less than 1 g d⁻¹ (Figure 9c). From spring to summer, mean net groundwater load increased by 26 g d⁻¹ (28%), while downstream load increased by only 6 g d⁻¹ (5%). Arsenic load from spring inputs in the spring season were more than twice that in other seasons (P < 0.0001), increasing by 15 g d⁻¹ from winter to spring, and then decreasing by 19 g d⁻¹ from spring to summer (Figure 9d).

4.1.3 Controls on Arsenic Loading

Net groundwater load showed a strong positive correlation with mean daily borehole temperature ($r^2 = 0.9107$, P = 0.0031, n = 6), with an increase of 2.9 g d⁻¹ per °C increase in borehole temperature while temperature varied from 7 to 20°C (Figure 10a). On average, mean daily borehole temperature was less than 0.5°C higher than mean daily groundwater temperature. Within season, there was no significant correlation between net groundwater arsenic load and downstream or groundwater discharge. When compared across seasons, net groundwater load showed a negative correlation with downstream ($r^2 = 0.6629$, P = 0.0076, n = 9) and groundwater discharge ($r^2 = 0.5623$ P = 0.02, n = 9; Figure 10b & c). Net groundwater load decreased with increasing water level elevation measured in the aquifer ($r^2 = 0.8457$, P = 0.027, n = 5; Figure 10c).

4.2. Arsenic in the Hyporheic Zone

4.2.1. Hyporheic Retention Terms

In general, measured arsenic concentrations in groundwater were similar to expected groundwater arsenic concentration derived from net groundwater load (Equation (9); Figure 11). On three sampling dates (June – August), measured mean groundwater arsenic concentrations were higher than expected groundwater arsenic

concentrations by an average of $840 \pm 74 \mu\text{g L}^{-1}$ in sub-reach 1 ($P < 0.05$). In May, measured groundwater concentration in sub-reaches 4 and 5 were lower than expected concentrations by 1800 and $460 \mu\text{g L}^{-1}$, respectively (P values = 0.0048 and 0.0081, respectively), while measured concentrations were only $23 \mu\text{g L}^{-1}$ greater than expected concentrations in sub-reach 1 ($P = 0.44$).

Reach-scale hyporheic retention in May 2005 was -33 g d^{-1} , suggesting that the hyporheic zone was a source of arsenic to the stream. During this time, reach-scale retention was dominated by release in sub-reach 4 (-30 g d^{-1}), representing 90% of the total release from the hyporheic zone (Figure 12a). From June to August 2005, the hyporheic zone was retaining arsenic as mean hyporheic retention for the study reach was $4.7 \pm 0.37 \text{ g d}^{-1}$ (Figure 12). Sub-reach 1 accounted for 100% of the hyporheic retention along the study reach as no other sub-reach retention terms were significant during this time. While the hyporheic zone in sub-reach 1 minimally affected reach-scale arsenic transport reducing the total gross groundwater load entering the study reach by less than 5%, it retained a large proportion of gross groundwater load entering in that sub-reach. The hyporheic zone was retaining 37% of gross groundwater load from sub-reach 1 in May, while in June it retained nearly 100%. By August, retention had declined to 76% in sub-reach 1.

4.2.2. Hyporheic microcosms

Sediments in the microcosms were exposed to conditions similar to the hyporheic zone in terms of biogeochemistry and source waters. Microcosm DO and pH were similar to those measured in hyporheic wells ($n = 11$). In the microcosms, mean DO and pH was 5.8 mg L^{-1} and 6.8, respectively, while in the hyporheic zone, DO varied from 3.6 to 6.5 mg L^{-1} and pH varied from 6.4 to 7.0. Arsenic concentrations increased in microcosms from four of the five mine-influenced sub-reaches following the 24-hour experiment (Figure 13). The average increase in mass of arsenic in the four increasing microcosms was $0.28 \mu\text{g As cm}^{-3}$ sediment. Following the 24-hour incubation, arsenic concentrations in microcosms from sub-reach 2 were not significantly different from

initial concentrations ($P = 0.26$) while concentrations in microcosms of sub-reaches 3 – 5 were significantly different ($P < 0.05$). Beginning with microcosms of sub-reach 2, arsenic release from microcosms of subsequent downstream sub-reaches increased with distance downstream. In contrast, microcosms from the upstream reference and sub-reach 1 consumed arsenic (Figure 13b). In sub-reach 1, mass of arsenic declined over 24 hours by $0.15 \mu\text{g As cm}^{-3}$ sediment ($P = 0.049$), a decrease of 36%. Over the course of the experiment, mass of arsenic in microcosms from upstream of the study reach declined by $0.30 \mu\text{g As cm}^{-3}$ sediment ($P = 0.0002$), a decrease of 58%.

5. Discussion

5.1. Sources of arsenic to the stream

The combination of the naturally-occurring arsenopyrite ore and the historic influence of mining activity has resulted in multiple sources of arsenic to the study reach. The alluvial aquifer adjacent to the stream, made up of mine tailings and regolith, contains various arsenic bearing minerals, including arsenopyrite, scorodite, and arsenic-rich iron hydroxides. Dissolution and oxidation of these minerals releases arsenic to groundwater over time. Aquifer sediments release arsenic to groundwater through dissolution of different source minerals including arsenopyrite and scorodite (Sengupta et al. 2004, Oremland and Stolz 2005, Saunders et al. 2005). Groundwater inflow is an important component of arsenic loading to the stream accounting for over 80% of total arsenic inputs to the stream in this study.

Springs contributed little to total discharge to the stream, but due to high arsenic concentrations, springs contributed a large proportion (5 – 25%) of overall arsenic load to the stream. Because spring loads enter the stream directly, arsenic from this source is relatively uninfluenced by hyporheic processes.

The limited input of arsenic from upstream results from the focused source of arsenic localized to the mine tailings area. Arsenic concentrations in surface waters are below detection upstream of the mine tailings piles (Lottig 2005). If there is a source of

arsenic upstream of the mine, dilution or adsorption onto sediments would result in natural attenuation.

5.2. Variability in Arsenic Loading

The high spatial variability of groundwater arsenic inputs along the study reach may be explained by the variability of arsenic concentrations of mine tailings sediments. Total arsenic concentrations of sediments at the Brinton mine site vary greatly depending location of sediments (Rocovich 1976). The mine tailings along the study reach are made of three distinct piles containing ore of different size classes and at various processing states. Differential weathering rates of minerals in these piles may result in the heterogeneity in net groundwater load between sub-reaches. Sources with relatively higher groundwater discharge are expected to contribute an equivalent proportion to net groundwater load (Kimball et al. 2002). In sub-reaches 1 and 5 groundwater and arsenic inputs were similar. While sub-reaches 2 and 3 contributed equivalent proportions of groundwater discharge and groundwater arsenic load, sub-reach 4 contributed an arsenic load disproportionate to its discharge. The incorporation of the spring at 254 m into net groundwater load contributes to the larger groundwater arsenic inputs in sub-reach 4.

Spring load varied greatly over the course of the study. Even though spring arsenic concentrations were highest in summer, spring load was lowest in this season because of low discharge during this time. Maximum spring load occurred in the spring season when discharge was high and arsenic concentrations were elevated. At the site, springs can be intermittent sources of arsenic as some springs are not present during the summer. Because spring discharge is highly responsive to changes in water table elevation, storm events will affect spring load.

5.3. Controls on Arsenic Loading to the Stream

Arsenic loads in surface and groundwater were elevated in summer. Others have shown that riverine arsenic concentration and load are higher in summer, although the

causal mechanism was unclear (McLaren and Kim 1995). Over the course of this study, increases in load were not due to increased discharge, because we documented a negative relationship between discharge and net groundwater load. While increased discharge may lead to increased transport of particulate arsenic (Pettine et al. 1992), increases in discharge did not increase dissolved arsenic loads in our study. The load of dissolved arsenic released to the stream is more likely controlled by dissolution rate of source minerals in the alluvial aquifer. The best predictor of net groundwater load was mean daily borehole temperature, which accurately represented mean daily groundwater temperature in the shallow alluvial aquifer. Higher groundwater temperatures have been associated with higher arsenic concentrations (Nadakavukaren et al. 1984, Armienta et al. 2001, Arnorsson 2003). Increased groundwater temperatures may increase arsenic concentrations through enhanced microbial activity and/or dissolution of arsenic from source minerals. Seasonal changes in arsenic concentration have been attributed to microbial activity (Andreae 1979, Howard et al. 1995), with increased arsenic concentrations observed in summer (Howard et al. 1988, Sohrin et al. 1997). The gradual establishment of conditions favorable to microbial growth from winter to summer may promote increases in microbially-mediated release of sediment-bound arsenic in the aquifer resulting in higher loads in summer. Alternatively, increases in temperature may cause an increase in dissolution rate of arsenic-bearing minerals, which has been shown for scorodite (Harvey and Schreiber 2004). In addition, increases in temperature may affect dissolution reactions indirectly through changes in redox state or increases in the size of microbial communities (McLaren and Kim 1995).

5.4. Hyporheic Retention vs Release

In May, hyporheic retention was negative at the study reach scale indicating that the hyporheic zone increased the load of arsenic received by the stream, while from June to August hyporheic retention was positive suggesting that the hyporheic was acting as a sink for arsenic. Most of the differences in gross and net groundwater load within a sub-reach were not significant. High variability of groundwater arsenic concentrations makes

it difficult to determine small differences in net and gross groundwater load. Nevertheless, this variability was accounted for in the significant differences between observed and expected arsenic concentrations, which indicate substantial retention of groundwater load in the hyporheic zone of sub-reach 1 and release of arsenic in the hyporheic zone of sub-reaches 4 and 5.

5.4.1. Hyporheic Retention

Two possible causes of gross groundwater load being larger than net groundwater load in sub-reach 1 are: (1) there has been retention of the solute in that sub-reach or (2) there are unsampled inflows with lower concentrations (Kimball et al. 2002). The possibility of significant unsampled inflows of low concentration in sub-reach 1 is unlikely given the extent of well coverage. The order of magnitude difference between expected and observed concentrations suggests the hyporheic zone was acting as a sink for arsenic in this sub-reach.

Hyporheic retention in sub-reach 1 is most likely associated with sorption of dissolved arsenic on hyporheic sediments. Arsenic sorption, often associated with iron oxides, is strongly influenced by pH, redox conditions, and presence of competing anions (Tadanier et al. 2005). In general, oxic conditions promote retention of dissolved arsenic on solid surfaces through sorption reactions (Devitre et al. 1991, Manning and Goldberg 1997, Dixit and Hering 2003). Results of the microcosm experiments support the possibility of hyporheic retention in sub-reach 1 as there were significant decreases in arsenic concentration over time. These observations suggest that dissolved arsenic can become sorbed onto hyporheic sediments from sub-reach 1. Based on microcosm results, the hyporheic zone in sub-reach 1 could retain 1 g d^{-1} assuming hyporheic depth of 0.35 m and width of 1.1 m which is similar to estimates produced by the mass balance. Sediments from upstream of the mine-influenced reach also showed the ability to retain dissolved arsenic. Because the reference reach has arsenic concentrations below detection, upstream sediments have had little exposure to arsenic and a high potential to

sorb arsenic. This resulted in hyporheic sediments from upstream retaining twice as much arsenic per gram sediment compared to sediments from sub-reach 1.

5.4.2. Hyporheic Release

With the mass balance approach, causes of net groundwater load being smaller than gross groundwater load include release of arsenic from the hyporheic zone or unsampled inflows of higher concentrations (Kimball et al. 2002). Sub-reach 4 was the most extensively instrumented sub-reach, with 13 wells used to sample groundwater arsenic concentration. However, the spring load at 254 m represented an unsampled inflow in this sub-reach. Accounting for this spring load as a surface water input instead of a groundwater input potentially could have resulted in a 60% reduction in the hyporheic retention term of sub-reach 4. If this load was accounted for in the mass-balance, the reach scale hyporheic retention term would be ca. -18 g d^{-1} instead of -33 g d^{-1} . This suggests that with the spring included, the hyporheic zone was still a source of arsenic, but on a smaller scale.

The release of arsenic from hyporheic sediments in sub-reaches 4 and 5 could occur via reductive dissolution of iron oxides under anoxic conditions (Brannon and Patrick 1987, Masscheleyn et al. 1991, Harvey et al. 2002). Arsenic release could also be caused by desorption of weakly bonded arsenic through ion exchange or more strongly bonded arsenic through pH change or competitive anion sorption (Tadanier et al. 2005). Due to the high DO and circumneutral pH observed in the hyporheic zone throughout the study reach, reductive dissolution is not a likely mechanism of arsenic release. However, microcosm experiments support the possibility of hyporheic release of dissolved arsenic in sub-reaches 4 and 5. Anoxic conditions necessary for reductive dissolution were not observed during the experiment, yet release of dissolved arsenic in microcosms of sub-reaches 2 – 5 still occurred. The most likely cause of arsenic release in microcosms was release of weakly bonded species from mineral surfaces, which is suggested by results of sequential extractions conducted on sediments from the site (Basu 2005). Based on microcosm results, the hyporheic zone along the study reach could be releasing 10 g d^{-1} ,

which is similar in magnitude to estimates produced by the mass balance for the study reach if the spring load at 254 m is accounted for in sub-reach 4.

5.5. Influence of Floods on Hyporheic Processes

Floods affect hyporheic retention of arsenic by transporting sediments from mine tailing piles to the stream and by decreasing hyporheic zone water residence time. Lottig (2005) classified floods for the study site as discharges exceeding 8 L s^{-1} which was the discharge necessary to move 50% of the benthic surface. Mass wasting of mine tailing piles during floods results in deposition of large volumes of arsenic-rich sediment in the stream. Stream and hyporheic sediments in the mine-influenced reach have high total arsenic concentrations varying from 2.6 to 5.2 g kg^{-1} (Valenti et al. 2005) and are likely derived from the mine tailing piles. Thus, floods represent a continuous source of arsenic-rich sediments to the stream which may release dissolved arsenic once incorporated in the hyporheic zone. Burial of arsenic-contaminated sediments in the hyporheic zone and lake sediments and subsequent reductive dissolution has been suggested as a possible source of dissolved arsenic to overlying surface waters (Bright et al. 1994, Nagorski and Moore 1999).

5.5.1 Sediment Transport

Sediment transport during floods provides relatively “clean” upstream sediments to sub-reach 1. These “clean” sediments have high sorption potential, resulting in significant hyporheic retention in this sub-reach. Although sub-reach 1 is adjacent to mine tailing piles, hillslope sediments in this sub-reach remain intact during floods and are relatively stable compared to other sub-reaches. Thus, most hyporheic sediments in this sub-reach appear to be derived from upstream of mining influences and have a high potential to sorb arsenic.

Recent floods may promote hyporheic retention by supplying upstream sediments to sub-reach 1. As time after a flood progresses, sorption sites on sediments may

eventually become filled resulting in conservative transport or release of arsenic in the hyporheic zone. Before sampling in May, there had been little deposition of new upstream sediments in sub-reach 1 due to absence of a recent (>29 days) flood. Therefore, hyporheic sediments may have had limited sorption capacity due to long-term exposure to groundwater arsenic, resulting in no significant retention of dissolved arsenic at that time. However, in between the May and June sampling, a flood resulted in a large amount of sediment deposition in sub-reach 1, leading to significant hyporheic retention in June. During subsequent months, the percentage of gross groundwater load retained by the hyporheic zone declined, suggesting that as time progressed, sorption sites on hyporheic sediment were filled. In the absence of mining activity, hyporheic sediments would have been derived from upstream sediments resulting in natural attenuation through greater retention of dissolved arsenic in both short- and long-term time scales.

5.5.2. Hyporheic Residence Time

Floods can alter not only the size and composition of the hyporheic zone, but also water residence times and exchange rates (Wondzell and Swanson 1999). A reduction in both size and water residence time of the hyporheic zone may have decreased the capacity for hyporheic transformation of groundwater-derived arsenic. With three large floods in late summer and fall of 2004, Lottig (2005) noted concomitant decreases in fine sediments and transient storage parameters representing the size of the hyporheic zone and the percentage of travel time due to the hyporheic exchange (Runkel 2002) along the study reach. Transient storage parameters estimated in July of 2004 and 2005 under baseflow discharge of 0.8 L s^{-1} showed a decrease of 51% in the size of the hyporheic zone and a 31% decrease in travel time due to hyporheic exchange. Human influence has been suggested to have potentially permanent effects on the size and function of the hyporheic zone (Wondzell and Swanson 1999, Hancock 2002). The combined effects of historic mining activity and floods may have differentially affected the mine-influenced reach as similar decreases in size and water residence time of the hyporheic zone in the reference reach were not seen (Lottig 2005). While pre-flood estimates of hyporheic

retention are not available, the effect of these floods on hyporheic residence time may have reduced the influence of the hyporheic zone on transport of groundwater arsenic.

6. Conclusions

A mass-balance approach was used to quantify arsenic loading to a mine-influenced stream and to estimate retention of arsenic in the hyporheic zone. At the study site, heterogeneity of arsenic in sediments results in high spatial variability of arsenic loading to the stream. While groundwater inputs constitute a large proportion of total arsenic load, spring load may alter downstream export depending on season. In general, arsenic loads in surface and groundwaters are higher during summer despite lower discharge, suggesting that arsenic release may be enhanced by mineral dissolution and/or microbial activity at higher temperatures.

There are many potential controls on hyporheic retention of redox-sensitive elements such as arsenic, such as hyporheic zone residence time and biogeochemical conditions including DO, pH, temperature, and oxidation-reduction potential. In this study, both the mass-balance and microcosm experiments suggest that within the mine-influenced reach the hyporheic zone acts as a source of arsenic to the stream within some sub-reaches. The source of release is likely desorption of arsenic from hyporheic sediments. The mine tailing piles supply arsenic-rich sediments to the stream and hyporheic zone during floods, which may enhance release of dissolved arsenic to the stream in some sub-reaches. In contrast, transport of upstream sediments to the study reach could result in hyporheic retention of arsenic as observed in the upstream most sub-reach. The effects of floods in combination with the historic influence of mining may have reduced the capacity for natural attenuation of arsenic in the hyporheic zone by decreasing hyporheic residence time and by scouring and depositing arsenic-rich mine tailings which subsequently release dissolved arsenic. These natural and anthropogenic alterations in physical and biogeochemical parameters of the hyporheic zone have resulted in increased loading of arsenic to the stream.

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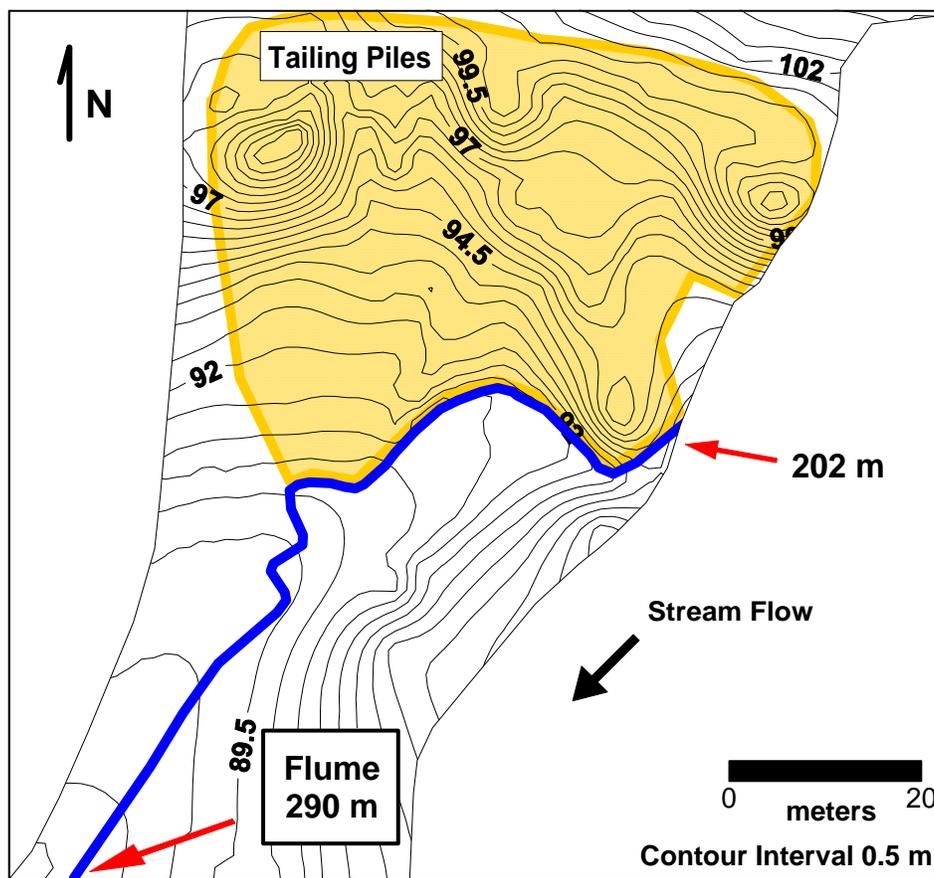


Figure 1. Topographic site map showing the start (202 m) and end (290 m) of the study reach. The spatial extent of the mine tailings pile is represented by the shaded area. Topographic relief (meters above a reference datum) was surveyed with a total station in October 2004.

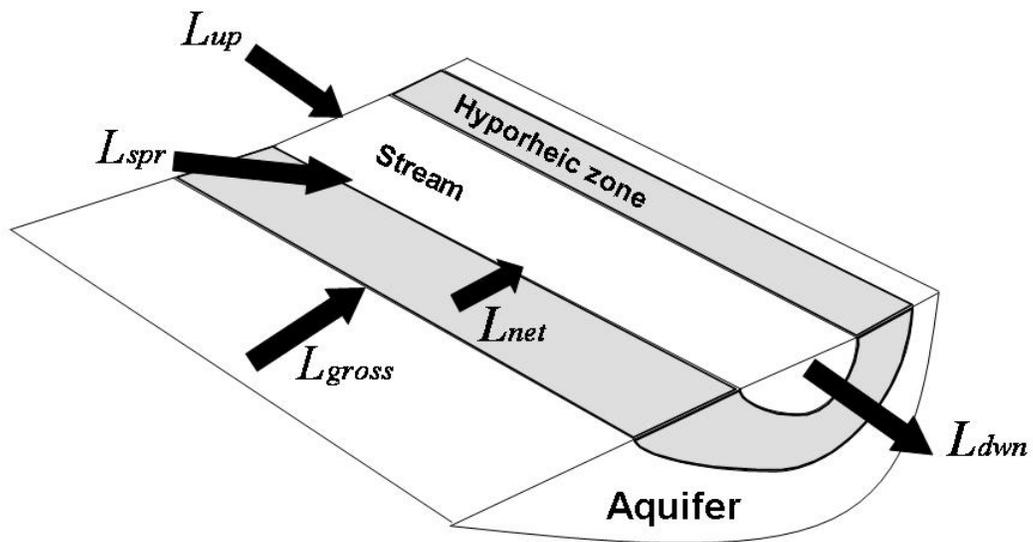


Figure 2. Compartment diagram depicting loads quantified through the mass-balance approach. All loads were measured empirically except for L_{net} which was determined by difference between surface water outputs and inputs.

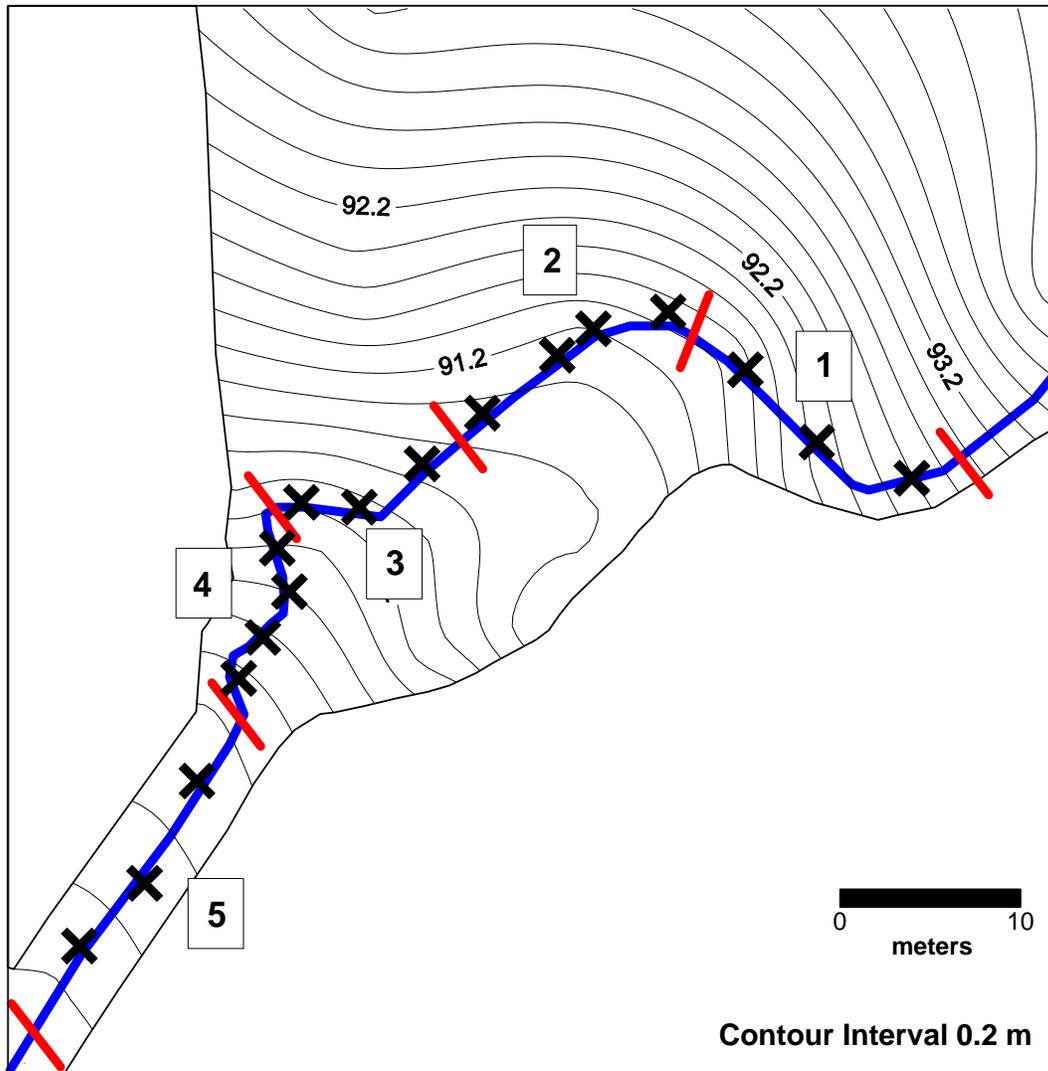


Figure 3. Water table map (meters above a reference datum) used in division of study reach (October 2005) and location of groundwater wells used in calculation of gross groundwater load. Each symbol represents location of a well pair (channel and bank). The seven additional wells installed in sub-reach 4 (May 2005) are not shown.

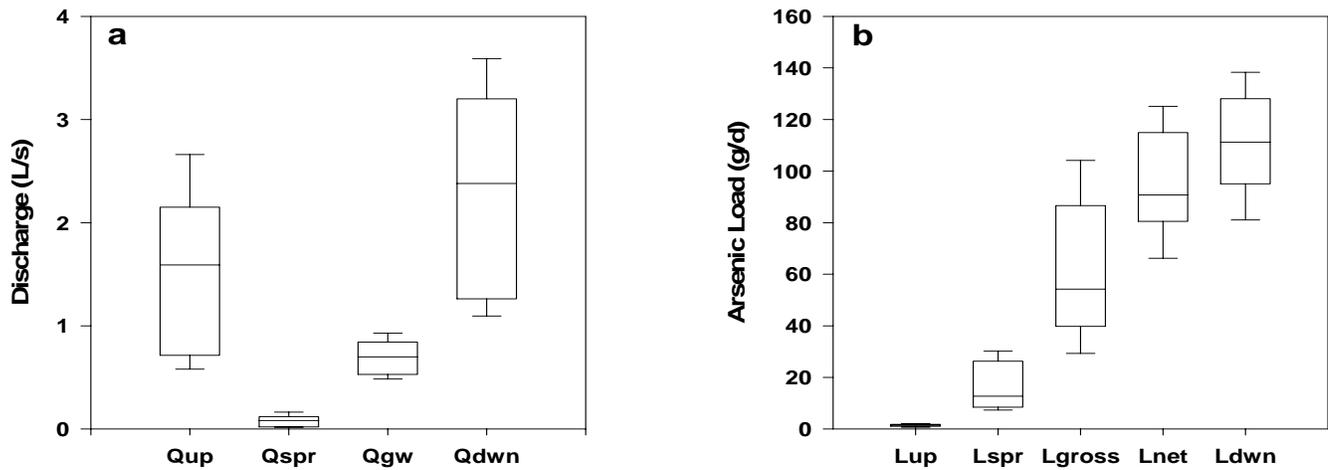


Figure 4. Boxplots of discharge (a) from upstream (Q_{up}), springs (Q_{spr}), groundwater (Q_{gw}), and downstream (Q_{dwn}) and arsenic load (b) from upstream (L_{up}), springs (L_{spr}), gross groundwater load which represents the groundwater load from the aquifer (L_{gross}), net groundwater load which represents the combined groundwater and hyporheic zone load (L_{net}), and downstream (L_{dwn}) from the nine sampling dates.

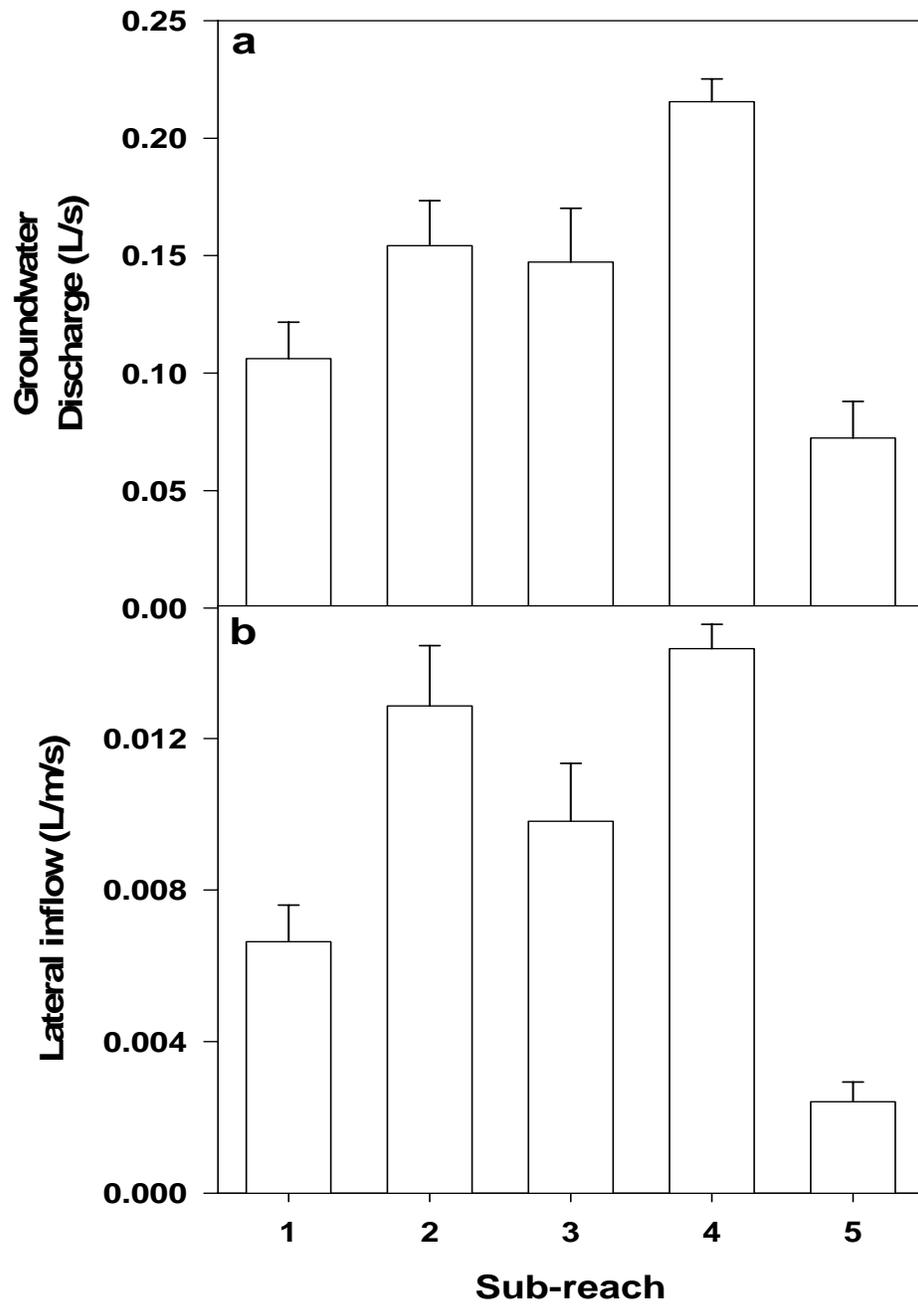


Figure 5. (a) Mean groundwater discharge of the five sub-reaches in the study reach from the nine sampling dates. (b) Mean lateral inflow of the five study reach sections. Error bars indicate standard error.

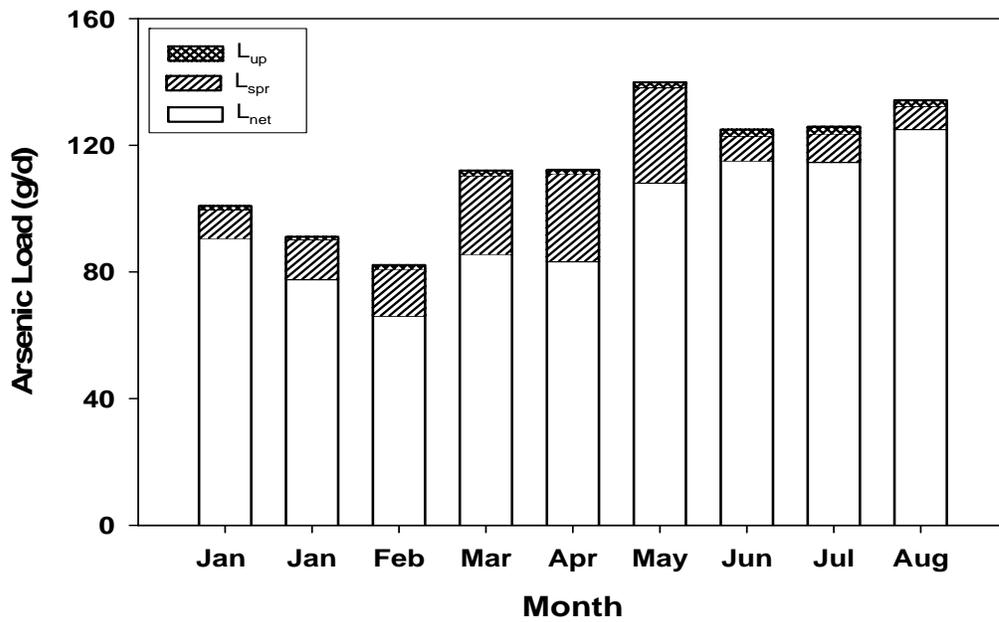


Figure 6 Arsenic inputs to the study reach from net groundwater, spring, and upstream load over the nine sampling dates.

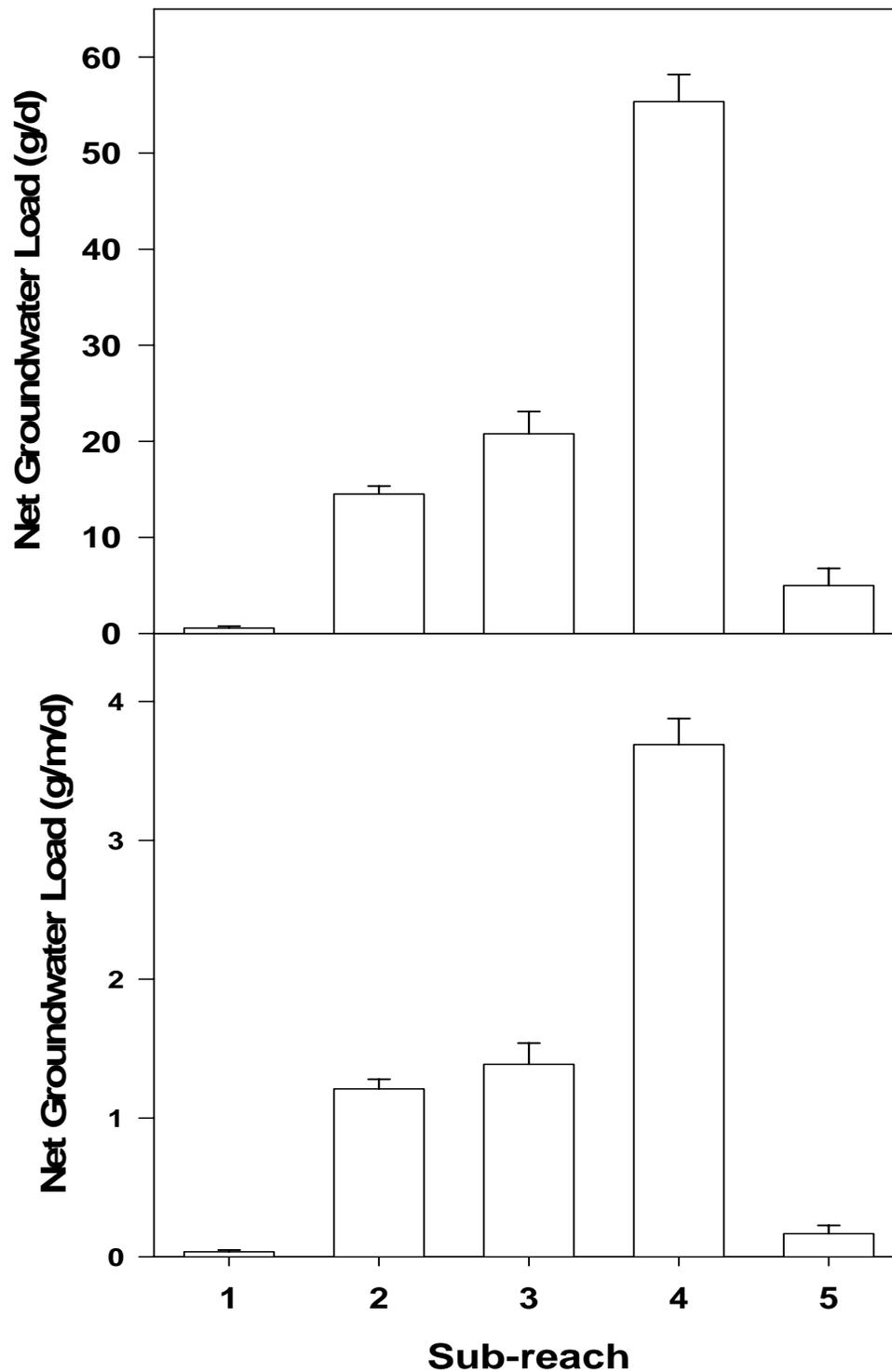


Figure 7. (a) Mean net groundwater load and (b) mean net groundwater load per meter stream length of the five sub-reaches. Error bars indicate standard error. Different letters in b indicate statistically significant differences among sub-reaches following Fisher's LSD ($\alpha < 0.05$).

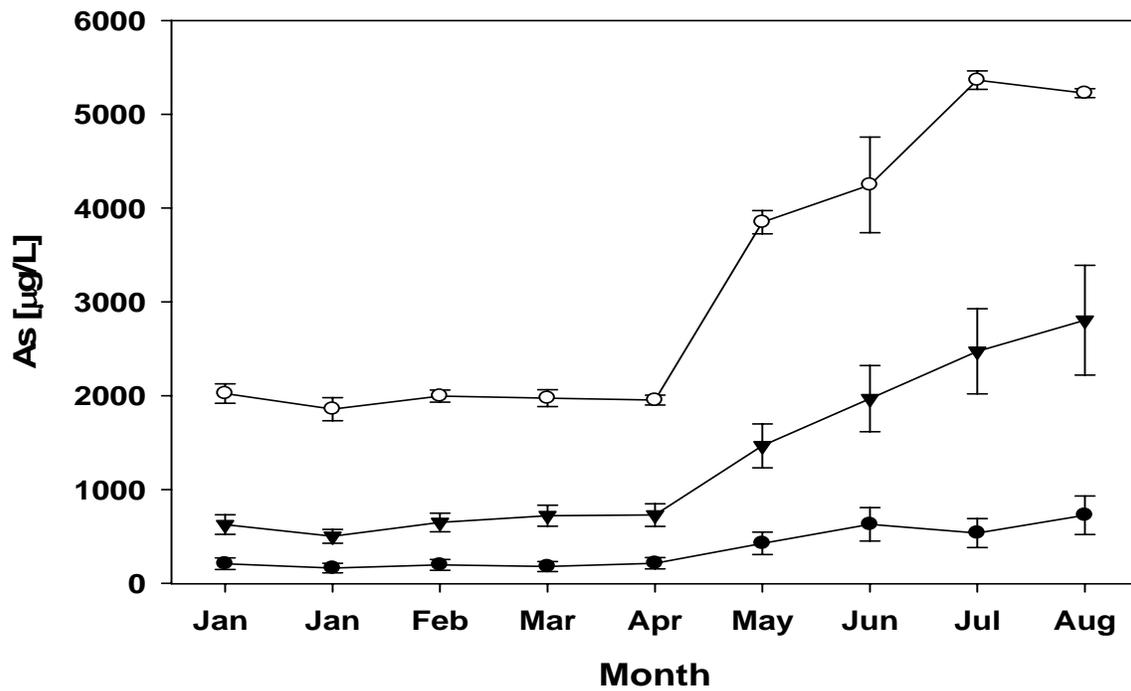


Figure 8. Mean arsenic concentrations of all sampling sites from surface water (●), groundwater (▼) and springs (○) over the nine sampling dates. Error bars indicate standard error.

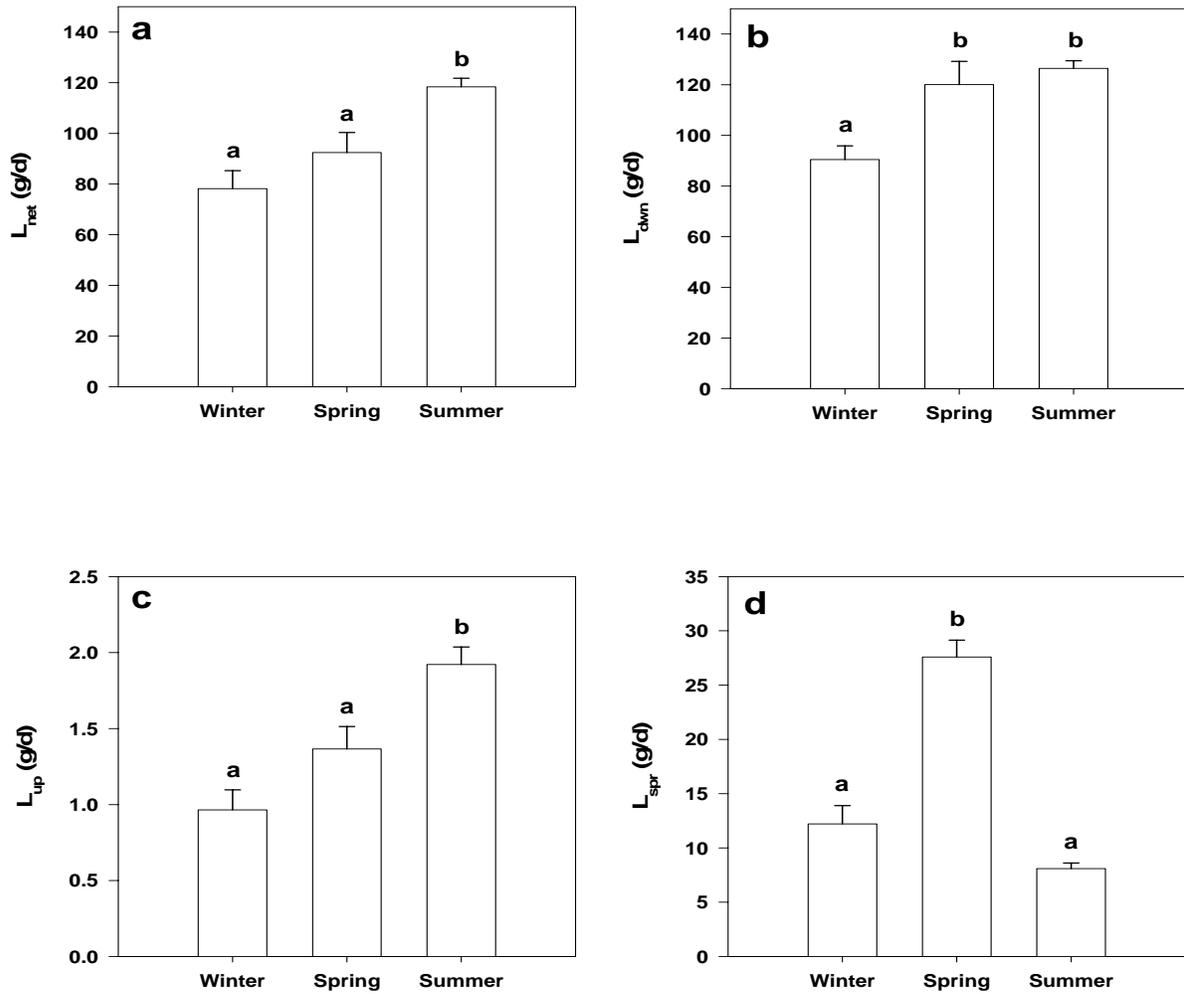


Figure 9. Seasonal means + SE of net groundwater load (a), downstream load (b), upstream load (c), and spring load (d). Within plots, columns with different subscripts are significantly difference following Fisher's LSD ($\alpha < 0.05$).

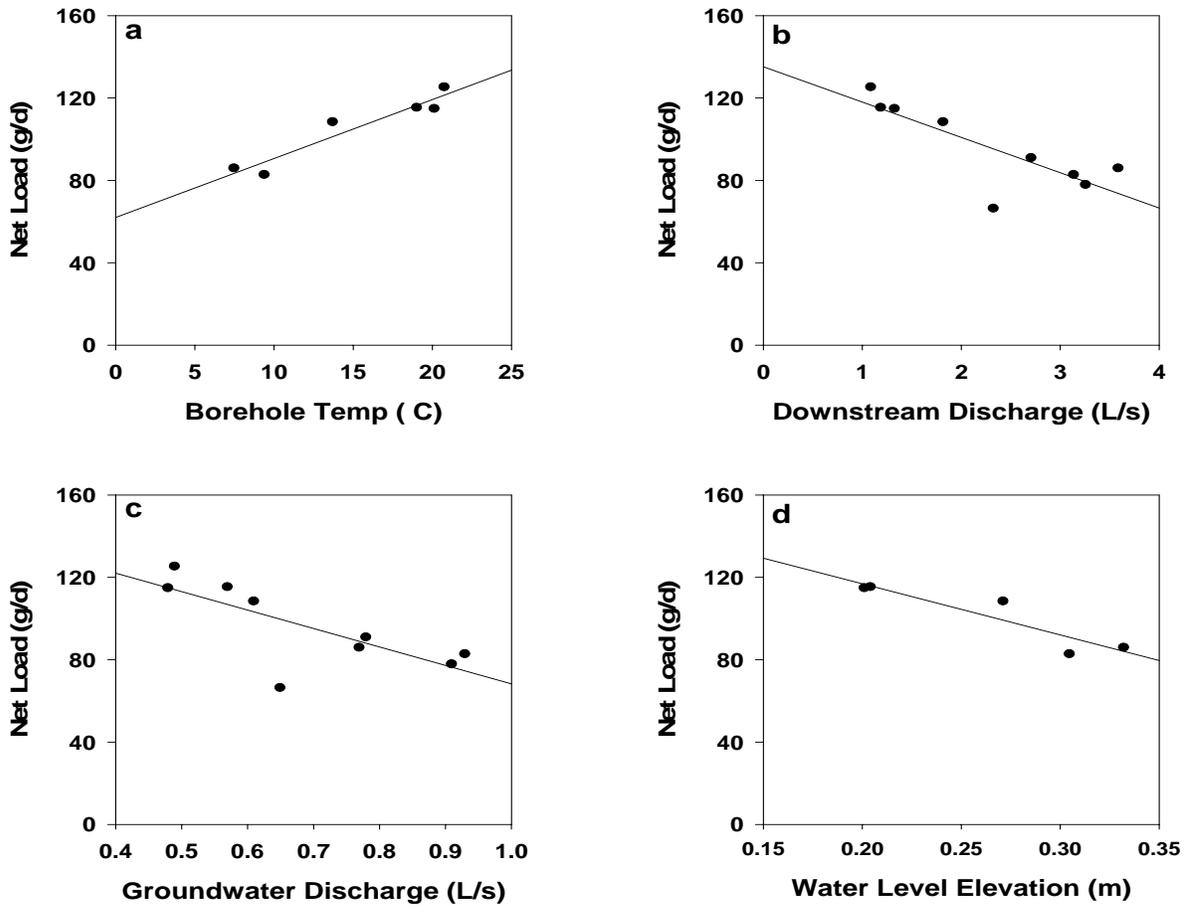


Figure 10. Linear regressions of net groundwater load and (a) mean daily borehole temperature, (b) downstream discharge, (c) total groundwater discharge, and (d) water level elevation relative to an established datum.

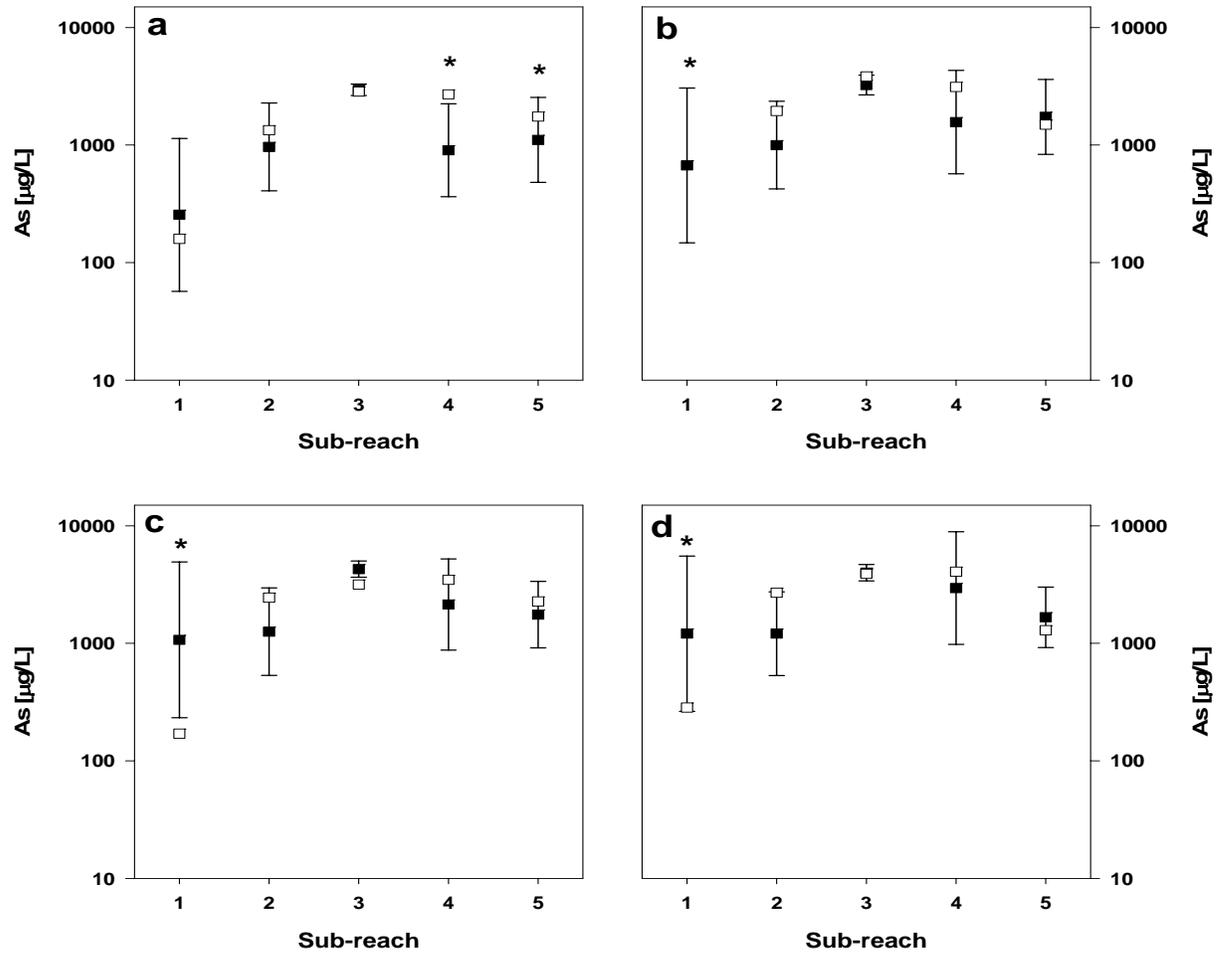


Figure 11. Measured geometric mean groundwater arsenic concentrations (■) and expected groundwater arsenic concentration (□) based on net groundwater load for each sub-reach samples in May (a), June (b), July (c), and August (d) 2005. Error bars show upper and lower standard deviation calculated from natural log transformed data. * Indicates significant differences between measured mean and expected groundwater arsenic concentrations in that sub-reach. Expected concentration for sub-reach 1 in June was zero and is not shown.

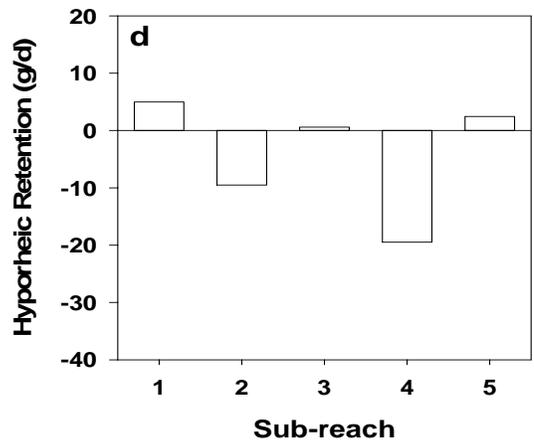
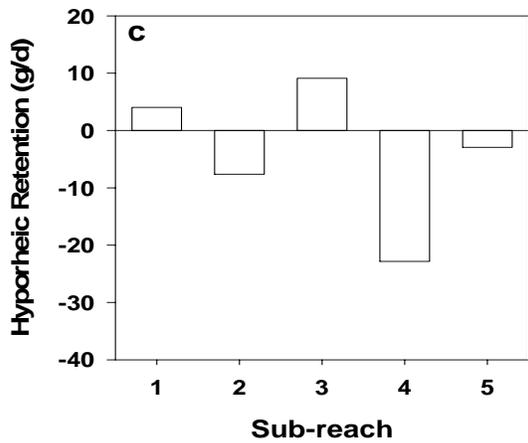
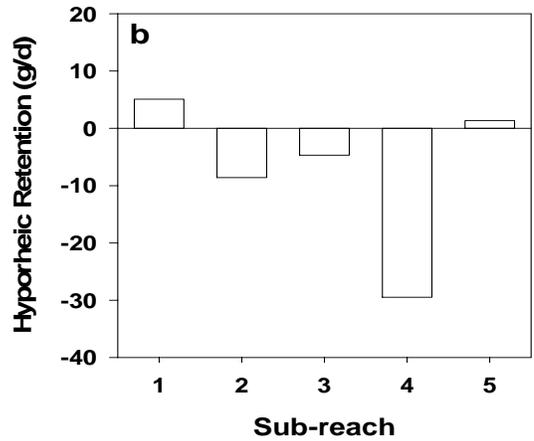
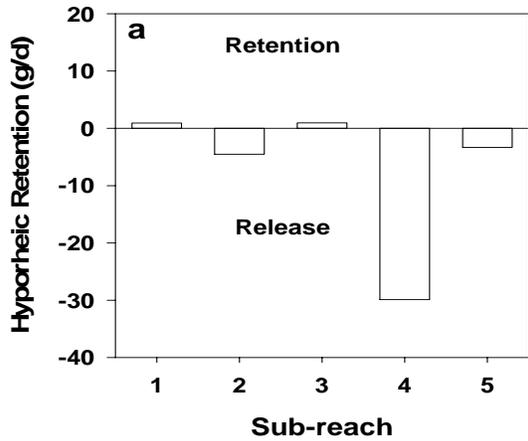


Figure 12. Hyporheic retention terms for the five sub-reaches in May (a), June (b), July (c), August (d). Positive values indicate hyporheic retention and negative values indicate hyporheic release.

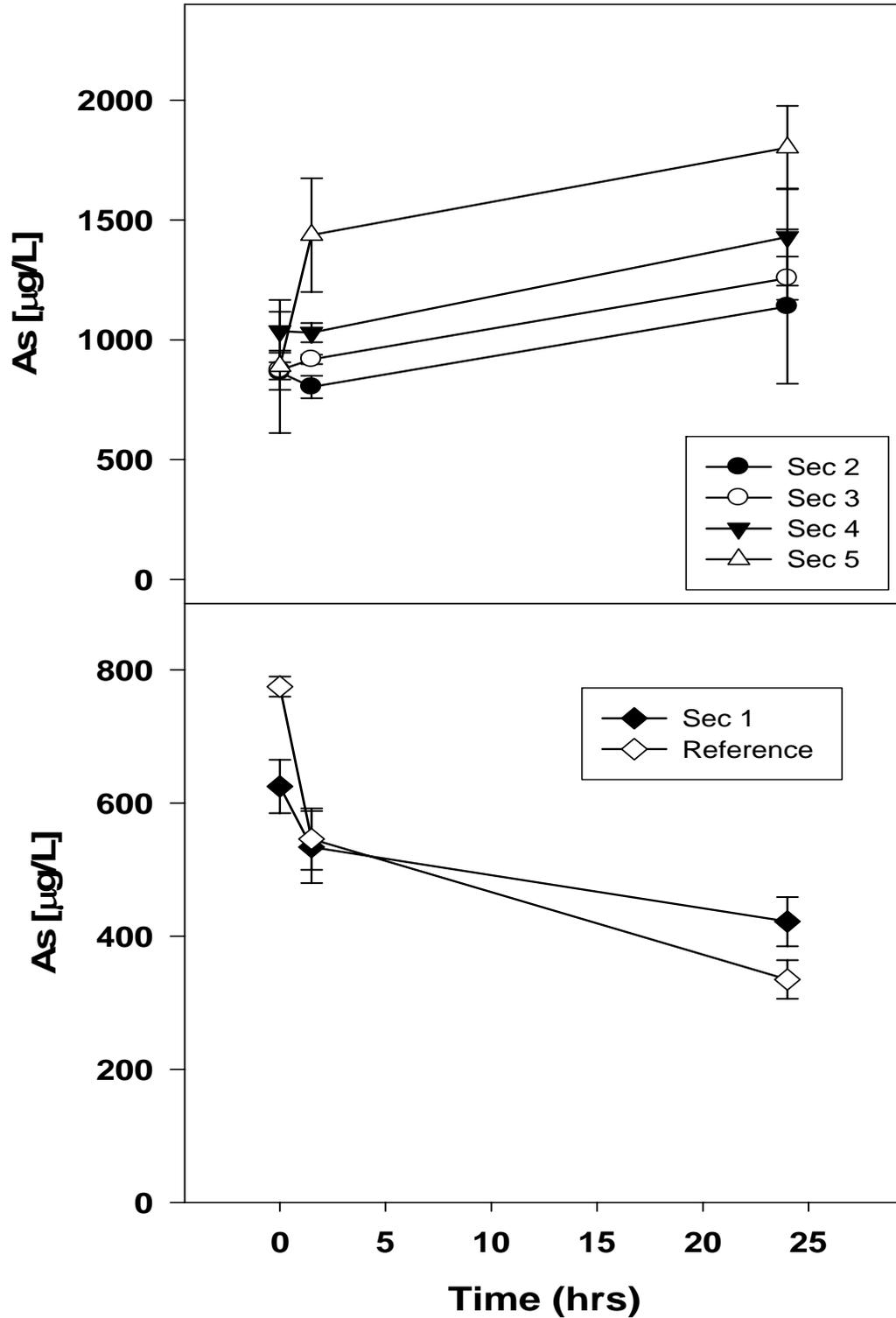


Figure 13. Dissolved arsenic concentrations in hyporheic microcosms from (a) sub-reaches 2 - 5 and (b) from sub-reach 1 and upstream reference. Symbols represent data means ($n = 3$) and error bars indicate standard error.

Table 1. Hydrologic data from March to December used to designate sub-reaches along the mine-influenced study site. Arsenic data from November 2004.

Sub-reach	VHG	Dominate Groundwater Flowpaths	% Groundwater Discharge	[As] Range ppb
1	0.24	Right Bank	15	20 – 580
2	0.14	Right Bank	19	320 – 1050
3	0.34	Right Bank	19	270 – 2800
4	0.1	Left Bank	35	50 – 1210
5	0.1	Right & Left Bank	12	600 – 3500

VITA

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Biologist, Sligh Environmental Consultants, Inc. Savannah, GA. Summer 2003. Experience with wetland delineation, water quality reports, endangered species surveys. Responsible for completion/submission of US Army Corps of Engineers permits.

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US Army Corps of Engineers permitting
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Transient storage modeling

Proficiency in Microsoft suite
General environmental monitoring:
Surface water/groundwater sampling
Water level meters, Hydrolab sonde

Research Interests:

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Trace metal transport and biogeochemistry

Relevant Course Work:

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Surface Hydrology
Statistics in Research I & II

Differential Equations
Wetlands
Soil and Site Assessment

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Amount – \$1600

Virginia Tech Graduate School, Graduate Research Development Program, 2005 Amount
– \$225

The Geological Society of America, Graduate Research Grant, 2005
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Annual meeting of The Geological Society of America. 2004. A mass-balance approach to assessing arsenic transport through the hyporheic zone of a mine-influenced mountain stream. Brown, B.V. (Presenter), H.M. Valett, M.E. Schreiber.

Joint meeting of North American Benthological Society and American Geophysical Union. 2005. A mass-balance approach to assessing arsenic transport through the hyporheic zone of a mine-influenced mountain stream. Brown, B.V.(Presenter), H.M. Valett, M.E. Schreiber.

Annual meeting of The Geological Society of America. 2005. Hyporheic transport of arsenic in a mine-influenced headwater stream: A mass-balance approach. Brown, B.V. (Presenter), H.M. Valett, M.E. Schreiber

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North American Benthological Society