SEDIMENT PORE-WATER INTERACTIONS ASSOCIATED WITH ARSENIC AND URANIUM TRANSPORT WITHIN A URANIUM MINING-IMPACTED WATERSHED IN SOUTH DAKOTA[1]

J.J. Stone[2], L.N. Larson, G.G. Kipp

Abstract: The extent of historical uranium mining impacts is well documented for the North Cave Hills region of Harding County, South Dakota. While previous studies indicate watershed sediment and surface water exhibit up to 90x established background concentrations for arsenic (As) and uranium (U), it was unclear whether or how localized changes in sediment redox behavior influence contaminant remobilization. Five pore-water equilibration samplers (peepers) were spatially and temporally deployed within the study area to evaluate seasonal solid-liquid equilibria as a function of sediment depth. At a sampling site 2 km downstream of the mine site within a wetlands-dominated deposition zone, seasonal variations of pore-water geochemistry were observed. Summer conditions promoted strongly reducing conditions, resulting in the remobilization of sediment-bound As(III). Fall conditions promoted oxidizing conditions within the sediments, resulting in decreased As (5x) and increased U (10x) concentrations within the sediment pore-waters. Peak pore-water U concentrations (781 μg/L) were 3.5x greater than observed within the surface water (226 μg/L) immediately above the sediments. Pore-water As(V) concentrations peaked directly below the sediment-water interface, suggesting As(V) was scavenged and accumulated by strong interactions with surficial iron (hydr)oxides. The study results suggest that localized redox conditions, especially those dominated by (bio)geochemically-influenced iron and sulfur reducing processes, may influence seasonal As and U behavior within these mining impacted alluvium sediments.

Introduction

Historical uranium mining within the North Cave Hills (NCH) region of northwestern South Dakota has led to pervasive contamination of surface water, sediment, and pore-water via hydraulic, erosional, and geochemical mechanisms. Mine spoils provide a source, by means of continual physical and chemical weathering, of As and U downgradient of the mining region of the NCH. This watershed has been extensively investigated as part of a Joint Venture Agreement between the United States Forest Service (USFS) and South Dakota School of Mines and Technology (SDSM&T) [e.g.(Kipp et al., 2009; Larson and Stone 2011; Stone et al., 2007; Tuombe 2008)], identifying areas of concern, extent of contamination, and transport mechanisms within the impacted watershed.

Physical weathering and off-site transport of spoils is facilitated by steep slopes, loose compaction, sparse vegetation, and intense storm events. Chemical weathering processes similar to acid mine drainage (AMD) formation have been observed within the soils directly adjacent to the mine sites (Kipp et al., 2009). Iron sulfides are common in the lower beds of sandstone and lignite in the Tongue River member, which comprises the majority of the mine tailings (King and Young 1956). Runoff appears to facilitate rapid oxidation of reduced iron sulfide minerals and subsequent pH reduction provides a mechanism for mobilization of mineral-bound As and U. The extent of pyrite oxidization is directly proportional to the exposure to water in contact with atmospheric oxygen, highlighting the role of hydrological processes responsible for off-site contaminant transport. High surface area to volume ratios of the finely disseminated overburden sediment and microbial activity would further catalyze oxidation of iron sulfides (Wanty et al., 1992).

Oxidized U(VI) is orders of magnitude more soluble than U(IV), hence acknowledged as highly mobile in most surface waters (Bargar et al., 2008). Oxic waters readily solubilize U to form a uranyl ion (UO_2^{2+}), forming highly mobile carbonate complexes in alkaline pH ranges, common to the NCH watershed (Stone et al., 2007) and promote the formation of uranyl-(bi)carbonate complexes $UO_2(CO_3)_2^{-2}$ (Wanty et al., 1992). While inorganic As naturally exists in oxidation states -3, 0, 3, 5, the As(III) and As(V) are the species are most commonly found within natural waters. Tri-valent arsenic primarily exists as H_3AsO_3 (pK$_1$ = 9.2), while penta-valent arsenic exists as $H_2AsO_4^-$ and $HAsO_4^=$ (pK$_1$ = 2.2, pK$_2$ = 7.0, pK$_3$ = 11.5) (Smedley and

Kinniburgh 2002). Arsenate is thermodynamically stable under oxidized conditions, while arsenite dominates in reducing conditions (Brookins 1988); however, arsenite may be significant in oxic waters due to slow abiotic oxidation kinetics (Campbell and Hering 2008).

Once As and U are released to surface water near the mines, the combination of intermittent fluvial processes and geochemical interactions largely control their fate and transport. Adsorption of arsenate to hydrous Fe(III) (hydr)oxides is well established at circumneutral pH values (Dzombak and Morel 1987) and occurs through inner-sphere complexation (Campbell and Hering 2008). On the other hand, arsenite generally forms weaker outer-sphere complexes. Sorption of both arsenate and arsenite to Fe(III)(hydr)oxides is highly dependent upon pH, competition from other anions for sorption sites, and solute concentrations (Hering and Dixit 2005).

Reductive dissolution of Fe(III) (hydr)oxides is recognized as a major re-mobilization mechanism for adsorbed As. The process is largely biotically driven, although disagreement arises over the precise reductive progression. There is mounting evidence that each mechanism is dependent on specific biotic and abiotic factors, including availability of metal reducing bacteria (MRB), accessibility of organic carbon substrate (either as a source of metabolic energy (electron donor) or complexing agent) and the amount and availability of reactive Fe present (Herbel and Fendorf 2005; Root et al., 2009). In common environmental systems, Fe(III) minerals typically exhibit poorly crystalline structures, and their ability to adsorb As varies dependent upon pH and differences in available surface areas (Kocar et al., 2010).

Arsenic mobility in anoxic environments has been linked to iron and sulfur cycling at redox boundaries (Root et al., 2009; Wilkin et al., 2003), whereas the distribution of free Fe^{2+} or total sulfide governs As behavior under anoxic sediment conditions commonly found beneath the sediment water interface (SWI). In free Fe^{2+} regions, either SO_4^{3-} reduction is depressed and/or abundant reactive Fe exists (Wilkin 2002). Free Fe^{2+} regions promote the formation of amorphous Fe monosulfides (FeS), which limit and exhibit control over the dissolved As(III) concentrations through adsorption and co-precipitation reactions (Gallegos et al., 2008; Farquhar et al., 2002). In contrast, free sulfide regions are typically supported by high activity of SO_4^{3-} reducing bacteria (SRB), high availability of SO_4^{3-}, and low abundance of reactive Fe (Wilkin et al., 2003). A significant increase in dissolved sulfide concentration promotes the formation of

orpiment ($As_2S_{3(s)}$), which may be considered as the controlling solid As phase in high SO_4^{3-} reducing conditions (O'Day et al., 2004). In general, free Fe regions sufficiently suppress As concentrations through the formation and uptake by iron sulfides while free sulfide regions tend to promote As mobility. In anoxic environments, where dissolved As concentrations do not exceed the solubility from arsenic sulfides, uptake of otherwise soluble arsenite is governed solely by adsorption reactions (O'Day et al., 2004). Seasonal shifts in the redox conditions due to changes in soil temperature, ion and oxygen availability, and flooding conditions may promote or hinder the ability of SRB sulfide production, shifting the iron/sulfide ion balance and affecting aqueous As mobility.

The focus of this study was to identify unique, localized geochemical regions within the impacted alluvium and develop further understanding of seasonal As and U cycling behavior within surface waters, sediments, and pore-waters. Biotic controls were expected to have a profound impact on the mobility of these contaminants, highlighting the importance of the variable NCH climate with respect to microbial kinetics. The objectives of this research were to: (1) investigate zones of geochemical importance within the watershed subject to seasonal cycling of As and U using pore-water sampling techniques and (2) predict As mobility due to seasonal biotic and abiotic dynamics.

Sampling Locations

The sampling locations (Fig. 1) were chosen based upon the unique and localized geochemical conditions that may promote contaminant transport, the extent of elevated As and U concentrations determined previously, observed seasonal variations of hydrologic flow regimes which may impact the degree of sediment saturation redox behavior, and the distance from the mining sites within the impacted watershed. The sedimentation pond site (Fig. 1) is located approximately 0.7 km from the eastern slope of the overburden. It is located so as to intercept and settle transported tailing and mine spoils prior to entering the headwaters of Pete's Creek. Approximately 2 km down gradient from the sedimentation pond, a wetland-dominated environment has formed where shallow stream gradients promote sediment deposition. This sampling site is referred to as Pete's Creek Wetlands (PCW).
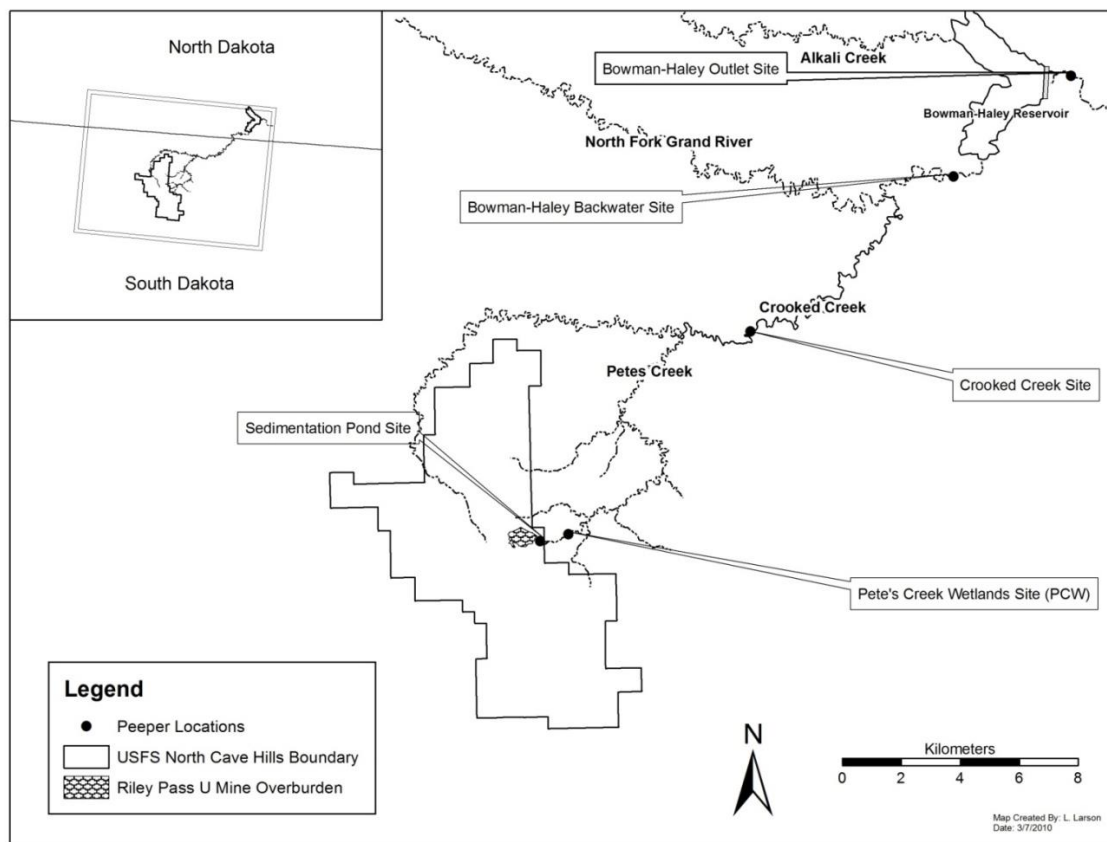
Figure 1: Peeper deployment locations (shown by black circles and corresponding labels) within the North Cave Hills mine region in northwestern South Dakota, USA. Only sedimentation pond and Pete's Creek Wetland sites are discussed within this paper. Topography of the North Cave Hills region dictates that the mine sites drain entirely to the east. The spoil of the Riley Pass Mine is the largest U mine site in the NCH region (0.42 km^2).

Materials and Methods

In situ membrane dialysis samplers (peepers) were constructed following a design modified from one originally by Hesslein et al. (1976). The peepers were constructed from plexiglass sheets with overall dimensions of 76.2 x 45.7 x 2.54 cm. Each contained 32 rows of 18-1.5 cm diameter, 4.5 mL volume chambers. Plexiglass overlays (3.175 mm thickness) were placed on either end of the base plate to hold the individual membranes (Whatman Nytran 0.45 μm) and fastened with nylon screws. The membranes were placed between the plexiglass cover and 2.54 cm thickness inner chamber on both sides (inlet and outlet). The 1.5 cm diameter cylindrical dialysis chambers were initially filled with distilled water, a water bath was purged with N_2 gas for approximately 12 hours prior to deployment, and peepers were submerged within the sealed

water bath until deployment in the field. Each peeper was deployed parallel to the flow direction at a depth ranging from approximately 25 to 40 cm below (from bottom of chamber) the sediment surface within the saturated sediments. Care was taken to minimize disturbance of *in situ* sediments during installation, with minimal excavation. The peeper had a sharp bottom edge which allowed easy placement within the sediments using a weighted hammer. The peepers were field equilibrated within the local *in situ* environment for 18 (summer) and 22 (autumn) days, after which sediment pore-water equilibrium was assumed achieved and the peepers were carefully removed from the site and immediately processed in the field as described below. Equilibration time was based on the design factor (F) which is the cell volume divided by the cell surface area (Johnston et al., 2009). Our design factor (2.54 cm) required longer equilibration than reported by Hesslein et al. (1976).

In processing the peepers, surficial sediments were carefully removed from the peeper surface. Individual 10 mL syringes were used to pierce the membrane and extract the contents of the dialysis chamber. Two chamber rows (~ 81 mL) were composited to comprise each sample for analyses. For the autumn deployments, approximately half of each composite sample was filtered through an ion exchange arsenic speciation cartridge for determination of As(III) concentration (Meng and Wang 1998), 5 mL was expended for pH, oxidation/reduction potential (ORP), conductivity, and total dissolved solids (Hanna Instruments probes HI 9025 and HI 3230; field calibrated), 100 µL was processed for Fe^{2+} by ferrozine analysis (Stookey 1970), and the remaining volume was reserved for total (dissolved) metals analysis. For the summer deployment, only As speciation, total aqueous metals, and total sediment concentrations (from sediments collected adjacent to the peeper) were determined.

For As(V) and As(III) speciation, aa pipette filter cartridge was used containing a selective alumino-silicate adsorbent which complexed and removed >99% of As(V) while passing As(III) (Meng and Wang 1998). The unfiltered sample was considered total dissolved As, filtered sample was As(III), and the difference was As(V) + organic-bound As. Methylated arsenic was not determined; however, As cartridges have a removal efficiency up to 80% at near neutral pH (Meng and Wang 1998). It should be noted that a small fraction of organic As may be present in the system, especially in the wetland environments (Gao et al., 2007); however for the purposes of this study, it was assumed that organic As concentrations were insignificant.

Arsenic speciation samples were processed within 30 min of extraction from the peeper, minimizing the potential of atmospheric oxidation, although abiotic As oxidation kinetics may be considered slow [on the order of weeks to months (Campbell and Hering 2008)]. Samples preserved with concentrated nitric acid were stored at 4^oC up to 30 days prior to analysis. Both the unfiltered (total dissolved metals, including total As) and filtered aliquots (analyzed as total As, representing As(III) concentration) were analyzed by Inductively Coupled Mass Spectrometry (ICP-MS) following EPA 200.3 methodology. Fe(II) was determined by the ferrozine method (Stookey 1970) where at least 100 µL of unfiltered sample was added to the ferrozine reagent and analyzed via UV spectrophotometer (Shimadzu UV-1601; 562 λ) within 24 hr of sample collection. Unfiltered surface water samples (500 mL) collected prior to peeper removal from a location adjacent to the peeper were analyzed for total metals.

Two –30 cm sediment core samples were collected directly adjacent to the peeper subsequent to its removal and preserved at 4^oC. In the laboratory, each core was sliced at 2 cm intervals and analyzed for total metals using an x-ray fluorescence spectrometer (XRF). XRF was previously found to correlate well with ICP-MS results for both sediment As and U concentrations (As: $r^2 = 0.83$, U: $r^2 = 0.81$) (Stone et al., 2007). All study sites were sampled in the summer and autumn. Sampling locations were identified using GPS and flagged in the field.

Results and Discussion

Sedimentation Pond

The sedimentation pond collects the drainages from the eastern face of the Riley Pass Mine (the largest mine site in the NCH region). Finely disseminated overburden material consists of remnants of the Ludlow member of the Fort Union Formation. Mining left loosely compacted spoils on naturally steep bluffs, resulting in ideal conditions for physical and chemical weathering, especially during frequent, high intensity thunderstorms common to the area in early summer. As sediment is transported down gradient from the spoils sites, chemical processes influence contaminant mobilization. Changes in available oxygen associated with sediment burial affect redox chemistry, while physical abrasion of secondary mineral rinds on clastic sediments can release As and U bearing colloids.

The sedimentation pond was partially dredged approximately 3 weeks prior to the autumn deployment in late September 2009, or approximately 2 months after the summer deployment.

The pre-dredging (summer) conditions represent approximately 7 years of sediment accumulation, while the autumn deployment reflects relatively fresh spoils and sediment only recently deposited. This comparison provides a unique opportunity to study geochemical signatures of similar source material over vastly differing time scales. In general, pre-dredging As and U concentrations were significantly higher than those observed post-dredging, with the exception of U dissolved concentration (collected within the peeper, U_{diss}). The dredging, as augmented by the differing summer/autumn conditions, decreased As and U surface water (As_{sw} and U_{sw}) by 8.5x and 6.5x, respectively, although background concentrations in the autumn samples were exceeded by 29x and 4x, respectively.

Although redox profiles were not determined during summer sampling, the pre-dredging results suggest oxygen availability within the sediments and pore-water was minimal. The peeper results shown in Fig. 2 indicate that As(III) was the predominant oxidation state of As within the sediment pore-waters, denoting reducing conditions. Low concentrations of U further confirm the existence of reducing conditions, as uraninite would be the thermodynamically expected specie. The distribution of As between As(III) and As(V) was nearly equal near the sediment water interface (SWI), both exceeded established background concentrations (~30x). At depth, As(III) clearly became predominant as reducing conditions prevailed. The total concentration of As(V) ($H_2AsO_4^{1-}$ and $HAsO_4^{2-}$) remained relatively constant throughout depth.

Interestingly, geochemical conditions changed near the 17 cm depth wherein As sediment pore water (As_{pw}) concentrations stabilized and U_{pw} simultaneously increased fivefold (from 10 to 53 µg/L). Several phenomena may account for the increased U, such as changing redox-driven formation boundaries, re-oxidation of U by iron (hydr)oxides (Sani et al., 2005), complexation of U by organic material, bicarbonate derived from microbial respiration, or simply the heterogeneous nature of the mine spoils and associated sediments. At the SWI, U_{diss} concentrations were 17.9 µg/L while the total U_{sw} concentrations were 38x higher (674 µg/L), indicating that the high surface water U concentrations were largely associated with suspended solids. These results suggest that minimal U was released from the spoils and sediments into the surrounding pore-waters. The prevailing sediment conditions suggest that physical sediment transport rather than geochemical weathering processes control As and U behavior under the conditions observed.
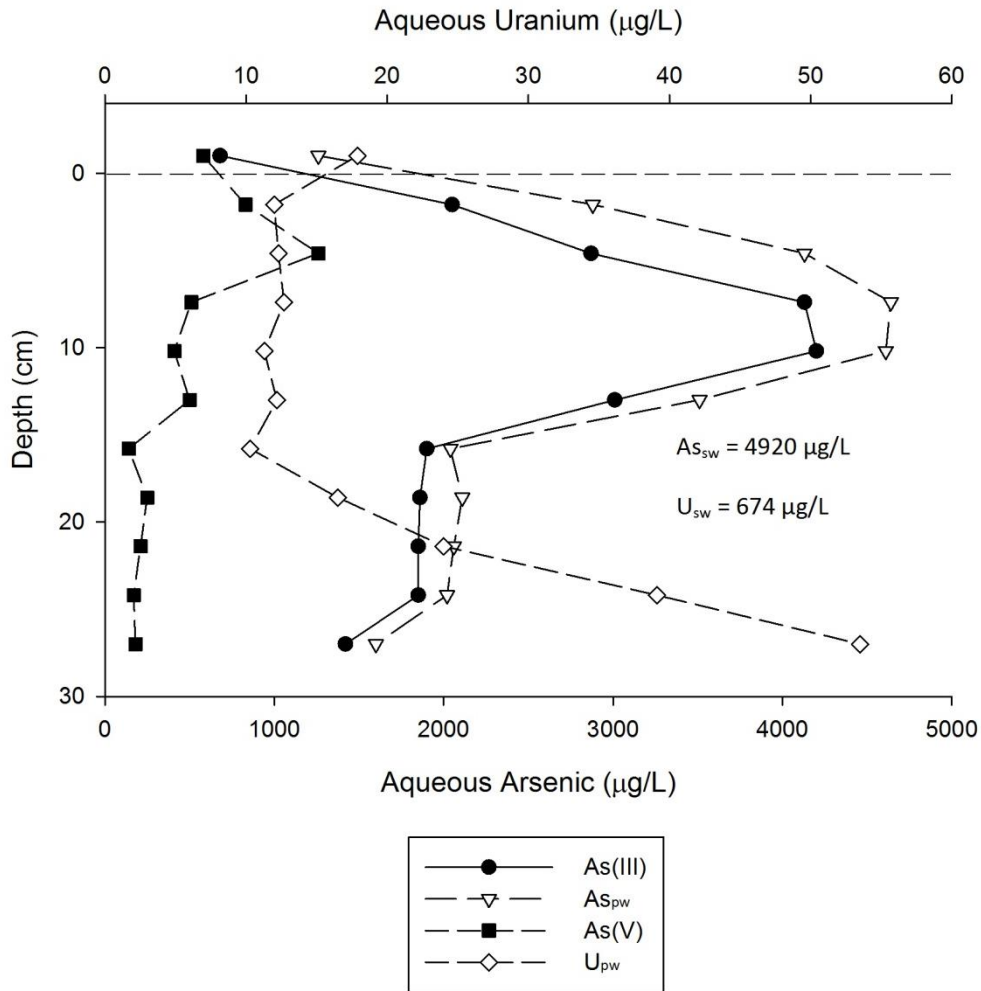
Figure 2: As and U concentrations as a function depth for the sedimentation pond sampling site, pre-dredging summer conditions. The horizontal dashed line with no symbols represents sediment-water interface. Surface water (sw) concentrations of total As and U (collected above the sediment water interface) were 674 and 4920 µg/L, respectively.

Post-dredging geochemical conditions observed during the autumn were slightly reducing, where ORP measurements ranged between 180 – 200 mV throughout the entire depth (Fig. 3). These findings are in contrast to the suspected reducing conditions based on the summer deployment. Oxidized conditions might suggest the sediment and spoils materials were freshly deposited. Dredging would have removed settled organic materials and acclimated microbes that would contribute to higher sediment oxygen demand. Fe(II) peaked at 8 cm depth, consistent with ORP water measurements at this depth where slightly reducing conditions and

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circumneutral pH (7.87) should promote Fe^{3+} hydrolysis and precipitation (Brookins 1988; Stumm and Morgan 1996). However, the production of Fe^{2+} in slightly reduced sediments provides valuable insight towards the geochemical composition and nature of the freshly deposited sediments. Pyrite and iron sulfide oxidation products have significant As(III) binding affinity (Kocar et al., 2010; Wilkin 2002), and oxidation of these materials could have profound influence upon As fate and transport. Pyrite was observed in the overburden material (King and Young 1956; Stone et al., 2007; Kipp et al., 2009) where dissolution would proceed according to well known AMD reactions. The kinetics of pyrite dissolution under high pH and alkaline conditions is slow (Huminicki and Rimstidt 2009), thus the potential for pyrite to serve as a primary transport vector would be considered minimal within the freshly deposited sediments, especially localized microenvironments around pyrite. On the other hand, the Fe^{2+} production observed may be the consequence of biotic reduction of meta-stable Fe^{3+} (hydro) oxides. Similar processes are well documented in AMD systems (Burton et al., 2007; Regenspurg et al., 2002).

As_{pw} existed entirely as As(V) near 14 cm depth. At shallower depths, sulfide oxidation (manifest in higher Fe^{2+}) increased releasing As(III). Peak Fe^{2+} concentration (presumably associated with the peak rate of sulfide oxidation or organic reduction of $Fe(OH)_3$) occurred near 9 cm coinciding with the peak As(III) concentration. Near the SWI, As(V) was the dominant As_{pw} species. Fe(II) concentrations decreased towards the SWI, likely due to amorphous Fe^{3+} (hydr)oxide formation. Alkaline pH conditions cause Fe^{3+} (hydr)oxides to repel As(V) species, as As(V) species and Fe^{3+} (hydr)oxide surfaces both become increasingly negatively charged at high pH (Bohn et al., 2001), and As(III) sorption becomes favored over As(V) adsorption above pH 9 (Herbel and Fendorf 2005), although both As(III) and As(V) sorption would be marginal due to the dominance of anionic arsenite (Pierce and Moore 1980). Regardless of the mechanisms responsible, at high pH, the system appears to reside in a transitory state encouraging poor As retention, allowing As_{pw} to exist in either oxidation state and largely unaffected by the presence of Fe^{3+} (hydr)oxides near the SWI. As_{sw} (579 µg/L) was 5x greater than As_{diss}, suggesting that As was primarily associated with suspended solids fraction of the surface water. A significant As_{diss} fraction (108 µg/L) existed, perhaps due to the poor adsorption affinity to Fe^{3+} (hydr)oxides at high pH.
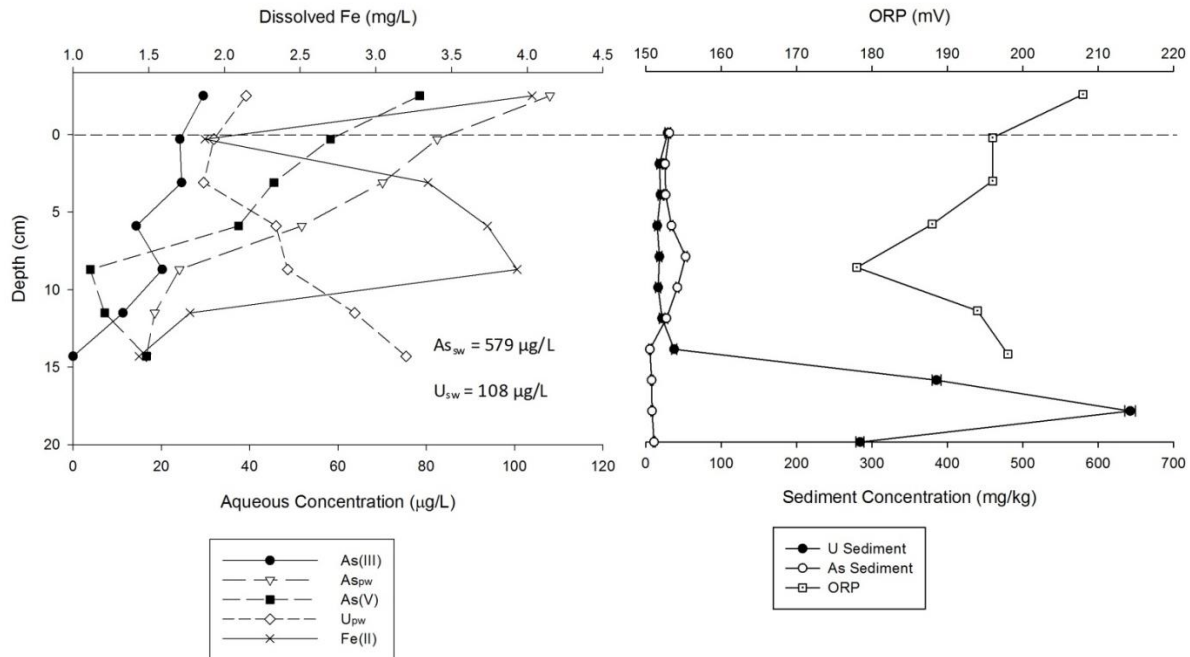
Figure 3: Constituent concentrations as a function depth for the sedimentation pond sampling site, autumn conditions. Dashed line with no symbols represents sediment-water interface (SWI). Surface water concentrations of As and U (collected above the SWI) were 579 and 108 µg/L, respectively.

Uranium sediment concentrations for the autumn deployment ranged between 25-30 mg/kg through approximately the 16 cm core depth, where an anomalous peak was observed near 15 cm (643 mg/kg). Again, the sediment composition was highly variable and the peak may have been attributed to the presence of an historical U(VI)/U(IV) redox boundary that was unaltered during dredging. Iron (III) (hydr)oxides in the oxidized sediments promote oxidation of U(IV) (Sani et al., 2005), likely accounting for the 2x increase of pore-water U(VI) concentrations compared to the pre-dredging conditions. The continual loading of fresh sediments and spoils and increased oxygen demand due to microbial respiration and sediment burial would eventually result in mimicking pre-dredge conditions, whereas low U_{pw} concentrations would exist relative to the watershed background concentrations as reducing conditions promote insoluble U(IV) formation. Over time, the sedimentation pond acts as a U sink as oxygen availability decreases. The U_{diss} was approximately 33% of the total U_{sw} concentration, indicating that U in the sedimentation pond was largely associated with solid phase particulates.

Pete's Creek Wetlands (PCW)

The PCW site located approximately 0.7 km downstream of the sedimentation pond provided optimal conditions for sediment deposition due to rapid bank widening and shallow slope. Discernible evidence of reducing conditions was present at the site, such as organic matter within the stream channel (dark, organic-rich sediments), excessive plant growth, and strong sulfide odor emanating from the sediments. Unlike the sedimentation pond, PCW was not disturbed between the summer and autumn deployments, allowing for seasonal changes to be investigated. Redox conditions changed from reducing (summer) to oxidizing (autumn) conditions, and were likely attributed to decreased kinetic activities of indigenous microorganisms due to lower temperatures (Borch et al., 2009). The reduced microbial oxygen consumption would allow for oxygen penetration deeper into the sediments and profoundly affect localized redox chemistry.

Pore-water As(III)/As(V) speciation ratios (1.37 – 10.8) suggest highly reducing conditions existed. For summer conditions, As_{sw} (468 µg/L) and As_{diss} (577 µg/L) were similar, suggesting that As existed predominately in the dissolved phase within the water column above the sediments. The high As_{sw} suggests that an As concentration gradient may have existed between the underlying sediment pore-water and surface water, resulting in the upward migration and liberation of As(III) from the sediments. While physical processes such as fluvial runoff and sediment transport were responsible for transporting As and U materials from the mine site overburden, the As-associated redox activity observed at the PCW site suggests the existence of geochemical transport mechanisms.

PCW autumn results are presented in Fig. 4. ORP results suggest slightly reducing conditions existed through the entire depth (+185 to + 220), with low As(III)/As(V) ratios (0 to 0.71). As_{diss} comprised entirely As(V) (151 µg/L) and represented ~70% of As_{sw} (226 µg/L), signifying As(V) found in the surface water may have been a product of desorption from surficial Fe(III) (hydr)oxides. Corresponding pH values (~8.4) support poor arsenate sorption to Fe(III) (hydr)oxides near the SWI interface. The remaining 30% of As_{sw} was likely adsorbed to a solid phase metal oxide or clay fraction of suspended solids. As(III) formation began near 3 cm depth (28.6 µg/L) which appears driven by biotic processes as redox conditions support As(V) formation. Below the SWI, the presence of As(III) may be associated with reductive dissolution of Fe^{3+} (hydr)oxides, as Fe^{2+} production increased 2-fold simultaneously with As(III) formation. Furthermore, the strong sediment sulfide odor that existed during the summer

suggests SRB activities were present; no sulfide odor was detected during the autumn deployment. Seasonally, As_{sw} were similar (summer - 468μg/L, autumn - 490 ug/L), however there were significant differences with As phase associations. As expected, As(III)/As(V) summer ratios confirm As(III) was predominant during reducing conditions, while As(V) dominate under oxidized autumn conditions. Total As_{pw} concentrations decreased ~4x when seasonal conditions changed from reducing to oxidizing.
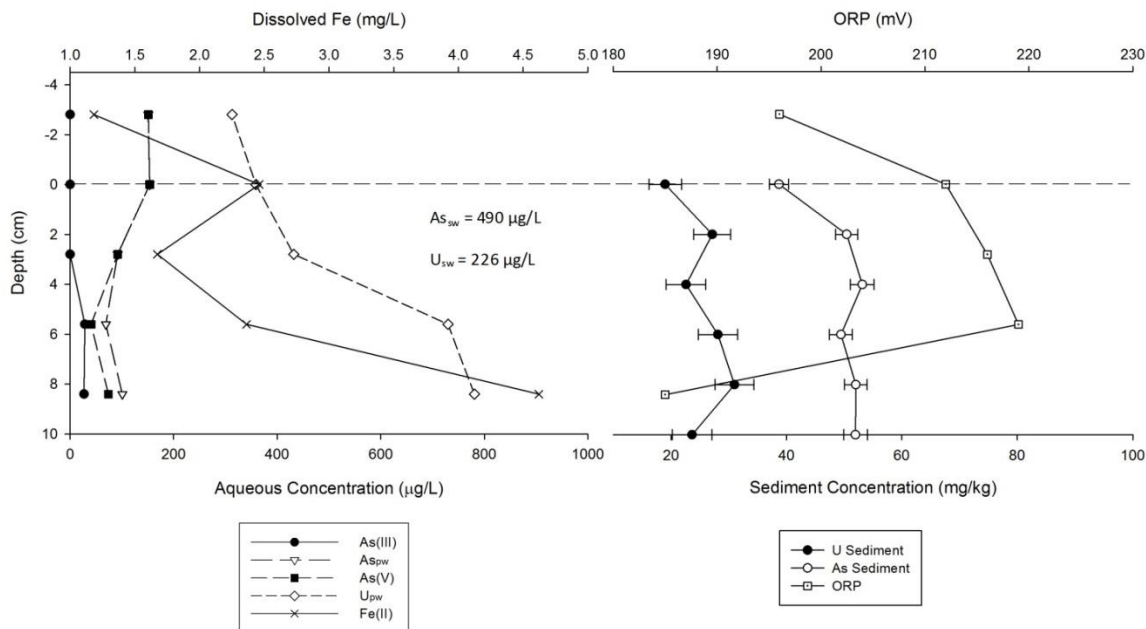

Figure 4: Constituent concentrations as a function of depth for the Pete's Creek Wetlands (PCW) sampling site, autumn conditions. Dashed line with no symbols represents the sediment-water interface (SWI). Surface water concentrations of As and U (collected above the SWI) were 490 and 226 μg/L, respectively. Error bars represent standard error from the XRF sediment analyses

Autumn U_{sw} concentrations were similar to U_{diss} (226 μg/L and 313 μg/L, respectively), indicating that U(VI) was the predominant U specie of the surface water. U_{pw} concentrations increased by 7x (summer - 110 μg/L, autumn - 800 μg/L) as redox conditions changed from reducing to oxidizing, implying that U mobility was highly dependent on seasonal changes in system (bio) geochemistry.

Conclusions

Natural environments are rarely at equilibrium, presenting challenging conditions for understanding the geochemical behavior of As and U; however, at the macroscopic scale most systems are generally not far removed from equilibrium, allowing the use of equilibrium geochemical models to gain understandings of factors controlling behaviors of contaminants in environmental systems. Fate and transport of As and U are dependent on various physical, chemical, and biological factors. Furthermore, these conditions are highly site specific, and may vary significantly at both the macro and micro-scale. Results from this sediment pore-water study demonstrate the variable spatial and temporal nature of geochemical conditions that influence attenuation and migration of As and U. In general, the results from this study were in general agreement with those of other As and U studies. Rapid physical erosion processes have transported As- and U-containing overburden sediments off-site where chemical leaching processes dominate.

Acknowledgements

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