EPA Public Access

Author manuscript

Appl Geochem. Author manuscript; available in PMC 2020 June 02.

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Published in final edited form as:

Appl Geochem. 2018 February 1; 89: 255–264. doi:10.1016/j.apgeochem.2017.12.011.

Groundwater co-contaminant behavior of arsenic and selenium at a lead and zinc smelting facility

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Abstract

Co-contaminant behavior of arsenic (As) and selenium (Se) in groundwater is examined in this study at a former lead and zinc smelting facility. We collected water quality data, including concentrations of trace metals, major ions, and metalloid speciation, over a 15-year period to document long-term trends and relationships between As, Se, geochemical parameters, and other redox-sensitive trace metals. Concentrations of dissolved As and Se were negatively correlated (Kendall's Tau B correlation coefficient, $r = -0.72$) and showed a distinctive L-shaped relationship. High-concentration arsenic wells ($>5 \text{ mg L}^{-1}$) were characterized by intermediate oxidation-reduction conditions ($75 < \text{Eh} < 275 \text{ mV}$), near-neutral pH (6.1–7.9), low Ca/Na ratios, elevated Fe and Mn concentrations, and high proportions of As(III) relative to total dissolved As. High-concentration Se wells ($>500 \text{ } \mu\text{g L}^{-1}$) were characterized by more positive Eh (305–500 mV), low Fe concentrations, and high proportions of As(V). Batch micocosm experiments showed that aquifer solids contain mineral surfaces and/or microbial communities capable of removing selenate from groundwater. Electron microprobe and Se *K*-edge X-ray absorption near-edge spectroscopic analyses demonstrated that Se was predominantly associated with elemental Se in the reduced aquifer solids. Factor analysis revealed three discernible groupings of trace metals. Group I includes U, Se, and nitrate-N, all of which are mobile under oxygenated to moderately oxygenated conditions. Group II includes elements that are mobile under Fe(III)-reducing conditions: Fe, total dissolved As, As(III), and ammonium-N. Group III elements (Mo, Sb, and V) showed mobility across the entire range of redox conditions encountered in site groundwater; As(V) clustered with this group of elements. Geochemical modeling suggests that As and Se species were in a state of disequilibrium with respect to measured parameters indicative of redox conditions, although predicted patterns of redox-controlled mobility and attenuation were confirmed. This analysis is important to better understand groundwater contaminant behavior in response to redox conditions ranging from oxic/suboxic to Fe(III)-reducing, but excluding sulfate-reducing conditions.

Keywords

Groundwater; Arsenic; Selenium; Trace metals; Metalloid speciation

1. Introduction

This study reports on co-contaminant behavior of arsenic (As) and selenium (Se) in a groundwater plume derived from a former lead and zinc smelting facility. Groundwater contaminant plumes typically contain mixtures of various organic and inorganic chemicals, the fate of which are affected by attenuation and mobilization processes. For example, environmental mobility of the metalloids As and Se is linked to pH/redox conditions and the relative tendencies of aqueous As and Se species to interact with aquifer particles through adsorption-desorption reactions and precipitation-dissolution reactions. Risk management approaches to restore contaminated groundwater are informed by holistic evaluations of co-occurring contaminants under prevailing geochemical conditions and the conditions that may be imposed during applied remediation efforts.

Arsenic and Se are potential inorganic contaminants in groundwater for which the U.S. Environmental Protection Agency has established drinking water standards at $10 \mu\text{g L}^{-1}$ and $50 \mu\text{g L}^{-1}$, respectively (USEPA, 2009). Contamination of groundwater with As is usually associated with anthropogenic activities such as mining, milling, smelting, production of pesticides and wood preservatives, nuclear testing, and disposal of spent nuclear fuel (Smedley and Kinniburgh, 2002, Essilfie-Dughan et al., 2013, Biswas et al., 2017). However, groundwater As concentrations in some regions across the United States exceed the EPA maximum contaminant level (MCL), in the absence of anthropogenic sources, indicating a natural source of As in the environment (USGS, 2000, Welch et al., 2000, Peters, 2008, Ayotte et al., 2003). Arsenic may be present in several oxidation states (-III, 0, III, V) depending on environmental conditions. In groundwater, the pentavalent and trivalent oxidation states are most often encountered (Cherry et al., 1979, Ferguson and Gavis, 1972, Welch et al., 2000, Smedley and Kinniburgh, 2002). The dominant form of As in oxic waters is the arsenate oxyanion, which can be present as various protonated species depending on pH: H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-} (Sigrist et al., 2013). In anoxic groundwater, the dominant form of As is arsenite, an uncharged oxyanion below pH 9.2 (H_3AsO_3 ; Sharma and Sohn, 2009). Because arsenite is typically uncharged in neutral or near-neutral pH groundwater systems, it is usually mobile and can develop persistent plumes (Nordstrom, 2002, Munk et al., 2011, Paktunc, 2013, Mladenov et al., 2014).

Toxicological studies show arsenite to be the most hazardous form of As (Sharma and Sohn, 2009, Marlborough and Wilson, 2015). Thus, reducing conditions which favor arsenic mobility also favor the formation of the toxic As(III) oxyanion. Organoarsenic species, such as monomethylarsonic acid and dimethylarsinic acid (Cullen and Reimer, 1989), are unusual in groundwater but have been reported in municipal landfill leachates (Li et al., 2010). Arsenic-sulfur species (thioarsenic species) provide additional complexity to arsenic speciation in reducing environments (e.g., Stauder et al., 2005, Helz and Tossell, 2008, Planer-Friedrich et al., 2010, Pi et al., 2017). Beak et al. (2008) concluded that thioarsenic species can dominant over As oxyanion species at sulfide concentrations $>100 \mu\text{M}$. Landfills containing construction and demolition debris are often highly sulfidic due to the dissolution of drywall gypsum and subsequent microbial reduction of sulfate and production of sulfide. Elevated levels of thioarsenic species have been observed in the leachate from such

environments due to reactions between aqueous sulfide and As oxyanions (Zhang et al., 2014). Under extremely reducing conditions elemental As and arsine may be present, although their occurrence in groundwater systems has not been widely documented.

Aquatic environments may contain Se due to mineral weathering processes and anthropogenic activities such as mining, nonferrous smelting, coal combustion, petroleum refining, fossil fuel power production, sewage treatment, agricultural drainage, and production of pesticides, fertilizers and metals (e.g., Wang and Gao, 2001, Cassella et al., 2002, Kulp and Pratt, 2004, Gerla et al., 2011, Santos et al., 2015, Schwartz et al., 2016, Hay et al., 2016). Selenium exists in four oxidation states in the environment: selenide [Se(-II)], elemental selenium [Se(0)], selenite [Se(IV)], and selenate [Se(VI)].

The aqueous speciation and redox states of Se species are generally similar to those of sulfur (i.e., sulfide, elemental sulfur, sulfite, and sulfate). In groundwater, dissolved inorganic Se is prevalent as selenate and/or selenite (Basu et al., 2007, Mills et al., 2016, Santos et al., 2015), depending on redox conditions and pH (Winkel et al., 2012). Selenate (SeO_4^{2-}) is stable in oxidizing conditions and at acidic to alkaline pH (Robberecht and Van Grieken, 1982). The affinity of selenate for oxide and clay mineral surfaces is weak and tends to decrease with increasing pH (Goldberg, 2014). Under intermediate redox conditions, the selenious acid species selenite (SeO_3^{2-}) and biselenite (HSeO_3^-) predominate depending on pH. Unlike selenate, selenite species are subject to irreversible sorption to iron oxides, clay minerals, and organic matter (Balistrieri and Chao, 1990, Goldberg, 2013). In contrast to elemental sulfur, which forms at low pH and intermediate redox conditions, elemental Se has a large stability region that covers the pH-Eh conditions encountered in reducing to moderately reducing groundwater systems (Winkel et al., 2012). Elemental Se formation can be driven by biotic processes and by abiotic mineral surface-mediated processes (Oremland et al., 1999, Nancharaiiah and Lens, 2015, Myneni et al., 1997, Kang et al., 2011, Chakraborty et al., 2010, Charlet et al., 2012, Finck and Dardenne, 2016). Selenide, primarily as biselenide above pH 4 (HSe^-), can form in organic-rich systems that are characterized by low Eh. Studies of selenide formation in groundwater are uncommon, although Basu et al. (2007) measured selenide concentrations in groundwater where sulfate reduction was a dominant terminal electron accepting process.

Here we investigate the co-occurrence of As and Se as well as the correlation of geochemical parameters associated with the mobilization and attenuation of these metalloids in a groundwater plume derived from leaching of lead and zinc smelting waste materials. Redox-sensitive parameters, including oxidation-reduction potential (Eh), nitrogen species, iron (Fe), manganese (Mn), As/Se speciation, and concentrations of other redox-sensitive trace metals were evaluated to understand the potential for changes in the mobility and distribution of As and Se species in groundwater. Our working hypothesis at the beginning of this study was that spatial and temporal variations in groundwater concentrations of As and Se at the site were mainly governed by oxidation-reduction conditions and proximity to contaminant source areas.

2. Site background

The ASARCO East Helena plant was a custom lead and zinc smelter located just south of East Helena, MT (USA; Fig. 1). The plant operated for over 100 years, starting around 1888 with operations ceasing in 2001. Groundwater beneath the site is contaminated in locations with inorganics including As, Se, lead (Pb), cadmium (Cd), and zinc (Zn); plumes of As and Se have migrated offsite whereas the occurrence of other metals is restricted within site property boundaries.

Contaminated groundwater flows through highly variable, unconsolidated alluvial deposits containing mixtures of cobbles, gravel, sand, and silt (Briar and Madison, 1992). Fine-grained Tertiary volcanic ash tuff deposits underlie the contaminated alluvial deposits and act as a lower confining layer. The ash deposits occur at a depth of about 7 m below ground surface under the plant and dip steeply to the north, reaching depths of about 20 m under East Helena. The direction of groundwater flow is to the northwest as inferred from gradients in groundwater elevation (Wilkin et al., 2009). The primary source area for As contamination in groundwater is located near the former speiss handling area (Fig. 1). Speiss is the lightest molten phase produced in lead smelting operations (Ettler et al., 2009). Characterization studies of speiss materials recovered from this site indicates mineralogy dominated by mullite, Ca-Fe silicates, Fe-Ti oxides, quartz, glass, and soluble Ca-Pb arsenates. The speiss is also enriched in Pb, Cd, and Zn, but these metals show limited mobility in groundwater except where pH conditions are below about 4.5–5. Leaching of speiss is not considered to be a source of Se. The release of Se to groundwater was apparently linked to uncontained plant process water (western lobe; Fig. 1) and to leaching of materials contained in the slag pile (eastern lobe; Fig. 1). Site restoration activities since 2012 have included the removal of all buildings and infrastructure except a water treatment system for storm water, construction of an evapotranspiration cover system, removal of contaminated soils and waste debris, and surface water diversion into Prickly Pear Creek around the eastern side of the slag pile (Fig. 1). Surface water diversion has led to the draining of wetlands and Lower Lake located to the south of the plant and water levels in the contaminated aquifer have decreased by up to 2.5 m, significantly reducing the volume of contaminated aquifer solids that contact groundwater.

3. Materials and methods

3.1 Groundwater sample collection and analysis

Groundwater samples were collected from 2001 to 2016 using submersible pumps (Fultz Pumps, Inc. or Proactive Mega Monsoon). During well purging flow rates varied between 200 and 800 mL min⁻¹ depending on well diameter and screen length. Drawdown of the water column during purging was typically negligible due to the highly conductive nature of the aquifer. Samples were collected after removing about 3 well volumes and following stabilization of geochemical parameters: dissolved oxygen (DO), pH, oxidation-reduction potential (ORP), and specific conductance, measured in a sealed flow-through cell (YSI 556). Field measurements were made for dissolved sulfide and ferrous iron using the methylene blue and 1,10-phenanthroline colorimetric methods, respectively (Hach DR2700 spectrometer). Alkalinity measurements were made by titrating groundwater samples with

standardized 1.6 N H₂SO₄ to the bromocresol green-methyl red endpoint with a digital titrator. Field quality control procedures are provided in the supplementary data (Appendix A).

Filtered samples (0.45 µm, Gelman Aquaprep) were collected for metals and cation analysis; these samples were preserved by acidification to pH < 2 with HNO₃ (Optima, Fisher Scientific). Analyte concentrations were measured using inductively coupled plasma – optical emission spectrometry (ICP-OES; analysis based on EPA Method 200.7) and/or inductively coupled plasma – mass spectrometry (ICP-MS; analysis based on EPA method 200.8).

Samples for As and Se speciation were filtered, acidified with HCl (Optima, Fisher Scientific), and retained chilled in amber-plastic bottles. Speciation analysis was carried out using liquid chromatography (LC) coupled on-line to ICP-mass spectrometry (LC-ICP-MS; Thermo Electron Spectra HPLC) using collision cell technology to remove spectral interferences. A He/H₂ gas mixture was used in the collision cell along with negative voltages applied to the quadrupole and hexapole. Chromatographic separation of As species was accomplished using a PRP-X100 guard column (Hamilton), a PRP-X100 separator column (Hamilton), and by pumping an isocratic eluent [1.0 mL min⁻¹, 10 mM (NH₄)H₂PO₄/NH₄NO₃]. Eluent was directly aspirated into a Thermo Electron X series II ICP-MS and As was detected by monitoring the *m/z* = 75 signal. In this study, groundwater samples were free of dissolved sulfide (<0.03 mg L⁻¹); thus, thioarsenic species were not expected and acidification was used to preserve the samples. Injection volumes ranged from 20 to 100 µL depending on sample concentration. Chromatographic separation of Se species was accomplished using an AG-16 guard column (Dionex), an AS-16 separator column (Dionex), and by pumping a gradient tetramethylammonium hydroxide eluent (1.0 mL min⁻¹, 0–4 min 17.5 mM, 4.1–12.0 min 17.5–100 mM, 12.1–15 min 17.5 mM). Se was detected by monitoring the *m/z* = 78 signal. In most cases, speciation measurements were completed within 8 d of sample collection. Over the course of this study the sum of speciated As or Se concentrations were in good agreement with total dissolved concentrations (Fig. S2, Appendix A).

Filtered and unacidified samples were analyzed for major anions by capillary electrophoresis (CE, Waters Quanta 4000E). Filtered samples were also collected for analyses of dissolved organic and inorganic carbon (Dohrmann DC-80 Carbon Analyzer). Nitrogen species (NO₃-N + NO₂-N, NH₄-N) were measured by flow injection analysis on a Lachat QuickChem 8000 Series flow injection analyzer. Quality control samples for laboratory measurements included laboratory/field duplicates, laboratory, field, and equipment blanks, matrix spikes, serial dilutions, interference check samples, calibration check standards, and second-source quality control samples (Appendix A).

Samples for stable oxygen and hydrogen isotopic compositions were collected into 20-mL glass vials and sealed to prevent evaporation that can potentially alter ¹⁸O/¹⁶O and ²H/H ratios. Oxygen- and hydrogen-isotopic ratios of H₂O were analyzed by isotope ratio mass spectrometry (Finnigan TC/EA, Finnigan Delta Plus XP IRMS; 2005–2009). Cavity ring-down spectrometry (CRDS) was used to measure isotope ratios in samples collected from

2010 to 2016 (Picarro L2120i). The oxygen and hydrogen isotope ratio values are reported in terms of permil (‰) notation with respect to the Vienna Standard Mean Ocean Water (VSMOW) standard.

3.2 Microcosm experiments

Aquifer solids were collected in 2004 near an area where a pilot-scale permeable reactive barrier was constructed as a potential treatment option for As in groundwater (Wilkin et al., 2009). Precautions were taken to minimize air exposure of the solids during collection and setup of microcosm experiments. Batch microcosm experiments were conducted in 60 mL glass serum bottles containing 1 g of sediment, plus solution containing 0.005 M Na₂SO₄, 0.01 M NaHCO₃, and 25 mg L⁻¹ Se from Na₂SeO₄·10H₂O. All solutions were purged with N₂ gas to remove dissolved oxygen. Container controls were prepared by spiking Na-SO₄-HCO₃-SeO₄ solutions into serum bottles without aquifer sediments. The bottles were sealed with butyl-rubber stoppers and crimp caps and their contents were mixed on a mechanical shaker within an anaerobic glovebox (Coy Laboratory Products) for the duration of the experiments. At selected time intervals, samples were collected from the serum bottles, filtered through 0.2-μm syringe filters and acid-preserved prior to sample storage and analysis by ICP-OES.

3.3 X-ray absorption spectroscopy experiments

Synchrotron-based X-ray absorption spectroscopy (XAS) was conducted on solid samples obtained from the microcosm experiments and on a suite of selenium reference standards [sodium selenate, Na₂SeO₄·10H₂O (Aldrich); sodium selenite, Na₂SeO₃ (Aldrich); elemental selenium (J.T. Baker); selenium sulfide, SeS₂ (Aldrich); and zinc selenide (Aldrich)] to determine the solid-phase Se speciation in the microcosm products. For data collection, samples and reference standards were ground to a fine powder using an agate mortar and pestle, and pressed into plastic sample holders using X-ray transparent polyimide tape. Se *K*-edge XAS data were collected at the bending magnet located at MRCAT Sector 10 (beamline 10-BM; Kropf et al., 2010) at the Advanced Photon Source (Argonne National Laboratory). At this beamline, a Si(111) double-crystal monochromator and a 50-mm-long second crystal provide a working energy range of 4.0–32 keV. Harmonic content of the incident X-ray beam was removed using the second crystal which has Bragg parallel and normal motions allowing for 50% detuning. Sample data for microcosm products were collected in fluorescence mode at ambient conditions using a 4-element Vortex energy detector with a monochromator step size of 0.5 eV in the X-ray absorption near edge spectral region (XANES). Sodium selenate was placed between the second and third ionization chambers for energy calibration (12665.7 eV). Gas mixtures of He-N₂-Ar were used in the ionization chambers during collection of Se *K*-edge data. Spectra for reference standards were collected in transmission mode.

XAS scans were collected and averaged to increase the signal-to-noise ratio; up to 10 scans were collected for each sample. Multiple successive sample scans did not show evidence of beam-induced oxidation or damage, i.e., progressive positive shifts in the Se *K*-edge position were not observed. IFFEFIT (Athena) software (Ravel and Newville, 2005) was used to analyze the Se *K*-edge XAS data. The data were first reduced to normalized spectra (edge

jump = 1) and then linear combination fitting (LCF) of the normalized XANES and k^3 -weighted extended X-ray absorption fine structure (EXAFS) spectra were used to determine the relative proportions of Se species in the microcosm samples. LCF analyses of XANES spectra were performed in the energy range from 12640 to 12690 eV and k^3 -weighted EXAFS spectra were fit over the range from 2 to 12 Å⁻¹. The goodness of fit in LCF analysis is measured using R factor values; smaller R factors indicate a better fit of the spectral data.

3.4 Scanning electron microscopy

Particle morphology and composition was studied using scanning electron microscopy (SEM, JEOL JSM 6360 microscope) coupled with energy dispersive X-ray spectroscopy (EDX, Oxford Instruments INCA Xact spectrometer). Sample powders were dispersed onto polished carbon planchets and coated with Au. An accelerating voltage of 20 keV was used and images were obtained with secondary and backscattered electron detectors. The X-ray spectrometer calibration was checked using a polished cobalt metal standard (Co K α , 6.925 keV) prior to obtaining energy dispersive spectra.

3.5 Modeling and statistics

Theoretical aqueous and mineral equilibrium speciation diagrams were created using ACT2 as part of the Geochemist Workbench (GWB) release 10.0 (Aqueous Solutions LLC) and the Lawrence Livermore National Laboratory thermodynamic database (thermo.com.v8.r6+). In order to develop insight into relationships between As, Se, and other geochemical data, the program SYSTAT (v. 13) was used to calculate Kendall's Tau B correlation coefficients and to conduct factor analysis. Principal Component Analysis (PCA) was utilized for building the correlation matrix and transforming data into the factors for evaluating associations between measured parameters.

4. Results and discussion

4.1 Stable isotopes of O and H

Stable isotope data for O and H in groundwater from the site and surface water from Lower Lake are shown on Fig. 2. The $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ trend for groundwater from the site plots below the local meteoric water line determined for south-central Montana (Benjamin et al., 2004), at a shallower slope (slope = 4.99) that compares well with the slope determined for surface water from Lower Lake (slope = 4.55). Due to evaporative processes, Lower Lake surface water is enriched in ^{18}O and ^2H compared to site groundwater. Water isotope trends on Fig. 2 show the influence of surface water on groundwater $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, which are controlled primarily by input from surface water and local recharge. The most depleted groundwater samples ($\delta^{18}\text{O} < -16.5$ permil) tend to come from the western and eastern Se plumes that were less influenced by surface water input from Lower Lake (see Fig. 1).

4.2 Distribution of As and Se in groundwater

Site groundwater was classified as Na–SO₄–HCO₃-type water. The highest dissolved solute levels were encountered around the former speiss handling area where specific conductance values ranged from 2.7 to 4.7 mS cm⁻¹ and As concentrations were as high as 112 mg L⁻¹.

Specific conductance values and As concentrations decreased along the flow path from the speiss handling area to downgradient regions (Wilkin et al., 2009). Long-term trends in major-ion chemistry within the center (well EPA04) and along the periphery (well PBTW-2) of the central As plume are plotted in Fig. 3. Both wells showed decreasing concentrations of Na, As, and sulfate over the 15-year sampling period. Decreasing concentration trends, modeled using first-order attenuation factors of $0.02\text{--}0.12\text{ y}^{-1}$, can reasonably be attributed to aquifer flushing with fresh recharge and limited new source contributions. The divalent cations, Ca and Mg, showed consistent time-dependent concentration profiles that are likely controlled by dynamic equilibria between groundwater and the aquifer solids (Fig. 3). In well PBTW-2, for example, groundwater was nearly saturated with calcite ($-0.1 > \text{Saturation Index} > -0.7$), suggesting that calcite dissolution played a role in regulating concentrations of Ca and bicarbonate.

Across the site, concentrations of dissolved As and Se showed a striking antithetical relationship (Fig. 4). Statistical analysis revealed a strong negative correlation between As and Se (Kendall's Tau B, $r = -0.72$). The non-linear L-shaped trend on Fig. 4 is produced by high As concentrations ($94 \pm 19\text{ mg L}^{-1}$) in the speiss handling area, elevated As ($\sim 5\text{--}45\text{ mg L}^{-1}$) and low Se ($< 5\text{--}120\text{ }\mu\text{g L}^{-1}$) concentrations in the plume core shown on Fig. 1, and low As ($< 2\text{ mg L}^{-1}$) and high Se (up to $7940\text{ }\mu\text{g L}^{-1}$) concentrations in the peripheral eastern and western Se plumes. Maximum concentrations of As tended to occur where the fractional abundance of As(III) relative to the sum of As(III) + As(V), i.e., $f[\text{As(III)}] = [\text{As(III)}] / (\text{As(III)} + \text{As(V)})$ was > 0.7 . Arsenic concentrations were enriched in Fe(III)-reducing portions of the aquifer. Approximately 71% of wells in which As concentrations exceeded the MCL were correlated to the presence of dissolved Fe ($\text{Fe} > 0.02\text{ mg L}^{-1}$, Kendall's Tau B, $r = 0.42$). Good agreement between colorimetric field results for Fe(II) and total dissolved Fe measured using ICP-OES indicated that the presence of dissolved Fe was largely due to Fe(II).

High-concentration arsenic wells ($> 5\text{ mg L}^{-1}$) were characterized by mildly reducing conditions ($75 < \text{Eh} < 275\text{ mV}$), near-neutral pH ($6.1\text{--}7.9$), low Ca/Na ratios, elevated dissolved Fe and Mn concentrations, and high proportions of As(III) relative to total dissolved As. Groundwater with moderately oxidizing potentials (range: $300\text{--}490\text{ mV}$) had lower arsenic concentrations (mean 1.7 mg L^{-1}) and $f[\text{As(III)}]$ values < 0.2 . More restricted mobility of As(V) aqueous species is generally considered to be due to As(V) oxyanion attenuation via adsorption to mineral surfaces (e.g., Mitsunobu et al., 2013). High-concentration Se wells ($> 500\text{ }\mu\text{g L}^{-1}$) were characterized by more positive Eh values ($305\text{--}500\text{ mV}$), low Fe concentrations, and higher proportions of As(V) relative to total dissolved As. Selenium was negatively correlated with Fe ($r = -0.44$) and positively correlated with Eh ($r = 0.72$). Detection of selenite was rare. Selenite was detected at concentrations above $10\text{ }\mu\text{g L}^{-1}$ in 13% ($n = 126$) of the Se speciation analyses and was typically associated with high total dissolved Se ($> 50\text{ }\mu\text{g L}^{-1}$) and low Fe concentrations ($< 0.02\text{ mg L}^{-1}$). When selenite was detected, in most cases (63%, $n = 19$), selenate was still the dominant Se species determined. Low selenite may be related to its propensity to react and/or sorb to aquifer solids (e.g., Goldberg, 2013).

4.3 Transect wells

To further examine the relationships between As, Se, and other geochemical parameters, results were examined from a transect of wells extending from the western Se plume to the eastern Se plume along an approximate west-east line (A-A' on Fig. 1). The transect includes six wells from the central As-rich plume. Across the transect, pH values were mainly within the range from 6 to 7 over the 7-y monitoring period indicating that spatial concentration trends and redox indicators shown in Fig. 5 were not significantly influenced by shifts in pH (Fig. S3). Groundwater transect data showed correlations between the concentrations of As, Se, and indicators of redox conditions. On the transect edges, Se concentrations were elevated ($500\text{--}5160\text{ }\mu\text{g L}^{-1}$) and As concentrations were low ($0.01\text{--}2\text{ mg L}^{-1}$), Eh values were $>300\text{ mV}$, Fe and Mn concentrations were low ($<0.1\text{ mg L}^{-1}$), and $f[\text{As(III)}]$, $f[\text{Se(IV)}]$, and $f[\text{NH}_4\text{-N}]$ were <0.4 (Fig. 5; $f[\text{Se(IV)}] = [\text{Se(IV)}]/([\text{Se(IV)} + \text{Se(VI)}])$ and $f[\text{NH}_4\text{-N}] = [\text{NH}_4\text{-N}]/([\text{NH}_4\text{-N} + \text{NO}_3\text{-N}])$). In the central region of the transect, moderately reducing conditions were encountered with Eh values ranging from 130 to 270 mV, concentrations of As, Fe, and Mn were elevated, as were $f[\text{As(III)}]$ and $f[\text{NH}_4\text{-N}]$ (Fig. 5). Measured dissolved oxygen concentrations within the As-rich plume were $<0.5\text{ mg L}^{-1}$ (anoxic/suboxic) and ranged between 1 and 5.5 mg L^{-1} (oxic) within the Se-rich peripheries. The relationship between As and Se in the transect wells mimics site wide behavior (Fig. 4) and further revealed the dependence of contaminant concentrations on groundwater redox conditions.

The spatial distribution of As concentrations along the transect was consistent over the 7-y period from 2008 to 2015 (Fig. 5). Concentrations of Se on the western transect margin were variable and positively correlated with Eh. Within the As-rich plume, redox conditions were consistently reducing as indicated by Eh, $f[\text{NH}_4\text{-N}]$, $f[\text{As(III)}]$, Fe, and Mn concentrations (Fig. 5; Fig. S3). The most notable time-related change occurred in well EPA07 located near the eastern margin of the As-rich plume (Fig. 1). In this well, concentrations of Se decreased from about 82 to $10\text{ }\mu\text{g L}^{-1}$ and redox indicators (Eh, $f[\text{NH}_4\text{-N}]$, $f[\text{As(III)}]$) showed a transition to more reducing conditions, indicating slight expansion of the reducing plume in this area that led to a reduction of soluble Se.

The origin of the reducing groundwater plume that coincides with maximum As concentrations, mainly as As(III), is not known with certainty. The reducing plume is believed to be related to historic fuel releases around the speiss handling area that occurred prior to the start of groundwater monitoring studies at the site in the 1980s. Groundwater from wells in the speiss handling area and transect wells within the reducing zone often had a characteristic odor of fuel. Interestingly, concentrations of dissolved organic carbon (DOC) were not significantly elevated in reducing groundwater downgradient from the speiss handling area (mean = 3.1 mg L^{-1} ; $n = 196$) compared to adjacent groundwater in the Se-rich regions (mean = 2.4 mg L^{-1} ; $n = 81$; $p = 0.535$; Kruskal-Wallis, Fig. S4). This statistical similarity suggests that the composition of DOC in the reducing plume was particularly conducive to microbial degradation reactions that resulted in Fe(III)-reducing conditions. Studies were not conducted to fully characterize the composition of groundwater DOC. Note that sulfate-reducing conditions were not apparent at the site as indicated by a lack of sulfate depletion and non-detection of dissolved sulfide; redox conditions remained within and

above levels characteristic of Fe(III) reduction. The reducing plume, however, exerts a major control on the occurrence and mobility of As and Se at the site.

4.4 Microcosm experiments and Se(0) formation

Microcosm experiments showed that aquifer solids from the site contain mineral surfaces and/or microbial communities capable of removing selenate. Selenate decreased from 25 mg L⁻¹ after 3 months to 0.4 mg L⁻¹ (Appendix A; Fig. S5). Eh measurements from microcosm experiments (160–170 mV) were within range of groundwater Eh values determined for the As-rich plume where Se concentrations were low (<50 µg L⁻¹; Fig. 5). Pseudo-first-order rate constants were determined by fitting Se concentration data in the initial non-linear decay period. Rate constants ranged from 0.07 to 0.15 d⁻¹ and are comparable to Se(IV) and Se(VI) loss rates observed in previous microbial transformation experiments (e.g., Lortie et al., 1992, Lai et al., 2016, Subedi et al., 2017).

Arsenic concentrations in the microcosm tests remained at low levels (<0.3 mg L⁻¹; Fig. S5). Arsenic was not spiked into the microcosms, so As concentrations presumably resulted from desorption and/or dissolution of the aquifer material. Examination of microcosm products by SEM in backscattered electron detection mode revealed bright spherical particles in the 1–2 µm size range (Fig. 6). X-ray mapping showed the particles were enriched in Se (Fig. 6) with associated solid-phase concentrations of Si, Al, Fe, Ti, Ca, and K (Appendix A; Fig. S6). The grains are similar in shape but slightly larger than Se spheres produced by Se-respiring bacteria (Oremland et al., 2004). The coarser particle size is important in maintaining Se sequestered in the immobile aquifer solids (Buchs et al., 2013).

XANES analysis was performed to identify the Se oxidation state in microcosm samples. Fig. 6 shows Se *K*-edge XANES spectra of a microcosm sample as well as reference materials: elemental Se, selenium sulfide, Na₂SeO₃, and Na₂SeO₄. The microcosm sample showed a strong white-line peak at 12660 eV matching the reference for elemental Se (Gibson et al., 2012). LCF of XANES data indicated that the microcosm was dominated by 98% Se(0), with minor amounts of Se sulfide and selenite (Fig. S6). Generally consistent results were obtained using combination fitting of EXAFS data, although greater proportions of Se sulfide (6%) and selenite (12%) were indicated in the fit results (Fig. S6). In order to further examine the Se retention mechanism, the *k*³-weighted χ spectrum was fit with a FEFF 8.2 file generated with the crystallographic structure of elemental Se. The EXAFS Fourier transform magnitude is dominated by one strong peak at 2.08 Å (uncorrected for phase shift; Fig. S6). A fit of this peak with a single scattering Se-Se path led to a coordination number (CN) of 2.2 and an atomic distance of 2.34 Å, supporting the presence of zero-valent Se (Breynaert et al., 2008). Based on the results of the microcosm studies, it can be concluded that Se retention by reductive precipitation of elemental Se is the predominant immobilization process for Se in the reducing portion of the aquifer.

4.5 Trace metal associations and redox controls on mobility

The co-occurrence of As and Se with major ions and other metals that form redox-sensitive oxyanions (e.g., U, Sb, Mo, and V) were evaluated using correlation statistics (Kendall's Tau B correlation coefficients) and principal component analysis (PCA). Kendall's Tau B

coefficients indicated significant positive correlations between As(III) and $\text{NH}_4\text{-N}$, and Fe. In both cases the magnitude of the correlation was $r > 0.47$, reflecting the tendency for high As concentrations to be associated with reducing conditions where Fe and nitrogen as ammonium are soluble and mobile. Correlation coefficients showed significant positive correlations between Se and U ($r = 0.14$), $\text{NO}_3\text{-N}$ ($r = 0.64$), V ($r = 0.35$), and negative correlations with Fe ($r = -0.44$) and Mn ($r = -0.28$). Oxyanions in the 6 + oxidation state of U, Mo, Sb, and V behave similarly and are mobile under moderately oxidizing conditions (e.g., Deverel and Millard, 1988, Leybourne and Cameron, 2008, Wright and Belitz, 2010). Results from this study indicated that U is moderately insoluble under iron-reducing conditions ($18 \pm 8 \mu\text{g L}^{-1}$); whereas, Mo, Sb, and V showed mobility across the range of groundwater redox conditions encountered at the site (Fig. S7).

PCA revealed three discernible correlated groupings of trace metals (Fig. 7). Group I includes U, Se, and nitrate-N, all of which are mobile under oxygenated to moderately oxygenated conditions. These elements also cluster with the divalent cations Ca^{2+} and Mg^{2+} . This correlation is particularly apparent in more oxidizing, Se-rich groundwater and possibly reflects the effect these divalent cations have on enhancing U mobility through the formation of Ca- and Mg-uranyl carbonate complexes (Bernhard et al., 2001, Lee et al., 2017). Group II includes elements that are mobile under reducing conditions: Fe, As, As(III), and ammonium-N (Fig. 7). Sodium is included in Group II, which reflects correlated source contributions of As and Na. Group III elements: Mo, Sb, and V, showed moderate mobility across the range of redox conditions encountered in site groundwater; As(V), Mn, and K clustered with this group of elements (Fig. 7). This finding is significant in that it reveals a redox window where Mo, Sb, V, and As(V) are mobile in groundwater; more reducing groundwater conditions (e.g., sulfate reduction) would be expected to render these oxyanions immobile (Willis et al., 2011, Smedley et al., 2014). The close relationship between As(V) and Mn (Fig. 7) is interesting and strengthens the proposed connection between As(V) production and Mn(IV) reduction (Amirbahman et al., 2006). Furthermore, it was anticipated that Cr(VI) would also associate with Group I (e.g., Izbicki et al., 2015); however, Cr concentrations were typically below the level of quantitation ($<1 \mu\text{g L}^{-1}$) indicating no significant natural or anthropogenic source of Cr at the site. It is emphasized that the specific pH/redox conditions over which these groupings were obtained are near-neutral pH and oxic to moderately reducing, excluding sulfate-reducing conditions.

4.6 Thermodynamic controls

Geochemical modeling was performed to provide insight into the thermodynamic controls on metalloid speciation and Se attenuation over site pH and redox conditions. At moderately reducing conditions, Se is expected to precipitate as elemental Se over the pH range from 6 to 8 (Fig. 8; shaded region). At higher redox potentials, Se(0) is soluble, and aqueous species of Se(IV) and Se(VI) are expected to dominate. Overlapping the predicted speciation of As shows that As(V) aqueous species, H_2AsO_4^- and AsO_4^{2-} , are expected to coexist with Se(IV) and Se(VI) aqueous species and the solid-phase field for Se(0) at redox potentials above about 0 mV at pH 7. Below about 0 mV and pH 7, arsenite and Se(0) are predicted. We used measured groundwater Eh values and As(V)/As(III) ratios to plot sample data on the equilibrium diagrams (Fig. 8). On both diagrams the filled circles represent samples in

which Se concentrations were below about $20 \mu\text{g L}^{-1}$ and presumably affected by Se reduction and precipitation; open-circle symbols represent samples in which aqueous Se concentrations were above $500 \mu\text{g L}^{-1}$ and Se speciation measurements indicated the presence of Se(VI) in groundwater. Neither redox probe (Eh measurements or As(V)/As(III) ratios) appears to accurately track the predicted equilibrium condition. The measured Eh/pH data for the low Se samples cluster around the pH-dependent Se(IV)/Se(0) boundaries, but the measured Eh data would predict higher Se concentrations in solution, mainly as Se(IV), then were measured in groundwater. In addition, field data plotted on Fig. 8 suggest that redox couples for As and Se are not in equilibrium. When the As(V)/As(III) ratio was used as a variable to define redox status, the measured data predicted Se(0) precipitation at all conditions encountered in the field which was not indicated in all cases by the groundwater Se concentration data. Nevertheless, field-scale gradients in soluble As and Se concentrations were generally consistent with measured differences in redox potential. Consequently, equilibrium models are helpful in providing insight to As and Se speciation and solubility across large gradients in redox but prove to be less predictive over narrow windows of pH and oxidation-reduction conditions.

5. Conclusions

This study presents groundwater chemistry results collected over a 15-y period to evaluate factors controlling the mobility and attenuation of As and Se. Groundwater redox conditions ranged from oxic/suboxic to Fe(III)-reducing, but excluded sulfate-reducing conditions. Redox potential was revealed to be the key determining factor in understanding the behaviors and distribution of As and Se, in agreement with previous studies (e.g., Schwartz et al., 2016). At this site, historic releases of fuel to groundwater created a reducing plume that enhanced As mobility, mainly as As(III), and also locally supported Se attenuation through reductive precipitation. Observed geochemical patterns generally tracked thermodynamic predictions: i) Se was present as Se(VI) in oxic groundwater; ii) low Se concentrations were observed in Fe(III)-reducing waters due to the formation of Se(0) as a natural attenuation process indicated by sediment microcosm tests; iii) reductive precipitation of Se(0) was indicated in As(III) dominated systems; and, iv) mobility of As(III) and As(V) was apparent over a range of redox conditions. In detail, however, although Se(IV) species were often predicted based on measured indicators of redox conditions, analytical detection of selenite was rare. In addition, measured concentrations of As(V) and As(III) species were not consistent with the predicted distributions of Se(0), Se(IV), and Se(VI).

Mobility of As is strongly controlled by speciation. In oxic/suboxic groundwater, As(V) species showed limited mobility compared to Fe(III)-reducing portions of the aquifer where As(III) was mobile, leading to concentrations of $\text{As} > 100 \text{ mg L}^{-1}$. Oxidation of reduced Se(0) could be a potential future source of Se to groundwater if reducing conditions transition to more positive Eh values. In addition, co-occurring redox-sensitive trace metals behaved in predicted manners. Uranium was apparently attenuated under reducing conditions along with Se. Molybdenum, V, and Sb, however, did not show patterns indicative of attenuation in Fe(III)-reducing or oxic/suboxic groundwater.

Extrapolating results from this study to applied remediation technologies suggests that in-situ chemical reduction technologies that promote Fe(III)-reducing environments can be particularly effective for Se contamination, as has been similarly documented for the treatment of hexavalent Cr (e.g., Ludwig et al., 2008). Manipulation of redox conditions to Fe(III)-reducing conditions, without the addition or formation of excess mineral surface substrate for adsorption, could lead to incomplete treatment of As, Sb, Mo, and V. Oxidative treatment of As, on the other hand, could lead to mobilization of Se via dissolution of Se(0). Thus, the selection criteria of technologies that utilize in-situ redox manipulation for removal of inorganic contaminants should consider possible co-contaminant behavior over variable redox conditions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgements

MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The EPA through its Office of Research and Development funded and conducted this research. The views expressed in this paper are those of the authors and do not necessarily reflect the views or policies of EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. The authors thank an anonymous reviewer for providing helpful comments on the manuscript.

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Fig. 1. Site map showing locations of groundwater monitoring wells sampled in this study, speiss handling area, Lower Lake, and outlines of the As ($>20 \text{ mg L}^{-1}$) and Se plumes ($>0.5 \text{ mg L}^{-1}$). The aerial site view represents conditions prior to the restoration activities that started in 2012.

Fig. 2.

Oxygen and hydrogen isotope compositions of groundwater and surface water from the site near East Helena, MT (USA). The local meteoric line is from Benjamin et al. (2004; $\delta^{18}\text{O} = 7.95 \times \delta^2\text{H} + 8.09$).

Fig. 3.

Time trends for sodium, sulfate, calcium, magnesium, and arsenic in two groundwater monitoring wells (EPA04 and PBTW-2). See Fig. 1 for location of the wells in relation to the As plume boundaries. The decreasing concentration trends for sodium, sulfate, and arsenic were estimated using attenuation factors of 0.02–0.12 y⁻¹. De-watering of Lower Lake began in 2012 and possibly impacted As concentration trends.

Fig. 4.
Relationship between total dissolved Se and As in groundwater.

Fig. 5.

Groundwater concentrations of As and Se across transect A-A' were determined from 2008 to 2015 (see Fig. 1 for the location of transect A-A'). Concentrations of the metalloids responded to indicators of groundwater redox conditions: Eh, Fe concentrations, fraction of As as As(III), and fraction of N as ammonium.

Fig. 6. Results of solid-phase characterization studies of the products from microcosm experiments. Spherical particles were observed in backscattered and secondary electron imaging. X-ray mapping indicated that the spherical particles were dominantly Se, with detected Al, Si, Ca, and Fe from nearby aquifer particles (Fig. S6). Also shown are XANES spectra of the microcosm products and Se reference materials. The white line shift to lower adsorption energy indicates reduction of Se(VI) to Se(0).

Fig. 7. Principal component analysis (PCA) of selected trace metals and major ions in groundwater from the East Helena, MT site. The percentage of variance explained by each factor is indicated on the axis labels (77% of the variance was explained by the 3 factors).

Fig. 8. Activity diagrams for the system H_2O -As-Se at 25 °C, $\Sigma\text{As} = 10^{-4}$, and $\Sigma\text{Se} = 10^{-3}$ to 10^{-8} . A) Eh – pH diagram with measured data plotted (data collected in 2015). Filled circles represent groundwater samples with Se concentrations $<20 \mu\text{g L}^{-1}$; open circles represent samples with Se concentrations $>500 \mu\text{g L}^{-1}$, mainly as Se(VI). Predominance areas are plotted showing the predicted fields for aqueous species of Se and As and the solid-phase field for Se(0) (shaded green). B) log ratio of $\Sigma\text{As(V)}/\Sigma\text{As(III)}$ is used as a master variable to define redox conditions. Data points correspond to measured ratios of As species. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)