THE BIOGEOCHEMISTRY OF SELENIUM IN THE US WESTERN PHOSPHATE RESOURCE AREA: SOURCES, PATHWAYS, RECEPTORS AND CONTROLS

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ABSTRACT

Selenium, a sulfur analogue, is often mobilized in mining impacted areas. Oxidation of the reduced forms of this metalloid can allow release into the local ecosystem with the potential for toxic impact. A large body of work in the scientific literature has documented the food chain effects of mobilized Se in certain types of aquatic environments, with endpoints that include reproductive failure in biological communities. This work explores the biogeochemical cycling and controls of Se in mining effected environments focusing on the Western US Phosphate Resource Area in Idaho. Unique in its terrestrial environment, this large-scale active and historical mining area is currently the focus of a study of selenium reaction pathways, environmental impacts and natural or accelerated controls. We have found chemical and microbial pathways are active in the Se cycle in both areas, however the regio-specific geochemistry, temperature, hydrograph and engineering operations dominate the local release and control dynamics. This work examines natural and "green" engineered Se control approaches explored in field and laboratory trials associated with this mining area.

INTRODUCTION

In the fall of 1997, the discovery of selenium toxicosis in livestock pastured downstream of a historic Idaho phosphate mine prompted regulatory action under the *Comprehensive Environmental Response Compensation and Liability Act* (CERCLA) by the United State Forest Service. This event initiated a focus towards the identification and characterization of selenium in the area and how its release is related to mining activities. Several studies throughout the last century have focused on the location and composition of phosphate reserves from the Phosphoria Formation of Idaho, Wyoming, Montana, and Utah (Weeks and Ferrier, 1907; Gale and Richards, 1910; Swanson, et al 1953; Service, 1967; Gulbrandsen and Krier, 1980). Studies begun after the Second World War were largely conducted in the search for reserves of useful trace elements such as uranium, vanadium, and rare earths (Lotspeich and Markward, 1963; Love, 1961; Gulbrandsen, 1967). Other studies looked at toxic plants growing in areas of high selenium and often mention the presence of selenium in bulk samples of soil and rock. These often specify total selenium, the amount of selenium that is water soluble, and whether it is present as selenate or selenite (Beath, et al 1946).

Active mining of the phosphate resource has occurred in the Caribou National Forest region for almost eighty years and five Jarge firms now control mine site operations management. In our continuing work, we have shown that the waste rock impoundments associated with phosphoria mining in the Western US Phosphate Resource Area to be the source of widespread selenium mobilization in the local environment (Moller, G. and P. Talcott. 1997; Möller, 1998; Bond, 1999; Munkers, 2000). The sedimentary phosphoria deposits are between chert, cherty shale, shale and limestone formations that result in waste rock generation in the recovery of the phosphate resource. Historical mining operations have resulted in large, waste rock canyon fills of approximately 1 km in length and 150 m in height. A typical active mine site can generate 10 million tons of waste rock in a year. Infiltration of precipitation and snowmelt mobilizes large amounts of leached selenium in the canyon drainages with the potential for significant environmental impact in the contiguous watershed ecosystems.

The middle waste shales, which are particularly high in selenium, have been selectively used as a surface dressing for the waste rock impoundments because of the enhanced fertility of these materials for reclamation activities. In historical retrospect, this has created a potential worst case since these shales are readily weathered and the selenium is rapidly mobilized in a surface environment. The mobilized Se from these surface soils on the reclaimed land allows for significant Se accumulation in forage plants and exposure to terrestrial fauna in addition to observed increases in some nearby aquatic environments.

Selenium, a sulfur analogue and a required trace element, has been shown to have the potential for chronic and acute toxicosis in environmental exposures (Ohlendorf and Santolo, 1994; Presser, et al. 1994; Frankenberger and Benson, 1994). Although there is healthy debate on the relative risks to different species and in different environments (Chapman, 1999), there is general agreement that environmental exposures to selenium require careful study and management. The management and control of selenium in mining impacted environments present significant challenges. In this work, we report on several laboratory and field studies that characterize the release and control of selenium in the Smoky Canyon region of the US Western Phosphate Resource Area.

MATERIALS AND METHODS

Samples were obtained and field studies were conducted in the Pole Creek Canyon waste rock impoundment of the J. R. Simplot Company Smoky Canyon mine site. This site is located in southeastern Idaho on the Caribou National Forest. For laboratory characterization studies, surface and shallow sub-surface (-0.5 to - 5 m) waste rock soils were screened to < 0.5 cm and homogenized by

mixing. The bulk samples were dried at 35°C and ground to 10 mesh. Five soil samples in five-gallon buckets were taken from the overburden piles in Pole Canyon. Two samples were collected at the upstream (upper) end of the piles at a depth of approximately 15 cm (PCO-01, PCO-02). A third sample was taken from the downstream (lower) end above the French drain that had slumped in the spring of 1997 (PCO-03). Prior to the slump, this sample site had been at a depth of approximately 6 m within the pile. We considère this to be an unweathered overburden sample. The fourth site was on an upper bench at the downstream end of the pile where topsoil application required excavation to about a one foot depth to reach overburden (PCO-04). A fifth sample was a channel sample taken from the central area on the top of the overburden pile (PC-CH). All samples were refrigerated and sent to the University of Idaho by air transport two days after collection.

All soil and water chemical analyses were performed by the University of Idaho Analytical Sciences Laboratory (UI ASL), a USEPA Drinking Water Program certified facility operating in compliance with Good Laboratory Practice standards. Total selenium in soils and water was analyzed by the method of Tracy and Môller, 1990. The samples are first digested with nitric acid and then boiled in perchloric and sulfuric acids to convert all species of Se to selenate. Selenate is then reduced to selenite with hydrochloric acid. Using hydride generation - ICAP analysis, the samples are then analyzed for total Se.

Neutron activation analysis

One air-dried and ground waste rock soil sample from each sample location was analyzed for Se^{75} using the TRIGA III reactor at Washington State University, Pullamn, WA. This reactor irradiates the soil samples, and the y-ray spectra are recorded using an ND6700 Ge(Li) γ-ray spectrometer.

Sequential extraction

The determination of selenium species in the overburden followed the sequential extraction outlined by Martens and Suarez, 1997. Air-dried, ground, 5 g samples were processed by three extraction and oxidation steps, each followed by centrifuging and decanting. Water-soluble selenium species were first extracted with 25 mL of 18 MΩ-crn water. Twenty-five milliliters of 0.1 M phosphate buffer (pH 7.0) extracted the selenium adsorbed to the soil, followed by the oxidation of insoluble selenium forms with 25 mL of 0.1 M persulfate. Samples were analyzed for selenite-Se and total selenium.

Scanning electron microscopy

Waste rock soil separates were analyzed by scanning electron microscopy with X-ray fluorescence (SEM-XRF) using an Amray model 1830 SEM with an acceleration potential of 20.0 kV. The rock was freshly fractured and mounted on carbon stubs with carbon tape.

Microprobe analysis

Polished thin sections of representative overburden samples were analyzed by electron microprobe at the University of Hawaii. A 20 nA, 15 kV electron beam was used, and intensities were converted to concentrations via a PAP correction scheme. Spot analyses of two microns in size were conducted repeatedly on the samples in order to create element maps. Professor Dennis Geist of the University of Idaho Department of Geology performed mass-balance calculations on the appearance of pyrite in the grab samples.

Drill-core analysis

The J. R. Simplot Company provided data on total selenium and total P_2O_5 content as a function of depth in a nearby sedimentary formation. Core samples were analyzed in 0.3 to 0.6 m segments to a depth of 107 m. This data was compared with the geologic description of the subsurface zones.

Amendments

The two types of iron used in the laboratory studies were colloidal iron (Micropowder iron, 1-3μm, grade S-3700, ISP Technologies, Inc.), and industrial mixed mesh scrap iron (100% passing 8 US Sieve; Master Builders, Inc., or Peerless, Inc.). The potato processing waste came as clarifier waste from the J.R. Simplot Company potato processing plant in Blackfoot, ID. Thermal polyaspartate (tpA) was obtained from the Donlar Corporation. Cheese whey was obtained from the Washington State University Creamery, Pullman, WA and from Star Valley Cheese, Star, WY.

Saturated soil paste with amendments

Ten treatment runs and one control run were performed in triplicate for two periods of time, 14 days and 28 days. For each run, 12.5 g of each soil (PCO-01, -02, -03, -04) were measured into a saturated paste cup and mixed with 30 mL of 18 MΩ-cm water. Dry amendments were added to the soil prior to addition of the water; wet amendments were added to the water prior to addition to the soil. Dry amendments were measured at 1.0% by weight; wet amendments were measured at 1.0% by volume, with the exception of potato waste amendment at 5.0% (by wet weight). Professor Frank Rosenzweig, of the University of Idaho Department of Biological Sciences, provided approximately 10,000-ceIls/mL suspension of a 50:50 mixed inoculum of *Desulfovibrio desulfuricans* and *Desulfatomaculum orientis,* that was used to inoculate some soil pastes. Pastes were sealed under nitrogen and two layers of parafilm and placed into an incubator at 25°C for either 14 days or 28 days. At the conclusion of the run, pastes were mixed and filtered. Filtrate was analyzed for selenium, dissolved multi-elements, and sulfate if there was enough filtrate left. Amendments tested included sulfate reducing bacteria inoculum (SRB), c-Fe, mb-Fe, mb-Fe plus SRB, potato starch, potato starch plus SRB, ferric ion chelated thermal polyaspartate (ferric tpA), ferric tpA plus SRB, potato processing waste, and potato processing waste plus SRB.

Four treatment runs and one control were performed in triplicate for 14 days. For each run, 12.5 g of soil was measured into a saturated paste cup and mixed with 30 mL of 18 MΩ-cm water. Dry amendments were added to the soil prior to addition of the water; wet amendments were added to the water prior to addition to the soil. The soil was amended with: Star Valley cheese whey, Washington State University cheese whey, Star Valley cheese whey plus Fe, Washington State University cheese whey plus Fe. The soil was amended with cheese whey measured at 3% wet weight. The iron amendment was measured at 1% dry weight. Pastes were sealed under nitrogen and two layers of parafilm and placed into an incubator at 25° C for 14 days. At the conclusion of the experiment pastes were mixed and filtered. The filtrate was analyzed for total selenium.

Surface amendments

A shallow subsurface field experiment examined the effects of granular iron and cheese whey on the shallow subsurface chemistry and forage uptake. Three fields were staked out with each measuring 7 m wide by 35 m long; 7 m separated each field. Each field has three suction lysimeters (Soil Moisture Equipment Model #1920F1 pressure-vacuum soil water sampler, ceramic), installed at a depth of 60 cm, with 7 m separating each lysimeter. The lysimeters are plumbed into a central sampling shed for

sampling. Approximately 450 kg of-8 +50 mesh iron granules were placed over the iron treatment field (0.54 kg Fe/sq m) using hand spreading. 15,000 Liters of cheese whey was sprayed through a 10-cm hose over the cheese whey treatment field (61 L whey/sq m). The final field acted as a control. The fields were then seeded with a typical variety mixture of seeds used during the normal reclamation activity (reclamation grass seed mix, Granite Seed Company, Lehi, UT). The suction lysimeters were then periodically sampled and the water samples were analyzed for selenium.

Subsurface amendment zone

In a subsurface zone, field amendment approach, we placed 4 treatment cells in a 150 m (1) x 15 m (w) x 6 m (d) excavation. We developed a subsurface sampling assembly (SSA, vide infra) that consists of a collection pan lysimeter, n = 4 in each cell, and suction lysimeter at - 3 m, n = 2 in each cell, connected to 250 L totalizing flow, collection barrel. All of the sampling areas in the SSA are accessible by wellhead or sampling tubing in a subsurface utility corridor. Homogenized waste rock soil (0.7 m) was laid directly over the sampling zone. This zone was further covered with homogenized waste rock soil (control, cell 2), 5 cm iron metal granules (cell 2), 5 cm of iron granules plus 0.7 m of potato waste amended soils (cell 3), or 0.7 m of potato waste amended soil (cell 4). Potato waste amendment rate to the soil layer is estimated at 5 % wet weight. Each of the cells was then covered to ground level with homogenized waste rock soil.

RESULTS AND DISCUSSION

Characterization

The neutron activation analyses of the waste rock soils show selenium concentrations that range from 0.218 mmol/kg (16 mg/kg) in sample PCCH to 0.922 mmol/kg (70 mg/kg) in sample PCO-04 (Table 1).

Sample	Se^{75}	units
PCO-01	0.431	mmol/kg-soil
PCO-02	0.484	mmol/kg-soil
PCO-03	0.681	mmol/kg-soil
PCO-04	0.922	mmol/kg-soil
PCCH	0.218	mmol/kg-soil

Table 1. Results of nuclear activation analysis performed on dried and ground Pole Canyon overburden

The sequential extraction scheme (SES) of Martens and Suarez identifies different extractable selenium species in a sample (Table 2). Results from applying this method to sample PCO-03 indicate that about 2% of the mass of selenium present in the sample is immediately leachable, and most of it appears to be selenite, SeO_3^{2-}. After all of the oxidation/extraction steps of the SES about 0.016 mmol-Se/kg soil is extracted. This is about 50 X less than the bulk selenium determined for this sample by NAA (0.68 mmol-Se/kg-soil). Of the total soil selenium determined by NAA, 2% is extractable selenite with the remaining selenium in the soil particles and probably present as either selenide (-II) or zero-valent selenium.

Extractant/Species	µmol-Se/L-Extract		mmol-Se/kg-Soil
Water/Se(IV)	0.322	0.213	0.00130
Water/Se(IV) and Se(VI)	0.234	0.198	0.00110
Water/Se(-II)	0.101	< 0.00890	0.000270
Buffer/Se(IV)	2.60	2.67	0.0130
Buffer/Se(IV) and Se(VI)	2.50	2.53	0.0130
Buffer/Se(-II)	< 0.00890	< 0.00890	< 0.0000450
Persulfate/Se(IV) and Se(-II)	0.238	0.175	0.00100
Total Extractable Se	-	-	0.0160

Table 2. Results of the sequential extraction procedure performed on unweathered Pole Canyon waste rock soil samples.

Analysis of the drill core data (not shown) for total Se and P_2O_5 demonstrates clear patterns of selenium abundance in the middle waste shales of the phosphoria formation. Concentrations exceeding 2.5 mmol-Se/kg-soil (200 mg/kg) are observed at several depths.

Professor Dennis Geist of the University of Idaho Department of Geology and Geological Engineering interpreted a limited microscopic and electron microprobe overburden study conducted by the University of Hawaii. Limestone and siltstone comprise the majority of the overburden. The lighter-colored limestones contain no visible sulfide and little organic matter, however, it appears that the siltstones are the host rock for pyrite (FeS_2) and sphalerite (ZnS) minerals and also contain hydrocarbons. Microprobe analysis indicates that the pyrite grains examined contain 0.66 wt % Se and that pyrite accounts for approximately 0.2% of the siltstone fraction. Selenium can replace sulfur in the crystal lattice by isomorphous substitution. When analyzed with the SEM, the morphology of pyrite inclusions were found as framboidal and cubic (Figure 1). Some grains analyzed showed selenium substituting for sulfur in

amounts as high as 6 %. The pyrite grains in samples analyzed by SEM-XRF ranged from O.I to 1 wt % selenium.
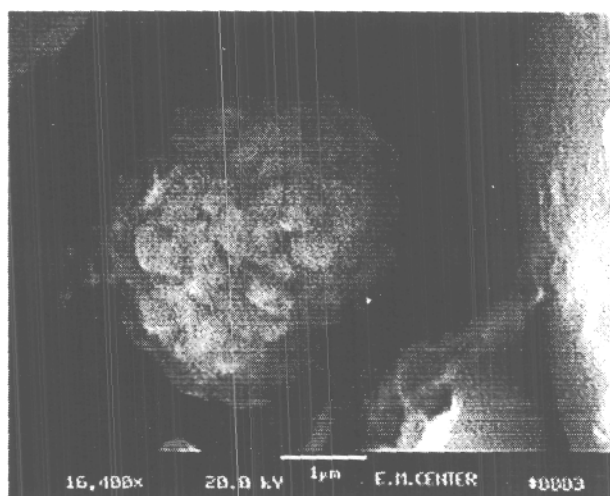

Figure 1. Scanning electron micrograph (16400X) of a framboidal pyrite granule containing 1-3% selenium.

The quantitative microprobe results show that the concentration of selenium in the pyrite grains is sufficient to account for most of the selenium concentration in the overburden. These results also support the hypothesis that "micro" pyrite oxidation is most likely occurring in the overburden even though there is no appreciable increase in acidity of Pole Creek. Limestone is an excellent neutralizer of acid rock drainage resulting from oxidation of the pyrite, and its presence is confirmed through this analysis. The USGS has observed Se(0) as the dominant species in their analysis of freshly sampled subsurface ore zones and have proposed a weathering and re-deposition of zero-valent selenium in fracture zones (Grauch, 2000). This is consistent with the overall reaction pathway of selenium and the thermochemically stable oxidation states in these systems (Table 3).

	+6		+4		0		-2
Acidic Solution	SeO_4^{2-}	1.15 $\leftrightarrow$	H_2SeO_3	0.74 $\leftrightarrow$	Se	-0.11 $\leftrightarrow$	H_2Se
Basic solution	SeO_4^{2-}	0.03 $\leftrightarrow$	SeO_3^{2-}	-0.36 $\leftrightarrow$	Se	-0.67 $\leftrightarrow$	Se^{2-}

Table 3. Standard reduction potentials (V) for the selenium oxidation - reduction pathway.
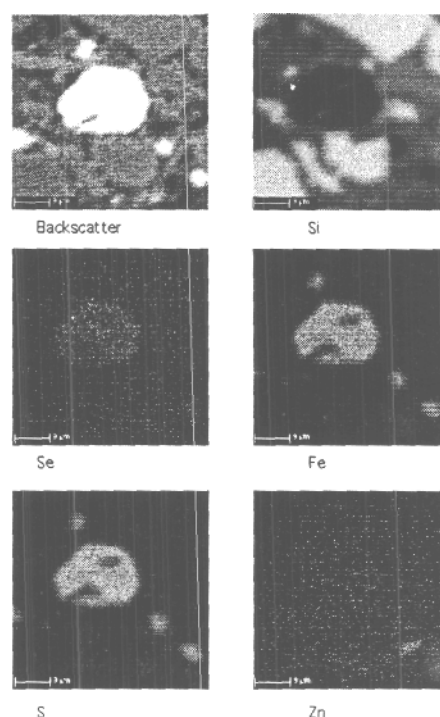
Figure 2. Element map showing a seleniferous pyrite grain from microprobe analysis of Pole Canyon overburden samples. White indicates presence and black indicates absence of the element. Backscatter view indicates area of highest metal density as white.

Laboratory amendment tests

The ten soil amendments used were anaerobic sulfate reducing bacteria inoculum (SRB), colloidal iron (c-Fe), mixed mesh scrap iron (mb-Fe), mb-Fe/SRB, potato starch (PS), PS/SRB, ferric thermal poly-aspartate (Fe(III)-tpA), Fe(III)-tpA/SRB, potato waste (PW), and PW/SRB. Figure 3 shows the effects of the ten soil amendment treatments on the amount of selenium leached after day 14. Fe(III)-tpA, Fe(III)-tpA/SRB, PW and PW/SRB all inhibited the amount of selenium leached by over 99 %. In the same time mb-Fe/SRB, PS, and PS/SRB reduced the amount leached by at least 95 %. Remaining amendments reduced the selenium leached from 56 % to 84 %. During this 14-day trial, the amendments that were mixed with SRBs outperformed those same treatments without SRB and the SRB alone. After 28 days, with the exception of PS, there was little difference between the amount of selenium leached in the samples treated with an amendment plus SRB and those with just the amendment. In some trials, the absence of SRB inoculation appears to have had a slightly lower Se concentration result. This may be due to the gradual infiltration of oxygen into the inoculated pastes, which limits the ability of the

anaerobic SRBs to maintain a viable population. Conversely, natural SRB populations in the non-inoculated media may have increased.

These approaches demonstrated varying ability to inhibit selenium release within the time frame of the experiment, and none of the approaches showed significant reversal of positive effects within the time frame of the study. In four weeks, all treatments except c-Fe (86 %) and SRB (82 %) showed the ability to inhibit selenium releases by at least 98 %.
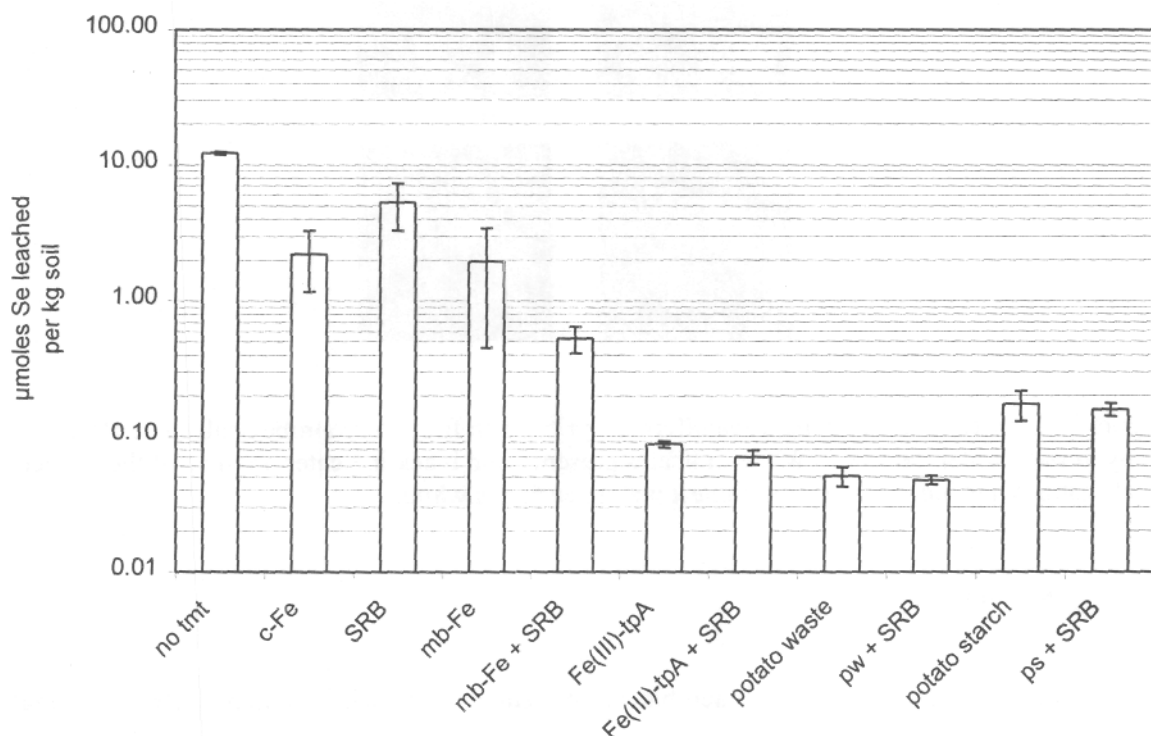

Figure 3.   Effects of amendments on amount of selenium leached from overburden saturated paste after 14 days, n=3.

In an additional experiment, waste cheese whey from two different creameries was applied to seleniferous waste rock soil. In 14 days, there was a decrease in selenium levels by all the treatments compared to the control (Figure 4). The greatest level of decrease was the combination of cheese whey and iron. The Star Valley whey plus Fe amendment had over a 99% removal of selenium compared to the control. These lower levels might suggest the possibility of a synergism between the two that facilitates microbial reduction and chemical reduction or co-precipitation. Another possibility is that the iron adds another energy source for selenium reducing microbes via the SRB hydrogenase pathway (Barton and Tomei,
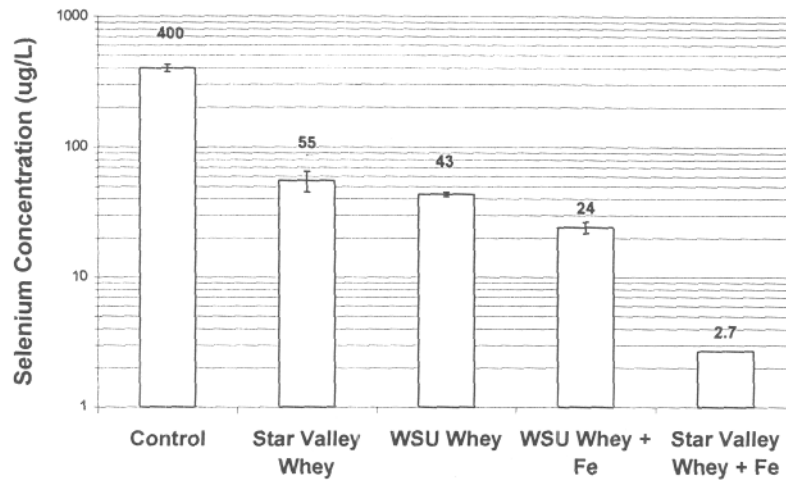
Figure 4. Effects of cheese whey and iron metal amendments on amount of selenium leached from overburden saturated paste after 14 days, n=3.

1995). As iron oxidizes it releases electrons as H_2 that are available to the microbes to use as a energy source. Alternatively, iron has been shown to co-precipitate selenium (Manning and Burau, 1995). It is also possible that the iron provides a reducing environment where oxidized selenium can be reduced chemically. It has been shown that reduction of selenium oxyanions to elemental selenium by zero-valent iron must be done under acidic conditions (Marchant, 1976; Murphy, 1992). The cheese whey might provide lower pH levels that are more conducive to chemical reduction of selenium by zero-valent iron.

Surface amendment trial

Figure 5 shows that both the cheese whey and iron granule surface amended soils were over four times lower in vadose zone dissolved selenium in the first sampling. Cheese whey appeared to largely limit any mobilization of selenium in the shallow subsurface. The results of the surface applied cheese whey indicate a 99% reduction of Se in the shallow subsurface water collection versus control. As the sampling season progressed, both the control and the amended soil levels decreased. This could indicate that the spring runoff in this mountainous area is important in the mobilization of oxidized selenium. The amendments may provide a chemical-microbial change in the soil environment that sequestered selenium or limited oxidation and mobilization. If the selenium in the soil were kept in a reduced or mineralized state by the cheese whey and iron, it would be less available to plant root systems in the shallow sub-surface. Amendments preventing the oxidation of selenium and uptake by plants may reduce the possible exposure pathway through re-vegetated forage on the reclaimed land.
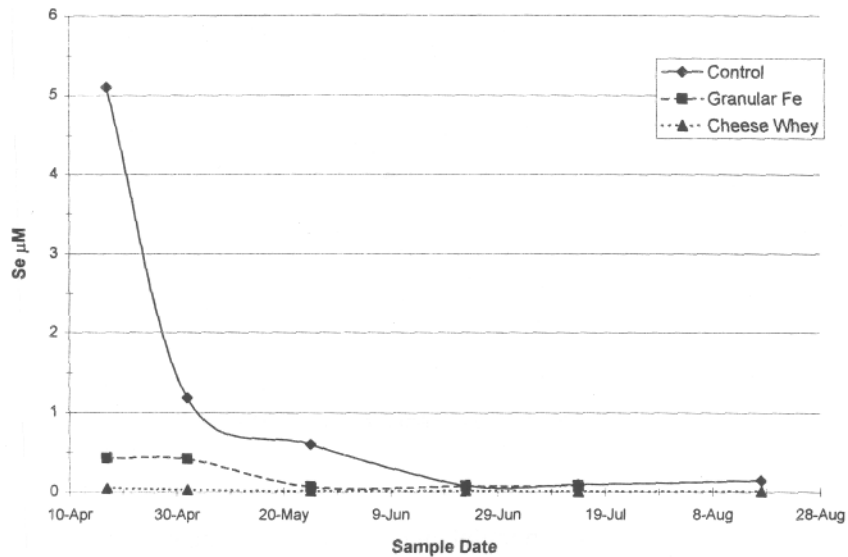
Figure 5. Surface amendment application results. Shallow sub-surface Se concentrations following cheese whey or iron granule amendment application in the previous August.

Subsurface amendment trials

The design of the subsurface sampling assembly is shown in Figure 6. The results of the 4 cells in the amendment trial are shown in Figure 7. Vadose zone, pore water levels of selenium are observed to be lower in the treatments compared to the control. The lowest levels were observed in the treatment zone that combined potato waste and iron metal. These data suggest that there is a synergism between the two chemistries that make for an environment conducive to selenium stabilization, thereby limiting leaching. Tracking of Se levels in the control and treatments is observed in the ceramic suction lysimeters and the collection pan lysimeters (data not shown) of the SSA.

Mobilized Se in waste rock soils is observed to be limited in zones amended with potato waste, potato waste-iron, iron and cheese whey. The reactive pathway is unclear at this time, however our laboratory experiments strongly suggest a combined chemical-microbial pathway. This pathway is currently under study. The results of this field experiment are encouraging since some success in altering large-scale soil chemistry, under difficult field conditions, was observed.
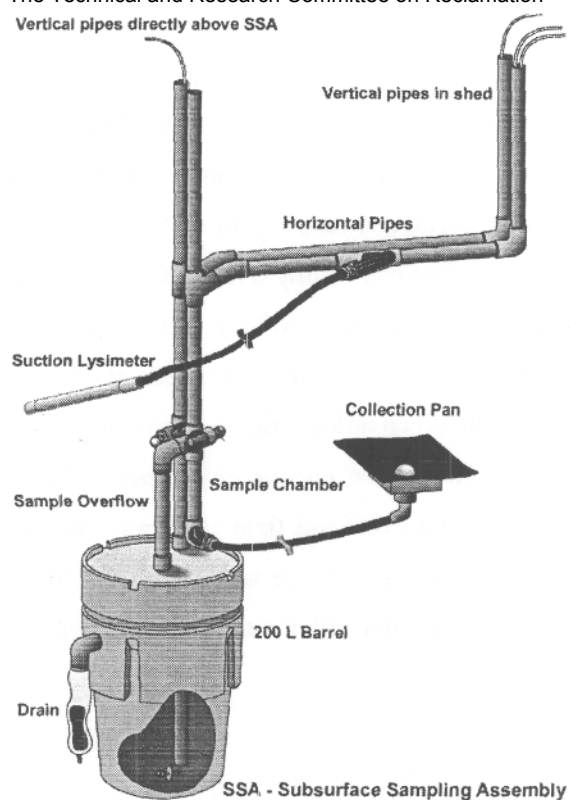
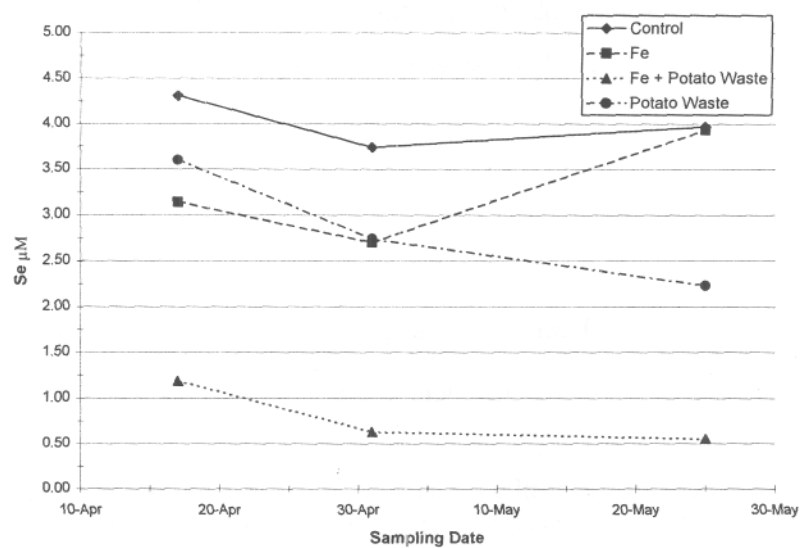Figure 6. Sub-surface sampling assembly (SSA).

Figure 7. Subsurface amendment application results. Shallow sub-surface Se concentrations following iron granule, potato waste, iron granule and potato waste amendment application in the previous August.

CONCLUSIONS

Selenium is readily mobilized from the waste rock soil at the Pole Canyon impoundment of the US Western Phosphate Resource Area. Selenium is observed in the middle shale fraction of the waste rock as the reduced species found in seleno-pyrite and zero-valent selenium. About 2 % of the waste rock Se is readily extractable as selenite. This selenite is readily oxidizable to selenate. Mobilized Se in waste rock soils is observed to be limited in zones amended with potato waste, potato waste-iron granules, iron granules and cheese whey. The reactive pathway is unclear at this time, however our laboratory experiments strongly suggest a combined chemical-microbial pathway. This pathway is currently under study. The results in these experiments are encouraging since success in altering large-scale soil chemistry and selenium mobilization under difficult field conditions, was observed. These studies assist in the evaluation of Se control approaches that use waste material amendments in mining impacted ecosystems, however it is recognized that controlling oxidative release in these disturbed ecosystems is a particularly difficult challenge.

ACKNOWLEDGEMENTS

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