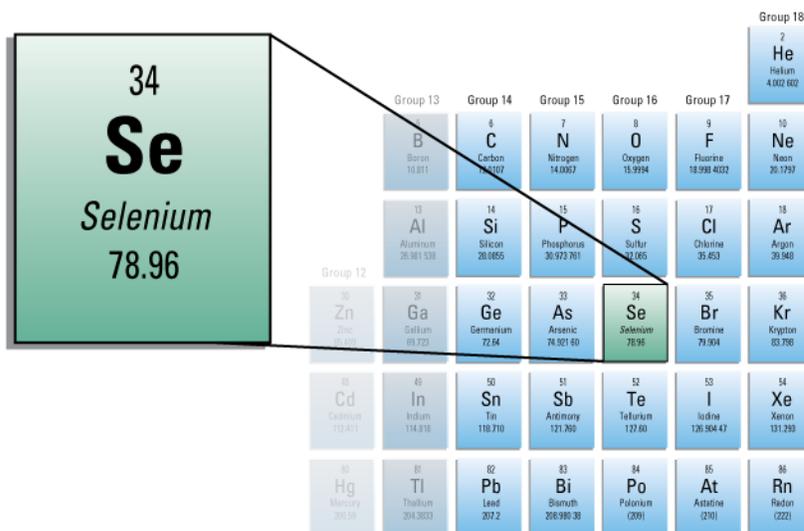




Prepared in cooperation with  
U.S. Environmental Protection Agency

# Preliminary Results of Sequential Extraction Experiments for Selenium on Mine Waste and Stream Sediments from Vermont, Maine, and New Zealand

By N. M. Piatak, R. R. Seal II, R.F. Sanzolone, P. J. Lamothe, and Z. A. Brown



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# Conversion Factors

## SI to Inch/Pound

<b>Multiply</b>	<b>By</b>	<b>To obtain</b>
<b>Length</b>		
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
<b>Volume</b>		
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
<b>Mass</b>		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound avoirdupois (lb)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:  
 $^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$

# Preliminary Results of Sequential Extraction Experiments for Selenium on Mine Waste and Stream Sediments from Vermont, Maine, and New Zealand

By N. M. Piatak<sup>1</sup>, R. R. Seal II<sup>1</sup>, R.F. Sanzolone<sup>2</sup>, P. J. Lamothe<sup>2</sup>, and Z. A. Brown<sup>2</sup>

## Abstract

We report the preliminary results of sequential partial dissolutions used to characterize the geochemical distribution of selenium in stream sediments, mine wastes, and flotation-mill tailings. In general, extraction schemes are designed to extract metals associated with operationally defined solid phases. Total Se concentrations and the mineralogy of the samples are also presented. Samples were obtained from the Elizabeth, Ely, and Pike Hill mines in Vermont, the Callahan mine in Maine, and the Martha mine in New Zealand. These data are presented here with minimal interpretation or discussion. Further analysis of the data will be presented elsewhere. The total concentrations of Se range from 0.43 to 44 mg/kg for stream-sediment samples (n=8), from 2.5 to 140 mg/kg for oxidized mine waste (n=7), and from 1.7 to 17 mg/kg for oxidized and unoxidized flotation-mill tailings (n=4). The highest total concentrations are for the burnt or roasted mine-waste samples from Vermont. The extraction technique employed the following dissolution reagents, each nominally targeting specific solid-phase forms (given in parentheses): 0.1 M  $\text{KH}_2\text{PO}_4$  (step 1- soluble and exchangeable), 15%  $\text{CH}_3\text{COOH}$  (step 2- carbonates), 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  (step 3- organic material), 0.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 0.10 M  $\text{HCl}$  (step 4- amorphous Fe- and Al-hydroxides and amorphous and crystalline Mn-oxides), 1.0 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 25%  $\text{CH}_3\text{COOH}$  (step 5- crystalline Fe-oxides),  $\text{KClO}_3$  + concentrated  $\text{HCl}$  (step 6- sulfides and selenides), and a mixture of concentrated  $\text{HF}$  +  $\text{HNO}_3$  +  $\text{HClO}_4$  (step 7- residual). The largest fractions of Se were extracted in steps 5, 6, and 7. For stream-sediment samples, Se was detected only in leachates from these last three steps in which more aggressive reagents were used. The last three steps liberated greater than 88% of the Se in oxidized mine-waste samples. Approximately half or more of the Se in the flotation-mill tailings from the Elizabeth and Callahan mines was found in leachate from step 6. In contrast, step 5 leachate for the Martha-mine tailings contains the majority of the Se. Overall, 10% or less of the Se was extracted in each of the first four steps for all media. Only oxidized mine waste from Vermont and the flotation-mill tailings from Maine contain detectable concentrations of Se in the ligand exchangeable fraction (step1). The results presented here have important implications for the release to the environment and potential bioavailability of Se from these mine-waste and stream-sediment samples.

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## Introduction

Sequential partial dissolutions were used to characterize the distribution of selenium in stream sediments, mine wastes, and flotation-mill tailings at several sites including the Elizabeth, Ely, and Pike Hill mines in Vermont, the Callahan mine in Maine, and the Martha mine in New Zealand. In general, extraction techniques are developed to extract metals associated with operationally defined solid phases giving insight into speciation. The release of Se to the environment and toxicity to the biosphere are related to its speciation and partitioning among various organic and inorganic solid phases, rather than to its total concentration. The oxidized form of selenium, selenate, is highly mobile and toxic and readily bioavailable because its salts are soluble and it is weakly adsorbed by particulates. Selenite predominates under mildly reducing conditions, is immobilized by adsorption onto particulates, and is less toxic than selenate. Under highly reducing, acidic or organic-rich conditions, elemental Se and selenide are the main forms of Se, and are generally insoluble and therefore not bioavailable (McNeal and Balistrieri, 1989). Selenide is the species expected to be present in solid solution in primary sulfide minerals such as pyrite, pyrrhotite, and chalcopyrite. Sulfate also plays a role in Se toxicity in that sulfate inhibits the uptake of selenate by microorganisms (Mayland and others, 1989).

This study was prompted by concerns for stream sediments raised by the preliminary Baseline Ecological Risk Assessment (BERA) at the Elizabeth mine. The results of this study will be used to characterize better the forms of Se in the sediment and relate this to its potential toxicity. Of the nineteen samples analyzed, six are stream-sediment samples from the Elizabeth mine. Samples of mine waste from the Elizabeth mine were included to constrain potential sources of Se found in the stream sediments. Samples from the others sites were included for comparison purposes.

## Methods

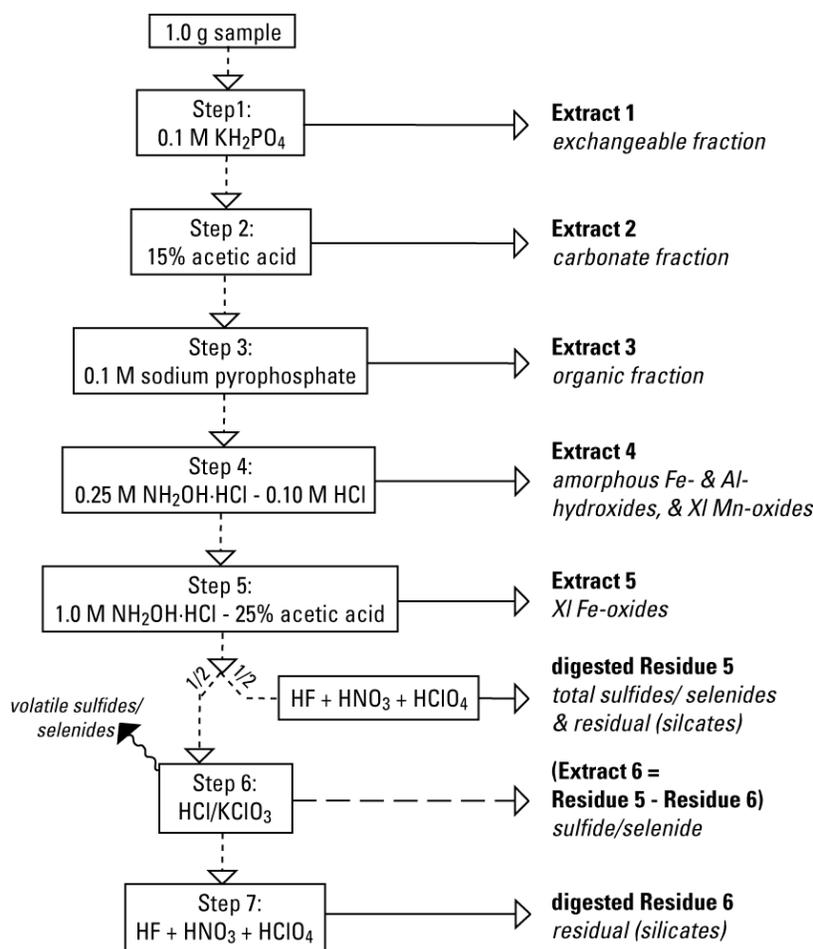
Minerals were identified by X-ray diffraction analysis (XRD). Powder patterns were collected using a Scintag X1 automated powder diffractometer equipped with a Peltier detector with  $\text{CuK}\alpha$  radiation. The XRD patterns were analyzed using Material Data Inc.'s JADE software and standard reference patterns. Relative amounts of phases were estimated using the Siroquant computer program that utilizes the full XRD profile in a Rietveld refinement (Taylor and Clapp, 1992). Amorphous content was determined using Siroquant on patterns of samples spiked with 15 wt. %  $\text{Al}_2\text{O}_3$ . The analytical uncertainty of the Siroquant results is approximately  $\pm 5$  wt. %. The colors of the samples were determined using soil color charts (Munsell Soil Color Charts, 1994).

Seven-step sequential extractions were performed on nineteen mine-waste and stream-sediment samples, on three duplicates, and on two blanks (Table 1). One blank was used for analytical calibration purposes. Samples are either grab or composites. Most composites consist of a minimum of 30 sample increments sampled over a measured area divided into a stratified grid. One stream-sediment composite (Ely-SD-09) consists of three increments from different depositional areas in the stream. Samples were air-dried, sieved to  $<2$  mm (or  $<180$   $\mu\text{m}$  for sample 1139830-SD, stream sediment from Pike Hill), and homogenized (Table 1). A split of the original untreated sample was analyzed for Se by hydride-generation atomic absorption spectrometry (HG-AAS) after digestion with a mixture of  $\text{HNO}_3$ -HF- $\text{HClO}_4$  (Hageman and others, 2002). Also, residues remaining after extraction steps 5 and 6 were analyzed after digestion by HG-AAS. Extraction solutes were analyzed for Se by inductively coupled plasma-mass spectrometry (ICP-MS) (Lamothe and others, 2002). The accuracy for ICP-MS and HG-AAS analysis is approximately  $\pm 10\%$ .

**Table 1. Sample descriptions.**

Sample ID	Extract ID	Mine	Type	Locations	Latitude	Longitude	Date	Method	Preparation
Blank	A	-	blank	Blank	-	-	-	-	none
EMV-SED-LOC05	B	Elizabeth	stream sediment	Copperas Brook below weir at sediment basin outlet.	43.82814	-72.32739	June-05	grab	dry sieved <2 mm
EMV-SED-LOC05-Dup1	C	Elizabeth	stream sediment	Copperas Brook below weir at sediment basin outlet. Duplicate.	43.82814	-72.32739	June-05	grab	dry sieved <2 mm
EMV-SED-LOC06	D	Elizabeth	stream sediment	Copperas Brook below flume at mouth.	43.83129	-72.32686	June-05	grab	dry sieved <2 mm
EMV-SED-04	E	Elizabeth	stream sediment	Copperas Brook upstream from flume at mouth.	43.83112	-72.32710	June-05	grab	dry sieved <2 mm
EMV-SED-06	F	Elizabeth	stream sediment	Copperas Brook down-gradient from decant and sediment basin drainage confluence.	43.82814	-72.32730	June-05	grab	dry sieved <2 mm
EMV-SED-701	G	Elizabeth	stream sediment	Copperas Brook at confluence with decant diversion.	43.82903	-72.32760	June-05	grab	dry sieved <2 mm
EMV-SED-702	H	Elizabeth	stream sediment	Copperas Brook downstream from confluence with decant diversion.	43.83050	-72.32746	June-05	grab	dry sieved <2 mm
Ely-SD-09	I	Ely	stream sediment	Ely Brook downstream of culvert, upstream from confluence with Schoolhouse Brook	43.91873	-72.28652	Dec-1-05	composite	dry sieved <2 mm
1139830-SD	J	Pike Hill	stream sediment	Pike Hill Brook above Richardson Road at weir.	44.06389	-72.30194	Aug-2-05	composite	dry sieved <180 µm
04Smith3	K	Pike Hill	mine waste	Lowermost mine-waste dump below main adit at the Smith mine.	44.05464	-72.30517	Oct-19-04	composite	dry sieved <2 mm
CLHN-TP-2	L	Callahan	tailings	Tailings pile at edge of wetlands.	44.34306	-68.80556	Jul-19-04	grab	dry sieved <2 mm
Blank	M	-	blank	Blank	-	-	-	-	none
EMV-SED-LOC05-Dup2	N	Elizabeth	stream sediment	Copperas Brook below weir at sediment basin outlet. Duplicate.	43.82814	-72.32739	June-05	grab	dry sieved <2 mm
TP1-S-unox	O	Elizabeth	tailings	Tailings pile 1 (TP1) near base of TP2.	43.82332	-72.32990	Jul-20-04	grab	air-dried
TP1-S-unox-Dup	P	Elizabeth	tailings	Tailings pile 1 (TP1) near base of TP2. Duplicate	43.82332	-72.32990	Jul-20-04	grab	air-dried
TP1-S-ox	Q	Elizabeth	tailings	Tailings pile 1 (TP1) near base of TP2.	43.82332	-72.32990	Jul-20-04	grab	air-dried
02TP3A	R	Elizabeth	mine waste	TP3 yellow pile below road.	43.82139	-72.33611	Oct-10-02	composite	dry sieved <2 mm
02TP3C	S	Elizabeth	mine waste	TP3 roasted pile below road.	43.82056	-72.33639	Oct-10-02	composite	dry sieved <2 mm
02Ely2A	T	Ely	mine waste	Upper mine waste pile.	43.92756	-72.28572	Oct-8-02	composite	dry sieved <2 mm
02Ely10A	U	Ely	mine waste	Roast beds.	43.92389	-72.28556	Oct-8-02	composite	dry sieved <2 mm
04PKHL9	V	Pike Hill	mine waste	Partly burnt red tailings pile above the mine road.	44.06258	-72.30519	Oct-20-04	composite	dry sieved <2 mm
04PKHL11	W	Pike Hill	mine waste	Large mine-waste dump below the mine access road.	44.06353	-72.30511	Oct-20-04	composite	dry sieved <2 mm
NZ-Newmont-A	X	Martha	tailings	Tailings pile.	-37.38592	175.84292	Dec-16-05	grab	air-dried

The selenium distributions determined by sequential extractions were operationally defined by the reagents used, the reaction times, temperatures, and sample to volume extract ratio for each step. Not one reagent, time, and temperature can be applied to all sample types to recover a given phase; extractions were matrix-dependent. Also, this extraction procedure attempted to differentiate the amorphous (step 4) versus crystalline (step 5) Fe-oxide and Fe-hydroxide phases. There is a gradation from amorphous to cryptocrystalline to crystalline Fe-oxides and hydroxides and Hall and others (1996a) discussed the subtleties in differentiating among the phases depending on reagent strength. Additional complicating factors included the possibility that occluded grains may persist past their designated dissolution step or factors such as grain size, mineralogy, or solid solution may affect the reactivity of phases. The sequential extraction procedure used in this study is outlined below and illustrated in Figure 1. The procedure was a combination of methods developed by Chao (1972), Chao and Sanzolone (1977; 1989), Chao and Zhou (1983), Chester and Hughes (1967), Hall and others (1996a, b), and Kulp and Pratt (2004). The hypothetically targeted species in each step are given in *italics*. The species or phases dissolved by each step will be investigated by chemical and mineralogical analysis and discussed in future studies.



**Figure 1.** Schematic of sequential extraction procedure. After extract step 5, half of sample was digested and analyzed by HG-AAS and the other half was treated in step 6. Because of the potential for Se volatilization in step 6, Se in extract 6 was calculated from the difference between Se in residue from step 5 and Se in residue from step 6.

- **Step 1:** (*soluble, adsorbed, and exchangeable Se fraction*) Combine 1.0 g of sample with 25 mL 0.1 M  $\text{KH}_2\text{PO}_4$ , agitate for 2 hours at 25°C. Centrifuge for 10 minutes (15,000 rpm, Sorvall RC2-B refrigerated supercentrifuge), decant extract and dilute with deionized water (DIW) to 50 mL. Add 500  $\mu\text{L}$  concentrated ultrapure  $\text{HNO}_3$ . Analyze extract by ICP-MS (**Extract 1**).
- **Step 2:** (*Se associated with carbonates*) Combine residue with 25 mL 15% acetic acid, agitate for 2 hours, centrifuge, decant, fill to 50 mL volume with DIW. Analyze extract by ICP-MS (**Extract 2**).
- **Step 3:** (*organic Se*) Combine residue with 25 mL 0.1 M sodium pyrophosphate and agitate for 1 hour. Centrifuge and decant. Add another 25 mL 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$  to residue, agitate for 1 hour, centrifuge, decant, add to first split and bring to 50 mL volume with DIW. Analyze extract by ICP-MS (**Extract 3**).
- **Step 4:** (*amorphous Fe- and Al-hydroxides and amorphous and crystalline Mn-oxides*) Mix residue with 25 mL 0.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  (hydroxylamine hydrochloride)- 0.10 M  $\text{HCl}$  for 30 minutes in a water bath at 50-54°C. Stir occasionally. Centrifuge, decant and fill to 50 mL with DIW. Add 500  $\mu\text{L}$  concentrated ultrapure  $\text{HNO}_3$  and analyze by ICP-MS (**Extract 4**).
- **Step 5:** (*crystalline “XI” Fe-oxides*) Combine residue with 20 mL 1.0 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25%  $\text{CH}_3\text{COOH}$ . Cap and shake. Place in boiling water (~90° C) bath for 3 hours uncapped, mix occasionally. Centrifuge and decant. Rinse residue with 10 mL 25%  $\text{CH}_3\text{COOH}$ , by hand-shaking and then centrifuge and decant into first split. Carry out a second leach with 20 mL 1.0 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25%  $\text{CH}_3\text{COOH}$  but heat in boiling water bath for 1.5 hours. Mix occasionally. Centrifuge and decant into first split. Fill to 50 mL with DIW. Analyze extract by ICP-MS (**Extract 5**).
- **Residue 5:** (*sulfides and selenides and residual Se*) Dry residue at approximately 100°F (~38°C) and then disaggregate to homogenize. Split residue in half. Analyze half by HG-AAS (**Residue 5**). Treat other half of residue in next step.
- **Step 6:** (*sulfides and selenides- acid volatile phases volatilized; step may potentially attack surfaces, corners, or edges of silicate minerals*) Add 0.5 g of  $\text{KClO}_3$  to residue and mix. Slowly add 10 mL concentrated  $\text{HCl}$  and mix. Let sit for 45 minutes with occasional gentle shaking. Add 10 mL of DI, mix, centrifuge, and discard. To the residue, add 10 mL 4 N  $\text{HNO}_3$  and heat in boiling water bath for 20 minutes, centrifuge and discard. Add 10 mL DI, shake and centrifuge for 10 minutes, also discard. Because some sulfide and selenides may be volatilized, calculate step 6 fraction by subtracting Se in residue from step 5 from Se in residue from step 6 (**Residue 5 – Residue 6**).
- **Step 7:** (*residual Se*) Dry residue at approximately 100°F (~38°C). Digest sample with mixture of  $\text{HF} + \text{HNO}_3 + \text{HClO}_4$  and analyze by HG-AAS (**Residue 6**) following procedure of Hageman and others (2002).

## Sample Descriptions

Samples used in the sequential extractions from the abandoned mines in Vermont include stream sediments, oxidized mine waste, and flotation-mill tailings, whereas only tailings were used from the Callahan mine in Maine and from the Martha mine in New Zealand (Table 1). The Elizabeth, Ely, and Pike Hill mines are Superfund sites in the Vermont copper belt that were mined intermittently from 1793 to 1958. These deposits, mined primarily for Cu and Zn, are Besshi-type

massive sulfides composed of pyrrhotite, chalcopyrite, and minor sphalerite and pyrite (Slack and others, 2001). Flotation-mill tailings from the Elizabeth mine include very dark gray sulfidic unoxidized tailings (TP1-S-unox) collected at depth and the overlying yellow oxidized material (TP1-S-ox) (Hammarstrom and others, 2001). Samples of oxidized mine waste (not processed in a flotation mill) include yellow jarositic waste (02TP3A) and yellowish red hematitic waste (02TP3C) that was partly roasted during copper production (Table 1; Hammarstrom and others, 2003). The six stream-sediment samples in Table 1 from the Elizabeth mine were collected in Copperas Brook downstream from the oxidized mine-waste piles and flotation-mill tailings. Colors of stream sediments include brownish yellow, dark yellowish brown, and strong brown based on soil color charts (Munsell Soil Color Charts, 1994). The chemistry of the mine drainage from Copperas Brook was described by Seal and others (2001).

Samples used in the extractions from the Ely mine include reddish yellow mine waste (02Ely2A) from the upper waste piles and red mine waste (02Ely10A) from roast beds in the lower waste piles (Table 1). Mine waste at this site was characterized in detail in Piatak and others (2004). One three-composite stream sediment from Ely Brook (Ely-SD-09) was collected downstream from the mine site and upstream from the confluence with Schoolhouse Brook (Table 1). The sample is strong brown probably because of Fe-rich precipitates coating the streambed.

Three samples of mine waste from the Pike Hill mines include olive yellow colored waste from the Smith mine (03Smith3), a partly burnt yellowish brown mine waste (04PKHL9), and a yellow oxidized mine waste (04PKHL11; Table 1). The two latter samples are from near the top of Pike Hill near the Union and Eureka mines. Locations and detailed characterizations of these samples were given in Piatak and others (2006). One strong brown stream sediment (1139830-SD) downstream from the Union and Eureka mines is also included in this study (Table 1).

The Callahan mine, a Superfund site in Brooksville, Maine, exploited a Kuroko-type massive sulfide deposit. Massive bodies of pyrite, sphalerite, and chalcopyrite were mined by open-pit methods and underground workings from 1968 to 1972 for Zn, Cu, Pb, and Au (Bouley and Hodder, 1984). Light gray, fine-grained tailings (CLHN-TP-2) were collected from the approximately 45,000 m<sup>2</sup> (11-acre) tailings pile at the Callahan mine (USEPA, 2005).

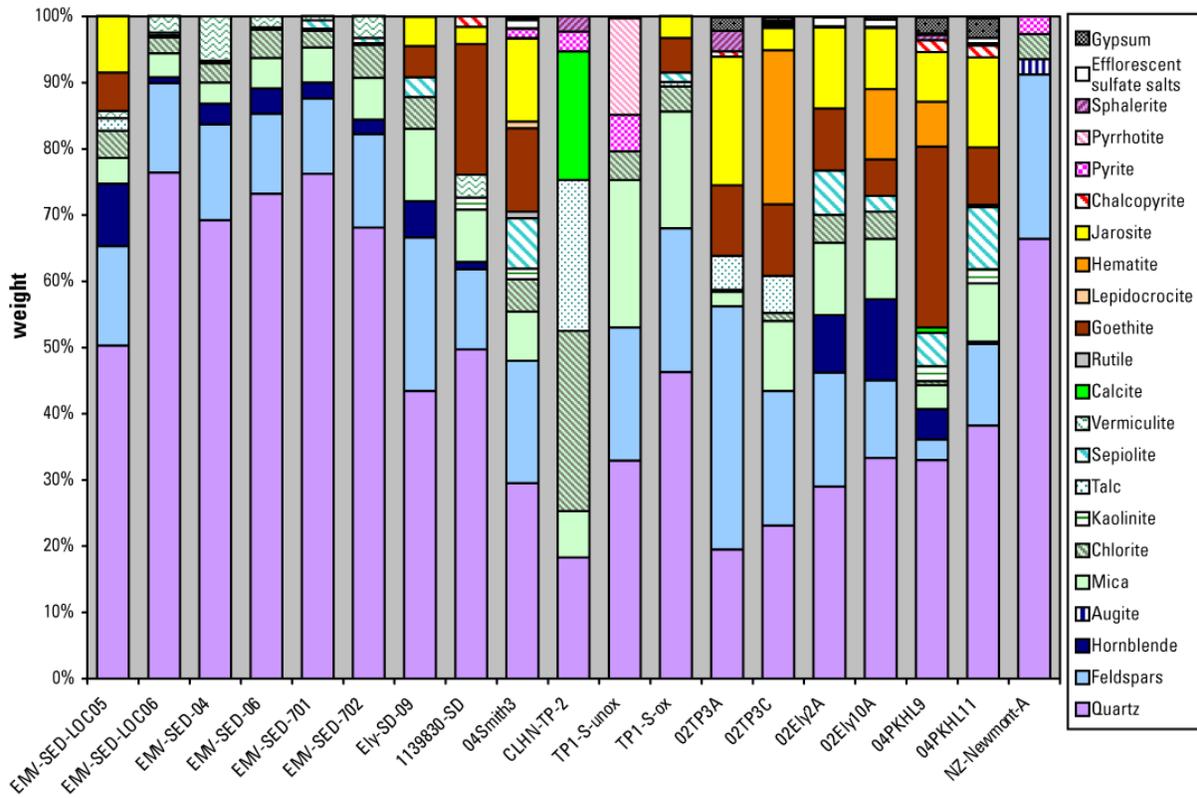
The Martha mine in Waihi, New Zealand, is an epithermal Au-Ag deposit that was mined by underground workings from 1878 to 1952. Mining recommenced in 1988 by open-pit methods and is planned to continue until 2007 (Castendyk and others, 2005). Light gray, fine-grained flotation-mill tailings (NZ-Newmont-A) were used in the extraction experiments for this study.

## Results

### Mineralogy

The quantitative mineralogy of the samples was determined by powder X-ray diffraction. The relative amount of phases in each sample in weight percent is given in Figure 2 and is for the crystalline part of the sample only. Estimates of the amorphous content were determined on spiked splits and are shown in Figure 3. The detection limit for XRD is on the order of a few weight percent and therefore phases present in trace amounts are likely below reliable detection. As shown, most samples primarily are composed of silicates including quartz, feldspar, hornblende, mica, chlorite, and clay. Phases such as quartz, feldspar, mica, and hornblende are expected to be resistant to extraction reagents in steps 1 through 6 and may persist until attack with concentrated acids in step 7. Additional studies will attempt to assess their dissolution behavior.

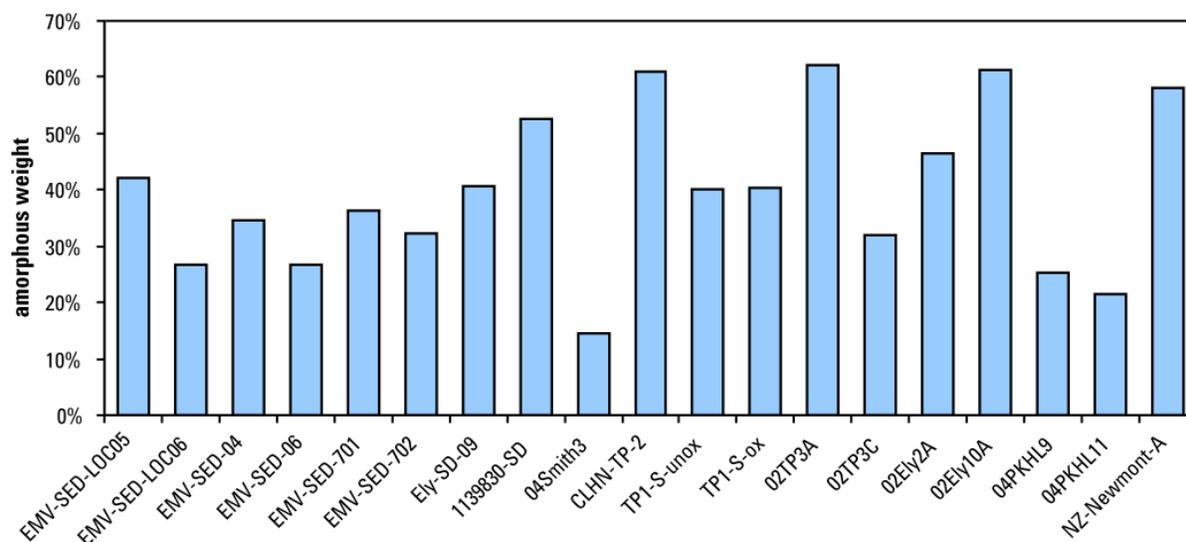
Based on XRD, most feldspars are plagioclase. The sample from the Martha mine is the only one that contains significant alkali feldspar. Muscovite is generally the most common sheet silicate. Chlorite is present in lesser amounts. The exception is the tailings from the Callahan mine that contains nearly 30 wt. % chlorite and only approximately 7 wt. % mica. Clay minerals include kaolinite, talc, vermiculite, and a phase having an intense broad peak at a spacing of approximately 11.5 to 12 Å, ascribed by the software to sepiolite in the XRD patterns (Figure 2). Sepiolite commonly forms in shallow seas and lakes and is not likely to be found in mine waste so this peak is assigned to hydrous altered biotite (Poppe and others, 2001). According to Rebertus and others (1986), biotite weathers to interstratified biotite-vermiculite (hydrobiotite), thus this low angle peak may be a result of varying degrees of biotite alteration. Hornblende was detected in most samples having a maximum of 12 wt. % in roasted mine waste (02Ely10A) from the Ely mine. The only sample containing detectable pyroxene is tailings from the Martha mine with ~2 wt. % augite.



**Figure 2.** Estimates of mineral abundances (wt. %) for the crystalline part of samples. Results based on a Rietveld refinement of powder X-ray diffraction patterns using Siroquant.

The only sample that contains significant carbonate is the tailings from the Callahan mine (CLHN-TP-2) having nearly 20 wt. % calcite. Based on Siroquant results, two mine-waste samples from Pike may contain trace calcite (<0.8 wt. %). The most intense diffraction peak spacing for calcite overlaps the most intense diffraction peak for chalcopyrite [CuFeS<sub>2</sub>]; these two Pike samples may contain minor (~2 wt. %) chalcopyrite. These estimated weight percentages are also near the reliable detection limits. The second step using acetic acid was aimed at dissolving carbonate minerals such as calcite [CaCO<sub>3</sub>] and dolomite [CaMg(CO<sub>3</sub>)<sub>2</sub>] (Kulp and Pratt, 2004).

Step 4 of the extraction procedure targeted amorphous Fe- and Al-hydroxides and amorphous and crystalline Mn-oxides (Chao, 1972; Chao and Zhou, 1983; Hall and others, 1996a). No crystalline Mn-oxide phases were detected by XRD. Using splits of the samples spiked with  $\text{Al}_2\text{O}_3$ , the amount of amorphous material in the samples was estimated using Siroquant. The amorphous fraction likely consists of Al, Fe, and Si-rich compounds for these samples and hypothetically includes the amorphous Fe- and Al-hydroxides targeted in step 4. The weight percentages of amorphous material in Figure 3 range from 15 to 62. Some of the lowest estimates are for mine waste from Pike Hill; some of the highest are for fine-grained flotation-mill tailings from the Callahan and Martha mines.



**Figure 3.** Estimates of amorphous content (wt. %) based on splits spiked with  $\text{Al}_2\text{O}_3$  and determined using Siroquant.

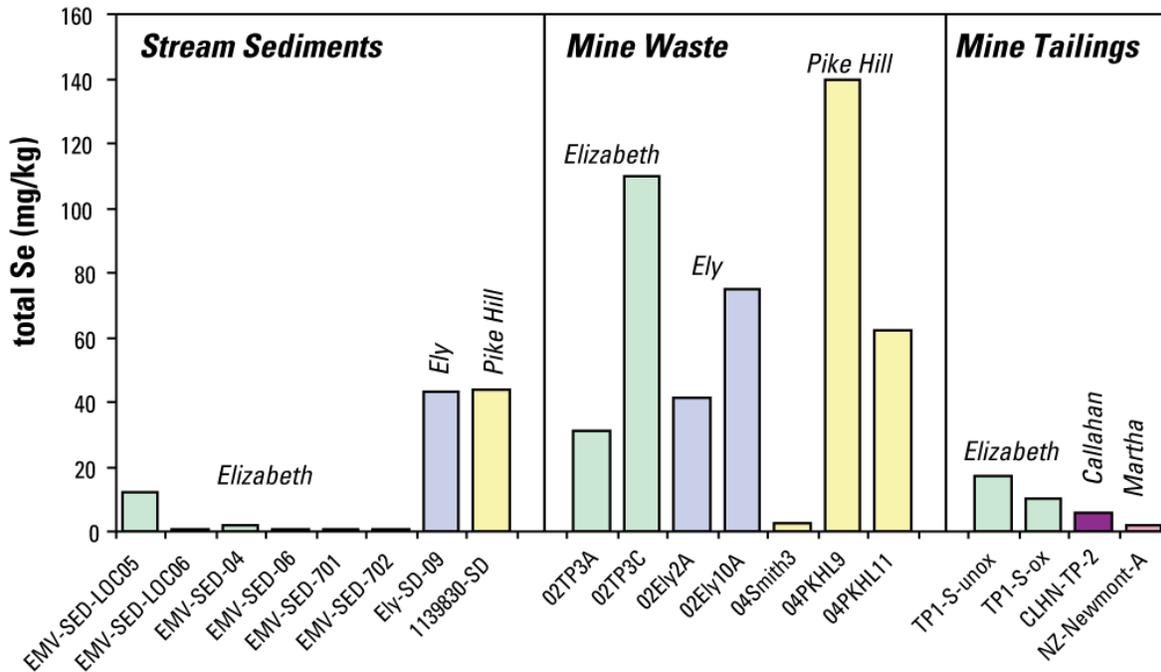
The crystalline Fe-oxide and Fe-hydroxysulfate minerals found in these samples include goethite [ $\text{FeOOH}$ ], hematite [ $\text{Fe}_2\text{O}_3$ ], and jarosite [ $\text{K}_2\text{Fe}_6(\text{SO}_4)_4(\text{OH})_{12}$ ]. Most stream-sediment samples from the Elizabeth mine do not contain detectable amounts of these phases. However, EMV-SED-LOC05 collected downstream from a sediment basin outlet below the tailings pile in Copperas Brook does contain nearly 6 wt. % goethite and 9 wt. % jarosite (Figure 2). The stream sediments from Ely and Pike Hill contain detectable goethite and jarosite. Both of these samples and EMV-SED-LOC05 were collected in areas of the stream where Fe-rich precipitates coated the streambed. Oxidized mine-waste samples and the oxidized tailings sample from the mines in Vermont contain detectable jarosite (3 to 20 wt. %) and goethite (5 to 27 wt. %). Significant hematite was found in three samples including 02TP3C (23 wt. %), 02Ely10A (11 wt. %), and 04PKHL9 (7 wt. %). All three are burnt or roasted mine waste. Hematite is not present in significant quantities in the ore or host rocks at these mines. Roasting or burning of the pyrrhotite-rich ores would have driven off much of the sulfur and left a residue of ferric oxide (hematite). Chester and Hughes (1967) reported the dissolution of crystalline Fe-oxide minerals (goethite and hematite) using the reagents in step 5. Only partial dissolution of jarosite was expected based on a study by Filipek and Theobald (1981).

Several samples likely contain minor to trace amounts of sulfides based on the semi-quantitative mineralogy. Estimates of ~2 wt. % chalcopyrite [ $\text{CuFeS}_2$ ] were determined for two

mine-waste and one stream-sediment sample from Pike Hill. Several samples contain ~3 wt. % or more pyrite [FeS<sub>2</sub>] and include tailings from the Callahan, Elizabeth, and Martha mines (Figure 2). The only sample having detectable pyrrhotite [Fe<sub>1-x</sub>S] is the unoxidized tailings from TP1 (TP1-S-unox) at the Elizabeth mine having nearly 15 wt. %. Sphalerite [ZnS] was found in a few weight percent in the Callahan tailings (CLHN-TP-2) and oxidized mine waste from Elizabeth (02TP3A). The reagent used in step 6 of the extraction procedure should have oxidized, possibly volatilized, and decomposed sulfides and selenides (Chao and Sanzolone, 1977).

## Total Selenium

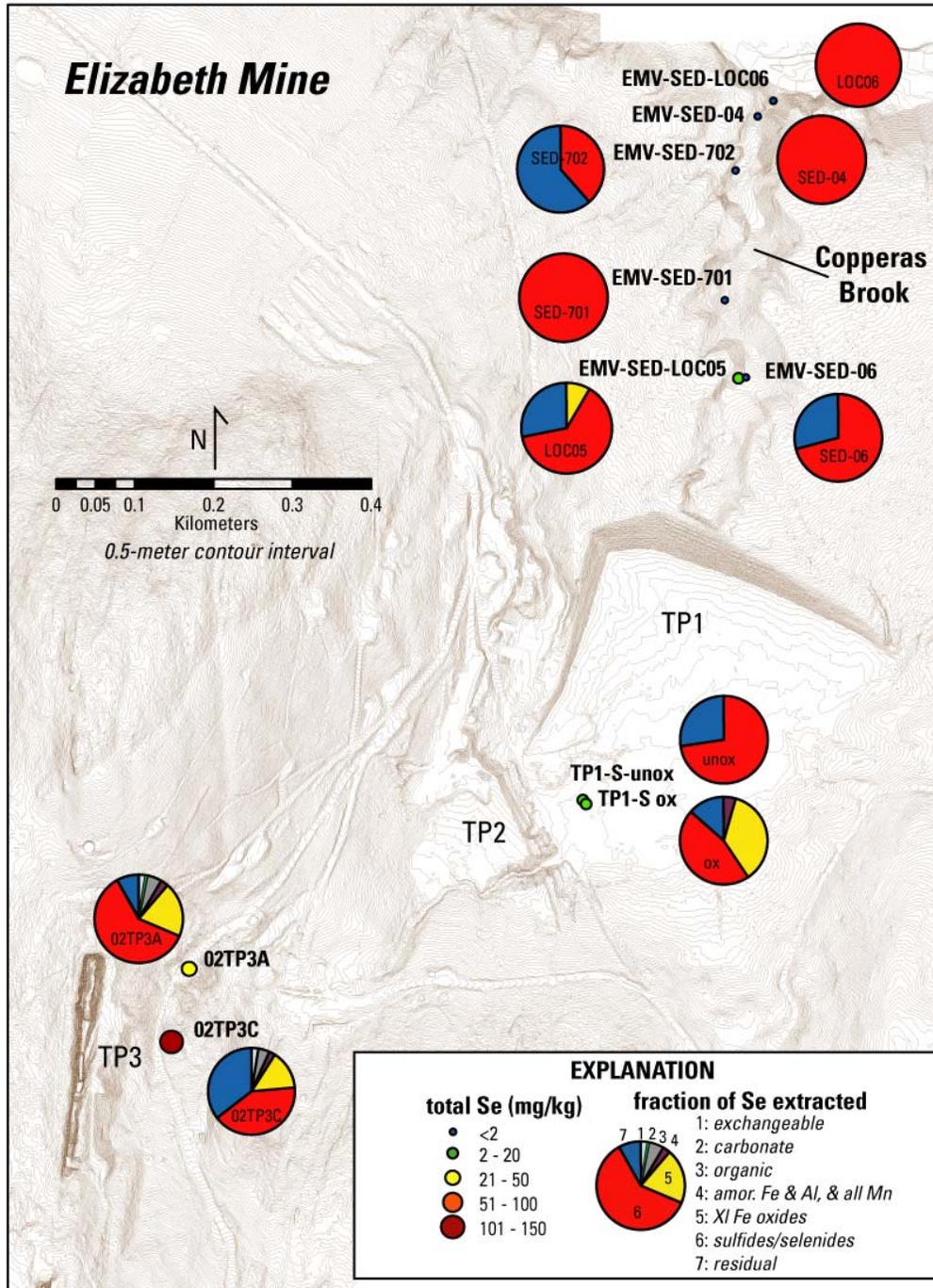
Total Se in the original bulk samples is illustrated in Figure 4 by sample type and mine site. Values are given in Table 2. Figures 5, 6, and 7 show locations and total Se concentrations for samples collected from the Elizabeth, Ely, and Pike Hill mines. (In Figure 5, the north toe of TP1 has been regraded to a less steep slope and stream-sediment samples were collected after regrading. Although the site was modified, the figure illustrates the overall site configuration.) The concentrations of Se in stream sediments from the Elizabeth mine found in this study range from 0.43 to 12 mg/kg. Most contain less than 2 mg/kg with the exception of EMV-SED-LOC05 with 12 mg/kg Se (Figure 5). This sample is unique mineralogically in that it is the only stream-sediment sample from Elizabeth that contains detectable goethite and jarosite. As shown in Figure 4, the concentrations of total Se in stream sediments from the Ely (43 mg/kg Se) and Pike Hill (44 mg/kg Se) mines are similar and are significantly higher than in those from the Elizabeth mine. These samples also contain detectable goethite and jarosite (Figure 2). The Pike Hill stream sediment is a finer-sized material than the others because it was sieved with a smaller mesh size. The effect of size fraction on Se concentrations was not examined in this study but may influence Se content.



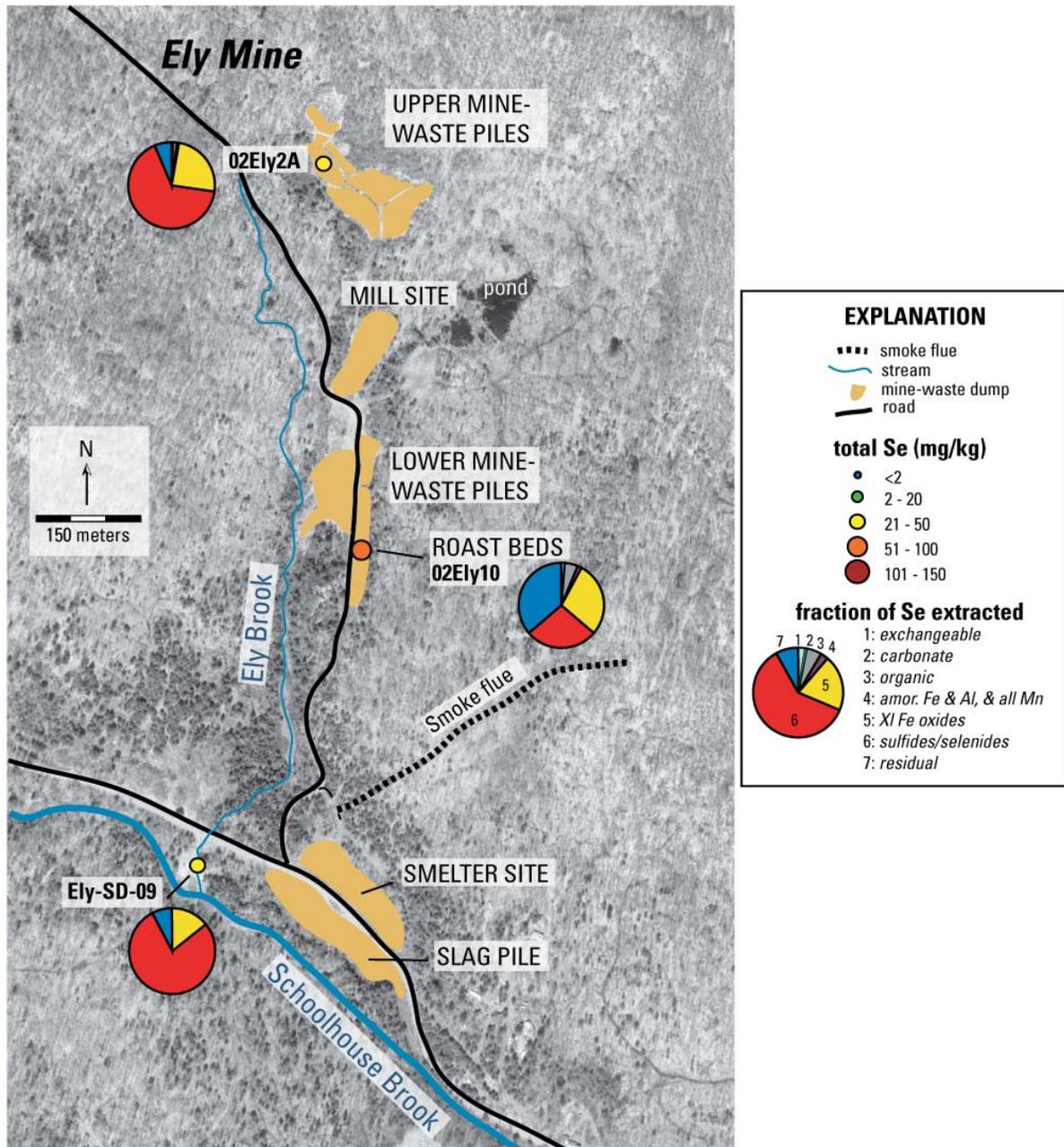
**Figure 4.** Total Se determined using HG-AAS. Samples are grouped according to sample type and color coded according to mine site.

**Table 2.** The results of sequential extractions experiments for Se. Concentrations (mg/kg) are for extracts 1 through 5 (given as concentrations in leached solid), for residues remaining after steps 5 and 6, and in the original bulk sample. Abbreviations include ICP-MS (inductively coupled plasma-mass spectrometry), HG-AAS (hydride-generation atomic absorption spectrometry), and XI (crystalline). Less than sign (<) is shown for concentrations below the detection limit. Sample A was a blank used for calibration for ICP-MS and therefore not given. Duplicate HG-AAS analysis of bulk sample EMV-SED-LOC05 is given in parentheses.

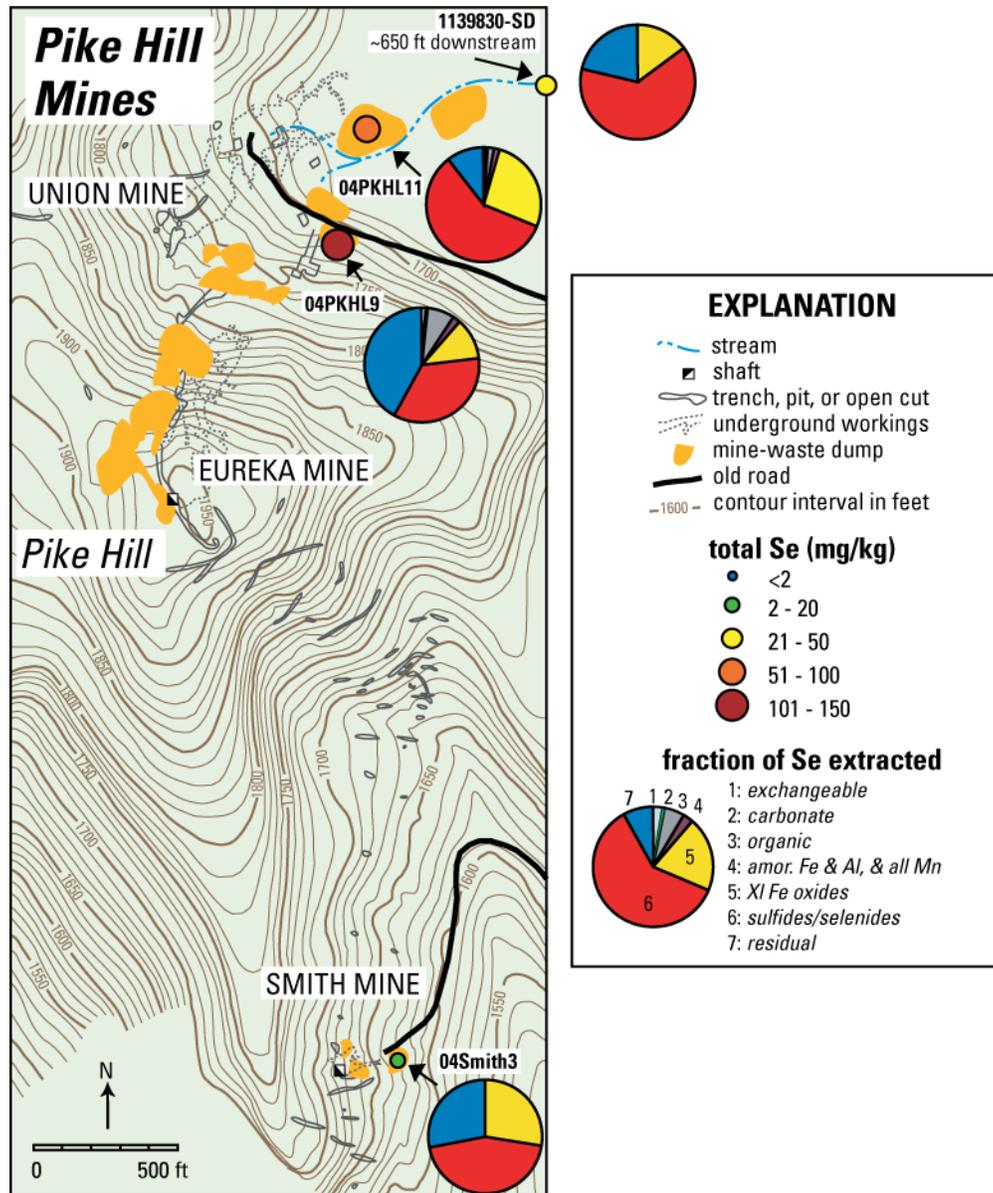
<b>extract/residue (step)</b>		<b>extract 1 (step 1)</b>	<b>extract 2 (step 2)</b>	<b>extract 3 (step 3)</b>	<b>extract 4 (step 4)</b>	<b>extract 5 (step 5)</b>	<b>residue 5</b>	<b>residue 5 - residue 6 (step 6)</b>	<b>residue 6 (step 7)</b>	<b>original (bulk)</b>
<i>fraction hypothetically extracted method</i>		<i>exchangeable</i>	<i>carbonate</i>	<i>organic</i>	<i>amorphous Fe &amp; Al, all Mn</i>	<i>XI Fe oxides</i>	<i>sulfides/selenides &amp; residual</i>	<i>sulfide/selenide</i>	<i>residual</i>	<i>total</i>
		ICP-MS	ICP-MS	ICP-MS	ICP-MS	ICP-MS	HG-AAS	<i>calculated</i>	HG-AAS	HG-AAS
<b>Sample ID</b>	<b>Extract ID</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>	<b>mg/kg</b>
EMV-SED-LOC05	B	<0.2	<0.2	<0.2	<0.2	0.7	7.4	5.1	2.3	12 (14)
EMV-SED-LOC05-Dup1	C	<0.2	<0.2	<0.2	<0.2	1.0	7.4	5.1	2.3	12 (14)
EMV-SED-LOC06	D	<0.2	<0.2	<0.2	<0.2	<0.2	0.31	>0.21	<0.1	0.82
EMV-SED-04	E	<0.2	<0.2	<0.2	<0.2	<0.2	0.52	>0.42	<0.1	1.6
EMV-SED-06	F	<0.2	<0.2	<0.2	<0.2	<0.2	0.75	0.53	0.22	0.66
EMV-SED-701	G	<0.2	<0.2	<0.2	<0.2	<0.2	0.15	>0.05	<0.1	0.43
EMV-SED-702	H	<0.2	<0.2	<0.2	<0.2	<0.2	0.47	0.18	0.29	0.77
Ely-SD-09	I	<0.2	<0.2	<0.2	0.2	4.9	29	26.5	2.5	43
1139830-SD	J	<0.2	<0.2	<0.2	<0.2	6.5	37	27.7	9.3	44
04Smith3	K	<0.2	<0.2	<0.2	<0.2	6.1	16	9.8	6.2	2.5
CLHN-TP-2	L	0.3	0.3	<0.2	0.4	0.8	2.9	>2.8	<0.1	5.8
Blank	M	<0.2	<0.2	<0.2	<0.2	<0.2	-	-	-	-
EMV-SED-LOC05-Dup2	N	<0.2	<0.2	<0.2	<0.2	1.2	9.6	8	1.6	12 (14)
TP1-S-unox	O	<0.2	<0.2	<0.2	<0.2	<0.2	16	11.6	4.4	17
TP1-S-unox-D	P	<0.2	<0.2	<0.2	<0.2	<0.2	16	12.9	3.1	17
TP1-S-ox	Q	<0.2	<0.2	<0.2	0.3	2.3	3.8	2.94	0.86	10
02TP3A	R	0.8	0.2	1.8	0.9	6.4	22	19.4	2.6	31
02TP3C	S	2.6	0.3	4.5	2.6	16.0	84	45	39	110
02Ely2A	T	0.3	<0.2	0.5	0.4	10.7	32	29.2	2.8	41
02Ely10A	U	1.1	<0.2	3.4	1.3	21.2	47	20	27	75
04PKHL9	V	1.8	0.3	10.4	2.7	15.3	100	45	55	140
04PKHL11	W	0.4	0.3	0.7	0.8	12.7	33	28	5.0	62
NZ-Newmont-A	X	<0.2	<0.2	<0.2	<0.2	2.7	0.60	0.38	0.22	1.7



**Figure 5.** Locations, total Se, and sequential extraction results for samples from the Elizabeth mine. Concentrations of total Se are shown as color-coded circles at sampling location. Relative amounts of Se extracted in each step are shown in pie graphs next to sampling site.



**Figure 6.** Locations, total Se, and sequential extraction results for samples from the Ely mine. Concentrations of total Se are shown as color-coded circles at sampling location. Relative amounts of Se extracted in each step are shown in pie graphs next to sampling site. Modified from Piatak and others (2004).



**Figure 7.** Locations, total Se, and sequential extraction results for samples from the Pike Hill mines site. Concentrations of total Se are shown as color-coded circles at sampling location. Relative amounts of Se extracted in each step are shown in pie graphs next to sampling site. Modified from Piatak and others (2006); original base map from White and Eric (1944).

The concentrations of Se are generally higher in mine waste compared to stream sediments (Figure 4). The three highest bulk concentrations, reaching 140 mg/kg Se, are for mine waste from Vermont that has been either roasted or burnt (02TP3C, 02Ely10A, 04PKHL9). These samples are also mineralogically unique in that they contain significant hematite that likely formed during roasting or burning (Figure 2). The mine waste with the least amount of Se is from the Smith mine (2.5 mg/kg Se), which is the smallest of the three mines at the Pike Hill site (Figure 7). At the Elizabeth mine, unoxidized tailings (17 mg/kg Se) and oxidized tailings (10 mg/kg Se) contain Se in concentrations close to those found in one stream sediment directly downstream of the tailings

piles (EMV-SED-LOC05; Figure 5). Tailings from the Callahan (5.8 mg/kg Se) and Martha (1.7 mg/kg Se) mines contain lower concentrations compared to Elizabeth tailings in Figure 4.

As stated earlier, the toxicity of Se is a function of its speciation and partitioning among various organic and inorganic solid phases, rather than its total concentration. Nonetheless, soil and sediment criteria or ratings have been set for total Se concentrations and are used here for comparison purposes. Mine waste and flotation-mill tailings are compared to soil criteria whereas stream sediments are compared to sediment hazard ratings. The guidelines set for the aquatic environment (sediment) are usually over an order of magnitude lower than those for the terrestrial environment (soil).

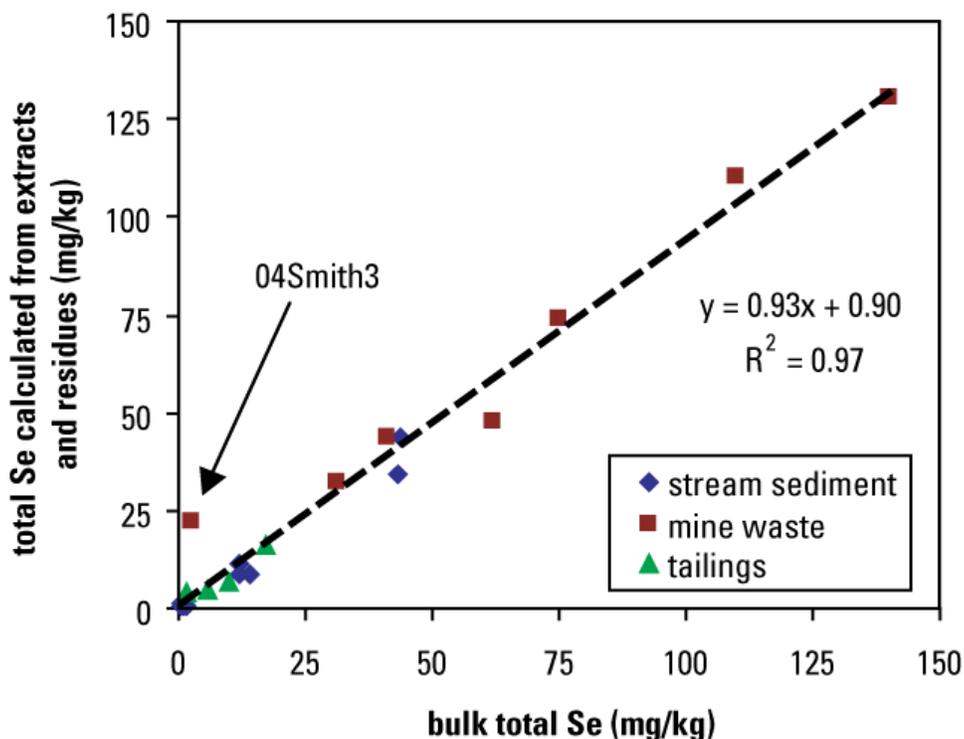
The USEPA Preliminary Remediation Goal (PRG) for industrial soil is 5,100 mg/kg Se and 390 mg/kg Se for residential soil (USEPA, 2004). PRGs are guidelines, not legally enforceable standards, used for initial evaluations of potentially contaminated sites. The total concentrations of Se in mine waste and tailings are well below the PRGs for both industrial and residential soils (Figure 4). The range in concentrations of Se found in soils in the Eastern United States is <0.1 to 3.9 mg/kg as reported by Shacklette and Boerngen (1984). Although the samples do not exceed PRGs, the concentrations in mine waste and tailings are higher than the range for eastern soils, except for the sample from the Smith mine and the Martha tailings (Table 2).

Selenium in sediments can be absorbed or ingested by aquatic organisms and bioaccumulates through the food chain (Lemly, 1997). A protocol for conducting a hazard assessment of Se was developed by Lemly (1995) based on five ecosystem components: water, sediments, benthic macroinvertebrates, fish eggs, and aquatic bird eggs. The hazard assessment is a sum of the hazard rating for all five categories to assess food-chain bioaccumulation and reproductive impairment in fish and aquatic birds. In this study, the hazard rating for the sediment component was examined. Selenium concentrations in four stream sediments from the Elizabeth mine are below the no-hazard rating of <1 mg/kg and one has a minimal hazard rating (1-2 mg/kg). Selenium concentrations in the sediment directly downstream from the sediment basin outlet below TP1 at Elizabeth (EMV-SED-LOC05) and in the sediment from Ely (Ely-SD-09) and Pike Hill (1139830-SD) fall in the high hazard rating field of >4 mg/kg.

## Extraction Experiments

The concentrations of Se leached from the solids in steps 1 through 5 are given in Table 2. Selenium extracted from the solid was calculated from extract concentrations and solid to extraction solution ratios. Selenium in residues from steps 5 and 6 and in original untreated samples determined after digestion with concentrated HF, HNO<sub>3</sub>, and HClO<sub>4</sub> are also in Table 2. The difference between the step 5 residue and the step 6 residue concentrations (Table 2; values in *italics*) is the Se extracted by step 6 solvents (selenide/sulfide fraction; see Figure 1). Direct measurement of Se in extract solution 6 was not used because some sulfides and selenides have been volatilized by the acids utilized in step 6.

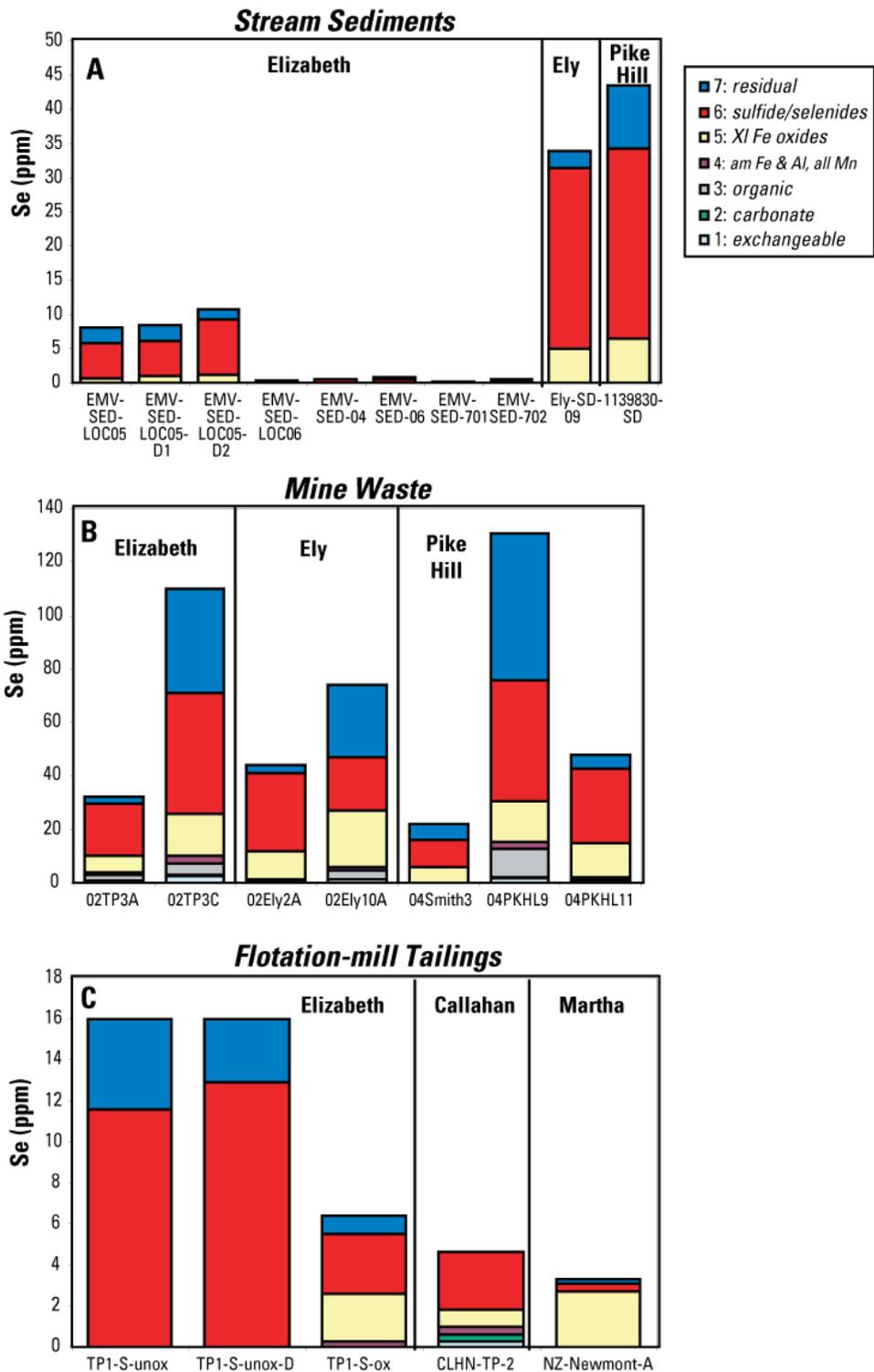
The sum of the concentrations of Se leached from the solids in steps 1 through 5 plus the residue after step 5 (calculated total) should be equal to the original total Se concentration of the solid (bulk total). In Figure 8, the calculated total Se correlates with the total Se in the untreated sample with a R<sup>2</sup> value of 0.97 for the linear regression. The only sample that significantly deviates from the trend is the mine waste from the Smith mine (04Smith3) that has a sum of Se from the extraction steps significantly higher than that found in the bulk sample.



**Figure 8.** Calculated Se totals from extractions versus total from untreated samples. Calculated total for each sample is the sum of Se in extracts 1, 2, 3, 4, and 5 and in the residue after step 5. For extracts with Se less than the detection limit, half of the detection limit was used in calculations. A linear regression (dashed line) and the equation for the line and  $R^2$  are also shown.

As mentioned previously, the fractions of Se leached were a result of extraction reagent, time, temperature, and sample to volume ratio. Each step of the extraction was designed to dissolve a specific fraction but the success must be investigated by chemical and/or mineralogical studies. This discussion focuses on the results of Se extracted in each step with only minor emphasis on implications of Se speciation and specific minerals or phases hosting the Se. References to specific phases are used liberally in the following discussion and dissolution of phases will be assessed in future studies.

Figure 9 shows the sequential partial dissolution results for Se in stream sediments, mine waste, and tailings from all the mines. Figures 5, 6, and 7, discussed above, show sampling locations, total Se, and fractionation of Se in extracts for the Elizabeth, Ely, and Pike Hill mines, respectively. The only detectable Se for stream-sediment samples is in extracts from steps 5, 6, and 7 where more aggressive reagents are employed (Figure 5-7 and 9). For most stream sediments, the highest fraction of Se (between 38% and 100%) was found in extraction step 6 using  $KClO_3$  and concentrated HCl (Figure 9). This procedure should have oxidized, possibly volatilized, and decomposed sulfides and selenides (Figure 1; Chao and Sanzalone, 1977). Based on mineralogy from XRD, these samples contain trace to non-detectable concentrations of sulfides such as chalcopyrite, pyrite, and pyrrhotite, and sphalerite. However, the detection limit for XRD is not low enough to exclude sulfides and selenides as potential sources.



**Figure 9.** Selenium concentrations from sequential extractions for (A) stream sediments, (B) mine waste, and (C) flotation-mill tailings.

In some stream sediments, Se was also found in the residual fraction (step 7; up to 62% Se extracted), likely in the structure of or as inclusions in silicates (i.e., quartz, feldspar, muscovite) or other refractory minerals (i.e., rutile), and in an acidic leach using hydroxylamine hydrochloride and acetic acid (step 5; up to 15% Se extracted). The solution in step 5 has been found to dissolve crystalline Fe-oxide minerals (Chester and Hughes, 1967). Goethite was the only Fe-oxide identified in the stream sediments by XRD. Jarosite is a Fe-hydroxysulfate found in several stream sediment samples, as well as mine waste and oxidized tailings. In a study by Filipek and Theobald (1981), only 20% of a nearly monomineralic jarosite sample was dissolved using an extractant solution similar but more dilute to the step 5 extract. Filipek and Theobald (1981) used a 0.25 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% acetic acid solution whereas the present study used 1.0 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 25% acetic acid. The extent to which jarosite is resistant to these dissolution reagents will be examined in future studies. These results suggest Se in the stream sediments is not easily leached.

Like the stream sediments, Se in mine waste was predominantly mobilized in the last few extracts that hypothetically target crystalline Fe-oxides such as goethite or hematite (step 5: 12-29% Se extracted), sulfides and selenides (step 6: 27-67% Se extracted), and residual minerals (step 7: 6-42% Se extracted) as shown in Figures 5, 6, 7 and 9. Like stream sediments, significantly more Se was extracted in step 6 compared to the other steps, except for roasted or burnt mine waste (02TP3C, 02Ely10A, and 04PKHL9) which contains comparable concentrations of Se in steps 6 and 7. Four to eight percent of the Se extracted from these three samples was found in the step 3 extract. According to Hall and others (1996b), the sodium pyrophosphate used in step 3 should target the organic component of the samples. The step 3 extracts for the other mine-waste samples contain between 1 and 6% of the total Se leached. Small fractions of Se were leached from extraction steps 1 and 4 suggesting a few percent of the Se may be found in the exchangeable/soluble fraction (step 1; Chao and Sanzolone, 1989) and the amorphous Fe- and Al-hydroxides and amorphous and crystalline Mn-oxides (step 4; Chao, 1972; Chao and Zhou, 1983; Hall and others, 1996a;).

Approximately three-fourths of the total Se in unoxidized sulfide-rich tailings (TP1-S-unox) from the Elizabeth mine was found in the step 6 extract (sulfides/selenides), the remainder being in the residual step 7 fraction (Figures 5 and 9). In the oxidized tailings (TP1-S-ox), Se was also found in significant concentrations in step 5, which targeted crystalline Fe-oxides (Figures 5 and 9). In contrast to the unoxidized tailings, TP1-S-ox contains up to 5 wt. % goethite and jarosite based on XRD.

Selenium in tailings from the Callahan mine predominately resides in the step 6 fraction (sulfide/selenide) with minor amounts being in steps 4 and 5 and below or near detection for steps 1 and 2 (Figure 9). In contrast to the tailings from Vermont and Maine, most Se in the Martha-mine tailings was extracted in step 5, which targeted the dissolution of crystalline Fe-oxide minerals. This is inconsistent with mineralogy based on XRD, which found no detectable crystalline Fe-oxide phases. The sample does contain a few weight percent pyrite.

## Conclusions

The results from the sequential extractions on stream sediments, mine waste, and flotation-mill tailings suggest that most Se in these samples was not found in the readily soluble or ligand exchangeable fractions that hypothetically should be leached with the potassium phosphate solution in first step of the scheme, presumably as selenate or selenite. For all stream-sediment samples, the concentrations of Se in this fraction is less than the detection limit. The highest concentrations in this fraction is from roasted or burnt mine waste from the Elizabeth (02TP3C: 2.6 mg/kg), Ely (02Ely10A: 1.1 mg/kg) and Pike Hill (04PKHL9: 1.8 mg/kg) mines. Only mine-waste samples

contain detectable Se in the extraction using sodium pyrophosphate, which has been shown to extract humic and fulvic complexes in soils (step 3, organic fraction). Again, the highest concentrations were leached from the burnt or roasted mine wastes and reach 10.4 mg/kg Se. These three samples also contain the highest bulk concentrations of Se (up to 140 mg/kg).

Generally, the largest fractions of Se were found in the leaches using the most aggressive reagents. These included potassium chlorate and concentrated hydrochloric acid to oxidize and decompose sulfides and selenides (step 6) and the concentrated multi-acid digestions used to decompose the final residual matrix (step 7). Selenium in stream sediments was predominantly mobilized in step 6 extract. In a few stream-sediment samples and in the mine waste and oxidized tailings, Se was also found in the extract from step 5. The solution for this step was hydroxylamine hydrochloride in dilute acetic acid and has been shown to extract metals bound to crystalline Fe-oxides such as goethite and hematite. Overall, these extraction results suggest that most of the Se in these samples was partitioned into crystalline Fe-oxides and insoluble sulfides, selenides, or silicates. Future efforts will investigate specific phases or species leached by each extraction step by conducting multielement chemical and mineralogical studies.

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