

SOIL SELENIUM: LABORATORY COMPARISONS AND SOIL/BACKFILL VARIABILITY¹

Roger N. Pasch and George F. Vance²

Abstract: Various analytical methods have been used to determine selenium (Se) in soils, overburden, and plants. Inter-Mountain Laboratories and the Soil and Environmental Chemistry Laboratory at the University of Wyoming conducted a study to determine the variability of soil Se by independently analyzing 20% of the soil/backfill samples from an Abandoned Coal Mine Land research project "Relationship Between Soil Selenium Concentrations and Selenium Uptake by Vegetation on Surface Coal Mine Lands in Wyoming". The quality control/quality assurance program for this project revealed excellent agreement between the two laboratories. For example, hot water, AB-DTPA, and phosphate extractable Se results from the two laboratories were found to be highly correlated ($R^2 \geq 0.95$) by linear regression analyses. Both laboratories followed "Standard Operating Procedures" (Spackman et al., 1994) which included determination of Se by atomic adsorption spectroscopy with hydride generation (Varian HGA-76).

Five methods used to determine soil Se (i.e., total Se and four methods of extractable Se - hot water, AB-DTPA, phosphate, and saturated paste) were compared among three cores sampled within a one meter triangle at different sites (native and reclaimed locations) and depths (5 at native and 3 at reclaimed sites). A wide range in the coefficient of variation (CV) was noted (0 to 118%); however, the larger CV's tended to be grouped at specific sites and depths, and with certain extractants. Of 831 CV's calculated, only 10 (or 1.2%) were greater than 100%. Average CV's for mine type and ecological system (i.e., native versus reclaimed) were approximately 25%. Overall, total Se varied the least among the five Se variables followed by phosphate < AB-DTPA < hot water < saturated paste extractable Se.

Additional Key Words: Atomic absorption spectroscopy, hydride generation

Introduction

Several areas within the western United States are known to contain high levels of Se in soils and geological formations. These areas can develop into potential problem spots to wildlife and livestock if high Se-containing vegetation ($>5 \mu\text{g/g}$ Se) growing on these sites is consumed over time (National Academy of Sciences, 1976). Areas adjacent to seleniferous regions may also be affected if Se is translocated to surface or ground water through wind or water movement. Several surface mines within Wyoming are in areas that contain seleniferous geological materials. During surface mining activities, materials previously in reducing environments are exposed to atmospheric oxygen. Upon oxidation, the reduced or immobile phases of Se (Se^{-2} and Se^0) can become more mobile Se species (SeO_3^{-2} and SeO_4^{-2}). The consequences of this may be increased Se availability to plants, which could result in greater plant Se uptake and the possibility of Se toxicity to animals in the reclaimed environments.

Seleniferous sedimentary materials are generally the greatest geological source of Se (Mayland et al., 1989). In Wyoming, Se concentrations range from <1 to over 300 mg Se/kg (ppm); the highest levels are typically found in Cretaceous black shales (Beath et al., 1937; National Academy of Sciences, 1983). Seleniferous geologic materials underlie approximately half of the land area of Wyoming, although Se in these geological materials is not necessarily in toxic forms. In fact, in geological materials Se exists primarily as metal complexes of selenide (Se^{-2} ; e.g., FeSe), or as elemental Se (Se^0) in most deep subsurface environments. The reduced forms found in anoxic environments are largely insoluble, and as such, are generally regarded as biologically impotent. Chemical and biological processes that transform reduced Se forms to more soluble oxidized forms increase the toxicity of Se (Rosenfeld and Beath, 1964).

¹Paper presented at the 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, Wyoming, June 5-8, 1995.

²Roger N. Pasch, Co-owner, Inter-Mountain Laboratories, Inc., Sheridan, WY 82801 and George F. Vance, Associate Professor of Soil and Environmental Chemistry, Department of Plant, Soil and Insect Sciences, University of Wyoming, Laramie, WY 82071-3354.

The relationship between soil Se and plant uptake is not well understood. Information from greenhouse and growth chamber studies (Soltanpour and Workman, 1980; Jump and Sabey, 1985; Wan et al., 1988) has shown better correlations than field studies (Lakin, 1961; Williams and Thornton, 1973). With greenhouse and growth chamber studies, experimental conditions are usually controlled (i.e., using similar soil and plant material, also regulating light, water and temperature), which reduces study variability. Factors and conditions of field studies may vary both spatially and temporally. A partial list of different Se extraction methods used to correlate soil-plant Se, and the study conditions (i.e., environment and vegetation) reported in the literature are presented in Table 1.

Table 1. A partial list of the different extraction methods, study conditions, and vegetation species used in various Se studies.

Method	Study	Vegetation	Reference
Water or Hot Water Soluble	Greenhouse - soils	None	Olson and Moxon, 1939
	Field	Western wheatgrass	Olson et al., 1942
	Greenhouse	Perennial ryegrass	Williams and Thornton, 1973
	Greenhouse - Se amended soils	Alfalfa	Soltanpour and Workman, 1980
	Greenhouse - high Se materials	Saltbush and Astragalus bisulcatus	Jump and Sabey, 1989
AB-DTPA	Greenhouse - Se amended soils	Alfalfa	Soltanpour and Workman, 1980
	Greenhouse	Saltbush and Astragalus bisulcatus	Jump and Sabey, 1989
	Field	Greasewood	Jump and Sabey, 1985
	Field	Winter wheat	Soltanpour et al., 1982
	Field	Variety	Producers and Munshower, 1991
Base Soluble (NaOH)	Greenhouse - soils	None	Olson and Moxon, 1939
	Field	Western wheatgrass	Olson et al., 1942
	Greenhouse	Perennial ryegrass	Williams and Thornton, 1973
DTPA	Greenhouse	Saltbush and Astragalus bisulcatus	Jump and Sabey, 1989
EDTA	Greenhouse	Perennial ryegrass	Williams and Thornton, 1973
Saturated Paste	Greenhouse	Saltbush and Astragalus bisulcatus	Jump and Sabey, 1989

Guideline No. 1 of the Wyoming Department of Environmental Quality - Land Quality Division (WDEQ-LQD, 1984) defines marginal Se levels in soil, spoil, and overburden as being < 0.1 mg/kg Se determined by ammonium bicarbonate-diethylenetriaminepentacetic acid (AB-DTPA) or hot water extraction. The choice of this level of extractable Se is based, in part, on a correlation between 0.1 mg/kg AB-DTPA extractable Se and 5 mg/kg Se in vegetation from greenhouse and growth chamber studies (see Soltanpour and Workman, 1980). The 5 mg/kg Se concentration in forage is believed to be toxic to animals consuming this vegetation over an extended period.

A recent review of WDEQ-LQD's marginal suitability level of 0.1 mg/kg extractable Se used for overburden, spoil, and soil was conducted by Vance (1990) who recommended that: 1) field studies be conducted that use well-

defined soil/overburden and plant sampling, and preservation methods, and 2) evaluation be made of prospective analytical methods that provide more meaningful and consistent results that can be used reliably for indications of soil-plant relationships. Vance (1990) suggested that AB-DTPA may not be the most appropriate extractant for assessing Se in soils, spoils, and overburden materials. For example, results of a multi-laboratory round robin study using soil and overburden samples found that AB-DTPA extractable Se analyses had tremendous variability ranging from a minimum to a maximum in one sample of 0.05 and 1.60 $\mu\text{g Se/g}$, respectively (Severson and Fisher, 1985, 1987; Fisher and Munshower, 1991). For this particular sample there was a 32-fold difference in the AB-DTPA extractable Se, whereas other samples reported in the Fisher and Munshower (1991) review revealed variability ranging from 10 to 50 times between minimum and maximum Se values.

Several analytical methods have been used over the past decade for quantifying Se in waters, soil extracts, and plant digests. Advantages and disadvantages of some of these methods are listed in Table 2. Fluorimetric measurements of Se have been used for many years due to the sensitivity of the analysis and the low cost of the equipment. Other analytical methods, such as atomic absorption (AAS) and inductively coupled plasma (ICP) spectrophotometry, both with and without graphite furnace (GF) or hydride generation (HG), are also commonly used for quantifying Se. A major advantage to the use of ion chromatography is the direct measurement of the Se species - selenite and selenate. Use of AAS-HG has been found to be both time efficient and useful in several analytical laboratories (e.g., Inter-Mountain Laboratories and the University of Wyoming Soil and Environmental Chemistry Laboratory) for measuring Se at low part per billion (ppb) levels.

Table 2. Advantages and disadvantages of several analytical methods that are common used for the quantification of selenium in waters, soil extracts and plant digests.

Method	Advantages	Disadvantages
Fluorometry	Low detection limits Inexpensive	Sample preparation time Interferences Unstable fluoro complexes
Atomic Absorption Spectrophotometry (AAS) or Inductively Coupled Plasma (ICP)	Rapid analysis time Multi element analysis (ICP)	High detection limits Interferences (Nitric and HF acid)
Graphite Furnace-AAS or Graphite Furnace-ICP	Low detection limits	Sample preparation time Cost Interferences (matrix effects and organics)
Hydride Generation-AAS or Hydride Generation-ICP	Low detection limits Some speciation capabilities	Digestion procedure Indirect and multistep speciation methodology
Ion Chromatography	Low detection limits Se Speciation capabilities Direct measurement of Se species	Interference from SO_4 and other anions at high concentrations

The objectives of this study were to: 1) examine the variability of different extractants used for the analysis of soil and backfill Se, which were conducted at Inter-Mountain Laboratories (Sheridan, WY) and the Soil and Environmental Chemistry Laboratory at the University of Wyoming and 2) evaluate the variation in Se, both within and amongst soils from reclaimed and native sites at two coal mines located in the Powder River Basin, Wyoming.

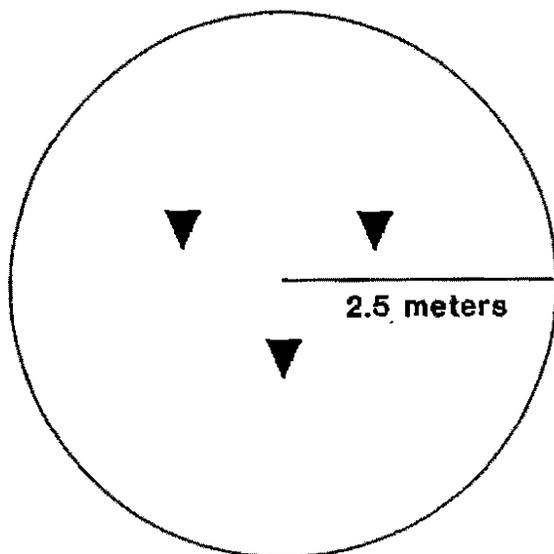
Materials and Methods

Reclaimed and Native Experimental Plots

Reclaimed and native experimental sites used in this study were approximately 20 m² in size, as shown in Figure 1. To verify the Se concentrations at each of the experimental sites, three cores, in a triangular pattern (one meter distance along each side), were drilled and sampled in 1991 and 1993. Samples were collected using a Giddings Soil Sampler (Ft. Collins, CO) equipped with a three inch core barrel and a sawtooth bit. Soil and backfill samples were placed in plastic bags, sealed, labeled and shipped to Inter-Mountain Laboratory in Sheridan, WY within 24 hours of collection.

EXPERIMENTAL PLOT DESIGN

Sample Plot Area = 20 m²



Sample Depths

Native = 30 cm (1 ft) increments
Reclaimed = 0 to ~30 cm (topsoil)
 0-30 cm backfill
 31-60 cm backfill

▼ Soil Sample Locations
○ Vegetation Sampling Area

Figure 1. Illustration of experimental plot design at field sites established within native and reclaimed areas at two active mines in the Powder River Basin, Wyoming. Approximately 20 native and 50 reclaimed plots were established.

Experimental plots on over 50 reclaimed sites were established and sampled according to the design in Figure 1. Topsoil depths on the reclaimed experimental plots varied from 40 cm (16 in.) to 75 cm (30 in.). A 60 cm (2 ft.) topsoil depth is most representative of actual reclamation practices being used in the Powder River Basin. After topsoil collection, regraded zone spoil material was sampled every 60 cm (2 ft.) to a total depth of approximately 180 cm (6 ft.), depending on topsoil depth. Thus, at each reclaimed site three soil/backfill samples were collected and analyzed as described in later sections.

Native sites adjacent to the two coal mines (Mines A and B) used in this study have abundant populations of *Astragalus bisulcatus*, a key Se indicator plant specie (Ihnat, 1989). Twenty of these sites were selected for comparison with reclaimed sites. Soil and geological parent materials were sampled at 30 cm (1 ft) increments to a depth of 180 cm (6 ft.). Total and extractable Se were analyzed in the native samples as well as the reclaimed samples.

Selenium Analysis

Several methods have been proposed for correlating soil Se concentrations to plant uptake. Soil Se has been characterized by extraction techniques such as hot water, AB-DTPA, DTPA, EDTA, Na_2CO_3 , and saturated paste extracts, as well as total Se levels (Jump and Sabey, 1989; see Table 1). For this study, soil and backfill samples were analyzed for total Se (after digestion) and hot water, AB-DTPA, saturated paste extract and KH_2PO_4 extractable Se. The objective of this research was to determine the variation in Se extraction methods used for Se analysis of mining soils. The four extraction methods have been suggested to represent plant available Se (Spackman et al., 1994). In order for any one extraction method to be valid for Se evaluation purposes, it must provide results that are comparable, reproducible, and representative of Se concentrations that can be correlated to plant uptake. The methods evaluated in this study included:

Total Se - Total soil and backfill Se concentrations were determined using perchloric and hydrofluoric acid digestion (Bajo, 1978) with subsequent analysis by AAS-HG. This total soil Se value was compared to the results obtained from the four extraction methods described below (Spackman et al., 1994).

Hot Water Soluble Se - This method has been used to measure available Se since the 1930's. Several states have guidelines for mining activities that regulate the placement of soil, spoil and overburden based on hot water soluble Se levels. Plant available Se was estimated using a hot water extractant containing 0.1% CaCl_2 . Hot water extraction methodology is listed in ASA Monograph 9, part 2, 1965, "Method 80-3.2" pg 1122.

AB-DTPA Extractable Se - Proposed by Soltanpour and Workman (1980) as a method for assessing soil Se, this method has been used extensively since the mid 1980's and has been used to generate a large amount of data on soils, spoils, and overburden materials from Wyoming coal fields. Specific greenhouse studies have shown a strong correlation between extractable Se and Se in study plant species. The method reference is ASA Monograph No 9, part 2, 1982, "Method 3-5.2.2" pg 55.

Saturated Paste Extraction - Currently this method is used for pH, EC, and soluble ions and metals, which would suggest it is also applicable for Se extraction. The procedure uses larger sample quantities (10-200 times greater than other methods) which should promote consistent results. Saturated paste extraction methodology is described in U.S.D.A. Agriculture Handbook 60 (U.S. Salinity Laboratory, 1954).

Potassium Dihydrogen Phosphate (KH_2PO_4) Extraction - This method has been demonstrated to be an effective extractant of Se species from certain minerals. The phosphate ion selectively replaces Se adsorbed on kaolinite and montmorillonite (Bar-Yosef and Meek, 1987). The U.S. EPA has used this extractant to assess extractable sulfate from soils throughout the U.S. Table 3 presents additional information for the justification of the use of phosphate extraction for characterizing soil and backfill Se. Method reference for phosphate extraction is "Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey" (Cappo et al., 1987) as modified by Spackman et al. (1994).

Table 3. Justification for Using Phosphate Extraction for Evaluation Selenium in Soils and Overburden Materials.

-
- Selenium chemistry similar to sulfur
 - Selenium and sulfur adsorb by Al and Fe oxides
 - Phosphate extractable SO_4 used by EPA in national acid deposition study
 - Phosphate will extract soluble and adsorbed Se
 - Preliminary results have suggested phosphate extractable Se is a better predictor of plant Se concentrations
-

The extraction procedures selected were chosen to allow us to compare current recommended methods (hot water and AB-DTPA) with two additional methods (phosphate and saturated paste) in order to evaluate their ability to index plant uptake of Se.

All soil and backfill digested and extracted solutions were pretreated with HCl and H₂O₂ to convert Se from the +6 to the +4 oxidation state for analysis of total soluble Se (Workman and Soltanpour, 1980; Spackman et al., 1994). Selenium was analyzed by the AAS-HG method, which is described in detail in Spackman et al. (1994).

Quality Control/Quality Assurance Program

Accuracy was evaluated within each laboratory by use of reference soil samples, duplicate analysis, and use of QA/QC standards. Duplicate analyses of approximately 20% of the soil and backfill samples were performed by the laboratory not in charge of the particular analysis. Therefore, approximately 20% of the samples were analyzed at both Inter-Mountain Laboratory (IML - Sheridan, WY) and the Soil and Environmental Chemistry Laboratory (SECL - University of Wyoming) and used for analytical comparison.

Results

Laboratory Comparisons

The quality control/quality assurance program for this project revealed excellent agreement between results for certain analyses conducted jointly by IML and SECL. For hot water, AB-DTPA, and phosphate extractable Se, linear regression analyses resulted in correlations greater than 0.95 (Figure 2). Total Se analysis was completed almost exclusively by IML, and therefore the number of samples that could be used for comparison were insufficient. The saturated paste extractable Se levels were low. Comparisons between the two laboratories indicated there was greater variability with the saturated paste Se results than with the other Se methods.

Se Variation

Coefficient of variations (CVs) were calculated for the five Se variables (i.e., total Se and the four extractable Se levels) at each site and depth. A large range in CV's was noted (0 to 118%); however, the larger CV's tended to be grouped at specific sites and depths, and with certain extractants. Of the 831 CV's calculated, only 10 (or 1.2%) were greater than 100%; only the results from hot water, AB-DTPA, and saturated paste extractable Se data had CV's greater than 100%. Average CV's for mine type and ecological system (i.e., native versus reclaimed) were approximately 25%. Overall, total Se varied the least among the five Se variables followed by phosphate < AB-DTPA < hot water < saturated paste Se (Table 4).

Using a significance level of $p=0.01$ and a correlation coefficient of 0.9 or greater, several trends were found when comparing soil/backfill extractable and total Se concentrations. When separating by mine or type, a consistent relationship was found, which indicated hot water, AB-DTPA, and phosphate extractable Se were all statistically correlated. Separation by mine and type indicated AB-DTPA and phosphate Se were highly correlated with samples collected from Mine A reclaimed and Mine B native and reclaimed; all correlation coefficients for Mine A native sites were less than 0.9.

Including depth as a variable in the above examples resulted in several significant correlations; however, the only logical combinations are between type, and mine and type because mine, type, and depth combinations are meaningless since depths for native sites are by 30 cm increments and depths for reclaimed are by approximately 60 cm increments. With native sites, significant correlations were found for hot water, AB-DTPA, and phosphate Se for all depths except depth 1 (top 30 cm of soil) which had correlation coefficients of ≤ 0.8 . Significant correlations were also determined for all reclaimed depths for hot water, AB-DTPA, and phosphate Se. Separating by mine, type, and depth indicated there were significant correlations ($r \geq 0.9$) among hot water, AB-DTPA, and phosphate Se at AN5 (i.e., Mine A native depth 5), AR2 and AR3, BN2 through BN5, BR2 and BR3. For the remaining comparisons, correlations were either significant between two variables or were lower than 0.9; several correlations were found with correlation coefficients of 0.7 or 0.8.

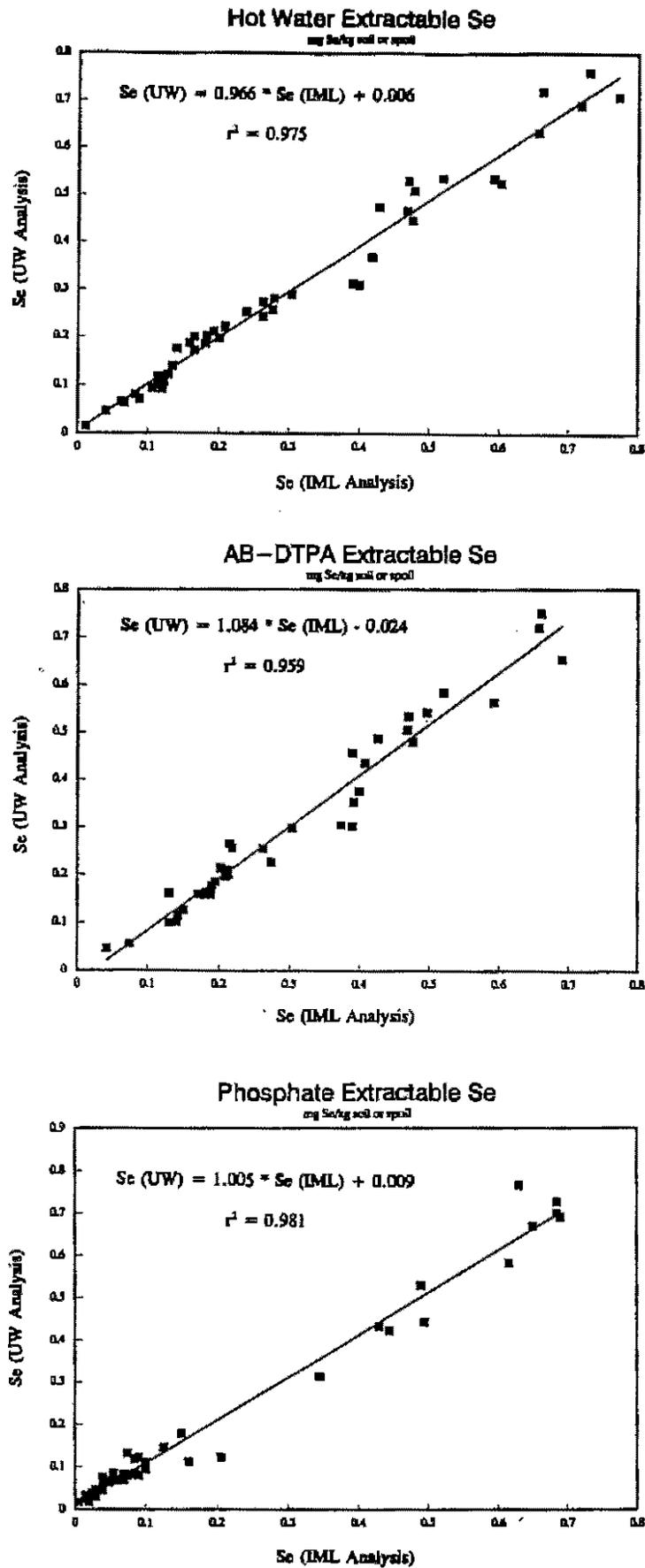


Figure 2. Results of hot water, AB-DTPA and phosphate extractable Se data determined at Inter-Mountain Laboratory (IML, Sheridan WY) and the Soil and Environmental Chemistry Laboratory (UW, University of Wyoming).

Table 4. Coefficients of Variation (CV) for total Se and hot water, AB-DTPA, saturated paste, and phosphate extractable Se determined on soil/backfill samples collected from three holes at different depth (3 to 5) at native (N) and reclaimed (R) sites within two mines (A and B) in the Powder River Basin, WY.

Mine	Type	Depths	Selenium Analysis				
			Total Se	Hot Water Se	AB-DTPA Se	Saturated Paste Se	Phosphate Se
			CVs ± standard deviation				
A and B	N and R	3 or 5	17 ± 14	31 ± 25	24 ± 21	36 ± 25	20 ± 15
A and B	N	1-5	19 ± 14	36 ± 27	27 ± 23	37 ± 25	21 ± 14
A and B	R	1-3	15 ± 14	27 ± 22	21 ± 18	35 ± 25	19 ± 18
A	N and R	3 or 5	16 ± 15	26 ± 20	22 ± 19	35 ± 23	19 ± 16
B	N and R	3 or 5	18 ± 12	39 ± 29	30 ± 23	39 ± 28	22 ± 13
A	N	1-5	19 ± 16	27 ± 15	23 ± 22	34 ± 18	20 ± 11
A	R	1-3	14 ± 13	25 ± 12	21 ± 18	36 ± 25	19 ± 18
B	N	1-5	19 ± 10	41 ± 30	30 ± 23	40 ± 29	22 ± 12
B	R	1-3	17 ± 17	34 ± 24	26 ± 18	31 ± 23	22 ± 18
A	N	1	10 ± 6	26 ± 20	20 ± 9	26 ± 11	14 ± 6
A	N	2	14 ± 11	25 ± 18	29 ± 27	36 ± 19	16 ± 7
A	N	3	27 ± 19	27 ± 9	17 ± 7	30 ± 17	21 ± 9
A	N	4	25 ± 21	27 ± 14	28 ± 31	32 ± 16	25 ± 12
A	N	5	21 ± 13	27 ± 13	22 ± 14	47 ± 16	23 ± 16
A	R	1	13 ± 15	32 ± 20	22 ± 17	43 ± 25	16 ± 17
A	R	2	17 ± 14	21 ± 20	19 ± 16	29 ± 24	17 ± 17
A	R	3	13 ± 9	23 ± 22	21 ± 20	35 ± 24	23 ± 20
B	N	1	19 ± 11	38 ± 25	39 ± 24	43 ± 29	25 ± 11
B	N	2	19 ± 6	59 ± 37	42 ± 31	54 ± 31	23 ± 11
B	N	3	19 ± 12	47 ± 24	28 ± 13	41 ± 11	24 ± 12
B	N	4	17 ± 10	23 ± 18	16 ± 10	27 ± 27	13 ± 7
B	N	5	17 ± 11	33 ± 31	24 ± 20	35 ± 35	22 ± 11
B	R	1	4 ± 2	39 ± 23	15 ± 6	32 ± 17	13 ± 13
B	R	2	21 ± 19	35 ± 23	31 ± 19	40 ± 31	22 ± 18
B	R	3	25 ± 15	26 ± 22	29 ± 19	21 ± 12	30 ± 18
A and B	R	2 and 3	16 ± 13	23 ± 22	21 ± 18	32 ± 25	21 ± 19

Discussion

The four extraction methods evaluated in this study provide different information concerning soil and backfill Se (Williams and Thornton, 1973). The water soluble fraction (i.e., saturated paste) is probably a better estimate of a true soil solution. The KH_2PO_4 extraction, however, may better estimate the Se concentration that should be related to plant uptake and mobility. Selenium determined by this extractant may approximate the amount of Se that will become accessible over time and which may be solubilized readily by plant-root interactions.

The use of AB-DTPA was introduced by Soltanpour and Schwab (1977), and subsequently modified by Soltanpour and Workman (1979), in order to combine four single extraction procedures into one. These included: (1) NH_4^+ for exchange of K^+ , (2) HCO_3^- for extraction of P, (3) DTPA for chelation of micronutrients (Cu, Fe, Mn, and Zn), and (4) as a substitute for water-soluble NO_3^- . Thus, one could measure several elements from a single extraction and save a considerable amount of time and effort. This approach would fit well into a soil testing laboratory that processes several thousands of samples yearly. Soltanpour and Workman (1980) used a modified AB-DTPA method (Soltanpour and Workman, 1979) to evaluate the availability and toxicity of Se (Se) to alfalfa plants. The conclusions presented in their paper were used, in part, by WDEQ-LQD to set marginal suitability at a level of 0.1 mg/kg AB-DTPA extractable Se for overburden, spoil, and soil materials (WDEQ-LQD, 1984).

Soltanpour and Workman (1980) proposed using the AB-DTPA soil extraction method to include the analysis of Se (presumably SeO_3^{2-} or SeO_4^{2-}) in soils, reconstructed coal mine soils and overburden materials. A main objective of their study was to assess the use of AB-DTPA extractable Se in determining its availability and toxicity to alfalfa plants. In two experiments, one with soil amended with sodium selenate, the other using coal mine soil and overburden materials, they found hot water extractable and AB-DTPA methods yielded mixed results for Se. Although hot water and AB-DTPA extracted similar amounts of Se from Se amended soils, AB-DTPA extracted greater amounts of Se than hot water from coal mine soils and overburden materials from coal mines in western Colorado.

The chemistry of Se is, in many respects, similar to sulfur (S). Thus, one might conclude that an extractant containing SO_4^{2-} may be useful for extracting Se. A study by Cary et al. (1967) found Se extracted from soils with K_2SO_4 was related to Se in alfalfa. Selenium extracted by K_2SO_4 is due to dissolution and exchange reactions involving the SO_4^{2-} ion. A problem associated with using K_2SO_4 is that many soil and overburden materials of arid and semiarid environments already contain very high levels of SO_4^{2-} . The U.S. Environmental Protection Agency, in conjunction with the National Acid Precipitation Assessment Program, conducted a tremendous amount of research on the problem of acid deposition (Direct/Delayed Response Project; Cappo et al. 1987). A method used extensively for determining soil extractable SO_4^{2-} utilized solutions containing phosphate (PO_4^{3-}). This would represent a logical choice of an extractant to determine extractable or plant-available Se. Phosphate extractable Se would include both water soluble and adsorbed Se species. The trivalent charge on the phosphate ion would enable phosphate to displace the divalent Se species from adsorption or complexing sites.

Jump and Sabey (1989) conducted greenhouse studies to compare several soil Se extraction methods for use in predicting plant Se concentrations. The soil Se analyses included total Se and Se extracted by hot water, AB-DTPA, saturated paste, DTPA, and Na_2CO_3 . Sodium carbonate extracted the greatest percentage of total Se. Saturated paste extracts, expressed in mg L^{-1} Se, were a better predictor of Se uptake by *Atriplex canescens* and *Astragalus bisulcatus*. Problems that could develop with this extraction method would be the lack of consistency in results between laboratories and lab workers from the use of unnormalized data and differences in preparing saturated pastes. Results of our study indicated saturated paste extractable Se concentrations were low and highly inconsistent between laboratories.

Soltanpour and Workman (1980) concluded that AB-DTPA and hot water-extractable Se were highly correlated, and that the former was useful for correlating Se uptake by alfalfa plants. After examining the effectiveness of five Se extractants, Jump and Sabey (1989) suggested that Se determined by saturated paste extraction was the best method for predicting Se concentrations in fourwing saltbush and *Astragalus bisulcatus*. The Environmental Protection Agency has used a phosphate extraction method for the analysis of soluble and adsorbed

SO₄²⁻ (Cappo et al., 1987). This method would therefore appear to be useful for determining extractable Se since sulfur and Se chemistry are very similar.

Many investigations claimed their extractable Se method is well correlated with soil and plant Se. However, when field tested the correlations are not as strong. For example, Olson and Moxon (1939) proposed water- and base-soluble extractable soil Se, which later when field tested indicated a relatively weak correlation with Se content of western wheatgrass (*Agropyron smithii*) (Olson et al., 1942).

Using 0.1 ppm AB-DTPA extractable Se as criteria for determining the suitability of soil and overburden materials for mine land reclamation may be more conservative than necessary (Vance, 1990). However, evidence presented suggests AB-DTPA may not actually be an appropriate extractant for assessing Se. If an interim criteria is to be used for classifying soils and overburden materials as suitable, one similar to that proposed by Fisher and Munshower (1991) may be a starting point. Any criteria implemented would have to be recognized as temporary until further research improves our understanding of soil-plant Se relationships.

Research is needed to define the relationship between soil and overburden Se concentration with plant uptake. Essentially, we need field studies that investigate possible interactions between Se and other soil chemical and physical properties over sites having diverse plant communities. At the same time we need to improve on methods for sampling, handling, preservation, extraction, and quantification of soil and plant materials. We have to develop extraction methods that provide meaningful representations of plant available soil Se that, above all, give consistent values.

Significant emphasis has been placed on the results obtained from the Soltanpour and Workman (1980) study for placing Se suitability limits on soils, overburden and regraded spoils. Although the findings of their study indicated soil Se levels correlate with plant Se concentrations, generalizations based on their results are not necessarily correct for all situations. First, their study was conducted in a growth chamber using North Dakota Mollisols that were amended with sodium selenate. The use of Mollisols, which have organic matter contents from 3.7 to 6.5%, as a replicate of mine land soils of Wyoming is unrealistic. Sodium selenate is very soluble in soils and more biologically active than is selenite, which may be an important Se species in Wyoming soils. Furthermore, the soil moisture for each pot was maintained daily at field capacity, a condition that is not found in the arid and semiarid soils of Wyoming.

Field studies using well-defined soil/overburden sampling and preservation methods are the initial step in contributing meaningful results for defining suitability criteria. Research is required for delineating better analytical methods that will provide consistent results that are reliable indications of soil-plant relationships. In addition, use of greenhouse or growth chamber studies should compliment field studies, if designed properly. These latter types of studies are useful for controlling chemical and physical soil and plant variables that may not be possible in the field. Additional studies are also needed for the analytical determination of soil and overburden Se that corresponds to plant availability. Due to the lack of consistency in methods for determining extractable Se concentrations, it behooves us to develop better analytical techniques so that Se results can be used with confidence. Results of the extraction analysis should provide information needed for understanding soil-plant relationships and guidelines for characterizing spoil materials for regulatory purposes.

Acknowledgements

This work was supported in part by the Abandoned Coal Mine Lands Research Program (ACMLRP) at the University of Wyoming and the National Science Foundation - EPSCoR ADP program. The ACMLRP support was administered by the Land Quality Division of the Wyoming Department of Environmental Quality from funds returned to Wyoming from the Office of Surface Mining of the U.S. Department of the Interior.

References

- American Society of Agronomy. 1965. L.O. Fine, Selenium - Chapter 80. In Monograph No. 9, Methods of Soil Analysis, Part 2, 1st ed., C.A. Black (ed.), Method 80-3: Hot Water Extraction. ASA. Inc., Madison WI.
- American Society of Agronomy. 1982. C.H. Lim, Dissolution for total elemental analysis - Chapter 1. In Monograph No. 9, Methods of Soil Analysis, Part 2, 2nd ed., A.L. Page (ed.), SSSA, Inc., Madison WI.
- Beath, O.A., C.S. Gilbert and H.F. Eppson. 1937 Selenium in soils and vegetation associated with rocks of Permian and Triassic age. *American Jour. Botany* 24:96-101.
<http://dx.doi.org/10.2307/2436728>
- Bar-Yosef and D. Meek. 1987. Selenium sorption by kaolinite and montmorillonite. *Soil Science* 144:11-19.
<https://doi.org/10.1097/00010694-198707000-00003>
- Cappo, K.A., L.J. Blume, G.A. Raab, J.K. Bartz and J.L. Engels. 1987. Extractable sulfate and nitrate. In Analytical Methods Manual for the Direct/Delayed Response Project Soil Survey. U.S. EPA Rep. 600/8-87/020. Environ. Monitoring Systems Lab., U.S. EPA, Las Vegas, NV. Section 12, 11 p.
- Cary, E.E., G.A. Wicczorek and W.H. Allaway. 1967. Reactions of selenite-selenium added to soils that produce low-selenium forages. *Soil Sci. Soc. Am. Proc.* 31:21-26.
<http://dx.doi.org/10.2136/sssaj1967.03615995003100010010x>
- Fisher, S.E. and F.F. Munshower. 1991. Selenium issues in drastically disturbed land reclamation planning in arid and semi-arid environments. Proceedings of the Billings Reclamation Symposium Proc., Billings, MT. U.S. Geol. Survey Circ. No. 1064. pp. 123-133.
- Ihnat, M. 1989. Occurrence and Distribution of Selenium. CRC Press, Boca Raton, FL.
- Jump, R. and B. Sabey. 1985. Evaluation of the NH_4HCO_3 -DTPA soil test for identifying seleniferous soils. *Amer. Soc. Surface Mining and Reclamation Proc.* Denver, CO, pp. 87-90.
<http://dx.doi.org/10.21000/JASMR85010087>
- Jump, R. and B. Sabey. 1989. Soil test extractants for predicting selenium in plants. In *Selenium in Agriculture and the Environment*, L.W. Jacobs (ed.). SSSA Special Publication No. 23. Soil Sci. Soc. Am., Inc. Madison, Wisconsin. pp. 95-106.
- Lakin, H.W. 1961. Selenium content in soils. In *Selenium in Agriculture*, M.S. Anderson et al. (eds.). USDA Handbook 200. U.S. Gov. Print. Office. Washington, D.C. pp. 27-34.
- Mayland, H.F., L.F. James, K.E. Panter, and J.L. Sondergger. 1989. Selenium in seleniferous environments. In *Selenium in Agriculture and the Environment*, L.W. Jacobs (ed.). SSSA Special Publication No. 23. Soil Sci. Soc. Am., Inc. Madison, Wisconsin. pp. 15-50.
- National Academy of Sciences. 1976. Selenium. Assembly of Life Sciences. NAS-NRC, Washington, D.C.
- National Academy of Sciences. 1983. Selenium in Nutrition. Rev. ed. Board on Agric. NAS-NRC, Washington, D.C.
- Olson, O.E. and A.L. Moxon. 1939. The availability to crop plants of different forms of selenium in the soil. *Soil Sci.* 47:302-311.
<http://dx.doi.org/10.1097/00010694-193904000-00005>
- Olson, O.E., E.I. Whitehead and A.L. Moxon. 1942. Occurrence of soluble selenium in soils and its availability to plants. *Soil Sci.* 54:47-53.
<http://dx.doi.org/10.1097/00010694-194207000-00004>

- Producers, R.A. and F.F. Munshower. 1991. AB-DTPA extractable soil selenium as a predictor of seleniferous vegetation. Proceeding of the Billings Reclamation Symposium Proc., Billings, MT. U.S. Geol. Survey Circ. No. 1064. pp. 65-71.
- Rosenfeld, I. and O.E. Beath. 1964. Selenium: Geobotany, biochemistry, toxicity, and nutrition. Academic Press, New York.
- Severson, R.C. and S.E. Fisher. 1985. Results of the third western round robin soil and overburden analysis program. U.S. Geol. Survey Open File Report 85-220, 54 p.
- Severson, R.C. and S.E. Fisher. 1987. Results of the third western round robin soil and overburden analysis program. U.S. Geol. Survey Open File Report 87-352, 18 p.
- Soltanpour, P.N., S.R. Olsen, and R.J. Goos. 1982. Effect of nitrogen fertilization of dryland wheat on grain selenium concentration. *Soil Sci. Soc. Am. J.* 46:430-433.
<http://dx.doi.org/10.2136/sssaj1982.03615995004600020044x>
- Soltanpour, P.N. and A.P. Schwab. 1977. A new soil test for simultaneous extraction of macro- and micro-nutrients in alkaline soils. *Commun. Soil Sci. Plant Anal.* 8:195-207.
<http://dx.doi.org/10.1080/00103627709366714>
- Soltanpour, P.N. and S.M. Workman. 1979. Modification of NH_4HCO_3 -DTPA soil test to omit carbon black. *Commun. Soil Sci. Plant Anal.* 10:1411-1420.
<http://dx.doi.org/10.1080/00103627909366996>
- Soltanpour, P.N. and S.M. Workman. 1980. Use of NH_4HCO_3 -DTPA soil test to assess availability and toxicity of selenium to alfalfa plants. *Commun. Soil Sci. Plant Anal.* 11:1147-1156.
<http://dx.doi.org/10.1080/00103628009367111>
- Spackman, L.K., G.F. Vance, L.E. Vicklund, P.K. Carroll, D.G. Steward, and J.G. Luther. 1994. Standard operating procedures for the sampling and analysis of selenium in soil and overburden/spoil material. Research Publication MP82. College of Agriculture, University of Wyoming, Laramie, WY. 13 pp.
- U.S. Salinity Laboratory Staff. 1954. Diagnosis and improvement of saline and alkali soils. U.S.D.A. Handbook No. 60. U.S. Gov. Print. Office, Washington D.C.
- Vance, G.F. 1990. Evaluation of Wyoming Department of Environmental Quality-Land Quality Division's "Marginal Suitability Level of 0.1 ppm AB-DTPA Extractable Selenium in Overburden, Spoil, and Soil". Wyoming Department of Environmental Quality, Cheyenne, Wyoming. 8 pp.
- Wan, H.F., R.L. Mikkelsen and A.L. Page. 1988. Selenium uptake by some agricultural crops from central California toxic soils. *J. Environ. Qual.* 17:269-272.
<http://dx.doi.org/10.2134/jeq1988.00472425001700020018x>
- Williams, C. and I. Thornton. 1973. The use of soil extractants to estimate plant available molybdenum and selenium in potentially toxic soils. *Plant Soil* 39:149-159.
<http://dx.doi.org/10.1007/BF00018053>
- Wyoming Department of Environmental Quality - Land Quality Division. 1984. Guideline No. 1, Topsoil and Overburden. Cheyenne, WY.

