

Soil Sulfur Amendments Suppress Selenium Uptake by Alfalfa and Western Wheatgrass

C. L. Mackowiak* University of Florida

M. C. Amacher USDA-FS

Selenium (Se) is a potential soil contaminant in many parts of the world where it can pose a health risk to livestock and wildlife. Phosphate ore mining in Southeast Idaho has resulted in numerous waste rock dumps revegetated with forages to stabilize the dumps and support grazing. Alfalfa (*Medicago sativa* L.), smooth brome (*Bromus inermis* Leyss.), and western wheat grass [*Pascopyrum smithii* (Rydb.) A. Löve] are the dominant forage species on these lands. To demonstrate the feasibility of using sulfur (S) as a soil amendment to restrict plant Se uptake, 3 kg pots containing 50:50 w/w soil and waste shale were uniformly mixed with 0, 0.5, 1.0, or 2.0 Mg ha⁻¹ S as either elemental S or gypsum. Pots were seeded with alfalfa or western wheat grass. Dry mass and tissue Se were monitored over several clippings. Soils were sampled at the conclusion of the study and analyzed for water-soluble, oxalate-extractable, and total Se. Sulfur amendments as either elemental S or gypsum at 1.0 Mg ha⁻¹ or greater equally suppressed Se uptake over 60% in both forage species. Alfalfa accumulated more Se than western wheat grass. Plant removal via successive clippings resulted in lower tissue Se accumulation over time than the use of S soil amendments alone. Alfalfa-planted soils contained lower water-soluble and oxalate-extractable Se than did the non-planted controls while western wheat grass-planted soils contained lower water-soluble Se. Applying S to these shale-based soils may be an economically viable option for treating Se-impacted, revegetated lands.

SELENIUM (Se) is an essential nutrient in animal systems but high concentrations can threaten biological systems when human activities, such as mining into shale for oil and phosphorus or irrigating arid and semiarid seleniferous soils occur (Lemly, 1997). The U.S. Western Phosphate Field is one of the largest sources of phosphate rock in the world and constitutes 30% of the total U.S. phosphate reserves. Similar marine shale deposits exist throughout the world, including Russia, Peru, and Australia (Cathcart, 1980). Many of these deposits contain elevated concentrations of selenium (Se) and other trace elements that may prove hazardous to the environment (Van Kauwenbergh, 1997; Presser et al., 2004).

Phosphate ore mining of sedimentary rock units of the Permian Phosphoria Formation in southeast Idaho has resulted in numerous large waste rock dumps. These dumps typically contain middle waste shale from between the upper and lower ore units in the Meade Peak member of the Phosphoria Formation, but they may also include mudstone, siltstone, chert, limestone, and dolostone (Moyle and Piper, 2004). Phosphatic shale, which is a major component of the waste rock dumps, is enriched in Se and other trace elements such as vanadium (V), chromium (Cr), molybdenum (Mo), nickel (Ni), zinc (Zn), cadmium (Cd), and uranium (U) (Herring and Grauch, 2004). The dumps are typically revegetated with a mixture of native and non-native plant species (Chambers et al., 1994). However, most of the historic dumps now consist of a tri-culture of alfalfa (*Medicago sativa* L.), smooth brome (*Bromus inermis* Leyss.), and western wheatgrass [*Pascopyrum smithii* (Rydb.) A. Löve]. Other native and non-native species comprise a minor component of this plant community. Many of the dumps exist on multi-use public lands, and support livestock grazing and recreational hunting.

In general, Se concentrations in phosphatic shale decrease with increasing degree of shale weathering (Herring and Grauch, 2004). Water-soluble Se is a significant fraction of the total Se in unweathered phosphatic shale (Herring, 2004), where it leaches from the waste rock (Stillings and Amacher, 2004) and becomes available for plant uptake (Mackowiak et al., 2004). Perkins and Foster (2004) found that most of the Se in the unweathered rocks is associated with the sulfide fraction with lesser amounts associated with organic matter and oxyhydroxide fractions and as elemental Se. In contrast, most of the Se in weathered rocks is found in the oxide fraction with lesser amounts in the organic matter fraction and as elemental Se. Thus, as mineral sulfide

Copyright © 2008 by the American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. All rights reserved. No part of this periodical may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the publisher.

Published in J. Environ. Qual. 37:772–779 (2008).

doi:10.2134/jeq2007.0157

Received 28 Mar. 2007.

*Corresponding author (echo13@ufl.edu).

© ASA, CSSA, SSSA

677 S. Segoe Rd., Madison, WI 53711 USA

C.L. Mackowiak, Univ. of Florida, North Florida Research and Education Center, 155 Research Dr., Quincy FL 32351-5677. M.C. Amacher, USDA-FS Rocky Mountain Research Station, Forestry Sciences Lab, 860 N 1200 E, Logan UT 84321.

weathering progresses, Se is released and re-incorporated into the weathered metal oxide fraction.

Even as shale Se release kinetics are largely unknown, plants have been found to accumulate Se from the impacted soil (Mackowiak et al., 2004). Plant accumulation and soil ingestion lead to bioaccumulation in livestock and wildlife (Witte and Will, 1993; Thomas et al., 2005). Chronic toxicity in cattle may occur with intakes as low as 0.4 mg Se kg⁻¹ body weight per day, and for sheep with intake as low as 0.08 mg Se kg⁻¹ body weight per day (Puls, 1994). The U.S. Food and Nutrition Board (1980) recommends plant tissue Se concentrations below 5 mg kg⁻¹ for grazing animals.

Remediation efforts may decrease Se bioavailability in forage plant communities on revegetated lands, thereby lessening animal exposure. One approach is to apply excess S to the waste rock-derived soil to suppress Se uptake. Sulfate (SO₄) is a structural analog of selenate [SeO₄ or Se(VI)], resulting in competitive uptake (Leggett and Epstein, 1956). Selenate uptake is via high affinity sulfate transporters but the transporters favor S over Se in nonaccumulating plants (Sors et al., 2005). Greater SO₄/SeO₄ ratios in soil solution may shift the balance toward greater SO₄ uptake, resulting in lower plant Se concentrations.

Incorporating gypsum (CaSO₄·2H₂O) or elemental S may be an economically attractive option (cost consists of materials and spreader-equipped all-terrain vehicles) for lessening Se uptake by plants growing on the waste shale if Se(VI) is the dominant plant-available species. Unfortunately, the literature on S suppressing Se uptake in the field is somewhat confusing and contradictory. Significant suppression has been reported in solution culture for nonaccumulating plant species (Bell et al., 1992; Hopper and Parker, 1999) and for plants growing in some field soils (Woodbury et al., 1999; Dhillon and Dhillon, 2000). However, Wu et al. (2003) found high soil S did not inhibit Se uptake in soil contaminated by drainage sediment. Milchunas et al. (1983) found S antagonism for Se uptake in *P. smithii* only in fields where high soil Se conditions were artificially created. Severson and Gough (1992) did not find a relationship between soil solution S and Se as it related to Se uptake by alfalfa under natural field conditions. They suggested that the interaction may be masked due to a wide range of soil chemical properties within their California soil/plant survey.

Amacher et al. (2001) found total S in the waste shale-impacted soils at one representative location averaged 3.4 g kg⁻¹ (range from 1.4 to 6.1 g kg⁻¹), while other Meade Peak rocks averaged 11 g kg⁻¹ (Herring and Grauch, 2004). These values should provide ample SO₄-S to compete against plant Se uptake. Yet weathering rates of pyrite and sphalerite, the principle forms of S in Phosphoria Formation rocks (Knudsen and Gunter, 2004; Grauch et al., 2004; Perkins and Foster, 2004), may not provide an ample supply of SO₄-S within the rhizosphere to sufficiently interfere with plant Se uptake.

To evaluate the ability of S to suppress plant uptake of Se from shale waste rock, we tested two S sources (elemental S and gypsum) at 4 application rates (0, 0.5, 1, 2 Mg S ha⁻¹) on Se aboveground tissue concentrations in multiple clippings from two commonly identified forage species, western wheatgrass and alfalfa.

Materials and Methods

Phosphatic Shale and Soil Collection, Preparation, and Analyses

Bulk phosphatic shale was collected from an exposed outcrop of a sedimentary rock unit within the Meade Peak Member of the Phosphoria Formation at Maybe Canyon, southeast Idaho. Topsoil was collected from an unmined area in nearby Dry Valley, Idaho. The shale and soil were screened to <0.6 cm in the field and placed in 20-gal tubs for transport to the lab for further processing. After air-drying under ambient conditions, a well-mixed subsample of shale and soil was screened through a 2-mm stainless steel sieve to remove coarse fragments. A well-mixed subsample of the <2-mm material was rolled in a glass scintillation vial with coated steel pins to pulverize the material to <100 mesh before digestion for total Se.

To determine total Se, a 0.500-g subsample of <100 mesh shale and soil was digested in 20 mL of a 3.5:1 mixture of concentrated HNO₃ + concentrated HClO₄ in glass digestion tubes in a graphite block digester at 95°C (Amacher et al., 2001; Amacher, 2003). Digestion was complete when the volume was reduced to <2 mL and HClO₄ fumes were visible. The digest was diluted to 50 mL with deionized water before analysis. To convert oxidized Se in the digest to Se(IV) for hydride atomic absorption spectrophotometry (AAS) analysis, equal volumes of digest and concentrated HCl + 1 mL of 0.1 mol L⁻¹ potassium persulfate were heated for 20 min at 80°C in a graphite block digester. Conversion efficiency was monitored by moving a Se(VI) standard through the procedure. Digestion and analysis accuracy was verified by analyzing three USGS sedimentary rock check samples that were collected, prepared, and analyzed for the Western U.S. Phosphate Project (Herring and Wilson, 2001).

Saturation extracts of shale and soil were prepared (Rhoades, 1996) and analyzed for total dissolved Se using the hydride AAS method. Briefly, deionized water was added to 200 g of shale/soil mixture until saturation. The soil/water mixture equilibrated for 24 h and then was suction filtered through a Whatman #40 filter paper to recover the soil solution for analysis. Oxalate-extractable Se was determined by shaking 0.500-g samples of <2-mm topsoil and shale with 25 mL of 0.2 mol L⁻¹ ammonium oxalate + 0.2 mol L⁻¹ oxalic acid for 2 h at 150 oscillations min⁻¹, filtering the suspensions through quantitative filter paper, and analyzing the extracts for total dissolved Se by hydride AAS. All extracts were filtered through 1.0-μm glass-fiber membrane filters before analysis. Extracts were prepared for hydride AAS analysis using the same procedure used for soil digests.

Glasshouse Pot Experiment

Meade Peak phosphatic shale was mixed with topsoil (all materials pre-screened <0.6 cm) from Dry Valley at a ratio of 1:1 (mass/mass) and 3 kg of shale/soil mixture was added to 15-cm diameter plastic pots. Earlier experiments showed that plant growth was improved in shale/soil mixtures versus 100% shale. Elemental S (S⁰) and gypsum (CaSO₄·2H₂O) were tested at 0, 0.62, 1.25, and 2.49 g S pot⁻¹ (0.0, 0.5, 1, and 2 Mg ha⁻¹)

Table 1. Effect of four rates (0, 0.5, 1, and 2 Mg S ha⁻¹) of elemental S and gypsum on total biomass harvested, total amounts of Se and S removed by harvesting, and S/Se ratios in total biomass harvested of *P. smithii* (wheatgrass) and *M. sativa* (alfalfa) from 3 kg pots.

Plant species	S source	S rate	Total biomass	Se removed	S removed	S/Se
		Mg ha ⁻¹	g	mg		mg:mg
Wheatgrass	Elemental S	0.0	58.3 a†	0.505 a	129.9 ab	240 c
		0.5	58.6 a	0.185 b	119.9 b	662 abc
		1.0	56.8 a	0.145 b	126.6 ab	1006 a
		2.0	57.4 a	0.140 b	129.1 ab	946 ab
	Gypsum	0.0	56.7 a	0.572 a	130.4 ab	254 c
		0.5	56.0 a	0.206 b	118.3 b	589 bc
		1.0	60.1 a	0.182 b	137.4 a	805 ab
		2.0	58.6 a	0.184 b	124.6 ab	695 abc
Alfalfa	Elemental S	0.0	95.6 a	2.277 a	425.0 a	132 d
		0.5	84.8 a	0.874 bc	449.5 a	493 ab
		1.0	97.6 a	0.776 bc	461.5 a	587 ab
		2.0	76.9 a	0.678 c	422.6 a	664 a
	Gypsum	0.0	90.8 a	2.189 a	404.0 a	142 cd
		0.5	86.0 a	1.172 b	414.1 a	358 bcd
		1.0	90.6 a	0.921 bc	313.5 a	450 abc
		2.0	91.1 a	0.903 bc	296.6 a	513 ab

† Within column means followed by the same letter are not significantly different by the Tukey-Kramer mean separation test ($P < 0.01$).

by uniformly mixing the amendments into four replicate pots of a 50:50, shale/soil mix. The four S rates were equivalent to 0, 3.35, 6.69, and 13.38 g gypsum pot⁻¹ (0.0, 2.5, 4.9, and 9.9 Mg gypsum ha⁻¹). After wetting each pot from below, *Pascopyrum smithii* (Rydb.) A. Löve (wheatgrass) or *Medicago sativa* L. (alfalfa) were seeded at a rate of 50 per pot into a pre-moistened 1-cm layer of a sphagnum peat/vermiculite seed germinating mix (Scotts Co., Marysville, OH) overlaying the shale/soil mix. The pots were arranged in a randomized complete block design with four blocks. The germination mix was kept moist until plants emerged. Plants were watered as needed throughout the course of the experiment and saucers were used to prevent leachate losses. Natural daylight was supplemented with 1000-W high-pressure sodium lamps to extend daylength to 15 h ($34 \pm 11 \text{ mol m}^{-2} \text{ d}^{-1}$). Greenhouse temperature ($22.1/16.1^\circ\text{C} \pm 1.7/2.8^\circ\text{C}$ light/dark) and humidity ($50/57\% \pm 20/16\%$ light/dark) were monitored throughout the experiment. Above-ground biomass was clipped at 51, 86, 110, 135, 166, 197, and 226 d after planting. Following each clipping, plants were fertilized with an $\text{NH}_4\text{NO}_3 + \text{KH}_2\text{PO}_4 + \text{KCl}$ nutrient solution to supply 100 mg/kg N, 50 mg/kg P_2O_5 , and 100 mg/kg K_2O to each shale/soil mixture.

Plant samples were dried in mechanical convection ovens at 60°C for 48 h, weighed, and ground to <20-mesh in a Willey mill before digestion. The $\text{HNO}_3 + \text{H}_2\text{O}_2$ digestion method of Jones (1989) was used to digest plant samples before analysis. Selenium in the digests was determined by hydride AAS. To convert oxidized Se in the digests to Se(IV) for hydride analysis, equal volumes of digest and concentrated HCl were heated for 20 min at 80°C in a graphite block digester. Conversion efficiency was monitored by carrying a Se(VI) standard through the procedure. Reagent blanks, method blanks and calibration standards were also included as part of the lab quality assur-

ance/control procedures. Digestion and analysis repeatability was verified by including an alfalfa check sample.

At the end of the glasshouse pot experiment, the shale/soil substrates were separated from the roots, aggregates were crushed, and the contents of each pot were re-mixed. Total, saturation extract, and oxalate-extractable Se were determined on the substrates as before. A single replicated set of unplanted controls containing the S amendments or no S was carried through the glasshouse study, including watering events, and were also analyzed for total, saturation extract, and oxalate-extractable Se. Soil data from the unplanted pot treatments were compared to data from soils containing plants.

Statistical Analysis

The Statistical Analysis System (SAS) Version 9.01 GLIMMIX model was used to determine the effects of S source and S rate on total biomass, total Se and S removed by top-growth harvesting, and total S/Se in harvested biomass (SAS, 2004). The Tukey-Kramer mean separation test was applied to treatment means at $P < 0.01$ probability level. Linear regression analysis was performed for each of the soil extractions; only equations with $P \leq 0.10$ are presented.

Results

Plants

Total aboveground biomass was greater for alfalfa than for wheatgrass, reflecting the different growth habit between the two species. There were no cumulative yield differences due to S treatments for either plant species (Table 1). Clipping yields increased over time for both plant species and eventually reached a plateau with the wheatgrass at 110 d and 135 d for the alfalfa (Fig. 1 and 2). The final wheatgrass biomass values were strikingly greater at the final harvest (226 d, Fig. 1). This was an artifact due to a more severe final clipping that included much of the crown biomass used to calculate cumulative aboveground yields and Se and S removal (Table 1). The alfalfa plants did not have a crown and so yield trends were not altered by the final clipping.

The cumulative aboveground biomass values for S treatments ranged from 56 to 60 g pot⁻¹ for wheatgrass and 85 to 98 g pot⁻¹ for alfalfa (Table 1). All three S application rates from either elemental S or gypsum suppressed Se uptake by wheatgrass and alfalfa for all seven clippings (Table 1 and Fig. 3 and 4). Above-ground plant Se concentrations declined with consecutive clippings, most notably with the 0 Mg ha⁻¹ S treatment (Fig. 3 and 4). This continued until the sixth clipping for alfalfa, when tissue Se in the non-supplemented soil increased with the final two clippings. The degree of Se uptake suppression was greatest with the first clipping for both plant species. Selenium concentrations in the first clipping of wheatgrass and alfalfa using 1 and 2 Mg S ha⁻¹ amendments were slightly lower than concentrations using 0.5 Mg S ha⁻¹ amendments, regardless of S source. Selenium concentrations in alfalfa were much greater than those in wheatgrass, which coincides with field survey results of plants growing on waste rock dumps at Wooley Valley (Mackowiak et al., 2004).

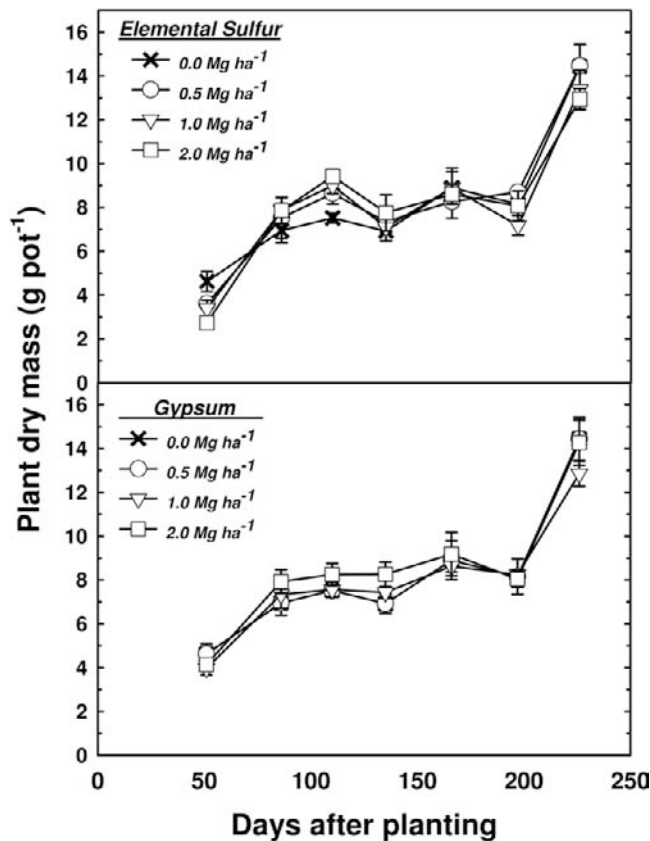


Fig. 1. Effect of four rates (0, 0.5, 1, and 2 Mg S ha⁻¹) of elemental S and gypsum on aboveground biomass of *P. smithii* at 51, 86, 110, 135, 166, 197, and 226 d after planting. Symbols represent the means from 4 pots $\pm$ standard errors.

Although elemental S and gypsum amendments strongly influenced Se concentrations, increasing S rates had minimal effect on S concentrations and uptake by wheatgrass and no effect by alfalfa (Table 1). Sulfur concentrations in wheatgrass and alfalfa tended to decrease with early clippings (one through three) and then S concentrations leveled off (data not shown). As with the tissue Se, alfalfa S concentrations and amounts exceeded those found in wheatgrass (Table 1). The wheatgrass and alfalfa S/Se tissue concentration ratios increased with S additions, mainly because of the decrease in Se concentrations (Table 1).

Soils

Soil total, oxalate-extractable, and saturation extract Se were measured in shale/soil mixtures from unplanted pots that were carried through the experiment and in the shale/soil mixtures after the final clipping of wheatgrass and alfalfa. Table 2 summarizes the Se extraction values of shale and the shale/soil mix without S amendments. Since the source of S did not have a significant effect on any of the measured soil Se pools at the end of the study, data from both sources were combined to compare soil Se pools (Fig. 5). Wheatgrass and alfalfa aboveground biomass removed only a small fraction of the total soil Se and therefore plant growth had no significant effect on the soil total Se measures. Saturation extract Se concentrations were lower in planted soils and there appeared to be a modest positive relationship ($r^2 = 0.42$) between saturation

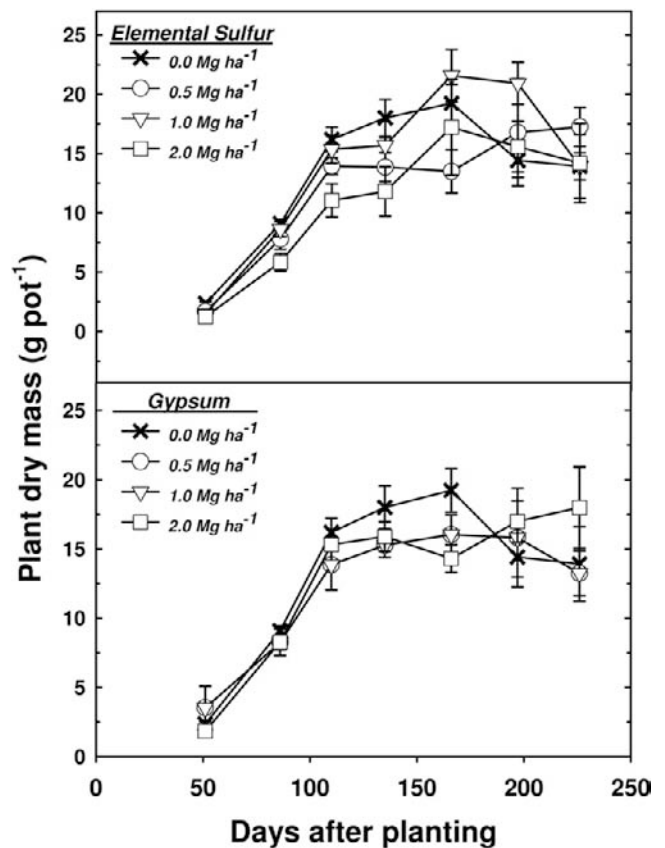


Fig. 2. Effect of four rates (0, 0.5, 1, and 2 Mg S ha⁻¹) of elemental S and gypsum on aboveground biomass of *M. sativa* at 51, 86, 110, 135, 166, 197, and 226 d after planting. Symbols represent the means from 4 pots $\pm$ standard errors.

extract and S application rate in the unplanted treatments (Fig. 5). The amounts of Se extracted with the saturation extracts were far less than the amounts of Se in the other pools (oxalate-extractable and total). Soil supporting alfalfa growth had less oxalate-extractable Se than soil from wheatgrass or unplanted pots. Sulfur applications resulted in a modest increase in oxalate-extractable Se from the unplanted and wheatgrass soils (Fig. 5).

Discussion

Sulfur Effects

Elemental S and gypsum were equally effective in suppressing Se uptake over 60% for wheatgrass and over 70% for alfalfa, when the materials were incorporated into the shale/soil substrate. Initially, the 1 Mg ha⁻¹ and 2 Mg ha⁻¹ S rates suppressed Se uptake more than the 0.5 Mg ha⁻¹ S rate, but differences among the rates diminished as Se was removed from the system with consecutive plant clippings. The initially larger suppression of Se uptake by adding 1 Mg S ha⁻¹ compared to 0.5 Mg ha⁻¹ S leads to a recommendation of 1 Mg S ha⁻¹ as either elemental S or gypsum to suppress Se uptake. Increasing the rate to 2 Mg S ha⁻¹ did not seem to have an additional effect. Gypsum and elemental S performed similarly, suggesting that conversion to SO₄-S was fairly rapid for elemental S. It is interesting to note that alfalfa tissue Se concentrations from the

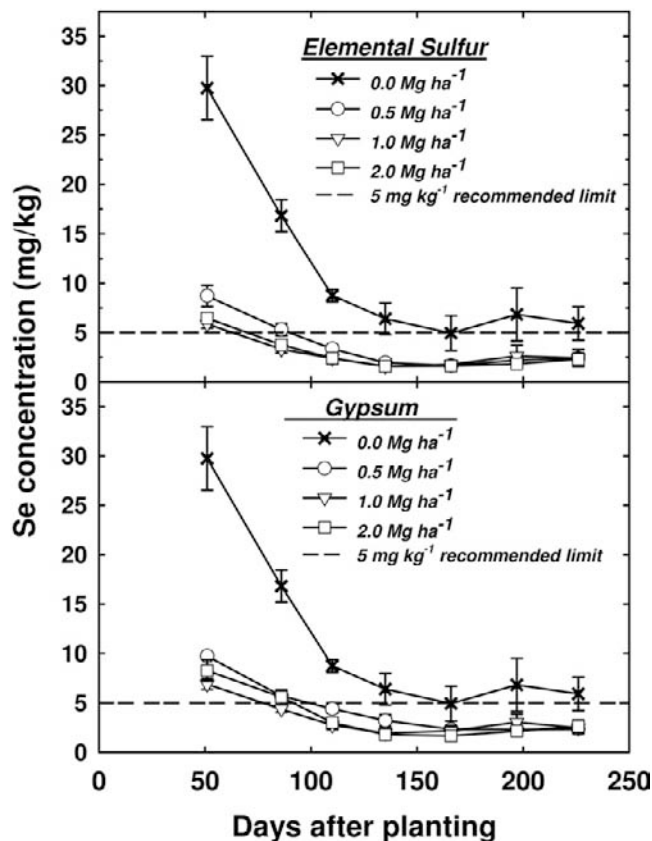


Fig. 3. Effect of four rates (0, 0.5, 1, and 2 Mg S ha⁻¹) of elemental S and gypsum on Se concentrations in *P. smithii* at 51, 86, 110, 135, 166, 197, and 226 d after planting. Symbols represent the means from 4 pots $\pm$ standard errors.

non-amended soil increased with the final two clippings (Fig. 4). This coincided with a lower relative growth rate, perhaps leading to a Se concentrating effect in the alfalfa tissue.

George (2002) reported that Se(VI) was the only detectable species in water from vadose zone samples of reclaimed soils directly impacted by waste rock dumps. Therefore, it is likely that Se suppression was primarily a result of SO₄-S successfully competing against Se(VI) for plant uptake (Gissel-Nielsen, 1973; Pezzarossa et al., 1999), while other Se species are relatively unaffected by soil SO₄-S status (Arvy, 1993; Zayed et al., 1998). It is well documented in crop plants that SO₄-S and Se(VI) are structural analogs likely sharing the same S transporters (Bell et al., 1992; Mayland, 1994; Wu et al., 1997; Zayed et al., 1998; Sors et al., 2005; White et al., 2007). However, Smith and Watkinson (1984) found that Se uptake had a synergistic effect on S uptake, suggesting that the uptake mechanisms between SO₄-S and Se(VI) may not be entirely identical. Past plant field surveys reveal that Se(VI) uptake was directly proportional to plant S requirement (Rosenfeld and Beath, 1964; White et al., 2007). Data from this study support past findings, showing that the higher S requiring alfalfa accumulated more Se and S and had lower S/Se ratios than grasses (Table 1).

Rhizosphere Effects

For the unplanted soils, there was a modest increase in soil saturation extract Se and oxalate extractable Se with increas-

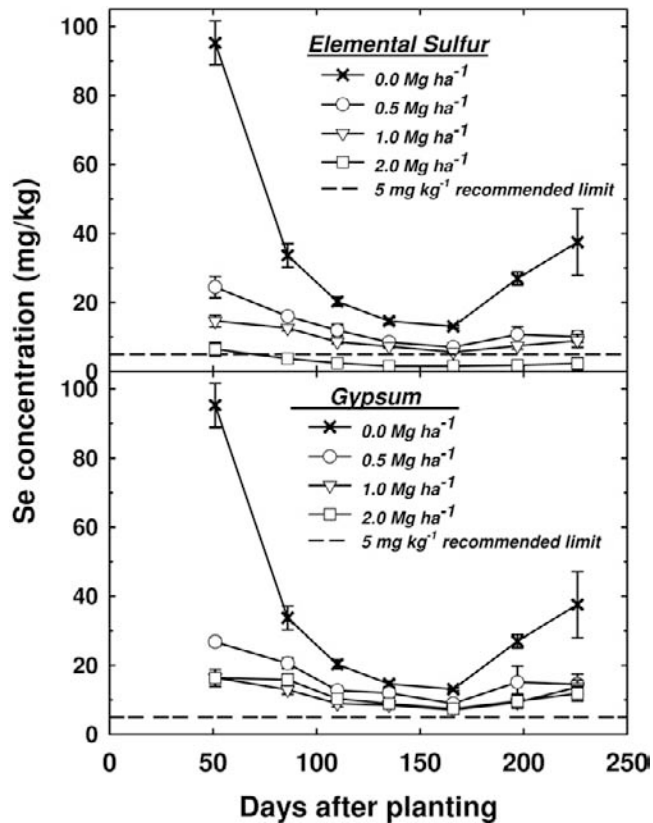


Fig. 4. Effect of four rates (0, 0.5, 1, and 2 Mg S ha⁻¹) of elemental S and gypsum on Se concentrations in *M. sativa* at 51, 86, 110, 135, 166, 197, and 226 d after planting. Symbols represent the means from 4 pots $\pm$ standard errors.

ing S rates (Fig. 5), which suggests some competition between S and Se for exchange sites. Additionally, the unplanted soils had greater saturated extract Se and oxalate-extractable Se than the planted soils. The lower oxalate-extractable Se values from planted soils suggests biologically enhanced weathering of the waste rock, where the released Se is then available for plant uptake and other Se transformation reactions. It is proposed that this weathering was accelerated through the release of root exudates. The alfalfa rhizosphere was particularly active, as final oxalate-extractable soil Se values were less than for the wheatgrass-planted or unplanted soils (Table 2). Additionally, legumes are noted for releasing more exudates than grasses, thereby supporting greater microbial activity (Odunfa, 1979).

The shift in soil Se pools shown by the data provides a view into the Se soil dynamics and suggests a hierarchical order of plant-available Se contributions to the rhizosphere. Continued Se removal via clippings likely accelerated the soil processes. As plant-available (saturated paste) Se was taken up, a chemical potential gradient was established between available and less available Se pools. The readily plant-available (saturated paste extract) soil Se value (Table 2) was much less than what was accounted for by the aboveground biomass (Table 1), supporting the concept that gradients between soluble and less soluble (oxalate extractable) pools existed in the rhizosphere. Others have observed similar results for metals in plant rhizospheres, where exchangeable fractions increased soon after seeding and

then decreased below initial concentrations as total biomass accumulated (Baylock and James, 1994; Knight et al., 1997; Tao et al., 2003). With depleted water-soluble Se fractions, the chemical gradient shifted toward the next most soluble fraction (i.e., oxalate extractable). Additionally, the legume rhizosphere enhanced biological weathering of this fraction even further.

A complete plant-soil Se budget cannot be created from the limited data and yet the data provide a feasible portrayal of Se plant-soil dynamics. The saturated paste Se was depleted in moist, unplanted soils by over 0.3 mg kg^{-1} (Table 2), suggesting that physical and microbially-mediated processes in the unplanted soils resulted in Se being volatilized, immobilized, and/or reduced. However, the oxalate-extractable Se pool was unaffected in the unplanted soils (Table 2). The difference in oxalate-extractable Se between unplanted and planted soils ($0.5 \pm 0.4 \text{ mg kg}^{-1}$ for wheatgrass, $3.7 \pm 0.7 \text{ mg kg}^{-1}$ for alfalfa, Table 2) was greater than plant uptake in the absence of S amendments ($0.18 \pm 0.02 \text{ mg kg}^{-1}$ for wheatgrass, $0.74 \pm 0.02 \text{ mg kg}^{-1}$ for alfalfa as calculated on a per kg basis from Table 1). Some of the missing Se likely resided in plant roots. Root Se(VI) concentrations have been reported as being similar to aboveground biomass concentrations while root Se(IV) concentrations are much greater (Arvy, 1993; Terry and Zayed, 1998; Hopper and Parker, 1999). Additional losses through volatilization (soil and plant) and reduction reactions within the rhizosphere may also factor into Se budget discrepancies, particularly with alternating soil wetting and drying (Terry and Zayed, 1998; Guo et al., 2000; Coppin et al., 2006).

Remediation Potential

In general, biomass removal was nearly as effective at reducing Se concentrations through subsequent clippings as were S amendments (Table 1 and Fig. 3 and 4). At this time, the longevity of using plant removal for remediating Se-contaminated soils is unknown. However, on a biological time scale as contrasted with a geologic time scale, this depletion strategy may protect grazing animals for substantial periods of time. Weathering rates in the field will dictate this process.

Where biomass removal is impractical, suppression of Se uptake by S additions has greater potential as a remediation strategy for revegetated landscapes. Dhillon and Dhillon (2000) obtained Se suppression for at least 2 yr when incorporating a single gypsum application into an alkaline, calcareous, silty loam. However, it is not known how long suppression may last. It should be noted that Se is continually being recycled in the plant/soil system on existing waste rock dumps. As plants go dormant and the top growth dies back each autumn, Se is released from decomposing plant tissue as non-selenate species and is available in various forms for subsequent uptake during the next grow-

Table 2. Selenium content of the soil, the waste rock shale and the shale/soil mixture without S amendments.

Material	Conditions	Saturated paste	Oxalate extractable	Total
		mg kg ⁻¹		
Soil	Initial	NA†	NA	0.55
Shale	Initial	0.72	27.8	111
50:50 mix	Final (no plants)	0.041	13.9	49.2
	Final (+ wheatgrass)	0.029 ± 0.013	13.4 ± 0.4	48.5 ± 1.6
	Final (+ alfalfa)	0.011 ± 0.004	10.2 ± 0.7	48.6 ± 0.2

† NA = not analyzed.

ing season. Some Se is lost via volatilization (Lamothe and Herring, 2004) and leaching (Stillings and Amacher, 2004), but in the absence of large-scale biomass removal, even highly mobile Se will likely be recycled within the root zone of plant communities as observed by the high concentrations of Se found in plants growing on waste rock dumps (Mackowiak et al., 2004).

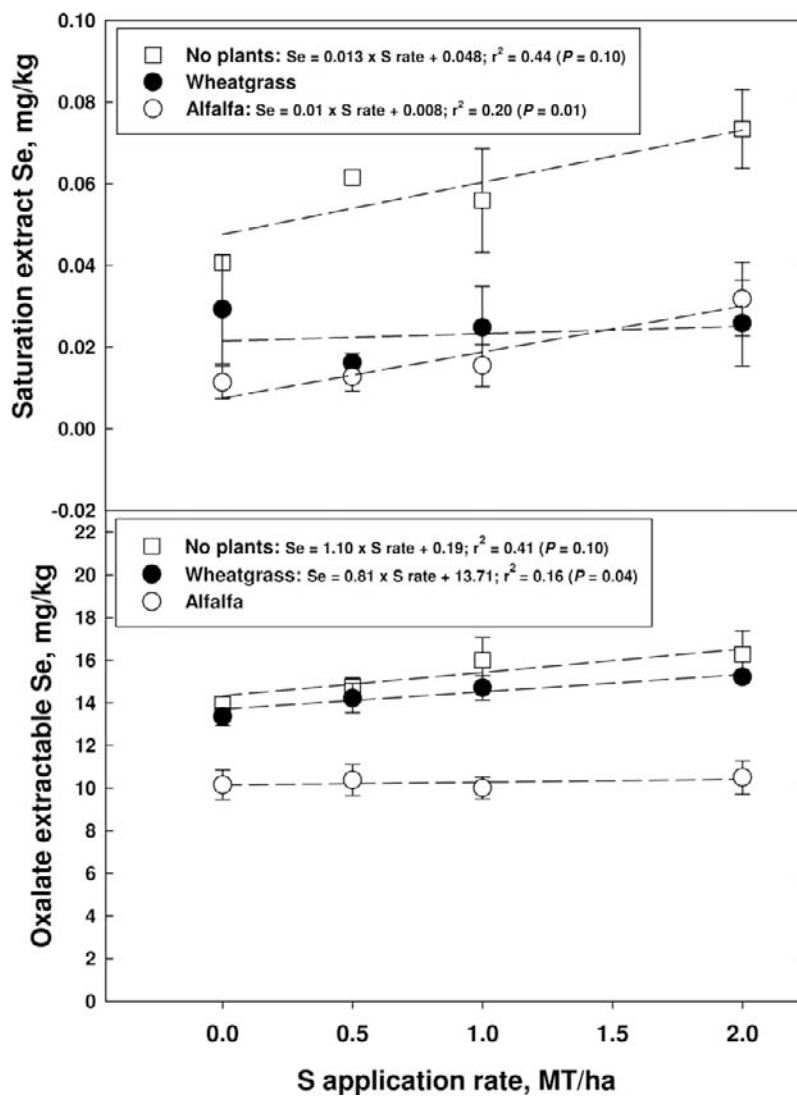


Fig. 5. Effect of seven clippings of *P. smithii* and *M. sativa* on soil saturation and oxalate-extractable Se in shale/soil mixtures with or without plants. Symbols for the planted treatments represent the means from 8 pots $\pm$ standard errors. Symbols for the unplanted treatments represent the means from 2 pots $\pm$ standard errors. Linear regressions at $P \leq 0.10$ are provided in the legends.

More than 57 km² of phosphate mining-related surface disturbances are documented in the spatial coverage of the core of the southeast Idaho phosphate resource area (Causey and Moyle, 2001). Internal U.S. Forest Service documents and communications estimate that total remediation costs under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund) could approach 1 billion dollars. Thus, low-cost remediation measures may be attractive, near-term alternatives. Pelletized gypsum is readily available (2007 retail cost was typically \$5 to \$8 per 23 kg bag with bulk quantity costs substantially less). This is easily applied to waste rock dump landscapes using broadcast fertilizer spreaders mounted to off-road '4-wheeler' vehicles. Evaluation of gypsum applications directly to field sites is ongoing.

Conclusions

Sulfur amendments potentially offer a low-cost alternative to other exceedingly expensive remediation methods (waste rock removal and/or capping) for controlling Se availability to plant communities in waste shale-impacted soils. Incorporating 1.0 Mg S ha⁻¹ as either elemental S or gypsum into a 50:50 soil/waste shale mix suppressed Se uptake over 60% in wheatgrass and alfalfa. It is not known how long Se uptake suppression will persist from a single S amendment application to the surface of waste rock dumps. Can infiltrating water carry soluble S into the rooting zone of the plant communities or are more expensive incorporation methods required? Experiments are underway to evaluate treatment effectiveness and longevity of surface applied S to impacted landscapes.

References

- Amacher, M.C. 2003. Manual of methods. 2003 ed. Open-File Rep. USDA Forest Service Rocky Mountain Research Station, Logan, UT.
- Amacher, M.C., J.R. Herring, and L.L. Stillings. 2001. Total selenium and other elements by HNO₃ and HClO₄ digestion and other soil characterization data from Wooley Valley Units 3 and 4 waste rock dumps and Dairy Syncline lease area soils, southeast Idaho. USGS Open-File Rep. 01-69. USGS, Denver, CO.
- Arvy, M.P. 1993. Selenate and selenite uptake and translocation in bean plants (*Phaseolus vulgaris*). J. Exp. Bot. 44:1083–1087.
- Baylock, M.J., and B.R. James. 1994. Redox transformations and plant uptake of selenium resulting from root-soil interactions. Plant Soil 158:1–12.
- Bell, P.F., D.R. Parker, and A.L. Page. 1992. Contrasting selenate-sulfate interactions in selenium-accumulating and nonaccumulating plant species. Soil Sci. Soc. Am. J. 56:1818–1824.
- Cathcart, J.B. 1980. The phosphate industry of the United States. p. 19–42. In F.E. Khasawneh et al. (ed.) The role of phosphorus in agriculture. ASA, Madison, WI.
- Causey, D.J., and P.R. Moyle. 2001. Digital database of mining-related features at selected historic and active phosphate mines, Bannock, Bear Lake, Bingham, and Caribou Counties, Idaho. USGS Open-File Rep. 01-142. USGS, Denver, CO.
- Chambers, J.C., R.W. Brown, and B.D. Williams. 1994. An evaluation of reclamation success on Idaho's phosphate mines. Restor. Ecol. 2:4–16.
- Coppin, F., C. Chabroulet, A. Martin-Garin, J. Balesdent, and J.P. Gaudet. 2006. Methodological approach to assess the effect of soil ageing on selenium behavior: First results concerning mobility and solid fractionation of selenium. Biol. Fertil. Soils 42:379–386.
- Dhillon, K.S., and S.K. Dhillon. 2000. Selenium accumulation by sequentially grown wheat and rice as influenced by gypsum application in a seleniferous soil. Plant Soil 227:243–248.
- Food and Nutrition Board. 1980. Recommended dietary allowances. p. 162–1654. Committee on dietary allowances. National Research Council, National Academy of Sciences, Washington, DC.
- George, J. 2002. Chemodynamic studies of selenium release, mineralization, and sorption-desorption pathways in the western phosphate resource area. M.S. thesis. Univ. of Idaho, Moscow, ID.
- Gissel-Nielsen, G. 1973. Uptake and distribution of added selenite and selenate by barley and red clover as influenced by sulphur. J. Sci. Food Agric. 24:649–655.
- Grauch, R.I., G.A. Desborough, G.P. Meeker, A.L. Foster, R.G. Tysdal, J.R. Herring, H.A. Lowers, B.A. Ball, R.A. Zielinski, and E.A. Johnson. 2004. Petrogenesis and mineralogic residence of selected elements in the Meade Peak Phosphatic Shale Member of the Permian Phosphoria Formation, southeast Idaho. p. 189–226. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Guo, L., W.A. Jury, W.T. Frankenberger, Jr., and Y. Zhang. 2000. Characterization kinetics of sequential selenium transformation in soil. J. Environ. Qual. 29:1041–1048.
- Herring, J.R. 2004. Rock leachate geochemistry of the Meade Peak phosphatic shale member of the Phosphoria Formation, southeast ID. p. 367–397. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Herring, J.R., and R.I. Grauch. 2004. Litho-geochemistry of the Meade Peak phosphatic shale member of the Phosphoria Formation, southeast Idaho. p. 321–366. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Herring, J.R., and S.A. Wilson. 2001. Phosphate shale analytical quality control materials of the USGS Western U.S. Phosphate Project: Bulk geochemical characterization and water leachate analysis. USGS Open-File Rep. 01-0024. USGS, Denver, CO.
- Hopper, J.L., and D.R. Parker. 1999. Plant availability of selenite and selenate as influenced by the competing ions phosphate and sulfate. Plant Soil 210:199–207.
- Jones, J.B., Jr. 1989. Soil testing and plant analysis laboratory manual. Benton Lab., Athens, GA.
- Knight, B., F.J. Zhao, S.P. McGrath, and Z.G. Shen. 1997. Zinc and cadmium uptake by the hyperaccumulator *Thlaspi caerulescens* in contaminated soils and its effects on the concentration and chemical speciation of metals in soil solution. Plant Soil 197:71–78.
- Knudsen, A.C., and M.E. Gunter. 2004. The effects of weathering on the mineralogy of the Phosphoria Formation, southeast Idaho. p. 169–187. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Lamothe, P.J., and J.R. Herring. 2004. Gaseous selenium and other elements in near-surface atmospheric samples, southeast Idaho. p. 427–435. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Leggett, J.E., and E. Epstein. 1956. Kinetics of sulfate absorption by barley roots. Plant Physiol. 31:222–226.
- Lemly, A.D. 1997. Environmental implications of excessive selenium: A review. Biomed. Environ. 10:415–435.
- Mackowiak, C.L., M.C. Amacher, J.O. Hall, and J.R. Herring. 2004. Uptake of selenium and other contaminant elements into plants and implications for grazing animals in southeast Idaho. p. 527–555. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Mayland, H.F. 1994. Selenium in plant and animal nutrition. p. 29–45. In W.T. Frankenberger, Jr. and S. Benson (ed.) Selenium in the environment. Marcel Dekker, New York.
- Milchunas, D.G., W.K. Lauenroth, and J.L. Dodd. 1983. The interaction of atmospheric and soil sulfur on the sulfur and selenium concentration of range plants. Plant Soil 72:117–125.
- Moyle, P.R., and D.Z. Piper. 2004. Western phosphate field-depositional and economic deposit models. p. 575–598. In R. Hein (ed.) Life cycle of the Phosphoria Formation: From deposition to the post-mining environment. Elsevier Science B.V., Amsterdam, The Netherlands.
- Odunfa, V.S.A. 1979. Free amino acids in the seed and root exudates in

- relation to the nitrogen requirements of rhizosphere soil *Fusaria*. *Plant Soil* 52:491–499.
- Perkins, R.B., and A.L. Foster. 2004. Mineral affinities and distribution of selenium and other trace elements in black shale and phosphorite of the Phosphoria Formation. p. 251–295. *In* R. Hein (ed.) *Life cycle of the Phosphoria Formation: From deposition to the post-mining environment*. Elsevier Science B.V., Amsterdam, The Netherlands.
- Pezzarossa, B., D. Piccotino, C. Shennan, and F. Malorgio. 1999. Uptake and distribution of selenium in tomato plants as affected by genotype and sulfate supply. *J. Plant Nutr.* 22:1613–1635.
- Presser, T.S., K.J. Piper, J.P. Skorupa, S.J. Hamilton, S.J. Detwiler, and M.A. Huebner. 2004. The Phosphoria Formation: A model for forecasting global selenium sources to the environment. p. 299–319. *In* R. Hein (ed.) *Life cycle of the Phosphoria Formation: From deposition to the post-mining environment*. Elsevier Science B.V., Amsterdam, The Netherlands.
- Puls, R. 1994. Mineral levels in animal health: Diagnostic data. *Sherpa International*, British Columbia, Canada.
- Rhoades, J.D. 1996. Salinity: Electrical conductivity and total dissolved solids. p. 417–435. *In* D.L. Sparks (ed.) *Methods of soil analysis*. Part 3. Chemical methods. SSSA, Madison, WI.
- Rosenfeld, I., and O.A. Beath. 1964. Selenium geobotany, biochemistry, toxicity, and nutrition. Academic Press, New York.
- SAS. 2004. SAS Version 9.1. SAS Inst., Cary, NC.
- Severson, R.C., and L.P. Gough. 1992. Selenium and sulfur relationships in alfalfa and soil under field conditions, San Joaquin Valley, California. *J. Environ. Qual.* 21:353–358.
- Smith, G.S., and J.H. Watkinson. 1984. Selenium toxicity in perennial ryegrass and white clover. *New Phytol.* 97:557–564.
- Sors, T.G., D.R. Ellis, and D.E. Salt. 2005. Selenium uptake, translocation, assimilation, and metabolic fate in plants. *Photosynth. Res.* 86:373–389.
- Stillings, L.L., and M.C. Amacher. 2004. Selenium attenuation in a wetland formed from mine drainage in the Phosphoria Formation, southeast Idaho. p. 467–482. *In* R. Hein (ed.) *Life cycle of the Phosphoria Formation: From deposition to the post-mining environment*. Elsevier Science B.V., Amsterdam, The Netherlands.
- Tao, S., Y.J. Chen, F.L. Xu, J. Cao, and B.G. Li. 2003. Changes of copper speciation in maize rhizosphere soil. *Environ. Pollut.* 122:447–454.
- Terry, N., and A. Zayed. 1998. Phytoremediation of selenium. p. 633–655. *In* W.T. Frankenberger, Jr. and R.A. Engberg (ed.) *Environmental chemistry of selenium*. Marcel Dekker, Inc., New York.
- Thomas, P., J. Irvine, J. Lyster, and R. Beaulieu. 2005. Radionuclides and trace metals in Canadian moose near uranium mines: Comparison of radiation doses and food chain transfer with cattle and caribou. *Health Phys.* 88:423–438.
- Van Kauwenbergh, S.J. 1997. Cadmium and other minor elements in world resources of phosphate rock. *Proceeding 400*. The International Fertilizer Society, London.
- White, P.J., H.C. Bowen, B. Marshall, and M.R. Broadley. 2007. Extraordinarily high leaf selenium to sulfur ratios define ‘Se-accumulator’ plants. *Ann. Bot. (Lond.)* 100:111–118.
- Witte, S.T., and L.A. Will. 1993. Investigation of selenium sources associated with chronic selenosis in horses of western Iowa. *J. Vet. Diagn. Invest.* 5:128–131.
- Woodbury, P.B., M.A. Arthur, G. Rubin, L.H. Weinstein, and D.C. McCune. 1999. Gypsum application reduces selenium uptake by vegetation on a coal ash landfill. *Water Air Soil Pollut.* 110:421–432.
- Wu, L., X. Guo, and G.S. Banuelos. 1997. Accumulation of seleno-amino acids in legume and grass plant species grown in selenium-laden soils. *Environ. Toxicol. Chem.* 16:491–497.
- Wu, L., X. Guo, and G.S. Banuelos. 2003. Selenium and sulfur accumulation and soil selenium dissipation in planting of four herbaceous plant species in soil contaminated with drainage sediment rich in both selenium and sulfur. *Int. J. Phytorem.* 5:24–40.
- Zayed, A., C.M. Lytle, and N. Terry. 1998. Accumulation and volatilization of different chemical species of selenium by plants. *Planta* 206:284–292.