Selenium Mobility in Soils and its Absorption, Translocation, and Metabolism in Plants

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ABSTRACT

Forms of selenium found in soils influence its mobility, uptake, and metabolism by plants. The major forms in alkaline, oxidizing environments which are available for plant uptake are selenium-VI (as selenate, SeO_4^{2-}) and selenium-IV (as selenite, SeO_3^{2-}). The major influences on uptake are soil pH and salinity. High salinity and pH favor selenium anion adsorption onto clays and metal oxides. Selenite is adsorbed much more strongly than selenate leaving selenate as the major form available for plant uptake. Some soil anions, such as phosphate, increase plant selenium uptake because increased soil-solution anion concentrations compete with selenium anions for adsorption sites. Other anions, such as chloride or sulfate, actually enhance or inhibit uptake by affecting plant metabolism.

Inorganic selenides and elemental selenium are mostly insoluble except under conditions of low pH in moist, reducing environments. In these conditions organic selenides may also be found as selenium amino acids, such as seleno-glutathione, and in various fractions of humic substances. Although it is unclear whether organic selenides are absorbed from soil by plants, they have been identified in soil solutions as products of bacterial and plant metabolism. Volatilization of organic selenium compounds makes mass balance studies of selenium difficult.

Selenate ions are rapidly absorbed and transported in plant xylem sap. Selenite absorption, on the other hand, is slower, but the selenium is more rapidly metabolized to organoselenium compounds and transported into upper portions of the plant.

Soil and plant management in seleniferous areas must take into account soil types and the genetic tolerance by plants of high selenium and salt concentrations. For example, plants will tolerate more selenium on high-sulfate soils than on low sulfate soils. Some plants, such as alfalfa, are very sensitive and will show signs of damage at low soil selenium concentrations while others, such as saltbush, may accumulate thousands of milligrams per kilogram of selenium without damage. Some arid and semiarid soils may need to be managed by prudent irrigation practices in order to reduce selenium and salinity to acceptable levels.

INTRODUCTION

A number of recent review articles detail the factors influencing selenium mobility, transport, and uptake by plants (Anderson and Scarf, 1983; Brown and Shrift, 1982; Girling, 1984; Gissel-Nielsen and others, 1984; Mayland and others, 1989; Peterson and others, 1981; and Sharma and Singh, 1983). In addition, Fisher and others (1987) examined selenium transport and uptake as it pertains to reclamation management problems and research needs. The purpose of the present report is to survey the literature published since 1983 (confirmation of toxic selenium levels in the Kesterson ecosystem) and discuss how this new information may refine approaches to land reclamation methods and management practices. Much useful information has come from greenhouse and plant culture experiments as well as field studies are included in this review.

MOBILITY IN SOILS

Selenium availability to vegetation is influenced by soil pH and Eh, mode of occurrence, soil weathering, and physiography and climate. Mobile selenium is defined here as those forms which are moved by water under oxic soil conditions and are available for plant uptake. Although selenium may exist in four oxidation states, selenium-VI (as selenate, SeO_4^{2-}) and selenium-IV (as selenite, SeO_3^{2-}) are the predominant mobile forms, and selenides (Se^{2-}) and elemental selenium (Se^{o}) are insoluble. Because selenate and selenite are the two most common selenium species encountered in solution in arid and semiarid regions their elution and sorption characteristics have received much attention in the literature.

Selenate and selenite compete with other anions, such as phosphate, sulfate, oxalate, and molybdate for adsorption sites. Selenite is sorbed more strongly than selenate onto

clays, but not as strongly as phosphate or fluoride (Barrow and Whelan, 1989a). Sorption of both selenite and selenate decreases with increasing pH. This decrease is most marked for selenate in low ionic strength sodium systems. Sorption of selenite by soil shows some analogies with the sorption of phosphate, whereas the sorption of selenate is closer to that of sulfate (Barrow and Whelan, 1989b).

Balistrieri and Chao (1987) found that selenium mobility, as opposed to adsorption on goethite (synthetic FeO(OH)), is favored by alkaline pH, high selenium concentrations, oxidizing conditions, and high concentrations of other strongly adsorbed anions.

Sorption studies with selenium anions have also been published for kaolinite and montmorillonite (Bar-Yosef and Meek, 1987; Bar-Yosef, 1987). Their purpose was to evaluate the role of adsorption in distributing selenium between solution and solid-soil phases. They found that between pH 4 and 8 selenium solubility is governed by adsorption; the hydroxyl ions are more effective in modifying the selenium ion's adsorption capacity than in competing with selenium for common adsorption sites.

Neal and others (1987a) reported that phosphate competitively inhibits selenite adsorption in two alluvial soils from the San Joaquin Valley but that chloride does not. Goldberg and Glaubig (1988) found that in addition to sorption on kaolinite and montmorillonite, selenite sorption on calcite is also important in calcareous soils. It is pH dependent, increasing from pH 6 to 8, peaking between 8 and 9, and decreasing above pH 9. Using a variety of semiarid soil types Singh and others (1981) found that selenate and selenite were sorbed in varying amounts according to the general soil sequence: high organic carbon > calcareous > normal > saline > alkali. Adsorption is influenced positively by organic carbon, clay content, $CaCO_3$, and cation-exchange capacity (CEC) and negatively by high salt, alkalinity, and pH.

Ylaranta (1983) found that selenate was reduced by added organic matter (peat) and subsequently rendered immobile by adsorption onto clay. Vuori and others (1989) noted that, 7 days after adding 5 mg Se/kg as selenate, as much as 25% of the selenate was sorbed and that the amount was positively correlated with sulfuric acid-extractable phosphorus. Neal and Sposito (1989), however, did not find positive selenate adsorption onto four soils from the San Joaquin Valley, California. However, these soils had shown adsorption traits for selenite (Neal and others, 1987a).

Elrashidi and others (1987, 1989) developed equilibrium reactions and constants for 83 selenium minerals and solution species in order to define selenium solubility in soils. They generalized that the redox (pe+pH) of soils controls selenium speciation in solution and classified soils into three categories: (1) arid regions with high redox (pe+pH >15.0) where selenate is most common; (2) humid regions with medium redox range (pe+pH =7.5–15.0) where, depending on pH, either selenite or biselenite ($HSeO_3^{1-}$) predominate; and, (3) gley soils or wetlands with a low redox (pe+pH <7.5), where monohydrogen selenide (HSe^{1-}) is the major solution species. They further noted that only in acid soils do H_2Se species contribute significantly to selenium in solution.

Masscheleyn and others (1990) showed that "***under reduced conditions selenium solubility was low and controlled by an iron selenide phase. Selenium (-2,0) comprised 80 to 100% of the total soluble selenium. Upon oxidation dissolved selenium concentrations increased. The oxidation of selenium (–2,0) to selenite was rapid and occurred immediately after the oxidation of iron. Above 200 mV, selenite slowly oxidized to selenate. Under oxidized conditions (450 mV) selenium solubility reached a maximum. Selenate was the predominant dissolved species present, constituting 95% at higher pH's (8.9,9.0) to 75% at lower pH's (7.5,6.5) of the total soluble selenium at 450 mV. Biomethylation of selenium occurred only under oxidized conditions."

Using a sequential partial-dissolution technique, Chao and Sanzolone (1989) also noted that in soils developed through intensive leaching and weathering, selenium tends to be associated with oxide minerals and is generally resistant to chemical dissolution. In soils with high pH and low content of oxide minerals, selenium is present as mobile selenate which is easily extracted.

In a study using saturated columns packed with overburden from cores acquired from a lignite outcrop in Texas, Ahlrichs and Hossner (1987) added selenium as the sodium salt of selenate or selenite, adjusted the pH from 2 to 9, and leached the columns with 1.5, 10, or 50 pore volumes of 0.01 M $CaCl_2$. They found that selenate was mobile at all pH values tested and was completely leached from columns with <3 pore volumes of solution. In contrast, selenite was rapidly sorbed at all pH values. In two separate but related studies, Fujii and others (1988) and Alemi and others (1988), found that most of the soluble selenium in saturated San Joaquin soils was present as selenate; whereas, most of the adsorbed selenium was selenite. Fujii and others (1988) also found that of the total concentration of selenium in soils from three fields, the proportion of adsorbed and soluble selenium, ranged from 1 to 11 and <1 to 63%, respectively.

In a study using $^{75}SeO_3$ spiked silt loam soils in England, van Dorst and Peterson (1984) found that after 2 days at pH 7, selenate and selenite made up 51 and 23%, respectively, of the soluble selenium compounds; after 105 days at pH 7 the ratio was 12 and 22%, respectively. This and other studies show that the loss of selenate with time from soil is due to direct leaching, biological and nonbiological reduction to selenite, subsequent sorption, and the volatilization of organoselenium metabolites.

EFFECTS OF pH ON SELENIUM AVAILABILITY

The chemical form of selenium in soil is largely controlled by the redox potential and soil pH. Selenate is the major form present in well aerated alkaline soils; whereas, selenite predominates in acid and neutral soils. The selenite form, however, is adsorbed to clays and hydrous Fe oxides and is generally unavailable for plant uptake.

Both selenite and selenate can be absorbed by plant roots. But, the net effect is that selenite does not remain available when added to soil, and at low concentrations, has minimal effect on selenium uptake and plant growth.

Selenate remains available and is readily absorbed by plants. Singh and Singh (1979) reported that selenium uptake resulting in reduced plant growth following the order: SeO_4^{2-} > $H_2SeO_3^{2-}$ > SeO_3^{2-} > Se^0. Higher concentrations of selenium were absorbed by Swiss chard (*Beta vulgaris* var. Cicla) when grown on acid soil (pH 5.4) than on neutral soil (pH 7.5) when selenate was added (Zhang and others, 1988). Additions of 1.0 mg Se/kg or more as selenate resulted in significant yield reduction in chard growing on the acid soil, but not when growing on neutral soil.

Atkins and others (1988) reported that selenate absorption by barley (*Hordeum vulgare* cv. Arivat) and soft chess (*Bromus mollis*) declined by a factor of 2 by increasing pH from 4 to 8. Thus, selenate seems to be more available at lower soil pH's than selenite. Mikkelsen and others (1987) reported that selenium accumulation in roots and tops was much greater at pH 7.0 than at 4.5 in sand culture experiments using either selenite or selenate.

Uptake of selenium from selenate by subclover (*Trifolium subterranean* L.) grown in the glasshouse for 3 months was 8–12 times greater than from selenite (Dimes and others, 1988). The pH for maximum selenite uptake was higher (pH=6.7) than for selenate (pH slightly less than 6). Nearly complete recovery of plants plus soil-selenium from both sources was possible early in the study. However, by the end of 12 weeks, less selenite than selenate in plant and soil was retrieved. This may have been caused by the immobilization of selenite.

Liming acid soils, inherently low in selenium, often increases availability and uptake of selenium by plants (Gupta and others, 1982). The observed response is likely due to the reduced adsorption capacity of clays and Fe oxides caused by the increased pH (Neal and others, 1987b) and exchange of hydroxyl ions for SeO_3^{2-}.

EFFECT OF SALINITY ON SELENIUM AVAILABILITY

In seleniferous areas, high selenium levels in soils and waters are generally accompanied by high salinity. Mikkelsen and others (1988a) measured selenium accumulation by alfalfa (*Medicago sativa* L.) grown in sand culture. Yields were significantly reduced by both salinity (0.5 and 5.0 dS/m as sodium and calcium sulfate) and selenium treatments (0, 0.25, 0.5, and 1.0 mg Se(VI)/L), but not by boron (0.5 and 3.0 mg/L). Plant selenium was reduced from 620 mg/kg to less than 7 mg/kg in the presence of sulfate. These same authors examined the effect of increasing the salinity by addition of Cl^- or SO_4^{2-} salts. They found that the biomass production of shoots and roots decreased with selenium and each of the anions. In the presence of selenium, the yield reduction was greater with Cl^- salinity than with SO_4^{2-} salinity. Nevertheless, the occurrence of high levels of SO_4^{2-} in seleniferous soils and waters should be considered when determining the availability and toxicosis of selenium in drinking water and forage for animal consumption.

CHARACTERIZATION OF SELENIUM FORMS IN SOIL

Yamada and Hattori (1989) determined the forms of selenium in three Japanese soils containing from 0.3 to 1.1 mg total Se/kg. Selenium soluble in hot water or sodium sulfate extractants ranged from 0.5–7.1% of the total soil selenium. A large proportion of this selenium occurred in organically bound forms and a small amount as inorganic selenium. Selenium in the organic fractions was mostly in proteins, peptides, or amino acids. One selenium-containing polypeptide was found with a molecular-weight of 3200 g/mole.

As noted previously (van Dorst and Peterson, 1984), the proportions of selenite and selenate in soils can change with time as a result of extraction by plants and biological and chemical changes in the selenium forms. They also noted the occurrence of selenoglutathione in the solution and that its concentration increased significantly during the growth of perennial ryegrass (*Lolium perenne*) plants.

Abrams and Burau (1989) described a procedure to fractionate, identify, and quantify organic selenium in soil extracts. The procedure separates humates, hydrophilic fulvates, and the acidic, neutral, and basic hydrophobic fulvates. Interferences were encountered in some soils; however, in one extensively studied soil, organic selenium was 20% of the extractable selenium and 7% of the total. About 20% of the hydrophilic selenium fulvates in this soil were in the form of selenomethionine.

A sequential partial dissolution technique was developed by Chao and Sanzolone (1989) to partition soil selenium into operationally defined solid phases. The procedure extracts soil selenium into five fractions: soluble (0.25 *M* KCl), ligand exchangeable (0.1 *M* KH_2PO_4), acid extractable (4 *M* HCl), and oxidative acid decomposable ($HF + HNO_3 + HClO_4$). The overall findings are consistent

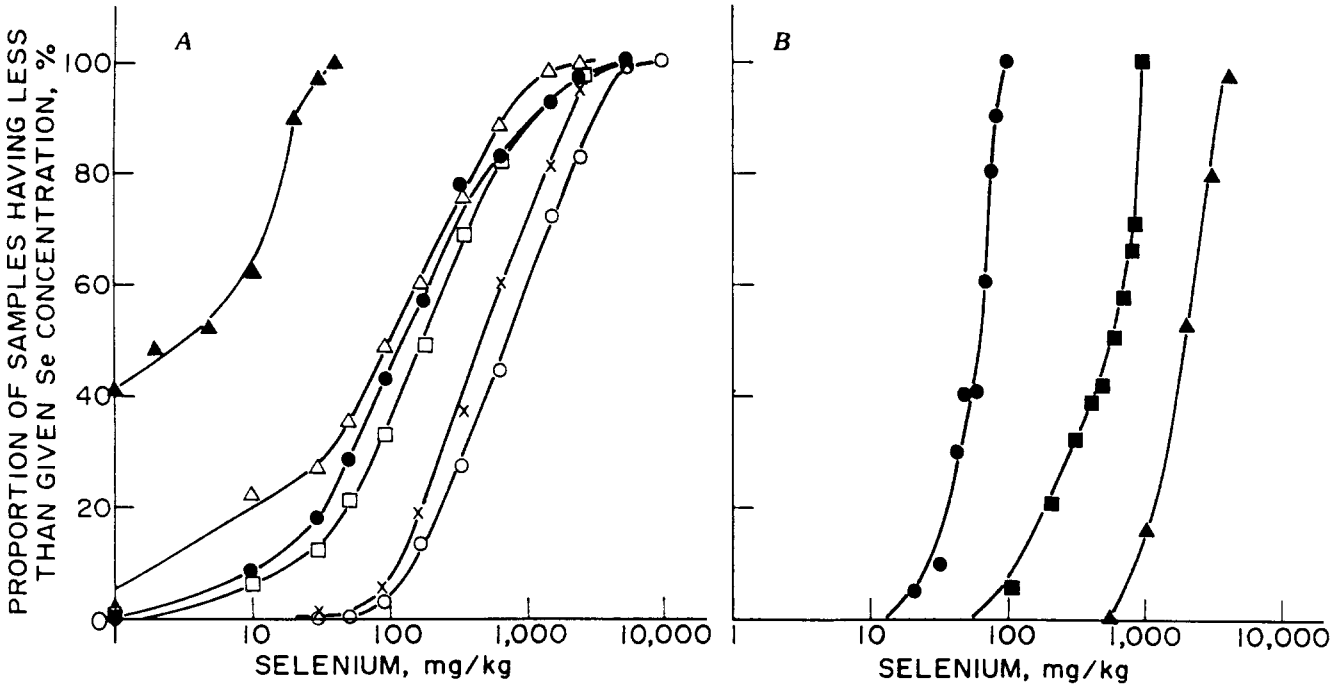

Figure 1 . Proportion of samples having less than given selenium concentration (Printed with permission of American Society of Agronomy). *A*, From left to right; Data for western wheatgrass (*Pascopyrum smithii*) plus Sandberg bluegrass (*Poa secunda*) sampled from seleniferous areas of Montana and Wyoming by H.F. Mayland, *Stanleya* spp., *Xylorhiza* section of *Machaeranthera*, *Astragalus bisulcatus*, *Astragalus pectinatus*, and *Oonopsis* section of *Haplopappus*, latter data adapted from Rosenfeld and Beath, 1964; *B*, Data for vegetative wheat (*Triticum aestivum*), *Astragalus bisulcatus*, and *Astragalus pectinatus* reported in plants from North Dakota by Lakin and Byers, 1941.

with the geochemical behavior of selenium in a soil environment. The five-step sequential extraction procedure is chemically sound, and should be useful in many different types of applications where selenium solubility is of interest.

SELENIUM UPTAKE

Although the essentiality of selenium as a micronutrient in plant growth has only been suggested and not substantiated, plants do absorb selenium from both the soil and the atmosphere (Zieve and Peterson, 1986). Some plants (fig. 1) have the ability to accumulate selenium to levels of hundreds or even thousands of milligrams per kilogram (Mayland and others, 1989). A second group rarely accumulates more than 50–100 mg Se/kg. Plants in a third group, in which most crop plants occur, do not usually accumulate selenium in excess of 50 mg/kg when grown on seleniferous soil. Selenium is a phytotoxin and yet is physiologically tolerated in low concentrations by some plants in this third group. Plants vary greatly in their ability to accumulate selenium. Genetic variation for selenium concentration in tall fescue (*Festuca arundinacea* Schreb.) has been found for low selenium concentrations (McQuinn and others, 1991). Presumably, genetic variability also exists in plants for increased tolerance or ability to prevent uptake from high selenium soils. Selenium uptake by human food crops occupies much of the ongoing research (Mikkelsen and others, 1989; Wan and others, 1988).

For any given concentration and oxidation state of added selenium; uptake will generally, but not always, be of the order Cruciferae > grass > legumes > cereal grains (Bisbjerg and Gissel-Nielsen, 1969; Banuelos and Meek, 1989).

Asher and others (1977) reported that concentrations of ^{75}Se in xylem exudate from tomato (*Lycopersicum esculentum*) was 6–13 times higher than in the nutrient solution when supplied as selenate. When selenium was supplied as selenite, xylem exudates contained lower concentrations of ^{75}Se than that provided in the nutrient culture. These authors suggested an active absorption of selenate by roots. Selenite absorption is often much slower than with selenate, but substantial inhibition of even selenite uptake occurred in the presence of various metabolic inhibitors. Thus, selenate and at least a portion of the selenite uptake is actively related to root metabolism. Similar findings have been reported for alfalfa where the ratio of ^{75}Se in roots/tops for plants receiving selenite was twice that of those receiving selenate (Asher and others, 1967). Gissel-Nielsen (1973) reported ratios of 2.5–3.6 for barley plants supplied with selenite compared to 1.5–1.9 for plants supplied with selenate.

Table 1. Selenium solubility in water and relative uptake of selenium by plants from different sources labeled with ^{75}Se in pot experiments using a loamy sand having 2.8 organic matter, 5.7 pH, and 0.12 mg Se/kg

[Adapted from Gissel-Nielsen and Bisbjerg, 1970]

Se source	Solubility of Se in cold water (g/L)	Se added to soil (mg/kg)	Uptake relative to added Se (in percent)		
			Clover	Barley	Mustard
Se----------	i[1]	2.5	0.005	0.02	0.07
SeO_2--------	i	0.5	1.0	0.9	1.2
K_2SeO_3------	22.4	0.5	1.0	1.1	1.3
Na_2SeO_3-----	s[2]	0.5	1.0	1.0	1.1
$BaSeO_3$------	0.05	0.37	0.9	0.9	0.9
$FeSeO_3$------	i	0.35	1.1	1.0	1.1
$CuSeO_3$------	i	0.30	0.8	0.8	0.7
K_2SeO_4------	390	0.50	24	12	24
$BaSeO_4$------	0.03	0.10	63	27	61
$CuSeO_4$------	68	0.13	53	28	48

[1] Insoluble

[2] Slightly soluble.

Studies on excised barley roots suggest that the mechanism responsible for selenate uptake is identical with that responsible for sulfate uptake (Asher and others, 1977).

ABSORPTION AND METABOLISM

Progress towards understanding selenium metabolism in plants has been slow because of the difficulty in isolating and identifying selenium compounds that are present in concentrations usually less than 1 ug Se/g. In almost all cases where a selenium compound was identified, the initial plant material contained unusually high levels of selenium (Ganther, 1986). Therefore, much of our knowledge of selenium metabolism is based on research using radioactive ^{75}Se.

Short-Time Studies

Root-absorbed selenium, either as selenite or selenate, is taken up and immediately translocated to plant tops (Gissel-Nielsen, 1979). Short-time experiments with plants grown in nutrient solutions have shown that selenium metabolism in plant roots, however, depends on the oxidation state of the applied selenium (table 1). Selenate is absorbed and translocated in xylem-sap as selenate, while selenite is quickly metabolized and is detected in the xylem-sap as seleno-amino acids within a few minutes after application (Gissel-Nielsen, 1979; Shrift and Ulrich, 1969).

Labeled selenite, once absorbed, is largely metabolized to water-soluble organic forms, and is moved through corn (*Zea mays*) roots at 1–2 cm per minute. Within 30 minutes after exposure, about 90% of the absorbed selenite detected in the foliar xylem sap was already metabolized to amino acids and some dipeptides and tripeptides (table 2). A major portion of the amino acid selenium was selenomethionine; less than 1% remained as selenite.

Gissel-Nielsen (1979) found traces of selenate in the xylem exudate of selenite-fed corn. Asher and others (1977), also found considerable selenate in selenite-supplemented tomato plants. They attributed this to oxidation of some of the selenite prior to, or shortly after absorption. There is also the possibility that appreciable amounts of selenate existed in the original selenite-stock chemical as a contaminant (Ahlrichs and Hossner, 1989).

Selenium absorption and transportation rates for selenate-fed plants were only 50–65% those for the selenite fed plants (Gissel-Nielsen, 1979). Only 5–6% of the selenate was incorporated into amino acids in contrast to the 90% found in that fraction when the plants were fed selenite-selenium. About 90%, however, was translocated as selenate.

Table 2. The effect of selenium speciation on the relative distribution of selenium fractions (1) in xylem sap, minutes after introducing the ^{75}Se to solution-fed corn (*Zea maize*) plants and (2) in tissues of soil-grown barley (*Hordeum vulgare*) and ryegrass (*Lolium multiflorum*) plants, more than 34 days after receiving soil- or foliarly-applied selenite or selenate

[Adapted from Gissel-Nielsen, 1987, and personal commun., 1990]

Fraction	Study 1 Short term: Corn Se source SeO_3	Study 1 Short term: Corn Se source SeO_4	Study 2 Long term[1]: Barley grain	Study 2 Long term[1]: Ryegrass herbage
	In percent			
Amino acid------	90	6	78	54
SeO_3----------	0	1	5	5
SeO_4----------	1	89	4	8
Residue[2]--------	2	3	10	14

[1]For barley grain in Study 1; values are means of application method (soil or foliar) and selenium source (selenite, selenate). For ryegrass grown in two separate studies; values are means of application method (soil or foliar), source (selenite, selenate), and three cuttings (2 and 3 of Study 1 and 2 of Study 2). In Study I; ^{75}Se fertilizer applied to soil day 0, barley and ryegrass sown day 2, foliar application of ^{75}Se day 34, first cutting of grass on day 44 was discarded, second and third cutting taken on day 68 and 89, while barley grain was harvested on day 106. In Study 2; ^{75}Se applied to soil day 0, ryegrass sown day 0, foliar application day 21, first cutting of grass discarded day 35, and cutting 2 on day 72 was characterized.

[2]Consists mainly of protein-bound Se.

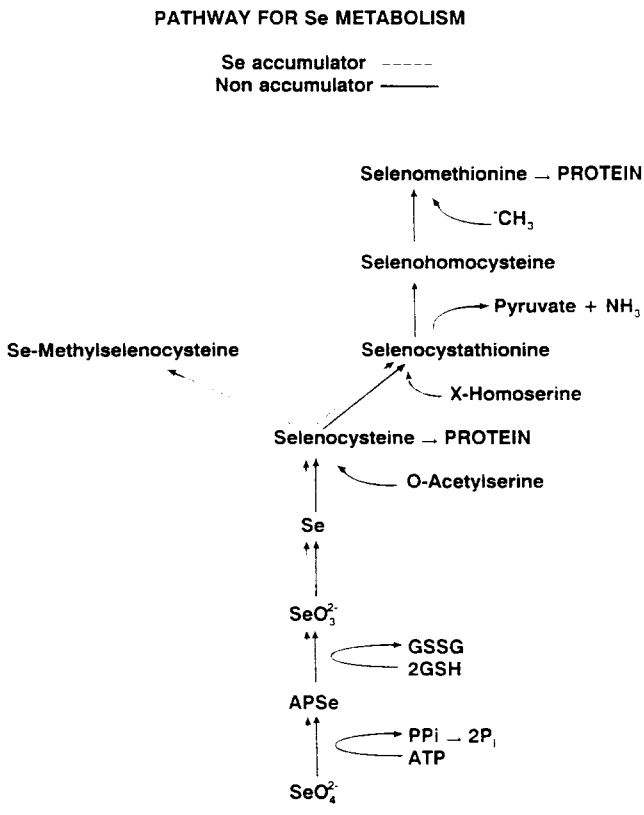

Figure 2. Suggested pathway for selenium metabolism in accumulator and nonaccumulator plants (adapted from Burnell, 1981).

Asher and others (1977) reported that the selenium concentrations in the xylem exudate of selenium-supplemented tomato plants were 6–13 times higher than in the external solution. They concluded that selenium, as selenate, was absorbed and transported similarly to sulfate sulfur. With selenite-supplemented plants, ^{75}Se concentrations in the exudate were always lower than in the external solution, and negligible amounts of selenium were transported as inorganic selenite, except at very high external concentrations (500 µM).

The uptake of selenate and translocation of selenium compounds are considerably reduced in the presence of sulfate (Gissel-Nielsen, 1979). Absorption of selenite in the root tips of both accumulator and nonaccumulators species is decreased by the presence of metabolic inhibitors (Shrift and Ulrich, 1969). This supports an active uptake mechanism. Figure 2 shows a suggested pathway for selenium metabolism in both accumulator and nonaccumulator plants.

The negative effect of nitrogen on the translocation of selenium from root to the top of plants may be mediated by increasing the uptake and concentration of sulfate in the plant.

Long-Time Studies

Gissel-Nielsen (1987) studied the "long time" (weeks or months) disposition of selenium absorbed as labeled selenite or selenate through roots or foliage (table 2). He found that, with one exception, there were no differences in the relative distributions of selenium fractions in the barley grain or grass herbage, that could be attributed to source or application method. The selenate form, which was transported as selenate in short-term studies, was now metabolized into products similar to those produced from selenite. In the one exception, selenate-treated plants contained about twice as much selenate as did the selenite-treated plants. However, this difference constituted only a few percent of the total selenium content and is probably of minor biological significance. He concluded that the distribution of selenium among different plant fractions was not significantly changed by the selenium source nor by the method of supplementation. In all cases, only 10% of the selenium was present in an inorganic form.

ASSIMILATION

In plants, selenium occurs as water soluble inorganic salts and amino forms, in simple or complex organic compounds. In nonaccumulating plants, 10–15% of the selenium is incorporated into protein. Because of similarities between sulfur and selenium, it is not surprising that the latter is converted into numerous selenium-analogs of sulfur compounds. However, these similarities should not be accepted in total, because exceptions in metabolism and functionality have been documented (Brown and Shrift, 1982).

Exclusion of selenium from proteins is characteristic of plant species able to tolerate high concentrations (>50 μg/g) of selenium. Se-methylselenocysteine and selenocystathionine have been isolated from species of *Astragalus* that accumulate selenium. Selenocystathionine has been found in seeds of a tropical nut tree (*Lechthis ollaria*, this may also be known as *Bertholletia excelsa*) that accumulates selenium (Aronow and Kerdel-Vegas, 1965). In seleniferous wheat (*Triticum aestivum*), about half of the selenium occurs as selenomethionine (Olson and others, 1970).

UPTAKE OF ORGANIC SELENIUM

Most studies involving selenium uptake have concentrated on inorganic processes. Abrams and Burau (1987), however, have identified selenomethionine in the soil. Van Dorst and Peterson (1984) identified selenoglutathione in soil solutions, and Yamada and Hattori (1989) found a significant proportion of organically bound selenium forms. Recent studies by M.C. Williams and H.F. Mayland (unpublished) have shown that selenomethionine and selenocystine, or the selenium from those molecules, is absorbed by both the selenium accumulator (*Astragalus bisulcatus*) and a nonaccumulator (*Pascopyrum smithii*). Besser and others (1989) added selenite, selenate, and selenomethionine to a closed-system microcosm. They reported that the selenomethionine was bioaccumulated preferentially to the added inorganic forms. However, volatilization was an important pathway for loss of selenium added as selenomethionine.

Volatilization of organo-selenium compounds from microbial activity into the gas phase of the soils and volatilization into the atmosphere from plant and animal metabolic activity has been known for some time (Hamdy and Gissel-Nielsen, 1976). These authors estimated that in the laboratory 8% of added selenium was volatilized. Dimes and others (1988) reported that the volatilization loss of unknown amounts of selenium was important in mass-balance studies involving subclover grown in the greenhouse. In the field, such parameters as soil moisture, soil microbial populations, and the presence of organic matter may affect selenium volatilization. Microbes as well as higher plants produce dimethylselenide that can subsequently be reabsorbed and metabolized by bacteria, fungi, and higher plants (Zieve and Peterson, 1986). These authors found that under typical conditions, 2% of the selenium in a plant can be derived from the atmosphere. In another study, Gissel-Nielsen (1986) reported that foliar absorption was involved in the uptake of selenium by barley and ryegrass when it was applied to the leaves as selenate.

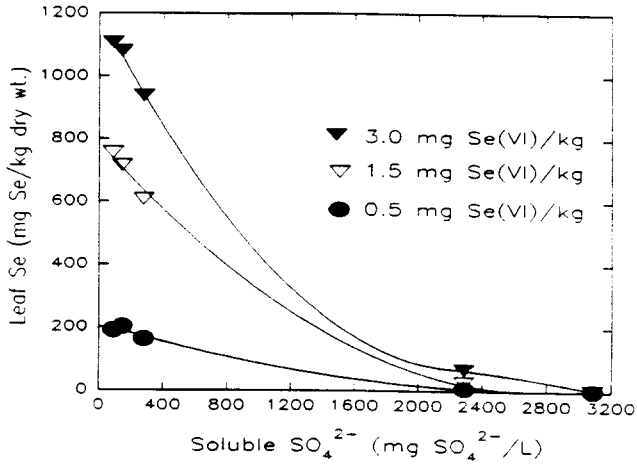

Figure 3. The effect of soluble sulfate in soil on selenate-selenium accumulation by alfalfa (*Medicago sativa*) shoots at three concentrations of added selenate (adapted from Wan and others, 1988).

UPTAKE OF INORGANIC SELENIUM

The interrelation of selenium and soil salinity is of concern in reclamation. In a study designed to assess this relation, Wu and others (1988) examined selenium uptake and selenium and salt (NaCl) tolerance of several forage and turf grasses. In general, they found that plant species with greater salt tolerances accumulated less selenium than did less salt-tolerant species. Combined selenium and salt treatments showed that selenium uptake was increased by addition of salt to the culture solution. Mikkelsen and others (1988b) measured selenium uptake by alfalfa in greenhouse sand cultures where salinity was increased by the addition of chloride or sulfate salts to the irrigation solutions. They found that in the presence of selenium, alfalfa yield reduction was greater with chloride salinity than with sulfate salinity. In a separate study Mikkelsen and others (1988a) reported that selenium concentrations in alfalfa tissue were positively correlated with selenium in irrigation water but negatively correlated with sulfate-salinity and boron.

Like salinity, the physiological interrelationship between selenium and sulfur has been reported in the literature for some time and is also of interest in

reclamation. In the presence of sulfate, Mikkelsen and others (1988b) found that selenium accumulation by alfalfa was reduced from 948 mg/kg to 6 mg/kg. A less antagonistic relationship was observed between chloride and selenium. A similar study by Wan and others (1988) found that alfalfa grown in low-sulfate soils accumulated 10–20 times more selenium (>1000 mg/kg) than did plants growing in high-sulfate soil (<100 mg/kg, figure 3). Gissel-Nielsen (1973) found that sulfate addition to the soil greatly decreased uptake of selenate by red clover (*Trifolium pratense*); whereas, selenite uptake was much less affected. Because of the common occurrence of sulfur-containing pyrite in coal overburden spoil materials in the arid and semiarid West, the addition of lime to these soils often mobilizes selenium by precipitating the sulfate ion. This results in greater selenium uptake by vegetation. The antagonistic effect of selenium and sulfate, therefore, can reduce selenium availability.

SELENIUM TOXICOSIS IN PLANTS

Shock and Williams (1984) reported that 20 μM selenate produced phytotoxic effects after 10 hours in filaree (*Erodium botrys*) and subclover. Roots began to darken and within 24 hours the plants were completely wilted and did not recover. Singh and Singh (1979) reported selenium toxicosis symptoms in cowpea (*Vigna sinensis*). Toxicity was in the order $SeO_4 > H_2SeO_3 > SeO_3 > Se^o$. In addition to decreased yield, yellowing, and black spots appeared on the leaves at 2.5 and 5.0 mg/L added selenium.

A 10% reduction in dry-matter yield of perennial ryegrass and white clover (*Trifolium repens*) was found for plants grown in sand culture and a range of selenite and selenate selenium concentrations (Smith and Watkinson, 1984). Selenite-treated plants had lower shoot concentrations of selenium than those treated with selenate. The critical toxic values for a 10% yield reduction were 48 and 320 μg selenite/g dry weight for ryegrass shoots and 160 and 330 μg selenate/g dry weight for white clover shoots for selenite and selenate, respectively. A greater proportion of the absorbed selenium was transported to the shoots of the selenate-treated plants than of those treated with selenite.

Smith and Watkinson also noted distinctive leaf symptoms developing on ryegrass and white clover plants that were most severely affected by selenate. A rose-colored pigmentation first appeared on the leaf margins of the more mature leaves. This color eventually covered the whole leaf. At a later stage of growth the younger leaves turned pale, while the older leaves lost all pigmentation and died.

SOIL:PLANT SELENIUM CORRELATIONS

The relation between soil selenium, both total and extractable, and plant selenium is generally strong. Robberecht and others (1982) reported that selenium concentrations in ryegrass were positively correlated with total soil selenium levels. Using the ammonium bicarbonate DTPA-extractable method Soltanpour and others (1982) found good correlation (r^2 = 0.82) between selenium in a 0–90 cm soil composite and wheat grown on the soil.

Jump and Sabey (1989) compared plant selenium concentrations in saltbush (*Atriplex canescens* (Pursh) Nutt.) and two-grooved milkvetch (*Astragalus bisulcatus* L.), grown in pots containing mine spoil material. Soil selenium was extracted by ammonium bicarbonate-DTPA, hot water, DTPA, or 0.5 *M* /L Na_2CO_3. Water soluble selenium was also determined in the saturated soil-paste extract. They reported that the saturated extracts were most useful (r^2 = 0.66 and r^2 = 0.78 for saltbush and milkvetch, respectively) in predicting mine spoil:plant selenium concentrations.

SOIL AND PLANT MANAGEMENT IN SELENIFEROUS AREAS

Alfalfa is one of the most sensitive crops to selenium accumulation. It can tolerate an average soil solution selenium concentration of 250 μg/L without exceeding the limit of 4 mg/kg in the dry forage set to protect ruminants. Studies by Albasel and others (1989) have shown that 20–30% of the irrigation water applied must be leached (leach fraction = 0.2–0.3) to maintain selenium concentrations below the above limit for soil solution when irrigation water contains no more than 100 μg/L.

Carlson and others (1989) noted that selenite is the more toxic form to plants grown in solution culture, but selenate is generally the more toxic form in soils, since selenite is immobilized by adsorption on clays and hydrous oxides. Seed germination and seedling radicle length were determined at concentrations of selenate or selenite up to 32 mg/L. Germination was unaffected by selenium treatment. Selenite treatment generally caused the greater decrease in radicle length. Plant sensitivity to selenate varied as follows: turnip > Sugar-Graze sorgrass (*Sorghum bicolor*, hybrid) = lettuce (*Lactuca sativa*) = cabbage (*Brassica oleracea*) > Dub-L-Graze sorgrass (*Sorghum bicolor*, hybrid) = wheat > radish (*Raphanus sativus*). Wheat was the least sensitive to selenite.

Limited information about the combined interaction of phosphorus and selenium shows that phosphorus decreases the harmful effects of selenium. But, the interactions are complex. The application of high amounts of phosphorus to reduce selenium uptake by plants, cannot be recommended with confidence (Singh and Singh, 1978).