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Proceedings of the 1990 Billings Land Reclamation Symposium on Selenium in Arid and Semiarid Environments, Western United States

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Proceedings of the 1990 Billings Land Reclamation Symposium on Selenium in Arid and Semiarid Environments, Western United States

By R.C. SEVERSON, SCOTT E. FISHER, JR., and
L.P. GOUGH, EDITORS

Proceedings of a plenary session held at the 1990
Billings Land Reclamation Symposium, March 25-30,
1990, Billings, Montana

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Introduction

By R.C. Severson, Scott E. Fisher, Jr., *and* L.P. Gough

The fifth edition of the *Billings Symposium* was held in Billings, Montana, from March 25 to 30, 1990. Previous symposia were held in 1980, 1982, 1984, and 1987. The traditional objectives of these meetings has been to provide a forum for the transfer of technology on disturbed land reclamation and to identify research needs relative to the reclamation of surface coal-mined lands. Development of the *Symposium* program over the years has resulted in increased numbers of technical sessions representing a wider diversity of resource areas. The meetings have been planned to meet a broad cross section of disciplines and professions by including those from the mining industry, consulting firms, academic institutions, and Federal and State agencies. In 1990, in response to participant interest and public concern, the topic areas were expanded to include hazardous materials, linear disturbances, and the reclamation or mitigation of hardrock mining and mineral processing waste. The 1987 program was the first *Symposium* to include a plenary session that was focused on a particularly important topic to western disturbed land reclamation: potentially acid-forming materials. This *Circular* contains papers from the 1990 plenary session, which was devoted to selenium in the arid and semiarid western United States.

The importance, and much of our understanding, of selenium in the western United States was accomplished initially through the work in the 1930's of Beath and Rosenfeld at the University of Wyoming and Byers and Knight at South Dakota State University. More recently, selenium problems related to Kesterson Reservoir in California have greatly increased both academic and public interest in the element. Contamination of wildlife refuges and elevated selenium levels in many irrigation return waters pose significant resource planning and management problems for this region of the United States. The Surface Mining Reclamation and Control Act of 1977 (SMCRA) requires the identification of potentially toxic materials such as selenium. Overburden analyses, completed for permitting under SMCRA, have provided evidence of elevated levels of selenium on some permit areas, and related ground water recharge monitoring data indicates the presence of elevated amounts of selenium on some mines. These events formed the basis for the establishment of the selenium plenary session of the *1990 Symposium.* The reports in this *Circular* provide information on global selenium cycles, discuss the chemistry of selenium in the near-surface environment, address selenium as it progresses through the food chain, detail field studies in areas where selenium has been reported to be an environmental problem, summarize studies on selenium in agricultural irrigation and drainage, and offer perspectives on managing selenium-affected lands.

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LIST OF CONTRIBUTORS

T.H. Brown
OSM-WTC
Brooks Tower
1020 15th Street
Denver, CO 80202

J.G. Crock
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

Johnathan P. Deason
Department of the Interior (6640-MIB)
18th and C Streets, N.W.
Washington, DC 20240

L.S. DeMarco
Environmental Sciences & Engineering Ecology
Colorado School of Mines
Golden, CO 80401
(Deceased)

J.C. Emerick
Environmental Sciences & Engineering Ecology
Colorado School of Mines
Golden, CO 80401

Richard A. Engberg
Department of the Interior (6640-MIB)
18th and C Streets, N.W.
Washington, DC 20240

J.A. Erdman
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

Herman R. Feltz
U.S. Geological Survey
412 National Center
Reston, VA 22092

Scott E. Fisher, Jr.
OSM-WTC
Brooks Tower
1020 15th Street
Denver, CO 80202

L.P. Gough
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

T.F. Harms
U.S. Geological Survey
Corbett Building
210 East 7th Street
Tucson, AZ 85705

James R. Herring
U.S. Geological Survey
Box 25046, MS 939
Denver, CO 80225–0046

L.F. James
USDA Agricultural Research Service
Poisonous Plant Research Laboratory
1150 East 1400 North
Logan, UT 84321

A. Dennis Lemly
U.S. Fish and Wildlife Service
National Fisheries Contaminant Research Center
4200 New Haven Road
Colombia, MO 65201

H.F. Mayland
USDA Agricultural Research Service
Route 1, Box 186
Kimberly, ID 83341

Frank F. Munshower
Reclamation Research Unit
Montana State University
106 Linfield Hall
Bozeman, MT 59717

Oscar E. Olson
Chemistry Department
South Dakota State University
Box 2170
Brookings, SD 57007–1217

Ivan S. Palmer
Chemistry Department
South Dakota State University
Box 2170
Brookings, SD 57007–1217

K.E. Panter
USDA Agricultural Research Service
Poisonous Plant Research Laboratory
1150 East 1400 North
Logan, UT 84321

T.S. Presser
U.S. Geological Survey
345 Middlefield Road
Menlo Park, CA 94025

Richard A. Prodgers
Consulting Plant Ecologist
2715 Ottawa
Butte, MT 59701

R.C. Severson
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

Gregory J. Smith
U.S. Fish and Wildlife Service
Patuxent Wildlife Research Center
Laurel, MD 20708

Kathleen C. Stewart
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

W.C. Swaine
U.S. Geological Survey
2800 Cottage Way
Sacramento, CA 95825

Marc A. Sylvester
U.S. Geological Survey (MS 470)
345 Middlefield Road
Menlo Park, CA 94025

R.R. Tidball
U.S. Geological Survey
Box 25046, MS 973
Denver, CO 80225–0046

CHAPTER A

Selenium Geochemistry—A Conspectus

James R. Herring

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Selenium Geochemistry—A Conspectus

By James R. Herring

ABSTRACT

Selenium is a dynamic element that is involved in many inorganic and biochemical processes on Earth. Much of the current interest in selenium geochemistry arises because of the element's critical nutritional requirement in animals along with its mixed blessings to many animals, including humans, wherein it has both toxic effects if assimilated in excess and equally severe consequences when nutritionally deficient. In the environment, four principal inorganic species exist: selenide (-2), elemental (0), selenite (+4), and selenate (+6). Partitioning among these species in a particular environment depends largely on the pH and Eh conditions and to lesser extent on the availability of other ligand- and complex-forming species. Common oxidizing crustal conditions favor the presence of selenite and selenate. Among selenium species, selenate is the most soluble and also commands the most societal attention and concern because of its mobility and toxicity, as well as its ease of uptake in plants and animals. In contrast, anoxic or dysaerobic conditions favor the existence of selenide. The reduced species is the form that occurs in organoselenium compounds, although the original metabolic uptake in organisms may include oxidized or reduced species. Selenium behaves like sulfur more than any other element. However, there is an important difference: selenium is more readily reduced than sulfur, or, conversely, sulfur is more readily oxidized than selenium. This allows divergence of their geochemical behaviors, particularly under strongly oxidizing conditions. The natural, overall geochemical cycle of selenium mainly involves crustal rock sources and oceanic sediment sinks. Subcycles of this overall cycle involve other inorganic sources and sinks; in addition, the overall crustal cycle also is strongly influenced by biochemical reactions that mobilize or fix selenium in organic compounds. Humans considerably modify this natural geochemical cycle by adding sources of selenium to the environment; these are principally by coal combustion, sulfide ore processing, and waste processing from the industrial use of selenium.

INTRODUCTION

Selenium is an element extensively involved in both inorganic and biochemical processes on Earth. Simplistically, selenium behaves similarly to sulfur and follows much of that element's geochemistry; however, certain chemical differences between the two elements allow subtle, but occasionally profound, divergence of their geochemical pathways. Most of the present interest in selenium concerns its biochemical behavior and stems from the discovery of its critical nutritional role, as well as its earlier discovered potential toxicity when present in excess. Consequently, selenium is the subject of much attention, particularly when natural or societal processes lead to dietary deficiencies or deleterious accumulations in organisms in various geographic locations or ecosystem levels. This review is intended to present background information on selenium's general chemical properties, worldwide distribution, use, production, and its natural and humanly modified geochemical cycles.

In this review, I emphasize those chemical and physical properties that determine the geochemical behavior of selenium and, hence, that govern interactions among the element, its geochemical environment, and humans. Information on many of the more complex chemical or thermodynamic properties lies outside the focus of this review and is not discussed. This material is readily available from other reference materials, for example in compilations on selenium and its properties (for example, Ihnat, 1989; National Research Council, 1976; Zingaro and Cooper, 1974; Rosenfeld and Beath, 1964), previous editions of this periodic review (McNeal and Balistrieri, 1989; Mayland and others, 1989), or summary articles (Lakin, 1973; Sarquis and Mickey, 1980). In addition, selenium has many interesting chemical and physical properties; for example, its photovoltaic, photoconductive, and semiconductive behavior, that likewise are peripheral to this review.

In the Earth's crustal rocks, most selenium occurs by substituting for sulfur in various sulfur compounds and minerals. The selenium occurs in elemental form occasionally or, most commonly, as selenides substituting in numerous sulfide minerals (Berrow and Ure, 1989). Elemental selenium has several allotropic forms: monoclinic (red) and hexagonal (black); and amorphous (red and black). However, at common crustal temperatures the most stable form is hexagonal, in which spiral chains of selenium atoms are arranged parallel to one another. A number of selenium minerals do exist (Sindeeva, 1964; Zingaro and Cooper, 1974; and Elkin, 1982), but few are common. One example is berzelianite, Cu_2Se, named for Jöns Berzelius, the discoverer of the element.

Uses of Selenium

The principal industrial uses of selenium include photovoltaic devices, for example, solar cells or exposure meters, semiconductor devices, and rectifiers. Selenium also has extensive use in xerography, in the decolorization of glass or production of black and smoky industrial glass, and as an additive to stainless steel. According to the U.S. Bureau of Mines (1990), the estimated U.S. end use of selenium was electronic and photocopier components, 40%; glass manufacturing, 20%; chemical and pigments, 20%; and other, 20%. Note that these nonagricultural applications are confined principally to technologically advanced or wealthy countries. Thus, problems of environment befouling from these selenium uses would be expected to be confined to the industrialized countries with little direct effect in the lesser developed countries. Other elements can be substituted for selenium in many of these industrial uses. For example, silicon can substitute for selenium in high-voltage rectifiers; silicon, cadmium, tellurium, gallium, and arsenic can substitute in photoelectric applications; cerium can substitute in glass manufacture; and tellurium can substitute in pigment use. Such substitutions could alter future production of or need for selenium, although the substitutions would not occur as a replacement for selenium's toxic properties as most of these substitute elements have toxic properties of their own.

Availability and Production

Selenium, when present, commonly occurs in sulfide minerals; thus, a principal source of selenium supply is byproduct to sulfide ore processing. Until recently, selenium has been obtained from flue dusts that condense after the roasting of sulfide ores, principally those of copper. Differences between the vapor and condensation properties of sulfur and selenium allow the two elements to fractionally distill and separate: selenium condenses as combustion emissions cool because of its higher boiling point; whereas, sulfur remains gaseous as the dioxide. Recently, however, most selenium has been obtained from electrolytic copper refining, wherein it is recovered from anode muds after the muds are roasted with soda or sulfuric acid or when smelted with soda and KNO_3. Note that both production techniques underscore the importance of high-temperature processes to selenium mobility and concentration, which suggests that volatility in natural processes, for example, volcanism, and in human activities, for example, fossil fuel combustion, will be important to the geochemical cycle of selenium.

In the United States during 1988, three copper refineries, one located in Utah and two in Texas, accounted for the primary domestic production of selenium. According to the U.S. Bureau of Mines (1988; 1989; 1990), U.S. selenium production for 1983 and 1984 was between 250 and 350 metric tons annually, with similar amounts imported into the country. The next 3 year's production was withheld to protect proprietary company data. Primary production for 1988 was 286 tons, and for 1989 was estimated to be 250 tons. During 1985 to 1988, U.S. selenium imports have generally increased, reaching a high of 496 tons in 1987, and imports came from Canada, 30%; United Kingdom, 23%; Japan, 17%; Belgium-Luxembourg, 17%; and other, 13%. For 1988, worldwide production was 1,500 tons (excluding the unavailable production from centrally planned economies), with the majority being produced by Japan, Canada, and Belgium at 471, 300, and 250 tons, respectively. These three countries and the U.S. accounted for 87% of 1988 World production. For 1989, global refinery production was estimated to be 1,450 tons. Countries with more than approximately 10% of the World reserves, each, are the U.S., Canada, Chile, and the group of Market Economy Countries. World reserves are estimated to be 80 kilotons (kT). In addition, this same group of countries, along with the group of Centrally Planned Economy countries, each contain more than 10% of the total World reserve base, estimated to be 130 kT (U.S. Bureau of Mines, 1990).

Finally, it interesting to consider coal as a resource of selenium. Worldwide, coal deposits contain about 80 times the selenium of the identified economic copper deposits. Lakin and Davidson (1973) provided estimates of the U.S. and World resources of selenium in coal as 2 and 11 megatons (MT), respectively. Compared against the annual selenium production for sulfide ores of about 1.6 kT globally, it appears that coal could provide, if economically feasible, an immense and long-term selenium reserve.

An interesting insight into possible future need for selenium is provided by examining the amount of selenium necessary as a supplemental plant nutrient to satisfy minimal nutritional needs (Lakin and Davidson, 1973). If, indeed, selenium can profitably and safely be added to soil in areas with selenium deficiency, for example, the Pacific Northwest or northeastern U.S., at the minimum ameliorative rate of 22 mg m^{-2} y^{-1} (applied as 110 mg m^{-2} at 5-year intervals because annual addition is unnecessary), then 5.7 kT of selenium would have to be applied to treat the selenium-deficient areas or 11.4 kT to reach optimal nutritional level in forage crops of just the United States. This amount of selenium exceeds current U.S. total production and imports of selenium by a factor of about 15.

Essential Nutrient Requirement and Toxicity

For selenium, an especially narrow interval of necessity exists between the levels of insufficiency and excess. Lakin and Davidson (1973) estimated that selenium deficiency diseases appear when animal dietary intake is <0.04 mg/kg, while toxicity diseases may appear in animals when the intake is >4 mg/kg. Animals, bacteria, and possibly higher plants all require trace amounts of selenium (Stadtman, 1974). The essential role of selenium in animal nutrition was identified in 1957 (Schwarz and Foltz, 1957), nearly a century after the toxicity effects from the element had been realized (Anderson, 1961a). Several selenium deficiency diseases have been identified (Oldfield, 1972; Wilber, 1983), such as degenerative disease of the cardiac and skeletal muscles; however, the most common deficiency is white muscle disease in sheep and cattle. In general, plants do not share this nutrient requirement, although selenium appears to provide a necessary function to some angiosperms (Stadtman, 1974).

Much discussion of these critical nutrient and toxic properties exists in the literature, for example by Jacobs (1989), and also occurs in other papers in the collection containing this report. Only brief mention is made here of selenium toxicity, as the topic has been extensively discussed elsewhere, for example in the review by Gough and others (1979) and references therein. In brief, selenium is not toxic to plants, but it can easily become toxic to animals through excessive dietary intake. The particular species of selenium is critical to toxicity—in fact, elemental selenium is considered to be practically nontoxic. However, when converted into more biologically assimilable forms, such as organoligand compounds, selenium can readily concentrate in organisms in toxic quantities. Some inorganic compounds of selenium are acutely toxic, as well. The well-known toxicity of hydrogen selenide, intolerable to humans above a level of about 1 part per million (ppm), is an example. Fortunately, concentrations of selenium combined with the reducing conditions necessary to produce this gas seldom exist naturally. There have been occasional reports, however, of unusual conditions leading to the natural release of hydrogen selenide into the environment. This occurred, for example, in Wyoming where changing water levels in an aquifer interacted with selenium-rich coal or the overburden rock of coal seams and stimulated the release of hydrogen selenide (Ensslin, 1987). A final toxicological consideration, but one that is not further discussed is that selenium toxicity, besides being a function of species, also depends on the dose and exposure length (Oldfield, 1972).

Table 1. Cosmic and terrestrial selenium abundance and S/Se ratios

	Selenium concentration (μg/g)	S/Se ratio (atomic)
Cosmic-------------------	25	1×10^4
Primordial Solar System Abundance----------	0.13	7.4×10^3
Earth's Crust-----------	0.05	1.3×10^4
Whole Earth-------------	6.1	7.4×10^3

Abundance

In the continental crust of the Earth, selenium occurs as a trace element with an abundance of about 50 parts per billion (ppb) (Taylor, 1964). For comparative purposes this abundance is similar to that of silver, or about ten times that of gold. Terrestrial and cosmic abundances of selenium, along with atomic S/Se ratios, are listed in table 1. These data were recalculated from the compilation by Henderson (1982), using data taken principally from Ganapathy and Anders (1974). Note that the crust is considerably depleted in selenium relative to the terrestrial abundance as a whole, and that the S/Se ratio remains fairly consistent at about 10^4 in all cases. Crustal depletion of selenium from the crust relative to the whole Earth likely occurred in the early stages of formation of the Earth when it and other volatile elements degassed from Earth's outer parts. These data foreshadow the importance of selenium's volatility and again suggest that major parts of the selenium geochemical cycle along with its human modifications will be closely tied to high temperature processes and volatile compounds.

Analytical Chemistry of Selenium

Many different analytical techniques have been used to measure selenium concentrations in various media. Early selenium measurements (Anderson, 1961b) were made using gravimetric, volumetric, wet chemical or spectrophotometric techniques, along with subsequently developed colorimetric methods used for analyzing selenium content of sea water, silicate minerals, and marine organisms (Chau and Riley, 1965). Cummins and others (1964) detailed a digestion and colorimetric method for determination of selenium in biological material. Modern analytical techniques include gas chromatography (GC), gas-phase vapor atomic absorption (AA), emission spectroscopy, X-ray emission, spark-source mass spectrometry, gas-liquid chromatography, high-pressure liquid chromatography, and electrochemical techniques (see, for example, Robberecht and Von Grieken, 1982, or Cooper, 1974). Instrumental neutron activation analysis (INAA) has been used for total selenium measurements in fossil fuels (Pillay and others,

Table 2. Some properties of the Group VI elements from Lof (1987)

Property	Element				
	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Electron configuration	$[He]2S^{2}2p^{4}$	$[Ne]3s^{2}3p^{4}$	$[Ar]3d^{10}$ $4s^{2}4p^{4}$	$[Kr]4d^{10}$ $5s^{2}5p^{4}$	$[Xe]4f^{14}5d^{10}$ $6s^{2}6p^{4}$
Electronegativity, kJ mol^{-1}	3.5	2.5	2.4	2.1	1.8
Ionization Potential, kcal/mole	314	239	225	208	194
Melting Point, ^{o}C	-219	119 (monoclinic)	217	450	254
Boiling Point, ^{o}C	-183	445	685	1390	962
Ionic Radius, X^{-2}, Å	1.40	1.84	1.98	2.22	2.30

1969; Ellrich and others, 1985). A review of inorganic analytical techniques for selenium analysis is given by Nazarenko and Remakov (1972) and more recently by Lewis and Veillon (1989).

Much interest now exists in analysis of selenium species and identification of the organometallic compounds of selenium, rather than measurement of total selenium. This interest has led to the development of new analytical techniques or combinations of other techniques, such as coupled GC/AA (Cooke and Bruland, 1987) or selective hydride generation followed by AA (Cutter and Bruland, 1984). Another recent experimental and analytical approach to understanding the behavior of selenium in soil has been the development of sequential extraction schemes to separate soil selenium into operationally-defined solid phases (Pickering, 1981; Chao and Sanzolone, 1989). A review of the analytical chemistry of organic and biochemical selenium compounds is presented by Tan and Rabenstein (1989).

FUNDAMENTAL CHEMICAL PROPERTIES

Jöns Berzelius discovered selenium in 1817; ironically, his discovery of this crustal trace element predates by several years his discovery of the major crustal cation, silicon. Selenium occurs in the Periodic Table in Group VI, along with oxygen, sulfur, tellurium, and polonium, and, as we shall see, it shares many of the characteristics of the elements in this group. Some of the fundamental chemical properties of the group are listed in table 2. Two chemical properties—valence electron configuration and oxidation potential—provide fundamental insight into selenium's similarities and differences with respect to the other elements in its group. Selenium's electron configuration explains many of the similarities shared with other elements of its group, especially sulfur, while the oxidation potential defines many of the differences, particularly those between selenium and the important and common crustal elements: oxygen and sulfur. In addition, these two chemical properties definen much of selenium's geochemical behavior in the environment.

The common s^2p^4 valence electron configuration in the group causes parallel valences and equivalent bonding structures among the group elements, and it also explains many of their similar chemical and physical properties. In turn, the similar chemical and physical properties explain commonality in the geochemical behaviors of selenium and the other elements of its group. Also, this electron configuration permits a variety of valence states for the group elements other than oxygen. In particular, selenium has three common oxidation states referred to as selenide (–2), selenite (+4), and selenate (+6), identical to sulfur and reiterating the rule that electrons commonly exist in pairs. Note also that elements with such a large range of oxidation numbers usually are biologically active because they can participate in extensive electron donor or receptor reactions. Thus, it is not surprising that selenium forms biologically active compounds (Shrift, 1973; and Reddy and Massaro, 1983).

Selenium readily reacts with water. It can oxidize then combine with water, similar to sulfur, forming selenic acid, H_2SeO_4. This acid, like H_2SO_4, attempts to protonate

Table 3. Volatility comparison between species of sulfur and selenium

[s = sublimes]

Species:	Elemental		Reduced		Oxidized	
	S	Se	H_2S	H_2Se	SO_2	SeO_2
Melting Point, °C	112-119	170-217	-85	-66	-76	340
Boiling Point, °C	445	684-688	-60	-41	-10	315, s
Vapor Pressure, °C for 100 mm Hg	327	554	-92, s	-74, s	-47	258, s

other species, while accepting an electron itself, leaving the acid with excess negative charge. Selenic acid is hydrophilic and is not so strong an acid (proton donor) as sulfuric acid, although it is a stronger oxidizing agent.

Volatility is another notable property of selenium and can be discerned from the data in table 3. Compared to most other elements, selenium's relatively low boiling point and high vapor pressure suggest clues as to its geochemical behavior. Specifically, selenium's boiling point of 684°C suggests enhanced mobility of the element in conjunction with volcanic or high temperature industrial processes and, as we shall see, this is indeed the case. It is useful to note, however, that selenium consistently is less volatile than sulfur. This becomes especially significant in common low temperature crustal environments where it is possible for SO_2 to stabilize as a gas, while SeO_2 does not.

Selenium and sulfur are very similar. For example, selenium, like sulfur, has many allotropic modifications. Also, selenium reacts with metals analogously to sulfur to form selenides, which can then further react in acidic solution to form gaseous hydrogen selenide, H_2Se. This dihydride is toxic, like H_2S, and can be oxidized to elemental selenium or to SeO_2. A principal difference between the hydrides of the two elements is that H_2Se is a stronger reducing agent (electron donor) than H_2S. Metal selenides, like the sulfides, range from sparingly soluble (with Na and K) to relatively insoluble (with Cu and Pb). Selenium, like sulfur, easily combines with certain amino acids to form peptides and becomes extensively incorporated in biochemical processes. The similarity between ionic radii of sulfide and selenide, 1.84 versus 1.98, respectively, also suggests that reduced selenium easily substitutes into compounds and mechanisms involving reduced sulfur. Other notable similarities between selenium and sulfur are their electronegativities and their molar ionization constants. Sulfur and selenium have the most similar electronegativities of any pair of elements in Group VI. Molar ionization values for sulfur and selenium differ by only about 10% for each of the first three successive ionizations, with the selenium values consistently lower, indicating slightly greater ease of ionization. Clearly, of all the pairs of elements in Group VI, sulfur and selenium share the greatest similarity.

Oxidation potential provides greatest insight into the differences in geochemical behavior among the elements in Group VI. Throughout the group the elements show decreasing oxidizing strength from oxygen to polonium, with differences between adjacent elements that range from subtle to substantial. This variation explains the transitional departure from similarity within the group, as well as the geochemical difference between sulfur and selenium. For example, oxidation potentials indicate that the dihydride of selenium, as well as that of Te and Po, is a better reducing agent (electron donor) than hydrogen itself. Selenous acid, H_2SeO_3, is a stronger oxidizing agent than sulfurous acid, H_2SO_3, and selenic acid, H_2SeO_4, is an even greater oxidizer than sulfuric acid, H_2SO_4. An important paraphrasing is that selenium compounds are more easily reduced than their equivalent sulfur compounds under natural conditions, and herein lies the key to geochemical differences between the two elements. This is illustrated by the following pair of reduction reactions and respective element potentials in volts, relative to the standard hydrogen potential:

$$H_2XO_3 + 4H^+ + 4e^- = X + 3H_2O; \quad S = +0.45, \; Se = +0.74$$

and

$$X + 2H^+ + 2e^- = H_2X; \quad S = +0.14, \; Se = -0.36.$$

Because of this difference, the co-occurrence of similar sulfur and selenium compounds can produce different reaction products for the two elements, as illustrated diagrammatically in the following disproportion reaction between identical-valence selenite and sulfite. The net result is that co-existence of similar phases can lead to oxidation of sulfur and reduction of selenium:

$$3H_2SO_3 + H_2SeO_3 = 3SO_4^{-2} + Se^o + 8H^+ + 2e^-.$$

(Note: the use of the term selenite here and at all other places in this work refers to Se^{+4} and not to a mineral sometimes known by this name.)

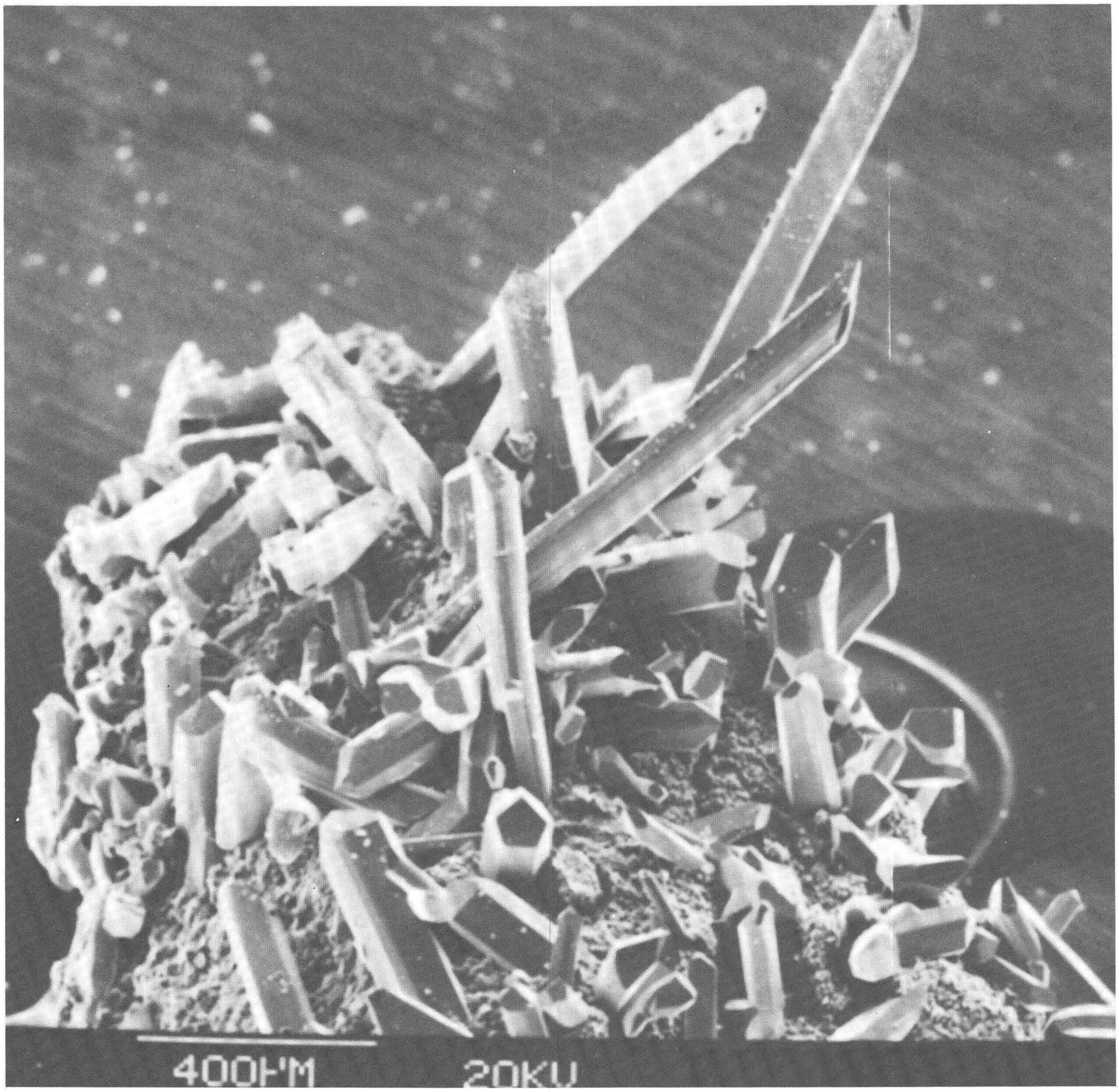

Figure 1. Scanning electron microscope (SEM) micrograph of an unusual occurrence of crystals of metallic, gray, hexagonal selenium. These crystals condensed from venting combustion gases onto the undersides of rocks overlying a pile of burning coal spoil in Pennsylvania. Crystal lengths ranged up to about 4 mm. The sample was analyzed uncoated due to the excellent conductive nature of the metallic selenium.

Selenium generally is regarded as nonmetallic, although its electron configuration places it in a transition zone between metallic and nonmetallic character. Some of the geochemistry of selenium is best explained assuming metallic rather than nonmetallic character. One interesting example of metallic occurrence is illustrated in figure 1, where metallic crystals of elemental selenium occurred in conjunction with a burning coal spoil (gob) pile in Pennsylvania. The spoil was burning at depth, releasing selenium vapor and other volatile elements from the coal and overlying shale. At the cooler surface of the spoil pile, the vapor condensed as crystals of black, metallic selenium. This phenomenon likely has occurred in conjunction with the many other natural coal burns that have happened throughout the world (Herring, 1980, 1981).

Selenium has several stable and two radioactive isotopes (Weast, 1988) that are of interest. The stable isotopes and their natural abundance are ^{74}Se (0.87%), ^{76}Se (9.02%), ^{77}Se (7.58%), ^{78}Se (23.52%), ^{80}Se (49.82%), and ^{82}Se (9.19%). It is important to note that the abundances of and mass separation between ^{76}Se and ^{82}Se are sufficient to be detected by mass spectrometric studies of the selenium system (Krouse and Thode, 1962). Isotopes of selenium offer the same opportunity as the highly studied system of sulfur isotopes (reduced isotopic mass of Se = 1.039; S = 1.031). The radioactive isotope, ^{75}Se with a halflife of 120.4 days, is of interest to experimentation in selenium uptake, partitioning, and tracer studies, while ^{79}Se, with a longer halflife of 6.5×10^4 years, can be produced by neutron activation of the common stable nuclide ^{78}Se and likewise is used for similar studies.

INORGANIC AND ORGANIC SPECIES OF SELENIUM

In common environmental conditions, selenium exists in the elemental state and in three charged states, –2, +4, and +6. The two positively charged forms can exist in anionic structures. Inorganic species are determined principally by the pH and Eh conditions, but competitive solubilities, complexation, biological interactions also play a part. In solution the dominant species is a function of pH and Eh. Even though thermodynamic considerations may dictate which species should be stable, reaction kinetics are sufficiently slow with selenium compounds that thermodynamic equlilibria are not rapidly obtained. Additional discussion of inorganic species is provided by Vokal-Borek (1979), Zingaro and Cooper (1974), Elrashidi and others (1987), Sarquis and Mickey (1980), Cutter (1982), and McNeal and Balistrieri (1989). Stability of various noncomplexed, inorganic species for a micromolar amount of selenium at various redox and pH conditions is shown in figure 2. The diagram was constructed from data and interpretations given by Wagman (1982), Elrashidi and others (1987), Geering and others (1968), and Lakin (1961c). Note that under usual aerobic conditions of redox and pH conditions, selenite will be the thermodynamically stable form. Low pH and Eh conditions favor reduced selenium species. In an earlier study of thermodynamic stability of selenium species, Lakin (1961c) concluded that more dilute systems will favor stability of the elemental and fully deprotenated species; however, this study may be compromised by dated stability-constant information. As a solid, selenate occurs far less commonly under crustal conditions and then only where unusually high redox conditions exist, as example in the Chilean niter beds. Sulfur's tendency to form catenated compounds is not shared by selenium; hence, the analogous selenium compound to sulfur's thiosulfate ($S_2O_3^{2-}$, where the two sulfur atoms are linked or catenated), does not exist in nature. There are no similar discussions of stability of organic selenium species under varying conditions of Eh and pH. However, the stability of the various inorganic species provides a clue as to the starting species for organic fixation. Most organoselenium compounds in organisms reside in reductive environments, which suggests the fixation of selenide directly or of reduction to selenide after fixation of an oxidized species.

Selenide

The acute toxicity of hydrogen selenide has already been mentioned. The compound forms a moderately strong acid when dissolved in water; one that is slightly stronger than hydrogen sulfide. Selenide ion is easily oxidized to elemental selenium. Metal selenides commonly occur by substitution in sulfide ores. Metallic selenides, especially of the heavy elements, are very insoluble.

Elemental Selenium

This species is stable in reducing environments. Also, it is very insoluble in aqueous systems and generally resistant to oxidation or reduction. Not surprisingly, it is therefore considered relatively nontoxic to organisms.

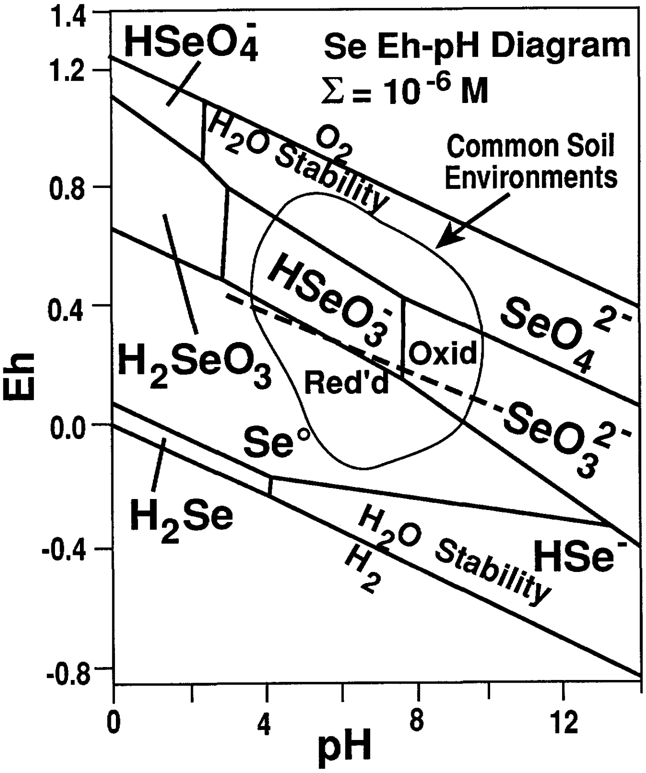

Figure 2. Stability diagram of inorganic selenium species. Eh values are in volts and are related to electron activity pE, by pE = Eh/0.059. The shaded area shows ranges of pH and Eh conditions for typical soil environments and, hence, the selenium species that would be in equilibrium with those conditions. The dashed line separates oxidized from reduced soils (Pearsall, 1938).

Although it could occur in the mildly oxidizing to oxidizing environments, it is not commonly found, however, because of slow oxidation kinetics. Thus, its presence may more signify sluggish reaction kinetics rather than stability for a given environment. Also, oxidizing environments facilitate the ease of bacterial oxidation of selenide to selenite, which effects a greater electron transfer and free energy by passing over the elemental end product. When burned in air, elemental selenium and selenide both form SeO_2. Remembering that selenium compounds are more easily reduced than their sulfur equivalents, results in an interesting situation wherein the co-occurrence of both dioxides results in the reduction of SeO_2 to elemental selenium and oxidation of sulfur. This can happen, for example, during the combustion of fossil fuels or roasting of sulfide ores, both of which produce abundant SO_2 for reduction of the SeO_2. This technique has been the basis for industrial production and recovery of selenium until recently.

Selenite

The oxide form of tetravalent selenium is SeO_2. In water this hydrates to form the weak selenous acid, H_2SeO_3. Once in solution, the inorganic selenites are highly toxic; however, we shall see that many factors tend to reduce the solubility of selenite compounds. For example, the ion can, in effect, be somewhat detoxified because of its tendency to form relatively insoluble complexes and compounds with iron and aluminum sesquioxides in certain soil environments (Hingston and others, 1968; Howard, 1972; Parfitt, 1979; Rajan, 1979; Hingston, 1981; Merrill and others, 1986; Balistrieri and Chao, 1987). In acidic environments, selenites readily and quickly reduce to elemental selenium in the presence of reducing agents (Sarquis and Mickey, 1980) or certain bacteria (Vokal-Borek, 1979). Also, most selenite salts are less soluble than the equivalent selenate salts. The net effect is that these considerations collectively render selenite unavailable to plants and minimize its deleterious effects on the environment.

Selenate

Selenate is the most mobile inorganic selenium species because the majority of selenates are highly soluble and do not form stable sesquioxide complexes. Because they are easily leached from the soil, selenates are also easily available to plants and are the form most readily assimilated by plants (Gissel-Nielsen and Bisbjerg, 1970; Eisler, 1985). Selenate compounds also are highly toxic. Consequently, selenate is the selenium species of greatest concern for its possible deleterious effect on the environment. Even changes in environmental parameters that favor more reduced selenium compounds will not immediately detoxify selenate because the kinetics of reduction are sluggish and the conversion is a slow process.

Organoselenium

Selenium forms organic compounds that are analogous to those of sulfur. These include seleno amino acids and their derivative proteins (Shrift, 1973), methyl selenides, methyl seleninic esters, methyl selenones, and methylselenonium ions. A variety of organoselenium compounds are synthesized in plants. Some plants so readily take up selenium that they are known as selenium accumulators and have been used as exploration guides for uranium deposits that associate with selenium in the Western United States (Cannon, 1957). Microbial processes can produce reduced organoselenium species, such as dimethyl selenide (Chau and others, 1976), and the ubiquity of these compounds in the environment suggests these processes are an important part of the aqueous geochemistry and geochemical cycle of selenium (Cooke and Bruland, 1987).

OCCURRENCE

Crustal Rocks

Data on abundance of selenium in crustal rocks are far more scarce than for many other trace elements due to selenium's volatility during emission spectrography, the classic technique used for rock analysis. Nonetheless, enough data exists to make simple inferences about the rock distribution and geochemical cycle of selenium. Lakin (1961a) gave an excellent, but now dated, compilation of selenium concentrations in rocks. Rosenfeld and Beath (1964), Lakin and Byers (1941), and Lakin (1972) have compiled selenium concentration data for a variety of rocks, soils, and associated vegetation. Ebens and Shacklette (1982) summarized data for rocks, soils, plants, and waters in the western United States. More recent compilations were given by Kabata-Pendias and Pendias (1984) and Berrow and Ure (1989). Mosher and Duce (1989) inventoried a general survey of concentrations in crustal rocks, soils, atmospheric dusts, coal, rivers, lakes, oceans, plants, algae, and animals.

Lakin (1973) listed a range of selenium concentrations in igneous rocks of 0.004 to 1.5 ppm, a great deal of variation in this rock type. Limestones and sandstones have relatively low concentrations of selenium, <0.1 ppm. Shales tend to have higher concentrations, about 0.6 ppm, presumably because the selenium associates with organic matter in the shale. However, shale contents of selenium also show an exceptionally wide range—from 0 to >100 ppm (Lakin, 1961a). In black shales, the correlation between organic matter and selenium concentration is more evident—in the Pierre Shale where organic carbon is <0.5%, the selenium is <0.5 ppm, but where organic carbon exceeds 1% of the shale the selenium concentration rises to 10 ppm and concentrations of up to 100 ppm occur (Tourtelot and others, 1960). Deep sea carbonates and deep sea clays both have typical selenium concentrations of about 0.2 ppm (Chester and Aston, 1976).

Robbins and Carter (1970) analyzed selenium concentrations in United States phosphate ore and found a range of 0.7 to 7 ppm in phosphate from the Pebble District of Florida, the area that currently produces most United States phosphate. Selenium in phosphate from the Western Phosphate Field of the U.S., a region that has now ceased significant production, has a higher concentration range of 1.4–178 ppm. This same study noted that 40–60% of the selenium in the phosphate rock extracted into the concentrated superphosphate, the typical fertilizer product. Thus, enriched selenium in phosphate rock transfers into the product fertilizer and later becomes available for crop uptake.

Fossil Fuel

In coal, selenium is enriched to nearly one hundred times its crustal abundance. Lakin (1973) listed selenium concentrations for United States coal as averaging 3.3 ppm with a range of 0.5 to 11 ppm. Japanese coal tends to have less selenium, averaging about 1 ppm. Representative concentrations for selenium in composite samples of oil shale from the Green River Formation range from 1.3 to 5 ppm with an average of 3.3 ppm, while concentrations in the extracted oil are about a factor of 10 lower (Poulson and others, 1977). The selenium here possibly associates with the higher molecular weight carbon compounds, as it does not extract with the oil. In 15 samples of crude oils from the Eastern Molasse Basin of Germany the selenium concentrations averaged 0.09 ppm (Ellrich and others, 1985), and the S/Se atomic ratio ranged from 1×10^5 to 3×10^5 with an average of 1.7×10^5. Selenium concentrations were enriched to an average of 0.31 ppm in 12 samples of the asphaltene fraction extracted from these crude oils, also suggesting association with the higher molecular weight compounds. In a compilation of United States crude oil, Pillay and others (1969) gave an average concentration of 0.17 ppm with a range of 0.06 to 0.35 ppm. In conclusion, selenium in fossil fuels seems to be enriched in those fuels derived from terrigenous organic matter (coal and some oil shale) and in the higher weight compounds in marine-derived petroleum.

From the selenium concentrations in fossil fuels and the amounts of the three fossil fuel types used worldwide, coal will be the principal fossil fuel source of selenium release into the environment. Furthermore, coal is used in a way that maximizes selenium release. Coal is burned mostly in steam power plants with high-temperature combustion conditions conducive to volatilization of selenium.

Marine Environment

The atomic ratio of dissolved sulfur to selenium in the ocean is 1.4×10^7. This ratio seems unusually large compared to other crustal environments; however, it is distorted by the sulfate abundance in the ocean, which results from sulfate's greater solubility. Weathering on land separates the two elements and preferentially removes sulfate to the oceans.

In the middle and deep parts of the open ocean water column, the concentration of total selenium is nearly constant at about 2 nmol/kg, although in the upper 200 m the concentration decreases progressively upward to about 1 nmol/kg at the surface. According to Measures and Burton (1980), the profile of total selenium suggests a nutrient-like behavior because of similarity to limiting nutrients, in particular that of phosphate. However, near the ocean surface subtle differences occur between the concentration profiles of selenium and phosphate that suggest non-nutrient behavior for selenium: dissolved phosphate is depleted at the surface and entirely fixed with organic matter, while total selenium decreases to only one-half of its rather consistent concentration in water deeper than 200 m. This surficial water difference between selenium and phosphate contraindicates the contention of selenium's nutrient-like behavior in the ocean. It may indicate that selenium is not a limiting trace element in the ocean, or another explanation is that the trace nutrient requirement for selenium is obtained from selenium's co-occurrence with particulate sulfur phases. Sulfur is abundant in the ocean, and it is easily and commonly metabolized. Consequently, inadvertent metabolic incorporation of occasional selenium in substitution for sulfur, even though selenium abundance relative to sulfur is low, may satisfy the trace level needs of organisms.

Three dissolved selenium species occur in the open ocean: selenite, selenate, and an organic form operationally named organic selenide (Cutter and Bruland, 1984). This latter species likely consists of seleno-amino acids in complex peptides. Dissolved elemental selenium does not occur in the open ocean because of its insolubility and tendency to associate with particles, although it might be present in negligible quantities as a pseudo-dissolved microcolloid. In surface waters, approximately the upper 200 m, biotic processes fix selenium. These waters are depleted in both higher oxidation states of selenium but enriched in organic selenide. The presence of the abundant dissolved reduced phase and absence of the higher oxidation states suggest reduction of the selenite and selenate as the mechanism of incorporation of selenium into biotic processes. Note that the reduced selenium is being generated in the most oxic zone of the ocean. Below this surface water layer the organic selenide is undetectable, and selenite and selenate constitute virtually all of the dissolved total selenium concentration. Particulate selenium consists mainly of organic selenide. The flux of particles and the associated selenide decreases downward with depth, presumably from particle dissolution that leads to regeneration of dissolved selenium. In reducing situations, for example in anoxic pore water, selenite and selenate can reduce and precipitate as elemental selenium. This may occur in organic-rich coastal waters (Takayanagi and Wong, 1984; and Takayanagi and Cossa, 1985), as well.

CRUSTAL GEOCHEMICAL CYCLE

In brief, the selenium cycle involves sources principally from igneous—but also from sedimentary and metamorphic—rocks and sinks of terrigenous or oceanic sediment, mainly in the biogenic sediment fraction. Both the atmosphere and ocean serve as selenium reservoirs with their own complex selenium subcycles. The atmosphere receives selenium from a variety of sources: volcanic, biotic, and anthropogenic. Selenium removal from the atmosphere presumably occurs in steady-state equilibrium with these sources and occurs via precipitation and/or sorption onto particles followed by particle removal. The oceans also receive selenium from a variety of sources and, like the atmosphere, must be in steady-state equilibrium with regard to input and output. Ultimately each reservoir must be in equilibrium with respect to influx and outgo of selenium, as neither one contains direct source or sink, or their total concentrations of selenium must change through time. Both reservoirs, however, may be evolving towards new equilibria with regard to amounts and throughputs due to the substantial and recent perturbation of the selenium cycle by humans. A recent synthesis discussion of the global cycling, reservoirs, and fluxes of selenium is given by Nriagu (1989). He listed the major crustal inventories of selenium in kT as lithosphere, 3×10^9; soils, 10^5; fossil fuel deposits, 1.4×10^5; terrestrial biomass 70; atmosphere, gaseous and particulate, 2; oceans, dissolved, 2×10^5; rivers, dissolved and particulate, 14; shallow groundwater, 0.8; and polar ice 400. Fluxes and interactions among the crustal sources and reservoirs of selenium are listed in table 4 and shown in figure 3.

The crustal geochemical cycle of selenium generally mimics that of sulfur, but there is some dissimilarity. Differences in oxidation/reduction potential between the two elements cause an important divergence of geochemical behavior. Selenium's ease of reduction compared to sulfur makes selenate less common in oxidizing environments than its sulfur equivalent, sulfate. Thus, the highly soluble sulfate is preferentially removed during weathering and occurs in the ocean and in salt deposits, but without an accompanying selenate phase.

Volcanoes

Volcanic plumes are often considerably enriched in selenium, and this has significance as a source of both particulate and vapor-phase selenium to the atmosphere. A recent summary of the considerations and amounts of volcanic injection of selenium into the atmosphere was given by Mosher and Duce (1989).

One quickly discovers the existence of an inadequate database on volcanic emissions of selenium and that selenium emission calculations from volcanoes are further compromised by the episodic and variable nature of volcanic emissions. However, even though selenium supply from volcanic emissions is uncertain, it is clear that even a single volcano can be large point source of selenium release into the environment. The concentration of particulate selenium in volcanic gas and particulate emissions varies tremendously—over a factor of nearly 5000, ranging from 1 ng/m^3 to 5 mg/m^3. In Hawaii, the Kilauea plume was enriched in selenium, relative to basalt, between a factor of 106 and 107, while the enrichment of particulate sulfur in the same plume, omitting the gaseous release that accounted for most sulfur emission, was only between a factor of 10 and 50 (Zoller and others, 1983). These data suggest that selenium is readily removed from the magma as particulate emissions; whereas, sulfur is emitted as a gaseous phase, a conclusion shared by Greenland and Aruscavage (1986). The volcanic release of selenium can be estimated by comparing selenium concentrations to sulfur dioxide emissions, which are moderately well characterized. Assuming the global volcanic flux of SO_2 to be about 20 MT/yr (Stoiber and others, 1987), the estimate of selenium emissions ranges from 50 kT/yr, in a case where the sulfur to selenium mass ratio of several sublimates averaged about 200 (Symonds and others, 1987), to the El Chichon eruption where the total sulfur to particulate selenium mass ratio was about 105 (Kotra and others, 1983), which would lower the global volcanic selenium release to 0.1 kT/yr. The difficulty with these types of calculations is that selenium may not consistently apportion its particulate and gaseous species in the same way as sulfur. Mosher and Duce estimate the range of annual volcanic emission of particulate selenium to be 0.04–1.2 kT, while Lantzy and Mackenzie (1979) provided a tenuous estimate of the annual gaseous selenium release from volcanoes as 0.013 kT, only about 1% of volcanic particulate emissions. Mount Etna in Sicily, has been estimated to emit 0.2 kT of particulate selenium annually (Buat-Menard and Arnold, 1979). In summary, the global emission of selenium from volcanism is not well

Table 4. Emissions of selenium, in kT/yr

[Quantities are abstracted from values discussed in this report and by Mosher and Duce (1989), Nriagu (1989), and sources therein.]

Source	Range	Average emission
Anthropogenic Emissions to Atmosphere		
Coal	0.42-9.5	3.2
Fuel Oil	0.03-0.5	0.2
Refuse Combustion		<0.0005
Metal Mining/Refining	0.29-2.1	1.5
Industrial	0.07-0.17	0.12
Total Anthropogenic	0.08-12	6
Natural Emissions to Atmosphere		
Particulate		
Mineral Dust	0.03-0.3	0.2
Sea Salt	0.004-0.55	0.2
Volcanic	0.04-1.2	0.4
Wood and Vegetative Combustion		0.5
Total Particulate Natural		1.3
Gaseous		
Marine	4.8-5.2	5
Continental	3.0-4.4	4
Volcanic		0.013
Total Gaseous Natural		9
Total Natural		10.3
Other Fluxes Rivers, dissolved	2-7	6
Rivers, particulate		12
to Oceanic Sediments		5.3
Oceanic Surface to Deep Layers		3.8

characterized; however, volcanism appears to contribute substantial selenium to the atmosphere, where it may be globally redistributed.

Atmosphere

The atmosphere receives selenium from a variety of sources, both natural and anthropogenic. A recent overview of these processes is provided by Mosher and Duce (1989), along with a compilation of measurements of particulate and gaseous selenium concentrations in the atmosphere. The key to understanding the geochemistry of selenium in the atmosphere is to remember that the atmosphere is neither source nor sink of selenium. Ultimately, the sum of all injection processes of both particulate and gaseous selenium compounds must equal all removal. Two other important points should be noted. First, the lower atmosphere, roughly 1 km above surface, contains considerable selenium even in remote locations. Thus, natural sources of atmospheric selenium are important and occur, or the selenium is disseminated, over large areas. Second, modern rainout fluxes are similar to preindustrial values for non-urban locations, underscoring the importance of natural processes. What makes the atmosphere difficult to understand in terms of the concentrations and dynamics of selenium is its multitude of sources, removals, and redistributive processes of both mass and species. Consequently, any locale may have gaseous and/or particulate selenium from a variety of origins and perhaps with an equal variety of residence times and removal processes. For example, boundary layer air concentrations of selenium may be used to calculate the gaseous marine emissions of selenium into the atmosphere, as done by Ross (1985) and Mosher and Duce (1989), but these measurements could have gaseous selenium components from additional sources, for example, coal combustion or volcanoes. Thus, these estimations of marine emissions of gaseous selenium may be too large.

At atmospheric urban and semirural sites, total particulate selenium generally averages between 1 and 10 ng/m^3, where the cutoff between particulate and gaseous

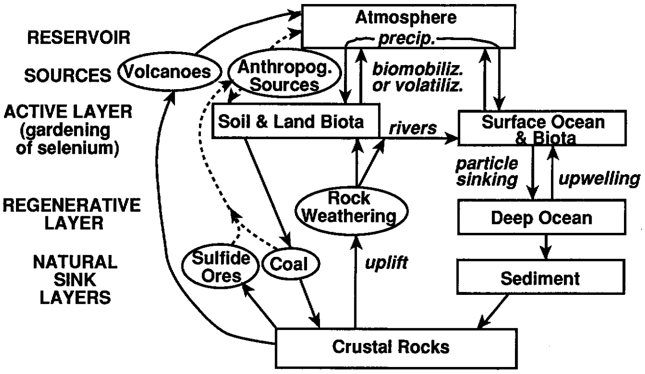

Figure 3. Generalized cycle of selenium on the Earth's crust, showing the sources, reservoirs, and processes of exchange and interaction among reservoirs. The chemical properties of selenium that most greatly influence the behavior of selenium and interaction with crustal processes are: volatility, redox properties, aqueous geochemistry, and organometallic complexing. Gardening refers to interacting processes among surface rock, soil, water, and plants. Solid arrows represent natural processes, while dashed arrows are anthropogenic processes. The overall geochemical cycle of selenium would be considerably simplified were it not for the anthropogenic activities.

material is generally considered to be 0.1 mm. A few particulate concentrations have been reported well above this range and document sampling proximal to sources such as smelters. Particulate selenium at marine and remote continental sites ranges between 0.03 and 0.6 ng/m^3. Particulate concentrations drop off radically and show less range with altitude for both marine and remote continental localities. For samples taken up to about 5 km height, the concentrations range between 0.01 and 0.05 ng/m^3; however, the paucity of samples with height precludes adequate assessment of the vertical distribution of particulate selenium in the atmosphere. Particle size data may provide information about the sources of selenium to the atmosphere, as well as the cycling of the element; however, few data exist and interpretation of size data is still incomplete. Nriagu (1989) estimated that the atmosphere receives 15×10^9 g/yr of natural and anthropogenic inputs of selenium. He estimated the anthropogenic component, which is 43% of total input, to be 60% particulate selenium, while the natural sources are only about 6% particulate selenium.

Vaporous selenium compounds exist in the atmosphere but their concentration, redistribution, and fluxes are not well characterized. Vaporous selenium compounds are usually operationally defined as <0.1 mm and typically comprise 10–40% of total selenium. These gaseous compounds include both organic forms, such as $(CH_3)_2Se$ and inorganic forms, for example gaseous SeO_2 or elemental selenium. A large component of selenium emitted to the atmosphere is thought to consist of the organic species produced by marine biogenic activity. With increasing altitude the concentration of gaseous selenium, like the particulate fraction, decreases radically, although the lack of information makes this consideration more suggestive than definitive.

Atmospheric particles from remote Northern and Southern Hemisphere sites are enriched in selenium by a factor of nearly 10^4, when normalized to Al, over a source from either crustal weathering or the ocean (Duce and others, 1975; Maenhaut and others, 1979). Furthermore, the atmosphere is enriched in selenium relative to sulfur. Particles sizes are such that atmospheric residence times are insufficient to allow much interhemisphere mixing; thus, the large selenium concentration for each hemisphere likely is a result of the processes occurring in that hemisphere. For the Northern Hemisphere, anthropogenic activities are suspect sources of this atmospheric enrichment. However, in the relatively unpolluted and unpopulated Southern Hemisphere, natural sources must be most significant. These include volcanism and biological mobilization. It may be more than fortuitous that the Southern Hemisphere, which is essentially an oceanic hemisphere, has significant selenium concentration in its lower atmosphere. Fewer volcanoes exist is this hemisphere to furnish selenium to the atmosphere; hence, the source of this atmospheric selenium could be the ocean, wherein biological activity in surface waters fixes dissolved selenium and the biofixation eventually produces volatile selenium compounds.

Once emitted into the atmosphere, selenium has a brief residence time, estimated as 45 days for total (particulate and vaporous) atmospheric selenium (Nriagu, 1989). The removal most likely occurs via condensation of vapor onto precipitation and settling particles or, in the case of particulate selenium, settling or scavenging by precipitation. Obviously, some process must continually remove selenium from the atmosphere or its atmospheric concentration would continually increase, which is not the case. Selenium enrichment factors of 800–3300, referenced to Mn, in preindustrial snow and ice deposits suggest that indeed precipitation is responsible for much atmospheric selenium removal (Weiss and others, 1978; Weiss and others, 1971).

Natural processes of atmospheric selenium supply and removal exceed those from anthropogenic activities. Presumably, much of the natural emission of selenium into the atmosphere is due to biogenic activity, principally from the oceans (Nriagu, 1989), that produces gaseous organoselenium compounds. The fate and removal of these compounds is uncertain, but their release into the atmosphere must be followed by sorption or condensation from the vapor in the atmosphere onto the particles, perhaps mediated by atmospheric photo-oxidation processes resulting in hygroscopic selenium oxides followed by sorption onto particles. Removal may then proceed through rain (Cutter and Church, 1986) or snow. Although this is the presumed fate of organoselenium compounds, few studies have attempted to measure organoselenium compounds in precipitation. The predominant species in urban and unpolluted marine rainwater samples is selenite (Cutter, 1989), with a selenite to selenate ratio ranging from 1 to 3. Selenium concentrations in various types of precipitation are summarized by Mosher and Duce (1989); they noted the following ranges and concentrations in ppb: continental rain (0.3–1.10); marine rain (0.04); Greenland ice (0.012); Antarctic ice, preindustrial (0.01); Antarctic ice, modern (0.01–0.03); and urban snow (0.08–0.2).

Other processes besides volcanic injection may lead to enrichment of selenium in the atmosphere. Goldberg (1976) has suggested that selenium and other volatile elements may be injected into the atmosphere simply by sublimation from crustal rock or soil. Using kinetic theory calculations similar to his computation of steady-state flux of volatile elements to the atmosphere, selenium vapor pressure is estimated as 10^{-9} atm at 300°K. This estimate of the vapor pressure directly depends on selenium concentration; it is substantially affected by choosing the concentration in average crustal rock as opposed to average crustal soil. Also, this vapor pressure release must be taken as very suggestive, due to the insufficiency of actual measurements of selenium vapor in the atmosphere. Nonetheless, this vapor pressure, if correct, is sufficient to continually sublimate small amounts of crustal selenium into the atmosphere, where the vapor could disperse worldwide. Perhaps this explains part of the ubiquity of selenium in the atmosphere, especially in areas remote from other potential sources. Most measurements of atmospheric selenium characterize only the particulate phase. Crustal vapor release and the subsequent sorption kinetics or degassing interaction between particles and the selenium vapor are poorly understood and little measured.

Another mechanism that may be responsible for refluxing selenium into the atmosphere is the release of volatile selenium compounds from land plants, measured by Lewis and others (1966). In this experiment the specific compounds responsible for the selenium volatilization were not identified; however, the important results were that both accumulator and nonaccumulator plant species released volatile compounds and that the amounts released were qualitatively related to the amounts of selenium in the plant. It is unknown whether marine plants also volatilize selenium in similar fashion, although the production of volatile organoselenium species in surficial marine water has been suggested as a source for injection of selenium into the atmosphere.

Rivers

Reported fluxes of riverborne, reactive selenium to the ocean, including dissolved and releasable adsorbed species but neglecting selenium that is sequestered within the mineral lattices of the suspended load, are about 6 kT/yr, according to Edmond and others (1979) or about 7 kT/yr using riverborne selenium concentration data from Kharkar and others (1968). These fluxes are based on global river concentration data and a flux of river water to the ocean of 3.5×10^{10} kT/yr. Neither selenium flux value includes the contribution transported to the oceans by groundwaters. This groundwater flux, which amounts to about 10% of the flux of river water to the ocean, is uncharacterized for its selenium contribution to the oceans. The average dissolved selenium concentration in streams and rivers given by Kharkar and others (1968) is 2–3 nmol/kg, which shows dissolved selenium in rivers and streams to be about one-tenth the total dissolved selenium concentration in average ocean water. However, this riverborne flux includes a component of selenium adsorbed onto clay, especially montmorillonite and illite, that could constitute 30–50% of the selenium in solution. Also, there is a major but presumably nonreactive particulate selenium component within the lattices of minerals of the suspended load or bedload; Nriagu (1989) estimated this combined load as 12 kT/yr. Dissolved organic and particulate organic material in rivers also contain and transfer some presumably minor amount of selenium to the oceans. It is crucial to the understanding of the selenium geochemical cycle that these mineral and organic phases become adequately characterized as to their release or sorption of selenium. A recent inventory of the dissolved selenium concentration and speciation of rivers worldwide is presented by Cutter (1989), who concluded that selenate and, occasionally, selenite are the dominant forms; whereas, colloidal selenium, equal to selenide plus elemental, is the least abundant species. Cutter also emphasized the uniqueness of each river with regard to selenium speciation and concentration. A final, important consideration of the global riverborne selenium budget is to remember that this flux contains a recycled component from other sources, such as atmospheric rainout, and does not simply result from the weathering of rock and soil. In addition, this recycled component could be both natural, for example, emissions from volcanoes or vaporous organoselenium compounds, or anthropogenic, for example, combustion of fossil fuel.

Oceans

Simplistically, the behavior of selenium in the marine environment largely parallels that on land, but with some subtle differences. Many overviews of selenium geochemistry ignore or discount selenium behavior in the oceans; however, this environment provides a useful insight into the overall geochemical cycle of selenium. In part, understanding the geochemistry of selenium is easier in the marine environment than on land. This occurs because of the gradual and minor change in redox and biochemical processes between surface and deep ocean waters compared to the radical temporal and spatial changes that these same conditions commonly have on land. Presumably, selenium has the same necessary trace element requirement for marine animals as those on land. Siu and Berman (1989) provided a recent summary of selenium geochemistry in the marine environment.

The sources and sinks of selenium in the ocean are varied. Among selenium sources to the ocean is submarine ridgecrest hydrothermal activity—the deepsea analog of volcanic emission of selenium on land. In studies of effluent particles from mid-ocean spreading ridges, selenium was found to be injected into the ocean in amounts ranging from 15 to 103 nmol/kg. The emission was solely particulate material—no dissolved selenium was detectable in filtered water samples obtained from these localities (Von Damm and others, 1985a). Some H_2Se apparently issues from these vents, as well (Von Damm and others, 1985b). A series of Pacific seafloor massive sulfide deposits, ranging between 30 to 50% sulfide, contained between 5 and 170 ppm selenium (Bischoff and others, 1983); whereas, average mid-ocean basalt contains about 0.2 ppm selenium (Hertogen and others, 1980). These ore-forming, metal-rich, and hydrogen sulfide-rich solutions that form the mid-ocean ridge deposits are a major sink for seawater sulfate and, presumably, the more readily reducible selenate as well. Much of this hydrothermal selenium injection into the ocean is recycled from interstitial seawater trapped in the heated sediments. Thus, hydrothermal sources can be discounted as having any significant influence on the geochemical cycle of selenium.

Strictly on the basis of the dissolved selenium flux given above and an average oceanic total selenium concentration of 2 nmol/kg, the residence time for selenium in the ocean is 3×10^4 years. Total oceanic content of selenium is approximately 2.2×10^5 kT. Nriagu (1989) separated the ocean into a surficial mixed layer and a deep layer of 75 and 3725 m thickness, respectively, and suggested that the residence time of selenium in the mixed layer is 70 years. Residence time is proportional directly to total amount and inversely to input; consequently, this brief residence time arises because most selenium input occurs into the mixed layer and because the selenium concentration of the mixed layer is much less than the deep layer. This latter consideration produces not only a smaller total amount in the mixed layer but also an even smaller total amount than dictated by the ratio of the respective volumes of the two layers.

In summary, selenium in the ocean cycles as a bioactive element that is biochemically fixed by reduction of the oxidized, inorganic species into a labile organic species. Marine organisms assimilate and incorporate selenium as particulate organic material in surficial waters that, upon death of the organism, sinks to deeper waters where dissolution and regeneration of the selenium occurs, perhaps as a multistep reoxidation of the reduced selenium mediated by opportunist organisms. Upwelling of deep waters resupplies this dissolved selenium to surficial waters where it is again incorporated, and the cycle repeats. It is important to remember that this biological incorporation maintains the oceanic profile of selenium with its surficial water depletion. Otherwise, vertical mixing of the ocean, in which downwelling and upwelling of water must equal, would lead to homogenized concentrations in the water column. The specific reactions and mechanisms of bioincorporation and regeneration of selenium from organic matter in the ocean are enigmatic. The major sources of selenium to the oceans are river transport and rainout of selenium from the atmosphere, although this latter term may contain a recycled component from the oceans wherein marine selenium volatilizes into the atmosphere. The arguments for gaseous marine emission of about 5 kT/yr organoselenium to the atmosphere are compelling, as summarized by Mosher and Duce (1989), but if this material is returned to the ocean via rainout or by sorption onto particles that fall back to the ocean, the net flux must be zero. Submarine volcanic injection seems only a minor source. The major sink, which must equal all source terms in order for the oceanic concentration to remain unchanged, is fixation of selenium into organic matter and eventual reposit in sediments. Organic matter cycles selenium into the sediments by a slow process; much of annual fixation of selenium by organic matter regenerates so that only a small fraction of the fixed selenium eventually transfers to the sediment. This fraction of selenium reposited in the sediment must equal the net transfer of all sources of selenium to the oceans. Human activities may have perturbed this equilibrium by increasing sources to the oceans, and the oceans may have yet to establish new equilibrium concentrations and fluxes.

Biogeochemistry

Microbial mediation of the geochemical cycle merits discussion. Some parts of the geochemical cycle, such as volcanic exhalations, are unaffected by microbial processes, but other aspects of the geochemical cycle clearly are governed by bacterial processes—for example, the release of volatile organoselenium compounds from the ocean to the atmosphere. The biological methylation of inorganic selenium species is well recognized, even though actual reaction pathways are unclear. Bacteria can effect other major changes in selenium speciation—for example, organic selenium compounds can be converted to inorganic products. Also, microbial mediation of oxidation of one inorganic species to another has been documented—as with selenide to selenate (Dart and Stretton, 1977) and elemental selenium to selenate (Sarathchandra and Watkinson, 1981). Stadtman (1974) considered the importance of biochemical behavior of selenium and concluded that enzymatic processes exist that cannot distinguish selenium from sulfur when the selenium is in >mM amounts; this selenium substitutes indiscriminately for sulfur in many cellular constituents. However, the biochemical role is not just one of indiscriminate substitution: selenium has a vital, irreplaceable role evidenced by its critical nutritional need for all animals. Among the possible advantageous reasons for existence of this latter reaction mechanism are facilitation of fixation for biologically needed selenium or, conversely, facilitating conversion of biotoxic levels of selenium into a volatile species that is more readily eliminated from an organism. Thus, bacterial involvement is extensive in the geochemical cycle of selenium; the geochemical cycle can not be viewed as simply inorganic.

Selenium Weathering—Content and Behavior in Soil

Only selenite and selenate commonly occur in the most typical soil conditions, as indicated in figure 2, but, given the range of conditions over which soils occur, any selenium species can be found, including elemental and organic forms (Berrow and Ure, 1989). Again, there are instructive differences and similarities between sulfur and selenium in soils. Sulfur, as a result of its different oxidation potential, is more easily oxidized to sulfate and transported to the ocean than selenium, which tends to oxidize less and remain fixed with less mobility. Thus, weathering separates the two elements, with the result that deposits of sulfates or sulfides derived from weathering contain little selenium. The differences in oxidation potential accentuates the differences in behavior between the two elements. Selenium, when oxidized to selenite, can adsorb on soil as a function of soil composition and pH (Neal and others, 1987a) and is readily trapped by metal hydroxides, especially $Fe(OH)_3$. Thus, enriched iron environments, such as ores or marine clays, can contain considerable amounts of selenium. These iron-rich deposits can produce large selenium concentrations in the soils associated with the deposits. Generally, the difficulty of oxidation from selenite to selenate (–1.15V) is the principal reason that selenates are less commonly encountered than sulfate in the environment; however, the ease of reduction of selenates when formed also contributes to its scarcity. Humid climates or those with substantial rainfall will readily oxidize and remove selenium in solution, most likely as selenite. Subsequent reduction of the solution may later lead to reprecipitation of the selenium. Conversely, hot, dry climates tend not to remove selenium, and, in the case of soil enrichment due to underlying source rocks, leave the selenium in place, poisoning the soil. Rajan (1979) showed that at slightly acidic pH selenite adsorbs onto positively charged hydrous alumina. During desorption, which showed mild hysteresis, the pH decreased slightly. Studies by Hingston and others (1968) showed ligand exchange to be the sorption mechanism for selenite in soils that contain abundant hydrous sesquioxides. In summary, soils with acidic, poorly aerated, and organic-rich conditions favor selenide, usually bound to heavy metals, and elemental selenium, both insoluble species. In contrast, well aerated, alkaline, oxidized soils favor occurrence of selenite, which can become an insoluble complex with iron, or selenate, which is readily leached.

Soil concentrations and concentration profiles of selenium are highly variable and depend on several factors, principally the concentrations of selenium in parent material, concentration of organic carbon, and pH and Eh conditions. The concentration of water-soluble selenium in the soil, typically 5–50% of the total, can have an interesting subsurface maximum—low values at the surface are followed by a maximum at a meter or so deeper, followed again by low concentrations at greater depth. Also of interest is to note the recent interest not only in the species of selenium in the soil but also in the particular compounds, along with their reactions, that contain those species (Chao and Sanzolone, 1989; Elrashidi and others, 1989). For example, soil selenium can be partitioned into the five following operationally defined phases: soluble, ligand exchangeable, acid extractable, oxidative acid decomposable, and strong mixed acid digestible.

In a compilation of worldwide soils, Vinogradov (1959) suggested that unenriched selenium concentrations are typically on the order of 0.01 ppm and that selenium-rich soils easily attain concentrations 103 to 104 times this value or more. He further noted an extraordinary enrichment in the Tuva area of the U.S.S.R., with soil-selenium enrichment to over 8000 ppm. Finland has a region impoverished with respect to selenium with concentrations of 0.005 ppm, while a seleniferous soil in Ireland, derived from upper Carboniferous limestone with an organic-carbon content of 5–15%, contains 30–324 ppm selenium (Walsh and others, 1951; Fleming, 1962; and Thornton and others, 1983).

U.S. Soils

In the United States, selenium enrichment in soil occurs when the soils are derived from shales and clays of the Upper Cretaceous Pierre, Steele, and Niobrara Shales; the Lower Permian Phosphoria Formation; the Lower Triassic Dinwoody Formation; and from other Triassic and Jurassic formations. Trelease (1945) attributed 70% of the seleniferous areas in the United States to be associated with Cretaceous shales, with the balance in either younger or older rocks. Obviously, those areas most prone to selenium enrichment in soil are areas underlain by seleniferous rocks and where the climate is arid and hot. Selenium tends to be low in the soils derived from glacial deposits due to the extensive reworking and leaching of those rocks. In his compilation of United States soils, Vinogradov (1959) listed average total soil selenium concentrations around 1 ppm for unaffected or unenriched soil; whereas, averages for enriched soils from Wyoming, Montana, New Mexico, and Utah ranged upwards to 60 ppm. Soil from the Wyoming phosphorite province, notably the Phosphoria Formation, had selenium enrichments up to 95 ppm with an average of 18 ppm. In contrast, well-leached glacial deposits within areas of selenium-enriched soil in South Dakota had maximum concentrations of only 9 ppm with an average concentration of 2 ppm. These glacial deposits, however, are of mixed blessing to agricultural selenium levels—glacial reworking and leaching of selenium-enriched source rocks indeed provide a soil that is relatively depleted in selenium, but the removed, leachate selenium can concentrate downdip hydrologically, allowing accumulation of harmful levels nearby. A final example of buildup of toxic levels of selenium is the occurrence in the Kesterson Reservoir area of the San Joaquin Valley, California. Irrigation waters leach and drain selenium from seleniferous rocks and soils of the region and cause buildup of dissolved selenium where the water accumulates (Sylvester, 1986). The dissolved species in this case is selenate, which further illustrates the mobility and toxicity of this form.

Assimilation and Availability

The final consideration of selenium behavior in soils is of assimilation and availability. The most important observation is that neither assimilation or availability of the element necessarily correspond to its soil concentration. This is noted, for example, in data presented by Mayland (1985). A soil containing <10 ppm selenium can produce toxic levels in plants, for example in South Dakota or Kansas, yet the soils from humid areas of Hawaii and Puerto Rico, containing up to 26 ppm, support nontoxic vegetation. In the latter two areas the soils are acidic and contain an abundance of iron. Presumably, iron selenite compounds or complexes form, and these are sufficiently insoluble to reduce the bioavailability of the selenium. Thus, acid soils favor the more reduced, complexed forms of selenium, such as ferric selenite, which are not readily available to plants. Conversely, oxidation by chemical and bacterial processes in alkaline soils favors the existence of selenate compounds or complexes, and these are soluble and readily assimilable by plants. Of the myriad of selenium forms in soil, the most bioavailable form to plants is considered to be the water soluble fraction (Kabata-Pendias and Pendias, 1984).

HUMAN ACTIVITIES LEADING TO SELENIUM RELEASE AND THEIR AMELIORATION

Anthropogenic emissions of selenium, as previously suggested, appear to be extremely large and rival many of the natural emissions. Nriagu (1989) summarized worldwide anthropogenic release of selenium as 6 kT/yr, estimated to consist of 60% particulate with the remainder as volatile emissions. He believed the major sources of anthropogenic emissions of selenium to be smelting (31%), fossil fuel combustion (37%), and wood and other combustion (26%). Note that this release is about 4 times higher than total world production. Nonetheless, the environmental problems caused by anthropogenic use and point-source release of excessive selenium or from selenium disposal are largely restricted at present to industrialized countries. Selenium emissions in less developed countries are usually small and mainly involve combustive processes that favor widespread dispersal of selenium. Only in those less developed countries with large amounts of seleniferous coal combustion or seleniferous ore smelting would selenium impact or disposal be potential problems.

Highly industrialized areas can become point source releases into the environment of selenium used in manufacturing and processing. For example, the municipal discharge of selenium into coastal waters offshore southern California has averaged about 14 tons annually over the past 14 years of measurement (Konrad, 1989). The total selenium concentration in the effluent averaged 120 nmol/kg, or about 60 times that of selenium concentration in open ocean seawater. For perspective, this annually released quantity of selenium would have to be diluted by 3×10^{14} kg of selenium-free seawater, a cube 6 km on edge, to achieve the open-ocean concentration. Discharges from densely populated areas with widespread industrial use of selenium, for example, the San Francisco Bay region with its variety of electronics industries, likely would be even greater than for southern California. Mayland and others (1989) discussed the bioavailability of selenium from municipal sewage sludges in the United States and concluded that selenium uptake in plants grown on sludge-amended soil is not of concern. They further identified about 0.1 kT of selenium as annually mobilized in the United States by this vector; however, their database is 2 decades old. Thus, the amount of selenium currently mobilized by municipal sewage effluents, as opposed to sludges, is unknown.

Another potential source of selenium emission into the environment is associated with municipal refuse. The amount of this potential source can be estimated assuming worldwide annual production of 5×10^{5} kT of refuse with a selenium concentration of 10 ppm. Thus, 5 kT of selenium annually is mobilized in refuse, which is an amount comparable to the river transport of selenium to the oceans.

Disposal of this material is problematic. If the refuse is burned, the selenium likely will be released to the atmosphere; whereas, if it is buried, the selenium could become a localized problem near landfills with the possible production of organoselenium compounds or H_2Se.

Selenium release in conjunction with fossil fuel combustion has already been mentioned, concluding that coal combustion accounts for the major release. The study by Weiss and others (1971) suggested that this selenium does not undergo the same long-range transport after fossil fuel combustion that is experienced by sulfur. Preindustrial values of the S/Se atomic ratios in high-latitude ice sheets are between 5×10^3 and 8×10^3, while subsequent values are around 2×10^4. These values show decreased mobility of selenium relative to sulfur and are consistent with the previous contention that sulfur is emitted from combustion as vapor capable of long-range transport, while selenium emissions are particulate and more locally confined. During coal combustion, selenium partitions into the fine fly ash typically in concentrations much greater than in the original coal; most of the selenium associates with the very small particles of fly ash and, thus, will not be trapped during electrostatic precipitation (Guntemann and others, 1976). In measurements taken during combustion at a single steam plant, Andren and others (1975) determined that 68% of the selenium in the coal associated with the fly ash, but 99.6% of the fly ash was removed by the precipitators and not emitted to the atmosphere. Thus, 32% of the total selenium in the coal was vaporized, and this vapor constituted 99% of selenium emissions to the atmosphere. They assumed uniform selenium distribution throughout the size range of the fly ash, however, and this may not be the case. Chiou and Manuel (1986) showed that 79% of the particulate selenium is in the very fine size fraction of the fly ash, <2 mm. Consequently, the small mass fraction of fly ash that escapes precipitation, 0.4% in the above example, may contain a significant fraction of the particulate-associated selenium.

Selenium associated with fly ash from coal combustion poses a problem for landfill disposal of the fly ash, but, on the beneficial side, can also serve as a source of the element. It is unclear how the selenium is sorbed onto the fly ash surface and whether the association with the fine fraction of the fly ash results simply from gaseous selenium condensation onto the large surface areas of the fine ash. The differences between condensive sorption versus chemical incorporation becomes important to subsequent release of selenium from the fly ash. Note the similarity that the ore roasting production technique for selenium has to modern environmental concerns wherein coal combustion leads to large amounts of selenium associated with the fly ash. Pillay and others (1969) estimated that about 4 kT of selenium are released annually from coal and oil burning in the United States. However, this rivals or exceeds the estimate of current global production.

Merrill and others (1986) showed that mainly dissolved—but also particulate—selenium could be effectively removed from aqueous waste discharges from coal-fired electric power plants by coprecipitation with amorphous iron oxyhydroxides. In this case the removal was a function of the selenium oxidation state, initial concentration, iron dosage, pH, and general solution composition. Selenium removal was optimized for pH values less than or equal to 6.2. Discharges containing selenium concentrations of 40–60 mg/L, with selenium predominantly in the dissolved form, showed removal efficiencies of 60–80%.

Another important anthropogenic source of selenium release to the environment is from the roasting and refining of sulfide ores (Mosher and Duce, 1989). The release is principally as particulate selenium, with perhaps only 10% emission as vaporous selenium. Mosher and Duce (1989) estimated this selenium source to be between 0.3 to 2×10^9 g/yr, about the same as from fossil fuel release. Presumably, the atmospheric emissions from this source will decrease with increasing pressure to curtail SO_2 emissions from smelting; however, this will simply trade one problem for another in that the selenium will become aqueous waste discharge rather than atmospheric discharge.

On seleniferous soils, plant uptake of selenium can be reduced by the addition of certain amendments. For example, Lakin (1961b) discussed the addition of sulfur to soils, which accomplishes two types of selenium reduction. First, the greater solubility of sulfur competes for the solubility of selenium taken into the plant. Second, the presence of sulfur can reduce the more mobile selenate ion to selenite, which has considerably less solubility. This type of soil amelioration is limited by cost and the consequent deleterious effect that sulfur in turn can impose by raising the salinity of soil water. Because many areas with seleniferous soil have limited rainfall and saline groundwaters, increased soil water salinity would be unacceptable. Thus, the lessening of selenium uptake in plants through sulfur addition to the soil may just trade one problem for another.

UNRESOLVED ISSUES

Several, profound gaps exist in the knowledge of selenium's behavior in the environment. Until these are bridged, the understanding of the pathways and fluxes between reservoirs of selenium is only an educated guess based on limited data. One of the largest gaps is the inadequate database concerning concentrations and fluxes for various selenium sources and reservoirs. Discussions of geochemical behavior, including this report, tend to heavily rely on a few classic studies that commonly are based on limited or possibly outdated measurements. For example, estimates of atmospheric selenium emissions from volcanoes are based on extrapolations of measurements from but a few volcanoes and from episodic events from those volcanoes. Overall volcanic emission rates of total selenium and selenium species are not well known; therefore, assessment of global emissions from this source is questionable. These releases need better characterization, especially in terms of global emission amounts, partitioning of emission amounts between vapor and particulate phases, and the temporal stability of the different phases. Until several of the selenium emissions into the environment are better characterized, the quantification, effect, and significance of many of these fluxes remain in doubt.

The anthropogenic contribution to the geochemical cycle of selenium needs to be separated from the natural cycle. Because of the recent nature of substantial anthropogenic effects, reservoirs with residence times longer than a few decades have not yet come to their reestablished equilibrium concentrations and fluxes. Consequently, estimates of reservoirs and fluxes may be in considerable error.

Selenium in the atmospheric reservoir must be categorized in terms of amounts, species, residence times, and fluxes. Particulate- and vapor-phase partitioning must be determined along with rates of transposition of vapor to particulate, and vice versa. The extent of uniform dispersion of these phases throughout the worldwide atmosphere must be resolved. Natural versus anthropogenic contributions must be differentiated, especially at remote sites, in the upper atmosphere, and in preindustrial precipitation samples. Land biota, soil, and oceanic mixed-layer sources of selenium to the atmosphere must be differentiated and better quantified.

Speciation in various reservoirs and during transit between reservoirs must be more carefully measured. This measurement should include the selenocomplexes and organocomplexes, which are important to considerations of soil-selenium mobility and selenium uptake into biota.

The partitioning or enrichment of selenium into certain composition or size fractions of industrial wastes must be understood in order for successful ameliorative procedures to work. Organoselenium compounds involved in both the natural- and human-affected geochemical cycles of selenium must be characterized along with determination of their biochemical fixations and pathways.

Pathways and mechanisms of transformation of inorganic selenium species to the various organic forms are not understood. For example, biomethylation of inorganic selenium is acknowledged to occur, but its significance and extent, especially in marine processes, is not well known. Furthermore, the marine fixation and regeneration of selenium, likely the most important step in the crustal cycle of selenium, occurs through a series of reactions or mechanisms that are unknown.

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CHAPTER B

Solubility, Sorption, and Redox Relationships for Selenium in Reclaimed Environments—A Review

T.H. Brown

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FIGURES

Solubility, Sorption, and Redox Relationships for Selenium in Reclaimed Environments—A Review

By T.H. Brown

ABSTRACT

Selenium contamination of terrestrial and aquatic ecosystems resulting from coal mining and related operations has become a major consideration when assessing the environmental impact of surface coal mining operations. Therefore, it is important to understand the behavior of selenium in the various depositional environments that may exist in reclaimed surface coal mining operations. This report provides a review of available information concerning the solubility, sorption, and redox relationships of selenium that effect three general depositional environments on reclaimed lands: (1) surface—minesoil zone; (2) subsurface—unsaturated zone; and (3) subsurface—saturated zone.

The amounts and forms of selenium found in the various depositional environments are primarily a function of mineral solubilities, redox potential, and pH. The differences in adsorption and/or sorption of selenate, selenite, and selenide are important considerations when assessing selenium chemistry in reclaimed environments. Selenium species have different mobilities in soil and overburden materials because of the different adsorption mechanisms involved for each species.

Of the three generally defined depositional environments discussed, the near-surface, minesoil environment has the greatest potential for adverse environmental impact. Placement of selenium minerals in the subsurface nonsaturated zone may be the most environmentally sound solution. A major factor that reduces environmental problems in this zone is the lack of water for transport in the western United States. The major area of concern is the ground-water recharge zone where selenium could be conveyed to the underlying aquifer.

INTRODUCTION

Much attention is being given to the high concentrations of selenium (Se) present in mine spoils, in reestablished ground water in reclaimed areas, and in fly ash from coal as possible sources of toxicity to fauna and flora. More and more evidence shows that selenium contamination of lakes and rivers adversely impacts the biota using these resources. Selenium toxicity problems have been directly linked to the contamination of lake waters by fly ash from coal-burning power plants (U.S. Department of the Interior, Fish and Wildlife Service, 1988). Elevated concentrations of selenium have also been observed in reestablished ground-water systems at mine sites (Naftz and Rice, 1988).

The possibility of selenium toxicity of terrestrial and aquatic ecosystems resulting from coal mining and related operations is a concern that requires our attention. Therefore, it is important to understand the behavior of selenium in the various depositional environments that may exist in reclaimed surface coal mining operations.

Most selenium is found associated with sulfide minerals, such as pyrite, or as metal selenides (Elrashidi and others, 1989). High levels of selenium found in overburden materials are often associated with uranium roll-front deposits. Selenium also commonly occurs with iron oxides, as it readily sorbs to available sites via ligand-exchange mechanisms (Geering and others, 1968). In addition, carbonaceous materials frequently contain high levels of selenium, and often shales contain significant amounts. In fact, shale materials are the primary sources of selenium in the Great Plains region of the United States (Adriano, 1986).

The geochemical behavior of selenium in both spoil and minesoil environments is seemingly complex. But the current understanding of selenium chemistry, although not complete, makes possible the attempt to predict selenium behavior under many conditions. This report discusses the chemistry of selenium in various depositional environments expected in reclaimed surface mined lands. Before addressing selenium behavior in depositional environments, however, the general solubility, redox, and sorption character of the selenium species should be considered. Redox potential and pH are the probable controlling factors for solubility relationships and speciation considerations (Cary and others, 1967; Geering and others, 1968; Elrashidi and others, 1989). Also, the solubility and redox relationships of selenium are anticipated to be the same in soils and spoil materials, except for differences in the initial mineral forms and the depositional environments.

SOLUBILITY AND SPECIATION OF SELENIUM UNDER VARIOUS REDOX AND pH CONDITIONS

The species of selenium most often found in soils and overburden environments are selenate(VI) (SeO_4^{-2}), selenite(IV) ($HSeO_3^{-1}$, SeO_3^{-2}), elemental Se(0), selenide(-II) (S^{-2}), and organo-selenium compounds (Lakin, 1961c; Adriano, 1986; Elrashidi and others, 1989). The degree of hydration of each species is directly related to the pH of the system being considered. Redox potential (pe or Eh) and pH are most likely the major parameters that control the solubility and speciation of selenium in the environment (Geering and others, 1968; Elrashidi and others, 1987). The effects of redox potential and pH on the selenium species expected in solution are presented in figure 1, (from Elrashidi and others, 1989). They plotted the -log (e) or pe in solution as a function of pH for the important selenium species expected in the soil environment. Soluble selenium is expected to be in the selenate form when the pe and pH value is between the $O_2(g)/H_2O$-couple line and the selenate/selenite couples line. Between the selenate/selenite couples line and the selenite/selenide couples lines, the soluble form of selenium will be selenite. Soluble selenium will be in the selenide form if values fall between the selenite/selenide-couples and the $H_2O/H_2(g)$ couple.

In general, selenate is usually found in well-oxygenated and alkaline conditions, that is, environments that have redox parameters (pe + pH) >14.5, conditions which seldom exist in acid or neutral soils (Elrashidi and others, 1989). Since selenate minerals are very soluble under such conditions and selenate is adsorbed in limited quantities by most materials (Neal and Sposito, 1989; Ylaranta, 1983), selenate compounds should be maintained in solution and are subjected to leaching and/or increased uptake by plant species. H_2SeO_4 has pK_1 and pK_2 values of -3 and 1.66, respectively. Therefore, the soluble inorganic species of selenium under normal pH conditions found in soils and spoil materials should be in the SeO_4^{-2} form. Organically complexed selenium would also be expected in the soluble phase under these conditions.

Under conditions of lower redox parameters (pe + pH = 7.5 to 14.5), selenite is expected to be the predominant selenium species (Elrashidi and others, 1989). The selenite form will exist as $HSeO_3^{-1}$ at pH values of less than about 7.3 and as SeO_3^{-2} at higher pH values. Elrashidi and others (1987) showed that metal selenite minerals are soluble in this environment and will not persist except as the more stable mineral forms. Geering and others (1968) demonstrated that selenite readily sorbs to ferric oxides, controlling solution levels of selenium in some instances.

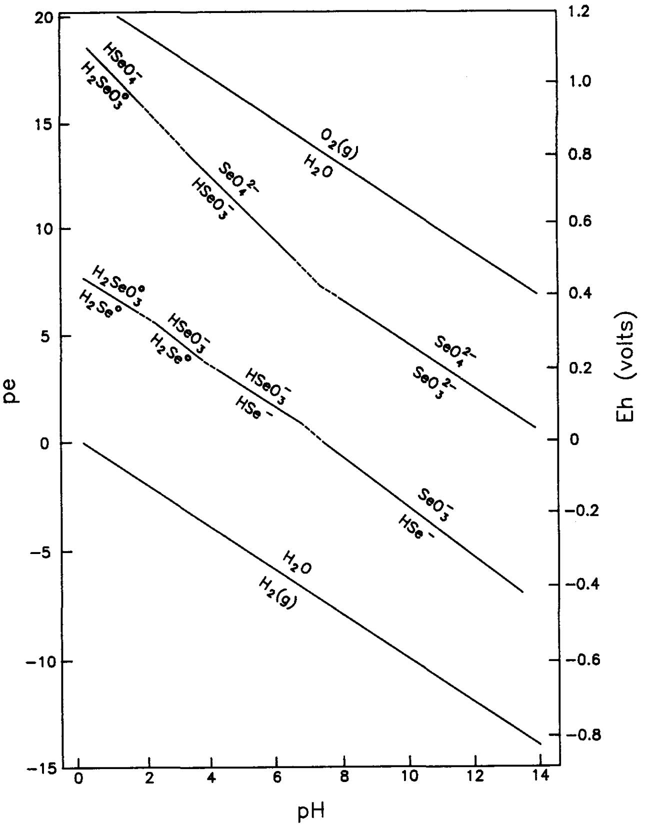


Figure 1. The effect of redox potential and pH on selenium speciation (Reproduced from *Selenium in Agriculture and the Environment,* Soil Science Society of America Special Publication 23, 1989, with permission of the American Society of Agronomy, Inc., and the Soil Science Society of America, Inc., Madison, Wisconsin.)

Elemental selenium and selenide minerals have very low solubilities and maintain low levels of selenium in solution. Therefore, conditions that promote their formation will help maintain low concentrations of selenium in solution. HSe^{-1} is the major selenide species expected to be found in solution, as the H_2Se form would only exist in very strongly acidic conditions. Elrashidi and others (1987) showed that elemental selenium and selenide minerals are formed at redox levels that are dependent on the total concentration of selenium in solution and on pH. The formation of elemental selenium and selenide minerals was calculated to occur at redox potentials of 9.6 in neutral soils that contain 10^{-7} M total selenium in solution (Elrashidi and others, 1987). At 10^{-7} M of total selenium in solution, they showed that elemental selenium would only form in soils after soluble Pb^{+1}, Cu^{+1}, Cu^{+2}, Sn^{+2}, and Cd^{+2} were converted to selenide forms or otherwise removed from solution. Such relationships are assumed to be maintained in minesoil and spoil environments. Rosenfeld and Beath (1964) have shown selenium can also be formed through microbial-mediated pathways. In addition, the oxidation of elemental selenium and selenides to selenite, and from selenite to selenate, appears to occur at a slow rate (Bar-Yosef and Meek, 1987; Rosenfeld and Beath, 1964). These factors may explain why elemental Se(c) and Se^{-2} are often present in well-oxidized materials and are commonly found in soils.

The conditions just described control the solubility relationships of the mineral forms of selenium and also influence the mobility, or lack thereof, of the selenium compounds formed. However, a major problem that exists when considering solubility relationships in materials is the lack of information available for the phases of selenium present, and the standard free energy of formation values (G) for selenium compounds (Essington, 1988). Until this void of information is filled, much of our knowledge of the solution chemistry of selenium will be based on conjecture.

ADSORPTION MECHANISMS

The differences in adsorption and/or sorption of selenate, selenite, and selenide are important considerations when assessing selenium problems in reclaimed environments. The redox potential and pH determine which selenium species will be found in solution and, therefore, determine the amount of influence that sorption will have on the mobility of selenium in the system.

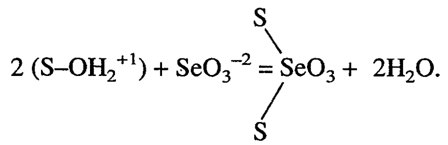
The adsorption and/or sorption of selenium species to materials found in soil environments has been a major topic of much recent selenium research (Neal and Sposito, 1989; Neal and others, 1987a; Goldberg and Glaubig, 1988; Ylaranta, 1983). Adsorption of selenium species to various sites on clay minerals, on the surfaces of aluminum and iron oxides, on the surfaces of calcite minerals, and on the organic matter complexes, have been studied. Sorption of selenium by the functional groups found in such materials may be the controlling factor in many instances for soluble selenium levels.

Soluble selenium species (selenate, selenite, and selenide) have different mobilities in soil and overburden materials because of the different sorption mechanisms involved for each species. Generally, it is thought that selenate can undergo anion exchange and is not specifically sorbed to ligand-exchange sites. Selenate is considered to be relatively mobile under normal circumstances. A highly oxidized, alkaline system will promote the formation of the selenate species. Therefore, the mobility of selenium is increased and the chances of environmental contamination are increased. Selenite, which is specifically sorbed, can be significantly hindered in comparison to selenate if sorption sites are available. However, selenite is also considered to be a mobile form of selenium (Adriano, 1986). Even though selenite is specifically sorbed, it can be removed from sorption sites and released into solution through ligand-exchange processes (Balistrieri and Chao, 1987). At low redox potentials selenide species are found in solution in low amounts, since metal selenides usually have very low solubilities. If present, the selenides would be readily adsorbed at anion exchange sites, if available, and would likely be found as soluble complexes with organics and metals.

Hayes and others (1987), usingx-ray absorption spectroscopy, reported that selenate adsorbs to exchange sites by forming outer-sphere complexes with particle surfaces. The selenate molecule maintains its hydration shell, forming a relatively weak selenate surface complex that is dominated by electrostatic bonding mechanisms (Sposito, 1984). Thus, the adsorbed selenate compound is held by relatively low binding forces and can be readily exchanged for other anions, such as SO_4^{-2}, Cl^{-1}. Adsorption of selenate is expected to react similarly to sulfate (Neal and Sposito, 1989; Alemi and others, 1988). Maximum adsorption would be expected at low pH where anion adsorption sites are more available. However, even at low pH, adsorption of selenate is expected to be minimal. Neal and Sposito (1989) found that selenate adsorption over the pH range of 5.5–9.0 was not detected in the soils collected from the San Joaquin Valley, California. Selenate reacted similar to sulfate in these soils. Ylaranta (1983) found no adsorption of selenate in soils having varying characteristics after a 1-month incubation. Balistrieri and Chao (1987) found that selenate adsorbs to goethite less strongly than selenite. Similar findings were shown by Ahlrichs and Hossner (1987) using overburden material. They found that selenate was mobile at all pH values and was completely leached from columns with <3-pore volumes of solution. Bar-Yosef and Meek (1987) found lesser adsorption of selenate than selenite by kaolinite and montmorillonite. Contrary to these findings, Singh and others (1981) found that selenate was always sorbed in higher amounts than selenite. This study was conducted using different soils with the following characteristics: high organic carbon, high salinity, high alkalinity, and calcareous. They showed that selenate was desorbed most effectively by orthophosphate. However, this fact cannot be used as evidence for specific adsorption of selenate. Hayes and others (1987) were also able to show that selenite is adsorbed to exchange sites by inner-sphere surface complexation—that is, the selenite compound does not maintain a hydration shell; rather, it complexes directly to surface oxygen atoms or other functional groups via ligand-complex formation. Inner-sphere complexation (chemi-sorption) involves either ionic or covalent bonding or a combination of the two (Sposito, 1984). This mechanism is primarily responsible for the sorption of selenite, reducing its mobility in the system. However, as indicated previously, selenite can be removed from such sites by competition with other species that readily form inner-sphere complexes with the surface (Balistrieri and Chao, 1987). Oxy-anion compounds, such as orthophosphate (PO_4^{-3}) and silicic acid (H_4SiO_4) species can remove selenite from most sorption sites. Therefore, the sorption of selenite in the root zone of plants, followed by desorption, could be responsible for increased availability of selenium for plant uptake.

Ahlrichs and Hossner (1987) found that selenite sorption on overburden material was maximum at a pH level of 3, decreasing with increased pH. Neal and others (1987a) found that the maximum selenite sorption on alluvial soils from the San Joaquin Valley, California, occurred at a pH level of about 4, with a rapid decline in selenite sorption at a pH level of 6 and a gradual decline at a pH level of 9. Goldberg and Glaubig (1988) also found selenite sorption by the Imperial soil series was greatest at low pH, with declines as pH increased. They found sorption to be greatest near pH 3, followed by a rapid decrease to pH 6.0, and a plateau at higher pH. They attributed the sorption at high pH to selenite sorbed to the surface of calcite. Pure calcite sorbed much more selenite than other minerals being studied, such as goethite. This finding was supported by the decline of selenite sorption at high pH values with the removal of the calcite from the material being studied. The sorption of selenite by goethite was also shown by Balistrieri and Chao (1987) and by Hingston and others (1968) to be directly related to pH levels. As noted previously, selenite will be in the $HSeO_3^{-1}$ form at pH values less than 7.3, and in the SeO_3^{-2} form at higher pH values.

Under some conditions, such compounds as orthophosphate and selenite may become very tightly bound to surface sites and cannot be removed by ligand exchange. Research has provided some evidence of bridging between two sorption sites at particle surfaces (that is, formation of binuclear surface complexes) that could render the sorbed selenite almost nonexchangeable.



$$2\,(S\text{–}OH_2^{+1}) + SeO_3^{-2} = \begin{matrix} S \\ \diagdown \\ SeO_3 \\ \diagup \\ S \end{matrix} + \; 2H_2O.$$

This type of mechanism has been shown by researchers to occur for orthophosphate species (Geering and others, 1968) and is responsible for its lack of desorption in many instances. Chadwick (1985) also suggested that silicic acid (H_4SiO_4) may bridge if adjacent sorption sites are present.

Several studies have suggested that sorption of selenite may occur in multilayer depositions or as amorphous coatings (Geering and others, 1968; Plotnikov, 1964). Multilayer sorption would result in the formation of an amorphous compound containing selenium at the particle surface. This has been suggested to occur at ligand-exchange sites in soils for orthophosphate (H_3PO_4) and H_4SiO_4 compounds (Hingston and Raupach, 1967); it is, therefore, reasonable to suggest that selenite compounds could react in a similar manner. Deposition of amorphous materials could affect solution composition of selenium through equilibrium relationships. This type of phenomenon was suggested by Brown and Mahler (1987) as a reason for increased solution levels of H_4SiO_4 associated with a zone of silica accumulation in the Palouse silt loam soil.

SELENIUM BEHAVIOR IN VARIOUS DEPOSITIONAL ENVIRONMENTS

Mineral solubility, redox conditions and adsorption /sorption phenomena interact to control the amounts and forms of selenium various environments. However, the chemical and physical nature of the environment, especially with regard to pH, redox condition, degree of water saturation, and the overall geochemistry nature of the system will dictate how a material deposited in a specific environment will react. For this discussion, three environments are considered: (1) the surface, or minesoil zone; (2) the subsurface-nonsaturated zone; and (3) the subsurface-saturated zone.

Surface Environments—Minesoil Zone

If selenium-bearing minerals are removed from deep within the overburden column and placed in a near-surface environment, significant changes can be expected in the solubility of the minerals and in selenium speciation of the soluble phase. The ultimate solubility of the minerals placed near the surface would be controlled by the redox potential and pH of their respective environments. Elrashidi and others (1987) showed in their theoretical development of the chemical equilibrium of selenium in soils that metal selenates were very soluble in well-aerated soils and were not expected to be stable in such environments. Similar conditions would be expected in mine spoil placed near the surface. As previously mentioned, Elrashidi and others (1987) also showed that metal selenites were soluble and are not expected to persist in soils, with the exception of $MnSeO_3(c)$ and $PbSeO_3(c)$. They also showed that metal selenides would be stable only under highly reducing conditions (pe + pH <7). If the system was well aerated, metal selenides would not be expected to persist. Most selenium minerals placed near the surface will be very soluble and tend to undergo dissolution, forming other minerals and/or mobile species of selenium. The nature of mineral formation and the speciation of the soluble species is dependent on the redox potential of the system. Soil solutions generally have redox parameters (pe + pH) that vary from –6.8 to 13.5 (Sposito, 1983). Soils that are either neutral or acidic and moderately well oxidized usually have redox parameters in the range of 7.0–13.5. Well oxidized, high pH materials can have redox parameters that exceed this range (Elrashidi and others, 1987). Poorly aerated, often water-logged materials are usually associated with low pe + pH values of <7.0.

The complexity of the system is compounded by the diverse spatial conditions expected to exist in the environment. For example, diverse assemblages of minerals can be expected in minesoils. Each mineral type (that is, metal selenate, metal selenite, and metal selenide) will react differently under varying redox potentials. Also, within these materials, micro-environments of considerable extent possess a range of redox conditions from aerobic to anaerobic (Bartlett, 1986). For example, materials close to a large pore may be well oxidized; whereas, the middle of an adjacent ped or particle of indurated spoil could be considered anaerobic. Presence of organic matter would significantly impact the variability, as it would promote conditions characterized by low pe values, thus lowering redox potentials. If the medium were alkaline, soluble selenium found in the immediate vicinity of the soil pore could be in the selenate form; whereas, selenium in an adjacent particle may be in the selenite and/or selenide form. Significant differences in selenium mobility would result in differences in availability for plant uptake and/or movement in the near-surface environment.

Drying of the surface environment can significantly influence the redox character of this zone, which, in turn, will impact the chemistry of selenium. Bartlett and James (1980) found that drying field-moist soils and rewetting them later have drastic effects on their redox behavior. They found that drying alters the chemical characteristics of surfaces such that the addition of water results in substantially different reactions from those of continuously moist soil. Drying results in the increased solubility and reducing ability of organic matter. In addition, manganese will be reduced, and its solubility will increase. Surface acidity will also increase. These effects were found to increase with storage time. Drying also causes a significant decline in microbial populations followed by an increased microbial activity when the soil is rewetted. Thus, reducing conditions may intensify immediately after the dried material is rewetted. The net effect is to lower the pe of the system, increasing the potential for oxidation.

The effect of drying on selenium chemistry is not entirely clear. During the drying process selenium could undergo oxidation from selenite to selenate if the pH of the system is high enough. However, the presence of Mg^{+2} and other reducing agents could result in the reduction of selenate to selenite. Following rewetting, selenium is expected to be present in the more reduced forms, inasmuch as the redox potential would decrease for the reasons discussed above. The effects of drying on selenium chemistry is an area that needs further evaluation.

Subsurface Environments—Unsaturated Zone

The unsaturated-subsurface zone can be characterized as a transition between the relatively well-aerated surface and the poorly aerated saturated zone below. Redox conditions would be expected to change with depth as the system would become more anaerobic. Initially materials found in this zone would contain significant amounts of oxygen as a result of the mining process (Groenewold and others, 1983). Selenium chemistry would initially react to a highly oxygenated system. If the pH were relatively high, the selenium minerals present would be unstable and dissolution would occur. Selenate could be the dominant species found in solution except in the micro-environments mentioned earlier, where more reduced selenium species could persist. The oxygenated condition would be expected to be short lived as the oxygen is depleted in reaction processes. With oxygen depletion, the redox potential of the system would decline and the selenate would be reduced to the selenite and selenide forms. Metal selenites and/or metal selenides would form, dependent on the local redox conditions and selenium levels existing in the vicinity of the respective selenium components. These minerals would control solution levels of selenium if sorption was not a controlling factor. If redox parameters were in the 7.0–14.0 range, metal selenites of varying solubilities would be formed, and the soluble species of selenium would generally be selenite. Lower redox potentials would favor the formation of selenide minerals and possibly elemental selenium, dependent on the presence of other elements in the system and total soluble selenium levels. If these minerals formed, solution levels of selenium would be low, due to the relatively low solubility of metal selenides and elemental selenium.

With consideration of the above discussion, the potential mobility of selenium in this zone is expected to be rather high during the initial period following mining. However, actual movement of selenium would be low due to the lack of a carrier phase (water), except in ground-water recharge zones. With time, the mobility potential of selenium is expected to decrease. This will be especially true if the material contains significant ligand-complexing sites that will sorb much of the selenium being solubilized.

Redox potentials found in the subsurface-unsaturated zone would generally be anticipated to be low, and solution levels of selenium would be maintained at low concentrations, due to sorption and/or the low solubilities of the selenium minerals formed in the system.

Subsurface Environments—Saturated Zone

Minerals and/or materials placed in what will be a saturated zone after mining have originated in environments characterized by gradations of reducing and/or oxidizing conditions. Therefore, such minerals may contain selenium in the form of selenate, selenite, elemental selenium, and selenide at the time of deposition. The stabilities of these minerals may change significantly, due to differences between the postmining, reclaimed (depositional) environment, and their original environment. During the mining process, the materials have been dewatered, and the system should be oxygenated due to entrapment of oxygen during mining (Groenewold and others, 1983). Such a condition would not only greatly influence the character of selenium in the system but also affect the total geochemistry of the system. As oxygen is removed, the depositional zone will revert to a more reduced condition. Re-establishment of a ground-water aquifer will contribute to the change in redox conditions of the system, directly influencing the geochemistry. The depositional environment will undergo significant changes with time as oxygen levels diminish and the system attempts to equilibrate, or reach an equilibrium. The chemistry of selenium will reflect these changes. A study made by Naftz and Rice (1988) in Wyoming demonstrated such changes in reclaimed coal and uranium mine pits. They found concentrations of selenium in the selenate form to be from 200 to 3,000 ppb in the ground water collected from four minesites shortly after reclamation was completed. With time, ground-water levels at the reclaimed minesites decreased. Such changes were observed within several months at three of the four mines studied. With the decline in oxygen levels, the pe of the system would decrease and the redox parameter would decline, causing selenate to reduce to the selenite form. Selenite would readily sorb to available exchange sites and could form less soluble metal selenites and other minerals of varying solubilities. However, sorption competition with compounds including silicic acid, orthophosphate, and organic acids, could result in decreased selenite sorption, reducing the influence that specific adsorption might have on solution levels of selenium. If a limited number of sorption sites exist and/or if competition removes selenite from the sorption sites, selenite would either form metal selenites or remain in solution in some form that allows easy transport (that is, selenite and soluble inorganic and organic complexes). Complexed selenium compounds may not be toxic in their complexed form; however, these compounds could change to toxic species if moved to a different environment or if a change in their current environment occurred.

If the geochemistry of the system allows, the redox potential could decrease below 7 and soluble selenite would be reduced to insoluble selenides. As previously stated, these reactions could promote the formation of metal selenides and elemental selenium resulting in decreased solution concentrations of selenium. In general, metal selenides are characterized by relatively low solubilities under highly reducing environments. The levels of selenium found in solution would be relatively low and would not pose a serious threat to the environment.

SAMPLE PREPARATION AND SELENIUM SPECIATION

Conceivably, sample preparation may mask differences in selenium availability that exist in the natural environment. That is, grinding, drying, and storage time could result in significant effects in the redox behavior of a soil (Bartlett, 1986). Bartlett and James (1980) showed that a dried sample will react much differently upon rewetting than a nondried sample. The differences have been discussed previously in this report. Therefore, it is conceivable that the analysis of samples collected from the field and prepared for use in the laboratory via grinding and drying, may greatly affect speciation of selenium found in such soils. If samples are stored for any length of time, changes in speciation may be great. Also, unpredictable results will be found if the system is evaluated while the rewetted sample is changing back to the metastable moist condition. If care is not taken to reestablish the metastable moist condition prior to analysis, the results would represent a rapidly changing state of disequilibrium, rather than a soil or spoil sample that represents actual field conditions. The results would be meaningless.

CONCLUSIONS

The amounts and forms of selenium found in the various depositional environments are primarily a function of mineral solubilities, redox potential, and pH. However, at moderate to high redox parameters ($pe + pH = 7$ to 15) sorption may also greatly influence the levels of selenium found in solution. Of the three generally defined depositional environments discussed, the near-surface, minesoil environment has the greatest potential for adverse environmental impact. Selenium minerals placed near the surface would be expected to undergo dissolution. Some of the selenium would be in the selenate and selenite forms. Selenate is very mobile and is easily taken up by plants; whereas, selenite is generally sorbed tightly to ligand-exchange sites. Some of the selenite would be sorbed from solution; however, ligand exchange with other species, such as orthophosphate, could make it available for plant uptake or movement in the system.

Placement of selenium minerals in the subsurface nonsaturated zone may be the most environmentally sound solution. Redox potentials would be low after trapped oxygen is removed from the system, and solution selenium would be expected to be in the selenite and selenide forms. Degradation of soluble minerals containing selenium would result in the formation of selenite and selenide minerals, and elemental selenium. These minerals would be characterized by low solubilities. If selenite was the primary form of selenium in solution, sorption would be expected to significantly decrease selenium mobility. A major factor that reduces environmental problems in this zone is the lack of water for transport. The major areas of concern are the groundwater recharge zones where selenium could be conveyed to the underlying aquifer.

Initially, the subsurface saturated zone could be oxygenated, causing dissolution of selenium minerals and resulting in selenate as the primary selenium species in solution. However, this is expected to be a relatively short-lived condition. As the redox potential of the system decreases, solution concentration of selenium will decrease. The formation of metal selenites, metal selenides, and elemental selenium will control solution concentrations of selenium which will be in the selenite and/or selenide form. Selenite can readily sorb to ligand-exchange sites, reducing solution concentrations. Selenide would be expected at very low levels due to the low solubility of the selenide minerals that would form under these conditions. Over the long term, environmental impacts will be relatively small. However, short-term impacts could be very serious, as the groundwater might not be suitable for use.

CHAPTER C

Geobotany of Selenium

J.C. Emerick and L.S. DeMarco

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Geobotany of Selenium

By J.C. Emerick *and* L.S. DeMarco[1]

ABSTRACT

Geobotanical relationships of certain elements are well known, particularly in the case of selenium. Selenium geobotany has been studied extensively since the 1930's in North America because selenium is toxic to livestock and because of its geochemical association with uranium. There are many plant species that are well known as primary selenium indicators that serve as reliable guides to areas of seleniferous soils. Thirty-five known selenium indicator species are contained in four plant families, including Compositae, Cruciferae, Leguminosae, and Rubiaceae. Most of these species are in North America. Additional species probably will be added to the list of selenium indicator plants as vegetation in other seleniferous areas of the World is studied. The largest single group are legumes of the genus *Astragalus*, of which 23 species are known selenium indicators.

INTRODUCTION

Rock and soil substrates exert a fundamental influence on the distribution of plant species across the landscape. Spatial changes in soil type, soil parent material, hydrologic condition, and other soil-related factors are often accompanied by corresponding changes in the plant community. People have recognized such relationships for centuries and have used vegetation as a guide to find water, as an aid to map geologic formations, to locate mineral deposits, to assess soil conditions that promote livestock diseases, and even to investigate environmental contamination by pollutant sources. Affinities of some plant species for certain elements in the substrate are well known, particularly regarding selenium (Brooks, 1983) (fig. 1).

The geobotanical investigation of selenium began in the Western United States in the early 1930's. At that time, it was observed that some livestock diseases were related to grazing on particular tracts of land. Selenium was implicated as a cause of some of the diseases (Franke and others, 1934), and subsequently A.O. Beath and coworkers identified a group of plants that were not only characteristic of certain soil conditions but also accumulated large amounts of selenium (Beath and others, 1934, and subsequent studies summarized in Trelease and Beath, 1949). More recently, geobotanical mapping has been combined with remote sensing studies to identify large areas of seleniferous soils for the purposes of grazing management (Kolm, 1975).

Beath's selenium indicator plants were useful not only in identifying areas of potentially toxic soils for farming and livestock, but for mineral prospecting as well. In specific geologic formations in the Western United States, including the Morrison Formation of Jurassic age, selenium, vanadium, and other elements are concentrated along with uranium. In a classic study on the Colorado Plateau in eastern Utah, Cannon (1952, 1957, 1964) was able to demonstrate that selenium indicator species could be used to locate economically important uranium deposits. Cannon and Starrett (1956) used similar methods to investigate uranium-bearing coal deposits in New Mexico north of Albuquerque, and Cannon (1971) reported on the successful location of a uranium ore body using geobotanical indicators near Grants, New Mexico.

During the past 2 decades, selenium has been studied because of its value as a micronutrient for humans and livestock (see reviews by Moxon and Olson, 1974; and Combs and Combs, 1986), and because of concern for selenium as an environmental contaminant (Peterson and others, 1981). Under some conditions, selenium can be concentrated in the food chain resulting in toxic conditions to higher organisms. In the San Joaquin Valley of central California, agricultural drainage water with high selenium concentrations emptying into closed basins has been linked to toxicity in waterfowl (Burau, 1985). The source of the selenium is apparently shales of Cretaceous age in the Coast Range. Izbicki and Harms (1986) studied the selenium content of the vegetation growing on these shales. Other such areas are now being investigated throughout the Western United States.

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[1] L. S. DeMarco, deceased.

Figure 1. Cisco woodyaster (*Xylorhiza venusta*), a primary indicator plant of seleniferous soils in eastern Utah.

PLANT RESPONSE TO SELENIUM IN THE SOIL

In discussing the role of geobotany in the study of selenium in the environment, it is useful to review the relationships between plants and seleniferous soils, and to consider the taxa that have proven to be reliable selenium indicators. The uptake of selenium by vegetation is governed by the presence of soluble selenium and not by total selenium in the soil. Selenium has been found in potentially toxic levels in the soils and plants in at least 17 countries and on virtually every continent (Lakin, 1972). In the Unites States, seleniferous soils have been found in 25 States.

The presence of selenium in the soil does not necessarily mean that it will be absorbed by vegetation; rather, the chemical form of the element is the key to its availability to plants. Selenium occurs as selenides and selenites in reduced conditions and is relatively unavailable to plants, particularly where soils contain appreciable concentrations of iron. In oxidized soils, particularly under alkaline conditions, selenium typically occurs in the water-soluble selenate form, which is the form most readily available to plants (Lakin, 1972; Moxon and Olson, 1974). Thus, some regions of highly seleniferous soils do not produce toxic vegetation. For example, soils reported from Hawaii and Puerto Rico where high concentrations of selenium occur as a basic iron selenite support vegetation with low selenium content (Lakin, 1972). On the other hand, the highly oxidized, alkaline soils of the western United States favor the formation of calcium and sodium selenates, which are readily absorbed by plants and often in great quantities. The occurrence of selenium in an organic form (from decaying seleniferous vegetation or micro-organisms, or perhaps as selenites bound to organic matter) also appears to enhance its availability to plants (Fleming, 1962).

There are many geological formations in the Western United States that produce seleniferous soils and support selenium indicator plants; most are of Pennsylvanian age or younger. Rosenfield and Beath (1964) described the distribution of known seleniferous formations in the United States, and the following summary is taken from their discussion. Among the most seleniferous of the rocks of Pennsylvanian and Permian age are the marine shales of the Hermosa Formation and the gypsiferous Paradox Formation, both in southern Utah and southwestern Colorado, and the sandstones, conglomerates, and shales of the Cutler Formation of the same region. Of the Mesozoic rocks, the Moenkopi and Morrison Formations are regarded as being highly seleniferous wherever outcrops occur. Both support many indicator species, and a large portion of Cannon's (1964) geobotanical investigations focused on the uraniferous Salt Wash Member of the Morrison Formation. The shales, sandstones, limestones, conglomerates, volcanic ash, and coal beds of Cretaceous age are the most widespread of the Mesozoic-age rocks in the Western United States. Nearly all are seleniferous to some degree, with the highest in selenium content being the Smokey Hill Member of the Niobrara Formation in the northern Great Plains region. Many rocks of Tertiary and Quaternary age are also seleniferous, particularly in localized areas where groundwater movement has produced concentrations of evaporite minerals. Of particular note are the Wind River Formation of southeastern Wyoming, the Bridger Formation of western Wyoming, and the Ogallala Formation in Texas and eastern Colorado.

Plant species have been grouped according to their ability to absorb selenium. Brown and Shrift (1982), summarizing the work of Beath and others, give the following categories:

1. *Primary selenium indicators*, also referred to as selenium accumulators: plants that grow only on seleniferous soils and that may accumulate selenium to several thousand µg Se/g of dry weight (and in some cases up to 1% of total plant weight).
2. *Secondary selenium indicators*, or moderate selenium accumulators: plant species that accumulate selenium up to 1000 µg Se/g dry weight. In general, these plants are not restricted to seleniferous areas, but may be useful as local indicators because of their tolerance to high selenium concentrations in the soil.
3. *Nonaccumulators*: plant species that occasionally grow on seleniferous soils, but rarely accumulate selenium to levels greater than 25–30 µg Se/g dry weight. The designation for this group is clearly a misnomer because these plants do cause toxicity in animals and are perhaps the most important group in this respect. A better name from a toxicologist's perspective would be "low selenium accumulators"; "non-indicator plants" might make sense from a geobotanical viewpoint.

Selenium accumulators not only have the ability to absorb the element to high concentrations, but also to metabolize it in a distinctive way, as described by Shrift (1969), and Brown and Shrift (1982). In contrast to other species, accumulator plants apparently survive by excluding selenium from their enzymes and other proteins, thereby preventing toxic effects that would normally result from high selenium levels. A byproduct of the biochemical reactions unique to selenium accumulators is a group of distinctive organic selenium compounds. Some of these compounds are volatile, such as dimethyl diselenide, and produce a characteristic garlic-like odor that is often strong enough to detect from a fast-moving car (the essence also pervades the laboratories of geobotanists who have collected specimens of selenophytes).

In discussing other physiological differences between selenium accumulator and nonaccumulator species, Rosenfield and Beath (1964) noted that nonaccumulator species of *Astragalus* typically have lower chromosome numbers. Seed germination of nonaccumulators is inhibited by the presence of selenium, but not those of accumulator species; this is the basis of a test devised by Trelease (1942) to differentiate between accumulator and nonaccumulator species.

There has been some discussion in the literature regarding the significance of selenium as an essential micronutrient for primary selenium indicator species. Trelease and Trelease (1938) conducted growth experiments on two species of *Astragalus*, one a selenium indicator (*A. racemosus*) and the other a nonaccumulator (*A. succulentus*). Their results seemed to indicate that growth of the indicator was stimulated by selenium (as selenite) and that of the nonaccumulator was inhibited. However, at phosphate concentrations lower than that used by Trelease and Trelease (1938), Broyer and others (1972a, b) failed to detect any effect on growth by selenium, but determined that phosphate ion absorption by *Astragalus* roots had been decreased. This led to a reinterpretation of the results of Trelease and Trelease (1938) that selenium levels may in fact have decreased absorption of potentially toxic levels of phosphate. Nevertheless, Brown and Shrift (1982) pointed out that the experiments of Trelease and Trelease (1938) still have some validity, and that they serve as evidence for a selenium requirement by indicator species. The growth of a number of *Astragalus* species can be highly stimulated by selenium, while growth of others is severely retarded by low levels of the element; a significantly higher incidence of floral initiation occurs in accumulator species stimulated by selenium, but not in nonaccumulators; and finally, numerous field studies have shown that primary indicator species are found only on seleniferous soils. It is clear that more work is needed regarding the role of selenium in plant physiology.

GEOBOTANICAL INDICATORS OF SELENIUM

Since Beath and his colleagues began their work on selenium indicators over 5 decades ago, surprisingly little new information has emerged that would add to their conclusions. Certain plant species exist that are reliable indicators of seleniferous soils; the number of known taxonomic groups is small and appears to be confined to only a few families. The largest group of indicator plants are legumes of the genus *Astragalus*; out of over 300 North

Table 1. Primary indicator plants of seleniferous soils

[AZ, Arizona; CO, Colorado; KS, Kansas; NM, New Mexico; SD, South Dakota; UT, Utah; WY, Wyoming]

Genus and Species	Locality	Reference
Family Compositae		
Haplopappus engelmannii (Gray) Hall	CO, KS	Rosenfield and Beath (1964).
H. fremontii (Gray)	do.	do.
H. multicaulis (Nutt.) Gray	WY	do.
Xylorhiza glabriuscula Nutt.	WY, SD, CO	do.
X. venusta (Jones) Heller	UT, CO	do.
Family Cruciferae		
Stanleya albescens (Jones)	CO, AZ, NM	Rosenfield and Beath (1964).
S. pinnata (Pursh) Britt.	Western U.S.	do.
S. integrifolia James	do.	do.
S. viridiflora Nutt.	do.	do.
Family Leguminosae		
Acacia cana	Australia	Brooks (1983).
Astragalus albulus Woot. and Stand.	NM, AZ	Cannon (1957).
A. beathi Porter	AZ	Trelease and Beath (1949).
A. bisulcatus (Hook.) Gray	Western U.S.	do.
A. crotalariae Gray	do.	do.
A. eastwoodae Jones	UT	do.
A. flavus Nutt. ex T. & G.	Western U.S.	Cannon (1957).
A. grayi Parry	WY, MT	Trelease and Beath (1949).
A. linifolius Jones	CO	Brown and Shrift (1982).
A. moencoppensis Jones	UT, AZ	Trelease and Beath (1949).
A. mollissimus Torr.	UT	Cannon (1957).
A. nelsonianus Barn.	Western U.S.	Brown and Shrift (1982).
A. oocalycis Jones	CO, NM	Trelease and Beath (1949).
A. osterhouti Jones	CO	do.
A. pectinatus Dougl.	Western U.S.	do.
A. pattersoni Gray	do.	Cannon (1957).
A. praelongus Sheldon	NM	Trelease and Beath (1949).
A. preussi Gray	Western U.S.	Cannon (1957).
A. racemosus Pursh	do.	Trelease and Beath (1949).
A. rafaelensis Jones	UT	Brown and Shrift (1982).
A. sabulosus Jones	UT	Trelease and Beath (1949).
A. saurinus Barn.	CO, UT	Brown and Shrift (1982).
A. toanus Jones	Western U.S.	Trelease and Beath (1949.)
A. woodruffi Jones	UT	Brown and Shrift (1982).
Neptunia amplexicaulis Domin.	Queensland, Australia	do.
Family Rubiaceae		
Morinda reticulata Benth.	Queensland	Brown and Shrift (1982).

American species recognized in this genus by Barneby (1964), about 23 are known selenium indicators. While more recent research has added a small number of new species, there are few reports that describe selenium indicator species elsewhere than in the United States. Descriptions of North American selenium indicator species by Trelease and Beath (1949), Cannon (1957), and Rosenfield and Beath (1964) remain as the most important works.

Known primary indicator species are listed in table 1. Of those species, *Haplopappus*, *Xylorhiza*, and most of the

Astragalus can be regarded as universal indicators (they indicate seleniferous soils wherever they occur). Cannon (1971) listed *Stanleya*, *Astragalus albulus*, *A. flavus*, *A. garbancillus*, and *A. mollissimus* as local indicators whose position as universal primary indicators is not established.

The taxonomic nomenclature of the *Compositae* listed in table 1 is particularly confused in the literature. The genus *Haplopappus* is listed as *Oonopsis* (Trelease and Beath, 1949; Weber, 1976), *Aplopappus* (Cannon, 1957, 1971), and *Haplopappus* (Rosenfield and Beath, 1964; McGregor and Barkley, 1986). *Xylorhiza* species have been listed under the genera *Aster* (Cannon, 1957, 1971), *Machaeranthera* (Rosenfield and Beath, 1964), and *Xylorhiza* (Trelease and Beath, 1949; McGregor and Barkley, 1986; Weber, 1987; Welsh and others 1987). Some confusion also occurs regarding some *Astragalus* species; nomenclature here generally follows Barneby (1964).

A number of species in several genera are capable of absorbing relatively large amounts of selenium when growing on seleniferous soils. These secondary selenium indicators are not limited to seleniferous regions, and they do not colonize extremely toxic soils as do the primary indicators. The genera containing secondary indicators are listed in table 2. Many of these species are hardy, widely distributed, and palatable to livestock. Nonaccumulator species consist mainly of crop and forage plants, including a wide variety of grasses and other types of vegetation. Growth of these plants is generally retarded in the presence of selenium under experimental conditions; however, some species along with secondary indicators will grow on mildly seleniferous soils and accumulate enough selenium to cause livestock poisoning (Brown and Shrift, 1982).

Table 2. Genera that include species in North America classified as secondary selenium indicators

[From Rosenfeld and Beath, 1964; and Brown and Shrift, 1982]

Genus	Family	Common Name
Aster	Compositae	Wild aster
Astragalus	Leguminosae	Milk vetch
Atriplex	Chenopodiaceae	Saltbush
Castilleja	Scrophulariaceae	Paintbrush
Comandra	Santalaceae	Toadflax
Grayia	Chenopodiaceae	Hop sage
Grindelia	Compositae	Gumweed
Guterrezia	Compositae	Snakeweed or matchweed
Haplopappus	Compositae	Goldenweed
Machaeranthera	Compositae	Aster

The relatively large proportion of known selenium indicator plants from the United States is probably the result of the attention given this element over the past several decades. As more geobotanical studies in other countries are reported in the literature, the list of selenium indicator species will certainly increase. Even in the United States, renewed interest in selenium as an environmental contaminant may lead to a more complete understanding of selenium geobotany.

CHAPTER D

Aquatic Cycling of Selenium: Implications for Fish and Wildlife

A. Dennis Lemly and Gregory J. Smith

CONTENTS

FIGURES

TABLES

Aquatic Cycling of Selenium: Implications for Fish and Wildlife[1]

By A. Dennis Lemly *and* Gregory J. Smith

INTRODUCTION

The processes by which selenium, a nonmetallic element, moves through the components of an aquatic habitat may affect fish and wildlife populations. Selenium occurs naturally in the environment in trace amounts and soil concentrations rarely exceed 2 µg/g (ppm) dry weight except where soils were produced by weathering of sedimentary rock. Such soils are widespread in the Western United States. Although selenium is a micronutrient that is essential for normal animal nutrition, concentrations not greatly exceeding those that are required may produce toxic effects. These effects may range from physical malformations during embryonic development to sterility and death. Industrial and agricultural practices produce selenium-laden wastewater that may be discharged directly or indirectly into lakes, rivers, and wetlands. Two major sources are agricultural irrigation return flows that originate from high selenium soils and drainage water from areas used for storage and disposal of ash produced by coal-fired power plants.

Selenium in aquatic systems is readily taken up by organisms, and concentrations can reach levels toxic to fish and wildlife. The degree of mobility or cycling rate of selenium in the system will, to a large extent, determine whether toxicity occurs and how long the environmental hazard remains. Cycling is important both when the selenium-laden wastewater is being discharged and after the discharge is stopped.

THE SELENIUM CYCLE

There are basically three things that can happen to dissolved selenium when it enters an ecosystem: (1) it can be absorbed or ingested by organisms,(2) it can bind or complex with particulate matter, or (3) it can remain free in solution. Over time, most of the selenium will either be taken up by organisms or bound to particulate matter. Through deposition of biologically incorporated selenium and settling of particulate matter (sedimentation), most of it will usually accumulate in the top layer of sediment and detritus. However, because biological, chemical, and physical processes move selenium out of, as well as into, the sediments (fig. 1), they represent only a temporary repository for selenium. Aquatic systems are dynamic and selenium can be cycled back into the biota and remain at elevated levels for years after waterborne inputs of selenium are stopped.

Immobilization Processes

Selenium can be removed from solution and sequestered in sediments through the natural processes of chemical and microbial reduction of the selenate form (Se VI) to the selenite form (Se IV), followed by adsorption (binding and complexation) onto clay and the organic carbon phase of particulates, reaction with iron species, and coprecipitation or settling (fig. 2). Regardless of the route, once in the sediments further chemical and microbial reduction may occur, resulting in insoluble organic, mineral, elemental, or adsorbed selenium. Most selenium contained in animal and plant tissues is eventually deposited as detritus and, over time, isolated through the process of sedimentation. Some selenium, particularly certain organic forms, may be released into the atmosphere through volatilization by chemical or microbial activity in the water and sediments, or through direct release by plants.

In total, immobilization processes effectively remove selenium from the soluble pool, especially in slow-moving or still-water habitats and wetlands. Ninety percent of the total selenium in an aquatic system may be in the upper few centimeters of sediment and overlying detritus.

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[1] This report is reprinted, with permission, from; U.S. Department of Interior, Fish and Wildlife Service: Fish and Wildlife Leaflet 12, Washington, D.C., 1988

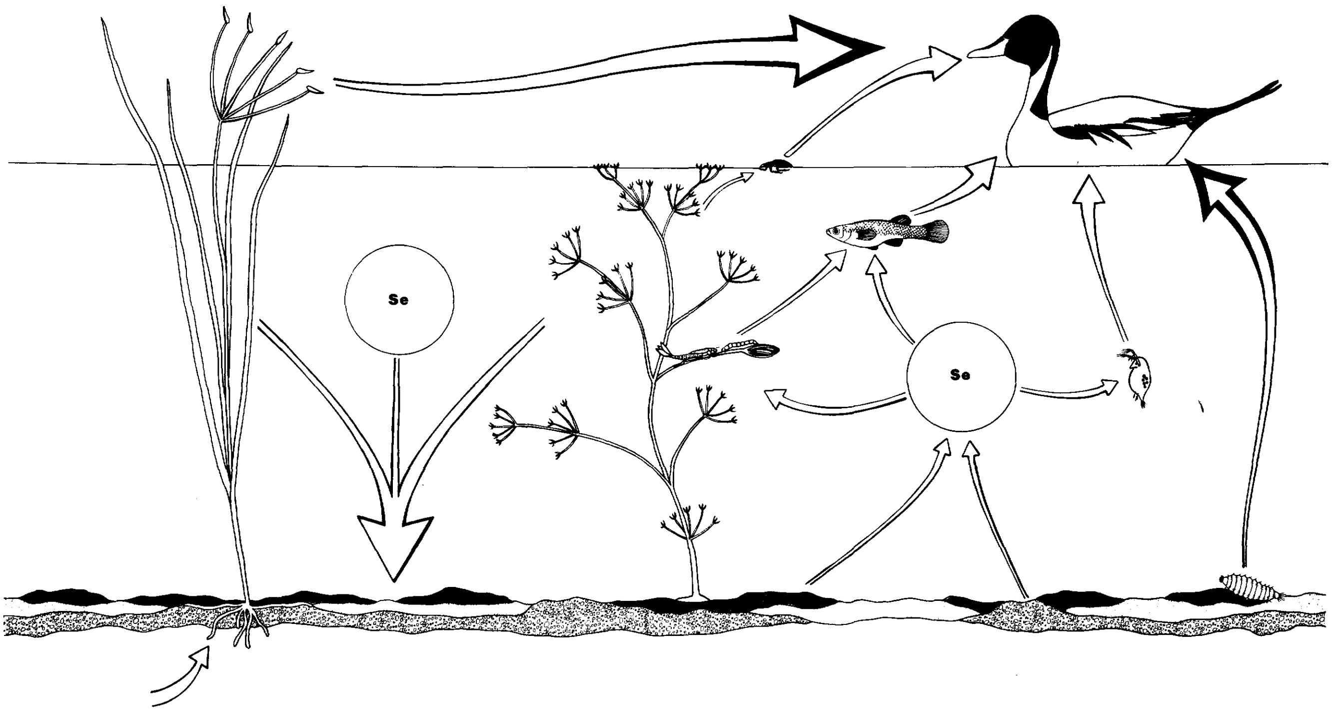

Figure 1. A highly dynamic system. Biological, chemical, and physical processes cycle selenium into and out of the water, sediments, and biota.

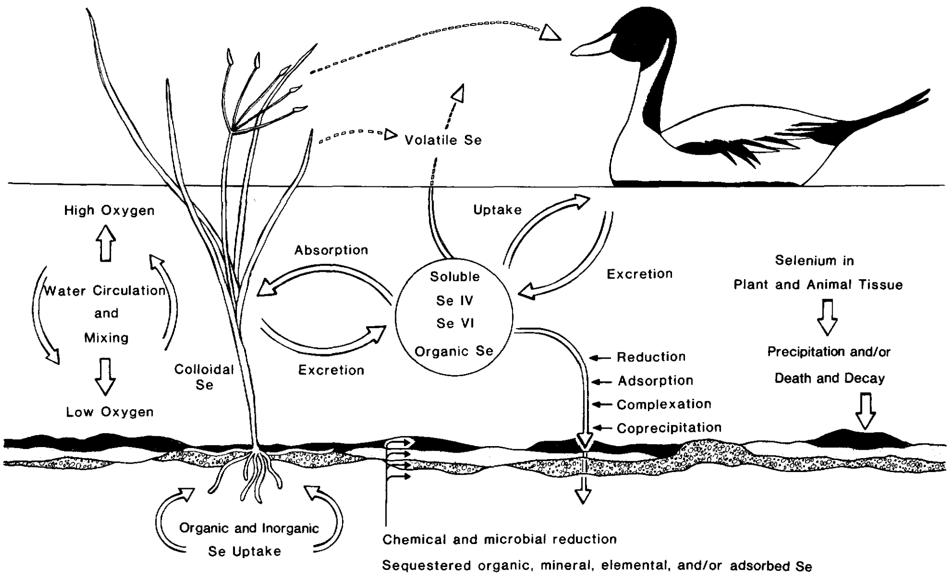

Figure 2. Processes for the immobilization of selenium include chemical and microbial reduction, adsorption, coprecipitation, and deposition of plant and animal tissue; mobilization processes include uptake of selenium by rooted plants and sediment oxidation due to water circulation and mixing.

Mobilization Processes

Selenium in sediments is particularly important to long-term habitat quality because mechanisms present in most aquatic systems effectively mobilize such selenium into food chains and thereby cause long-term dietary exposure of fish and wildlife.

Selenium is made available for biological uptake by four oxidation and methylation processes (figs. 2–4). The first process is the oxidation and methylation of inorganic

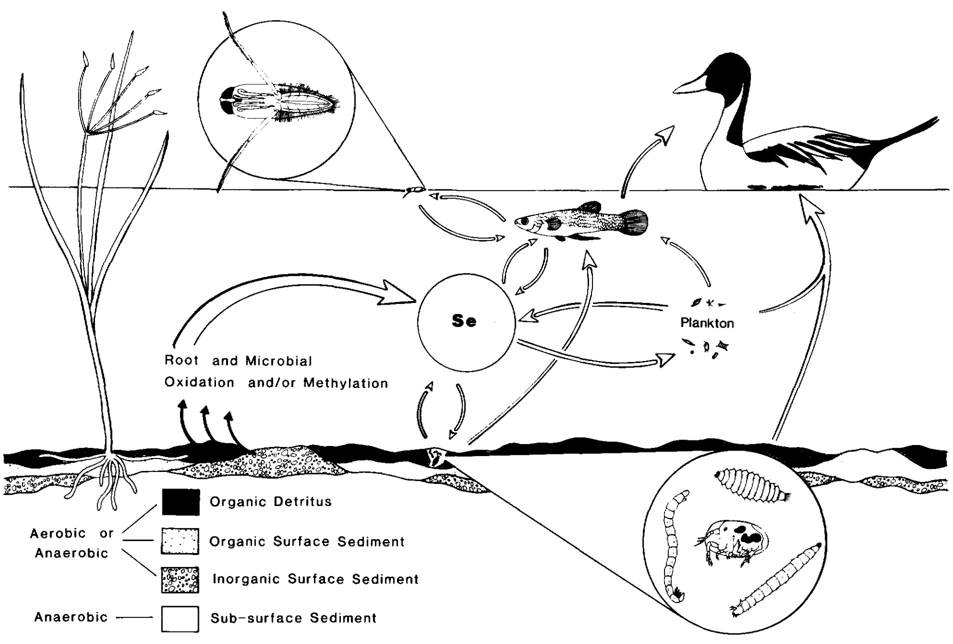

Figure 3. Additional mobilization processes include direct uptake of selenium by benthic invertebrates and oxidation of sediments resulting from plant roots, micro-organisms, and the burrowing activity of benthos.

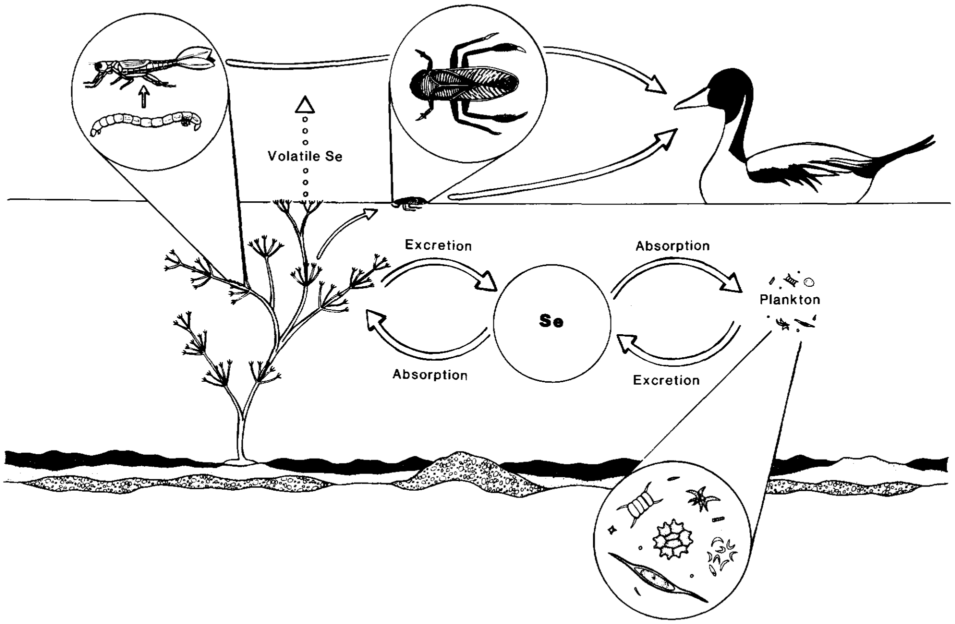

Figure 4. Dissolved selenium, whether introduced from wastewater discharge or mobilized from sediments, is readily taken up by aquatic organisms and concentrated in food chains. These pathways converge on top consumer species of fish and wildlife. The effects may be severe even when the concentration of waterborne selenium is very low.

and organic selenium by plant roots and micro-organisms. Oxidation refers to the conversion of inorganic or organic selenium in the reduced organic, elemental, or selenite forms to the selenite or selenate forms. Methylation is the conversion of inorganic or organic selenium to an organic form containing one or more methyl groups which usually result in a volatile form. A second process is the biological mixing and associated oxidation of sediments due to the burrowing of benthic invertebrates and feeding activities of fish and wildlife. Physical perturbation and chemical oxidation associated with water circulation and mixing (current, wind, stratification, precipitation, and upwelling) represent another type of process. Finally, sediment oxidation may be caused by plant photosynthesis.

Two additional pathways provide for direct movement of selenium from sediments into food chains even when the surface water does not contain selenium. These pathways are uptake of selenium by rooted plants and uptake of selenium by bottom-dwelling invertebrates and detrital-feeding fish and wildlife. These two pathways may be the most important in the long-term cycling of potentially toxic concentrations of selenium. Thus, rooted plants and the detrital food pathway can continue to be highly contaminated and expose fish and wildlife through dietary routes even though concentrations of selenium in water are low.

Role of Habitat Variability

The processes regulating selenium cycling are similar in all aquatic habitats, but the relative contribution of each process may vary from habitat to habitat. In fast-flowing waters, fine organic sediments, such as those produced by the deposition and decay of particulate matter and of plant and animal tissue, may be rare because they are continually flushed from the system. In such waters, there is little opportunity for a contaminated surface layer of sediment to develop and rooted plants are often scarce. Thus, the benthic-detrital components of the system and the associated food pathways play a smaller role in the selenium cycle in flowing waters than in standing water habitats, such as wetlands or reservoirs.

Perhaps the aquatic systems that accumulate selenium most efficiently are shallow with standing or slow moving waters that have low flushing rates. In these systems, biological productivity is often high and selenium may be trapped through immobilization processes or through direct uptake by organisms. Sediments build up a selenium load that can be remobilized gradually, yet continually, through detrital and planktonic food. These habitats are also some of the most important feeding and breeding habitats for fish and wildlife, especially waterfowl and shorebirds.

Several habitat types often occur together in one aquatic system. For example, rivers may have fast flowing waters, slow moving pools, and standing backwater areas all within a few hundred meters. The degree of fish and wildlife exposure to selenium will vary among habitats according to intensity of use, type of use, and the relative contributions of the various processes that regulate selenium cycling. Assessment of selenium contamination must consider variation among habitat types. Assessment of toxicological risk must consider how individual species utilize different habitats, as well as the role of the physical environment in the selenium cycle.

TOXICOLOGICAL IMPLICATIONS

Bioaccumulation

Perhaps the most important factor in selenium cycling and toxicity in aquatic systems is the ability of aquatic organisms to accumulate this element to concentrations one or more orders of magnitude greater than water or food sources. This extensive bioaccumulation may result because selenium is chemically similar to sulfur and because it is an essential micronutrient. Where fish have experienced chronic toxicity, selenium in the water has been concentrated from 100 to over 30,000 times depending on the species and tissue sampled. Selenium accumulation by organisms consumed by fish and wildlife is the major pathway leading to toxicity in most cases.

Biomagnification of selenium (the accumulation of progressively higher concentrations by successive trophic levels of a food chain) usually ranges from 2–6 times between the producer (algae and plants) and lower consumer (invertebrates and forage fish) levels. For example, fish eating contaminated plankton or benthic invertebrates may contain 4 times the selenium concentration in their diet which could contain 500 times the selenium concentration in the water. The total bioconcentration factor for the fish would be 2000 (4×500); the food chain biomagnification factor would be 4. These relationships are important in natural systems because they can cause top-level consumers, such as predatory fish, birds, and mammals, to receive toxic selenium levels in the diet even though the concentration in water is low. Moreover, the risk of toxicity through the detrital food pathway will continue despite a loss of selenium from the water column as long as contaminated sediments are present.

Residues and Toxicity

Toxic effects of selenium fall into two categories: (1) mortality of juveniles and adults, and (2) reproductive effects. Reproductive failure, whether through effects on the adult ovary or on the embryonic development and survival of young, may be the first obvious biological symptom of a selenium contamination problem. Complete reproductive failure can occur with little or no tissue pathology or mortality in the adult population. Selenium concentrates in bird and fish eggs and is passed to the developing embryo where it may cause death or developmental malformations. Reproductive failure accompanied by deformities in embryos and young signals possible selenium toxicity.

Field and laboratory data suggest that selenium at greater than 2–5 µg/L (parts per billion) in water can be bioconcentrated in food chains and cause toxicity and reproductive failure in fish. About 10 mg/kg (parts per million, dry weight) of selenium (as selenomethionine) of diet caused adverse reproductive effects when fed to mallards. Three to eight mg/kg in food items represent contamination which could cause toxic effects in fish and wildlife. Further guidelines for assessing potential selenium toxicity are given in tables 1 and 2. These guidelines should be applied with caution because the actual concentrations of selenium that are toxic may be enhanced or diminished by several other factors or other contaminants in the system. Selenium may interact with several metals which can alter the expression of biological effects. Moreover, several factors including temperature, nutrition, disease, differences in species sensitivity, differences in the relative toxicity of the various chemical forms of selenium, and other environmental stresses may affect the actual concentration of selenium that produces toxicosis.

ECOSYSTEM RECOVERY

Immobilization and mobilization processes occur simultaneously in aquatic systems, and the physical and biological characteristics of the environment including season, climate, and habitat determine which process dominates at any given time. Continuous inputs of selenium at relatively constant levels generally result in an equilibrium in which the two groups of processes become more or less offsetting and selenium continues to cycle. When inputs stop, four processes operate to permanently remove selenium from the system and gradually reduce the residual contamination: (1) movement of selenium-contaminated organisms out of the system, such as with the emigration of fish and wildlife or the emergence of aquatic insects, (2) release of volatile selenium from plants and the water directly into the atmosphere, (3) removal by sediment and water transport (flushing) and groundwater seepage, and (4) burial by the process of sedimentation.

The rate at which an ecosystem recovers from selenium contamination depends on such factors as the degree of contamination, habitat type, annual productivity, flushing rates, and climate. The time necessary for these natural processes to lower selenium concentrations to non-toxic levels in specific habitats can presently not be estimated accurately. However, field evidence suggests that such time intervals may range from several years to several decades. In general, recovery will be much slower in shallow impoundments and wetlands than in fast flowing rivers and streams.

Because of its propensity to bioaccumulate, to move from sediments to biota, and to produce severe adverse reproductive effects as well as adult mortality, selenium should be recognized as a contaminant with the potential to markedly impact fish and wildlife populations.

ACKNOWLEDGMENTS

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Table 1. Concentrations of selenium known to be hazardous to fish and wildlife

Source	Concentration µg/L (water) or µg/g dry wt (mean)	Exposure setting duration, and test conditions	Species and life stage	Toxic effect	Tissue residue	Reference
Water[a]	1100	Laboratory, 48 days, flow-through. Hardness = 330 mg/L.	Fathead minnow, <u>Pimephales</u> <u>promelas</u>, larvae	50% mortality	--	Adams, 1976.
Water[a]	400	Laboratory, 48 days, flow-through. Hardness = 330 mg/L.	Bluegill, <u>Lepomis</u> <u>macrochirus</u>, larvae	50% mortality	--	Adams, 1976.
Water[a]	500	Laboratory, 48 days, flow-through. Hardness = 330 mg/L.	Rainbow trout, <u>Salmo</u> <u>gairdneri</u>, larvae	50% mortality	--	Adams, 1976.
Water[a]	160	Laboratory, 48 days, flow-through. Hardness = 330 mg/L.	Coho salmon, <u>Oncorhynchus</u> <u>kisutch</u>, larvae	50% mortality	--	Adams, 1976.
Water[a]	30-170 (80)	Laboratory, 60 days, flow-through. Hardness = 28 mg/L, temperature = 11°C.	Rainbow trout, eggs	Significant number of deformities	--	Goettl and Davies, 1976.
Water[a]	30-170 (80)	Laboratory, 12 months, flow-through. Hardness = 28 mg/L, temperature 11°C.	Rainbow trout, eggs	Significant mortality	--	Goettl and Davies, 1976.
Water[a]	47	Laboratory, 90 days, flow-through. Hardness = 272 mg/L, temperature = 12°C.	Rainbow trout, sac fry	Significant mortality	Whole body =1.07 µg/g wet wt (survivors).	Hunn and others, 1977.
Water[a]	28	Laboratory, post-fertilization through hatching, flow-through. Hardness = 135 mg/L, temperature = 0°C.	Rainbow trout, eyed eggs	Significantly reduced hatching	--	Hodson and others, 1980.
Water[a]	17	Laboratory, 30 days, flow-through. Hardness = 371 mg/L, temperature = 12°C, sulfate - 200 mg/L.	Chinook salmon, <u>Oncorhynchus</u> <u>tshawytscha</u>, fry	Significant mortality	--	Hamilton and others, 1986.
Water[b]	90	Laboratory, post-fertilization through 60 days post-hatch, flow-through. Temperature = 20-26°C, salinity = 3.5-5.5 °/oo.	Striped bass, <u>Morone</u> <u>saxatilis</u>, 24-hr post-fertilization eggs	Significant number of deformities	--	Klauda, 1986.

Source	Concentration µg/L (water) or µg/g dry wt (mean)	Exposure setting duration, and test conditions	Species and life stage	Toxic effect	Tissue residue	Reference
Diet[a]	8.9	Laboratory, 42 weeks, flow-through. Hardness = 28 mg/L, Temperature = 11°C.	Rainbow trout, juveniles	Significant mortality	--	Goettl and Davies, 1978.
Diet[c]	13	Laboratory, 6 weeks, flow-through, 3% body wt per day feeding. Hardness = 74 mg/L, temperature = 10°C.	Chinook salmon, parr	Reduced smolting success	Whole body= 2.9 µg/g wet wt, 13.4 µg/g dry wt. (survivors).	Hamilton and others, 1986.
Diet[c]	54	Laboratory, 44 days, flow-through, satiation feeding temperature=21°C.	Bluegill, juveniles	75% mortality	Skeletal muscle= 5.0-7 µg/g wet wt; liver = 8-86 µg/g wet wt.	Finley, 1985.
Diet[c]	45	Laboratory, 7 days, flow-through, satiation feeding; Hardness=18 mg/L, sulfate= 5.7 mg/L, temperature=25°C.	Bluegill, juveniles	100% mortality	Whole body = 21-32 µg/g dry wt.	Carolina Power and Light Co., 1984.
Diet[c]	25-70	Laboratory, 61 days, flow-through, satiation feeding; Hardness=19 mg/L, sulfate= 5.4 mg/L, temperature=25°C.	Bluegill, juveniles	100% mortality	Whole body = 44-53 µg/g dry wt.	Carolina Power and Light Co., 1985.
Water[d] and diet[c]	8.9-12 µg/L (10) 21-73 µg/g	Field (reservoir), 14 days; Alkalinity = 26 mg/L, temperature = 26°C.	Bluegill, juveniles	100% mortality	Muscle = 13.1-17.5 µg/g dry wt; viscera=27.5-37.5 µg/g dry wt.	Duke Power Co., 1980.
Water[d] and diet[c]	5-22 µg/L (10) 15-70 µg/g	Field (reservoir), 2 years. Alkalinity = 20-38 mg/L, sulfate = 5.5-17.1 mg/L.	All life stages of centrarchids, percichthyids, ictalurids, cyprinids, percids, clupeids, catostomids.	Mortality and deformity of fry, juveniles and adults; total reproductive failure.	Skeletal muscle= 3.2-22.3 µg/g wet wt; viscera minus gonad) = 13-52.4 µg/g wet wt; ovary = 5.2-41.7 µg/g wet wt; testis = 15-22.8 wet wt. (survivors).	Cumbie and Van Horn, 1978; Lemly, 1985a.
Water[e] and diet[c]	8-12 µg/L (10) 25-45 µg/g	Field (reservoir), 2 years, alkalinity = 20 mg/L avg, sulfate = 27 mg/L avg.	Bluegill, adults exposed in the field and spawned in the laboratory.	Mortality and deformity of larvae; total reproductive failure.	Carcass (minus gonad) = 5.9-7.8 µg/g wet wt ovary = 6.9-7.2 µg/g wet wt (38-54 µg/g dry wt); testis = 4.3 µg/g wet wt.	Gillespie and Baumann, 1986.

Table 1. Concentrations of selenium known to be hazardous to fish and wildlife—Continued

Source	Concentration µg/L (water) or µg/g dry wt (mean)	Exposure setting duration, and test conditions	Species and life stage	Toxic effect	Tissue residue	Reference
Diet	10[h]	Reproductive study	Mallard, <u>Anas platyrhynchos</u> adults received treated diets.	Productivity and duckling survival reduced.	Concentrations in eggs ranged from 2.9 to 5.6 µg/g (wet wt) and wet wt concentration ranges in adult male and female livers were 6.1 to 12.0 µg/g and 2.6 to 6.2 µg/g, respectively (use 71% moisture for conversion to dry wt).	Heinz and others, 1987.

[a] In the form of selenite.

[b] In the form of selenate.

[c] Selenium source was food organisms from selenium-contaminated habitats.

[d] Measured as total recoverable selenium in filtered (0.45 µm) samples.

[e] In the form of selenite (57%), selenate (34%), and selenide (9%).

[f] In the form of selenomethionine.

[g] Converted from 13.6 µg/g wet weight assuming 75% moisture. Formula for converting wet weight to dry weight:

$$\text{Dry weight conconcentration} = \frac{\text{wet weight concentration}}{1 - \%\text{ moisure of sample}}.$$

[h] Fresh weight, diet contained about 10% moisture.

Table 2. Selenium levels of concern for fish and wildlife

Source or tissue residue	Concentration (µg/L for water or µg/g dry weight)	Affected group	Suspected toxic effect	Reference
Water	> 2-5	Fish and waterfowl	Reproductive failure and/or mortality due to food-chain bioconcentration	Heinz and others, 1987; Lemly, 1985a, 1985b.
Sediment	≥4	Fish and waterfowl	do.	Duke Power Co., 1980; Finley, 1985; Garrett and Inman, 1984.
Food	≥5	Fish	do.	Cumbie and Van Horn, 1978; Lemly, 1987.
	≥3	Waterfowl	do.	Heinz and others, 1987.
Whole body[a] residue	≥12	Fish	Reproductive failure	Gillespie and Bauman, 1986; Lemly, 1985a.
Visceral residue[a]	≥16	Fish	do.	do.
Skeletal muscle residue[a]	≥8	Fish	do.	do.
Egg	≥15-20[b]	Waterfowl (Mallard)	Teratogenesis or embryo mortality	Heinz and others, 1987.

[a] Approximate conversion factors for fish:
Whole body to muscle = whole body x 0.6
Vicera (liver or female gonad) to muscle = Viscera x 0.25
Vicera to whole body = Viscera x 0.33.

[b] Converted from a mean wet weight concentration of 4.6 µg/g using a 71% moisture content.

Note: The 85th percentile whole-body concentration of selenium in fish tissues measured in the National Contaminant Biomonitoring Program was 0.82, 0.70, and 0.71 µg/g wet weight for the years 1976-77, 1978-79, and 1980-81, respectively.

Formula for converting wet weight to dry weight:

$$\text{Dry weight concentration} = \frac{\text{wet weight concentration.}}{1\text{-\% moisture of sample}}$$

CHAPTER E

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

H.F. Mayland, L.P. Gough, and K.C. Stewart

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FIGURES

TABLES

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

By H.F. Mayland, L.P. Gough, *and* K.C. Stewart

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 selenoglutathione, 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: $SeO_4^{2-} > H_2SeO_3^{2-} > SeO_3^{2-} > Se^o$. 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

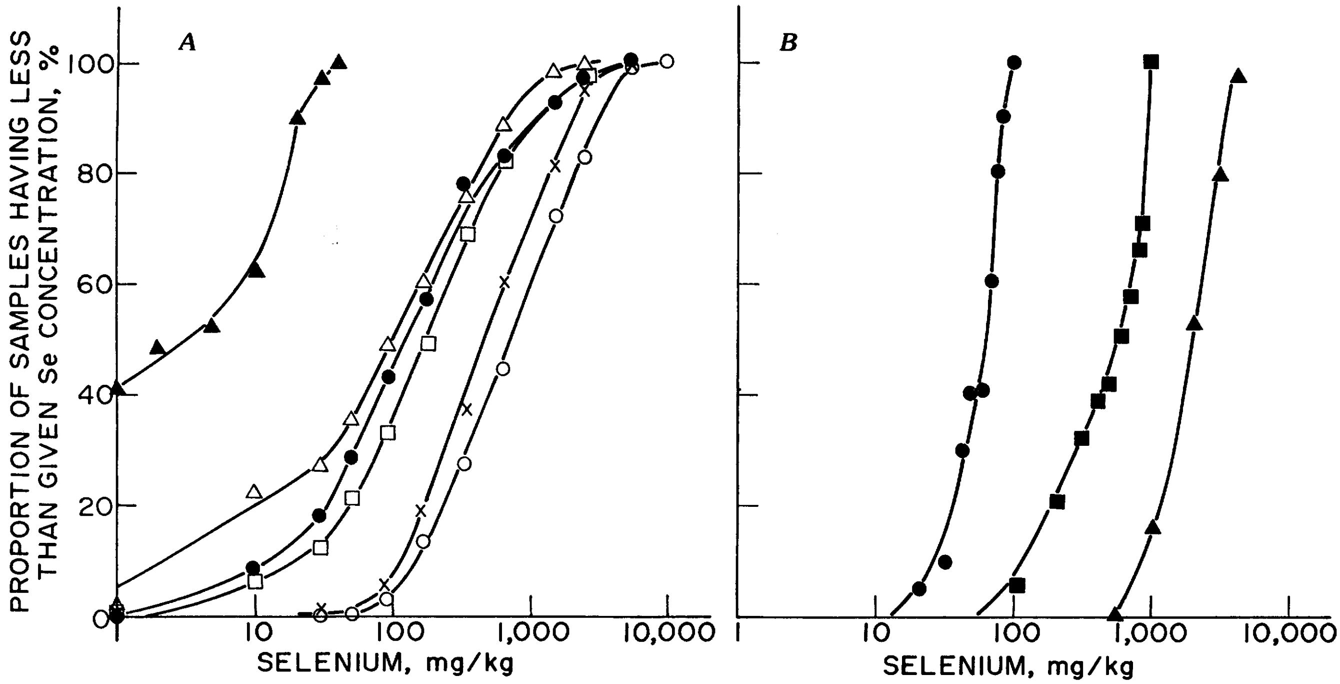


Figure 1 . Proportion of samples having less than given selenium concentration (Printed with permission of American Society of Agronomy). *A*, From left to right; Data for western wheatgrass (*Pascopyrum smithii*) plus Sandberg bluegrass (*Poa secunda*) sampled from seleniferous areas of Montana and 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]

	Study 1 Short term Corn Se source		Study 2 Long term[1]	
Fraction	SeO_3	SeO_4	Barley grain	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

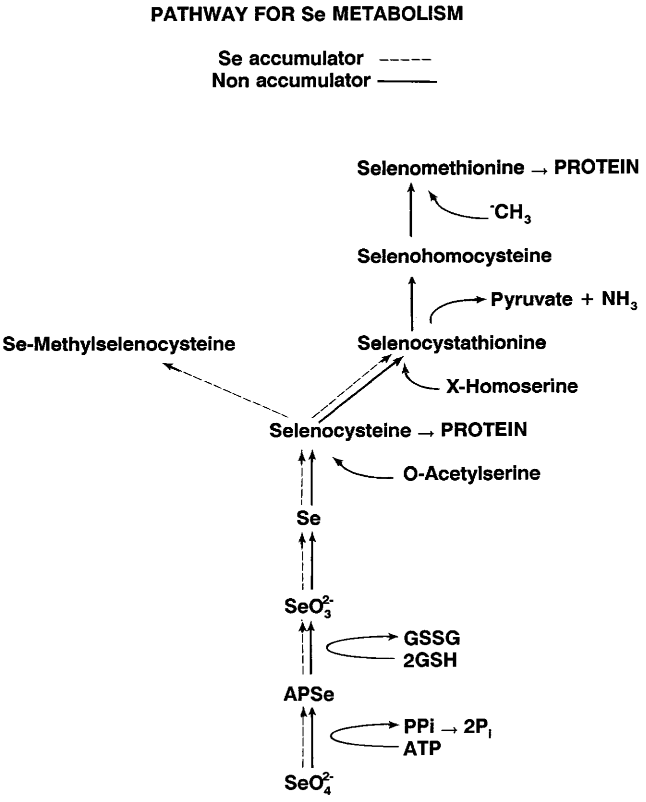
[1] For barley grain in Study 1; values are means of application method (soil or foliar) and selenium source (selenite, selenate). For ryegrass grown in two separate studies; values are means of application method (soil or foliar), source (selenite, selenate), and three cuttings (2 and 3 of Study 1 and 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.

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.



Burnell, 1981

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

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.

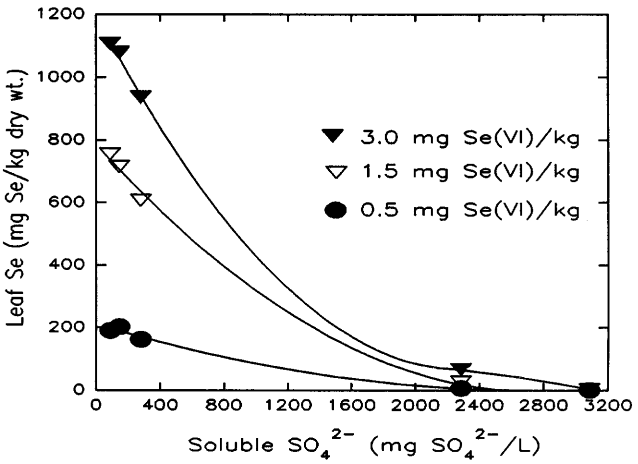


Figure 3. The effect of soluble sulfate in soil on selenate-selenium accumulation by alfalfa (*Medicago sativa*) shoots at three concentrations of added selenate (adapted from Wan and others, 1988).

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 $SeO_4 > H_2SeO_3 > SeO_3 > Se°$. 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).

CHAPTER F

AB-DTPA Extractable Soil Selenium as a Predictor of Seleniferous Vegetation

R.A. Prodgers and F.F. Munshower

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By R.A. Prodgers *and* F.F. Munshower

ABSTRACT

Twenty-nine soils were sampled near Lysite and Chalk Bluff, Wyoming, where livestock mortalities have resulted from toxic (presumably seleniferous) forage. Ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA) was used to extract selenium from each soil horizon. Samples of foliage associated with these soils were collected. Plant species were assigned to one of three groups based on selenium concentrations. Relationships between extractable soil selenium and plant tissue selenium were statistically evaluated using linear regressions and analyses of variance. For each group of plant species, plant tissue selenium was regressed on each of five estimates of extractable soil selenium. The five estimates were extractable soil selenium concentrations for (as many as three) half-meter depth increments, average extractable selenium for the soil profile, and highest selenium concentration from any horizon in each profile.

Near Lysite, where extractable soil selenium concentrations were rather low, significant soil/plant relationships were calculated for common, nonindicator species. The regression equation indicated that an extractable soil selenium concentrations of 0.06–0.07 μg Se/g soil (weighted average for the soil profile) would result in a plant tissue selenium concentration of 5 μg Se/g tissue, commonly considered to be a minimum toxic level. At Chalk Bluff, where soil selenium concentrations were much higher, significant soil/plant relationships were found for selenium accumulator species, but not for nonaccumulators. However, nonaccumulator plant species had revealed an average selenium concentration of 27.6 μg/g plant tissue; the average soil concentration was 0.78 μg Se/g.

INTRODUCTION

Mining has contributed to seleniferous soils and plants (Rosenfeld and Beath, 1964). A direct relationship between extractable soil selenium and selenium concentrations in plants would be useful to evaluate the potential of mine soils to produce toxic seleniferous vegetation. Toxic seleniferous forage is defined as plant tissue with more than 5 μg Se/g dry tissue (National Research Council, 1976; Levander, 1986). Selenium in soils is commonly extracted using hot water or AB-DTPA. These two extractants removed similar amounts of selenium from Mollisols, but AB-DTPA extracted about 1.5 times more selenium than hot water from mine soils and overburden materials (Soltanpour and Workman, 1980).

An AB-DTPA extractable soil selenium concentration of 0.1 μg/g was associated with toxic alfalfa forage in a greenhouse study. The authors (Soltanpour and Workman, 1980) treated the soils with sodium selenate. In natural environments, the pattern is less clear. Jump and Sabey (1985) found a significant relationship between extractable soil selenium and the concentration of selenium in *Sarcobatus vermiculatus* leaves, but their data for *Elymus smithii* grown in a greenhouse on naturally seleniferous soils did not demonstrate a significant linear relationship. One soil with 0.08 μg/g AB-DTPA extractable selenium produced plants with an average of 2.0 μg Se/g tissue, while another soil with the same concentration of extractable selenium produced plants with 8.5 μg Se/g tissue. To further complicate the pattern, a soil with 0.84 μg Se/g produced grass foliage containing only 1.5 μg Se/g tissue.

The field study reported in this report investigated the relationship between AB-DTPA extractable soil selenium and plant tissue selenium for range species grouped by their proclivity to accumulate selenium. That is, plant species were grouped as selenium accumulators, intermediate selenium accumulators, and nonaccumulators.

METHODS

Twenty-nine soil pits were subjectively located in two seleniferous areas of Wyoming. Sample locations were selected to include a variety of plant communities and topoedaphic sites. Sixteen soils were sampled near Lysite in Fremont County (Sections 27 and 34, T. 40 N., R. 91 W.), and 13 soils were sampled near Chalk Bluff in Albany County (Section 7, T. 21 N., R. 74 W.). About 1 kilogram of soil was collected from each recognizable horizon down to lithic or paralithic material, in some cases over 1.5 meters deep. Approximately 23 cm of the terminal shoot from grasses and forbs and nonwoody new growth from shrubs were collected. Flowers and stems over 2 mm in diameter were excluded from plant tissue samples used to determine foliar selenium concentrations.

AB-DTPA was used to extract soil selenium (Soltanpour and Schwab, 1977, as modified by Soltanpour and Workman, 1979). Extracts were analyzed by atomic absorption spectroscopy after generation of selenium hydride (H_2Se). The detection limit was 0.004 μg Se/g soil, and the value 0.003 μg/g was used in statistical analysis for concentrations below the detection limit.

Foliage samples were totally digested in a mixture of nitric and perchloric acids (Behan and Kincaide, 1970). A second plant tissue sample of equal weight at field moisture content was dried at 70°C and weighed to estimate the oven-dry weight of tissue. Digestates were analyzed by atomic adsorption spectroscopy after generation of H_2Se. The detection limit was 0.1 μg/g, and all plant samples revealed selenium concentrations above the detection limit.

Some plant species were sampled at several soil pits. Sufficient data were not available to derive individual soil/plant selenium analyses for each species. Because of the highly variable ability of different plant species to accumulate selenium from a given soil, plant species were assigned to one of three groups. Group I selenium accumulators exhibited concentrations of more than 500 μg Se/g dry weight. Group II species revealed selenium concentrations from 100 to 500 μg/g tissue. Group III plants are nonaccumulators and revealed selenium levels below 100 μg/g. These three groups are roughly analogous to the accumulator and nonaccumulator species group of Beath (Trelease and Beath, 1949).

The actual amount of selenium in a given plant tissue reflects two major factors: selenium available to the plant and the accumulating proclivity of that plant. To emphasize the plant's contribution or ability to accumulate selenium, only selenium concentrations above the median value for each species were averaged to determine selenium concentration values used to assign each species to one of the three groups. Tissue samples collected in May, July, and Aμgust were used to provide a large data base for assigning species to groups. Owing to limited sampling and the chance that a species may have been sampled only on nonseleniferous soils, some species may have been assigned to a lower concentration group than might be warranted by more extensive sampling of plants on seleniferous soils.

Plant tissue selenium concentrations were regressed separately on each of five estimates of soil selenium. The five estimates were as follows: (1) weighted average selenium for the entire profile, (2) weighted mean selenium for the 0–50 cm increment, (3) the 51–100 cm increment, (4) the 101–150 cm increment, and (5) highest extractable selenium concentration in any horizon in the profile. For a depth increment to be statistically evaluated relative to plant selenium concentrations, more than 25 cm of that 50 cm interval must have been identified in the field as a soil horizon and sampled. Average selenium concentrations for each profile were calculated using every identified horizon. Only plant tissue samples collected in July were used for statistical analysis, so season of collection was not a variable. Using analysis of variance, the regression residual (that is, all factors other than extractable soil selenium) was partitioned into site-to-site and plant-to-plant components. If the site-to-site residual was greater than the plant-to-plant residual, the F-ratio was computed using site-to-site mean squares in the denominator. If the plant-to-plant residual was greater than the site-to-site residual, the average residual (regression residual) was used to compute the F-ratio. Only results significant at $P > 0.025$ have been reported.

RESULTS

Plant Species Groups

Six species were selenium accumulators and placed in Group I. Above-median plant selenium concentrations for these species averaged more than 500 μg/g tissue. Species in Group I include *Aster adscendens, Astragalus bisulcatus, A. grayi, A. pectinatus, Castilleja linariifolia,* and *Haplopappus wardii* (Nomenclature follows Dorn, 1988). The highest concentration in a plant sampled for this study was an *Astragalus bisulcatus* specimen collected in May that contained 12,000 μg Se/g tissue. However, only plant samples collected in July were used for statistical analysis.

The five species in Group II had above-median average selenium concentrations of several hundred micrograms per gram of plant tissue, but one sample of *Atriplex gardneri* tissue collected in July at Chalk Bluff contained over 1,000 μg Se/g tissue. Two species, *Stanleya pinnata* and *Xylorhiza glabriuscula*, may be indicative of available soil selenium, but the other three species in this group—*Atriplex gardneri, Gutierrezia sarothrae* and *Haplopappus nuttallii*—are widely distributed across the Great Plains.

Group III species typically did not accumulate more than 60 μg Se/g plant tissue on any soil sampled. This group includes many common range and revegetation species of the western Great Plains and intermountain valleys: *Elymus trachycaulus, E. lanceolatus, E. smithii, E. spicatus, Artemisia pedatifida, A. tridentata, Astragalus kentrophyta,* another unidentified *Astragalus, Carex filifolia, Krascheninnikovia lanata, Cirsium undulatum, Chrysothamnus nauseosus, C. viscidiflorus, Comandra umbellata, Distichlis spicata, Eriogonum brevicaule, Glycyrrhiza lepidota,*

Table 1. Comparison of AB-DTPA extractable soil selenium concentrations at Chalk Bluff and Lysite study areas

[µg/g oven dry wt]

Extractable soil selenium	Chalk Bluff area	Lysite area
Average in soil profile[1]----	0.78 (N=13)	0.05 (N=16)
Highest in soil profile-----	2.41 (N=13)	0.09 (N=16)
Average in upper 50 cm soil[1]	0.13 (N=13)	0.03 (N=16)
Average in 51-100 cm soil[1]--	0.92 (N=10)	0.07 (N=12)
Average in 101-150 cm soil[1]--	1.01 (N=5)	0.02 (N=3)

[1] Values are weighted averages based on selenium concentrations in each horizon.

Gutierrezia sarothrae, Haplopappus multicaulis, Linum lewisii, Oryzopsis hymenoides, Phlox muscoides, Psoralea lanceolata, Stipa viridula, and *Tetradymia canescens.*

Predicting Plant Tissue Selenium Using Soil Selenium

Each species group exhibited different relationships (or no relationship) between AB-DTPA extractable soil selenium and plant selenium concentrations. Results were not consistent from Lysite to Chalk Bluff, probably because of the order-of-magnitude difference in extractable soil selenium at the two sites (Table 1). The average selenium content of plant groups sampled at the two sites are compared in Table 2.

Chalk Bluff

At Chalk Bluff, extractable soil selenium was not linearly related ($P > 0.025$) to nonaccumulator plant tissue selenium. The lack of predictive ability for Group III plants at Chalk Bluff indicates that AB-DTPA extractable soil selenium data alone are insufficient to predict the foliar content of common range and revegetation plant species when average extractable soil selenium concentrations are high (0.1–5 µg Se/g soil).

It is possible that as extractable soil selenium concentrations reach and exceed some threshold level, nonaccumulator plants selectively discriminate against further absorption and transport, or at least any linear pattern of increased uptake with increased availability being disrupted. It is also possible that other soil factors in addition to AB-DTPA extractable soil selenium influence plant uptake enough to confound a simple availability/uptake model.

Accumulator and intermediate accumulator species selenium contents were significantly related to average soil selenium and highest extractable soil selenium from any horizon in a profile at this site. Group I species' selenium concentrations were also related to extractable selenium in the 51–100 cm depth interval. Accumulator species appear to increase selenium absorption and transport as availability

Table 2. Average plant tissue selenium concentrations at Chalk Bluff and Lysite for each species group

[µg/g dry wt]

Species group	Chalk Bluff area	Lysite area
Group I------	2620 (N=18)	405 (N=13)
Group II-----	294 (N=18)	79 (N=5)
Group III----	27.6 (N=64)	2.9 (N=24)

Table 3. Summary of significant ($P < 0.025$) analyses of variance and linear regressions relating plant tissue selenium to AB-DTPA extractable soil selenium

Site/ group	Extractable selenium	r^2	Regression equation[1]
Chalk Bluff/ Group I	51-100 cm	0.41	Y=1835 + 834X
Chalk Bluff/ Group I	Average	.40	Y=1811 + 758X
Chalk Bluff/ Group I	Highest	.40	Y=1853 + 232X
Chalk Bluff/ Group II	Average	.30	Y=162 + 29.4X
Chalk Bluff/ Group II	Highest	.30	Y=166 + 26.0X
Lysite/ Group I	51-100 cm	.89	Y=41.8 + 6464X
Lysite/ Group III	Upper 50 cm	.79	Y=1.01 + 97.4X
Lysite/ Group III	51-100 cm	.83	Y=1.59 + 36.6X
Lysite/ Group III	Average	.81	Y=1.08 + 59.3X
Lysite/ Group III	Highest	.73	Y=0.97 + 33.2X

[1] X = AB-DTPA extractable soil selenium in µg Se/g soil.

increases throughout the range of extractable soil selenium concentrations at Chalk Bluff. Group I and II species also appear capable of extracting selenium from anywhere in the soil profile, given adequate root contact.

Extractable soil selenium never accounted for more than half of the selenium in Group I or Group II species (table 3). Plant-to-plant variance was high compared to site-to-site variance for these species. The plant-to-plant residuals associated with Group II species was greater than the site-to-site residual. This suggests that species-specific relationships would give better predictions of plant selenium concentrations.

On the basis of an average extractable soil selenium concentration of 1.3 µg/g, which is typical for soils on which accumulator and intermediate accumulator species were found at Chalk Bluff, the equations in table 3 predict plant selenium concentrations in Group II species of 200 µg/g and in Group I species of 2,800 µg/g. Other significant regression equations are presented in table 3. Predictions based on regression equations are most properly applied to values for independent variables within the range of values used to calculate the regressions.

Lysite

Results at Lysite differed greatly from Chalk Bluff. Soils in each area developed from different parent materials under varied combinations of soil forming factors. Soil and plant selenium concentrations were much lower at Lysite than at Chalk Bluff (tables 1 and 2).

At Lysite, nonaccumulator species selenium concentrations exhibited significant relationships with AB-DTPA extractable soil selenium in the 0–50 cm and 51–100 cm depth increments, average soil selenium and highest concentration of selenium in any horizon. In many cases, selenium content of most or all of these soil categories was near the detection limit.

On the basis of the regression equations in table 3, extractable soil selenium values at Lysite that predict approximately 5 µg Se/g foliage in Group III plants are 0.04 µg Se/g soil for the upper 50 cm, 0.09 µg Se/g soil for the 51–100 cm interval, and 0.07 µg Se/g soil average for the profile. The AB-DTPA extracted concentration of 0.07 µg Se/g soil, weighted average for the profile is slightly less than the value tentatively suggested by Soltanpour and Workman (1980) as the level associated with toxic forage.

Insufficient data for Group II species prevented evaluation of soil/plant relationships. Only one statistically significant regression equation was identified for Group I species: extractable soil selenium in the 51–100 cm depth interval (table 3). An average extractable soil selenium concentration of 0.07 μg Se/g soil is associated with 490 μg Se/g plant tissue for accumulator species.

DISCUSSION AND SUMMARY

The most significant relationships between extractable soil selenium and plant selenium are for nonaccumulator species at Lysite, where soil selenium concentrations are typically low. Extractable soil selenium concentrations below 0.1 μg Se/g soil are associated with plant tissue concentrations above the threshold toxic level of 5 μg Se/g foliage. The intercept values are low, but the slope of the regression equations are rather steep, so small increases in extractable soil selenium are associated with rather large increases in foliar selenium. These relationships may be of interest when evaluating allowable soil selenium concentrations in the rooting media of plants in reclaimed landscapes.

One apparent anomaly in table 3 warrants further elaboration because it illustrates limitations that should be observed when applying the results of regression equations. Table 3 contains two very different equations for accumulator species wherein the foliar concentration of accumulator species is related to extractable soil selenium in the 51–100 cm depth interval. One equation was derived from data at Lysite, the other from data at Chalk Bluff.

At Lysite, the intercept value is low (41.8) and the slope of the regression equation is very steep ($Y = 41.8 + 6464X$). Obviously, this equation is not valid for a soil selenium concentration of 4 μg Se/g soil, for it would predict a foliar concentration in accumulator species of 26,000 μg Se/g foliage. The actual soil selenium concentrations used in the 51–100 cm depth regression calculation ranged from the detection limit (<0.004 μg Se/g soil) to 0.076 μg Se/g soil. This tight range of selenium concentrations helps explain the high predictive value of the regression equation ($r^2 = 0.89$). However, this equation should be used only for soils with <0.1 μg Se/g soil. In other words, it should be used for soil selenium concentrations similar to those used in the regression calculation.

At Chalk Bluff, the intercept for accumulator species (1835) for the 51–100 cm soil depth is quite high. This equation ($Y = 1835 + 834X$) is obviously inappropriate for soil selenium concentrations near zero. The soil selenium concentrations upon which this equation is based ranged from 0.024 to 5.17 μg/g soil, with an average concentration of 1.06 μg Se/g soil. This equation is obviously more appropriate for soil selenium concentrations of 0.1 to 3 μg Se/g soil than for concentrations below 0.1 μg or above 5 μg Se/g soil. With only eight soil samples and the large observed range in soil selenium concentrations, one would anticipate poor predictive ability from the regression equation, and the r^2 value of 0.41 indicates that this is the case.

Taken together, the two equations suggest that selenium uptake in accumulator species increases very rapidly with increased availability when soil selenium concentrations are low. At higher soil selenium concentrations, accumulator species continue to utilize additional available selenium, but at a slower rate. However, sufficient data from this study were not available to statistically evaluate this trend.

The reader is advised that table 1 should be consulted and similarities or differences noted between those soil selenium concentrations and soil selenium concentrations the reader may wish to use in the regression equations reported in table 3. Even if concentrations are similar, other soil properties may modify the relationship between soil selenium and foliar selenium reported here.

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CHAPTER G

Selenium Poisoning in Livestock

L.F. James, H.F. Mayland, and K.E. Panter

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Selenium Poisoning in Livestock

By L.F. James, H.F. Mayland, and K.E. Panter

ABSTRACT

Selenium in certain soils may be taken up by plants in amounts sufficient to make forage toxic to animals. Seleniferous forage can be found in semiarid areas on soils typically derived from Cretaceous geologic material in the Western United States and Canada. Intoxication of livestock by seleniferous plants has been classified as acute or chronic. Acute poisoning results from consuming plants containing high selenium concentrations. Chronic selenium poisoning has been described in two forms: alkali disease and blind staggers. Alkali disease results from prolonged ingestion of plants containing 5–40 ppm selenium in inorganic or organic forms. Alkali disease causes loss of hair, lameness, weight loss and probably reduces reproductive efficiency. Blind staggers is said to result from the consumption of selenium indicator plants. These plants, in contrast to the nonaccumulators, contain selenium in water soluble, nonprotein forms. Blind staggers causes animals to wander, walk in circles, and to have difficulty in swallowing; in addition, it may cause blindness. Information is presented that questions the attribution of blind staggers to selenium toxicosis.

INTRODUCTION

Selenium has long been recognized as being toxic to animals. Marco Polo had probably seen selenium poisoning during his travels through western China, circa 1295 (Lantham, 1958). He described a condition where his horses' hooves dropped off after grazing certain plants of the region. Polo's travels took him through an area of northwest China which recently has been identified as containing high to excessive soil selenium levels (Jian-An and others, 1987). The area is bounded by 36° and 45° North latitude and 75° and 107° East longitude.

In 1560, Father Pedro Simon of Columbia described a condition in livestock and humans which today is recognized as selenium poisoning (Simon, 1953). A marked loss of hair and sloughing of the hooves of cavalry horses were described by United States Army physician Dr. T.C. Madison (1860). He was stationed at Fort Randall on the Missouri River near the South Dakota and Nebraska State line. Settlers in this and adjacent areas in the northern Great Plains observed similar symptoms in their livestock. These people called the condition 'alkali disease' because of its association with alkaline seeps. It is possible that many of these seeps were used as watering sources for the animals.

The seriousness of alkali disease stimulated initiation of research by the late 1920's to determine the cause of the problem. In the early 1930's, H.G. Knight of the United States Department of Agriculture Bureau of Chemistry and Soil suggested that selenium was the cause of alkali disease (Anderson and others, 1961). Later, high concentrations of selenium were found in some small grains grown in the area. Proof was soon obtained that selenium was the cause of alkali disease. It was also shown that certain plants accumulated selenium in relatively large concentrations. Selenium toxicosis occurred when animals consumed these plants.

During the following 15 years, intensive research was conducted by the Agricultural Experiment Stations in Wyoming and South Dakota and by the United States Department of Agriculture and U.S. Geological Survey. They described the factors governing its occurrence in soil, accumulation in plants, and toxic effects on animals. Excellent reviews of this early research are given by Anderson and others, (1961), Rosenfeld and Beath (1964), Zingaro and Cooper (1974), National Research Council (1976), Moxon and Rhian (1943), and Moxon (1937).

Selenium in Soil

The Earth's surface contains an average of 0.1 ppm selenium. Some soils contain less and some considerably more. Soil selenium concentration varies over short distances. Some soils contain selenium in amounts and forms available to plants, causing them to be toxic to animals. Selenate is the most soluble inorganic form, while selenite is less soluble. Each is readily absorbed by plants. Selenium is also present as elemental selenium or as iron selenide in certain unweathered rocks, but these forms are highly insoluble and are not absorbed by plants.

Soils containing high levels of available selenium are usually alkaline and usually receive less than 50 cm annual precipitation. The soluble selenium may be found in lower portions of the profile, where it is only available to deeply rooted perennial forbs and shrubs. Reviews of selenium in soils have been prepared by Anderson and others (1961), National Research Council (1976), Sharma and Singh (1983), and Jacobs (1989).

Selenium in Plants

Selenium is readily absorbed by all members of the plant kingdom (Anderson and others, 1961). However, in this report we are primarily concerned with plants that accumulate selenium at levels toxic to animals. Plants, even of the same species, may differ in their selenium concentration because of differences in available soil selenium, interfering anions at the soil-root interface, root absorption, translocation from roots to tops, and dilution in the plant tops.

Plants have been divided into three groups, based upon their selenium-accumulating ability (Rosenfeld and Beath, 1964; National Research Council, 1976).

1. Primary selenium-accumulator or indicator plants may contain up to several thousand parts per million selenium. This group includes species of the genera *Astragalus*, *Machaeranthera* (section *Xylorrhiza*), *Haplopappus* (section *Oonopsis*), and *Stanleya*. Selenium accumulated by these plants is largely water soluble and in the form of low molecular weight organic compounds and selenate (National Research Council, 1983). The selenium is not incorporated into protein.
2. Secondary selenium absorbers may contain up to several hundred parts per million selenium, but lesser amounts are much more common. This group includes species of the genera *Aster*, *Atriplex*, *Castilleja*, *Comandra*, *Gyria*, *Grindelia*, *Gutierrezia*, *Machaeranthera*, and *Mentzelia*. As in the first group, selenium appears primarily as water soluble selenate with smaller amounts of low molecular organic forms.
3. The nonaccumulator group includes grasses, small grains, and alfalfa. Selenium absorbed by these plants is metabolized into plant proteins. These plants rarely accumulate more than 50 ppm selenium and usually only 5–12 ppm. The majority of selenium intoxications probably result from the grazing of plants in this category.

These groupings are somewhat arbitrary because some plants appear in more than one group. There is, however, greater tendency for plants in group 1 or 2 to accumulate a much higher level of selenium than those in group 2 or 3.

The toxicity of selenium-accumulating plants cannot be evaluated solely on the basis of the total selenium concentration. Various selenium compounds are likely to exhibit different intensities of toxicosis to animals. Also, plants, such as *Astragalus* and *Happlopappus*, contain other nonseleniferous constituents that may be toxic to animals.

SELENIUM IN LIVESTOCK

Selenium Deficiency

Selenium has long been recognized as a mineral toxic to animals, but only recently has it been shown to be a nutritional requirement. Selenium was reported essential for animal health in 1957, nearly three decades after its implication with alkali disease and animal death (Schwartz and Foltz, 1957). Selenium deficiency (Combs and Combs, 1986) has been implicated in retained placenta in cattle, persistent diarrhea in young calves, and white muscle disease in young calves and lambs. Deficiency can cause exudative diathesis, nutritional muscular dystrophy, and nutritional pancreatic dystrophy in poultry. Hepatoses dietetica, mulberry heart disease, nutritional muscular dystrophy, and infertility may occur in ewes not receiving enough selenium.

Selenium concentrations required in the diet range from 0.05 to 0.10 ppm, depending on availability to the animal. Dietary sulfur has been shown to compete with selenium absorption, both by the plant and the animal. The interaction of selenium and vitamin E in animal metabolism is discussed by Combs and Combs (1986).

Selenium Intoxication

Toxicosis occurs when an animal's diet contains more than 3–8 ppm selenium (National Research Council, 1980). The actual concentration may vary between and within animal species. Some individuals may be conditioned to tolerate higher levels of selenium than others (Lynn James and others, unpubl. data, 1989). The concentration in forage plants leading to animal toxicosis is thus only 30–160 times that required for adequate nutrition. This window is not as narrow as that for copper toxicosis/essentiality which is less than 10 for sheep (National Research Council, 1980). Much work has been done to determine the geographical distribution (mapping) of selenium deficiency or excesses (R. W. Welch, E. E. Cary, W. H. Alloway, and J. Kubota, unpubl. data).

All animals, including man, are susceptible to selenium poisoning (National Research Council, 1980; Combs and Combs, 1986). However, poisoning occurs most frequently in animals grazing seleniferous forages. Although much emphasis has been placed on plants that accumulate selenium in thousands of parts per million, we believe that most selenium poisonings result from grazing plants containing 5–20 ppm selenium. Consumption of seleniferous grains can cause poisoning in poultry and swine. According to Rosenfeld and Beath (1964), selenium is one of the few elements absorbed by plants in sufficient concentrations to create a toxicity hazard to foraging animals.

Rosenfeld and Beath (1964) provided a widely accepted classification of selenium intoxications in livestock. The classification is as follows:

1. Acute intoxication
2. Chronic intoxication
    a. Alkali disease
    b. Blind staggers.

Acute Selenium Poisoning

Acute selenium poisoning often results from short-term foraging of highly seleniferous plants such as the indicator plants (Rosenfeld and Beath, 1964). This occurs principally when animals are very hungry and ingest seleniferous plants of low palatability but with high levels of selenium. Poisoning in cattle, horses, and swine is characterized by an abnormal posture, unsteady gait, diarrhea, abdominal pain, increased pulse and respiratory rate, prostration, and death. Sheep do not show signs of selenium poisoning as distinctly as do other species of domestic animals. Often all that will be seen in sheep is depression and sudden death.

Cattle at the Poisonous Plant Research Laboratory fed a high dose of seleniferous *Astragalus* plants over several days quite suddenly started bellowing with a high-pitched voice as if distressed, became excited, increased their respiratory rate, became prostrate and died (Lynn James, unpubl. data, 1982–86). Swine fed a selenium deficient diet are later more susceptible to acute intoxication than normal pigs.

Gross pathological changes include petechial hemorrhages in the endocardium, acute congestion and diffuse hemorrhages in the lungs, enteritis and passive congestion in the liver. Acute congestion of the endocardium occurs. The lungs evidence congestion and hemorrhaging in the alveoli. The mucosa of the stomach and intestine manifest edema, hemorrhage, and necrosis. The signs of poisoning in sheep are primarily increased respiration and sudden death. The gross and microscopic lesions reflect the marked congestion and edema of the lungs.

Chronic Intoxication

Chronic selenium poisoning has been divided into two syndromes—alkali disease and blind staggers. This separation is based on the type of forage eaten (Rosenfeld and Beath, 1964). Alkali disease, which has been described in cattle, swine, and horses, is associated with the consumption of seleniferous forages (Group 2 and 3 plants) like hay, grain, grasses, and palatable forbs for days, weeks, or even months. In these forages, the selenium is largely incorporated into the protein and is not water soluble. Blind staggers has been described in cattle, and possibly sheep, and is associated with the consumption of selenium indicator plants over days or weeks. Selenium in these plants is largely water soluble.

Alkali Disease

The condition, described as alkali disease by T.C. Madison in 1857, is now recognized as a type of chronic selenium poisoning. This disorder, according to Rosenfeld and Beath (1964), results from the consumption of seleniferous grasses, grains, and forbs that contain 5–40 ppm selenium. The forage is usually consumed over a period of weeks or more. Alkali disease has been produced by feeding inorganic sodium selenate and sodium selenite (Moxon, 1937; Hartley and others, 1985). Alkali disease is characterized by dullness, lack of vitality, emaciation, rough hair coat, loss of hair (especially the long hair of mane or tail), and lameness. Cattle, horses, and swine all develop alkali disease when fed seleniferous feeds. Sheep do not respond in the same manner, they neither lose wool nor develop hoof lesions.

Reduced reproductive performance could be the most significant effect of chronic selenium poisoning (Olson, 1978; Ort and Latshaw, 1978; Wahlstom and Olson, 1959). It apparently occurs at levels of dietary selenium lower than that required to produce typical signs of alkali disease. Adverse effects on animal reproduction may occur at forage selenium levels less than 2 ppm (National Research Council, 1976). Additional verification is needed on the effects of selenium on reproduction. Alkali disease may be the principle chronic manifestation of selenium poisoning.

Blind Staggers

According to Rosenfeld and Beath (1964), blind staggers results from grazing moderate amounts of indicator plants over a period of days or weeks. Selenium in these plants is readily extractable in water. Blind staggers has been observed in cattle and sheep but not in horses, swine, or poultry.

In cattle, blind staggers appears in three stages. In the first or early stage the animal may demonstrate impaired vision, disregards objects in its path, and stumbles over them or walks into them. The body temperature and respiration are normal, but the animal has little interest in eating or drinking. The clinical signs intensify as the animal enters phase 2. The front legs weaken, failing to support the animal. The animal becomes anorectic.

During phase 3, the tongue and mechanism for swallowing become partially or totally paralyzed. The animal is nearly blind. Respiration becomes labored and rapid. Abdominal pain is apparent. The body temperature drops below normal. The cornea becomes cloudy, and death may come suddenly. The animal dies of respiratory failure.

Often, a loss of weight occurs during the process so the animal appears emaciated. Cattle may show no outward sign of poisoning but suddenly develop severe clinical signs and die within a few days. Beath reported that this has been known to occur in cattle shipped to feed lots for fattening (Beath, 1982). Recovery only occurs during phases 1 and 2.

In sheep, the blind staggers form of chronic selenium poisoning is not easily diagnosed, and the three stages are not distinct. However, the pathological lesions are the same in sheep as in cattle (Rosenfeld and Beath, 1964).

Microscopic changes, as described in blind staggers, include necrosis and cirrhosis of the liver, nephritis, and impaction of the digestive tract (Rosenfeld and Beath, 1964). Nothing is known of neurological changes even though neurological aberrations are indicated by the signs of poisoning.

Blind staggers, while presently attributed to selenosis, may be a disease of unknown etiology in which selenium may or may not be involved.

Is Blind Staggers a Misnomer?

Some question exists as to whether blind staggers as described by Rosenfeld and Beath is a condition associated with selenium intoxication (National Research Council, 1976; James and others, 1983; Jensen and others, 1956). Alkali disease may be the principle chronic manifestation of selenium poisoning; whereas, "blind staggers" may be a disease condition of unknown etiology in which selenium may or may not be involved.

This section includes several quotations illustrating the confused descriptions of selenium-induced blind staggers. The reader should be aware that blind staggers has never been experimentally produced using selenium compounds.

Beath claimed to have induced blind staggers in cattle by feeding selenium-containing plants. These plants may have contained other toxins in addition to selenium. This work has not been verified (National Research Council, 1976). Beath described a treatment for blind staggers as follows:

> TREATMENT—In the treatment of a type case of blind staggers some success can be expected by following this schedule. First of all, one should not allow a time lag to develop after the first suggestion of illness is noticed. Drenching with copious amounts of lukewarm water is an important step to take. This should be followed with foodstuffs, such as corn syrup (glucose), along with baby calf feed. When the digestive tract has been cleared, an animal should be offered some green, succulent forage. In the meantime, it is advisable to inject a small amount of strychnine to stimulate certain body functions. One of the accompanying disorders in this malady is an impaction of the fourth stomach. The use of laxatives should be considered advisedly so as not to bring on excessive irritation. Recovery is slow in most cases; but, when the animal regains its normal appetite and can find its way around, one can consider the illness arrested.

There would seem to be little justification for this treatment for simple selenium toxicosis. However, the treatment is very appropriate for cases of impaction of the digestive tract.

Tansy mustard (*Descurainia pinnata*) causes a condition in New Mexico that is very similar to so-called selenium-induced blind staggers (Hershey, 1945). The syndrome was called woody tongue, paralyzed tongue, or blind staggers. Kingsbury (1964) summarized the tansy mustard condition as follows:

> POISONOUS PRINCIPLE—unknown. Despite similarity of the symptoms with those produced in one type of selenium poisoning, tansy mustard's selenium content is insufficient to produce the disease.
> TOXICITY, SYMPTOMS, AND LESIONS—Continued ingestion of large quantities of this plant over a relatively long period of time is required before symptoms appear. In cattle on range the symptom first observed is partial or complete blindness. This is followed by, or accompanied with, inability to use the tongue or to swallow. the disease is popularly termed "paralyzed tongue." Because of blindness, animals may wander aimlessly until exhausted, or stand pushing against a solid object in their path for hours. Because of inability to swallow, animals may be observed standing at water unable to drink, or unsuccessfully cropping forage. Animals become thinner and weaker, and death will eventuate if treatment is not undertaken. Treatment is simple and effective. It consists of administering 2 to 3 gallons (7.6 to 11.4 liters) of water (with nourishment such as cotton seed meal in it if the animals are seriously weak) twice daily by stomach tube. This gets the digestive system functioning again and symptoms gradually disappear.

Treatment by Southwestern ranchers and veterinarians for tansy mustard poisoning is the same as that recommended by Beath (1982) for treatment of blind staggers. Hershey (1945) suggested that elements other than selenium may also be involved in the blind staggers described by Beath (1982).

Jensen and others (1956) reported a polioencephalomalacia in pasture and feedlot cattle in Colorado, which was not associated with seleniferous forage. The problem was clinically identical to blind staggers as described by Rosenfeld and Beath (1964). Jensen and others (1956) noted that:

> Polioencephalomalacia, a noninfectious disease of pasture and feedlot cattle and sheep, is characterized by multiple foci of necrosis in the cerebral cortex. In Colorado, the disease is known as "forage poisoning." In Wyoming, where the disease has been studied extensively, it is known as "blind staggers" and (is said) results from selenium poisoning. The clinical syndromes of the disease in Colorado and Wyoming are identical. The cause of the disease in cattle and sheep of Wyoming has not been reported. Although it is assumed that blind staggers reported from Wyoming and forage poisoning reported from Colorado are a single entity, the appellation polioencephalomalacia is appropriate until the etiological and pathological factors are clearly established.

Beath (1982, p. 20–22) in an apparent response to Jensen's report (Jensen and others, 1956) wrote:

> The action of the poison may be delayed, so that several weeks or several months may elapse before the attack occurs. Cattle may show no outward sign of poisoning until severe symptoms develop suddenly, with death following within a few days. This has been known to occur after cattle have been shipped to a feedlot and are being fattened for the market. Diagnosis would obviously be impossible by one not familiar with this type of delayed poisoning.
>
> QUESTIONABLE INTERPRETATIONS— Some investigators think of blind staggers as a form of arrowgrass poisoning. Others merely refer to it as a kind of forage poisoning***Perhaps such an experiment should be undertaken to either prove or disprove the role of arrowgrass as a forage capable of inducing a chronic form of injury to cattle. The term forage poisoning is so all inclusive that any abnormal behavior, of an animal might come under this classification.

This response did not account for Jensen's observations nor was any justification given for assuming that the delayed action response was selenium related.

Kochia (*Kochia scoparia*) weed poisoning in cattle has been shown to produce a condition characterized by progressive central nervous system dysfunction, blindness, gastrointestinal disorders, and jaundice (Dickie and Berryman, 1979; Dickie and James, 1983). Post-mortem findings included edema of the brain, fatty, cirrhotic, and enlarged livers, gastrointestinal inflammation, and rumen impaction. In addition, polioencephalomalacia has also been associated with kochia poisoning. High sulfate drinking water is thought to aggravate kochia poisoning (Dickie and James, 1983).

High sulfate water is also a potential cause of polioencephalomalacia or blind staggers syndrome (Raisbeck, 1982). The work of Sadler and others (1983) supports that hypothesis. Blind staggers has been repeatedly noted in cattle drinking water from wells or saline seeps in Montana. These saline waters may contain high concentrations of magnesium sulfate (L.F. James, and H.F. Mayland, unpubl. data, 1987). The hypothesis is that ingestion, by ruminants, of large amounts of sulfur, either in the forage or water, results in sulfur reduction by specific rumen flora (Coleman, 1960) to hydrogen sulfide. The H_2S escapes to the oral cavity. The toxic gas is then absorbed by the respiratory system, causing symptoms similar, in many respects, to those of blind staggers (National Research Council, 1980).

Blind staggers was produced experimentally by feeding indicator plants to animals but not by administering pure selenium compounds (Rosenfeld and Beath, 1964). The presence of toxins, in addition to the selenium in the indicator plants, may have been involved in the intoxication (National Research Council, 1976). For example, two-grooved milkvetch (*A. bisulcatus*) contains swainsonine, which is the toxin in locoweeds (James and others, 1983). Broom snakeweed (*Gutierrezia* spp.) contains various organic toxins (Kingsbury, 1964). Rosenfeld and Beath (1964) erroneously indicated that selenium was the only toxin present in *A. bisulcatus.*

Hartley and others (1985) fed swine various sources of selenium including sodium selenite, sodium selenate, *A. bisulcatus*, *A. praelongus*, and seleniferous wheat (*Triticum aestivum*) to test the hypothesis that accumulator plants produced one type of intoxication (blind staggers) and nonaccumulators produced another (alkali disease). They concluded that selenium in experimental diets was responsible for the poisoning that occurred in swine. Feeding swine different sources of either organic or inorganic selenium produced similar selenium toxicoses. This is contrary to Rosenfeld and Beath (1964) who said "It is well known that alkali disease or hoof injury occurs when selenium is in the organic form." "Blind staggers occurs in connection with indicator plants which contain some inorganic selenium compounds and some in the organic form" (Maag and Glenn, 1967).

Maag and others (1960) fed sodium selenite to steers. The animals did not develop signs of alkali disease, blind staggers, or forage poisoning, although 2 of 8 steers fed the selenite developed microscopic lesions of polioencephalomalacia.

CONCLUSIONS

Alkali disease, a chronic selenium poisoning, has been produced by feeding inorganic selenium compounds or seleniferous plants. Alkali disease seems to be the principal manifestation of selenium intoxication.

Blind staggers describes various disease conditions. It has not been reproduced by feeding selenium compounds, and it is highly questionable if it has been produced using selenium-accumulating plants. Conditions resembling blind staggers include forage poisoning in Colorado, tansy mustard poisoning in the Southwest, and kochia poisoning. High sulfate in water and feed should also be added to the list of potential causes of so-called blind staggers.

CHAPTER H

Selenium Research at the South Dakota Agricultural Experiment Station

Ivan S. Palmer and Oscar E. Olson

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TABLES

Selenium Research at the South Dakota Agricultural Experiment Station

By Ivan S. Palmer *and* Oscar E. Olson

ABSTRACT

A brief historical review of some of the contributions to selenium research by the South Dakota Agricultural Experiment Station (Chemistry Department) is presented. A more detailed description of the research conducted in the last decade is given. The research areas reported include 1) the development and comparison of analytical methods; 2) the determination of the selenium content of regional foods and feeds and the estimation of selenium intakes; 3) the determination of the forms of selenium in plants; 4) the study of the relationship between soluble soil selenium and plant selenium content. Some previously unpublished data are given.

INTRODUCTION

In reporting the selenium research in progress in South Dakota, a general historical review will be given, followed by a more detailed report concerning the areas currently under study.

There has been a selenium project in our Experiment Station since the 1930's. Depending on the interests of the personnel and the nature of concurrent problems, this area of research has resulted in varying amounts of productivity. However, some significant contributions have been made.

In the 1930's, Franke (1934) was one of the workers who demonstrated that selenium was the toxic principle that caused "alkali disease". Moxon (1938) demonstrated that arsenic could partially protect against the toxic symptoms of selenium toxicity. In a study of the effects of various protein sources, he found that flax provided some protection against selenium toxicity in experimental animals (Moxon, 1941). In the late 1930's and the 1940's, several workers were involved in mapping the selenium-bearing strata in the western part of the State (Moxon and others, 1939). During this period, several studies were performed to elucidate the mechanism of selenium toxicity.

In the 1950's, workers, such as Bonhorst, Halverson, Kamstra, Olson and Whitehead carried out a variety of basic studies. These included documentation of signs of selenium toxicity from studies on a seleniferous ranch (Dinkel and others, 1957), studies on the mechanism of the protective action of arsenic (Kamstra and Bonhorst, 1953), further characterization of the protective principle in flax (Halverson and others, 1955), studies on the distribution of the element in experimental animals (Palmer and Bonhorst, 1957) and the demonstration of antagonisms between selenium and various other anions besides arsenite and arsenate (Bonhorst, 1955; Bonhorst and Palmer, 1957).

Near the end of the 60's decade, continuous work on an analytical method by Olson led to the acceptance of a fluorometric method as an official AOAC method for the determination of selenium in plants (Olson, 1969). A urinary metabolite, trimethylselenonium ion, was also successfully isolated and identified (Palmer and others, 1969) simultaneously with workers at the University of Wisconsin. This was really only the second well characterized metabolite of selenium found in animal tissues at that time.

The most rewarding accomplishment in the 1971–1980 period was the completion of the isolation and identification of the protective substances in flax. They were shown to be the cyanogenic glycosides, linustatin, and neolinustatin (Palmer and others, 1980; Smith and others, 1980). Further studies showed that the protective action was apparently the result of the release of cyanide from the glycosides and the subsequent reaction with endogenous selenium to form selenocyanate. This hypothesis was supported by the observation that cyanide itself showed protection against selenium when administered orally or by injection (Palmer and Olson, 1979). Other studies in this time period established the toxicities of various selenium compounds (Palmer and others, 1973), investigated forms of selenium in wheat protein (Olson and others, 1970), demonstrated the potentiation of the toxicity of methylated selenium derivatives by arsenic (Obermeyer and others, 1971), demonstrated methylation of selenium by bacteria (Hwang, 1977), and modified the fluorometric method of analysis (Olson and others, 1975). These studies present a representative overview of the research conducted at the South Dakota Agricultural Experiment Station from 1930 to 1980.

CURRENT RESEARCH

The work we have been involved with in the last decade is what I want to report in more detail. For purposes of this discussion the research will be organized into four areas: (1) the development and comparison of analytical methods; (2) the determination of the selenium content in regional foods and feeds and estimation of selenium intakes; (3) the determination of the forms of selenium in plants; (4) the study of the relationship between soluble soil selenium and plant selenium content.

Analytical Methodology

The method of choice in the South Dakota work has been the fluorometric method developed by Olson and others (1975) and modified according to the conditions described by Koh and Benson (1983). The method involves the digestion of all samples in a nitric acid-perchloric acid system. The normal acid ratio is 1:1 or 4:1 depending on the amount of organic material. The digestion is carried out in 20× 150 mm Pyrex tubes that are placed in a 12 inch× 12 inch aluminum block containing 80 sample holes. This arrangement allows for two batches of 40 tubes to be digested. Each batch contains at least two blanks, three standards, and two to three reference materials. The block is gradually raised in temperature to 210°C and maintained at this temperature for 10 minutes (a total of 2 hours). The block is then cooled to 110–130°C and 0.5 mL of concentrated HCl is added to each tube. The reduction step is allowed to proceed for 30 minutes. To each tube is added 15 mL of 0.01M EDTA and 2 mL 0.1 2,3-diaminonaphthalene. The tubes are mixed on a vortex mixer and incubated in a 60°C water bath for 30 minutes. After cooling, 5 mL of cyclohexane are added, and the tubes capped with Teflon-lined caps. Each rack of 40 tubes is mixed in a rotating device for 5 minutes to extract the selenium complex. The cyclohexane is withdrawn and read in a automated fluorometer with excitation wavelength at 375 nm and emission wavelength at 550 nm.

The method has a detection limit of 4–8 nanograms and a coefficient of variation (CV) of 5% at the 50 ng level. It has been found suitable for water, plant tissue, animal tissue, feedstuffs, premixes, and various other sample matrices. Soil is the one sample matrix that seems to have an interfering substance(s). The interfering substances apparently can be removed by pretreatment of the digest by cation exchange chromatography.

The fluorometric method has been compared with a continuous hydride generation atomic absorption method (HGAA). For the HGAA method, digestion and reduction procedures are identical to those used for the fluorometric method. After reduction, the samples are diluted to 20 mL with 1:1 HCl, and the selenium determined with a Varian Spectr20 Atomic Absorption Spectrometer.

In a collaborative study we have recently gathered the comparative data shown in table 1 on three types of sample matrices. The two methods agree quite well on all three types of samples. It should be noted that in this study the soil digests were subjected to cation exchange treatment prior to fluorometric analysis while the HGAA analyses were performed directly on the digests. Other work and preliminary results with these samples indicated that the lack of ion exchange treatment of the soil with low selenium content would result in very low values by the fluorometric procedure. Spike recoveries as determined by fluorometry are also very low when ion exchange treatment was not included. Soils with high selenium content do not always show this phenomenon, since their digests are diluted to provide the appropriate selenium concentration and the interference is apparently diluted to an ineffective level. In this study, the ratios of the results obtained by the two methods are very close to 1.0 with only a few exceptions. In another more extensive study involving a greater variety and number of samples, Olson has found that HGAA results are more typically 5 higher than those obtained by fluorometry (unpublished results).

In summary, the fluorometric and HGAA methods give very similar results on a wide variety of samples (assuming digestion is by a HNO_3+$HClO_4$ mixture). We still prefer the fluorometric procedure in our laboratory because of the availability of perchloric acid-handling facilities, stability of instrumentation, linearity of standard curve, and the fact that the highly corrosive 1:1 HCl solutions, necessary for HGAA, are not required. Laboratories with different designs and equipment may reach a different conclusion.

Selenium Content of Regional Foods and the Effect of Processing

The fluorometric method of selenium analysis has been applied to the analysis of a great variety of foods purchased in local markets. Many of the data have been reported and compared to studies made in Washington, D.C., Ohio, and Canada (Olson and Palmer, 1984). The selenium content of fruits, vegetables, fish, and cereal products were very similar for all regions. There is no doubt that the similarities resulted from our system of processing and distribution of these items. In the case of meats and dairy products, there is a greater possibility of local production and processing; therefore, these products may

Table 1. Comparison of selenium analysis by fluorometry and HGAA on a variety of sample matrices

Sample		Se content[a]		Ratio
		Fluorometry	HGAA	Fluor/HGAA
		Values given in µg/g		
Vegetation	1	2.99 ± 0.10	2.80 ± 0.13	1.06
	2	2.78 ± 0.02	2.84 ± 0.06	0.98
	3	2.72 ± 0.03	3.58 ± 0.01	0.76
	4	25.5 ± 0.10	24.6 ± 3.0	1.04
	5	22.6 ± 0.4	23.1 ± 0.4	0.98
	6	25.6 ± 0.3	22.3 ± 0.4	1.15
Spike Recovery[b]		96.4% ± 1.4	102.2% ± 1.4	
Soil[c]	1	1.12 ± 0.10	1.08 ± 0.03	1.04
	2	2.86 ± 0.22	3.25 ± 0.01	0.88
	3	3.05 ± 0.05	3.58 ± 0.01	0.85
	4	46.7 ± 0.1	45.2 ± 4.6	1.03
	5	39.8 ± 0.6	41.1 ± 1.1	0.97
	6	21.8 ± 0.7	22.3 ± 0.1	0.98
Spike Recovery[b]		87.9% ± 11.4	91.9% ± 10.0	
		Values given in ng/mL		
Water	1	5.7 ± 0.3	5.1 ± 0.4	1.12
	2	0.36 ± 0.32	0.34 ± 0.50	1.06
	3	5.3 ± 0.2	6.3 ± 0.6	0.84
	4	108.0 ± 1.5	105.0 ± 2.5	1.03
	5	106.0 ± 1.0	103.0 ± 8.0	1.03
	6	113.0 ± 3.0	120.0 ± 6.0	0.94
Spike Recovery		100.3% ± 4.2	102.1% ± 2.8	

[a] Values are means of 3 replicates ± SD.

[b] Samples were spiked with selenate at a level similar to the original content.

[c] Values for fluorometry were obtained after pretreatment of the digest by cation exchange chromatography.

show a difference in selenium content depending on the selenium status of the production area. This can be demonstrated by comparing the selenium contents of the common items analyzed in the studies previously mentioned. The South Dakota study analyzed 36 items in common with the Washington study, 60 items in common with the Canadian study, and 36 items in common with the Ohio study. The mean selenium content of the South Dakota items in comparison with the other sites were 0.294 versus 0.236, 0.231 versus 0.297, and 0.235 versus 0.149, respectively. These data show there can be regional differences in selenium intake.

Of interest relative to the analysis of selenium and the estimation of intake is the possibility of losses of the element due to heat drying or cooking. Olson has conducted a study on various grains or plant tissues to determine the effect of heat drying. Samples with at least 10 ppm selenium were chosen to facilitate the study. The data are shown in table 2.

The data show that at a high temperature, such as 250°C, a high loss of selenium occurs. The samples were severely charred at this temperature; experience with wet digesting samples has indicated that charring should be avoided to minimize loss of selenium. The *Astragalus* species, which are selenium accumulator plants, showed considerable loss of selenium at all temperatures except the lowest. Cereal grains and alfalfa showed only a small loss at 105°. Since this is a common temperature for drying in the laboratory, in is unlikely that routine drying will reduce the selenium content of usual types of foods and feeds.

Table 2. Selenium loss from plant materials as related to drying temperature

Plant material	Original Se content (μg/g)	Percent of Se lost while heating at the following temperatures for 22 hr (°C)[a]				
		75	105	130	155	250
Oats grain----	10.5		0.2^{0}			71.5^{4}
Wheat grain---	15.5		2.6^{0}		15.0^{3}	74.2^{4}
Corn grain----	25.9		0.6^{0}		9.3^{3}	77.0^{4}
Alfalfa hay---	18.1		3.0^{0}		21.0^{2}	77.0^{4}
Astragalus bis.	641	0.0	11.2^{1}	22.6^{2}	47.0^{3}	92.2^{4}
Astragalus rac.	1510	4.9	17.4^{1}	43.9^{2}	60.8^{3}	96.4^{4}

[a] The superscripts represent the degree of charring, 0 = none, 4 = very black.

Also of concern to nutritionists is whether or not cooking processes modify the selenium content of foods. To study this, representative portions of various foods were analyzed for selenium. Duplicate portions were then cooked in the normal fashion. After the cooking process, samples were weighed, analyzed for selenium and the selenium content corrected for the loss in moisture (weight). The data are shown in table 3.

The data indicate that conventional methods od cooking do not result in the loss of selenium. Cooking results in a loss of moisture and therefore the content of selenium in cooked food is higher than the original item. Correcting for the weight loss during cooking gave selenium content values essentially identical to the original content. The major exception occurred when boiling was the method of cooking and the water was discarded (see spaghetti). Analysis of the water used for boiling accounted for the lost selenium. Except when cooking methods are used that involve large amounts of water that are later discarded, it appears that the measurement of the original selenium content of uncooked food is a reasonable measure of selenium intake of ingested food.

Forms of Selenium in Plants

Much work has been done in determining bioavailability of various forms of selenium. The common approach has been to feed every source of interest to some experimental animal and measure the intake and excretion. Another approach is to examine the form of selenium in the feed/food and then make estimates of availability from the specific form.

Previous work by Olson and others (1970) on the form of selenium in wheat gluten, showed that 55.7% of the total selenium was found as selenomethionine (Se-met), and the remainder of the selenium was unidentified. Lee (1986)

Table 3. Effect of cooking on the selenium content of some foods

Food	Method of cooking	No. of trials	Se content μg/g Original	Se content μg/g After cooking	Percent of original
Bread------	Toasted	3	0.25	0.24	96
Spaghetti--	Boiled 8 min. liquid discarded	5	0.59	0.47[a]	80
Spaghetti--	Boiled 8 min. liquid retained	3	0.64	0.64	100
Oat meal---	Brought to boil in 4X weight of H_2O	3	0.25	0.24	96
Fish-------	Fried sticks	5	0.14	0.14	100
Ground beef	Fried, well done	4	0.28	0.27	97
Bacon------	Fried to crisp	7	0.21	0.19	92
Pork-------	Fried, well done sausage	5	0.23	0.24	104
Beef liver-	Fried well	4	0.64	0.63	98
Eggs-------	Scrambled	3	0.32	0.33	103

[a] Significantly different ($P < 0.05$) than uncooked food by "*t*" test.

reevaluated this work and examined the form of selenium in high-selenium yeast used in making human supplements. She derivatized selenocysteine (Se-cys) before hydrolysis by converting it to the carboxymethyl derivative, a technique used by others in identifying Se-cys as a component of glutathione peroxidase (Forstrom and others, 1978). Lee (1986) found that in wheat gluten, 52.8 + 10.6% of the total selenium was present as Se-met, confirming the work of Olson and others (1970). In addition, 24.8 + 1.4% was present as Se-cys. In high-selenium yeast, 68.4 + 9.2% of the total selenium was accounted for by Se-met, and 7.00 + 0.8% was present as Se-cys. In these food sources, at least 75% of the selenium was present as the common selenium-amino acids. Olson has compiled other data (unpublished results) which indicate that 30–50% of the selenium in the vegetative parts of plants may be selenate. This is consistent with the earlier work by Hamilton and Beath (1964).

The information now available appears to indicate that the bioavailability of selenium in most foods and feeds could be estimated from the relative content of Se-met, Se-cys, and selenate. An obvious exception to this generalization would be the selenium-accumulator plants which contain other unusual forms of selenium (Shrift and Virupaksha, 1965).

Relationship of Soluble Soil Selenium and Plant Content

Over many years great interest has been maintained in determining the relationship between soil selenium content and selenium content of plants grown on the soil. This is of major importance in predicting problem areas which occur naturally and in assessing the potential impact of reclamation activities in certain areas. There remains some difference of opinion as to whether total selenium or soluble selenium is the most important factor.

Byers (1936) suggested that selenate probably accounted for the greatest amount of selenium taken up by plants. This form is easily leached, therefore, as Olson and others (1942a) pointed out, it was important to consider the soluble selenium in the second and third foot of soil. It has been difficult to obtain definitive field data relative to the actual level of soil selenium that will produce toxic vegetation. In 1985, our laboratory attempted to gather this type of information.

A study was made on a ranch in southwestern South Dakota that was known to have selenium problems. Soil cores were collected at 25 locations and divided into various horizons. Samples of western wheatgrass were collected as close to the soil core site as possible. The soil horizon samples were analyzed for total selenium and soluble selenium as extracted by 0.1M $CaCl_2$. The specific data will not be shown, but no clear correlations could be obtained. Plants ranged in selenium concentration from 1.1 to 23.9 ppm. Total soil selenium ranged from 1.0 to 28 ppm, and soluble selenium ranged from 0.01 to 19 ppm depending on the horizon. In sites where total selenium was elevated, generally all horizons were found to have elevated levels; whereas, soluble selenium sometimes was only elevated in the deeper horizons. It was concluded that when soluble selenium averaged at least 0.1 ppm within the top 3 feet, the plants growing on the site would usually contain elevated selenium levels. There were exceptions to this generalization in that plant selenium levels were not elevated on sites that appeared to contain >0.1 ppm soluble soil selenium. On the other hand, an instance was observed where plants contained 20.3 ppm selenium while the soil contained 0.13 ppm selenium in the first 13 cm and <0.04 ppm in the lower horizons. The conclusions reached from this study, which included well-planned sampling, was that the best estimate of potential selenium toxicity problems would be obtained by extensive mapping of plant selenium content. Analysis of total selenium content of soil will give an estimate of potential trouble areas and further determination of soluble selenium will refine the estimate. However, the only reliable indication of areas that produce toxicity in animals will be obtained by plant analysis.

We have more recently conducted a study that provides information as to the relationship of soil selenium and plant selenium content. The original objective of the study was to evaluate the availability of elemental selenium to plants. It constituted the research for a M.S. Thesis (Tseng, 1988).

A local soil composite that was a sandy clay loam texture (30% clay, pH = 6.4) was mixed with sand (2:1). This mixture was amended with an "elemental Se" preparation produced by precipitating selenium in the presence of a silicic acid slurry. The soil was amended at levels of 0, 5 and 10 ppm Se, and 18.2 kg were added to each of 10 trays (18 in. ×13.5 in. ×4 in.) for each selenium level. The trays contained no drainage openings and so watering was carefully controlled. Three rows of wheat seeds were planted with the seeds spaced 1.5 in. The trays were arranged randomly in three rows on an outside cement patio. When 50% of the plants were in the boot stage (42 days), two rows from each pot were clipped and analyzed for selenium. The remaining plants were grown to maturity (12 weeks). The grain and straw were separated and analyzed for selenium. Total and soluble soil selenium were determined at the beginning and termination of the experiment. The results are shown in table 4.

The surprising observation from this study was the availability of selenium from the "elemental Se" preparation that was added to the soil. This will have to be discussed at another time. It is evident that the soluble soil selenium increased over the 12-week experimental period. The

Table 4. Selenium content of wheat grown on soil amended with elemental Se

Total Se applied to soil (ppm)		Se content (ppm)				
		Soluble soil Se		Wheat plants[a]		
Theory	Actual	Initial	Final	Fresh tissue	Grain	Straw
0	0.20	0.006	0.014	0.068	0.38	0.30
5	5.23	0.017	0.08	1.54	13.0	9.63
10	11.40	0.023	0.17	3.77	27.0	23.0

[a] Selenium content of fresh tissue was on the as received basis (71-77% moisture). Selenium content of the other material is on dry weight basis.

increase was essentially proportional to the original level of amendment. Furthermore, regardless of whether one considers the fresh tissue, grain or straw, the selenium content of the plants increases in proportion to the soluble soil selenium. This would seem to indicate soluble soil selenium should be a reasonable predictor of plant selenium content. The data also show that soluble soil selenium levels of 0.1 ppm are capable of producing vegetation with a selenium content higher than what one observes in the field. It should be noted that leaching was not possible in the experimental trays and so all selenium remained in the root zone as it became available.

When these results are compared with the field studies, it becomes apparent that the conditions existing in the natural environment are considerably more complicated than they appear to be in a closed system (tray). These data support the conclusion given earlier, that the best estimations of potential selenium toxicity problems in the field are obtained from the determination of the selenium content of plants grown in the area.

FUTURE STUDIES

Although the direction of any Agricultural Experiment Station research program is somewhat subject to the needs of the clientele served, it is our intent to continue studies in the following areas:

1. To further evaluate the apparent high availability of the "elemental Se" used to produce the data in table 4.
2. To elucidate the mechanisms by which arsenic potentiates the toxicity of methylated selenium derivatives in animals.
3. To study Vitamin E-selenium interrelationships in order to explain the field reports of selenium deficiency signs in animals that have more than adequate tissue selenium levels.

CHAPTER I

Selenium in Soils and Plants from Native and Irrigated Lands at the Kendrick Reclamation Project Area, Wyoming

J.A. Erdman, R.C. Severson, J.G. Crock,
T.F. Harms, and H.F. Mayland

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Selenium in Soils and Plants from Native and Irrigated Lands at the Kendrick Reclamation Project Area, Wyoming

By J.A. Erdman, R.C. Severson, J.G. Crock, T.F. Harms, *and* H.F. Mayland

ABSTRACT

In response to earlier findings of elevated levels of selenium in the Kendrick area, two detailed geochemical surveys were conducted in 1988 to study the distribution of selenium in soils (0–1 m depth), and new growth of associated big sagebrush (*Artemisia tridentata* Nutt.) and alfalfa (*Medicago sativa* L.). A survey of the native rangeland focused on specific geologic units as sources of selenium; whereas, a gridded survey of the irrigated lands assessed the extent of its mobilization, transport, and concentration.

Only three of the approximately 200 soil samples contained total selenium slightly greater than the 3.3 ppm maximum baseline established for soils from the northern Great Plains. In contrast, selenium concentrations in about one-fifth of the big sagebrush samples exceeded the 1.1 ppm maximum baseline established for this species from the West. Selenium tended to be elevated, but not uniformly so, in both soils and sagebrush collected from areas underlain by the Cody Shale of Cretaceous age.

Alfalfa from about 15% of the irrigated fields contained selenium in excess of about 4 ppm, levels reported to be potentially hazardous to livestock if fed over prolonged periods. Most of these samples were concentrated in an area of 11 contiguous sections where selenium-enriched surface and drain waters also occurred. The agricultural soils just to the north of this seleniferous area had slightly higher levels of selenium compared to those elsewhere in the irrigated lands. At present, the cause for this displaced anomaly is unclear.

Followup sampling in 1989 of two fields where selenium levels in alfalfa collected in 1988 were 25 and 15 ppm yielded samples that contained only 0.2 and 0.7 ppm, respectively. This dramatic and puzzling temporal disparity may be explained by marked differences in weather patterns and irrigation practices for the 2 years. Such a disparity underscores the need to monitor a potentially seleniferous area over an extended period.

INTRODUCTION

The Kendrick Reclamation Project Area was one of nine areas selected in 1985 by the Department of Interior for a field-screening study to investigate the possibility of elevated selenium concentrations in irrigation drainage. This reconnaissance investigation of the Kendrick area showed anomalous levels of selenium in bottom sediments (Severson and others, 1987b), water, and biota (Peterson and others, 1987).

On the basis of these findings, the Department of Interior's Irrigation Drainage Task Group selected Kendrick as one of four areas for more detailed study. Detailed studies focus on the following goals: (1) determine the magnitude and extent of irrigation-induced water quality problems, and (2) provide the scientific understanding needed to mitigate or resolve identified problems. The working objective for each of the four detailed studies was to determine the extent, magnitude, and effects of contaminants associated with agricultural drainage, and, where effects are documented, to determine the sources and exposure pathways that cause contamination.

In the mid-1930's, the Bureau of Reclamation began the Kendrick irrigation and drainage project in Natrona County, Wyoming (fig. 1). An area of approximately 24,000 acres near Casper, Wyoming, has been under irrigation since about 1946.

Two detailed geochemical surveys were conducted in 1988 to study the distribution of selenium and other elements in native and agricultural soils and plants of the Kendrick Reclamation Project Area (hereafter abbreviated to "Kendrick Project").

The native, nonirrigated soils have developed on different geologic units, including several marine Cretaceous formations containing carbonaceous shales and coals (Mesaverde Formation, Lance Formation, Meeteetse Formation and Lewis Shale [combined], and the Niobrara Formation), and several Tertiary formations containing bentonite, claystone, shale, and sandstone or siltstone (White River Formation, Wind River Formation, and the Fort Union Formation). A study that focused on the local geology was judged essential to identify specific geologic

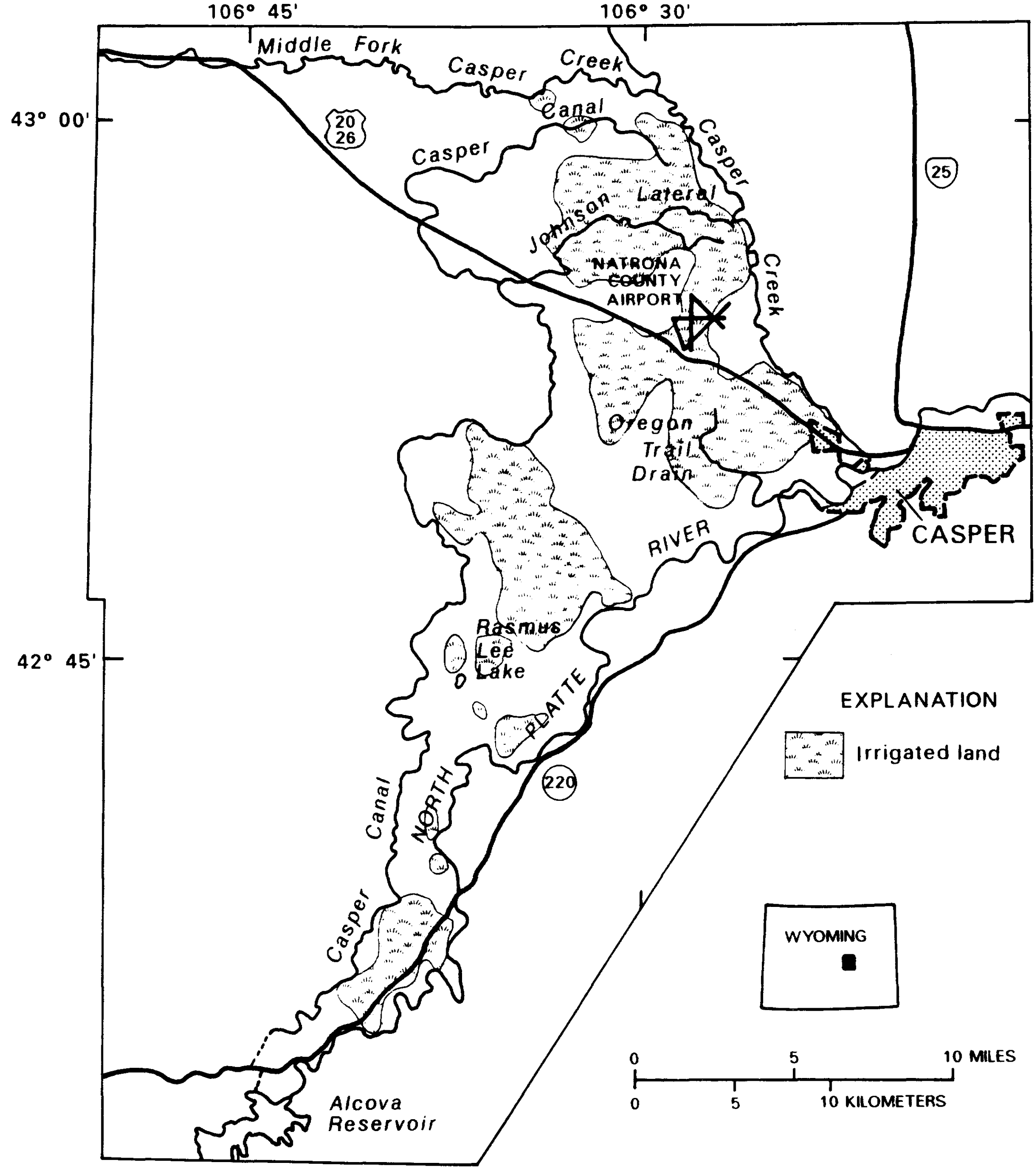

Figure 1. Index map of the Kendrick Reclamation Project Area.

units as sources of the elevated selenium found in the screening studies. A geologic map of the Kendrick Project, simplified from a map of Natrona County (Lageson, 1980), is shown in figure 2.

The agricultural portion of the Kendrick Project comprises a patchwork of irrigated land surrounded by uncultivated native rangeland. Irrigated soils are generally confined to two dominant geologic units: Cody Shale of Cretaceous age and Quaternary alluvial deposits. The alluvium is derived largely from the Cody Shale. We felt that information on agricultural soils and alfalfa might reveal the extent of mobilization, transport, and concentration of selenium and other trace elements resulting from irrigation.

A synthesis of the results from both detailed geochemical studies might serve to segregate the effects of irrigation from those attributed to natural environmental processes.

These soil and plant surveys were conducted concurrently with independent water and wildlife surveys

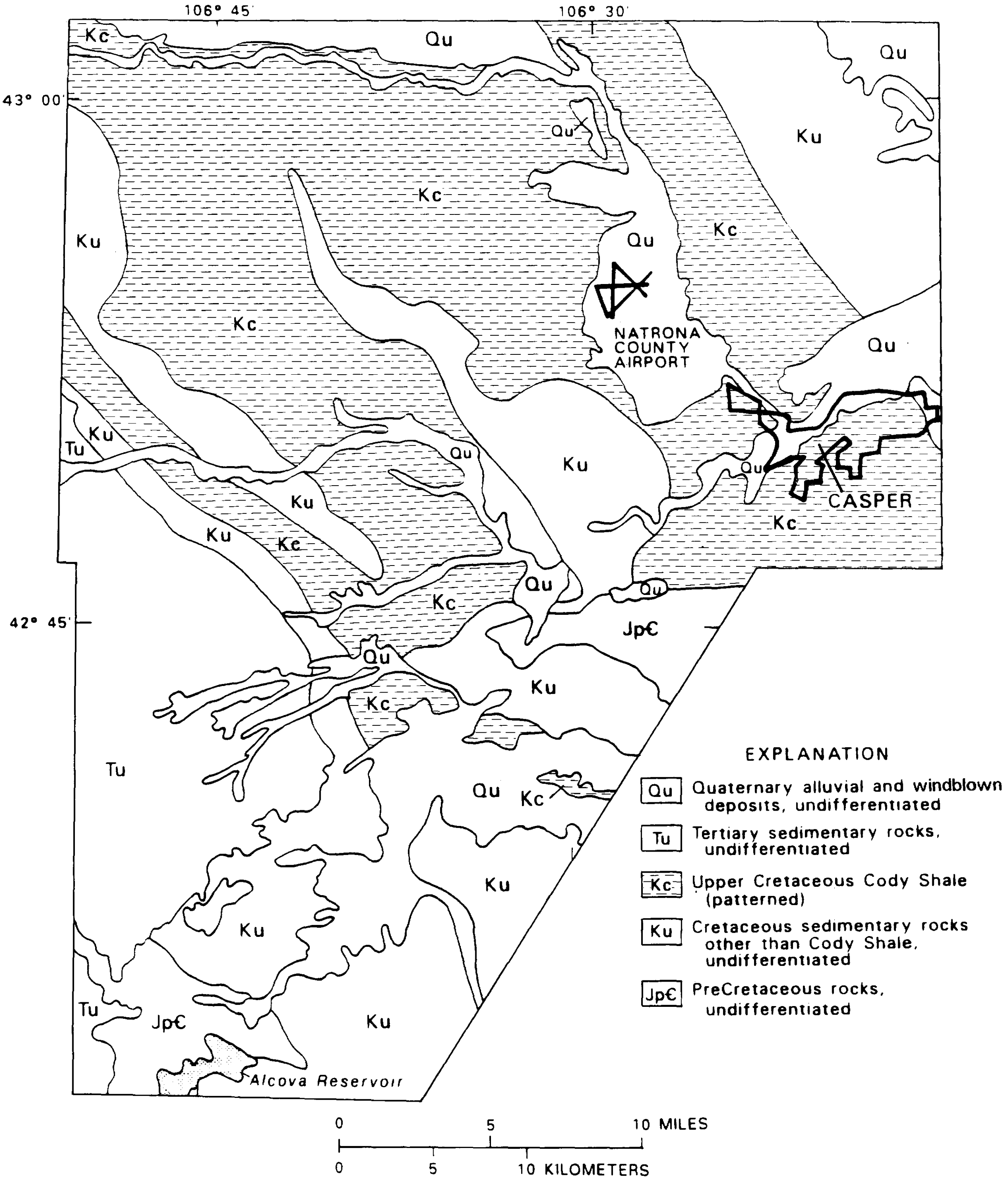

Figure 2. Simplified geologic map of the Kendrick Reclamation Project Area (adapted from Lageson, 1980).

by personnel of the Water Resources Division (USGS) and the United States Fish and Wildlife Service, respectively. A future summary report will integrate the results of this multidisciplinary effort.

The intent of the present report is to discuss the significance of the selenium data that were released earlier (Erdman and others, 1989).

METHODS

Field Sampling

Separate sampling plans were designed for the irrigated agricultural lands and the surrounding native rangelands. Field sampling was conducted by Severson, Erdman, and Crock during the spring and early summer of 1988.

Native Soils and Big Sagebrush

A four-level, stratified random sampling design was used to assess the variability in trace element content of native soils and big sagebrush (*Artemisia tridentata* Nutt.) among and within geologic units that occur in the Kendrick Project. The Kendrick Project area encompasses approximately 25 townships. Twelve of the townships were selected randomly for sampling (fig. 3). A total of 14 geologic units was identified for sampling within the area, but not all geologic units occurred in each township. The distribution of geologic units occurring within each township is shown in table 1. Within a township, each of the geologic units present was sampled at two randomly selected locations. A sampling location was chosen by randomly selecting a section with reasonable accessibility and by identifying the geologic units within that section. Successive sections were selected randomly within each township until all geologic units occurring within the township had been sampled twice.

The purpose of this geochemical survey was to identify the possible source rocks of selenium, not to produce geochemical maps. Two questions we sought to answer were (1) Is a specific geologic formation more seleniferous than others? (2) If so, is the selenium uniformly distributed throughout the unit?

Field work began April 12, 1988, and lasted almost the balance of the month. At each of the 120 sites selected, we used a 3.5-inch bucket auger to collect a sample of the uppermost meter of the soil horizon. The 1-meter channel sample was then mixed in the field and a 1-kg sample collected. Only 101 of the sites supported big sagebrush, thus resulting in 19 "non-response" sites for the plant portion of the study. The previous year's growth was clipped from several shrubs within about a 10-m radius of the soil-auger hole and placed in cloth HUBCO bags. Most plants were still essentially dormant at the time and many had been heavily browsed by antelope.

Estimates of analytical precision for the soils and sagebrush analyses were based on 15 splits and 10 splits, respectively.

Agricultural Soils and Alfalfa

Geobotanical mapping of areas of selenium deficiency and excess is a proven technique, as described recently by Combs and Combs (1986, p. 29):

> ***Kubota and others (1967) surveyed the distribution of selenium in more than 1000 samples of forages (primarily alfalfa) from different parts of the USA. They used the results of the survey to produce a generalized map of the distribution of selenium in United States crops. Because their map was based upon crop selenium data, it has greater relevance to considerations of nutritional aspects of selenium than would one based upon geological data, inasmuch as it represents the distribution of selenium in the particular terrain (i.e., valleys and plains) used for food and feed production.

On a much smaller but more detailed scale, we collected samples on an approximate grid-interval of 1 mile that would allow the preparation of geochemical maps identifying areas of low and high concentrations of selenium and other environmentally important trace elements, based on soils and alfalfa throughout the irrigated lands. An efficient sampling plan is dictated by an optimum grid size which, in turn, depends on knowing where most of the geochemical variation occurs spatially throughout the landscape. Because this information was unavailable for the Kendrick Project, we selected a grid size of 1 mile based on previous studies in the northern Great Plains (Severson and Tidball, 1979) and in the San Joaquin Valley (Severson and others, 1987a).

Although the irrigated lands of the Kendrick Project encompass about 38 square miles (sections), only portions of most sections are currently irrigated, and those portions under irrigation are not contiguous. We superposed a map of irrigated areas (1:24,000 scale), which lacked essential access details, over the appropriate topographic maps of the same scale. Sections that contained less than 40 acres of irrigated land were rejected. For the most part the locality selected in the office proved to be suitable to sample when we arrived at the site.

From June 7–17, 1988, we collected samples of soils and associated alfalfa (*Medicago sativa* L.), mostly in the 10% bloom stage, from fields in 109 sections, beginning at the south end of the Kendrick Project and completing the sampling at the north end. Four sections lacked any alfalfa, although evidence of previous irrigation required that we sample at least the soils. Alfalfa was sampled from 105 fields and soils from 109 fields.

Within each field, two sites approximately 100 meters apart were selected and sampled. In later preparation of the samples, half of each soil and alfalfa sample from the two within-field sites was retained for possible separate analysis while the other half was blended with its field pair; this composite sample was then analyzed. Each alfalfa sample was a collection of several individual plants within a few meters of the soil-auger hole. The top 20 cm of the plants were sampled. The 1-m soil core sample was similar to that described above for the native soils, but sampling often proved to be more time consuming especially in clay-rich soils that had been heavily irrigated.

A three-level analysis-of-variance design was incorporated into this geochemical study to estimate the within-field variance and analytical error. For the soils, the estimate of within-field variance was based on site pairs

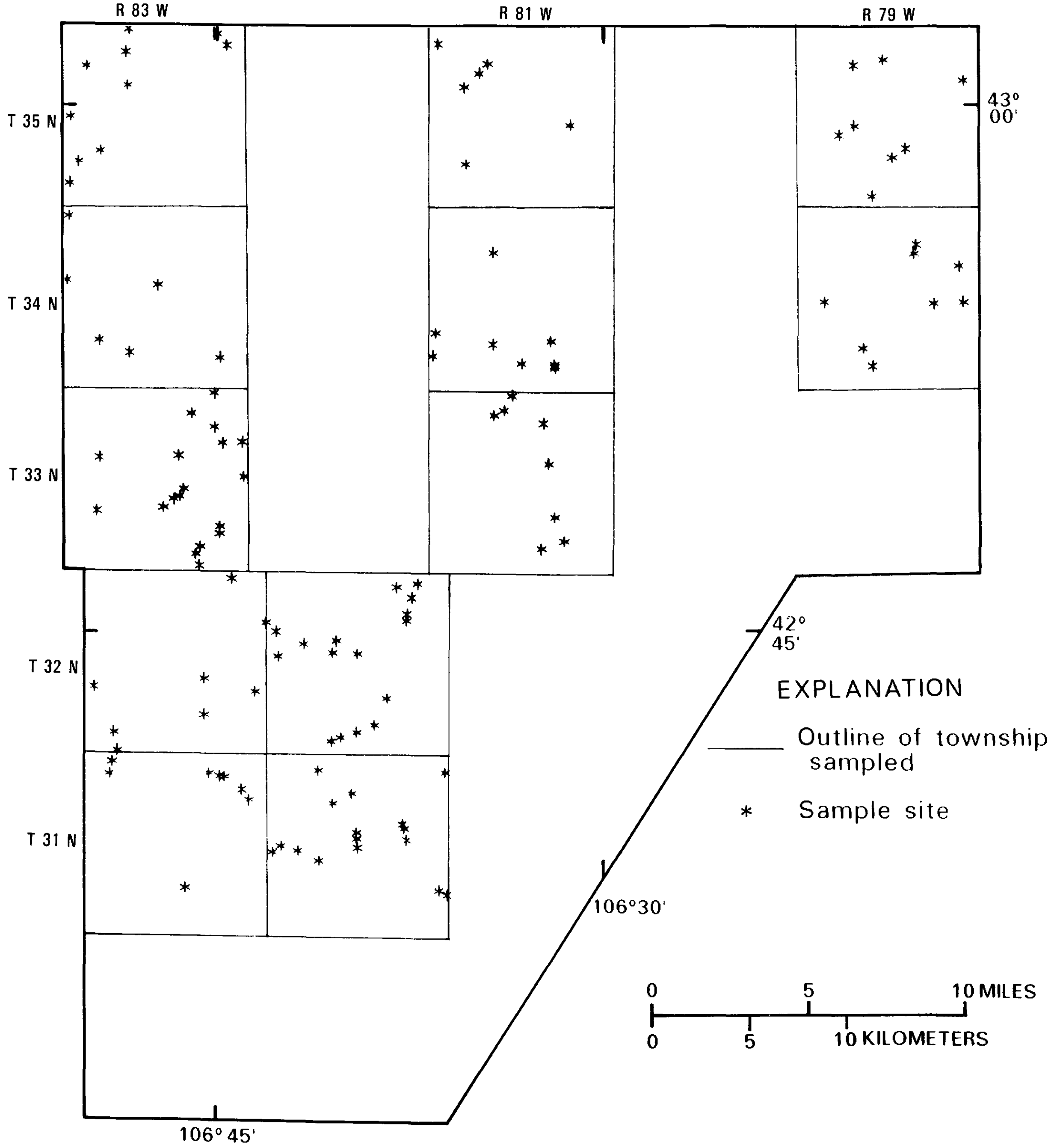

Figure 3. Locations of townships and sites sampled in the geologic-source study.

from eight fields, and analytical error was based on 15 analytical splits. For the alfalfa, site duplicates from seven fields were retained; each of the 14 samples was split in order to estimate the analytical error.

Field-sampling conditions were optimum: first cutting of the alfalfa was not to begin for another week, access to most fields was ideal, weather conditions were virtually perfect, and the selenium indicator plants, mainly two-grooved poisonvetch (*Astragalus bisulcatus* [Hook.] Gray) and woody aster (*Xylorrhiza glabriuscula* Nutt.), were at their peak bloom period.

On June 6, 1989, field sampling was repeated by H.F. Mayland in two localities where alfalfa, sampled in 1988, contained 15 and 25 ppm selenium. Both localities occur on Cretaceous Cody Shale. The forage mixtures contained about 85% alfalfa and 15% smooth bromegrass (*Bromus*

Table 1. Distribution of geologic units sampled from randomly selected townships at the Kendrick Reclamation Project Area

[Numbers in body of table indicate number of sample sites from each geologic unit within each township. Explanation of geologic units: Qal, Quatenary alluvium; Qs, Quaternary sand dunes; Twru, Tertiary White River, upper unit; Twrl, Tertiary White River, lower unit; Twdr, Wind River Formation; Tfu, Tertiary Fort Union Formation; Kl, Cretaceous Lance Formation; Kfh, Cretaceous Fox Hills Sandstone; Kml, Cretaceous Meeteetse Formation; Kmv, Cretaceous Mesaverde Formation; Kc, Cretaceous Cody Shale; Ks, Cretaceous Steele Shale; Kf, Cretaceous Frontier Formation; Kmt, Cretaceous Mowry and Thermopolis Shales]

Township North	Range West	Geologic Units													
				Twr											
		Qal	Qs	Twru	Twrl	Twdr	Tfu	Kl	Kfh	Kml	Kmv	Kc	Ks	Kf	Kmt
35	79	-	2	-	-	-	-	-	2	2	2	-	-	-	-
35	81	2	2	-	-	-	-	-	-	-	-	2	-	-	-
35	83	2	2	-	-	-	-	-	-	-	-	2	-	2	2
34	83	-	-	-	-	-	-	-	-	-	-	2	-	2	2
34	81	2	2	-	-	-	-	-	-	-	-	2	-	2	-
34	79	-	2	-	-	-	-	-	-	2	2	2	-	-	-
33	81	2	-	-	-	-	-	-	-	-	-	2	-	2	2
33	83	2	-	-	-	2	2	2	-	2	2	2	-	2	2
32	83	2	-	-	2	2	2	-	-	-	-	-	-	-	-
32	82	2	-	-	-	2	2	2	-	2	2	2	-	2	-
31	82	2	-	-	2	2	1	2	-	2	3	-	2	-	-
31	83	2	-	2	2	2	-	-	-	-	-	-	-	-	-

inermis Leyss.). Plants were 30- to 35-cm tall and were in early bud and flower stage, respectively. The first harvest of the season occurred 2 weeks after sampling. Selenium indicator plants in this area were in early bloom stage.

Two to four tillers (above 4-cm stubble height) each of alfalfa and bromegrass were collected from each of approximately 50 subsites on each of four sampling sites. One of these sites was a 40-acre field having 1.5% slope and easterly aspect. The three remaining sites were part of a 40-acre field containing 10 acres having 2–3% slope on a northerly aspect and an upper and lower site on the other 30 acres, having a 2–4% slope and a southeasterly aspect.

Laboratory Methods

Sample Preparation

Soil samples were sent to the United States Geological Survey laboratories in Denver for preparation and analysis. After the samples were air dried under forced air at ambient temperatures, they were disaggregated with a mechanical mortar-and-pestle, sieved at 2 mm (10 mesh), and the minus 2 mm material saved for analyses. A split of the minus 2 mm material was ground in a ceramic plate grinder to minus-100 mesh, and this material was used for all chemical analysis.

All plant samples were washed (to avoid any possible surface contamination), dried, and pulverized to a 2-mm size in a Wiley mill by the sample preparation laboratory of Minerals Exploration Geochemistry, Carson City, Nevada. Drying was at ambient temperature for 24 hours followed by 15 minutes in a microwave oven. The alfalfa samples were mailed in the cloth sample bags to the preparation laboratory within 1–2 days of collection.

After milling, 10 of the 101 sagebrush samples collected from the native rangeland were split into two parts in the laboratory to provide an estimate of the analytical precision. The total number of sagebrush samples, then, was 111; these were submitted for analysis to the United States Geological Survey laboratories in Denver in a randomized sequence.

The alfalfa samples from each site (two sites per field) were separated into two parts with a Jones splitter, and one part of each field pair was then combined for analysis. The other part of each pair was placed in the original sample bag to allow for later analyses of the site samples, if needed. Alfalfa samples from two sites in each of seven fields were analyzed separately in order to estimate local variation. Splits of these 14 samples were made to estimate analytical error. The total number of alfalfa samples was 126; these samples came from 105 fields.

The 1989 forage samples were cut into 1- to 2-cm lengths, mixed thoroughly, subdivided into approximately 200 g subsamples, and submitted to one of three drying methods: (1) oven drying in forced draft (100°C for 90 minutes followed by 65°C for 30 hours), (2) microwave drying (200 g sample for 15 minutes in 1.22 kw household microwave oven at 2450 MHz), and (3) freeze drying. Samples were then ground to pass a 1-mm sieve in an intermediate Thomas-Wiley mill.

Analytical Techniques

The selenium analyses were performed by two techniques: continuous-flow hydride generation atomic absorption spectroscopy (HGAAS) for soils (Crock and Lichte, 1982; Sanzolone and Chao, 1987), and fluorometry for plants (Harms and Ward, 1975).

A 0.25-gram soil sample was digested with nitric, perchloric, and hydrofluoric acids. After digestion, the sample was diluted to 50 mL with 6*N* HCl. In the procedure, the sample solution was reacted with sodium borohydride in order to generate the gaseous hydride which was swept into the heated quartz furnace of an atomic absorption spectrometer. Selenium was determined using an aqueous standard calibration curve. The determination limit for selenium in soils is 0.1 ppm. The relative standard deviation for duplicate determinations was about 10%.

One gram of dried, ground vegetation was digested with 10-ml nitric and 2-ml perchloric acids; hydrogen peroxide was used to help break down resistant waxes. Selenium was then complexed with 2,3-diaminonaphthalene, and the complex extracted into cyclohexane. The determination limit for selenium in plants is 0.01 ppm; the relative standard deviation for duplicate determinations was 10–15%.

Selenium concentrations in the 1989 forage samples were determined by HGAAS after a similar digestion was used for the fluorometric determination. Several forage samples, including the two collected from the same areas in 1988, were included as unknowns with the 1989 sample set.

Quality Control

Soil Materials

Statistical techniques and reference samples were used to assess accuracy and precision of the selenium analyses. Subsets of samples from each of the two geochemical studies were selected to be split into two parts after grinding and analyzed separately to estimate errors associated with sample preparation and analysis (often referred to as procedural error rather than analytical error). The samples from each study, plus sample splits, were arranged in a randomized sequence and prepared and analyzed in that sequence to convert any systematic errors in preparation and analysis to random errors, and to estimate relative laboratory precision. Samples of United States Geological Survey standard reference material SCo-1 Cody Shale were inserted at random intervals into the soil-sample sequence to estimate laboratory accuracy. Reported consensus values from the literature, when compared with our laboratory determinations (table 2), show that the determinations were highly accurate.

Plant Materials

Several biological standard reference materials from the National Bureau of Standards were analyzed for selenium by the fluorometric method. Gladney (1980) analyzed these same materials by neutron activation analysis. The close agreement between the certified values, the values determined by Gladney (1980), and those determined by the United States Geological Survey laboratories are shown in table 2.

RESULTS AND DISCUSSION

Geologic Units In Native Rangeland

Native Soils

Background ranges for selenium in soils of the northern Great Plains, as well as those for soils from three other regional studies in the West, are given in table 3. An explanation of the data in table 3 is necessary before any comparisons can be made. The computed values are referred to as baselines rather than backgrounds because they represent the concentration measured at some point in time. Background values, in contrast, are intended to represent natural concentrations that exclude man's influence, and are rarely obtainable. The sampling media for each of the studies in table 3 differ from one study to another. Samples from the western half of the United States (Shacklette and Boerngen, 1984) were collected from the B horizon, or below 20 cm where the B horizon was undefined. Surface or A-horizon samples were collected for the northern Great Plains study (Severson and Tidball, 1979). And the surface 0–20 cm was collected for the San Joaquin Valley study (J.M. McNeal, United States Geological Survey, Reston,

Table 2. Analysis of standard reference materials for selenium

[All values are expressed in parts per million]

Reference materials	National Bureau of Standards certified values	Literature values	This study determined values
SCo-1 (Cody Shale)[1]	Not determined	0.89±(0.06)[4]	0.82±(0.117)[6]
#1567 Wheat flour[2]	1.1±(0.2)	1.12±(0.01)[5]	0.97
#1571 Orchard leaves[2]	0.08±(0.01)	0.08±(0.009)[5]	0.075
#1575 Pine needles[2]	Not determined	0.049±(0.004)[5]	0.056
#1570 Spinach[2]	Not determined	0.039±(0.015)[5]	0.032
#1572 Citrus leaves[2]	0.025[3]	Not determined	0.038±(0.002)[7]

[1] U.S. Geological Survey reference material.
[2] National Bureau of Standards reference material.
[3] Non-certified value.
[4] Gladney and Roelandts, 1988.
[5] Gladney, 1980.
[6] Based on six analyses.
[7] Based on five analyses.

VA, unpubl. data, 1987). Samples of soils from a depth of 66–72 inches were collected from the Panoche Fan, located on the west side of the San Joaquin Valley, California (Severson, Tidball, and Wilson, 1987). These baselines are valid for comparing analyses of the same kind of sample from within the area where the baseline was developed. They should be applied with caution to different sample media or to samples collected outside of the baseline area. They are presented here to show what ranges in selenium values have been determined in soils from different parts of the Western United States.

Additional data on selenium in world soils are summarized by Berrow and Ure (1989). Some reported values for soils exceed those shown in table 3 (this report).

All the native, rangeland soils that we sampled contained total selenium within the 3.3 ppm norm established for soils from the northern Great Plains (fig. 4), the most appropriate baseline with which to compare our data. The relative normalcy of the Kendrick soils is quite surprising in light of the clearly anomalous concentrations of selenium found in the associated sagebrush collected in our study. A comparison of the ranges and means for selenium in soils collected from the various geologic units (fig. 4) shows that soils from the Cody Shale are higher in selenium than those from the other units, and only the mean from the Cody Shale exceeds that for soils from the northern Great Plains.

Results of the analysis-of-variance, expressed as a percent of the total variance, are as follows:

	Geologic Units	Townships	Sections	Analyses
Native soils	34*	11	45*	10

*Differences within a category are significant at the 0.05 level.

An *F*-test of the variance components shows statistically significant differences in selenium concentrations in the native soils among geologic units and between sections within townships. This result suggests that the geology plays an important role as a source of selenium, but a specific unit, such as the Cody Shale, is not uniformly seleniferous. In fact, the small-scale variation that occurs between sites from randomly selected sections in townships exceeds that between geologic units. (For the few samples in which selenium was reported to be less than the detection limit, we replaced the "less than" values with an arbitrary

Table 3. Geochemical baselines for selenium in soils from selected studies in the Western United States

[Detection ratio, number of samples in which the element was found in measurable concentrations to number of samples analyzed; GM, geometric mean; GD, geometric deviation; baseline, expected 95-percent range]

Reference and general location of the study area	Detection ratio	GM	GD	Baseline	Observed range
Shacklette and Boerngen (1984) western half of the United States.	590:733	0.23	2.43	0.039-1.4	<0.1-4.3
Severson and Tidball (1979) northern Great Plains, parts of Montana, Wyoming, and N. Dakota.	104:136	0.45	2.72	0.061-3.3	<0.1-20
McNeal (unpublished data) San Joaquin Valley, California.	240:328	0.14	2.56	0.021-0.92	<0.1-2.8
Severson, Tidball, and Wilson (1987) Panoche Fan, San Joaquin Valley.	713:721	0.68	1.94	0.1-2.2	<0.1-4.5

value of 0.07 ppm; noncensored data are required in the analysis-of-variance.) Analytical error contributed only 10% of the total variance; the analytical precision, then, was quite satisfactory.

Big Sagebrush

In the Kendrick Project, the geometric mean for selenium in big sagebrush is 0.41 ppm—four times higher than the norm of 0.11 reported by Gough and Erdman (1983) for big sagebrush from the Western United States. Concentrations of selenium in sagebrush from the Kendrick Project ranged from 0.06–9.5 ppm (fig. 5), the maximum value far exceeding the 1.1 ppm upper baseline threshold. A total of 13 samples exceeded the normal range expected, and the four clear outliers—9.5, 7.5, 6.5, and 5.5 ppm—came from sites mapped as Cody Shale. Our results indicate that sagebrush from the Cody Shale typically contains selenium at levels close to the upper limit of the normal range (fig. 5).

If we look at selenium in big sagebrush from the nearby Powder River Basin, however, the concentrations in sagebrush from the Kendrick Project are not quite so extreme. In a reconnaissance study of the Powder River Basin of Wyoming and Montana, Connor and others (1976) reported a geometric mean of 0.43 ppm selenium, almost identical to that for sagebrush from the Kendrick Project, and an observed range of 0.08–4.8 ppm for samples of sagebrush from 41 localities.

As with the native soil results, the most seleniferous vegetation comes from areas underlain by Cody Shale. In contrast to the soil results, many of the sagebrush samples contained anomalous levels of selenium when compared to norms. Yet some of the sagebrush sampled from the Cody Shale contained the lowest concentrations. Sagebrush from five other geological units, including alluvium deposits of Quaternary age, also contained selenium that exceeded the established baseline. Low-selenium sagebrush tended to occur at sites mapped as Quaternary alluvium or dune-sand deposits.

Results of the analysis-of-variance, expressed as a percentage of the total variance, are given as follows:

	Geologic Units	Townships	Sections	Analyses
Big Sagebrush	10*	18	70*	3

*Differences within a category are significant at the 0.05 level; test result among geologic units was performed on a pooled variance estimate.

As with the results given for the native soils, the largest variation for selenium in sagebrush occurred between sections, but to a much greater extent and with the largest disparities from sites in the Cody Shale.

In brief, then, the Cody Shale is the most seleniferous of the geologic units in the Kendrick Project, especially in terms of availability; but it is clearly not uniformly so. The four most selenium-rich sagebrush samples were taken from fairly widespread localities. This precludes narrowing the source in the nonirrigated native rangelands to a specific area.

We found a significant (P=0.05) but low correlation (r=0.34, n=101 pairs) for selenium in soils versus sagebrush. Such poor correlations have been widely reported in

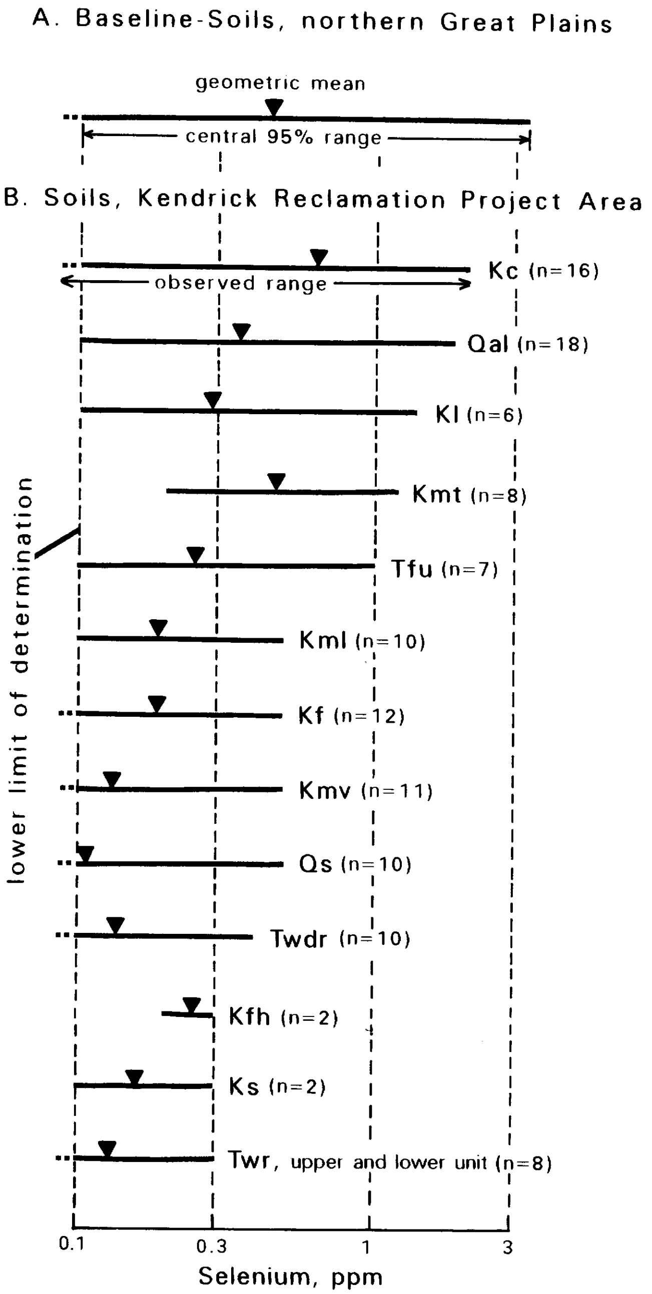

Figure 4. Bar plots of selenium in native soils from geologic units in the Kendrick Reclamation Project Area, arranged in order of decreasing maximum concentrations. Baseline data are from Severson and Tidball (1979). Dashes indicate that the lower end of the range was below the 0.1 ppm lower limit of determination. (See table 1 for explanation of geologic symbols.)

the literature. Olson and others (1942b) found a poor correlation between water-soluble selenium in the surface soil and the selenium content of plants growing in the soil. Still, three of the four sites where sagebrush contained extremely high selenium also had soils with elevated selenium.

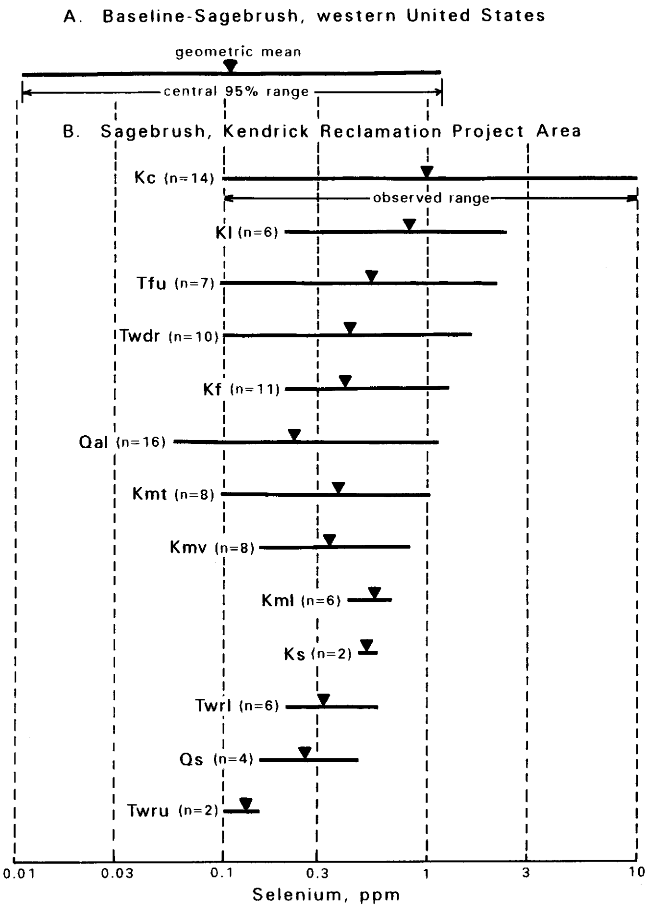

Figure 5. Bar plots of selenium in big sagebrush from geologic units in the Kendrick Reclamation Project Area, arranged in order of decreasing maximum concentrations. Baseline data are from Gough and Erdman (1983). (See table 1 for explanation of geologic symbols.)

Summary statistics for selenium in the native soils and big sagebrush from the various geologic units are given in table 4.

Irrigated Lands

Agricultural Soils

Results of the analysis-of-variance for selenium in agricultural soils, expressed as a percentage of the total variance, are as follows:

	Fields (sections)	Sites	Analyses
Agricultural soils	75*	13	12

*Differences within a category are significant at the 0.05 level.

Table 4. Average and range of selenium concentrations (ppm) in soil and sagebrush determined from stratified random sampling of geologic units at the Kendrick Reclamation Project Area

[Analytical duplicates not included; explanation of geologic units: Qal, Quaternary alluvium; Qs, Quaternary sand dunes; Twr, White River Formation, upper and lower units combined; Twdr, Wind River Formation; Tfu, Fort Union Formation; Kl, Lance Formation; Kfh, Fox Hills Sandstone; Kml, Meeteetse Formation; Kmv, Mesaverde Formation; Kc, Cody Shale; Ks, Steele Shale; Kf, Frontier Formation; Kmt, Mowry and Thermopolis Shales. Detection ratio, number of samples in which the element was found in measurable concentrations relative to the number of samples analyzed]

Geologic unit	Native soil			Sagebrush		
	Detection ratio	Geometric mean	Observed range	Detection ratio	Geometric mean	Observed range
Qal------	18:18	0.35	0.1-1.9	16:16	0.22	0.06-1.2
Qs-------	7:10	.11	<0.1-0.5	4:4	.25	0.15-0.45
Twr------	7:8	.14	<0.1-0.3	8:8	.24	0.1-0.55
Twdr-----	8:10	.14	<0.1-0.4	10:10	.41	0.1-2.0
Tfu------	7:7	.25	0.1-1.0	7:7	.52	0.1-2.2
Kl-------	6:6	.28	0.1-1.4	6:6	.79	0.2-2.2
Kfh------	2:2	.24	0.2-0.3	1:1	.3	0.3-0.3
Kml------	10:10	.19	0.1-0.5	6:6	.53	0.4-0.65
Kmv------	10:11	.13	<0.1-0.5	8:8	.32	0.15-0.8
Kc-------	15:16	.64	<0.1-2.1	14:14	.96	0.1-9.5
Ks-------	2:2	.17	0.1-0.3	2:2	.50	0.45-0.55
Kf-------	11:12	.19	<0.1-0.5	11:11	.39	0.2-1.6
Kmt------	8:8	.47	0.2-1.2	8:8	.36	0.1-1.0

As 75% of the variance can be attributed to differences among irrigated fields, we can contour the concentrations of selenium in soils with reasonable certainty that the map pattern is real. The map contours were computed by averaging the four nearest neighbors and applying an inverse-distance-squared algorithm. Only a small percentage of the variance observed can be attributed to analytical error.

A contour map of selenium in the irrigated soils (fig. 6) shows four areas where peak values exceeded 2 ppm: the southernmost field in the irrigated area (selenium value, 2.2 ppm); Rasmus Lee Lake (a single-point anomaly of 3.6 ppm), Oregon Trail Drain, west of the confluence of Casper Creek with the North Platte River (a single-point anomaly of 3.8 ppm—the maximum observed), and the Johnson Lateral northwest of the Natrona County Airport (a multipoint anomaly with values ranging from 2.2 to 3.2 ppm). We have used 2 ppm as a threshold because soils in North America that are associated with selenosis usually contain 2–6 ppm or more of total selenium (Thornton, 1981, p. 14). Composited soils from only ten of the fields sampled contained selenium in excess of the 2 ppm threshold. As with the results from the native soils in the project area, the concentrations of selenium from the irrigated soils, by themselves, would probably not arouse much interest when compared with the baselines reported for the northern Great Plains (table 3). However, total selenium in soil may not directly reflect irrigation-induced effects, such as increased solubility, transport, and accumulation by an irrigation drainage, nor would it reflect selenium uptake by native and agricultural plants and subsequent utilization by wildlife and livestock.

Alfalfa

Selenium levels in alfalfa ranged from 0.1 to 40 ppm; the median was 0.9 ppm, and 25th and 75th percentiles were 0.4 ppm and 2.0 ppm, respectively. Highly elevated concentrations of selenium in alfalfa were found in three of the four areas identified by the irrigated soil results: Rasmus Lee Lake; near the terminus of the Oregon Trail Drain; and an extensive area underlain by Cody Shale west of the airport (fig. 7) and offset slightly to the south of the seleniferous (>2 ppm) soil area. The extensive area consists of 11 contiguous sections where selenium in alfalfa ranged from 4 to 40 ppm, concentrations that are potentially

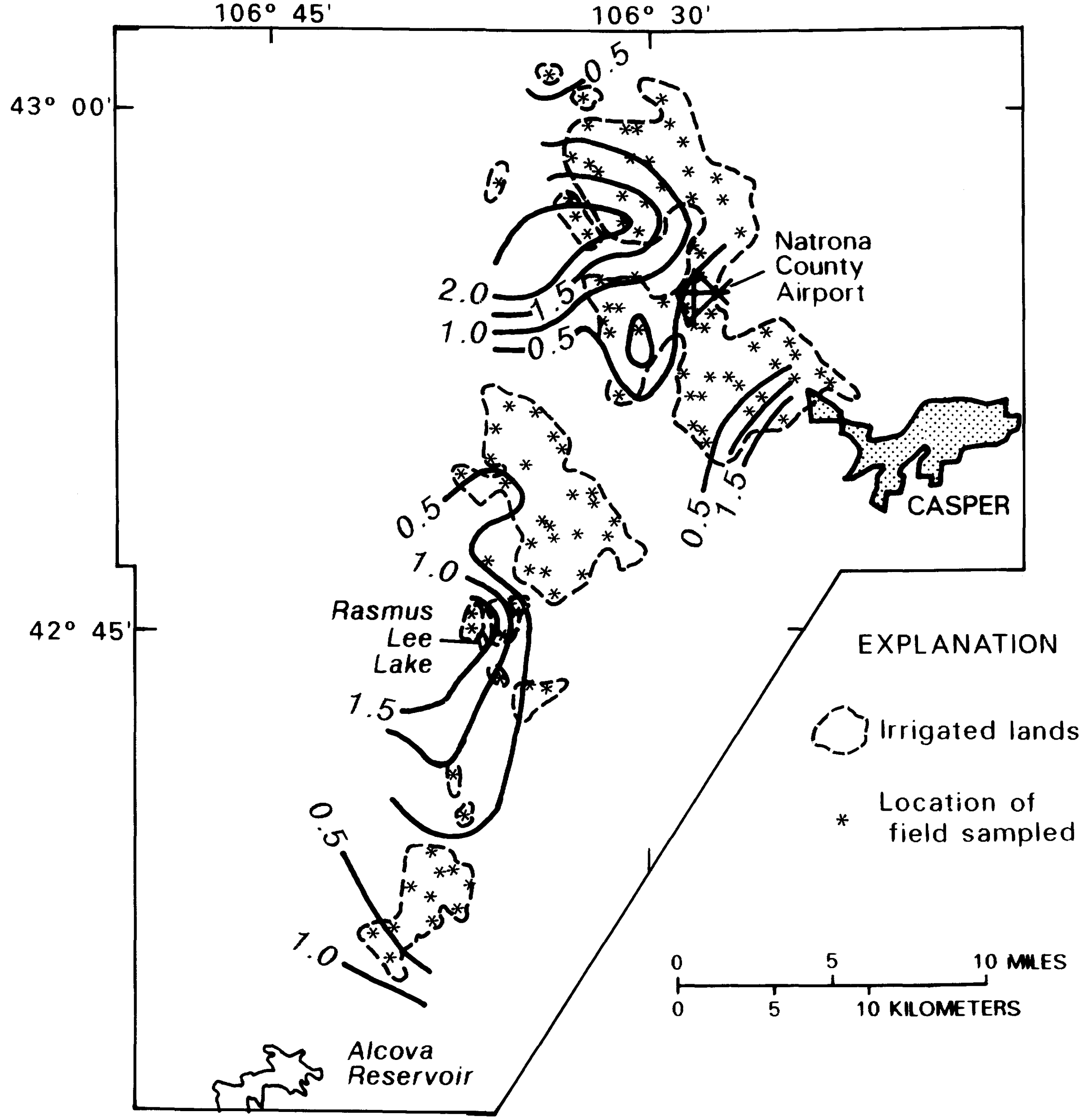

Figure 6. Contour map showing the distribution of total selenium (ppm) in agricultural soils collected from irrigated lands.

hazardous to livestock when consumed over extended periods of time (see Kingsbury, 1964, p. 47; Church and others, 1971, p. 506; Lakin, 1973, p. 96; and Combs and Combs, 1986, p. 26). According to Church and others (1971), alkali disease (manifested by loss of hair and sloughing of hooves) is due to consuming hays and grasses with selenium levels of 10–30 ppm.

The only evidence of selenosis in cattle and horses on the two farms sampled again in 1989 was some hardening of the horses' hoofs. Infrequent incidences of selenosis (alkali disease) have been reported on the Kendrick Project. Tolerance to high selenium levels varies considerably between individual animals. In addition, experimental evidence suggests that some animals may be able to accommodate high levels of dietary selenium after evidencing some symptoms of chronic toxicosis like lameness and hair loss (L.F. James, Poisonous Plant Research Laboratory, United States Department od Agriculture-Agricultural Research Service, oral commun., 1989).

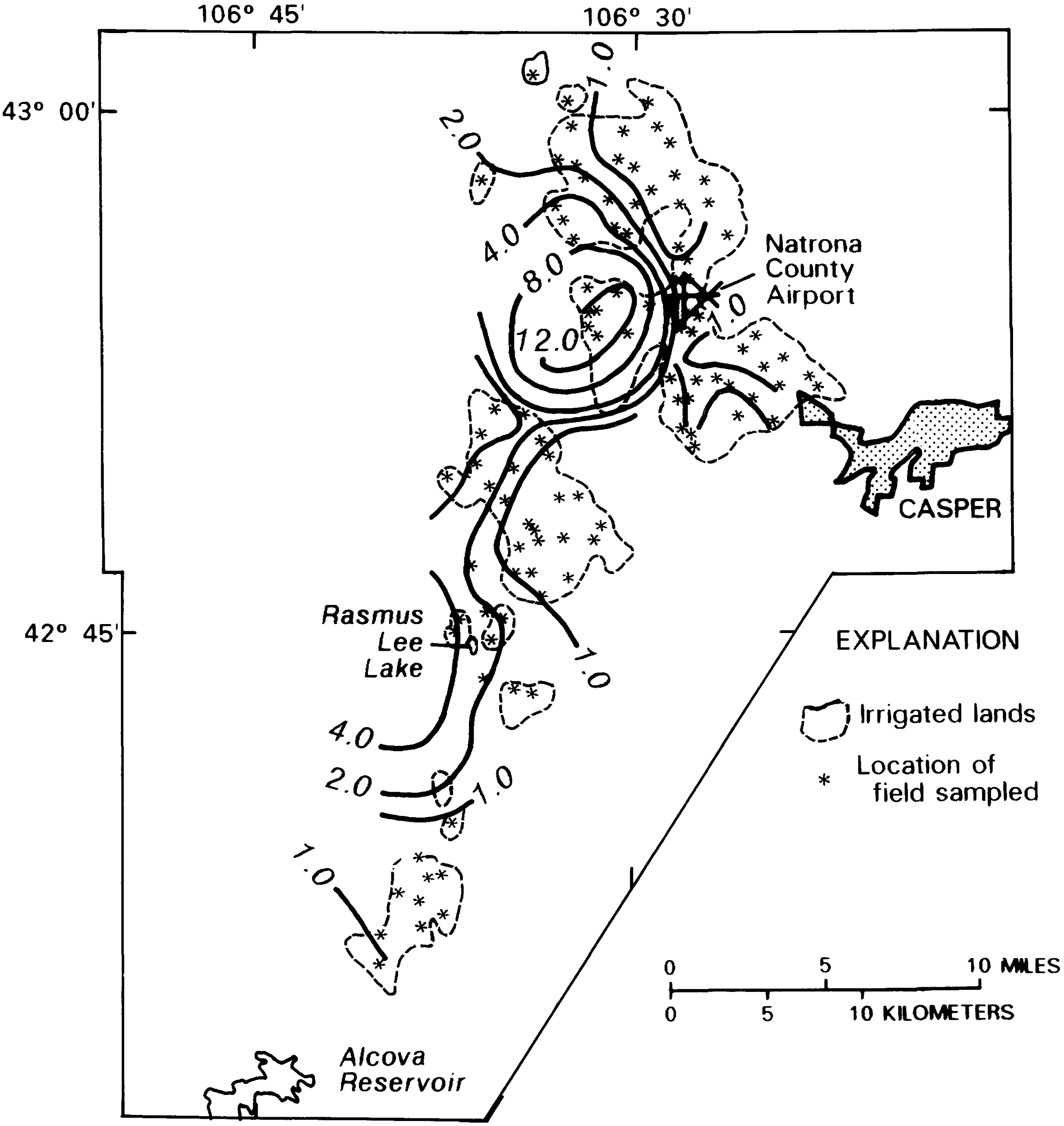

Figure 7. Contour map showing the distribution of selenium (ppm, dry-weight basis) in alfalfa collected from irrigated lands.

The extensive selenium anomaly in alfalfa west of the airport was independently confirmed by water-quality data provided by David Naftz and his associates with the Water Resources Division of the United States Geological Survey. Dissolved selenium concentrations ranged from 0.12 to 0.98 mg/L in drain-water samples and from 1.7 to 5.3 mg/L in ponded-water samples. These concentrations exceed the 0.100 mg Se/L guideline for irrigation water used in the production of alfalfa (Albasel and others, 1989). Drinking water and domestic-livestock water standards are 0.01 mg/L and 0.05 mg/L, respectively (U.S. Environmental Protection Agency, 1977).

Clearly, some of the alfalfa produced in the Kendrick area contains selenium above most reported concentrations. It is difficult to assess the importance of the high values because most published studies on selenium in alfalfa are from selenium-deficient or nonseleniferous regions (Ihnat and Wolf, 1989). Several exceptions include an early study by Byers and others (1938) that reports a maximum concentration of 7 ppm selenium in alfalfa from southeastern Colorado. A second exception is a report of up to 44 ppm selenium in alfalfa grown in Israel (Ravikovitch and Margolin, 1957). We also have a record (Oscar Olson, South Dakota State University, written commun., 1975) of an alfalfa sample that contained 27.3 ppm selenium. Concentrations of 12 and 13 ppm were found in two samples of alfalfa collected from Wallace Meadows northeast of Lusk, Wyoming (by H.F. Mayland, unpubl. data, 1989).

On the other hand, we found alfalfa from eight fields that is marginally deficient (0.10–0.20 ppm) in selenium. According to Allaway and Hodgson (1964), Westermann and Robbins (1974), and Fisher and others (1987), minimal dietary selenium concentrations—critical levels needed to prevent white muscle disease (a form of muscular dystrophy) in livestock—are about 0.1 ppm. Alfalfa that contained selenium below 0.5 ppm generally came from fields in the southern half of the Kendrick Project.

Results of the analysis-of-variance simply confirm the strong differences among fields shown in figure 7 and also reflected in the soils, although not quite so strongly. The distribution of the variance, expressed as a percentage of the total variance, follows:

	Fields (sections)	Sites	Analyses
Alfalfa	60	39*	<1

*Differences within a category are significant at the 0.05 level.

Our results from the Rasmus Lee Lake area provide an example of the extreme differences observed among fields. The composite alfalfa sample from a pasture just northwest of the lake contained 15 ppm selenium; whereas, a sample from a heavily irrigated hay field to the east contained only 0.25 ppm.

Of nine bottom-sediment samples collected from the Kendrick area during an earlier field-screening study (Severson and others, 1987b), the sediment from Rasmus Lee Lake contained 17 ppm, second only to a sample from the mouth of Poison Spring Creek that contained 25 ppm. Recent unpublished results of pore-space analyses (David Naftz, oral commun., April 1989) showed 30 mg/L dissolved selenium in a sample of pore water 15 feet below land surface in a sand lens near the field where the alfalfa contained 15 ppm selenium. In marked contrast, a pore-water sample contained only 0.150 mg Se/L from the field in which the alfalfa sample contained 0.25 ppm. Alfalfa, a deep-rooted plant, seems to provide a good indirect measure of soluble selenium in the pore spaces at depth. As Fisher and others (1987, p. 124) stressed: "the ability of selenium-accumulating plants to absorb selenium from sources deep within the soil profile indicate that surface soil elemental analyses have serious limitations as a means of forecasting toxicity problems."

Unlike the results for selenium in the agricultural soils, we found strong differences in selenium from alfalfa taken within the same field. The largest disparity occurred between the two sites from a field where the sample from the first site contained only 0.85 ppm selenium; whereas, the sample from the second site contained 7.0 ppm. These results, although disturbing, simply support those reported by Olson and others (1942b) who also found large variations in the selenium content of plants over relatively short distances on soils derived from the same parent material. Differences between site pairs from the other six fields where such comparisons can be made were considerably less extreme.

Results of a correlation analysis that compared total selenium in the agricultural soils with selenium in alfalfa from the same fields were similar to those found between native soils and sagebrush. The correlation coefficient in this case was 0.43 (n=105 pairs); although the correlation is significant (P=0.05), the soil selenium explains only about 16% of that found in the alfalfa.

The offset or displacement of a large zone of seleniferous alfalfa and selenium-laden surface waters from a possible source area of slightly seleniferous soils to the north is difficult to explain. Almost 50 years ago, however, Olson, Whitehead, and Moxon (1942) seemed to have dealt with similar patterns. They concluded (p. 52):

> During the weathering of seleniferous rock to soil in the region in which these studies were made, a large part of the selenium is oxidized to the selenate form. As the selenate, it is leached from the surface to subsurface soils or *removed by run-off waters and redeposited at lower elevations*, where it may finally leach from the surface and be deposited in subsurface soil. [emphasis added.]

Much more recently, Tidball and others (1989b) reported what appears to be a very similar situation in an irrigated area of the San Joaquin Valley, California. Elevated levels of selenium in soils have been dispersed downslope toward areas where the water table is close to the surface and where the groundwater is extremely seleniferous. At present this displacement seems to be the only explanation for the major selenium anomaly at Kendrick.

Selenium concentrations in the alfalfa samples collected from the two fields in June 1989 were less than 5% of the concentrations found in alfalfa sampled from the same fields in June 1988. In the field where the 1988 sample contained 25 ppm selenium, the three 1989 samples contained only 0.2 ppm; whereas, in the field where the 1988 sample contained 15 ppm, the single 1989 composite sample had 0.7 ppm. Differences in selenium concentrations owing to drying methods were not significant at the 0.05

probability level. The analyses were verified by data obtained from six laboratory-reference alfalfa samples, two of which were from the 1988 sampling of these two fields.

This large temporal variation, as measured at the two fields sampled in 1988 and again in 1989, was entirely unexpected. The following examination of weather patterns and managerial practices may, however, explain the results. Discussions with the owners of both farms revealed that the fields were quite dry during the 1987–88 winter and were not irrigated until after the initial sampling in early June 1988. Irrigation water management was then improved by installation of gated pipe on one farm resulting in more timely and adequate irrigations on both farms. Fields were watered in late 1988 and twice again during the subsequent spring before the June 6, 1989, sampling. On one field, alfalfa hay yields were fair in 1988 and very good in 1989; whereas, the 1989 yields on the second field were expected to quadruple those of 1988 because of better water management.

We suggest that selenate selenium may have been concentrated in the minimal pore water in the soil profiles preceding the 1988 sampling and that the selenium was readily absorbed by the alfalfa plants. The relatively dry soils limited plant growth to the extent that the selenate was concentrated in the plant tissue collected in early June 1988. Subsequent irrigations in the late fall of 1988 and twice before sampling on June 6, 1989, may have leached the selenate below the rooting zone. Soil-moisture profiles were likely saturated in early 1989, which resulted in further dilution of soluble selenium. The vigorously growing plants absorbed less total selenium than in the previous year and further diluted that which was absorbed because of the greater production of dry matter. The net effect would explain the precipitous drop in selenium concentrations in the 1989 alfalfa compared to that from the previous year.

These results underscore the importance of irrigation practices on selenium concentrations in crops grown in arid environments and clearly point to the need to design detailed studies of the possible change in selenium levels in alfalfa between same-year cuttings and from year-to-year cuttings.

SUMMARY

Probably the most important result of the soil sampling at Kendrick is the fact that, with few exceptions, none of the samples were abnormally high in total selenium. Selenium tended to be elevated in soils derived from the Cody Shale, but it was not uniformly so.

In contrast, selenium in many samples of big sagebrush tended to be considerably higher than the norm, and some samples from 6 of the 14 geologic units exceeded the maximum baseline established for this species.

Large differences in selenium concentrations were found in samples of alfalfa from different fields in the Kendrick Project. Some of the samples (15% of the total) contained selenium at levels potentially hazardous to livestock if fed over prolonged periods. However, reported incidences of selenosis are not common in the study area.

Seleniferous alfalfa and surface and drain waters were found in an extensive area west of the Natrona County Airport. However, significant temporal variation in selenium concentration in alfalfa were documented. These changes may be attributed to hydrologic and crop management factors.

The agricultural soils just to the north of this seleniferous area had slightly higher levels of selenium compared to those elsewhere in the study area. This may relate to the lesser amount of irrigation water available or applied to soils. Forage production is generally restricted on some of the farms northwest of the airport by low soil fertility and inadequate irrigation.

CHAPTER J

Selenium Sources in the Diablo Range, Western Fresno County, California

R.R. Tidball, R.C., Severson, T.S. Presser, and W.C. Swain

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Selenium Sources in the Diablo Range, Western Fresno County, California

By R.R. Tidball, R.C. Severson, T.S. Presser, *and* W.C. Swain

ABSTRACT

A selenium anomaly occurs in San Joaquin Valley soils in western Fresno County, California. An investigation of the geologic source of this anomaly included reconnaissance sampling of soils and weathered rock material in several geologic formations in the vicinity of Monocline Ridge. The Ridge is a series of steeply dipping sedimentary beds ranging in age from Late Cretaceous to Quaternary that border the westside of the valley. In general, the nonmarine rocks of Pliocene and younger age tend to be nonseleniferous, and marine rocks of Oligocene to Upper Cretaceous age are variously seleniferous. The Tumey Formation of Oligocene age, the Kreyenhagen Shale of Eocene age, and the Moreno Shale of Late Cretaceous age contain the highest amounts of selenium. The wide range of total selenium found, 2.5–12 ppm in the Tumey Formation, 0.8–35 ppm in the Moreno Shale, and 0.3–45 ppm in the Kreyenhagen Shale, indicates that the distribution is not uniform within these formations. Dissolved selenium appears to be concentrated where sulfate salts are precipitated either in seeps or in the sediments of ephemeral streams that receive drain water from these rocks. Dissolved selenium transported to the valley floor in muddy debris flows by ephemeral streams tends not to reach the groundwater because of restricted through-flow potential. Dissolved selenium transported by intermittent streams, however, apparently recharges groundwater and moves by artesian flow to the lower end of the alluvial fans.

INTRODUCTION

Elevated levels of selenium were found in irrigation drainage water being delivered to the Kesterson National Wildlife Refuge, Merced County, in California's San Joaquin Valley through June 1986. The drainage water was received from the San Luis Unit of the United States Bureau of Reclamation's Central Valley Project in western Fresno County. The irrigation water originates in the Sacramento–San Joaquin delta area and is delivered to the project area largely by the San Luis Canal and the Delta-Mendota Canal.

Because of the warm, arid climate in conjunction with a high water table near the valley trough, dissolved solids migrate to the surface soil by capillarity and are precipitated by evaporation. Thus, salt-affected soils and high water tables have long been known as agricultural problems in the valley (Kelley and Nye, 1984). The design of the irrigation system, therefore, provided for subsurface drains and a canal, the San Luis Drain, to remove the excess water and dissolved solids leached from the soils. The drainage water was transferred to holding ponds known as Kesterson Reservoir in western Merced County. Kesterson was jointly managed by the United States Bureau of Reclamation as a drain-water facility and by the United States Fish and Wildlife Service (FWS) as the Kesterson National Wildlife Refuge. After high concentrations of selenium were detected in the drainage water, the Bureau of Reclamation closed the drain and reservoir in June 1986, in compliance with directives from the State of California.

Investigations along the basin trough and the basin rim at the foot of the alluvial fans that extend from the western side of the valley showed that median concentrations of *dissolved* selenium in shallow ground water are about 10 µg/L and maximum values are in excess of 3000 µg/L (Deverel and others, 1984). Selenium content is highly correlated with salinity (Deverel and Fujii, 1988). The higher concentrations of dissolved selenium occur along the toe of the alluvial fans near the valley trough. In contrast, the distribution of *total* selenium in soils measured at the 66–72-inch (168–183-cm) depth shows that the higher concentrations (up to 4.5 ppm) occur near the westside valley margin, particularly adjacent to Monocline Ridge (Tidball and others, 1989b).

The total-selenium anomaly occurs in soils developed on mud-flow deposits transported by ephemeral streams. These deposits form small fans that coalesce with the larger fans created by Panoche and Cantua Creeks (Bull, 1964). The selenium distribution on the mud flows indicates that a geologic source for selenium must lie within rock units in the nearby coast ranges. The purpose of this report is to describe the selenium concentrations in samples of weathered surficial rock and soil materials and stream sediments in the foothills bordering the west side.

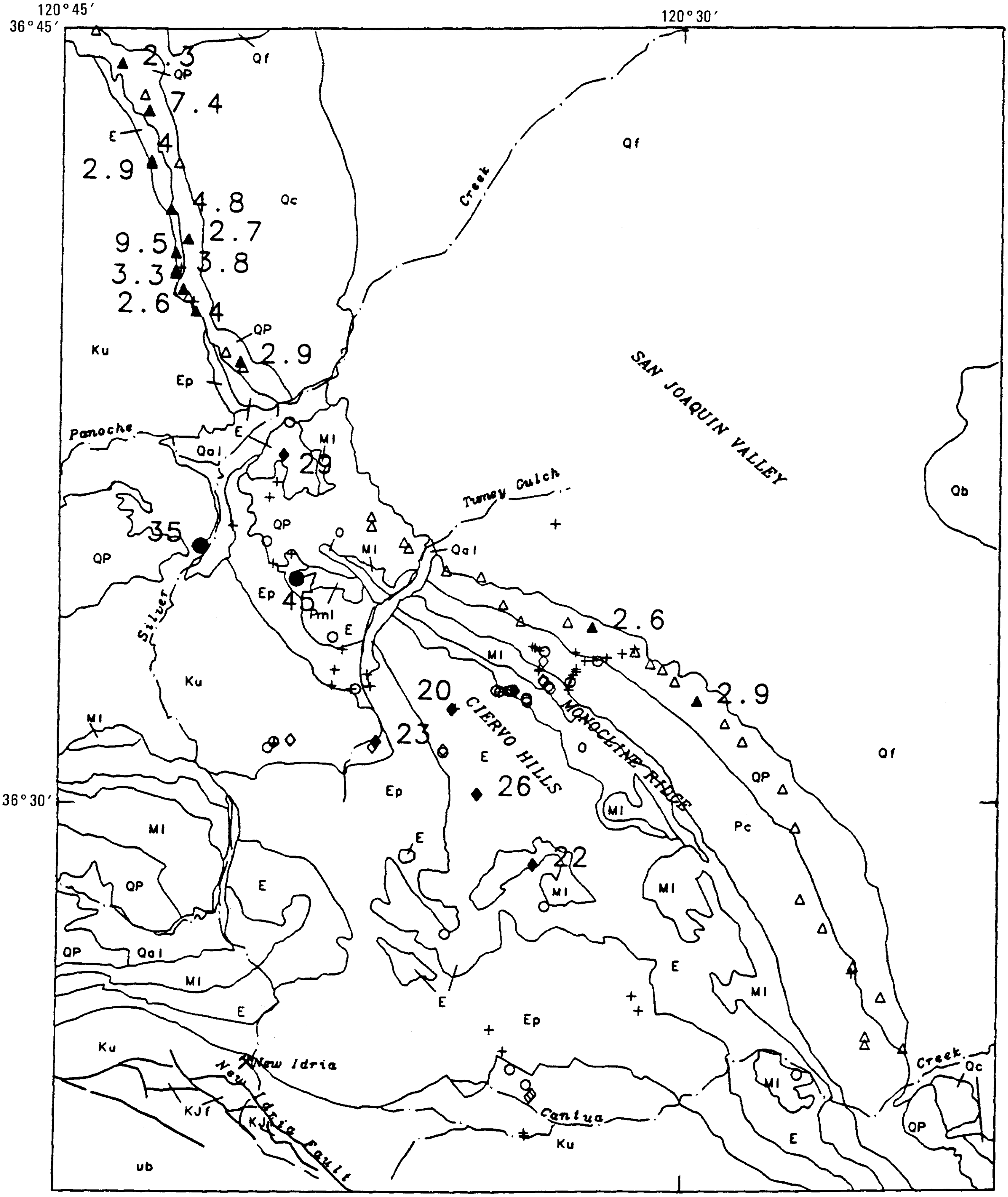

Figure 1 (above and facing page). Geologic map of Monocline Ridge area, part of the Diablo Range (map-unit symbols and stratigraphic nomenclature slightly modified from Jennings and Strand, 1958). Site locations of rock, soil, and stream sediment samples with selenium concentrations shown by classes (some larger values are posted.)

EXPLANATION

Sedimentary rocks

Qal	Quaternary alluvium
Qb	Quaternary basin deposits
Qf	Quaternary fan deposits
Qc	Pleistocene nonmarine
QP	Pleistocene and Pliocene nonmarine
Pc	Undivided Pliocene nonmarine
Pml	Middle and (or) lower Pliocene marine
Ml	Lower Miocene marine
O	Oligocene marine
E	Eocene marine (seleniferous)
Ep	Paleocene marine
Ku	Late Cretaceous marine (seleniferous)

Igneous rocks

KJf	Early Cretaceous and Late Jurassic Franciscan assemblage
ub	Mesozoic ultrabasic intrusions (serpentinite)

ROCK AND SOIL SITES

Selenium, ppm	
0.1 - 2.0	+
2.0 - 10	○
10 - 20	◇
20 - 30	◆
30 - 50	●

STREAM SEDIMENT SITES

Selenium, ppm	
0.1 - 2.0	△
>2.0	▲

STUDY AREA

The Monocline Ridge area consists of those foothills along the eastern flank of the Diablo Range that lies approximately between Panoche Creek on the north and Cantua Creek on the south and is bounded by the San Joaquin Valley on the east. Tumey Gulch is a principal drainage between Panoche and Cantua Creeks. The name, Monocline Ridge, refers to the line of foothills to the east of the higher parts of the Ciervo Hills where the topographic change from a moderate upland slope to a steep slope reflects the structure of underlying strata that are bent into a sharp monoclinal fold dipping to the northeast. The Ciervo Hills divide the drainage that flows east to the valley from that which flows west into Silver and Panoche Creeks. The study area also includes an extension of the mountain front north from Panoche Creek to latitude 36° 45′ N.

GEOLOGY

The rocks of the area include a series of sedimentary strata that range in age from Late Cretaceous to Quaternary. Formations that were sampled are listed in table 1. Rocks of middle Pliocene age and older are of marine origin. The lithology includes massive concretionary sandstone, siltstone, and shale. Diatomaceous earth is common in some shale units. The geology of Monocline Ridge area is shown in figure 1 as time-stratigraphic units.

Immediately southwest of the mapped area near the head of Silver Creek lies an extensive outcrop of serpentine intruded into rocks of the Franciscan assemblage of Jurassic age. The intrusion possibly occurred between the end of the Cretaceous and the middle of the Tertiary (Eckel and Myers, 1946, p. 94). Both upward and horizontal components of movement resulted in high angle faults around the sides of the intrusion, and the New Idria thrust fault is along the northeast flank of the serpentine dome. The thrust overturned the sandstone and shale strata of the Panoche Formation creating a porous zone where hydrothermal fluids deposited cinnabar ore with minor amounts of pyrite (Coleman, 1986) in the New Idria mining district.

METHODS

The formations and lithologic units (Dibblee, 1971, 1975) that were sampled include several time-stratigraphic units as shown in table 1. Samples mostly represent weathered rock or soil material (hereafter called soil) developed from the specified lithology. Stream sediments are whole samples of less than 2-mm particles. All streams channels were dry at the time of sampling. In some cases the sediments were variously coated with the white efflorescence of readily soluble evaporative salts.

All samples were air dried, sieved through a 2-mm stainless steel screen, and a subsample was ground in a ceramic mill to pass a 100-mesh screen. The sample was digested in acids (HF, HCl, HNO_3, and H_2SO_4) and total selenium was determined by hydride generation-atomic absorption spectrometry after volume adjustment in 6 M HCl (Briggs and Crock, 1986). The lower limit of determination of the method is 0.1 ppm.

RESULTS

The sampling sites for soils and stream sediments are shown in figure 1 superimposed over the geologic map units. Soil samples greater than 30 ppm selenium are annotated. Other concentrations are shown by class symbols. The stream-sediment samples are located along the valley margin (shown by triangles), and those samples with greater than 2.0 ppm selenium are annotated. Stream sediments with the higher concentrations of selenium occur north of Panoche Creek where the ephemeral streams cut across steeply dipping beds of both the Kreyenhagen Shale and the easily eroded Moreno Shale. These high concentrations are upstream from a selenium anomaly of limited area in nearby valley soils (Tidball and others, 1989b).

The selenium concentrations in samples of soils are summarized by geologic units in figure 2 as geometric means and expected ranges at the 95% confidence level.

Table 1. Formations and lithologic units sampled within each time-stratigraphic unit

[Map-unit symbols and stratigraphic nomenclature from Jennings and Strand (1958) and Dibblee (1975)]

QP--Pleistocene and Pliocene nonmarine sedimentary rocks:
QTt--Tulare Formation, terrestrial gravel, sand, clay, and caliche

Pc--Undivided Pliocene nonmarine sedimentary rocks:
Tun--Unnamed sand, gravel, and clay
Tuc--Unnamed clay, minor sand

O--Oligocene marine sedimentary rocks:
Ttu--Tumey Formation, semi-siliceous shale

E--Eocene marine sedimentary rocks:
Tk--Kreyenhagen Shale, clayey shale
Tki--Kreyenhagen Shale, semi-siliceous shale
Tke--Kreyenhagen Shale, semi-siliceous shale and clayey shale
Ep--Paleocene marine sedimentary rocks:
Tl--Lodo Formation, claystone, undifferentiated
Tlc--Lodo Formation, Cantua Sandstone Member

Ku--Late Cretaceous marine sedimentary rocks:
Km--Moreno Shale, undifferentiated micaceous claystone
Kp--Panoche Formation, clay shale

Only one sample was reported as less than 0.1 ppm, the lower limit of detection, but 55% of the samples were less than 2.0 ppm.

The analysis of variance, which is shown in table 2, indicates a highly significant difference between the means of geologic units that indicates a significant difference exists between the largest and the smallest mean. Duncan's multiple range test (Duncan, 1955), however, shows that the means fall into one of two groups; within each there are no significant differences. These groups are indicated by the underscores in figure 2. On the basis of the samples at hand, the division appears to reflect parent material: in general, the lower group of values is largely for nonmarine rocks, and the higher group of values is for marine rocks. The apparent marine and nonmarine division has one exception at the boundary: the Lodo Formation (Tl and Tlc) is of marine origin, but it groups with the nonmarine rocks. The claystone (Tl) has the highest average selenium (1.2 ppm) of the nonmarine group. The Lodo Formation is extensive in outcrop area, so the impact of its moderate selenium content on the gross material balance is of some concern. On the basis of additional observations of geologic units not covered here (Presser and others, 1990), the nonmarine rocks tend to be consistently nonseleniferous, but marine rocks are variably seleniferous.

Selected larger values of selenium in the Kreyenhagen Shale and the Moreno Shale, which are the predominant host rocks for selenium, are given in table 3. The largest selenium value found, 45 ppm, is in a clayey shale facies of the Kreyenhagen Shale. The Kreyenhagen Shale dominates the high selenium source rocks on the east side of the Ciervo Hills drainage divide. The largest value found in Moreno Shale, 35 ppm, is in subsoil material exhumed along a pipeline installation west of Silver Creek. The Moreno Shale has limited exposure near the head of Tumey Gulch, but most of the exposure is in the Silver Creek–Panoche Creek drainage. The water in Tumey Gulch was found to contain the highest amount of selenium among several streams along the valley margin (Presser and others, 1990).

DISCUSSION

An earlier study by Lakin and Byers (1941) reported 28 ppm of selenium in the Moreno Shale of Late Cretaceous age at Hospital Creek near the northwestern edge of the San Joaquin Valley. The results of this study confirm that marine shales of Late Cretaceous and Eocene age are enriched in selenium.

The selenium-enriched soils that occur in the valley adjacent to the Monocline Ridge area contain total selenium concentrations of about 2–5 ppm (Tidball and others, 1989b). The parent materials of these soils appear to be mudflow deposits derived largely from Kreyenhagen Shale,

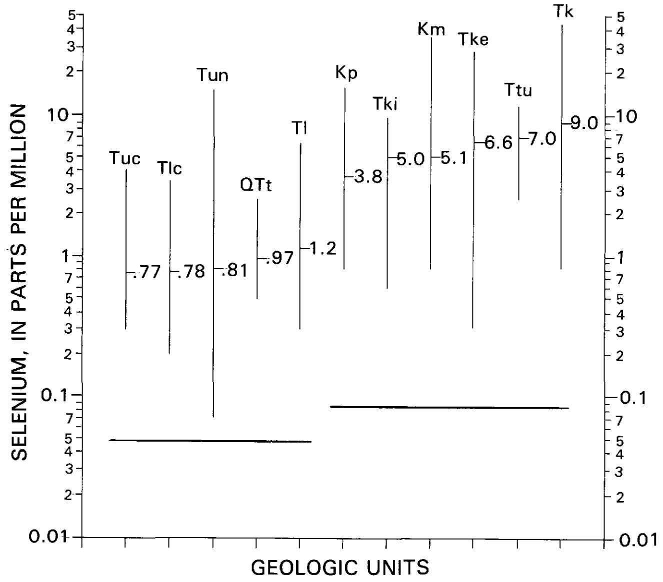

Figure 2. Summary of selenium in samples of geologic units from the Monocline Ridge area. Horizontal bar, labelled geometric mean. Vertical bar, 95-percent expected range. Underline, group of means with no significant differences. Geologic units abbreviations are defined in table 1.

which outcrops extensively in the watershed, and to a lesser extent from the Moreno Shale. Measurements of suspended sediment load in Panoche Creek (Presser and others, 1990) show that it contains 1.2–3 ppm selenium of which about 0.05 ppm occurs in a dissolved form.

A model for selenium mobilization as proposed by Presser and others (in press) is summarized here. Heavy winter rains penetrate surface cracks to destablize the poorly consolidated and steeply dipping marine shales. Pyrite is oxidized to sulfate to form an acid water (pH 4). Selenium can substitute for sulfur as in the pyrite analog, ferroselite ($FeSe_2$). The oxidation potential for the transformation sequence selenide-selenite-selenate at low pH is relatively high, but as the pH becomes more alkaline, the oxidation potential diminishes. Thus, the reaction is shifted toward the more mobile selenate form by neutralizing acid waters with existing bicarbonate waters derived from the Franciscan assemblage and the Panoche and the Lodo Formations. Soluble selenium along with other soluble salts, such as Na_2SO_4 and $MgSO_4$, then appear in seeps particularly along the base of landslides. A cycle of evaporative concentration and precipitation under a semiarid climate produces hydrated evaporative minerals, such as, mirabilite and bloedite. Such minerals serve as a temporary sink for selenium by substitution of selenate for sulfate in the crystal lattice. Evaporites from acid seeps in the Moreno Shale averaged 8.5 ppm (maximum of 25 ppm) selenium and from the Kreyenhagen Shale about 5 ppm selenium (Presser and others, 1990).

At least two transport mechanisms are probable. First, occasional flood events carry a significant sediment load derived from landslides and mass wasting that includes both reduced and oxidized selenium to the valley floor. Subsequent oxidation of the reduced forms in these mud flows can then occur on the valley floor. Second, an annual surge of dissolved salts including selenium appears in the ephemeral streams as the winter and spring rains remobilize the evaporative minerals. The larger streams may extend to the valley where the water could either infiltrate and recharge groundwater, or run off, or evaporate. Most of the small streams fail to reach the valley, and the salts are reprecipitated in the stream bed.

In general, the Coast Ranges have been shown to be a more significant source of selenium for valley soils than is the Sierra Nevada (Tidball and others, 1989b). Compared to the whole west side of the valley, the anomaly adjacent to the Monocline Ridge area is notable. What unusual features are there in this area?

First, a large exposure of serpentine occurs nearby that intruded into the Franciscan assemblage plus an associated mercury mineralization that developed on the northeast flank of the intrusion. Metacinnabar in certain of the ore veins contains selenium as an impurity in amounts of 0.30–6 weight percent (Boctor and others, 1987). Because the serpentine apparently intruded over an extended period, evidence of serpentine can be found among the sediments of several younger overlying rock strata and particularly on the alluvial fan of Cantua Creek. An outwash pattern of mercury is also found on both the Cantua Creek and Panoche Creek fans (Tidball, Severson, McNeal, and Wilson, 1989, p. 79). The origin of this mercury is taken to be the mineralized zone at New Idria. If the mineralized zone is also to be judged as a significant source of selenium, then we should expect to find a selenium pattern on both fans similar to the mercury. This is not the case as selenium is more prominent on the Panoche Creek fan than on the Cantua Creek fan. Although it is not possible to distinguish between selenium originating in the mineralized area from that originating in sedimentary rocks in the same watershed, it is concluded that the mineralized area is not a significant source of selenium.

Second, the area of exposed seleniferous marine shales is considerably larger in the Monocline Ridge area than anywhere else along the western margin of the valley. Also, the chance juxtaposition of acid seep waters from these easily eroded seleniferous shales and bicarbonate stream waters creates an alkaline environment that enhances the oxidation to soluble selenate. Because of low stream flow to the valley floor, limited through-flow potential probably exists from the alluvium into the groundwater system. Nevertheless, given a very long time, either surface flow or artesian flow have transported dissolved selenium to the lower perimeter of the alluvial fans where significant accumulations currently exist.

Table 2. Analysis of variance of log Se concentration in geologic units

Level	Sum of squares	Degrees of freedom	Mean square	Unit size	Variance component	*F*
1------	13.9265	10	1.3926	11	0.1610	5.69**
2------	16.6378	68	.2447	79	.2447	
Total	30.5634	78			.4057	

Table 3. Selected larger values of Se found in weathered samples of Kreyenhagen Shale (Tk, Tke) and Moreno Shale (Km) in the Monocline Ridge area

Location	Geologic unit	Selenium, (ppm)
NW¼ sec. 3, R. 12 E., T. 16 S.	Tk	45
SW¼ sec. 29, R. 13 E., T. 16 S.	do.	26
SE¼ sec. 4, R. 13 E., T. 17 S.	do.	22
NE¼ sec. 19, R. 13 E., T. 16 S.	do.	20
SW¼ sec. 19, R. 13 E., T. 16 S.	do.	13
SE¼ sec. 17, R. 13 E., T. 16 S.	Tke	29
Do.	do.	16
Do.	do.	13
Do.	do.	11
NE¼ sec. 31, R. 12 E., T. 15 S.	Km	35
SE¼ sec. 23, R. 12 E., T. 16 S.	do.	23
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CHAPTER K

Preliminary Results of the Department of the Interior's Irrigation Drainage Studies

Marc A. Sylvester, Jonathan P. Deason, Herman R. Feltz, and Richard A. Engberg

CONTENTS

Preliminary Results of the Department of the Interior's Irrigation Drainage Studies[1]

By Marc A. Sylvester, Jonathan P. Deason,
Herman R. Feltz, *and* Richard A. Engberg

ABSTRACT

Responding to increasing concern about the quality of irrigation drainage and its potential effects on human health, fish, and wildlife, the Department of the Interior, in 1986, began irrigation drainage studies in nine areas in seven Western States. These studies were done to determine whether irrigation drainage has caused or has the potential to cause harmful effects on human health, fish, and wildlife, or might reduce the suitability of water for beneficial uses. Results of the seven studies completed in 1987 are presented and are compared to baselines, standards, criteria, and other guidelines helpful for assessing the potential of observed constituent concentrations in water, bottom sediment, and biota to result in physiological harm to fish, wildlife, or humans. Selenium is the constituent most commonly found at elevated concentrations in water, bottom sediment, and biota in the study areas. Yearly variation in precipitation and streamflow, geologic sources of trace elements, arid to semiarid climate, internal drainage basins, irrigation drainage, and pesticide usage were the factors that affected concentrations of constituents in water, bottom sediment, and biota in the study areas.

INTRODUCTION

Responding to increasing concern about the quality of irrigation drainage and its potential effects on human health, fish, and wildlife, the Department of the Interior, in 1986, began irrigation drainage studies in nine areas in seven Western States. These studies were done to determine whether irrigation drainage has caused or has the potential to cause harmful effects on human health, fish, and wildlife or, might reduce the suitability of water for beneficial uses.

Seven of the studies were completed during 1987 and the remaining two (Salton Sea area in California and Stillwater Wildlife Management Area in Nevada) will be completed in 1988. Studies at ten additional areas were started in 1988. More detailed studies in four of the areas studied in 1986 and 1987 also were started in 1988. These four studies are being done because results of the 1986–87 studies in these areas indicate that irrigation drainage might be causing harmful effects on human health, fish and wildlife, or beneficial uses of water.

SUMMARY OF RESULTS

A brief summary of the most significant results from each of the reconnaissance investigations completed in 1987 is presented. The page limitations of this report preclude anything more than an overview of the most significant findings. Readers should refer to the referenced reports to obtain a full discussion of the results of each investigation and to Deason (1988) for a description of the sampling and analysis protocol.

Lower Colorado River, Arizona, and California

The lower Colorado River study area (Radtke and others, 1988) included the mainstream Colorado River and adjacent land from Davis Dam, just north of the Arizona-California border, downstream to Imperial Dam just north of the Mexican border.

With the exception of one water sample having a cadmium concentration of 69 ppb, no trace elements were found in concentrations exceeding State of Arizona maximum allowable limits for protected uses of surface water. In addition, the only organic pesticides detected in water were the short-lived organophosphorus compounds diazinon, methylparathion, parathion, and chlorpyrifos.

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Concentrations of barium, molybdenum, vanadium, and zinc in water were substantially greater at stations directly receiving irrigation drainage but were not found to be at elevated levels. Selenium concentrations, conversely, were lower at stations directly receiving agricultural discharges and did not increase from Davis Dam to Imperial Dam. Thus, selenium concentrations in water appear to be derived from sources upstream of Davis Dam and are not enriched by agricultural activities in the lower Colorado River valley.

Selenium concentrations in bottom sediment at mainstream stations equaled or exceeded the 95-percent baseline (1.4 ppm dry weight) for soils in the Western United States (R. C. Severson, United States Geological Survey, written commun., 1987). Selenium concentrations in bottom sediment at stations directly receiving agricultural discharges were lower than at mainstream stations and did not exceed the 95-percent baseline for soils in the Western United States. The largest concentrations of selenium in bottom sediment (up to 7.1 ppm dry weight) were found in backwater areas of the mainstream of the Colorado River. Thus, bottom sediment in the mainstream of the lower Colorado River appears to be acting as a sink for selenium. Organochlorine pesticides and other synthetic organic compounds were detected in bottom sediment in the study area. DDE was found at all stations and ranged from 0.1 to 7.5 ppb, dry weight.

Except for selenium, no inorganic constituents exceeded guidelines for the protection of fish and wildlife resources. Mean selenium concentrations in carp ranged from 0.62 to 4.0 ppm wet weight, generally exceeding the 85-percent national baseline of 0.71 ppm, wet weight for fish collected in the National Contaminant Biomonitoring Program from 1978 to 1981 (Lowe and others, 1985). Selenium concentrations in fish of 2 ppm, wet weight or greater, can result in reproductive impairment or lack of recruitment in fishes (Baumann and May, 1984). Carp having concentrations equal to or greater than 2 ppm, wet weight, were collected from backwater or oxbow lakes that receive inflow from the main river.

Organic compounds do not appear to present environmental problems for fish in the lower Colorado River. Organochlorine pesticide concentrations in biota generally were less than 1.0 ppm, wet weight.

Tulare Lake Area, California

The Tulare Lake study (Schroeder and others, 1988) was conducted in the southern portion of the dry Tulare Lake Bed, which is located at the southern end of the Central Valley in California. Specific sites included in the study were the Kern and Pixley National Wildlife Refuges and the Westfarmers evaporation pond system, which is about 5 miles west of the Kern Refuge.

Trace-element concentrations in water, bottom sediment, and biota were found to be comparatively low at Kern and Pixley National Wildlife Refuges and high at Westfarmers evaporation ponds. Concentrations of trace elements at Kern and Pixley National Wildlife Refuges did not exceed baselines, drinking-water standards, or criteria for protection of aquatic life. Concentrations of several trace elements did exceed such guidelines at Westfarmers evaporation ponds. For example, concentrations of selenium, the constituent of greatest concern in the study area, ranged from 110–360 ppb in water from the Westfarmers evaporation ponds, far exceeding the U.S. Environmental Protection Agency (1986) criterion of 35 ppb for protection of aquatic life. In contrast, selenium concentrations in water at Kern and Pixley National Wildlife Refuges were less than 1 ppb.

Few pesticides were detected in water, bottom sediment, or biota, and where found, their concentrations were much less than those at which adverse effects would be apparent.

Low concentrations of trace elements and pesticides at Kern and Pixley National Wildlife Refuges indicate that these constituents pose little threat to wildlife there. Much higher concentrations of trace elements (particularly selenium) in water, bottom sediment, and biota at Westfarmers evaporation ponds suggest that health and reproduction of wildlife there could be threatened. Preliminary results of bird censuses and nesting and brooding surveys in 1987 indicate that there are adverse physiological effects on shorebirds nesting at Westfarmers evaporation ponds.

Sun River Project, Montana

The Sun River study area (Knapton and others, 1987) was composed of three areas in Teton and Cascade counties of west-central Montana: (1) the Greenfield–Fort Shaw Irrigation Districts, (2) Freezeout Lake Game Management Area (including Priest Butte Lake) and (3) Benton Lake National Wildlife Refuge (NWR). Each of these areas is directly affected by irrigation practices and return flows.

Based on a comparison with baselines, criteria, and standards, concentrations of constituents in water, bottom sediment, and biota within the Greenfields–Fort Shaw Irrigation Districts do not indicate a threat to human health, fish, or wildlife. Both the Freezeout Lake Game Management Area and the Benton Lake NWR, however, were found to contain elevated levels of several constituents in water, bottom sediment, and biota. The highest concentrations of trace elements in water and bottom sediment were associated with saline seeps, which are common throughout the northern Great Plains. For example, concentrations in water as high as 580 ppb selenium, 660 ppb cadmium, 7,000 ppb nickel, 2500 ppb boron, and

19,000 ppb zinc were detected in saline seeps in the Benton Lake NWR. These concentrations far exceed Montana standards or criteria for the protection of human health, aquatic life, or agricultural crops. However, flow volumes from such seeps were very small relative to total inflows. The highest selenium concentration in bottom sediment was 6.7 ppm, which is greater than the 95-percent baseline of 1.4 ppm for soils in Western United States.

Boron concentrations in sago pondweed from Freezeout Lake and Benton Lake were at levels (230–990 ppm, dry weight) that might be toxic to consumer organisms limited to an aquatic vascular plant diet for an extended period of time (Knapton and others, 1987). Several bird livers and eggs contained boron concentrations at or approaching levels (6–89 ppm and 26–31 ppm, dry weight, respectively) found in diet studies to reduce hatching success and decrease survival of mallard ducklings (Patuxent Wildlife Research Center, 1987), while other bird livers and eggs were below such levels.

Selenium was found in the majority of biological samples. The highest levels of fish were found in Priest Butte Lake. Selenium concentrations (dry weight) in fish (up to 48 ppm in yellow perch and 35 ppm in white sucker), invertebrates (up to 32 ppm in insects), bird livers (up to 32 ppm in avocets, 28 ppm in coots, and 46 ppm in eared grebes), and bird eggs (up to 68 ppm in avocet eggs, 7.8 ppm in coot eggs, and 18.0 ppm in eared grebe eggs) indicate that levels are present that could have toxic effects on fish (Gillespie and Baumann, 1986; Goettl and Davies, 1978) and birds (Heinz and others, 1987). Other trace elements and pesticides either were not detected or generally were at low concentrations.

Milk River, Montana

The Milk River study area (Lambing and others, 1987) is centered around the Bowdoin NWR in northeastern Montana, about 7 miles east of the town of Matta.

In general, concentrations of trace elements, radiochemicals, and pesticides in the refuge lakes were not found to be greatly elevated compared to upstream water supplies. Very few exceedances of water quality guidelines were detected, and none were prevalent at any particular site. High streamflows in the study area in 1986 probably resulted in lower than normal concentrations of dissolved constituents.

In bottom sediment, trace element concentrations were generally similar to background concentrations found in soils, and pesticides were not detected. Concentrations of trace elements and pesticides in biological organisms generally were less than values known to adversely affect growth or reproduction. Maximum concentrations of several trace elements were considered elevated, but the occurrences generally were random among sites. Arsenic was found in all biological samples analyzed except for bird eggs, walleyes, and hemipterans, and was highest in plants and net plankton. The highest arsenic concentration measured was 21 ppm dry weight in net plankton. Boron was found in all organisms sampled but one, and generally was found in higher concentrations in sago pondweed and filamentous algae than in other trophic levels sampled. The highest boron concentration (810 ppm dry weight) was detected in sago pondweed. Mercury was below detectable levels in plants and invertebrates and was found at relatively low concentrations in bird eggs, bird livers, and fish. The highest mercury concentration (1.6 ppm dry weight) was in an avocet egg. Selenium was found in all classes of organisms sampled, with the highest concentrations (2.6–13 ppm dry weight) occurring in net plankton.

Laguna Atascosa National Wildlife Refuge, Texas

The Laguna Atascosa study (Wells and others, 1987) was conducted in the lower Rio Grande Valley, which is located principally in the four southernmost counties of Texas: Starr, Hidalgo, Cameron, and Willacy. It includes the Laguna Atascosa NWR along the Gulf of Mexico in Cameron and Willacy Counties.

Results of sampling in the lower Rio Grande Valley and Laguna Atacosa NWR indicate that concentrations of dissolved trace elements in water generally are not elevated. The most significant trace element appears to be boron, the concentrations of which increase significantly from west to east. Concentrations of boron ranged from 220 ppb to 5,300 ppb at all sampling locations except for Athel Pond, a lake in the refuge that receives little freshwater inflow, where concentrations of dissolved boron as high as 11,000 ppb were detected. No chlorophenoxy herbicides or carbamate insecticides were detected. Low concentrations were detected of triazine herbicides (less than 0.1 to 1.7 ppb), organophosphorus insecticides (less than 0.01 to 0.75 ppb), and organochlorine insecticides (DDE only, from less than 0.01 to 0.01 ppb).

Concentrations of trace elements in bottom sediment were less than the 95-percent baselines for soils in the Western United States, except for manganese (maximum concentration exceeded the 95-percent baseline of 1,500 ppm). The only pesticides detected in bottom sediment were chlordane, DDT, DDE, DDD, and dieldrin. Concentrations ranged from 0.1 to 34 ppb, dry weight.

Concentrations of trace elements in fish were low. Only maximum concentrations of arsenic, mercury, selenium, copper, and zinc exceeded the 85-percent baselines for fish in the United States (Lowe and others, 1985). No concentrations were at levels known to be harmful to fish. The only pesticides detected were toxaphene, DDT, DDE, and DDD concentrations ranging from less than detection to 9.9 ppm, wet weight. Some concentrations exceeded baselines for fish in the United States (Schmitt and others, 1985).

Concentrations of trace elements in birds also were low. For example, the selenium concentration in a composite of five black-necked stilts was only 0.47 ppm, wet weight. No concentrations were at levels known to be harmful to birds. Concentrations of DDT, DDD, and DDE in the black-necked stilt composite were 0.036, 0.053, and 3.3 ppm wet weight, respectively.

Middle Green River, Utah

The Middle Green River Basin area consists of about 25,500 square miles along the mainstream of the Green River and its tributaries south of Flaming Gorge Reservoir and north of the town of Green River, Utah. The study (Stephens and others, 1988) focused on the Ouray National Wildlife Refuge and the Stewart Lake Waterfowl Management Area within the middle Green River Basin.

Generally, concentrations of all constituents except boron, selenium, zinc, and gross alpha radiation were less than guideline values in water, sediment, and biological tissues. Of these, selenium appeared to be the principal constituent of concern. Concentrations of selenium entering Stewart Lake from subsurface drain pipes ranged from 14 to 140 ppb. Selenium concentrations in bottom sediment in the alluvial areas where the drains enter Stewart Lake ranged from 10 to 85 ppm. Liver tissue collected from coots at Stewart Lake contained from 4.9 to 26 ppm selenium, dry weight. These concentrations are similar to those in coots from Kesterson NWR (Ohlendorf and others, 1986a) and indicate that adverse effects on wildlife reproduction and growth from selenium may be occurring.

At the Ouray NWR, concentrations of selenium in water ranged from less than 1 to 93 ppb, with the higher values occurring in the North Roadside Pond, which receives only irrigation drainage water. Liver tissue from coots on the North Roadside Pond contained a geometric mean concentration of 32 ppm selenium, dry weight, whereas liver tissue from coots collected in areas of the refuge that receive water from the Green River contained less than 5 ppm selenium, dry weight. Several embryonic deformities also were found in the North Roadside Pond.

At a few sites, concentrations of boron and zinc exceeded Utah standards for agriculture and wildlife protection, respectively. Gross alpha radiation in drain water samples generally exceeded the Utah standard of 15 picocuries per liter for protection of aquatic life and domestic water supplies.

Kendrick Project, Wyoming

The Kendrick study area (Peterson and others, 1987) was defined as the Kendrick Reclamation Project service area, just west of Casper, Wyoming. The study area is bounded on the east by the North Platte River and Casper Creek, and on the west by the Casper Canal. Analyses of water, bottom material, and biological samples for trace elements, pesticides, and radiochemicals indicated that the main constituent of concern is selenium. Concentrations of dissolved selenium in water ranged from less than 1 ppb to 300 ppb, with a medium concentration of 7.5 ppb. The higher selenium concentrations were found in creeks, a drain, a well, and a lake. Concentrations of dissolved selenium in the North Platte River, which supplies drinking water for several municipalities, ranged from less than 1 to 4 ppb.

Bottom material samples contained selenium concentrations of 0.9–25 ppm, with the highest levels found in the places that contained the higher concentrations of dissolved selenium in water.

Selenium concentrations in fish and invertebrate samples taken at some lakes were at levels (greater than 8 ppm, dry weight) that could cause adverse physiological effects to birds (Heinz and others, 1987; Patuxent Wildlife Research Center, 1987). Most bird liver and egg samples from lakes contained selenium concentrations that could have toxic effects. For example, selenium concentrations ranged from 51 to 170 ppm (dry weight) in avocet livers from Rasmus Lee Lake and were 43 to 56 ppm (dry weight) in two mallards from Illco Pond.

Other than selenium, the only constituent that might be of concern is boron. Boron concentrations in rooted aquatic plants were found at levels (390–630 ppm, dry weight in sago pondweed) that might be toxic to birds limited to a diet of aquatic vascular plants for an extended period of time.

FACTORS AFFECTING RESULTS

Several factors appear to be involved in determining the concentration of constituents associated with irrigation drainage that were found in water, bottom sediment, and biota during the 1986–87 reconnaissance studies of irrigation drainage areas conducted by the Department of Interior.

One of the factors is the yearly variation in precipitation and streamflow. The Milk River, Colorado River, and Green River basins had greater than normal precipitation prior to or during the studies, which resulted in greater than normal streamflows. Generally, constituent concentrations were not elevated or were not at levels known to produce harmful effects on growth or reproduction of organisms in the Milk River or Lower Colorado River study areas. However, in the Middle Green River study area, a few trace elements, principally selenium, occurred at elevated concentrations in water, bottom sediment, and biota. Deformed coot embryos were found, and selenium concentrations in biota were at levels that can result in adverse effects on wildlife reproduction. Larger than normal flows in the Milk and Colorado Rivers raised refuge water levels and helped flush accumulated salts from the wetlands. The flushing of Stewart Lake WMA due to large flows in the Green River since 1982 probably has diluted concentrations of trace elements in the lake. Thus, greater than normal precipitation and streamflow decreased constituent concentrations, but elevated concentrations of trace elements in water, bottom sediment, and biota still were observed in the Middle Green River study area.

Geologic sources of trace elements is another factor. Kendrick Reclamation Project area, Middle Green River basin, and west side of the Tulare Lake basin contain geologic formations known to be sources of trace elements, particularly selenium. In each case, the source rocks are pervasive, and soils in the area are primarily derived from such rocks. In the Kendrick Reclamation Project area, soils are derived from Cretaceous formations of marine origin, several of which are known to be seleniferous (Crist, 1974; Rosenfeld and Beath, 1964, p. 23). Soils in the area are known to be high in selenium (3.7–37 ppm, Rosenfeld and Beath 1964, p. 45). Irrigated lands in the Middle Green River basin are located on soils that overlie the Mancos Shale. This shale is known to contain high concentrations of selenium (140 ppm at a site in Colorado) (Coleman and Delevaux, 1957, p. 519) and is the formation in which the Green River flows in much of the study area. Soils in the western part of the Tulare Lake basin are derived from Cretaceous and Tertiary marine rocks that contain selenium. Soils on the west side of the basin are high in selenium (Tidball and others, 1986). As mentioned previously, Kendrick Reclamation Project area, Middle Green River, and Westfarmers ponds in the western part of the Tulare Lake basin have elevated concentrations of trace elements, principally selenium, in water, bottom sediment, and biota. Concentrations are at levels that could result in harmful effects to wildlife.

Although geologic formations that contain selenium and other trace elements do occur in the other study areas, elevated selenium concentrations in bottom sediment occur only in the Lower Colorado River basin. The source of these elevated concentrations appears to be upstream of Davis Dam, which is outside of the study area. Elevated selenium concentrations in soils have not been documented in any of these areas. Except in a few localized places, selenium concentrations in water and biota also were not elevated at any of these other study areas. Thus, geologic sources of trace elements (particularly selenium) appear to be directly related to elevated concentrations of these elements in the study areas, especially and perhaps only, if such sources are pervasive and substantial enough to have a primary effect on concentrations of trace elements in soils and bottom sediments.

A third factor is an arid to semiarid climate where precipitation is low (that is, less than or equal to 12 inches per year) and evaporation or evapotranspiration is high (several times precipitation). These conditions apply to all the study areas except Laguna Atascosa, where the average annual precipitation is between 22 and 30 inches, depending on location in the study area. Evaporation of water in streams, ponds, and wetlands in the study areas no doubt increased salt concentration in water and soil. Nevertheless, evaporation or evapotranspiration do not appear to be the primary factors controlling trace-element concentrations in the study areas, because some areas had relatively low concentrations and others had relatively high concentrations despite similar precipitation and evaporation conditions.

Another factor is internal drainage basins or sinks. Indeed, the greatest trace element and dissolved solids concentrations in the Milk and Sun River study areas generally were found in terminal drainages with no outlet (Dry Lake Unit and Benton Lake, respectively). Also, selenium concentrations in biota were greatest in Westfarmers Ponds (evaporation ponds with no outlet) in the Tulare Lake study area, and in the shallow ponds and reservoirs with little or no flow through or surface water release in the Kendrick Reclamation Project area. These areas had elevated selenium concentrations that could result in adverse effects on wildlife reproduction and growth. In the Middle Green River study area, Stewart Lake and ponds and wetlands in the Ouray NWR are managed water bodies with inlets and outlets; they do not function as internal drainages. Wetlands and ponds along the Lower Colorado River are not internal drainages either. However, the only elevated selenium concentrations detected (> 2 ppm, wet weight) were from backwater or oxbow lakes that receive inflow from the main river. Despite some nonconforming situations, most of the information from the reconnaissance studies shows that internal drainages with terminal ponds and wetlands (especially shallow ones) and backwater or oxbow lakes (in the case of the Lower Colorado River study) are related to elevated trace-element and dissolved-solids concentrations. This is not unexpected, as effects of evaporation and evapotranspiration would be greatest in such areas under arid or semiarid climatic conditions.

The amount and proportional contribution of irrigation drainage to wetlands, ponds, and refuges in the study areas is another factor. Irrigated agriculture occurs in all of the study areas. The amount of irrigation drainage and the proportion it contributes to the water supply of refuges and wetlands varies considerably among the study areas.

In study areas where concentrations of selenium were elevated and at levels that could adversely affect wildlife reproduction and growth (Kendrick Reclamation Project, Middle Green River, and Tulare Lake study areas) extensive irrigation and drainage do occur. The contribution of irrigation drainage to receiving waters in these areas ranged from none at Goose Lake in the Kendrick Reclamation

Project area to all at Westfarmers Ponds in the Tulare Lake area. Except for Goose Lake, the amount of irrigation drainage received by wetlands, ponds, and reservoirs in the Kendrick Reclamation Project area is not well documented. North Roadside Pond, where elevated selenium concentrations in water and biota were noticed at Ouray NWR in the Middle Green River study area, receives irrigation tailwater and likely some shallow ground water. Except during periods of overflow from the Green River, the source of water to Stewart Lake primarily is irrigation drainage from the lands within the service area of the Jensen Unit of the United States Bureau of Reclamation's Central Utah Project.

In other study areas where concentrations of selenium generally were not elevated (Milk River, Sun River, Laguna Atascosa, and Lower Colorado River areas), a consistent pattern is not apparent. Irrigation and drainage generally are not extensive in the Milk and Sun River study areas, but are in the Lower Colorado and Laguna Atascosa study areas. Irrigation drainage comprises 15–40% of the water supply to Bowdoin NWR in the Milk River study area. It is a minor source of water to Freezeout Lake Game Management Area and a major source of water to the Benton Lake NWR in the Sun River study area. Major sources of irrigation drainage contribute water to the Laguna Atascosa NWR and wetlands and refuges in the Lower Colorado River study area, although the proportion it contributes to the total supply is undetermined. A clear relation cannot be determined between elevated trace-element concentrations and the amount and proportional contribution of irrigation drainage to receiving waters in the study areas because of the paucity of quantitative information and the apparent lack of consistent patterns among study areas.

The last factor considered is pesticide application. Little or no quantitative information on pesticide application was obtained during the reconnaissance studies. Thus, no quantitative relations can be determined between usage and occurrence in water, bottom sediment, or biota. Nevertheless, some qualitative statements can be made. Organochlorine pesticides generally were detected only in study areas where applications have been large (Lower Colorado River and Laguna Atascosa). DDE was the principal compound detected. Concentrations were low in water and sediment (<0.01 ppb and generally less than 10 ppb, dry weight, respectively). Concentrations in biota also were low (generally less than 1.0 ppm, wet weight). The occurrence of DDE is indicative of the persistence of this breakdown product of DDT, which was widely used from the 1940's to the early 1970's (when it was banned in the United States). Other pesticides either were not detected or their occurrence was localized.

GENERAL OBSERVATIONS AND RELATIONS

Although the evaluation process described here has not yet been completed, several observations about the nature of irrigation-induced contamination problems can be made.

First, it appears that selenium is the constituent most commonly found at elevated concentrations. Although selenium was not detected at elevated concentrations in all areas nor was it found to be the constituent of greatest concern in all areas with elevated concentrations, it clearly was the constituent most frequently detected at elevated levels.

Another significant observation concerns the variability of concentrations found within the study areas. Concentrations of analytes were found to vary widely on a spatial basis in all environmental media sampled. This observation leads to the conclusion that, at least in some cases, irrigation-induced contamination problems are likely to be site specific. Thus, problems can be severe on a localized basis while having a low level of relative significance on a regional basis.

Other inferences can be made from the results of the reconnaissance investigations that may enhance our ability to predict where irrigation-induced contamination problems will occur from planned or existing irrigation developments. For example, irrigated areas in internal drainage basins appear to have high concentrations of trace elements in water, bottom sediment, and biota. The Tulare Lake, Milk River, Kendrick, and Sun River study areas all contain internal drainage basins or bodies of water having no surface-water outlets. In each case, the closed bodies of water contained some of the highest concentrations of constituents within the study areas.

Other hydrologic and geochemical characteristics also can serve as indicators of possible problems. The presence of alkaline, seleniferous soils in arid or semiarid environments (low precipitation with high evaporation rates) is an example.

One fairly consistent pattern that should be of interest to scientists and resource managers alike is the apparent inverse relation between selenium and arsenic concentrations. The inverse relation appears to be consistent among study areas and within the various media analyzed (water, bottom sediment, and biota). This apparent relation is being investigated further.

CHAPTER L

Selenium Issues in Drastically Disturbed Land Reclamation Planning in Arid and Semiarid Environments

Scott E. Fisher, Jr., and Frank F. Munshower

CONTENTS

TABLES

Selenium Issues in Drastically Disturbed Land Reclamation Planning in Arid and Semiarid Environments

By Scott E. Fisher, Jr., *and* Frank F. Munshower

ABSTRACT

Selenium is a potentially toxic microelement of concern in drastically disturbed land reclamation in the arid and semiarid environments of the Western United States. An important aspect of this reclamation is the planning of material selection for minesoil construction to prevent production of forages having toxic selenium concentrations. Many factors influence uptake and incorporation of selenium by plants. These factors make the evaluation of relationships between soil selenium and plant tissue selenium difficult. Analytically based selenium values are suggested to prevent the development of potential herbivore toxicities under four disturbed land reclamation land use options.

INTRODUCTION

Selenium is an essential microelement for fauna but if found in sufficiently high dietary concentrations it may be toxic. The differences between selenium deficiency and toxicity in animals are relatively narrow. A dietary level of 0.1 ppm in the diet is generally considered essential and 5.0 ppm potentially toxic (Whanger, 1974). Herbivore selenium deficiencies have been well documented, are important economically, and are relatively widespread in humid regions of the United States. Lakin (1961b) stated that deficiency is the most widespread and important issue related to selenium in animal nutrition.

While deficiency is a more widespread livestock problem, selenium toxicities are the major problem in the Great Plains. Both chronic and acute types of livestock losses from consumption of forage grown on seleniferous western soils have been reported (Rosenfeld and Beath, 1964). Chronic forms of selenium toxicity are difficult to isolate but are potentially more important economically to western agriculture than acute poisoning.

Plant tissue concentrations of greater than 5.0 ppm are considered capable of producing chronic toxicities if provided for sustained consumption by herbivores (National Research Council, 1976). This toxicity value serves as the basis for the suggested selenium levels for reconstructed plant growth media in this report.

The primary objectives of current land reclamation planning are to (1) confine the environmental impact to the original disturbance area, (2) mitigate or detoxify environmental hazards related to the initial disturbance, and (3) return the disturbed site to productive land use. These reclamation efforts do not attempt to restore the predisturbance soils or biotic communities, but concentrate instead on reestablishing functional ecosystems capable of sustaining the postmining land use. Inherent in this type of reclamation planning is the need to provide long-term relief from environmental impacts resulting from earlier developments or activities.

Relative to potentially toxic microelements such as selenium, the disturbed land reclamation goal is to reconstruct ecosystems that will support the defined land use for extended time periods. Meeting these requirements in the arid and semiarid environments of the Western United States includes forage production that will not induce either acute or chronic toxicity in herbivores. The potential for chronic microelement impacts on livestock thrift and productivity are critically important in today's highly competitive agricultural marketplace.

Successful reclamation in the Western States is dependent upon control and/or appropriate placement of materials containing potentially acid-forming and/or toxic microelements. Selenium, along with boron, appears to be among the most important of the potentially toxic microelements in this region. Four components of the many selenium issues are particularly important in arid and semiarid disturbed land and waste reclamation planning.

- The total amount of selenium in a soil is not consistently correlated to vegetation levels. Some fraction of the total selenium is available for plant uptake, and this fraction varies with the redox potential, pH, and other less well understood conditions in the plant growth media.

- The widespread use and successful establishment of western wheatgrass (*Pascopyrum smithii*) and four-wing saltbush (*Atriplex canescens*) in reclamation efforts are widely accepted. Both species are quite palatable to livestock and have been described as secondary selenium accumulators (Rosenfeld and Beath, 1964). Both species have demonstrated capacities to accumulate relatively high concentrations (over 100 ppm) of selenium in their tissues (Munshower and Prodgers, 1990).
- Some of the species of *Astragalus*, a group known to accumulate selenium, appear to be more frequently encountered in disturbance areas; therefore, they may be among the early native pioneer species in revegetated and reclaimed areas. Observations of the distribution of *Astragalus bisulcatus* (two grooved milkvetch) on disturbed areas throughout the Great Plains support this thesis (Rosenfeld and Beath, 1964).
- The proposed introduction of intensive short duration grazing systems on revegetated areas could bring about greater utilization of the relatively unpalatable primary selenium accumulator species. Less intensive management systems and forms of forage utilization, such as those associated with wildlife land uses, would result in greater selection and use of more palatable plant species expressing lower selenium concentrations.

SELENIUM DISTRIBUTION, FORMS, AND UPTAKE BY PLANT SPECIES

Selenium is often found associated with pyrite enrichments in metalliferous deposits. Spoils and processing waste materials from these minerals often contain potentially toxic amounts of selenium. Boon and Smith (1985) reported selenium enrichments in coals and carbonaceous materials. Lithochromic or carbonaceous materials and coal stringers occur in the overburden and spoil of some surface mines. Placing these materials into the near-surface portions of minesoils may result in the incorporation of potentially toxic concentrations of selenium and other microelements in plant tissue.

Overburden and spoil materials are frequently composed of reduced materials where selenium occurs in the elemental, selenide, and selenite forms. In some cases, such as the southern Powder River Basin of Wyoming, much of the selenium in overburden material appears to be in an organic detrital form (Naftz and Rice, 1988). Determination of potential selenium toxicities in overburden and spoil is difficult but important in hydrologic restoration, minesoil construction, and related revegetation portions of reclamation planning for disturbed lands and potentially toxic material disposal.

The intensity of chemical and physical weathering systems, as well as, the degree of expression of pedogenic processes, are climatically limited. Therefore, soils developing under drier regimes often closely reflect the chemical and physical properties of the soil parent materials. Soils developing under western arid and semiarid environments from geologic formations that contain parent rocks of relatively high selenium concentration have similarly elevated selenium levels. Western soils derived from the Pierre, Niobrara, and Greenhorn Formations (Cretaceous Age) and various Jurassic and Triassic formations often reveal elevated soluble selenium concentrations (Rosenfeld and Beath, 1964; Lakin, 1961a).

Selenium concentrations range widely in representative western soils—from high levels in excess of 40 ppm AB-DTPA (ammonium bicarbonate-diethylenetriaminepentaacetic acid) extractable to nondetectable levels (< 100 ppb). The higher values are from samples collected from the C_r horizons from a loamy, mixed (calcareous), frigid, shallow, Aridic Torriorthent from the Poison Draw drainage northwest of Lysite, Wyoming. Analysis was accomplished by several methods at Intermountain Laboratories, Sheridan, Wyoming, and the Reclamation Research Unit Laboratory, Montana State University, Bozeman, Montana. Selenium is not uniformly distributed in soil profiles. Pedogenic activities distribute soluble selenium in a manner similar to sulfur, with enrichments occurring well below the zone of carbonate enrichment.

Spoils, tailings, mineral processing wastes, fly ash, and other materials disposed of in near-surface environments can differ widely in selenium content and ion species present. The total selenium concentration and ion species are important in defining any potential selenium problems. However, the nature of the depositional environment is also important in defining potential toxicity problems (P. J. Sullivan, Western Research Institute, Laramie, Wyoming, oral commun., 1988). The depositional environment will influence conversion of insoluble selenium species to the more soluble forms and vice versa. In any plant growth media, the equilibrium developed between the mineral and solution phase, as well as the redox conditions in the root environment, will be important in defining the potential for uptake and incorporation of selenium into plant tissues. Nevertheless, the conversion of insoluble selenium forms to plant-available selenium is an oxidation process that appears to occur relatively slowly.

The amount and form of selenium in plant root growth media, and the plant species present, are the primary factors controlling selenium concentrations in plant tissues. Selenium forms in soil and geologic materials generally

Table 1. Plant tissue selenium concentrations of the dominant plant species near Chalk Bluff, Wyoming (July 1987 collection)

[Dashes (---) indicates plant species not present]

Species	Plant tissue selenium concentration (ppm)		
	Site No. 3	Site No. 4	Site No. 5
Agropyron spicatum	---	28	---
Pascopyrum smithii	12	---	8
Artemisia tridentata	11	---	33
Astragalus bisulcatus	7,300	---	7,600
Astragalus pectinatus	3,300	4,400	3,600
Atriplex gardeneri	---	---	1,500
Ceratoides lanata	33	77	50
Chrysothamus viscidiflorus	11	---	32
Eriogonum brevicaule	16	6	---
Gutierrezia sarothrae	---	208	50
Linum lewisii	---	50	---
Machaeranthera grindeloidies	300	380	630
Oryzopsis hymenoides	55	40	---
Tetradymia canescens	11	6	44
Xylorhiza glabriuscula	---	---	473

include selenate, selenite, elemental selenium, selenide, and organoselenium compounds. Brown (1991) has reviewed the factors influencing selenium solubility in primary and secondary minerals. Selenate is thought to be the dominant species of selenium in alkaline western soils (Elrashidi and others, 1989). In some areas, it is thought that selenium-containing organic compounds compose a significant portion of the soluble selenium fraction in naturally occurring soils. Lithochromic/carbonaceous or high clay content plant growth media frequently contain higher selenium concentrations (Boon and Smith, 1985).

Plant species range widely in their ability to absorb selenium from the soil solution as is indicated by the plant tissue selenium concentrations in table 1. Selenium speciation, generally controlled by oxidative status and reaction of the plant growth medium, is also important in determining the amount of selenium a plant will absorb. Changes in tissue selenium concentrations within a plant occur through the growing season, frequently decreasing with maturity. This phenomenon has been used by ranchers to limit potential livestock toxicities.

ACQUISITION OF SELENIUM DATA FOR RECLAMATION PLANNING

Determining the selenium content of the soil resource or other proposed plant growth media to describe potential toxicities is more important in arid and semiarid regionsthan in humid regions. Sampling restricted to surface horizons of naturally occurring soils is not adequate for selenium characterization, as the element is often concentrated in lower lying horizons (below the soil solum and near or below the strata of sulfate enrichment in the C horizon). This situation is most frequently observed where significant pedogenic activity has occurred over extended time periods. Under higher precipitation regimes, selenium is frequently leached from the soil solum and underlying horizons. Where lower lying horizons and/or strata of the regolith, overburden and/or spoil materials are to be used in minesoil construction or other related reclamation activities, selenium contents should be determined even in more humid environments.

Before environmental samples are collected, some thought should be given to what form of selenium is of interest: total, inorganic (primarily selenate and selenite), or organic. Detection techniques, sample preparation, digestion, and extraction methods differ for the various forms and affect analytical results and interpretation of data. Plant analyses are done almost always for total selenium. Soil analyses usually include detecting extractable, water soluble, or total selenium types.

Soil taxonomic units (soil series) and mapping units cannot be consistently correlated with microelement concentrations, toxicities, or deficiencies. To guide the baseline soil sampling program, two approaches are available: (1) gridding of the soil landscape within the proposed disturbance area with subsequent description, sampling, and analysis of the pedon at each point on the grid, and (2) conducting a geobotanical inventory to compliment selenium analysis of typifying soil profiles or other proposed plant growth materials. The geobotanical inventory should be based on the presence, distribution, and selenium content of selenium-indicators and/or secondary selenium-accumulator plant species (Rosenfeld and Beath, 1964). Supporting analysis of plant tissue and soils found in locations where these plant species occur is an important part of the program. Selenium indicators (plant species restricted to high selenium soils) include species within the genera *Astragalus*, *Stanleya*, *Xylorhiza*, *Machaerantera*, *Oonopsis*, and *Haplopappus*. Secondary accumulators (plants known to accumulate significantly elevated levels of selenium but species not restricted to seleniferous soils include some species of the following genera: *Aster*, *Atriplex*, *Castilleja*, *Commandra*, *Grayia*, *Grindelia*, *Gutierrezia*, and *Mentzelia* (Rosenfeld and Beath, 1964). Many of these genera have widespread regional distribution, and species from the Atriplex are widely established during revegetation of drastically disturbed lands.

Several difficulties exist in making interpretations of selenium analytical data. The problems are partially based on plant species that have differing capacities to extract and incorporate selenium into their tissues (table 1). As in most toxicity studies, understanding the concentrations and chemical forms of the potentially toxic compounds in the materials, as well as the nature of the depositional environment into which they will be placed, are essential to predicting their potential impacts. Such information is equally important in identifying and handling these materials during reclamation.

ANALYTICAL TECHNIQUES

Significant differences of opinion exist about the proper procedures for the collection and preparation of plant tissue samples for selenium analysis. Selenium compounds are generally volatile and care must be exercised to prevent losses of this element from environmental samples (Gissel-Nielsen, 1970). Vegetation with high selenium concentrations (100 ppm or more) gives off a strong odor. This odor is selenium volatilizing from the plant. To reduce this loss, it is appropriate to refrigerate (4°C) all environmental samples, especially vegetation, from the time of collection to initial laboratory preparation. If drying is to be undertaken, it should be carefully controlled to minimize selenium losses (Gissel-Nielsen, 1970). Long-term storage (>90 days from time of sampling or coring) is unacceptable. Plant tissue analysis should be conducted on a wet-weight basis; that is, samples should be analyzed "as-received" in the laboratory. A second portion of the sample can be air-dried to provide data for dry-weight concentration, if required. Soil samples should also be analyzed on an as-received basis, with dry-weight determinations made on a separate subsample.

Preparation of plant tissues for selenium analysis usually involves acid digestion. If an oxidizing environment is maintained in the acid, the selenium will not be lost from the digestate. Vegetation should be analyzed on a wet-weight basis after digestion in a combination of $HClO_4$ (perchloric acid), HNO_3 (nitric acid), H_2O_2 (hydrogen peroxide), and H_2SO_4 (sulfuric acid).

Soil selenium is usually determined in samples weighed on an as-received basis. Dry weight conversions can be calculated by simultaneously determining water loss from an additional aliquot of the original sample. Selenium is usually extracted into a liquid that complexes or dissolves the element. Common extractants are hot water and AB-DTPA. Again, the maintenance of an oxidizing environment prevents the loss of selenium from the extracting solution. After the extraction is complete, the solution should be digested with an acid prior to analysis. This will insure that all the selenium forms are oxidized and in an inorganic form. For total soil selenium determination, the soil sample should be digested in a combination of acids including hydrofluoric (HF), HNO_3, and $HClO_4$. It is important to maintain oxidizing conditions throughout the digestion procedure, especially for soils high in organic matter, or losses of selenium may occur. A digestion mixture of HNO_3, H_2O_2, $HClO_4$ and H_2SO_4 is recommended for such materials.

The digestate or extracting solution containing selenium can be analyzed by ICP (inductively coupled plasma emission spectrometry), HGAAS (hydride generation atomic absorption spectrometry), FAAS (furnace atomic absorption spectrometry), or NAA (neutron activation analysis) (Van Loon, 1985). The FAAS may be the most sensitive analytical tool for determination of concentrations in dilute solutions. Successful FAAS analysis may require use of chemical modifiers, background correction and/or determination of selenium by the method of standard additions.

Analyses of extractable selenium attempt to show consistent relationships between the amount of selenium in the plant and the amount of selenium extractable from the soil. In most soils, the concentration and ionic species of selenium present in a horizon are a reflection of the amount of selenium in the parent material/rocks, the nature of the biological and physical environment found in the horizon, pedogenic activities, and time. In spoil, overburden, and waste materials, the equilibrium between selenium ion species and related soil minerals—that is, the balance between selenium and the biophysical environment—has not been reached. Analysis using extractable procedures will provide information about selenium soil-plant relationships at one point in time. However, using these types of analysis on spoil, overburden, and waste materials will not provide an indication of the amount of selenium

Table 2. Methods of sample preparation and analysis for selenium in materials being evaluated for use as a plant growth medium

Nature of material	Sample preparation	Sample selection and methods of analysis[1]
Soil solum and parent material (<1.5m) samples.	Flail to <2 mm; continuous sample removal; discard >2mm lithic fraction.	Extractable Se determination; total analysis on suspect samples.
Deeper lying oxidized regolith[2].	Flail to <2 mm; continuous sample removal; discard <2mm lithic fraction.	Extractable Se determination; total analysis of 25% of samples randomly selected.
Near-surface paralithic[3] materials samples.	Grind to <60 mesh; continuous sample removal.	Extractable Se determination; total analysis of 25% of samples with clay content, randomly selected.
Tailings, fly and/or metal processing wastes.	Grind to <60 mesh; continuous sample removal.	Extractable and total Se analysis on all samples.
Oxidized high chroma overburden spoils[4].	Grind to <60 mesh; continuous sample removal.	Extractable Se determination; total Se analysis of 25% of samples with <40% clay, and 50% of samples with >40% clay, randomly selected.
Reduced and high chroma overburden.	Grind to <60 mesh; continuous sample removal.	Randomly select 50% samples for extractable Se analysis; total analysis all samples with >40% clay content, and 50% of samples with <40% clay content.

[1] Extractable Se: AB-DTPA extractable Se (Soltanpour and Schwab, 1977; Soltanpour and Workman, 1980); total analysis for Se acid digestion (Pitt and others, 1986).

[2] Regolith: unconsolidated debris overlying bedrock.

[3] Paralithic materials: sedimentary bedrock materials having a hardness of <3 on the Moh's scale, generally soft weakly cemented sedimentary rock.

[4] High chroma: materials having Munsell chromas of greater and moist colors lighter than 3/2 for all hues; low chroma: all chromas of less than 2 and all others with hues of 3 or less.

potentially available for plant uptake. The lack of sufficient time for selenium species to reach chemical equilibrium prevents the analyst from making an accurate interpretation of extractable selenium data from such materials. Therefore, analysis for total selenium in reduced overburden and spoil materials should be used as the basis for determining potential selenium toxicity. These tests should be supplemented with other evaluations, including pot culture and greenhouse tests, artificial weathering, long-term column leach studies, and selenium partitioning studies.

Suggested methods for sample preparation and analysis of a variety of materials encountered in disturbed land reclamation are found in table 2. Near-surface or oxidized materials are disaggregated but not ground. Grinding changes the physical nature of the materials and will influence chemical properties. Flailers produce less

Table 3. AB-DTPA selenium analyses of five round robin soil/spoil/overburden samples (Severson and Fisher, 1985, 1987)

[Extremes are in bold print]

Round Robin No. 1			Round Robin No. 3	
Sample (1)	Sample (2)	Sample (3)	Sample (4)	Sample (5)
<0.01	**0.10**	<0.100	**1.60**	**1.00**
0.01	0.030	0.130	0.05	-.-
<0.005	0.087	0.010	0.38	0.49
<0.025	0.085	0.140	0.34	0.63
<0.01	0.06	0.060	**<0.05**	**<0.05**
0.038	<0.013	0.013	0.36	0.64
<0.02	<0.020	<0.020	0.15	0.19
<0.005	**0.010**	**<0.005**	0.22	0.55
0.240	0.020	**0.250**	0.37	0.44
		0.37		0.64
		0.16		0.21
		0.23		0.30

change in the size of primary particles and less change in the chemical state of the materials than grinding (Munshower and Prodgers, 1990).

Soil, waste, spoil, and overburden samples collected for selenium analyses should be dried at low temperatures when drying is required. If these samples are relatively dry at the time of collection, it is preferable that they be analyzed on an "as received" basis. Air drying is the best option when sample moisture reduction is required. Drying in a circulating oven at relatively low temperatures (<70% C) is a less favorable option. Samples should be transported from the field to laboratory under controlled conditions, such as those provided by large coolers. Analyses of the samples should be completed as quickly as possible, with lapsed time limited to a month or less. Storage, after sample preparation, should not allow exposure to temperature extremes. Reporting of the analytical data should include dates of sampling and analysis accompanied by full description of the conditions of sample transport, sample preparation techniques, nature of storage conditions, method of subsampling, and condition of the sample (fineness, moisture content, and so on) at the time of analysis.

Fundamental to any reclamation or disposal planning effort is the acquisition of reliable data upon which the operations will be designed. Such is particularly true in the case of selenium. A detailed quality assurance and quality control (QA/QC) program must be developed before any selenium analytical work is undertaken. Important elements of this program include analysis of reference samples; analysis of NBS standards; utilization of a secondary quality control laboratory for duplicate analysis of samples; spike and recovery work on randomly selected samples (both pre-extraction and at solution extract phases); and internal replication of sample analyses. All such data must be reported and evaluated along with the routine sample selenium concentrations. Table 3 provides an indication of the range in results that has been reported from characterization of the selenium content of soil or overburden samples in multiple laboratories.

EVALUATION AND INTERPRETATION

Providing accurate and precise values or methods for the determination of existing or potential selenium toxicities in materials proposed for use as a plant growth medium is difficult because of the current state of knowledge of selenium and its biology. However, drastically disturbed land reclamation planning and execution are ongoing processes, and the sciences must provide the best available information to these operations. Much is being learned about selenium in the environment, and suggestions for the types of evaluations of materials and material suitabilities can be expected to change in the next few years. Many important questions remain unresolved about the chemistry and biology of selenium as related to minesoil construction, potential plant uptake, and herbivore toxicities. In light of these uncertainties, the suggestions outlined in table 5 are presented to provide initial directions for selenium investigations and to assist in planning for the reclamation of drastically disturbed land and reclamation of waste disposal.

Much of the technical basis for published western selenium suitabilities stems from the work of Soltanpour and Workman (1980). Numerous samples from North Dakota Mollisols—minesoils created in coal mine reclamation—and overburden materials from western Colorado were extracted with AB-DTPA. Analysis was accomplished using a hydride generator attached to an inductively-coupled plasma spectrometer. The authors concluded as follows:

Table 4. Soil selenium concentrations near Chalk Bluff, Wyoming

Site 3		Site 4		Site 5	
Depth (cm)	AB-DTPA Se extract (ppm)	Depth (cm)	AB-DTPA Se extract (ppm)	Depth (cm)	AB-DTPA Se extract (ppm)
0-2	<0.004	0-2	0.12	0-4	0.04
2-18	0.004	2-13	0.20	4-9	0.04
18-46	0.004	13-28	0.10	9-25	0.02
46-64	0.80	28-46	0.11	25-38	0.02
64-86	0.10	46-71	0.11	38-58	0.03
86-107	7.63	71-97	0.37	58-86	0.09
107-127	5.17	97-122	0.04	86-124	19.0
127+(150)	3.11	122-152	0.10		
Weighted mean-----	2.35		0.15		5.86

1. Alfalfa plants growing in soils containing over 100 ppb (0.1 ppm) of AB-DTPA extractable selenium produced plant tissue selenium concentrations of 5 ppm or more,

2 A strong correlation ($r^2 = 0.96$) was found between selenium uptake by alfalfa and AB-DTPA extractable selenium,

3. Soils with 2.0 ppm of extractable selenium (from addition of 4 ppm selenate) were toxic to alfalfa plants and resulted in plant tissue selenium concentrations exceeding 1000 ppm.

Field studies of two sites in Wyoming (Chalk Bluff near Rock River and Poison Draw near Lysite) identified as having toxic (seleniferous) vegetation have been undertaken in recent years by F.F. Munshower and R.A. Prodgers of Montana State University, and S.E. Fisher of the Office of Surface Mining. Extensive use of this data has been made in the development of the following suggestions for determining the suitability of plant growth material with respect to selenium. The selenium concentrations in soil horizons or strata reported in table 4 correspond to the sites at which the plant tissues were collected and selenium concentrations were reported in table 1. All plant tissue was collected during a 2-day sampling period in July and transported to the laboratory in iced coolers. Tissue samples were obtained from at least two plants occurring within 10 meters of the soil pit. Preliminary conclusions from the above study, parts of which are reported elsewhere in this document (Munshower and Prodgers, 1990), are as follows:

1. Native plant species differ strongly in their capacity to incorporate selenium into plant tissue.
2. Soils having relatively low AB-DTPA extractable selenium concentrations (<0.1 ppm) can support primary and secondary selenium accumulating plant species which contain toxic levels of selenium (tables 1 and 4).
3. Selenium is not uniformly distributed throughout a soil profile (table 4). Some evidence exists to suggest that it follows a pattern similar to sulfate. In soils classified as Entisols, strata or horizons having higher levels of selenium are frequently encountered at depths greater than 1 meter.
4. Plant tissue selenium content varies widely throughout the growing season. The general trend is a lowering of selenium concentrations later in the growing season.

Our present state of knowledge about soil and plant selenium relationships indicates that we cannot rely solely on extractable selenium concentrations in plant growth media as a basis for selection of material for minesoil construction in disturbed land reclamation. We propose to use the post-reclamation land use, associated plant species, total and extractable selenium content, and intensity of use and management to guide the selection of materials for minesoil construction. Suggestions for the use of these criteria and related rationale are shown in table 5.

These suggestions for minesoil material selection must be tempered by an understanding that the pedogenic and related biological processes will result in redistribution of the selenium in near-surface materials selected for use as a plant growth medium. Some volatile losses of selenium, probably in the form of dimethylselenide, will take place, with larger losses occurring with the presence of the primary selenium-accumulator plant species. Certainly, downward movement of soluble forms of selenium with percolating waters will occur during pedogenesis and plant succession. These processes can lead to the concentration of

Table 5. Suggested values for selenium content of plant growth media proposed for use in reclamation

[Note: Extractable selenium to be based on AB-DTPA extractions following procedures of Soltanpour and Schwab (1977) and Workman and Soltanpour (1980)]

Item No.	Land use or type of reconstructed ecosystem and/or management system	Selenium suitability levels
A	Grazing land--dominantly native grass species with rooting depths to 1.5 m common. Primary goal: moderately intensive livestock grazing.	<0.15 ppm extractable Se; if >0.8 ppm total Se, additional limited shrubs; sampling and analysis required.
B	Pastureland--hay crop land dominated by introduced grass species; grass rooting depths to 1.5 m and legumes to 3.0 m.	<0.1 ppm extractable Se; if >0.5 ppm total Se, additional sampling and analysis required; for high sulfur feeding plant species, such as alfalfa, suitability value may need to be reduced.
C	Grazing land ecosystems with significant shrub and/ timber cover; grass roots extensive to depths of 1.5 m and shrubs to 6 m; primary goal: livestock and wildlife utilization.	<0.2 ppm extractable Se; <0.8 ppm total Se, additional or sampling and analysis required.
D	Stabilization/isolation of disturbed materials and/ products to restrict impacts; primary preservation of watershed values, restrict toxic impacts and limited wildlife use.	<0.25 ppm extractable Se; total Se analysis of available waste materials to isolate those with the lowest risk factor for goal incorporation into plant root zone.

COMMENTS

A. Grazing land is here defined as land used for grasslands and/or forest lands where the indigenous vegetation is actively managed for grazing, browsing, or occasional hay production.

The intermediate value of <0.15 ppm is suggested because a) the relatively intensive form of forage utilization can deprive herbivores of the option to select the more palatable species and reject the generally less palatable selenium accumulator species; b) the more intensively used grazing lands in the region frequently are dominated by some form of wheatgrass, a genus from which several species are known to accumulate relatively high concentrations of selenium; c) the cool season mid-grass prairie species which will be expected to dominate, when forage production is the primary revegetation goal, will have rooting systems more extensive at greater depths than other native species; d) acreages within individual pastures envisioned here will generally be limited to less than 160 acres and the potential for significant herbivore selection of low selenium concentration forage is less than in extensive paddocks.

B. Pastureland is here defined as land used primarily for the long-term production of adapted, domesticated forage plants to be grazed by livestock or occasionally cut and cured for livestock feed.

The pasture and hayland scenario will involve both legumes and forage grass species; we have continued to rely on the definitive work of Soltanpour and Workman (1980) on alfalfa which will be an important component of many of these forage systems.

C. The grazing ecosystems being reconstructed under this scenario will encompass large areas, ranging from one to several sections in size. The reasons for allowing increased amounts of selenium in minesoils include a) extensive pastures utilizing less intensive forms of grazing will allow herbivore selection of the more palatable plant species (under high levels of management), thereby reducing utilization of the relatively unpalatable primary selenium accumulator species; b) establishment of plant communities having greater diversity and seasonality will result in inclusion of plant species which are shallower rooted and potentially have less opportunity to reach deep-lying accumulations of selenium salts in the minesoil profile. Revegetation efforts would need to be redirected from the primary emphasis on establishment of saltbush (Atriplex) species for shrub community re-establishment because several of the species in the genus are known to accumulate higher concentrations of selenium.

D. The primary goal in this scenario is to attempt to isolate and prevent the previously disturbed or waste disposal area from contaminating the surrounding landscape and/or to limit percolation and contribution of selenium to ground water systems. The higher selenium levels do not suggest that wildlife is of lesser value than domestic livestock, but rather is based on the larger home ranges of many wildlife species, enabling them to potentially use adjacent areas having lower soil and plant concentrations of selenium.

selenium in horizons or strata of the minesoil or plant growth media on the reclaimed site. Such concentrations can result in increased incorporation of selenium into plant tissue. (See table 4, Site 5.)

The importance of the potential concentration or redistribution of selenium in reclaimed plant growth materials is illustrated by the selenium distribution in native soils data in table 4. The weighted mean values for extractable soil selenium are 2.35, 0.15, and 5.86 ppm for Sites No. 3, 4, and 5, respectively. The concentration of selenium in lower strata or horizons is probably the product of pedogenic processes as suggested, but it could have resulted from differing parent material chemistry and deposition. Site No. 5 has very low selenium concentrations in the upper 58 cm of the profile, yet all of the plant tissue collected during midsummer exceeded the 5 ppm limitation. Major involvement of the 58–124 cm horizon or strata on this site in plant uptake of selenium must have taken place.

The inclusion of total selenium analyses is essential to define potential toxicities in plant growth materials that are reduced or have been removed from reducing conditions. The data cannot be directly used to predict plant uptake of selenium but are important in describing the potential problem or in selecting materials which will pose less risk of plant uptake of toxic levels of selenium. The values appearing in table 5 indicate where additional sampling needs to be undertaken to describe the range of values present in proposed plant growth media, and to identify those materials with lower total amounts of selenium for use as the preferred material for minesoil construction.

The following are some suggestions that we have drawn about the design and evaluation of selenium studies including the application of results into drastically disturbed land reclamation planning.

1. Compositing samples for evaluation of selenium content of disturbed materials or native soils should be restricted to horizons or strata of less than 20 cm, preferably 10 cm or less.
2. Minesoil, disturbed materials, or soil sampling should minimally take place to depths of 1.2 m, with 2 m being preferable. Sampling should include paralithic materials as well as parent materials.
3. The suitability values proposed must be integrated throughout the depth of the plant rooting material. How this is to be accomplished cannot be precisely defined at this time. It is known that strata or horizons of limited thickness but having elevated levels of extractable selenium (in the range of >0.1 ppm) can potentially produce toxic vegetation.
4. Plant tissue selenium concentrations differ significantly over the season. In the case of most western native species, the highest concentration occurs at the point of maximum standing crop near the flowering stage. There are important exceptions to this rule—note curly cup gumweed (*Grindelia squarrosa*) (Munshower and Prodgers, 1991).
5. Soil selenium concentrations can vary widely over very short geographic distances. Distribution of total and extractable selenium throughout the soil profile varies considerably within pedons of the same series.

Given the range of selenium values found in some soil series and mapping units, monitoring of the selenium content of materials salvaged for minesoil construction seems to be prudent. Strict reliance on monitoring of vegetation established during reclamation has significant limitations. Plant root systems will take several years to become fully established, and changes in the ionic species of selenium present will continue to take place over extended periods of time. Pedogenic processes that result in enriched zones of selenium occur over many years, and plant succession, with associated invasion of species not seeded during revegetation efforts, will proceed with the pedogenic changes. All these activities will change the selenium distribution within the reclaimed ecosystem over time.

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