

**EVALUATION OF SELENIUM MOBILITY IN SOIL USING
SORPTION EXPERIMENTS AND A NUMERICAL MODEL,
WESTERN SAN JOAQUIN VALLEY, CALIFORNIA**

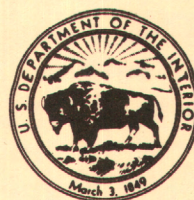
U.S. GEOLOGICAL SURVEY

Open-File Report 90-135

REGIONAL AQUIFER-SYSTEM ANALYSIS

**Prepared in cooperation with the
SAN JOAQUIN VALLEY DRAINAGE PROGRAM**

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This report was prepared by the U.S. Geological Survey in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer-System Analysis (RASA) Program of the U.S. Geological Survey.

The San Joaquin Valley Drainage Program was established in mid-1984 and is a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the program are to investigate the problems associated with the drainage of agricultural lands in the San Joaquin Valley and to develop solutions to those problems. Consistent with these purposes, program objectives address the following key concerns: (1) public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

Inquiries concerning the San Joaquin Valley Drainage Program may be directed to:

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2800 Cottage Way, Room W-2143
Sacramento, California 95825-1898

The RASA Program of the U.S. Geological Survey was started in 1978 following a congressional mandate to develop quantitative appraisals of the major ground-water systems of the United States. The RASA Program represents a systematic effort to study a number of the Nation's most important aquifer systems, which in aggregate underlie much of the country and which represent an important component of the Nation's total water supply. In general, the boundaries of these studies are identified by the hydrologic extent of each system, and accordingly transcend the political subdivisions to which investigations were often arbitrarily limited in the past. The broad objectives for each study are to assemble geologic, hydrologic, and geochemical information, to analyze and develop an understanding of the system, and to develop predictive capabilities that will contribute to the effective management of the system. The Central Valley RASA study, which focused on the hydrology and geochemistry of ground water in the Central Valley of California, began in 1979. Phase II of the Central Valley RASA began in 1984 and is in progress. The focus during this second phase is on more detailed study of the hydrology and geochemistry of ground water in the San Joaquin Valley, which is the southern half of the Central Valley.

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By John L. Fio, Roger Fujii, and S.J. Deverel

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6439-77



**Sacramento, California
1990**

DEPARTMENT OF THE INTERIOR

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CONVERSION FACTORS

For use of readers who prefer inch-pound units rather than metric (International System) units, conversion factors for terms used in this report are listed below.

Multiply	By	To obtain
centimeter (cm)	0.394	inch
centimeter per day (cm/d)	0.394	inch
cubic centimeter per cubic centimeter (cm ³ /cm ³)	1.0	cubic foot per cubic foot
gram (g)	0.0022	pound
kilometer (km)	0.6214	mile
meter (m)	0.305	foot
milliliter (mL)	0.0038	ounce
millimeter (mm)	0.0394	inch
square centimeter per day (cm ² /d)	0.155	inch

Concentrations in solution are given in micrograms per liter (µg/L) or micrograms per milliliter (µg/mL). Micrograms per liter is equivalent to "parts per billion" and micrograms per milliliter is equivalent to "parts per million."

Concentrations in soil are given in micrograms per kilogram (µg/kg) or micrograms per gram (µg/g). Micrograms per kilogram (µg/kg) is equivalent to "parts per billion" and micrograms per gram (µg/g) is equivalent to "parts per million." One thousand micrograms per kilogram is equivalent to 1 milligram per kilogram.

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation:

$$^{\circ}\text{F} = 1.8(^{\circ}\text{C}) + 32$$

Abbreviations used:

d (day)
dS/m (decisiemen per meter)
h (hour)

meq/L (milliequivalent per liter)
min (minute)
M (molar concentration)
mL (milliliter)

EVALUATION OF SELENIUM MOBILITY IN SOIL USING SORPTION EXPERIMENTS AND A NUMERICAL MODEL, WESTERN SAN JOAQUIN VALLEY, CALIFORNIA

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ABSTRACT

Sorption experiments and a numerical model were used to assess the effects of irrigation and drainage on the depth distribution of selenite and selenate in soils from the western San Joaquin Valley, California. The sorption studies show that selenate (15 to 12,400 micrograms per liter of selenium) is not adsorbed to soil, whereas selenite (10 to 5,000 micrograms per liter of selenium) is rapidly adsorbed. The time lag between adsorption and desorption is considerable, indicating nonreversible sorption, and an equation describing the desorption reaction is determined by the concentration of adsorbed selenite prior to desorption. A numerical model was used to qualitatively evaluate the nonreversible sorption reaction and its affect on selenite mobility during leaching by irrigation water. Model results show that selenite is resistant to leaching and therefore can represent a potential long-term source of selenium to ground water. In contrast, selenate behaves as a conservative constituent under alkaline and oxidized conditions and is easily leached from soil.

Chemical analyses of soils from irrigated and non-irrigated sites confirm the experimental and modeling results. Increasing salinity and soluble concentrations of selenate at a site irrigated for more than 40 years indicated leaching and downward displacement by irrigation water. Decreasing salinity and soluble concentrations of selenate at a nonirrigated site probably resulted from evaporation from the shallow water table. Adsorbed selenium in the irrigated and nonirrigated soils is mostly selenite and has been minimally affected by irrigation and drainage.

INTRODUCTION

Drainage systems have been installed in some agricultural fields in the western San Joaquin Valley,

California, where shallow ground water has become detrimental to crop production. These drainage systems generally maintain the water table about 1.5 m below land surface. Leaching of soluble salts by irrigation water and evaporative concentration of solutes in ground water near the water table have resulted in high concentrations (20 to 1,000 $\mu\text{g/L}$) of selenium (Se) in ground water in low-altitude areas of the western valley (Deverel and Gallanthine, 1989). Irrigation water is displacing the saline, high Se water towards the drain laterals (Deverel and Fujii, 1988). Discharge from the drainage systems has been identified as the primary source of Se to the Kesterson National Wildlife Refuge (Deverel and others, 1984; Presser and Barnes, 1984), where Se was implicated in the deformity and mortality of waterfowl hatchlings (Ohlendorf and others, 1986). An understanding of Se mobility and the effects of irrigation on the downward movement of Se concentrations in soil will be useful for the development of management practices aimed at reducing concentrations in agricultural drain water.

This report presents results from sorption experiments and a numerical model used to evaluate Se mobility in soil. The results provide insight into the effects of irrigation and drainage on the depth distribution of salinity and Se in soil samples collected from the western San Joaquin Valley, California (fig. 1). This study is part of a comprehensive investigation of the hydrology and geochemistry of the San Joaquin Valley by the U.S. Geological Survey. The studies are being done in cooperation with the San Joaquin Valley Drainage Program and as part of the Regional Aquifer-System Analysis Program of the U.S. Geological Survey.

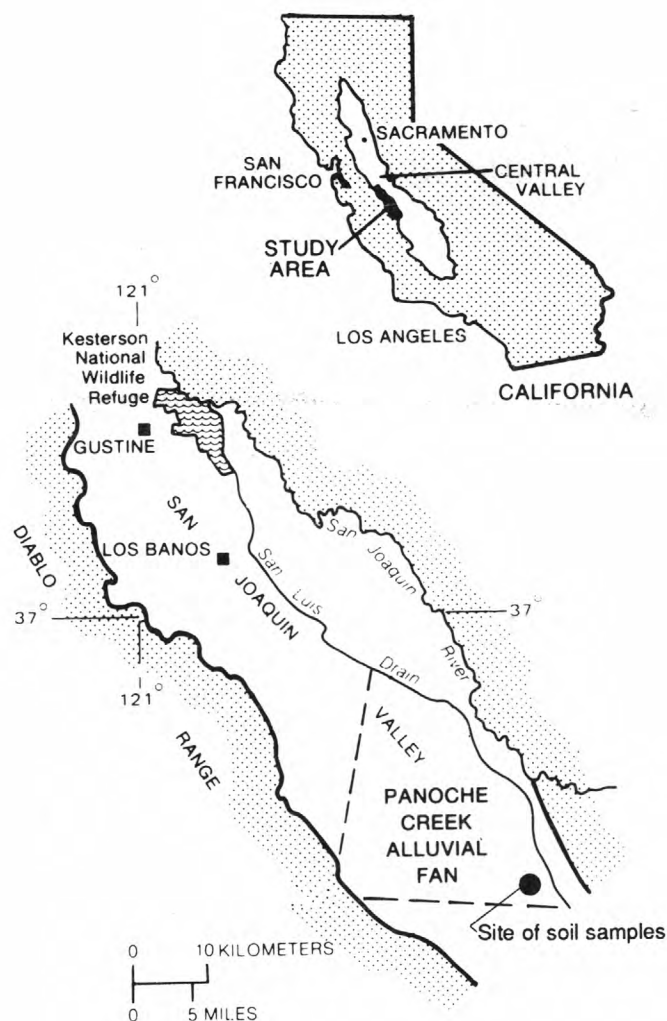


Figure 1. Study area and sampling site.

BACKGROUND ON SELENIUM MOBILITY AND GENERAL STUDY APPROACH

In natural systems, Se exists in four oxidation states: selenite (+4), selenate (+6), elemental selenium (0), and selenide (-2). The selenate (SeVI) species is thermodynamically favored in alkaline-oxidized environments (Geering and others, 1968), and about 98 percent of the Se in ground water from the western San Joaquin Valley is SeVI (Deverel and Millard, 1988). Soluble selenite (SeIV) was detected in some saturation extracts of soils from the western San Joaquin Valley (Fujii and others, 1988; Fio and Fujii, 1990).

Fujii and others (1988) used data from sequential extractions of soils to conclude that SeIV comprised most of the adsorbed fraction of Se. Adsorbed SeIV represents a potential source of Se to ground water. Burau and others (1987) measured equilibrium SeIV adsorption isotherms for eight soils representing a toposequence of major soils in the western San Joaquin Valley. (Equilibrium adsorption isotherms refer to the relation between the equilibrium partitioning of adsorbed and soluble Se concentrations at constant temperature.) They found that adsorption isotherms for each soil were different. The slopes of the isotherms were positively correlated to surface area and oxalate-extractable iron in the soils and negatively correlated with organic matter and soil pH. Desorption studies showed that 70 to 85 percent of the adsorbed SeIV is desorbed with a saturated gypsum (CaSO_4) solution, thus indicating that adsorption and desorption isotherms are different. In contrast, Burau and others (1987) and Sposito and others (1987) reported no net adsorption of SeVI in soil.

These sorption studies showed that Se mobility in soil and ground water is species dependent. Microbial reactions affect the quantity and form of Se, thereby influencing Se mobility. Frankenburger and others (1986 and 1987) reported that SeIV, SeVI, and organic Se in soil and evaporation-pond waters from the western San Joaquin Valley were transformed to volatile dimethylselenide by fungi under aerobic conditions. Under anaerobic conditions, SeVI was reduced by bacteria to immobile elemental Se (Oremland and Hollibaugh, 1988).

The existing data on Se mobility and speciation indicate that modeling the movement of water and Se through soil requires a full understanding of complex physical, chemical, and biological processes. Quantifying these processes in western San Joaquin Valley soils is beyond the scope of this report, but instead we use results from a relatively simple model to interpret the concentrations of adsorbed and soluble Se measured in selected samples of soil. The soil samples were collected from sites that have historically undergone varying amounts of leaching by irrigation water. Sorption experiments were done to quantify equilibrium adsorption and desorption isotherms for SeIV, and the isotherm data were used in a numerical model to qualitatively simulate the relative mobility of SeIV and SeVI in saturated soil. The model was used to evaluate differences in salinity and Se concentrations between the soils resulting from irrigation and drainage.

METHODS TO EVALUATE SELENIUM MOBILITY IN SOIL

COLLECTION AND PREPARATION OF SOIL SAMPLES

Soil samples were collected from the southern part of the Panoche Creek alluvial fan in the western San Joaquin Valley, California. Samples were collected from three sites within 1 km of each other in an area with a water table currently at a depth of about 2 m below land surface. The sampling sites are all on soils of the Ciervo silty clay series (Typic Torriothent). Site 1 is in an agricultural field that has been irrigated for more than 40 years and artificially drained since 1980. Site 2 is in an area that, according to the landowner, was never irrigated and represents non-irrigated soil conditions. Four incremental soil samples were hand augered at 30-centimeter intervals from the surface to a depth of 120 cm at sites 1 and 2. Site 3 is in an area that was irrigated prior to 1980 but not irrigated since 1980. Site 3 has never been artificially drained. Only one sample of the top 30 cm of soil was collected at site 3.

The chemical composition of the soil and background solution determines the composition of constituents occupying potential sorption sites for Se, and consequently can influence the reactions studied in the sorption experiments. Because of variability in the chemical composition of soil from the three sampling sites, a subsample of soil from site 3 was equilibrated with a 0.005 M CaSO_4 solution, herein referred to as soil CS. Equilibration with CaSO_4 resulted in soil with a relatively homogeneous chemical composition and negligible amounts of extractable Se. The equilibration of soil CS was done by placing the soil from site 3 in CaSO_4 solution at a 2:1 solution to soil ratio (w/w). The mixture was periodically stirred for a minimum of 8 h, allowed to settle, and the solution was decanted. This procedure was repeated five times. The soil was then rinsed three times with 0.005 M CaSO_4 and the rinse removed by vacuum filtration.

Soil CS and the samples from sites 1, 2, and 3 were air dried and ground to pass through a 1-millimeter sieve. The authors recognize that air drying and sieving the soil samples can potentially alter the forms and amounts of Se in the soil by oxidation of reduced forms of Se and loss of Se by volatilization. With the

exception of the short-time intervals following irrigation, the alkaline-oxidized soils sampled from these fields generally are unsaturated. Chemical changes resulting from air-drying are therefore probably negligible, but Se concentrations measured in the soil extracts should be interpreted with caution.

ANALYSES OF SOIL AND SOIL EXTRACTS

The total, water-soluble, and adsorbed fractions of Se and other chemical constituents in soil were measured to provide data on the distribution of Se in the irrigated and nonirrigated soils. Total Se in soil samples was determined using a method modified from Briggs and Crock (1986). The modifications described by Fujii and others (1988) increased Se recovery presumably by reducing Se losses by volatilization during digestion of soil. The total carbon content of the soils was determined by combustion of the soil sample in a Leco Total Combustion Analyzer¹ that measures the release of carbon dioxide (CO_2) with an infrared detector. Inorganic carbon was determined on a split sample by gravimetrically measuring the CO_2 released from the reaction of inorganic carbon with acid. Organic carbon content in the soils was calculated as the difference between the total and inorganic carbon analyses.

Water-soluble constituents were determined on extracts of saturated soil pastes as described by Rhoades (1982). The saturation extracts were divided into two parts. Specific conductance and pH were measured on one part of the extract. The remaining extract was filtered through 0.45-micrometer filters and split into two subsamples (the filters contributed less than 3 percent of the dissolved-organic carbon in the samples). One subsample was refrigerated for analysis of major cations and anions and the other subsample was acidified with concentrated hydrochloric acid (HCl) to a pH less than 2 and refrigerated for determination of dissolved-organic carbon (DOC) and Se species. Major cations (calcium, magnesium, potassium, and sodium) and anions (chloride, sulfate, and nitrate) were determined by ion chromatography and dissolved-organic carbon was measured with a Dohrman DC-80 total carbon analyzer. The concentration of inorganic carbon species (carbonate plus bicarbonate) was estimated from the difference between the cation-anion balance.

¹The use of brand, firm, or trade names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

Dissolved Se species in the soil extracts (SeIV, SeVI, and hydrophobic-organic Se) were determined by the method described by Fio and Fujii (1990). The extracted solutions (pH less than 2) were passed through XAD-8 resin to remove hydrophobic organic matter, which can interfere with Se analysis by hydride generation atomic absorption spectrometry (Roden and Tallman, 1982). Hydrophobic-organic Se is retained by the XAD-8 resin (Leenheer and Huffman, 1976; Cutter, 1985). An aliquot of the effluent solution was analyzed directly for SeIV, and another aliquot was analyzed after chemical digestion and reduction of the total forms of Se in the effluent. The concentration of SeVI was estimated from the difference between the two analyses. Substantial quantities of hydrophilic-organic Se and/or elemental Se in the column effluents can result in erroneous estimations of SeVI. The contribution of colloidal elemental Se is assumed negligible, but speciation results from the XAD-8 method must be interpreted with consideration of the limitations of the method. Hydrophobic-organic Se was sequentially eluted from the XAD-8 resin with 0.1 M sodium hydroxide (NaOH), deionized water, and methanol. The eluates were digested and analyzed for Se.

Selenium species sorbed to soil surfaces were estimated by extractions with phosphate solution (15 g soil: 150 mL solution) adjusted to pH 8 using a method similar to the one described by Fujii and others (1988). The procedure requires initial extraction of the soil with 0.25 M potassium chloride (KCl) to remove substantial amounts of soluble and exchangeable calcium (Ca). Decreasing Ca concentrations reduces the potential for precipitation of low solubility Ca phosphates on addition of the phosphate extracting solution (Fujii and others, 1988). The KCl extracts were equilibrated for 1 h in a mechanical shaker and the samples were then centrifuged ($17,600 \times g$) for 15 min, pH measured, and the supernatant filtered through 0.45-micrometer filters. The filtrate was preserved and analyzed as described above for Se species.

Next, 150 mL of phosphate solution (0.1 M KH_2PO_4) was added to each sample, resuspended, and the suspensions were adjusted to a pH of 8 after 0, 5, and 20 h with 1.0 or 0.1 M HCl or NaOH. The extraction procedure was complete after 24 h of shaking, and the samples were treated as described above for the KCl extracts. The concentration of SeIV and SeVI in the phosphate extracts was corrected for carry-over of Se from the KCl extracts (Fujii and others, 1988).

SORPTION EXPERIMENTS WITH SELENITE AND SELENATE

Sorption experiments were done at constant temperature ($25 \pm 1^\circ\text{C}$) to evaluate the equilibrium partitioning of adsorbed and soluble Se species in the soils and provide input to the numerical model. Because it was necessary to determine the time required to reach equilibrium or steady-state conditions, both rate and equilibrium sorption studies were done. The sorption experiments were done by adding about 7.5 g of soil to 150 mL of 0.1 M sodium chloride (NaCl) or 0.005 M CaSO_4 background electrolyte in 250 mL centrifuge bottles. The pH (8.2 to 8.4) and specific conductance of the 0.1 M NaCl (10.5 dS/m) and 0.005 M CaSO_4 (1.1 dS/m) background solutions were in the range of those determined from the soil saturation extracts. Selenium (SeIV or SeVI) was added to the centrifuge bottles containing the soil and background solution and placed in a reciprocating shaker. At the end of the shaking period, the samples were centrifuged, pH was measured, and the supernatant was filtered through a 0.45-micrometer filter. The samples were then acidified with concentrated HCl to a pH less than 2 for analysis of Se species.

The rate of Se sorption was studied by measuring the change in soluble Se concentration with time. The soil from site 3 (and soil CS) was used for the sorption rate study because of its intermediate composition of soluble salts and Se relative to the other samples. About 50 $\mu\text{g/L}$ of SeIV and 260 $\mu\text{g/L}$ of SeVI were added to replicate centrifuge bottles containing soil and background solution. The bottles were removed from the shaker after 0.5, 1, 2, 4, 8, 16, 32, 64, and 124 h and solutions were analyzed for Se species. A decrease in the concentration of Se in solution was attributed to adsorption. The rate of Se desorption was measured using a similar procedure. Desorption was measured by replacing 100 mL of the solution in the centrifuge bottles after the adsorption step with 100 mL of 0.005 M CaSO_4 solution. The centrifuge bottles were returned to the shaker and the concentration of Se was measured after 0.5, 1, 4, 8, and 24 h.

Comparison of results from sterile and unsterile rate experiments were used to assess microbiological transformations of Se species. A subsample of soil from site 3 was sterilized by exposure to a cobalt-60 source for 24 h. All the glassware, centrifuge bottles, deionized water, and other pertinent materials used for the sterile experiment were autoclaved. Sterile soil and solutions were combined under a hood equipped with an ultra-violet light to prevent microbial contamination.

Adsorption isotherms were determined for all the surface soils (0- to 30-centimeter depth) to assess the affinity of soils with different leaching histories to Se species. Solutions containing 15; 1,400; 2,200; 3,100; 4,500; 6,300; 8,500; and 12,400 µg/L of SeVI and 10; 50; 100; 500; 1,000; and 5,000 µg/L of SeIV were added to centrifuge bottles containing soil. The bottles were shaken for 24 h, and the difference in initial and final Se concentrations were attributed to adsorption. The adsorption isotherms show the affinity of soil for Se over a large range of concentrations. Large concentrations of SeVI were used because adsorption was not detected in the rate study (260 µg/L) and concentrations as great as 11,800 µg/L were reported for shallow ground water in the western San Joaquin Valley (Deverel and Fujii, 1988). The concentrations of SeIV are substantially larger than what exist in the western San Joaquin Valley, but are feasible should conditions occur that are favorable for the reduction of existing SeVI to SeIV.

Adsorption and desorption isotherms were determined for soil CS to provide the necessary sorption data for input to the numerical model. Desorption isotherms were measured using a procedure similar to the one used in the desorption rate study. After a 24 h equilibration with 8, 50, 90, or 150 µg/L of SeIV, about 100 mL of solution in the centrifuge bottles was replaced with 100 mL of 0.005 M CaSO₄ solution. After 2 h, the increase in SeIV concentration was measured. This procedure was repeated eight times for each concentration, and the desorption experiment was terminated after 24 h.

DESCRIPTION OF EQUILIBRIUM SORPTION ISOTHERMS USING THE FREUNDLICH EQUATION

The Freundlich equation (Grove and Stollenwerk, 1984) is used to describe the equilibrium sorption isotherms for soluble and adsorbed fractions of a constituent

$$S = K_i C^{N_i} \quad (1)$$

where

- S is adsorbed concentration of the constituent, in micrograms per gram,
- C is soluble concentration of the constituent, in micrograms per milliliter, and
- K_i and N_i are empirical constants (for adsorption reactions, $i = a$, and for desorption reactions, $i = d$).

A log-log plot of S compared to C yields a straight line, and the values of K_i and N_i are the intercept and slope of the line, respectively. For reversible sorption reactions, adsorption and desorption isotherms follow the same line. However, if sorption reactions show a substantial time lag and are essentially nonreversible, adsorption and desorption reactions will follow different isotherms. Two equations in the form of equation 1 are therefore needed to describe nonreversible adsorption and desorption.

The adsorption and desorption isotherms of a non-reversible reaction will intersect at the relative maximum adsorbed concentration before desorption (S_m). For these conditions, the Freundlich desorption constant k_d is a function of S_m and the ratio of the slopes of the adsorption and desorption isotherms (Van Genuchten and others, 1974):

$$k_d = k_a N_d / N_a \cdot S_m^{(1 - N_d / N_a)} \quad (2)$$

NUMERICAL MODEL USED TO SIMULATE MOVEMENT OF SELENIUM IN SATURATED SOIL

A one-dimensional transport model for reactive constituents was used to simulate Se movement in saturated soil. The governing equation for the transport model is the one-dimensional advection-dispersion equation:

$$\partial C / \partial t = (D / \theta R) \partial^2 C / \partial Z^2 - (q / \theta R) \partial C / \partial Z, \quad (3)$$

where

$$R = 1 + (\rho_b / \theta) N_i k_i C^{(N_i - 1)}$$

- R is the retardation factor,
- θ is the volumetric water content, in cubic centimeters per cubic centimeter,
- ρ_b is the bulk density, in grams per cubic centimeter,
- D is the dispersion coefficient, in centimeters squared per day,
- Z is the depth below land surface, in centimeters, and
- q is the volumetric flux, in centimeters per day.

The affinity of soil for the constituent is described by the retardation factor. The retarded dispersion coefficient ($D / \theta R$) and retarded velocity ($q / \theta R$) is affected by the value of R . For a nonreactive constituent, the retardation factor is equal to 1, and dispersion and velocity are not affected by sorption reactions.

An approximate solution to the advective-dispersion equation was obtained using the finite-difference method where the continuous system described by equation 3 was replaced by a finite set of discrete points in space (Grove and Stollenwerk, 1984). Equation 2 was incorporated into the finite-difference equation to simulate equilibrium-controlled adsorption and desorption of constituents from soil during leaching.

The transport model assumes that initial soluble and adsorbed concentrations of constituent in the soil profile are negligible. A pulse of water containing the constituent at concentration C_i is introduced instantaneously at the soil surface for a prescribed period of time (t_1). Water and constituent flow continuously into the soil profile until replaced by constituent-free water after t_1 . The input boundary condition is described by flux continuity and the output boundary assumes no concentration gradient of constituent at an effectively infinite depth in the soil profile (Grove and Stollenwerk, 1984).

During the pulse interval from 0 to t_1 , the increasing concentration of constituent adsorbed to the soil is calculated with equation 1. After t_1 , input of the constituent to the soil ceases, and leaching by constituent-free solution causes the soluble concentration of constituent to decrease in the soil profile. The relative maximum adsorbed concentration before desorption (S_m) is used with equation 3 to calculate the desorption isotherm for each finite-difference point (modification of Grove and Stollenwerk, 1984). Decreasing concentrations of adsorbed and soluble constituent are calculated with the desorption isotherm after t_1 .

We compared the transport model results to miscible displacement data of Van Genuchten and others (1974) for nonreversible sorption of picloram in a soil column. Van Genuchten and others (1974) described their data with a transport model similar to the one used in this study. The results from our transport model compare favorably with their experimental data and model results.

SORPTION OF SELENITE AND SELENATE TO SOIL

Figure 2 shows the change in adsorbed and desorbed concentrations of SeIV with time. The data show rapid

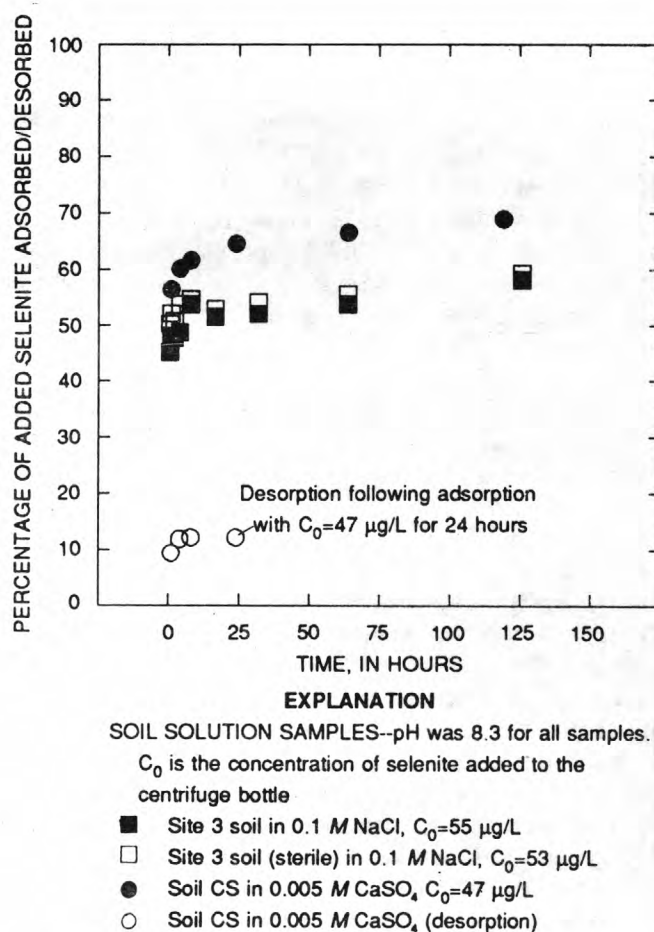
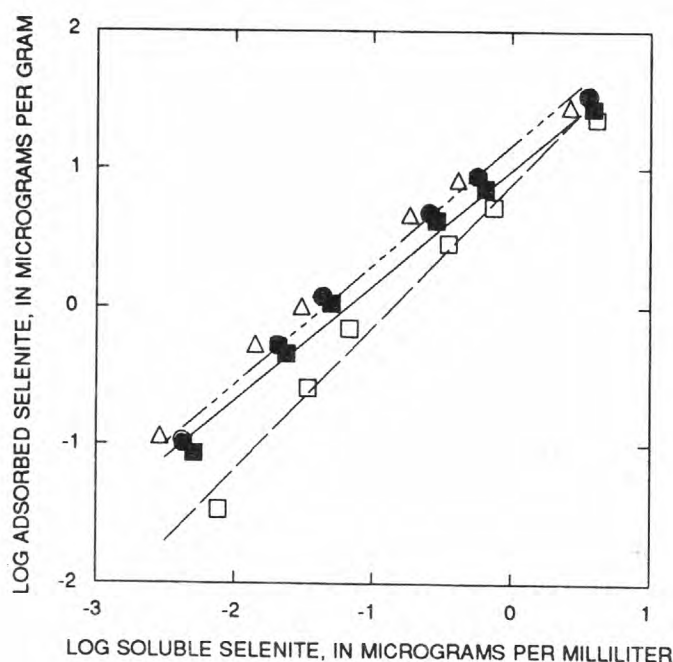


Figure 2. Change in adsorbed and desorbed concentrations of selenite with time from site 3 soil and soil CS.

and substantial adsorption of SeIV to the soil. More than 50 percent of the SeIV was adsorbed after 8 h, and equilibrium conditions were essentially reached after about 24 h. The similar adsorption rates and equilibrium partitioning in sterile and unsterile conditions indicate that biological activity did not alter the concentration of SeIV during the 124-hour experiment. Desorption of SeIV from soil CS in 0.005 M CaSO_4 solution also is rapid, and equilibrium conditions were essentially reached after 2 h. About 88 percent of the SeIV remained adsorbed to the soil at the end of the desorption experiment indicating the sorption reaction is nonreversible. In contrast, SeVI did not appreciably adsorb to soil during the rate or equilibrium experiments (data not shown). Negligible adsorption of SeVI was reported in four San Joaquin Valley soils for pH's ranging from 2 to 12 (Sposito and others, 1987) and an Imperial Valley soil (Goldberg and Glaubig, 1988).

Equilibrium adsorption of SeIV on soil samples from sites 1, 2, 3, and soil CS are plotted on a logarithmic scale in figure 3. On the average, 43 to 27 percent of the added SeIV was adsorbed to the soils (10 to 5,000 $\mu\text{g/L}$ added concentrations of SeIV, respectively). The data in figure 3 are curvilinear, which suggests multiple sorption sites or sorption mechanisms over the range of coverages in the adsorption experiment. The Freundlich model does not fully describe the physiochemical reactions associated with the adsorption process, but it does describe the strong affinity these soils have for SeIV. The Freundlich model was used to provide information on the relative affinity of these soils for SeIV.

Least-squares regression was used to determine the intercept (k_a) and slope (N_a) of the data in figure 3 (table 1). The adsorption isotherms for the soils from sites 1 and 3 have slopes that are similar (0.85 and



EXPLANATION

SOIL SOLUTION SAMPLES--pH was 8.2 for all samples.

Line symbols indicate results of least-squares regression analysis for samples

- — Site 1 soil in 0.1 M NaCl
- — Site 2 soil in 0.1 M NaCl
- --- Site 3 soil in 0.1 M NaCl
- — Soil CS in 0.1 M NaCl
- △ --- Soil CS in 0.005 M CaSO₄

Figure 3. Equilibrium adsorption isotherms for selenite on soil samples from sites 1, 2, 3, and soil CS.

Table 1.--Slopes and intercepts of the selenite adsorption isotherms determined from least-squares regression

Site	Intercept (k_a)	Slope (N_a)	Coefficient of determination (r^2)	Background solution
1	10.5	0.85	0.99	0.1 M NaCl
2	7.1	1.01	.98	.1 M NaCl
3	13.5	.86	.99	.1 M NaCl
3*	13.5	.85	.99	.1 M NaCl
3*	13.5	.81	.99	.005 M CaSO ₄

*Site 3 soil equilibrated with 0.005 M CaSO₄ (soil CS).

0.86), but smaller in magnitude than the slope of the adsorption isotherm from site 2 (1.01). The intercepts were different for all three of the adsorption isotherms. The soils are all from the same depth (0 to 30 cm below land surface) and are similar in texture.

Analysis of covariance (Steel and Torrie, 1960) was used to evaluate the differences between the adsorption isotherms for the soil samples. The slope and intercept of the isotherm for nonirrigated soil (site 2) were significantly different ($\alpha=0.001$) from the irrigated soils (sites 1 and 3). Adsorption isotherms show that more SeIV is adsorbed to the irrigated soils than the nonirrigated soil at a given concentration of SeIV (fig. 3). The reason for enhanced adsorption of SeIV in the irrigated soils is uncertain. Irrigation and leaching probably increased the weathering and dissolution of surface precipitates in these soils relative to the nonirrigated conditions at site 2. The increased weathering may have increased the content and/or surface areas of minerals such as iron and manganese oxides and hydrous oxides, which would increase the number of specific adsorption sites in these soils.

Adsorption isotherms for the site 3 soil and soil CS were not significantly different ($\alpha=0.001$) in 0.1 M NaCl background solution and show that adsorption characteristics were not altered after removal of Se and salts by equilibration with 0.005 M CaSO₄. However, the adsorption isotherm for soil CS in 0.005 M CaSO₄ background solution was significantly different from the one in 0.1 M NaCl ($\alpha=0.05$). This is in agreement with data reported by Neal and others (1987), who attribute greater adsorption of SeIV in the presence of substantial amounts of calcium ion

due to the formation of a surface precipitate ($\text{CaSeO}_3 \cdot 2\text{H}_2\text{O}$) or an increase in the surface charge of soil by adsorption of calcium ions to soil surfaces.

Equilibrium adsorption and desorption isotherms for SeIV on soil CS are plotted on a logarithmic scale in figure 4. The desorption isotherms substantially deviate from the adsorption isotherm indicating nonreversible sorption. The desorption isotherms are slightly nonlinear, but the errors associated with linearizing the desorption data are small relative to assuming reversible sorption reactions. The intercepts (k_d) and slopes (N_d) of the desorption isotherms were determined by least-squares regression (table 2). The intercept of the isotherm generally increased (1.21 to 4.34), and the slope generally decreased (0.40 to 0.28) as the relative maximum adsorbed concentration

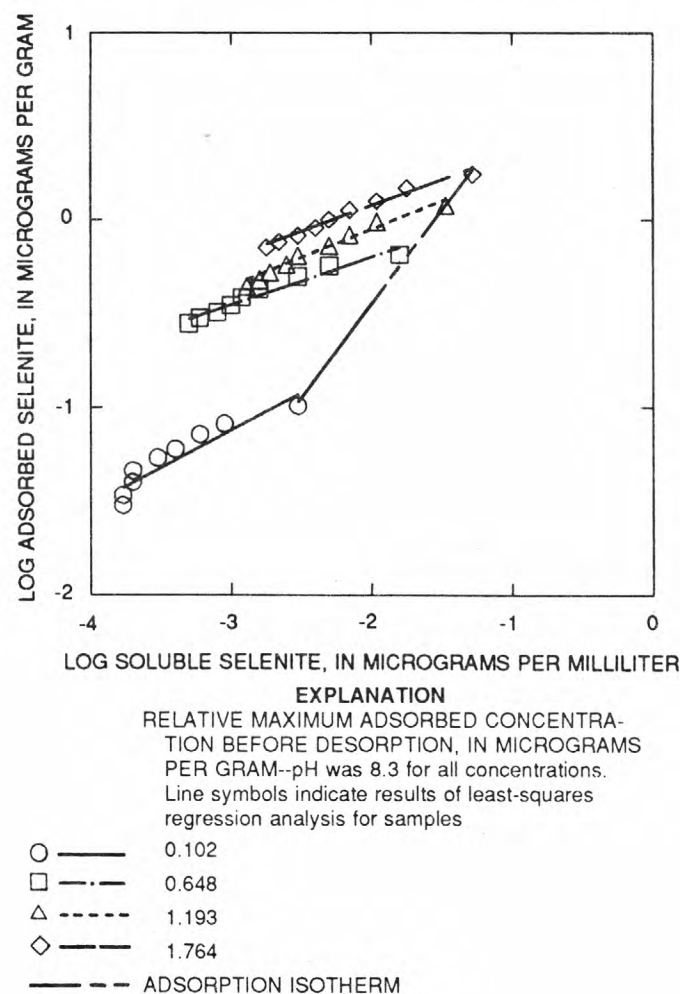


Figure 4. Equilibrium adsorption and desorption isotherms for selenite on soil CS.

Table 2.--Slopes and intercepts of equilibrium desorption isotherms determined from least-squares regression and predicted with equation 2

[$\mu\text{g/g}$, microgram per gram]

Relative maximum adsorbed concentration before desorption ($\mu\text{g/g}$) [S_m]	Intercept (k_d)	Slope (N_d)	Coefficient of determination (r^2)	Predicted intercept (k_d)	Predicted slope (N_d)
0.102	1.21	0.40	0.87	0.70	0.31
.648	2.01	.25	.95	2.18	.31
1.193	3.75	.31	.97	3.18	.31
1.764	4.34	.28	.98	4.05	.31

before desorption increased from 0.102 to 1.764 $\mu\text{g/g}$, respectively. The increased deviation from reversible sorption may indicate specific adsorption sites selective for SeIV.

The limited data from the sorption experiments make it impossible to develop a complete physical and chemical understanding of the nonreversible sorption of SeIV. The Freundlich model used in this study does provide qualitative information on SeIV mobility and its resistance to leaching by irrigation water. Because the results are qualitative, we used the average slope of the desorption isotherms in table 2 (0.31) and the slope of the adsorption isotherm for soil CS (0.81) to estimate the ratio N_d/N_a (0.38) for the nonreversible sorption model. The approach calculates values of k_d that are slightly lower than the measured values (table 2), but generally reproduces the nonreversible characteristic of SeIV sorption.

MODEL RESULTS TO EVALUATE SELENIUM MOBILITY UNDER LEACHING CONDITIONS

The concentrations of Se in a dynamic system changes in space and time making it difficult to evaluate the net result of physical and chemical processes on the depth distribution of Se under leaching conditions. The numerical model was used to simulate the combined effect of chemical and physical processes on Se concentrations in a hypothetical soil profile. Nonreversible sorption was included

in the model to show the movement of the SeIV specie relative to the conservative SeVI specie during continuous leaching by irrigation water.

Leaching by irrigation water is not a continuous process because these agricultural soils experience alternating periods of irrigation and drainage during a typical growing season. The resulting variability in soil moisture content and water residence time greatly complicate the transport of water and solutes in the soil. The numerical model does not simulate Se movement in soil under these complex conditions. The model cannot be used to determine Se travel times during leaching but instead estimates the net distribution of soluble and adsorbed Se in soil after extended periods of time. References to time therefore are not quantitative and must be interpreted on a qualitative basis.

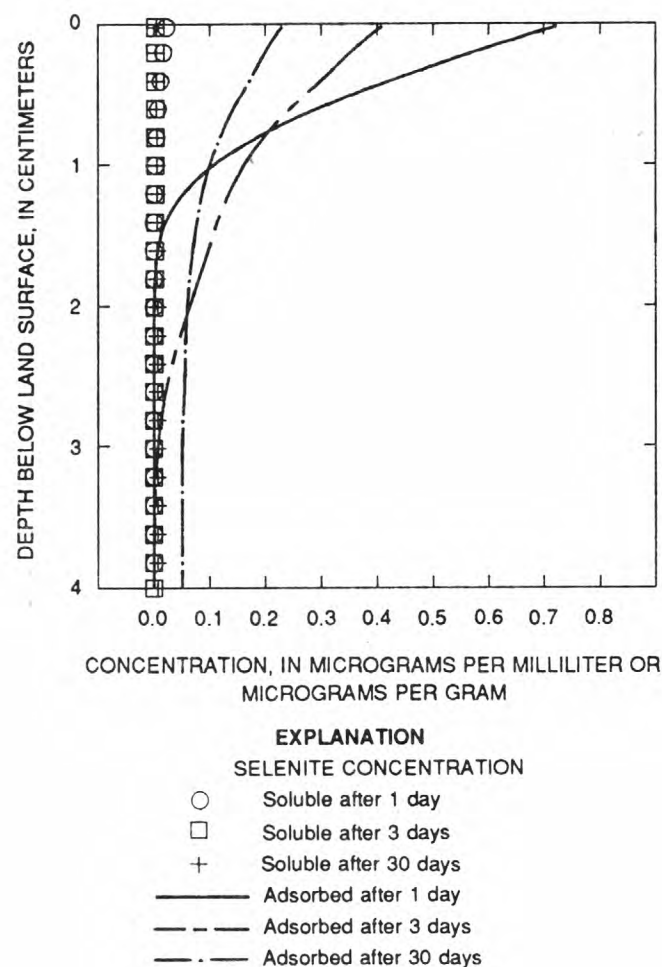


Figure 5. Depth distribution of soluble and adsorbed selenite simulated by the numerical model with nonreversible sorption reactions after 1, 3, and 30 days of continuous leaching.

Two model simulations were done to assess SeIV transport in hypothetical profiles of saturated soil. The first simulation shows the distribution of adsorbed and soluble SeIV resulting from nonreversible sorption (fig. 5). The second simulation assumes that sorption reactions are reversible, and comparison of simulations 1 and 2 (fig. 6) allows for qualitative assessment of the effect of the nonreversible reaction. Input to the transport model was as follows: input concentration (C_i), 0.10 $\mu\text{g/mL}$; volumetric flux (q), 6.1 cm/d ; volumetric water content (θ), 0.43 cm^3/cm^3 ; pulse interval (t_1), 1 d; dispersion coefficient (D), 14.3 cm^2/d ; and Freundlich parameters k_a , N_a , and N_d/N_a were 13.5, 0.81, and 0.38.

The model results show the strong affinity these soils have for SeIV. Most of the SeIV entering the profile in the first simulation is adsorbed near the

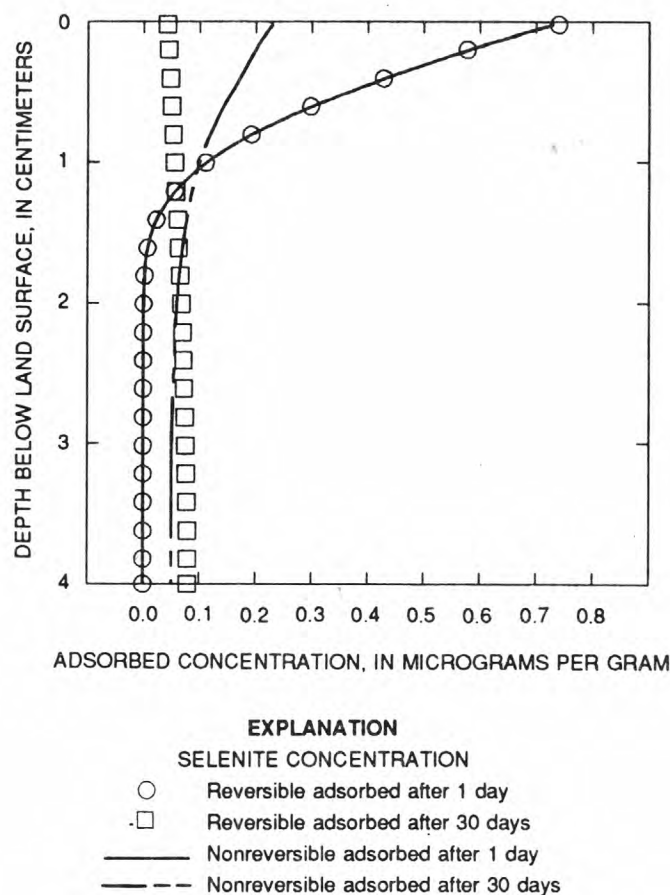


Figure 6. Comparison of soluble and adsorbed distributions of selenite simulated by the numerical model with reversible and nonreversible sorption reactions after 1 and 30 days of continuous leaching.

surface (fig. 5). Soluble concentrations of SeIV are uniformly low and do not substantially change during the 30-day simulation. The concentration of soluble SeIV provides minimal insight into the quantity of SeIV adsorbed to the soil. The model shows that adsorbed SeIV can represent a substantial reservoir of Se. Leaching does result in significant movement of adsorbed SeIV, and the SeIV adsorbed at the shallow depths is desorbed and subsequently re-adsorbed to soil at deeper depths. Redistribution of adsorbed SeIV during leaching is substantially greater for a reversible reaction (fig. 6), and thus nonreversible sorption reactions have an important role in limiting SeIV mobility. The simulation for SeVI (results not shown) indicate most of the SeVI is leached from the soil profile before 1 day. Leaching by irrigation water should have a substantial effect on the depth distribution of SeVI. Chemical analyses of soils with different leaching histories were done to assess the effects of irrigation and drainage on the depth distribution of salinity and selenium.

DEPTH DISTRIBUTION OF SALINITY AND SELENIUM IN TWO SOIL PROFILES WITH DIFFERENT LEACHING HISTORIES

The chemical analyses of soil samples reported in table 3 show the distribution of salinity and selenium resulting from different leaching histories. The salinity of the saturation extracts, as measured by specific conductance, increases with depth at the irrigated site (site 1) indicating leaching of soluble and slightly soluble salts. Decreasing salinity with depth at the nonirrigated site (site 2) probably is the result of evaporation from a shallow water table (Bohn and others, 1979).

Chemical equilibrium calculations using the computer code WATEQF (Plummer and others, 1976) were done with the major cation and anion data from the saturation extracts (table 4). The equilibrium calculations indicate that the soil solution from site 1 is undersaturated with respect to gypsum. In contrast, the soil solution from site 2 is supersaturated with respect to gypsum. The calcium ion activity calculated for the extracts of soil from the two sites is about the same, but the calculated sulfate ion activity at site

1 is about 10 times lower than at site 2. Irrigation at site 1 has probably leached soluble and slightly soluble salts containing sulfate. The soil solution from site 3 is saturated with respect to gypsum and its composition is intermediate between the irrigated and nonirrigated soils. Site 3 was irrigated in the past, but nonirrigated since 1980. These results support the effect of leaching histories on the distributions of salts and salinity at the three sites.

Analysis of the saturation extracts (table 3) show that SeVI is the predominant form of Se in the soil solution. The distribution of SeVI in the two soil profiles almost parallels the salinity distributions ($r^2=0.73$), and indicate that leaching by irrigation water percolating through the root zone can contribute significant quantities of salt and SeVI to shallow ground water. In contrast, concentrations of soluble SeIV generally are low in the soil samples and SeIV probably is resistant to leaching. The concentration of SeIV was relatively high (2 $\mu\text{g/L}$, or 29 percent of the total Se in the saturation extract) in the soil solution of the most leached soil (0- to 30-centimeter depth sample from site 1). Extensive leaching of this surface soil relative to the samples collected at the deeper depths and at the nonirrigated site resulted in a low concentration of SeVI. The SeIV thus represents a higher percentage of the total Se in the soil solution.

The selenium sorbed to soil surfaces was estimated by extraction with phosphate solution. Most of the Se in the phosphate extracts is SeIV, but significant quantities of SeVI were extracted from some of the samples (table 3). The extract from the deepest depth at site 1 is about 50 percent SeIV and 50 percent SeVI. Because selenate is not significantly adsorbed, the SeVI in the phosphate extracts may represent Se released by mechanisms other than desorption (for example, dissolution of solid phases).

The distribution of adsorbed SeIV estimated by the phosphate extracts generally decreases with depth at site 2. At site 1, adsorbed SeIV increases from 0.044 mg/kg at the 0- to 30-centimeter depth to 0.058 mg/kg at the 31- to 60-centimeter depth, then decreases below the 60-centimeter depth. The application of irrigation water at site 1 for the past 40 years may

Table 3.--Chemical analyses of soil saturation extracts, sequential extractions, and soil of soil samples from sites 1, 2, and 3

[cm, centimeter; mL/g, milliliter per gram; dS/m, decisiemen per meter; mg/L, milligram per liter; µg/L, microgram per liter; mg/kg, milligram per kilogram; --, not analyzed. <, value is less than actual value shown]

Sample depth (cm)	Soil saturation extracts							
	Water content (mL/g of soil)	Specific conductance (dS/m)	pH	Dissolved organic carbon (mg/L)	Selenite (µg/L)	Selenate (µg/L)	Organic selenium (µg/L)	Soluble selenium (µg/L)
Site 1								
0-30	0.483	1.40	8.4	53	2	4	1	7
31-60	.663	5.94	8.1	43	1	99	1	110
61-90	.515	12.60	8.0	48	<1	446	<1	420
91-120	.813	12.70	7.8	28	<1	546	2	540
Site 2								
0-30	0.567	10.30	8.1	69	4	620	1	640
31-60	.413	7.10	8.1	36	1	216	1	220
61-90	.502	6.64	7.9	22	<1	97	<1	96
91-120	.675	7.48	7.9	19	1	72	<1	74
Site 3								
0-30	0.626	4.80	8.1	39	<1	24	<1	24
*0-30	.625	.90	8.2	--	--	--	--	<1
Sequential extractions								
Sample depth (cm)	Sequential extractions				Soil			
	0.25 M KCl		0.1 M H ₂ PO ₄ ²⁻		Total carbon (percent)	Organic carbon (percent)	Inorganic carbon (percent)	Total selenium (mg/kg)
Selenite (mg/kg)	Selenate (mg/kg)	Selenite (mg/kg)	Selenate (mg/kg)					
Site 1								
0-30	<0.006	0.014	0.044	0.019	0.85	0.62	0.23	1.3
31-60	<.006	.083	.058	.018	.78	.43	.35	1.5
61-90	<.006	.240	.032	.014	.56	.26	.30	1.4
91-120	<.006	.444	.023	.025	.64	.30	.34	1.6
Site 2								
0-30	0.012	0.407	0.059	0.032	1.02	0.59	0.43	1.7
31-60	<.006	.123	.024	.010	.64	.31	.33	1.3
61-90	<.006	.097	.012	.006	.63	.30	.33	1.1
91-120	<.006	.086	.016	.006	.66	.27	.39	1.1
Site 3								
0-30	<0.006	0.022	0.008	<0.006	0.74	0.38	0.36	1.2
*0-30	<.006	<.006	<.006	<.006	--	--	--	1.1

*Equilibrated with 0.005 M CaSO₄ solution (soil CS).

Table 4.--Major cations and anions in saturation extracts of surface soils (0- to 30-centimeter depth)

[meq/L, milliequivalent per liter]

Sample site	Anions (meq/L)				Cations (meq/L)			
	Chloride	Nitrate	Sulfate	Bicarbonate plus carbonate	Potassium	Sodium	Calcium	Magnesium
1	3.7	2.2	2.6	3.2	0.4	5.2	4.7	1.4
2	40.5	10.7	61.4	8.9	8.3	64.5	36.8	11.9
3	14.9	3.1	38.0	1.7	.9	26.1	25.4	5.3
CS	.6	.0	8.6	1.2	.4	2.5	7.2	1.0

have leached adsorbed SeIV near the surface to the deeper depths where it was readsorbed. The redistribution of adsorbed SeIV at site 1 seems to have been small, probably because of nonreversible sorption reactions. The contributions of SeIV to Se concentrations in shallow ground water from irrigation water percolating through the root zone should be minimal under the alkaline-oxidized conditions in this field.

The soil extractions removed a small proportion of the total Se in the soils (table 3). On the average, about 85 percent of the Se in the soil samples was resistant to extraction by either the KCl or phosphate solutions. This fraction represents a substantial reservoir of Se in the soil that is resistant to leaching. The extraction data and model results (fig. 5) emphasize the need to accurately assess concentrations of adsorbed Se and the rate at which Se is oxidized to SeVI under alkaline and oxidized soil conditions. This information will provide estimates of the quantity of Se potentially available for leaching to the shallow ground water by the continued irrigation of soils in the western San Joaquin Valley.

SUMMARY AND CONCLUSIONS

Results from sorption experiments and a numerical model were used to assess the effect of irrigation and drainage on the depth distribution of selenium in soils from the western San Joaquin Valley, California. Sorption studies showed that selenate (15 to 12,400 µg/L of selenium) is not adsorbed to soil. In contrast, selenite (10 to 5,000 µg/L of selenium) is rapidly adsorbed and the time lag was considerable between the adsorption and desorption reactions, indicating nonreversible sorption of selenite. Selenite adsorption was greater in the irrigated soil than the nonirrigated

soil, and adsorption seems to be enhanced by substantial concentrations of calcium ion. Slopes and intercepts are different for selenite adsorption and desorption isotherms. The desorption isotherm is dependent on the quantity of adsorbed selenite in the soil prior to desorption.

Results from model simulations qualitatively evaluate the mobility of selenite during leaching by irrigation water. The resistance of selenite to leaching is enhanced by the nonreversible characteristic of the sorption reaction, and desorption of selenite can therefore represent a long-term source of selenium to shallow ground water. Selenate behaves as a conservative constituent under alkaline-oxidized conditions and is rapidly leached from soil. This explains why depth distributions of adsorbed selenite generally were similar in irrigated and nonirrigated soils, whereas the soluble selenate and salinity distributions were substantially affected by leaching history.

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