COMPARISON OF METHODS TO DETERMINE SELENIUM SPECIES IN SATURATION EXTRACTS OF SOILS FROM THE WESTERN SAN JOAQUIN VALLEY, CALIFORNIA

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

U.S. GEOLOGICAL SURVEY
Open-File Report 88-458
REGIONAL AQUIFER SYSTEM ANALYSIS

Prepared in cooperation with the
SAN JOAQUIN VALLEY DRAINAGE PROGRAM

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 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 areas: (1) Public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

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The Regional Aquifer System Analysis (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 have often arbitrarily been limited in the past. The broad objective for each study is 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 an effective management of the system. The Central Valley RASA study, which focused on studying 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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CONVERSION FACTORS

Metric (SI) units are listed in this report. For readers who prefer inch/pound units, the conversion factors for the terms used in this report are listed below.

Multiply	By	To obtain
cm (centimeter)	0.3937	inch
cm^3 (cubic centimeter)	0.0610	cubic inch
g (gram)	0.0022	pound
km (kilometer)	0.6214	mile
mL (milliliter)	0.0038	ounce
mm (millimeter)	0.03937	inch

Selenium concentrations in solution are given in micrograms per liter (µg/L). One thousand micrograms per liter is equivalent to 1 milligram per liter. Micrograms per liter is equivalent to "parts per billion." Milligrams per liter is equivalent to "parts per million."

Concentrations of selenium in soil are given in micrograms per gram (µg/g). Micrograms per gram is equal to parts per million.

For temperature, degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) by using the formula:

$$°F=[(1.8)(°C)]+32.$$

ABBREVIATIONS USED

decisiemen per meter (dS/m)
hour (h)
minute (min)
micrometer (µm)
molar concentration (M)

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ABSTRACT

Methods to determine soluble concentrations of selenite, selenate, and organic selenium were compared on saturation extracts of soil samples collected from three sites on the Panoche Creek alluvial fan in the western San Joaquin Valley, California. The methods were used in combination with hydride-generation atomic-absorption spectrometry for detection of selenium and included a selective chemical digestion method and three chromatography methods using XAD-8 resin, Sep-Pac C_{18} cartridge, and a combination of XAD-8 resin and activated charcoal.

Undigested organic matter in some of the extracts inhibited selenium detection when using the digestion and Sep-Pac C_{18} methods, but the interference was removed by using the XAD-8 method. Combining XAD-8 resin and activated charcoal was an unacceptable method, because the activated charcoal removed selenite and selenate. Ninety-eight percent of the selenium in the extracts was selenate and about 100 percent of the isolated organic selenium was associated with the humic acid fraction of dissolved-organic matter.

INTRODUCTION

Selenium (Se) in subsurface agricultural drain water from soils in the western San Joaquin Valley has entered the food chain of wetland habitats and caused a high incidence of deformity and mortality in waterfowl hatchlings at the Kesterson National Wildlife Refuge near Gustine, California (Ohlendorf and others, 1986). Though saline soils and the disposal of saline drain water have caused water-management problems for agriculture in the region for decades, Se was not recognized as a problem or studied until recently (1983). An understanding of the mobility of Se in soil and ground water is essential for the development of management practices aimed at decreasing the amount of Se in drain water.

Selenium exists in four oxidation states in natural systems: +6 (selenate, SeO_4^{2-}), +4 (selenite, SeO_3^{2-}), 0 (elemental selenium, Se^0), and -2 (selenide, Se^{2-}). In the alkaline-oxidized soils of the arid western San Joaquin Valley, SeO_4^{2-} has been reported as the dominant soluble form of Se, and estimates of the adsorbed Se species have been reported to be comprised of mostly SeO_3^{2-} (Fujii and others, 1987). Organic Se has been measured in some San Joaquin Valley soils, and it may represent a significant source of soluble Se (Burau and others, 1986). Therefore, at least three soluble Se species are in soils of the San Joaquin Valley, and the determination of soluble SeO_3^{2-}, SeO_4^{2-}, and organic Se is necessary to conduct meaningful studies on Se mobility in soil and ground water.

In this paper, methods for determining concentrations of soluble SeO_3^{2-}, SeO_4^{2-}, and organic Se in soil saturation extracts are compared. The methods differ in the manner in which the Se that is associated with dissolved-organic matter is assessed. The methods are (1) determination of organic Se by calculating the difference between total Se and the sum of SeO_3^{2-} and SeO_4^{2-}, as measured with sequential chemical digestions (digestion method); (2) determination of organic Se by isolation of dissolved-organic matter with an acrylic ester polymer resin of intermediate polarity (XAD-8[1] method); (3) determination of organic Se by isolation of dissolved-organic matter with octadecylsilane bonded phase packings (Sep-Pac C_{18} method); and (4) determination of soluble organic Se by isolation of dissolved-organic matter with a combination of XAD-8 resin and activated charcoal (XAD-8/AC method).

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.

BACKGROUND ON SPECIATION METHODS

The four methods used in this study to speciate Se require the measurement of Se concentrations in aqueous samples. Selenite in aqueous samples can be analyzed by generating Se hydride (H_2Se), which is detected by atomic-absorption spectrometry. The hydride-generation atomic-absorption spectrometry (HGAAS) method only measures SeO_3^{2-} (Simenus and others, 1981), and in order to determine total Se, all Se present must be transformed to SeO_3^{2-}.

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[1] The 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.

When using HGAAS for Se analyses on water from the Kesterson National Wildlife Refuge, samples were oxidized and reduced to measure SeO_3^{2-}, the sum of SeO_3^{2-} and SeO_4^{2-}, and total Se. For example, three aliquots of a water sample from pond 2 in the Kesterson Refuge were analyzed for Se by HGAAS as follows: (1) generation of H_2Se from an untreated aliquot measured SeO_3^{2-} (6 µg/L), (2) generation of H_2Se from an aliquot after reduction of the SeO_4^{2-} to SeO_3^{2-} measured the sum of SeO_3^{2-} and SeO_4^{2-} (300 µg/L), and (3) oxidation of all Se in an aliquot to SeO_4^{2-}, and then reduction of the SeO_4^{2-} to SeO_3^{2-} before generation of H_2Se measured total Se (350 µg/L) (Presser and Barnes, 1984). This demonstrated that the selectivity of HGAAS for SeO_3^{2-} could be used to analyze various oxidation states of Se in this water.

Use of the HGAAS method to measure Se species in soil saturation extracts is questionable because of potential interferences caused by dissolved-humic substances. In one example, only 2 percent of 0.1 µg of SeO_3^{2-} was reportedly recovered from 50 mL of a ground-water sample (Roden and Tallman, 1982). After removing the dissolved-humic substances with XAD-8 resin, accurate determination of the added SeO_3^{2-} was possible. The Se interference was hypothesized to result from the formation of an adduct between dissolved-humic substances and H_2Se. The humic substances removed with the XAD-8 resin were not analyzed for Se, and the fraction of dissolved-organic matter removed from the ground-water sample was not reported.

The XAD-8 resin has been used to separate dissolved-organic matter into hydrophobic (adsorbed to XAD-8 resin) and hydrophilic (not adsorbed to XAD-8 resin) acids, bases, and neutrals (Leenheer, 1981; Thurman and Malcolm, 1979). The selectivity of the XAD-8 resin for hydrophobic-organic matter in a water sample is inversely related to the solubility of the organic matter (Thurman and others, 1978). Therefore, adsorption is affected by factors which affect solubility such as solvent type, pH, and ionic strength. For example, the compounds that are adsorbed to the XAD-8 resin at low pH (for example, protonated humic acids) are subsequently desorbed (eluted) with a basic solution by deprotonation.

Because the XAD-8 resin is selective for a portion of the dissolved-organic matter (hydrophobic-organic matter), it probably will not remove all of the dissolved-organic carbon (DOC) from soil saturation extracts. Thurman and Malcolm (1979) removed 63.2 percent of the DOC in a water sample from the South Platte River, Colorado, with XAD-8 resin. Leenheer (1981), also using XAD-8 resin, removed 49.6 percent from another South Platte River water sample and 54.6 percent from an oil-shale retort wastewater sample.

Despite the inability to remove and isolate all dissolved-organic matter in a sample, the measurement of Se associated with the hydrophobic-organic matter isolated with the XAD-8 resin (hydrophobic-organic Se) has been operationally defined as the concentration of organic Se in natural water samples (Cutter, 1985 and 1986). Similarly, Sep-Pac C_{18} cartridges made from octadecylsilane bonded phase packings also have been used to isolate hydrophobic-organic Se in aqueous samples (Cutter, 1986). Like XAD-8 resin, adsorption to the Sep-Pac C_{18} cartridge resin is determined by solubility. The XAD-8 and Sep-Pac C_{18} methods have not been compared on the basis of their ability to remove and isolate dissolved-organic matter.

The quantity of soluble-organic matter removed from seawater using XAD-2 resin (a styrene-divinylbenzene polymer with a less polar structure than XAD-8) was improved by combining XAD-2 resin with activated charcoal (Fu and Pocklington, 1983). Ninety-eight percent of the DOC in seawater was isolated using this method. However, the effect of the XAD-2 resin and activated charcoal on the composition of the inorganic constituents in the seawater was not reported. Combining the XAD-8 resin with activated charcoal should isolate greater quantities of organic matter than the XAD-8 resin alone, but any effect the activated charcoal may have on inorganic Se must be tested.

MATERIALS AND METHODS

Speciation Using the Digestion Method

Separation of Se oxidation states in aqueous samples with selective chemical digestions uses the specificity of HGAAS for SeO_3^{2-}. The concentration of SeO_3^{2-} is determined by HGAAS on an aliquot of sample made acidic with hydrochloric acid (HCl) by generating H_2Se with sodium borohydride ($NaBH_4$). The H_2Se is stripped from solution with argon gas and detected by atomic-absorption spectrometry. Concentrated HCl is added to another aliquot of sample resulting in a concentration of 4 M HCl and boiled for 46 min to reduce any SeO_4^{2-} to SeO_3^{2-} (Presser and Barnes, 1984). The solution is then analyzed by HGAAS and the resulting Se concentration is considered the sum of SeO_3^{2-} and SeO_4^{2-}. Total Se is determined on a sample after oxidation of organic matter and Se by digestion with HCl and potassium persulfate, followed by digestion with oxalic acid [this digestion procedure is a modification of the method described by Presser and Barnes (1984)]. The sample is then reduced with HCl so that all the Se is present as SeO_3^{2-}. The difference between the reduction only analysis (the sum of SeO_3^{2-} and SeO_4^{2-}) and the undigested analysis (SeO_3^{2-}) is equal to the SeO_4^{2-} concentration. The difference between the concentration of total Se and the reduction only analysis is assumed equal to the organic Se concentration (Presser and Barnes, 1984).

Speciation Using Chromatography Methods

Column chromatography was used to isolate hydrophobic dissolved-organic matter in aqueous samples. The organic matter adsorbed to the column packings was desorbed, and the Se concentration of the isolated organic matter was the hydrophobic-organic Se in the original sample (Cutter, 1985 and 1986; Leenheer and Huffman, 1976). Dissolved-organic carbon concentrations in the column effluents and eluates were used to trace the dissolved-organic matter during the speciation procedure. Therefore, the materials used in the chromatography columns were cleaned to prevent carbon contamination, which would interfere with the tracing of dissolved-organic matter.

Soluble carbon was removed from the XAD-8 resin by first soaking it in 0.1 M sodium hydroxide (NaOH) for 5 days. The solution was decanted and the resin was then rinsed with deionized water before being sequentially Soxhlet extracted with acetone, hexane, and methanol (CH_3OH) each for 24 h (Leenheer, 1981). Clean resin was stored in a CH_3OH/deionized water mixture and refrigerated. The activated charcoal used in the XAD-8/AC method was soaked in 1.0 M NaOH followed by 1.0 M HCl. It was then rinsed with deionized water, drained, dried in an oven at 110 °C, and washed again with deionized water (Fu and Pocklington, 1983).

The columns were constructed from polypropylene drying tubes (1.0-cm diameter, 4.0-cm length), and packed with XAD-8 resin, or XAD-8 resin and activated charcoal. Glass wool was used to plug end caps and separate the XAD-8 resin and activated charcoal. The resulting XAD-8 and XAD-8/AC columns had a bed volume of about 3.1 cm³. The Sep-Pac C_{18} cartridges are factory packed with a bed volume of about 0.8 cm³. Columns were rinsed with 500 mL of deionized water, attached to all-plastic syringes with Tygon tubing, and placed in a mechanical vacuum extractor. The XAD-8/AC columns were positioned so that the water sample passed through the XAD-8 resin and then the activated charcoal. The vacuum extractor was set at a constant flow rate of 2.5 mL/min for sample application and elution.

Before use, the XAD-8 resin and XAD-8/AC columns were sequentially rinsed three times with 50 mL of 0.1 M NaOH followed by 50 mL of 0.1 M HCl (Thurman and Malcolm, 1979). The Sep-Pac C_{18} cartridges were sequentially rinsed with 20 mL deionized water, 20 mL 1.0 M HCl, 20 mL deionized water, 20 mL CH_3OH, 10 mL deionized water, and finally 10 mL 0.1 M HCl (Cutter, 1986). Dissolved-organic carbon concentrations in the HCl and NaOH rinses from the XAD-8 resin prior to sample introduction were less than 0.5 mg/L. Dissolved-organic carbon concentrations in the HCl and NaOH rinses from the XAD-8/AC column prior to sample application were less than 1.0 and 0.5 mg/L, respectively. Dissolved-organic carbon concentrations in the water and HCl rinses from the Sep-Pac C_{18} cartridges before the CH_3OH rinse were less than 0.5 mg/L. Low concentrations of DOC in these rinses indicated negligible contribution of carbon from column materials.

To separate Se species for analysis, 50 mL of acidified sample (pH less than 2) was passed through a chromatography column and followed with 10 mL of 0.1 M HCl. The resulting 60 mL of column effluent was divided into two parts: 20 mL for undigested HGAAS analysis (SeO_3^{2-}), and 40 mL for Se analysis after digestion and reduction (the sum of SeO_3^{2-} and SeO_4^{2-} and any hydrophylic-organic Se).

The adsorbed hydrophobic-organic matter was recovered from the chromatography columns by reversing and sequentially eluting them. The elution schemes were assumed to recover all hydrophobic-organic matter (Thurman and Malcolm, 1979). The XAD-8 resin was eluted with 40 mL 0.1 M NaOH, 40 mL deionized water, and 10 mL CH_3OH. This elution procedure was later modified by deleting the CH_3OH elution and used a combined 40 mL eluate consisting of 25 mL 0.1 M NaOH followed by 15 mL deionized water. The XAD-8/AC columns were eluted with 50 mL 7 M ammonium hydroxide (NH_4OH), a mixture of concentrated NH_4OH and CH_3OH (resulting in a 7 M NH_4OH concentration), and CH_3OH (Fu and Pocklington, 1983). The XAD-8 resin elution procedure using 0.1 M NaOH, deionized water, and CH_3OH also was tested on the XAD-8/AC column. The Sep-Pac C_{18} cartridges were eluted with 10 mL CH_3OH (Cutter, 1986). All eluates were digested and analyzed for total Se by HGAAS, and their sum was considered equal to the hydrophobic-organic Se isolated from the original sample.

Comparison of the sum of SeO_3^{2-}, SeO_4^{2-}, and hydrophobic-organic Se to the total Se determined by the digestion method on an aliquot of the original sample provided a mass-balance check of the results. The CH_3OH present in some of the eluates was evaporated before digestion by placing the sample in a 250 mL Erlenmeyer flask on a hot plate at 40°C. Sample volume was maintained with periodic additions of deionized water. Volatile losses of Se during the evaporation of the CH_3OH were assumed negligible because the quantity of hydrophobic-organic Se obtained from the digestion of organic compounds eluted with CH_3OH from

Sep-Pac C_{18} cartridges was similar to that eluted with NaOH and deionized water from the XAD-8 resin.

Soil Sample Collection and Analyses

A total of nine soil samples were collected from three sites on the Panoche Creek alluvial fan in the western San Joaquin Valley, California (fig. 1). All sampling sites were on soils of the Panoche and Ciervo clay series [soil classification Typic Torriorthent (Harradine, 1950)].

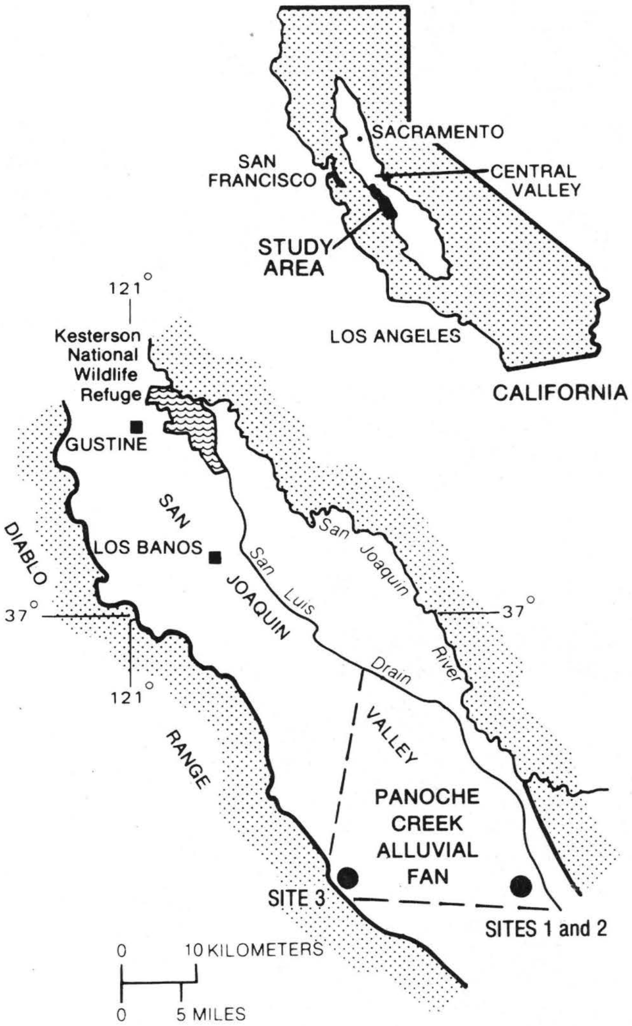

FIGURE 1. - Study area and sampling sites

Two of the three sampling sites were on Ciervo silty clay soils within 1 km of each other near the southern edge of the alluvial fan. The water table in this area is at an average depth of 2 m below land surface. Site 1 is in an agricultural field which has been irrigated for about 40 years and artificially drained since 1980. Four incremental soil samples were hand augered at 30-cm intervals from the surface to a depth of 120 cm. Site 2 is in an area that probably has never been irrigated and may represent unirrigated soil conditions. Four 30-cm incremental samples were collected to a depth of 120 cm at site 2.

Site 3 is near the head of the Panoche Creek alluvial fan on Panoche silty clay soil. Unlike the Ciervo soils at sites 1 and 2, this soil is well drained and has not been affected by shallow ground water; therefore, only one sample of the top 30 cm of soil was collected at site 3.

All soils were air dried and ground to pass through a 1-mm sieve. The three surface samples (0- to 30-cm depth), one from each site, were analyzed for total Se and total and inorganic carbon at the Geologic Division laboratory of the U.S. Geological Survey in Denver, Colorado. Total Se was determined by HGAAS after the soil was digested by a modified method of Briggs and Crock (1986). The modifications are described in Fujii and others (1987) and are intended to increase Se recovery by presumably reducing Se losses by volatilization. Total carbon was determined by combustion of the soil in a Leco Total Combustion Analyzer that measured the released carbon dioxide (CO_2) with an infrared detector. Inorganic carbon was determined on an identical sample by gravimetrically measuring the CO_2 released from digestion of the inorganic carbon with acid. Organic carbon was calculated as the difference between the total and inorganic carbon analyses.

Soil saturation extracts were obtained from saturated soil pastes prepared and extracted by the conventional method described by Rhoades (1982) using about 400 g of soil and are assumed to contain the soluble constituents in soil. For each soil sample, replicate extracts were composited to obtain an adequate volume of solution for multiple analyses. The extracts were passed through a 0.45-µm filter. The solutions were split, and one part was acidified with HCl to a pH less than 2 for Se analyses. Dissolved-organic carbon also was measured in the acidified extracts with a Dohrman DC-80 Total Organic Carbon Analyzer, which oxidizes the dissolved-organic matter in an aqueous sample with persulfate solution and ultraviolet light. The CO_2 released is then measured with an infrared detector. Specific conductance and pH were measured on unacidified extracts.

The soil saturation extracts from the nine soil samples used to test the Se speciation methods varied in the quantities of soluble salts (specific conductance), DOC, and Se as shown in table 1. The 640 µg/L of Se in the saturation extract from site 2 surface soil represented about 23 percent of the total Se in the soil on a mass basis. The Se in the saturation extracts of the site 1 (7 µg/L) and site 3 (9 µg/L) surface soils represented less than 1 percent of the total Se in the soils on a mass basis. Also, less than 1 percent of the total organic carbon on a mass basis was removed from the three surface soils by the saturation extracts.

Table 1. *Chemical analyses of soil and soil saturation extracts of nine samples used in the comparison of methods study*

[--, no data]

Soil saturation extracts						Soil			
Sample depth (cm)	Water content (mL/g of soil)	Specific conductance (dS/m)	pH	Dissolved organic carbon (mg/L)	Soluble Se (µg/L)	Total carbon (percent)	Organic carbon (percent)	Inorganic carbon (percent)	Total Se (µg/g)
					Site 1				
0-30	0.483	1.40	8.45	53	7	0.88	0.63	0.25	1.3
31-60	.663	5.94	8.11	43	110	--	--	--	--
61-90	.515	12.60	7.96	48	420	--	--	--	--
91-120	.813	12.70	7.89	28	540	--	--	--	--
					Site 2				
0-30	0.567	10.30	8.14	69	640	1.05	0.60	0.45	1.6
31-60	.413	7.10	8.13	36	220	--	--	--	--
61-90	.502	6.64	7.90	22	96	--	--	--	--
91-120	.675	7.48	7.94	19	74	--	--	--	--
					Site 3				
0-30	0.373	0.77	8.44	93	9	0.59	0.40	0.19	1.2

EXPERIMENTAL APPROACH

Comparison of Chromatography Methods for Interactions of Selenite and Selenate with Column Materials

The removal of hydrophobic-organic matter from solution, without altering the concentration of inorganic Se species, was tested by analyzing standard Se solutions prepared in the laboratory. A solution containing 24 µg/L of Se (9 µg/L as SeO_3^{2-} and 15 µg/L as SeO_4^{2-}) was passed through the XAD-8, Sep-Pac C_{18}, and XAD-8/AC columns to evaluate reactions between these Se species and the column materials. The retention of SeO_3^{2-} and SeO_4^{2-} complexed by dissolved-organic matter also was tested. Under acidic conditions such as those used for the chromatographic separation of hydrophilic- and hydrophobic-organic matter (pH less than 2), SeO_3^{2-} is predominantly present as H_2SeO_3 (pK_1 of 2.6) and SeO_4^{2-} is about equally distributed between $HSeO_4^{1-}$ and SeO_4^{2-} (pK_2 of 1.9). Protonation of organic acids under acidic conditions will reduce their net negative charge and may then form hydrogen-bonded organic complexes with H_2SeO_3 and $HSeO_4^{1-}$. Removal of these complexes by the chromatography columns will remove inorganic Se. When the adsorbed materials are eluted and digested for Se analysis, the complexed H_2SeO_3 and $HSeO_4^{1-}$ would erroneously be interpreted as hydrophobic-organic Se.

To test for the removal of organically complexed Se, dissolved-organic matter in a 1:10 soil water extract from a sample low in total soluble Se (site 1, 0-to 30-cm sample) was isolated with the XAD-8 resin. The solution of isolated hydrophobic-organic matter contained 10 µg/L of total Se. Ten mL aliquots of this solution were spiked with Se and diluted to 50 mL with deionized water resulting in the following concentrations: (1) 5 µg/L of SeO_3^{2-} (solution A), (2) 14 µg/L of SeO_3^{2-} and 2 µg/L of SeO_4^{2-} (solution B), and (3) 5 µg/L of SeO_4^{2-} (solution C). The solutions were acidified to a pH less than 2 and speciated by the XAD-8 method.

Comparison of Methods for Determining Selenium Species in Saturation Extracts of Soils

The speciation methods were used to determine SeO_3^{2-}, SeO_4^{2-}, and organic Se in saturation extracts of surface soils (0- to 30-cm depth) from sites 1, 2, and 3. Results from the chromatography methods evaluated the presence of interferences from dissolved-organic matter during SeO_3^{2-} and SeO_4^{2-} determinations using the digestion method. The chromatography methods were compared on the basis of their ability to remove these interferences and isolate hydrophobic-organic Se from solution without altering SeO_3^{2-} and SeO_4^{2-} concentrations.

The ability of the chromatography methods to isolate hydrophobic-organic matter from soil saturation extracts was evaluated by calculating the carbon-adsorption efficiency. The DOC concentration measured in the soil saturation extracts (DOC_{in}) and column effluents (DOC_{out}) was used to calculate the carbon-adsorption efficiency, and is represented by the ratio of the DOC removed by the column and the DOC in the original sample $[(DOC_{in} - DOC_{out})/DOC_{in}]$. The average carbon-adsorption efficiency was calculated for each chromatography method with results from all analyses. The number of analyses used to calculate the average value varied depending on the number of samples (n) analyzed with each method. A low carbon-adsorption efficiency would indicate that a large part of the organic matter from the soil saturation extracts was hydrophylic-organic matter. Selenium associated with the hydrophylic-organic matter that passed through a chromatography column would cause erroneous speciation results.

The elution schemes used on the chromatography columns were assumed to quantitatively recover the adsorbed organic matter removed from the sample, which is represented by the carbon-adsorption efficiency (Thurman and Malcolm, 1979; Cutter, 1986; Fu and Pocklington, 1983). Organic matter in the NaOH, deionized water, and CH_3OH elutions from the XAD-8 method were digested and analyzed for Se separately. The organic matter in the NaOH elution contains high and low molecular-weight acids, including compounds with carboxyl and phenolic hydroxyl functional groups, such as humic acids (Thurman and Malcolm, 1979). The water elution contains materials with 8 to 10 carbon atoms per functional group and require a reduction in the ionic strength of the eluting solvent for desorption. The CH_3OH elution removes the remaining adsorbed materials, which are hydrophobic neutrals such as long-chain fatty acids (Thurman and Malcolm, 1979). The fractionation of hydrophobic-organic matter was not possible with the digestion, Sep-Pac C_{18}, or XAD-8/AC methods.

ASSESSMENT OF METHODS

Reactions of Selenite and Selenate with Chromatography Column Materials

Results from the speciation of standard solutions containing SeO_3^{2-} and SeO_4^{2-} by the digestion and chromatography methods are shown in table 2. Dissolved-organic matter was not present in the standard solution, and the digestion method results represented the correct Se speciation. Selenite concentration in the standard solution was not changed by the XAD-8 method, but decreased 1 μg/L with Sep-Pac C_{18} and 6 μg/L with XAD-8/AC. The sum of SeO_3^{2-} and SeO_4^{2-} was not changed by the XAD-8 or Sep-Pac C_{18} methods, but was reduced 15 μg/L (6 μg/L of SeO_3^{2-} and 9 μg/L of SeO_4^{2-}) by the XAD-8/AC method. Negligible quantities of Se were measured in eluates from the XAD-8 and Sep-Pac C_{18} methods, and 8 μg/L Se was measured in the XAD-8/AC eluate.

Table 2. *Results from the speciation of standard solution containing only selenite and selenate with the digestion, XAD-8, Sep-Pac C_{18}, and XAD-8/AC methods*

[Number in parentheses is percentage recovered from the applied solution. Digestion method results are considered the standard solution concentrations]

Method	Selenite (μg/L)	Selenite plus selenate (μg/L)	Selenium eluted (μg/L)
Digestion	9	24	--
XAD-8	9(100)	24(100)	<1
Sep-Pac C_{18}	8(88)	24(100)	<1
XAD-8/AC	3(29)	9(39)	8

These results indicate that the XAD-8 method did not alter SeO_3^{2-} or SeO_4^{2-} concentrations. The Sep-Pac C_{18} and XAD-8/AC methods did alter SeO_3^{2-} and SeO_4^{2-} concentrations. A 1-μg/L decrease in SeO_3^{2-} in the Sep-Pac C_{18} effluent was interpreted as a 1-μg/L increase in SeO_4^{2-} because the sum of SeO_3^{2-} and SeO_4^{2-} was not changed. The decrease of 6 μg/L of SeO_3^{2-} and 9 μg/L of SeO_4^{2-} in the XAD-8/AC effluent was not measured in the column containing only XAD-8 resin, which indicates that the activated charcoal was responsible for the Se loss. These SeO_3^{2-} and SeO_4^{2-} losses most likely resulted from diffusion of Se into the pores of the activated charcoal. Selenium detected in the column eluate was probably inorganic Se diffusing back into the main flow paths of the charcoal matrix, and was erroneously interpreted as hydrophobic-organic Se.

Retention of Organic Selenite and Selenate Complexes

A comparison between the calculated and measured Se species (XAD-8 method) of three solutions containing hydrophobic-organic matter spiked with SeO_3^{2-} and SeO_4^{2-} is shown in table 3. Increased concentrations of hydrophobic-organic Se were not measured when the solutions containing hydrophobic-organic matter were spiked with Se. Note that SeO_4^{2-} was not detected in solution B, and that the hydrophobic-organic selenium in solution B equalled the calculated concentration. Also, the concentration of SeO_4^{2-} in solution C equalled the calculated concentration. Therefore, the difference between the measured and calculated SeO_4^{2-} concentrations in solution B probably is due to analytical error and did not reflect removal of the 2 µg/L of SeO_4^{2-} by formation of organic complexes. The absence of the hydrogen-bonded organic complexes between H_2SeO_3, $HSeO_4^{1-}$ and hydrophobic-organic matter indicates that these complexes are not present, and the low pH used in the speciation procedure probably destroys more complexes than it forms (J.A. Leenheer, U.S. Geological Survey, written commun., 1988). Therefore, this mechanism seems to be insignificant and does not adversely affect the measurement of Se species.

Table 3. *Results from the XAD-8 method speciation of solutions containing isolated hydrophobic-organic matter spiked with selenite and selenate*

[Concentrations in micrograms per liter (µg/L)]

Solution	Calculated Se in solution: Selenite	Selenate	Organic selenium	Total selenium
A	5	<1	2	7
B	14	2	2	18
C	0	5	2	7

Solution	Results from XAD-8 speciation: Selenite	Selenate	Organic selenium	Total selenium
A	4	<1	2	6
B	14	<1	2	16
C	0	5	2	7

Determination of Selenium Species in Saturation Extracts of Soils

The speciation results from the four methods used to analyze saturation extracts from the 0- to 30-cm depth samples at sites 1, 2, and 3 are shown in table 4. Results were similar for samples from sites 1 and 2 with the digestion, XAD-8, and Sep-Pac C_{18} methods, but not with the XAD-8/AC method. All four speciation methods produced different results for the sample from site 3.

Total Se (640 µg/L) and the sum of SeO_3^{2-} and SeO_4^{2-} (640 µg/L) determined by the digestion method for the site 2 sample do not detect the presence of organic Se when the difference between the two digestion method analyses are calculated. The magnitude of analytical error associated with the determination of total Se and the sum of SeO_3^{2-} and SeO_4^{2-} by using the digestion method on the site 2 sample was probably greater than the magnitude of the organic Se concentration in the sample. Isolation of hydrophobic-organic matter with the XAD-8 and Sep-Pac C_{18} methods did detect organic Se in the site 2 sample at a concentration that was orders of magnitude smaller than the sum of SeO_3^{2-} and SeO_4^{2-}.

Reduced detection of inorganic Se species by the digestion method were measured for samples from site 1 (less than 1 µg/L SeO_3^{2-}) and site 3 (less than 1 µg/L SeO_4^{2-}). The presence of hydrophobic-organic matter in the saturation extract samples (for example, humic

Table 4. *Comparison of four methods to determine dissolved selenite, selenate, and organic selenium in three saturation extracts of surface soils (0 to 30 cm)*

[All selenium concentrations are in micrograms per liter]

Method	DOC removed with column (mg/L)	Selenite	Selenate	Organic selenium	Sum of selenium species
		Site 1			
	53 mg/L of DOC; 7 µg/L of total selenium				
Digestion	--	<1	5	2	7
XAD-8	28	2	4	1	7
Sep-Pac C_{18}	25	1	4	2	7
XAD-8/AC	41	1	2	3	6
		Site 2			
	69 mg/L of DOC; 640 µg/L of total selenium				
Digestion	--	3	640	<1	643
XAD-8	44	4	620	2	626
Sep-Pac C_{18}	37	3	620	3	626
XAD-8/AC	60	3	590	39	632
		Site 3			
	93 mg/L of DOC; 9 µg/L of total selenium				
Digestion	--	<1	<1	9	9
XAD-8	48	<1	3	4	7
Sep-Pac C_{18}	33	<1	<1	4	4
XAD-8/AC	66	<1	2	6	8

acids) may have inhibited the formation or the stripping of H_2Se in these samples prior to detection by HGAAS (Roden and Tallman, 1982). Therefore, selenite was not detected in the site 1 sample, and the low SeO_4^{2-} concentration measured for the site 3 sample resulted in an erroneous calculated concentration of 9 µg/L of organic Se.

A concentration of 4 µg/L of hydrophobic-organic Se and negligible concentrations of SeO_3^{2-} (less than 1 µg/L) and SeO_4^{2-} (less than 1 µg/L) were measured in the site 3 sample with the Sep-Pac C_{18} method. As with the digestion method, inhibited Se detection during the SeO_4^{2-} analysis on the site 3 sample produced erroneous speciation results. The sum of Se species determined with the Sep-Pac C_{18} method (4 µg/L) was lower than the total concentration of soluble Se (9 µg/L). The XAD-8 method seemed to remove this interference by adsorbing 15 µg/L more DOC from the sample than the Sep-Pac C_{18} method and measuring 3 µg/L more SeO_4^{2-}. The higher sum of Se species from the XAD-8 method (7 µg/L) was still lower than the 9 µg/L of total Se.

The average carbon-adsorption efficiency calculated for the XAD-8 method (55±14 percent of the DOC removed from soil saturation extract samples; 11 analyses) was greater than the average carbon-adsorption efficiency calculated for the Sep-Pac C_{18} method (49±19 percent of the DOC removed from soil saturation extract samples; 10 analyses). A larger quantity of DOC was removed from the samples by the XAD-8 method than by the Sep-Pac C_{18} method, however, this did not necessarily result in a larger quantity of isolated hydrophobic-organic Se.

The XAD-8/AC method had the largest average carbon-adsorption efficiency (75±8 percent of the DOC removed from soil saturation extract samples; four analyses). This method eluted larger quantities of Se (calculated as hydrophobic-organic Se) than the other chromatography methods. Larger Se concentrations in XAD-8/AC eluates corresponded to lower effluent concentrations of SeO_3^{2-} and SeO_4^{2-}, when compared to the XAD-8 method. For example, 39 µg/L of Se was eluted by the XAD-8/AC method during the analysis of the site 2 sample (37 µg/L more than the XAD-8 method). The SeO_4^{2-} measured in the XAD-8/AC effluent (590 µg/L) was 30 µg/L less than the SeO_4^{2-} concentration in the XAD-8 effluent (620 µg/L). These measurements are consistent with retention of inorganic Se by the activated charcoal (table 2) and are not attributed to more isolated hydrophobic-organic Se.

The fractionation of hydrophobic-organic Se in the XAD-8 method eluates of the three samples (0- to 30-cm depth, sites 1, 2, and 3) are reported in table 5. Most DOC (on the average, about 60 percent) and Se (about 100 percent) eluted from the XAD-8 resin columns were in the NaOH elutions. Both water and CH_3OH elutions contained negligible Se (less than 1 µg/L), and about 40 percent of the DOC adsorbed by the XAD-8 method. Therefore, the hydrophobic-organic Se isolated by the XAD-8 method was associated with the humic acid fraction of the dissolved-organic matter in the samples (Thurman and Malcolm, 1979).

FIELD APPLICATION OF XAD-8 SPECIATION RESULTS ON SOIL SATURATION EXTRACTS

The XAD-8 method was considered the most successful of the four methods compared for Se speciation analyses for the following reasons: (1) XAD-8 resin did not affect SeO_3^{2-} or SeO_4^{2-} concentrations (SeO_3^{2-} and SeO_4^{2-} concentrations were not altered by complexation with hydrophobic-organic matter and subsequent removal of complexes by the XAD-8 resin); (2) XAD-8 resin removed hydrophobic dissolved-organic matter from soil saturation extracts, which eliminated interferences during analyses for Se by HGAAS; and (3) the XAD-8 resin removed about 55 percent of the DOC, which contained some Se from soil saturation extracts.

Results from using the XAD-8 resin method to speciate the saturation extracts of the soil profile samples from sites 1 and 2 demonstrate that SeO_4^{2-} was the dominant Se species, and SeO_3^{2-} and

Table 5. *Concentrations of selenium and dissolved-organic carbon in XAD-8 column eluates*

[Number in parenthesis is the amount of DOC in the eluate divided by the total amount of DOC removed with the XAD-8 method, expressed as a percentage]

	Sodium hydroxide		Deionized water		Methanol		Sum	
Site	Se (µg/L)	DOC (mg/L)	Se (µg/L)	DOC (mg/L)	Se (µg/L)	DOC[1] (mg/L)	Se (µg/L)	DOC (mg/L)
1	1	17 (61)	<1	2 (7)	<1	9 (32)	1	28 (100)
2	2	29 (66)	<1	2 (4)	<1	13 (30)	2	44 (100)
3	4	24 (50)	<1	2 (4)	<1	22 (46)	4	48 (100)

[1] The CH_3OH was assumed to elute the adsorbed DOC remaining after the NaOH and water eluates. The concentration of desorbed carbon in the CH_3OH was therefore determined by the difference between the concentration of carbon adsorbed with the XAD-8 column and the combined concentration of carbon eluted with NaOH and deionized water.

hydrophobic-organic Se concentrations were uniformly low at all depths. Selenite concentrations with decreasing depth (0 to 120 cm) from site 1 were 2, 1, less than 1, and less than 1 µg/L, and with decreasing depth (0 to 120 cm) at site 2 were 4, 1, less than 1, and 1 µg/L. Hydrophobic-organic Se concentrations with decreasing depth (0 to 120 cm) from site 1 were 1, 1, less than 1, and 2 µg/L, and with decreasing depth (0 to 120 cm) at site 2 were 2, 1, less than 1, and less than 1 µg/L. Selenate was the dominant Se species; at least 98 percent of the soluble Se (soluble Se in table 1) in the soil saturation extracts was SeO_4^{2-}.

The distribution of SeO_4^{2-} in soil saturation extracts from the soil profiles at sites 1 and 2 were almost inversely distributed and are shown in figure 2.

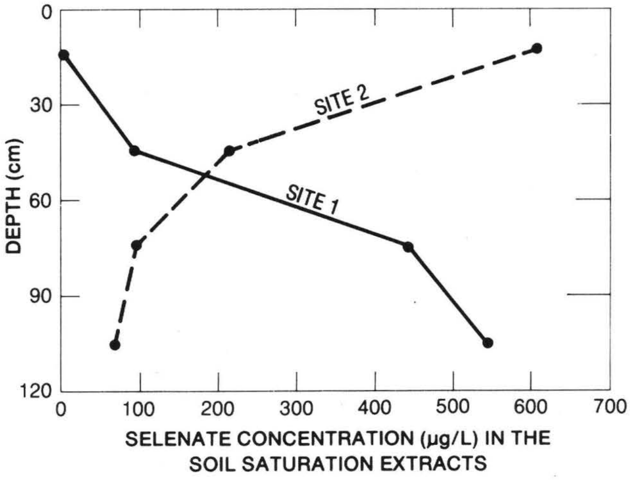

FIGURE 2. - Selenate concentrations from the XAD-8 method speciation of soil saturation extracts of 0- to 120-cm depth soil profiles from sampling sites 1 and 2.

The greatest SeO_4^{2-} concentrations were in the extract of the 0- to 30-cm depth of surface soil from site 2 (620 µg/L) and 90- to 120-cm depth of soil from site 1 (550 µg/L). The smallest SeO_4^{2-} concentrations were in the extract of the 90- to 120-cm depth of soil from the site 2 profile (72 µg/L) and the 0- to 30-cm of surface soil at site 1 (4 µg/L). The SeO_4^{2-} distributions almost parallel the salinity distributions measured on the same soil saturation extracts (table 1).

Increasing salinity with depth at site 1 implies downward leaching of salts from the upper soil horizons by less saline irrigation water. This site has been irrigated for 40 years and drained since 1980. Decreasing salinity with depth at site 2 is consistent with evaporation from a shallow water table in arid environments (Bohn and others, 1979). Site 2 may represent unirrigated soil conditions; the water table at this site is currently at a depth of about 2 m, but may have been closer to the soil surface in the past (U.S. Bureau of Reclamation, 1953).

The salinity and SeO_4^{2-} concentrations in the soil saturation extracts from sites 1 and 2 support the hypothesis that attributes high soluble Se and salinity concentrations in shallow ground water and soil in the western San Joaquin Valley to evaporation from a shallow water table (Fujii and others, 1987; Deverel and Fujii, 1988). The downward displacement of SeO_4^{2-} in the soil profile at site 1 is from leaching of Se salts by less saline irrigation water low in Se concentration. The predominance and mobility of the SeO_4^{2-} is consistent with this hypothesis because SeO_4^{2-} is mobile and thermodynamically predicted in alkaline-oxidized environments (Geering and others, 1968).

IMPROVING THE XAD-8 METHOD

Maximum adsorption and recovery of hydrophobic-organic matter with XAD-8 resin is achieved with optimum column dimensions, sample flow rates, and sample volumes. Optimizing these details for the XAD-8 method will ensure maximum isolation of hydrophobic-organic Se.

The XAD-8 columns used in this study have a height to diameter ratio of 4:1, which is less than the maximum limit recommended by researchers for the greatest adsorption of organic matter, less than 14:1 (Leenheer and Huffman, 1976; Mantoura and Riley, 1975). Thurman and others (1978) suggests flow rates of 10 bed volumes per hour or less for adsorption and desorption reactions to approach equilibrium. Reducing the rate of the vacuum extractor (from 2.5 to 0.5 mL/min) could improve the quantity of dissolved-organic matter isolated from the soil saturation extracts by ensuring that the reactions are complete.

Smaller sample volumes or larger XAD-8 resin columns will increase the resin quantity to sample volume ratio and possibly increase the quantity of DOC adsorbed with the XAD-8 method (Thurman and Malcolm, 1979). In this study, the magnitude of the sample volume was determined by requirements for the analysis of SeO_3^{2-} and the sum of SeO_3^{2-} and SeO_4^{2-} by HGAAS and were fixed. Increasing the resin quantity to sample volume ratio by using larger columns with greater bed volumes would require larger volumes of eluate to quantitatively recover adsorbed organic matter. The larger volume of eluate would dilute the hydrophobic-organic Se concentration, and reduce the detection limit of the method. Therefore the ratio of resin quantity to sample volume was constrained by the volume requirements for Se determination by HGAAS. Decreasing the volume of sample used for the HGAAS analysis will allow smaller sample volumes to be treated with the XAD-8 method. This will then increase the resin quantity to sample volume ratio and the quantity of DOC adsorbed by the XAD-8 method.

SUMMARY AND CONCLUSIONS

This study found a column of XAD-8 resin to be the most reliable method of speciating Se in soil saturation extracts when compared to Sep-Pac C_{18} cartridges, a column combining XAD-8 resin and activated charcoal (XAD-8/AC), and a chemical digestion method. This conclusion was based on the following three results:

(1) The XAD-8 method had no effect on standard solutions containing SeO_4^{2-} and SeO_3^{2-}, whereas, the XAD-8/AC method altered the standard solutions making it an unreliable method to determine Se species.

(2) Selenate and SeO_3^{2-} in acidic solutions (pH less than 2) containing hydrophobic-organic matter were not removed from solution during isolation of dissolved-organic matter with the XAD-8 method. This indicated that organic SeO_4^{2-} and SeO_3^{2-} complexes are not removed by isolation of a part of the dissolved-organic matter during Se speciation with XAD-8 resin.

(3) Hydrophobic-organic matter in some undigested soil saturation extracts seems to interfere with Se analyses by hydride-generation atomic-absorption spectrometry. This interference caused unreliable speciation results when using the chemical digestion method. Sample treatment with XAD-8, but not Sep-Pac C_{18}, prior to Se analysis removed this interference from all samples tested.

The XAD-8, Sep-Pac C_{18}, and XAD-8/AC methods removed on the average 55, 49, and 75 percent of the DOC in soil saturation extracts, respectively. The hydrophobic-organic matter associated with the DOC isolated by the XAD-8 and Sep-Pac C_{18} methods contained measurable quantities of Se (hydrophobic-organic Se) and represented a minimal estimation of the organic Se in the extracts.

Speciation of saturation extracts from selected San Joaquin Valley soils with the XAD-8 method showed that soluble Se was present in the SeO_3^{2-}, SeO_4^{2-}, and hydrophobic-organic Se forms. The isolated hydrophobic-organic Se (less than 1 to 4 µg/L concentration range) was associated with the humic acid part of the dissolved-organic carbon in the saturation extracts (representing a small fraction of the total organic carbon in the soils). Selenite concentrations in the extracts also were low (less than 1 to 4 µg/L concentration range), and 98 percent of the soluble Se was SeO_4^{2-} (4 to 640 µg/L concentration range). The depth distribution of Se concentrations in the saturation extracts (representing a small fraction of the total Se in the soil) support a hypothesis that states that the distribution of soluble Se and salinity in soils are mainly the result of evaporation from a shallow water table and leaching by irrigation water low in Se and salinity.

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