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DETERMINATION OF SELENIUM LEACHING USING BATCH TESTS AND
COLUMN EXPERIMENTS

A Thesis

Presented to

The Department of Geology

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Evangelos Kakouros

May 2001

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ABSTRACT

DETERMINATION OF SELENIUM LEACHING USING BATCH TESTS AND COLUMN EXPERIMENTS

By Evangelos Kakouros

Selenium is a biologically essential element, but can become a potent toxin even at low concentrations. In the vicinity of Stewart Lake and Jensen, located in the Middle Green River Basin, Utah, selenium has been mobilized by irrigation and has accumulated in Stewart Lake Waterfowl Management Area, resulting in problems for the wildlife. Batch tests in soil and weathered Mancos Shale samples indicated that selenium occurs primarily as selenium associated with organic matter and elemental selenium. Column experiments indicated that selenium could be leached rapidly from the soil horizon below the root zone, where a significant quantity of soluble selenium was present. The amount that could be leached from the surface soil horizon and the weathered shale was considerably smaller for the same leaching period, but the leaching rate remained constant. The leaching rate increased when irradiation limited microbial activity, indicating its importance on selenium mobility.

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TABLE OF CONTENTS

	Page
INTRODUCTION.....	1
Background	1
Purpose of the Study	4
Selenium Geochemistry	4
METHODS.....	11
Field Sampling	11
Batch Tests	14
Column Experiments.....	20
RESULTS.....	28
Field Sampling	28
Water Samples.....	28
Soil and Mancos Shale Samples.....	33
Batch Tests	40
Column Experiments.....	48
DISCUSSION	67
Field Sampling	67
Water Samples.....	67
Soil and Mancos Shale Samples.....	70
Batch Tests	78

Selenium Forms in the Core Samples	78
Effect of Grinding and Drying on the Se Distribution	79
Distribution of the Se Forms in the Soil Samples	80
Column Experiments.....	82
Electrical Conductance and pH of the Effluent, Applied Water Solutions..	82
Selenium in the Effluent.....	85
Non-Irradiated Samples	85
Irradiated Samples	90
Forms of Se Leaching and Application to Natural Conditions	92
Column Experiments and Batch Tests	95
CONCLUSION	97
REFERENCES CITED	99
APPENDIX A: SORPTION PROCESSES	105
APPENDIX B: CORE AND SEDIMENT ANALYTICAL METHODS.....	108
I. Sequential Extraction Technique	108
II. Wet Digestion of Samples for Total Selenium Analysis	110

LIST OF ILLUSTRATIONS

Figure	Page
1. Location of Stewart Lake and Jensen Study Area and Sampling Points	3
2. Eh-pH Diagram for Part of the System Se-O-H.....	7
3. The Effect of Redox on Se Species in Solution at pH 7	8
4. Location of Core and Water Samples Relative to Irrigated Areas.....	12
5. Selenium Related to TDS, Chloride and Sulfate.....	32
6. Normalized Selenium and Selected Elements in Borehole JM-17	36
7. Normalized Selenium and Selected Elements in Borehole JM-16	38
8. Normalized Selenium and Selected Elements in Borehole JM-11	39
9. Se Extracts and Total Extracted Selenium as a Percentage of Total Se.....	42
10. Vertical Distribution of the Different Forms of Selenium	46
11. Electrical Conductance and pH of the Effluent from JM-17	50
12. Electrical Conductance and pH of the Effluent from Surface Soil from JM-16 ..	51
13. Electrical Conductance and pH of the Effluent from Deeper Soil from JM-16...	52
14. Br Concentration in the Effluent from JM-17	53
15. Br Concentration in the Effluent from Surface Soil from JM-16	54
16. Br Concentration in the Effluent from Deeper Soil from JM-16	55
17. Se Concentration in the Effluent from JM-17	56
18. Se Concentration in the Effluent from Surface Soil from JM-16	58
19. Se Concentration in the Effluent from Deeper Soil from JM-16	59

20.	Se Production and Cumulative Production from JM-17	61
21.	Se Production and Cumulative Production from Surface Soil from JM-16.....	63
22.	Se Production and Cumulative Production from Deeper Soil from JM-16	64
23.	Se Production Rate from JM-17.....	65
24.	Se Production Rate from JM-16.....	66
25.	Mobility of Se in the Surface Soil and the Soil Below the Surficial Root Zone..	96

LIST OF TABLES

Table	Page
1. Location of Sampling Sites near Jensen, Utah, 05/25-06/06/1999	13
2. Location of Sampling Sites near Jensen, Utah, 09/06-09/12/1999	13
3. Reagents Used and Se Fractions Obtained from the Sequential Extraction	15
4. Sampling Information for the Batch Test Samples	19
5. Composition of Water Applied to the Columns.....	21
6. Field Water Quality Parameters Obtained during 05/25-06/06/1999	29
7. Field Water Quality Parameters Obtained during 09/06-09/12/1999	30
8. Selected Constituents from Jensen-Stewart Lake Water Analysis.....	31
9. Selected Constituents from Jensen-Stewart Lake Soil Analysis.....	34
10. Concentrations and Percentages of the Selenium Forms	41
11. Location, Material and Physical Properties of the Columns.....	49
12. Pore Volume, Flow Rate and Residence Time for Columns	60
13. Trend Lines of Se versus TDS, SO_4^{2-} and Cl^- for the Water Samples	70
14. R^2 Values for Correlation between Se and other Elements for All the Samples .	72
15. R^2 and $\rho(x, y)$ Values for Se and other Elements at Individual Boreholes	73
16. $\rho(x, y)$ Values for Organic C and Selected Elements for Shale and Soil	75
17. Se Concentration in the Effluent.....	86
18. Se Production	88

19.	Se Production Rates	89
20.	Minimum Time and Water Quantity Required for the Se Leaching.....	94

INTRODUCTION

Background

Selenium (Se) is an essential element for humans, livestock, waterfowl, plants and certain bacteria, but it can become a potent toxin even at low concentrations. The present U.S. Environmental Protection Agency (USEPA) drinking water standard for selenium is 50 µg/L. The chronic water-quality criterion that is protective of wildlife and aquatic life is 5 µg/L (Kharaka et al., 2000). The properties of selenium make the boundary between toxicity and deficiency narrow, with both phenomena common around the globe (McNeal and Balistrieri, 1989).

The toxic effects of Se were not recognized until 1931 when researchers identified in the northern Great Plains what was known from mid-nineteenth century as “alkali disease” to be chronic Se toxicosis (selenosis), characterized by hair and hoof loss and poor growth and reproduction in livestock. Marco Polo described these symptoms during his travels in western China in the thirteenth century, and he associated the problem with the ingestion of certain plants. In 1560 Father Pedro Simon described the same symptoms in Colombia (Mayland, 1994). In 1983 incidences of mortality, abnormalities (64% rate of embryonic deformity and mortality) and reproductive failure in waterfowl attributed to irrigation drainage water with high concentrations of selenium were discovered at the Kesterson National Wildlife Refuge in the western San Joaquin Valley, California (Ohlendorf et al., 1986). A major Federal program was initiated to determine

whether high concentrations of selenium existed at other irrigation projects, national wildlife refuges, or other Federal wetland areas in the western United States.

Among these projects is the study area of Stewart Lake and Jensen, located in the middle Green River Basin, Utah (Fig. 1). The study area is agricultural, irrigated on a sustained basis for more than 60 years. The irrigation season starts in mid-April and ends in mid-October, the exact dates depending on precipitation. Since 1979 the majority of the irrigation water has been provided from Red Fleet Reservoir via Brush Creek (Stephens et al., 1992). The climate is arid to semi-arid with average annual precipitation 19 cm (7.5 in) and potential evapotranspiration 170 cm (68 in) (Stephens et al., 1992).

The Cretaceous Mancos Shale is the most ubiquitous formation in the Jensen area where it is overlain by Quaternary alluvium and terrace deposits close to Green River and area streams (Untermann and Untermann, 1965; Carrara, 1980; Hintze, 1993). The Mancos Shale can be 5,000 feet thick and is pyritic and organic rich, with high Se content (Hintze, 1993). High selenium concentrations have been mobilized by irrigation and have accumulated in Stewart Lake Waterfowl Management Area, resulting in problems for the wildlife. For this area, one detailed study of selenium occurrence has been performed; this previous study mainly focused on biological observations and the contamination of biota with selenium and selected other elements (Stephens et al., 1992).

This investigation is part of a broader research into the occurrence of selenium and its relationship with sulfur in this area conducted by the U.S. Geological Survey and the Bureau of Reclamation (Kharaka et al., 2001). This study employed sequential extractions with batch tests and column experiments on core samples. In addition, the

Figure 1. Location of Stewart Lake and Jensen study area and sampling points (modified from the U.S. Geological Survey 7.5-minute maps: Dinosaur Quarry, Jensen, Naples and Rasmussen Hollow).

results from the analyses of the water and core samples for total selenium and selected other constituents, performed by U.S. Geological Survey Menlo Park, California and Denver, Colorado, were used.

Purpose of the Study

The purpose of this study was to obtain information on the selenium geochemistry and leaching rates in the research area. The purpose of the batch tests was to quantify the various forms in which selenium occurs in the soil and the Mancos Shale (weathered and intact) of the study area. These forms include soluble selenium, adsorbed selenium, elemental selenium and selenium associated with organic matter, which were sequentially extracted from the core samples. Total selenium analysis with wet digestion provided the concentration of Se in the samples, so that the degree of selenium recovery from the sequential extractions was determined. The purpose of the column experiments was to determine the rate and extent of selenium leaching from the soil and the major factors that have an effect on this leaching.

Selenium Geochemistry

Selenium occurs in nature in four oxidation states as elemental selenium (Se^0), selenide (Se^{-2}), selenite (Se^{+4}) and selenate (Se^{+6}); the occurring organic selenium is also in one of those oxidation states even if covalently bonded. It is known to have volcanic, magmatic and hydrothermal sources (Trelease and Beath, 1949; Coleman and Delevaux, 1957). Selenium enrichment of geologic material occurred during the Cretaceous Period

and was related to volcanic emission of selenium-rich ash and gases (Butler et al., 1996). The environment of the Cretaceous sea bottom was reducing and organic rich so it favored the precipitation of sulfide minerals, such as pyrite (FeS_2) or chalcopyrite (CuFeS_2). Selenium is isomorphous with sulfur and so can substitute for sulfur in the crystalline structure of the sulfide minerals in Cretaceous shale.

The average concentration of selenium in the crust is 0.05 ppm, in seawater is 0.0002 ppm and in shale is 0.6 ppm (Krauskopf and Bird, 1995). The geometric mean concentration of selenium in Western soils is 0.23 ppm (Butler et al., 1996). Selenium is present as a trace element in the Cretaceous Mancos Shale, which is known as seleniferous. In the Uncompahgre Project area of Colorado, Butler et al. (1996) observed Se concentrations between 0.1 and 8.6 ppm (geometric mean 1.4 ppm) in 142 soil samples. The concentration of selenium from the present study has been found to be up to 3.0 ppm in shale and soil samples (Kharaka et al., 2001). Stephens et al. (1992) have found selenium concentrations up to 4.0 ppm in Mancos Shale.

When the seleniferous shale is exposed to weathering, selenium is mobilized by oxidation because the solubility of Se minerals is higher with increased valence. Sorption also decreases as selenium valence increases, thus the overall effect of increased valence is increased mobility in the oxidized environment. Selenium can be viewed as cycling geochemically between the species in the different oxidation states, depending on external biogeochemical constraints. Selenium or metallic and organically bound selenides in parent rocks weather to selenite under acidic oxidizing conditions and to selenate under neutral and alkaline oxidizing conditions (Presser et al., 1990). The

concentration of the aqueous selenium species after weathering and oxidation depends on the pH and the redox potential of the geochemical environment, the solubility of the Se species, the presence of adsorbing minerals, the existence and concentration of other competitive anions, the vegetative uptake and transformation, and the microbial activity.

The redox potential and the pH control the Se speciation in solution (Figs. 2 and 3). Selenate (SeO_4^{2-}) is the major species in solution at high redox conditions, for soils in arid regions. In the medium redox range, for soils in humid regions, either SeO_3^{2-} or HSeO_3^- is predominant depending on the pH. At low redox conditions, for soils in wetlands, HSe^- is the major species in soil solution. Hydrogen selenide (H_2Se) contributes significantly to Se in solution only in strongly acid soils (Elrashidi et al., 1987). Under moderate to highly oxidizing conditions, commonly occurring in irrigated arid to semi-arid areas, sorption mechanisms can control distribution of Se between solid surfaces and the solution phase (Elrashidi et al., 1987). The low concentration of Se in acid or neutral soil solutions has been attributed to its presence as selenite in combination with ferric iron; selenite ions have more affinity for iron oxyhydroxides than for clays and oxides of other metals (e.g., Mn). Solubility of ferric selenite ($\text{Fe}_2(\text{SeO}_3)_3$) is very low under conditions of variable ionic strength (Chukhlantsev and Tomashevsky, 1956) and basic ferric selenite ($\text{Fe}_2(\text{OH})_4\text{SeO}_3$) is even less soluble (Williams and Byers, 1936). Selenite concentrations may be further lowered because it forms strong adsorption complexes with ferric oxides (Geering et al., 1968). At low redox conditions (e.g., anaerobic conditions at the bottom of ponds rich in organic material), the less soluble elemental Se or metal selenide minerals (e.g., FeSe , Cu_2Se) may control Se distribution.

It is also found that the oxidation of selenite to selenate occurs at a higher Eh than the sulfide to sulfate oxidation (Masscheleyn et al., 1990).

Figure 2. Eh-pH diagram for part of the system Se-O-H at 25° C, P = 1 bar, and activity of dissolved Se = 10^{-6} showing stability fields of selenium species (modified from Hitchon et al., 1999).

Figure 3. The effect of redox on Se species in solution at pH 7 (modified from Elrashidi et al., 1987).

In addition to the redox conditions and the solubility, sorption-desorption processes, which are also dependent on speciation, affect selenium mobility (details in Appendix A). Selenite adsorbs much more strongly than selenate, as selenate adsorbs only weakly on clays, iron oxyhydroxides and other soil components at neutral pH (Neal and Sposito, 1989). In addition, competitive effects with sulfate (which are much more

competitive to selenate than to selenite) suppress this limited sorption capability, so that the adsorption is not capable of retarding selenate migration in the sulfate-rich groundwater commonly associated with elevated Se concentrations. This difference in sorption affinities can explain why the selenate/selenite ratios are often higher in groundwater than in surface water; the low selenite concentration in the groundwater is due to a stronger sorption affinity in the aquifer. Therefore, the conditions that favor the mobility of selenium with respect to adsorption are alkaline pH, high selenium concentrations, oxidizing conditions and high concentrations of additional anions that can be strongly adsorbed.

In addition to the inorganic forms of Se, nonvolatile organic selenides such as selenoamino acids (e.g., dimethylselenonium, an organic decomposition product) and volatile methylated forms of selenides, such as dimethylselenide (CH_3SeCH_3), dimethyl selenyl sulfide ($\text{CH}_3\text{SeSCH}_3$), and dimethyl diselenide ($\text{CH}_3\text{SeSeCH}_3$), can occur in surface water and in groundwater. Organisms can take up inorganic Se and reduce it in a variety of organoselenide compounds. The uptake of selenium by plants differs by species, the soil pH, the soil texture and the soil organic matter. Seleniferous plants can convert the inorganic selenium (as Se^0 , SeO_3^{-2} or SeO_4^{-2}) into organic selenium, such as selenomethionine, selenocysteine and selenocystine (Frankenberger and Karlson, 1994). In addition, there is an association between Se sorption and humic substances (Chasteen, 1998). Bacteria and fungi can volatilize Se^0 , SeO_3^{-2} , SeO_4^{-2} and organoselenides into mobile methylated derivatives, such as dimethylselenide and dimethyl diselenide (Frankenberger and Karlson, 1994). Oxidized forms can be reduced to less mobile forms

(Se^0 and SeO_3^{2-}) by anaerobic or facultative bacteria (Oremland et al., 1989).

Autotrophic bacteria can oxidize the reduced selenium species and form mobile selenium species (Sarathchandra and Watkinson, 1981).

METHODS

Field Sampling

Undisturbed cores that were about 13 cm (5 in) in diameter and about 75 cm (2.5 ft) long were obtained from boreholes near Stewart Lake-Vernal, Utah (Fig. 1). Drilling was performed with a hollow-stem auger and a split-barrel sampler equipped with a clear PVC tube as a liner. No drilling fluids were used. Field conditions (pH, Eh, water content, hydraulic properties, microbial activity) were preserved in the cores by sealing the cores in the PVC tubes directly after drilling and storing them in the dark and at a temperature of about 4 °C (Cutter, 1985; Zhang and Moore, 1998). In addition, cores that were about 6 cm (2 3/8 in) in diameter were obtained using a smaller auger when hard material prohibited the use of the larger auger. The smaller cores were preserved in core boxes under the same conditions as the cores in the PVC tubes.

Core samples consisted of soil and/or Mancos Shale obtained from above and below the water table. They were taken from both irrigated and non-irrigated areas (Fig. 4), so that a comparison was possible. Core and water samples were spatially distributed to represent the entire area of study. Water samples were obtained from all the boreholes where cores were taken. In addition, water samples were obtained from existing wells, from surface water bodies, and from study wells from which cores had not been recovered. Water sampling was conducted at the same sites in two phases, prior to (Table 1) and at the end (Table 2) of the irrigation season. The field parameters of electrical conductance (E.C.), dissolved oxygen (D.O.), temperature (T), redox (Eh) and

Figure 4. Location of core and water samples relative to irrigated areas (modified from the U.S. Geological Survey 7.5-minute maps: Dinosaur Quarry, Jensen, Naples and Rasmussen Hollow).

Table 1. Location of sampling sites near Jensen, Utah, 05/25-06/06/1999.

Well I.D. or surface water site	Water sample	Latitude	Longitude	Elevation m above MSL+	Core
Groundwater					
E-1	99SL-107	40° 21' 26"	109° 20' 49"	1440	NO
W-3	99SL-106	40° 20' 56"	109° 22' 03"	1439	NO
K-6	99SL-101	40° 21' 34"	109° 21' 42"	1442	NO
99JM-11	99SL-104	40° 21' 31"	109° 21' 51"	1442	YES
99JM-12	99SL-103	40° 21' 31"	109° 21' 50.5"	1442	YES
99JM-13	99SL-105	40° 21' 46"	109° 22' 44"	1448	YES
99JM-14	99SL-114	40° 22' 22"	109° 23' 05"	1474	YES
99JM-15	99SL-110	40° 21' 28"	109° 22' 27"	1443	YES
99JM-16	99SL-111	40° 22' 10"	109° 21' 50"	1455	YES
99JM-17	99SL-113	40° 21' 43.5"	109° 22' 53"	1457	YES
99JM-18	99SL-115	40° 24' 25"	109° 20' 28"	1472	NO
Snow well	99SL-102	40° 21' 29"	109° 22' 20"	1442	NO
Surface water					
Green River	99SL-108	40° 21' 05"	109° 20' 57"	1439	-
Ashley Creek	99SL-109	40° 21' 32"	109° 23' 11.5"	1445	-
# Brush Creek	99SL-112	40° 29' 39"	109° 23' 04"	1561	-

Table 2. Location of sampling sites near Jensen, Utah, 09/06-09/12/1999.

Well I.D. or surface water site	Water sample	Latitude	Longitude	Elevation m above MSL+
Groundwater				
E-1	99SL-211	40° 21' 26"	109° 20' 49"	1440
W-3	99SL-210	40° 20' 56"	109° 22' 03"	1439
K-6	99SL-207	40° 21' 34"	109° 21' 42"	1442
99JM-11	99SL-206	40° 21' 31"	109° 21' 51"	1442
99JM-12	99SL-205	40° 21' 31"	109° 21' 50.5"	1442
99JM-13	99SL-204	40° 21' 46"	109° 22' 44"	1448
99JM-14	99SL-209	40° 22' 22"	109° 23' 05"	1474
99JM-15	99SL-201	40° 21' 28"	109° 22' 27"	1443
99JM-16	99SL-208	40° 22' 10"	109° 21' 50"	1455
99JM-17	99SL-203	40° 21' 43.5"	109° 22' 53"	1457
99JM-18	99SL-212	40° 24' 25"	109° 20' 28"	1472
Snow well	99SL-202	40° 21' 29"	109° 22' 20"	1442
*well 5500S/9000E	99SL-218	40° 22' 38"	109° 21' 16"	1493
**spring in canyon	99SL-217	40° 25' 03"	109° 26' 01"	NM
***seep	99SL-219	40° 25' 22"	109° 27' 05"	NM
Surface water				
Green River	99SL-215	40° 21' 05"	109° 20' 57"	1439
Ashley Creek	99SL-216	40° 21' 32"	109° 23' 11.5"	1445
# Brush Creek	99SL-213	40° 29' 39"	109° 23' 04"	1561
canal by 99JM-18	99SL-214	40° 24' 16"	109° 20' 35"	1463

+ For surface water, elevation of water surface; for well, elevation of ground at well head.

* close to Burns Canal; possibly is K-7 U.S. Geological Survey well

** not in Figs. 1 and 4, close to sewer ponds, approx. 7 km NW from JM-14

*** not in Figs. 1 and 4, about at Ashley Creek level and approx. 8 km NW from JM-14

not in Figs. 1 and 4, from Brush Creek approx. 15 km N from the Hwy 40 and St. Rd. 149 intersection.

MSL: mean sea level, NM : not measured

Coordinates and elevation determined combining 7.5 min USGS topographic map and GPS site location.

pH were obtained using a flow-through cell. The depth to water (DTW) was measured using a stainless steel measuring tape, and the discharge was measured using a flow meter and data from the USGS gaging stations when available.

Batch Tests

Soluble Se, adsorbed Se, elemental Se and Se associated with organic material were extracted sequentially from batch tests using methods summarized in Table 3, with details in Appendix B. Recovery of Se was adequate, so additional extractions for Se in oxides (easily reducible, amorphous and crystalline fractions) and Se in amorphous aluminosilicates were not necessary. For the determination of Se associated with pyrite, there is a less frequently used sequential extraction method (Velinsky and Cutter, 1990) that follows the elemental Se extraction. Although pyrite (FeS_2) with a similar chemical structure to ferroselite (FeSe_2) is the dominant form of sulfur, pyrite-Se is only a minor fraction of the total Se in soils (Velinsky and Cutter, 1991). The pyrite-Se extraction was not performed because of the ambiguous results of the analysis, the small fraction of pyrite-Se in the soils that are the main focus of this study, the possibility of extracting part of the Se associated with organic matter along with the pyrite-Se, and the probable importance of the Se associated with organic matter (details in Appendix B). Most likely for the reasons mentioned above, the pyrite-Se was not extracted in the detailed sequential extractions of Se from soils and bottom sediments in studies elsewhere by Tokunaga et al. (1991), Zawislanski and Zavarin (1996), and Zhang and Moore (1996).

Table 3. Reagents used and Se fractions obtained from the sequential extraction of the batch tests.

Reagent	Fraction Extracted	References
0.25M KCl	Soluble Se	Fujii et al. (1988), Stephens et al. (1992), Zhang and Moore (1997d).
0.1M K ₂ HPO ₄ solution at pH 8 adjusted with KH ₂ PO ₄	Adsorbed Se	Barrow and Shaw (1979), Balistrieri and Chao (1987), Fujii et al. (1988), Butler et al. (1996). Martens and Suarez (1997).
1M Na ₂ SO ₃ solution at pH 7 adjusted with HCl	Elemental Se	Warren (1968), Velinsky and Cutter (1990).
4-6% NaOCl solution at pH 9.5 adjusted with HCl	Se associated with organic matter	Anderson (1963), Tokunaga et al. (1991), Zhang and Moore (1997c, d).

Twelve samples consisting of soil and weathered and intact Mancos Shale were selected for the batch tests, following the sampling methods of Butler et al. (1996), Goldberg and Glaubig (1988), Neal et al. (1987a, b), Neal and Sposito (1989), and Presser et al. (1990). Samples were taken from the same parts of the cores as the samples used for total Se analysis. Samples were not dried (Cutter, 1985; Zhang and Moore, 1997b) or ground (Butler, 1996; Neal et al., 1987a, b; Neal and Sposito, 1989). Drying and grinding oxidize and volatilize selenium species; these would not only affect selenium speciation and concentration (Fujii et al., 1988), but also the selenium distribution in different fractions, which is controlled by the Se oxidation state (Zhang and Moore, 1997a, b). The results from the batch tests were compared with those from the column experiments, so the geochemical conditions of the samples had to be similar. Drying and grinding would have changed these conditions. In addition, this unaltered

core was much closer to the field conditions and reflected the actual selenium leaching potential.

About 200 g of sample were obtained from the cores for splits, as archival material and for other tests. The water content of the samples was determined by oven drying a weighed split of the sample at 105 °C until a constant weight was obtained. For each batch test, 10 to 15 g of dry sample (equivalent weight based on the water content of a sample split) were used depending on the Se concentration, the heterogeneity of the core, and available equipment. The sample quantity used for Se sequential extractions in previous studies ranged from 1.2 g (Goldberg and Glaubig, 1988) to 40 g (Stephens et al., 1992). The samples were gently disaggregated with a stainless steel spatula just before starting the test to minimize contamination, volatilization and oxidation. At this point the reagent solutions were already made and samples, flasks, filters, etc. were weighed. The mass-to-mass ratio of sample and reagent solution was 1:10 (Stephens et al., 1992), selected based on reagents used (the sample to reagent solution ratios in previous studies ranged from 1:2, Alemi et al., 1991, to 1:25, Neal et al., 1987a), the analytical accuracy and Se detection limit, and the sample quantity.

All the solutions (Table 3) were filtered through a 0.45- μ m membrane filter (Supor®-450, 47 mm in diameter) with a vacuum-filtering unit. The solution and soil mixture was shaken to ensure mixing in previously acid-washed, 250 ml centrifuge bottles, where they remained for a short time period (only during shaking and centrifugation). Use of a swinging arm shaker at a rate of 100-excursions min⁻¹ for 30 min to 2.0 h for each fraction (Appendix B; Fujii et al., 1988; Martens and Suarez, 1997)

was adequate to ensure mixing and to provide sufficient reaction time for each fraction, considering that the samples were disaggregated with a spatula, but not ground. Excessive retention in the containers (Cutter, 1978; Zhang and Moore, 1997b) or vigorous and extensive shaking (Neal et al., 1987a) would change the redox status and, especially extensive shaking, could lead to particle abrasion and the exposure of fresh adsorbing surfaces, thus increasing adsorption considerably. Agitation methods as gentle as possible are more likely to mimic field behavior and to minimize effects associated with the solution/soil ratio, particularly at lower ratios (Barrow and Shaw, 1979). After each extraction (added solution and shaking), the mixture was centrifuged at 1850 to 2500 g relative centrifugal force (RCF) for 30 to 60 min (Fujii et al., 1988). The slurry was retained and the supernatant was filtered through the 0.45- μ m membrane filter (Fujii et al., 1988). Immediately after the filtration, the supernatants were acidified to pH 1 with HCl and were stored at a temperature of 4°C for preservation (Cheam and Agemian, 1980) and Hydride Generation Atomic Absorbance Spectrometry (HGAAS) analysis. Tests were conducted at ambient temperature. Reagent and equipment blanks were analyzed to control possible contamination from reagents, bottles, glassware, etc.

All extracts were analyzed for total Se by HGAAS, following a modified technique of Presser and Barnes (1984). For the batch tests, the high concentration of the reagents prohibited the use of the Inductively Coupled Plasma Mass Spectrometry technique (ICP-MS). HGAAS measures the H_2Se formed when selenite reacts with $NaBH_4$ ($NaBH_4$ was added with an automated system during the HGAAS analysis). The detection limit for Se was 0.03 μ g/L in a 1:1 dilution. According to this technique 2 ml

of 2.5% wt/v $K_2S_2O_8$ was added to 25 ml of the acidified sample; the solution was slowly heated and then was boiled for 10 min to oxidize the organo-seleno compounds to selenate. Ultimately the reduction of selenate to selenite occurred with the addition of 8.25 ml of concentrated HCl and boiling for 46 min. Finally the sample was made up to 50 ml with de-ionized water and analyzed with HGAAS. Three replicates of each sample were analyzed with HGAAS. During the analysis, the atomic absorbance peaks and the standard deviation (SD) as an absolute value and as a percentage (%) of each sample were examined. If the Se concentration in the sample was more than the highest standard (20 $\mu\text{g/L}$), the peak of one of the three replicates was disturbed, or the SD was more than 2.5% (or more than 0.05 $\mu\text{g/L}$ in the samples with low Se concentration), the sample was re-analyzed (8 of the 96 processed samples).

Twelve samples were used for the batch tests (Table 4). Eight of these samples consisted of soil from irrigated (boreholes JM-13, JM-15 and JM-16) and non-irrigated (boreholes JM-14 and JM-17) areas (Table 4, Fig. 4). Four samples consisted of Mancos Shale from a borehole (JM-17) in a non-irrigated area (Table 4, Fig. 4). Two samples, consisting of weathered shale, were splits of the same sample but one of them (JB-99041D) was ground (USGS Laboratory, Denver, CO) and the other (JB-99041) was not, so the selenium recovery of the unground samples and the effects of grinding and drying could be determined. Selected samples from each extraction were spiked with Se^{+4} and Se^{+6} before the final potassium persulfate oxidation and the HCl reduction to determine the recovery of each extract and whether the reagents interfered with the HGAAS.

Table 4. Sampling information for the batch test samples.

Core sample	Depth, (m BLS)	DTW (m BLS)	Material	Batch test sample
99JM-13B 9916	0.12	5.73	Soil-surficial root zone	JB-99070
99JM-13 9918	1.92	5.73	Soil-below surficial root zone	JB-99080
99JM-14 9925	0.06	9.85	Soil-surficial root zone	JB-99100
99JM-15 9921	0.0	1.77	Soil-surficial root zone	JB-99090
99JM-16 9915	0.0	2.13	Soil-surficial root zone	JB-99050D
99JM-16 9914	0.76	2.13	Soil-below surficial root zone	JB-99060D
99JM-17 9910	0.0	-2 (artesian)	Soil-surficial root zone	JB-99011
99JM-17 9909	0.60	-2 (artesian)	Soil-below surficial root zone	JB-99021
99JM-17 9908	2.90	-2 (artesian)	Weathered shale and sand	JB-99031
99JM-17 9907	3.60	-2 (artesian)	Weathered shale	JB-99041
99JM-17 9907D	3.60	-2 (artesian)	Weathered shale	JB-99041D
99JM-17 9901	9.77	-2 (artesian)	Shale (intact)	JB-99110

(m BLS): meters below land surface,

DTW: depth to water (artesian well's hydraulic head was 2 m above land surface)

Recovery of each extract (as determined from the spikes) ranged from 93% to 101%.

The concentration of selenium in the soil and shale samples was found from the values of selenium concentration in the extracts corrected for the reagent blanks and the recovery from the spikes, the known total volume of each extract and the known dry weight of each sample. Ultimately, the percentage of each selenium form (soluble, sorbed, elemental and organic, as percentage of total selenium) was determined by dividing the value of each Se fraction by the total selenium concentration from the HGAAS analysis (wet digestion at USGS Laboratory, Denver, CO). The sum of the selenium extracted relative to the total Se analysis was used to determine the total selenium recovery for each sample.

Column Experiments

Seven undisturbed core samples, which were 13 cm (5 in) in diameter and from 7 to 15 cm (3-6 in) long, were used for the columns. The length depended on the visually-estimated permeability of each core. Six of the columns consisted of soil samples and one column consisted of weathered Mancos Shale. The cores for the column experiments were selected according to the following criteria.

- Importance: As defined by the total selenium concentration (more than 0.9 ppm), the type of material (soil or shale), and the site location (irrigated or non-irrigated, soil from surface or below the surficial root zone) so that differences could be evaluated.
- Suitability: Undisturbed, properly-preserved core in the PVC tube so that the hydraulic properties, chemical composition and field conditions had not been altered: core in good contact with the PVC tube walls so that the applied water had to pass through the material; material permeable enough so that the water could be applied without pressure, because pressure would alter porosity, residence time, etc.
- Uniformity: Material in the column as uniform as possible, so that the leaching effect of the applied water was equally distributed through the entire column.

Before the column set-up, the sample was weighed (total weight of column minus weight of PVC, ceramic porous plate, etc.). During the experiments, irrigation water with distinct, modified compositions was used to evaluate the factors that could affect the selenium leaching (Table 5). Initially, columns were saturated from the bottom up with filtered irrigation water. The irrigation water with differing compositions was applied sequentially at the top of the column.

Table 5. Composition of water applied to the columns.

Column	Water 1	Water 2	Water 3	Water 4
1	Irrigation water 0.1mM NaBr, pH 7.13	Irrigation water 0.1mM NaBr, pH 8.72	Irrigation water 0.1mM NaBr, pH 5.5	De-ionized water
2	Irrigation water 0.1mM NaBr, pH 7.13	Irrigation water 0.1mM NaBr, pH 8.72	Irrigation water 0.1mM NaBr, pH 5.5	De-ionized water
3	Irrigation water 0.1mM NaBr, pH 7.13	Irrigation water 0.1mM NaBr, pH 8.68	De-ionized water	
4	Irrigation water 0.1 mM NaBr, pH 7.11	Irrigation water 0.1 mM NaBr, pH 7.11, 110 mg/L NO_3^-	De-ionized water	
5 Sterilized	Irrigation water 0.1 mM NaBr, pH 7.11	Irrigation water 0.1 mM NaBr, pH 7.11, 110 mg/L NO_3^-	De-ionized water	
6	Simulated irrigation water, pH 7.17, 0.05 mM NaBr,	Irrigation water 0.05 mM NaBr, pH 7.23, 55 mg/L NO_3^-		
7 Sterilized	Simulated irrigation water, pH 7.17, 0.05 mM NaBr,	Irrigation water 0.05 mM NaBr, pH 7.23, 55 mg/L NO_3^-		

To determine when the applied water exited the column and to determine the effective pore volume of the column, a 0.1 mM or a 0.05 mM sodium bromide (NaBr) solution was used as a conservative tracer. The tracer solution was slightly alkaline (pH 7.9), so the pH was adjusted closer to the field conditions of pH 7.1 (Table 5). For all the pH adjustments, dilute solutions of 0.25% NaOH and 5% HCl were used. In general, the concentration of the applied reagents was less than 10 mg /L. All the applied solutions had been filtered through a 0.45- μm membrane filter (Supor®-450, 47 mm in diameter)

with a vacuum-filtering unit. All solutions passed through the column solely by gravity flow so the residence time was as close as possible to that occurring in the field. The residence time of the various waters in a given column was the same, because the columns were continuously saturated and the flow rate was constant for each individual column. Each type of water was applied until at least 1.5 pore volumes had flowed through. For the individual experiments, 4 to 8 pore volumes of water flowed through each column. Changes in the Se concentration as a function of the applied water chemistry were evaluated.

To evaluate the effect of microbial activity on selenium leaching, two columns (column 5 and column 7) were sterilized. The best way to sterilize the soil, without causing major alteration, was by ionizing radiation (Eno and Popenoe, 1964). A cobalt-60 source, with a dose of 2.8 Mrads at a rate of 0.2 to 0.3 Mrads/h, was used at Argonne National Laboratory. This was sufficient for the sterilization of the soil without altering the physical and chemical properties (Powelson and Jenkinson, 1976; Ostlund et al., 1989). In particular for the sterilized columns, a sterile filtering unit equipped with a 0.2- μm membrane filter was used, so that bacteria were not introduced. The same procedure was followed on the sterilized columns as for the rest of the columns, and the results were compared with the non-sterilized columns (column 4 and column 6), which corresponded to the sterilized columns (columns 5 and 7, respectively).

The columns were constructed with clear PVC so that the core could be continuously observed. During the test the leachate was analyzed and both the leachate and the core sample were observed for color changes and precipitates. For most of the

column experiments, the initial applied water was the same as the irrigation water in the study area. Water was collected in June 1999 from Brush Creek above the irrigated areas, before any return flows from irrigation to the creek. The water was stored in the dark at ambient temperature. Simulated irrigation water was used for the first applied water series for columns 6 and 7, because the quantity of irrigation water was not sufficient to complete the experiment. The simulated irrigation water was made to match the chemistry of the corresponding irrigation water sample 99SL-112. The effluent from the columns was analyzed for total selenium and Br by ICP-MS with Flow Injection Analysis System (FIAS-ICPMS). This ICP-MS technique is effective because it has acceptable detection limits (0.1 to 0.3 $\mu\text{g/L}$ for Se and 0.5 to 1 $\mu\text{g/L}$ for Br), can function with total dissolved solids (TDS) up to 1,200 mg/L, and can analyze bromine along with selenium. Steady-flow ICP-MS analysis was used when the TDS of the effluent was low (columns 6 and 7), probably due to fewer soluble solids in the soil. The detection limit was 0.2 to 0.4 $\mu\text{g/L}$ for Se and 5 to 10 $\mu\text{g/L}$ for Br. During the ICP-MS analysis, HBr is formed with the ^{81}Br isotope and interferes with the analysis of the ^{82}Se isotope because they have the same molecular weight. Selenium concentration values were corrected for the formation of HBr. Blanks were analyzed to control for possible contamination from reagents, bottles, glassware, etc.

The data for each column include leachate volume, concentration of Se and Br, readings of the measured parameters (pH, conductance, flow rate), and the production of selenium. The production of selenium was evaluated for production ($\mu\text{g Se per kg of}$

sample dry weight and liter of effluent), cumulative production ($\mu\text{g Se/kg}$ of sample dry weight), and production rate ($\mu\text{g Se per kg of sample dry weight per min}$).

The flow rate was determined by collecting a calculated volume of effluent at known time periods and was approximately constant for each column during the experiment. The average flow rate is used for the determination of the hydraulic conductivity. Hydraulic conductivity (K) was found using Darcy's law:

$$K = -\frac{Q}{A \frac{dH}{dL}},$$

where:

Q = the flow rate (L^3T^{-1})

$A = \pi \times D^2/4$ = the surface area of column of D diameter normal to the flow (L^2)

dL = the length of the column (L)

dH = the hydraulic head difference between the top and the bottom of the core in the column (L).

The number of pore volumes (T) was calculated by dividing the amount of water leached through the column (V) by the pore volume (V_0) of the column $T = V/V_0$ (Van Genuchten and Wierrega, 1986). The pore volume used for the Se and Br concentration curves was based on the concept that the pore volume (V_0) equals the volume of the effluent, when $C_{\text{effluent}} = 0.5 \cdot C_{\text{input}}$ if a non-reacting tracer is applied to a continuously saturated column (Van Genuchten and Wierrega, 1986). Br was used as a non-reacting tracer. The assumption was that the tracer had not sorbed or reacted with the material in

the column, a safe assumption for the conservative bromide tracer. The value of the pore volume based on the bromide tracer was compared with the value of pore volume based on the effective porosity (n_e):

$$V_0 = V_t \times n_e,$$

where:

$V_t = A \times L$ the total volume of the column (L^3), where L is the length of core in the column.

The effective porosity was calculated following a modified technique of Fetter (1994). According to this technique, the known volume of the column (V_t) was saturated from the bottom up with a measured volume of irrigation water (V_a). The water content (V_w) of the material in the column was found after completion of the experiment by drying the core at 105 °C until a constant weight was obtained. Effective porosity (n_e) was found by:

$$n_e = (V_a + V_w) / V_t,$$

Lastly, the pore volume of the column based on the total porosity (n_t) was determined by:

$$V_0 = V_t \times n_t,$$

and was also compared with the pore volume values based on the two previous methods.

Total porosity was calculated by:

$$n_t = (1 - \rho_b / \rho_p),$$

where ρ_b and ρ_p are dry bulk density (ML^{-3}) and the particle density (ML^{-3}), respectively (Danielson and Sutherland, 1986). Dry bulk density was calculated (Blake and Hartge,

1986a) by dividing the mass of the dry solids (dried at 105 °C until a constant weight was obtained) by V_t . Particle density was calculated by the pycnometer method (Blake and Hartge, 1986b).

The buffering capacity of the soil was determined by adding 100 ml of irrigation water at pH adjusted to 8.85 to 5 g of soil (equivalent dry weight). The pH of the water was monitored for 15 min. The water was removed and then 100 ml of irrigation water at pH 5.5 were added and the process repeated. Results were monitored to determine if the soil was capable of buffering both the acidic and the basic solution to a similar pH.

The residence time of the applied water solutions was also determined. The residence time of a substance (here water) in a reservoir is obtained by dividing the volume of the substance in the reservoir by the volumetric flux rate of the substance into the reservoir (Drever, 1982). The flux into the column was equal to the flux out of the column, so the time (t) that the molecules of the solute stayed in the columns was calculated by:

$$t = V/Q.$$

The time (t_L) and water quantity (Q_L) required for leaching 1 kg of dry soil until the arbitrary value of the average concentration of Se in the Western soils (0.23 µg/kg) were estimated by:

$$t_L = m_r/P$$

$$Q_L = Q \times t_L,$$

where:

$$P = 1 \text{ kg dry soil} \cdot \text{production rate at steady state (MT}^{-1}\text{)}$$

$$m_r = \text{mass of Se required to be leached} = 1 \text{ kg} \cdot [C_{\text{total}} - (C_{\text{leached}} + 0.23 \text{ } \mu\text{g/kg})]$$

(M)

C = Se concentration in $\mu\text{g /kg}$ (dimensionless).

Tests were continued as long as the data indicated that there were changes in water quality, for instance if the pH was decreasing (Broughton et al., 1992), if leachate electrical conductance was constant or increasing, or if the selenium concentration of the effluent was fluctuating or increasing. Tests were run continuously until all the water series had been applied to each column. Tests were interrupted only when necessary, such as overnight on some occasions, because an automated system to collect the effluent was not available. The experiment was stopped for about two hours after collecting 1.5, 2.9 and 4.3 pore volumes from column 1, and overnight (approximately 8 hours) after collecting 1.9, 2.1 and 1.9 pore volumes from columns 2, 6, and 7, respectively.

RESULTS

Field Sampling

Water Samples

The chemical composition of ground and surface waters in the area (Tables 6, 7 and 8) was determined for the broader U.S. Geological Survey study (Kharaka et al., 2001). They are included in this report for completeness of data and a better interpretation of the batch tests and column experiments. The relationship of the water samples to the sampling sites is shown in Tables 1 and 2.

Field data (Tables 6, 7) indicated that the electrical conductance for the surface water samples ranged between 220 and 1,810 $\mu\text{S}/\text{cm}$ and for the groundwater samples ranged between 1,544 and 17,130 $\mu\text{S}/\text{cm}$. The surface water samples measured were saturated with oxygen, with concentrations greater than 8 mg/L, and most of the groundwater samples had dissolved oxygen (DO) concentrations less than or equal to 0.3 mg/L. The pH of the groundwater samples was about 7 (except JM-14 which had pH of about 7.5), and the pH of the surface water samples was about 8.3. Redox conditions in the surface water samples measured were oxidizing ($+110\text{ mV} < \text{Eh} < +205\text{ mV}$); in the groundwater samples measured, redox conditions varied from reducing to oxidizing ($-530\text{ mV} < \text{Eh} < +250\text{ mV}$), although in general the Eh field values are ambiguous. For instance, there was poor correlation between DO and Eh values, when at least some correlation would be expected. Temperatures ranged between 9 and 22 °C, in most cases being several degrees (2-5 °C) warmer in late summer than late spring for both surface and

shallow groundwater. Exceptions were the samples from the artesian well JM-17 with almost constant temperature and the surface water from Ashley Creek, where the temperature increased about 13 °C.

Results of laboratory water quality analyses are given in Table 8. The concentration of selenium in the water samples (HGAAS analysis) ranged from less than 0.5 µg/L to 153 µg/L. The average concentration was 37.7 µg/L, and the geometric mean was 11.7 µg/L. The relationship between selenium and TDS, chloride and sulfate concentrations for samplings before and after the irrigation season are shown in Figure 5.

Table 6. Field water quality parameters obtained during 05/25-06/06/1999.

Location	Water sample	E. C. µS/cm	D.O. mg/L	pH	Temp °C	Eh mV	Water elevation (m MSL)	
Groundwater								Well DTW
E-1	99SL-107	4,670	0.11	6.95	9.0	-25	NM	NM
W-3	99SL-106	4,370	0.11	7.13	10.4	-160	1439	-0.08 m
K-6	99SL-101	4,150	0.15	6.98	10.6	+181	1442	0.05 m
99JM-11	99SL-104	4,350	0.05	6.88	11.2	+40?	1439	2.74 m
99JM-12	99SL-103	3,400	0.04	6.98	11.8	-530?	1439	2.74 m
99JM-13	99SL-105	4,550	0.21	7.14	12.3	-220	1442	5.73 m
99JM-14	99SL-114	*10,960	NM	*7.65	NM	NM	1465?	9.42 m?
99JM-15	99SL-110	5,150	0.00	7.05	10.2	-110	1441	1.76 m
99JM-16	99SL-111	2,100	0.01	7.15	12.3	-480	1453	2.29 m
99JM-17	99SL-113	17,130	0.03	7.11	11.6	+130	1459	-2 m
99JM-18	99SL-115	3,130	5.00?	6.98	14.0	+125?	1471	1.41 m
Snow well	99SL-102	5,180	0.00	7.04	10.2	+150	1440	2.1 m
Surface water								Discharge
Green River	99SL-108	320	8.75	8.34	12.0	+155	-	510 m ³ /sec
Ashley Creek	99SL-109	220	10.27	8.29	9.6	+205	-	15.7 m ³ /sec
Brush Creek	99SL-112	290	9.12	8.33	11.5	+110	-	17 m ³ /sec

E. C.: Electrical Conductance

D.O.: dissolved oxygen

DTW: depth to water below ground surface

MSL: above mean sea level

(-) indicates above ground surface

* not enough flow for field measurements, value refers to laboratory values

? uncertain values

NM: not measured

Table 7. Field water quality parameters obtained during 09/06-09/12/1999.

Location	Water sample	E. C. $\mu\text{S/cm}$	D.O. mg/L	pH	Temp. $^{\circ}\text{C}$	Eh mV	Water elevation (m MSL)	
Groundwater								Well DTW
E-1	99SL-211	4350	0.07	6.89	10.8	-33	1438	1.7 m
W-3	99SL-210	4850	0.05	7.03	12.5	-185	1438	1.14 m
**K-6	99SL-207	4320	0.30	6.92	15.0	+140	1442	0.35 m
99JM-11	99SL-206	4560	0.13	6.82	13.1	+157	1439	2.73 m
99JM-12	99SL-205	3340	0.07	6.85	17.5	+145	1439	2.67m
99JM-13	99SL-204	4250	0.08	7.05	16.0	+22	1442	5.74 m
99JM-14	99SL-209	10800	*2.50	7.51	16.0	+193	1464	9.85 m
99JM-15	99SL-201	4100	0.18	*7.26	15.3	+95	1441	1.63 m
99JM-16	99SL-208	2190	0.06	7.04	14.0	+250	1453	1.8 m
99JM-17	99SL-203	16610	0.04	7.09	11.2	+200	1459	-2 m
99JM-18	99SL-212	2090	*1.70	6.98	17.0	+100	1470	1.98 m
Snow well	99SL-202	4730	0.05	6.98	15.5	+155	1440	1.9 m
Well 5500S.9000E	99SL-218	NM (lab 1544)	NM	NM	NM	NM	1489	4.12 m
Spring in canyon	99SL-217	~1800	NM	NM	16.0	NM	-	~250 cm^3/sec
Seep	99SL-219	~3980	NM	NM	16.0	NM	-	~670 cm^3/sec
Surface water								Discharge
Green River	99SL-215	NM (lab 691)	NM	NM	16.0	NM	-	~56.6 m^3/sec
**Ashley Creek	99SL-216	1810	9.00	8.28	22.4	NM	-	0.65 m^3/sec
Brush Creek	99SL-213	NM (lab 332)	NM	NM	12.5	NM	-	~0.71 m^3/sec
Canal by 99JM-18	99SL-214	NM (lab 455)	NM	NM	15.0	NM	-	NM

E. C.: Electrical Conductance

D.O.: dissolved oxygen

DTW: depth to water below ground surface

MSL: above mean sea level

(-) indicates above ground surface

NM: not measured

lab values measured in the lab (lab-truck in the field)

* calibration of pH electrode after field measurements indicated that it was reading pH=7.3 instead of 7.0

** direct measurements (without flow through cell)

• high dissolved oxygen concentration possibly due to proximity of submerged pump to water surface (not much water in the well)

Table 8. Selected constituents from Jensen-Stewart Lake water analysis (U.S. Geological Survey, Menlo Park, CA).

Location	Sample	TDS mg/L	Na mg/L	Mg mg/L	Ca mg/L	Mn mg/L	As μg/L	* Se μg/L	U μg/L	Cl mg/L	NO ₃ mg/L	SO ₄ ²⁻ mg/L	HCO ₃ mg/L	SiO ₂ mg/L	DOC mg/L
Groundwater															
E-1	99SL-107	4394	474	260	452	3.65	1.6	<0.5	16	74	0.06	2400	690	19	9.9
E-1	99SL-211	4085	431	240	424	3.47	1	<1	14	70	<0.05	2160	679	20	11
W-3	99SL-106	4040	526	244	295	3.24	4	1	8	75	<0.05	1940	900	28	13
W-3	99SL-210	4685	627	276	359	2.66	8.9	1	11	106	<0.05	2350	888	29	15
K-6	99SL-101	4252	461	218	490	0.87	7	5.9	40	61	0.5	2500	473	14	5
K-6	99SL-207	4057	395	205	497	0.86	1	11	43	73	1.2	2340	500	16	6.2
99JM-11	99SL-104	4069	372	228	509	0.84	0.4	1.5	49	81	24.5	2380	435	9	4.9
99JM-11	99SL-206	4253	429	228	499	0.92	0.5	1.5	51	98	32	2480	444	9	6
99JM-12	99SL-103	3184	217	129	527	0.99	0.4	49	50	61	15.1	1690	504	18	5.7
99JM-12	99SL-205	3153	213	126	510	0.82	<1	56	51	56	21.3	1660	522	20	6.2
99JM-13	99SL-105	4167	450	221	487	0.8	0.5	90	39	97	53.7	2510	305	12	3.3
99JM-13	99SL-204	4088	432	203	475	0.65	0.5	92	44	100	56.6	2460	322	12	3.1
99JM-14	99SL-114	10065	2090	430	430	2.09	1	85	31	305	160	6160	415	11	17
99JM-14	99SL-209	10078	2070	410	419	2.85	1.1	11	22	330	128	6220	435	10	13
99JM-15	99SL-110	4674	691	202	439	0.1	1	78	55	82	15.7	2640	580	18	5.7
99JM-15	99SL-201	3729	493	176	351	0.01	1	78	49	68	28.3	2050	525	20	6.6
99JM-16	99SL-111	1862	127	92	260	1.54	0.5	39	25	38	15.9	807	470	17	4
99JM-16	99SL-208	1973	138	96	277	1.52	0.5	43	30	37	19.6	877	496	18	5
99JM-17	99SL-113	16292	4179	402	390	0.39	0.5	26	40	282	930	9390	620	8	17
99JM-17	99SL-203	15605	3930	385	391	0.42	<2	22	40	271	843	9080	635	9	18
99JM-18	99SL-115	3008	206	156	415	0.01	0.6	140	49	35	24	1550	600	13	6.1
99JM-18	99SL-212	1809	167	82	225	0.02	0.5	22	31	15	4	763	523	15	5.8
Snow well	99SL-102	4619	596	238	441	1.24	0.7	100	65	87	12.3	2620	580	19	5.5
Snow well	99SL-202	4342	629	205	379	1.67	1.2	89	61	87	12.2	2430	551	21	7
5500S/9000E	99SL-218	1329	75	52	193	0.01	1.2	28	20	66	84.1	316	502	30	NM
Spring in canyon	99SL-217	1536	131	89	180	<0.01	0.5	8	30	56	1.6	715	334	16	4
Seep	99SL-219	3873	342	216	505	<0.01	0.7	153	55	70	42.2	2300	344	26	10
Surface water															
Green River	99SL-108	260	20.6	11.2	31.9	0.004	1.1	0.7	1.5	7.3	0.3	68.6	112	8	5.2
Green River	99SL-215	555	58	21.2	56	<0.01	2	1.3	3.9	22	0.6	156	232	6	4
Ashley Creek	99SL-109	186	8.2	8.5	26.4	0.02	0.5	3.7	1.9	2.1	1.1	60.9	74	5	7.8
Ashley Creek	99SL-216	1539	109	106	181	0.01	1.6	38	26	29	9.6	826	254	14	7.4
Brush Creek	99SL-112	259	5	11.5	41.2	0.01	0.7	0.7	1.2	1.6	0.4	45.4	140	6	3.3
Brush Creek	99SL-213	253	6.3	9.5	44	0.01	0.6	<1	1.2	1.5	0.2	68.1	117	5	4.8
Canal by JM-18	99SL-214	353	12.9	13.5	58	0.01	0.7	3	2.3	2.2	0.4	114	144	6	NM

Samples 99SL-101 to 99SL-115 from May-June 1999, 99SL-201 to 99SL-219 from September 1999.

Analytical methods used: Ion Chromatography for the anions and Inductively Coupled Plasma Mass Spectrometry for the cations.

*Selenium by Hydride Generation Atomic Absorbance Spectrometry (HG-AAS), U.S. Geological Survey Laboratory, Denver, CO.

NM: not measured

Figure 5. Selenium related to TDS, chloride and sulfate for the Stewart Lake-Jensen water samples

Soil and Mancos Shale Samples

Samples taken from all the cores were analyzed for total selenium, inorganic and organic carbon and other elements at the U.S. Geological Survey Laboratory, Denver, CO. The determination of the spatial and vertical distribution of total selenium in the study area and the relationship with the distribution of other elements were based on these analyses. Analysis with wet digestion (Appendix B) provided the total selenium concentration of all the core samples. The total selenium concentration in the core samples (Table 9) ranged from 0.18 ppm to 3.0 ppm, with an average of 1.1 ppm and a geometric mean of 1.0 ppm. The total selenium concentration in the soil samples ranged from 0.32 ppm to 1.9 ppm; average concentration of Se in all the soil samples was 1.1 ppm and geometric mean was 1.0 ppm. In the surface soil samples, the average concentration of Se was 1.3 ppm in the boreholes JM-13, JM-13B, JM-15, JM-16 from the irrigated areas (borehole JM-13B, located immediately adjacent to JM-13, was drilled to recover the undisturbed core from 0.1 to 0.9 m below land surface; the boreholes are essentially the same) and 1.5 ppm in the non-irrigated areas (boreholes JM-11, JM-12, JM-14, JM-17). In the samples taken from the deeper soil the average Se concentration was 0.9 ppm in both irrigated and non-irrigated areas.

In addition to the location-based statistical analysis, the normalized concentrations (C_n) of selenium, C-carbonate, C-organic and selected other elements (As, Mo, U, Ca and also V, Cr and Cu for JM-17) as a function of depth were determined at the boreholes JM-17, JM-16 and JM-11 (Figs. 6 to 8), where:

$$C_n = C_i / C_{\max} ,$$

Table 9. Selected constituents from Jensen-Stewart Lake soil analysis.

Sample	Material	Depth (m BLS)	Na ppm	Mg ppm	Al ppm	K ppm	Ca ppm	Cr ppm	Mn ppm	Fe ppm
99JM-11 9927	Weathered and intact shale	6.3	4570	17700	65400	24200	48300	61.8	227	22400
99JM-11 9928	Intact shale	6.5	4400	16500	62600	22300	53800	60.1	212	21900
99JM-11 9929	Weathered shale	6.7	4310	16300	61900	22400	53400	63.8	239	26700
99JM-11 9930	Weathered shale	7.7	4310	14700	54800	20000	80200	51.8	302	22300
99JM-11 9931	Intact shale	8.8	4910	17500	65800	23700	56000	66.3	231	23700
99JM-12 9923	Coarse - medium sand, gravel	3.4	9210	5400	35000	19300	27600	15	168	7300
99JM-12 9924	Shale and sand	4.9	6020	12400	69300	26500	32100	52.8	320	26600
99JM-13B 9916	Sandy soil, yellowish	0.1	5180	15400	47600	19100	49200	46.3	327	18600
99JM-13B 9917	Silty- loamy soil	0.9	9360	13600	49100	17200	40800	48	262	19300
99JM-13 9918	Silty soil	1.9	7430	11200	37500	15800	41500	31.2	258	13300
99JM-13 9919	Silty soil	2.7	6310	5790	35500	15500	15800	33	202	11400
99JM-13 9920	Loamy silt	8.3	7290	12300	53600	19600	44800	49.5	279	20200
99JM-14 9925	Loamy-silty soil	0.06	6140	14600	52100	19000	44400	53.1	314	23000
99JM-14 9926	Weathered shale	0.9	2880	9120	42500	13300	113000	51.4	341	26000
99JM-14 9932	Weathered shale	1.5	7680	14800	54700	17800	68300	64.4	343	26300
99JM-14 9933	Weathered shale	2.2	8140	17500	55100	19000	48200	59.7	346	24400
99JM-15 9921	Gravelly-silty brown soil	0.0	3800	17400	65800	23800	43600	71.7	354	26100
99JM-15 9922	Gravelly sandy soil	0.8	10100	4560	39100	21600	21300	15.2	177	9350
99JM-16 9915	Yellowish surface soil	0.0	4480	13500	47200	17800	44100	45.9	326	18300
99JM-16 9914	Sandy- silty soil	0.8	5570	16400	60300	22000	63000	61.4	381	24400
99JM-16 9913	Sandy silt (saturated)	1.5	6530	12400	59600	20800	36900	58.9	319	22000
99JM-16 9912	Silty sand (saturated)	2.3	11500	5480	43500	19900	20600	22.9	223	10100
99JM-16 9911	Silty sand (saturated)	3.0	12300	4760	42900	19600	17800	18.7	172	8650
99JM-17 9910	Surface soil (roots, gray)	0.0	3660	16000	60100	20900	44300	74.9	295	23400
99JM-17 9909	Sandy soil (reddish)	0.6	4450	7540	29400	12500	32200	31.1	230	13900
99JM-17 9908	Weathered shale and sand	2.9	5160	13800	42100	14800	81000	52.4	226	21300
99JM-17 9907	Weathered shale	3.7	4980	17200	67200	22800	28700	90.6	146	31100
99JM-17 9906	Weathered shale	4.4	4900	17800	65200	20400	48600	74.9	205	26500
99JM-17 9905	Weathered shale	5.2	4560	16600	58600	19600	44100	71.7	189	23700
99JM-17 9904	Weathered shale	5.9	5320	17500	61200	21500	51600	81.7	184	25000
99JM-17 9903	Weathered shale	8.2	5150	16200	63000	22400	59100	84.8	394	28900
99JM-17 9902	Weathered shale	8.8	5170	16600	62000	21500	58500	82.7	374	27200
99JM-17 9901	Intact shale	9.8	4620	16000	63700	22100	56800	87.6	293	29900

The first six digits from the sample I.D. indicate the year and the borehole I.D. (locations in Table 1) where the sample was obtained.

m BLS: meters below land surface

Table 9 (continued). Selected constituents from Jensen-Stewart Lake soil analysis.

Sample	Material	Depth (m BLS)	As ppm	* Se ppm	Mo ppm	Pb ppm	U ppm	C- Carbonate %	C-organic %
99JM-11 9927	Weathered and intact shale	6.3	6.6	0.82	1	13.2	4.3	1.76	0.27
99JM-11 9928	Intact shale	6.5	9.3	2.0	1.3	14.2	4.5	1.93	0.96
99JM-11 9929	Weathered shale	6.7	15.2	1.1	7.5	14.8	4.9	1.66	0.48
99JM-11 9930	Weathered shale	7.7	10.1	0.94	3.8	14.2	4.1	2.31	0.28
99JM-11 9931	Intact shale	8.8	8	1.3	0.77	13.7	4.4	1.95	0.92
99JM-12 9923	Coarse - medium sand, gravel	3.4	2.6	0.18	0.77	10.9	1.3	0.75	0.08
99JM-12 9924	Shale and sand	4.9	12.9	1.9	2.2	16.3	5.1	0.99	0.39
99JM-13B 9916	Sandy soil, yellowish	0.1	6.7	1.6	1.8	17.9	2.8	1.55	2.85
99JM-13B 9917	Silty- loamy soil	0.9	7.8	1.4	1.1	13.4	3.1	1.31	0.1
99JM-13 9918	Silty soil	1.9	4.8	1.0	1	11.6	2.3	0.95	0.09
99JM-13 9919	Silty soil	2.7	4	0.64	0.81	9.25	1.6	0.37	0.08
99JM-13 9920	Loamy silt	8.3	6.5	0.7	1.3	13.8	3	1.16	0.24
99JM-14 9925	Loamy-silty soil	0.06	9.4	1.1	1.9	16.7	3.1	1.41	0.43
99JM-14 9926	Weathered shale	0.9	11.8	1.2	1.5	13	2.8	0.95	0.17
99JM-14 9932	Weathered shale	1.5	10.6	1.5	1.3	14.9	3.8	1.2	0.22
99JM-14 9933	Weathered shale	2.2	10.8	1.3	1.4	15.1	3.8	1.47	0.1
99JM-15 9921	Gravelly-silty brown soil	0.0	7.1	1.3	1.4	22.1	3.2	1.31	2.75
99JM-15 9922	Gravelly sandy soil	0.8	3.6	0.32	0.63	12.7	1.6	0.59	0.3
99JM-16 9915	Yellowish surface soil	0.0	7.1	1.0	1.7	14.2	2.7	1.38	0.7
99JM-16 9914	Sandy- silty soil	0.8	10.6	0.98	2.5	16.8	3.2	1.83	0.37
99JM-16 9913	Sandy silt (saturated)	1.5	8.6	0.9	2.5	16.6	3.1	1.02	0.29
99JM-16 9912	Silty sand (saturated)	2.3	3.5	0.41	0.65	12.9	2.2	0.63	0.2
99JM-16 9911	Silty sand (saturated)	3.0	2.4	0.38	0.45	12.4	1.5	0.61	0.13
99JM-17 9910	Surface soil (roots, gray)	0.0	8.5	1.9	1.9	17.3	3.4	1.4	1.92
99JM-17 9909	Sandy soil (reddish)	0.6	6.6	0.93	0.94	10.7	2.1	0.95	-0.02
99JM-17 9908	Weathered shale and sand	2.9	9.1	1.0	2.0	13.6	2.8	1.46	0.23
99JM-17 9907	Weathered shale	3.7	16.2	3.0	3.5	15.1	4.6	0.85	0.44
99JM-17 9906	Weathered shale	4.4	10.1	0.5	1.7	16.7	4.2	1.62	0.44
99JM-17 9905	Weathered shale	5.2	11.8	1.0	2.3	14.9	3.3	1.55	0.36
99JM-17 9904	Weathered shale	5.9	9.4	0.68	1.1	15.6	3.6	1.8	0.35
99JM-17 9903	Weathered shale	8.2	10	1.1	0.7	17	3.6	1.71	0.38
99JM-17 9902	Weathered shale	8.8	10	0.9	1	17.7	3.7	1.72	0.46
99JM-17 9901	Intact shale	9.8	11.2	1.9	1.8	17.3	3.9	1.98	1.34

The first six digits from the sample I.D. indicate the year and the borehole I.D. (locations in Table 1) where the sample was obtained.

m BLS: meters below land surface

* Se by HGAAS analysis

where:

C_i is the concentration of the element

$C_{\max}$ is the maximum concentration of the element found at the specific borehole.

This normalization was used to evaluate whether the distributions of Se and the selected elements as a function of depth were following similar patterns in the studied boreholes.

The pattern of Se distribution (Figs. 6 to 8) was similar with those of As, Mo, U (and with V, Cr and Cu in JM-17) and to a lesser extent with C-organic; it was dissimilar with those of Ca and C-carbonate.

Figure 6. Normalized selenium and selected elements in borehole JM-17.

m BLS: meters below land surface

Figure 6 (cont.). Normalized selenium and selected elements in borehole JM-17.

m BLS: meters below land surface

Figure 7. Normalized selenium and selected elements in borehole JM-16.

Figure 8. Normalized selenium and selected elements in borehole JM-11.

Batch Tests

Results of analysis with wet digestion (Appendix B), performed in U.S. Geological Survey Laboratory, Denver, CO, for the total selenium concentration of the soil and shale samples and results of the batch tests for the extracted selenium fractions are given in Table 10. The concentration of total selenium for the twelve samples used for the batch tests ranged from 0.93 ppm to 3.0 ppm (Table 10). Selenium recovery from the sequential extractions ranged from 60 to 101% of the total selenium value (Table 10).

The soluble Se form contributed 0.8 to 48% of total Se; the adsorbed Se 0.2 to 9% of total Se; the elemental Se 17 to 67% of total Se and the Se associated with organic material contributed 19 to 79% of total Se (Table 10, Figs. 9 and 10). The majority of Se in the analyzed samples occurred as elemental Se and as Se associated with organic matter. In addition, a significant fraction of soluble Se was found in the soil below the surficial root zone.

Sample 99JM-17 9907, consisting of weathered Mancos Shale taken from borehole JM-17 at a depth of 3.6 m (Table 9), was selected to determine the effect of grinding on the selenium recovery and distribution in various forms. The specific sample was selected based on its adequate total Se concentration, the abundance of Mancos Shale and its importance for the Se distribution in the study area, and the fact that this sample was difficult to disaggregate properly without grinding. Analysis of the ground (JB-99041D) and not ground (JB-99041) pair of samples (Table 10) indicated that selenium recoveries were almost the same: 101% for the ground sample JB-99041D and 97% for the unground sample JB-99041. Analysis of the unground sample (JB-99041, Table 10)

Table 10. Concentrations (ppb) and percentages of the selenium forms.

Borehole	Depth (m BLS)	Sample	Se concentration (ppb)					Total Se (ppm)*
			Soluble	Sorbed	Elemental	In organic matter **	Sum. of extracted Se	
JM-13B	0.12	JB-99070	25.7	89.9	648.4	509.8	1273.7	1.6
JM-13	1.92	JB-99080	481.8	56.9	174.7	205.2	918.6	1.0
JM-14	0.06	JB-99100	8.9	32.3	188.4	873.7	1103.3	1.1
JM-15	0.0	JB-99090	11.4	55.6	476.2	240.6	783.8	1.3
JM-16	0.0	JB-99050D	20.6	92.3	254.7	596.8	964.4	1.0
JM-16	0.76	JB-99060D	167.5	39.2	169.7	416.0	792.4	0.98
JM-17	0.0	JB-99011	50.5	141.7	614.0	938.1	1744.2	1.9
JM-17	0.60	JB-99021	292.0	3.4	156.1	241.5	693.0	0.93
JM-17	2.90	JB-99031	182.3	60.6	189.4	512.4	944.7	1.0
JM-17	3.60	JB-99041	64.4	5.8	1019.0	1812.3	2901.4	3.0
JM-17	3.60	JB-99041D	86.8	35.6	2003.4	913.9	3039.7	3.0
JM-17	9.77	JB-99110	231.4	146.2	410.9	1041.0	1829.6	1.9

Borehole	Depth (m BLS)	Sample	% of total Se *				
			Soluble	Sorbed	Elemental	In organic matter **	Total recovery
JM-13B	0.12	JB-99070	1.6	5.6	40.5	31.9	79.6
JM-13	1.92	JB-99080	48.2	5.7	17.5	20.5	91.9
JM-14	0.06	JB-99100	0.8	2.9	17.1	79.4	100.3
JM-15	0.0	JB-99090	0.9	4.3	36.6	18.5	60.3
JM-16	0.0	JB-99050D	2.1	9.2	25.5	59.7	96.4
JM-16	0.76	JB-99060D	17.1	4.0	17.3	42.5	80.9
JM-17	0.0	JB-99011	2.7	7.5	32.3	49.4	91.8
JM-17	0.60	JB-99021	31.4	0.4	16.8	26.0	74.5
JM-17	2.90	JB-99031	18.2	6.1	18.9	51.2	94.5
JM-17	3.60	JB-99041	2.1	0.2	34.0	60.4	96.7
JM-17	3.60	JB-99041D	2.9	1.2	66.8	30.5	101.3
JM-17	9.77	JB-99110	12.2	7.7	21.6	54.8	96.3

* value of total Se from wet digestion and HGAAS analysis at U.S. Geological Survey, Denver, CO.

** Selenium associated with organic matter
(m BLS): meters below land surface

Figure 9. Se extracts and total extracted selenium as a percentage of total Se.

Figure 9 (cont.). Se extracts and total extracted selenium as a percentage of total Se.

Figure 9 (cont.). Se extracts and total extracted selenium as a percentage of total Se.

Figure 9 (cont). Se extracts and total extracted selenium as a percentage of total Se.

Figure 10. Vertical distribution of the different forms of selenium.

Figure 10 (cont.). Vertical distribution of the different forms of selenium.

indicated that 60% of total Se was Se associated with organic material, 34% was elemental Se, and the rest of the recovered Se was soluble and sorbed Se. In the ground sample (JB-99041D, Table 10), 31% of total Se was Se associated with organic material, 67% was elemental Se, and the rest of the recovered Se was sorbed and soluble Se. Comparison of the two samples indicated a significant decrease of the Se associated with organic matter and a significant increase of the elemental Se in the ground sample.

Column Experiments

Seven core sections were used for the column experiments. Three of the columns (columns 1 to 3) were from borehole JM-17, in a non-irrigated area, and four of the columns (columns 4 to 7) were from borehole JM-16 in an irrigated area. Two columns (column 5 and column 7 from JM-16) were sterilized with Co-60 gamma radiation at Argonne National Laboratory, IL. Location, type of material and physical properties of the columns are shown in Table 11.

The electrical conductance and the pH of the effluent were monitored during the experiments (Figs. 11 to 13). Testing for each applied water solution was continued if the pH was changing or if electrical conductance was constant or was increasing.

Determination of the pore volume was based on the value from the bromide concentration of the effluent (Figs. 14 to 16), except for column 4, where the average of the three values (based on the total porosity, the effective porosity and on the bromide concentration) was used. For column 4, channeling in the beginning of the experiment was possibly responsible for the lower values of pore volume and porosity based on $0.5 \cdot C_{Br}$ (Table 11). The pore volume values based on the effective porosity were generally smaller than the values based on the $0.5 \cdot C_{Br}$. In general, the pore volume values based on the concentration of a conservative tracer are considered as more accurate, since the effective porosity values can be ambiguous because of incomplete saturation due to entrapped air in the sample and/or because of errors in the determination of the water volume used for the saturation (Van Genuchten and Wierrega, 1986).

Selenium concentration of the effluent was based on the ICP-MS analysis (Figs. 17 to 19) and ranged between 1.5 and 870 $\mu\text{g/L}$ with an average of 50 $\mu\text{g/L}$ Se. The error bars on the selenium concentrations are based on the analytical precision and the dilution of the effluent before the analysis. Splits from the same samples analyzed for Se and Br have been used (before the acidification-preservation) for the determination of the electrical conductance and the pH of the effluent.

Table 11. Location, material and physical properties of the columns.

Borehole		JM-17			JM-16			
Column number		1	2	3	4	5	6	7
Core depth (cm BLS)		0-10cm	60-75cm	360-370cm	20-30cm	30-40cm	65-70cm	70-75cm
Material in column		Surface soil	Deeper soil *	Weathered shale	Surface soil	Surface soil, irradiated	Deeper soil *	Deeper soil *, irradiated
Volume (cm ³)	dry	1279.8	1849.5	1001.0	1475.4	1164.8	846.0	812.4
	wet	1316.6	1884.7	1157.6	1517.1	1232.5	881.2	875.6
Dry weight (g)		1533	3211.4	1480.7	1801.7	1361.5	1129.9	1029.5
Water content (%)		8.17	6.95	22.35	10.07	13.46	3.35	3.28
Bulk density (g/cm ³)		1.20	1.74	1.48	1.22	1.17	1.34	1.27
Particle density (g/cm ³)		2.66	2.69	2.75	2.70	2.70	2.71	2.71
Porosity	Total (n _t)	0.55	0.35	0.46	0.55	0.57	0.51	0.53
	Effective (n _e)	0.46	0.19	0.30	0.37	0.42	0.40	0.42
	Based on 0.5C _{Br}	0.46	0.28	0.41	0.16	0.45	0.41	0.44
Flow rate (cm ³ /min)		11.15	1.38	0.06	17.71	12.82	5.21	3.48
Hydraulic conductivity	(cm/s)	1.3x10 ⁻³	1.6 x 10 ⁻⁴	6.7 x 10 ⁻⁶	2.0 x 10 ⁻³	1.4 x 10 ⁻³	5.5 x 10 ⁻⁴	3.7 x 10 ⁻⁴
	(m/day)	1.08	0.14	0.01	1.74	1.24	0.48	0.32
Pore volume (cm ³)	based on n _t	702	655	462	809	661	429	432
	based on n _e	590	360	305	550	495	340	342
	based on 0.5C _{Br}	591	520	412	260	525	350	360

cm BLS: centimeters below land surface

* deeper soil is characterized as the soil below the surficial root zone

Figure 11. Electrical conductance and pH of the effluent from columns from borehole JM-17.

Figure 12. Electrical conductance and pH of the effluent from the surface soil columns from borehole JM-16.

Figure 13. Electrical conductance and pH of the effluent from the deeper soil columns from borehole JM-16.

Figure 14. Br concentration in the effluent from columns from borehole JM-17.

Figure 15. Br concentration in the effluent from surface soil columns from borehole JM-16.

Figure 16. Br concentration in the effluent from deeper soil columns from borehole JM-16.

Figure 17. Se concentration in the effluent from columns from borehole JM-17.

Figure 17 (cont.). Se concentration in the effluent from columns from borehole JM-17.

Figure 18. Se concentration in the effluent from surface soil columns from borehole JM-16.

Figure 19. Se concentration in the effluent from deeper soil columns from borehole JM-16.

Results indicate that a number of factors have an effect on the Se concentration of the effluent and the Se production from each column. These factors include the sample quantity (Table 11), the residence time (Table 12) and the volume of effluent (Figs. 11 to 13). To examine leaching of Se independent of those factors, Se production, in μg Se per Kg of dry soil per liter of effluent, and cumulative Se production, in μg Se per Kg of dry soil, were determined (Figs. 20 to 22). The Se production from all the columns ranged between 1 and 270 $\mu\text{g}/(\text{Kg}\cdot\text{L})$. The Se cumulative production at the end of each experiment ranged between 5.6 and 119 $\mu\text{g}/\text{Kg}$, with an average of 36 $\mu\text{g}/\text{Kg}$.

Table 12. Pore volume, flow rate and residence time for columns.

Column	Depth (cm BLS)	Material	Pore volume (cm^3)	Flow rate (cm^3/min)	Residence time		
					min	hr	d
1	0-10	Surface soil	591	11.15	53	0.88	0.037
2	60-75	Deeper soil	520	1.38	377	6.28	0.262
3	360-370	Weathered shale	412	0.06	6867	114.44	4.769
4	20-30	Surface soil	540	17.71	30	0.51	0.021
5	30-40	Surface soil (irradiated)	525	12.82	41	0.68	0.028
6	65-70	Deeper soil	350	5.21	67	1.12	0.047
7	70-75	Deeper soil (irradiated)	360	3.48	103	1.72	0.072

cm BLS: centimeters below land surface

Considering the variability of the flow rate, the Se production rate, in μg Se produced per Kg of dry soil per elapsed minute, was also determined (Figs. 23 and 24). The Se production rate from all the columns ranged between 1.8×10^{-4} and 3.7×10^{-1} $\mu\text{g}/(\text{Kg}\cdot\text{min})$.

Figure 20. Se production and cumulative production from columns from borehole JM-17.

Figure 20 (cont.). Se production and cumulative production from columns from borehole JM-17.

Figure 21. Se production and cumulative production from surface soil columns from borehole JM-16.

Figure 22. Se production and cumulative production from deeper soil columns from borehole JM-16.

Figure 23. Se production rate from columns from borehole JM-17.

Figure 24. Se production rate from columns from borehole JM-16.

DISCUSSION

Field Sampling

Water Samples

The surface water samples taken from the Green River and Ashley Creek in September 1999 had higher TDS than those taken in May-June 1999 (Tables 1, 2 and 8). This is inferred to be due to irrigation drainage water with high salinity and to evaporation. Irrigation drainage was possibly the main reason for the TDS increase in Ashley Creek with evaporation being less significant. In contrast, the samples from the Brush Creek had TDS values of 259 and 253 mg/L for June and September 1999, respectively. Brush Creek is connected with Red Fleet Reservoir in order to provide the irrigation water for the study area, and so it was not affected by evaporation or irrigation drainage because the sample was obtained above the irrigated land.

Compared to samples taken in May-June 1999, the TDS of the groundwater samples taken in September 1999 decreased for seven sampling locations, increased for three sampling locations, and remained almost constant for two sampling locations (Table 8). This fact, along with the water chemistry, indicated that some of the wells were influenced by irrigation (increase in water levels and decrease in TDS) and others were not. In addition, the water chemistry indicated that recharge by irrigation, mixing of water with different water-qualities, and evaporation were responsible for the variability of the groundwater composition in the study area.

The average concentration of Se for the surface water samples was $7.6 \pm 14 \mu\text{g/L}$ ($1.7 \pm 1 \mu\text{g/L}$ for the May-June 1999 sampling and $13 \pm 17 \mu\text{g/L}$ for the September 1999 sampling, Table 8). The average Se concentration in the groundwater samples was $43 \pm 40 \mu\text{g/L}$ ($51 \pm 45 \mu\text{g/L}$ for the May- June 1999 sampling and $36 \pm 33 \mu\text{g/L}$ for the September 1999 sampling, Table 8). The changes in the Se concentration indicate that irrigation return and evaporation increased the concentration of Se in the surface water samples for the sampling of September 1999 in relation to the sampling of May-June 1999, particularly for Ashley Creek. Recharge by irrigation decreased the Se concentration in the groundwater samples for the sampling of September 1999 in relation to the sampling of May-June 1999. These results indicated that Se enrichment of the groundwater was controlled by in-situ leaching of Se from the area and not by Se transported in surface water from other areas.

The average Se concentration in the groundwater samples within the irrigated areas (Fig.4) was $77 \pm 33 \mu\text{g/L}$ ($89 \pm 33 \mu\text{g/L}$ for the May-June 1999 sampling and $65 \pm 28 \mu\text{g/L}$ for the September 1999 sampling, Table 8). The average Se concentration in the groundwater samples outside of the irrigated areas was $19 \pm 25 \mu\text{g/L}$ ($24 \pm 30 \mu\text{g/L}$ for the May-June 1999 sampling and $15 \pm 18 \mu\text{g/L}$ for the September 1999 sampling, Table 8). The greater concentrations of Se in the irrigated areas indicate that irrigation had an effect on the occurrence of Se in the groundwater. The concentration of Se in the irrigated areas was possibly increased either directly by dissolution of soluble Se species or indirectly by seasonal variations of the water table level that caused suitable redox conditions for the Se leaching. Cycling between oxidation when the water level was low

and reduction when water level was elevated could form suitable redox conditions for leaching. However, there is not a clear distinction between the samples from irrigated and non-irrigated areas; for example, samples from the non-irrigated areas were possibly influenced by the irrigation to some extent because they were obtained relatively close to irrigated areas (Fig. 4).

The relationship of the selenium concentration with the concentrations of other elements (Fig. 5) indicates that the selenium distribution in the majority of the water samples approximates a linear trend line. This trend line is formed by the surface water samples and the water samples from the wells located in both irrigated and non-irrigated areas: JM-12, JM-13, JM-15, JM-16, JM-18, 5500S/9000E and Snow well (values from Table 8, sampling location and water sample numbers in Tables 1 and 2). The rest of the water samples (from wells in non-irrigated areas: E-1, W-3, K-6, JM-11, JM-14 and JM-17) did not follow the same trend line, but formed a less obvious trend line (passing through the cluster of points at TDS of about 4,000 mg/L or sulfate of about 2,300 mg/L). The trend lines are the same for most of the major anions and cations and for the trace constituents. Equations of the trend lines and R^2 values are shown in Table 13.

Evaporation is possibly one of the controlling factors for the Se distribution in the water samples. The relationships between Se and SO_4^{2-} , Cl^- and TDS in ground water, however, are more complex as indicated from the two or more trends and significant scatter depicted in Figure 5.

Table 13. Trend lines of Se versus TDS, SO_4^{2-} and Cl^- for the water samples.

Date (trend line)	TDS (mg/L)		SO_4^{2-} (mg/L)		Cl^- (mg/L)	
	equation	R^2	equation	R^2	equation	R^2
June 99 (1)	$y = 0.02x + 2.4$	0.67	$y = 0.04x + 8.4$	0.64	$y = 0.9x + 14$	0.47
September 99 (1)	$y = 0.02x - 5.8$	0.96	$y = 0.04x + 2.6$	0.96	$y = 0.9x + 0.5$	0.83
June 99 (2)	$y = 0.004x - 5.7$	0.29	$y = 0.006x - 6.8$	0.34	$y = 0.25x - 16$	0.73
September 99 (2)	$y = 0.002x - 3.1$	0.77	$y = 0.003x - 2.6$	0.77	$y = 0.05x - 0.06$	0.46

(1) trend lines for samples from surface water and JM-12, JM-13, JM-15, JM-16, JM-18, 5500S/9000E and Snow well

(2) trend lines for samples from E-1, W-3, K-6, JM-11, JM-14 and JM-17.

y = Se concentration in $\mu\text{g/L}$, x= mg/L of the constituent selected for comparison

Samples taken from JM-14 (September 1999 sampling) with total dissolved solids about 10,000 and JM-17 (June and September 1999 sampling) with total dissolved solids of 15,000 mg/L and 16,000 mg/L, respectively, had relatively low selenium concentrations and do not follow the same pattern (outliers in Fig. 5). Furthermore, water quality for JM-14 and JM-17 was different from that of the rest of the groundwater samples (for example, nitrate concentrations of about 150 mg/L and 900 mg/L in JM-14 and JM-17, respectively; also, the stable water isotope ratios deviated from those of the rest of the samples, Kharaka et al., 2001). Most likely local conditions such as leaching of fertilizers, seepage from sewer ponds or septic tanks, etc. were responsible for these differences.

Soil and Mancos Shale Samples

Concentrations of Se and the other elements in the core samples were used in a statistical analysis to determine their relationship. The relationships were analyzed with

respect to all samples and individually for shale and soil samples (Table 14). The R^2 values were used to examine the linear (first order) relationship, where:

$$R^2 = \left(\frac{n(\sum xy) - (\sum x)(\sum y)}{\sqrt{[n\sum x^2 - (\sum x)^2][n\sum y^2 - (\sum y)^2]}} \right)^2.$$

The relationship of Se to the other elements was also evaluated for individual boreholes (Table 15) in the boreholes JM-11, JM-13, JM-14, JM-16, and JM-17. The data from JM-17 were the most significant because 10 samples were obtained. Only 4 or 5 samples were obtained from each of the other boreholes. The values of R^2 and $\rho(x, y)$ (correlation coefficient) were used for the location-based statistical analysis, where:

$$\rho(x, y) = \frac{\text{cov}(x, y)}{\sigma_x \times \sigma_y}, \text{ and } \text{cov}(x, y) = \frac{1}{n} \times \sum_{i=1}^n (x_i - \mu_x) \times (y_i - \mu_y) .$$

where:

μ_x = the mean of the individual element data set

μ_y = the mean of the selenium data set.

The $\rho(x, y)$ (correlation coefficient) values were used to determine if the concentrations of Se and other elements had a non-linear relationship (e.g., second or third order). In general, the $\rho(x, y)$ is used to determine whether two sets of data vary together. If large values of one set are associated with large values of the other the correlation coefficient is positive. If small values of one set are associated with large values of the other the correlation coefficient is negative, and if values in both sets are unrelated the correlation coefficient is near zero.

Table 14. R^2 values for correlation between Se and other elements for all the samples.

Element	All samples	Shale	Soil
Li	0.36	0.09	0.64
Be	0.20	0.01	0.49
Na	0.20	0.01	0.26
Mg	0.27	0.01	0.61
Al	0.25	0.08	0.33
P	0.29	0.01	0.63
K	0.07	0.07	0.04
Ca	0.03	0.12	0.34
Sc	0.32	0.04	0.53
Ti	0.32	0.06	0.50
V	0.34	0.08	0.51
Cr	0.32	0.04	0.59
Mn	0.03	0.02	0.31
Fe	0.39	0.21	0.46
Co	0.34	0.14	0.46
Ni	0.40	0.24	0.51
Cu	0.28	0.01	0.45
Zn	0.34	0.05	0.55
Ga	0.26	0.05	0.38
As	0.43	0.32	0.30
Rb	0.26	0.09	0.29
Sr	0.01	0.00	0.08
Y	0.26	0.02	0.41
Mo	0.09	0.02	0.28
Cd	0.05	0.01	0.24
Sb	0.18	0.01	0.34
Cs	0.31	0.04	0.56
Ba	0.01	0.12	0.18
La	0.15	0.03	0.11
Ce	0.14	0.05	0.10
Tl	0.29	0.10	0.32
Pb	0.15	0.00	0.34
Bi	0.23	0.01	0.61
Th	0.15	0.03	0.21
U	0.38	0.16	0.66
C-Carbonate	0.06	0.19	0.43
C-Organic	0.16	0.13	0.42
C-Total	0.17	0.01	0.55

Table 15. R^2 and $\rho(x, y)$ values for Se and other elements at individual boreholes.

Element	Borehole									
	JM-11		JM-13		JM-14		JM-16		JM-17	
	R^2	$\rho_{(x,y)}$	R^2	$\rho_{(x,y)}$	R^2	$\rho_{(x,y)}$	R^2	$\rho_{(x,y)}$	R^2	$\rho_{(x,y)}$
Li	0.05	0.23	0.33	0.58	0.86	0.93	0.91	0.95	0.19	0.44
Be	0.16	0.40	0.02	0.14	0.18	0.43	0.67	0.82	0.02	0.13
Na	0.00	0.01	0.00	-0.01	0.28	0.53	0.99	-0.99	0.09	-0.30
Mg	0.00	0.06	0.65	0.80	0.09	0.29	0.94	0.97	0.02	0.14
Al	0.03	0.17	0.10	0.31	0.21	0.46	0.56	0.75	0.09	0.31
P	0.03	0.17	0.62	0.79	0.10	0.32	0.90	0.95	0.04	0.19
K	0.00	-0.01	0.09	0.30	0.01	0.11	0.01	0.11	0.14	0.37
Ca	0.05	-0.22	0.38	0.62	0.00	0.02	0.78	0.89	0.17	-0.41
Sc	0.07	0.27	0.24	0.49	0.72	0.85	0.86	0.93	0.08	0.29
Ti	0.02	0.14	0.22	0.47	0.64	0.80	0.71	0.84	0.11	0.33
V	0.05	0.22	0.23	0.47	0.76	0.87	0.86	0.93	0.20	0.44
Cr	0.03	0.16	0.17	0.41	0.85	0.92	0.86	0.93	0.15	0.39
Mn	0.29	-0.54	0.51	0.71	0.49	0.70	0.90	0.95	0.03	-0.16
Fe	0.05	-0.23	0.21	0.46	0.50	0.70	0.87	0.93	0.20	0.44
Co	0.58	0.76	0.13	0.36	0.68	0.82	0.84	0.92	0.04	0.21
Ni	0.68	0.83	0.29	0.54	0.50	0.70	0.87	0.93	0.15	0.38
Cu	0.18	0.42	0.58	0.76	0.57	0.76	0.88	0.94	0.01	0.08
Zn	0.34	0.58	0.42	0.65	0.95	0.98	0.89	0.94	0.08	0.28
Ga	0.01	0.08	0.06	0.24	0.44	0.67	0.58	0.76	0.09	0.31
As	0.00	0.002	0.44	0.66	0.06	0.25	0.84	0.92	0.46	0.68
Rb	0.01	0.12	0.08	0.28	0.39	0.62	0.52	0.72	0.13	0.36
Sr	0.05	-0.23	0.00	-0.03	0.55	0.74	0.12	-0.34	0.00	-0.03
Y	0.02	0.04	0.23	0.48	0.13	0.36	0.82	0.91	0.02	0.14
Mo	0.08	-0.27	0.45	0.67	0.76	-0.87	0.83	0.91	0.53	0.73
Cd	0.09	0.31	0.43	0.65	0.36	-0.60	0.91	0.95	0.07	0.26
Sb	0.00	0.03	0.56	0.75	0.00	-0.05	0.74	0.86	0.05	0.23
Cs	0.03	0.18	0.25	0.50	0.86	0.93	0.87	0.93	0.09	0.30
Ba	0.29	0.54	0.35	-0.59	0.20	0.44	0.85	-0.92	0.11	0.33
La	0.05	0.22	0.28	0.53	0.15	0.39	0.17	0.41	0.05	0.22
Ce	0.09	0.30	0.21	0.45	0.13	0.36	0.09	0.30	0.04	0.21
Tl	0.33	0.57	0.46	0.68	0.00	-0.03	0.79	0.89	0.13	0.36
Pb	0.07	0.27	0.59	0.77	0.05	-0.22	0.68	0.82	0.02	0.12
Bi	0.01	0.08	0.65	0.81	0.09	0.29	0.46	0.68	0.00	0.06
Th	0.00	0.01	0.33	0.57	0.41	0.64	0.01	0.11	0.05	0.22
U	0.03	0.16	0.34	0.58	0.58	0.76	0.78	0.88	0.21	0.46
C-Carbonate	0.00	-0.01	0.65	0.81	0.01	-0.09	0.76	0.87	0.20	-0.44
C-Organic	0.75	0.86	0.47	0.69	0.24	-0.49	0.60	0.78	0.20	0.44
C-Total	0.52	0.72	0.61	0.78	0.09	-0.31	0.84	0.92	0.02	0.13

Statistical analysis of samples from the entire study area indicated that the selenium concentrations were not strongly correlated with the concentrations of the other elements. The R^2 values (Table 14) were too small to prove a positive or negative relationship. The greatest R^2 value (0.66) was found for uranium and selenium for the soil samples. The weak relationship can be explained by the fact that the samples consisted of different materials. In addition, the geochemical conditions varied within the study area and a variety of factors, such as the evaporation of different waters, the microbial activity or uptake by plants, contributed to the selenium occurrence at each sampling site.

In general, the R^2 values were much greater for soils than for shale (Table 14). The shale samples consisted of intact and weathered shale samples. The geochemical conditions that caused the Se enrichment of Mancos Shale were related to the deposition of selenium-rich volcanic detritus at the reducing and organic-rich Cretaceous sea bottom. Processes such as ionic substitution for sulfur, reactions with organic material and sorption were involved (Butler et al., 1996). Molybdenum, arsenic, uranium and sulfur usually have a positive correlation with Se in shale, because they have similar sources and depositional environments. However, the geochemical conditions that favored the mobilization of U, As, Cr, V, Mo and Se were possibly different, so the R^2 values for Se and these elements were small in the weathered shale samples of the shale data set. Conversely the geochemical conditions that favored the accumulation of U, As, Cr, V, Mo and Se in soil were similar, so the R^2 values for Se and these elements in the soil samples were greater. In addition, the $\rho(x, y)$ values for all the elements listed

above and the organic carbon were higher in the soil samples than in the shale samples, indicating an increased positive relationship with organic carbon in soil samples relative to the shale samples (Table 16). For example, $\rho(x, y)$ values for U and organic C were $\rho = 0.31$ for the shale samples and $\rho = 0.49$ for the soil samples; $\rho(x, y)$ values for V and organic C were $\rho = 0.34$ for the shale samples and $\rho = 0.53$ for the soil samples; and $\rho(x, y)$ values for Se and organic C were $\rho = 0.36$ for the shale samples and $\rho = 0.65$ for the soil samples. Probably the relationship with organic C was the reason for the greater R^2 and $\rho(x, y)$ values for Se with U, As, Cr, V, Mo in the soil samples.

Table 16. $\rho(x, y)$ values for organic C and selected elements for shale and soil samples.

Element	U	As	Cr	V	Mo	Se
Sample						
Shale	0.31	-0.05	0.38	0.34	-0.05	0.36
Soil	0.49	0.17	0.60	0.53	0.37	0.65

The relationship of the selenium distribution with the other elements on a location basis (Table 15) has been evaluated in the boreholes JM-11, JM-13, JM-14, JM-16 and JM-17. The values of R^2 for individual boreholes were significantly larger than the values for all the samples (Table 14). This can be explained if the geochemical conditions are similar throughout each individual borehole and dissimilar between the different boreholes. In addition, the larger values of $\rho(x, y)$ were observed when Se and elements with similar geochemistry such as U, As, Cr, V, Mo were compared. Although

the number of samples from each borehole (except JM-17) was rather small for a confident statistical analysis, it can be inferred based on the $\rho(x, y)$ values for JM-17 (Table 15) and the average $\rho(x, y)$ values for all the boreholes that the selenium occurrence was positively related with the concentrations of uranium (average $\rho(x, y) = 0.57$), arsenic (average $\rho(x, y) = 0.50$), chromium (average $\rho(x, y) = 0.56$), vanadium (average $\rho(x, y) = 0.59$), molybdenum (for JM-17 $\rho(x, y) = 0.73$) and organic carbon (average $\rho(x, y) = 0.46$).

The selenium concentrations did not correlate, or were negatively correlated, with the concentrations of sodium (average $\rho(x, y) = -0.15$ and for JM-17 $\rho(x, y) = -0.30$), calcium (average $\rho(x, y) = 0.18$ and for JM-17 $\rho(x, y) = -0.41$) and carbonate carbon (average $\rho(x, y) = 0.23$ and for JM-17 $\rho(x, y) = -0.44$). The high $\rho(x, y)$ values for elements with a geochemistry different from that of selenium (for example, Sc, Zn) that were found in the samples from JM-14 and JM-16 (Table 15) were probably attributable to the small number of samples analyzed (4 and 5, respectively).

Statistical analysis, especially when a small number of samples is involved, is not always an accurate method to determine the relationship between selenium and the other elements. Therefore, the relationship between Se and U, Mo, As, Ca, organic C and carbonate C was also determined using the normalized concentrations ($C_i/C_{\max}$) as a function of depth at the boreholes JM-17, JM-16 and JM-11 (Figs. 6 to 8). Selenium had a positive relationship with the elements with geochemical similarities (U, Mo and As) and with organic carbon, indicating that a fraction of Se was in the organic form.

Selenium had a negative relationship with Ca and carbonate carbon, indicating that Se was not associated with carbonate minerals. Similar patterns have been observed in the rest of the boreholes. Increased concentrations of U, Mo and As along with Se were also found in soils from West-Central Colorado (Butler et al., 1996). The positive relationship of the Se occurrence with U, Mo, As and organic carbon was also observed in studies related with the transportation and precipitation of uranium at low temperatures (Langmuir, 1997). These results (organic Se occurrence and the absence of Se associated with carbonates) were used for the determination of the Se sequential extraction method used for the batch tests.

Although the number of samples was rather small for a confident evaluation, the comparison of the Se concentration in the soil from irrigated and non-irrigated areas indicated that a fraction of Se had already leached from the soil in the irrigated areas. The average Se concentration in the soil from the irrigated areas was slightly lower (1.0 ± 0.4 ppm, $n = 8$) than the average Se concentration in the soil from the non-irrigated areas (1.3 ± 0.4 ppm, $n = 3$). The Se concentration in the surface soil and in the soil below the surficial zone from irrigated and non-irrigated areas was also compared. The comparison indicated that a small fraction of Se had already leached from the surface soil in the irrigated areas; Se had not leached from the soil horizon below the surficial root zone. The average Se concentration in the surface soil from the irrigated areas was 1.3 ± 0.2 ppm ($n = 3$) and in the surface soil from the non-irrigated areas was 1.5 ± 0.4 ppm ($n = 2$). The average Se concentration in the deeper soil (below the surficial root zone) was

the same in both cases (0.9 ± 0.3 ppm, $n = 5$ for the irrigated areas, $n = 1$ for the non-irrigated areas).

Batch Tests

Selenium Forms in the Core Samples

The Se forms obtained by the sequential extractions were the soluble Se, sorbed Se, elemental Se and Se associated with organic matter. Selenium recovery from the sequential extractions of the batch tests ranged from 60% to 101% of the total Se value with an average of 89% (Table 10, Fig. 9). The Se recoveries indicated that the major part of the Se inventory consisted of the extracted forms in the samples analyzed. The one low recovery (60%, sample JB-99090) is probably attributable to the selenium bound in oxides, which was not extracted. Results from the batch tests indicated that selenium in the tested soil and weathered shale samples occurs mainly as selenium associated with organic material and as elemental selenium (Table 10, Figs. 9 and 10). Elemental Se and Se associated with organic matter were the major fractions of the total Se in sediment and core samples from Benton Lake, MT (Zhang and Moore, 1996) and in soil samples from a vegetated area at Kesterson, CA (Tokunaga et al., 1991). The Se associated with organic matter was also the major fraction in river and estuarine sediments from Québec, Canada and reservoir sediments from Hyco, NC (Cutter, 1985). The distribution of selenium in the various forms was not uniform in the tested samples in this study, but depended mainly on the material (soil or shale) and the location of the sample relative to the surficial root zone (Tables 4 and 10). For example, smaller percentages of soluble Se

were found in the surface soil samples (average 1.6% of total Se) and the weathered shale samples (average 2.5%) than in the soil samples below the surficial root zone (average 32.2%).

Effect of Grinding and Drying on the Se Distribution

The effect of grinding and drying on the distribution of Se into various forms was evaluated (Table 10). Although the recoveries for the unground and ground samples were almost the same (97% and 101% of the total Se, respectively), the distribution of Se in the ground sample had significantly changed from the unground. In the unground sample, 60% of total Se was associated with organic matter and 34% was elemental Se: in the ground sample, Se associated with organic matter was 31% of total and elemental Se was 67%. Selenium and organic matter most likely were oxidized during grinding and drying. The most strongly affected was the selenium associated with the organic material, which was oxidized to elemental Se, because of the oxidation of the organic material. Further oxidation to the forms of Se^{+4} and Se^{+6} is a very slow process (McNeal and Balistrieri, 1989) and occurred to a much lesser extent. Zhang and Moore (1997b) had also observed changes in the Se distribution into various forms because of drying. The Se results indicate that the samples used for sequential extractions should not be ground or dried, if an adequate recovery of Se can be achieved from the unground samples.

Distribution of the Se Forms in the Soil Samples

Of particular interest is the fact that the concentrations and the percentages of the soluble selenium form, selenate (SeO_4^{2-}) and soluble organic Se species, were elevated in the soil samples taken below the surficial root zone (samples JB-99021, JB-9960D, JB-99080) but above the water table (Tables 4 and 10, Figs. 9 and 10). This indicates that depletion of soluble Se from the surface soil and accumulation of soluble Se in the soil below the surficial root zone occurred. However, total selenium concentration in the samples below the root zone was smaller than the total selenium concentration in the samples taken from the surface soil horizon at the same sites (surface soil samples JB-99011, JB-99050D and JB-99070). Total Se should be increased if only soluble Se was leached from the surface soil and then accumulated in the soil below the surficial root zone; this indicates that other processes were also involved. The surficial root zone soil consisted of the surface soil where the roots of the grass plants were abundant, in a depth less than 0.5 m below land surface. The root zone depths could be visually identified, because clear PVC tubes were used as a core barrel liner.

The elevated total Se concentration and decreased soluble Se concentration in the surficial root zone soil most likely were caused by processes such as leaching and vegetative uptake of Se and the accompanying transformation to Se associated with organic matter (immobilized in organic forms). Decay of organic matter and leaching of the soluble Se forms (oxidized Se^{+6} and soluble organic Se) by the percolation of the precipitation and irrigation water decreased the soluble Se concentration in the surface

soil. Accumulation of the Se leached from the surface soil increased the soluble Se fraction in the soil below the surficial root zone.

There are a number of reasons that could explain the decreased total Se concentration in the soil below the surficial root zone. Possibly during dry periods in this arid to semi-arid area, water with increased soluble Se concentrations migrated from the moist deeper soil to the dry surface soil where plants used it and immobilized the soluble Se into organic forms, thus increasing the total Se concentration in the surface soil. During wet periods or for the duration of the irrigation season, soluble Se was possibly leached deeper. Fluctuation of the water table is not likely to be responsible for the Se distribution in the samples tested because all the soil samples used for the batch tests were taken above the water table (Table 4) and observed water level fluctuations between May-June 1999 and September 1999 were small. However, the capillary fringe could be responsible for a part of the accumulation of soluble Se in the soil below the surficial root zone. Soil samples taken below the water table had concentrations of Se (Tables 1 and 9) less than the arbitrary limit selected for the batch tests (0.9 ppm Se). The fact that the total Se concentration in the soil below the root zone was smaller than in the surface soil (Table 10, Fig. 10) is an indication that the vegetative uptake near the soil surface is an important factor influencing the Se distribution because that vegetative uptake immobilizes Se, as does the microbial activity. The results from the column experiments also indicated the importance of the microbial activity because the Se leaching from the irradiated/sterilized columns was greater. All these processes were involved in the Se distribution in the soil, although the significance of each process could not be determined.

In previous studies of soils in seleniferous areas from California (Zawislanski and Zavarin, 1996) and South Dakota (Olson et al., 1942; Abu-Erriesh et al., 1968), it was also found that the soluble Se content of the upper part of the soil profile was considerably lower than the soluble Se content of the lower part.

In general, the processes controlling the distribution of Se in different forms were similar in the soil samples taken from both irrigated and non-irrigated areas (Tables 4 and 10, Fig. 4), but the number of analyzed samples was too small to compare accurately the Se distribution in soils from irrigated and non-irrigated areas. Possibly irrigation had mobilized a small part of the soluble Se from the surface soil as total Se analysis and batch tests indicated (Tables 4 and 10, Fig. 4), but this is ambiguous because of the small number of the analyzed samples.

Column Experiments

Electrical Conductance and pH of the Effluent, Applied Water Solutions

Electrical conductance, which is directly related to the amount of dissolved ions, indicated that the greater part of the soluble salt load was released in the first two pore volumes of the effluent (Figs. 11 to 13). The electrical conductance of the effluent from all columns was initially low except for column 1. The water solution that initially exited from the columns was the water solution used for the saturation of the columns from the bottom up, so it had not passed through the entire column but only through a small part of it. The irregular distribution of the soluble salts in column 1 possibly was the reason for the increased electrical conductance in the beginning of the experiment. A temporary

increase in the electrical conductance of the effluent of column 1, and to a lesser extent of columns 6 and 7, occurred when the experiments were stopped (an automated system for the collection of the effluent was not available), increasing the residence time of the first one or two samples collected after the experiments were resumed. The experiment was stopped after collecting 1.5, 2.9 and 4.3 pore volumes (for about two hours in each case) from column 1. The experiment was stopped overnight after collecting 1.9, 2.1 and 1.9 pore volumes from columns 2, 6, and 7, respectively. The effects can be observed in the electrical conductance curve of column 1 (Fig. 11) where the curve showed temporary small increase upon recommencing flow, and to a lesser extent in the electrical conductance curves of the columns 6 and 7 (Fig. 13). The overnight stop of the experiment also temporarily increased the Se concentration in the samples from the columns 6 and 7 collected at pore volumes 2.3 and 2.2, respectively (Fig. 19). The irregular pattern of the selenium concentration curve for column 1 (Fig. 17) is probably attributable to the non-uniform distribution of Se through the column and to stopping flow. Channeling during the experiment is not likely to have occurred, because this would have resulted in a small calculated pore volume value based on the Br concentration of the effluent, such as for column 4 (Table 11).

De-ionized water was applied to the columns 1 through 5 before collecting the final three samples (three final points on the curves). De-ionized water did not affect the electrical conductance and the Se concentration of the effluent. Other researchers (Alemi et al., 1988) have found increased Se concentrations in the effluent when they compared applied de-ionized water with saline water. The differences in the Se concentration of the

effluent caused by the irrigation water and de-ionized water were probably too small to be observed because the irrigation water used for the column experiments had low TDS (259 mg/L). The temporary increase of the electrical conductance and the small increase of the Se concentration in the effluent from column 5 at the point corresponding to 3.8 pore volumes (Figs. 12 and 18) was attributed to the increased residence time when collecting that specific sample (a decreased flow rate was observed at that time). This increase is not observed in the production rate curve (Fig. 24), indicating that the increased residence time was the only reason for the increased Se concentration.

Changes in the pH (columns 1, 2 and 3) of the applied water did not affect the Se concentration of the effluent. The buffering capacity of the soil was determined, and the results indicated that 5 g of dry soil could buffer sequentially at least 100 mL of irrigation water from pH 8.85 to pH 7.78 and 100 ml from pH 5.5 to pH 7.75, within 10 min. The volume of the applied irrigation water was about 1,000 mL, for the pH-adjusted series in columns 1, 2 and 3, and the soil dry weight ranged from 1,480 g to 3,211 g. Based on the buffering capacity, the soil buffered the pH in the first 2-3 mm of the core, so the effect along the length of the core was negligible. The relatively constant pH of the effluent (Figs. 11 to 13), independent of the pH of the applied water, is caused by the great buffering capacity of the soil. Because of this buffering effect, pH-adjusted irrigation water was not applied to the rest of the columns (columns 4 through 7).

Nitrate was applied only to columns 4 through 7. Columns 1 through 3 were obtained from JM-17 and were already exposed to high nitrate concentrations since the concentration of nitrate in groundwater ranged from 840 mg/L to 930 mg/L (Table 8).

The nitrate addition to columns 4 through 7 had no effect on the selenium leaching rate possibly because the presence of dissolved oxygen in the applied water (about 8 mg/L) kept the environment from being significantly reducing. Highly reducing conditions would decrease the mobility of Se because of the reduction of the mobile oxidized Se forms. In addition, the nitrate in soil was abundant for the microbial activity and the residence time of the nitrate in the column possibly was not sufficient for the oxidation of the reduced Se forms, although results (NO_3^- in the effluent) indicated that the residence time was sufficient for a small consumption of nitrate (close to the detection limit) by the microbial activity in the non-sterilized columns. However, the redox conditions inside the columns were not determined because this would require a major disturbance of the core.

Selenium in the Effluent

Non-Irradiated Samples. The selenium concentration in the effluent was significantly higher for the columns consisting of soil below the surficial root zone (deeper soil) at both boreholes JM-17 and JM-16 (Figs. 17 to 19, Table 17). This is in agreement with the results from the batch tests (Tables 4 and 10), where it was found that the percentage of the soluble selenium was greater in the samples below the surficial root zone. The total selenium concentration in the surface soil was greater than in the deeper soil, but the increased contribution of the soluble selenium form in the deeper soil accounted for this increase in selenium leaching. Most of the selenium from the deeper soil and the weathered shale columns was released within the first one to two and a half

pore volumes (Figs. 17 to 19). For the non-irradiated surface soil, at least three pore volumes were necessary to release most of the selenium (Figs. 17 to 19). By the end of the experiments, when the selenium concentration of the effluent remained approximately constant (approximating a steady-state indicative of the long-term Se leaching), the selenium concentration of the effluent from the deeper soil and the weathered shale columns was smaller than the concentration from the surface soil columns.

Table 17. Se concentration in the effluent.

Column No.	Borehole	Material-depth (cm BLS)	Se (µg/L) max	Se (µg/L) at approx. steady state	Pore volumes to approx. steady-state
1	JM-17	Soil 0-10	26.3	6.3	3.6
2	JM-17	Soil 60-75	867	3.5	3.7
3	JM-17	Weathered Shale 360-370	13.7	4.5	4
4	JM-16	Soil 20-30	5.3	3.5	4.5
5	JM-16	Soil 30-40 [#]	28.2	4.9 [#]	4.8 [#]
6	JM-16	Soil 65-70	23.5	1.7	7.9
7	JM-16	Soil 70-75 [#]	50.8	3.6	8.2

cm BLS: centimeters below land surface

[#] Sterilized (irradiated) soil columns

[#] [#] Not at steady-state by the end of the experiment; Se concentration was still decreasing.

The Se results indicated that the selenium from the soil below the surficial root zone leached rapidly and so increased significantly the selenium concentration of the percolating water for the initial pore volumes of soil, but then the leaching decreased abruptly. Selenium concentration in the effluent from the surface soil was smaller for the initial pore volumes, but was relatively constant through the experiment.

In terms of the selenium production, the results were similar (Figs. 20 to 22). The production was much greater for the initial pore volumes from the deeper soil than from the surface soil (Table 18). By the end of the experiment, the surface soil was producing more selenium than the deeper soil and the weathered shale. A small percentage of total Se was leached from the surface soil in the initial pore volumes. Production was more constant throughout the experiment, most likely because the soluble Se concentration was smaller and the total Se concentration was greater in the surface soil than in the corresponding soil below the surficial root zone. The curve of the Se production for the column consisting of weathered shale (Fig. 20) has a pattern intermediate between the surface and deeper soil columns. Although there is a rather small percentage of soluble Se in weathered shale (2%), the high total Se concentrations (3.0 ppm) possibly could increase slightly the production for the initial pore volumes and also keep a relatively constant production.

In terms of the selenium cumulative production, much more selenium had been leached from the deeper soil than from the surface soil on the time frame of the experiment (Figs. 20 to 22). The cumulative production curves for the deeper soil are steep for the initial pore volumes and flatten toward the ending of the experiment, indicating that the majority of Se was produced in the initial pore volumes and a small amount was produced in the final pore volumes. For the JM-17 deeper soil, 99% of the total leached Se had leached with the first two pore volumes out of 3.7 pore volumes in total. The cumulative production curves for the surface soil have a more constant slope, indicating that the Se production was more evenly distributed throughout the experiment.

For the JM-17 surface soil, 50% of the total leached Se had leached with the first two pore volumes (out of 5.5 pore volumes in total). The cumulative production curves for the surface soil did not flatten toward the end indicating that the Se production had not decreased as much as the Se production from the deeper soil columns had decreased by the end of the experiment. The Se cumulative production curve for the weathered shale column had a pattern intermediate between the curves for the surface and the deeper soil, possibly for the same reasons as for the production curve.

Table 18. Se production.

Column No.	Borehole	Material-depth (cm BLS)	Se production, max [$\mu\text{g}/(\text{kg}\cdot\text{L})$]	Se production, approx. steady state [$(\mu\text{g}/(\text{kg}\cdot\text{L}))$]
1	JM-17	Soil 0-10	16.6	3.3
2	JM-17	Soil 60-75	269.9	1.7
3	JM-17	Weathered Shale 360-370	9.3	2.7
4	JM-16	Soil 20-30	2.9	1.9
5	JM-16	Soil 30-40 [#]	20.7	3.6 ^{# #}
6	JM-16	Soil 65-70	20.8	1.5
7	JM-16	Soil 70-75 [#]	50	3.4

cm BLS: centimeters below land surface

[#] Sterilized (irradiated) soil columns

^{# #} Not at steady-state by the ending of the experiment; Se concentration was still decreasing.

The columns consisted of different material, so they had different permeabilities (Table 11), and the residence time of the water solution within each column was different. The Se production rates were determined to obtain the time frame of Se production, to compare accurately the Se productions from all the columns, and to

evaluate the effect of the residence time on Se leaching (Figs. 23 and 24). Comparison of the Se concentration and production curves (Figs. 17 to 22) with the production rate curves (Figs. 23 and 24) indicated that when residence time was increased Se concentration and production were also increased. The production rates were greater for the deeper soil columns and smaller for the corresponding surface soil columns for the initial pore volumes (Figs. 23 and 24). When a steady-state was approached at the end of the experiment, the production rates for the surface soil columns were greater than for the corresponding deeper soil columns (Table 19, Figs. 23 and 24). The production rates for the surface soil columns were more constant throughout the experiment, when compared with the corresponding production rates in the deeper soil columns.

Table 19. Se production rates.

Column No.	Borehole	Material-depth (cm BLS)	Se production rate,max [$\mu\text{g}/(\text{kg}\cdot\text{min})$]	Se production rate, approx. steady state [$(\mu\text{g}/(\text{kg}\cdot\text{min}))$]
1	JM-17	Soil 0-10	0.17*	0.0259
2	JM-17	Soil 60-75	0.37	0.0025
3	JM-17	Weathered Shale 360-370	0.0006	0.0002
4	JM-16	Soil 20-30	0.05	0.0306
5	JM-16	Soil 30-40 [#]	0.26	0.0257 [#]
6	JM-16	Soil 65-70	0.12	0.0073
7	JM-16	Soil 70-75 [#]	0.18	0.0103

cm BLS: centimeters below land surface

* average of the three higher values, because of the irregular pattern of the curve

[#] Sterilized (irradiated) soil columns

[#] Not at steady-state by the ending of the experiment; Se concentration was still decreasing

The differences in the production rates between surface and deeper soil columns were probably attributable to the different percentages of soluble Se (greater in the deeper soil columns) and the total Se concentration (greater in the surface soil columns). The weathered shale had a relatively small production rate, most likely due to its very low permeability (Table 19, Fig. 23).

Irradiated Samples. An important result from the column experiments is the significantly increased selenium concentration of the effluent (Figs. 18 and 19) and the Se production (both as production and as cumulative production) from the sterilized soil columns (Figs. 21 and 22), when compared with the paired non-sterilized columns (Tables 17 and 18). This indicates that the microbial activity immobilized a significant portion of the Se. When this activity was prevented by sterilization, more Se could be leached. To compare precisely the two column pairs (columns 4 and 5 and columns 6 and 7), the Se production is normalized as production per minute (Fig. 24), because the 5 to 10 cm greater depth from the corresponding non-sterilized columns, and to a lesser extent the Co-60 irradiation, had slightly decreased the permeability of the sterilized columns (Table 11). It has been observed in laboratory experiments (Bowen and Cawse, 1963) that the rate of percolation of water through soils treated with 2.5 Mrads was reduced, probably because of decomposition or deconstruction of soil organic matter.

The difference, both in terms of production and maximum production rate, was greater for the pair of surface soil columns (Fig. 24). The major forms of Se in the surface soil columns were the Se associated with organic matter and the elemental Se; the

soluble Se was an insignificant fraction of the total Se at shallow depths (Table 10). The difference was smaller (in terms of production and maximum production rate) for the deeper soil (Fig. 24), where the soluble Se was a significant fraction of the total Se (Table 10). By the end of the experiment, the Se production rate (Table 19, Fig. 24) for each pair of columns (sterile and non-sterile) was almost the same, when the steady-state rate of long-term leaching was approached. After the sterilization, part of the Se was released, primarily because of the lack of microbial activity and, to a lesser extent, because of a small degree of decomposition or deconstruction of soil organic matter caused by the irradiation. The selected irradiation dose and rate most likely had a minimal effect on the soil organic matter (Bowen and Cawse, 1963; Ostlund et al., 1989). The released selenium most likely consisted of a variety of Se species bound by the organic matter and organic Se held in the cells of the organisms; the exact contribution of each process is unknown, but the latter probably predominated. In addition, the environment in the columns possibly became more oxidizing because the microbial activity was eliminated by the irradiation; consequently the mobility of Se was further increased. Previous studies (Alemi et al., 1988) indicated that Se concentration in the effluent from sterilized columns exceeded the Se concentration from the non-sterilized paired columns; the increased Se concentration in the effluent from the sterile columns was attributed to the limited microbial reduction of Se.

The Se portion leached from the sterile columns within the first 3 to 4 pore volumes and the production rates for the paired columns were almost equal toward the end of the experiment. The greater Se concentrations and productions for the sterilized

columns but the almost equal production rates for the sterile and non-sterile paired columns at the end of the experiment indicated that the increased Se concentration and production from the sterile columns at the end of the experiment were caused only by the increased residence time of the applied water in the columns. The irregular pattern of the selenium production rate curve from column 7 (Fig. 24) is attributed to a small fluctuation in the flow rate for the part of the experiment between two and two and a half pore volumes.

Results indicated that the Se production rates for the soil columns from JM-17 (from a non-irrigated area) were initially slightly greater than the production rates for the non-sterilized columns from JM-16 (from an irrigated area), but at the end of the experiment production rates were similar in both cases (Table 19, Figs. 23, 24). A small fraction of the soluble Se had previously been leached from the irrigated areas, but it was not large enough to alter the Se leaching rates, except during the initial pore volumes.

Forms of Se Leaching and Application to Natural Conditions

Leaching of soluble Se probably dominated a major portion of the experiment. Therefore, most of the results represent the short-term Se leaching rate, which can provide high Se concentration to the aquifers from the initial pore volumes of the soil below the surficial root zone. At the end of the experiments, the Se concentrations in the effluent and the production rates were roughly constant and so steady-state, indicative of long-term leaching, was approached.

It is likely that two different kinds of leaching occurred during the experiment: a short-term leaching of the soluble Se and the Se forms mobilized by the irradiation, and a long-term leaching of the much less mobile Se forms, including selenite, elemental Se and organic Se. After the partial removal of the soluble species, the slow mobilization of the less mobile forms responsible for the long-term leaching possibly dominated. Mobilization of these Se species probably occurs by two processes: a slow oxidation of the organic Se, elemental Se and selenite to form the soluble selenate (McNeal and Balistrieri, 1989); or the mobilization of the much less soluble and easily sorbed selenite (Elrashidi et al., 1987), elemental Se (very insoluble, McNeal and Balistrieri, 1989), or organic Se. Oxidation is most likely to be the major process controlling the long-term Se leaching. In previous studies (Alemi et al., 1988), the Se availability for transport was found to be greatly enhanced by oxidation of the Se in sediments in columns because of air-drying, indicating that oxidation is a major factor that affects the leaching of selenium.

A leaching calculation was made to evaluate whether the results from the column experiments would apply to natural conditions and if flushing of the soil could be a method for possible remediation. The average concentration of Se in the Western soils is 0.23 ppm (Butler et al., 1996). An estimation of the quantity of water and time required for leaching 1 kg of dry soil with the same physical and chemical properties as the soil used in the columns until this arbitrary Se concentration is reached is shown in Table 20. It was assumed that the leaching rate would be constant and the same as that determined at the end of the column experiments (steady-state) and that the water will percolate

through the columns continuously. It was also assumed that the geochemical conditions (Eh, pH, etc.) would be constant and the same as during the experiments, and that the percolating water would be the same as the water used for the experiments. The already leached Se, which ranged from 0.3 to 13% of the total Se, was taken into account.

Table 20. Minimum time and water quantity required for the Se leaching from 1 kg of dry soil.

Borehole	Material, depth BLS	**Water quantity (L)	Time (yr)
JM-17	Soil, 0-10 cm	707	0.12
JM-17	Soil, 60-75 cm	322	0.44
JM-17	Weathered shale 360-370 cm	850	26.9
JM-16	Soil, 20-30 cm	442	0.05
* JM-16	Soil, 30-40 cm	373	0.06
JM-16	Soil, 65-70 cm	521	0.13
* JM-16	Soil, 70-75 cm	236	0.19

BLS: below land surface

* Sterilized columns

** Considering the Se already leached

The time required increases for the soil below the surface mainly because of its lower permeability and the lower leaching rate at steady-state, although a fraction of Se had already been leached. The concentrations of total Se were similar for the deeper soil of both boreholes and slightly greater at the surface soil of the non-irrigated area (Table 9). In general, the order of magnitude of the time required for the leaching is the same for soils both in irrigated and non-irrigated areas and much greater for the weathered shale.

Some of the assumptions indicated above may not apply to the field conditions. In particular, the time required for leaching does not agree with the roughly equal Se concentrations in irrigated and non-irrigated samples and the fact that Se was not leached from the area after at least 60 years of irrigation. Certainly a much longer time is required. In reality, the water is not percolating continuously nor at a constant rate through the soil, and the leaching rate at the end of the experiment is only an approximation of a steady-state rate, so this table has many uncertainties and shows only the minimum time and water quantity required for the Se leaching to average background concentrations. Although a greater water quantity most likely is required, the estimated quantity of water required for leaching indicates that a very large volume of water is required for leaching. It is probable that flushing of Se-rich soils for remediation requires very large amounts of water.

Column Experiments and Batch Tests

Results from the column experiments were in agreement with the results from the batch tests. The differences in the production rates for the columns from different soil depths can be explained considering the differences in the Se distribution and total concentration (Fig. 25). In addition, the effect of the irradiation was greater on the surface soil columns than on the deeper soil columns, because the concentrations of Se associated with organic matter were greater in the surface soil columns. Other factors that could potentially affect the Se production rates include the microenvironments in each column and the heterogeneity of the column.

Soil Depth	Experiment type	
	Batch tests	Column experiments
Surface soil	Results: Greater total Se concentration. Greater Se associated with organic matter. Lesser soluble Se concentration.	Results: Almost constant Se production rate. Greater Se production rate at steady-state.
	Processes: Immobilization of Se by vegetative uptake and microbial activity. Leaching of soluble Se forms (mainly selenate and organic Se).	
<i>Root zone</i>		
Soil below the surficial root zone	Results: Greater soluble Se concentration. Lesser total Se concentration.	Results: Greater Se production rate for the initial pore volumes. Lesser Se production rate at steady-state.
	Processes: Accumulation of the soluble Se forms leached from above. Migration of water with high Se concentration from the moist deeper soil to the dry surface soil during dry periods and/or deeper percolation of soluble Se due to precipitation or irrigation.	

Figure 25. Mobility of Se in the surface soil and the soil below the surficial root zone.

CONCLUSION

The Cretaceous marine Mancos Shale is the source of selenium in the soils and rocks of the study area in the middle Green River Basin, Utah. Greater Se concentrations have been found in the surface soil and in the shale than in soils at intermediate depth. The distribution of the different forms of Se is the most important controlling factor on Se mobility. The batch tests indicated that selenium in the analyzed samples occurs as soluble Se, sorbed Se, elemental Se and as Se associated with organic matter. The spatial and vertical distribution of Se in different forms is not uniform. Although the majority of the Se is present as elemental Se and Se associated with organic matter, a significant fraction of the Se occurs as soluble Se in the soil below the surface root zone.

The Se concentrations in the effluent from the column experiments ranged from 1.5 $\mu\text{g/L}$ to 870 $\mu\text{g/L}$ and the production rates from 1.8×10^{-4} to 3.7×10^{-1} $\mu\text{g}/(\text{kg}\cdot\text{min})$. Soluble Se has accumulated below the root zone. This fraction accounts for the elevated Se concentrations in the effluent and the increased Se production in the initial pore volumes from the columns containing soil below the surface root zone, although the total Se concentration in that soil is smaller. Long-term leaching occurs at a higher rate from the surface soil columns because of higher residual Se compared to the deeper soil columns once a significant fraction of the soluble Se form is leached from the deeper soil columns.

Another controlling factor on Se mobility is microbial activity. This was more pronounced for the initial pore volumes where the maximum Se concentration in the

effluent of the sterilized columns was five and two times greater, respectively, than in the non-sterilized paired soil columns from the surface and below the surficial root zone. In addition, the production, the cumulative production and the production rate were increased for the irradiated columns. At the end of the experiment, when the Se mobilized by irradiation had been already leached, the Se production rates of the sterilized and non-sterilized paired columns were approximately equal.

In general, the batch tests and the column experiments indicated that the spatial and vertical distribution of Se in different forms is not uniform. This variability, together with the vegetative uptake and the microbial activity, are the most important controlling factors on Se mobility.

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APPENDIX A: SORPTION PROCESSES

Sorption occurs by three principal processes. The first is by formation of a surface precipitate that has a structure or composition different from that of the host mineral. The second is by incorporating solute species into the mineral structure, either by diffusion or by dissolution of the mineral and reprecipitation, a mechanism called absorption or coprecipitation. A third process is the accumulation of aqueous species on the mineral surface without formation of a three-dimensional molecular arrangement typical of a mineral, a process referred to as adsorption (Krauskopf and Bird, 1995).

Adsorption takes place by electrochemical reactions between a solution and a mineral in which the solute is removed from the bulk solution and is concentrated on the mineral surface. The stable molecular unit that forms is called a surface complex, of which there are two common types based on atomic arrangement and bonds formed between the solute and the mineral. In one type, called inner-sphere complex, ionic or covalent bonds are formed between the solute species and a specific crystallographic site on the mineral surface. This complex has no water molecules positioned between the mineral surface and the adsorbed species. Another type is the outer-sphere complex, where one or more water molecules are located between the mineral and the solute species. Outer sphere complexes are loosely attached to the mineral surface by electrostatic bonding and are not constrained to specific crystallographic sites on the mineral surface. A third type of adsorption refers to ions in the diffuse layer farther from the mineral surface that contribute to the net surface charge of the diffuse outer or Gouy

layer. These diffuse-ion swarms do not form discrete complexes attached to the mineral surface, but are solvated ions weakly attracted by electrostatic forces to the charged mineral surfaces.

The amount of adsorption depends, in general, on the relative concentrations of the adsorbate, on the surface area and the nature of the adsorbent, the temperature, the pressure, the pH, the Eh, the ionic strength of the solution and the extent of the hydrolysis or complexation of the adsorbate ion (Krauskopf and Bird, 1995). Adsorption of inorganic oxyanions by soil materials involves a ligand exchange reaction or surface complexation (Sposito, 1989). Davis and Leckie (1980) considered three types of surface complexation for selenate adsorption: adsorption of selenate on protonated surface sites, adsorption of protonated selenate, or bridging of selenate between two protonated hydroxyl sites. X-ray absorption spectroscopy showed that selenate forms a weakly bonded outer-sphere complex, but selenite forms a strongly bonded inner-sphere complex (Hayes et al., 1987).

According to Balistrieri and Chao (1990), negatively charged selenate oxyanions adsorb primarily by electrostatic interaction. In the case of selenite adsorption by goethite Balistrieri and Chao (1987) described the following sequence.

- Selenite adsorbs almost completely if the pH of the solution (0.65 μ M selenite and 30 mg/L goethite) is less than 5 and desorbs if the pH of the solution is greater than 9; the adsorption of selenite is completely reversible with respect to pH.
- The removal of selenite from solution increases with decreasing pH (pH in the range 4 to 9) and increasing particle concentration.

- The adsorption edge for selenite shifts to lower pH values with increasing total selenite concentration.
- The influence of additional anions on selenite adsorption depends on the relative concentrations of the anions. For a given anion concentration ratio, the competition sequence with selenite is: phosphate>silicate>citrate>molybdate>bicarbonate/carbonate>oxalate>fluoride>sulfate>selenite.

APPENDIX B: CORE AND SEDIMENT ANALYTICAL METHODS

I. Sequential Extraction Technique

1. 0.25M KCl solution, 120 min shaking for soluble Se (Fujii et al., 1988; Stephens et al., 1992; Zhang and Moore, 1997d). Calcium phosphates are expected to precipitate on addition of large concentrations of phosphate during the next extraction because of the low solubility of calcium phosphate (Fujii et al., 1988), therefore soil was equilibrated with KCl before the phosphate extraction attempting to remove soluble and exchangeable Ca from the soil (Stephens et al., 1992; Fujii et al., 1988) to prevent calcium phosphate precipitation.
2. 0.1M K_2HPO_4 solution adjusted to pH 8 with KH_2PO_4 , 180 min shaking for adsorbed Se (Fujii et al., 1988, Martens and Suarez, 1997). Selenite (SeO_3^{2-}) adsorbs much more strongly than selenate (SeO_4^{2-}). Adsorption of selenite is completely reversible with respect to pH; if the pH of a given solution is changed selenite sorbs or desorbs according to the pH changes. Selenite adsorption decreases with increasing pH in the range of 4 to 9. Finally, for a given concentration, phosphate is the most competitive with adsorbed selenite (Balistrieri and Chao, 1987).
3. 1M Na_2SO_3 solution adjusted to pH 7 with HCl for elemental Se, 60 min shaking and 330 min ultrasonic bath repeated twice. After that the slurry was rinsed twice with DI water, with ultrasonic bath and shaking repeated for each rinse (Velinsky and Cutter, 1990). The approach used for the determination of elemental selenium

involves the formation of soluble selenosulfate at pH 7 by the reaction of elemental selenium with sulfite (Warren, 1968). This reaction is similar to that between elemental sulfur and sulfite in which thiosulfate is formed. The sulfite solution is then treated with nitric acid to oxidize the sulfite to sulfate. Without this step, elemental sulfur precipitates and a significant amount of hydrogen sulfide is formed that interferes with the determination of selenium by HGAAS. The nitric acid also interferes and is removed before the $K_2S_2O_8$ oxidation and HCL reduction. The effect of the sulfite leach (1M Na_2SO_3 solution, pH 7) on sedimentary organic selenium has been examined (Velinsky and Cutter, 1990). Results indicated that very little organic selenium is mobilized by the sulfite leach.

4. 4-6% NaOCl solution adjusted to pH 9.5 with HCl, 30 min boiling repeated twice (Anderson, 1963; Tokunaga et al., 1991; Zhang and Moore; 1997c, d) for Se associated with organic matter.

In the study area there was no indication of a Se-carbonate occurrence. In such a case, an additional sequential extraction would be necessary using a 1 M sodium acetate solution and then a 0.1M K_2HPO_4 solution (Tokunaga et al., 1991) after the adsorbed Se extraction.

For the pyrite-Se determination, there is a less frequently used sequential extraction method (Velinsky and Cutter, 1990) that follows the elemental-Se extraction. Pyrite-Se is usually a small fraction in soils, although pyrite, which has a similar chemical structure to ferroselite, is the dominant form of sulfur (Velinsky and Cutter, 1991). In addition, the absolute detection limit for the chromatographic-AAS procedure

is high (2 ppb Se) and the relative standard deviation for the pyrite-Se determination is about 16% (Velinsky and Cutter, 1990), indicating ambiguous results. Ultimately, it is possible that part of the Se associated with organic matter may be extracted along with the pyrite-Se. Because of the ambiguous results of the analysis, the small fraction of pyrite-Se in soils, the possibility of extracting part of the Se associated with organic matter along with the pyrite-Se, and the importance of the Se associated with organic matter, the pyrite-Se extraction was not performed.

If selenium recoveries are low, sequential extraction can be extended (Zhang and Moore, 1996) to Se in:

- Easily reducible oxides (after soil organic matter extraction): 0.1M NH_2OH , then 0.1M KOH.
- Amorphous oxides: 0.25M $\text{NH}_2\text{OH} \cdot \text{HCl}$ (Hydroxylamine hydrochloride), then 0.1M KOH.
- Crystalline oxides: 4M HCl.
- Amorphous aluminosilicates (after Se-oxide extractions): 0.5M NaOH (Tokunaga et al., 1991).

II. Wet Digestion of Samples for Total Selenium Analysis

For the determination of total selenium content in environmental materials, samples should be digested with an acid mixture prior to application of the AAS method. To decompose the silicate matrix of the rock and sediment samples, a hydrofluoric-nitric-perchloric mixture (Tamari, 1998) was used for the core samples. For the wet digestion

of core samples the technique described by Tamari (1998) was used. According to this technique the mixture is heated to 200° C and a small amount of nitric acid is added to avoid carbonization; the mixture is heated until white fumes of the perchloric acid appear and continue to evolve (Tamari, 1998). During digestion small amounts of perchloric acid are added to avoid dryness or near dryness, because perchloric acid is slowly consumed by heating and dryness can result in volatilization of selenium. The nitric acid interferes with the determination of selenium by HGAAS and is removed before the $K_2S_2O_8$ oxidation and HCl reduction. After boiling the sample for 30 min with 6M HCl, selenium species are reduced to selenite (Martens and Suarez, 1997).