

## Selenium Speciation of Marine Shales, Alluvial Soils, and Evaporation Basin Soils of California

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### ABSTRACT

The surface exposed shales of the Moreno and Kreyenhagen Formations are considered to be the sources of selenium (Se) that have enriched soils of the west-central San Joaquin Valley of California. Although the total Se content for the source shales and the resulting alluvial, seleniferous soils has been reported, the distribution of Se oxidation states has not been determined in these materials. This study investigates the Se speciation trends in the seleniferous source shales, the adjacent alluvial soils, the San Luis Drain sediment to the Kesterson evaporation pond soils. The surface-exposed Moreno shales (5.21 mg total Se kg<sup>-1</sup>) had half of the Se content of the less exposed Kreyenhagen shale (10.94 mg total Se kg<sup>-1</sup>). The elemental Se (Se<sup>0</sup>) concentration was similar in the two shales, but the selenate (Se+VI), selenite (Se+IV), and selenide (Se-II) concentrations were lower in the Moreno shale as compared with the Kreyenhagen shale. The Se in the San Luis Drain sediment (83.8 mg total Se kg<sup>-1</sup>) was enriched in the Se<sup>0</sup> and the Se-II fractions (91.4% of Se inventory). The soils of the Kesterson evaporation pond 4 (47.8 mg total Se kg<sup>-1</sup>), 7 (6.7 mg total Se kg<sup>-1</sup>), and 11 (5.4 mg total Se kg<sup>-1</sup>) were also enriched in Se with 86, 76, and 48% of the Se inventory present in the Se<sup>0</sup> and Se-II fractions, respectively. The organic C content also decreased in the sequence, San Luis Drain, Kesterson pond 4, 7, and 11, from 33.3, 26.7, and 19.3 g C, to 15.1 g C kg<sup>-1</sup> soil material, respectively, suggesting a relationship between Se concentrations and organic C levels. A linear relationship between the sum of (Se-II and Se<sup>0</sup>)-Se and organic C levels ( $R^2 = 0.96$ ; significant at the 0.05 level) was noted for the analyzed San Luis Drain sediment and the Kesterson soils. For the nine soil materials, an exponential relationship ( $R^2 = 0.96$ ) was determined for the sum of (Se-II and Se<sup>0</sup>)-Se and organic C contents, suggesting that the Se in the materials tested was highly associated with the soil organic matter fraction. An additional 12 Se analyses and organic C contents from Se contaminated semiarid and irrigation drainage water evaporation basin soils obtained from the literature closely fit the exponential function established for the nine soil materials. The results suggest that an initial release of organic-associated Se would be expected with increased C oxidation, along with a slower, long-term release of the refractory Se, due to the reversion of the former Kesterson wetland evaporation pond ecosystem back to a native semiarid grassland.

THE GEOLOGIC SETTING and climate of the west-central San Joaquin valley of California has resulted in soil salinization. Agricultural engineering solutions to natural salinity problems have themselves at times created problems with the disposal of highly saline irrigation return waters. A major problem with disposal of irrigation return waters from the west-central San Joaquin Valley of California is the inadvertent cycling and concentration of the trace element Se in evaporation pond sediments. In environmental samples, any or all of the four Se oxidation states, selenate (Se+VI), selenite (Se+IV), elemental (Se<sup>0</sup>) and selenide (Se-II), may be present. The mobility, bioavailability, and toxicity of Se is controlled by its chemical speciation (Geering et al., 1968; Elrashidi et al., 1987) indicating that it is desirable to determine the concentration of individual Se species in a sample rather than a total Se content.

A reconnaissance study conducted by the U.S. Geological Survey (Presser et al., 1990) determined that the primary source of Se to the west-central San Joaquin Valley that resulted in Se contamination at the Kesterson National Wildlife Refuge (KNWR) was the nearby Diablo Range of the California Coastal Range (Fig. 1). Presser et al. (1990) established that elevated concentrations of Se were present in the extensive shale exposures of the Upper Cretaceous-Paleocene, Moreno, and Eocene-Oligocene, Kreyenhagen formations. The Se present in these sedimentary, pyritic shales was released by oxidative weathering and the resulting Se + VI was transported via solid and soluble phases to the alluvial soils that compose the valley floor. Recent availability of irrigation water and installation of subsurface drainage for salinity control, subsequently enabled these saline alluvial soils that contained shale-derived Se to be brought into cultivation. Since 1960, 35 000 ha have entered cultivation by installation of drains and it was estimated that 154 000 ha will be under subsurface drainage by the year 2020 (U.S. Bureau of Reclamation, 1984; Presser et al., 1990).

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**Abbreviations:** KNWR, Kesterson National Wildlife Refuge; SOM, soil organic matter.

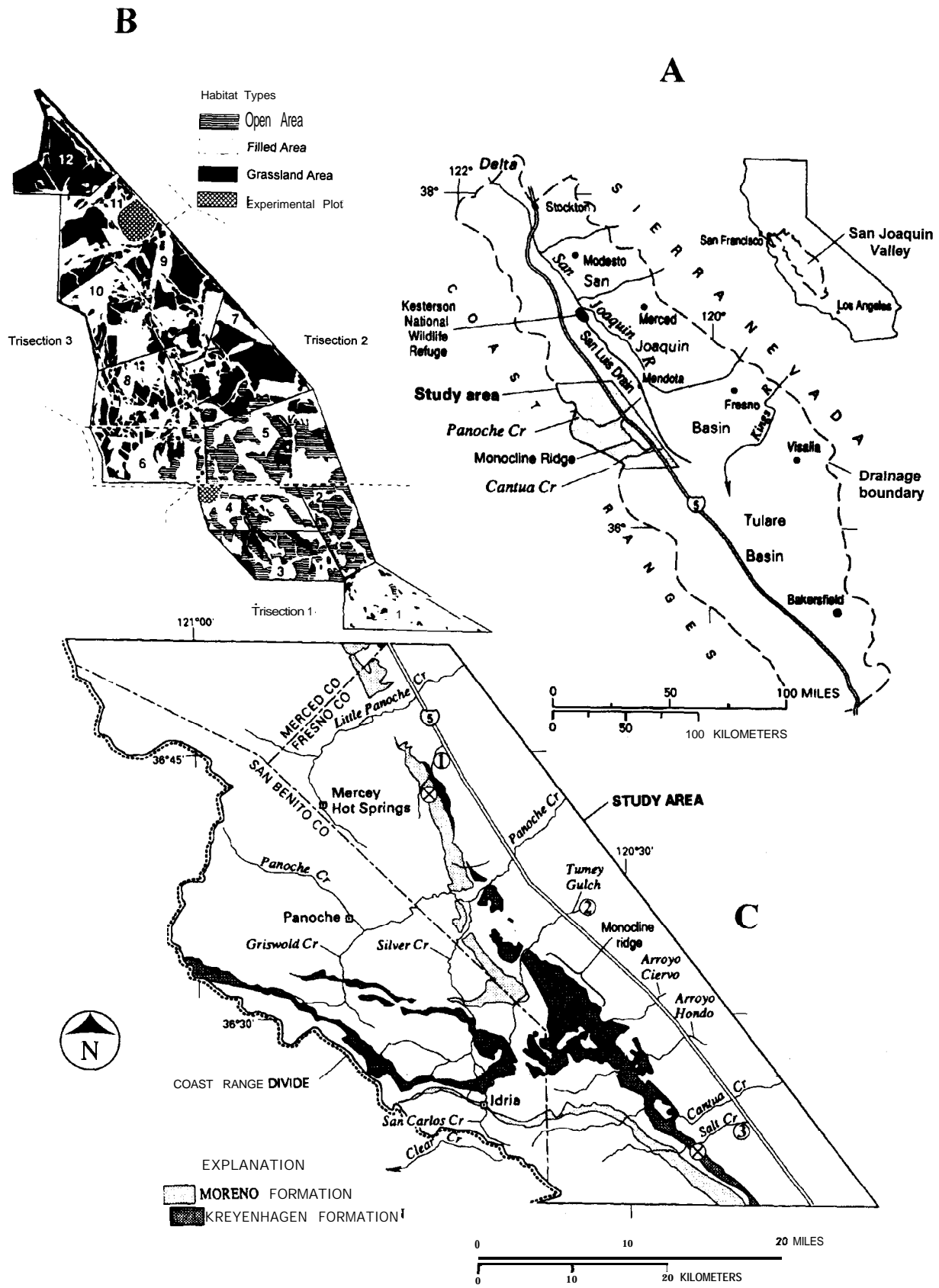


Fig. 1. Location of (A) the San Joaquin Valley of California, the San Luis Drain and the proximity of (B) the Kesterson evaporation pond system of the KNWR and (C) the Se source shales in the Diablo Coastal Mountain range. The numbers next to the open circles indicate the soil sampling location. The circles with the cross-hatch indicate the sampling location for the Moreno and Kreyenhagen shales (fig. adapted from Presser et al., 1990; Ohlendorf and Santolo, 1994).

The total Se content of the marine shales has been reported (Presser et al., 1990), but no information is available pertaining to the distribution of Se species in these marine shales or the resulting Se contaminated alluvial soils.

The San Luis Drain was constructed between 1968 and 1975 to extend the subsurface drainage system from the hydrologically closed basins to the south of the San Joaquin River, including the Se-containing alluvial soils, north to the San Francisco Bay delta estuary. The construction of the drain was stopped at the KNWR due to environmental and appropriation restrictions. The KNWR began to receive agricultural drainage waters via the San Luis Drain in 1978. Agricultural discharge to the KNWR was terminated in 1986 with the discovery of extensive migratory waterfowl deformities as early as 1983. The deformities were determined to be caused by elevated Se concentrations in the waterfowl as a result of Se present in the drainage waters (Ohlendorf et al., 1986). An estimated total of 9 t of Se was delivered via irrigation drainage water to the KNWR via the San Luis Drain (Tokunaga et al., 1994a). Previous research has shown that San Luis Drain sediment was highly enriched in refractory forms of Se (Calderone et al., 1990), but no results are available on the distribution of Se oxidation states of the Drain sediment.

Analysis of Se inventories of the Kesterson evaporation ponds has shown that the majority of the Se present as Se +VI and Se +IV during irrigation water discharge between 1978 and 1986 became concentrated in the surface 15 cm of soil (Ohlendorf and Santolo, 1994). Selenium analysis now shows that the soluble Se+VI and +IV accounts from approximately 10 to 50% of the total Se inventory in the contaminated soil (Weres et al., 1989; Tokunaga and Benson, 1992; White and Dubrovsky, 1994; Martens and Suarez, 1997a). Thermodynamic stability data predicts that in the oxidizing soil conditions present in semiarid environments, the majority of the Se should be Se+VI (Geering et al., 1968; Elrashidi et al., 1987). However, prolonged ponding in water containment facilities profoundly affected the Se speciation in the Kesterson evaporation pond soils enabling biological reduction of Se +VI and +IV to Se-II (Mairis et al., 1988) as well as to Se<sup>0</sup> (Oremland et al., 1989). Oremland et al. (1989) demonstrated that bacterial reduction of Se +VI can produce Se<sup>0</sup> and suggested that dissimilatory reduction of Se+VI and +IV to Se<sup>0</sup> can be an important mechanism for the incorporation and retention of Se in sediments. Other explanations for the low levels of Se +VI and +IV measured in these soil samples include removal of soluble Se species from solution by immobilization with organic matter (Calderone et al., 1990; Neal and Sposito, 1991) and/or by soil microbial metabolism to gaseous Se forms such as dimethylselenide (Calderone et al., 1990).

Although the Kesterson Reservoir has been closed to additional inputs of irrigation drainage water since 1986 and allowed to revert back to an upland semiarid habitat, the Se introduced via the San Luis Drain remains in forms whose mineralization and mobilization potential are not well understood. This study was conducted to

determine the distribution of Se oxidation states in a series of geological materials, the Se source rocks (Moreno and Kreyenhagen shales), the resulting alluvial fan soils, the contaminated San Luis Drain sediment and soils of the Kesterson Reservoir. Understanding the processes that enriched the Kesterson soils with Se and the redistribution of Se species is important since these processes are continuing at numerous other local evaporation ponds used for agricultural drainage disposal in the western USA. The processes are also applicable to prediction of the long-term fate of Se in such environments upon termination of use for drainage water disposal.

## MATERIALS AND METHODS

The shales and alluvial soils (0-15 cm) were collected from the sites shown in Fig. 1 and stored until processing in polyethylene plastic bags (4°C). The shales were collected from sites described by Presser et al. (1990). Excess water in the collected pond soil (0-15 cm depth) and sediment samples was allowed to drain, then the samples were air-dried. The Kesterson soil samples are original seleniferous sediments collected before remediation procedures were conducted at the KNWR. The shales, sediment, and soils were ground with an agate mortar and pestle, passed through a sieve (250 µm openings), dried at 40°C to constant weight and stored in polyethylene, wide mouth bottles. Soil pH was determined on a 2.5:1 water to soil ratio, total C content was determined by dry combustion (935°C) with a Coulometric C analyzer (UIC, Inc., Joliet, IL), and inorganic C content was determined by CO<sub>2</sub> evolved by acid treatment. Organic C content was determined by subtracting inorganic C content from total C content. Total N was determined by the method of Bremner and Mulvaney (1982). Total Se content was determined by placing the prepared soil material (0.20-0.50 g) in a 100 mL PTFE (teflon) beaker with 5 mL aqua regia (3: 1; HCl/HNO<sub>3</sub>) and 2 mL HF, covered with a watch glass and heated at 110°C in a sand bath for 2 h (Nham and Brodie, 1989).

## Apparatus

Hydride generation atomic absorption measurements (HGAAS) were made with a Perkin Elmer 3030B spectrophotometer (Perkin-Elmer Corp., Norwalk, CT) equipped with a Varian Model VGA-76 (Mulgrave, Victoria, Australia) vapor generation apparatus. A Se electrodeless discharge lamp (Perkin-Elmer) operated at 6 W was used as the radiation source. The operational conditions were as follows: acetylene flow, 2.4 L min<sup>-1</sup>; air flow, 6.0 L min<sup>-1</sup>; purge gas flow, argon, 90 mL min<sup>-1</sup>; sample flow, 1.0 mL min<sup>-1</sup>; 6 M HCl flow, 1.0 mL min<sup>-1</sup>; reagent flow, 0.6% NaBH<sub>4</sub>-0.5% NaOH, 0.33 mL min<sup>-1</sup>; wavelength, 196 nm; and slit width, 2.0 nm. A quality assurance procedure for Se analysis by HGAAS was employed as follows: Duplicate samples were analyzed with calibration, reagent blanks, NIST samples and spikes (20 ng Se mL<sup>-1</sup>) to check for interferences at the beginning and end of each HGAAS run. Acceptable data quality objectives were as follows: spike recovery, 90 to 103%; precision, 10%; detection limit, 0.01 mg kg<sup>-1</sup>. All glassware used was cleaned with detergent, rinsed, soaked overnight in 0.5 M HNO<sub>3</sub>, rinsed six times with deionized (DI) water (<10<sup>-5</sup> dS m<sup>-1</sup>) and air-dried prior to use.

<sup>†</sup>Trade names and company names are included for the benefit of the reader and do not imply any endorsement or preferential treatment of the product listed by the U.S. Department of Agriculture.

### Reagents and Standards

Stock solutions (1000 mg Se L<sup>-1</sup>) of Se (+IV and +VI) were prepared by dissolution of Na<sub>2</sub>SeO<sub>3</sub> and Na<sub>2</sub>SeO<sub>4</sub> (Aldrich Chemical Co., St Louis, MO) in DI water. Working standards of lower concentrations were prepared by serial dilution of stocks using DI water. Baker (J.T. Baker, Inc., Buffalo Grove, IL) intra-analyzed grade HCl, HF, and HNO<sub>3</sub> were used for all specified analyses. The NaBH<sub>4</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> were used as received from Aldrich and the K<sub>2</sub>HPO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> were obtained from Baker.

### Selenium Extraction and Speciation

A sequential extraction scheme was used for analysis of Se + VI, Se +IV, Se-II and Se<sup>0</sup> present in seleniferous samples (Martens and Suarez, 1997a).

**Water and Phosphate Extraction.** Prepared material (5.0 g) was placed into a 40 mL PTFE centrifuge tube and fractionated as follows: A 25 mL aliquot of DI water was added to the material and shaken (130 oscillations min<sup>-1</sup> at ambient temperature) on a horizontal shaker for 1 h. The sample was then centrifuged (10 000 x g; 20 min) and the supernatant was decanted to a 30 mL polyethylene bottle. A 25 mL aliquot of 0.1 M (pH 7.0) K<sub>2</sub>HPO<sub>4</sub>-KH<sub>2</sub>PO<sub>4</sub> buffer (P-buffer) then was added to the pelleted material and shaken for 1 h (130 oscillations min<sup>-1</sup> at ambient temperature), the sample was then centrifuged (10 000 X g; 20 min) and the supernatant was decanted to a 30 mL polyethylene bottle. The P-buffer-sample was then shaken for 2 min with 5 mL DI water, centrifuged and the supernatants combined.

Selenium speciation was determined by HGAAS on three treatments of the water and P-buffer extract. This procedure enables speciation of Se+IV, Se+VI, and Se-II solubilized by the extractions. We added from 0.1 to 2.0 mL of the specified extract to 25 mL graduated glass test tubes and: 1) 6 M HCl for Se +IV concentration (25 mL total); 2) 6 M HCl heated at 90°C for 30 min for Se+IV and Se+VI concentrations (25 mL total); 3) 1 mL 0.1 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (90°C) for 30 min then addition of 6 M HCl (25 mL total; 90°C) for 30 min to determine Se + IV, Se + VI, and Se-II concentrations. Persulfate oxidation results in conversion of all soluble Se species to Se + VI. The Se-II concentration was determined by subtraction of the Se + IV and Se + VI concentration (analysis no. 2) from the persulfate oxidation (analysis no. 3). The Se + VI concentration was calculated by subtracting the Se+IV (analysis no. 1) from the Se +IV and Se+VI (analysis no. 2). Recovery tests with Se + IV, Se + VI, or selenomethionine (Se-II) spiked to a nonseleniferous soil and extracted with the P-buffer resulted in >95 % spike recovery rates by the listed HGAAS speciation procedure.

**NaOH Oxidation.** The material remaining after the P-buffer extraction was then treated with 25 mL 0.1 M NaOH (90°C) for 2 h. The NaOH-soil suspension was centrifuged (10 000 x g; 20 min), the supernatant decanted, the sample mixed with 5 mL DI water, shaken, centrifuged and the supernatants combined in a 30 mL polyethylene bottle. We added from 0.1 to 2.0 mL of the NaOH extract to 25 mL graduated glass test tubes and: (i) 6 M HCl for Se+IV concentration (25 mL total); (ii) 1 mL 0.1 M K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (90°C) for 30 min then addition of 6 M HCl (25 mL total; 90°C) for 30 min to determine Se+IV, and Se-II concentrations. The NaOH extraction has been shown to recover tightly held Se +IV and inorganic and organic Se-II (Martens and Suarez, 1997a).

**Nitric Acid Oxidation.** The material remaining after NaOH extractions was treated with 2.5 mL 17 M HNO<sub>3</sub> and heated to 90°C for 30 min, thoroughly cooled, then 20 mL DI water

was added and the sample heated at 90°C for 1.5 h. The resulting 2 M HNO<sub>3</sub> solution was cooled to ambient temperature and centrifuged (10 000 x g; 20 min), decanted and Se analysis performed on sample aliquots (0.1-1.0 mL) treated with 6 M HCl (total 25 mL) heated at 90°C for 30 min. The HNO<sub>3</sub> extraction accounts for the remaining Se inventory in the sequential extraction method as Se<sup>0</sup> (Martens and Suarez, 1997a). All allotropes of Se<sup>0</sup>, insoluble S-Se associations and possible S amino acid-Se complexes are grouped together in the Se<sup>0</sup> fraction (Weres et al., 1989).

## RESULTS

Figure 1 (adapted from Presser et al., 1990; Ohlendorf and Santolo, 1994) shows the proximity of the source shales of the Diablo Range of the California Coastal Ranges, to the San Joaquin Valley, the San Luis Drain and the KNWR which includes the Kesterson evaporation ponds. The chemical properties of the materials used in this study are presented in Table 1. The Moreno and Kreyenhagen shales sampled for this study contained 5.2 and 10.9 mg total Se kg<sup>-1</sup>, respectively (Table 1). The distribution of Se in the different sequential fractions of the two shales appear to reflect the degree of surface exposure and weathering. The Moreno Formation shale is extensively exposed to weathering processes at the surface with evidence of leaching (Presser, 1994). The sampled Kreyenhagen Formation shale was less exposed to weathering and located in a steep-sided arroyo where erosion provided a relatively fresh rock surface. The Moreno shale contained lower Se concentrations in the water, P-buffer and NaOH extractions than did the Kreyenhagen shale, but the Moreno and Kreyenhagen shale contained comparable refractory Se<sup>0</sup> concentrations (Table 2; Fig. 2). The extraction protocol showed that both shales contained >80% of the Se inventory in the sum of the NaOH and HNO<sub>3</sub> extractions. However, a greater percentage of the NaOH extractable-Se was found to be Se + IV (45.6%) in the Kreyenhagen shale, compared to Se + IV (22.3 %) extracted from the Moreno shale (Table 2).

The Tumey Gulch, Moreno Gulch, and Salt Creek alluvial soils were found to contain 1.06 mg total Se, 0.58 mg total Se, and 0.41 mg total Se kg<sup>-1</sup>, respectively.

**Table 1. Chemical properties of materials used.**

Material	pH†	Organic‡	Inorganic§	Total N¶	Total Se#
		C	C	g/kg	mg/kg
Kreyenhagen shale	3.83	14.0	ND	2.43	10.90
Moreno shale	4.10	17.4	ND	2.33	5.20
Tumey Gulch soil	8.30	5.8	0.7	1.25	1.46
Moreno Gulch soil	6.87	5.7	ND	1.23	0.59
Salt Creek soil	8.45	2.9	0.6	0.90	0.45
San Luis Drain sediment	7.91	33.3	56.5	9.51	83.80
Kesterson pond no. 4	7.63	26.7	3.3	4.96	47.20
Kesterson pond no. 7	7.28	19.3	3.0	4.80	6.70
Kesterson pond no. 11	7.70	15.1	2.8	3.61	5.20

† The pH values were determined on a 1:2.5 soil to water ratio.

‡ Organic C content was determined by difference between total C content and inorganic C content by Coulometric C analyses.

§ Inorganic C content was determined by Coulometric C analysis.

¶ Total N was determined by block digestion and colorimetric NH<sub>4</sub> determination.

# Total Se content was determined by mixed acid digestion.

**Table 2. Selenium speciation of the Moreno and Kreyenhagen shales and Panoche Fan alluvial soils.t**

Material	Water		P-buffer		NaOH		HNO <sub>3</sub>	ΣSe
	SeO <sub>3</sub> <sup>-</sup>	SeO <sub>4</sub> <sup>-</sup>	SeO <sub>3</sub> <sup>-</sup>	Se-II	SeO <sub>3</sub> <sup>-</sup>	Se-II	Se <sup>0</sup>	
	mg kg <sup>-1</sup>							
Kreyenhagen shale	0.03 (0.00)	0.47 (0.04)	1.35 (0.06)	0.36 (0.00)	3.98 (0.30)	2.98 (0.41)	1.77 (0.05)	10.94
Moreno shale	0.03 (0.01)	0.10 (0.03)	0.49 (0.02)	0.20 (0.01)	0.98 (0.28)	1.57 (0.23)	1.84 (0.28)	5.21
Tumey Gulch soil	ND‡	0.09 (0.01)	0.02 (0.01)	0.02 (0.01)	0.04 (0.01)	0.33 (0.02)	0.56 (0.05)	1.06
Moreno Gulch soil	ND	0.05 (0.01)	0.01 (0.01)	0.02 (0.01)	0.01 (0.00)	0.18 (0.01)	0.31 (0.02)	0.58
Salt Creek soil	ND	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.01 (0.01)	0.10 (0.01)	0.27 (0.03)	0.41

t The shales and soils (5 g) were placed in 40 mL teflon centrifuge tubes and sequentially extracted with water (25 mL), P-buffer (25 mL), NaOH (25 mL; 90°C) and nitric acid (2.5 mL + 20 mL water; 90°C). Selenium speciation in the extractants was determined by HGAAS. The value in parentheses indicates relative standard deviation of the mean.

‡ ND, not detectable.

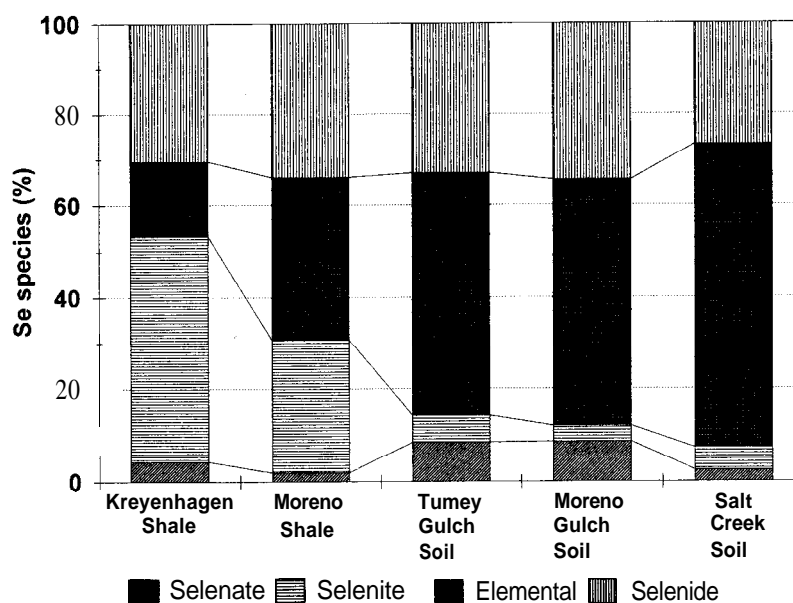
The results of this speciation procedure show the concentration of soluble Se is low, with >88% of the Se inventory present as nonwater-soluble Se +IV, Se-II and Se<sup>0</sup> in the alluvial soils tested (Table 2). An interesting trend is evident when the percentage of each Se species is plotted in order of descending Se content (Fig. 2). The Kreyenhagen shale was found to contain >50% of the Se inventory as Se+VI and +IV with a decreasing trend to <8 % of the Se inventory as Se +VI and +IV in the Salt Creek soil. The percentage of Se<sup>0</sup> increased in this sequence from 16% in the Kreyenhagen shale to 66% of the Se inventory in the Salt Creek soil. Organic C content was also noted to decrease with the decreased Se concentrations (Table 1).

The San Luis Drain sediment and the series of Kesterson evaporation pond soils were enriched with 83.8 mg total Se, 47.2 mg total Se, 6.7 mg total Se, and 5.2 mg total Se kg<sup>-1</sup>, respectively (Table 1). The San Luis Drain sediment contained very low levels of Se+VI or +IV,

with 92% of the Se inventory as Se-II and Se<sup>0</sup> (Table 3 and Fig. 3). The Kesterson soils also contained >50% of the Se inventory as Se-II and Se<sup>0</sup>, levels of inorganic Se +VI and +IV increased from 14% in the pond 4 soil and 24 % in the pond 7 soil, to nearly 50% of the Se inventory in the pond 11 soil (Fig. 3). Concentrations of Se also decreased with decreased organic C content of the sediment and pond soils (Table 1).

## DISCUSSION

The shales, alluvial soils, San Luis Drain sediment, and Kesterson soils were included in this study to determine if trends in the distribution of Se oxidation states exist from the Se source (shales) to the Se sink (evaporation ponds) in this drainage series. The speciation data provide much information on the potential mobility and availability of Se present in the tested materials. The Se+VI fraction which is very mobile is found only in the water extraction along with low levels of water-soluble Se + IV. Selenite



**Fig. 2. The percentage composition of Se species in the shales and nearby alluvial soils.**

**Table 3. Selenium speciation of the San Luis Drain sediment and the seleniferous Kesterson evaporation pond soils.†**

Material	Water		P-buffer		NaOH		HNO <sub>3</sub>	Total Se
	SeO <sub>3</sub> <sup>2-</sup>	SeO <sub>4</sub> <sup>2-</sup>	SeO <sub>3</sub> <sup>2-</sup>	Se-II	SeO <sub>3</sub> <sup>2-</sup>	Se-II	Se <sup>0</sup>	
	mg kg <sup>-1</sup>							
San Luis Drain sediment	0.11 (0.01)	2.15 (0.01)	3.23 (0.31)	1.71 (0.16)	1.05 (0.28)	42.23 (0.16)	32.16 (3.71)	83.24
Kesterson pond no. 4	0.49 (0.00)	2.48 (0.08)	1.42 (0.11)	0.77 (0.12)	2.45 (0.20)	12.46 (0.13)	27.13 (1.23)	47.80
Kesterson pond no. 7	0.10 (0.01)	0.51 (0.01)	0.51 (0.01)	0.24 (0.00)	0.50 (0.12)	2.56 (0.04)	2.29 (0.45)	6.70
Kesterson pond no. 11	0.11 (0.01)	0.92 (0.06)	0.43 (0.01)	0.29 (0.06)	1.34 (0.08)	0.46 (0.03)	1.80 (0.23)	5.3s

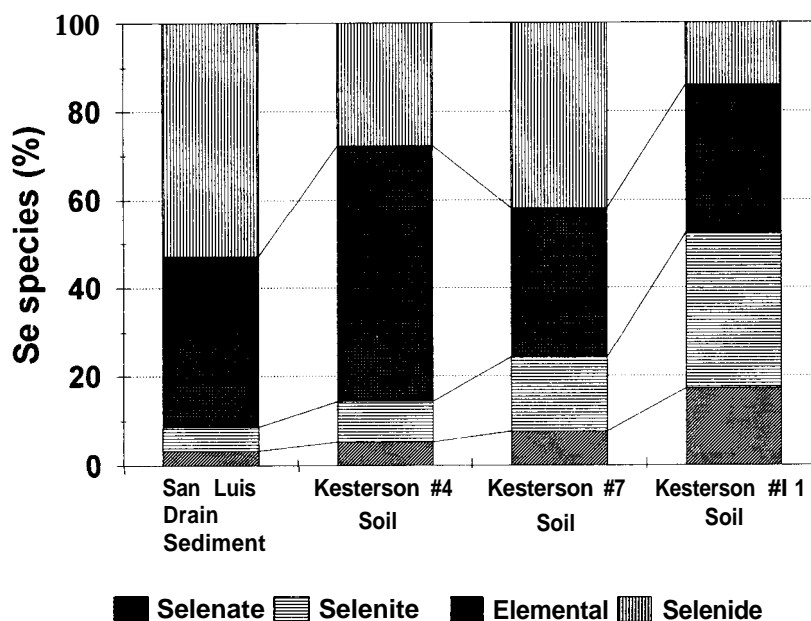
† The soils (5 g) were placed in 40 mL teflon centrifuge tubes and sequentially extracted with water (25 mL), P-buffer (25 mL), NaOH (25 mL; 90°C) and nitric acid (2.5 mL + 20 mL water). Selenium speciation in the extractants was determined by HGAAS. The value in parentheses indicates relative standard deviation of the mean.

was found in all samples as water soluble, ligand-exchangeable and very tightly held Se + IV. The sum of water-soluble and exchangeable Se in the materials tested was low in comparison to the total Se contents. The source shales and resulting alluvial soils contained approximately the same percentage of the Se inventory in the Se-II form, although this trend was not evident for the San Luis Drain sediment and Kesterson soils. Martens and Suarez (1997b) established that Se-II in the form of the selenoamino acids, selenomethionine and selenocystine, was rapidly mineralized to Se +VI, +IV, Se<sup>0</sup>, and Se-II, in addition to the volatilized Se-II species. If amino acid Se-II is present in samples, this Se-II fraction would be recovered in the P-buffer extraction. The presence of very low concentrations of P-buffer soluble Se-II in the samples tested (Tables 2 and 3) indicates that the amino acid form of Se-II does not persist in soil or sediment, as was noted in laboratory studies (Martens and Suarez, 1997b). However, low levels of the Se-containing amino acid, selenomethionine have been unequivocally shown to occur in soils and drain sediments exposed to Se (Abrams et al., 1990; Rael and Franken-

berger, 1995). The extraction procedure employed here also suggests that a large portion of the Se inventory is present in these materials as Se<sup>0</sup>. Evidence for the presence of Se<sup>0</sup> in the Kesterson soils was determined by synchrotron radiation based x-ray absorption spectroscopy (Pickering et al., 1995).

Presser et al. (1990) determined that the Moreno and Kreyenhagen Formations were the Se source that eventually contaminated the Kesterson sediments and ranged up to 35 and 45 mg total Se kg<sup>-1</sup>, with a median Se concentration of 6.5 and 8.9 mg Se kg<sup>-1</sup>, respectively. The Se content determined in our shale samples were very close to the median levels measured by Presser et al. (1990) suggesting that our samples were representative of the shales in question. Presser's study determined that alternative Se source materials, such as nearby sandstones, continental rocks, acid mine drainage and serpentine rocks were comparatively barren of Se when compared to the marine shales. Our sampling also found that the adjacent rocks (sandstone and serpentine) were almost devoid of Se (data not reported, 1996).

Total Se inventories for the alluvial soils tested have



**Fig. 3.** The percentage composition of Se species in the San Luis Drain sediment and the Kesterson evaporation pond soils.

been reported to range from 1.14 to 2.38 mg Se kg<sup>-1</sup> in the Tumey Gulch alluvial soils to 0.32 to 0.80 mg Se kg<sup>-1</sup> in the Salt Creek and Moreno Gulch alluvial soils (Presser et al., 1990). The low soluble Se concentrations for these soils may reflect the active cultivation, irrigation, and subsurface drainage at the locations in question that would be expected to leach soluble Se as well as slowly convert insoluble Se to soluble Se forms. Consistent with this, >84% of the Se inventory was determined as insoluble Se-II and Se<sup>0</sup>. The increased percentage of insoluble Se present in this sequence indicates that a large portion of the soluble Se has been leached from the alluvial soils and the extensively weathered Moreno shale formation. The data also suggests that the insoluble Se-II and Se<sup>0</sup> concentrations in semiarid soils are relatively stable. The time required to mineralize these Se forms has not been fully described.

Ponds 1 to 4 at KNWR received the most Se-contaminated drainage water, resulting in nearly continuous open water present with aquatic plant species such as cattails as the dominant vegetation. Ponds 5 to 7 and ponds 8 to 12 received the next highest amount of drainage water with variable, ponded water, and little standing water, respectively (Ohlendorf and Santolo, 1994). Previous research has shown that the series of evaporation ponds exposed to the greatest amounts of irrigation water via the San Luis Drain retained the highest concentrations

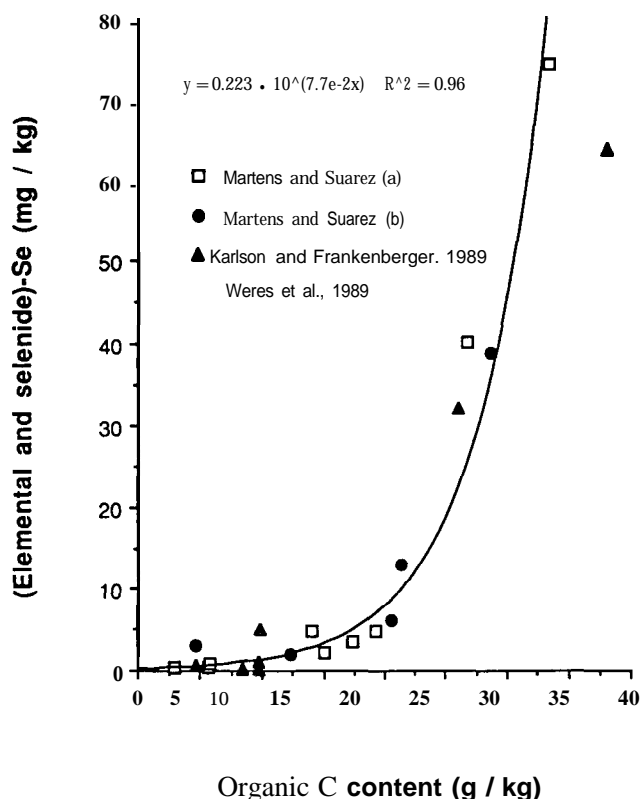


Fig. 4. The relationship between (a) the sum of the Se-II and Se<sup>0</sup> concentrations and the organic C content in the nine soil materials tested here, (b) additional evaporation pond Se and organic C values (data not reported here) and Se and organic C values from previous research with western San Joaquin Valley alluvial soils (Frankenberger and Karlson, 1989) and the Kesterson evaporation ponds (Weres et al., 1989).

of Se (Weres et al., 1989). Soil organic C contents also increased with increased inputs of irrigation drainage water (Table 1). Tokunaga et al. (1991) found that in the surface 0.2 m in the pond 11 soil, >70% of the total Se inventory was determined by a sequential extraction procedure to be associated with the soil organic matter (SOM) fraction, highlighting the importance of organic matter in the retention and biochemistry of Se. Tokunaga et al. (1991) described the possible Se species associations with SOM as Se-II and Se<sup>0</sup> and Se +IV incorporation with the SOM matrix. Immobilization of soluble Se by organic C has been shown to be an important process in soils exposed to Se (Calderone et al., 1991; Neal and Sposito, 1991). The distribution of Se species found in the pond 11 soil reported here confirms these Se associations with soil organic C. Of the Se inventory recovered from the pond 11 soil, 67 % was recovered in the NaOH and HNO<sub>3</sub> extractions as Se +IV (25 %), Se-II (8.6%) and Se<sup>0</sup> (33.6%).

Selenium has been found to be chemically similar to S and many of the reactions involving Se species are assumed to follow the reactivity of S analogs. Previous research has shown that soil organic matter is the predominant factor for retention of S in nongypsiferous soils (Tabatabai and Bremner, 1972). Weres et al. (1989) noted a relationship for seleniferous Kesterson soils (total Se content) and organic C contents and theorized that Se was initially deposited with the organic fraction of the sediment. In the San Luis Drain sediment and Kesterson soils, the Se<sup>0</sup> content, the Se-II content and the sum of (Se-II and Se<sup>0</sup>)-Se were highly correlated with organic C content ( $R^2 = 0.90^*$ ,  $0.86^*$ , and  $0.96^*$ , respectively). Other research (Elsokkary, 1980; Naftz and Rice, 1989; Abrams et al., 1990) has also reported that total soil Se content was correlated with organic matter content. A different relationship emerges when all nine soil materials employed here are considered. An exponential function ( $R^2 = 0.96^{**}$ ) rather than a linear relationship was noted when the sum of (Se-II and Se<sup>0</sup>)-Se was plotted against the organic C content of nine soil materials investigated here. To further test the observed Se and organic C relationship, an additional 12 Se and organic C content values (evaporation pond and alluvial soil data from the western San Joaquin Valley obtained from our research and reported values taken from Karlson and Frankenberger, 1989 and Weres et al., 1989) were added to our data set, as shown in Fig. 4. The close approximation of the additional data points to the determined exponential relationship suggests that concentrations of Se rapidly increased as organic C contents increased above 20 g organic C kg<sup>-1</sup> (2% organic C) in evaporation pond soils. This increase in the Se/organic matter ratio may be related to the change from aerobic conditions (nearly all values with <20 g organic C kg<sup>-1</sup>) to anaerobic conditions (all samples with more than 20 g organic C kg<sup>-1</sup>) which were reported to occur in evaporation pond soils. Such a relationship is expected to be found only when the materials have similar inputs of Se (i.e., C content is not a general predictor of Se content).

Not all irrigation drainage water evaporation ponds that received seleniferous inputs accumulated high levels

of insoluble Se. Martens and Suarez (1997a) determined that the distribution of Se species from a San Joaquin Valley evaporation pond soil remained as 75% Se+VI and +IV with only 18% present as Se<sup>0</sup> after exposure to water ponding for 10 yr. The pond was located on the Sumner Peck ranch (described in Thompson-Eagle and Frankenberger, 1990) and had a total Se content of 11.7 mg kg<sup>-1</sup> with a low organic C content (4.6 g organic C kg<sup>-1</sup>). Frankenberger and Karlson (1995) determined that 58% of the Se present in the top 1 m in the Peck soil, was contained in the 0 to 15 cm depth. In comparison, 80% of Se content in the top 1 m of the Kesterson ponds was retained in the 0 to 15 cm depth (Tokunaga et al., 1994a). The main difference between the Peck evaporation pond and the Kesterson evaporation ponds was the pronounced lack of plant growth and plant residues in the Peck pond soil (W.T. Frankenberger, Jr, personal communication, 1996). Even though the two evaporation pond systems were managed differently, the Peck soil and the Kesterson soils both fall very close to the regression line presented in Fig. 4. Limited research also supports the influence of plant communities on Se cycling in natural systems. Tokunaga et al. (1994b) determined that soil aggregates embedded with plant roots and saturated with a Se +VI solution rapidly developed large accumulations of total Se surrounding the root tissue. Synchrotron x-ray spectroscopic analysis showed that the Se + VI was reduced to Se<sup>0</sup> in the presence of plant roots. In contrast, selenate permeated into soil aggregates without plant roots was found as Se +VI under the same experimental conditions. Little research is available describing the role of plants and plant residues on the cycling of soluble Se into the Se forms now present in the Kesterson evaporation pond system. Yet, the observed Se (Se-II and Se<sup>0</sup> contents) and C relationship suggests that plant growth with concomitant Se assimilation from the irrigation evaporation ponds and C accumulation with plant residue decomposition has an impact on the Se inventories. Research is specifically needed to understand the complex cycling of Se-II present in seleniferous plant residues upon decomposition in soil.

The statistical relationship determined between Se concentrations and organic C content indicates that Se accumulation and/or mobilization from contaminated evaporation pond soils is controlled by the organic C mineralization rate. Field and laboratory decomposition studies with <sup>14</sup>C plant residues in cultivated soils has shown that the C decomposition rate is strongly influenced by climate and plant residue addition rate (Jenkinson and Ayanaba, 1977; Ladd et al., 1981). Previous <sup>14</sup>C-organic matter decomposition studies determined that organic residues released 70% of added <sup>14</sup>C in the first 2 mo with about 12% remaining in the soil after incubation for 10 yr because of physical inaccessibility and (or) a chemical protection mechanism (Jenkinson, 1977). The turn-over time of organic matter in grassland soils is estimated to occur every 30 to 40 yr and is independent of residue type with turnover times much shorter for soils with low initial organic matter contents (Jenkinson, 1981). Recent research has found that mineralization of leachable and easily hydrolyzed compounds from fresh

plant residues is equally fast under aerobic or anaerobic conditions (Kristensen et al., 1995). The distribution of Se species and the relationship of the Se concentrations with organic C levels in the series of soil materials studied suggests that two stages of Se release should be noted in soils of recently drained evaporation pond systems contaminated with Se. First, an initial release of organic associated-Se due to oxidation of C accumulated during anaerobic conditions along with a slower, long-term release of the refractory Se from the former Kesterson evaporation pond ecosystem (1978-1986), with reversion back to the native semiarid grassland (1986-present). The data suggests that long-term management of contaminated Kesterson sediments will be required to avoid refractory Se oxidation and limit the impact of soluble Se in the environment.

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