Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

**Soil Water and Vegetation Management for
Cleanup of Selenium Contaminated Soils**

Progress Report

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- Progress Report -

**Soil Water and Vegetation Management for Cleanup
of Selenium Contaminated Soils**

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University of California

and

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Berkeley, California 94720

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Executive Summary

Over the past year scientists at Lawrence Berkeley Laboratory and the Division of Agriculture and Natural Resources at the University of California have initiated a new effort aimed at developing a soil water and vegetation management plan for Kesterson Reservoir. The goal of the management plan is two-fold. First, the plan is intended to result in a gradual depletion of the inventory of soluble selenium at the Reservoir through a combination agriculturally oriented practices that enhance dissipation of selenium from near surface soils. Agriculturally oriented processes that will contribute to depletion include microbial volatilization from the soils, direct volatilization by living plants, decomposition and volatilization of selenium-bearing vegetation, harvest and removal of seleniferous vegetation, and leaching. The benefits of using this integrated approach are that (1) no single mechanism needs to be relied upon to detoxify the soils, (2) a stable plant community can be established during this period so that impacts to wildlife can be more easily evaluated and controlled, and (3) cleanup and management of the site can be carried out in a cost-effective manner. The management plan is also intended to facilitate control over wildlife exposure to selenium contaminated biota by creating a well managed environment. By managing the type of vegetation growing at the site, and by using vegetation to assist in soil moisture control, and consequently surface water accumulation during the wet season, biotic exposure to seleniferous food-chain items can be controlled.

The majority of research associated with this new effort is being carried out at a 200 m by 50 m test plot in Pond 7. A two-line irrigation system, providing local groundwater as an irrigation supply, has been installed. Through an intensive program of soil water sampling, soil gas sampling, vegetation sampling, groundwater monitoring, and soil moisture monitoring, the

mass balance for selenium under irrigated conditions is being evaluated. These studies, in conjunction with supplementary laboratory experiments will provide the information needed to develop an optimal management plan for the site. Research activities, which began in July 1988, are just getting underway. This progress report provides information on the current status of the individual components of the integrated research program.

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1.0. Introduction

One way to reduce selenium contamination in near surface soils is through a combination of agriculturally oriented practices that stimulate selenium cycling in soil/soil water/plant systems. Transformation of selenium in the soil, soil water, and plants results in a cycling and redistribution of selenium within and between each component of the system (Sharma and Singh, 1983). Uptake by soil microorganisms and plants alters the speciation of selenium in the soil. Evapotranspiration, irrigation and drainage control soil water movement, selenium mobility, and selenium transport. Plant uptake mines the soluble species of selenium from the root zone. Both microbial activity and plant growth can result in a net loss of selenium through volatilization.

A new effort is underway to evaluate how a combination of soil water and vegetation management can be optimized to manage selenium contaminated soils in a practical and cost-effective manner. It should be recognized that depletion of the soluble species of selenium through soil water and plant management is a slow process which will take tens of years to complete. Nevertheless, the potential benefits of this integrated approach are substantial. These include the potential for thorough depletion of the excess soil selenium (even at depths to 1 m), minimal disturbance of wildlife habitat, and low costs.

The basic components of the selenium mass balance for the soil/soil water/plant system are shown in Figure 1 (note that this figure depicts unfilled conditions at Kesterson Reservoir). The primary processes that can be used to deplete the selenium inventory in the vadose zone soils include microbial volatilization from the soils, volatilization from the plants, harvest and removal of seleniferous vegetation, and leaching. The primary means of redistributing selenium in the soil profile are infiltration of rainfall and irrigation water, transpirative fluxes, evaporative fluxes, drainage, and the seasonal rise and fall of the water table. Soil microorganisms play a continuing role in transforming selenium from inorganic forms to volatile and non-volatile organic forms. Simultaneously, mineralization of organic matter transforms organically bound selenium back

Figure 1. Components of the selenium mass balance in a soil water and vegetation management scheme.

into inorganic forms. Some inorganic species of selenium such as selenate and selenite are relatively soluble and available for plant uptake and transport. On the other hand, inorganic species such as elemental selenium and metal selenides are relatively non-toxic, unavailable for plant uptake and are immobile in some soil environments.

The objective of this cleanup strategy is to manipulate these processes to simultaneously accelerate microbial and plant volatilization of selenium in the near-surface soils and enhance root extraction and/or leaching to prevent accumulation of selenium at the soil surface. Table 1 lists factors that will contribute to depletion of the inventory and the management practices that would accelerate depletion. Note that all of the processes that contribute to depletion of the selenium inventory are relatively slow and each individually may only remove on the order of a percent per year. This expectation is compatible with recent investigations presented by Gillian et al. (1989). These studies indicate that after about 15 years of irrigated agriculture, a large fraction of the initial inventory remains, although much of soluble inventory has been removed from the root zone, largely by leaching. Wildlife exposure to selenium contaminated food during the cleanup can be minimized by choosing the appropriate plant species and/or manipulating the growing environment to achieve safe levels in food-chain organisms. Benefits of using an integrated approach to cleanup of selenium contaminated soils include (1) no single mechanism needs to be relied on to detoxify the soils, (2) a stable plant community can be established during the cleanup operations so that impacts to wildlife can be more easily evaluated and controlled, and (3) by combining several mechanisms the rate of depletion from the near-surface soils may be accelerated.

1.1. Vegetation Management

Plants are an important component of this cleanup strategy because they provide the primary means of extracting soluble selenium from the root zone and they are an inexpensive organic amendment for enhancing microbial volatilization rates. The plant community also plays an important biological role, affecting both the habitat value and wildlife exposure to selenium contaminated vegetation. Two basic options are available for managing the plant community in

Table 1. Factors and management options for accelerating depletion of selenium from contaminated soils.

Factors which Favor Dissipation of Selenium	Method of Management	How the Management Method Will Optimize Volatilization?
1. Organic matter with Se	Grow a crop with high biomass production. Incorporate crop residue. - OR - Use existing vegetation and incorporate.	Provide organic Se compounds which are easily metabolized by microbes.
2. High water soluble Se in surface soils	Grow a crop with deep feeding root system and incorporate crop residue.	Plant uptake and incorporation will bring deep Se to surface soils. By mineralization water soluble Se concentration increases.
3. High temperature	Grow the crop during winter, spring (i.e., during periods of low temperature. Select crops that can grow during winter and spring. Incorporate during the periods of high temperatures (summer).	Microbial volatilization increases with increase in temperature. Use the seasonal temperature variations to optimize volatilization.
4. Optimum moisture	Provide irrigation.	During summer, the volatilization is not favored due to lack of moisture for microbial activity. Therefore, sufficient moisture for volatilization is provided by irrigation.
5. Drying and wetting	Plan the irrigation schedule.	Drying and wetting cycles may release more easily available organic matter and more water soluble Se compounds.
6. Aeration	Tillage during summer, several times after the incorporation of plant material.	Volatilization is mainly a process mediated by fungi. By tillage the soil system becomes aerobic for fungal activity.

Table 1. Factors and management options for accelerating depletion of selenium from contaminated soils (continued).

Method of Management	Advantages
1. Cropping during winter/spring	Provide biomass for incorporation. Bring deep Se to the surface. Reduce water ponding during wet periods. May have plant volatilization during periods which do not favor microbial volatilization. May provide some yield benefits.
2. Incorporation of crop residue during summer	Provide organic Se for volatilization. Provide a method of disposing of crop residue.
3. Irrigation	Provide water for plant growth. Provide optimum moisture for volatilization.
4. Tillage	Provide necessary aerobic condition for volatilization.

Crop	Time of Establishment	Time of Harvest	Special Feature
Barley (Se non-accumulator)	Winter	Mid-July	Good for salinity. Good for poor soil condition. Produces high biomass. Gives a yield. Disadvantages: Seeds may encourage birds. Surface feeding root system.
Alfalfa (Se non-accumulator)	Spring, March/April Fall	?	No need of N fertilizer. High biomass production. Deep feeding root system.
Tall fescue (Se non-accumulator)	Spring, March/April	?	High biomass production. Good for high levels of salinity and Se.

selenium contaminated soils. Plants that accumulate high levels of selenium may be cultivated. Alternatively, non-accumulators, plants that do not accumulate high levels of selenium may be encouraged. Selenium concentrations in the plants can be manipulated to some extent by irrigation and cultivation practices.

Plant species which accumulate selenium may be useful in rapidly depleting the inventory of soluble selenium in the soils by removing soluble selenium from the root zone and transporting it to the leaves and stems. Some plant species can also convert relatively insoluble forms of selenium to soluble forms that are extracted by root uptake (Anderson et al, 1961). Some fraction of the selenium taken up by the plants will also volatilize. Primary accumulator plants include species of *Astragalus*, *Stanleya*, *Machaeranthera*, and *Happlopappus* (Sharma and Singh, 1983; Anderson et al., 1961). Secondary accumulators include species of *Atriplex*, *Grindelia*, and *Aster* (Sharma and Singh, 1983). Seleniferous vegetation could be harvested or incorporated back into the soil to provide a source of organic matter for enhancing microbial volatilization and concentrating the selenium at shallow depths where microbial volatilization is most effective. Alternatively, the vegetation could be harvested and used as a soil amendment and food supplement for livestock in selenium deficient areas, or as a biofuel.

As an alternative to growing selenium accumulator plants, plant species that do not accumulate high concentrations of selenium may be cultivated to protect wildlife from hazardous exposure to selenium-contaminated food. Salt grass (*Distichlis*) and alkali weed (*Cressa*), which grow abundantly at Kesterson Reservoir, are examples of non-accumulator plants which may be cultivated in seleniferous soils. Concentrations of selenium in the leaves, stems, and seeds are typically less than 3 ppm even in soils with selenium concentrations of 5 ppm (USBR, 1988). These plants will slowly extract selenium from depth and translocate it to the stems and leaves. Some fraction of the selenium will also volatilize directly from the plants. The plants could be used as a soil amendment for enhanced volatilization. Laboratory experiments have demonstrated that by amending the soil with salt grass and a nitrogen fertilizer, volatilization rates can be increased to 10 times the rate in unamended soils (LBL, 1987).

1.2. Soil Water Management

Soil moisture and chemical composition of the soil water play an important role in microbial volatilization, plant productivity, and plant uptake. Adequate moisture and nutrients are needed for stimulating volatilization and for enhancing the productivity of the plant community. In addition, in saline soils such as those at Kesterson Reservoir, salt concentrations must be controlled to avoid excessive accumulation that would inhibit microbial activity in the soil and thwart plant growth. Irrigation can provide the moisture needed for microbial volatilization and plant growth. Irrigation water also provides a means of leaching salts and soluble forms of selenium from surface soils and in the root zone. Nitrogen fertilizers can enhance volatilization rates, maintain oxidizing conditions in the soil water, and increase plant productivity. Addition of nitrogen fertilizers may affect plant tissue selenium concentrations and increase the rate at which selenium is leached from the root zone. Drainage may be desirable for water table control and leachate collection.

A positive salt balance in the root-zone must be maintained. Chemical precipitation (except for the most insoluble minerals) and plant uptake usually make relatively small contributions to the removal of soluble salts from the soil, so that a mass of salt approximately equal to that added in irrigation water must be carried below the root-zone by water applied in excess of that needed for evapotranspiration. If watering is frequent during periods of high evaporative demand, then a salt balance may be achieved by the efflux of a small volume of highly saline water from the root-zone. If this water cannot be accepted without raising the watertable, then subsurface drainage may be needed. However, installation of a drainage system requires careful consideration of the options available for disposal of the leachate, and at present, this appears to be a serious obstacle due to concerns not only about selenium concentrations but boron and total dissolved solids as well.

1.3. Project Status

Evaluation of options for an integrated approach to soil water and vegetation management has only recently begun. A systematic approach to evaluating each component of the mass

balance shown in Figure 1 is underway.

The majority of research effort is being conducted in a 183 m by 46 m test plot in Pond 7. A dual-line sprinkler system has been installed, along with various sampling/monitoring systems for measuring the parameters needed to understand the behavior of selenium when the Kesterson soils are irrigated. To supplement these field investigations, laboratory studies are also being conducted. Laboratory experiments will provide information on the processes that accelerate selenium dissipation in a more controlled environment. All of these experiments are described in greater detail in the following sections.

2.0. Test Plot Studies for Soil-Water and Vegetation Management

2.1. Introduction

The primary test plot for the soil water and vegetation management investigations is located on the eastern border of Pond 7, approximately midway between Ponds 5 and 9 (see Figure 2). The plot covers a 183 by 46 m area that was originally vegetated with salt grass. Initial concentrations of water-extractable selenium average 0.35 ppm in the surface-most 0.15 m of the test plot. Analyses to determine the average total selenium concentration are underway.

A dual line sprinkler system was installed that utilizes local well water for irrigating the test plot. The system is designed to provide a uniform application of irrigation between the sprinkler lines. Outside the lines the application decreases. The irrigation water has an electrical conductivity of about 12 dS/m (12,000 micromhos/cm) and a boron concentration of 10.5 ppm.

Preliminary studies at the test plot were designed to provide first-cut information on:

- The spatial variability of selenium concentrations under present conditions;
- Redistribution of soluble selenium in response to irrigation;
- Infiltration characteristics of the Kesterson soils;
- The effect of vegetation on soil-water movement;
- The influence of irrigation rates on microbial volatilization of selenium;
- The effectiveness of incorporating the native vegetation into the soils for promoting volatilization of selenium;
- Biomass of the native vegetation under irrigated and non-irrigated conditions, and
- The correlation between selenium concentrations in the soil water and vegetation.

In the sections to follow, methods and preliminary results from the investigations are described. Due to the relatively short period over which these investigations have been

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Figure 2. Location of the test plot for soil water and vegetation management studies.

underway, it is too early to attempt to infer potential rates of selenium dissipation. Instead, the early studies are aimed at identifying processes and quantifying the rates of the processes under the narrow range of conditions that have been tested to date.

2.2. Soil Sampling

On July 7, 1988, before the irrigation began, soil samples were taken along three transects, a main transect parallel to the irrigation lines and two subtransects perpendicular to the irrigation lines, as shown in Figure 3. The main transect is located midway between the dual line sprinkler system. Soil samples were collected every 3 m along the main transect over a length of 183 m. The subtransects which were perpendicular to the main transect were located 60 m apart, dividing the main transect into three parts. Soil samples were collected at 1 m intervals in the subtransect. At each sampling site, the soil samples were taken at depth intervals of 0-15, 15-30, 30-60, 90-120 and 120-150 cm.

A second set of soil samples were taken on October 16, 1988, after application of a total of 22 cm of water over a three-month period. Comparison between the two data sets provides a means of evaluating the redistribution of the inventory as a result of irrigation. During the second sampling, samples were collected along the main transect and one of the subtransects with the same frequency as the initial sampling. Soil samples were only collected at depths of 0-15, 15-30 and 30-60 cm.

2.2.1. Soil Sample Preparation and Extraction

Soil samples were immediately air dried, ground, and passed through a 2-mm sieve. The extractions were performed with a homogenized subsample of the soil.

Selected soil samples were extracted at water contents equivalent to (a) 1:5 soil:water extract, and (b) saturation extract. The 1:5 soil water extract was prepared with 25 g of a homogenized soil sample with 125 ml of water in a plastic container. The samples were vigorously shaken for 2 hours, centrifuged for 1/2 hour at 9,000 rpm and vacuum filtered through a millipore filter with 0.45 μ filter paper. Electrical conductivity and pH were measured in the extract and

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Figure 3. Schematic diagram of the main transect and subtransects showing relative positions of the sprinkler lines and soil sampling sites

approximately 60 ml of it was stored in plastic bottles at room temperature for selenium and boron analyses. The soil extracts were obtained in all sites, to a depth of 150 cm along the main transect and every alternate site to a depth of 60 cm along one of the subtransects. From the final sampling, the samples were analyzed at the same frequency but only to a depth of 60 cm.

2.2.2. Method of Analysis

pH was measured with a combination pH electrode and a pH meter (Model Beckman, 41). EC was measured with conductivity meter (Model YSI 32). Selenite was measured directly with the AAS/hydride generation method. Total selenium was measured by oxidizing the organic matter with ammonium persulfate, reducing the selenate with HCl, followed by AAS/hydride generation. Ca^{2+} , Mg^{2+} , Na^+ , K^+ and B were measured by ICP and SO_4^{2-} , Cl^- , and NO_3^- were measured by ion chromatography (Wescan Ion Analyzer).

2.2.3. Soil Sampling Results

Figures 4a-e present the mean and an error bar representing the standard error of the mean for each depth for water extractable selenium, selenite, boron, EC, and pH, respectively, in the 1:5 soil water extract for the main transect. Similar results for one of the subtransects are presented in Figures 5a-e for water extractable selenium, selenite, boron, EC and pH, respectively. Values for water extractable selenium, selenite, and boron are reported in terms of ppm dry-weight of the soil. The EC and pH values are reported for the 1:5 soil water extract.

Figures 6, 7 and 8 present data from the main transect data for water extractable selenium at six depths, and for selenite and EC at three depths. As indicated in the figures, the physicochemical properties and concentrations vary with location. The variations have been analyzed using geostatistical methods.

As an example, water extractable selenium measured at 3 meter intervals were estimated at 1.5 meter intervals using state space methods. A second order equation was selected as adequate, based on the Akaike Information Criteria (Akaike, 1973). Figure 9 presents the resultant transect for the 0-15 cm depth and Figure 10 the measured and estimated selenium which when

Figure 4a. Mean water extractable selenium concentrations (main transect).

Figure 4b. Mean selenite concentration (main transect)

KESTERSON RESERVOIR : POND 7

Figure 4c. Mean boron concentration (main transect).

KESTERSON RESERVOIR : POND 7

Figure 4d. Mean electrical conductivity (main transect)

KESTERSON RESERVOIR : POND 7

Figure 4e. Mean pH [1:5] (main transect)

KESTERSON RESERVOIR : POND 7

Figure 5a. Mean water extractable selenium concentrations (sub transect).

Figure 5b. Mean selenite concentration (sub transect)

Figure 5c. Mean boron concentration (sub transect)

KESTERSON RESERVOIR : POND 7

Figure 5d. Mean electrical conductivity (sub transect)

KESTERSON RESERVOIR : POND 7

Figure 5e. Mean pH (sub transect)

KESTERSON RESERVOIR : POND 7

Figure 6. Water extractable selenium concentrations (main transect: 0-150 cm).

KESTERSON RESERVOIR : POND 7

Figure 7. Selenite concentration (main transect: 0-60 cm).

KESTERSON RESERVOIR : POND 7

Figure 8. Electrical conductivity [1:5] (main transect: 0-60 cm)

Figure 9. Estimated water extractable selenium (main transect: 0-15 cm).

correlated gave an $r^2 = 0.94$. The auto correlation function for water extractable selenium drawn in Figure 11 suggests samples are correlated to distances of about 18 m using both estimated and measured data. Similar analyses have been done for other parameters and for some plant data. Semi-variograms have been prepared but models have not been fit to the data yet.

Figure 12 represents the mean water extractable selenium in the initial and final sampling for the 0-60 cm interval. It shows that the water extractable selenium concentration in the 0-15 cm in depth has decreased while the concentration in the 30-60 cm depth has increased, which suggest that a fraction of soluble selenium has leached to deeper layers by irrigation. A small fraction of selenium lost from the 0-15 cm interval may be explained by microbial and/or plant volatilization.

Figure 13 shows the changes in mean selenite concentration before and after irrigation. As shown, the selenite concentration has increased in the surface layer (0-15 cm) while remaining nearly the same in the 30-60 cm depth. Increases in selenite concentration may be due to reduction of selenate to selenite or oxidation of elemental selenium. At this time we do not know which of these two processes is the dominant one.

Figures 14 and 15 show an increase in EC_{25} (1:5) and B concentration in the 0-60 cm depth as a result of irrigation. Irrigation water with an average EC_{25} of 11.7 dS/m, and B concentrations of 10.4 ppm most likely lead to increased EC and B concentrations (see Table 2).

Table 2. Properties of irrigation water.

Date Collected	EC_{25} (dS/m)	B (ppm)	SO_4^{2-} (me/l)	Cl^- (me/l)	Se (ppb)
07/01/88	11.64	10.3	83.7	58.9	<1
08/31/88	11.90	10.3	91.9	70.1	<1
09/16/88	11.77	10.6	95.6	71.0	<1

Figure 10. Regression of estimated and measured water extractable selenium.

Figure 11. Autocorrelation of water extractable selenium (0 - 15 cm).

Figure 12. Initial and final mean water extractable selenium in the main transect (0-60 cm).

Figure 13. Initial and final selenite concentration in the main transect (0-60 cm).

Figure 14. Initial and final electrical conductivity in the main transect (0-60 cm).

Figure 15. Initial and final mean boron concentration in the main transect (0-60 cm).

2.3. Volatilization Studies at the Pond 7 Test Plot

Selenium volatilization measurements were made under several conditions in the test plot. The various treatments tested were: bare soil, soil with native vegetation; and disked soil with incorporated plant residue. One additional plot with disked native vegetation was also tested, but with a lower rate of irrigation. All of the other treatments received the same amount of irrigation water (see Figure 20 for a complete record of the irrigation schedule).

The volatile selenium was trapped in a chimney fitted with a charcoal filter trap. Selenium was then extracted from the filters with deionized distilled water. Two methods of extractions were used, namely (a) syringe and (b) shaker. In both methods, approximately the same amount of selenium was extracted. However, it was found that selenium recovery from the filters was incomplete. Further studies are underway to determine a more efficient method of extracting volatilized selenium from charcoal filters.

Figure 16 summarizes the results of the volatilization measurements. The highest rate of volatilization was found in the disked soil with incorporated plant residue which also received high amounts of irrigation water. Volatilization rates in this plot were ten times greater than any of the other plots, thus confirming earlier laboratory experiments that identified disking native vegetation into the soil as a promising stimulation for volatilization of selenium (LBL, 1987). Small but measurable rates were detected at all of the plots. The volatilization rates at the disked plot with a low rate of irrigation was similar to the other plots, demonstrating that soil moisture is an important stimulant for volatilization. This observation is in general agreement with the results reported by Frankenberger and Karlson, 1988.

2.4. Irrigation System and Soil Water Movement

2.4.1. Irrigation System

The irrigation water for the test plot is pumped from a well located along the road parallel to the San Luis Drain near Pond 7. A gate valve, totalizing flow meter, air release valve, and butterfly valve were installed in the 6-inch (.15 m) mainline which carried water to the two 3-

Figure 16. Volatilization of selenium under various treatments in Pond 7.

inch (0.076 m) aluminum irrigation laterals located about 10 m apart. Both laterals were equipped with pressure gages, totalizing flow meters, and butterfly valves and an air release valve was placed in lateral 2. Impact sprinklers (Rainbird 20-14 H) with 3/32-inch nozzles were installed on 18-inch (0.46 m) high risers every 4.6 m along the 200 m laterals. A schematic of the irrigation system and the location of measuring station is provided in Figure 17.

The layout and numbering sequence for the catch cans is shown in Figure 18. Water application profiles are shown in Figure 19 for rows of catch cans normal to the lateral. Can number 13 is at lateral 1 and can 25 is a lateral 2. Application is nearly uniform between cans 17 and 21 and decreases to the edges of the profile. Profile shape changes little along the laterals. The 2 laterals will be placed closer together in the future to obtain more uniform distribution between the two sprinkler lines.

Shallow irrigations were applied initially to prevent overirrigation. Later the water application was increased to approximately 5 cm per irrigation at the midpoint between the laterals where application was greatest (see Figure 20). Total application was nearly the same for the vegetated and non-vegetated portions of the test plot.

2.4.2. Soil Water Monitoring

Neutron probe access tubes were installed to 150 cm depth every 18 m midway between the lateral lines (sites 4 through 58). Ten access tubes each were installed at 30 cm spacing along the same transect in the area where vegetation was scraped off then the area disked (NV) and in two areas where the vegetation was undisturbed. The first vegetated location was adjacent to the scraped treatment (veg) and the second was upstream (USV) and normal to another transect of neutron probes. Access tubes along the transverse transect were spaced every 3 m and were numbered 65 through 106. Probe measurements were taken at 15-, 30-, 60-, 90-, 120-, and 150-cm depths. The probe was calibrated to determine the relationship between count ratio and volumetric water content.

The mean and variability of water application were measured with catch cans placed at

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Figure 17. Schematic of the irrigation system at the test plot in Pond 7.

Figure 18. Layout of three row catch can test.

Figure 19. Water distribution profiles from the irrigation system.

each moisture probe site. A can was placed on top of each tube and the amount of water collected was measured.

Soil moisture content was integrated over the monitoring depth to give total soil water in the 150 cm profile for vegetated and non-vegetated treatments (see Figure 21). Large increases in stored water corresponded to the amount of irrigation water that was applied (see the arrows in Figure 21). Comparison between the data from the vegetated and non-vegetated plots shows that the vegetated plot was considerably drier throughout the irrigation period. Differences between total water storage of vegetated and non-vegetated areas can be largely attributed to root water extraction and transpiration by the vegetation.

The total amount of soil water stored in the profile was also measured on a transect perpendicular to the sprinkler lines (see Figure 22). Moisture storage was high between laterals and decreased away from the lines as would be anticipated with the dual-line system. As shown in Figure 22, water applied during irrigations between August 19 and 26 increased the total amount of water storage, especially between the laterals where water application was greatest.

To examine the distribution of water content within the soil profile in the vegetated and non-vegetated areas, water content data from 10 closely-spaced tubes (see Figure 17) was averaged at each depth (see Figures 23 and 24 respectively). The soil was drier near the surface and water content was generally lower for the vegetated area compared to the non-vegetated area. Comparing Figures 23 and 24 indicates that water was extracted and/or evaporated from deeper layers in the vegetated treatment, as compared to the non-vegetated treatments. Irrigations caused approximately equal increases in water content to 90 cm. Small changes in water content at and below 120 cm between the two dates shown, together with the large decrease in water content above 120 cm suggests little deep percolation.

2.4.3. Groundwater Monitoring

In June of 1988, 21 observation wells screened over a depth of 1.5 to 4.5 m were installed at the test plot in Pond 7. The wells were arranged in 3 rows of 7 wells each. The rows were

Figure 20. Cumulative water applied for vegetated and no vegetation areas.

Figure 21. Total soil water in profile for vegetated and no vegetation areas (arrows represent irrigations).

Figure 22. Total soil water to 150 cm along a transect perpendicular to sprinkler lines for the vegetated area before and after irrigations (arrows are line locations).

Figure 23. Average water content profile for the vegetated area.

spaced 6 m apart and individual wells were 9 m apart. This grid of wells was nearly centered on to the irrigation system.

Groundwater levels and electrical conductivity (EC) measurements were taken occasionally from September 1 1988 through January 31, 1989. As shown in Figures 25 and 26 depths to groundwater ranged from approximately 1.5 to 2.5 m. EC values ranged from 10 to 35 dS/m during this period (see Figure 27). Consistent with seasonal fluctuations due in part to flooding of duck club lands adjacent to the Reservoir, groundwater levels rose from September to January by nearly one meter. Though groundwater levels changed, the spatial variation of the water levels remained unchanged as can be seen in the contour plots. Groundwater salinity was greatest near the road, and declined with distance into the pond to a relatively constant level at the center of the observation well grid. The reason for this spatial variation in salinity is uncertain but most likely is due to the recent period (1986 to 1987) during which lower salinity was used to flood some of the Reservoir. These data provide a baseline for assessing groundwater salinity and water table elevation changes in response to future irrigation at the test plot.

2.5. Vegetation Sampling

2.5.1. Introduction

Plant growth and ability of colonization are often severely inhibited by high concentrations of soil salinity and toxic elements. Yet almost inevitably, contaminated soils are colonized by a variety of plant species. These species either have an innate adaptive nature or have developed tolerance through the processes of selection and evolution (Goodman, 1983; Rozema et al., 1978; Wu, 1981). The richness of species diversity and biomass production of the vegetation in the contaminated soil is a result of direct interaction between the plants and the physical environment of the soil which may influence plant population growth and individual survival (Dodd and Coupland, 1966; Power, 1978). In soils at Kesterson Reservoir, both high concentrations of salinity and selenium are present, and the distribution of plant species in the area is very distinctive (CH₂M Hill, 1986).

Figure 24. Average water content profile for no vegetation area.

Figure 25. Water table depth and electrical conductivity averaged for all wells and for well 10.

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Figure 26. Water table depth contours (m) for September 19, 1988.

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Figure 27. Electrical conductivity contours (dS/m) for September 19, 1988.

This section of the report presents the results of field studies on biomass distribution, species diversity and selenium accumulation by plants in this Pond 7 test plot.

2.5.2. Diversity, Biomass and Selenium Concentrations in the Pond 7 Test Plot

Plant species diversity and biomass distribution of native-grown plants were measured at the test plot in Pond 7 on two occasions, the first on July 13, 1988 and the second on November 21, 1988. The above-ground plant tissue was collected from 62 sites along a 183 m north-south transect crossing the center of the 46 m-wide field plot. Plant samples also were collected along two 46 m east-west transects. Samples were collected in 9 m intervals. The species diversity is presented as percent area of vegetation coverage by each plant species. Plant materials were oven dried, and percent dry weight of each species was calculated. Plant tissue selenium concentration was measured.

The average biomass production was found to be approximately 800 g/m², and the three transect sampling sites presented a similar value of biomass production (see Table 3). The average ground coverage by the vegetation was about 90 per cent. Salt grass (*Distichlis spicata*) composed about 80 per cent of the total vegetation. *Atriplex tularensis* is the second most common species and composed about 20 percent of the vegetation. *Juncus balticus* was only found in small areas confined by high soil moisture. Biomass dry weight production of these three plant species is positively correlated with their vegetative coverage.

The plant tissue selenium concentration of salt grass was found to be between 1 to 2 ppm, with an average of 1.5 ppm. *Atriplex tularensis* had about 4 ppm tissue selenium concentration, and *Juncus balticus* had a similar tissue selenium concentration as salt grass. Figures 28, 29, 30 show the distribution of biomass and tissue selenium concentration of salt grass along the sampling transect. There appears to be a positive correlation between these two parameters found in transect 1 ($r = 0.49$, $P < 0.01$). However, no significant correlation was found between tissue selenium concentration and biomass production for samples collected from transects 2 and 3. For *Atriplex* (Figures 31, 32, and 33) no significant correlation was detected for any of the three transect samples.

Table 3. Biomass production, species diversity and plant tissue Se concentration of vegetation grown in evaporation Pond 7 at Kesterson Reservoir

	Transect 1 Mean±SD	Transect 2 Mean±SD	Transect 3 Mean±SD
Number of samples taken	62	12	12
Average Biomass (g/m ²)	799±86	803±172	801±131
Average ground coverage(%)	86.9±18.1	94.1±5.5	90.6±9.8
Species diversity			
Area(%)			
<i>Distichlis spicata</i>	81±21	76±32	79±27
<i>Atriplex tularensis</i>	18±11	28±32	33±22
<i>Juncus balticas</i>	0±0	0±0	10±0
Biomass (g/m ²)			
<i>Distichlis spicata</i>	740±145	638±242	684±177
<i>Atriplex tularensis</i>	59±53	120±145	114±69
<i>Juncus balticas</i>	0±0	0±0	53±0
Se conc. in tissue (ug/g)			
<i>Distichlis spicata</i>	1.54±0.31	1.71±0.24	1.43±0.41
<i>Atriplex tularensis</i>	3.63±1.53	4.11±2.05	2.32±0.51
<i>Juncus balticas</i>	0±0	0±0	1.25±0

salt grass

Figure 28. Biomass and selenium concentrations in salt grass samples along transect 1.

salt grass

Figure 29. Biomass and selenium concentrations in salt grass samples along transect 2.

Figure 30. Biomass and selenium concentrations in salt grass samples along transect 3.

Atriplex tularensis

Figure 31. Biomass and selenium concentrations in *Atriplex tularensis* samples along transect 1.

Atriplex tularensis

Figure 32. Biomass and selenium concentrations in *Atriplex tularensis* samples along transect 2.

Atriplex tularensis

Figure 33. Biomass and selenium concentrations in *Atriplex tularensis* samples along transect 3.

Data on the soil selenium concentrations presented in Section 2.2 showed that the water extractable selenium of the top 15 cm soil ranged from 0.15 to 0.65 ppm (ppm of the air-dried soil). The soil salinity at the experimental plot was generally high and ranged from 1.5 dS/m to 3.5 dS/m in the 1 to 5 soil water extracts. A positive correlation between soil selenium concentrations and EC of the soil extract was found ($r = 0.46$, $P < 0.01$). Plant biomass was not significantly correlated with soil selenium concentration, except the salt grass biomass in transect 1, which showed a positive correlation with the soil selenium concentration (see Table 4). Tissue selenium concentrations of both salt grass and *Atriplex* were positively correlated with soil selenium concentrations (see Table 4).

The second sample collection was conducted in September of 1988. A summary of the data from the second sampling period is shown in Table 5. At this time the total soil soluble selenium concentration ranged from 88 to 252 ppb, and selenate concentration ranged from 27 to 137 ppb. The biomass production was about 200 g/m^2 , with a tissue selenium concentration of about 2 ppm.

Several tentative conclusions may be drawn from the above studies:

1. Pond 7 was represented by a dense vegetation coverage with an average biomass of 800 g/m^2 dry weight.
2. The plant species diversity in Pond 7 was represented by only a few species, and salt grass composed 80 per cent of the vegetation. *Atriplex* composed about 20 per cent. Both species are adaptive to high soil salinity. The tissue selenium concentration was about 1.5 ppm for salt grass and 4 ppm for *Atriplex* species.
3. Salt grass collected in the fall of 1988 had slightly but significantly higher tissue selenium content.

2.6. Biological Sampling at the Pond 7 Test Plot

Biological sampling in the Pond 7 test plot was initiated in January 1989. The biological monitoring plan is modeled after the ongoing monitoring plan described in USBR (1988). Sam-

Table 4. Linear regression and significant levels generated between biomass, plant tissue Se concentration and soil extract Se contents for plant and soil samples collected from Kesterson Evaporation Pond 7 field plot.

Species and Correlation	Correlation Coefficient	Degree of Freedom	Significance Level
<i>Saltgrass</i>			
soil Se ⁴⁺ /biomass	r=0.106	29	NS
soil Se ⁴⁺ /tissue Se concentration	r=0.304	29	NS
Soil total Se/biomass	r=0.556	29	**
soil total Se/tissue Se concentration	r=0.535	29	**
<i>Atriplex</i>			
soil Se ⁴⁺ /biomass	r=0.295	13	NS
soil Se ⁴⁺ /tissue Se concentration	r=0.504	13	NS
Soil total Se/biomass	r=0.265	13	NS
soil total Se/tissue Se concentration	r=0.533	13	*

Table 5. Selenium concentration (ng/g dry weight or ppb), pH, and electrical conductivity [mmhos/cm.(EC)] of soil extracts of soils and biomass production and tissue Se concentration of plants collected from the Kesterson evaporation Pond 7.

Measurement	Sample Collected in June 1988		Sample Collected in September 1988		Sign. Level
	Mean	SD	Mean	SD	
Soil					
Total Se	376	170	139	58	**
Selenate			66	40	
Selenite	33	25	37	30	NS
pH	7.10	0.39	7.02	0.18	NS
EC	2.38	0.59	1.94	0.38	*
Saltgrass					
Biomass (g/m ²)	740	145	200	47	**
Se conc. (ppb)	1.54	0.31	2.13	0.63	**

*Significantly different at the 90% confidence limit.

**Significantly different at the 95% confidence limit.

ples of salt grass, *Frankenia* and soil were collected in two locations; one between the two sprinkler lines, and one on the periphery of the plot. Two pitfall traps for catching invertebrates were also installed at these locations.

Selenium concentrations in the soil were low, less than 1 ppm in the two samples collected from the top 0.15 meters of soil. *Frankenia* and salt grass were slightly higher, with concentration of 2.8 ppm and 1.2 ppm, respectively. To date, a total of 5 spiders have been collected from the plot. The selenium concentration in a composite sample of these 5 spiders was 8.9 ppm. All of the above analysis were determined with the XRF method described in the LBL QA/QC program. Selenium concentration in the above ground vegetation and spiders are typical of the upland environment at Kesterson Reservoir (USBR, 1988).

Collection of vegetation and invertebrates will continue. As treatments are added and/or identified as a promising component of a vegetation management plan, biological monitoring will be intensified to identify biological impacts of the various management options.

3.0. Laboratory Investigations

3.1. Introduction

The following section describes the results of 5 laboratory investigations, namely:

- Selenium volatilization from plants;
- Identification of salt and boron tolerant plant species that may be grown at Kesterson;
- Laboratory leaching and column volatilization experiments;
- Selenium uptake and tolerance of salt grass; and
- Resorption of volatilized selenium in Kesterson soils.

3.2. Selenium Volatilization from Plants

3.2.1. Introduction

The main objectives of this effort are (1) to determine the rates of volatilization of selenium (Se) for a range of plant species including selenium accumulators, crop plants and native species, and (2) to determine the relationship of selenium volatilization to selenium uptake and partitioning. This data will provide one piece of information needed to assess the selenium mass balance for a particular species when grown at Kesterson Reservoir.

3.2.2. Plant Materials and Methods

The selenium accumulators being evaluated include *Astragalus bisulcatus*, *Astragalus cymocarpus*, and *Astragalus hamosus*. The selenium nonaccumulator crops include cotton (Acala SJ-2) and barley (UC 337). The range plant species include *Brassica juncea* and *Atriplex nummularia*. Plants were grown in nutrient solution culture containing 20 μM sodium selenate in 1/2 strength Hoagland solution. For the *Astragalus* species, 50 μM phosphorous was used in the nutrient solution. Higher phosphorus concentrations were found to be toxic to *Astragalus*

species. The plants were grown in growth chambers at $500 \mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ photon flux density (PFD), 25°C and 16 hour photoperiod.

The growing conditions were standardized for all of the plant species mentioned above. A gas exchange system was developed for measuring the selenium volatilization rates from an intact plant for a prolonged time under controlled environmental condition (light, air temperature, leaf temperature and relative humidity). This whole plant gas exchange system can measure the selenium volatilization rates very accurately. The system is comprised of a plant chamber made with plexiglass and a light source (water-cooled xenon-arc illumination system) that is attached to a conventional leaf gas exchange system. The rate of air flow in the system was maintained at 6 L/min. A small fan was placed inside the plant chamber to circulate air. The leaf temperature was monitored by using a thermocouple.

Selenium volatilization rates were measured by passing the air through the whole plant into an alkaline peroxide solution (100 ml: 80 ml of 0.05 N NaOH + 20 ml of 30% H_2O_2). To analyze the selenium trapped by the solution, samples were boiled for 15 minutes to drive off the residual H_2O_2 , cooled, made up to 100 ml, mixed with an equal volume of HCl, boiled for an additional hour and then measured by AAS/hydride generation.

3.2.3. Results

After determining selenium volatilization rates, the plant was removed from the chamber and separated into roots, leaves, and stems. Leaf area was determined using a Delta-T leaf area meter so that volatilization rates could be expressed per unit leaf area. The plant samples were dried at 50°C , weighed, and tissue selenium concentrations were determined using acid digestion followed by AAS/hydride generation (Mikkelsen, 1987). Selenium volatilization rates have been monitored for 7 test plants, including 3 Se accumulators, 2 range and 2 crop species. Volatilization rates, expressed on a per plant and per leaf area basis are presented in Figures 34a,b. Selenium accumulators outperformed other plant species in terms of Se volatilization.

Table 6. Plant growth and Se uptake for 7 different plant species. Plants were grown in growth chambers in 1/2 strength Hoagland solution with 20 μ M sodium selenate.

Plant Species	Age (days)	Total dry matter (gplant ⁻¹)	Total leaf area (cm ² ·plant ⁻¹)	Se uptake (mg·plant ⁻¹)
<i>Astragalus Bisulcatus</i>	55	2.31	195	2.59
<i>Astragalus hamosus</i>	41	4.2	206	1.06
<i>Astragalus cymbocarpus</i>	49	4.06	294	2.23
<i>Atriplex numularia</i>	38	5.61	704	1.32
<i>Brassica juncea</i>	43	3.38	627	2.0
Cotton	36	5.43	669	0.89
Barley	36	9.17	934	3.31

Astragalus bisulcatus was the champion volatilizer volatilizing more Se than any other species tested ($0.6 \mu\text{g Se}\cdot\text{plant}^{-1}\cdot\text{day}^{-1}$; $31 \mu\text{g Se}\cdot\text{m}^{-2} \text{ leaf area}\cdot\text{day}^{-1}$). We were surprised to find however, that the two crop plants, cotton and barley, volatilized almost as much Se per plant as the remaining four species which included two accumulator species, *Astragalus hamosus* and *Astragalus cymbocarpus* (Figure 34a). Although the Se accumulator species outperformed the crop plant species on a per unit leaf area basis (Figure 34b), the crop plants had faster growth rates and greater total leaf areas (Table 6) so that the rates of Se volatilized per plant by the crop plants were comparable to those of the other 4 species. (The crop plants were grown for 5 weeks compared to 6 to 8 weeks for the accumulator plants.)

There seems to be little relation between the rate of Se volatilization and the amount of Se present in the leaf. In barley, large amounts of Se were transported to leaves (see Figure 335a), yet the rate of Se volatilization per area was the lowest of all the species tested (Figure 34b). Cotton has the lowest leaf Se concentration (Figure 35a), but volatilized Se at a faster rate per area than barley. Similarly, there appeared to be little evidence that the rates of volatilization

Figure 34a,b. The rates of Se volatilization per plant (A) and per unit leaf area (B) for six different plant species including Se accumulators (*Astragalus hamosus*, *Astragalus cymbocarpus*), range plants (*Atriplex numularia*, *Brassica juncea*), and crop species (cotton, barley). The rate of Se volatilization for *Astragalus bisulcatus* was $0.6 \mu\text{g Se} \cdot \text{plant}^{-1} \cdot \text{day}^{-1}$ or $31 \mu\text{g Se} \cdot \text{m}^{-2} \cdot \text{leaf area} \cdot \text{day}^{-1}$. Plants were grown in growth chambers for 5 to 8 weeks in 1/2 Hoagland solution with $20 \mu\text{M}$ sodium selenate.

Figure 35a,b,c. Tissue Se levels in leaves (a), stems (b) and roots (c) for six different plant species. The tissue Se levels for *Astragalus bisulcatus* leaves, stems and roots were 1417, 1333 and 592 mg·dry wt, respectively. Plants were grown in growth chambers in 1/2 Hoagland solution with 20 μ M sodium selenate.

among the 6 species (excluding *A. bisulcatus*) were correlated with the total uptake of Se per plant in each case (Figure 34a, Table 6). *A. bisulcatus*, however, had the highest concentration of Se in leaves and this was correlated with the highest rate of Se volatilization (Table 6; Figure 34).

Barley is an interesting crop species in terms of its potential ability to remove Se from soils. This is because it volatilized Se at rates comparable to the other species except *A. bisulcatus* (Figure 34). This was due in part to the high rate of expansion of the total leaf surface which was exhibited by barley. Furthermore, barley accumulated high concentrations of Se in leaf tissue (Figure 35a). This in turn could potentially contribute to the removal of Se from seleniferous soils since leaves and stem could be harvested and removed from the site.

3.3. Accumulation of Selenium by Perennial Forage Species

Efforts for this task have only recently begun. To date, seed supplies for a number of cultivars and lines have been procured, catalogued, and placed in cold storage. Included are 13 lines across 8 species of grass and 13 lines across 4 legume species. Efforts to obtain three *Astragalus* species are underway.

Preliminary experiments have been conducted to develop and optimize germination methods and standard procedures have been adopted. In addition, germination rate experiments have been completed for 11 grass and legume lines, and optimum seed pretreatments and incubation conditions have been identified. Salinity and boron tolerance tests for germination are currently underway.

3.4. Effect of Irrigation Strategy on Dissipation of Selenium from Contaminated Pond

Sediments

The effect of surface and subsurface irrigation and irrigation frequency on the vertical movement, plant uptake, and volatilization of selenium in Kesterson Reservoir sediments is being evaluated under greenhouse conditions using large soil columns planted with salt grass. The following treatments are being evaluated

1. Surface irrigation
 - Three irrigation frequencies
 - Sediments from filled and unfilled areas
2. Subsurface irrigation
 - Sediments from filled and unfilled areas.
 - Vegetated (salt grass) and non-vegetated sediments.

Sediment columns approximately 1 m in length and 15 cm in diameter have been prepared and placed in a controlled temperature chamber inside a greenhouse under conditions which will be similar to dry season at the Kesterson Reservoir. Native plants (salt grass) were planted in these columns. Two different methods of irrigation, and three different frequencies will be used. Water is applied at a rate less than or equal to the infiltration rate to simulate the sprinkler irrigation. Water is applied at zero and negative pressures from the bottom of the soil profile in another set of columns to simulate subsurface irrigation and create an upward flux of water. Soil columns were wetted in upward direction by applying water at zero pressure from the bottom of the soil profile. Tensiometers, soil solution samplers, redox electrodes, and thermocouples were installed after the soil wetting was finished. Soil gas samplers have been installed at various depths to determine the soil zone from which selenium volatilization might occur. A plant canopy and glass hood assembly has been constructed to trap volatile selenium from the soil surface. Gaseous selenium is trapped in a hydrogen peroxide solution. Concentrations of water extractable selenium in the sediments were determined prior to and after wetting (Figure 36). As expected, capillary rise draws the more seleniferous fluids up through the soil column, creating a dramatic increase in the soluble selenium content in the upper portions of the soil columns. Similar consequences of capillary rise were noted in LBL Progress Report 9.

Experiments are now underway to assess the effects of different irrigation strategies on the redistribution and volatilization of selenium.

Figure 36. Concentration of total water-extractable selenium with depth prior to and after capillary rise in filled and non-filled sediments (microgram per kilogram).

3.5. Selenium Uptake and Tolerance of Salt Grass

3.5.1. Introduction

Salt grass is one possible cornerstone of a soil water and vegetation management scheme at Kesterson Reservoir. Its benefits include salt tolerance, demonstrated ability to grow in the Kesterson environment, and its relatively low uptake of selenium into the above-ground plant tissue. Laboratory studies are underway to assess selenium uptake and tolerance of salt grass, to better understand how it will survive anticipated future conditions at the Reservoir.

3.5.2. Materials and Methods

Plant samples were collected as single pieces of rhizomes. Three or four shoots were attached with each piece of rhizome. Salt grass rhizomes were collected from three sites within Pond 6, covering a soil selenium concentration gradient. The high soil selenium site was a 25 m by 30 m island about 45 meters from the south edge of the pond. The second site was a 3 m wide and 45 m long strip of vegetation along the southern edge of the pond. The third site was a 0.5 m wide strip of vegetation along the roadside. Five pieces of salt grass rhizomes were collected at 5 m intervals from the island, and at 10 m intervals at the other two sites. Plant samples were also collected from a site about 300 meters from Pond 6 where the soil selenium was low, and from a vernal pool in Dixon, California. Plant samples collected from these two sites were used as controls. Three soil samples from the surface most 15 cm were collected 5 m apart in the center of each site. Soils were dried at room temperature before water extractable selenium concentrations were measured.

The plant samples were propagated by transplanting them into 5 liter plastic pots filled with greenhouse potting soil. For selenium tolerance and selenium accumulation studies, tillers of comparable size including a two node section of rhizome were collected from the greenhouse propagated clones. Three tillers were transplanted into a supporting medium of black polystyrene beads. The beads were contained in a hole 8 cm wide in the center of a 12 cm diameter, 2.5 cm thick styrofoam disc. The whole disc was floated on nutrient solution in a 2.5 liter plastic container. One quarter strength of Hoagland nutrient solution was amended with 0 or 2 ppm

selenium. The culture solutions were replaced every four days. The plants were kept in a greenhouse (20°C day and 18°C night). After a 40-day growth period, the plants were harvested and separated into shoots (including rhizome) and roots. Selenium tolerance was measured based on dry weight, and expressed as a tolerance ratio. The tolerance ratio is defined as the ratio between the dry weight of the plant grown in the selenium amended solution and the dry weight of the plant in the unamended solution.

For the selenium accumulation measurements, the plant tissue was dried at 65°C for 48 hours. An acid digestion method (Ganje and Page, 1974) was used for selenium extraction. The final analysis was made by hydride generation flame atomic absorption (Perkin-Elmer).

For soil analysis, the water extractable selenium was measured. A five to one, distilled water to dry soil, ratio was used for soil extract preparation.

For data analysis, analysis of variance, correlation coefficient analysis and Duncan's new multiple range test were performed (Duncan, 1955).

3.5.3. Results

In Pond 6 the highest water extractable selenium concentration was found in the soils collected from the island (2758 ppb dry weight for selenate and 360 ppb dry weight for selenite). These concentrations were about 10 times higher than the water extractable selenium concentration at the edge site, and 100 times higher than the water extractable selenium concentration at the roadside site. The concentrations at the two control sites were low, ranging from 10 to 40 ppb.

The salt grass collected from the island of Pond 6 produced a dry shoot weight of about 2,000 mg for 3 plants in a 2 ppm selenium solution (see Table 8). The plants from the edge site of the pond, cultured under similar conditions, had about 1,500 mg (for 3 plants). The road side plants produced about 1,000 mg (3 plants). Root dry weights were about 1/10 that of the shoot dry weight and showed a similar difference between the three sites. The shoot tissue selenium concentration was in the range of 300 to 500 µg/g dry weight, and the root tissue selenium con-

Table 7. Selenium concentration ($\mu\text{g/g}$ dry weight), pH, and electrical conductivity [mmhos/cm.(EC)] of soil extracts of soils collected from the Kesterson evaporation ponds and from control sites.

Location	Soil measurement	Site					
		Roadside		Pond edge		In the pond	
		Mean	SD	Mean	SD	Mean	SD
Kesterson Pond 2	Selenate	38	6	138	11	1601	58
	Selenite	14	5	231	56	2101	294
	pH	6.88	0.43	7.20	0.15	7.15	0.21
	EC	0.28	0.04	2.35	0.38	0.87	0.09
Kesterson Pond 6	Selenate	32	5	233	19	2758	221
	Selenite	-	-	73	37	360	14
	pH	7.26	0.43	7.44	0.28	7.39	0.09
	EC	0.28	0.10	2.19	1.51	6.61	0.39
Kesterson Control Site	Selenate	38	4				
	Selenite	10	-				
	pH	6.87	0.04				
	EC	0.38	0.09				
Dixon Control Site	Selenate					19	4
	Selenite					13	-
	pH					6.70	0.07
	EC					0.19	0.05

Table 8. Dry weight production and tissue selenium concentration of salt grass collected from three sites along a soil selenium concentration gradient in each of the two evaporation ponds grown in culture solution supplemented with 2 ppm selenium as sodium selenate.

Site	Pond 2		Pond 6	
	Dry weight(mg)	Se (ug/g)	Dry weight(mg)	Se (ug/g)
	Shoot		Shoot	
In the pond	1684.9 ^a	574.2 ^a	1983.1 ^a	640.9 ^a
Pond edge	1223.9 ^a	445.9 ^b	1477.8 ^b	529.6 ^b
Roadside	724.6 ^b	323.5 ^c	879.1 ^c	458.6 ^c
	Root		Root	
In the pond	164.3 ^a	238.8 ^a	206.0 ^a	456.4 ^a
Pond edge	129.3 ^a	254.7 ^a	111.2 ^b	301.3 ^b
Roadside	61.9 ^b	277.7 ^a	67.6 ^b	219.6 ^c

Note: means in a column followed by the same letter are not significantly different at the 5 percent probability level according to Duncan's multiple range test.

centrations ranged from 200 to 450 $\mu\text{g/g}$ dry weight. The selenium tolerance of the plants displayed a positive relationship with the soil selenium gradient across the three sites in the pond. The results of Duncan's New Multiple Range Test shows that the mean selenium tolerance between sites are significantly different.

The correlation coefficient analysis showed that the tissue selenium concentration is positively correlated with the selenium tolerance ratios and the dry weight production of the plants (Figures 37 and 38). The positive correlation between the selenium tolerance of the plants and the soil selenium concentration suggests that the soil concentration was sufficiently high to provide a selection pressure on salt grass. The positive relationship between selenium uptake and tolerance suggests that a cellular tolerance mechanism may be involved.

3.6. Resorption of Volatilized Selenium in Kesterson Reservoir Soils

3.6.1. Introduction

While volatilization of selenium from soils is recognized as an important pathway for dissipation of the selenium inventory at Kesterson Reservoir, processes which can retard the efficiency of this mechanism also require quantification. Among these mechanisms is resorption of volatilized selenium within the soil profile, which reduces the effectiveness of volatilization by allowing selenium recycling within the soil. Several researchers have observed this mechanism in previous studies. However, few systematic studies directed specifically at resorption of volatile selenium in soils appear to have been performed. In view of the importance of volatilization as a component in managing the residual selenium inventory at the Reservoir, and the potential importance of volatile selenium resorption, a study of this process is warranted.

Previous researchers have noted the importance of organic matter and clay contents of soils in resorbing volatilized selenium, and thus retarding its emission from soil surfaces (Zieve and Peterson, 1985). These variables will be included in the present study. Two additional variables which apparently have not been investigated previously will also be included in the present study. These variables are (1) the effect of the soil profile depth, and (2) the effect of diffusive versus convective soil gas flow. Due to the distribution of selenium at depth in Reservoir soils,

Figure 37. The joint distribution and correlation coefficient of tolerance ratio and dry weight production of salt grass grown in culture solution supplemented with 2 ppm selenium as sodium selenate.

Figure 38. The joint distribution and correlation coefficient of tolerance ratio and tissue selenium accumulation of salt grass grown in culture solution supplemented with 2 ppm selenium as sodium selenate.

the variable of soil profile depth is of relevance in estimating selenium depletion times. In light of the potential importance of volatile selenium resorption in soils, the depth variable appears to be comparably significant. This preliminary evaluation is based upon the fact that opportunities for resorption are at least linearly proportional to the distance (i.e. depth) traversed. Simple arguments are also available which support an even stronger depth-dependence for volatile selenium resorption (specifically, that resorption will be at least proportional to the depth squared). The second new variable to be investigated is that of diffusive versus convective transport of volatilized selenium. This aspect of the work focuses on the effect of soil gas flow rates on net release of volatile selenium. This component of the study is of practical importance in assessing volatilization rate estimates based upon field or laboratory methods which induce flow of soil gas. In the natural field setting, bulk flows of soil gas are generally considered to be insignificant below the very near-surface. By inducing flow of soil gas, net emission of volatile selenium may be significantly increased above rates associated with the undisturbed soil environment. When gas sampling involves active pumping of soil gas, the resorption probability (i.e., gas residence time) is reduced substantially (due to being inversely related to pumping rates). The present set of experiments will provide quantitative information addressing the magnitude of bias associated with selenium volatilization rates based upon active pumping.

3.6.2. Materials and Methods

In order to investigate the abovementioned processes and variables, Kesterson Reservoir soils will be used in laboratory column studies. Seleniferous surface soils will be packed into columns containing different amounts of organic matter. Columns of different lengths, ranging from 0.10 m to 0.60 m will be studied. For studying volatilization under purely diffusive conditions, the bottom end of the columns will be sealed, and the headspace gas at the top end of each soil column will be circulated within a closed loop containing a filter/trap for volatile selenium. System temperatures will be controlled, and pressures will be monitored to assure that bulk flow does not occur. The same columns in which diffusive fluxes of selenium are measured will also be used to measure volatile selenium emissions under various soil gas flow rates. These flow rates will span the range of 0 mm/s (purely diffusive), up to 1.0 mm/s.

4.0. Supplemental Studies

In addition to the field and laboratory studies presently underway as part of this effort, three supplemental investigations are being carried out. All of these investigations stem from the fact that in addition to selenium, large quantities of salts, and lesser quantities of trace elements were delivered to Kesterson in the drainage water. The first of these investigations aims to assess the concentration of a wide range of trace constituents in the Kesterson soils. The second investigation focuses on characterizing the chemistry and mineralogy of the evaporites that form as the soil solution becomes saturated with respect to various mineral assemblages. The third investigation aims to determine the rate at which these constituents will accumulate at the soil surface in response to evaporative fluxes from the shallow water table. Preliminary descriptions and results from these studies are described below.

4.1. Trace Element Concentrations in Kesterson Soils

Thirty-six surface (<5 cm depth) samples of the organic-rich layer overlying the mineral sediments (three from each pond), collected in October 1988 by John Fields (USBR) were analyzed to determine the concentration of trace constituents in the surface soils. One-to-one (mass/volume) water extracts were prepared and separate aliquots taken for selected trace element analyses by ICAP. Aliquot #1 was pretreated by chelation and solvent extraction to separate and concentrate several trace elements. Aliquot #2 was analyzed by hydride generation for selenium, arsenic, antimony, bismuth, germanium, tellurium and mercury. Aliquot #3 was diluted and analyzed by direct nebulization. One-gram portions of each sample were dissolved by HNO_3 , HCl , and HF treatment and analyzed for total trace element content (Bakhtar et al., 1989). Table 9 lists the water-soluble trace elements dissolved in a 1 to 1 sediment to water mixture and total trace element contents of selected elements.

Table 9. Trace elements in Kesterson sediments (mg/L)

	Water extracts (1:1 m/v)			Total		
	Range	Mean	Median	Range	Mean	Median
B	3.0-242.	61.0	39.0	34.-578.	200.	160
Mo	0.01-45.0	10.5	3.0	0.4-49.	13	7
Se	0.01-6.0	.378	1.09	8.-306.	66	54
As	0.001-0.089	0.017	0.015	.17-2.56	.86	.65
V	0.001-0.135	0.048	0.025	8.0-97.	38	34
Pb	0.001-0.90	0.0025	0.012	<10-75	16	<10
Cr	0.001-0.012	0.004	0.002	8.5-85.	26	15
Ni	0.001-0.375	0.104	0.030	4.3-45.	19	13
Co	0.001-0.034	0.014	0.015	0.2-11.	3.0	2
Zn	0.001-0.048	0.010	0.005	10.-65.	44	42
U*	0.030-1.8	0.476	0.150	-	-	-
EC, dS/m	0.5-115.	37.	7.	-	-	-

*Water extract values for uranium are for nine samples only due to insufficient sample. Values for total uranium in sediments have not yet been determined.

Concentrations of boron, molybdenum, selenium, vanadium and uranium are elevated well above background levels. Analysis of potential concerns associated with the presence of these constituents are underway.

4.2. Effect of Evaporite Formation and Dissolution on Salinity and Toxic Element

Management in Surface Soils

Evaporites are one of the principal sinks as well as sources of dissolved mineral salts in Kesterson Reservoir. Associated with these evaporites are unknown amounts of toxic trace elements that may be either coprecipitated or adsorbed. The results from this study are important for understanding the surface accumulation of salts and toxic elements as well as leaching into the subsoil for both upland and filled areas, establishment and growth of vegetation, and potential salinity impacts on microbial volatilization of selenium and arsenic from soil.

Efforts thus far have been focused on the "C-Salt" computer program. C-Salt (Smith, et al., 1988) is a thermodynamic equilibrium chemistry model that calculates chemical speciation of the solution phase and mineral solubility in the solid phase in hypersaline systems up to 20 molar in ionic strength and for a temperature range of 10° to 40°C. The model considers in the solution phase free ions, ion pairs and triplets, and total salinity in terms of ionic strength, specific gravity and osmotic coefficient. In addition, this model calculates the precipitation and/or dissolution of more than 30 evaporite minerals.

An early version of C-Salt for evaporative salinization of brines has been partially tested for pH in carbonate systems (Nakayama, 1968), speciation of an A1-F water sample computed by GEOCHEM (Sposito and Mattigod, 1980), single ion activity coefficients in sea water using the Pitzer equation as reported by Whitfield (1979), and evapoconcentration of sea water up to 50 times and sequence of mineral precipitation (Harvie, et al. 1980).

C-salt has been utilized to calculate evapoconcentration of tile drainage effluents in the Peck Pond evaporation facility, south of Mendota. The Peck Ranch is located adjacent to Westlands Water District's regional tile-drainage collector system which contributed the subsurface

drainage waters to Kesterson Reservoir. The tile effluents disposed in the Peck pond have nearly identical chemical composition and concentration as was discharged into Kesterson.

The early version of C-Salt when applied to evapoconcentration of Peck pond water predicted the precipitation of dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), magnesite (MgCO_3), and mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) in that order. Since the precipitation of dolomite has not been observed in Peck pond and is limited by kinetic considerations, a new run of evapoconcentration without the precipitation of dolomite gave a more realistic sequence of mineral precipitation over a concentration factor (CF) from one through 50 (see Table 10).

Most recently, boron, the most dominant trace element in Peck and Kesterson ponds has been incorporated into C-Salt. Table 10 gives the speciation of borate ions including polymeric forms as well as a $\text{CaB}(\text{OH})_4$ complex for CF 1 through 50.

The illustrative computed data in Table 10 provides a powerful tool in predicting the solubility of evaporite minerals in an environment such as Kesterson. In the coming months this model will be used to compute solution and mineral speciation under evapoconcentration and dilution dissolution.

4.3. Studies of Salt, Selenium, and Boron Movement in Near Surface Soils

Due to the combination of high pan evaporation rates and a shallow water table, evaporatively driven flow is an important component of the hydrologic system at Kesterson Reservoir. Evaporation of water from the soil surface creates an upward soil water potential gradient which leads to the accumulation of solutes at and near the soil surface. Along with salt accumulation, which is a common occurrence in parts of the San Joaquin Valley, trace elements will also be transported towards the surface. Understanding of how salts and selenium behave near the soil surface under seasonally varying conditions is important for making decisions regarding the management of the Reservoir.

Such an understanding is being currently gained through detailed studies of evaporation rates and species reconcentration rates at two plots in the Reservoir (plot 8EP, in Pond 8, and plot

Table 10. Illustrative example showing the results from a C-salt run for the Peck evaporation pond.

Thermodynamic Data									
Concentration Factor	1	2	5	10	15	20	30	40	50
Ionic Strength (m)	0.15984	0.31927	0.79793	1.5108	2.1466	2.8471	4.7367	6.406	7.8705
CO ₂ (atm)	0.00034	0.00034	0.00034	0.00034	0.00034	0.00034	0.00034	0.00034	0.00034
pH	8.18	8.1	8	8.1	8.1	8.1	8.1	8.1	8.1
Density (g/cm ³)	1.009	1.0156	1.0354	1.068	1.1002	1.1319	1.1939	1.254	1.3123
Osmotic Coefficient	0.836	0.8038	0.7559	0.7221	0.7156	0.7057	0.6681	0.6735	0.689
Activity of Water	0.9975	0.9952	0.9888	0.9793	0.9701	0.9608	0.9418	0.9214	0.9019
Temperature (°C)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0

Activity Coefficients of Ions									
Concentration Factor	1	2	5	10	15	20	30	40	50
Na	0.7498	0.7007	0.6334	0.5865	0.5562	0.5357	0.5139	0.5024	0.5019
K	0.7343	0.677	0.5959	0.538	0.5006	0.473	0.4358	0.4062	0.3852
Mg	0.6914	0.7343	0.8981	1.1793	1.4398	1.7618	2.8617	4.2717	6.1234
Ca	0.1898	0.1385	0.0927	0.0733	0.0655	0.0621	0.0657	0.0712	0.0801
B(OH) ₄	0.6767	0.5919	0.4634	0.3634	0.3075	0.2626	0.1877	0.1448	0.1169
Cl	0.7243	0.666	0.5896	0.5344	0.5277	0.5249	0.513	0.5476	0.5911
SO ₄	0.2608	0.1819	0.1006	0.06	0.0449	0.0345	0.0198	0.0147	0.012
H	0.715	0.6512	0.5693	0.5288	0.5221	0.5244	0.5437	0.5955	0.664
OH	0.7024	0.6358	0.545	0.496	0.4815	0.4689	0.4273	0.4225	0.4202
HCO ₃	0.701	0.631	0.532	0.4442	0.4091	0.3809	0.3263	0.3001	0.2822
CO ₃	0.2773	0.1943	0.1096	0.0701	0.0556	0.0454	0.0296	0.0259	0.0253
H ₂ CO ₃	1.0306	1.0613	1.158	1.3207	1.4994	1.4144	2.356	3.1856	4.1334

Ion Concentrations (moles / kg water)									
Concentration Factor	1	2	5	10	15	20	30	40	50
Na	0.093854	0.18789	0.47111	0.94724	1.4292	1.9176	2.9176	3.9542	4.8537
K	0.00019173	0.00038382	0.00096239	0.001935	0.0029195	0.0039174	0.00596	0.0080776	0.010287
Mg	0.0038423	0.0053244	0.0070698	0.0033258	0.0027241	0.0022264	0.0013706	0.00091816	0.00064051
Ca	0.0037494	0.0075658	0.018346	0.014352	0.016031	0.016919	0.016005	0.014759	0.013119
B(OH) ₄	5.692E-06	9.699E-06	0.00002038	0.00005567	0.00009019	0.00012957	0.00023453	0.00037118	0.00054351
Cl	0.020266	0.040571	0.10173	0.20454	0.3086	0.41408	0.62999	0.85383	1.0873
SO ₄	0.045235	0.090555	0.22706	0.43326	0.59294	0.78429	1.4062	1.9058	2.3361
H	9.144E-09	1.218E-08	1.775E-08	1.502E-08	1.521E-08	1.515E-08	1.461E-08	1.334E-08	1.196E-08
OH	2.183E-06	1.983E-06	1.804E-06	2.497E-06	2.548E-06	2.592E-06	2.788E-06	2.758E-06	2.715E-06
HCO ₃	0.0010999	0.0010073	0.00093753	0.0014284	0.0015513	0.0016658	0.0019447	0.0021142	0.0022486
CO ₃	0.00001989	0.00001929	0.00002107	0.00005334	0.0000672	0.00004047	0.00012616	0.00014452	0.00014769
H ₂ CO ₃	0.00001141	0.00001105	0.00001007	8.742E-06	7.627E-06	6.607E-06	4.713E-06	0.00000341	2.572E-06

Table 10. Illustrative example showing the results from a C-salt run for the Peck evaporation pond (continued).

Activity Coefficients of Complexes									
Concentration Factor	1	2	5	10	15	20	30	40	50
MgB(OH)4 complex	0.6840	0.6593	0.6451	0.6547	0.6653	0.6801	0.7329	0.7864	0.8459
MgCO3 complex	0.6989	0.6233	0.5139	0.4356	0.3945	0.3636	0.3139	0.2871	0.2703
MgOH complex	0.6969	0.6833	0.6996	0.7648	0.8327	0.9089	1.1058	1.3435	1.6041
CaB(OH)4 complex	0.6989	0.6233	0.5139	0.4356	0.3945	0.3636	0.3139	0.2871	0.2703
CaCO3 complex	0.2294	0.1640	0.1008	0.0716	0.0603	0.0531	0.0441	0.0429	0.0450
B(OH)3 complex	0.6956	0.6208	0.5136	0.4384	0.4007	0.3710	0.3195	0.2936	0.2786
B3O3(OH)4 complex	0.5992	0.4836	0.3230	0.2120	0.1549	0.1194	0.0803	0.0554	0.0417
B4O5(OH)4 complex	0.2224	0.1344	0.0563	0.0256	0.0153	0.0100	0.0051	0.0031	0.0021
HSO4 complex	0.7326	0.6760	0.5955	0.5227	0.4989	0.4751	0.4094	0.3830	0.3637

Amounts of Compounds (moles) or (moles / kg water)									
Concentration Factor	1	2	5	10	15	20	30	40	50
Mirabilite_Na2SO4.10H2O						0			0.090867
MgB(OH)4 complex	3.749E-07	8.532E-07	0.00000233	3.037E-06	4.096E-06	4.917E-06	5.904E-06	6.716E-06	0.00000738
MgCO3 complex	0.00001777	0.00001992	0.00002416	0.00002851	0.00003147	0.00003415	0.00003955	0.00004325	0.00004594
MgOH complex	9.011E-07	1.112E-06	1.375E-06	9.794E-07	8.911E-07	8.086E-07	6.514E-07	5.246E-07	4.301E-07
Magnesite_MgCO3	0.00082496	0.0040353	0.016426	0.043939	0.0686	0.093484	0.14426	0.19647	0.25074
CaB(OH)4 complex	1.752E-07	4.309E-07	1.397E-06	2.181E-06	3.296E-06	4.391E-06	6.583E-06	8.785E-06	0.00001103
CaCO3 complex	0.00002423	0.00003389	0.00005515	0.00007765	0.00009204	0.0001047	0.00012606	0.00012957	0.00012349
Calcite_CaCO3	0.0080054	0.015981	0.040724	0.081174	0.067374	0.083708	0.35003	0.48137	0.61872
Gypsum_CaSO4.2H2O				0.023279	0.095866	0.13994			
B(OH)3 complex	0.00006276	0.00012715	0.00032225	0.00063553	0.00095313	0.0012628	0.0018979	0.0025203	0.00314
B3O3(OH)4 complex	6.296E-13	3.803E-12	4.118E-11	3.807E-10	1.342E-09	3.215E-09	1.036E-08	2.729E-08	5.983E-08
B4O5(OH)4 complex	2.806E-17	3.373E-16	9.58E-15	2.74E-13	1.62E-12	5.608E-12	3.115E-11	1.14E-10	3.185E-10
HSO4 complex	1.006E-08	1.846E-08	3.702E-08	3.773E-08	4.047E-08	4.323E-08	5.163E-08	5.535E-08	5.836E-08

Volume of Solids (cm3)									
Concentration Factor	1	2	5	10	15	20	30	40	50
Mirabilite_Na2SO4.10H2O								0.000	19.998
Magnesite_MgCO3	0.024	0.115	0.468	1.253	1.955	2.665	4.112	5.601	7.148
Calcite_CaCO3	0.296	0.590	1.504	2.998	2.488	3.092	12.928	17.779	22.852
Gypsum_CaSO4.2H2O			0.000	1.728	7.114	10.385			
Total	0.319	0.705	1.972	5.978	11.558	16.142	17.040	23.379	49.997

9BE, in Pond 9). Descriptions of the methods used in these field studies may be found in LBL Annual Report, October 1988, and LBL Progress Report No. 9. A more detailed summary of the findings may also be found in the aforementioned reports. Over the summer and early fall months of 1988 (July through October), increases in concentrations of salts had been observed in the top 9 cm of soil at both plots. Average increases were on the order of 15 to 25% of the concentrations found in July 1988. The large spatial variability in selenium concentrations made similar interpretation of the data difficult.

Bare soil evaporation rates have been measured since July 1988, with a break during the rainy months. These rates provide another method for estimating a solute flux towards the soil surface (see LBL Progress Report No. 9 for details on approach and results). Comparison between the two methods yields good agreement, thus confirming the general trend and providing a first-cut estimate on anticipated rates of accumulation.

During the rainy season (late October to March), the surface concentrations of all species, including selenium, fell sharply due to the downward flux created by infiltrating rainwater (salt mass per soil mass ratio averaged over the surface 9 cm fell from approximately 80-90 mg/g to 30-40 mg/g). It is expected that a reconcentration of all species will occur during the remainder of the spring and summer months. Field studies will continue to determine the rates of species reconcentration at the soil surface. Numerical modeling of fluid flow will be used to simulate and predict bare soil evaporation rates. If successful, predictions for other parts of the Reservoir will be made.

5.0. References

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