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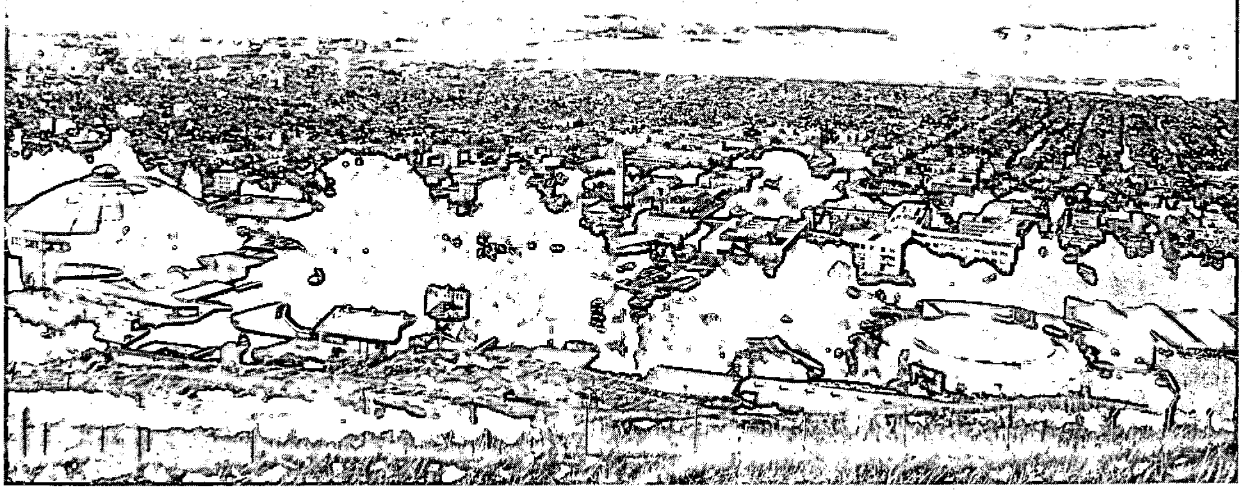

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Hydrological and Geochemical Investigations of Selenium Behavior at Kesterson Reservoir

Annual Report
October 1, 1989, through September 30, 1990

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Table of Contents

List of Figures

List of Tables

EXECUTIVE SUMMARY

Sally M. Benson
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This is the fourth in a series of Annual Reports describing research and monitoring activities carried out at Kesterson Reservoir by scientists in the Earth Sciences Division (ESD) at Lawrence Berkeley Laboratory (LBL, 1987; 1988; 1990). From 1985 to the present we have studied the behavior of selenium in various habitats and environments at Kesterson, shifting emphasis as remedial actions altered the physical setting. Investigations have been directed towards evaluating the efficacy of several remedial alternatives, from innovative techniques relying on the complex geochemical behavior of selenium in aquatic environments to conventional excavation schemes. Ultimately, results of these studies supported two cost-effective remedial measures; drain water deliveries were terminated in 1986 and, in 1988, 1 million cubic yards of soil were imported and used to fill the low lying areas of the former Kesterson Reservoir. To date, these two actions appear to have eliminated the aquatic habitat that caused waterfowl death and deformity at Kesterson from the early 1980's to 1987. As anticipated from scientific investigations carried out at Kesterson, biological, surface water and groundwater monitoring data collected by the USBR indicate that Kesterson is now a much safer environment than in past years when drainage water containing 300 μg/l of selenium was delivered to the Reservoir.

However, the continued presence of a large inventory of selenium within the upper portions of unfilled areas of Kesterson Reservoir and immediately below the fill material requires that a continued awareness of the status of this inventory be maintained and improved upon. Of particular concern from the perspective of potential future exposures to selenium are (1) the distribution of soil selenium among fractions of differing availability, (2) transformations of the presently large insoluble fraction of this selenium inventory into more mobile and bioavailable soluble forms, (3) movement of this soluble selenium inventory up and down the soil profile, (4) mixing of selenium into rainwater pools, (5) leaching of selenium into the shallow water table, and (6) uptake of selenium through the food chain. Consequently, our investigations are now directed to monitoring and predicting the fate of the selenium inventory residing in the surface soils at Kesterson. Of particular concern is the likelihood of surface ponding during particularly wet years, where surface pools may contain levels of selenium in excess of ''safe'' concentrations of 2 to 5 µg/l. These issues are being addressed in a number of ways through our research programs, from long-term monitoring of selenium concentrations in the vadose zone, to field trials of selenium dissipation through microbial volatilization. Field experimentation and monitoring activities are supported by laboratory investigations of these same processes under better controlled conditions.

Major topics of these investigations are discussed in the following 6 sections:

Section 2 - chemical evolution of the inventory of selenium residing in Kesterson soils, including physical redistribution within the soil profile, biological and geochemical transformation from immobile to mobile forms, and transformation to volatile forms;

Section 3 - transport of selenium from soils to surface water pools formed by ponding of rainwater on Kesterson soils;

Section 4 - processes and rates of processes leading to dissipation of the surficial inventory of selenium through microbial volatilization;

Section 5 - feasibility of land disposal of seleniferous San Luis Drain sediments, including evaluation of potential application rates, transport to groundwater, and biological uptake in grasses and shrubs; and

Section 6 - a Reservoir-wide assessment of total selenium concentration and the fraction of this inventory that is soluble.

Conclusions of these investigations and implications for management of the former Kesterson Reservoir are summarized below:

- Four years of data are now available for assessing trends in selenium and salt concentrations in a *Distichlis* and *Cressa*- vegetated region of Pond 11. Shortly after drying out the Reservoir, rapid increases in salt and selenium concentrations were observed in the vadose zone. However, over the past year this trend either slowed or leveled off. Overall, about 6% of the initially insoluble inventory solubilized over the past three years, increasing the soluble fraction to about 15% of the total selenium inventory. In the same period, dissolved salt concentrations increased by about 50%, largely due to plant uptake of soil moisture from the saline groundwater. Increases in dissolved salt concentrations have slowed due to less vigorous plant growth. Years of higher than average rainfall are expected to periodically reverse these trends towards increased selenium and salt concentrations. The net trends resulting from a sequence of wet and dry years, such is expected to occur in the Central Valley, remain uncertain.

- Continued monitoring of two test plots, one in Pond 8 and one in Pond 9, show that large increases in dissolved selenium and salt concentrations are associated with revegetation of playa areas within the Reservoir. These trends appear to be associated with drying of the soil profile caused by plant root uptake of soil moisture and consequent oxidation of the soil environment. The magnitudes of salt and selenium increases in these environments are similar to those observed in the in the Pond 11 test plot described above. Future trends in recently re-vegetated areas are expected to slow down as a stable soil-moisture regime is established.
- Soil selenium concentrations in the top 0.15 m are strongly influenced by rainfall infiltration. Selenate, in particular, is readily leached down deeper into the soil profile with winter rains. This will tend to decrease the inventory of soluble selenium that is available for dissolution in rainwater pools that form at Kesterson.
- Soil selenium concentrations in the fill areas are increasing as a result of evaporative and transpirative flux of soil moisture from the watertable towards the soil surface and plant-root zone (molecular diffusion will also tend to increase soil selenium concentrations in the fill material). At two monitoring sites, one in Pond 5 and one in Pond 7, dissolved selenium concentrations within the root zone of

Kochia scoparia, the dominant plant in the filled areas, are now nearly the same as in the unfilled areas (e.g., thousands of µg/l). A Reservoir-wide sampling of filled areas (18 sample sites) indicate that these elevated levels of soluble selenium have not yet reached the surface of the fill-dirt.

- Selective extraction procedures have been developed and applied in an effort to determine the dominant forms of selenium in Kesterson soils. These experiments indicate that within surface soils, the dominant forms of selenium are extracted with a solution commonly believed to dissolve soil-organic matter. The precise forms of selenium associated with this pool have not been resolved, but likely forms include elemental selenium, organic forms of selenium, and adsorbed selenite. The strong association between selenium and soil organic matter is consistent with the processes that lead to accumulation of selenium in the organic-rich marsh-bottom sediments present when Kesterson was in operation. It also suggests that the evolution and fate of selenium in Kesterson soils is closely coupled to cycling of soil organic matter. Implications of this association are being pursued in a set of laboratory experiments.

- From a Reservoir-wide synoptic sampling of selenium concentrations in the top 0.15 m of soil the following information has been obtained. Representative mean values (and ±95% confidence intervals) for the total selenium values are <2, 2.8 (±3.8), and 9.3 (± 11.8) mg/kg-soil, in the fill, grassland, and open areas, respectively. Representative mean values for the water-extractable total selenium values are 0.04 (± 0.14), 0.15 (± 0.15), and 0.33 (± 1.0) mg/kg-soil, in the fill, grassland, and open areas, respectively. Within any "habitat" selenium concentrations range over an order of magnitude, making conclusions on appropriate management action by "habitat" type unreliable. The fraction of the total selenium inventory in Kesterson soils that is water-extractable is about 5%, indicating that only a limited amount of the selenium is currently mobile and available for plant uptake and dissolution in rainwater pools. No significant changes in total or water-extractable selenium concentrations have been observed between the 1989 and 1990 data sets.

- The cumulative evidence available to-date indicates that the total inventory of selenium, fractions that are in water soluble forms, and distribution of selenium within the soil profile will evolve slowly in the Kesterson environment. Processes contributing to this evolution include microbial transformation of organic and inorganic forms of selenium to volatile forms that may dissipate in the atmosphere, cyclic oxidation and reduction of selenium resulting from seasonal variations in soil moisture content, mineralization of soil organic matter, and physical redistribution resulting from root uptake of soil moisture and rainfall infiltration. The net effect of all these will be to eventually decrease the amount of selenium in this environment. However, in the interim, increases in the quantities of readily available selenium may be observed. Nevertheless, these changes are expected to occur slowly. Areas covered with fill are expected to undergo more rapid changes because of the large gradients in selenium concentrations at the fill-native soil interface.
- During years with annual rainfall in excess of 350 mm (about 50% more than normal), surface water pools up to 5 cm deep are expected to occur over large areas within the Reservoir. In the event of a 500 mm rainfall (100-year event), pools from 10 to 25 cm deep are expected to occur over the majority of the Reservoir. The water in the pools will be derived from rainwater ponding at the soil surface. Selenium and salts present at the soil surface will dissolve in these pools, creating selenium concentrations ranging from less than detection to several hundred µg/l. Estimates of a Reservoir-wide average selenium concentration have been made. For 20 cm-deep pools covering the entire Reservoir, estimates of the average selenium concentrations range from about 10 to 30 µg/l. Given the sparcity of data from which these estimates were developed it is not possible to narrow the

expected range of average concentrations. These concentrations are in the range of values measured in surface waters near Kesterson, including Mud Slough, Fremont Canal, and the San Luis Canal.

- To prevent formation of aquatic habitat at Kesterson that may attract nesting birds during spring, provisions for draining surface waters from the Reservoir are prudent. Direct discharge of surface drainage into Mud Slough, or discharge through the San Luis Drain into Mud Slough would be the most practicable solution for an emergency drainage plan. Given the high levels of selenium observed in Mud Slough over the past year (up to 50 μg/l), it is unlikely that the incremental loading of selenium due to surface drainage from Kesterson during unusually wet years would contribute significantly to degradation of this waterway. If necessary, the array of 10 wells that the USBR drilled along the San Luis Drain may provide a source of dilution water for lowering selenium concentrations.
- An experiment is underway to evaluate the potential risks and benefits of land disposal of San Luis Drain sediments. Selenium concentrations in the San Luis Drain sediments average above 100 mg/kg-soil. This experiment demonstrates that applying a 7.5 cm-thick layer of these sediments to soils with low concentrations of selenium results in selenium concentrations in soil water and upland vegetation similar to levels observed throughout Kesterson. This indicates that San Luis Drain Sediments are an effective soil supplement for increasing selenium concentrations in upland vegetation, and may provide an economical soil supplement for the selenium-deficient east side of the San Joaquin Valley. At the same time, selenium concentrations may be elevated enough so that unmonitored exposure to such vegetation may pose a hazard to wildlife. Decreasing the application rate should result in lowering the quantity of selenium available for plant uptake. Monitoring will continue in order to establish time-trends in soil water, soil, and biotic concentrations of selenium in the experimental plots.

1. INTRODUCTION

Sally M. Benson
Earth Sciences Division
Lawrence Berkeley Laboratory

This is the fourth in a series of Annual Reports describing research and monitoring activities carried out at Kesterson Reservoir by scientists in the Earth Sciences Division (ESD) at Lawrence Berkeley Laboratory (LBL, 1987; 1988; 1990). Throughout this period we have studied the behavior of selenium in various habitats and environments at Kesterson, shifting emphasis as remedial actions altered the physical setting. Investigations have been directed towards evaluating the efficacy of several remedial alternatives, from innovative techniques relying on the complex geochemical behavior in aquatic environments to conventional excavation schemes. Ultimately, results of these studies supported two cost-effective remedial measures; drain water deliveries were terminated in 1986 and, in 1988, 1 million cubic yards of soil were imported and used to fill the low lying areas of the former Kesterson Reservoir. To date, these two actions appear to have eliminated the aquatic habitat that caused waterfowl death and deformity at Kesterson from the early 1980's to 1987.

As anticipated from scientific investigations carried out at Kesterson, biological, surface water and groundwater monitoring data collected by the USBR indicate that Kesterson is now a much safer environment than in past years when drainage water containing 300 μg/l of selenium was being delivered to the Reservoir. However, the large inventory of selenium, residing largely in the top six inches of soil warrants continued attention. Over time, the fraction of the selenium inventory that is now immobile (est. at 90%) may oxidize to more mobile and bioavailable forms. This in turn may lead to increased risk of wildlife exposure to unacceptably high levels of selenium. Consequently, our investigations are now directed toward monitoring and predicting the fate of the selenium inventory residing in the surface soils at Kesterson. Of particular concern is the likelihood of surface ponding during particularly wet years, where surface pools may contain levels of selenium in excess of ''safe'' concentrations of 2 to 5 μg/l.

Major topics of these investigations during the past year are:

Section 2 - chemical evolution of the inventory of selenium residing in Kesterson soils, including physical redistribution within the soil profile, biological and geochemical transformation from immobile to mobile forms, and transformation to volatile forms;

Section 3 - transport of selenium from soils to surface water pools formed by ponding of rainwater on Kesterson soils;

Section 4 - processes and rates of processes leading to dissipation of the surficial inventory of selenium through microbial volatilization;

Section 5 - feasibility of land disposal of seleniferous San Luis Drain sediments, including evaluation of potential application rates, transport to groundwater, and biological uptake in grasses and shrubs;

Section 6 - a Reservoir-wide assessment of the fraction of the selenium inventory that is currently in mobile forms in the top 6 inches (0.15 m) of Kesterson soil; and

Section 7 - documentation of the performance of our analytical laboratory for measuring selenium and boron concentrations in Kesterson samples.

Although our Annual Progress Reports are the primary means of disseminating the results of our research efforts to the USBR and other concerned agencies, we also attempt to publish topical reports in more widely distributed journals and conference proceedings. Several topical papers have been written and presented at workshops or conferences over the past year. Titles of these include:

- Soil selenium fractionation, depth profiles and time trends in a vegetated upland site at Kesterson Reservoir. Presented at the International Conference on Metals in Soils, Waters, Plants, and Animals held in Orlando, Florida on April 30 to May 30, 1990 and submitted to the *Journal of Water, Air and Soil Pollution*.

- Selenium immobilization in a pond sediment at Kesterson Reservoir. Published in the *Journal of Environmental Quality*, Vol. 19, no. 2, pp. 302-311.

- Kesterson crisis: Sorting out the facts. Presented at the American Society of Civil Engineers National Conference on Irrigation and Drainage in Durango, Colorado and submitted to the *Journal of Irrigation and Drainage Engineering*.

- Groundwater contamination at the Kesterson Reservoir, California. Part 1: Hydrogeologic setting and conservative solute transport. Submitted and accepted for publication in *Water Resources Research.*

- Groundwater contamination at the Kesterson Reservoir, California. Part 2: Geochemical parameters influencing selenium mobility. Submitted and accepted for publication in *Water Resources Research.*

- Selenium in Kesterson Reservoir ephemeral pools: No. 1. A field study of ponding resulting from shallow water table raise. To be submitted to *Journal of Environmental Quality*.

- Selenium in Kesterson Reservoir ephemeral pools: No. 2. Laboratory Experiments. To be submitted to *Journal of Environmental Quality*.

2. SOIL SELENIUM AND SALINITY MONITORING AND EVALUATION

Tetsu Tokunaga
Earth Sciences Division
Lawrence Berkeley Laboratory

The continued presence of a large inventory of selenium within the upper portions of unfilled areas of Kesterson Reservoir and immediately below fill material requires that a continued awareness of the status of this inventory be maintained and improved upon. Of particular concern from the perspective of potential future exposures to selenium are (1) the distribution of soil selenium among fractions of differing availability, (2) transformations of the presently large insoluble fraction of this selenium inventory into more mobile and bioavailable soluble forms, (3) movement of this soluble selenium inventory up and down the soil profile, (4) mixing of selenium into ephemeral pool waters, (5) leaching of selenium into the shallow water table, and (6) uptake of selenium through the food chain. Items 1, 2 and 3 are addressed in a variety of ways in this chapter. Item 4 is addressed in parts of the present chapter and more completely in Chapter 3. Item 5 is addressed in Chapter 6. Item 6 is under investigation by CH2M Hill and the University of California, ANR.

In addition to concerns over the fate of the selenium inventory at Kesterson Reservoir, temporal and spatial patterns in soil salinity also warrant continued monitoring. At high concentrations, soluble salts and trace elements such as boron will constrain the possible plants species to those which can tolerate such conditions. Even among the group of plants which are capable of growing in the generally saline environment of Kesterson Reservoir soils, it is expected that periods of increased soil salinity will impair growth rates. While plants are greatly influenced by soil salinity, plants also exert significant influences on the distribution of salts within the soil profile through evapotranspirative concentration of solutes (including selenium) within the root zone. This effect have been observed at many of the monitoring sites, and will be described in various portions of the present chapter. In contrast to the majority of areas at Kesterson Reservoir which have been vegetated for various periods of time (including the recently (1988) filled areas), three soil monitoring sites have been maintained under essentially unvegetated conditions for the past 4 years. The distribution patterns of salts in these plots provide a contrast to those of the vegetated regions.

Materials presented in the following sections include reviews of water-soluble selenium profiles and soil water salinity from several soil monitoring sites, information on selenium fractionation in soils, and projections concerning the long term fate of the selenium inventory at Kesterson Reservoir. The sites to be described will include continuously vegetated uplands in Pond 11 (Section 2.1), recently revegetated playas in Ponds 8 and 9 (Section 2.2), filled sites which have revegetated in Ponds 5 and 7 (Section 2.3), and excavated sites (devegetated and vegetated) in Pond 6 (Section 2.4). These sections addressing field observations will be followed by a presentation of a soil selenium fractionation study (Section 2.5), and a discussion of the possible long-term behavior of the selenium inventory at Kesterson Reservoir (Section 2.6).

2.1. Pond 11 Saltgrass Upland Soil Sites

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Earth Sciences Division
Lawrence Berkeley Laboratory

Presently, four years of soil solution data are available from the 5 monitoring sites located in the *Distichlis*- and *Cressa*-vegetated uplands of the southwest section of Pond 11. Background information on these sites has been provided in previous annual reports. Increases in soil solution selenium concentrations and salinity at all of these monitoring sites have been described in previous reports. During the 1990 soil solution samplings these trends appear to have either continued at slower rates, or have levelled off. Sample recoveries were in some cases incomplete, thus prohibiting comprehensive comparisons with past conditions. Examples of Pond 11 soil solution selenium profiles are provided in Figures 2.1a and 2.2a. Relative changes in soil solution selenium at each of the Pond 11 sites are presented in Figure 2.3a. The relative soil solution selenium concentrations shown in the figure were obtained for each site by averaging two or three characteristic soil solution profiles within a particular year, then divided by the profile-averaged soil solution selenium concentration at the particular site obtained during the first monitoring year (1987). An average relative increase in the soil solution selenium inventory of 140% in the Pond 11 study area is indicated by the soil solution data. The seleniferous soil crust present in some other areas of Kesterson Reservoir is not present in the Pond 11 monitoring area. The general increases of soil solution selenium concentrations with time appear to result primarily from oxidation of previously reduced selenium. Since the present soil solution selenium inventory amounts to only about 10% of the total soil selenium in the Pond 11 study area, the observed increases in soil solution selenium amount to an approximate 6% decrease in the initially (1987) insoluble selenium inventory.

Depth and time trends for soil solution salinity in the Pond 11 study area, as reflected in soil

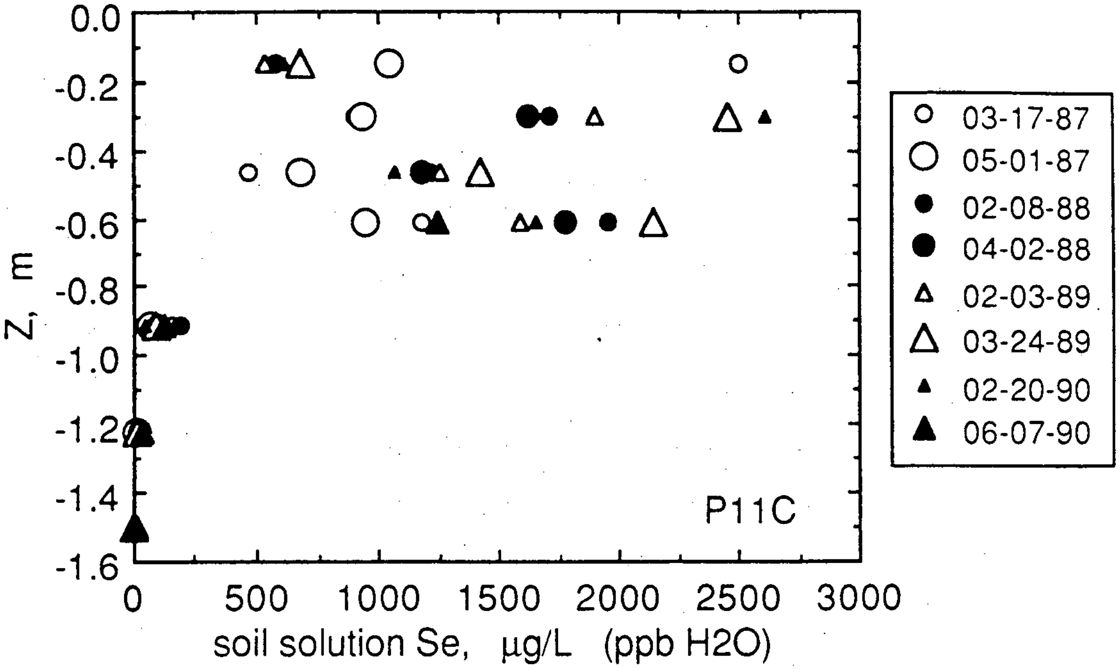


Figure 2.1a. Upland saltgrass site P11C, soil solution selenium concentration profiles.

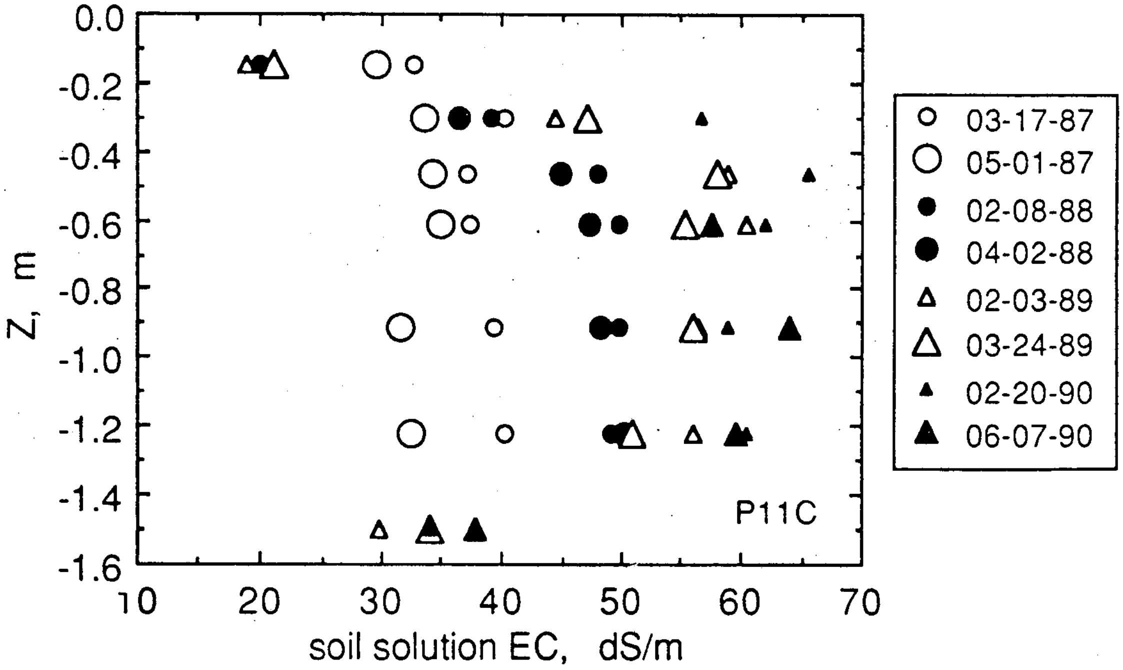


Figure 2.1b. Upland saltgrass site P11C, soil electrical conductivity profiles.

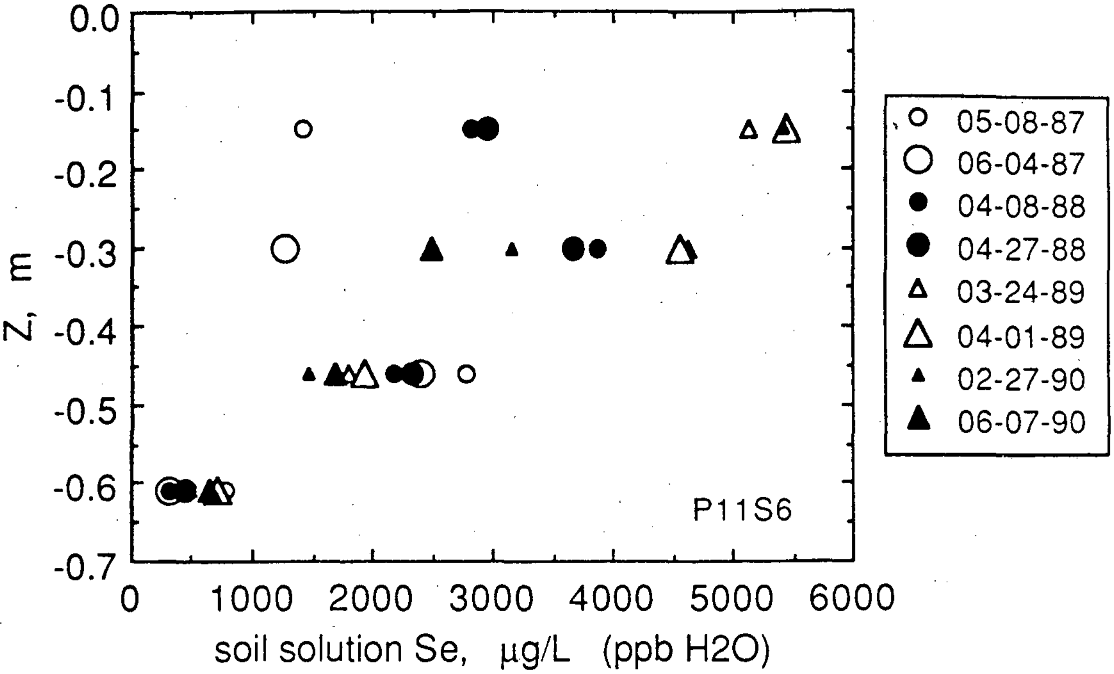


Figure 2.2a. Excavated (to 0.15m) upland site P11S6, soil solution selenium profiles.

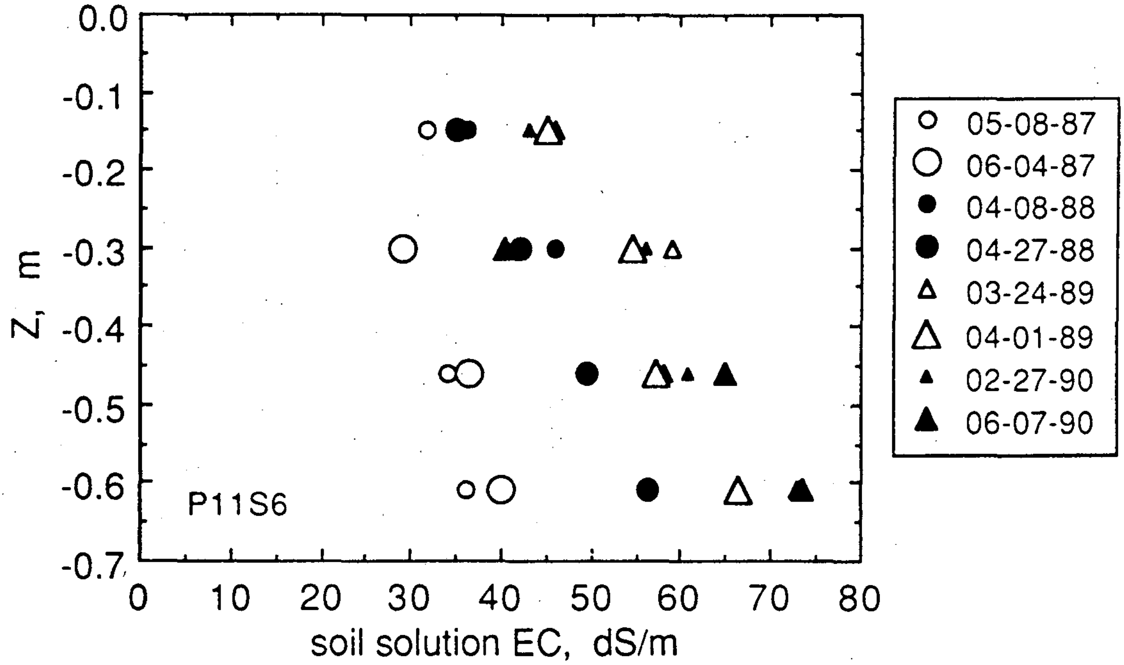


Figure 2.2b. Excavated (to 0.15m) upland site P11S6, soil solution electrical conductivity profiles.

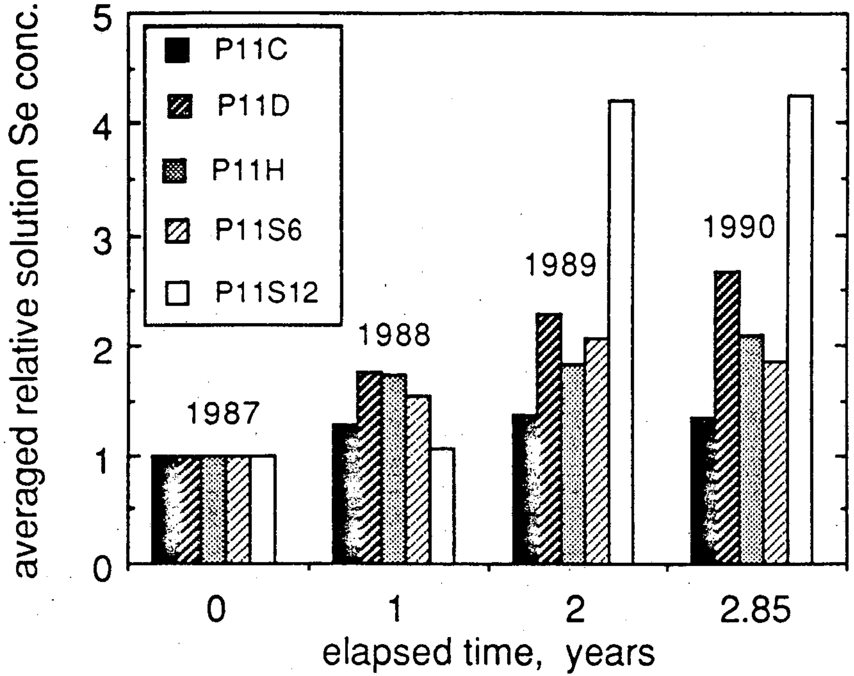


Figure 2.3a. Pond 11 upland soil monitoring sites, relative changes in profile-averaged soil solution selenium.

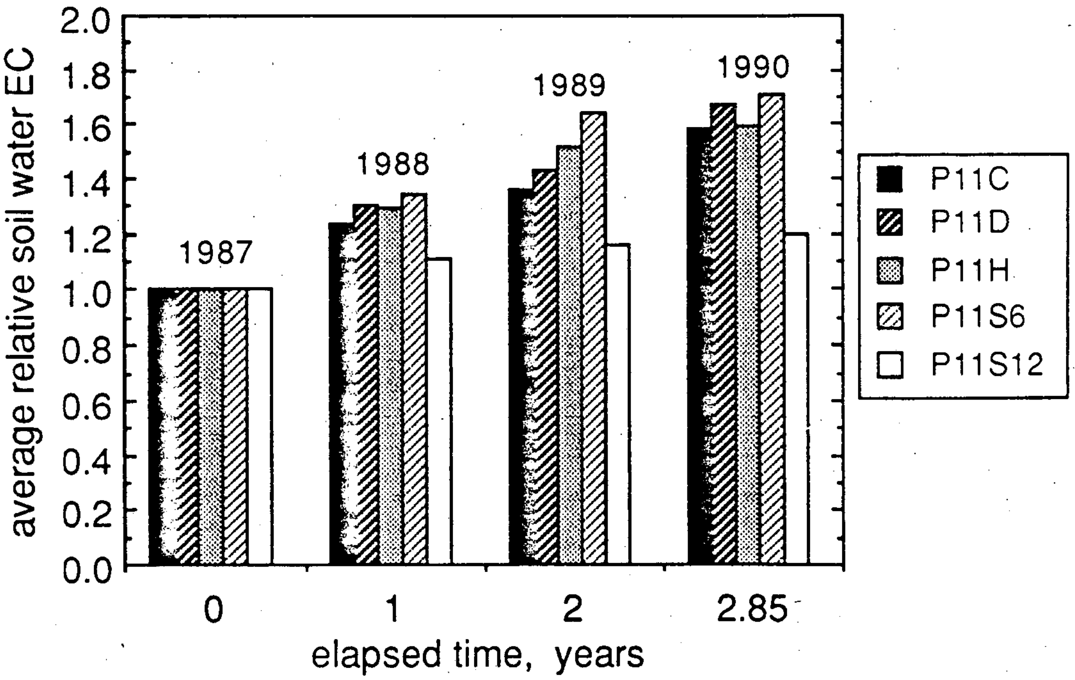


Figure 2.3b. Pond 11 upland soil monitoring sites, relative changes in profile-averaged EC.

solution electrical conductivities (EC), are typified by the two profiles presented in Figures 2.1b and 2.2b. Decelerating rates of soil profile salinization have been observed during the 1987-1990 period. Salinities of soil solutions in the Pond 11 sites commonly exhibit maxima in the 0.46 m to 0.91 m depth range, reflecting evapotranspirative concentration of salts in the root zone. A summary of relative changes in soil solution EC for the 5 Pond 11 sites is provided in Figure 2.3b. The soil solution EC data for this figure have been processed in a manner analogous to that for the relative changes in soil solution selenium. Thus, profile-averaged soil solution EC data from a particular year are divided by corresponding averages from the first (1987) year. It should be noted that the soil solution EC data (Figures 2.1b, 2.2b and 2.3b) are less than proportional to soil solution salinity at the high values encountered here. Changes in soil solution salinity estimated through changes in chloride concentrations are indicative of relative changes that are approximately twice those implied from the EC changes in these Pond 11 soils (DANR/LBL Annual Report, 1989). Trends in tensiometer responses during the growing season, and visual observations of the saltgrass and alkali weed at these sites over the past 4 years indicate that plant growth rates have declined during this period. Increased salinization presumably contributes significantly to the observed decline in plant growth. Years of higher than average rainfall can be expected to periodically reverse the observed trend.

2.2. Revegetated Playa Site in Ponds 8 and 9

Peter Zawislanski
Earth Sciences Division
Lawrence Berkeley Laboratory

Beginning in the summer of 1988 two field plots, one in Pond 8 (Plot 8EP) and one in Pond 9 (Plot 9BE), were established to evaluate evapotranspirative accumulation of salts and selenium in surface soils. These studies which were described in Zawislanski (1989) and the 1990 LBL Annual Report, indicated that while seasonal fluctuations in surface inventories of these constituents were relatively large, the net yearly differences were small. In effect, the competing processes of downward infiltration were nearly balanced by the counteracting evaporation fluxes towards the soil surface. During this past year, we have continued these studies, shifting our emphasis to include the effects of revegetation by the plant *Kochia scoparia.* Over the past two years much of the playa and filled areas of Kesterson Reservoir have been revegetated by this plant. These studies help to assess the impact of revegetation on salt and selenium distribution in Kesterson soils. The following sections described data collections over the past year and discuss potential impacts of revegetation on the behavior of selenium resulting from this occurrence.

2.2.1. Vadose Zone Monitoring in Plot 9BE

Over the past twelve months, the soil chemistry and moisture regime of plot 9BE have been affected by the following factors: fluctuations in the elevation of the groundwater table; rainfall and the subsequent infiltration of rainwater; evaporation of water from the soil surface; transpiration of soil water by plants. In 1988 there was only sparse vegetation in this plot. After the filling operation late in 1988, plants began to emerge on the fill material surrounding the plot and on the boundary between the fill material and the playa. These plants were predominantly *Kochia scoparia.* After the summer of 1989, these plants died out. In the spring of 1990, a new generation of *Kochia scoparia* emerged within the plot itself. (Figure 2.4) shows the growth of these plants as measured by the height of the tallest specimens within the plot. As is apparent, the growth rate was highest between April and June. This gave the opportunity to observe changes in soil chemistry, including selenium redistribution in a profile before and during transformation from barren to vegetated. Such observations are pertinent to other parts of the Reservoir undergoing similar changes.

Electrical conductivity (EC) of soil water is commonly used in assessing variations in soil salinity. The EC of soil water in plot 9BE from May of 1989 to July of 1990 is presented in Figure 2.5. Since soil water composition will vary seasonally depending on the position of the groundwater table (Figure 2.6) and rainfall, it is best to compare EC profiles at the end of the summer. Unfortunately, it is difficult and sometimes impossible to collect soil water samples during the driest months; this was the case in 1989. Therefore, a comparison between late May 1989 and late May 1990 will have to suffice. Such a comparison reveals a doubling to tripling of EC during that period in the upper meter or so of the soil. It should be noted that the most dramatic increase in EC began to occur in early May of 1990, at approximately the same time that the *Kochia scoparia* plants established themselves. Also, extremely high ECs (60 to 100 dS/m) are limited to the top 60 cm of soil, suggesting the position of the root zone. While EC is a good indicator of total salinity, its relationship to salinity is not linear, i.e., a doubling in EC would be equivalent to more than a doubling in salinity. Examination of changes in chloride concentrations in soil water of this plot (Figure 2.7) shows a six-fold increase at the 45 to 60 cm depth between 5/24/89 and 7/18/90. Such an increase can be explained by root extraction of soil water; such extraction would result in a soil water hydraulic head gradient directed toward the root zone (see Figure 2.8). Flow of water from deeper in the soil profile would provide the salts necessary to so dramatically increase the EC in the root zone. A comparison of selenate profiles (May 1989-May 1990) reveals a similar pattern through early May 1990, and a different pattern afterward (Figure 2.9). While selenate concentrations increased in the root zone until early May, they did not change significantly in the following two months, while soil water salinity was skyrocketing. This may be explained by the fact that soil water below the root zone contains very

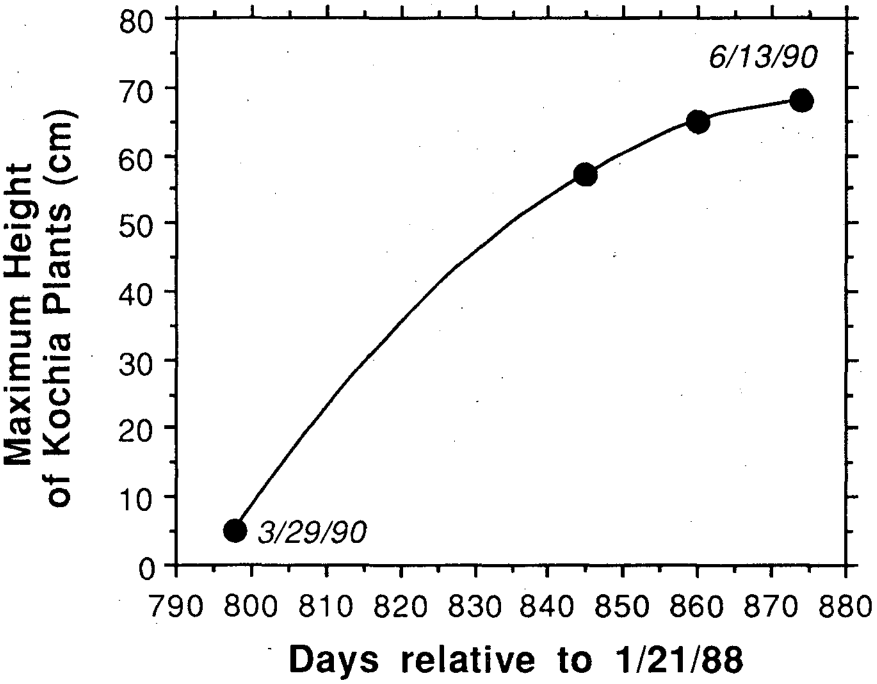


Figure 2.4. Changes in the maximum height of *Kochia* plants in plot 9BE: Spring 1990.

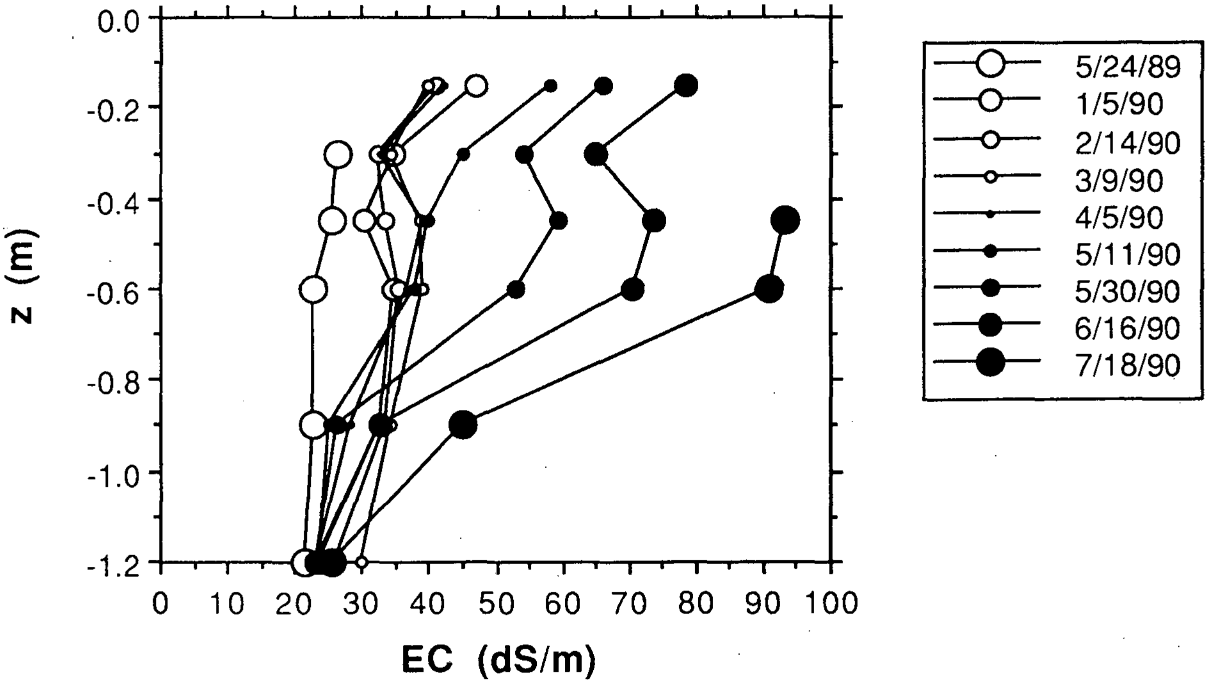


Figure 2.5. Changes in electrical conductivity of soil water in plot 9BE.

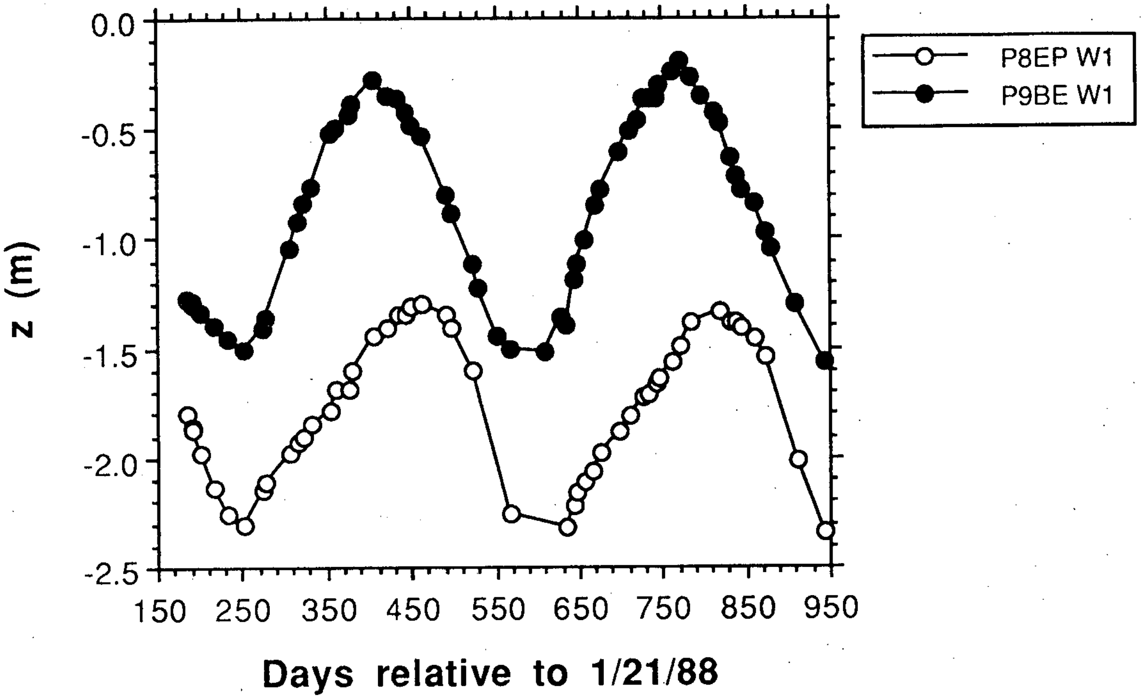


Figure 2.6. Depth to the water table in wells P8EP-W1 and P9BE-W1.

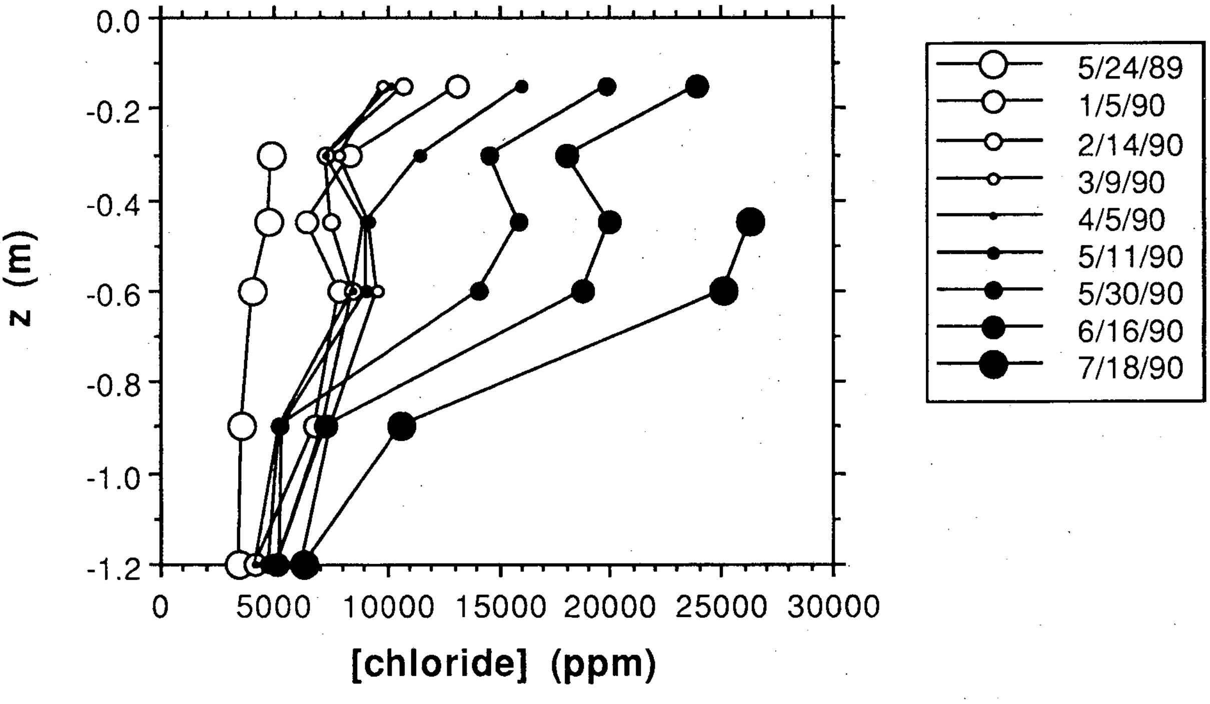


Figure 2.7. Changes in chloride concentrations in soil water in plot 9BE.

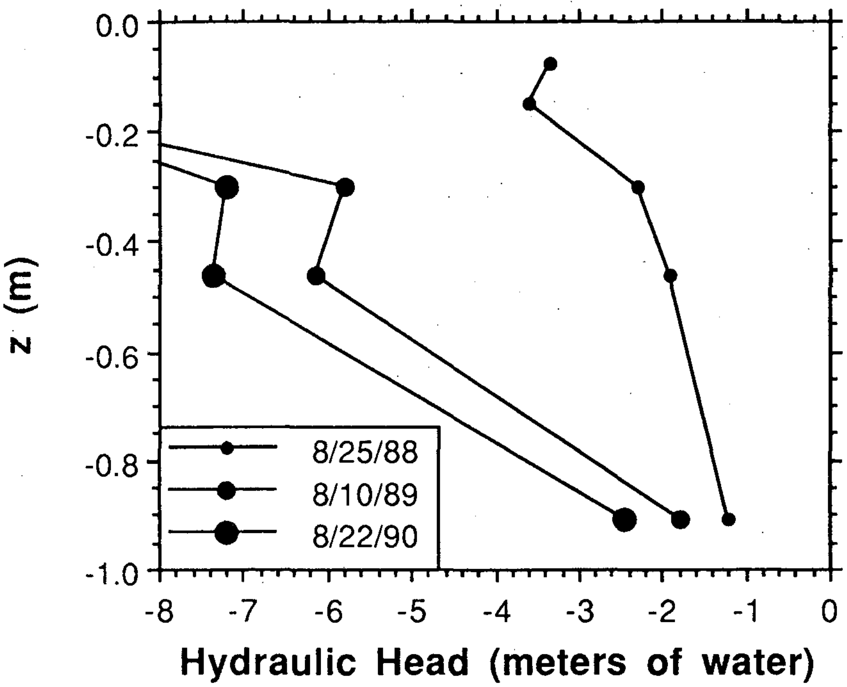


Figure 2.8. Hydraulic head profiles as measured via tensiometers in plot 9BE. Effects of drying out of the soil profile are apparent.

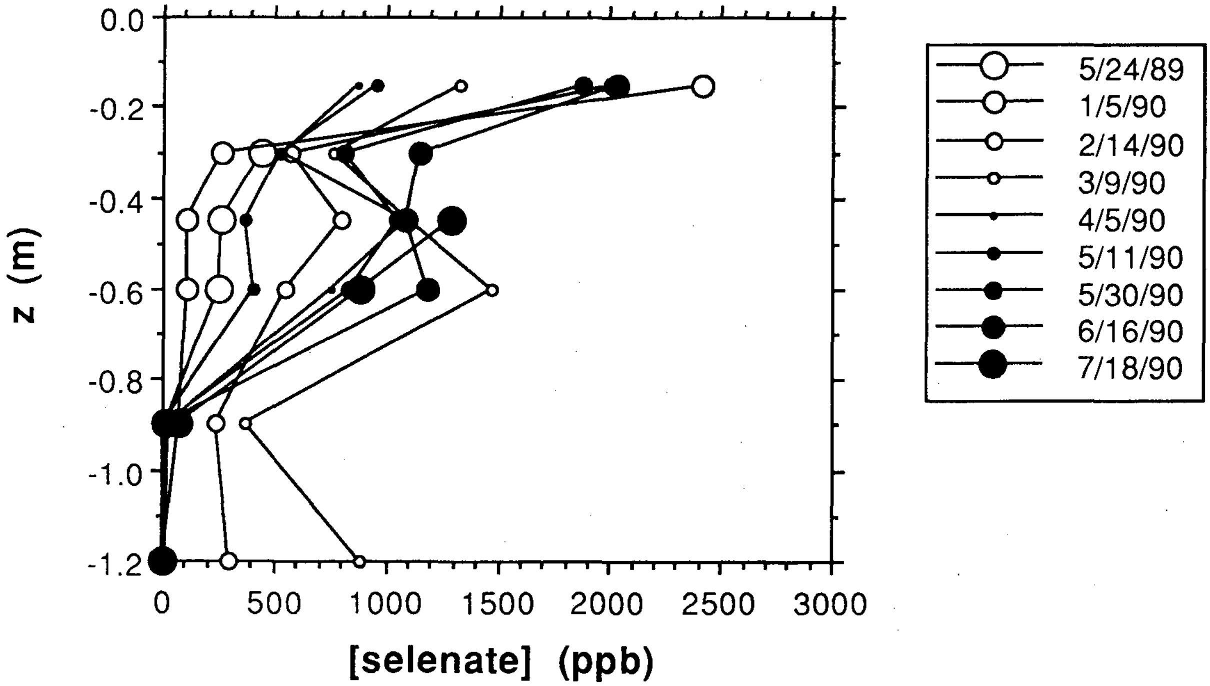


Figure 2.9. Changes in selenate concentrations in soil water in plot 9BE.

low concentrations of selenium (usually <50 ppb). Therefore, a transpirative concentration of such water would not add relatively significant amounts of selenium to the root zone over a 2-3 month period. In fact, since selenium is subject to changes in solubility due to varying redox conditions, it is not clear how much of the increase of selenate in the soil profile was due to physical and how much to chemical redistribution. The following paragraphs outline changes in selenium and salt distribution in the soil profile as influenced by the rise of the water table and rainfall infiltration during the wet season.

The combined effect of rainfall infiltration and the coincident, though not resultant, rise of the water table are clearly reflected in the increase of soil moisture, as charted by hydraulic head (Figures 2.10a,b). By comparing the timing and intensity of rainfall events with the response of soil moisture, one may get an idea of the kind of rainfall events which may significantly displace soil solution deeper into the profile. For example, single rainfall events of less than 5 mm appear to have a negligible effect on the soil moisture regime in this plot, even at the shallow depth of 8 cm. On the other hand, larger rainfall events may have an effect as deep as a meter below the soil surface. Concentrations of chloride and other salts are not as significantly affected by rainfall infiltration as selenium, simply due to the fact that the selenium concentration gradient in the soil profile is much steeper (compare Figures 2.11-13). It appears that the first significant rainfall events of late 1989 (around Day 615) caused a flushing down of salts and selenium, which had accumulated at and near the soil surface, deeper into the profile; this took place when the water table was at its deepest (-1.5 meters relative to soil surface). Following Day 615, the water table began to rise until it reached its highest level of -0.2 meters around Day 770 (3/2/90). During this period, redox conditions in the soil profile must have changed from oxidized to more reducing, although it is unlikely that completely reducing conditions were set up in this short time. Such conditions undoubtedly led to the reduction of a certain percentage of the selenate inventory. However, changes in selenate concentrations during this period match fairly well the changes in chloride concentrations, suggesting that they were driven by processes of physical redistribution and the rise of less saline and less seleniferous groundwater. The greater sensitivity of selenate

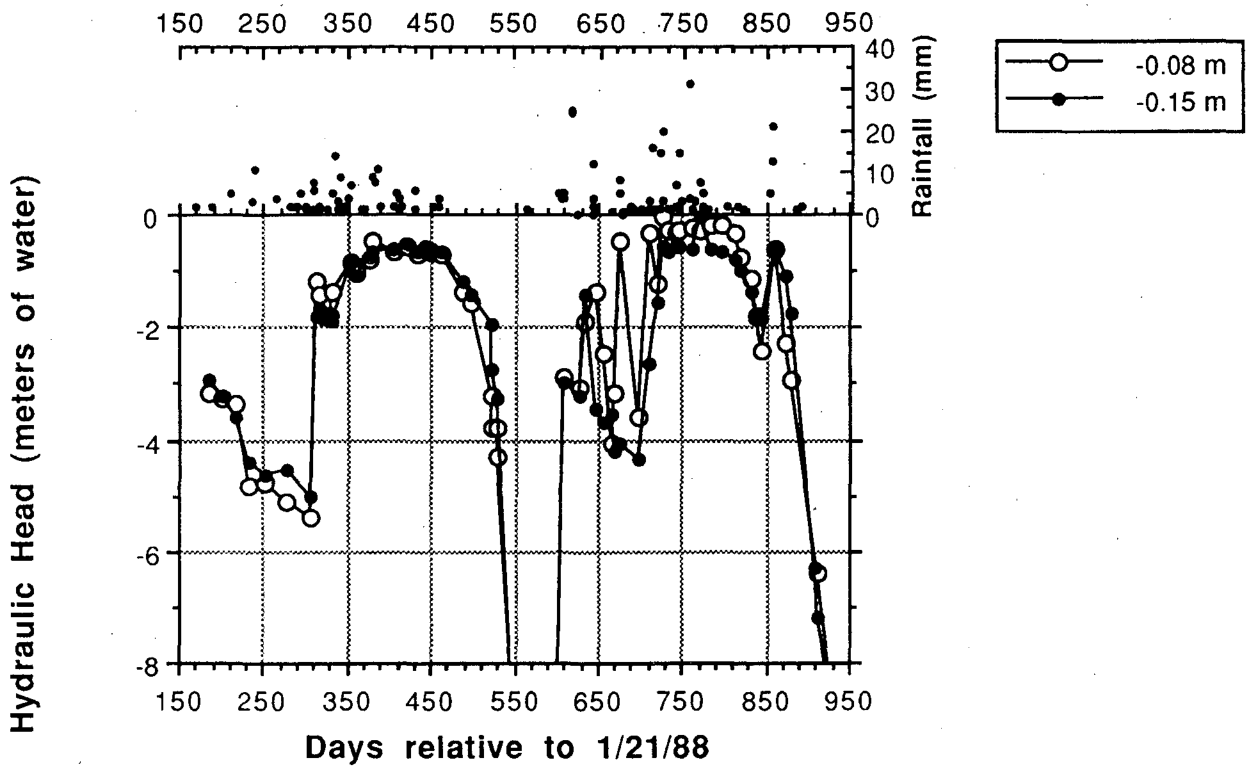


Figure 2.10a. Hydraulic head at 8 and 15 cm below the soil surface in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

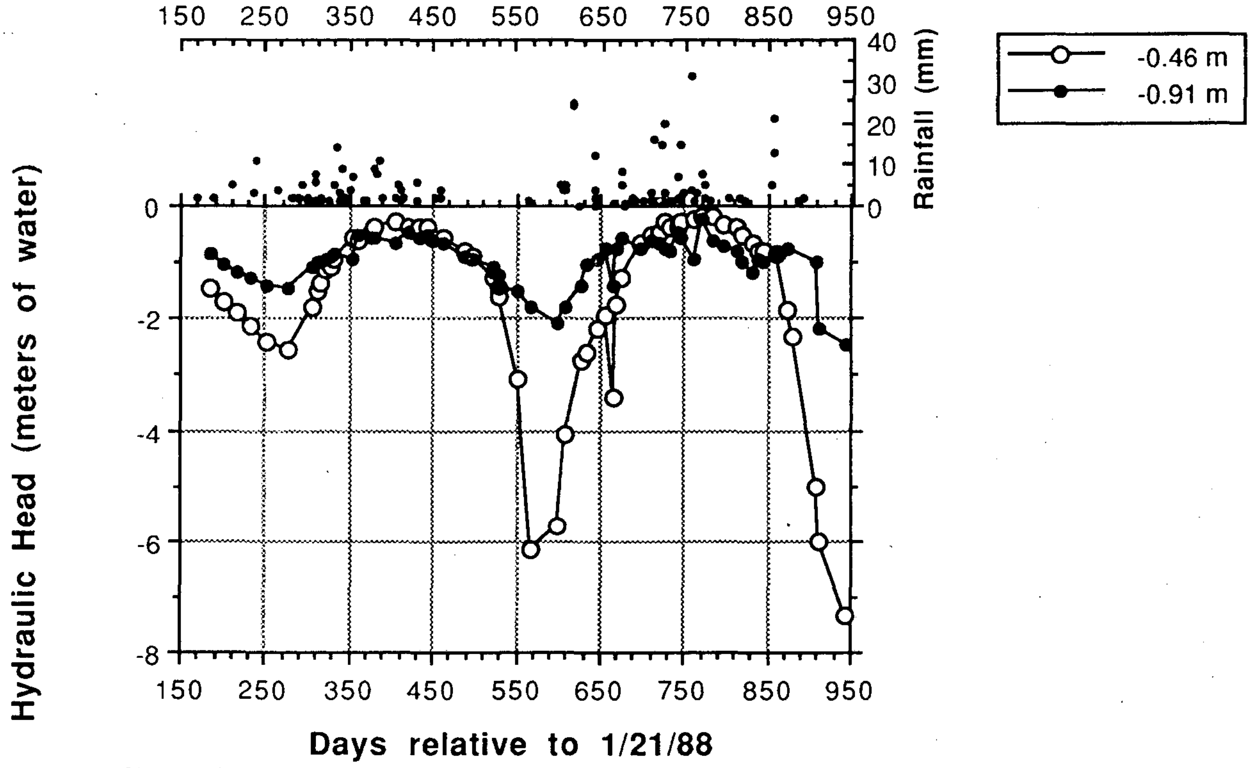


Figure 2.10b. Hydraulic head at 46 and 91 cm below the soil surface in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

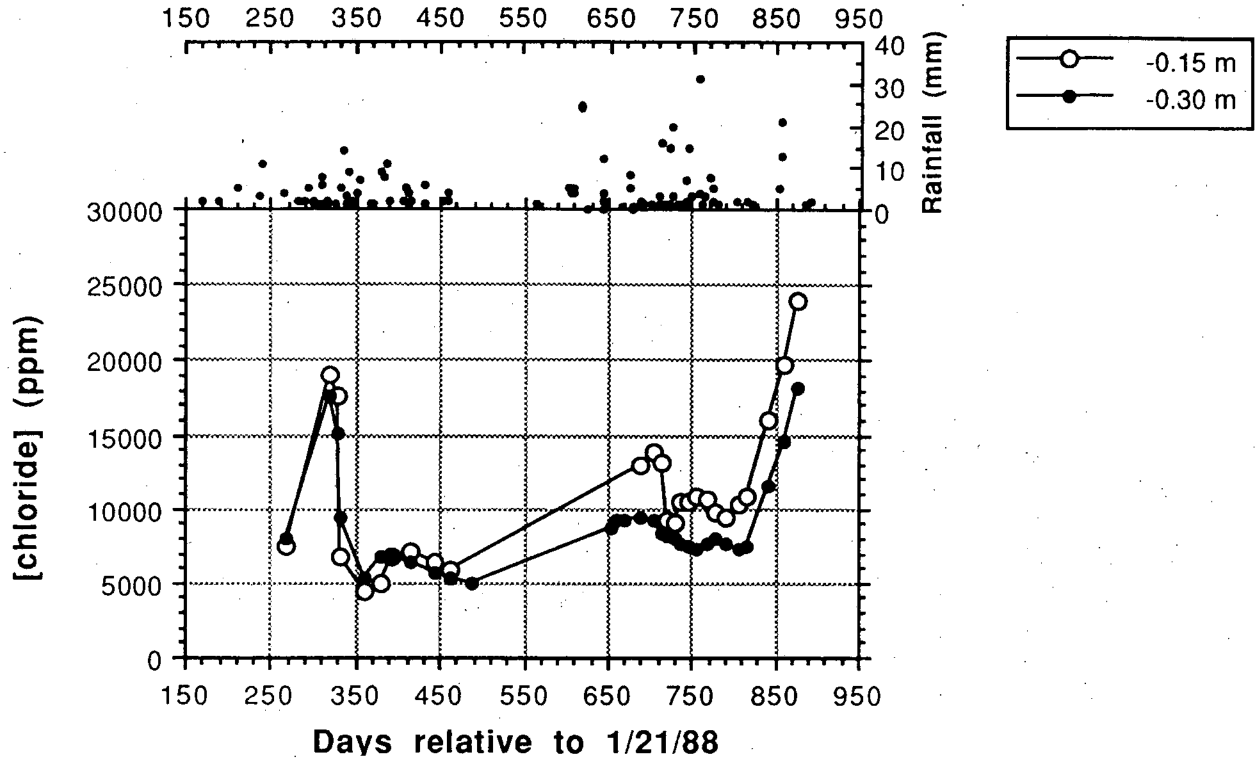


Figure 2.11a. Changes in chloride concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

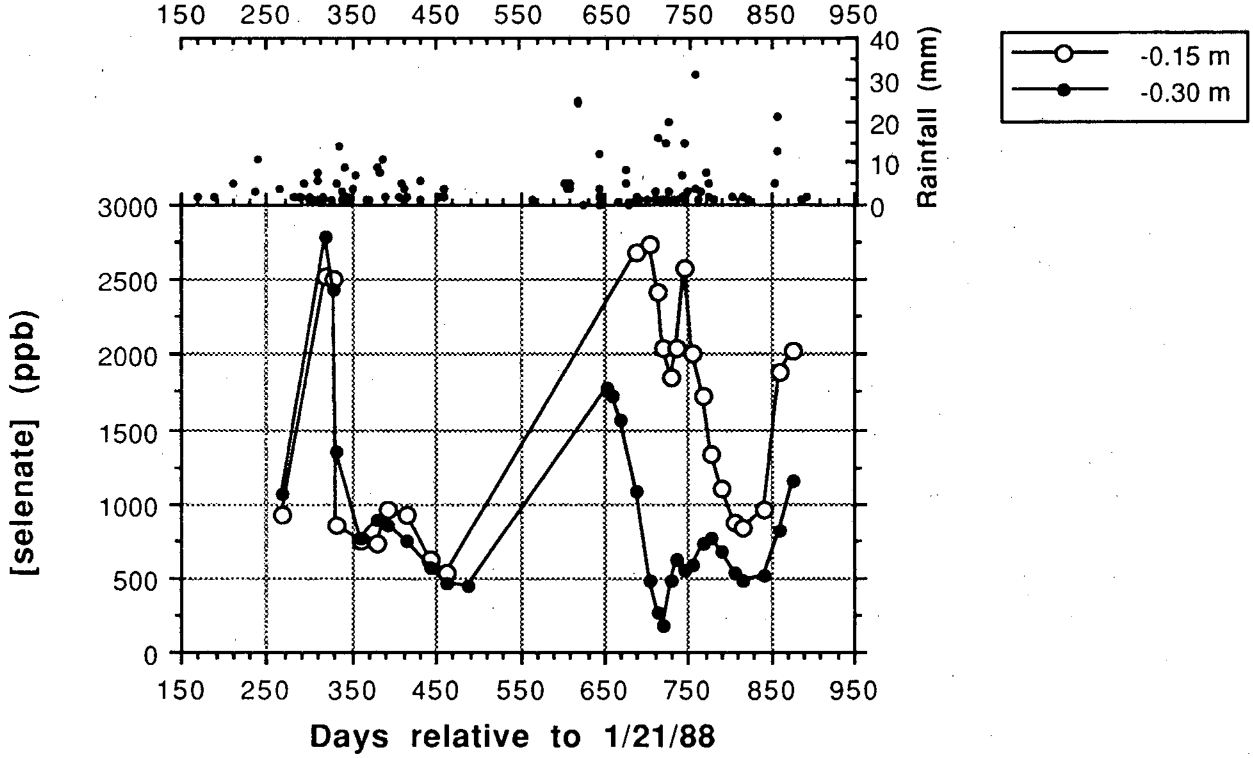


Figure 2.11b. Changes in selenate concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

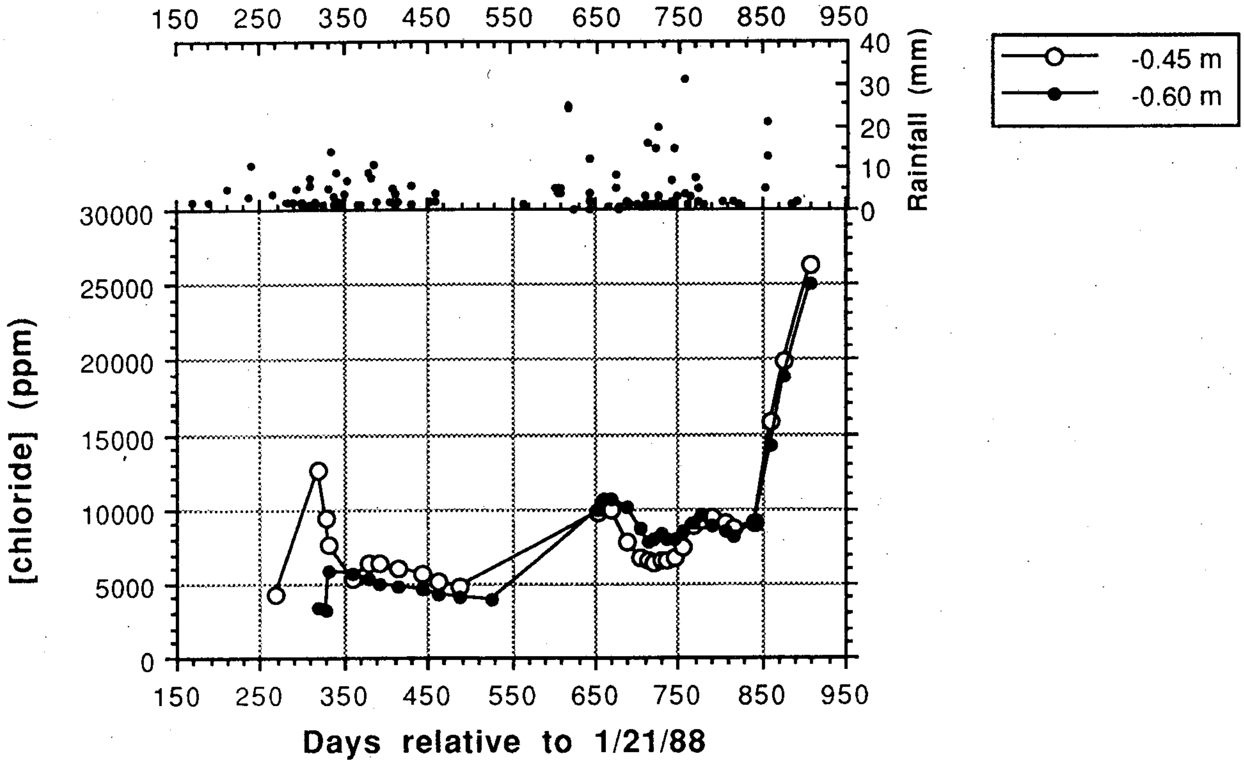


Figure 2.12a. Changes in chloride concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

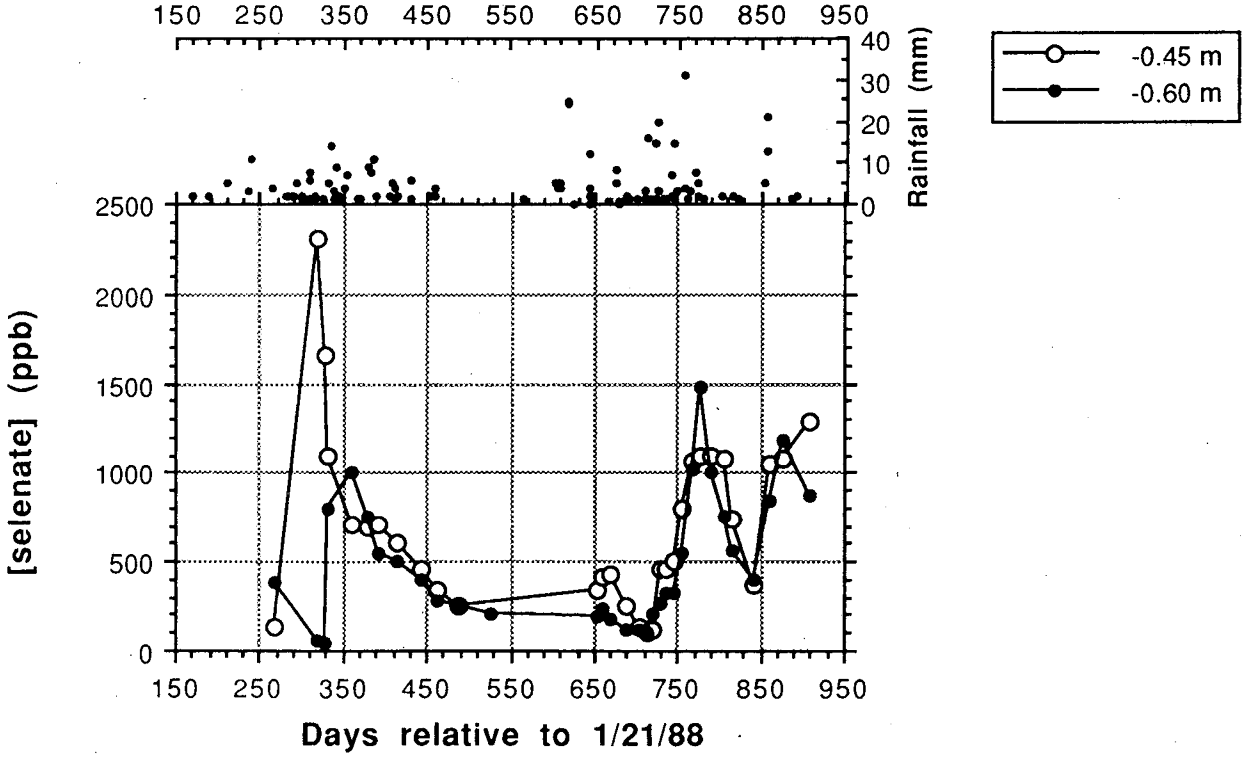


Figure 2.12b. Changes in selenate concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

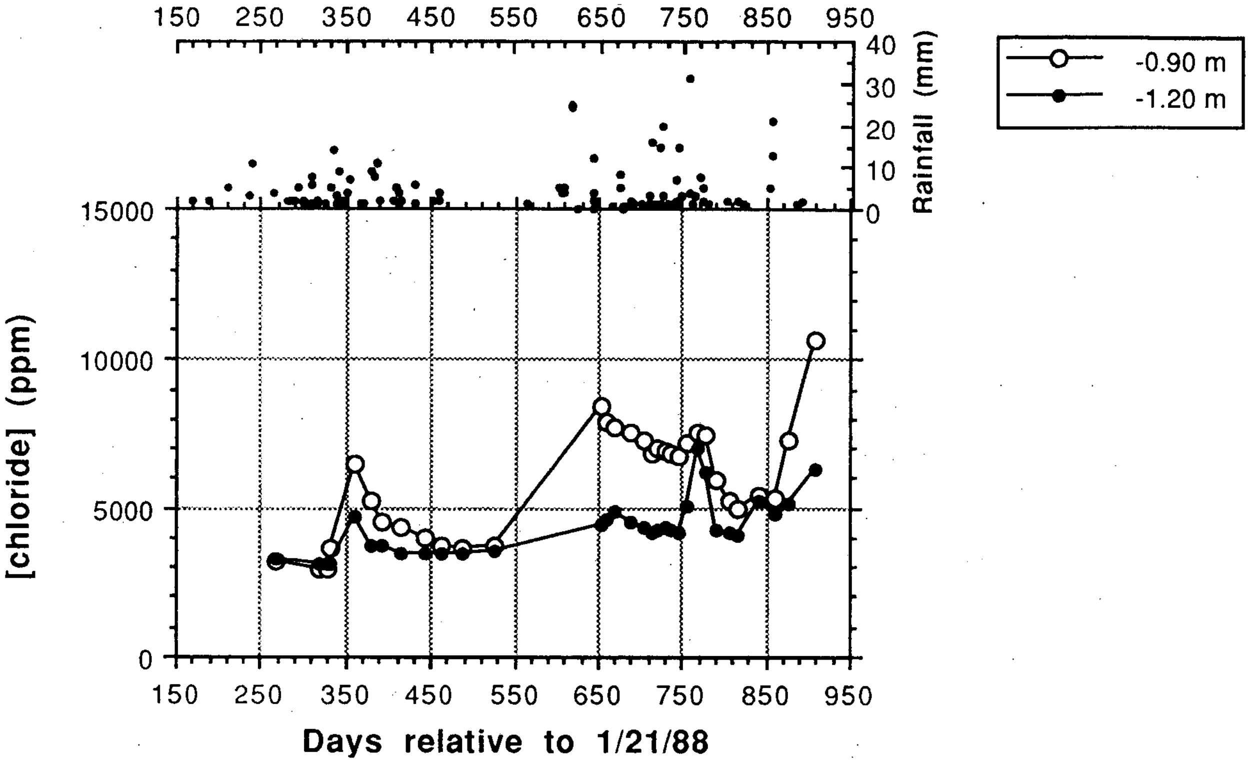


Figure 2.13a. Changes in chloride concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

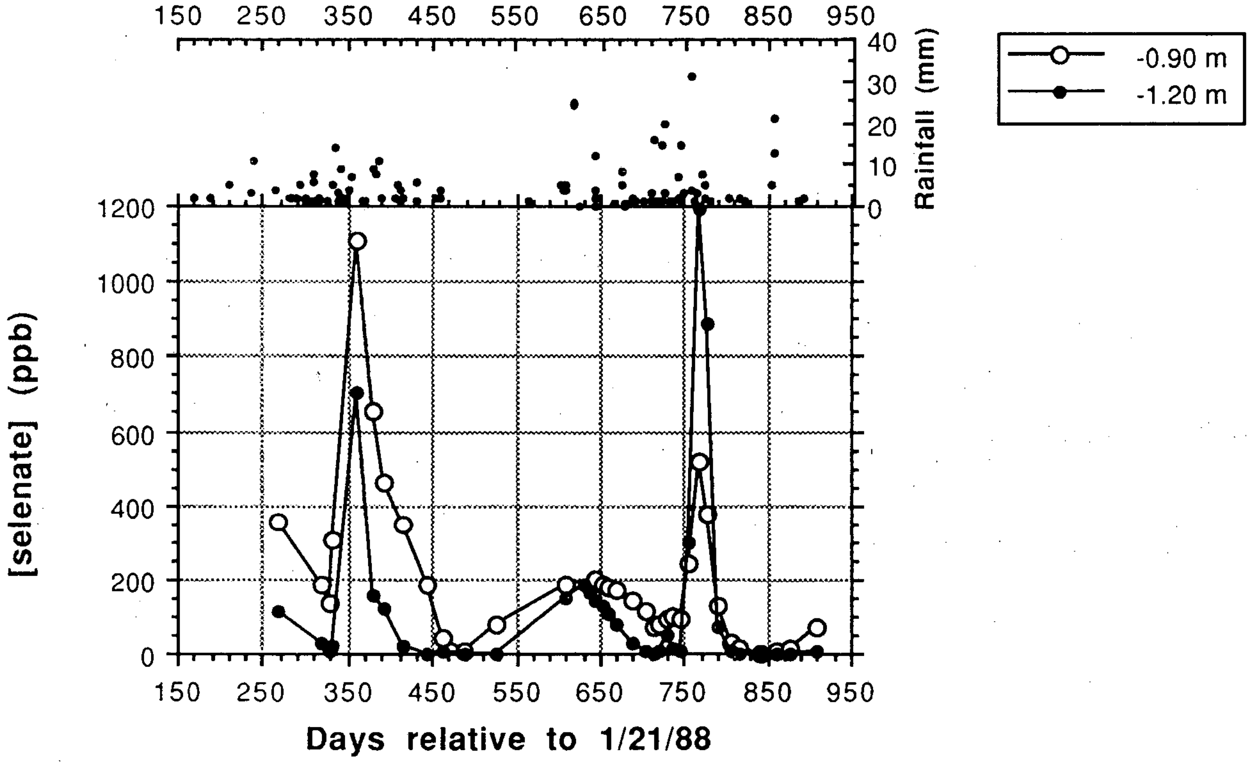


Figure 2.13b. Changes in selenate concentrations in the soil water samplers in plot 9BE (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

redistribution to rainfall infiltration is well illustrated by the events following a series of major rainfalls around Day 755. While the changes in chloride concentrations were minor (a decrease in the 15 cm sampler due to the influx of rainwater and an increase in the deeper samplers due to the downward displacement of soil water), changes in selenate concentrations were dramatic. Most surprisingly, the effect of these rainfall events was felt at depths which were below the groundwater table, including the 1.2 meter depth, which at this time was almost 1 meter below the groundwater table. A similar event also took place the preceding wet season (around Day 340- 360). Such penetration into the saturated zone cannot be easily explained, and is most likely not a natural process. In fact, it would appear that by removing soil water via soil water samplers, a ''pipe'' effect may be created which would result in the sub-water table flow through macropores. In other words, macropores which come into contact with the ceramic cup of the soil water sampler may be drained rapidly relative to the surrounding matrix and water present in the macropores in the unsaturated zone may be channeled below the water table. This bias will only be significant during and after major rainfall events, but nevertheless needs to be considered when interpreting the effect of rainfall infiltration on species redistribution.

2.2.2. Vadose Zone Monitoring in Plot 8EP

Revegetation at plot 8EP followed a slightly different pattern, in that a sparse growth of small plants was present in this plot since the fall of 1988. However, those parts of the plot which were monitored were kept devegetated until the summer of 1989. Similar to the sequence of events in plot 9BE, growth of *Kochia scoparia* greatly intensified in the spring of 1990. The soil in the top 2 meters of plot 8EP is of considerably finer texture than soil of plot 9BE. Finally, the soil profile of plot 8EP was more saline than that of plot 9BE in 1988 (see LBL, 1990).

One set of tensiometers and two sets of soil water samplers (nests ''C'' and ''ML'') were used to monitor variations in hydraulic head and salt and selenium concentrations. As in plot 9BE, soil drying over the last two years is apparent from hydraulic head data (Figure 2.14). The greatest increase in soil suction between 1988 and 1990 occurred at a depth of 60 cm, suggesting the influence of plant roots. The net increase in EC between 7/88 and 6/90 ranged from 30 dS/m

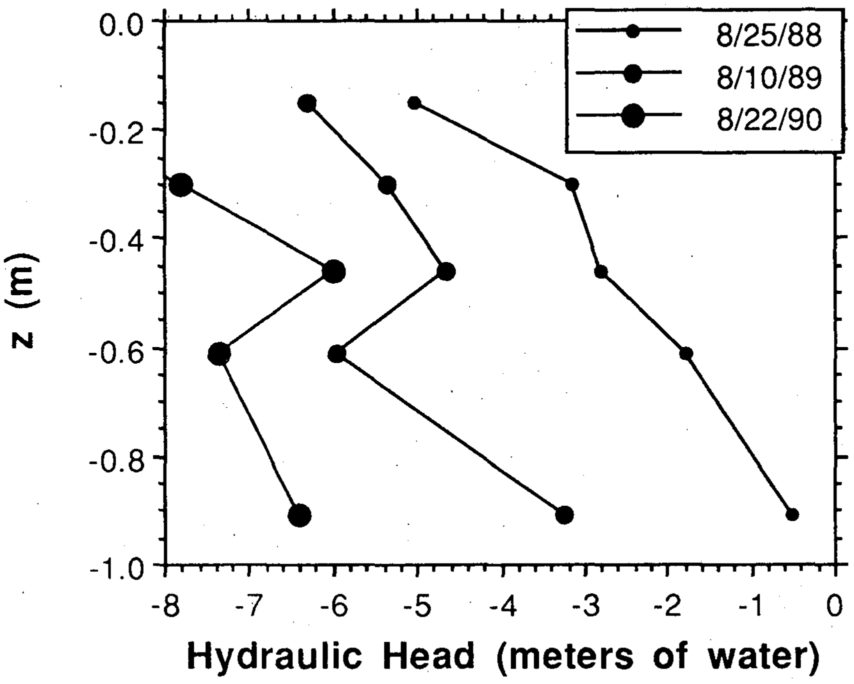


Figure 2.14. Hydraulic head profiles as measured using tensiometers in plot 8EP. Drying out of the soil profile is apparent.

at 15 cm to 20 dS/m in the remainder of the soil profile down to 61 cm (Figure 2.15; note that data from nest ''ML'' were not collected until 1/90). Not unlike in plot 9BE, soil salinity increased significantly in the last 3 months at depths of 30, 46, and 61 cm, apparently due to root extraction of soil water. This increase is seen clearly in chloride data from both nests of samplers (Figure 2.16). For example, chloride concentrations increased from about 15,000 ppm to 21,000 ppm between 5/11/90 and 7/5/90 at a depth of 45 cm in nest ''ML'' (approx. 40%). On the other hand, selenate concentrations at the same depth increased from about 550 to 650 ppb (approx. 20%) (Figure 2.17); the change in nest ''C'' was even less. This, once more, may be explained by transpirative concentration of solutes from a deeper soil water, relatively low in selenium.

Since the water table in plot 8EP does not rise higher than to 1.4 m below the soil surface, one would expect to see effects of rainfall infiltration in the vadose zone. Based on comparisons between hydraulic head readings and rainfall data (Figure 2.18), it appears, however, that rainfall did not infiltrate significantly below 46 cm or it did so slowly enough that it is not possible to distinguish one pulse from another. Furthermore, there are no apparent effects of rainfall infiltration on salt or selenate concentrations except at the 15 cm depth (Figure 2.19). All of this may be due to the very fine texture of soil in this profile and the apparent lack of a continuous macropore structure capable of channeling infiltrating rainwater.

In summary, the following general statements may be made regarding the changes in selenium and salt distribution in the vadose zone of plots 9BE and 8EP:

- Over the last two years, both selenate and salt concentrations have increased in the vadose zone. The greatest increases have taken place in the root zone, or in the top 60 cm of soil. There, soil solution salt concentrations have risen up to sixfold, while selenate concentrations have doubled to tripled. Increases in salt concentrations may be attributed primarily to root extraction of soil water, while changes in selenate concentrations are the result of a combination of root extraction, oxidation of less soluble selenium forms, and rainfall infiltration.

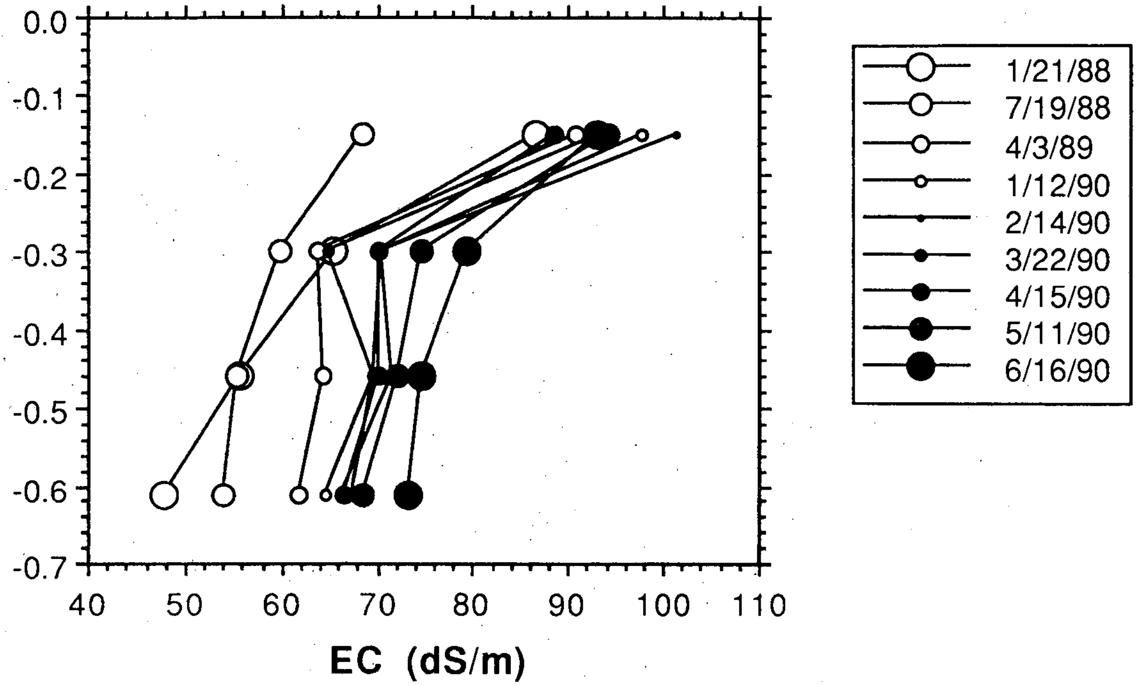


Figure 2.15a. Changes in electrical conductivity of soil water in plot 8EP, sampler nest "C."

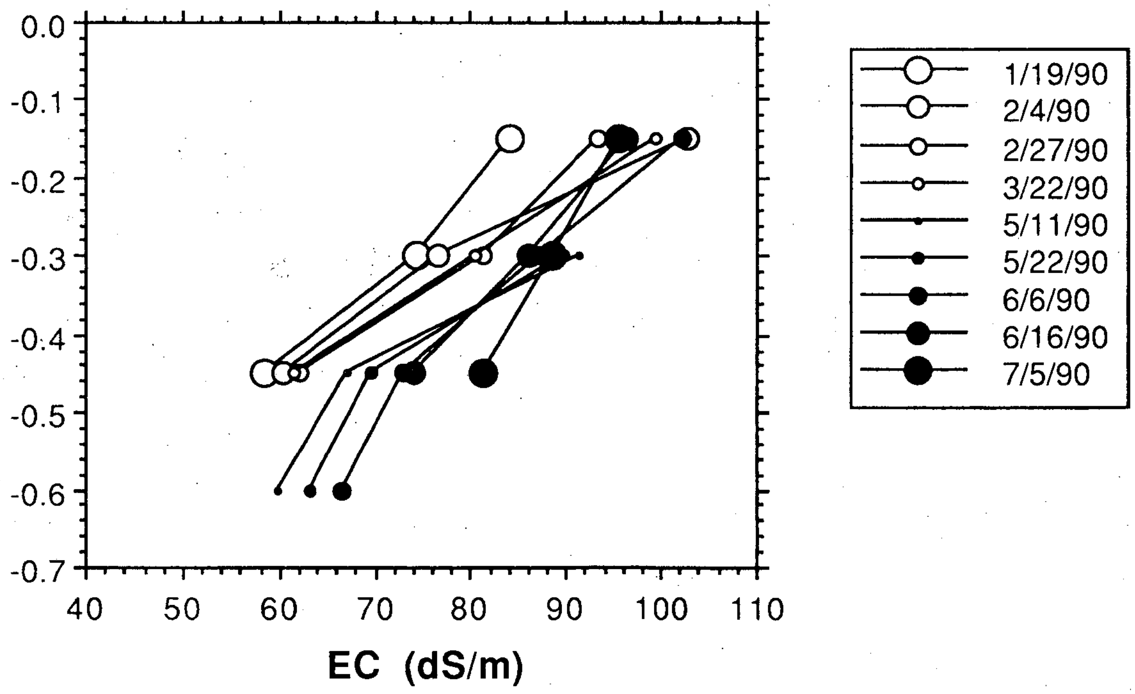


Figure 2.15b. Changes in electrical conductivity of soil water in plot 8EP, sampler nest "ML."

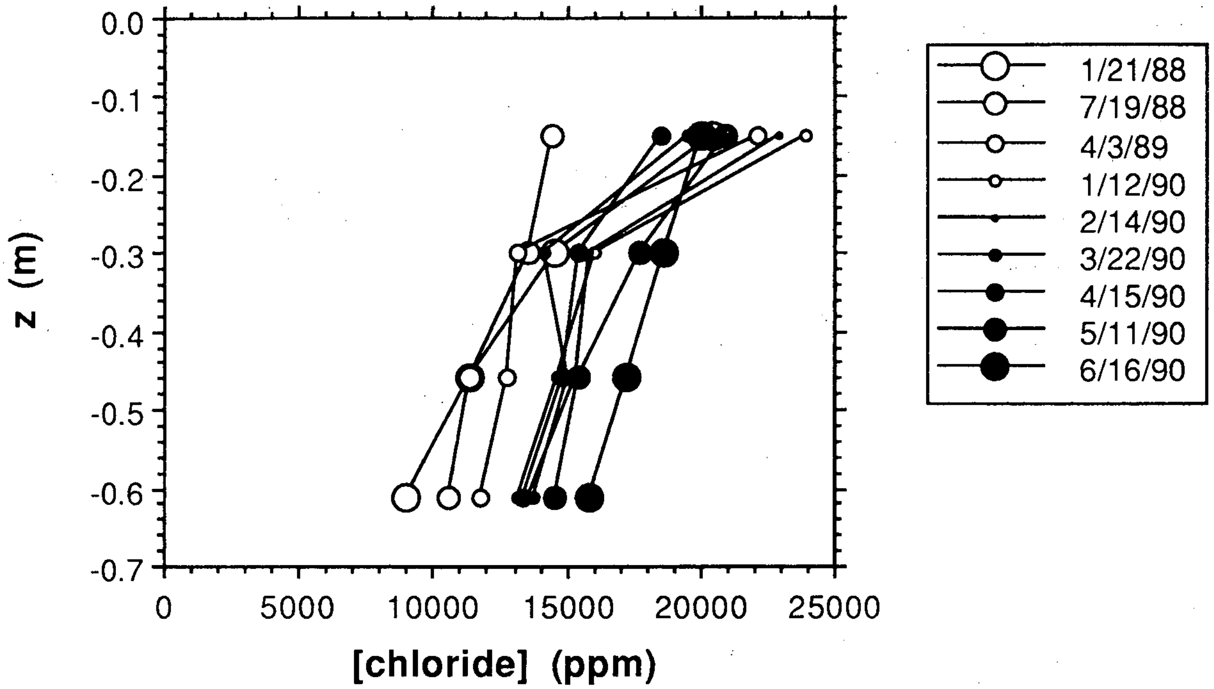


Figure 2.16a. Changes in chloride concentrations in soil water in plot 8EP, sampler nest "C."

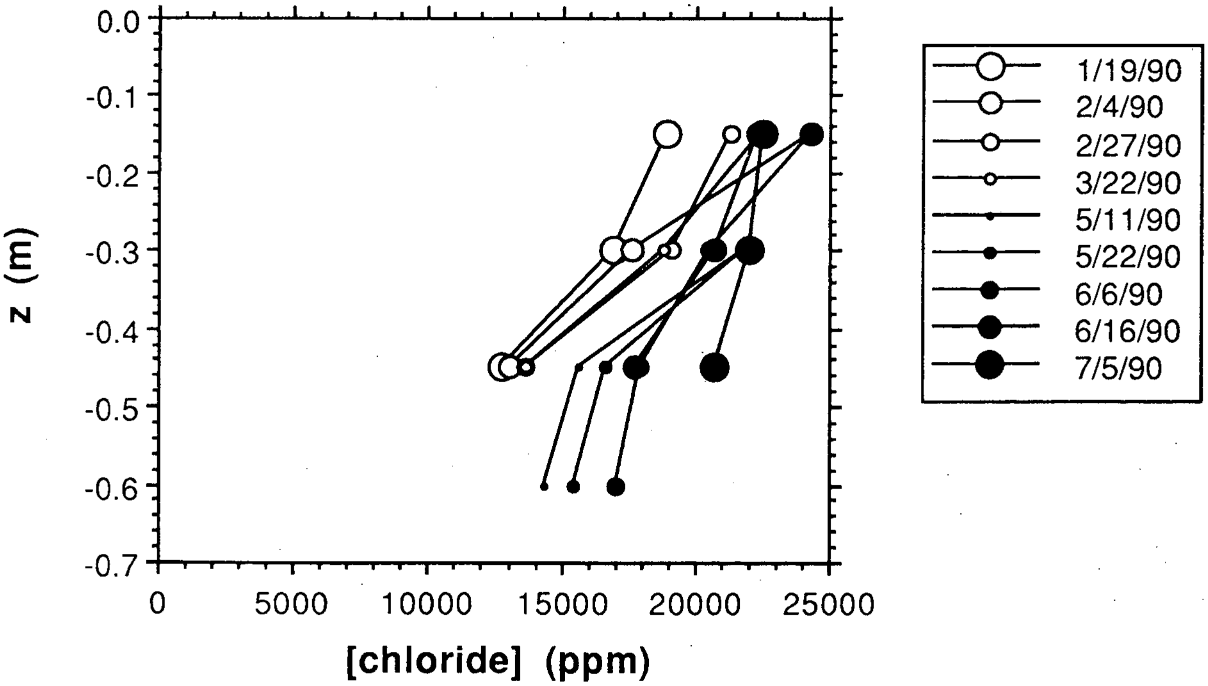


Figure 2.16b. Changes in chloride concentrations in soil water in plot 8EP, sampler nest "ML."

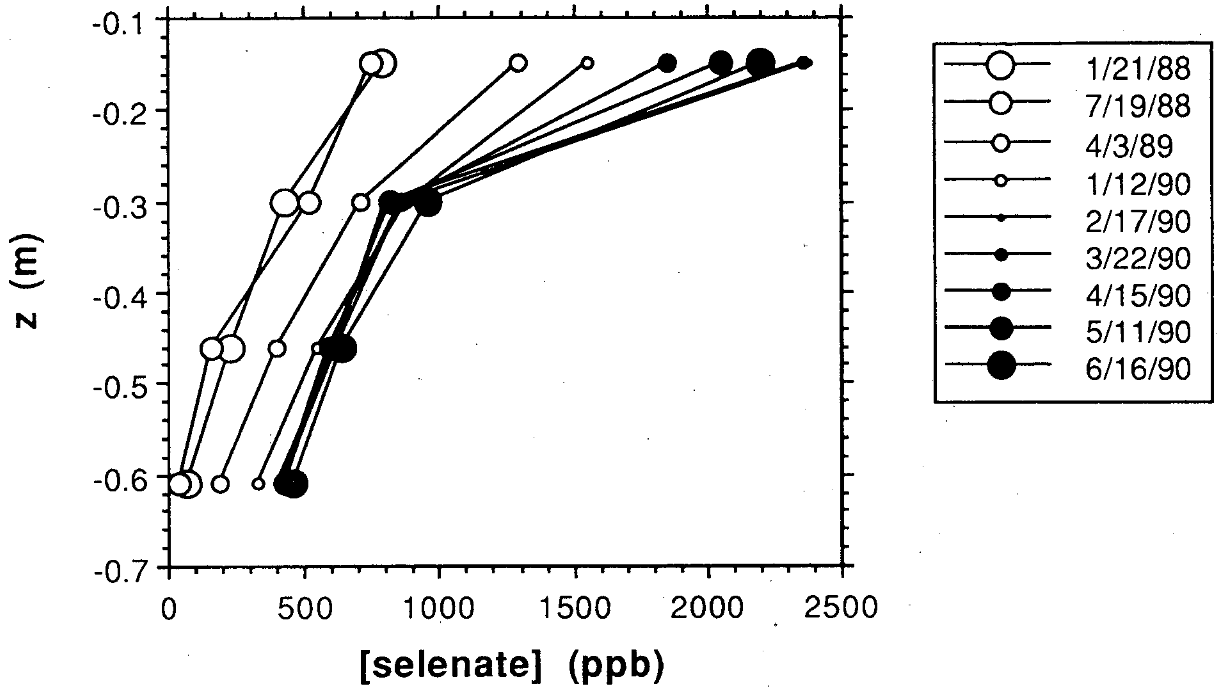


Figure 2.17a. Changes in selenate concentrations in soil water in plot 8EP, sampler nest "C."

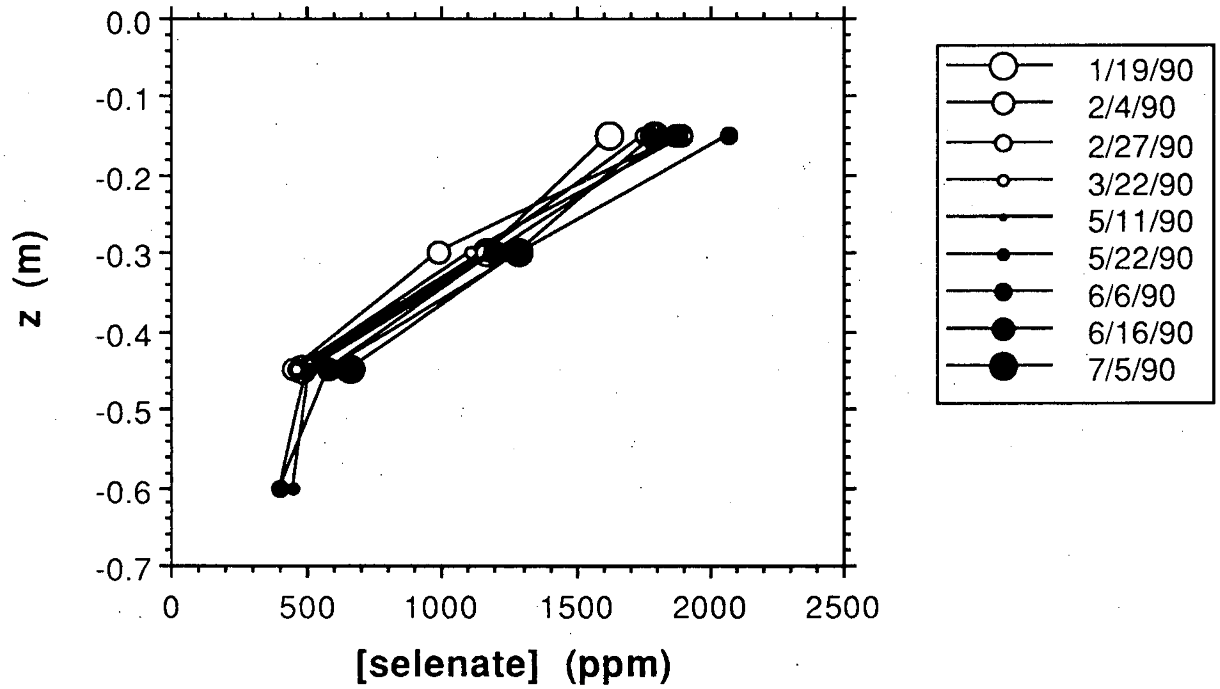


Figure 2.17b. Changes in selenate concentrations in soil water in plot 8EP, sampler nest "ML."

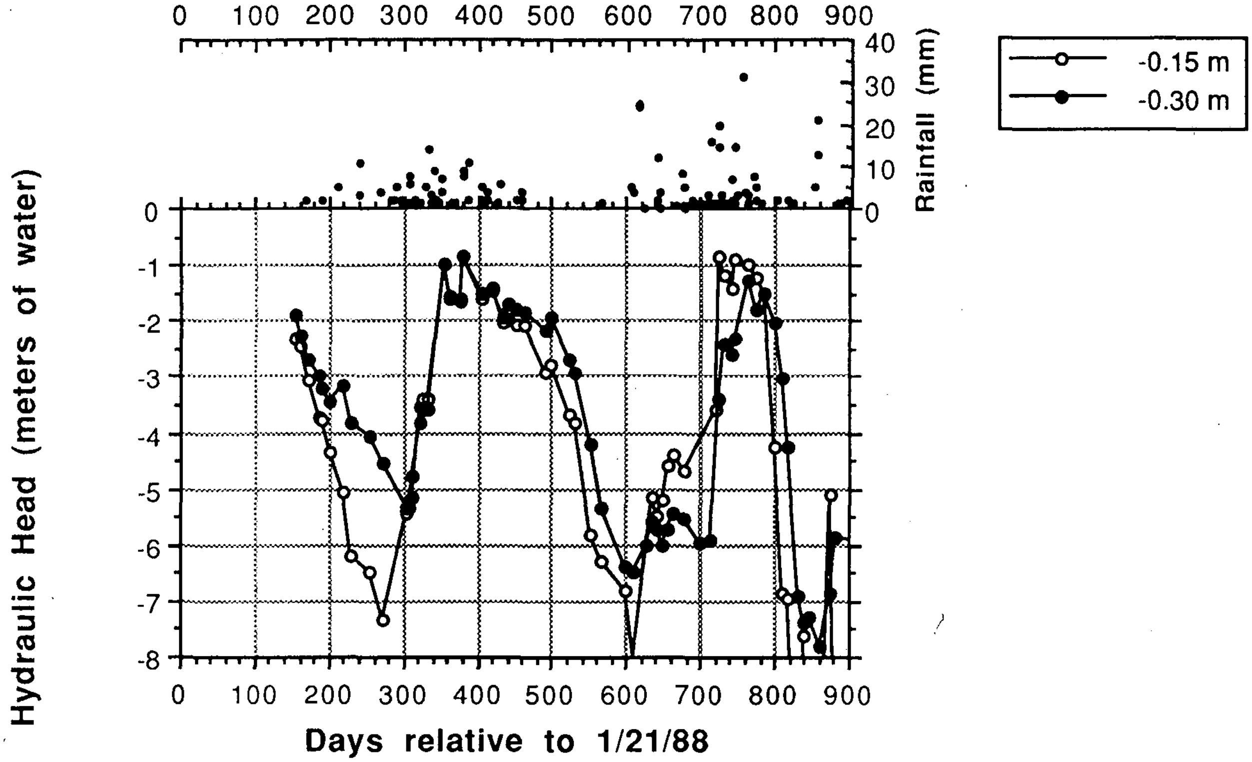
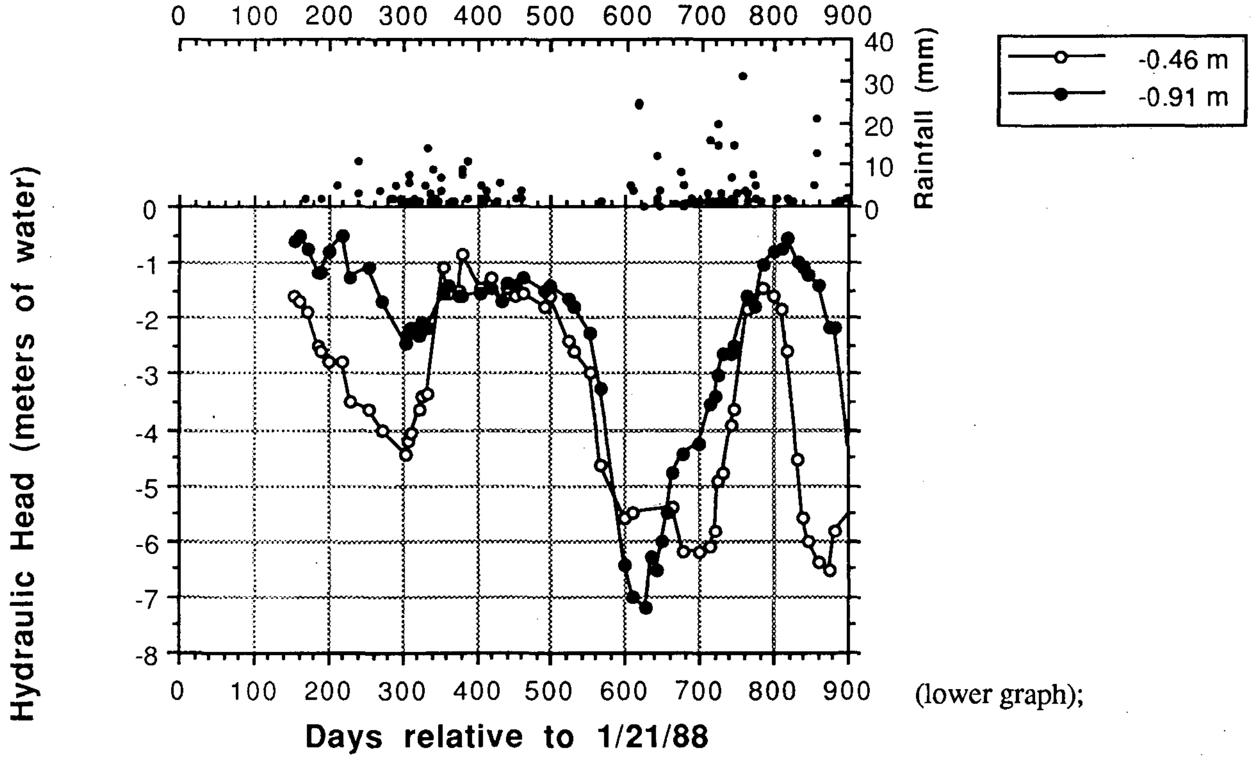


Figure 2.18a. Hydraulic head at 15 and 30 cm below the soil surface in plot 8EP (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).



(lower graph);

Figure 2.18b. Hydraulic head at 46 and 91 cm below the soil surface in plot 8EP (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

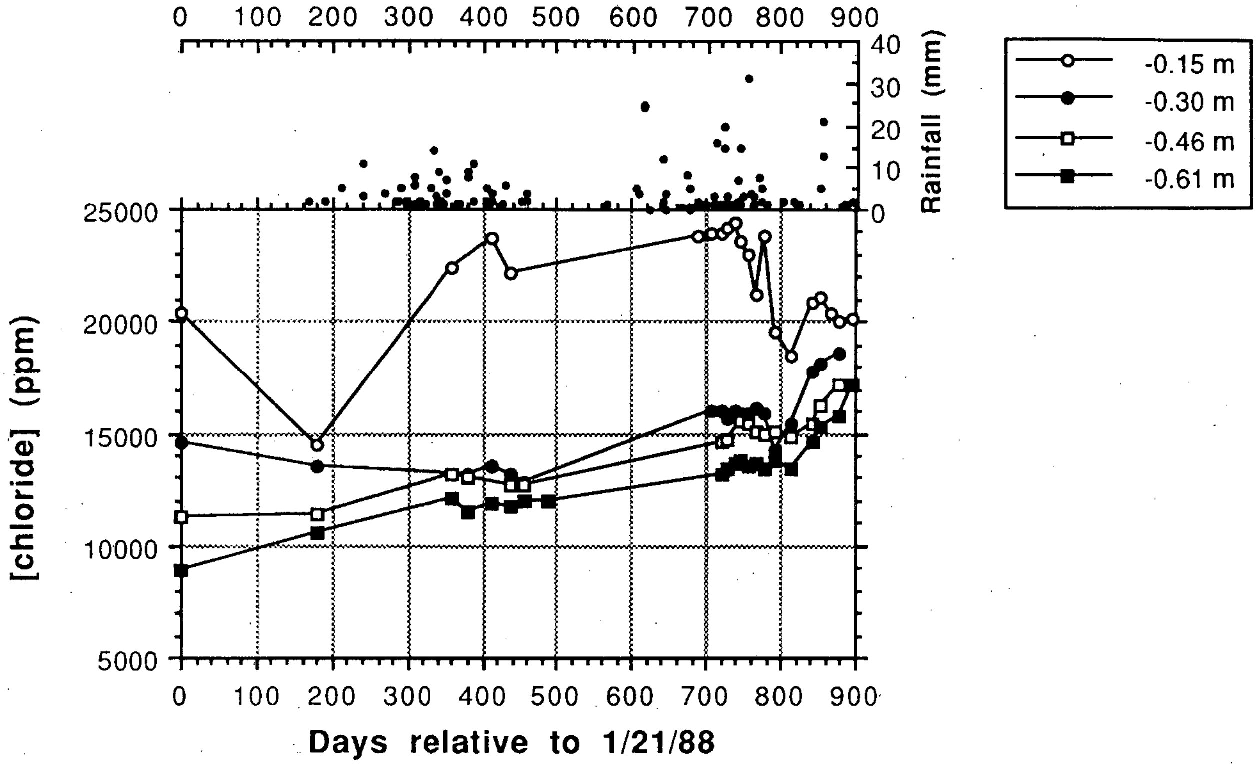


Figure 2.19a. Changes in chloride concentrations in soil water samplers in plot, nest "ML" (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

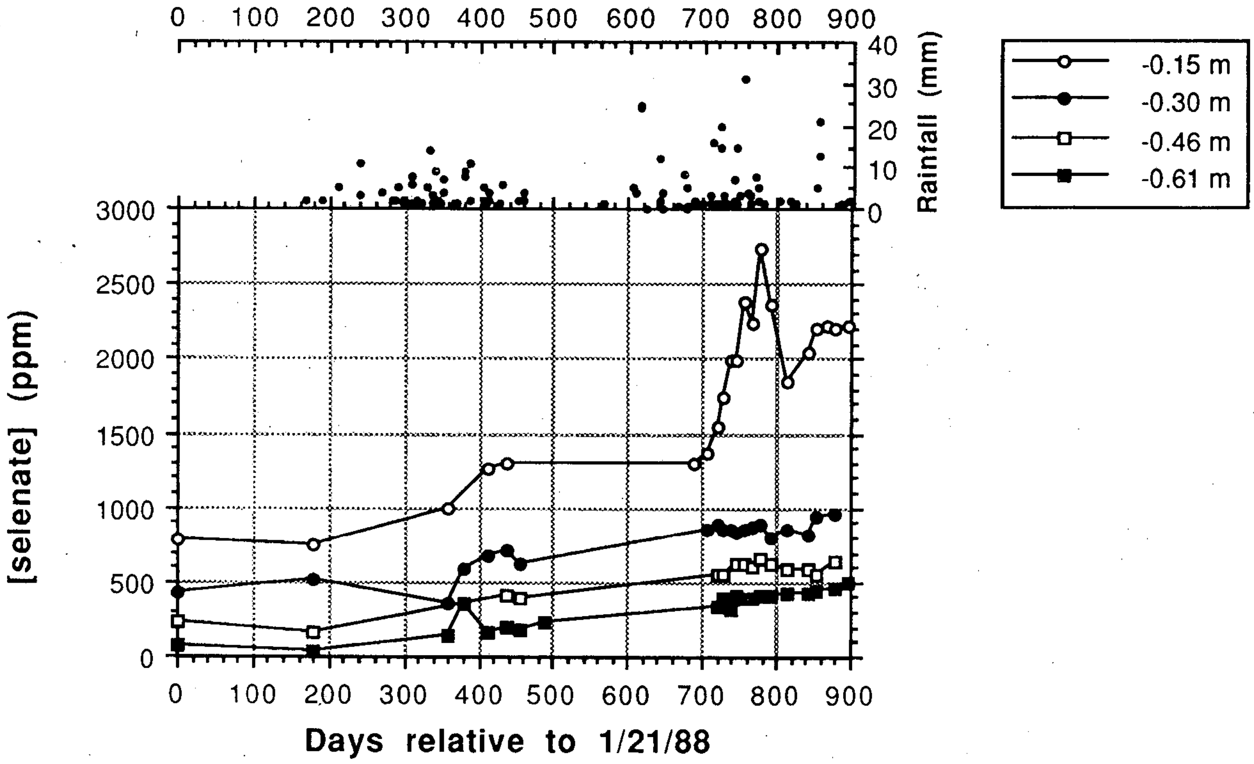


Figure 2.19b. Changes in selenate concentrations in soil water samplers in plot, nest "C" (lower graph); cumulative daily rainfall at Kesterson Reservoir (upper graph).

- Selenate concentrations in the vadose zone may be significantly affected by rainfall infiltration. This will be especially apparent in soil profiles with very strongly skewed selenium distributions and coarser soil texture, both of which are true in plot 9BE. Several small rainfall events may have a negligible effect, while a single large event may be significant, especially when macropores provide a major flow pathway. On the other hand, in very fine texture soils with poor structure, rainfall infiltration may move solutes down to only very shallow depths. What must be kept in mind is that the winter of 1989/1990 was only average in terms of total rainfall. During wetter years, or following a particularly intense rainfall, these effects may be magnified.
- Rapid salinization in the root zone will likely slow down future growth of *Kochia scoparia* and other equally or more salt-tolerant plants may become more common.

2.2.3. Measurement of Chemical Changes in Near-Surface Soils of Plots 8EP and 9BE

Beginning in July 1988 and ending in July 1989, samples of the top 9 cm of soil were taken from plots 8EP and 9BE for analysis on a monthly basis. The impetus for this sampling strategy was to track changes in chemical species concentration in these surface soils as affected by bare soil evaporation and rainfall infiltration. The 1988/89 series of samples yielded data which suggested that while seasonal fluctuations in this interval were significant (species flushed down deeper into the soil profile during the wet season, and evaporatively concentrated during the dry season), the net differences over a twelve month period were very small; these changes were recognized to be strongly dependent on atmospheric conditions, especially rainfall amount and intensity. In summary, salt concentrations over that twelve month period dropped slightly, while water-extractable selenium concentrations did not change significantly (for a full discussion see LBL, 1990). Since then, two more sets of samples have been taken from those plots (9/89; 4/90).

The following is a brief description of the soil preparation and analysis procedures. After each sample was homogenized, a subsample of known mass (on the order of 10 to 20 g) was used to prepare a 1:10 soil:water extract which was stirred for 2 hours. Subsequently, the suspension was centrifuged at between 3000 and 6000 revolutions per minute for 5 to 20 minutes, depending on the texture of the soil. The supernatant liquid was then poured off and filtered through a 0.45 µm filter in preparation for chemical analysis. Three analytical methods were used for the analysis of water samples. Sodium, calcium, magnesium, sulfate, and boron were analyzed using an Inductively Coupled Plasma Spectrophotometer (ICP) produced by Applied Research Laboratories. Potassium, selenite, and selenium were analyzed for using atomic absorption spectroscopy (AAS) coupled with a hydride generator. Chloride was analyzed for using Mohr titration, as described by Flaschka and others (1969).

The last set of samples was taken toward the end of the rainy season (April 1990). Because of variations in rainfall patterns from year to year, it is best to compare samples taken during the summer or early fall: the sample set taken in October 1990 has not yet been processed. Nevertheless, some comparisons may be made between the salt and selenium concentrations in 4/90 and 4/89.

Figure 2.20 shows the changes in chloride concentrations in the top 9 cm of soil in plot 8EP. The concentrations in 4/90 are essentially within the range of those in 4/89. This suggests that near-surface salt movement patterns have not changed significantly over that period. The same comparison of selenium concentrations (Figure 2.21) reveals a very slight increase over the same period (range of values in 4/89: 0.65-1.10 µg/g; range of values in 4/90: 1.00 to 1.17 µg/g). Such small changes should not be given much consideration in light of the evident spatial variability. While spatial variability in both chloride and selenium concentrations is even greater in plot 9BE (Figures 2.22,2.23), chloride concentrations were significantly higher in 4/90 than in 4/89. This may be due to the shallow roots of the emerging *Kochia scoparia* plants (see Figure 2.4) in addition to bare soil evaporation, and differences in rainfall distribution. Selenium concentrations, however, did not increase as significantly (range of values in 4/89: 1.4 to 2.0 µg/g; range of values in 4/90: 1.65 to 2.35 µg/g).

Further monitoring of the surface soil in these plots will reveal changes influenced by an additional factor not present in the 88/89 sampling period: plant transpiration. Some effects of this process may have manifested themselves in the data from plot 9BE presented above. As

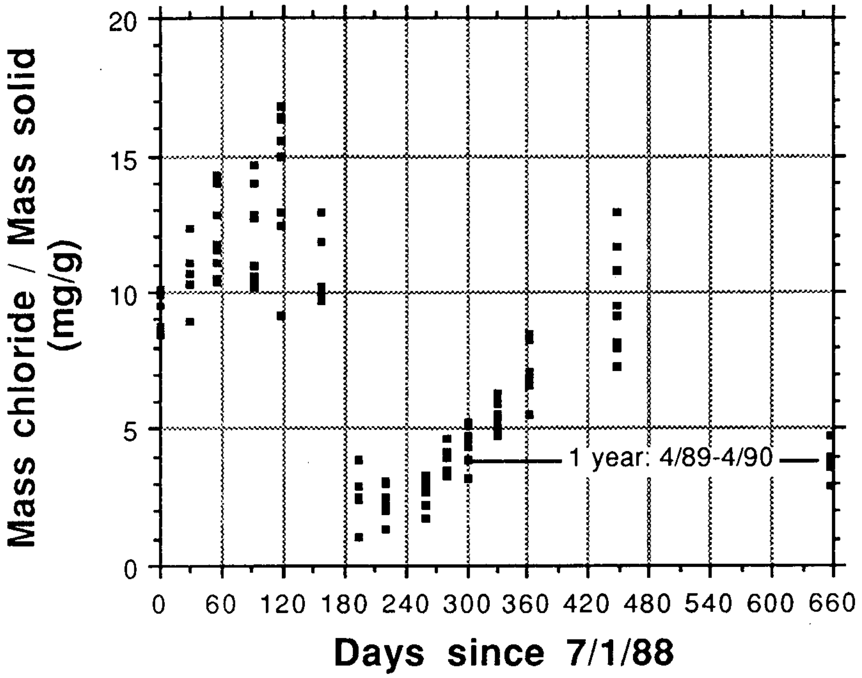


Figure 2.20. Changes in chloride concentration in the top 9 cm of soil in plot 8EP; July 1988 - April 1990.

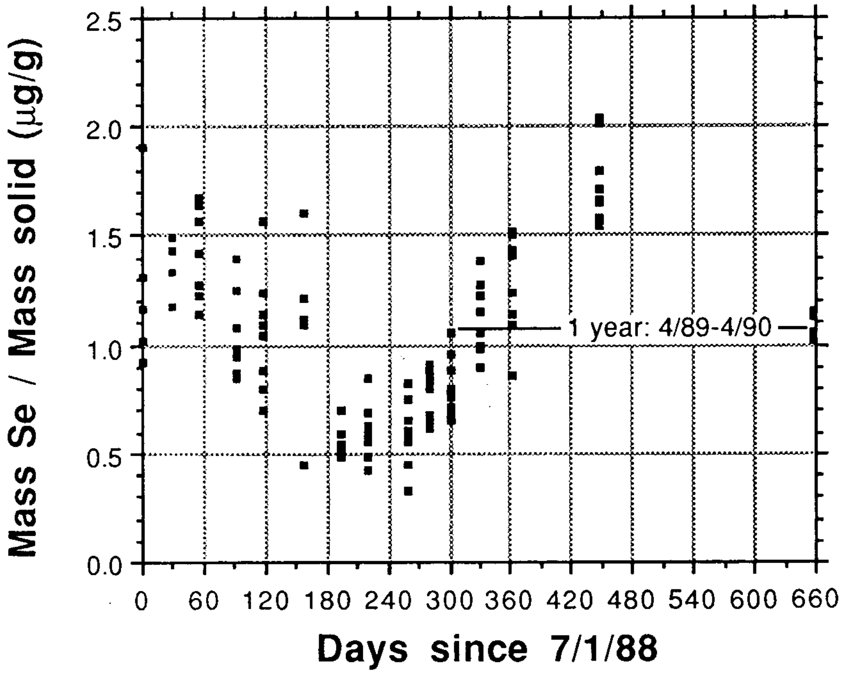


Figure 2.21. Changes in water-extractable selenium concentration in the top 9 cm of soil in plot 8EP; July 1988 - April 1990.

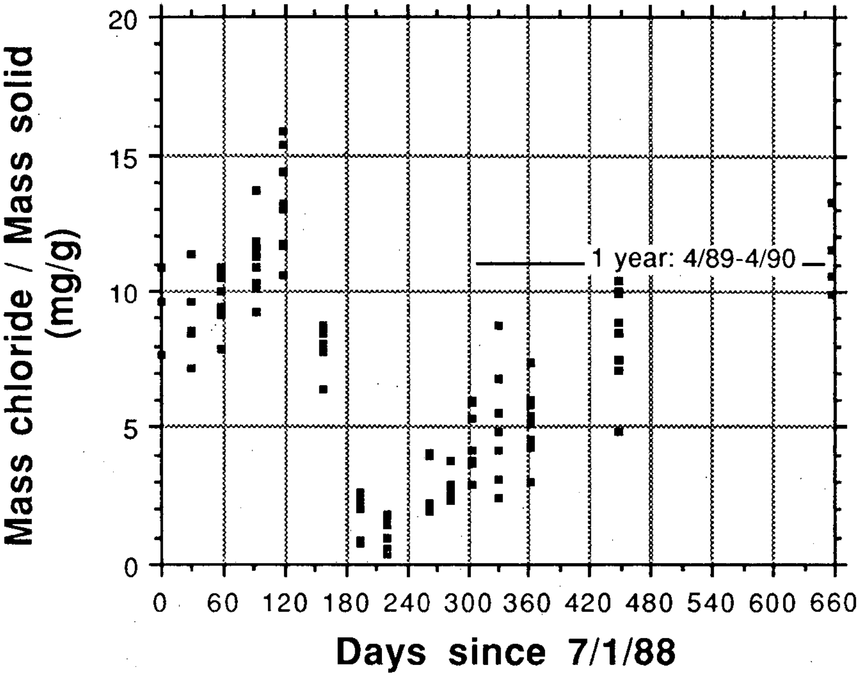


Figure 2.22. Changes in chloride concentration in the top 9 cm of soil in plot 8EP; July 1988 - April 1990.

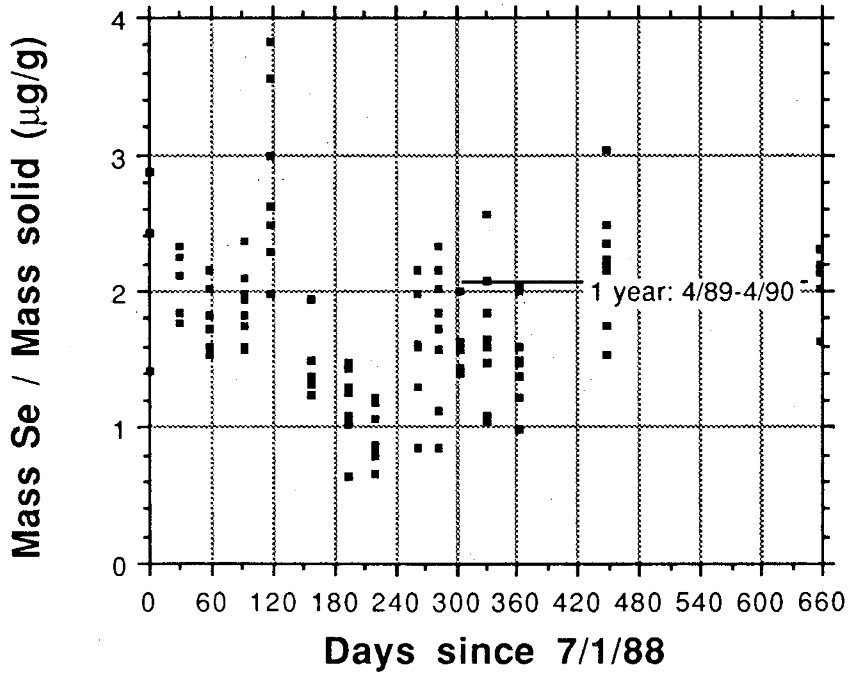


Figure 2.23. Changes in water-extractable selenium concentration in the top 9 cm of soil in plot 8EP; July 1988 - April 1990.

Kochia plants grow in size, their roots tap water deeper in the soil. Therefore, their effect in the long run may be to decrease evaporation from the soil surface and thereby reduce the rate of salt accumulation at the soil surface during the dry season.

2.3. Pond 5 and Pond 7 Fill Sites

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Since approximately half of the Reservoir area has been covered with fill dirt during the summer of 1988, it was warranted to establish monitoring sites in such environments. During December 1988 and March 1989, soil profiles in filled areas of Ponds 5, 6, and 7 were sampled (one profile in each pond). Analysis of the Pond 6 fill material indicated that it was largely comprised of Kesterson Reservoir soils (i.e., the selenium content and salinity of the fill was too high to have been associated with fill dirt borrowed from areas external to the Reservoir). Analyses of the Pond 5 and Pond 7 profiles indicated that filling had occurred to depths of 0.52 m and 0.30 m respectively (with uncertainties of ± 0.02 m in both cases). In both of these sites, the fill consisted of initially clean material obtained from spoil banks of the Delta-Mendota Canal. The primary motivation for establishing monitoring sites in filled areas was for the purpose of detecting changes in the selenium content and salinity of initially clean fill soils. Therefore, monitoring has been continued in the Pond 5 and Pond 7 sites, while the Pond 6 fill profile has been abandoned. Data from soil water samplers installed in the Pond 5 and Pond 7 fill sites, referred to as P5F and P7F respectively, will be presented here. In addition, water-extracts of core profiles at site P5F, taken in September of 1989 and 1990 have been analyzed for trends in redistribution of selenium and salts during a one year time interval.

Depth profiles and time trends for soil water selenium in the P5F and P7F sites are presented in Figures 2.24a and 2.26a respectively. Included in all figures relevant to filled sites are lines demarcating the boundary between fill dirt and the original soil surface. A significant increase in the soil solution selenium concentrations was observed in the P5F site. The originally clean fill at site P5F now contains soil solution selenium concentrations in the range of 300 to 8000 $\mu g\ L^{-1}$ (ppb) (Figure 2.24a).

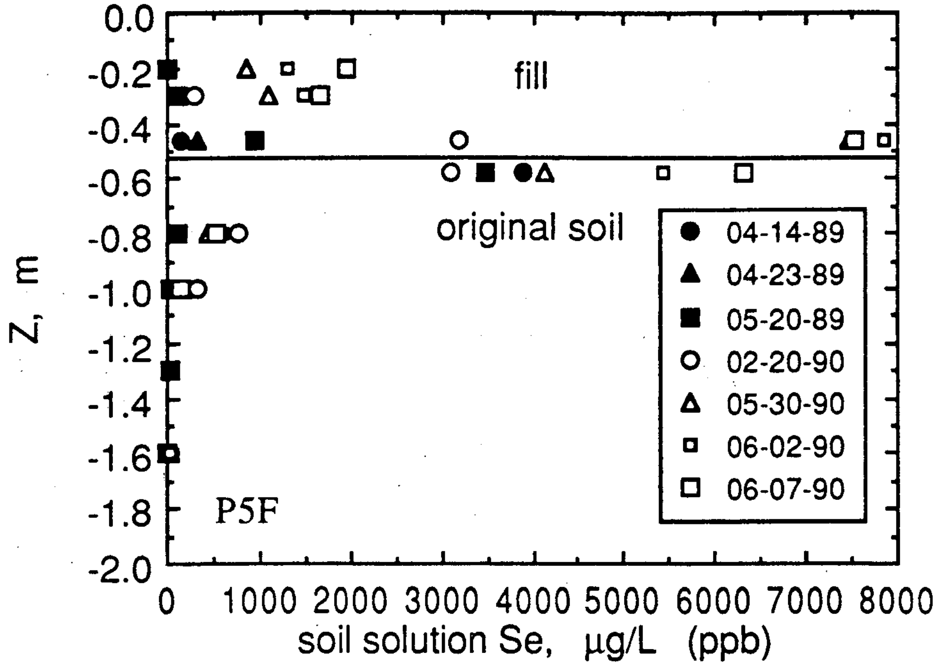

Figure 2.24a. Pond 5 fill monitoring site, soil solution selenium profiles.

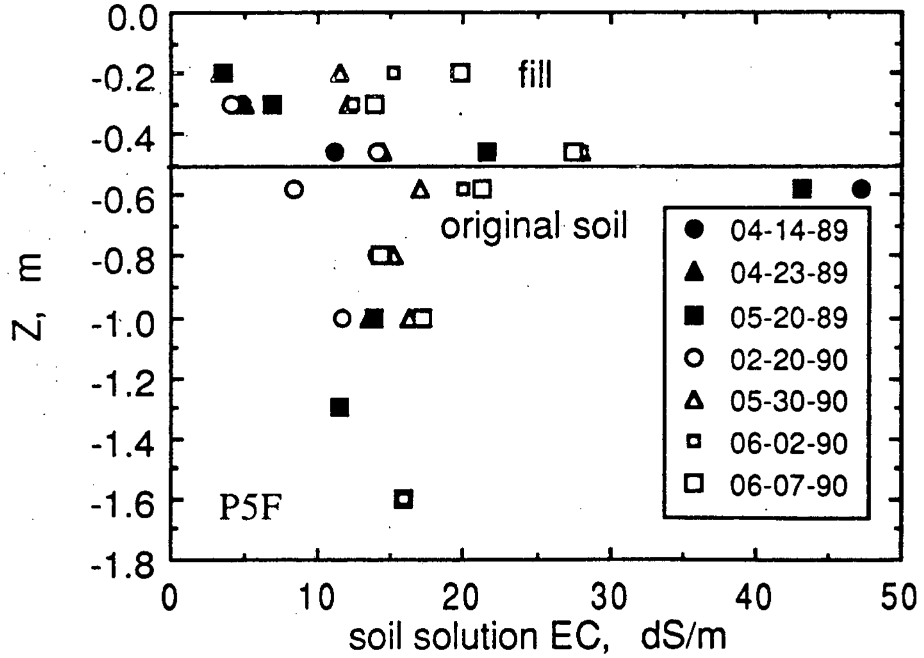

Figure 2.24b. Pond 5 fill monitoring site, soil solution electrical conductivity profiles.

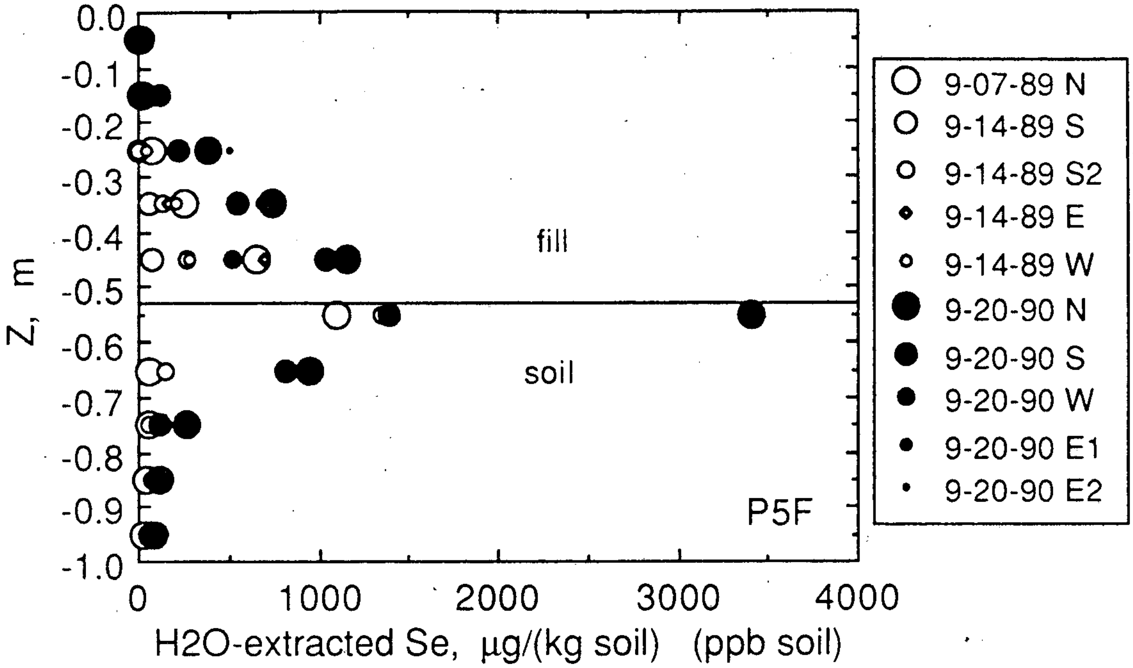

Figure 2.25a. Pond 5 fill monitoring site soil core profiles, water extracted selenium profiles.

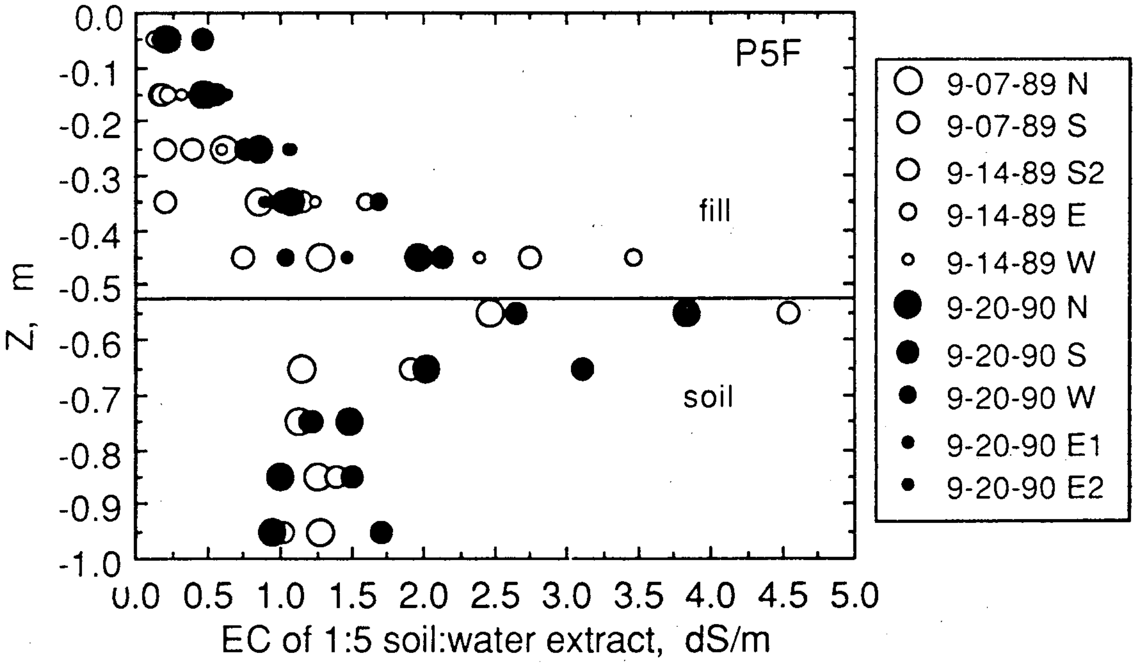

Figure 2.25b. Pond 5 fill monitoring site soil core profiles, water-extract electrical conductivity profiles.

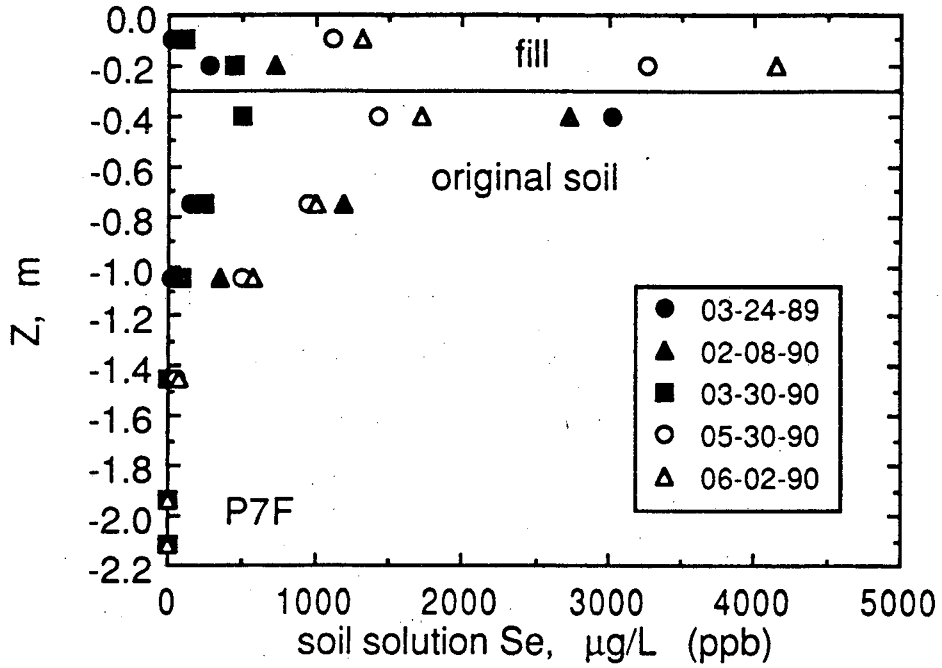

Figure 2.26a. Pond 7 fill monitoring site, soil solution selenium profiles.

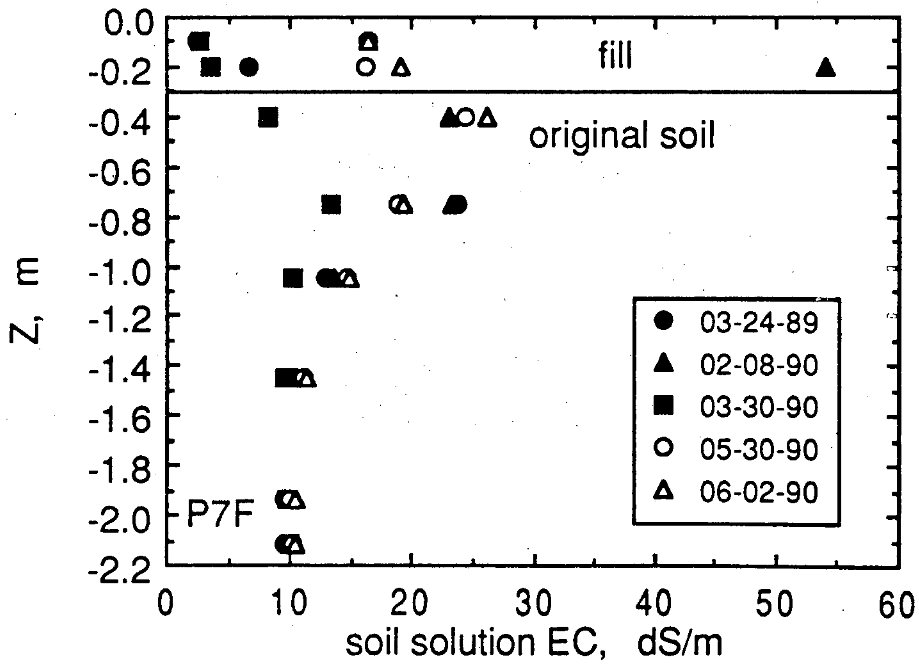

Figure 2.26b. Pond 7 fill monitoring site, soil solution electrical conductivity profiles.

The fill sites have also been monitored through collections of soil profile samples at the end of each summer. The sampling time was selected to minimize the variable influence of rainfall, in order to attempt to detect more general changes in distributions of selenium and salts. Yearly auger samples are collected at 4 to 5 points at sites P5F and P7F. Two of the profiles at each site and time are collected to a depth of 1.00 m below the present (fill) surface, such that both fill material and the underlying soil are sampled in 0.10 m intervals. The remaining 2 to 3 profiles at each sampling site and time are taken to a depth at or near the fill-soil interface. The Sept. 1989 and Sept. 1990 core profile data for water-extracted selenium at site P5F are presented in Figure 2.25a. Similar analyses for site P7F are currently in progress. (Note that water-extracted selenium concentrations for auger profiles are normalized to the dry mass of soil, rather than to the soil water content. The latter is the normalization used for data from soil solution samplers. Approximate conversions from the former to the latter can be made by multiplying by the field soil:water mass ratio, which commonly ranges from 3 to 12.) A general agreement in depth and time trends for soluble selenium profiles from field soil solution samplers and from water-extraction of soil samples is seen in comparing Figure 2.24a and 2.25a.

The soluble selenium concentrations in the initially clean fill obtained from both soil water samplers and soil water extracts are in the range of values associated with the original Reservoir soils following their exposure to agricultural drainage waters. It is emphasized that only the soluble selenium fractions of the P5F soils and original Kesterson Reservoir soils are of similar concentrations. Total selenium analyses of the P5F fill material have not been completed at this time. However, phosphate extractions of the fill soil as well as total selenium analyses from other fill sites indicate that in most fill areas increases in selenium are largely associated with the soluble inventory. Thus, in most fill areas, the total selenium concentrations are lower than those of the underlying original soils.

The increase in soluble selenium in the fill appears to result primarily from evapotranspirative flow from the buried soil. Although filled areas were initially unvegetated, prolific plant growth occurred during both 1989 and 1990. A commonly observed revegetation sequence during these years is the initial growth of annual grasses and forbs during April and May, followed by shrubs (dominated by *K. scoparia*, but also including *Salsola kali* (tumble weed) and other unidentified species). The extent of upwards movement of soil water into the fill is difficult to determine from increases in selenium or other solutes since gradients of these constituents are extremely high at the original soil underlying the fill. Unlike some other areas of the Reservoir, increases in fill dirt selenium concentrations can not be attributed to downwards leaching from an overlying seleniferous crust. For similar reasons, auger samples of the fill material are not likely to be cross-contaminated with more seleniferous soil materials since the latter are located deeper in the profile.

Data from the P7F site (Figure 2.26a) appear to show increases in fill soil solution selenium concentrations similar to those observed at site P5F. The P7F data are regarded as less conclusive at this time, since only one complete profile sampling was obtained during the beginning of monitoring (1989). The completion of water-extractions of yearly soil samples at P7F will help assess the extent of changes with respect to soluble selenium profiles.

Profiles of soil solution salinity from sites P5F and P7F are presented in Figures 2.24b and 2.26b. The changes in fill soil solution salinity, as estimated through solution electrical conductivities, are qualitatively in agreement with the trends observed with respect to soluble selenium. Changes in salinity profiles are also indicated from the EC data from water-extractions of yearly soil samples at site P5F, as shown in Figure 2.25b. Increased salinization from evapotranspirative flow of salts into the fill is indicated from the data. Again, the data from P7F must be regarded as less conclusive. An estimate of the rate of evapotranspirative movement of seleniferous soil solutions into the fill material was not attempted. Estimation of evapotranspirative fluxes across the fill-soil interface based upon changes in the selenium content and salinity of the fill are complicated by the fact that the gradients in these solutes within the original soil surface are extremely large.

2.4. Pond 6 Excavated Test Plots

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The 1/2 and 1 foot deep excavations in Pond 6 (referred to as sites P6S6 and P6S12, respectively) have now been under study for nearly 4 years. The surface soils at these sites were removed (excavated) during May 1987. The P6S6 plot remained devegetated during 1987 and 1988, then was allowed to revegetate (primarily with *Kochia scoparia*) since the early spring of 1989. The P6S12 plot has been maintained in a relatively devegetated condition throughout this study. The original purpose of these plots, along with other excavated sites in Ponds 9, 10 and 11, was for observing the effects of the proposed Onsite Disposal Plan on the residual soil environment. More recently, these sites are serving to provide additional information on time trends for selenium, salinity, and other constituents in soil profiles. A summary of such trends in the 1/2 and 1 foot excavation plots at Pond 6 is presented here.

Time trends for soil solution selenium concentrations at sites P6S6 and P6S12 are presented in Figures 2.27a and 2.28a. Considerable variation in depth distributions of soluble selenium have been observed in the P6S6 site (Figure 2.27a). Oxidation and evapotranspirative concentration of selenium appears to have taken place within the upper portion of the profile. The fluctuations in soluble selenium concentrations obtained at intermediate depths (0.46 and 0.61 m) may reflect fluctuations in redox conditions. The profiles of soil solution selenium concentrations obtained in the P6S12 site exhibit a somewhat systematic trend, becoming generally more concentrated with time. Again, both selenium oxidation and evaporative concentration appear to explain the general pattern.

Time trends in soil solution salinities (as indicated through electrical conductivities) at the P6S6 and P6S12 sites are shown in Figures 2.27b and 2.28b. Significant, systematic increases in

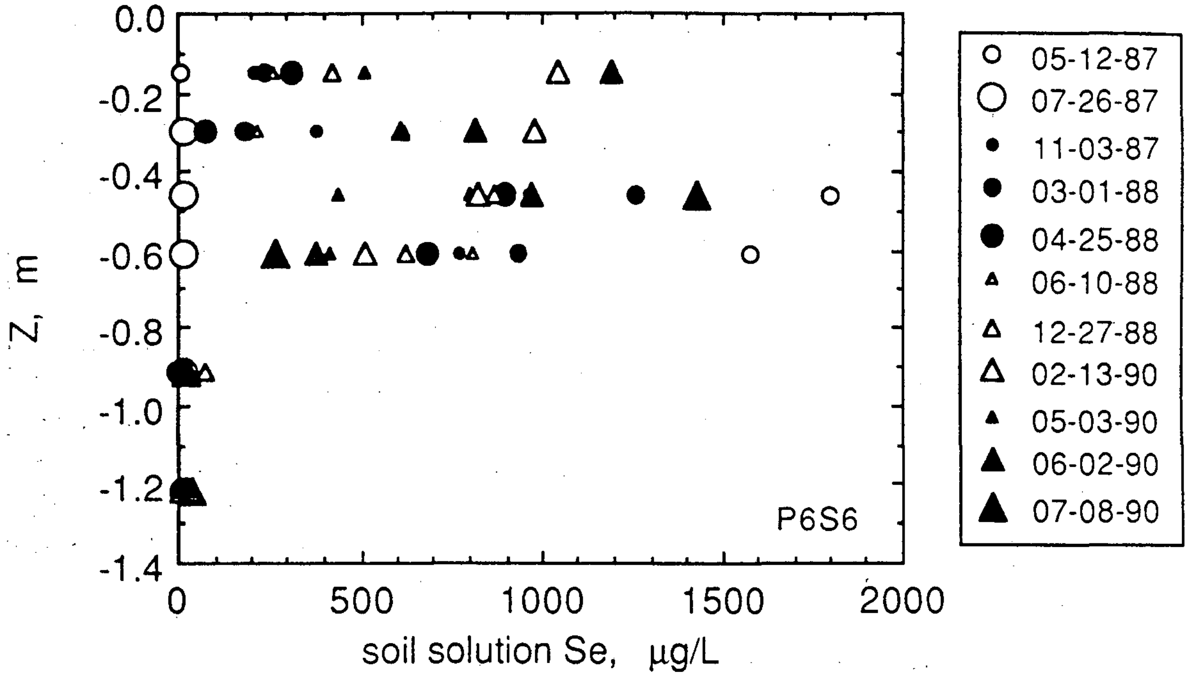

Figure 2.27a. Revegetated Pond 6 test plot excavated to 0.15 m deep, soil solution selenium profiles.

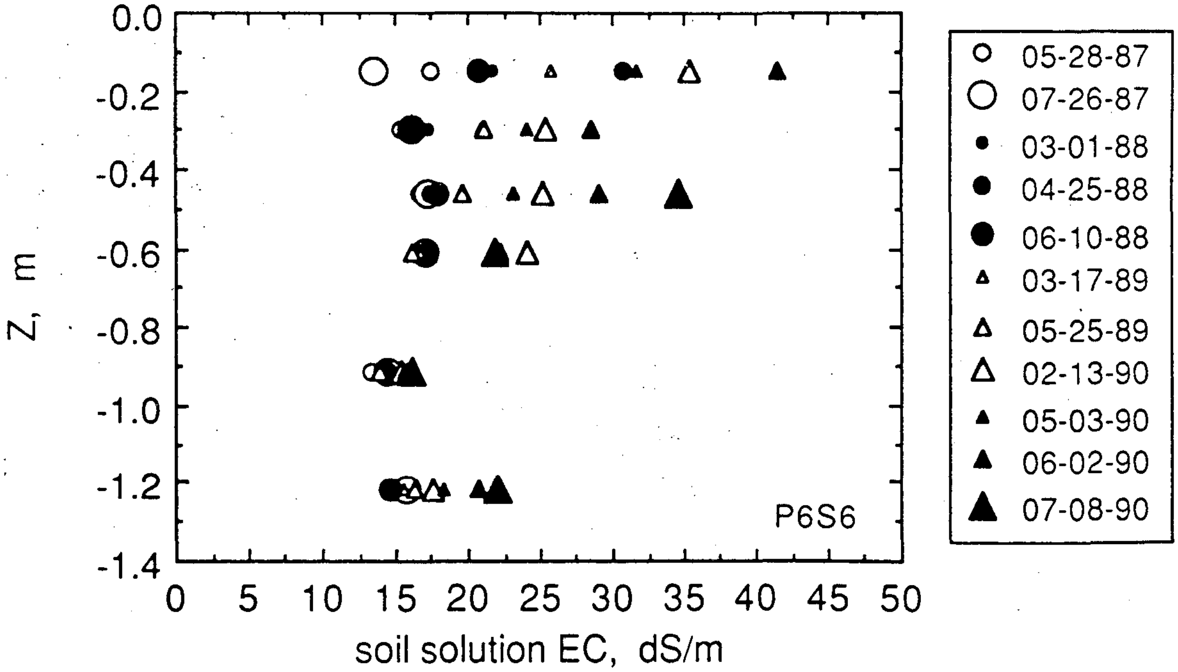

Figure 2.27b. Revegetated Pond 6 test plot excavated to 0.15 m deep, soil solution electrical conductivity profiles.

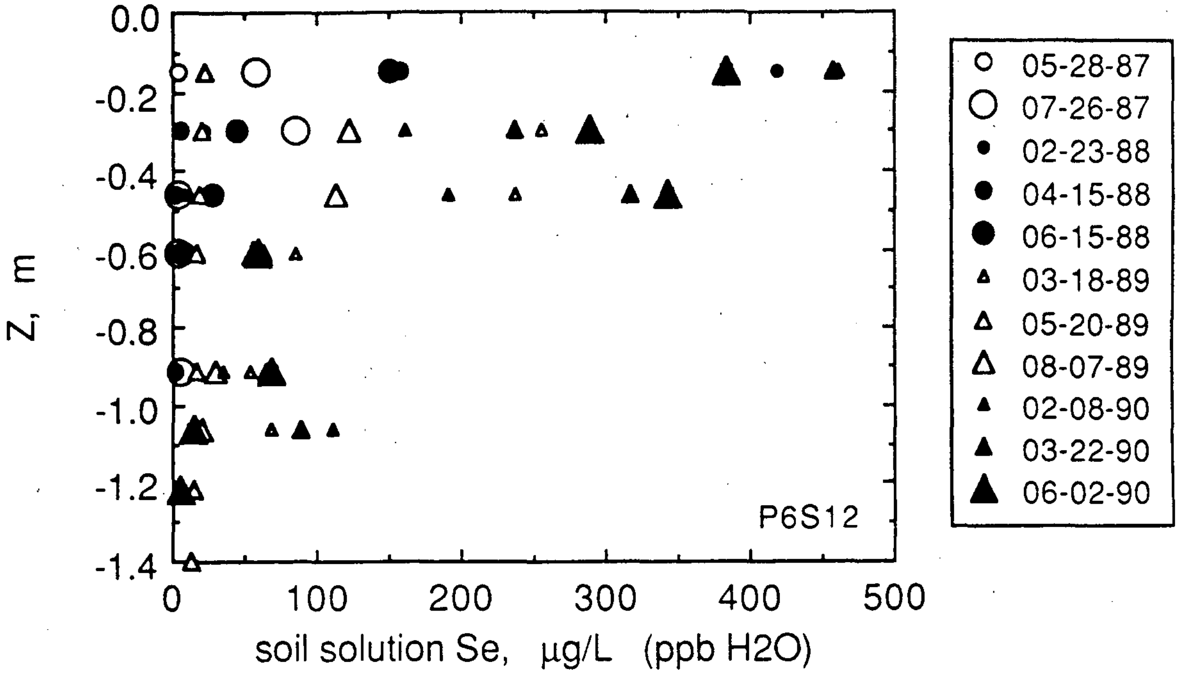

Figure 2.28a. Unvegetated Pond 6 test plot excavated to 0.30 m deep, soil solution selenium profiles.

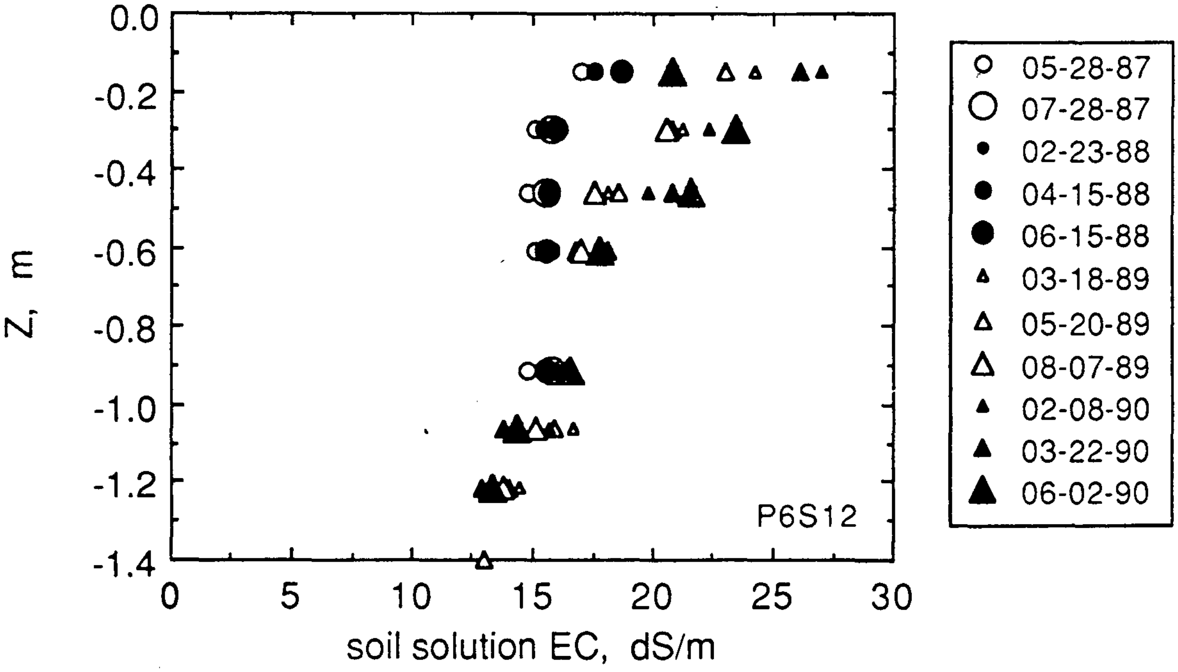

Figure 2.28b. Unvegetated Pond 6 test plot excavated to 0.30 m deep, soil solution electrical conductivities

salinity of these profiles are illustrated in the electrical conductivity (EC) data. The EC data obtained during 1987 are indicative of the salinities observed in drain waters ponded at the Reservoir during its operation. Increases in EC values in the devegetated site P6S12 reflect evaporative concentration, whereas in the revegetated site P6S6 both evaporation and transpiration contribute to increased salinization. The greater increases in EC values in site P6S6 (relative to those observed in the adjacent site P6S12) appear to result from the additional net upwards water movement associated with the invading *Kochia scoparia*. From considerations of changes in soil solution EC and chloride concentrations from 1987 through 1990, average net evapotranspiration rates of 0.10 and 0.05 m y^{-1} (in net excess of annual rainfall) are estimated for sites P6S6 and P6S12 respectively.

2.5. Fractionation of Selenium in Kesterson Soils

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As a result of the processes leading to accumulation of selenium in surface soils and subsequent processes leading to selenium redistribution, selenium is present in a variety of dissolved and solid forms in the Kesterson soils. The distribution of selenium between these various forms controls its mobility, its rate of volatilization, toxicity to wildlife and availability for plant uptake. Changes in distribution will affect the future impacts of selenium on the wildlife community supported by these lands. Over this past year we applied several sequential extraction methods in an attempt to identify and quantify the dominant forms of selenium in Kesterson soils. Conventional sequential extraction techniques commonly employed for trace metal fractionation in soils and sediments (Tessier, 1979; Chao, 1984) are inappropriate for elements like selenium that can be released from a solid phase and readsorbed by undissolved surfaces during a particular extraction, and which can undergo oxidation state changes in others (Gruebel et al., 1989). As a result, a sequential extraction procedure developed by Lipton (1990) for specifically fractionating soil selenium in arid, alkaline soils was used in this study. This section describes the methods used for sequential extraction and one of the soil profiles to which it was applied. Section (2.7) describes the remainder of the fractionation studies and implications thereof.

2.5.1. Soil Description

Soil samples used for selenium extraction studies were obtained by hand augering at 0.10 m intervals down to 1.70 m below the soil surface. Physical characterization of the soils included particle-size analyses, identification of evaporite and clay minerals, and measurements of hydraulic conductivities. The soils in the Pond 11 test area, which are described here, were relatively homogeneous with respect to physical, and many chemical, characteristics when compared with other Kesterson sites. Clay and silt contents throughout the profile were in the range of 23±4% and 24±5% respectively (sandy loam to sandy clay loam U. S. D. A. textures). Field-saturated hydraulic conductivities ranged from 2×10^{-8} to 6×10^{-7} m/s in 15 replicated measurements within the upper 1.3 m of the site. Gypsum and calcite are distributed over the upper 1.2 m of the profile (Flexser, 1988). The site is very saline, with all soil solutions and the shallow groundwater characterized by electrical conductivities exceeding 14 dS/m, sodium absorption ratios (SAR) exceeding 30, and slightly alkaline pH. Roots of *Distichlis, Cressa,* and *Frankenia* permeate the upper 1.0 m of the soil. A distinct surface salt crust was absent at the Pond 11 site, unlike more frequently ponded areas of the Reservoir.

2.5.2. Extraction Procedure

Soils were air-dried and ground to pass through a 0.5 mm sieve for the sequential extraction. A soil:solution ratio of 1:10 (2.5 g/25 m/l) was used for all extractions except for the NaOCl boil, used to remove soil organic matter (SOM), which employed a 1:4 ratio. Supernatant solutions were collected by centrifugation (20,000 × g, 10 min) and the soil residue was rinsed with 0.25 mol/l KCl after each step. The rinses were combined with the preceding extraction, filtered (0.45 μm), and analyzed for selenium (by HGAAS) and other elements (by inductively coupled plasma spectrometry) within 2 weeks of collection.

Table 2.1 lists the fractions of selenium that were isolated, in the order extracted. It must be emphasized clearly that the names applied to the isolated selenium fractions represent the best estimates of the pools of selenium that would be removed by the respective extractant and do not imply perfect selectivity. For example, selenium associated with the SOM (SOM-Se) may include various forms of selenium that can be intimately associated with SOM; organic selenium, elemental selenium and adsorbed Se(IV) that may be protected from being released into the preceding extractions by a ''protective'' coating of SOM. Organic selenium removed by phosphate extractants was determined using the hydrophobic XAD-8 resin and subtracted from the total selenium measured in the adsorbed and carbonate pools, and added to the SOM-Se pool as described by Lipton (1991). For a more detailed and critical discussion of the sequential

Table 2.1. Methods used to extract soil Se fractions. Fractions are listed in the order extracted.

Fraction	Extraction Method	Name
Soluble	0.25 mol/l KCl (2 h) (Fujii et al., 1988)	(KCl)
Adsorbed	0.1 mol/l K_2HPO_4 (pH 8, 20 h)	(P8)
Carbonate	1 mol/l Na-acetate (pH 5, 1 + 4 h) followed by 0.1 mol/l K_2HPO_4	(OAc/P8)
Soil Organic Matter (SOM)	NaOCl (pH 9.5, 0.5 h boil, repeated once) (Anderson, 1963)	(NaOCl)
Easily Reducible Oxides	0.1 mol/l NH_2OH (pH 2, 0.5 h) followed by 0.1 mol/l KOH (20 h)	
Amorphous Oxides (Am-Ox)	0.25 mol/l NH_2OH/HCl (0.5 h @50°C) followed by 0.1 mol/l KOH (20 h)	
Crystalline Oxides (Cryst-Ox)	4 mol/l HCl (0.5 h boil) (Chao and Sanzalone, 1989)	
Amorphous Aluminosilicates (Alk-sol Al/Si)	0.5 mol/l NaOH (0.2 h boil) conducted following SOM, Am-Ox, and Cryst-Ox extractions	

extraction procedure and the associations of soil selenium with the isolated fractions, the readers are referred to the above paper.

2.5.3. Distribution of Soil Selenium Fractions in Pond 11 Soil

The distribution of selenium in soil fractions at the surface (0 to 0.1 m) of the P11C site, according to the sequential extraction procedure described earlier, is presented in Table 2.2. Important elements (Ca, Mg, Al, Fe, Mn, Si, and S) that were released with each extraction are also presented in Table 2.2 so that the selectivity of each fraction can be evaluated.

The selenium extracted by KCl (soluble selenium) was found to be comprised of 77% Se(VI) and 23% Se(IV), consistent with the higher solubility of the former and the greater tendency for adsorption of the latter. The large amounts of KCl-extracted Ca and S (virtually all SO_4^{2-}) indicate the dissolution of evaporite minerals such as gypsum. Other Kesterson soils that have extensive salt crusts have been found to contain KCl-extractable selenium at levels greater than 7 mg kg/l soil, and Se(VI) and Se(IV) at about the same relative concentrations as reported above for site P11C. The potential for precipitating gypsum to remove Se(VI) and Se(IV) from solution by occlusion and/or coprecipitation reactions is suggested from results of laboratory investigations (D. Suarez, U.S. Salinity Laboratory, U. S. D. A. - A. R. S., Riverside, CA, personal communication; LBL 1990).

The P8-extracted selenium pool (designated as adsorbed selenium) was comprised predominantly of Se(IV) (65%), which reflects the greater tendency of Se(IV) to be adsorbed by charged surfaces. The negligible amounts of S in the P8 extract indicates that the preceding KCl extraction was effective in removing most of the soluble sulfate salts. The large amount of Se(VI) observed in the adsorbed pool was surprising given that it is not strongly sorbed by alkaline soils (Neal and Sposito, 1989), and that, according to the small quantity of S in the P8 extract, a minor amount of evaporite salts were dissolved. The source of the P8-extracted Se(VI) is currently being investigated.

In the following OAc/P8 extraction to remove selenium associated with carbonates (P8 was

Table 2.2. Total Se, Se(IV), and some important elements removed by the sequential extraction of site P11C (0 to 0.1 m).

Soil Fractions Extractant(s)	Se_T	Se(IV)	Ca	Mg	Al	Fe	Mn	Si	S
	µg/kg*					mg/kg*			
Soluble:									
KCl	298	68	3,738	621.7	3.6	<0.5	<0.5	31.8	1,778
Adsorbed:									
P8	417	269	100.9	28.8	<0.5	1.9	<0.5	63.8	22.5
Carbonate:									
OAc	124	80	1,763	68.9	12.7	0.8	4.1	99.4	37.8
P8	104	58	1.0	<0.5	4.4	5.3	<0.5	61.0	<0.5
SOM:									
NaOCl	4,341	NA	41.3	19.8	5.2	<0.5	<0.5	61.1	31.7
ER-Oxide:									
NH_2OH/HCl	<4	NA	29.4	38.2	77.0	156.0	1.7	168.4	NA
KOH	8	NA	<0.5	<0.5	52.8	<2.0	<0.5	510.9	NA
Am-Oxide:									
NH_2OH	14	NA	110.4	331.9	980.7	1,059	7.0	951.7	NA
KOH	10	NA	<0.5	<0.5	10.0	<0.5	<0.5	1,749	NA
Cryst-Oxide:									
HCl	5	NA	477.3	4,069	10,049	18,476	111.8	924.4	NA
Alk-sol Al/Si:									
NaOH-1	38	NA	<0.5	3.5	342.4	11.0	<0.5	1,972	NA
NaOH-2	<4	NA	<0.5	<0.5	203.8	6.0	<0.5	1,007	NA
NaOH-3	<4	NA	<0.5	<0.5	143.6	13.9	<0.5	28,623	NA

*kg of air-dried soil.

Data are means of duplicate samples with relative percent differences usually < 10% and always < 30%.

NA: not analyzed.

used to remove Se(IV) that readsorbs significantly at pH 5 during OAc extraction), the relative proportion of Se(IV) and Se(VI) was found to be similar to that reported for the adsorbed pool. Evidence for the removal of Se(IV) and, to a lesser degree, Se(VI) from solutions in which calcite is precipitating has been observed in laboratory investigations (Lipton, 1991; Suarez, personal communication). The substantial amount of Se(VI) in the carbonate fraction of the P11C soil was unlike that reported for 2 irrigated Western San Joaquin Valley agricultural soils by Lipton (1991) in which Se(IV) accounted for virtually the entire carbonate selenium pool. This disparity is possibly a result of the higher Se(VI) content of the drainage waters that entered into Kesterson (≈300 μg/L), relative to the concentrations of Se(VI) in surface soils of irrigated agricultural fields. With depth, in the P11C soil profile, the proportion of carbonate--associated Se(VI) decreased to levels that more closely approached that observed in the surface soils of the agricultural fields.

Clearly, the largest amount of soil selenium, more than 4 mg kg/l soil, was extracted by NaOCl. The ability of this SOM extractant to minimize the dissolution of hydroxides and aluminosilicates while oxidizing organic C (>95% removed) is reflected in the small levels of NaOCl-extractable Fe, Al, Mn, and Si, especially when the amounts are compared to that removed by the subsequent extractions (Table 2.2). The pool of selenium solubilized by NaOCl, as described in section 2.2, is considered to include forms of selenium that are closely associated with the SOM (SOM-Se); organic selenium, Se(IV) "protected" by a coating of SOM, and elemental selenium whose production depends on the microbial respiration of organic compounds (Doran, 1982). A more detailed description of SOM-Se in Kesterson sediments, using a combination of methods developed by Weres et al. (1990) and Lipton (1991), will be presented in a future paper.

The selenium associated with refractory inorganic soil constituents (ER-Ox + Am-Ox + Cryst-Ox + Alk-sol Al/Si) was found to comprise an insignificant proportion of the total soil selenium (<2%). (The recovery of total soil selenium from the surface soil by the sequential extraction procedure was 95.0% for the 0 to 0.1 m depth, and was generally 90% to 110% for all other depths.) Trivial amounts of selenium in the refractory inorganic soil constituents were also observed throughout the rest of the profile. It can be concluded from the sequential extraction procedure, therefore, that virtually all of the soil selenium inventory was accounted for in the soluble, adsorbed, carbonate, and SOM fractions. This observation was distinct from investigations of surface California agricultural soils in which refractory inorganic pools (hydroxides and amorphous aluminosilicates) have been reported to play a prominent role in the retention of soil selenium (Chao and Sanzalone, 1989; Lipton, 1991). This disparity is probably a consequence of the forms of the selenium source, rather than any physicochemical differences between the Kesterson soils and the agricultural soils, as the majority of the selenium was introduced to the former via drainage waters in its most mobile form, Se(VI), while selenium in the latter was derived from refractory selenium-bearing sulfidic minerals originating from marine sediments. It is conceivable that over time some of the selenium in the Reservoir soils may be incorporated into refractory inorganic soil constituents although this possibility is not likely to play an important role in the mitigation of selenium pollution in the short term. The kinetics of selenium transformations in soils, however, have not been elucidated for the wide range of expected conditions at the Reservoir.

The depth distribution of the major selenium fractions at site P11C is illustrated in Figure 2.29. Total extractable selenium is presented along with soluble, soluble + adsorbed, soluble + adsorbed + carbonate, and SOM pools of selenium so that the relative importance of the soil fractions can be visualized throughout the profile. The general decrease in the quantities of selenium with depth reflects the practice by which selenium was introduced into this site, i.e. from surface applications of drainage waters, and the capacity of the Kesterson soil environment to immobilize large amounts of selenium, notably in the SOM. In the top 0.2 m, more than 70% of the total selenium inventory was observed to be associated with the SOM fraction, highlighting the importance of the SOM in the biogeochemistry of selenium. The relative significance of SOM-Se at about 0.5 m depth, however, declined markedly (to about 20%) as the soluble and adsorbed pools of selenium increased proportionally. Interestingly, this trend was reversed deeper in the profile (0.7 to 1.0 m) as selenium in the soluble and adsorbed pools were found in small amounts

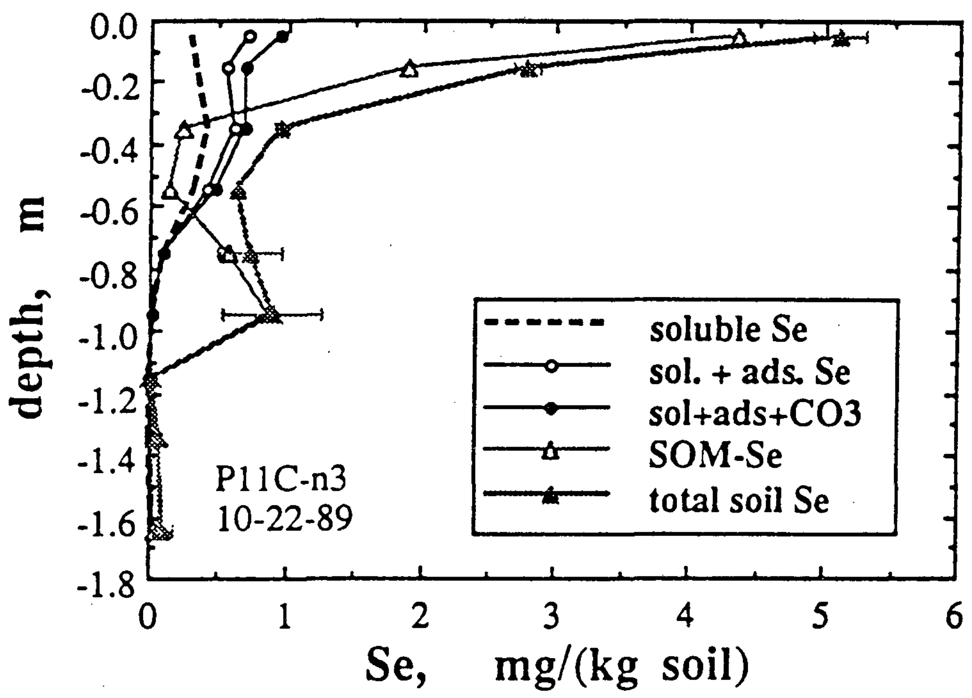

Figure 2.29. Depth profile of soil-Se concentrations at the P11 study site.

while SOM-Se was observed to reach a second maximum of almost 1.0 mg kg/l soil. This portion of the profile corresponds to the region influenced by the annual maximum height of the water table. Preliminary investigations, using a combination of methods developed by Weres et al. (1989) and Lipton (1990), have indicated that the SOM-Se at the 0.7 to 1.0 m depth was largely elemental selenium while at the surface it was primarily organic selenium and SOM-associated Se(IV) (data to be presented in a future paper). This apparent increase in the percentage of elemental selenium (relative to the total selenium inventory) with depth concurs with investigations of other Reservoir soils profiles (Weres et al., 1989), and may have resulted from reducing conditions at the fluctuating water table.

The presence of selenium in soluble, adsorbed, carbonate, and SOM fractions, and its relative absence in refractory inorganic soil constituents, reflects the manner by which selenium entered the Kesterson Reservoir environment. Their potential lability under common cultural and pedogenic processes (e.g. oxidation of SOM by tillage and drying, dissolution of carbonates and other evaporite minerals by acidification from plant roots and fertilizers, and displacement of adsorbed selenium by phosphate fertilizers), suggests that the distribution of selenium within Reservoir soils will change over time. Although, as indicated by the monitoring activities described in Sections 2.1 and 2.2, these changes are slow. As discussed in the following section, the complexity of this soil system, with its competing processes of volatilization, microbial reduction, oxidation, accompanied by seasonal transport of selenium within the soil profile, make this an extremely difficult environment for predicting long term evolution of the selenium inventory.

2.6. Multiple Extractions of Surface Salt Crust and Soil for the Determination of Selenium Associations

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In order to improve the understanding of the future distribution of selenium in Kesterson soils, past and current research has often focused on the speciation and association of selenium in the soil profile. In the recent past, sequential extractions of soils have used deionized water or KCl solution washing of the soil in order to remove readily soluble and/or dissolved selenium, although the interpretation of these results is often debated (LBL, 1990; Tokunaga and others, 1991). Following this extraction, a sodium or potassium phosphate solution of varying molarity has been used to liberate selenite ligand exchange of phosphate for Se(IV) is assumed to be the mechanism responsible (e.g. Lipton, 1990; LBL, 1990; Neal and others, 1987). Any number of extractions have followed, depending on the desired selenium fraction to be extracted. It has been suspected, however, that highly saline soils may require more than a single water or KCl solution wash in order to dissolve all precipitated salts, especially those with moderate to low solubilities, e.g. gypsum ($CaSO_4 \cdot 2H_2O$) and calcite ($CaCO_3$). While the nature of this association is not yet clear, selenium has been found to be associated with precipitated salts (e.g. Goldberg and Glaubig, 1988; Tanji, 1990).

In this study, the top 20 cm of Pond 9 soil (plot 9BE) was repeatedly extracted with deionized water and at different stages extracted with Na_2HPO_4. Each of the four soil intervals (0-2 cm, 2-4.5 cm, 4.5-9.5 cm, 10-20 cm) was washed with deionized water (1:10 soil:water, 2 hours on a reciprocating shaker table), centrifuged, the supernatent solution removed, and more water at a 1:10 ratio was added to the soil; this procedure was repeated until the total dissolved solids were significantly and consistently below the solubility of gypsum (as judged by measurements of electrical conductivity (EC)). [A duplicate sample was extracted each time with a calcite-saturated solution in order to suppress the dissolution of soil calcite. This apparently had little effect, probably due to the variability of calcite solubility with pH, ionic strength, and temperature. Most of the apparent calcite concentrations in extracted solutions were above calcite ''solubility.''] When EC came to an apparent steady state, the soil was extracted with 1mM Na_2HPO_4 (1:20 soil:solution, 24 hours on a reciprocating shaker table). selenium liberated in this extraction is usually considered to come from an adsorbed phase. In addition, sub-samples of the same soil were extracted with 1mM Na_2HPO_4 after a varying number of water extractions. This was done in order to determine how much of the selenium liberated during the water washes was coming out of the ''adsorbed pool.'' During any extended periods between extractions, the soil samples were refrigerated. However, during the many hours of actual extractions and centrifugation (as many as 72 hours), the soil was not refrigerated, thereby potentially allowing for aerobic biological activity which may have some effect on selenium distribution. selenium was analyzed for using atomic absorption spectroscopy (AAS); chloride was analyzed using Mohr titration; all other major ions were analyzed via inductively coupled plasma spectrophotometry (ICP), except bicarbonate (HCO_3^-) which was calculated by difference.

The results of selected extractions are contained in Figures 2.30 through 2.37. Most of the following discussion focuses on the 0 to 2 cm soil interval which includes a salt crust. The following data will demonstrate the strong influence of salt crust dissolution. As expected, selenate (Se(VI)) concentrations were very high in the first water extract (4.3 ppm relative to soil mass) and then dropped off dramatically to between 0.6 and 0.7 ppm in the second extraction. In all the following extractions, selenate concentrations remained below 0.5 ppm (see Figure 2.30). This trend may be explained by selenate's high solubility: most was flushed out in the first wash. Nonetheless, a significant amount (2.8 ppm) of selenate had seen extracted in the next nine water extractions, suggesting an association of Se(VI) with a salt or possibly Se(VI) adsorption. 0.4 ppm of selenate was extracted with the phosphate solution.

A different picture emerges from the selenite extraction data (see Figure 2.31). Se(IV) concentrations, at first in the 1.0 to 1.5 ppm range, gradually drop to around 0.5 ppm after the 6th

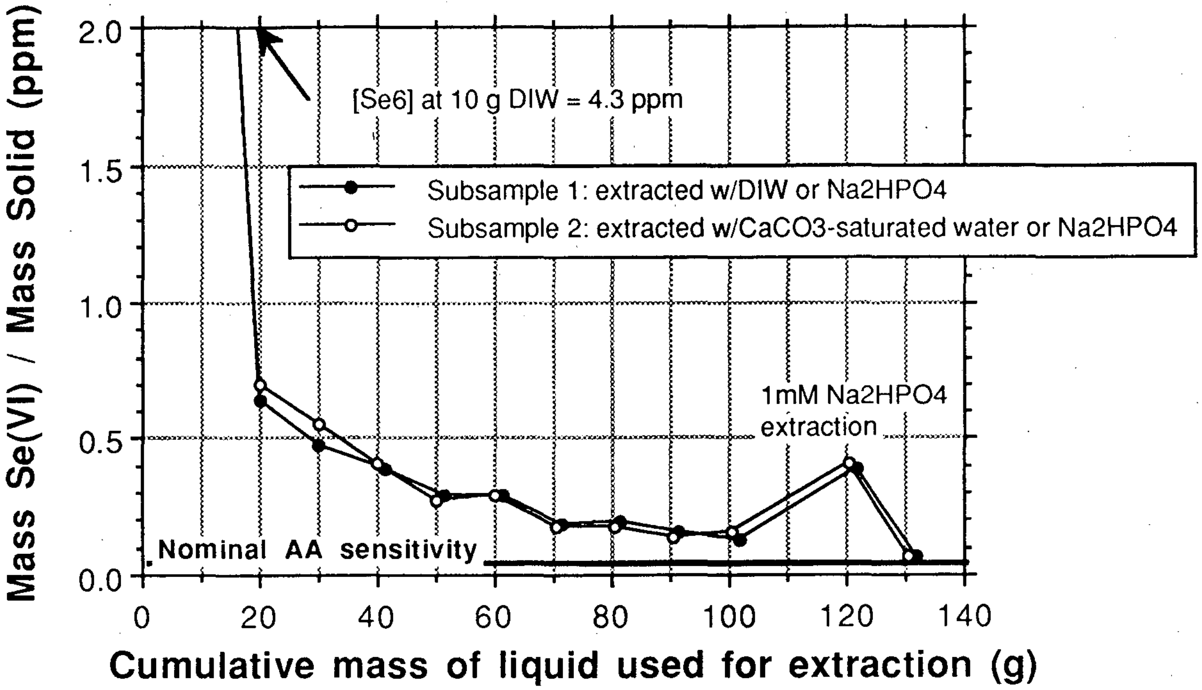

Figure 2.30. Sequential selenate extraction from a saline soil: P9BE, 0.000-0.020m depth interval.

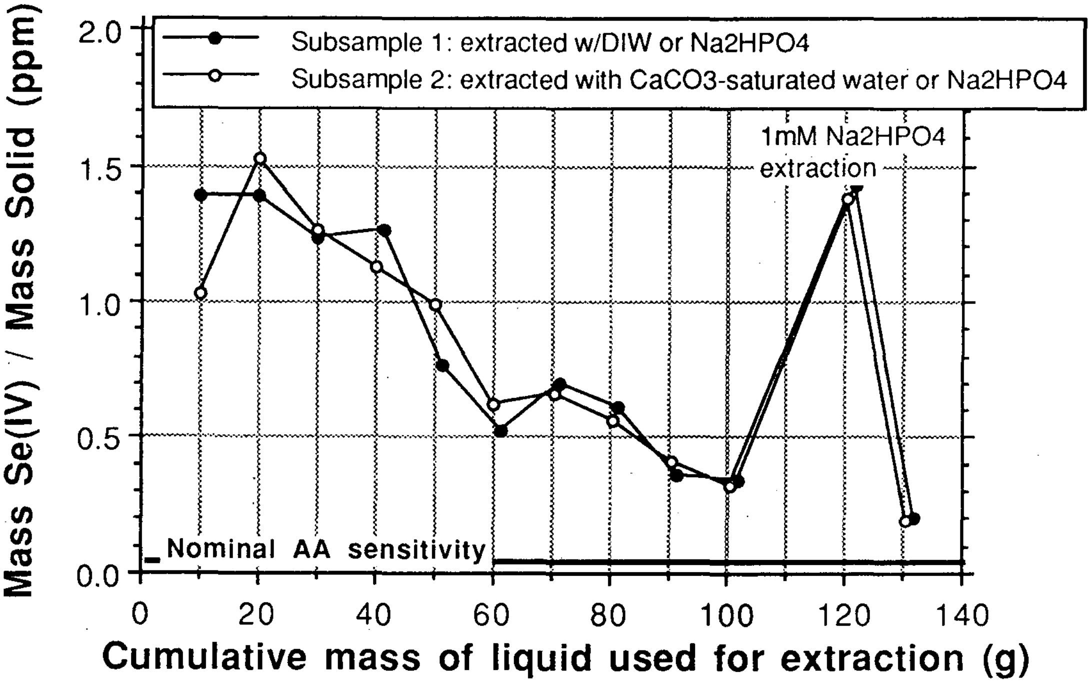

Figure 2.31. Sequential selenite extraction from a saline soil: P9BE, 0.000-0.020m depth interval.

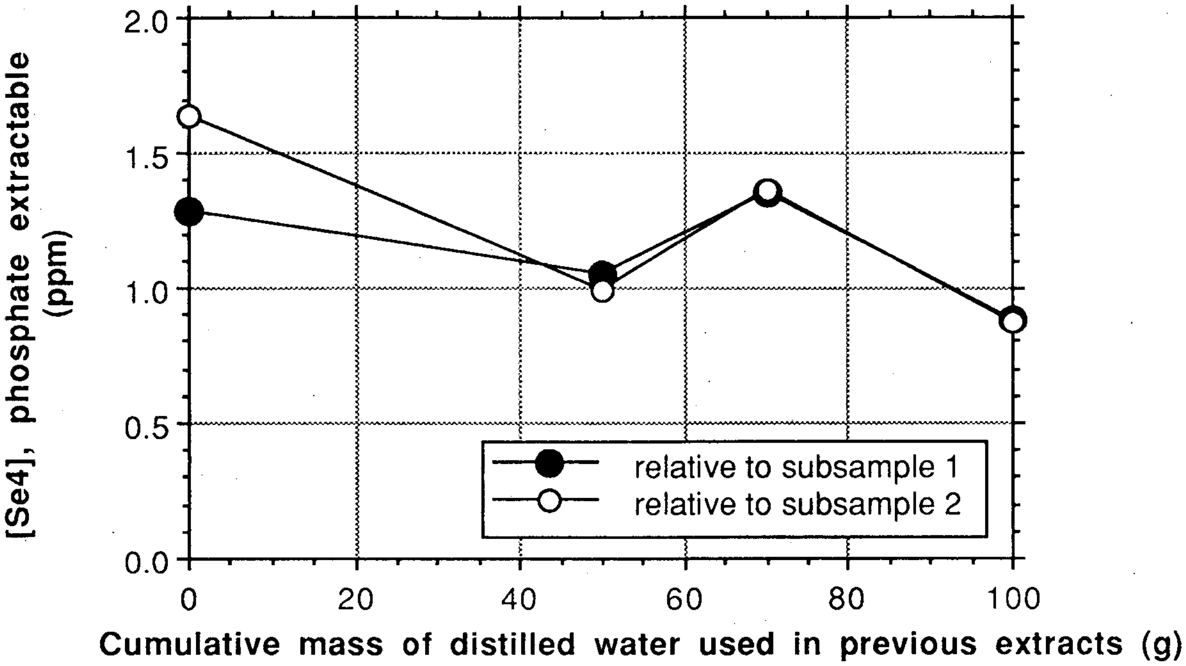

Figure 2.32. Phosphate-extractable selenite from 0-2 cm soil interval from P9BE, following given number of water extracts.

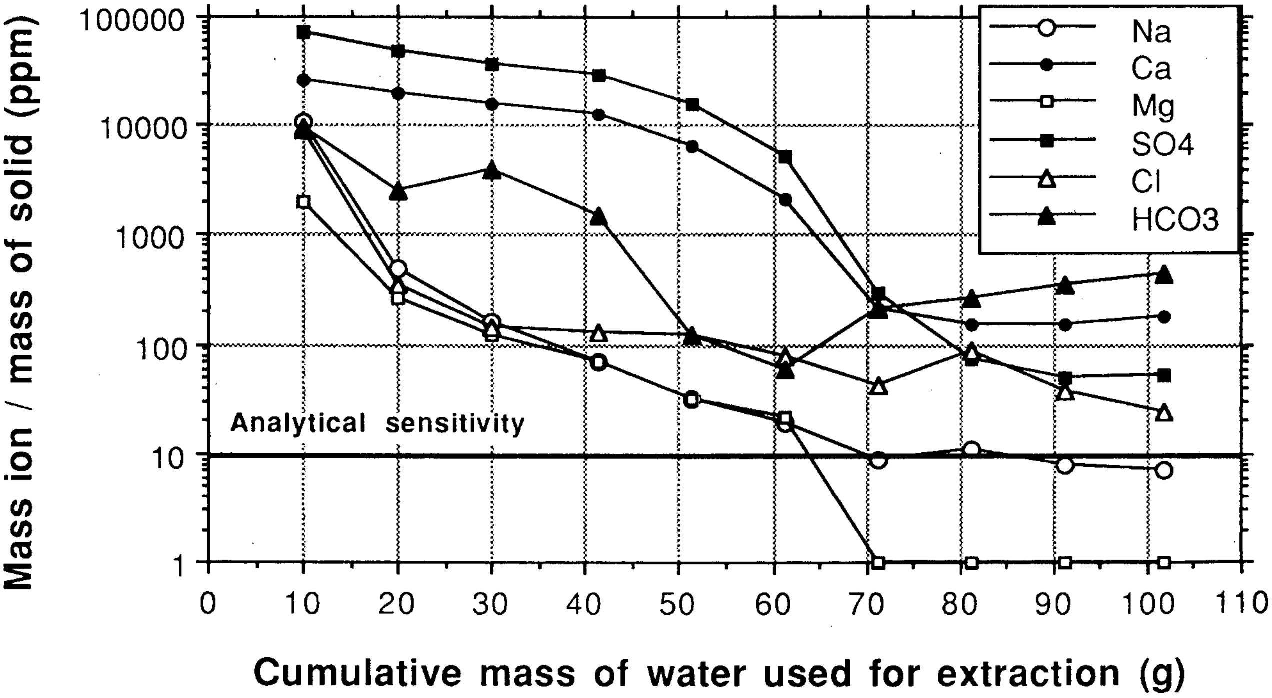

Figure 2.33. Sequential salt extraction from a saline soil: P9BE, 0-2 cm interval. HCO_3 calculated by difference.

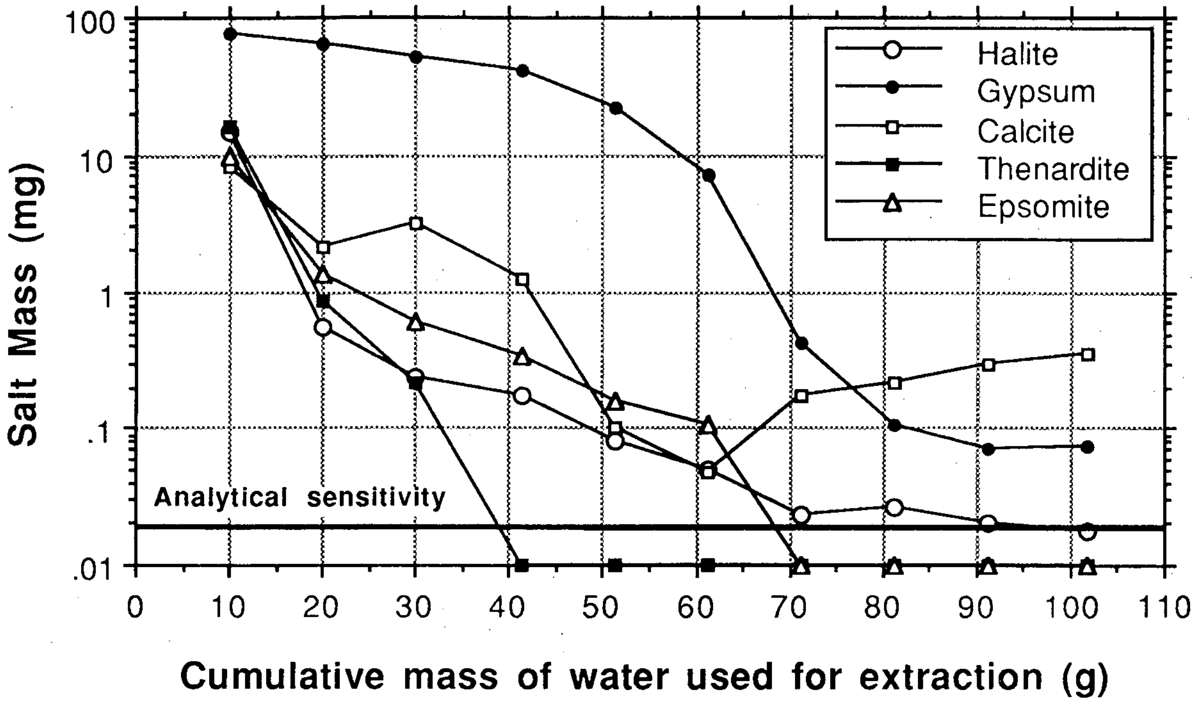

Figure 2.34. Sequential extraction from a saline soil: P9BE, 0-2 cm interval. Calculated salt masses extracted from 1 gram of soil by water washes.

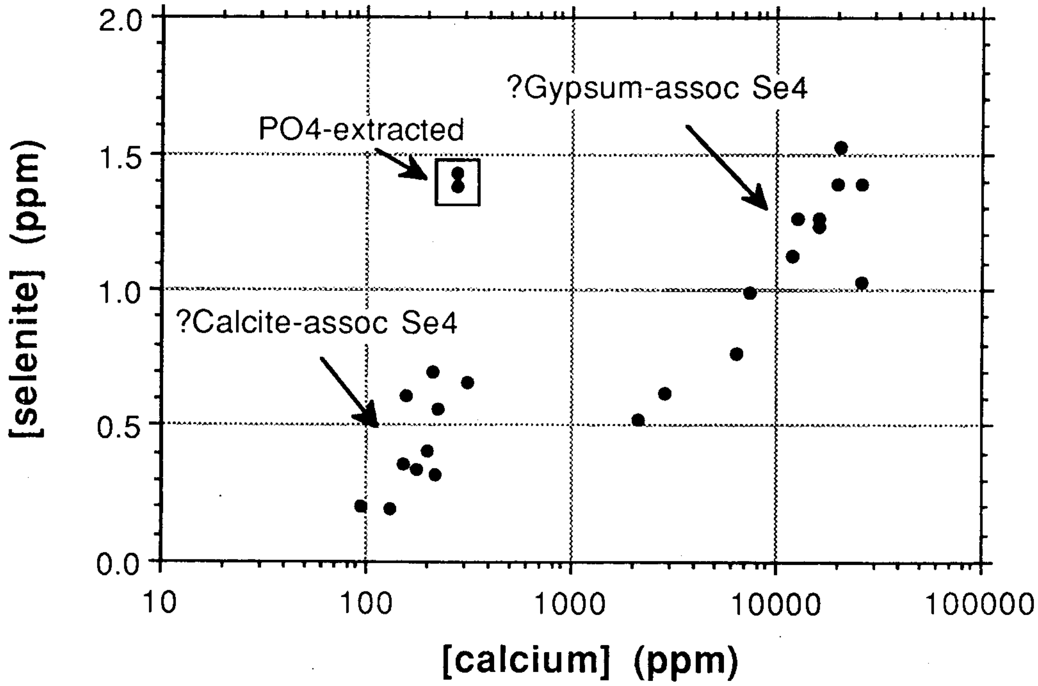

Figure 2.35. P9BE, 0-2 cm soil interval, results of sequential extractions.

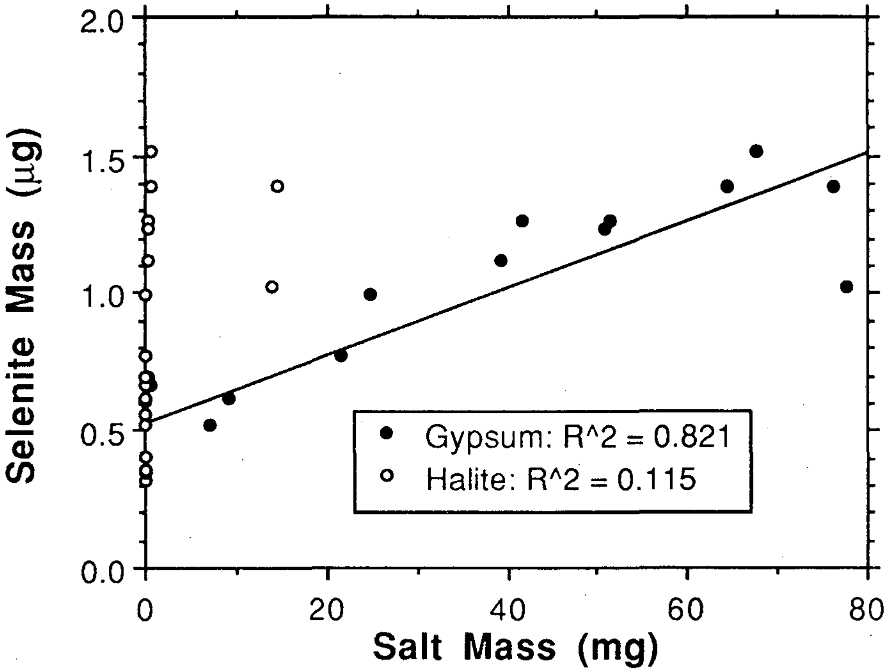

Figure 2.36. P9BE, 0-2 cm soil interval: mass of selenite vs. mass of gypsum and halite dissolved.

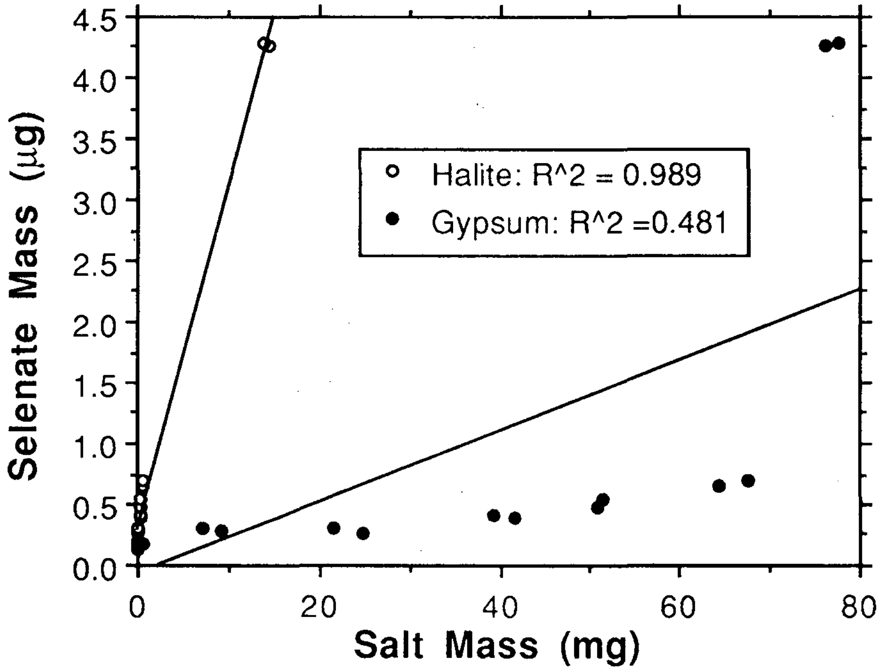

Figure 2.37. P9BE, 0-2 cm interval, mass of selenate vs. mass of halite and gypsum dissolved.

water extraction. 1.4 ppm of selenite was extracted by phosphate solution; this was expected as selenite has a tendency to strongly sorb onto oxide and clay surfaces. However, a total of 8.7 ppm selenite was liberated in the first 10 (water) extractions, suggesting a different selenite association. In order to determine whether some adsorbed selenite was being removed during the water washes, three phosphate extractions on other sub-samples of the same soil were made after 0, 5, and 7 water washes (see Figure 2.32). Water-extracted selenite concentrations were subtracted from the results of phosphate extractions in order to account only for non-water extractable selenite. These results suggest that the change in the amount of phosphate-extractable selenite is considerably too small to account for the 8.7 ppm of selenite liberated during the first 10 water extractions.

Major ion data shed some light on the possible selenium associations in this soil. Figure 2.33 shows concentrations of major ions relative to soil mass as a function of the water mass used for extraction. Clearly, calcium and sulfate are the dominant ions until after the 7th extraction when calcium and bicarbonate dominate. It needs to be noted that concentrations of calcium in the first five water extracts exceeded calcium solubility with respect to gypsum, as much as five-fold; this has not yet been explained.

Based on the data from this study and other efforts (e.g. LBL, 1990), a set of likely major salts was selected. These, in decreasing order of their solubilities, are: halite (NaCl), thenardite (Na_2SO_4), epsomite ($MgSO_4 \cdot 7H_2O$), gypsum, and calcite. All but epsomite have been positively identified in Kesterson salt crusts, but epsomite is the most likely magnesium evaporite, (Bresler et al., 1982). Magnesite ($MgCO_3$) may also be present but since most of the Mg was flushed from the soil in the early extraction and magnesite has a relatively low solubility magnesite is not a major salt in this system. The data of Figure 2.33 was used to calculate masses of salts washed out during each extraction, based on their respective solubilities, in the following way: chloride was balanced with sodium (to form halite); any leftover sodium was balanced with sulfate (to form thenardite); any leftover sulfate was balanced with magnesium (to form epsomite); any further leftover sulfate was balanced with calcium (to form gypsum); any leftover calcium was considered to have come from calcite. Such a calculation required several assumptions to be made, e.g., all chloride was considered to have come from halite, none of the phases were occluded within other phases, and only the listed solid phases were present. The results are presented in Figure 2.34. As expected, gypsum is the dominant salt being dissolved in each extraction until the 7th extraction, after which calcite dominates. There appears to be a positive correlation between calcium and selenite concentrations. Figure 2.35 shows an apparent separation between selenite association with gypsum and calcite. Whether selenite is associated with gypsum or calcite is simply inferred from when a given phase is dominant. In general, as shown by both Figures 2.35 and 2.36, selenite concentrations are strongly correlated with gypsum concentrations when [Ca]>300 ppm (relative to soil mass) or so [$R^2 = 0.821$], while not being correlated with the more soluble salts (here halite is used as an example, though a similar correlation coefficient [$R^2 \approx 0.1$] was found for thenardite and epsomite). As shown in Figure 2.37, selenate concentrations are strongly correlated with halite (and thenardite and epsomite) [$R^2 \approx 0.99$] and weakly correlated with gypsum [$R^2 = 0.481$]. Based on data in Figure 2.36, the selenite to gypsum ratio is around 0.0125 µg/mg or 12.5 ppm. Selenate associations with the more soluble salts are indicative of most of the selenate being readily removed with a single water wash. Similar correlations were found for the other three depth intervals in this short profile, with one very notable exception: in all three intervals, calcium concentrations fell below gypsum saturation after the first or second extraction.

Several conclusions may be drawn from the above data and interpretations. First, this study confirms the need to consider whether all readily soluble salts have been flushed out of the soil before proceeding with other extractions which would be expected to liberate selenium from other pools (e.g. adsorbed, organic, etc.). Second, it appears that in salt crusts a substantial portion of the selenium inventory may be associated with the less soluble salts: gypsum and calcite. The nature of this association is not clear at this point. It is possible that selenium may coprecipitated with or occluded within these salts, or, as suggested by Goldberg and Glaubig (1988), adsorbed onto calcite. Third, washing a salt-encrusted soil with water, even repeatedly, removes very little of phosphate-extractable selenium. Fourth, the fact that even after several washings sodium, chloride, and magnesium salts were still present, albeit at small concentrations, suggests that these salts were occluded within less soluble salts and may be a source of selenate after as many as ten water extractions. Finally, all of the above conclusions apply to highly saline soils, most likely within centimeters of the soil surface, although many soil profiles in the Reservoir are gypsum and/or calcite saturated at depths of 1 m or more (e.g. Flexser, 1988). A more detailed analysis of this data along with data on selenium potentially associated with other constituents in this soil profile is forthcoming.

2.7. Discussion of Processes Affecting Long-Term Evolution of the Selenium Inventory at Kesterson Reservoir

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2.7.1. Impetus for Study

A long-term management strategy for Kesterson Reservoir must depend on chemical, physical and biological changes likely to occur in the soil system. Over the past four years, field and laboratory data have been collected on the distribution of selenium species at the Reservoir. These data describe the regime only within this narrow time frame and provide limited information about long-term changes in selenium concentrations, speciation, and distribution. Therefore, an attempt has been made to construct possible scenarios for the long-term evolution of the selenium inventory at Kesterson Reservoir by gathering available site-specific information and relevant references from the soil chemistry, soil microbiology, and geochemistry literature.

2.7.2. Brief Summary of Selenium Chemistry in the Vadose Zone of Kesterson Reservoir.

Before discussing potential changes in the selenium inventory, various pools of selenium need to be defined. The following major selenium species need to be considered:

- Selenate (Se^{+6}) - will occur mostly as a solute, although it will sorb very slightly and may precipitate or co-precipitate or be occluded with evaporites under extremely dry conditions ($HSeO_4^-$, SeO_4^{-2}).
- Selenite (Se^{+4}) - will occur mostly as species adsorbed onto oxides, organic matter and clays in the soil, although a significant fraction will be dissolved, and some may be associated with evaporites ($HSeO^{-3}$, SeO_3^{2-}).
- Elemental selenium (Se^0) - may be precipitated on mineral surfaces in an insoluble form; may occur in association with soil organic matter (SOM).

- Organic Se - will occur mostly within SOM, also may be found in the soil solution.

Therefore, the following pools of selenium in soils of the vadose zone may be defined:

- dissolved selenium (mostly selenate; also selenite and to a small degree organo-selenium compounds)
- adsorbed selenium (mostly selenite and to a lesser degree selenate)
- soil organic matter-associated selenium (SOM-Se) (the most ambiguous category, includes all selenium species which are either chemically or physically incorporated into SOM; these species include: elemental selenium (Se^0), organic Se ($Se^?$), selenite, and possibly selenate, possibly in that order of predominance; each specie could actually be chemically bound within SOM or could be physico-chemically associated, e.g. adsorbed Se^{+4}.)
- evaporite-associated selenium (mostly selenite and selenate, either occluded within or coprecipitated with such minerals as gypsum, calcite, thenardite, and halite)
- refractory pool [precipitated elemental Se; oxide-associated Se; aluminosilicate-associated Se]

It is currently believed that, at Kesterson Reservoir, the last two pools of selenium are minor compared with the first three, although evaporite-associated selenium may be significant in the salt crusts present at the soil surface (see Section 2.6 of this report). While selenium is likely to be found coprecipitated with salts, most of these will have very high solubilities; in the event of increased moisture content (e.g. due to rainfall), selenium in this pool will be liberated (see Section 2.2). The following paragraphs will outline available data on selenium speciation in the vadose zone at Kesterson Reservoir.

Most work in the past has been focused on the dissolved pool of selenium, for three reasons: (1) dissolved selenium is most accessible to biota, (2) dissolved selenium moves with soil water and therefore its vertical distribution changes on a short time scale, and (3) dissolved selenium is most easily and unambiguously detected and quantified. To a lesser extent, the adsorbed selenium pool has been investigated (LBL, 1990). Only in a few profiles has SOM-Se been studied; in these cases there is still much ambiguity as to the true nature of selenium species (see previous section; Tokunaga and others, 1991). Figures 2.38 through 2.42 show examples of selenium distributions in selected profiles; in Figure 2.42, possible distribution of SOM-Se and the more refractive pools are included. As is apparent from these figures, water-soluble, phosphate-extractable (approximates adsorbed pool), and SOM-Se dominate, with each one of these pools being predominant at different depths in various profiles.

Since the discontinuation of water deliveries to the Reservoir, soil profiles have been drying out and progressively more oxidized conditions exist in the vadose zone. Thermodynamically, such conditions would favor the existence of selenium as selenate, the most soluble and mobile form. Therefore, the soil system appears to be out of equilibrium with respect to selenium and further changes in selenium speciation should be expected to take place in the future. Furthermore, in the Fall of 1988 approximately 50% of the Reservoir was covered by non-native material which originated from the excavation of the nearby Delta-Mendota Canal. The addition of up to 1 meter of this material onto the top of the soil surface, put the system out of hydrological and chemical equilibrium, whereby upward movement of solutes into the fill material is expected to occur in the near future (data confirming this may be found in Section 2.3). Such physical redistribution will have an effect on physico-chemical processes controlling transformations of selenium in the soil system. These processes are described in the following section.

2.7.3. Past Research on Selenium Transformations

A conceptual representation of the likely Se cycle at Kesterson Reservoir is presented in Figure 2.43. (DMSE is dimethyl selenide, a product of biologically mediated volatilization.) These processes may be grouped as follows: (1) plant and fungal volatilization, (2) reduction and (3) oxidation (Se^0 + Se(IV) + Se(VI)), (4) adsorption (mostly selenite), (5) Se uptake by plants, (6) organic Se mineralization. While a detail description of each process at the most basic level is beyond the scope of this report, a brief review of research emphasizing the rates of selenium transformations is presented.

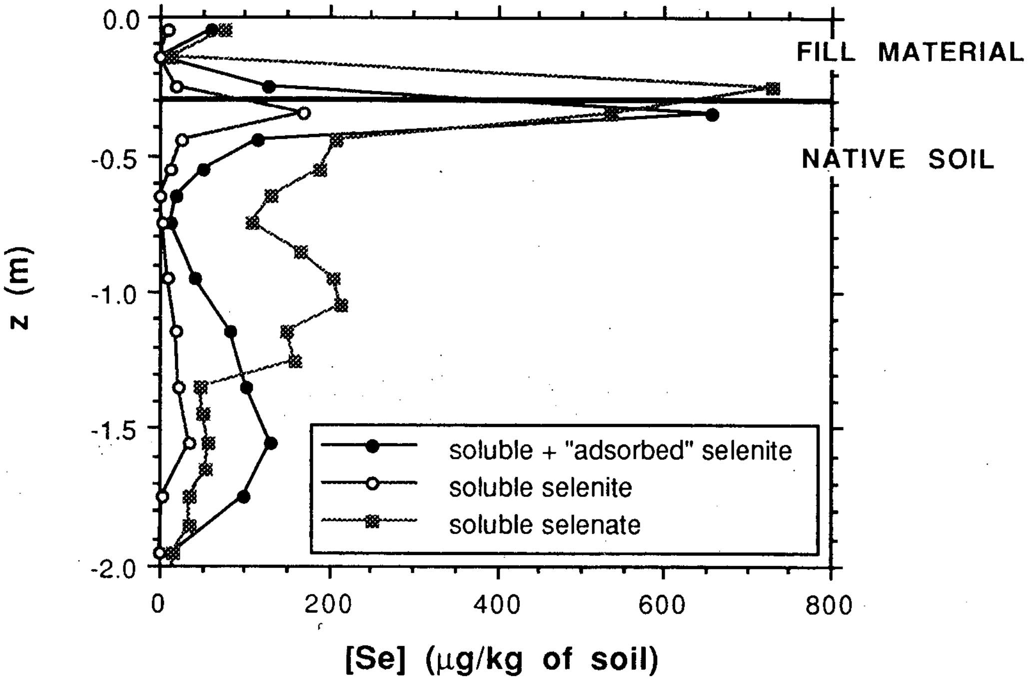

Figure 2.38. Soluble selenate and soluble and "adsorbed" (phosphate extractable) selenite concentrations in the soil profile of plot 7f (pond 7), 12/88.

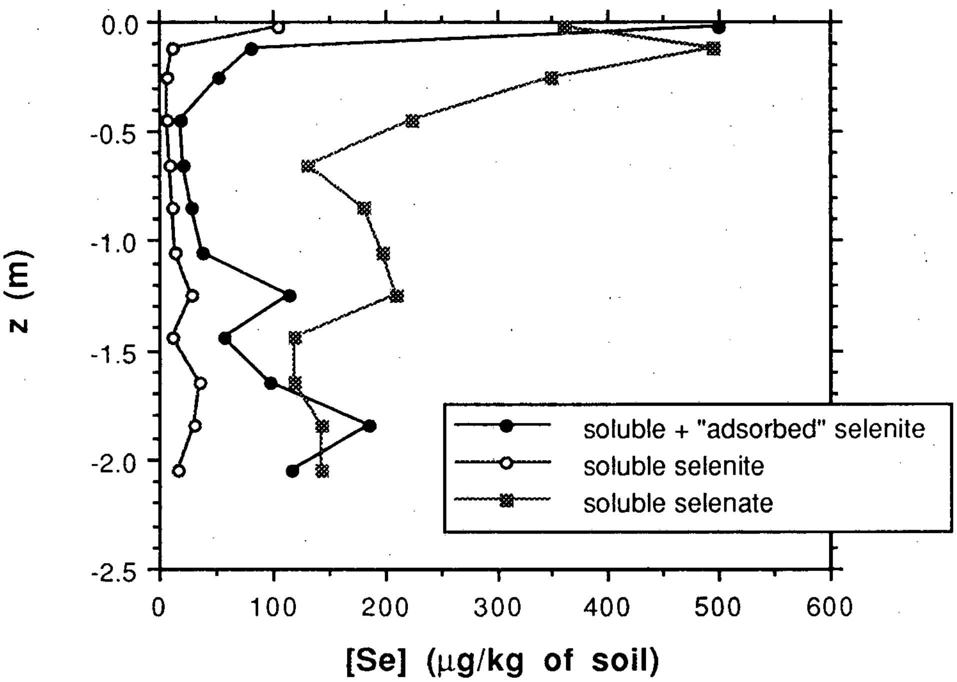

Figure 2.39. Soluble selenate and soluble and "adsorbed" (phosphate extractable) selenite concentrations in the soil profile of plot 9c (pond 7), 12/88.

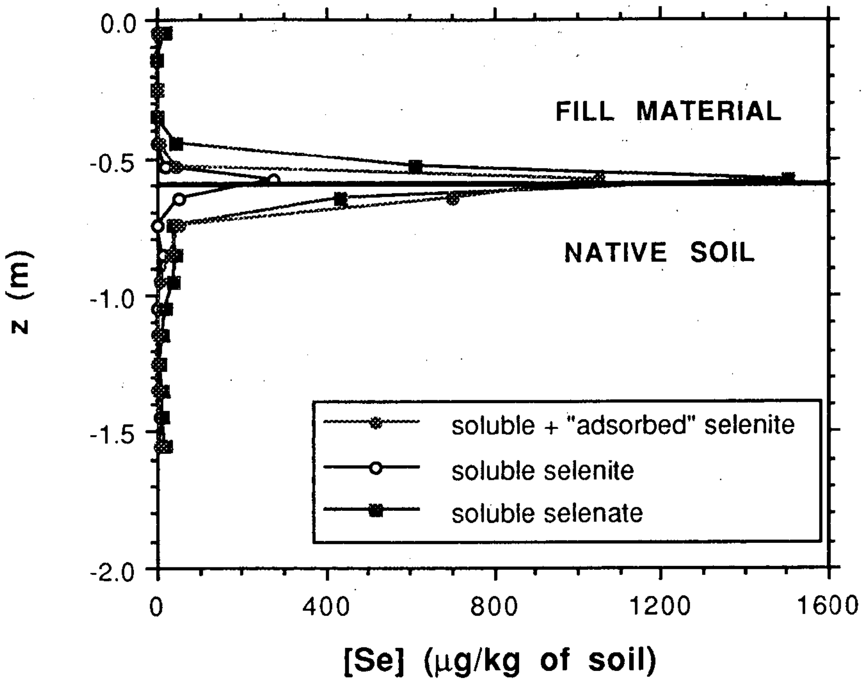

Figure 2.40. Soluble and "adsorbed" (phosphate extractable) selenite and soluble selenate concentrations in the soil profile of plot 5f (pond 5), 3/89.

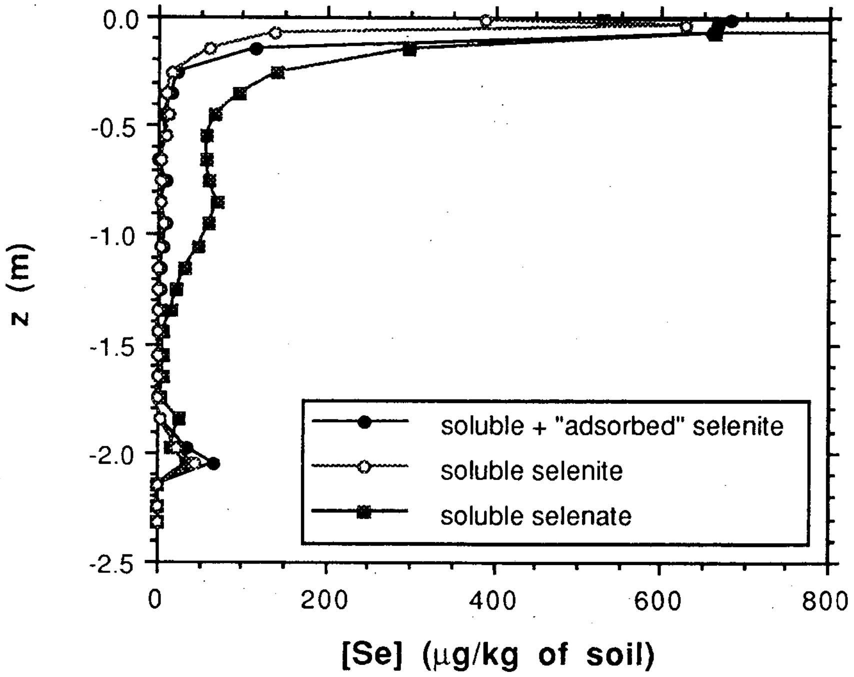

Figure 2.41. Soluble and "adsorbed" (phosphate extractable) selenite and soluble selenate concentrations in the soil profile of plot 8EP (pond 8), 11/89.

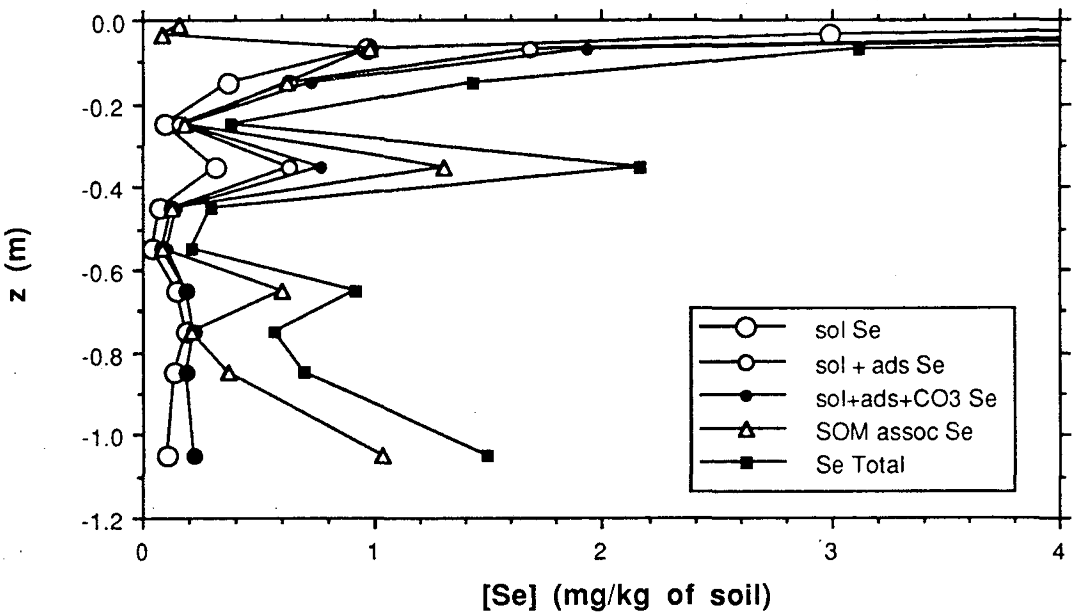

Figure 2.42. Soil-Se concentrations in soil profile of plot 9BE (pond 9), 11/89.

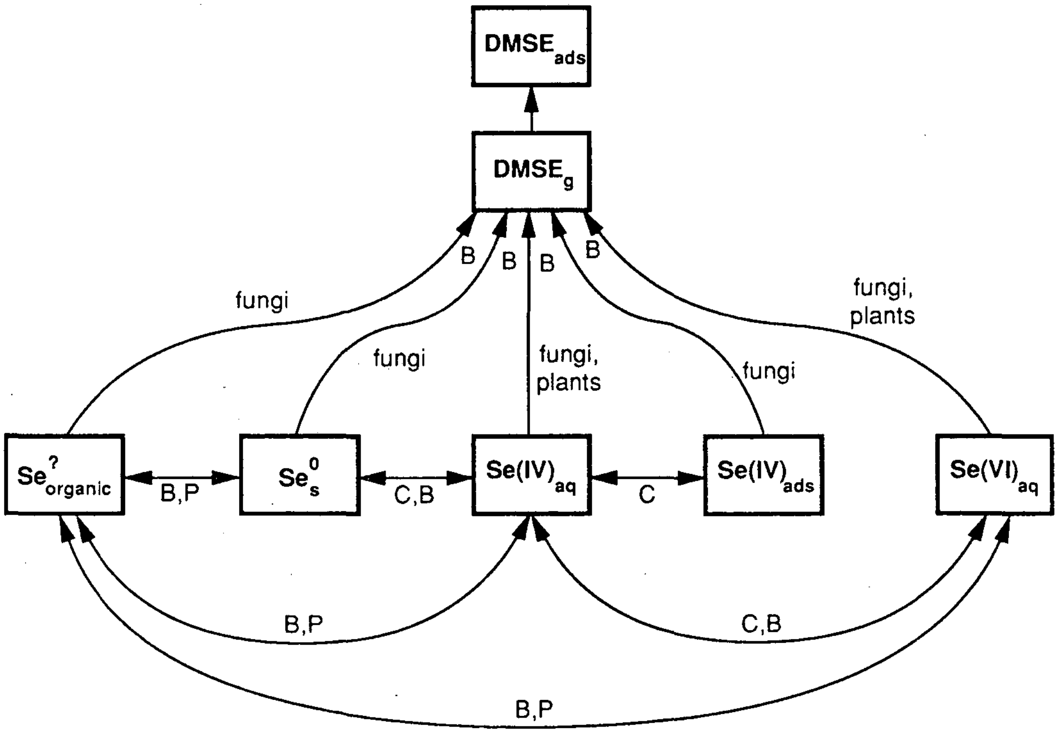

Figure 2.43. Likely components of the selenium cycle at Kesterson Reservoir. Arrows show the direction in which the processes will take place. Letters indicate nature of process: B = biochemical, C = chemical, P = physical.

2.7.3.1. Plant and Fungal Volatilization of Selenium

Selenium volatilization is a process by which microbes or plant tissue convert inorganic and organic selenium into a methylated species, dimethyl selenide (DMSE). In soil, fungi appear to have the greatest capacity to form dimethyl selenide, although the ability to volatilize selenium is considered to be a "general phenomenon ... not restricted to any one group of microorganisms" (Doran, 1982). Methylation of selenium in plants greatly reduces the toxicity of the trace element in the plant itself. Since methylation is endothermic, both in microorganisms and plants, the detoxification aspect is considered to be the most likely reason for the process (Shrift, 1973). A mechanistic description of selenium methylation is offered by Doran, 1982 (pp. 18-22). As shown in Figure 2.43, fungi are likely able to volatilize all of the major forms of selenium present in Kesterson soil. This ability has been documented in past and current laboratory research. Doran and Alexander (1977) showed that a strain of Corynebacterium, isolated from soil, formed DMSE from selenate, selenite, elemental selenium, and three organic selenium compounds: selenomethionine, selenocystine, and methaneseleninate. Se-compounds were placed in flasks containing 4 ml of nutrient solution buffered at pH 7.0 and bacterium cell suspension. The head-space in the flasks was periodically sampled and the DMSE in the gas was quantified using GC-MS. Table 2.3 contains data collected on the final hour of the experiment (hour 16) and the relative effectiveness of volatilization of the various Se compounds.

From the above data it is clear that while all selenium fractions were volatilized, the effectiveness varied, with methaneseleninate being completely volatilized and elemental Se only slightly so. Considering the very short run of this experiment it is not possible to speculate on the long term effectiveness of volatilization on the more slowly methylated fractions. Laboratory experiments similar in concept to the one above, except utilizing fungi believed to be of primary importance in Se volatilization in the soils of Kesterson Reservoir (Karlson and Frankenberger, 1989) and using Kesterson soil as a substrate, have been performed by scientists at LBL and some preliminary results are discussed in Section 4.2. These investigations also confirm the ability of fungi to volatilize all Se fractions with varying efficiency. On the other hand, plant volatilization only affects the dissolved Se pool; plants can only volatilize Se which is present in the root-extracted soil solution. This obviously is further constrained by the soil depths from which plants and fungi can draw Se. Plants will only be effective at volatilizing Se dissolved in soil solution within the root zone. Fungi will most effectively volatilize selenium within centimeters of the soil surface, being that they are obligate aerobes. Through moisture movement due to root extraction, plants may actually access a Se inventory which goes beyond the root zone at one time or another.

Table 2.3. Quantities of various selenium species volatilized in a 16 hour period (after Doran and Alexander, 1977).

Se compound used as substrate	Mass Se (μg)	DSME after 16h μg	Se-equiv. after 16h μg	Percentage volatilized	Percent volatilized minus control
None	0	2.36	1.7	NA	0
Elemental Se	192	4.23	3.05	1.6	0.7
Selenite	12.0	7.47	5.38	45	31
Selenate	10.8	14.5	10.4	97	81
Selenocystine	9.2	4.99	3.59	39	21
Selenomethionine	7.6	6.95	5.00	66	43
Methaneseleninate	12.0	19.5	14.0	117	103

What rates of selenium volatilization by fungi and plants can be assumed to be realistic under field conditions? It has been well established that these rates are strongly dependent on how the soil is treated (moist vs. dry, type and amount of carbon source, aeration, temperature, etc.) (Frankenberger and Karlson, 1989; Zieve and Peterson, 1981; Doran and Alexander, 1976). At first, we will assume that no action is taken to enhance volatilization: the soil system is natural and unmanaged. The soils literature is generally lacking in field data on in situ selenium methylation. Zieve and Peterson (1984) measured selenium volatilization from soil and plants (barley) under greenhouse conditions but did not normalize results to surface area of soil (selenium from soil containing 5 ppm Se as sodium selenite was volatilized at a rate of roughly 0.01% per day for 20 days). Such data has been collected at Kesterson Reservoir in a variety of environments. Frankenberger and Karlson (1988) measured selenium volatilization rates from undisturbed soil in Pond 4 and Pond 11. The most important difference between these two sites is that the top 6 inches in Pond 4 contains, on average, 50 ppm Se, while in Pond 11 it contains an average of 4 ppm Se. A twelve month survey revealed an average volatilization rate in Pond 4 of 3.53 $\mu g\ m^{-2}\ h^{-1}$ with measurements made over a one hour period; in Pond 11 the corresponding average was 0.80 $\mu g\ m^{-2}\ h^{-1}$. Since most of these measurements were made during the hotter parts of the day, the values should be divided by 2 to give an approximate daily average. Seasonal variations were not very significant in either of these sets of data. Measurements of selenium volatilization were also made in Pond 7 (DANR, 1989) on undisturbed bare soil (soil Se in top 0.15 m is < 1 mg/μg-soil) and showed a volatilization rate of 0.13 $\mu g\ m^{-2}\ h^{-1}$. This data suggests a probable range of Se volatilization rates from undisturbed soils at Kesterson Reservoir of 0.10 to 10.0 $\mu g\ m^{-2}\ h^{-1}$. They also suggest a strong dependence of volatilization rates on soil Se concentrations. Since the average Se concentration in the top 6 inches is approximately 5 mg/kg, this range is not likely to be exceeded under unmanaged conditions.

By managing moisture and aeration (through disking or rototilling) and the introduction of additional carbon sources, the growth of fungi can be stimulated. This in turn increases the rate of selenium volatilization. Based on data from Ponds 4, 7, and 11, under managed conditions, rates generally go up one to two orders of magnitude, although during winter months, when temperatures drop significantly, volatilization rates drop back down to unmanaged levels. Therefore, a likely range of rates from managed soils would fall between 1.0 and 100 $\mu g\ m^{-2}\ h^{-1}$.

The rate of plant volatilization is dependent on a number of variables: (1) plant species, (2) plant tolerance to Se and salinity, (3) competing ion concentrations (sulfate), (4) concentration of dissolved selenium in the root zone, (5) moisture content in root zone. Plant volatilization data has been collected by researchers affiliated with the Kesterson project. *Astragulus* plants are generally considered to be effective selenium volatilizers. In the laboratory, Norman Terry (U. C. Berkeley) has found that certain *Astragulus* species are far better than others. Some *Astragulus* species are no better at selenium volatilization than crop plants (DANR, 1989). *Astragulus bisulcatus* volatilized up to 0.6 μg Se $plant^{-1}\ day^{-1}$; assuming 10 to 100 plants per square meter, selenium would be volatilized at rate of 0.25 to 2.5 $\mu g\ m^{-2}\ h^{-1}$. These plants were grown under idealized, laboratory conditions and both their growth rate and volatilization rate could be reduced under highly saline and arid field conditions. Measurements of plant volatilization of Se have been made in Pond 7 by Gamani Jayaweera (U. C. Davis); barley was found to volatilize approximately 0.5 μg Se $m^{-2}\ h^{-1}$, saltgrass volatilized 1.0 μg Se $m^{-2}\ h^{-1}$, tall fescue volatilized 4.9 μg Se $m^{-2}\ h^{-1}$. The soluble selenium concentrations in the root zone of this plot were between 50 to 200 mg/l. It may be concluded that even though the ability of a plant to volatilize Se varies tremendously from species to species, the probable range for rates of Se volatilization by plants falls in the range of 0.1 to 10.0 $\mu g\ m^{-2}\ h^{-1}$.

2.7.3.2. Selenium Reduction and Oxidation

As mentioned previously in this section, due to the progressive drying out of Kesterson soils in the last few years, conditions in the vadose zone have become increasingly oxidized. This, by the way, is a not a statement of directly determined fact, but rather of a generally construed notion of oxidation in soils (e.g. Bohn and others, 1979). This change in redox conditions should result in the progressive oxidation of the selenium inventory (Elrashidi and others, 1987). As can be seen from Figures 2.38 through 2.42, most of the selenium inventory at this point is not in its most oxidized state, Se(VI), or selenate. Therefore, further change in this direction should be expected and has been observed in a few profiles (LBL, 1988, 1990; Tokunaga and others, 1991). On the other hand, the seasonal rise in the groundwater table as well as influx of rainwater lead to more reducing conditions, which probably result in reduction of selenate to selenite, and possibly all the way to elemental selenium. The literature has been scanned for studies of selenium reduction and oxidation, with an emphasis on measured or estimated rates.

The presence of both organic forms of selenium and elemental selenium is a relict of the former hydrogeochemical regime at Kesterson. Organic-rich pond bottoms and a fully saturated soil profile were ideal environments for the conversion of incoming selenate to reduced forms (Weres and others, 1989). It has been shown by numerous authors that both the reduction and oxidation of selenium are microbially mediated in soils. This has been especially well documented for the reduction of selenate and selenite (e.g. Oremland and others, 1989, 1990; Moss and Gibbs, 1987; Macy and others, 1989; Bautista and Alexander, 1972; Maiers and others, 1988). As pointed out by Doran (1982), microbial oxidation of selenium has received much less attention than reduction, mostly because of the desire to find a Se removal process. This is especially unfortunate since then net redox change in Kesterson soils is in the positive direction. In addition, many studies focus on a qualitative identification of the process and microorganism and not on the reaction rate.

Maiers and others (1988), collected soil samples from nearby Kesterson Reservoir. Eight soils were inoculated into basal salts media containing 100 mg/l of selenate and carbon source (2 g lactate). After three weeks of incubation, selenate had been reduced to other forms: selenite ranging from 40 to 80 mg/l, and more reduced forms from 20 to 60 mg/l. The partial pressure of oxygen in this experiment was not controlled. A *Pseudomonas sp.* was found to reduce 50% of the selenate in a 7 mM selenate solution to selenite in 2 hours in an experiment conducted by Macy and others (1989). Better controlled experiments were performed by Oremland and others (1989, 1990). Selenate (approx. 400 μM) was added to a sediment slurry and incubated under varying conditions. All of the selenate was reduced under a nitrogen or hydrogen atmosphere in 7 days. In an autoclaved control, selenate concentrations dropped to around 200 μM after 4 days and appeared to remain at that concentration until day 7, when the experiment was terminated. In another laboratory experiment, Oremland and others (1990), found a selenate "turnover time" of 82.4 days in evaporation pond sediments ($[SeO_4^{-2}] \approx 17$ μM. Sposito (1990), incubated a saturation extract with 2 μM sodium selenate. Soluble selenium gradually decreased to zero over a period of 160 hours. These results demonstrate the relatively fast rates of these reactions and underscore the importance of microbial mediation in selenate reduction.

A rare laboratory study of Se oxidation was performed and described by Masscheleyn and others (1990). Under controlled redox and pH conditions, the solubility and speciation of Se in a soil suspension was studied. The soil was collected from the northeastern corner of Pond 2 and originally contained 9 ppm total Se. Selenium speciation in the original soil was not determined, and all selenium which was insoluble under given Eh conditions was assumed to be elemental. Oxidation of some of these insoluble species to selenite was found to occur rapidly under moderately oxidized conditions. After 2 days of incubation at ''natural'' pH ($\approx$7.7) and Eh = 200 mV, approximately 200 μg selenite (kg of dry sediment)$^{-1}$ were found in solution. This concentration did not change significantly over the next 18 days. On the other hand, selenate did not show up in the solution until Day 12, at a concentration of about 100 μg kg^{-1}. On Day 28 (final day), the selenite concentration rose to approximately 1000 μg kg^{-1}, while the selenate concentration went up to only 200 μg kg^{-1}. At a redox potential of 450 mV, both selenite and selenate concentrations reached roughly 100 μg kg^{-1} after 2 days and subsequently, selenite concentrations dropped to about 30 μg kg^{-1} on Day 20, while selenate concentrations rose to roughly 1500 μg kg^{-1} on that day. By Day 28, selenate dropped slightly to 1400 μg kg^{-1}, while selenite rose back up to roughly 100 μg kg^{-1}. Due to the lack of Se speciation in the soil, it is not possible to say what pool of Se was being oxidized or whether Se release into solution was strictly due to oxidation. Furthermore, ''oxidation'' rates at Eh = 450 mV were rapid during the first few days, after which concentrations did not change. Since the experiment was terminated after only 28 days, it is difficult to say whether selenium oxidation ceased or slowed down to very low rates. Except at Eh = 450 mV, the percentage of total Se which became ''oxidized'' is small: 17% at Eh = 200 mV, and much less at lower Eh. In the same experiments run at higher and lower pH (6.5, 8.5, 9.5) as much as 67% of the selenium was solubilized at Eh = 450 mV. The authors theorized that at pH 6.5 iron sulfide solubility increased leading to a release of Se, while at higher pH Se release was due to desorption.

Sarathchandra and Watkinson (1981) found that a heterotrophic bacterium (Bacillus megaterium) very significantly increased the rate of oxidation of Se^0 to Se(IV). Nonetheless, the rate was very slow: after 45 days, 1.5% of the added Se^0 (init. conc. = 0.01% by wt.) had been oxidized. Also, an order of magnitude less selenate was produced. Furthermore, in the absence of the given bacterium, Se^0 oxidation took place at rates one order of magnitude slower. This suggests that the oxidation process of Se^0 to Se(IV) is very slow and that Se(IV) is stable enough under oxidized conditions that its transformation to selenate is even slower. Purely inorganic oxidation of Se^0 may not be significant.

A field experiment performed by Long (1988) in Pond 1 focused on the effects of flooding on Se transformations in soil water. The study showed that the reduction of selenate to selenite and possibly beyond (elemental Se) is extremely fast under saturated conditions (on the order of 25 days). The results suggested that under moderate to low flow rates through the soil profile, between 90% and 100% of the soluble selenate will become "immobilized," i.e., either reduced to selenite and adsorbed or reduced to elemental selenium and precipitated. The aspect of this experiment more applicable to the current hydrological setting of Kesterson Reservoir, is the monitoring of soil water after pond drying. Within approximately 10 days after drying out the pond, selenate concentrations rose from 150 ppb to as much as 1500 ppb in the 15 cm soil water sampler; selenate concentrations in deeper samplers doubled during the same interval. The five different sites in this experiment were dry for 80 to 180 days before a second flooding event. Within 100 to 150 days of drying, soluble Se concentrations in most samplers were in the range of pre-flooding levels.

2.7.3.3. Adsorption/Desorption of Selenite

Selenite adsorption in soils is thought to occur mostly on iron oxides (e.g. goethite, Hingston and others (1968); Balistrieri and Chao (1987)) and to a lesser extent on clay minerals and soil organic matter (Hamdy and Gissel-Nielsen, 1977; Rajan and Watkinson, 1976; Bar-Yosef and Meek, 1987). Variables which affect the amount of selenite adsorption include: pH; competing anions; ionic strength of the soil solution; soil composition; and, of course, selenite concentration. In laboratory studies, selenite adsorption declines with pH and is usually negligible above pH 9 (Neal and others, 1987). This does not agree with field data from Kesterson (see Figures 2.38 to 2.42) where soil pH usually averages around 8, yet only a small fraction of the selenite inventory is found in solution. This may be related to very high solution salinity or sorption on calcite which, in the laboratory, has been found to peak between pH 8 and 9 (Goldberg and Glaubig, 1988). Whatever the case, usually between 60 and 90% of the non-refractory selenite in

Kesterson soil is found to be phosphate-extractable and no significant changes over time have been observed. The latter fact is not surprising since selenite adsorption is considered a very fast process. Bar-Yosef and Meek (1987) found that selenite at an initial concentration of 1.58 μM came to equilibrium with a 1:100 kaolinite suspension in approximately 300 hours (78% adsorbed; pH 6.2, Eh 390 mV), although 68% had already become adsorbed after around 10 hours. In experiments conducted by Neal and others (1987), maximum sorption was reached after 2 hours. Kinetic experiments performed by Balistrieri and Chao (1987) indicated equilibrium in 2 hours as well. All of these experiments were performed in soil suspensions and slurries which were vigorously shaken: how this relates to a field setting is not clear, although certainly the kinetics will be slower.

A few studies have been conducted using laboratory columns, which may be a better representation of field conditions. Ahlrichs and Hossner (1987) found selenite to be completely adsorbed by a sandy loam-textured strip-mine overburden, at pHs ranging from 2 to 9. However, their detection limit was very high (320 ppb), so it is very likely that some selenite moved through the column. Short column experiments performed by LBL (1986), in which inflow and outflow selenium and selenite concentrations as well as Eh were monitored, showed outflow selenite concentrations falling below inflow concentrations after as few as 1 to 2 pore volumes were passed through the system, even when both the inflow and outflow Ehs were greater than zero. This suggests that selenite was being rapidly adsorbed, since the high Eh most likely precluded the reduction of selenite to elemental selenium.

Selenite desorption is not much discussed in and of itself, although under laboratory conditions (a vigorously agitated soil slurry) the kinetics are similar. Balistrieri and Chao (1987) increased the pH of an equilibrated soil solution by 0.5 of a pH unit to 2.5 pH units and found that desorption was completed (or adsorption was reversed) within 24 hours.

2.7.3.4. Selenium Uptake by Plants

Plant uptake of selenium will be limited to soluble selenium species within the root zone. The abilities of certain plants to take up and accumulate selenium are not always related since some plants are very efficient selenium volatilizers. A few studies have been performed to determine the fate of selenium once it enters a plant. It appears that speciation of selenium is species-specific. Gissel-Nielsen (1979) found that in corn grown in nutrient solution containing 75Se in both selenate and selenite forms, the selenite was ''metabolized immediately to ... a Se-amino acid, while ... selenate was found in the xylem-sap as selenate ions.'' In similar experiments with barley and rye-grass (Gissel-Nielsen, 1987), 60 to 80% of selenium was converted to amino acid form, 10 to 25% became protein-bound and the rest remained inorganic, regardless of whether selenite or selenate was applied. The prevailing notion regarding Se storage by Se accumulator plants is that the toxicity is minimized by the reduced incorporation of the element into protein (Brown and Shrift, 1981; Eustice and others, 1981). Non-accumulator species of the *Astragulus* genus averaged approximately ten times the concentration of protein-bound Se relative to accumulator species when both were grown under the same conditions. It is clear then that no general conclusions may be made with respect to Se speciation in plant tissue, except that potentially a large fraction may become organically bound.

A sizable body of research exists on the ability of Se accumulation by various plant species. Wu and others (1988) studied Se accumulation in five grass species: tall fescue, crested wheatgrass, buffalograss, seaside bentgrass, and bermudagrass. Table 2.4 summarizes the range of measured rates and their dependence on Se concentration in nutrient solutions.

Table 2.4. Selenium uptake in plants grown at a range of selenium concentrations in nutrient solutions (from Wu et al., 1988).

Selenium in nutrient solution	0.5 mg/l	1.0 mg/l	2.0 mg/l
Range of accum. rates (μg Se 10 plants^{-1} day^{-1})			
Low	2.1	2.7	1.3
High	6.7	7.5	8.0

All plants, except for tall fescue, were not able to withstand Se concentrations above 2 mg/l. Assuming 100 plants per square meter of soil, these rates translate to between 0.54 μg Se m^{-2} h^{-1}

and 3.3 μg Se m^{-2} h^{-1}. Sulfate was not included in the nutrient solution; sulfate is known to compete with selenate and would likely cause a decline in accumulation rates. For example, Wan and others (1988) found that increasing soluble sulfate concentrations from 300 to 2300 mg/l in a soil containing 3.0 mg kg^{-1} selenate resulted in a decrease of selenium accumulation in alfalfa shoots from 1,100 mg kg^{-1} to 100 mg kg^{-1}. Sulfate concentrations in Kesterson soil water are usually in the range of 3,000 to 10,000 mg/l. Dimes and others (1989) observed *Astragulus asymetricus* accumulate as much as 2,310 mg Se (kg shoot)$^{-1}$ in a period of 9 weeks, in a soil treated with a solution containing 15.0 mg/l selenium. This was equivalent to an accumulation rate of 3.7 μg Se plant^{-1} day^{-1}. Assuming from 10 to 100 plants m^{-2}, this amounts to 5 to 15.4 μg Se m^{-2} h^{-1}. Accumulation rates were markedly lower at lower selenium concentration treatments. Sulfate concentrations were very low.

The above data suggest that plant accumulation of Se could extract between 0.1 and 100 μg Se m^{-2} h^{-1} from the soil. The upper part of this range is quite unlikely in a sulfate-rich environment such as Kesterson. Plants collected at Kesterson usually contain from 0 to 30 mg/kg Se (LBL, 1990); at their given biomass, this translates to 0 to 10,000 μg Se m^{-2}, with most values in the range of 10 to 100 μg Se m^{-2}. Given that most of the plants have one major growth cycle per year, hourly uptake rates (averaged over a year) are in the range of 0.001 to 0.01 μg Se m^{-2} hr^{-1}. These rates are small compared to rates of uptake and dissipation by microbial volatilization.

2.7.3.5. Organic Se Mineralization

Possibly one of the slowest, and therefore most significant processes over the long run may be the mineralization of Se-containing SOM. Mineralization refers to the process by which organic matter in soil is converted to the inorganic state (Alexander, 1977). The process of organic selenium formation under natural conditions would usually involve processes described in the previous section. The introduction of large amounts of selenium in Kesterson Reservoir through ponding created conditions ideal for the formation of organic Se compounds. This resulted in a very large proportion of Se associated with soil organic matter (see and Section 2.5). The microbial decomposition of plant and animal residues results in the release of, among other compounds, inorganic elements (Doran, 1982). The literature is replete with studies on the mineralization of carbon and nitrogen, but information on Se mineralization is scarce. Organic Se compounds are believed to be metabolized in ways similar to organic sulphur (Shrift, 1973), although much uncertainty about this likeness remains. If this parallel is assumed, then the primary products of aerobic mineralization of organic selenium would be selenate, selenite, elemental Se, dimethyl selenide, and dimethyl diselenide. The actual pathway for microbial metabolism of organic Se compounds will depend on the nature of the compound, for there are several organic Se compounds likely to form in soil. In addition to the three listed in Table 2.4, trimethylselenonium and Se-methylselenomethionine may also be significant in soil organic matter. Table 2.5 pairs the ''parent'' with probable ''product'' of the mineralization processes of the above compounds. The above table makes it clear that most organic-Se compounds will not actually be ''mineralized'' in microbial metabolism, but rather converted to gaseous organic-Se compounds, which in turn are released to the soil gas phase; how much of this gas phase escapes to the atmosphere is unknown, though the percentage will decline with depth in the soil profile, as significant quantities of DMSE may become adsorbed (LBL, 1990). This is in fact the process described under the heading Plant and Fungal Volatilization of Selenium in this section, however the transformation rates described therein only apply to fungal processes taking place near the soil surface under aerated conditions. Deeper in the soil profile, bacterial transformations may be more significant than fungal volatilization, but their rates have not been measured. In addition to organic-Se, inorganic forms may be associated with SOM, either through adsorption onto its surface or occlusion within. Their release, most likely in their given oxidation state, would also occur during organic matter mineralization. There is no data regarding rates of mineralization of organic-Se compounds to selenite, selenate, and elemental selenium. One may get a general idea of these rates based on measurements made of soil organic carbon turnover. These rates are often taken to represent the cycles of SOM itself.

Table 2.5. Products of microbial metabolism of various forms of selenium.

Organic-Se Compound	Product of Microbial Metabolism	Chemical State	Reference
selenomethionine	dimethyl diselenide	gaseous	a
selenocystine	H2Se, Se^0 * SeO_3^{-2}, SeO_4^{-2}†	gaseous, solid aqueous	a b
trimethylselenonium	dimethyl selenide	gaseous	a
methaneseleninate	?	?	-
Se-methylselenomethionine	?dimethyl selenide	gaseous	c

[a] Doran and Alexander (1977)
[b] No data -- inference based on parallel to sulfur (cystine)
[c] Doran (1982)
* under anearobic conditions
† under aerobic conditions

Rates at which SOM is mineralized may range from months to years, although in general, SOM turnover is on the order of 10 to 100 years (Alexander, 1977; Bohn and others, 1979; Jenkinson, 1981; Ross, 1989), turnover being the time required to mineralize all of the SOM present initially. Based on field data, 2 to 5% of the organic carbon in humus can be mineralized per year (Alexander, 1977). The average half-life of organic carbon in soils is considered to be approximately 30 years (Bohn and others, 1979). These rates were measured in environments considered to be in steady-state, which is certainly not the case at Kesterson Reservoir. Therefore, SOM mineralization may be more rapid due to the past accumulation of organic material at and near the soil surface. Unfortunately, data on SOM mineralization in playa and grassland environments has not been found so only a very wide range of mineralization rates may be assumed. After microbial metabolism of organic-Se compounds, the aqueous products (selenate, selenite) will likely go into the soil solution; gaseous products will be released into the soil and eventually escape into the atmosphere, although adsorption of DMSE onto soil may be significant; solid products (elemental selenium) will likely precipitate onto the surface of soil minerals. Non-gaseous products will be available for plant and microbial uptake (as part of the soil solution) and will continue to be cycled in the soil. Therefore, initial rates of SOM mineralization may lead only to a reduction of the selenium inventory, although this process will take decades. Furthermore, there is no direct information as to the actual organic forms of Se in SOM, which means that we do not know what percentage will be methylated and how much will return to the soil in an inorganic form.

2.7.4. Summary

Based on the presented data, the above processes may be grouped according to their short-term and long-term significance in either reducing the Se inventory or causing changes in Se speciation. Unmanaged fungal volatilization, plant volatilization, bacterial volatilization, and groundwater transport will slowly dissipate the surficial inventory of selenium. Due to the large spatial variability in soil selenium concentrations (see Section 7), statistically significant declines are not expected to be observed before 10 or 20 years. Over the long-term (100 years), these processes will significantly reduce the selenium inventory. The effects of SOM-Se mineralization and Se^0 oxidation may substantially alter the chemical distribution of Se in the next 10 years. A more quantitative assessment of the effects of these processes is not possible without data collected over a similar time-span. A laboratory experiment is currently being designed to estimate long-term rates of SOM-Se and Se^0 oxidation by accelerating rates of selenium transformations relative to field rates; knowing that microbial activity increases proportionally with temperature, we will able to speed up the metabolism of organic-Se and Se^0 by exposing subsamples of the same soil to a variety of environmental conditions (humidity, temperature).

Other studies could improve our understanding of Se transformations and render it easier to predict the evolution of the selenium inventory:

- continuation of ongoing field experiments to determine the trends in microbial volatilization rates; in order to make long-term predictions, the dependence of volatilization rates on soil-Se concentrations must be made.
- further laboratory experiments to improve our understanding of the availability of various Se fractions for fungal volatilization; such knowledge could help us better

assess the feasibility of microbial volatilization as a remedial technique in Kesterson soils.

- laboratory experiments designed to distinguish the solid onto which selenite is adsorbed; if selenite is predominantly adsorbed onto calcite, its desorption may be more sensitive to soil acidification.

3. SURFACE WATER SELENIUM CONCENTRATIONS IN AND AROUND KESTERSON RESERVOIR

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Biological monitoring data collected over the last 7 years at Kesterson indicates that the aquatic food chain is the most significant exposure pathway for selenium contamination. Therefore, actions were taken in 1986 and later, in 1988, to eliminate the aquatic food chain at Kesterson. Specifically, in 1986 drain water deliveries to Kesterson ceased. In 1988, low lying areas in the former Reservoir were filled with soil to prevent formation of ephemeral pools caused by rising groundwater. Section 3 describes our efforts to:

- evaluate the effectiveness of these measures;
- understand physical, chemical and biological processes leading to elevated selenium concentrations in pools that do or may form at Kesterson; and
- predict the likely concentrations of selenium and salts in pools that form in years of exceptionally heavy local rainfall.

In the winter following completion of the filling operation, an extensive effort was undertaken by the USBR and LBL to locate, sample, and survey the surface water pools that formed within the Reservoir. Numerous pools were observed, mostly in areas covered with fill-dirt. The majority of these were small, covering and area of less than 20 by 20 m. The total area occupied by these pools was estimated at less than 1% of the area of the Reservoir. The majority of the pools did not persist more than several days after a rainfall event. There were however several pools that persisted over the majority of the winter months. Water quality sampling and watertable elevation data indicated that these pools were formed by ponded rainfall. In general, electrical conductivities were less than 1 dS/m, far less than the 15 dS/m typical of drain water and the 10 to 60 dS/m observed in soil-water. Selenium concentrations averaged less than 10 μg/l. Again, far less than the 300 μg/l in drain water and thousands of μg/l in soil-water. The areas with pools that persisted though the winter were disked and or covered with additional soil to minimize the likelihood of pool formation over the past winter (1989-90). Section 3.1 provides information collected over the past winter (1989-1990) regarding occurrence and water quality of surface pools in areas covered with fill-dirt.

Sections 3.2, 3.3 and 3.5 describe field and laboratory studies designed to improve our understanding of the chemical, physical and biological processes leading to selenium transport into surface water pools. These provide the basis for distinguishing pools formed by rising groundwater from pools formed by rainfall ponding and clearly demonstrate that since the filling operation, watertable rise has not contributed significantly to pool formation. The data also provide early indications of temporal trends in surface water selenium concentrations.

During 1989, mass balance models and numerical simulation studies were used to investigate the hydrologic factors leading to watertable fluctuations in and around Kesterson (LBL, 1990). These studies and a large body of waterlevel data indicate that flooding of nearby duck clubs is responsible for the majority of the rise in watertable elevation. Rainfall is a significant source of watertable rise only when it exceeds normal values by more than 50%. Model predictions indicated that in years with twice the average annual rainfall of 240 mm, much of the Reservoir could be covered with standing water during winter. However, selenium and salt concentrations in these pools are expected to be low compared to past levels because they form from rainwater ponding, rather than by rising soil-waters from below. Nevertheless, surface water selenium concentrations may exceed the recommended safe levels of 2 to 5 μg/l. Moreover, direct transport of selenium from the soils to vegetation and/or insects may create an environment which is hazardous to waterfowl and/or small mammals residing in this temporary aquatic habitat. For these reasons, drainage of surface water has been recommended for very wet years. Section 3.4 provides some results of recent water quality monitoring of nearby surface water conveyances. These data provide a reference point for selenium concentrations in nearby waterways. Section 3.6 provides an assessment of likely concentrations of selenium and salts in the pools that form during very wet years. This information may provide a basis for regulatory considerations of surface water discharges from Kesterson Reservoir into Mud Slough or the San Luis Canal.

3.1. Selenium and Salinity in Kesterson Reservoir Fill Pools

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During the past 2 years following the completion of filling at Kesterson Reservoir, occasional ponding of rainfall has been observed. Surface water samples from a limited number of these pools have been collected during these past 2 years, and analyzed for selenium and salinity. More comprehensive sampling has been performed by the USBR. Background information on fill sites where ponding has been observed is provided in the 1989 Annual Report. A brief review of this background information is provided here, followed with presentation and review of the LBL fill pool water sample data.

Fill dirt, largely obtained from nonseleniferous spoil banks of the Delta-Mendota Canal, was distributed in topographically low regions of Kesterson Reservoir in order to prevent seasonal ponding of the shallow watertable and associated ponding of seleniferous soil waters. During the 1988-1989 wet season following completion of filling, occasional ponding of rain water has been observed, primarily in fill areas with low permeability. The maximum areal extent of ponding was limited to about 1% of Kesterson Reservoir, with no ponding associated with the rising watertable. The average selenium concentration from 34 samples was 10 µg/L (ppb), with higher selenium concentrations associated with pools formed over fill material composed of original Kesterson Reservoir soils. In these latter pools, selenium concentrations ranged up to 50 µg/L.

During the 1989-1990 wet season, a smaller sampling of surface waters was obtained by LBL. Fewer pools were observed during the more recent wet season, despite the fact that approximately 50% more rainfall occurred (240 mm during 1989-1990, versus 163 mm during 1988-1989). The fewer observations of ponding events may possibly be attributed to a combination of several factors associated with vegetation influences. The extensive invasion of vegetation (dominated by *Kochia scoparia*) in filled areas may have facilitated infiltration of rain water through

(1) evapotranspiratively drying the soil profile during the growing season to moisture contents below that of the original fill conditions, (2) the persistence of standing dead vegetation minimizing direct raindrop impacts on the fill surface, thereby minimizing puddling of the surface, and (3) creation of some preferential flow paths for water infiltration. Items (1) and (3) above may need further elaboration. Although the fill was brought into Kesterson Reservoir as relatively dry material, it is likely that only the surface portions of the Delta-Mendota Canal spoil banks were as dry as the surfaces of in-place fill material at the end of the first year (1989) drying cycle. In other words, fill materials originating from deeper regions of the spoil banks may have contained relatively high moisture contents such than the average initial moisture content of the fill was higher than the moisture content at the end of the summer of 1989 (i.e., after the first spring and summer of evapotranspirative water removal from the fill). In addition, some water was applied to the fill material while it was being deposited and leveled. Thus the average surface fill water content may have been higher during the beginning of the first post-fill wet season than during the beginning of the second season. When all other variables are kept constant, initial infiltration rates into drier soils are higher than rates into more moist soils. Concerning item (3), drying of the soil profile by evapotranspiration is likely to be accompanied with some shrinkage of soils, leaving macropores. In addition, permeation of the soil profile by plant roots may provide additional channels for enhanced water infiltration. An additional factor associated with the persistence of dense stands of dead *K. scoparia* is the greatly diminished visibility of any ponding in these settings.

Of the limited observations of ponding in filled areas, only 16 samples were collected. Of these, 10 samples were collected on the same day (Feb. 17, 1990). Thus the more recent data set is not a representative sampling for the 1989-1990 wet season. Sampled waters are filtered (0.45 μm) or pre-digested with hydrogen peroxide (30%) and then filtered prior to analyses. The average selenium concentration for this set is 3.1 μg/L. The only high selenium concentration, 22 μg/L, was collected from the northeast corner of Pond 3. This Pond 3 site appears to have been filled with seleniferous Kesterson Reservoir soil, and has experienced ponding with seleniferous waters (44 to 50 μg/L) during the first year following filling also. Selenium concentrations in the sampled fill pools from both wet seasons are summarized in Figure 3.1a. Given the small number of surface water samples obtained during the past year, interpretations of differences between the selenium concentrations in the fill pools during the two wet seasons are limited.

Measurements of electrical conductivities (EC) of ponded waters serve as a simple general indicator of surface water salinity. EC data from fill area pools from the 1988-1989 and 1989-1990 wet seasons are summarized in Figure 3.1b. These EC data are generally relatively low, with most values in the range of 0.1 to 1 dS/m. The few higher EC data (2 to 6 dS/m) are associated with samples collected on fill material comprised of original Kesterson Reservoir soils. The generally low EC values are indicative of waters in which rainwater has mixed with small quantities of surface salts and surface pore waters. These fill EC data may be contrasted to ephemeral pool EC data from other unfilled Kesterson Reservoir sites and to EC data from other local surface water features. These other data will be presented in following sections.

The only general conclusions which can probably be made are that the extent of ponding was less during the 1989-1990 wet season than in the 1988-1989 wet season, and that these waters consisted largely of rainwater with commonly low concentrations of solutes mixed in from the fill surface. The apparent decrease in pool formation during the 1989-1990 wet season appears significant in view of the greater precipitation which occurred. It appears that selenium concentrations in fill surface waters were less during the 1989-1990 wet season than in the 1988-1989 wet season, although the sampling population is insufficient for substantiating this relation. The extent to which future surface water selenium concentrations in filled areas will be influenced by upwards movement of selenium from the original Kesterson Reservoir soils into the fill material (section 2.3) remains to be seen.

In order to put these fill surface water sample data into perspective, comparisons with selenium concentrations in ephemeral pools formed on unfilled areas of Kesterson Reservoir as well as in other local surface water bodies are useful. These data will be presented in following sections.

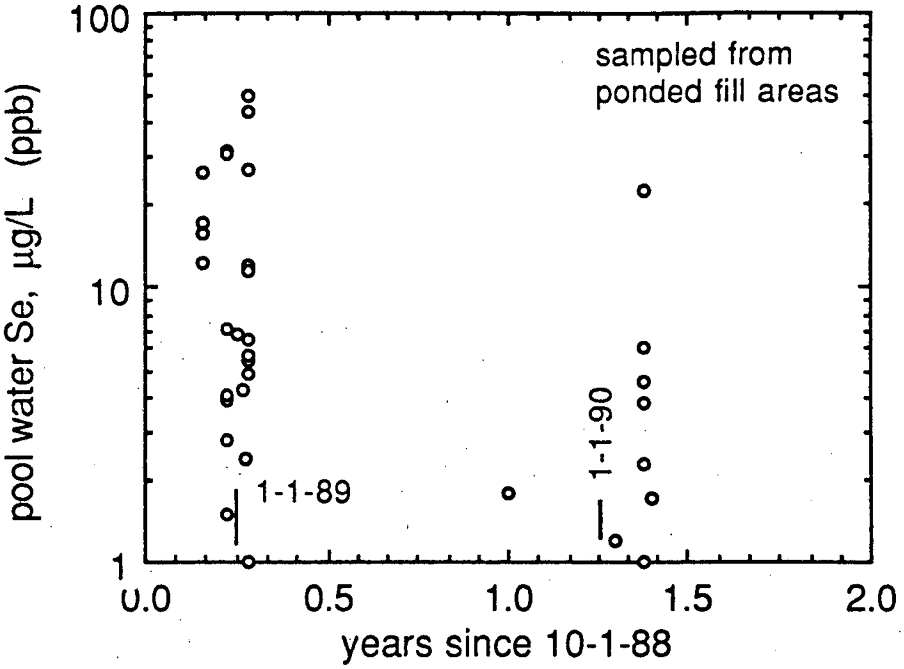

Figure 3.1a. Ephemeral pool water samples from filled sites, surface water selenium concentrations.

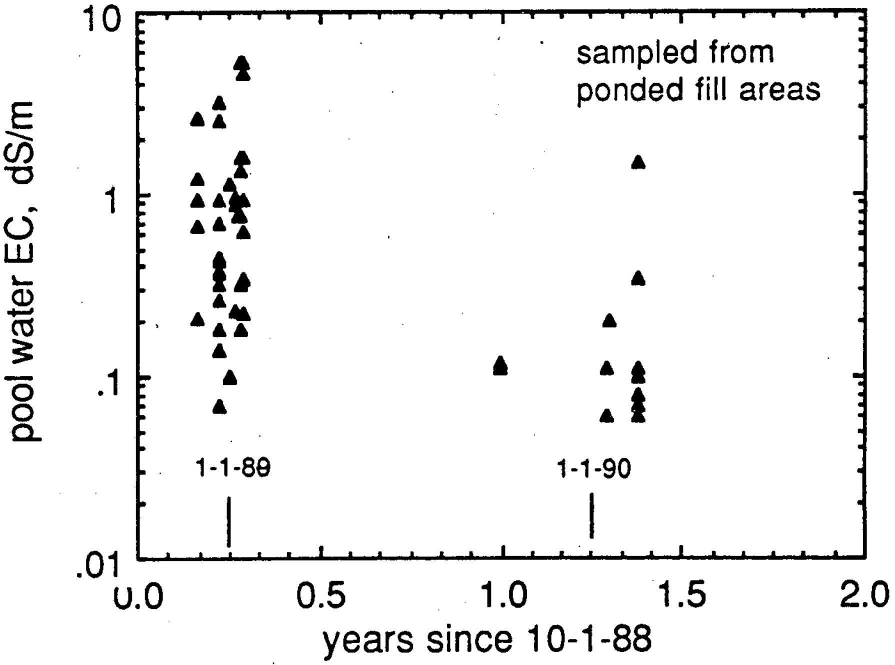

Figure 3.1b. Ephemeral pool water samples from filled sites, surface water electrical conductivities.

3.2. Time Trends in Surface Water Selenium Concentrations in the Pond 6, 1 ft Excavation Test Plot

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During the past two wet seasons, infrequent ponding of rainfall has been observed in the devegetated Pond 6, 1 ft excavation test plot, P6S12. Soil solution selenium and salinity profiles for this site were reviewed in section 2.4. During the 1987-1988 wet season, watertable rise caused surfacing of pore waters at this site, resulting in highly seleniferous and saline ephemeral pools. Rainfall dilution provided some moderation of high concentrations of dissolved selenium and salts, yet concentrations of selenium in particular remained high during this period. The extent of watertable rise was greater than in more recent years because of intentional ponding in the adjacent Pond 5 until the middle of 1988. The maximum heights of the watertable at this site during the 1988-1989 and 1989-1990 wet seasons were 0.53 m and 0.47 m below the excavated surface. Therefore, waters which have ponded at this site during the past two wet seasons are completely attributed to rainfall. The solutes in the ponded waters, however, are largely derived from dissolution of (excavated) surface soil salts and mixing of surface soil solutions into the ponded rainfall. Surface water samples were collected from the interiors of cylindrical sampling rings embedded into the excavated soil surface. Rings of 0.29, 0.33 and 0.56 m diameters were used. These rings served to isolate the surface water samples from potential lateral contamination. Selenium and EC analyses of samples of surface waters collected from isolated pools on the exteriors of the rings indicated that samples obtained within the rings were representative of the test plot.

The collective data on selenium concentrations from all surface waters sampled at P6S12 are shown in Figure 3.2a. The high selenium concentrations in the initial samplings are all associated with the mechanism of watertable rise displacing seleniferous soil solutions to the surface.

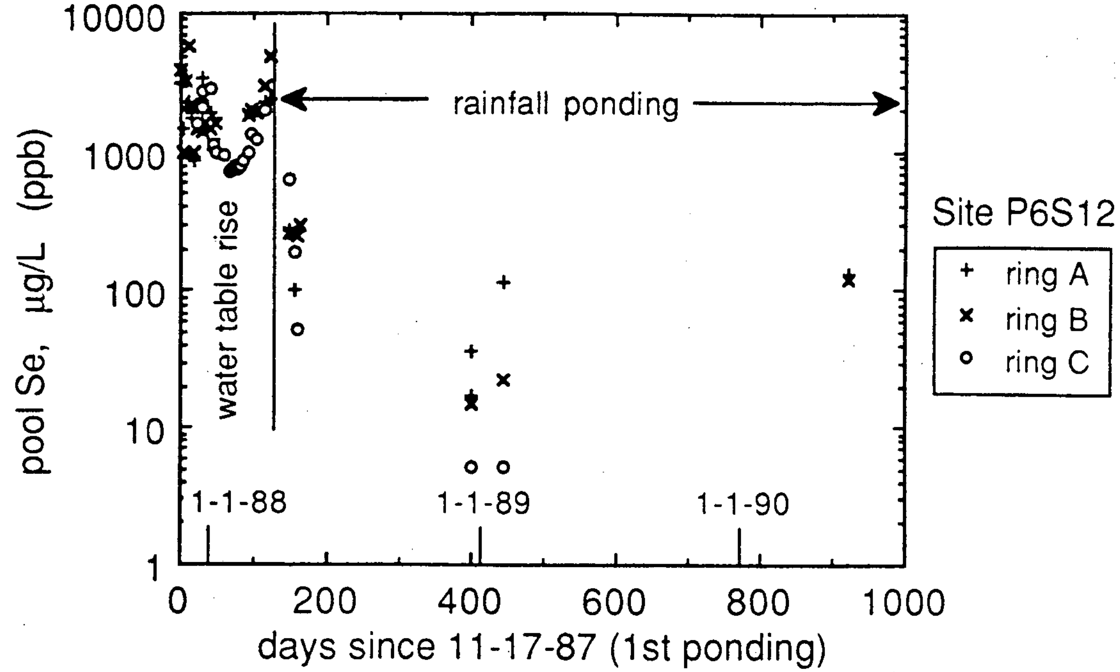

Figure 3.2a. Ephemeral pool water samples collected from the 1 ft (0.30 m) excavation test plot P6S12, surface water selenium concentrations.

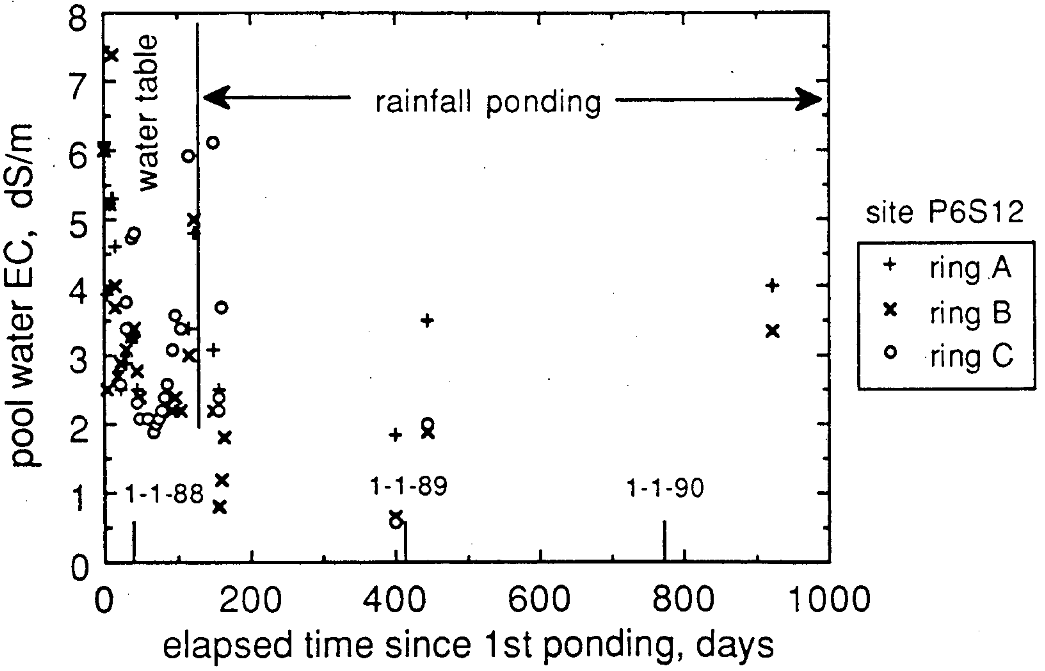

Figure 3.2b. Ephemeral pool water samples collected from the 1 ft (0.30 m) excavation test plot P6S12, surface water electrical conductivities.

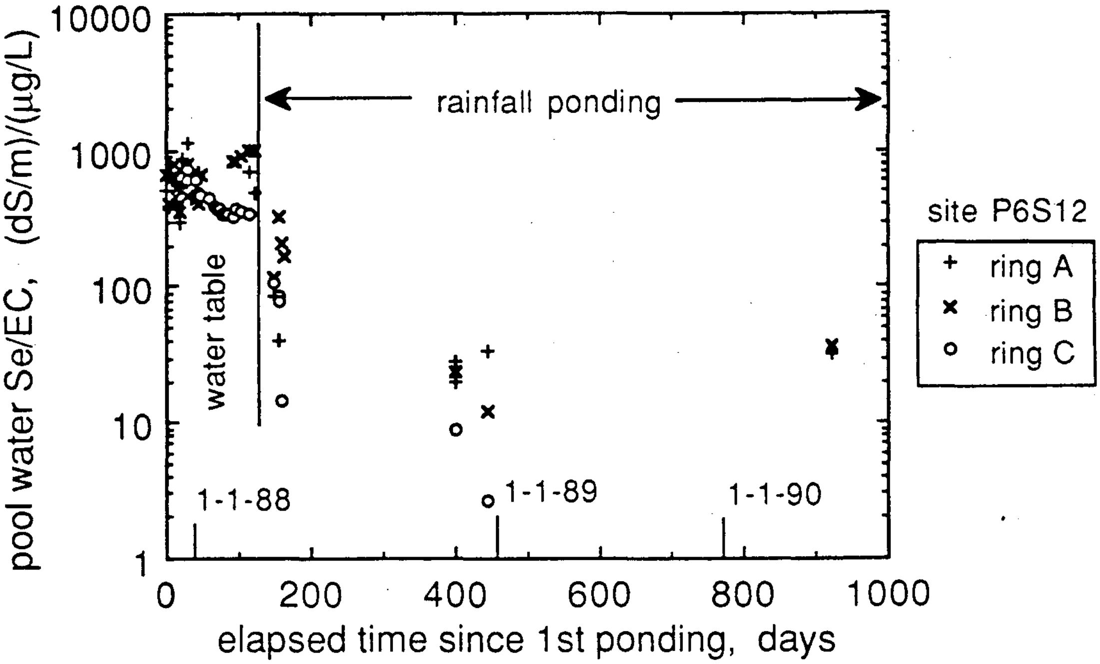

Figure 3.2c. Ephemeral pool water samples collected from the 1 ft (0.30 m) excavation test plot P6S12, ratios of selenium concentration to electrical conductivity of surface waters.

These selenium concentrations were on the order of 1000 µg/L. Such high concentrations are characteristic of the original Kesterson Reservoir surface soil pore waters, and are several times more concentrated with respect to selenium than the original drain waters which were disposed of at Kesterson. Very little rainfall ponding has occurred during the past 2 wet seasons at P6S12. The few surface water samples collected had selenium concentrations ranging from 5 to 118 µg/L. The average selenium concentration during the 1988-1989 season was 32 µg/L (7 samples). Only 2 surface water samples were collected at P6S12 during the 1989-1990 season. These were both collected on May 28, 1990, and had selenium concentrations of 122 and 132 µg/L. Neither sampling season provided large enough populations to make meaningful inferences concerning time trends. However, the data from both seasons do demonstrate the ability to dissolve relatively high selenium concentrations in rainfall pools. The data also indicate that rainfall-induced pools are generally less seleniferous than the pools formed from upwards displacement of pore waters.

EC data for the ponded waters collected at site P6S12 are summarized in Figure 3.2b. During the 1987-1988 wet season when ponding resulted from a watertable rise, EC values ranged from 1.9 up to 7.4 dS/m. The range of values reflected varying influences of rainfall dilution and evaporative reconcentration of dissolved salts. For pool samples collected during the 1988-1989 and 1989-1990 wet seasons, EC values ranged from 0.6 to 4.0 dS/m. Again, the small number of samples collected during these two more recent years prevent assessment of a time trend.

The ratio of selenium concentration to EC in the pool waters may provide an indication of the extent to which surface water selenium inventories are changing over time with respect to concentrations of major ions. A plot of this ratio for the P6S12 data discussed earlier is provided in Figure 3.2c. During the 1987-1988 season when displaced pore waters contributed significantly to ponding, the Se:EC ratio ranged from 300 to 1000 (µg/L)/(dS/m). This ratio fell to ranges of 10 to 300, and 3 to 40 (µg/L)/(dS/m) during the spring 1988 rainfall ponding, and the later 1988-1990 rainfall ponding events respectively. A loss of soluble selenium from pool waters relative to other salts is indicated by the trends in these data. Mechanisms consistent with this pattern are (1) volatilization, (2) net leaching of selenium deeper into the soil profile, and (3) a proportionally larger evaporative influx from the subsoil of major ions than selenium, relative to their surface soil inventories. The second effect could in principle operate even with a net upwards movement of major ions if the periodically leached selenium becomes reduced at depth. The expected greater increase of the near surface soluble selenium inventory as a result of reoxidation may obscure this effect.

The possibility that volatile losses could contribute significantly to the observed decline of the Se:EC ratio is indicated from a simple calculation. Assuming an initial water-soluble selenium inventory of 400 μg/(kg soil) in the upper 0.15 m of the test plot, with a soil bulk density of 1.5×10^3 kg m^{-3}, the soluble selenium inventory contained in a 0.15 m deep, 1 m^2 unit of soil will be 9×10^4 μg. An average volatilization rate of only 10 μg m^{-2} h^{-1} would deplete this initial inventory in about 1 year. It is recognized that other transformations are actually taking place simultaneously (such as oxidation as well as leaching of selenium), and that volatilization rates vary considerably. Nevertheless, the above considerations indicate that volatilization may be significant in diminishing the selenium inventory, even under unmanaged conditions, such that concentrations of soluble selenium in ephemeral pools will decline. It is emphasized that the above considerations are speculative, and that more complete data sets and longer elapsed times are needed to realistically assess long-term impacts of soil selenium redissolving in ephemeral pools. The only other sites at Kesterson Reservoir where the soil environment is suited for such observations are in Pond 10. Surface water data from these sites will be reviewed in the following section.

3.3. Ephemeral Pool Water Quality in a Small Cut-off Tributary to Mud Slough

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A small channel which appears to be a former tributary to Mud Slough is found near the west edge of Pond 10. Direct surface runoff into Mud Slough from this channel has ceased due to construction of the berm which encloses Pond 10. The remnant channel within Pond 10 is an environment conducive for both ephemeral pool formation and salt accumulation since both processes are favored in local depressions. Two monitoring sites were established in the channel in June 1987. One site, designated P10GC was instrumented with tensiometers and soil water samplers with minimal site disturbance. The second site, designated P10GS, was excavated to a depth of approximately 0.15m to remove the seleniferous saline crust, then equipped with soil water samplers and tensiometers. In both sites, soil water samplers were placed at 0.15, 0.30, 0.46, 0.61, 0.91 and 1.22 m depths. Tensiometers were placed at depths ranging from 0.08 to 1.22 m at site P10GC, and 0.15 to 0.76 m in P10GS. The excavated site was separated from the rest of the channel through the installation of sealed plywood barriers. Surface water samples have been collected during each wet season in this channel since March 1987. In this section, a summary of soil water selenium and salinity profile data from the P10GC and P10GS sites will be provided, followed by surface water quality information.

The P10GC and P10GS sites undergo extreme annual fluctuations associated with cycles of watertable height and precipitation. The watertable drops below 1.5 m of the channel bottom by the end of each summer, and rises above the soil (channel bottom) surface in late winter and early spring. The extent to which ponding at these sites results from the water table rise versus rainfall ponding is not clear. Tensiometer data indicate that there are periods where each factor is dominant. As is typical of many other closed depressions in the region, considerable salt accumulation has occurred at these sites. EC values ranging from 40 to 100 dS/m (increasing towards the soil surface) typify the 0.15 to 1.22 m depth intervals. At the surface, evaporites (primarily thenardite, with lesser amounts of gypsum and halite) are precipitated throughout most of the year (except during extensive ponding).

Along with fluctuations in soil moisture profiles, annual fluctuations in the soluble selenium profiles are also observed. A typical drying and wetting cycle in P10GC is depicted in Figures 3.3a,b. Similar trends are seen at site P10GS. Yearly cycles of profile-averaged soil solution selenium concentrations for both sites are depicted in Figure 3.4a. A number of sampling periods were not included in this plot because only incomplete profile samples were obtained. The P10GS data are generally associated with lower selenium concentrations. While this is consistent with the fact that the P10GS site had the highly seleniferous surface 0.15 m of soil removed, the observed differences are well within the range associated with spatial variability within a common environment. The annual profile-averaged selenium concentration maxima appear to occur in late summer to fall months. The late summer and early fall months correspond to times when the profile is expected to be most aerated, hence tending to be more oxiding, favoring soluble selenate in the soil profiles. The fall months also are associated with leaching of selenium from the salt crust into the regions at and below 0.15 m from the soil surface, thus potentially contributing to higher concentrations in the soil water samples. Local minima for profile-averaged selenium concentrations occur during spring months, when the soil profile is most water saturated, and probably least aerated.

Salinities of the P10GC and P10GS sites are summarized as times trends of profile-averaged EC values. Again, the P10GS profile-averaged values are lower than those for P10GC, for reasons of (1) removal of the salt crust upon excavation, and/or (2) spatial variability. A general pattern of increased salinity is apparent. It should be noted that actual salinities in these profiles have increased to a greater extent than indicated by the EC data. This greater increase is associated with increased proportions of salts remaining in solution as more neutral complexes with counterions, and precipitation from solution (most often associated with gypsum in this environment). EC data are not sensitive to either of these processes. It should be noted that the observed

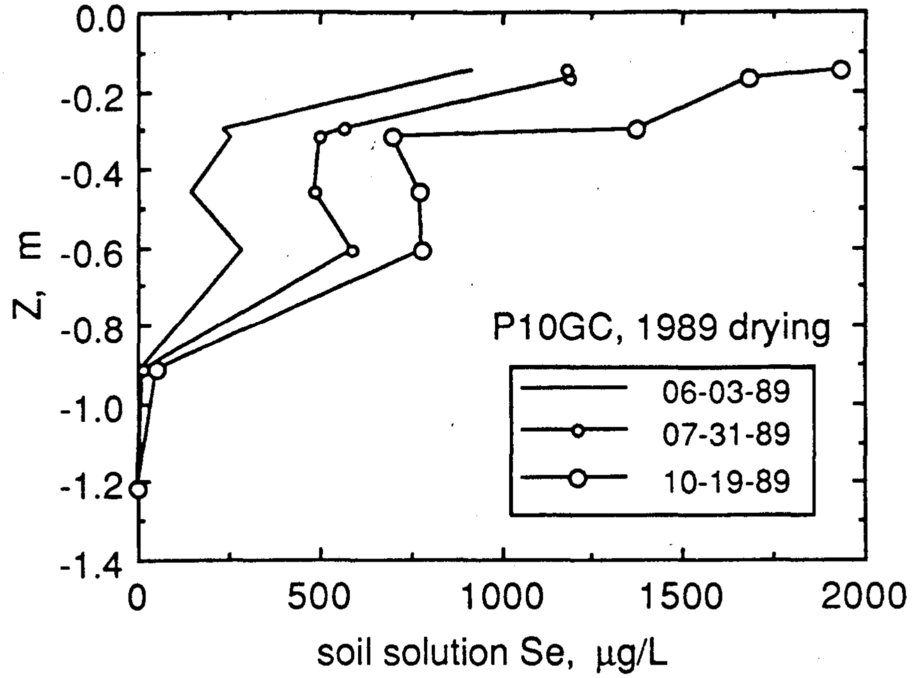

Figure 3.3a. Pond 10 channel site P10GC, 1989 soil solution profiles during the drying cycle.

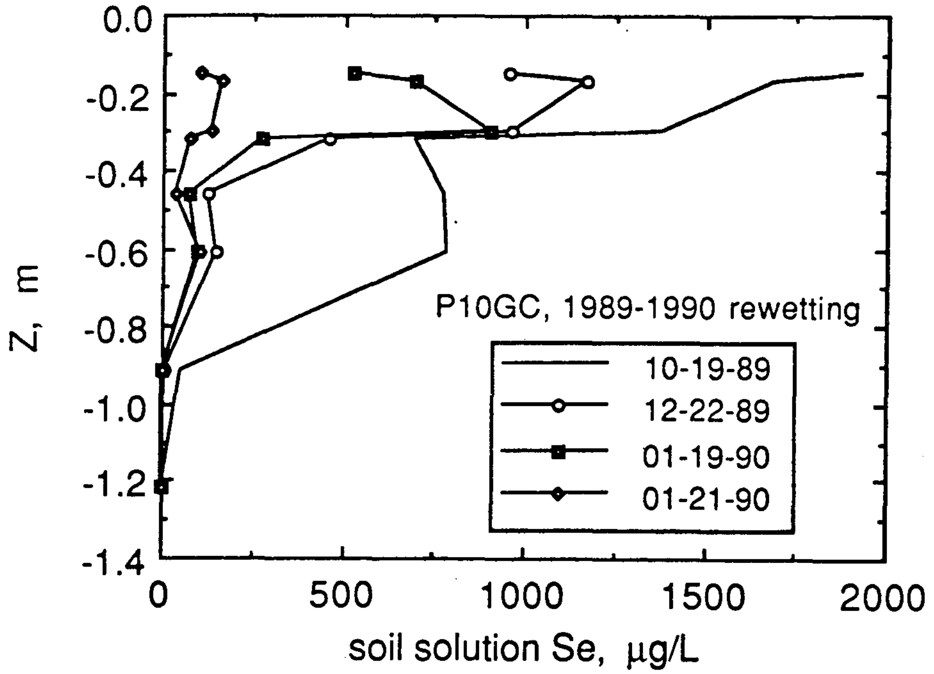

Figure 3.3b. Pond 10 channel site P10GC, 1989-1990 soil solution profiles during the wetting cycle.

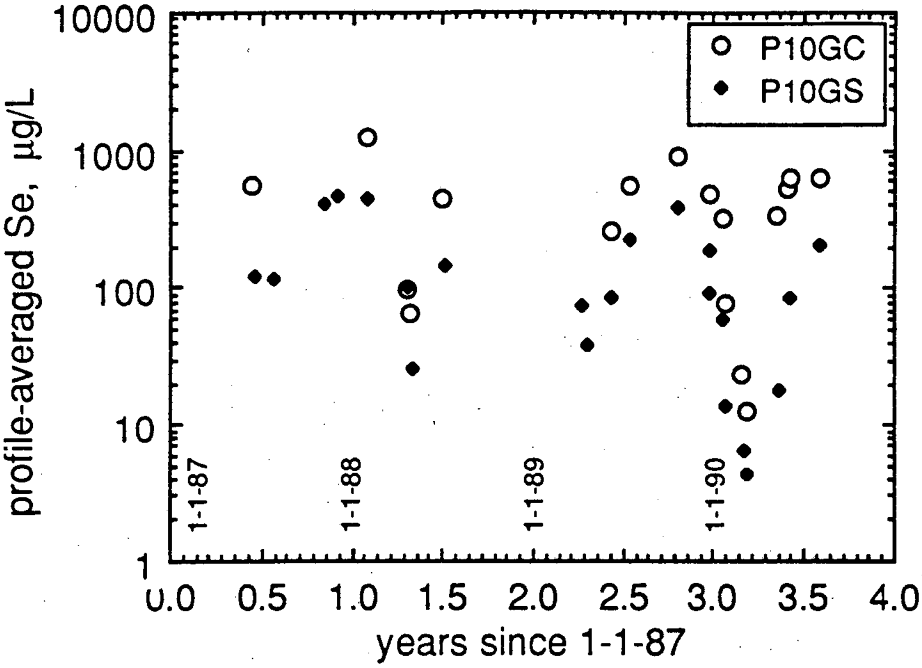

Figure 3.4a. Pond channel sites P10GC and P10GS, time series for profile averaged soil solution selenium concentrations.

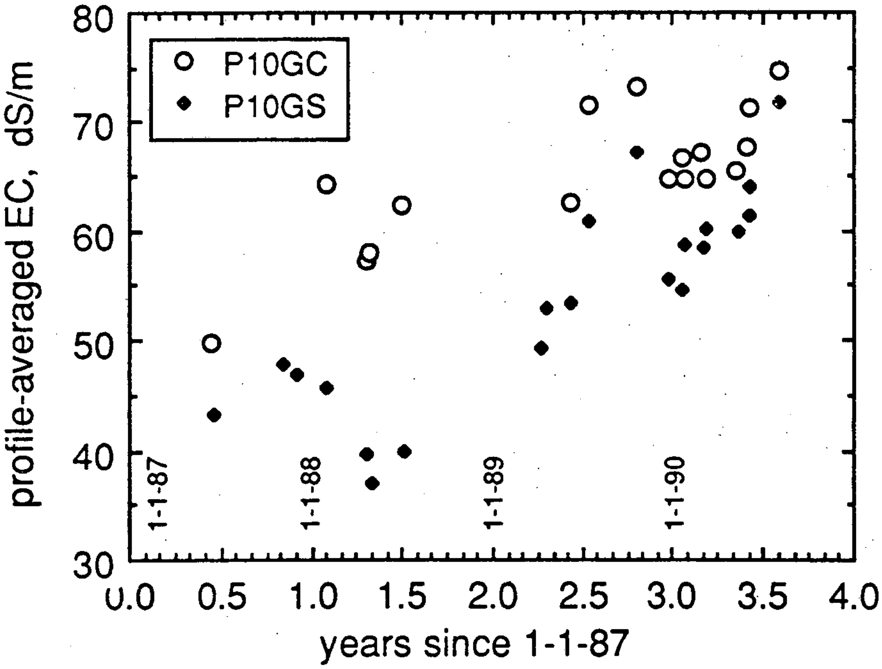

Figure 3.4b. Pond channel sites P10GC and P10GS, time series for profile averaged soil solution electrical conductivities.

increases in salinity at this and other sites has taken place during years of less than average rainfall. The extent to which above-average rainfall years are effective in desalinizing soil profiles at Kesterson Reservoir remains to be seen.

Ponding in the P10GC and P10GS sites has generally been observed at various times during the months of January through May. As noted earlier, ponding at these sites is caused by both the annual rise of the watertable and rainfall ponding. Selenium concentrations in ponded waters from both sites are summarized in Figure 3.5a. Concentrations of selenium in the ponded waters ranged from 10 up to 1700 μg/L. Selenium concentrations ranging between 100 and 1000 μg/L are common for these surface waters. Such high selenium concentrations are generally associated with environments where either the watertable rise has displaced seleniferous soil waters to the surface, or where rainfall has leached seleniferous evaporites off banks into localized depressions. Again, both mechanisms are in operation at the P10GC and P10GS sites. Note that these pool water selenium concentrations are considerably higher than those of the fill pools and the rainfall pools formed at site P6S12. The P10GS surface water selenium concentrations have generally been lower than those from site P10GC. Again, while this is reasonable from the perspective that the seleniferous surface has been removed at site P10GS, such differences in concentrations are also within the realm of observed spatial variability in apparently uniform regions.

The salinities of the ponding waters at the P10GC and P10GS sites also tend to be considerably higher than in other ephemeral pools. This is expected because of the significantly lower topographic position of these sites, which permits considerable evaporative accumulation of salts. The EC data from the surface waters collected at these sites is summarized in Figure 3.5b. The higher salinities are indicative of waters dominated by displaced soil water and dissolved salt crusts, while the few low EC values are indicative of newly ponded rainfall in which earlier stages of the rainfall event effectively leached surface salts into the soil profile.

Trends in pool water selenium and EC at the P10GC and P10GS sites are individually difficult to discern (Figures 3.5a,b). Plots of the ratio Se:EC at these sites however do exhibit a decline with time (Figure 3.5c). As noted in section 3.2, such a pattern may be indicative of a net

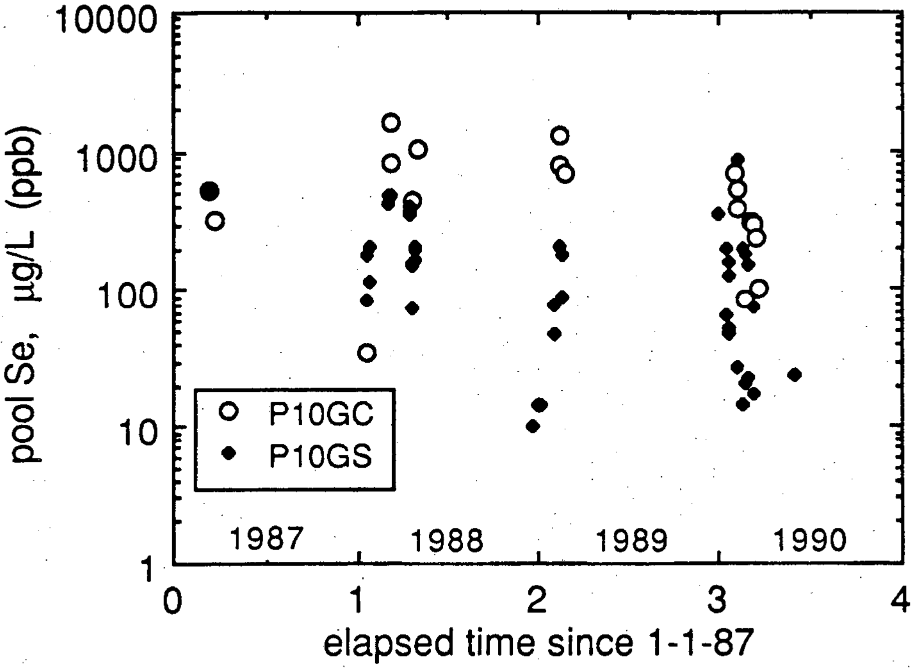

Figure 3.5a. Pond 10 channel sites P10GC and P10GS, ephemeral pool water selenium concentrations.

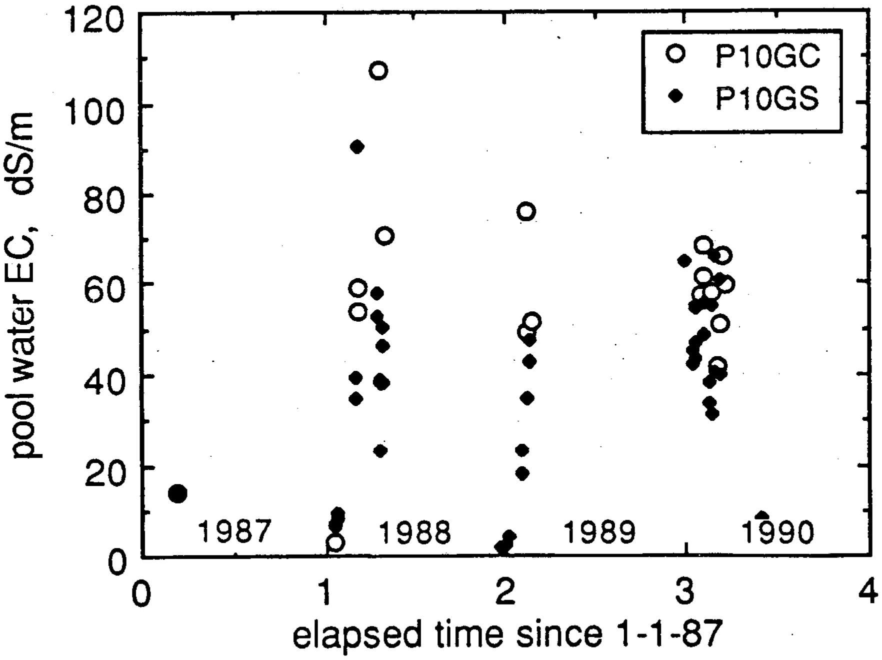

Figure 3.5b. Pond 10 channel sites P10GC and P10GS, ephemeral pool water electrical conductivities.

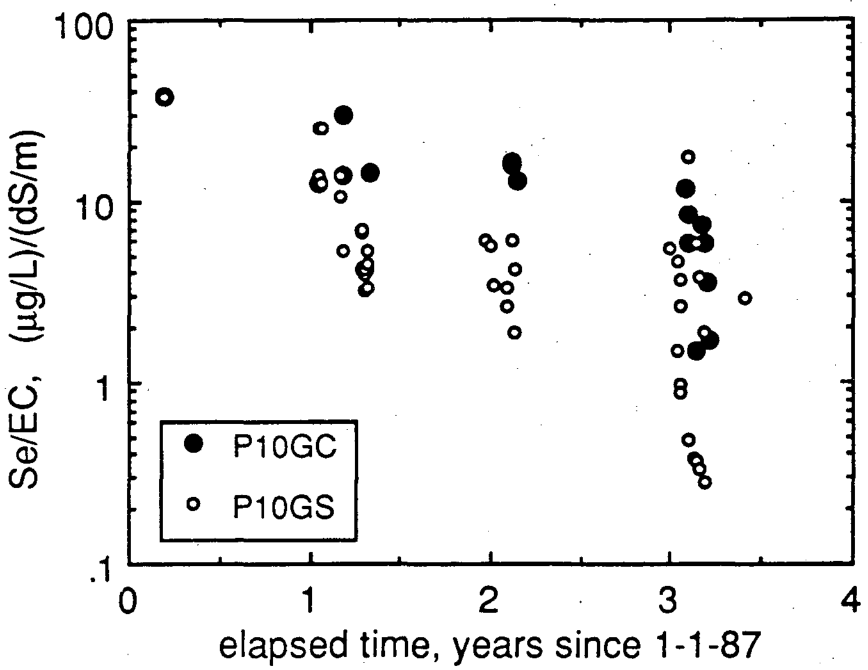

Figure 3.5c. Pond 10 channel sites P10GC and P10GS, ratios of selenium concentration to electrical conductivity in pool waters.

loss of selenium from the uppermost portion of the soil profile, through a combination of volatilization and deeper leaching, and may also be indicative of increased salinization (at a greater rate than increases in soluble selenium concentrations) of the surface. The extremely high salinities of these Pond 10 sites are likely to limit the effectiveness of microbial selenium volatilization. The latter process of greater increases in salinity relative to selenium for evaporative fluxes is likely to be more significant in the excavated P10GS site where the original salt crust has been removed.

3.4. Selenium and Salinity in Various Surface Waters near Kesterson Reservoir

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In order to gain a perspective on the relative magnitudes of selenium concentrations in Kesterson Reservoir ephemeral pools, samples from various surface water features nearby Kesterson Reservoir have occasionally been collected over the past 2 years. The sample collections were initiated informally, and conducted primarily when planned work at Kesterson Reservoir was completed. Therefore, collections did not follow a prescribed schedule. Collection sites included Mud Slough along the west side of Kesterson Reservoir, the Fremont Canal southwest of Kesterson Reservoir, Salt Slough near the San Luis National Wildlife Refuge, the San Luis Canal at various points between the San Luis National Wildlife Refuge and Highway 152, and the San Luis Drain at various points between Kesterson Reservoir and Highway 152. It is emphasized that the sample set is small, yet replicate samples collected at intervals spanning several months have been obtained. Thus it is believed that the ranges of selenium and EC values obtained in this set of samples do provide an indication of representative ranges of these water quality parameters for the sampled systems. All of these sites are continuous waterways which are water-filled to various levels, hence not representative of regional ephemeral pool environments. While these off-site surface water features are not intended to represent local ephemeral pool environments, both the extensiveness of these surface water features and their essentially continuous availability for use by wildlife suggest that comparisons of water quality in these systems and those of Kesterson Reservoir ephemeral pools would be of interest.

Information concerning sampling site locations, dates, selenium concentrations and electrical conductivities are provided in Table 3.1. The selenium concentration and EC data are also summarized in Figures 3.6a and 3.6b respectively. The data from these off-site surface water systems indicate that these sites often had selenium concentrations in excess of 10 μg/L. In fact, the

Table 3.1. Off-site surface water sampling locations, dates, selenium concentrations and electrical conductivities

System	Site	Date	EC. dS/m	Se4 µg/L (ppb)	Total Se µg/L (ppb)
San Luis Canal	inflow into Los Banos W.A.	5/28/90	2.74	1.1	35.7
	at Wolfsen Rd.	6/25/90	3.21	1.2	23.0
	at Wolfsen Rd.	6/25/90	ox*	ox*	24.7
	at LBWA, rep. 1	9/1/90	3.93	2.1	57.5
	at LBWA, rep. 2	9/1/90	3.78	1.7	55.7
	at Wolfsen Rd., rep. 1	9/1/90	3.07	3.4	45.9
	at Wolfsen Rd., rep. 2	9/1/90	3.07	3.2	45.5
Fremont Canal	SW of KR Pond 3	1/27/89	3.3	1.5	39.4
	near KR Pond 4	2/18/89	3.1	0.6	6.2
	near KR Pond 3	4/14/89	3.8	3.8	9.1
	SW of KR Pond 3	4/14/90	3.33	3.5	13.2
	SW of KR Pond 3, rep. 1	9/1/90	2.91	5.2	55.9
	SW of KR Pond 3, rep. 2	9/1/90	2.91	5.3	54.7
Mud Slough	at Gun Club Road	1/27/89	3	1.0	1.0
	at KR Pond 12	2/4/89	3.39	0.6	1.4
	at KR Pond 12	4/14/89	6.4	1.2	2.4
	W. of KR Pond 8	1/15/90	2.38	0.3	2.2
	W. of KR Pond 10	8/2/90	2.68	3.2	31.0
	W. of KR Pond 8	9/1/90	3	5.6	53.0
Salt Slough	at San Luis N.W.R.	5/28/90	1.8	0.5	13.1
	at SLNWR	6/25/90	2.04	0.2	8.3
	at SLNWR	6/25/90	ox*	ox*	11.4
San Luis Drain	at KR Pond 9	1/27/89	22.8	2.4	7.5
	at Gun Club Road	4/14/89	12.2	5.5	8.5
	at KR P12	4/23/89	23.1	3.0	6.6
	at KR P7	1/15/90	38.1	8.2	13.3
	at Wolfsen Rd.	5/28/90	12.8	2.6	4.1
	at Wolfsen Rd.	6/25/90	14.5	1.2	23.0
	at Wolfsen Rd.	6/25/90	ox*	ox*	24.7
	at Wolfsen Rd.	9/1/90	21	3.9	6.1
	W. of LBWA, rep. 1	9/1/90	31.1	7.3	10.2
	W. of LBWA, rep. 2	9/1/90	31.1	7.5	9.0
	at Hwy 152, rep. 1	9/1/90	15.7	1.7	2.8
	at Hwy 152, rep. 2	9/1/90	15.6	1.6	2.6

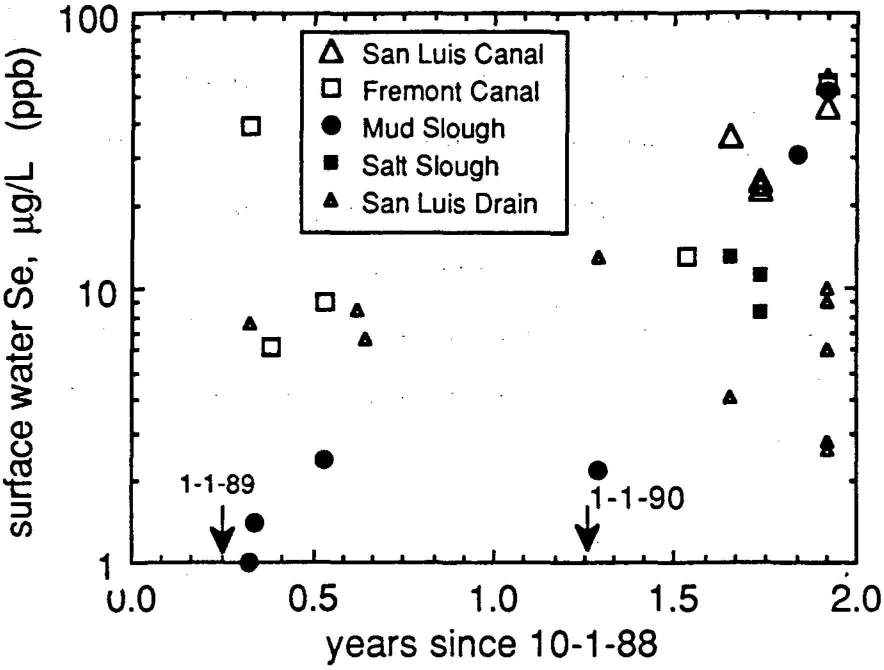

Figure 3.6a. Surface water samples from sites in the vicinity of Kesterson Reservoir, selenium concentrations in waters.

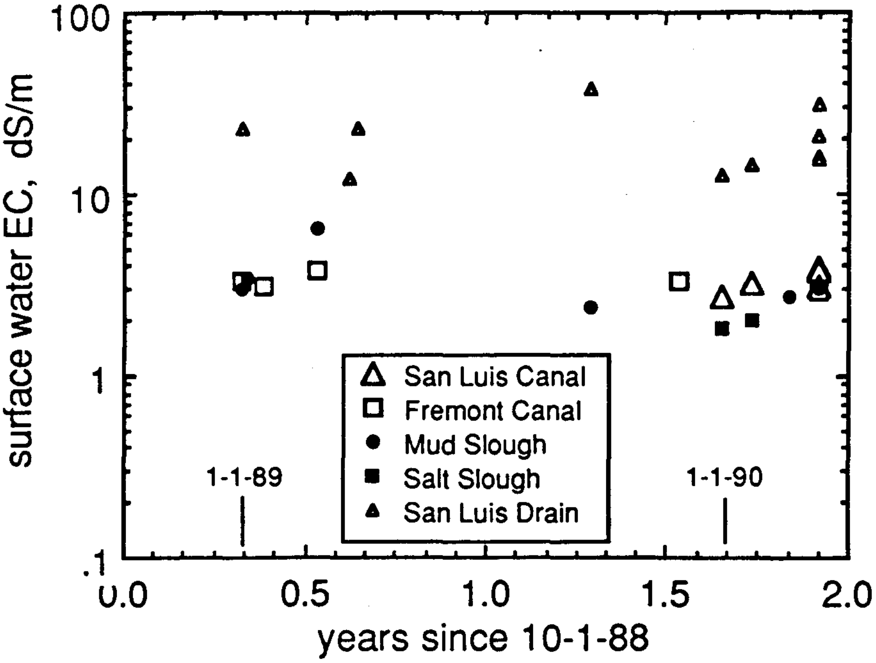

Figure 3.6b. Surface water samples from sites in the vicinity of Kesterson Reservoir, electrical conductivities of waters.

San Luis Drain, formerly used to convey seleniferous drain waters to Kesterson Reservoir, is now often less seleniferous than the other waterways. The salinities of the San Luis Drain water samples on the other hand remain quite high. It is of interest to note that the ephemeral pool waters sampled from fill sites during the past two years are generally cleaner with respect to selenium and salts than many of the major local surface water features surrounding Kesterson Reservoir. However, the extent to which future upwards movement of selenium and salts into the fill will be reflected in future selenium and salt concentrations in pools formed over filled areas remains to be seen.

3.5. Laboratory Experiments on Selenium in Ephemeral Pools

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The rise of a shallow watertable through a seleniferous soil can result in ephemeral pool formation with selenium concentrations in the surface waters which pose a hazard to wildlife. Surface soil depressions within Kesterson Reservoir, California provided an environment conducive to such a process. Monitoring of both excavated and unexcavated depressions (Sections 3.2 and 3.3 respectively) demonstrated the potential for selenium concentrations in excess of 1000 $\mu g\ L^{-1}$ to occur in ephemeral pools at Kesterson Reservoir. The most seleniferous ephemeral pool waters formed as a result of upwards displacement of soil water by the rise of the shallow watertable. In such pools, the composition of the ponded waters was similar to that of the near-surface soil solution, with moderate dilution of all solutes due to rainfall, and variable depletion of dissolved selenium due to selenate reduction. Selenate (Se(VI)) commonly comprised the largest fraction (80 ±20%) of the soil solution selenium inventory, with the remainder of the dissolved selenium inventory composed primarily of selenite (Se(IV)) and to a lesser extent, various unidentified organic selenium compounds (Weres et al., 1989b; Long et al., 1990). It should be noted that the dissolved selenium inventory in Kesterson Reservoir soils generally amounted to only about 5% to 10% of the total soil selenium (Weres et al., 1989b).

While it was clear from the field observations discussed earlier that the shallow water table rise which displaced seleniferous soil water to the surface was responsible for the highly seleniferous ephemeral pools, the influence of numerous parameters on this process remained to be evaluated. In this section, results of laboratory experiments designed to assist in understanding field observations related to ephemeral pool selenium concentrations which arise solely from shallow watertable rise are presented. While the movement of selenium through soils is dependent on a large number of variables, a subset of these was tested in this study. The variables selected in this study include the depth of the soil interval, the rate of soil water (groundwater) rise and temperature. Numerous other important factors such as the selenium inventory (soluble, adsorbed and various insoluble forms), organic matter content and composition, soil texture and mineralogy, and soil solution composition are clearly included in the variable of soil depth, but were not independently varied in this work. Numerous studies have demonstrated the central role which the redox status of soils play in controlling microbially mediated selenate transformations, and consequently the transport of selenium (e.g. Geering et al., 1968; Ahlrichs and Hossner, 1987; Elrashidi et al., 1987; Neal et al., 1987; Alemi et al., 1988a,b; Deverel and Millard, 1988; Fujii et al., 1988; Oremland et al., 1989; and Masscheleyn et al., 1990). The rate of watertable rise was expected to have a significant influence on selenium concentrations in waters which emerge at the soil surface since the time-dependent process of Se(VI) reduction competes with Se(VI) transport. A faster rate of flow (watertable rise) will allow less time for Se(VI) reduction to Se(IV), and permit more of the former to be carried with the bulk flow of water towards the soil surface. Conversely, a slower rate of flow permits Se(VI) reduction to proceed to a greater extent for two principle reasons. First, the longer residence time of solutes (including Se(VI)) in the soil permits reactions in general to proceed further. Secondly, the slower rate of watertable rise permits more complete water saturation (air displacement) in the soil, and more complete removal of oxygen (both through displacement and respiration). Thus, the reducing conditions necessary for immobilizing selenium in the soil are favored with low flow rates. As with most reactions, a strong temperature-dependence is also expected.

3.5.1. Materials and Methods

The Pond 1 site from which the soil samples were collected was largely unvegetated, and was in this respect typical of many areas of Kesterson Reservoir which were subjected to alternating periods of flooding with drain waters and subsequent drying. This soil is mapped under the Turlock series (Albic Natraqualf) in a recent (draft) soil survey. The previous flooding history of Pond 1 is provided in Long et al. (1990). Seleniferous drain waters were periodically ponded from approximately 1981 to 1986. During most of the subsequent period from October 1986 to

April 1988, Pond 1 was intentionally flooded with saline, nonseleniferous waters. Two surface soil intervals were sampled from the southwest corner of Pond 1 on June 17, 1988. At the time of sampling, two months had elapsed since the most recent occurrence of ponding (with nonseleniferous waters) at the site. The 0.00-0.15 m surface soil and 0.15-0.30 m subsurface depth intervals were sampled from a projected surface area of approximately 0.10 m^2. In addition, the salt crust present on the soil surface was sampled separately. The soil samples were homogenized by coarse crushing and passed through a 4.75 mm sieve. This procedure for soil preparation was selected to provide homogeneous subsamples for soil columns and for water-extractions of the soil. Preservation of some micropore structure with this coarse crushing may be an advantage from the perspective of constructing laboratory columns which preserve some features of the field setting. Various soil physical and chemical properties associated with the sampled intervals are presented in Table 3.2.

The initial water-soluble selenium contents of the soils were determined from water extracts of duplicate subsamples. 20 g soil samples were magnetically stirred in 1:5 (soil:water mass ratio) suspensions for 1 h. Later tests demonstrated the equivalence of extracted selenium obtained from this method and from the more commonly used reciprocating shaker. The extract solutions were centrifuged and filtered (0.45 μm). Selenium concentrations were measured by hydride generation atomic absorption spectroscopy (HGAAS), utilizing digestion procedures outlined in Weres et al., 1989a.

The homogenized soils were packed in 0.034 m inner diameter, 0.24 m long sections of PVC pipe. The vertically oriented columns were capped on the bottom, and open to the atmosphere on the top. A rubber septum stopper was fitted to each bottom endcap to facilitate periodic injection of prescribed quantities of simulated soil water. A stainless steel wire screen covered with filter paper was placed inside each endcap to provide a uniform distribution of water across the bottom end of the soil packings. Platinum electrodes were imbedded into the soil columns at distances of 0.030, 0.085 and 0.140 m from the bottom of each soil core. These electrodes were used to measure redox potentials during the course of the experiment. Twenty-four columns were constructed to provide duplicates for twelve configurations to be described.

Three different soil environments were studied with these columns. In the first group, the 0.00 to 0.15 m soil interval was used. The prehomogenized soil was packed into eight identical columns to an equivalent dry bulk density of 1.03 mg m^{-3}, and a height of 0.15 m. Over the surface of each of these columns, 2.29 g of the previously separated salt crust was applied. This application was equivalent to the original local field salt crust surface density of 2.5 kg m^{-2}. The second group of eight soil columns were identical to the first set, with the exception that the salt crust was not included. The third group of eight columns contained soil excavated from a depth interval of 0.15 to 0.30 m. No salt crust was included in the third set. This last set was included to simulate ephemeral pool formation under conditions where the upper 0.15 m of Kesterson Reservoir soils have been removed. Such a procedure for selenium removal was given serious consideration as a site cleanup method, and was referred to as the Onsite Disposal Plan (ODP) (USBR, 1986a; Tokunaga and Benson, 1990 manuscript). The rationale for excavation as a cleanup method was provided by the fact that approximately 75% of the selenium inventory resided within the uppermost 0.15 m of the Kesterson Reservoir soils. This fact was coupled with the opinion that the selenium concentrations of < 4 mg kg^{-1} in the residual (post-excavation) soils would result in a considerable decrease in wildlife exposure to selenium relative to unexcavated conditions. Properties of the soil columns are included in Table 3.2.

To examine the influence of various rates of watertable rise, each column was injected through the rubber septum with a quantity of water to result in a daily rise in the watertable at one of three different rates: 3, 10 and 30 mm d^{-1}. These rates are equivalent to average pore water velocities rather than darcy velocities since injection rates were based on the initial air-filled porosity. The intermediate rate of 10 mm d^{-1} corresponds roughly to the maximum rate of annual watertable rise at Kesterson Reservoir. At the Reservoir, peak rates of watertable rise generally occur during the months of October and November, in response to intentional flooding of neighboring wetlands. The annual maximum extent of watertable rise commonly occurs during the months of January through March. It should be noted that upon reaching the soil surface, the rate of pond surface rise is, at most, about 50% of the rate of the imposed watertable rise due to the equivalent air-filled porosity being equal to unity above the pond surface. Evaporation would further diminish the actual rates of watertable rise. The injection water was prepared to provide a composition with respect to the major ions which approximated Kesterson Reservoir soil solutions, with the exclusion of selenium. The exclusion of selenium from the inflow solution permitted unambiguously assigning any selenium in ponding waters to have originated from the soil. The composition of the injection water is given in Table 3.3.

To examine the effect of temperature on selenium transport to the soil surface, a set of columns was stored at 5°C and injected with water at the same temperature. The 5°C columns were all composed of the 0.00 - 0.15 m soil interval (without salt crust), and were run at the three aforementioned flow rates.

Various combinations of these three variables (soil type, temperature, and watertable rise rate) were tested in duplicate columns to decrease the impact of experimental variability and error.

Redox potential within the columns were measured daily. Contact between the soil solution and the calomel reference electrode was achieved through a solution-filled line connected to the column inlet via a hypodermic needle. The line solution was of the same composition as the injected water, and was connected to the column only during the brief periods needed to take redox potential readings.

Subsequent to the emergence of water at the upper surface of the soil columns, small subsamples of the ponded water (approximately 5 g) were periodically removed with a syringe and analysed for selenium and salinity (electrical conductivity, EC). selenium concentrations were measured by HGAAS as previously noted. EC measurements were temperature-corrected to 25°C.

3.5.2. Results and Discussion

It will be convenient to consider effects of the variables of soil composition, rate of watert-

Table 3.2. Various physical and chemical properties of the Kesterson Reservoir soil samples used in the experiments. Soils were sampled at the southwest corner of Pond 1 on June 17, 1988.

Field depth	Units m	Surface soil 0.00-0.15	Surface + crust 0.00-0.15	Subsurface 0.15-0.30
Water soluble selenium	µg/kg	958 ± 48	1072 ± 54	117 ± 6
	µg/column	166.9 ± 8.4	187.1 ± 9.4	20.6 ± 1.0
Percent Se(IV)	% of soluble	26%	24%	4%
Percent Se(VI)	% of soluble	≈74%	≈76%	≈96%
Temperature	°C	5°,≈25°	≈25°	≈25°
Initial soil moisture	kg/kg	0.0395	0.0239	0.0239
Solid phase density	Mg/m^3	2.76	2.76	2.69
Dry bulk density	Mg/m^3	1.22	1.21	1.22
Total porosity	m^3/m^3	0.56	0.56	0.55
Initial gas porosity	m^3/m^3	0.51	0.53	0.52
pH(1:5 extract)		6.8	6.8	7.2

Table 3.3. Composition of the solution injected into the bottoms of the columns.

Na+	$mol(\pm)/m^3$	167
Ca2+	"	27
Mg2+	"	48
K+	"	0
SO4 2-	"	167
Cl-	"	75
SeO3 2-	"	0
SeO4 2-	"	0
pH		8.0
EC	S/m	1.81

able rise, and temperature individually. The most complete data set was obtained on the columns subjected to a watertable rise rate of 10 mm d^{-1}. A sparse sampling frequency and leakage from one of the columns compromised the data from the 30 mm d^{-1} columns. At the slowest watertable rise rate (3 mm d^{-1}), evaporation from the ponded surface severely minimized the effective height of ponding. Consequently, in addressing the effects of soil composition and temperature, most of the discussion will focus on the columns with the intermediate rate of watertable rise (10 mm d^{-1}).

Before proceeding to the results, it will be useful to comment on the actual rates of pond surface advance. As noted earlier, in the absence of evaporation, the ponded surfaces would advance at approximately 50% of the imposed watertable rise rates. Thus, the pond surfaces would rise at 1.5, 5 and 15 mm d^{-1} in the absence of evaporation. Evaporation rates from the room temperature columns were measured to be 0.9 ± 0.2 mm d^{-1}, while the 5°C pond evaporation rates were measured to be 0.33 ± 0.05 mm d^{-1}. Thus the actual rates of pond surface rise were 0.6, 4.1 and 14.1 mm d^{-1} (all within $\pm$ 0.2 mm d^{-1}) for the room temperature columns. The corresponding pond surface advance rates in the 5°C columns were 1.2, 4.7 and 14.7 mm d^{-1} (all within $\pm$ 0.05 mm d^{-1}).

The effect of the soil composition with respect to water-soluble selenium concentrations in ponded waters of the 10 mm d^{-1} water table rise columns ($\approx$25°C) is shown in Figure 3.7a,b. Figure 3.7a summarizes instantaneous ponded water selenium concentrations as a function of depth of ponding. The initial selenium concentration maxima observed in all cases were due to the dominating effect of advective transport of selenium to the surface in the rising wetting front, followed by inflows of less selenium-concentrated soil solutions. Lower selenium concentrations in the subsequent soil solutions resulted from both preleaching of the local soil water-soluble selenium inventory by earlier waters, and by the development of reducing conditions within the columns. Similar trends in salinity of the ponded waters are indicated by the EC data shown in Figures 3.11a,b. The movement of selenium and major ions into the ponded waters does differ in at least two important ways. First, the initially soluble selenium is subject to removal from solu-

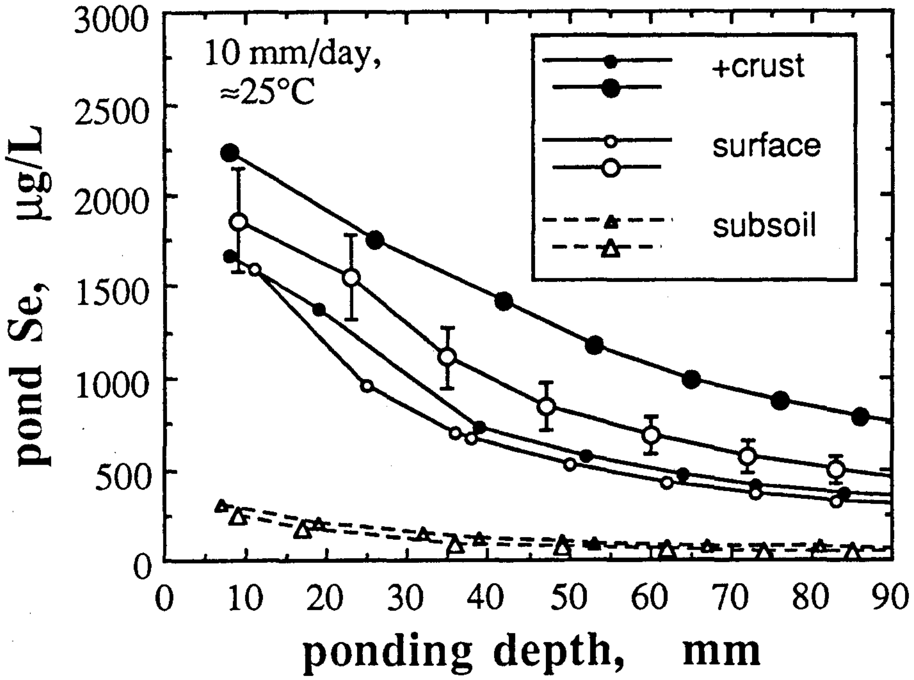

Figure 3.7a. Se in ponded waters of replicate 10 mm/day columns (25°C). Instantaneous pond Se concentrations in crusted, uncrusted and subsoil columns.

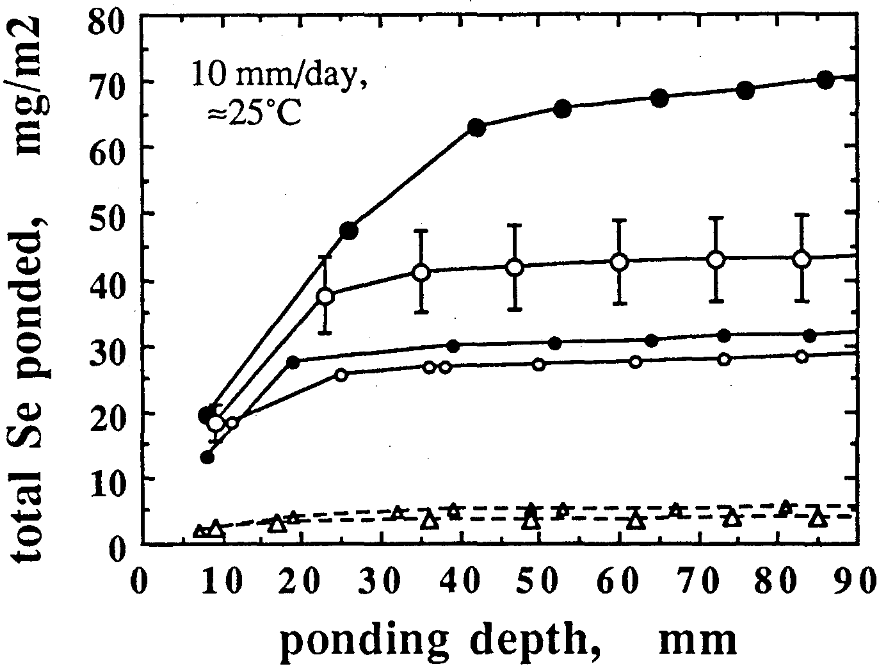

Figure 3.7b. Cumulative selenium leached from ponded waters in replicate columns with a 10 mm/day flow rate. See Figure 3.7a for legends corresponding to crusted, uncrusted and subsoil.

tion through reduction and adsorption or precipitation. Second, under the experimental conditions a substantial, steady supply of major ions is provided in the supply water, while no additional selenium is introduced. Another selenium removal mechanism is provided by volatile losses (e.g. Doran and Alexander, 1977; Cook and Bruland, 1987; and Frankenberger and Karlson, 1989). While this pathway was not monitored, volatile selenium emission rates were expected to be minor (relative to the selenium in ponded waters) over the course of this experiment, especially due to the ponded conditions.

At any stage in the ponding process, roughly an order of magnitude higher selenium concentration was observed in the columns packed with surface soils (with or without the crust) compared with the subsurface soils. Slightly higher average selenium concentrations were observed with the crusted surface soils than the noncrusted surface soils. The ratios of selenium concentrations in waters overlying the crusted surface, uncrusted surface and subsurface soils at any given ponding depth fall in the ranking of (1):(0.7):(0.1) when replicate columns are averaged. These relative concentrations are similar to the corresponding ranking of the initial water-extractable selenium inventories, (1):(0.89):(0.12) (obtainable from Table 3.2). Quantitative agreement of the observed and water-extractable ratios was not expected when normalizations were performed relative to the crusted surface soils. This is because the uncrusted surface and subsurface soil columns were initially homogeneous with respect to selenium distribution, whereas the crusted surface soils include an exceptionally high soluble selenium inventory at the soil surface. Under the conditions of the experiment, the selenium inventory in the crust is not subject to reductive immobilization to the same extent as selenium originating deeper in the columns. Thus, soluble selenium initially in the crust is expected to have a greater contribution to the pond water selenium than an equivalent amount originating from deeper in the soil profile. This expected behavior was only observed in one of the duplicate crusted columns. On the other hand, comparison of the uncrusted surface and subsurface soil columns is more justifiable since both are initially homogeneous with respect to selenium distribution. The ratio of pond selenium concentrations in this case yields an average value of (1):(0.14) (surface:subsurface) at any given ponding depth. The corresponding ratio of water extractable selenium is (1):(0.13). However, large relative percent differences within duplicates, some of which reached 50%, limit interpretations to a qualitative nature. While other variables including microbial respiration rate, organic matter content and mineralogy were not identical in the surface and subsurface soils, the results indicate that the initial soluble selenium inventories in these two soils was the dominant variable under the given conditions (prescribed flow rate, temperature and column length). The relatively small differences in the behavior of the surface soil columns with and without inclusion of the salt crust is probably partially a reflection of the flooding with nonseleniferous waters in Pond 1 prior to collection of the soils. Since only minor differences were observed in the average behavior of the surface soils with and without crusts, only the uncrusted soils will be addressed in the remainder of this discussion for the sake of brevity.

The effects of the rate of watertable rise on pond selenium concentrations are summarized in Figures 3.8a,b, and Figures 3.9a,b. In Figures 3.8a,b, selenium concentrations in the ponded waters are presented in the same manner as in Figure 3.7a. In Figures 3.9a,b, the ponded selenium is expressed as a fraction of the water-extracted selenium within each column. In general, higher rates of watertable rise resulted in higher concentrations of selenium in the ponded waters. The selenium eventually transported into the ponded waters comprised from 5% up to 60% of the initial water-extractable selenium inventories. The correlation between watertable rise rates and selenium transported into ponding waters was expected for reasons previously discussed. It is expected that with field soils of larger characteristic aggregate size, the flow-rate dependence of selenium transport will be significantly affected by kinetic limitations associated with mixing of micropore and macropore soil solutions. This limitation was moderated in the present experiment by the small aggregate dimensions (≤4.75mm).

It is worth noting that the surface water quality goal for wildlife of 2 to 5 $\mu g\,L^{-1}$ is exceeded under all experimental conditions. This aspect of selenium transport in Kesterson Reservoir soils indicated that ephemeral pool formation due to the rise of the shallow watertable would certainly expose wildlife to high concentrations of selenium. Furthermore, the fact that

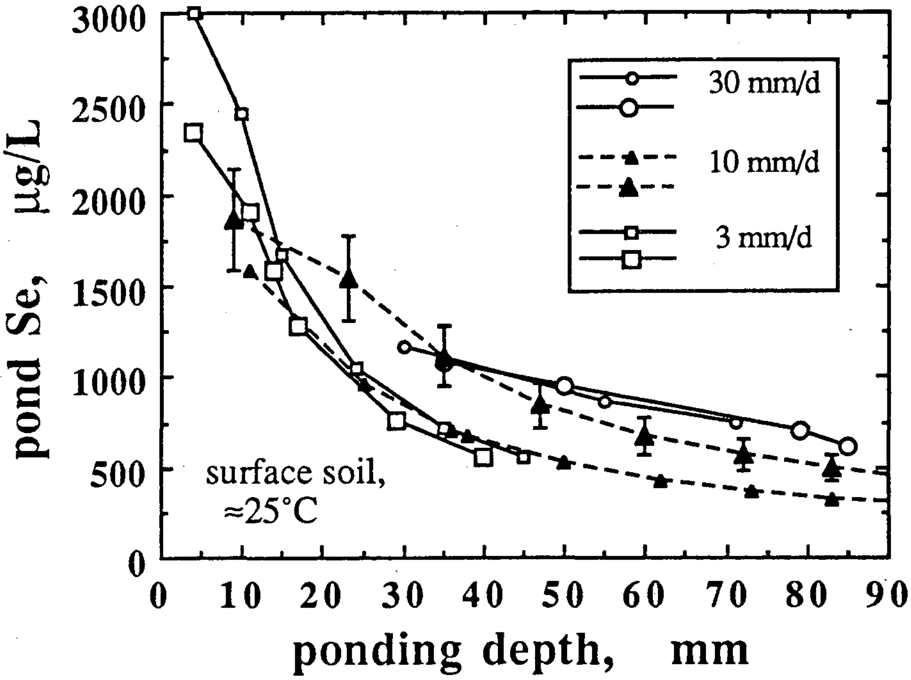

Figure 3.8a. Instantaneous Se concentrations in pond waters resulting from water table rise rates of 3, 10 and 30 mm d^{-1} (replicate columns, all at ≈25°C) on the surface soil (without crust).

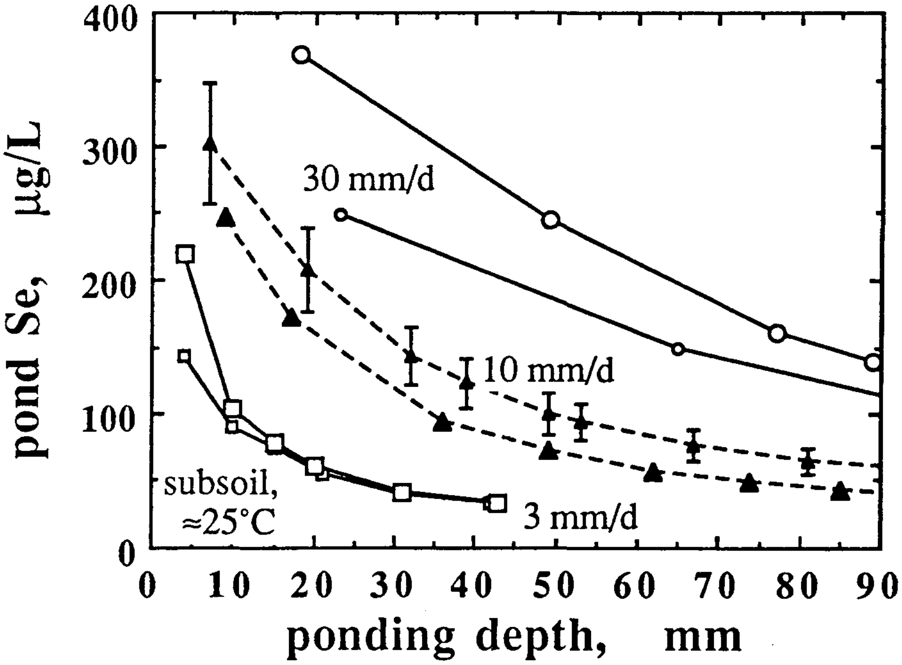

Figure 3.8b. Instantaneous Se concentrations in pond waters resulting from water table rise rates of 3, 10 and 30 mm d^{-1} (replicate columns, all at ≈25°C) on the subsoil.

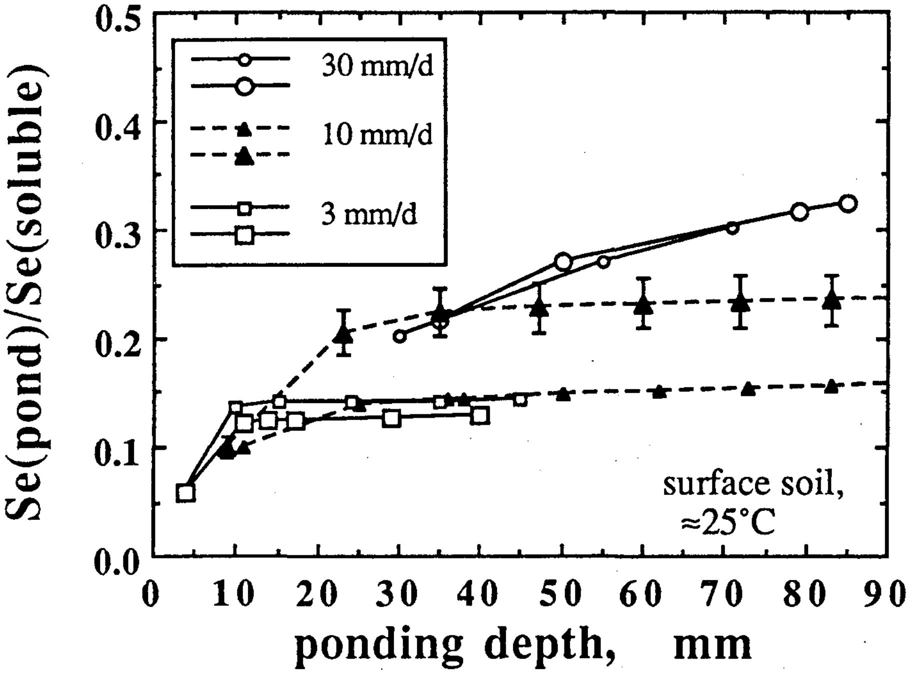

Figure 3.9a. Cumulative Se in ponded waters on surface soil (without crust) relative to the initial water-soluble Se inventory in the soils, at 3, 10 and 30 mm d^{-1} water table rise rates (replicate columns, all at ≈25°C).

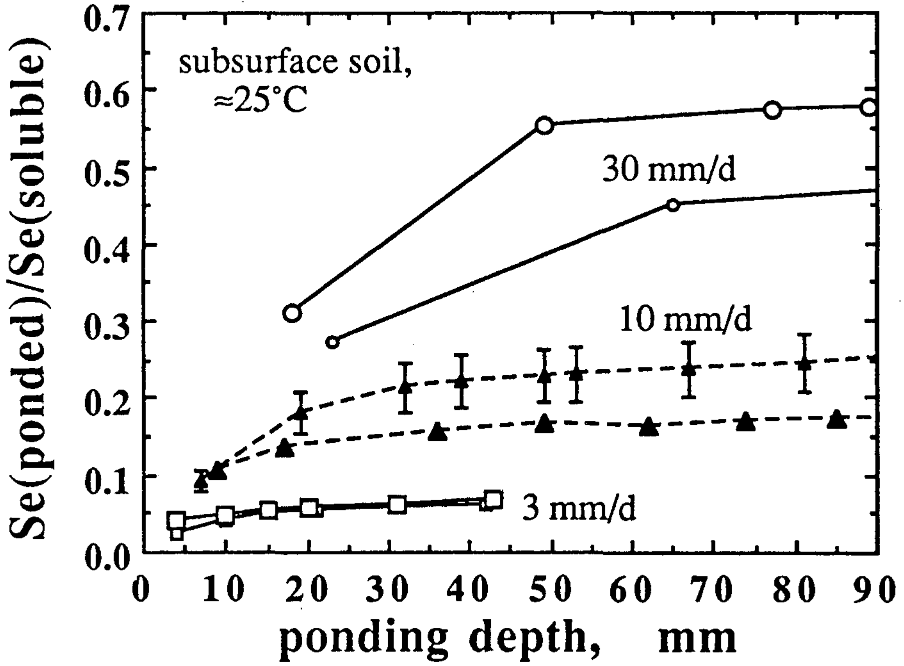

Figure 3.9b. Cumulative Se in ponded waters subsoil relative to the initial water-soluble Se inventory in the soils, at 3, 10 and 30 mm d^{-1} water table rise rates (replicate columns, all at ≈25°C).

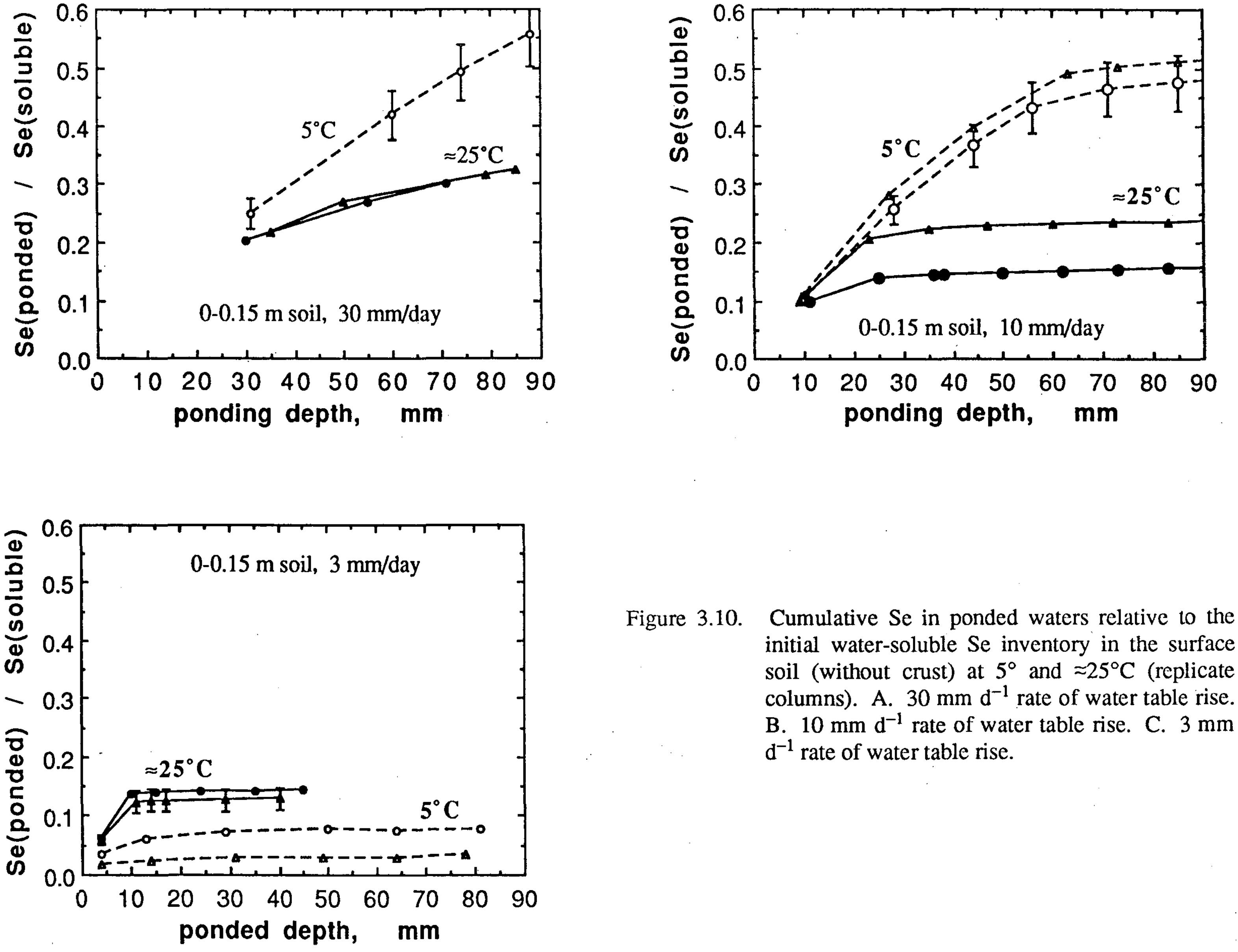

Figure 3.10. Cumulative Se in ponded waters relative to the initial water-soluble Se inventory in the surface soil (without crust) at 5° and ≈25°C (replicate columns). A. 30 mm d^{-1} rate of water table rise. B. 10 mm d^{-1} rate of water table rise. C. 3 mm d^{-1} rate of water table rise.

water quality goals with respect to selenium were exceeded in columns comprised only of the less seleniferous subsurface (0.15-0.30 m) Kesterson Reservoir soils indicated that excavation of the surface (0-0.15 m) soils would not provide sufficient moderation of selenium exposures to wildlife. Similar observations were noted in ephemeral pool waters formed from watertable rise in the 0.30 m (1 ft) excavation test plot (Section 3.2).

The influence of soil temperature on selenium transport and subsequent pond selenium concentrations is illustrated in Figures 3.11a,b,c for the three rates of watertable rise. The emergence of selenium in ponding waters at low temperatures can be of interest in environments where the period associated with the annual rise of the watertable coincides with the colder late fall and winter months. Such conditions prevail at Kesterson Reservoir. In the 10 and 30 mm d^{-1} columns, the resulting pond selenium concentrations indicated an enhancement of selenium transport at lower temperatures. This behavior is consistent with a positive temperature-dependence of Se(VI) reduction. The enhanced breakthrough of selenium in the 5°C columns suggests a decrease in the rate-controlling steps of Se(VI) reduction with decreased temperature. The opposite conclusion is suggested by the data from the 3 mm d^{-1} columns. This latter result suggests that factors other than the rate of Se(VI) reduction are important at the lowest flow rates. The greater influence of evaporative concentration of ponded selenium at the lowest flow rate, combined with lower evaporation rates in the 5°C columns is evident in the electrical conductivities of the ponded waters (see Figure 3.11a and 3.11b), and contributes toward the reversal depicted in Figure 3.10c. However, the magnitude of the evaporative concentration effect is insufficient for accounting for the observed reversal. The insignificance of differences arising from evaporation at the two different temperatures in the higher flow rate columns is apparent in Figure 3.11a, for the 10 mm d^{-1} columns. Similar reproducibility was obtained in the 30 mm d^{-1} columns. In both of these latter cases, the rate of soil solution inflow was sufficiently high, thus minimizing the impacts of evaporation rate differences at the two temperatures.

Redox potential measurements yielded results which were commonly in qualitative agreement with expected trends. Quantitative interpretation of these redox data is unjustified (e.g.

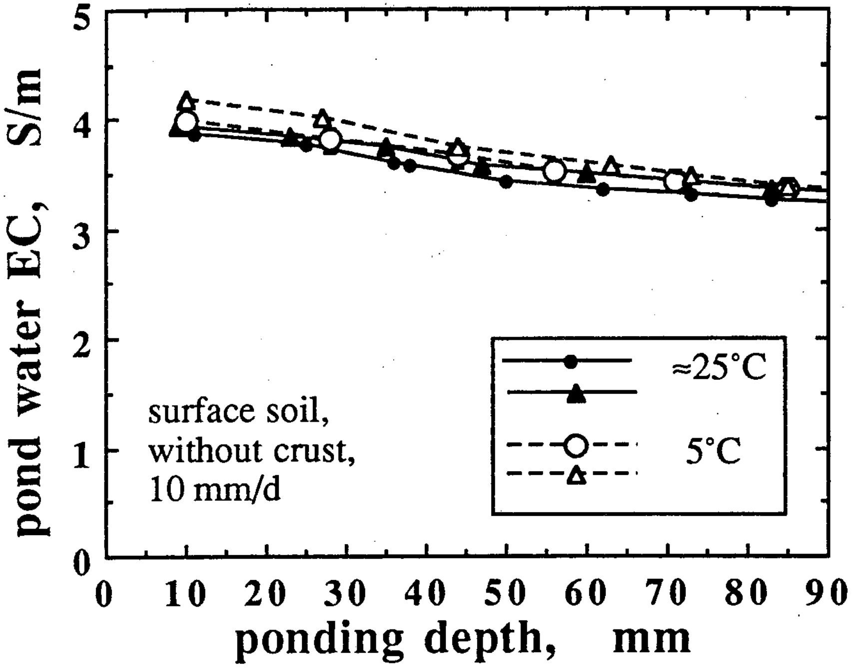

Figure 3.11a. Electrical conductivities (EC) of ponded waters in the surface soil columns (without crusts) at 5° and ≈25°C (replicate columns) with 10 mm d^{-1} rate of water table rise.

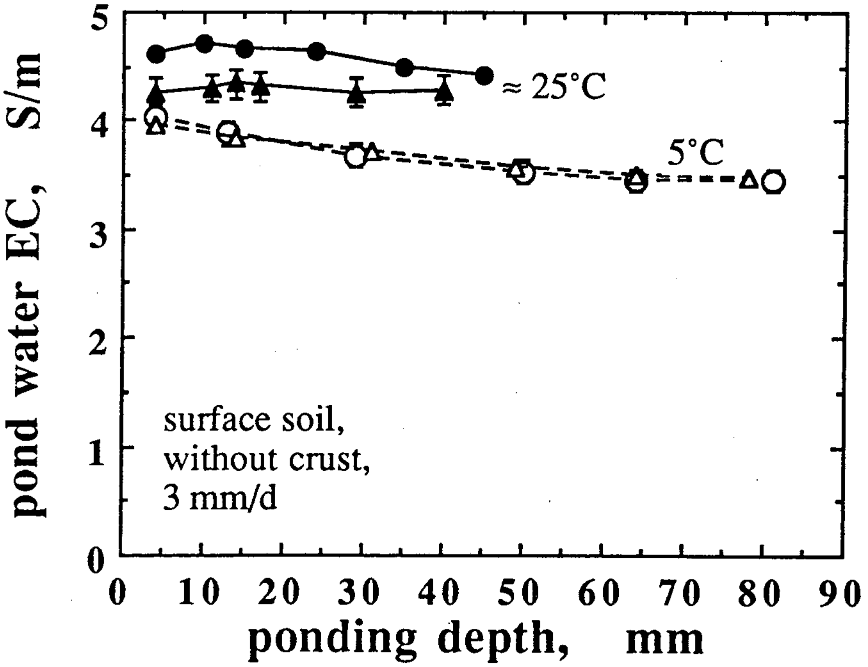

Figure 3.11b. Electrical conductivities (EC) of ponded waters in the surface soil columns (without crusts) at 5° and ≈25°C (replicate columns) with 3 mm d^{-1} rate of water table rise.

Bohn, 1971). The observed general trends included (1) the development of more completely reducing soils with the lowest flow rates, (2) the more rapid development of reducing conditions at the higher temperature, and (3) the progressive growth of the reducing zone from the bottom of the column upwards. However, the redox potential measurements also exhibited considerable scatter, as indicated by the data from replicate 3 mm d^{-1} (25°C) columns (0-0.15 m soils) shown in Figures 3.12a,b. Equilibrium analyses of selenium redox in neutral to slightly alkaline environments indicate that Se(VI) to Se(IV) transformations will occur in the vicinity of 400 mV (Geering et al., 1968; Elrashidi et al., 1987). In reoxidation experiments on Kesterson Reservoir sediments by Masscheleyn et al. (1990), Se(IV) to Se(VI) transformations began at approximately 200 mV.

3.5.3. Summary

Ponding conditions were generated by watertable rise through laboratory columns packed with soils from Kesterson Reservoir. The tested variables (1) soil depth interval, (2) the rate of watertable rise, and (3) temperature, all influenced the resulting selenium concentrations in the ponded waters. Selenium concentrations in ponded waters were roughly proportional to the initial water-extractable selenium inventories of the different soils. While considerable variation in pond water selenium inventories was observed between duplicate columns, the surface soils (0.00-0.15 m, with and without crusts) contributed approximately 10 times more selenium into ponding waters than the subsoils (0.15 to 0.30 m). Nevertheless, pond water selenium concentrations ranging from 30 to 400 $\mu g\,L^{-1}$ associated with the subsoil columns are in considerable excess of surface water goals of 2 to 5 $\mu g\,L^{-1}$. Similar results from the P6S12 excavated field plot were observed during the 1987-1988 wet season (Section 3.2). The field study was conducted in an environment quite different from that from which the laboratory column soils were sampled, hence the field and laboratory results are not directly comparable. The field study was conducted in a 0.30 m deep excavation, in an area formerly vegetated with cattails (Typha), and not subjected to flooding with nonseleniferous waters after termination of seleniferous drain water inputs. As noted earlier, the soils used in the laboratory studies were sampled in an

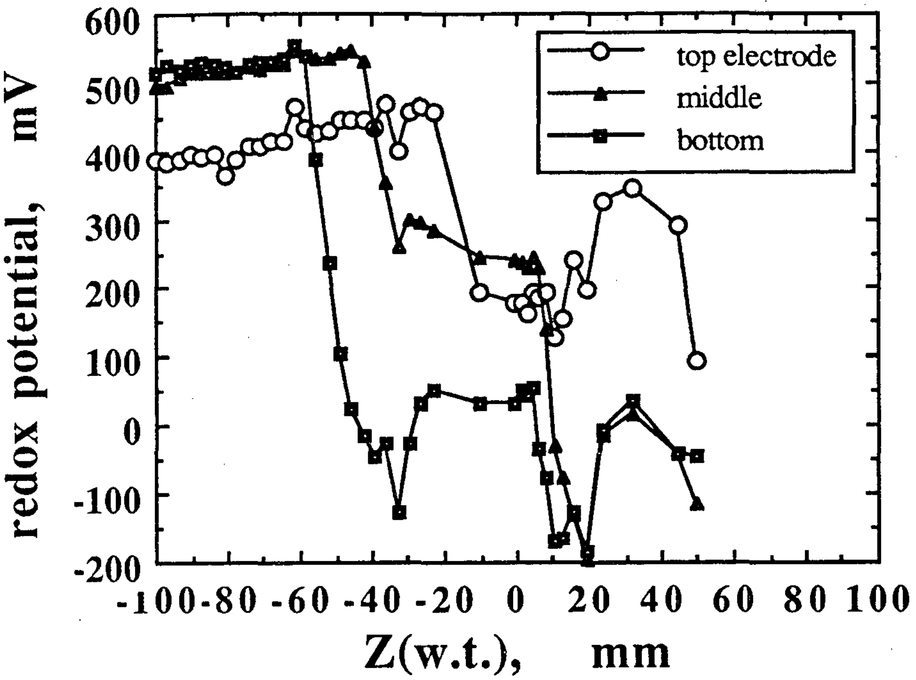

Figure 3.12a. Redox potentials in surface soil (without crust) columns (≈25°C). Z(w.t.) denotes the elevation of the water table relative to the soil surface.

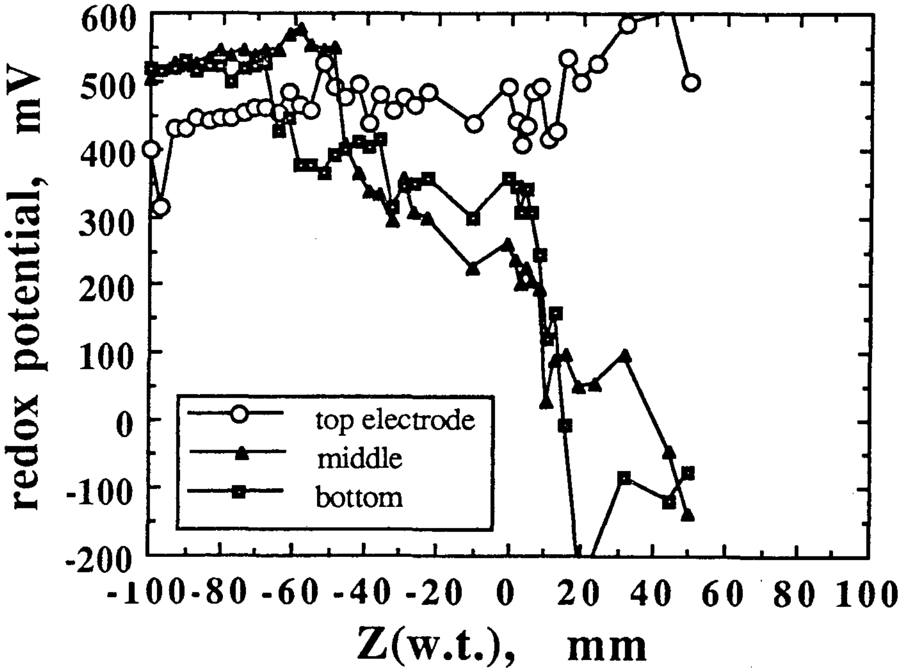

Figure 3.12b. Redox potentials in replicate columns with same conditions described in Figure 3.12a.

unvegetated region of Pond 1, which had been relatively recently flooded with nonseleniferous waters for approximately 1.5 yr. Nevertheless, similar results from both studies indicate that watertable rise through excavated soils at Kesterson Reservoir could result in future wildlife exposures to selenium in ephemeral pools.

Higher rates of watertable rise resulted in higher concentrations of selenium in ponded waters, presumably because the competing influences associated with the development of reducing conditions for Se(VI) depletion were minimized under the higher flow rates. The magnitude of this effect can be summarized by comparing the highest (30 mm d^{-1}) to the lowest (3 mm d^{-1}) rates of watertable rise. Approximately twice as much selenium was mobilized from the surface soil into the ponded waters under the 30 mm d^{-1} rate relative to the 3 mm d^{-1} rate. With the subsurface soils, an approximately six-fold difference was observed under the above conditions.

Two different sets of results were obtained from the experiments directed at investigating the effects of temperature. For the 10 and 30 mm d^{-1} columns, larger quantities of selenium were mobilized from the soils into the ponded waters at 5°C than at room temperature (≈25°C). Such behavior was expected, based upon the assumption that the kinetics of Se(VI) reduction would be decreased at lower temperatures, thereby allowing more of the initially water-soluble soil selenium to be transported into the ponding waters. In the cases of the 10 and 30 mm d^{-1} rates of water table rise, approximately twice as much selenium was transported up into the ponded waters at 5°C relative to the soil columns maintained at room temperature. A reversal of this pattern was observed in the columns subjected to the lowest rate of watertable rise (3 mm d^{-1}). Higher pond water selenium concentrations were observed in the room temperature columns than in the 5°C columns. An explanation for this behavior is presently lacking since, as noted in the discussion, evaporative concentration of selenium under room temperature conditions can not account for the magnitude of the observed reversal.

3.6. Estimated Selenium Concentrations in Surface Water Pools at Kesterson

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Although significant surface water ponding has not been observed at Kesterson since the fill operation in 1988, the potential for creating these pools in wetter-than-average years remains. Mass balance models and numerical simulation studies were used to anticipate when such pools would form, and by what mechanism. From these studies, which were presented in the 1989 Annual Report (LBL, 1990), we concluded:

- surface pools are unlikely to form from rising groundwater;
- pools that form are mostly likely caused by ponding of rainwater;
- in years with 50% greater-than-average rainfall (which are expected to reoccur once in 10 years), soils between the watertable and the ground surface may become fully saturated over one-half of the Reservoir, leaving excess rainwater to form surface water pools; and
- in the event of a 100-year rainfall (500 mm), surface ponding over most of the former Reservoir can be anticipated.

On average, selenium concentrations in these pools are expected to be lower than the historic levels associated with waterfowl death and deformity at Kesterson. Nevertheless, because of the substantial inventory of selenium in Kesterson soils, it is certain that at least some of the surface waters will contain in excess of recommended levels of 2 to 5 μg/l.

In response to these concerns, plans are being made to develop a surface water drainage scheme for the Reservoir, to eliminate aquatic habitat that may attract wildlife. As part of this effort we have attempted to estimate the likely range of selenium concentrations in these pools, and provide an overall average value that could be used as the basis for a surface water discharge permit. This effort is by nature speculative because little to no data are available on surface water selenium concentrations in rainfall pools on native Kesterson soils. Nevertheless, we have drawn on data collected from a variety sources over the years at Kesterson in an attempt to represent the range of conditions that may occur. The following sections describe the approach and results of this effort.

3.6.1. Estimated Depths of Rainwater Pools

As a first step in estimating surface water selenium concentrations, likely depths of rainwater pools were calculated. Numerous simplifying assumptions were used and are described below.

1. All rainfall either infiltrates into the soil, evaporates, or forms a surface water pool (e.g. no run-off occurs).
2. The quantity available for ponding is equal to rainfall, minus the quantity that can be stored in the soil at 100% saturation, minus the potential evaporation.
3. The porosity of the surface soil is 35%.
4. The profile-averaged fraction of pore space available for storage of infiltrated rainwater at the beginning of the rainy season is 40% (e.g. assuming a vegetated soil, see Section 2.3).
5. The total soil storage is equal to the depth to the watertable multiplied by the porosity times the fraction of pore-space available for water storage at the beginning of the rainy season.
6. Average potential evaporation for the 5 month period between November and March is 1.5 mm day^{-1} (see LBL, 1990, p. 67). Potential evaporation rates decline linearly from 3.0 mm/day to 0 mm/day over the 2 1/2 month period from November 1 through January 15. Rates then increase linearly back to 3.0 mm/day by March 30.
7. Plant uptake of soil moisture from November through March is negligible.

8. Daily rainfall varies linearly from a maximum value at the beginning of November to zero at the end of March. The results of these calculations were compared to ones assuming a constant rainfall over the 5 month period. Results varied between these two cases but overall conclusions about ponding depths and likely periods of maximum ponding did not change significantly.

With these assumptions it is possible to estimate ponding depths, for a range of rainfall and depth to the watertable. For example, if the minimum depth to the watertable is 0.9 m in a normal water year, 300 mm annual rainfall may create pools 1 cm deep. Similarly, annual rainfall of 350, 400, and 500 mm may create pools that are 5, 15, and 25 cm deep, respectively. The most extensive ponding is anticipated to occur from early February to mid-March. The calculations neglect the potentially important effect of local depressions that may create deeper pools from collection of surface runoff. They do however provide a range of expected values and a reasonable estimate of the quantity of water that may pond at Kesterson.

Because the depth to the watertable ranges from about 0.3 to 1.5 m at Kesterson, it is not possible to determine a single representative ponding depth (e.g., during the 1989-90, pond-averaged minimum depths to the watertable ranged from 0.6 to 1.4 m). Therefore, calculations covering a range of annual rainfall and depths to the watertable were made. These simple calculations indicate that for 350 mm annual rainfall, ponding depths will range from 0 to 5 cm. For 400 mm annual rainfall, ponding depths will range from 0 to 15 cm. Ponds from 10 to 25 cm deep are expected to cover the Reservoir in the event of a 500 mm annual rainfall (100 year rainfall). Local topographic irregularities will expand this range of values. In all cases, maximum pond depths are anticipated to occur in the late-February, early-March time period.

3.6.2. Estimated Selenium Concentrations in Surface Pools

As stated initially, there is little data on which to base predictions of surface water selenium concentrations at Kesterson, due largely to the recent succession of drought years. However, limited data are available and these have been drawn on heavily to arrive at the forthcoming estimates. Specific data drawn upon include:

- samples from rainwater pools formed on fill-dirt during the winters of 1988-89 and 1989-90 (see LBL, 1990; and Section 3.1, this report);
- samples from ephemeral pools formed in 1987 from a combination of rising groundwater, rainfall, and overland flow of water from intentionally flooded areas (LBL, 1987);
- experimental laboratory and field data collected from seasonally ponded areas (see Section 3.2, 3.3 and 3.5, this report);
- soil cores showing the influence of rainfall infiltration on driving surficial inventories of selenium deeper into the soil profile (Zawislanski, 1989; also see Section 2.2, this report);
- samples collected from Pond 1 when it was intentionally flooded with selenium-free water (< 1 μg/l) (Long, 1988); and
- samples collected from Pond 7 when is was seasonally flooded with water containing about 5 μg/l selenium (LBL, 1987).

Before describing the procedure and philosophy used to estimate selenium concentrations in these pools, the physical and chemical processes taking place as these pools form will be reviewed. Early in the rainy season the watertable is typically from 0.7 to 1.5 m below the ground surface. As the rain falls on the ground surface, salts that have accumulated at the soil surface dissolve and are transported deeper into the soil profile. As described in Section 2.6, relatively large quantities of selenate, probably associated with readily soluble sodium and magnesium salts, can be dissolved and transported into the soil profile by this process. Information on the depth to which these penetrate into the soils is limited but available data suggests that from 50 to 75% of the water extractable selenium inventory can be driven out of the top 9 cm of soil by this process (Zawislanski, 1989). However, as also described in Section 2.6, selenium (largely as selenite) may be associated with less soluble salts (e.g. gypsum) that will only slowly be leached from the soil surface by infiltrating rainfall. As the rainy season progresses, the air-filled void space in the soil will fill with rain water. When the cumulative rainfall (minus evaporation) exceeds the storage capacity of the soil, surface ponding will occur.

The inorganic selenium dissolved in these pools will be derived from soluble forms residing at the soil surface when the pools begin to form, dissolved selenate and selenite residing in the fully saturated pore spaces that can diffuse from the soils into the overlying surface water, and selenite associated with moderately soluble salts the have not fully dissolved prior to the time when the pool forms. Organic forms of selenium may also be present in these pools, derived from solubilization of organically associated or bound selenium and microbial activity. A potentially large pool of selenium is available for entry into the surface water by this pathway, but the extent to which this will occur is uncertain. Mitigating processes include volatilization of organic selenium and reduction of selenate and selenite to less mobile forms when fully saturated conditions are established.

Note that temporary ponding is expected to occur during and following major rains, regardless of availability of soil storage capacity. However, these pools are expected to persist only for several days to as long as a week or two. These short-lived pools are not expected to pose a significant biological hazard and are consequently not the focus of this discussion. This discussion pertains to large, long-lasting pools that are biologically productive enough to create a significant attractive nuisance to wildlife.

In describing likely concentrations of selenium in pools at Kesterson we will divide the discussion into two parts. First, likely ranges of selenium concentrations in filled areas will be discussed. There is a reasonable body of data from which to make the projections, at least for the coming wet season, and perhaps for several years following. Next, selenium concentrations in the unfilled areas will be described. These projections are far more speculative because few, if any, rainfall pools have occurred in on native Kesterson soil since monitoring began in 1988. Since approximately 50% of the Reservoir is covered with fill-dirt, and assuming equal probability of pool formation in both areas, the Reservoir-wide average concentration of selenium in surface water pools will be equal to the average of the values forming on each of these surfaces.

In the winter of 1988-89, surface water samples were collected from about 30 rainwater pools that formed in the filled areas (LBL, 1990). A similar but significantly smaller set of samples was collected this year (see Section 3.1). Selenium concentrations in these pools range from less than detection to about 50 µg/l. The average concentration in the 1988-89 season was 9.3 µg/l. The depths of these pools were also measured, values ranged from 1 to 6 cm, with an average value of 3 cm. Assuming that the same quantity of selenium is available for dissolution into these pools regardless of its depth, it is possible to extrapolate this data set to calculate the range of expected concentrations in deeper pools. For example, for the average concentration of selenium in pools of 5, 10, 15, and 20 cm deep, are expected to be 6.4, 3.2, 2.1 and 1.6 µg/l, respectively. Note that these values are based on extrapolation over a very narrow time frame (e.g. two years). The amount of selenium available for dissolution in surface pools may increase over time as evaporatively driven transport of soil water carries selenium up to the top of the fill surface (see Section 2.2). Nevertheless, over the next few years these values provide our best estimates of average selenium concentrations in pools that form in filled areas of the Reservoir. Selenium concentrations in individual pools are expected to range of a similar set of values as observed over the past two years (e.g., less than detect to tens of µg/l).

In the following paragraphs, various sources of information relevant to predicting surface water selenium concentrations on native Kesterson soil are reviewed. Specific information include: data from surface water pools collected in the winter of 1987-88; samples from Ponds 1 and 7 collected when they were intentionally flooded with water containing little selenium; and surface water samples collected from the experimental plot in Pond 6 (see Section 3.2).

Samples were collected from about 30 pools found at Kesterson during the 1987-88 winter season. These pools formed from a combination of rising groundwater, overland flow from adjacent flooded ponds and rainfall. Selenium concentrations in these pools ranged from 30 to 2500 µg/l with an average value of 373 µg/l. It is not possible to determine the dominant process responsible for ponding in these areas. However, about 30% of the pools were clearly formed primarily from rising groundwater and contained very high concentrations of salts and selenium. Discounting the data collected from these pools, the average selenium concentrations from the remaining pools was 216 µg/l. An alternative approach to discriminating between rainfall and groundwater pools is based on the electrical conductivity or salt contents (i.e., rainfall pools are expected to contain relatively low dissolved solids). In this case, neglecting all pools with electrical conductivities greater than 10 dS/m, the remaining 15 pools had an average selenium concentration of 133 μg/l. The average depth of these pools was about 10 cm. Assuming that the same quantity of selenium could dissolve in 5, 10, and 20 cm deep pools, selenium concentrations would be 260, 130, and 65 μg/l, respectively. These numbers provide a conservative estimate of potential selenium concentrations because some these these pools were undoubtably formed at least partially from rising groundwater or overland flow.

Data are also available from intentional seasonal flooding of Ponds 1 and 7 with low selenium water. In both 1986 and 1987 Pond 1 was flooded to an average depth of 60 cm with groundwater pumped from wells located along the San Luis Drain (Long, 1988). Water from these wells contained less than 1 μg/l selenium and a total dissolved solids concentration about 1/2 that of drainage water. Surface water selenium concentrations ranged from 20 to 40 μg/l in consistently flooded areas, with an average value of about 25 μg/l. Normalizing these values to depths of 5, 10 and 20 cm, expected selenium concentrations are 300, 150 and 75 μg/l, respectively. Similar data were obtained from Pond 7, where average selenium concentrations were 20 μg/l in an area flooded to a depth of 30 cm. Expected concentration in pools with depths of 5, 10 and 20 cm, are 120, 60, and 30 μg/l, respectively. The extent to which these data provide a reliable model for rainfall pools is uncertain because unlike rainfall pools, both of the ponds were flooded quickly, over a period from several days (Pond 1) to weeks (Pond 7). The potential for dissolution of the salt crust and overland flow are significantly greater under these conditions.

A final source of information about likely concentrations of selenium in rainfall pools comes from the experiment described in Section 3.2. Here, in Pond 6, rainfall pools have actually formed on a non-filled surface. However, as described, 0.3 m (12 inches) of the soil were excavated. Nevertheless, comparison between the selenium inventory in the soils with the selenium concentrations in rainfall pools provides a basis for assessing what fraction of the soluble inventory of selenium in the top 0.15 m of soil may be dissolved in rainwater pools. In this test plot, the soluble selenium inventory in the top 0.15 m of soil is 400 μg/kg–soil. For a soil bulk density of 1500 kg/m^3, this is equivalent to 0.09 g/m^2 of soluble selenium in the top 0.15 m. The concentration of selenium in the overlying 10 cm-deep pool was 140 μg/l. This indicates that only 15% of the soluble selenium in the top 0.15 m of soil dissolved in the overlying rainwater pool. Although this is an extremely limited data set and can not be considered to be representative of the Reservoir as a whole, it can be used to make a first guess at selenium concentrations in rainwater pools on native Kesterson soil.

As described in Section 7, average water extractable selenium concentrations in the grassland and open areas are approximately 150 and 330 μg/kg–soil, respectively. Assuming a bulk soil density of 1500 kg/m^3, this translates to 0.035 and 0.074 g/m^2 of selenium, for the grassland and open areas, respectively. Assuming that 15% of this is dissolved in the overlying pools, we can calculate the concentration of selenium, depending on their depth. In the grassland areas, expected concentrations for 5, 10 and 20 cm-deep pools are 105, 50, and 25 μg/l, respectively. In the open areas, expected concentrations for 5, 10 and 20 cm-deep pools are 220, 110, and 55 μg/l, respectively.

Three vastly different data sets have drawn upon to provide estimates of potential selenium concentrations in rainwater pools formed on native soil at Kesterson. Estimates developed from these data sets for selenium concentrations range from 105 to 300 μg/l for 5 cm-deep pools, from 50 to 150 μg/l for 10 cm-deep pools, and from 25 to 65 μg/l for 20 cm-deep pools. Most likely, these estimates provide a reasonable range of values that will occur during a year with exceptionally heavy rainfall.

It is more difficult to arrive at a representative average value that can be used as the basis for obtaining a surface water discharge permit. However, several factors render this a somewhat easier task. First, experience obtained during the dewatering operations carried out in the spring of 1988 indicated that it is difficult to drain shallow pools at the Reservoir because of the hummocky nature of the terrain. Therefore, it is unlikely that pools of less than 10 to 20 cm deep will be drained. This lessens the range of expected concentrations to 25-150 μg/l. Second, since only

1/2 of the Reservoir is covered with native soil, and selenium concentrations in areas covered with fill-dirt are expected to be in the range of 1 to 3 μg/l for 10 to 20 cm-deep pools, Reservoir-averaged selenium concentrations will be only about 1/2 the values observed in unfilled areas. For example, if the entire Reservoir were covered with 20 cm of water, the average concentration is expected to range from 12 to 32 μg/l.

As is clear from the above discussion, precise estimates of selenium concentrations under extremely wet conditions are not possible. However, the ranges and likely averages are our best estimates at this time. Another factor to consider in pursuing a discharge permit is the on-site dilution capacity presently available from the 10 pumping wells located along the San Luis Drain. Dilution within the Reservoir or at the discharge point into Mud Slough are both possible. Moreover, during a very wet year flows in Mud Slough should be relatively high, presenting a significant natural dilution potential. In addition, the data presented in Section 3.5 clearly show that selenium levels in surface waters surrounding Kesterson are already relatively high, higher in fact than surface waters recently observed within Kesterson and the San Luis Drain. Significant degradation of water quality in Mud Slough from discharge of Kesterson waters during wetter-than-normal years seems unlikely.

4. VOLATILIZATION STUDIES AT KESTERSON RESERVOIR

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Microbial volatilization is a demonstrated process for dissipating selenium from soils at Kesterson Reservoir (Frankenberger and Karlson, 1989; LBL, 1990). However, questions remain about a number of factors, including:

- dissipation rates;
- physical, biological and chemical processes controlling volatilization rates;
- cost effective strategies for enhancing volatilization rates;
- costs associated with implementation of a large-scale remediation program using this technique; and
- effectiveness of volatilization for removing refractory forms of selenium from soils.

LBL scientists have conducted two types of experiments to address these issues. The first of these, a pilot-scale field test of microbial volatilization of selenium, is being carried out in collaboration with faculty from the Davis and Riverside campuses of the University of California. This experiment will provide information for evaluating optimal strategies and costs for implementing volatilization as a remedial measure at Kesterson Reservoir. As such, it addresses questions regarding dissipation rates, effectiveness of irrigation and disking to enhance volatilization rates, and costs associated with full scale implementation. Section 4.1 defines LBL's role in this experiment and provides a status report on related activities.

Three years of laboratory experiments have improved our understanding of the physical, biological and chemical processes leading to dissipation of soil selenium (Frankenberger and

Karlson, 1988; Frankenberger and Karlson, 1989; Karlson and Frankenberger, 1989; LBL, 1990). However, we have not addressed one major issue adequately. To what extent can selenium can be removed from Kesterson soils by microbial volatilization? Although we now have a large body of data regarding volatilization rates, we have not demonstrated that Kesterson soils containing tens to hundreds of mg/kg selenium can be reduced to the several mg/kg believed to be environmentally "safe." Experiments have been either been terminated after removal of 50%, at the most, or have simply not progressed to the extent that more than this fraction of selenium has been removed (Frankenberger and Karlson, 1988; Frankenberger and Karlson, 1989a; Karlson and Frankenberger, 1989; Frankenberger, 1990). There are several reasons for this, the principle one being that at least several years would be required to fully dissipate the initial inventory of selenium.

As an alternative to this time consuming approach, we have addressed this issue in a different way. Selenium exists in a variety of forms in Kesterson soils (see Section 2.3). Each form volatilizes at a different rate. With depletion of the initial inventory, the relative fractions of selenium in the soil change, leading to changes in the overall volatilization rate. Consequently, extrapolation of volatilization rate measurements obtained during the initial phases to the entire dissipation process is subject to large uncertainty. To help resolve some of this uncertainty, we have carried out experiments aimed at evaluating volatilization rates from the different forms of selenium present in Kesterson soils. Comparing volatilization rates for these different forms assists in extrapolating volatilization rates over the full dissipation process. Section 4.2 describes these experiments and provides and assessment of relative volatilization rates for several of the "pools" of selenium found in Kesterson soils.

4.1. Pilot Scale Volatilization Experiment in Pond 2

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Small-scale field and laboratory experiments sponsored by the Kesterson Program from 1987 to 1990 suggest that microbial volatilization may provide an effective means of dissipating selenium from Kesterson soils. Volatilization trials in Pond 4 show that selenium concentrations in the top 0.15 m of soil have declined by up to 50% in several of the test plots (Frankenberger, 1990). However, comparison of the soil depletion data to measured gaseous emissions suggests that only part of this decline can be attributed to microbial volatilization. The remainder of these losses are attributed to the dilution effect of disking and perhaps, a small amount of leaching below the sampled interval. Nevertheless, the rapid depletion of selenium concentrations in the surface soils and encouraging data from volatilization of selenium from San Luis Drain sediments (Frankenberger, 1990) suggest that this remedial strategy warrants additional evaluation. A pilot-scale test of microbial volatilization is being carried out to better quantify selenium depletion mechanisms and to provide information for estimating costs of implementing this remedial technique on a large scale. The test plot is located in highly seleniferous soils in an area previously vegetated by cattails. This site was selected because of concerns regarding wildlife exposure to this and similar regions throughout the southern part of the Reservoir (CH2M Hill, 1989).

The site chosen for this study is an 80 m by 100 m plot in the northern end of Pond 2, an area which was almost always flooded during operation of the Reservoir and supported primarily cattail vegetation. Results of preliminary soil sampling in this plot in November 1989 are shown in Figure 4.1. The sample set contained some of the highest Se concentrations ever observed at Kesterson: the mean Se concentration in the top 15 cm (5 6" samples) was 291 ppm; in the 15 to 30 cm (6-12") interval it was 27.3 ppm (analyzed via XRF). The soil was found to be less saline

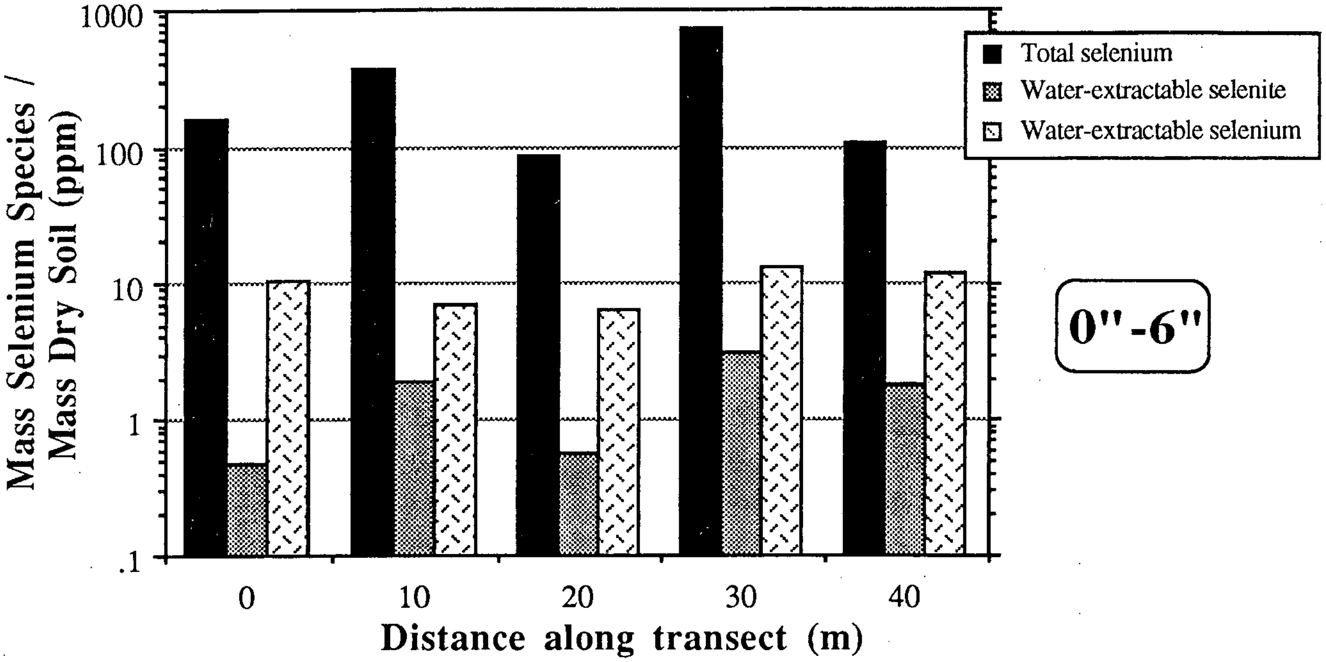

Figure 4.1a. Selenium concentrations in the top 6 inches of soil in Pond 2 along an west-east transect, 11/7/89.

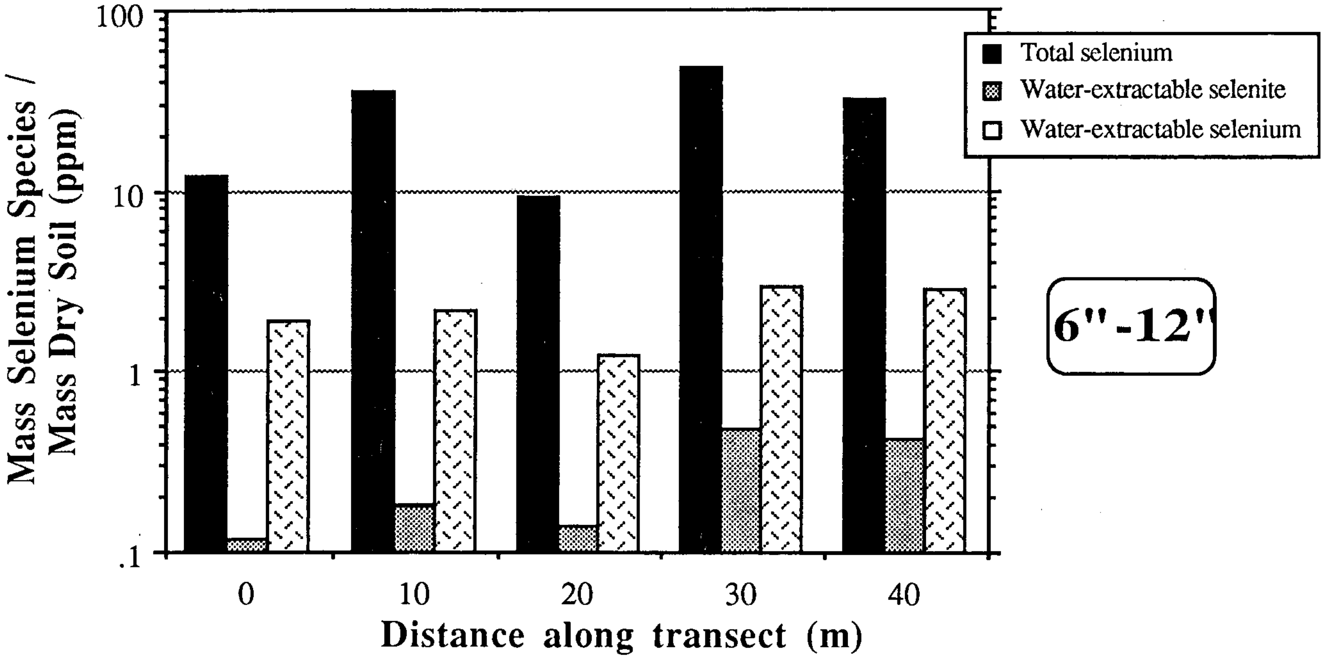

Figure 4.1b. Selenium concentrations in the soil interval of 6 to 12 inches, in Pond 2 along an west-east transect, 11/7/89.

than most Kesterson soils (1:10 soil:water extract electrical conductivities normalized to field water content ranged from 23 dS/m to 69 dS/m). In preparing this plot, cattail remains on the soil surface were incorporated into the top 20 cm or so of soil by disking and rototilling. As shown in Figure 4.2 the plot was then divided into four subplots, each being reserved for a particular treatment: irrigation only (I), irrigation and disking (ID), disking only (D), and control or no treatment (C). An 11.6 meter buffer zone was set up between the irrigated and non-irrigated plots in order to prevent irrigation water from falling onto the disked plot. The irrigation system is currently under construction. When completed, it will deliver sufficient water to keep the top 15 cm of soil moist.

Information regarding mechanisms of selenium dissipation will be collected by comparing data from three treatment plots and one control plot. By treating each of the subplots in a different way, information will be gathered on the effectiveness of water and aeration (disking) on microbial volatilization. Soil will be sampled over a defined profile (down to 60 cm or deeper), with controlled intervals which will be analyzed separately for selenium; this will reveal any redistribution of selenium between those intervals. By integrating the concentrations of selenium over the entire sampled profile, any loss of selenium may be accounted for. Losses of selenium in the soil will be monitored by annual sampling along selected transects and quarterly sampling in randomly selected subplots. There are 10 such subplots (5 by 5 meters in size) in each treatment. A random number generator was used to locate these plots. Along with total selenium analysis (to be performed by CSU Fresno), a subset of these samples will be analyzed for water soluble and potentially adsorbed selenium. This will provide information on selenium dissipation from different pools and will improve our understanding of which pools are more easily volatilized. Emissions of gaseous selenium are being monitored using two methods: results will aid in constructing an accurate selenium mass balance. In addition, monitoring of the vadose zone for potential short-term and long-term leaching of selenium deeper into the profile is being conducted. In order to determine how much of the near-surface selenium is actually lost to volatilization, it must be known how much was displaced by irrigation water below the sampled interval.

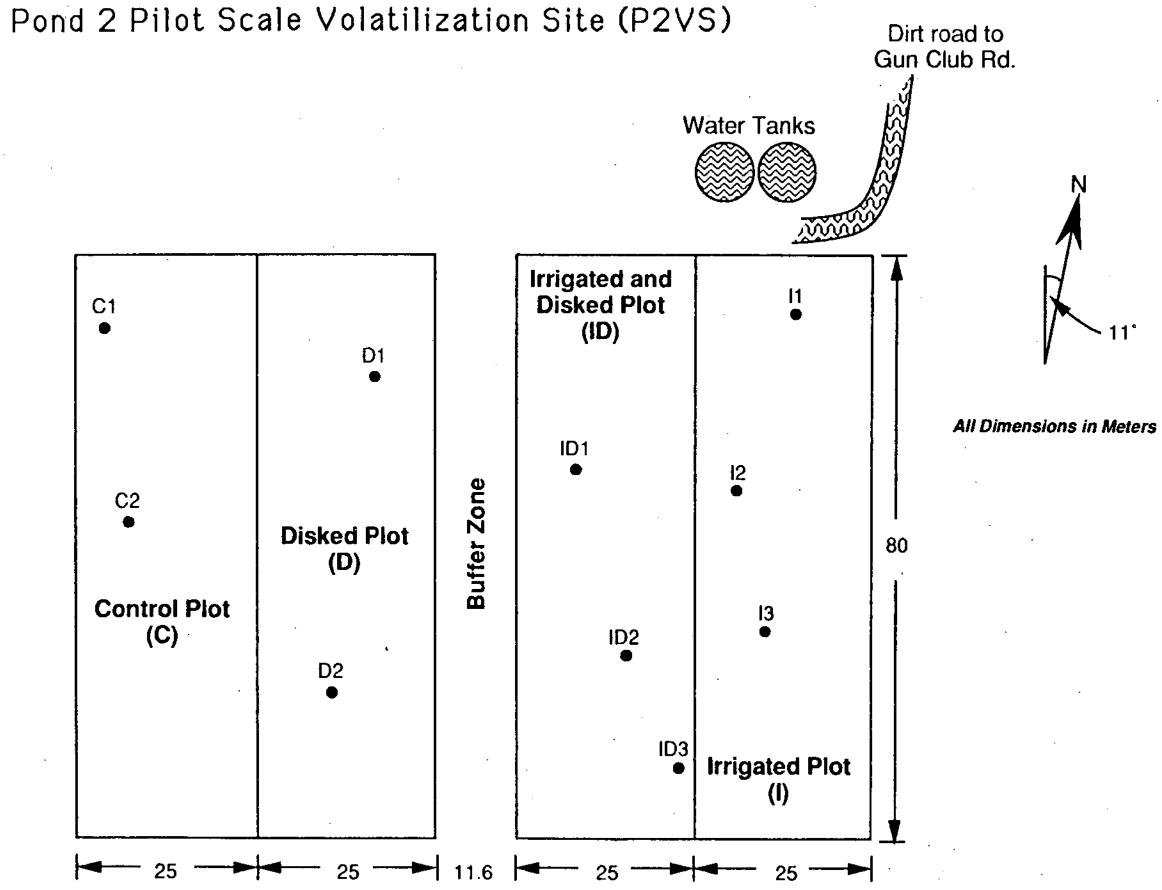

Figure 4.2. Map of the Pilot Scale Volatilization Site in Pond 2 (P2VS). Points mark locations of nests of tensiometers and soil water samplers.

Tensiometers and neutron probe measurements will also give short term indications of overirrigation.

In order to minimize future soil sampling intensity, it would be advantageous to know the degree of mixing which takes place during soil disking. By introducing a solid, insoluble tracer (silica sand) to the soil surface, and periodically sampling that soil for tracer concentration, the degree to which the surface soil (and the tracer with it) is being diluted with deeper, less seleniferous soil will be determined. This tracer will be applied in the next few weeks.

The responsibilities of Lawrence Berkeley Laboratory include: design and installation of a vadose zone monitoring system (soil water samplers and tensiometers); solid tracer experiment; soil water and groundwater sampling and analysis; participation in quarterly and annual soil sampling; preparation and analysis of a subset of the above soil samples for water-extractable and phosphate-extractable selenium.

The vadose zone monitoring system was installed in July 1990. A total of 10 nests of tensiometers and soil water samplers have been installed, three clusters in each of the irrigated plots and two in each of the other two plots. The locations of these devices were chosen to coincide with locations of both soil and gas sampling. All soil water samples and tensiometer readings will be taken on a monthly basis. In addition, readings will be taken strategically, relative to irrigation and rainfall events. Each nest consists of 4 tensiometers and 4 soil water samplers with porous cups at the following depths: 0.425 m, 0.60 m, 0.80 m, and 1.00 m. All of the instruments are buried at least 30 cm below the soil surface in order to allow disking machinery to pass over the soil. Tubing is routed 1 meter away from the tensiometers and soil water samplers to a common standpipe through which the samplers are sampled and the tensiometers are read. The first set of data was collected between 7/31/90 and 8/10/90.

Tensiometer data reveal a ''flat'' hydraulic head profile in most nests (Figure 4.3), with head ranging roughly from -1.6 m to -2.7 m. The nature of the matric potential profile is typical of unvegetated soils; the magnitude of the readings, i.e. the high hydraulic head, even at the relatively shallow depth of 42.5 cm, suggests that bare soil evaporation is not particularly significant

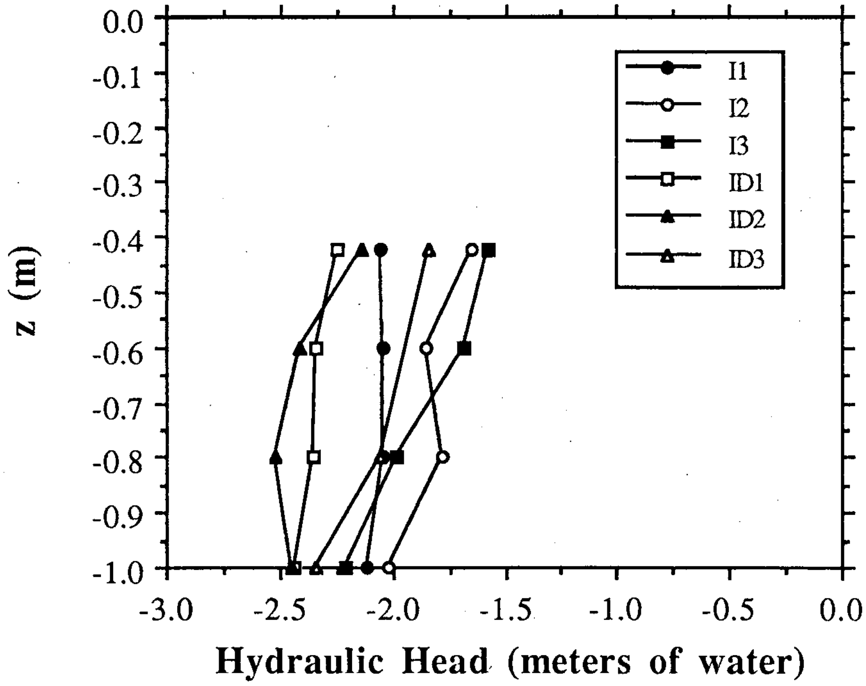

Figure 4.3a. Hydraulic head in soil profile of "Irrigation Only (I)" and "Irrigation and Disking (ID)" plots, as measured using tensiometers, 8/90.

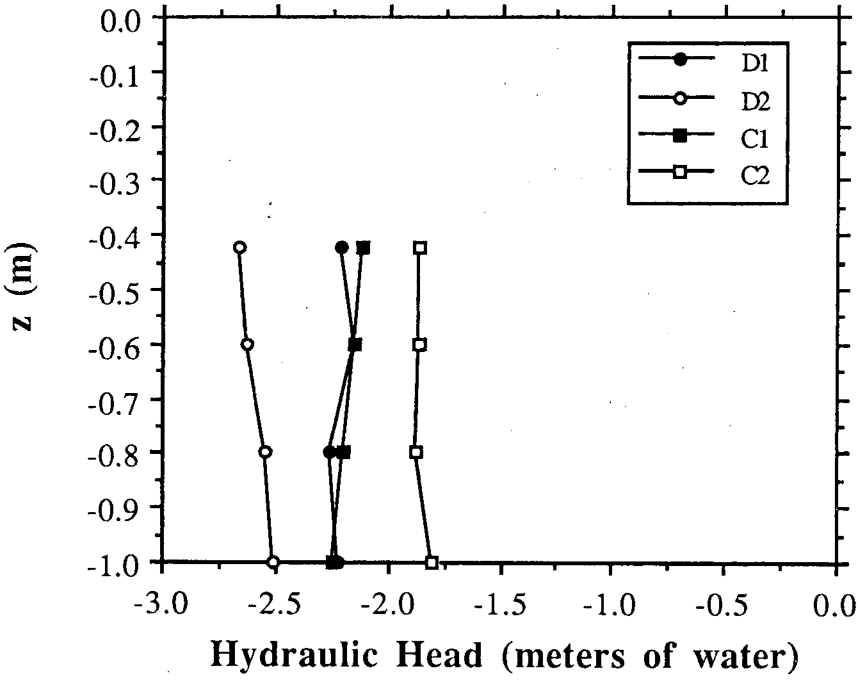

Figure 4.3b. Hydraulic head in soil profile of "Disking Only (I)" and "Control (C)" plots, as measured using tensiometers, 8/90.

compared to other unvegetated plots in the Reservoir. This may be explained by the presence of loose organic material on the soil surface, which acts as a mulch. Adding a mulch on top of a soil is an approach used commonly to minimize water loss through evaporation (Gardner and Fireman, 1958). Therefore, the matric potential below -42.5 cm is probably close to equilibrium with respect to the water table. At the time of measurement, the water table at Kesterson Reservoir was still falling. This may explain the pattern in a few of the profiles where soil suction actually increases with depth.

The first set of samples from soil water samplers was discarded since it would have been affected by the instrument installation procedure. Electrical conductivity and selenium data from the second sample set are presented in Figures 4.4 through 4.6. Relatively flat EC profiles are consistent with the fact that Pond 2 had been flooded from August 1986 until the spring of 1988 with moderate EC and close to selenium-free water ([Se]≤5 ppb), which would have resulted in low vertical variability in salinity. ECs range from 9.5 dS/m to 18.5 dS/m, with most values clustered within 2 dS/m of 12 dS/m. On the other hand, selenium concentration data (see Figures 4.4b, 4.5b, and 4.6b) illustrate the tremendous variability in soil-water selenium. At the depth of 0.425 m, selenium concentrations range from 760 ppb (nest D2) to 11,240 ppb (nest ID3). At the depth of 1.00 m, selenium concentrations range from 280 ppb (nest ID2) to 3,180 ppb (nest I1). While there is only slight correlation between selenium concentrations and electrical conductivity within a given nest, i.e. location, there is virtually no correlation from nest to nest, that is, a location with a relatively high EC will not necessarily have a high selenium concentration. Such variability necessitates intensive soil sampling within chosen areas. Analysis of transect soil samples (currently underway) will reveal spatial variability of selenium in the surface soil. The baseline information described here will provide a means of evaluating temporal changes in the distribution of selenium throughout the profile.

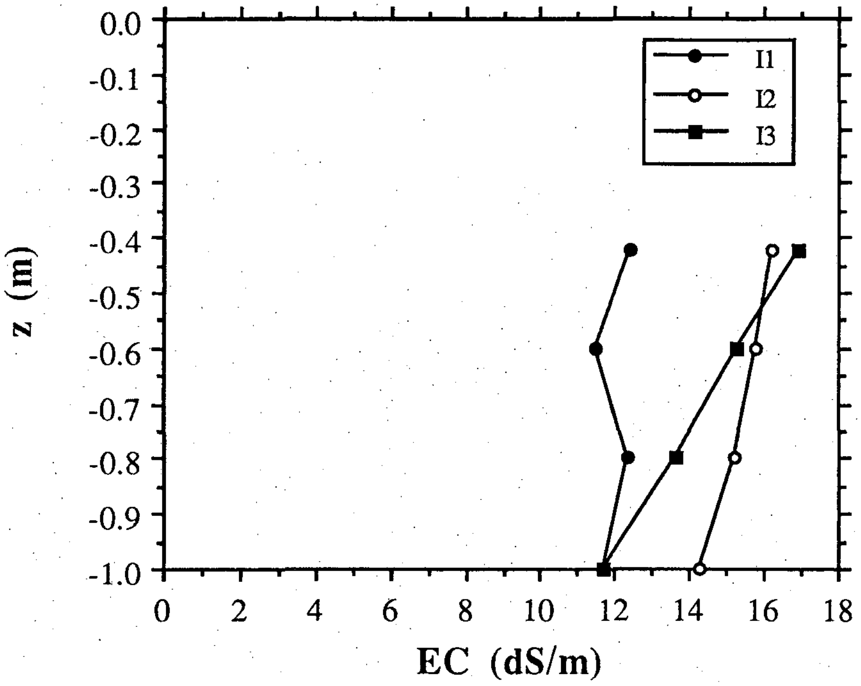

Figure 4.4a. Electrical conductivity of soil water of "Irrigation Only (I)" plot as sampled via soil water samplers, 8/90.

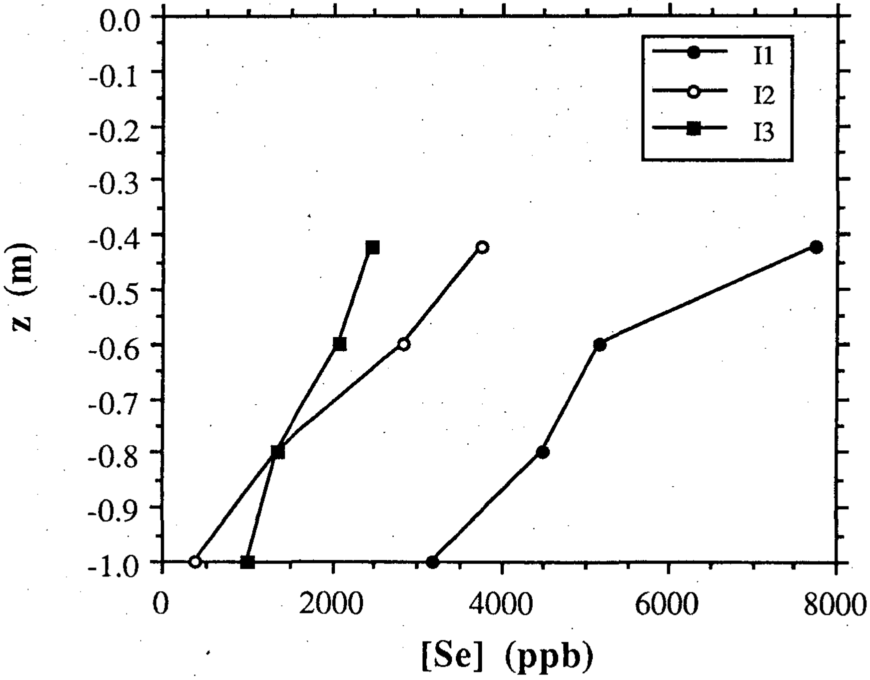

Figure 4.4b. Selenium concentrations in soil water of "Irrigation Only (I)" plot as sampled via soil water samplers, 8/90.

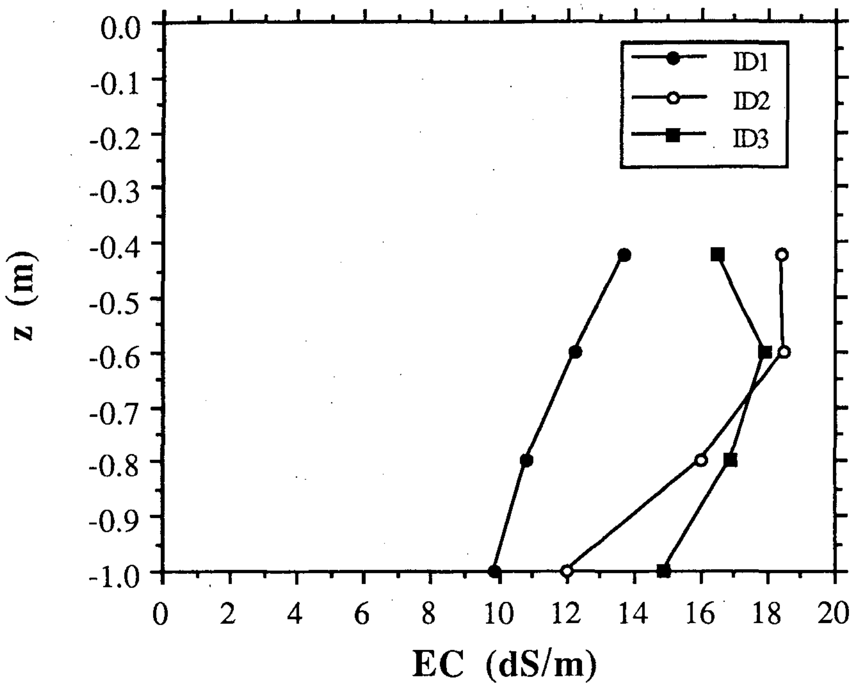

Figure 4.5a. Electrical conductivity of soil water of "Irrigation and Disking (ID)" plot as sampled via soil water samplers, 8/90.

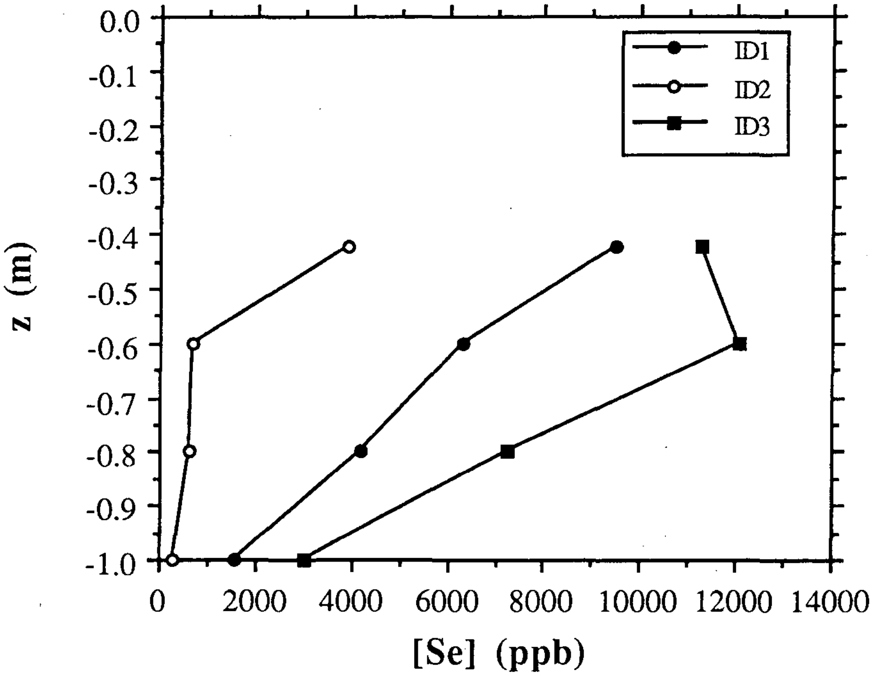

Figure 4.5b. Selenium concentrations in soil water of "Irrigation and Disking (ID)" plot as sampled via soil water samplers, 8/90.

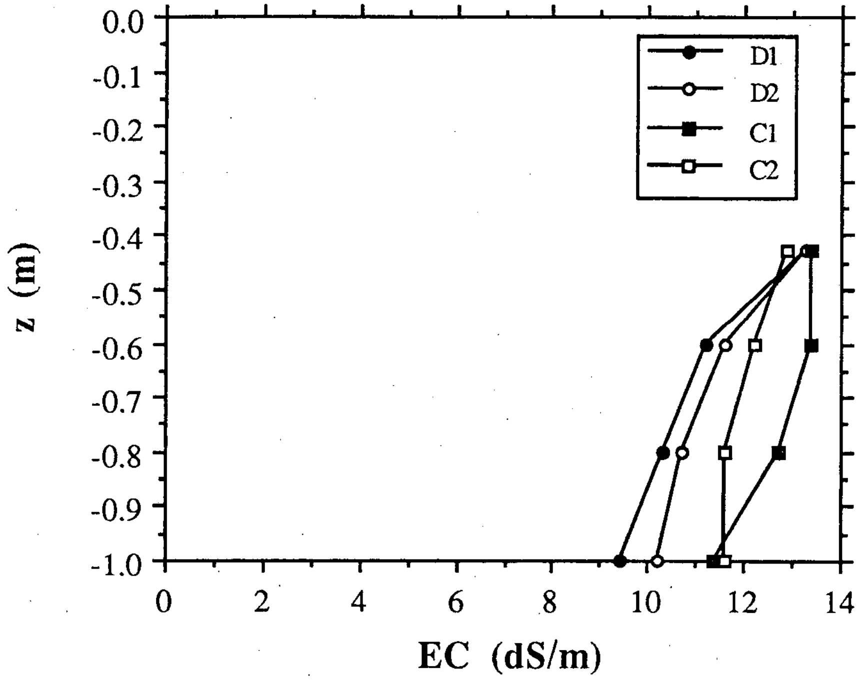

Figure 4.6a. Electrical conductivity of soil water of "Disking Only (D) and Control (C)" plots as sampled via soil water samplers, 8/90.

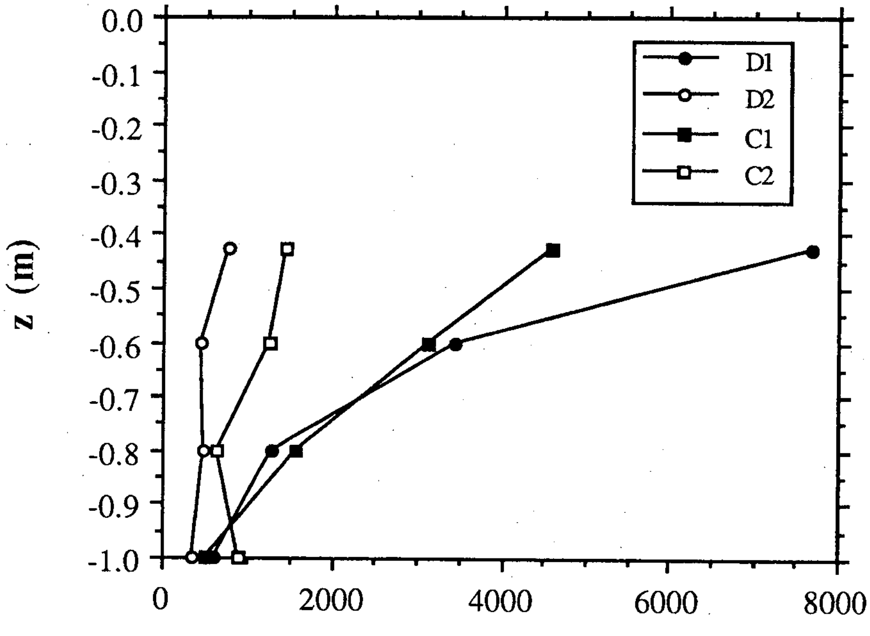

Figure 4.6b. Selenium concentrations in soil water of "Disking Only (D) and Control (C)" plots as sampled via soil water samplers, 8/90.

4.2. Selenium Volatilization from Fractionated Soil

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4.2.1. Introduction

The objective of this effort focuses on the microbial volatilization and mobilization of selenium from various pools in the Kesterson soil. From previous studies we have classified the selenium pool into three fractions based on solvent extraction (LBL, 1990). These were referred to as soluble, labile, and refractory. Note that this is a simpler classification scheme than the more detailed one described in Section 2.5. However, there is general correspondence between the water extractable pools, the labile, and the refractory pools described in Section 2.5. The soluble fraction consists primarily of inorganic selenate and selenite salts which can be easily extracted by washing the soil with water or with 0.1M KCl. The labile portion of the selenium, which has never been well characterized, is generally believed to be associated with the soil's organic matter and clays. This portion of the selenium can be displaced from the soil by phosphate anions or by dilute sodium hydroxide. The remaining selenium in the soil, which is resistant to almost any solvent extraction is the refractory portion. This portion is believed to be composed at least partially of elemental selenium which is derived from microbial metabolism of inorganic selenate and selenite.

To investigate the fungus' ability to volatilize the various forms of selenium we inoculated a fungal suspension grown in a nutrient broth to each soil fraction. The nutrient broth serves to accelerate the growth of the microorganism. At the beginning of the experiment serum bottles were used as the culture chamber. These bottles were tightly fitted with Mininert valves (Supelco, PA) made of teflon. Daily head space measurement for dimethylselenide (DMSe), dimethyldiselenide (DMDSe), and carbon dioxide was performed by gas chromatography.

Monitoring for CO_2 is important because it correlates directly with the metabolic rate and growth of the microorganisms, hence the rate of DMSe volatilization.

In later experiments, serum bottles were replaced by Warberg flasks to improve the precision for DMSe determination. In the Warberg flasks an alkaline peroxide solution was placed in the side-arm to absorb the DMSe slowly liberated over a twenty four hour period. Then the absorbent was aspirated with a syringe and analyzed for total selenium by the hydride generation method, and fresh alkaline peroxide solution was added to the Warberg flask.

At the end of the incubation period the soil samples were sequentially extracted and the amount of selenium in each pool was determined. Finally, the remaining selenium in the residual samples were determined by X-ray fluorescence and by acid digestion methods.

From these data we may be able to draw some conclusions concerning rates of microbial volatilization of selenium, and more importantly, the mobilization of selenium mediated by microbial metabolism, and the fate of selenium in the Kesterson Reservoir.

4.2.2. Materials and Methods

4.2.2.1. Soil Processing

The soil used in the experiment was collected from the top 5 cm in Pond 1. After removing the coarse organic litter, it was air dried and sieved through a No. 48 mesh screen. Total selenium determined by XRF was 42.5 ± 2.2 ppm ($n = 3$), and by acid digestion method, 40.2 ± 0.55 ppm ($n = 6$). This otherwise unprocessed soil was used as a control in these experiments.

To obtain a soil from which the ''water extractable'' pool was removed the following procedure was used. Three hundred grams of the untreated soil (air-dried sieved) was washed 2 times with 0.1M KCl and rinsed once with de-ionized water in a 4 liter beaker. The soil was agitated with a stirring motor for about 4 hours and then allowed to settle for two days before decanting the supernatant. After a water rinse the sediment was left in the beaker to dry. The hardened cake was broken up with a mortar and pestle and sieved again through a No. 48 mesh screen. The coarse material remaining on the screen was discarded. The final material was stored in a plastic jar. The yield was about 220 grams. Selenium content of the extracted soil was 43.8 ± .4 ppm (n = 2) by XRF. Note that the total selenium concentration of the untreated and KCl extracted soil are not significantly different, indicating that the KCl extractable fraction from this soil is very small.

The sample containing only the refractory pool was processed in the following way. One hundred fifty grams of the untreated soil was washed with 0.2N NaOH followed by a water rinse and dried. After grinding and sieving through a No. 48 mesh screen, the selenium content was determined. Total selenium in this pool was 16.0 ± 0.8 ppm (n = 1) as determined by XRF analysis.

4.2.2.2. Fungal Inoculum

The native fungus, Acrimonium falciforme, was a gift to us by Professor Frankenberger of UCR. To maintain the culture we periodically transferred the fungus to Sabouraud (supplied by BBL) agar plates and nutrient broth. To use this fungus in our experiment a specimen was prepared in a fungal suspension two days in advance by inoculating the fungus to 100 ml of sterile Sabouraud broth. After two days at room temperature the media was overgrown with hyphae and ready for soil inoculation.

4.2.2.3. Preparation of Soil Samples for Volatilization Experiments

Three grams from each of the fractionated soils were placed in small serum bottles (37 ml capacity) and 1 1/2 ml of the fungal suspension was gently layered over the entire surface of each sample. The bottles were then capped with Mininert valves (Supelco, PA). The culture bottles were placed on top of a vacuum oven warm enough to serve as an incubator. The soil temperature was 30° C.

4.2.2.4. Gas Chromatography of Dimethyl Selenium and CO_2

The method used for DMSe analysis was similar to one described by Frankenberger and Karlson (1989). We used a Gow Mac series 750 gas chromatograph equipped with dual flame ionization detectors (FID). On one detector we installed a 3 m by 0.3 cm i.d. stainless steel column packed with a 10% Carbowax 1000 on a Chrom W-AW 60/80 mesh support. This column was used for DMSe analysis. On the second FID detector we installed a 1.83 m× 0.3 cm Poropak N column in series with a 7.62 cm Ruthenium catalytic column for the reduction of CO_2 to methane. The catalytic column had an independent temperature control and was insulated from the other column. Also, the hydrogen line supplying the FID detector was re-routed to mix with the carrier gas at the end of Poropak column with a stainless ''T'' connector. Hydrogen was used for the CO_2 reduction. The chromatographic conditions were: oven temperature, 65°C; Helium carrier gas, 30 ml/min.; injector port temperature, 120°C; detector temperature, 200°C.; catalytic column temperature, 350 C.; Peak areas and retention times were measured with a HP3390A integrator. DMSe, DMDSe, and CO_2 reference standards were obtained from Alfa Ventron.

4.2.2.5. Selenium Volatilization, Modified Method, Alkaline Peroxide Absorption

Substituting Warberg flasks for serum bottles, and employing alkaline peroxide instead of gas chromatography for selenium determination greatly simplied the monitoring procedure, and at the same time yielded more reliable volatilization data. As with the serum bottles, the same amount of soil and inoculum were placed in the Warberg flasks. One half ml of alkaline-peroxide mixture (4:1 v/v ratio of 0.05N-NaOH to 30% hydrogen peroxide) was placed in the side arm of the flask to absorb the DMSe liberated by the fungus. The flasks were capped with glass stoppers and incubated as before. After twenty-four hours the alkaline peroxide was removed and replaced with a fresh solution with the aid of a syringe. The old solution was placed in a culture test and digested for 15 minutes in a boiling water bath to oxidize the DMSe to inorganic selenate. The selenate was then determined by the HG-ICP method described in Section 4.2.2.7.

4.2.2.6. Alkaline Peroxide Absorption Efficiency

A saturated DMSe vapor standard was prepared by placing one gram of liquid DMSe into a 137 ml serum bottle capped with a Mininert valve. After equilibration at room temperature 10, 20, 30, 40, and 50 microliters of the vapor were withdrawn using a gas tight syringe and injected into smaller (37 ml) serum bottles containing 5 ml of alkaline-peroxide mixture. After standing for one hour the contents were removed and transferred to regular digestion tubes and heated in a boiling water bath for 15 minutes. Selenium was determined by the HG-ICP.

4.2.2.7. Selenium Analysis by HG-ICP

Aqueous selenium determinations were made using HG/ICP. Performing these analysis required a small modification to the ICP. The very simple device shown in Figure 4.7 consisting of a regular 3-channel peristaltic pump and a gas-liquid separator is needed for these analyses. As shown in Table 4.1 operating conditions are identical to HG-AAS except for the argon flow. The hydride outlet consists of a 1/4'' teflon tubing connected directly to the injector tube of the plasma torch. The instrument detection limit of the HG-ICP is 0.1 µg/L with a background equivalent concentration (BEC) of 4 µg/L. The linear range is from 0 to 4,000 µg/L.

Table 4.1. Comparison between operating conditions for selenium analysis by HG-ICP and HG-AAS.

	HG-ICP ml/min	HG-AAS ml/min
Sample flow rate	7	7
Acid flow rate	1	1
borohydride	1	1
Argon	1,000	30

4.2.2.8. Soil Fractionation after Incubation

(1) Soluble selenium by KCl extraction: After drying the incubated soil in an oven (90°C) overnight, 0.5 gm of the soil was removed and placed in a teflon centrifuge cone and extracted with 35 ml of 0.1M KCl on a shaker for two hours. After centrifugation the supernatant was analyzed for selenium by HG-AAS or by HG-ICP.

(2) Selenium associated with Soil Organic Matter: The same soil after KCl extraction was extracted with 20 ml of 0.1N NaOH and analyzed for selenium.

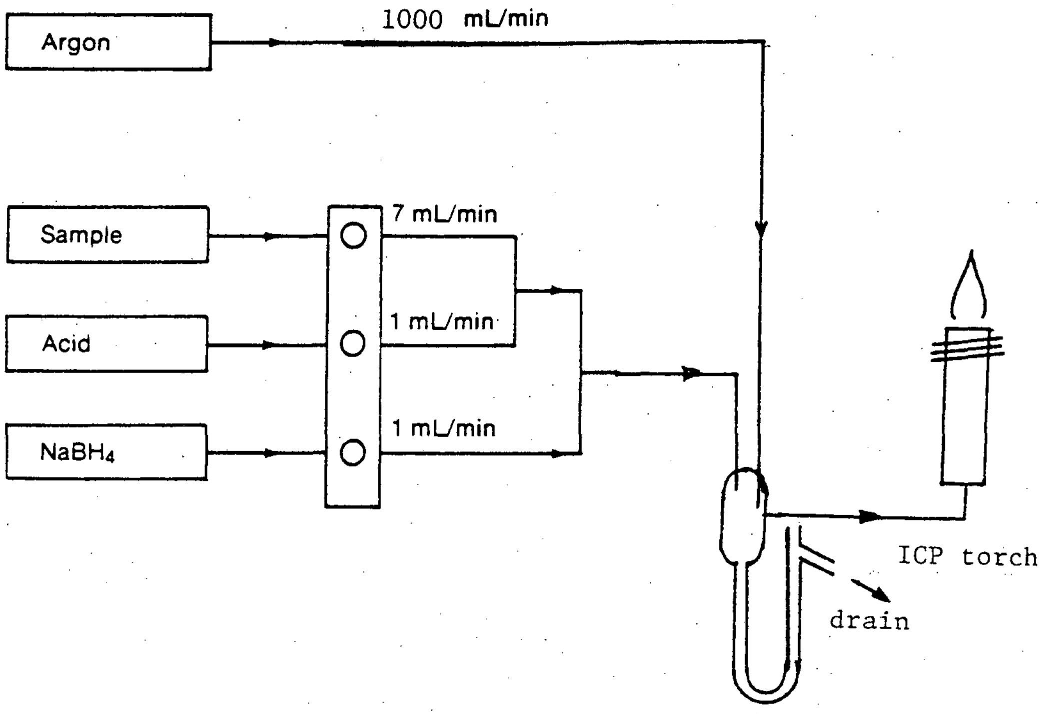

Figure 4.7. Schematic diagram of a continuous HG-ICP system using a 3-channel peristaltic pump and a gas-liquid separator.

(3) Refractory Pool Remained in Soil Sediment: A nitric-peroxide digestion was first carried out to convert all the selenium into the +6 oxidation state. 4.5 ml of concentrated nitric acid + 0.5 ml 30% hydrogen peroxide were added to each soil residue and slowly digested in a heated aluminum block until fully dried. This step can take more than 24 hours. A 10 ml aliquot of 6N-HCl was then added and a hot extraction continued for 30 minutes. Then the acid was carefully decanted into a 100 ml volumetric flask and the same procedure was repeated until the last extract showed a very faint yellow color. To the combined extract, 1 ml 8 M urea was added before diluting to 100 ml. Addition of urea eliminates nitrate interference in the selenium analysis.

4.2.3. Results and Discussions

4.2.3.1. CO_2 and DMSe Volatilization

The daily gas chromatographic monitoring of CO_2 in Figure 4.8 shows that all the soil fractions yielded the same rate of CO_2 emission, indicating all the cultures were equally active and multiplying at the same rate. Data points for average values and bars indicating 1 standard deviation among treatments are shown in Figure 4.8. Note that all reported values are averages obtained from triplicate samples. Maximum CO_2 emissions occurred on the second day of incubation and after that rates gradually declined to a steady level in about 10 days.

DMSe emission from all three soils followed the same general course as CO_2, but different amounts were volatilized from each treatment. As shown in Figure 4.9 untreated and KCl extracted soils evolved about the same amount of DMSe, but emissions from the NaOH extracted soil were significantly lower. The general patterns of volatilization may be explained through kinetics of enzyme reactions. In the first two soil samples the initial substrate concentration (or the available selenium), was much greater than the enzyme concentration (here represented by the number of microorganisms). Therefore, the rate of DMSe emission depends on the concentration of the enzyme (a variable in this case). As the fungal culture grew in number the amount of DMSe increased also. After two days the culture began to die off or decrease activity due to aging, the overall results being diminished enzyme concentration in the system.

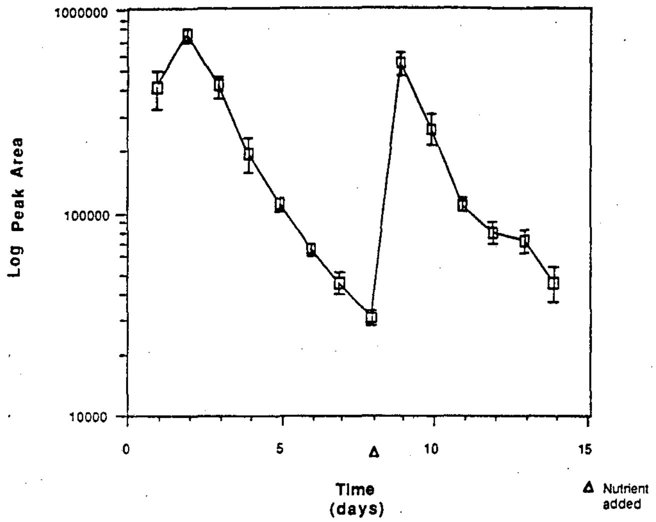

Figure 4.8. CO_2 volatilization of soil fractions inoculated with the fungus Acrimonium falciforme. Δ indicates additional nutrient added to the culture.

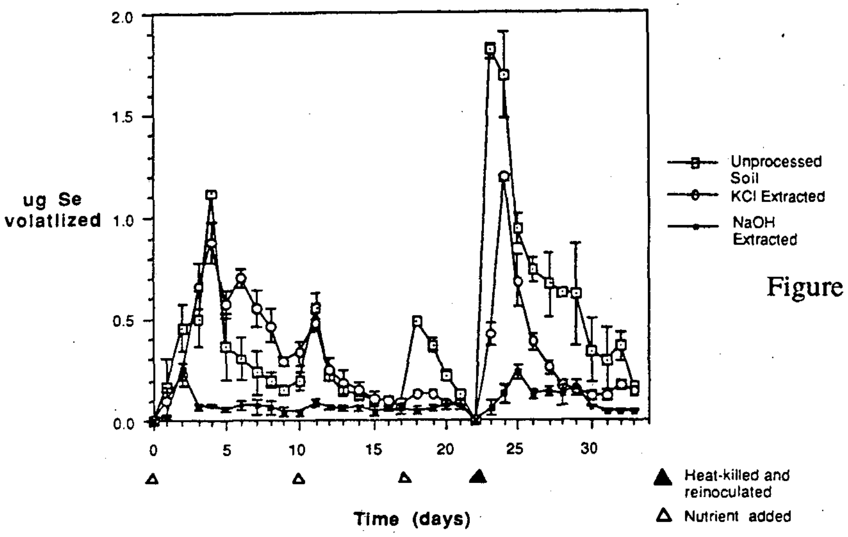

Figure 4.9. Daily volatilization of DMSe from soil fractions. Δ indicates addition of nutrient supplement. ▲ indicates termination of culture and reinoculation with new fungus.

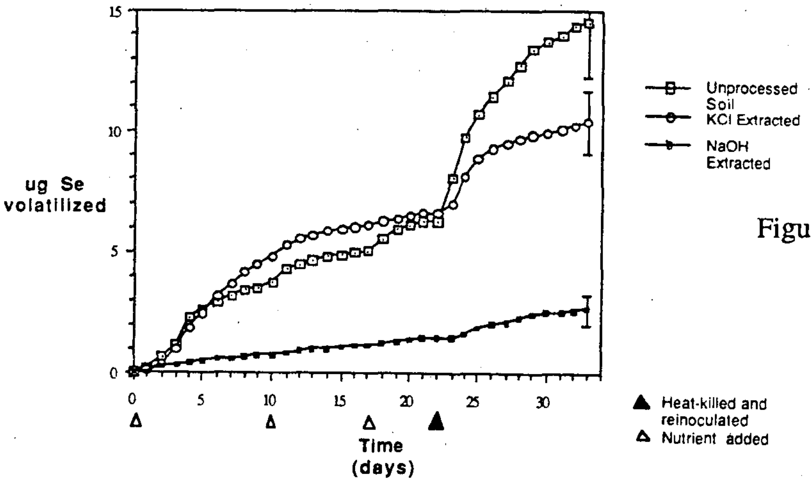

Figure 4.10. Cumulative plot of DMSe volatilization vs. time and effect of nutrient supplement and reinoculation.

DMSe emission declined with diminished enzyme concentration. With the NaOH extracted soil, the concentration of available selenium may have been less than the enzyme concentration, and therefore resulted in all the substrates tied up the enzyme-substrate complex, and with the resultant DMSe emission following a zero order kinetics (with respect to fungi). When fresh nutrient broth was added to the aging cultures, DMSe release again increased, but the amount did not match the previous emission rates. The lowered metabolic rate was probably due to accumulation of metabolic by-products in the culture media, suppressing the normal growth of the fungus. When the culture was terminated by drying the inoculum in a vacuum oven and reinoculated with a new culture, DMSe emissions were much higher then before (see Figure 4.10, day 22, Figures 4.9 and 4.10). This phenomenon can be explained by the presence of growth promoting substances derived from the previous cultures and the new cultures just took advantage of the accumulated nutrients.

The similarity in emission rates between the unprocessed soil and the KCl extracted soil is of interest. It suggests that the fungus can metabolize the adsorbed or organically bound selenium just as easily as the soluble inorganic selenium in the unprocessed soil. The refractory portion of the selenium (NaOH extracted) was only metabolized at a low rate. The low but measurable emission rates from the NaOH extracted soil may be due to two causes:

(1) mobilization of the refractory selenium in the soil into the soluble pool by some unknown processes, and the newly available Se immediately converted to DMSe by the fungus;

(2) incomplete extraction of labile fraction in the NaOH wash, and trace amount of Se slowly leached out of the soil aggregates was responsible for the selenium volatilization.

Mobilization of selenium from the refractory pool is of concern because this soil fraction represented a major portion (almost 50%) of the total selenium inventory. To deplete this portion of the selenium may require a long period of time. As shown in Table 4.2, over a 33 day period the unprocessed soil lost 9.3% of the total selenium; the KCl extracted soil lost 6.6%; and the NaOH extracted soil, 3.9%. It is to be noted that these figures represents ideal laboratory conditions and are in no way equivalent to field trials.

4.2.3.2. Fractionation of Selenium after Incubation

To demonstrate the mobilization of Se from various pools the incubated soils were fractionated and analyzed for soluble and labile pools of selenium. Results are listed in Table 4.3. The control (unprocessed soil) did not show an increase in the soluble or in the labile portion of the selenium. The KCl extracted soil showed an increase in the soluble portion but the labile portion remained the same. The NaOH extracted soil showed a dramatic increase in the soluble and the labile portions of the selenium.

Table 4.2. Selenium loss in 3 gram soil samples after 33 days incubation with fungus Acrimonium falciforme. Selenium in soils analyzed by the acid extraction method.

	Unprocessed soil	KCl extracted	NaOH extracted
Initial Se µg	156.3 ± 12.6 µg	158.7 ± 1.2 µg	67.5 ± 1.8 µg
Loss as DMSe	14.5 ± 2.3	10.4 ± 1.3	2.6 ± 0.6
Percent Volatilized	9.3	6.6	3.9

Table 4.3. Changes in selenium pool after 33 days incubation with fungus. Figures represent percent of total selenium.

	KCl Extractable Se		NaOH Extractable Se	
	before	after	before	after
Unprocessed soil	10%	10%	10%	10%
KCl extracted	5%	9%	10%	10%
NaOH extracted	5%	25%	5%	10%

4.2.3.3. Alkaline-Peroxide Absorption of Dimethyl Selenide

Alkaline-peroxide solution was found to be an excellent absorbent for DMSe. As shown in Figure 4.11, even at very high vapor concentration absorption was virtually complete. Se determination based on alkaline-peroxide absorption is more reliable than gas chromatographic analysis, because it is independent of temperature and pressure variations, which affects the volume of gas withdrawn from the culture chamber. When uncorrected for temperature and pressure, selenium values were about 18% higher than Se determined from alkaline peroxide absorption.

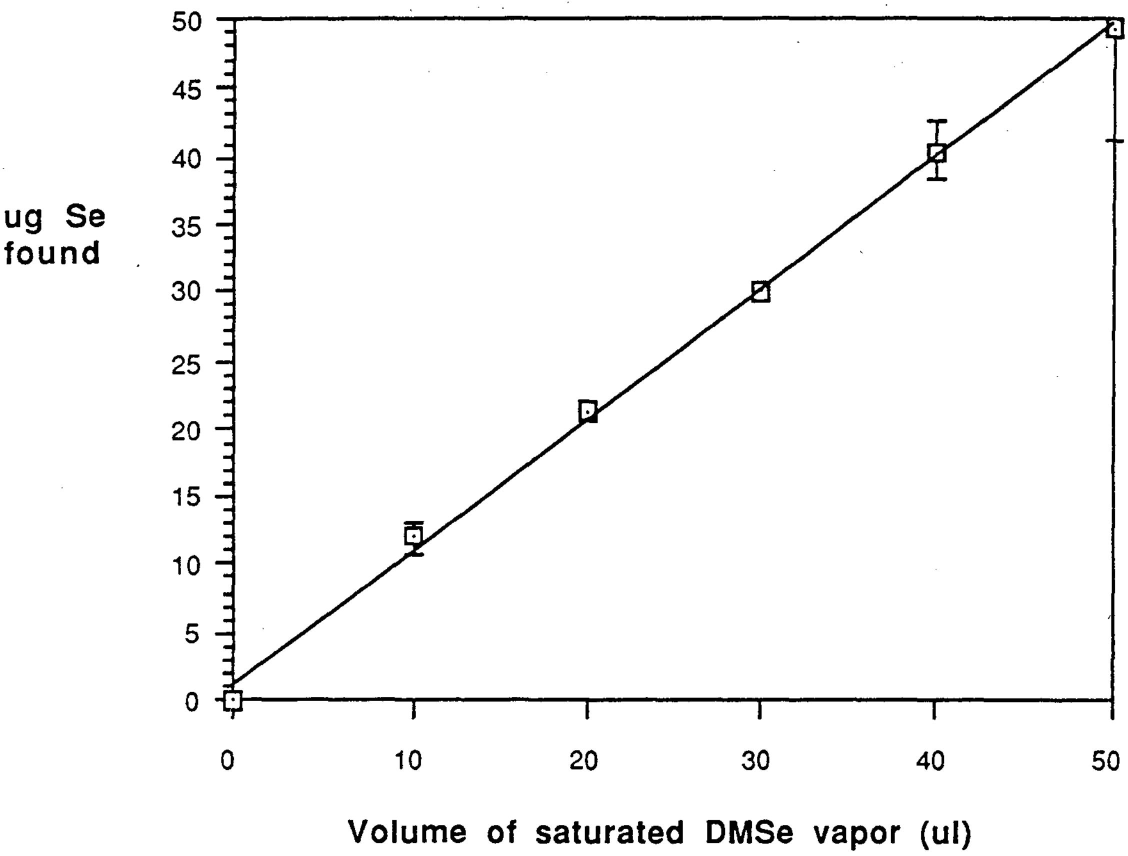

Figure 4.11. Absorption of DMSe by hydrogen peroxide/NaOH. (Analyzed by hydride generation method on ICP-AES.)

4.2.4. Conclusions

The results of this study demonstrate that all of the ''pools'' of selenium defined for this study were amenable to volatilization by microorganisms. However, the rates of volatilization varied from pool to pool, with the lowest rates being associated with what is referred to as the ''refractory'' pool. Equally importantly, the results of this study suggest that microorganisms are also active in converting this pool, or fractions of selenium within this pool to forms that are more amenable to volatilization. Due to the small size of the samples used for these experiments (3 grams), quantification of the precise amount of selenium volatilized was limited. Replication of similar but better controlled experiments with larger soil samples will provide a more accurate assessment of these processes.

5. LAND APPLICATION OF SAN LUIS DRAIN SEDIMENTS

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5.1. Introduction

A potentially effective and cost efficient method of disposing of sediments in the San Luis Drain (SLD) is being investigated. As of 1986, 134 kilometers of the SLD contain roughly 174,000 cubic meters of sediment. Much of this sediment has high levels of selenium and other trace elements. Selenium concentrations as high as 190 parts per million dry weight have been measured in SLD sediments (USBR, 1986b). The average selenium concentration in the northern part of the SLD measured in 1986 was 85 ppm dry weight (USBR, 1986b). Currently, there is no known technique for the disposal of these sediments excluding the use of microbial volatilization techniques (Frankenberger and Karlson, 1988) or their removal and placement in a landfill. Time and cost restraints have stimulated the search for alternative solutions.

A possible solution lies in the land application of SLD sediments. If SLD sediments were to be spread upon nearby land, the vegetation which would grow on these sediments could be used as a nutrient supplement for domesticated animals. Land application of SLD sediments would be most beneficial to the selenium deficient eastern side of the California Central Valley. The feasibility and biological impact of this idea is the focus of an experiment now in progress.

5.2. Purpose

The purpose of this experiment is to investigate the environmental effects of applying SLD sediments to soils. Specifically, the objective is to evaluate the potential for ground water contamination and wildlife exposure to unacceptably high levels of selenium.

5.3. Experimental Plan

Two sites at Kesterson Reservoir have been chosen for evaluating the effects of applying SLD sediments to soils. The first of these sites is in a filled area in Pond 5, the second is in an upland area in Pond 7. An additional site or sites might be chosen in the future, perhaps off of Kesterson Reservoir, such as on the selenium deficient east side of the valley. A map indicating the location of these plots is provided as Figure 5.1. Each of the sites consists of three strips, each covering 25 meters by 10 meters. Contained within each strip are three 8.33 meter by 10 meter subplots (see Figure 5.2). As indicated in Figure 5.2, the test strips will be used to monitor the effects of:

- applying a 7.5 cm layer of drain sediments to the top of the soil;
- applying a 7.5 cm layer of drain sediments and tilling to a depth of 15 cm, and;
- applying a 7.5 cm layer of drain sediments and ripping and tilling to a depth of 30 cm.

5.4. Monitoring Program

A comprehensive monitoring program is planned for these plots. The data that we collect will address several issues, including migration of selenium from the drain sediments down into the soil profile and groundwater; changes in the quality and speciation of selenium; selenium uptake by plants; and accumulation of selenium in invertebrates. A schematic highlighting the elements of the monitoring plan is provided in Figure 5.3. The following data will be collected from the test plots.

5.4.1. Soil Sampling

Soil samples are collected initially and biannually from depths of 0 - 15 cm, 15 - 30 cm, 30 - 45 cm, and 45 - 60 cm. Three samples are collected for each depth interval within each test strip. Each sample is a composite of 4 smaller samples (see Figure 5.3). Soil water extracts (1:5 mass of soil to mass of water) of these samples are analyzed for total selenium, water extractable selenium, sulfur, boron, and chloride. Additional selenium speciation and more comprehensive chemical characterization will be performed on a subset of the samples.

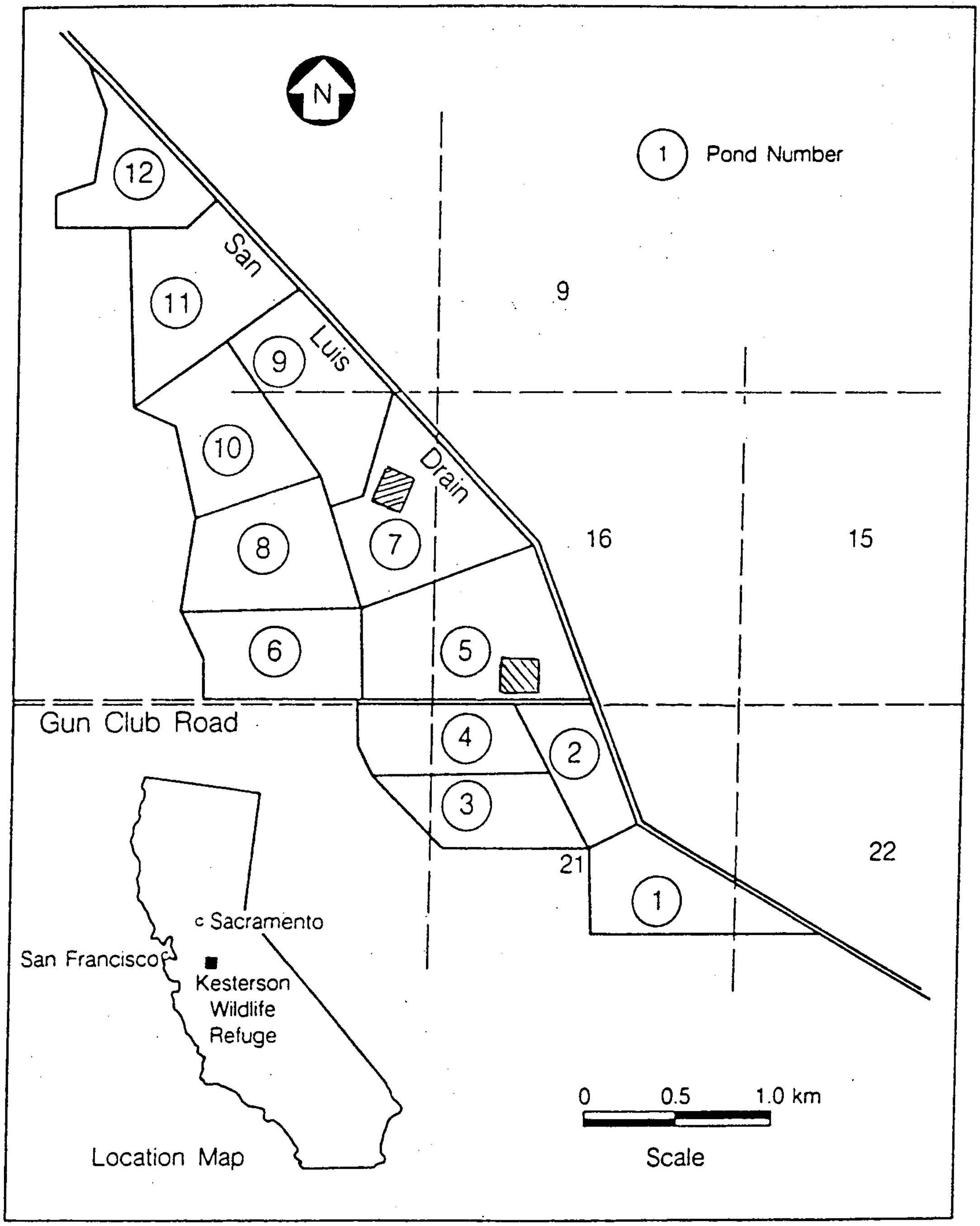

Figure 5.1. Location of the drain sediments experimental plots.

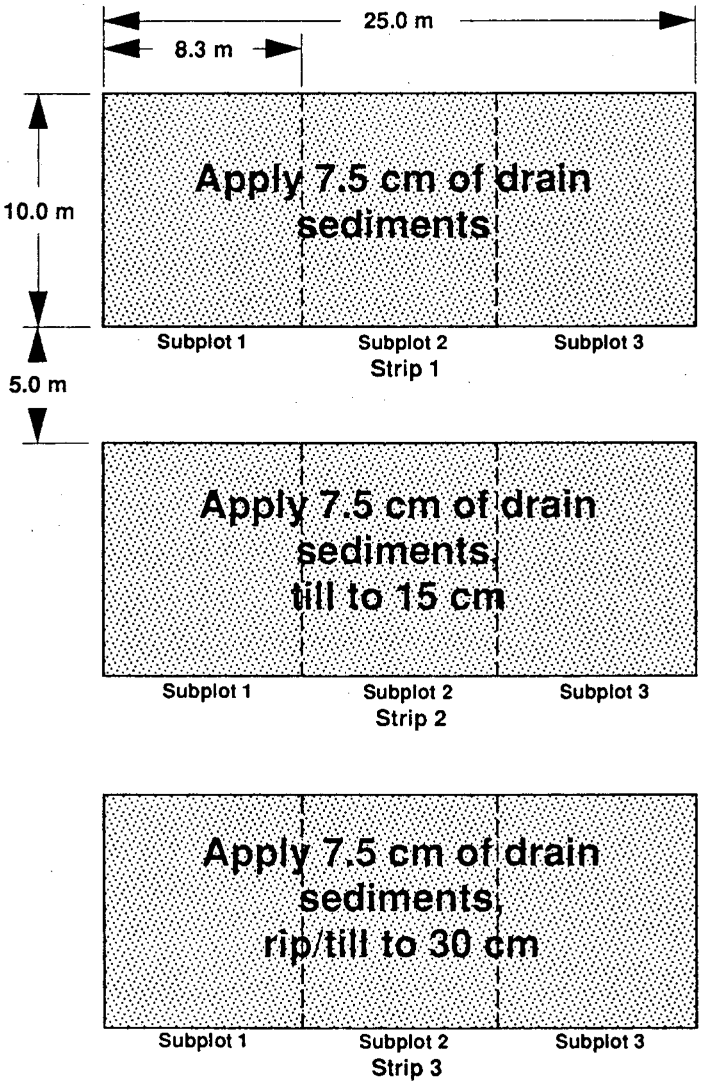

Figure 5.2. Schematic of a drain sediments experimental site.

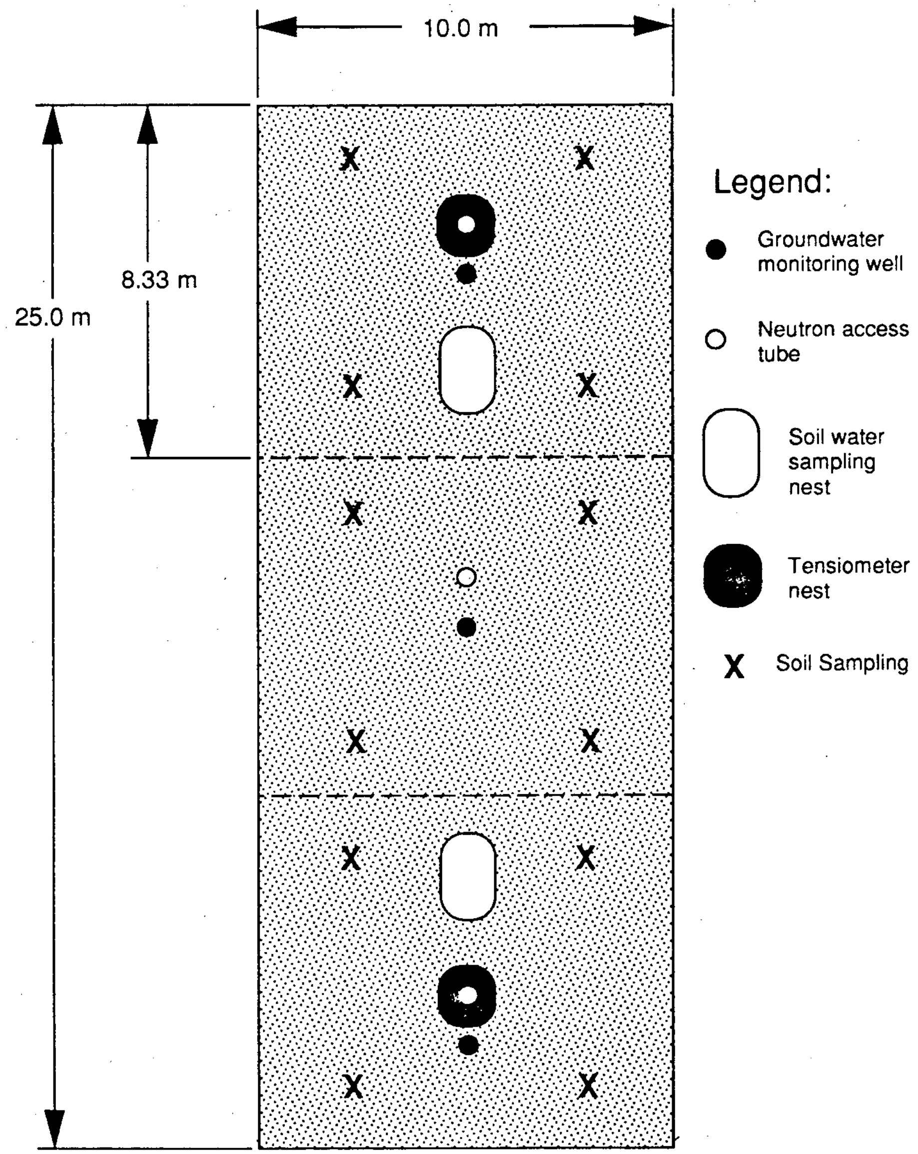

Figure 5.3. Detail of a single strip at a drain sediments experimental site.

5.4.2. Soil Water and Groundwater Sampling

Soil water samples are collected with ceramic cup suction samplers biannually from each subplot to a depth of 1.5 meters. Samples are collected quarterly from one subplot on each strip. Samples are analyzed for selenite, total selenium, and organic selenium. Selected samples are to be analyzed for boron, chloride, molybdenum, vanadium, and uranium.

Fluid potential and neutron probe water content measurements are obtained biannually from each strip, and quarterly from one subplot on each strip.

Shallow groundwater samples from an array of three meter deep wells on each site are collected biannually. Samples are analyzed for selenite, total selenium, nitrate, boron, sulfate, and chloride.

5.4.3. Biological Monitoring

Samples of vegetation are collected biannually at each of the sites. The vegetation sampling of each strip will include major and minor types of vegetation. Samples are analyzed for total selenium. Nonflying invertebrates are collected from pit-fall and debris traps on a biannual basis. One debris and three pit-fall traps are installed on each subplot. Biological samples are analyzed for total selenium.

5.5. History of Initial Work

The initial shallow soil samples were collected from the Pond 5 and Pond 7 experimental sites in August of 1989. In September of 1989, three meter deep groundwater monitoring wells were installed on each subplot. These wells were then sampled and capped below grade so that the San Luis Drain sediments could be applied using heavy equipment. During the well installation, three meter shelby tube cores were also collected from each subplot.

Beginning in late September 1989, roughly 380 cubic meters of San Luis Drain sediments were removed from the drain and placed in a ‘‘mixing area’’ in Pond 7. These sediments were removed from the drain between ‘‘Check 2’’ (at the very southern tip of the reservoir), and the northern end point of of the drain. In mid October the average selenium concentration in these

SLD sediments was measured to be 59.3 ± 15.8 (n=5) ppm per dry weight of sample. Average total water extractable selenium and selenite concentrations were 3.4 ± 2.5 ppm per dry weight and 0.55 ± 0.26 ppm dry weight respectively. After extensive homogenization by "wind rolling" the sediments with a large grader in the mixing area, land application in Pond 5 and Pond 7 was completed in late November 1989. The first strip of each site had 7.5 cm of drain sediments applied to it with no other treatment. The second strip of each site had the same application of sediments but was tilled repeatedly to a depth of 15 cm. The third strip of each site had equivalent sediment application but was repeatedly ripped and tilled to a depth of 30 cm. Pore water samplers, fluid potential meters, neutron probe access tubes, and pit-fall/debris traps were then installed on each of the strips on these sites.

5.5.1. Soil, Groundwater, and Biological Sampling Prior to Application of SLD Sediments

Prior to application of SLD sediments in Pond 5 and Pond 7, soil samples were collected from the experimental sites in August 1989 as per the procedure outlined previously. Plots of total water extractable selenium and selenite and electrical conductivity are shown in Figures 5.4 through 5.9. A complete and accurate set of total selenium data is not available for these samples because the XRF method of analysis, with its detection limit of 1 ppm, is not reliable below 2 ppm.

The plots show measured data at the depth intervals 0 - 15 cm, 15 - 30 cm, 30 - 45 cm, and 45 - 60 cm. The points at the centers of the depth intervals on each curve have plus or minus one standard deviation attached to them. This deviation represents the spread in measured data in the three samples analyzed. Each of the three samples is a composite of four samples collected on a single subplot. (The points at the center of each depth interval have been shifted slightly so that the standard deviations do not overlap.) All concentrations are normalized to parts-per-billion (ppb) or parts-per-million (ppm) per dry weight of sample.

The plots show average total water extractable selenium in the 0 - 15 cm interval to be about 100 ppb dry weight and 150 ppb dry weight for Ponds 5 and 7 respectively. Water extractable selenite concentrations in the top interval in Ponds 5 and 7 average 5 ppb dry weight and 45

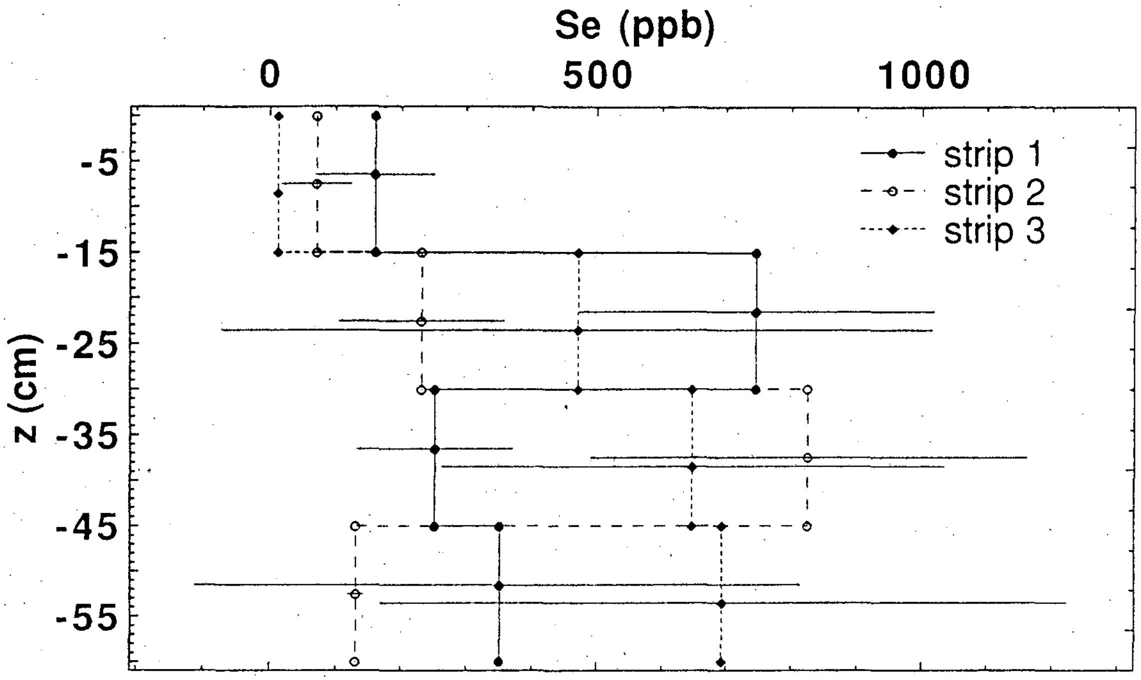

Figure 5.4. Pond 5 pre-SLD application total water extractable selenium (ppb dry weight) vs. depth.

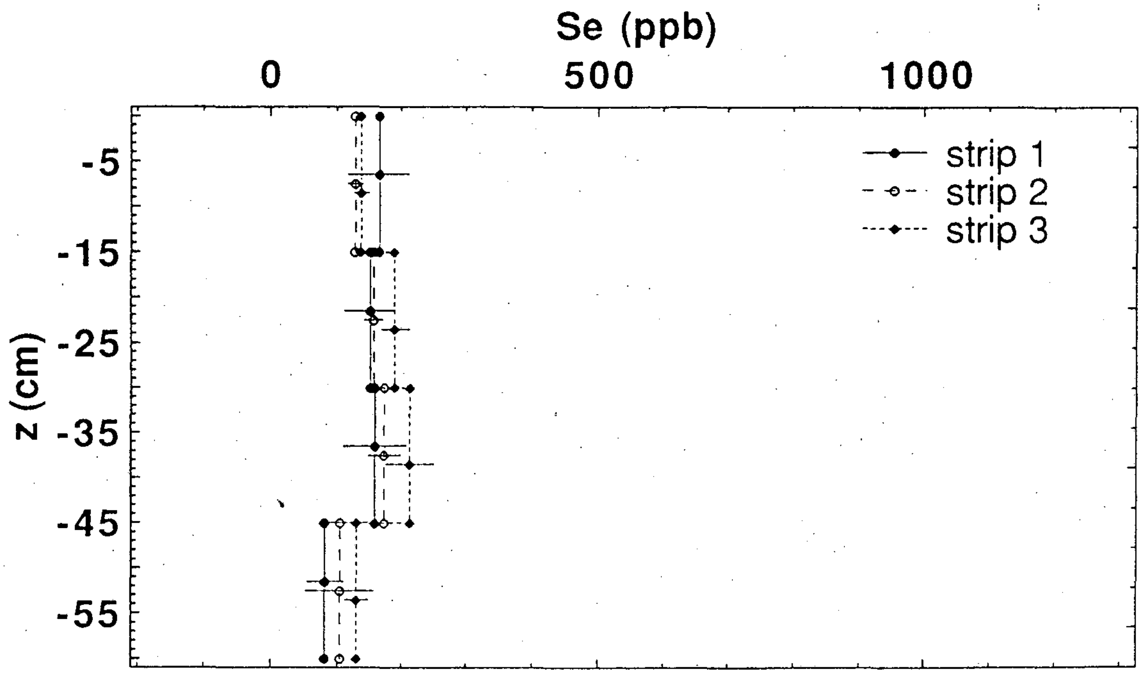

Figure 5.5. Pond 7 pre-SLD application total water extractable selenium (ppb dry weight) vs. depth.

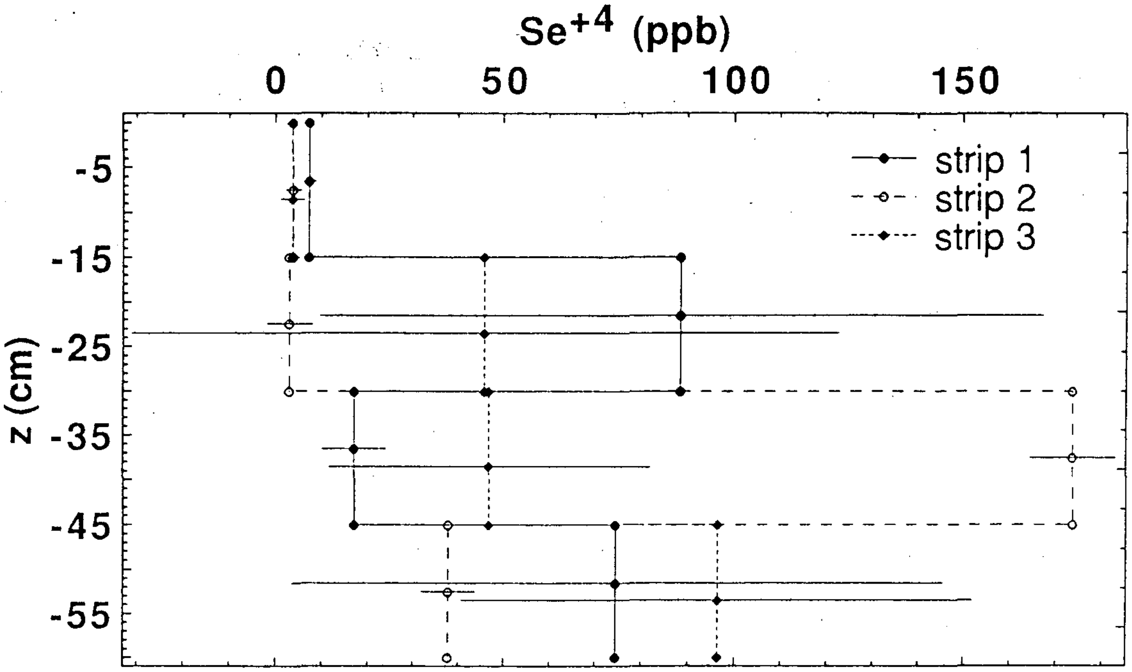

Figure 5.6. Pond 5 pre-SLD application water extractable selenite (ppb dry weight) vs. depth.

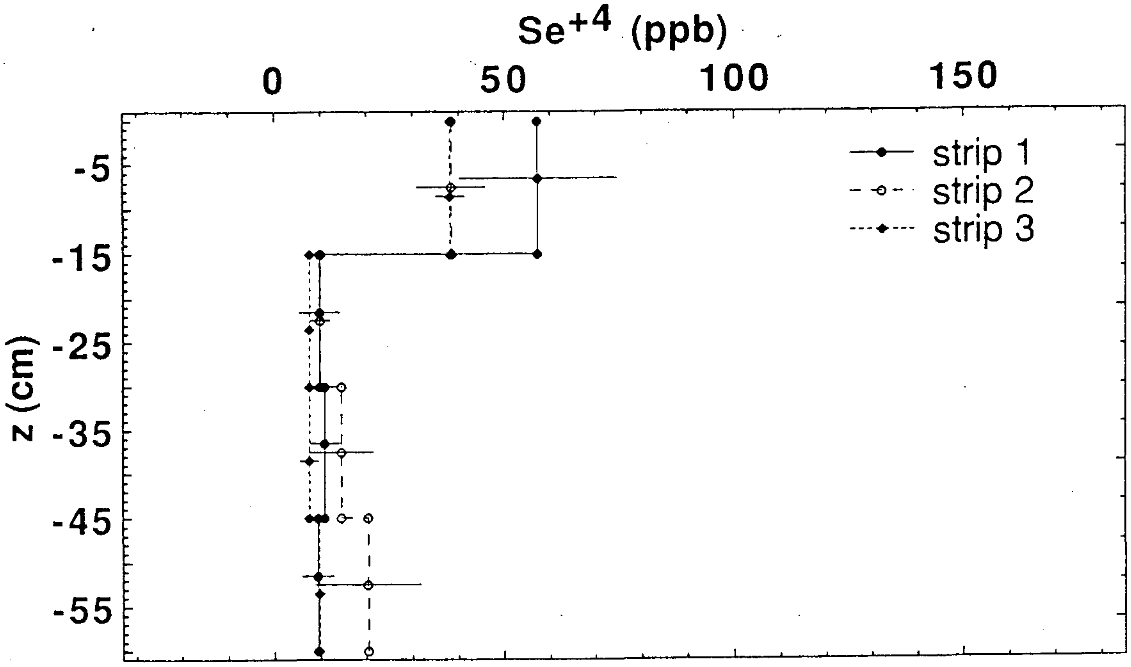

Figure 5.7. Pond 7 pre-SLD application water extractable selenite (ppb dry weight) vs. depth.

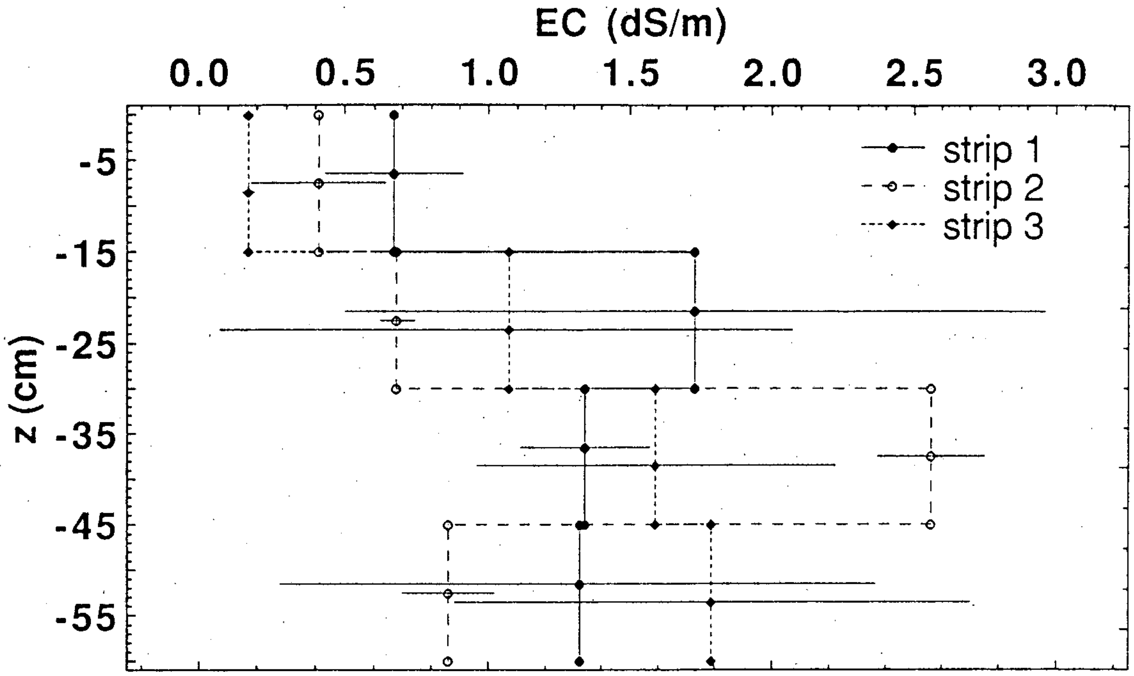

Figure 5.8. Pond 5 pre-SLD application (1:5 mass of soil to mass of water extract) electrical conductivity vs. depth.

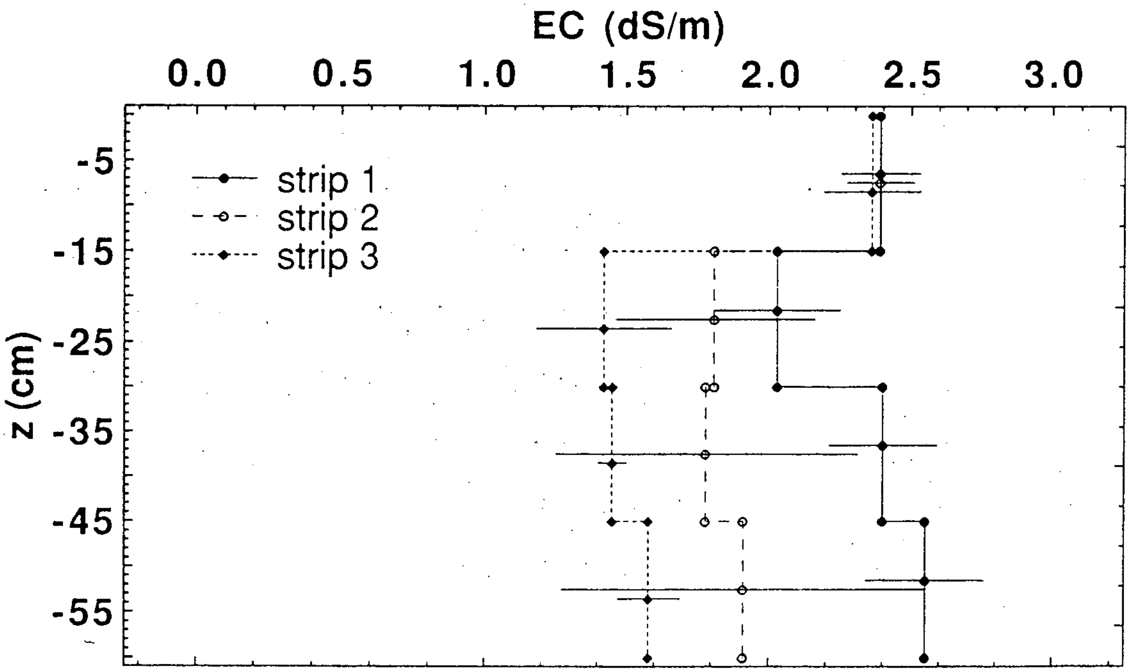

Figure 5.9. Pond 7 pre-SLD application (1:5 mass of soil to mass of water extract) electrical conductivity vs. depth.

ppb dry weight. The concentration of total water extractable selenium and selenite measured in the Pond 5 and Pond 7 test plots are typical of filled and grassland areas, respectively (see Chapter 6). The presence of fill material is clearly evident in Pond 5; Figure 5.4 shows soil with low water extractable selenium concentration underlain by soil of higher water extractable selenium concentration (up to 750 ppb dry weight). The total water extractable selenium and selenite data show much greater variability in Pond 5 than in Pond 7. This is because fill material of different composition, packing, and depth has been laid upon the experimental site in Pond 5. Average depths of the fill on strips 1, 2, and 3 in Pond 5 are 25.4 cm, 33.7 cm, and 47.6 cm respectively.

The plots of electrical conductivity in the surface 15 cm indicate a much more saline environment in Pond 7 than in Pond 5. These plots in Figures 5.8 and 5.9 are the EC's of 1:5 soil to water extracts (normalized to 25 degrees centigrade). A linear extrapolation of these electrical conductivities to a 1:1 soil to water extract yields average EC's of about 2 dS/m and 12 dS/m in the 0 - 15 cm interval for Ponds 5 and 7 respectively. It is recognized that this extrapolation yields EC's that are probably slightly higher than would truly be found in a 1:1 extract and is done here for purposes of comparison.

Shallow groundwater was sampled in October 1989 from 18 three meter deep wells on the experimental sites and from two wells in the "mixing area." Groundwater samples from Pond 5 contain concentrations of selenium between 0.4 and 2.4 ppb with an average concentration of 1.0 ppb. Samples from wells in Pond 7 contain concentrations of selenium between 0.7 and 1.3 ppb with an average concentration of 1.0 ppb. These low selenium concentrations are typical of Kesterson Reservoir groundwater. Nitrate concentrations were measured in the Pond 5 wells from below 0.03 ppm up to 2.17 ppm with an average of about 0.57 ppm. Nitrate concentrations ranged from less than 0.03 up to 0.11 for an average of 0.05 ppm in Pond 7. Analyses of boron and sulfate (as sulfur) were also performed and yield values expected for infiltrated drainage water.

Large composite vegetation samples were collected from each site before the drain sediments were applied. These first samples were composed entirely of *Kochia*. The total selenium in these samples were 3.5 and 1.2 ppm per dry weight of sample for Pond 5 and Pond 7 respectively.

5.6. Post SLD Sediment Application

5.6.1. Sampling and Analysis

Soil samples were collected from the the experimental sites in September 1990 after application of SLD sediments. Total selenium, total water extractable selenium, selenite, boron, sulfur, electrical conductivity, selenite fraction of total water extractable selenium, and total water extractable selenium fraction of total selenium are shown in Figures 5.10 through 5.25.

Pond 5 total selenium data shows little difference in the concentrations in strips 1 and 2 for the 0 - 15 cm interval (about 22 ± 3.6 ppm per dry weight, n=3). The selenium concentration in the 0 - 15 cm sample for the third strip in Pond 5 is 13 ppm dry weight. Total selenium concentrations in the 0 - 15 cm samples from Pond 7 are 36 ± 6.5, 23.6 ± 7.0, and 16.8 ± 3.8 ppm dry weight for strips 1, 2, and 3 respectively (n=3).

Total water extractable selenium concentrations range from 0.4 to 1.2 ppm dry weight for Pond 5 and from 0.7 to 1.5 ppm dry weight for Pond 7 after SLD sediment application. A linear extrapolation of the electrical conductivities in Figures 5.20 and 5.21 to a 1:1 soil to water extract yields average EC's of about 13.4 dS/m and 18 dS/m in the 0 - 15 cm interval for Ponds 5 and 7 respectively. (Again it is recognized that this extrapolation yields EC's that are probably slightly higher than would truly be found in a 1:1 extract and is done here for purposes of comparison.) Boron concentrations in the 0 - 15 cm intervals in Ponds 5 and 7 average 7 and 11 ppm dry weight. Sulfur concentrations in the 0 - 15 cm intervals in Ponds 5 and 7 average 2300 and 3000 ppm dry weight. Figures 5.24 and 5.25 show the fraction of total water extractable selenium to total selenium in the 0 - 15 cm samples to be about 4% for all strips in both ponds, again typical of Kesterson Reservoir. Interestingly, Figures 5.22 and 5.23 show high fractions of water extractable selenite compared to total water extractable selenium (up to 45% in Pond 5). This fraction of water extractable selenite is very high compared to more typical values measured elsewhere at

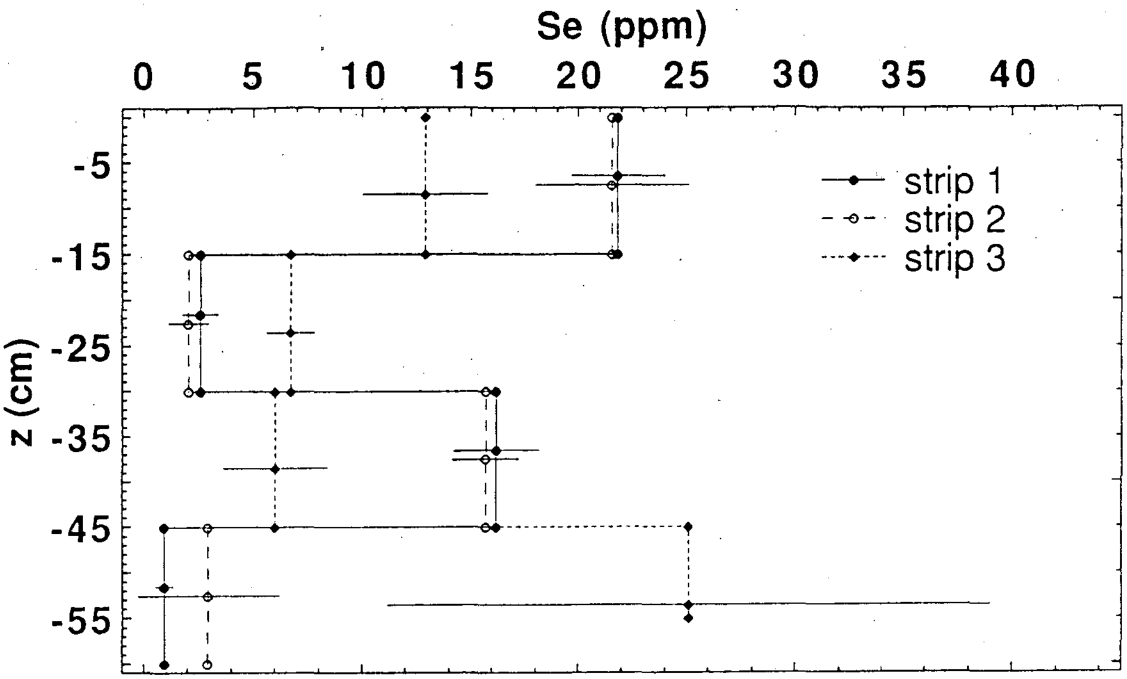

Figure 5.10. Pond 5 post-SLD application total selenium (ppm dry weight) vs. depth.

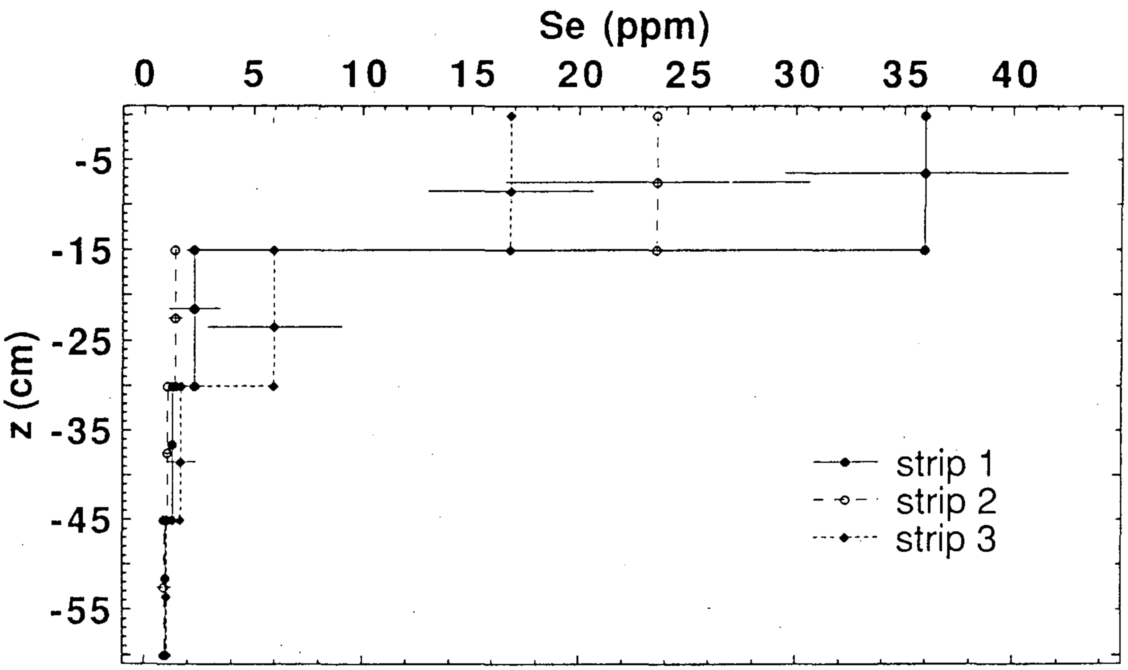

Figure 5.11. Pond 7 post-SLD application total selenium (ppm dry weight) vs. depth.

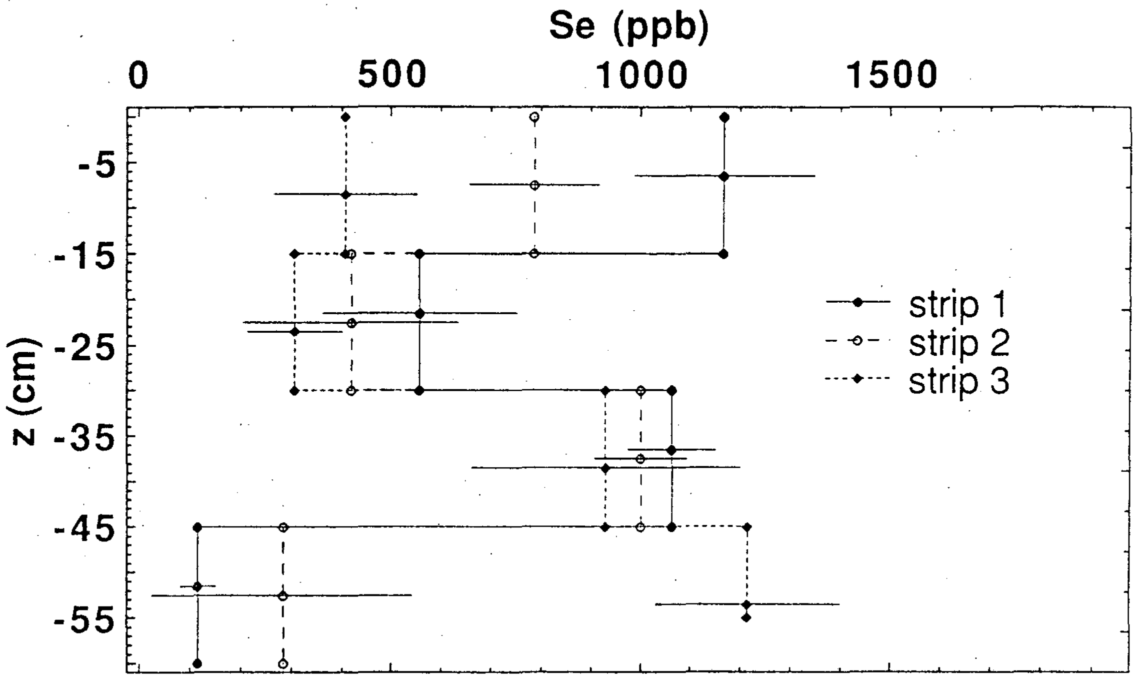

Figure 5.12. Pond 5 post-SLD application total water extractable selenium (ppm dry weight) vs. depth.

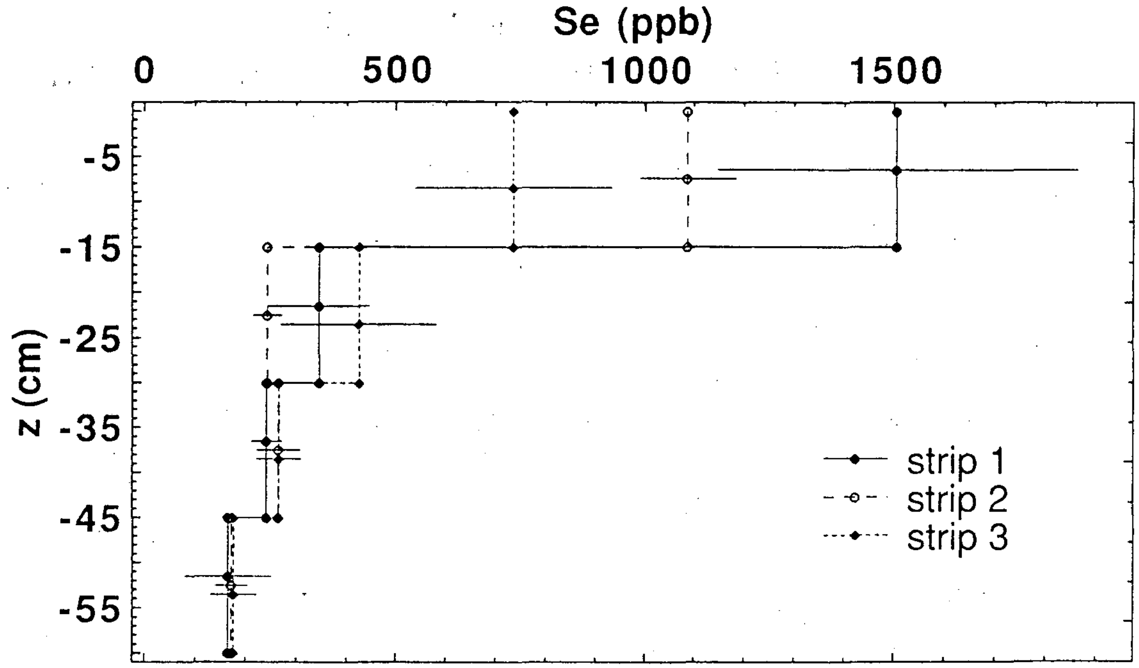

Figure 5.13. Pond 7 post-SLD application total water extractable selenium (ppm dry weight) vs. depth.

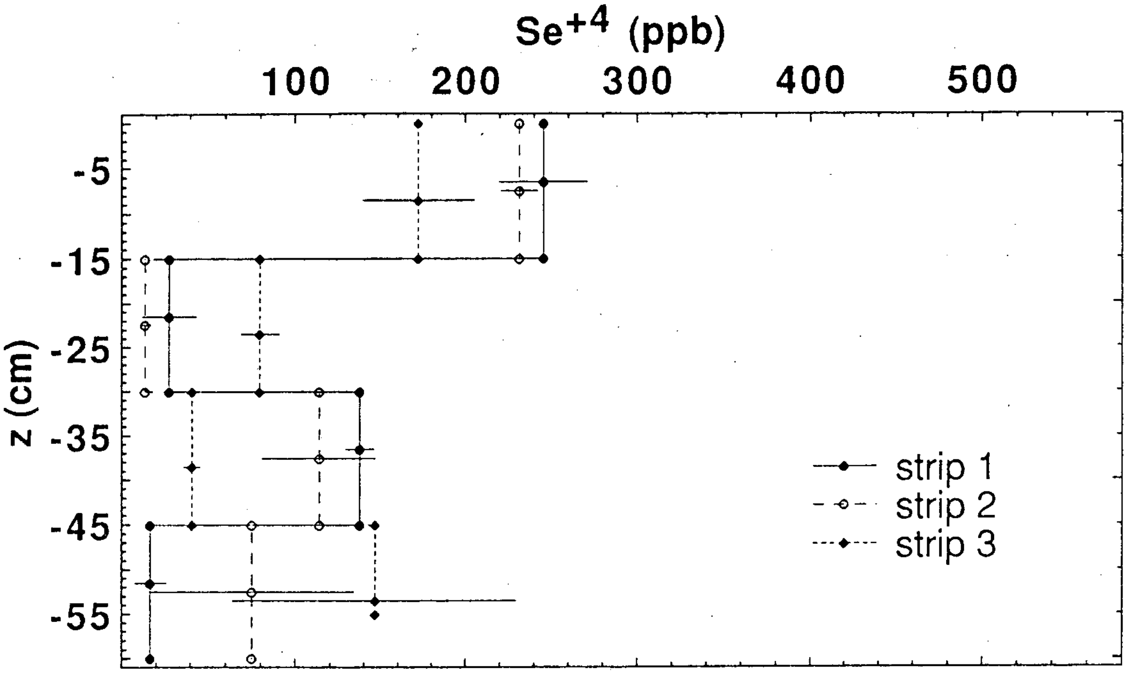

Figure 5.14. Pond 5 post-SLD application water extractable selenite (ppm dry weight) vs. depth.

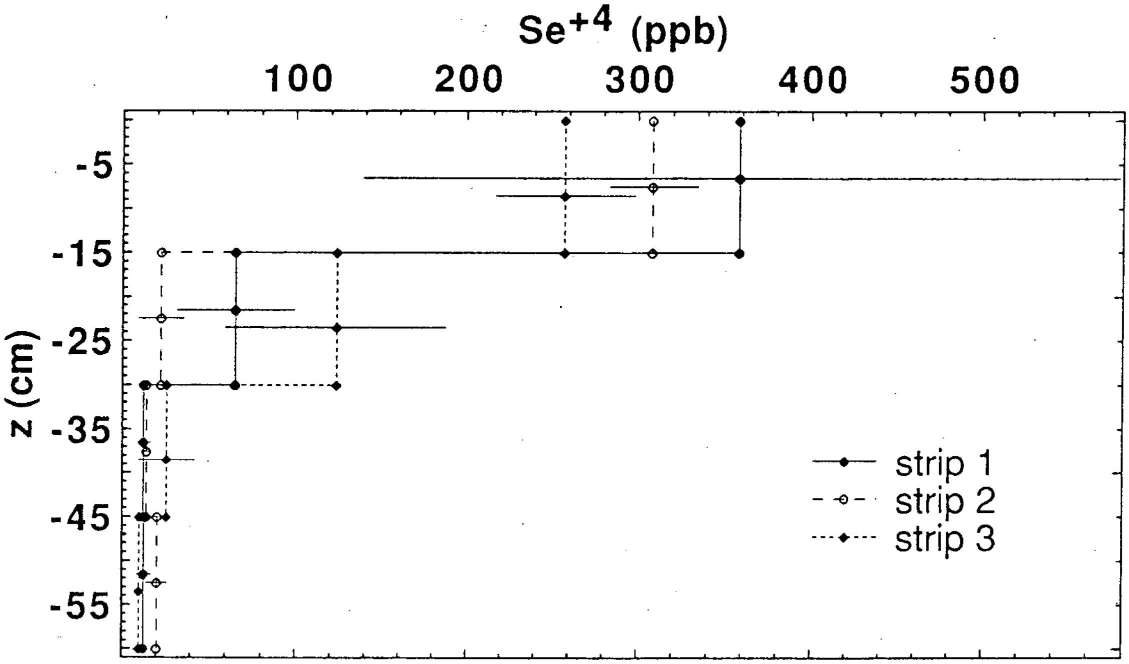

Figure 5.15. Pond 7 post-SLD application water extractable selenite (ppm dry weight) vs. depth.

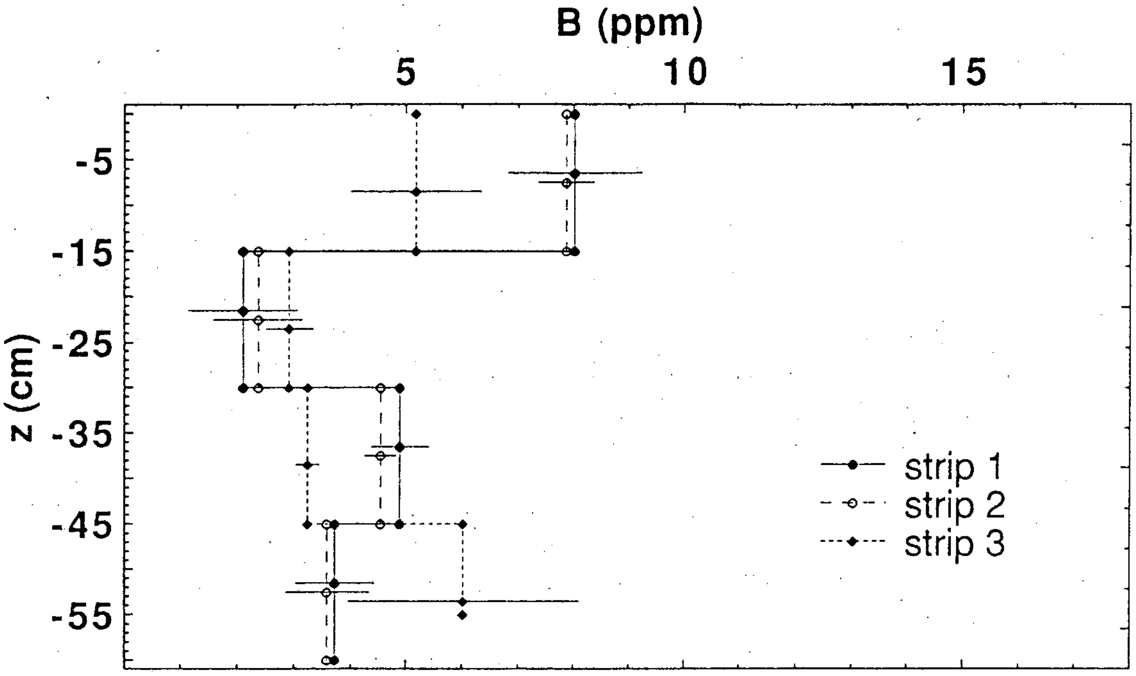

Figure 5.16. Pond 5 post-SLD application water extractable boron (ppm dry weight) vs. depth.

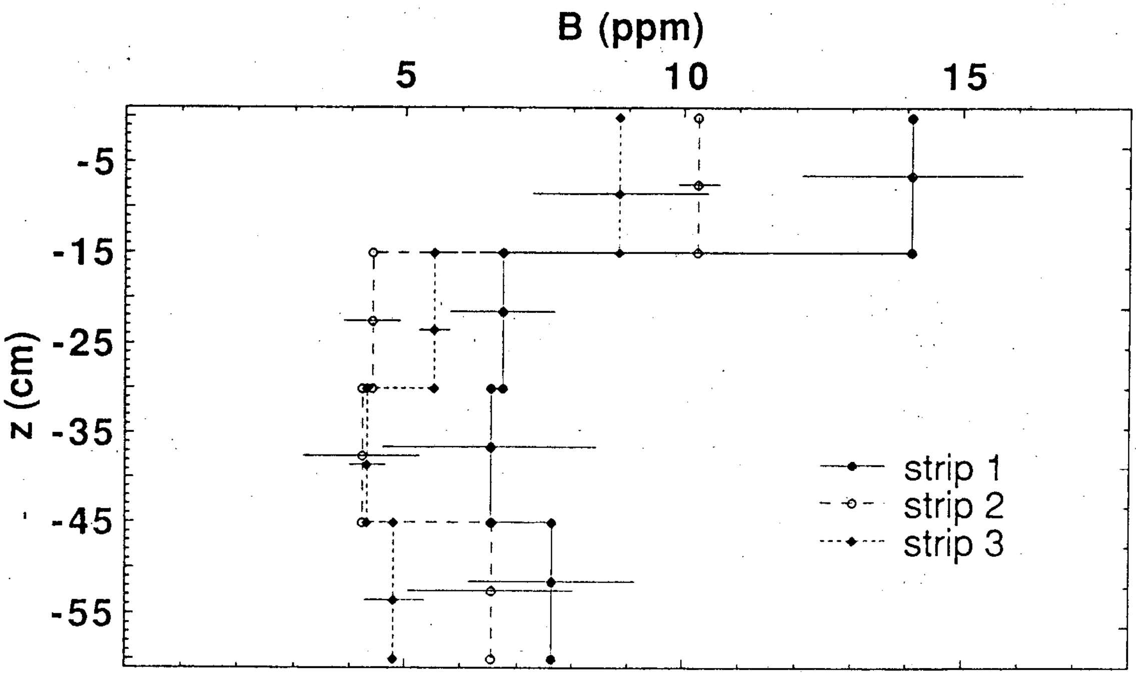

Figure 5.17. Pond 7 post-SLD application water extractable boron (ppm dry weight) vs. depth.

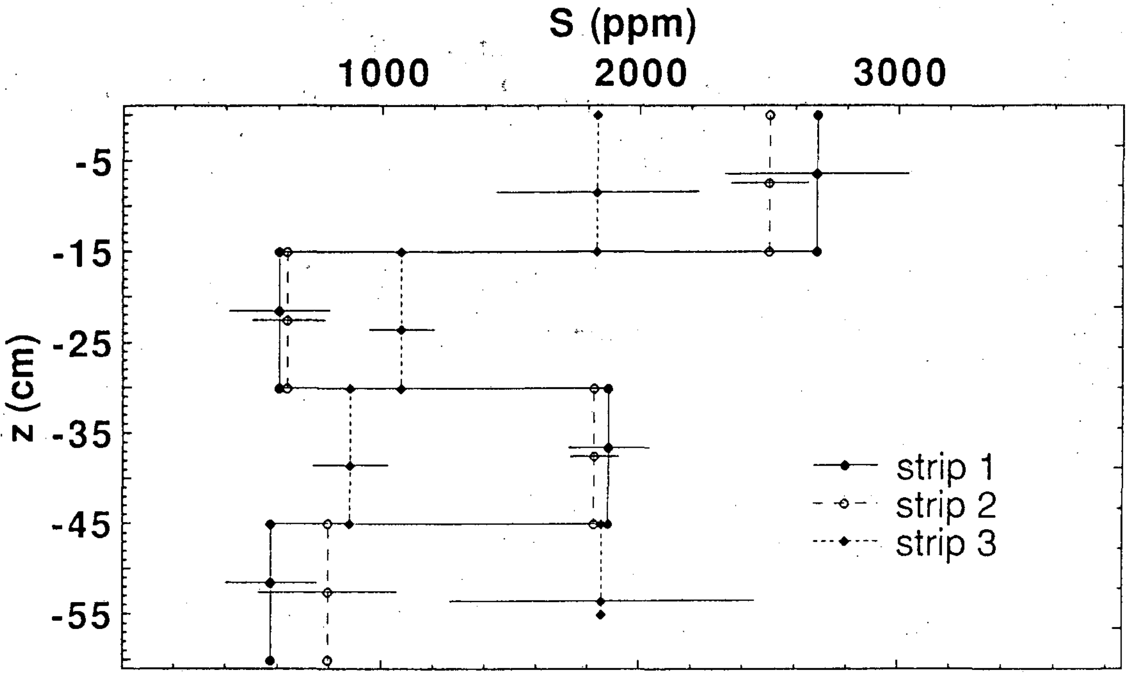

Figure 5.18. Pond 5 post-SLD application water extractable sulfate (as sulfur) (ppm dry weight) vs. depth.

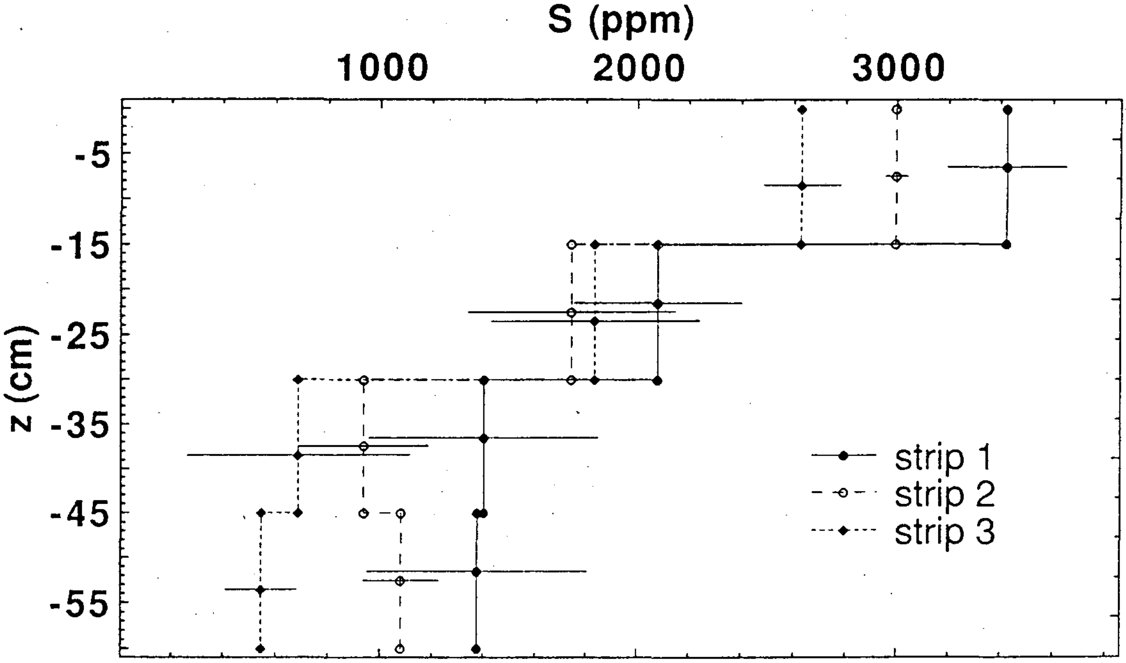

Figure 5.19. Pond 7 post-SLD application water extractable sulfate (as sulfur) (ppm dry weight) vs. depth.

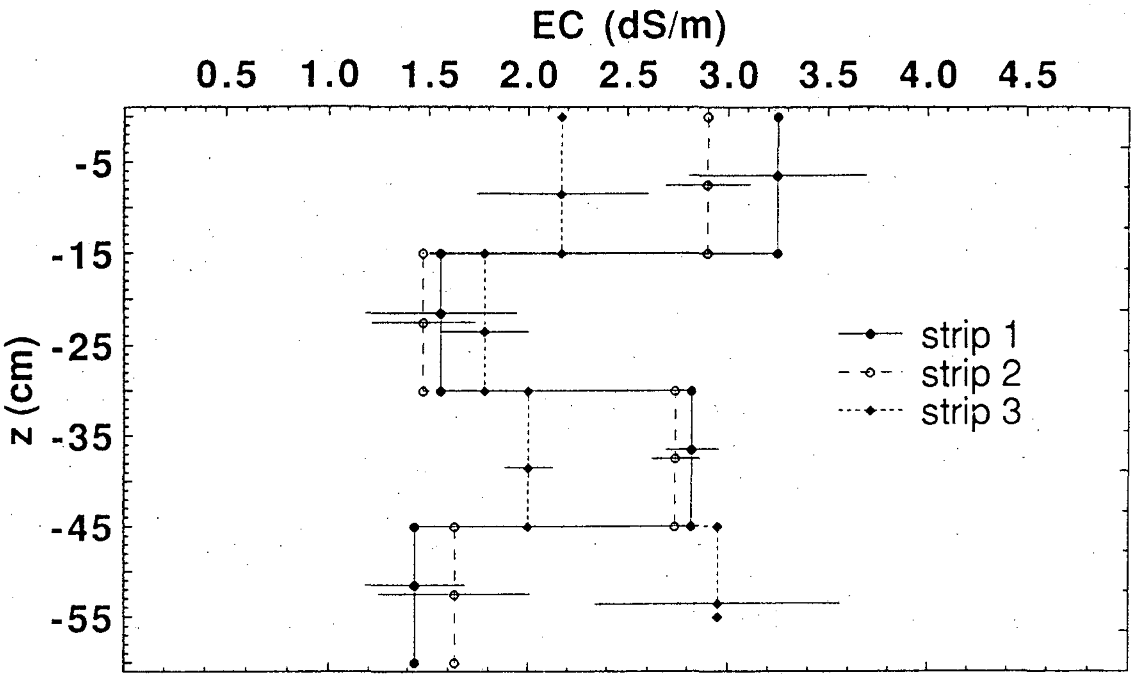

Figure 5.20. Pond 5 post-SLD application (1:5 mass of soil to mass of water extract) electrical conductivity vs. depth.

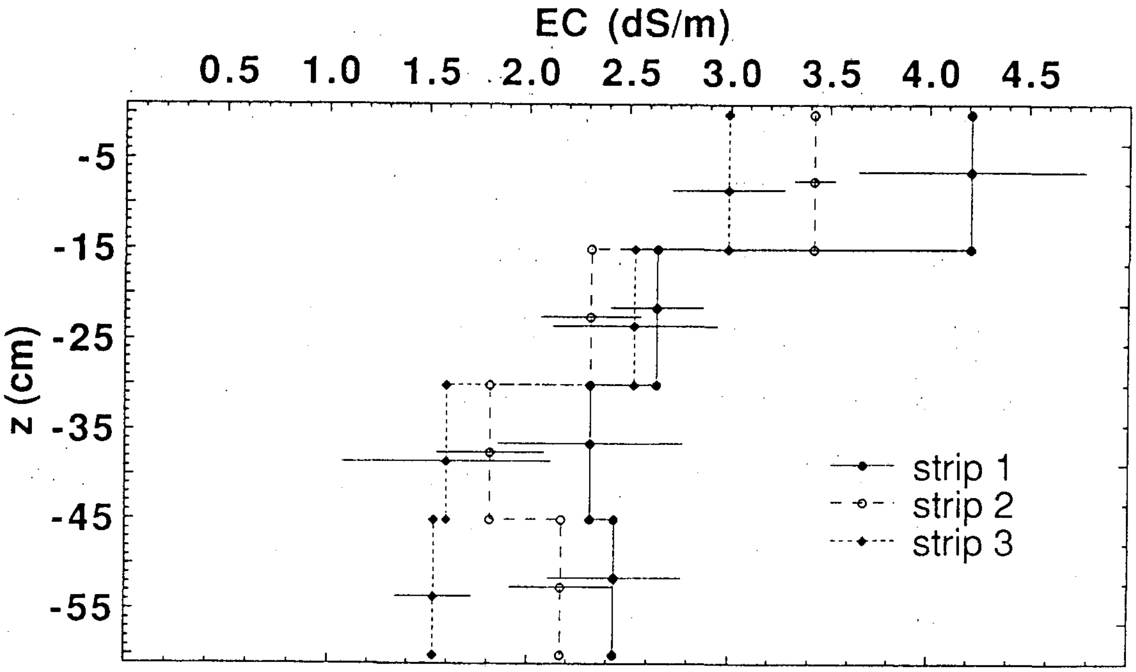

Figure 5.21. Pond 7 post-SLD application (1:5 mass of soil to mass of water extract) electrical conductivity vs. depth.

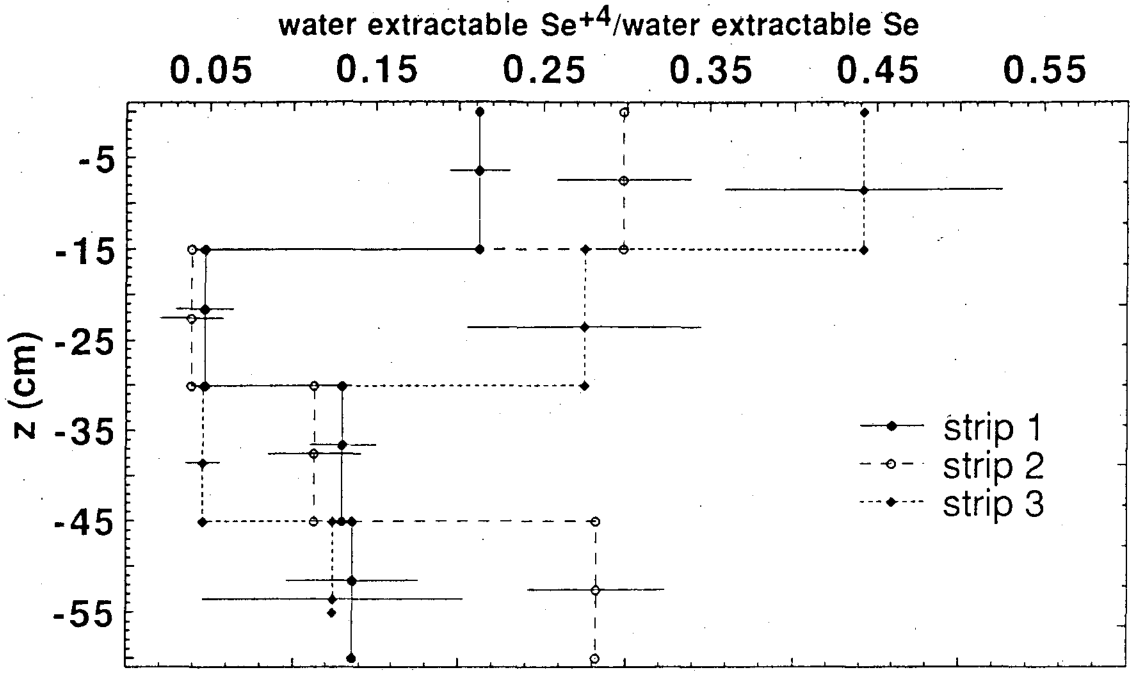

Figure 5.22. Pond 5 post-SLD application fraction of water extractable selenite as compared to total water extractable selenium vs. depth.

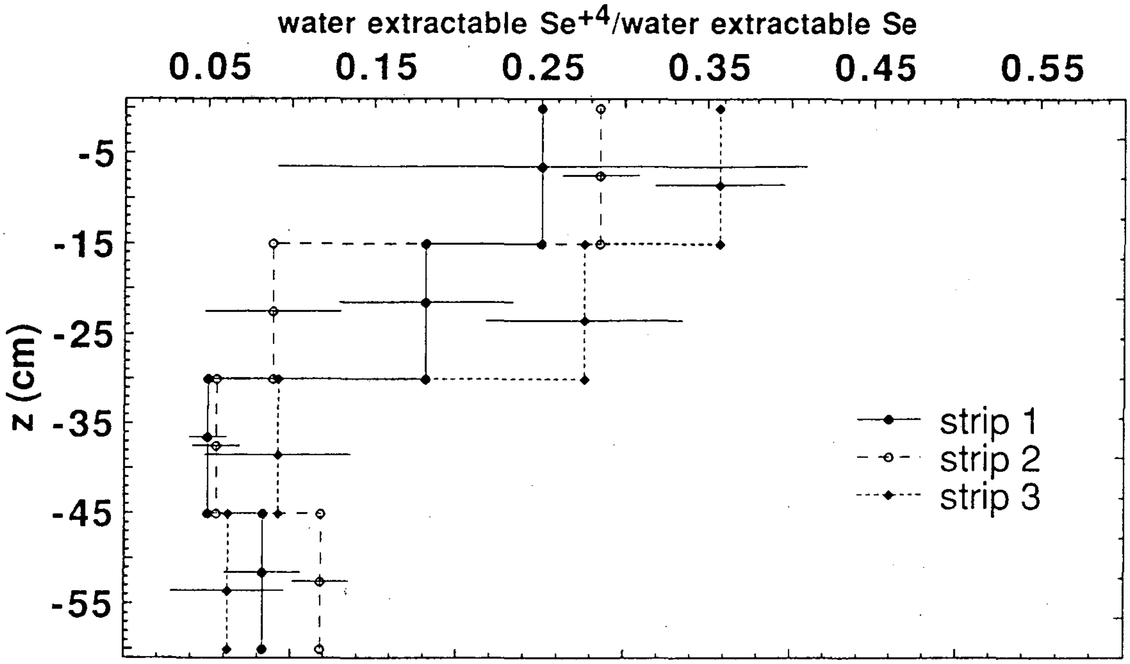

Figure 5.23. Pond 7 post-SLD application fraction of water extractable selenite as compared to total water extractable selenium vs. depth.

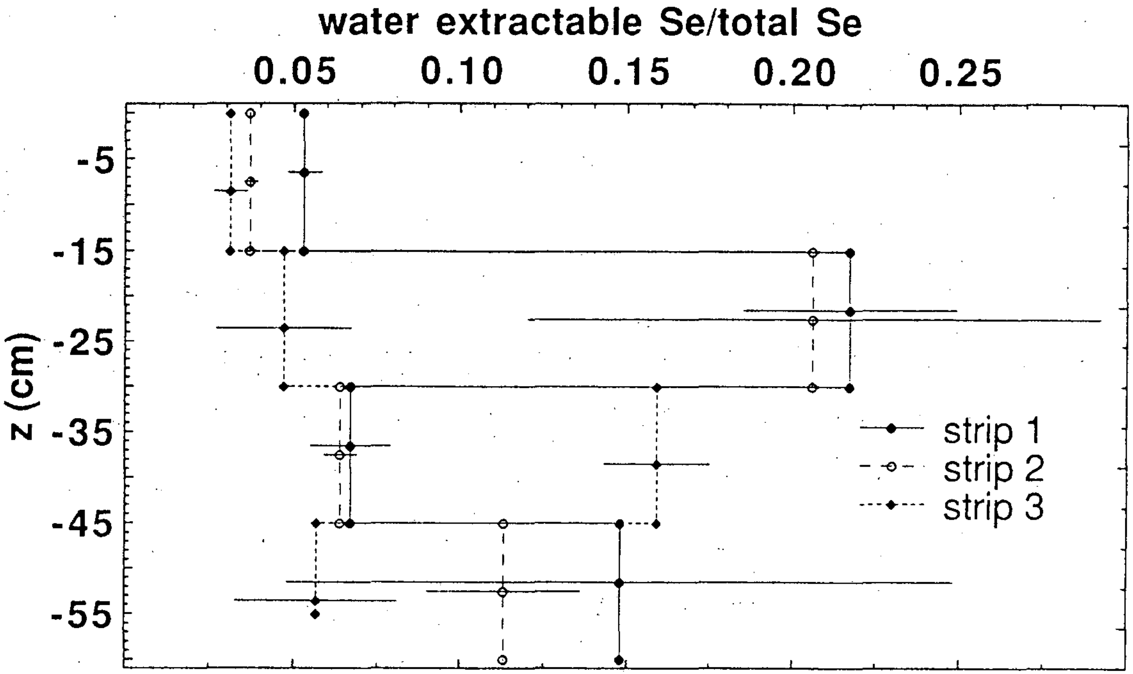

Figure 5.24. Pond 5 post-SLD application fraction of water extractable selenium as compared to total selenium vs. depth.

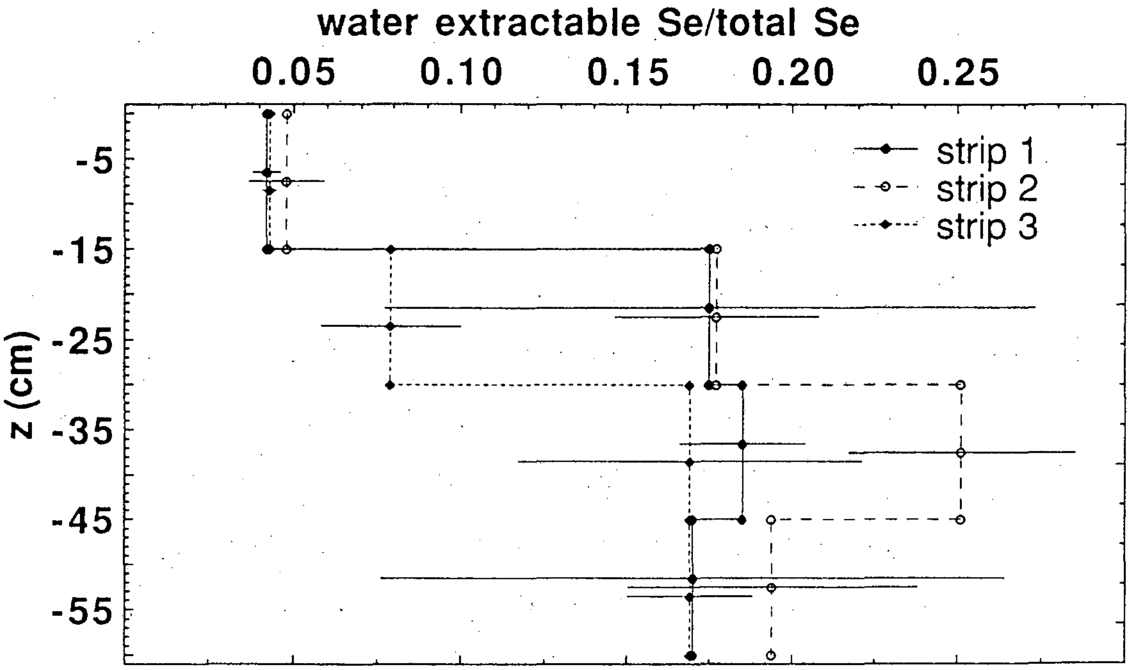

Figure 5.25. Pond 7 post-SLD application fraction of water extractable selenium as compared to total selenium vs. depth.

the reservoir of 20%. Processes leading to this are being investigated.

In an effort to evaluate how effective we were in meeting our objective of spreading an even layer of SLD sediments on each of the experimental sites, we calculated the mass of selenium laid down upon each strip. Table 5.1 shows the mean mass of selenium in the top 15, 30, 45, and 60 cm for each strip of each interval in units of g/m^2. Regardless of the different treatments given to each strip, the selenium mass should be about the same in the top 30 cm for each strip for each pond if an even application of SLD sediment was achieved. The mean selenium masses in the top 30 cm intervals for each strip were compared to each other to see if they are statistically different. This comparison was done using a 95% confidence rating applied to the difference in means of Student-t distributions. All of the mean masses of selenium in the top 30 cm interval for each strip in Pond 5 are found to be statistically identical except for strip 3 which was found to be statistically different from strip 1. All of the mean masses of selenium in the top 30 cm interval for each strip in Pond 7 are found to be statistically identical. The soil sampling procedure is such that the mass of selenium in the top 15 cm for strips 1 and 2 for both ponds should be equal. The same statistical comparison was made for the top 15 cm intervals of the first and second strips. The mean selenium concentrations in the shallow intervals of strip 1 and strip 2 in both Ponds 5 and 7 are found to be statistically identical. Table 5.1 also shows the mass of selenium in the 0 - 15 cm intervals of the third strips in Ponds 5 and 7 to be about 64% of the masses in the first and second strips, as would be expected with deeper ripping and tilling. Correspondingly, selenium concentrations in the 15 - 30 cm intervals for both the third strips (Figures 5.10 and 5.11) are higher (6-7 ppm dry weight) than those in the first and second strips (2-3 ppm dry weight) due to the deeper ripping and tilling.

The total selenium concentrations seen in Figure 5.11 show a wide variability in the concentrations in the 0 - 15 cm samples from Pond 7. This variability can be explained by examining the topography and vegetation at the experimental site in Pond 7. In contrast to Pond 5's smooth surface before SLD sediment application, the surface of Pond 7 was very uneven due to its many tufts of salt grass. Some of these tufts were as much as 15 cm higher than the surrounding ground. In both ponds, the drain sediments were spread out leaving a smooth flat surface. Doing so in Pond 7 resulted in a an uneven spreading of the sediments such that the thickness of sediment for each sample depended upon whether the sampling point was at a ''crest'' or a ''valley'' near or on a tuft of salt grass. Table 5.2 shows expected selenium concentrations depending upon the depth of the sediment application, which for Pond 7 could range from less than 7.5 cm up to roughly 12.7 cm. These concentration ranges were calculated taking into account the density differences between the drain sediments and the in situ material and the relative amounts of drain sediments and in situ material in the interval. The calculated possible concentration ranges in Table 5.2 are in good agreement (given standard deviations) with the measured data in Figures 5.10 and 5.11.

Table 5.1. Mass of selenium (g/m^2) in the top 15 cm, 30 cm 45 cm, and 60 cm of each strip in Ponds 5 and 7.

Location		Mass of Se in top 15 cm	Mass of Se in top 30 cm	Mass of Se in top 45 cm	Mass of Se 0-60 cm
Pond 5	Strip 1	3.2 ± 0.3	3.7 ± 0.5	6.6 ± 0.8	6.8 ± 0.9
	Strip 2	2.8 ± 0.4	3.1 ± 0.5	5.8 ± 0.7	6.4 ± 1.4
	Strip 3	1.9 ± 0.4	2.9 ± 0.6	4.0 ± 1.0	7.8 ± 2.7
Pond 7	Strip 1	4.3 ± 0.8	4.8 ± 1.0	5.0 ± 1.0	5.3 ± 1.0
	Strip 2	3.2 ± 0.7	3.5 ± 0.8	3.7 ± 0.8	3.9 ± 0.9
	Strip 3	2.4 ± 0.4	3.4 ± 0.9	3.7 ± 1.0	3.9 ± 1.1

Table 5.2. Expected selenium concentrations (ppm dry weight) in the 0-15 cm interval as a function of SLD sediment application depth for the first and second strips of Ponds 5 and 7.

Location	7.5 cm of drain sediments applied	12.7 cm of drain sediments applied
Pond 5 Strip 1	27.4 ± 1.7	
Pond 5 Strip 2	21.2 ± 1.8	
Pond 7 Strip 1	18.8 ± 3.9	29.7 ± 6.5
Pond 7 Strip 2	21.1 ± 2.7	33.3 ± 4.6

Further soil monitoring over time at the experimental sites will lend insight to changes in the chemical processes which govern chemical speciation, soil quality, microbial volatilization, leaching, and biological uptake of selenium.

5.6.2. Soil Water and Groundwater Sampling

Soil pore water samples, fluid potential measurements, and soil moisture measurements were taken after the installation of the instrumentation. Shallow pore water could not be collected due to the summer's extreme dryness. Further monitoring over time of pore water, fluid potential, and soil moisture content will aid in our efforts to track the processes governing chemical speciation, volatilization, and leaching.

Groundwater was again sampled (from the three meter deep wells) in May 1990 after the application of SLD sediments to Ponds 5 and 7. Selenium concentrations in these wells are found to be in the same range of values recorded in 1989 before the SLD sediments were applied to the experimental sites. The average selenium concentrations in the Pond 5 and 7 wells are 1.0 and 2.0 ppb respectively.

5.6.3. Biological Data

Vegetation and invertebrate samples were collected from each strip of both experimental sites in May 1990 after the drain sediments were applied. These total selenium concentration data are shown in Table 5.3. Selenium concentration in *Kochia* ranges from 5.3 to 14.0 ppm dry weight. Selenium concentrations in the less abundant *Distichlis* and Mustard range from 3.0 to 11.5 ppm and 20.1 to 42.9 ppm, respectively. Interestingly, as of this writing much of the *Kochia* on the experimental sites in both Ponds 5 and 7 still persists while the *Kochia* on the fill material surrounding the experimental site in Pond 5 has died off. A possible explanation of this may lie in the fact that the *Kochia* on the experimental sites got a late start in its germination compared to the relatively older *Kochia* on the surrounding fill material in Pond 5. Invertebrate selenium concentrations range from 12 ppm (Grasshopper, n = 2), 21.0 to 26.0 ppm (Beetles, n = 135), and 2.2 to 18.2 ppm (Stink Bugs, n = 2). Concentrations for most types of vegetation and invertebrates are generally inside the ranges of selenium concentrations measured previously across the Reservoir (CH2M Hill, 1989; and CH2M Hill, 1990). *Distichlis* and beetle selenium concentration ranges, however, are slightly higher than those found reservoir wide.

Table 5.3. Total selenium concentrations (ppm dry weight) of post-SLD application vegetation and invertebrates.

Species	Pond 5			Pond 7		
	Strip 1	Strip 2	Strip 3	Strip 1	Strip 2	Strip 3
Kochia	7.7	12.2	14.0	5.6	6.9	5.3
Distichlis	4.3	11.5	9.4	3.0	3.2	4.9
Mustard	42.9	25.0	-	20.1	23.4	-
Grasshoppers	12.0	-	-	-	-	-
Beetles	21.0	25.6	-	-	26.0	-
Stink bugs	-	18.2	-	-	-	2.2

5.7. Conclusion

The experimental test plots in Ponds 5 and 7 are not unlike the rest of Kesterson Reservoir. The application of a thin layer of SLD sediments to these test plots yields surface selenium concentrations in the same ranges as those observed elsewhere on the reservoir. Augmentation of selenium levels by land application of SLD sediments is effective, yet levels in the biota are sufficiently high such that there is concern for unmonitored wildlife exposure. Groundwater will continue to be sampled in order to confirm or rule out leaching of selenium into the shallow groundwater. Further monitoring of these experimental sites will provide information about the temporal and spatial changes of the selenium applied to the experimental plots, and how these changes affect concentration in plants and invertebrates residing therein.

6. SYNOPTIC SURVEY OF WATER-EXTRACTABLE AND TOTAL SELENIUM CONCENTRATIONS IN KESTERSON SOILS

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As part of a Reservoir-wide monitoring program carried out by the USBR, soil samples from each of three tri-sections covering Kesterson Reservoir are collected annually by CH2M Hill. Tri-sections of the Reservoir include: one below Gun Club Road, covering the former Ponds 1, 2, 3 and 4; one covering former Ponds 5, 6, 7, and 8; and one covering former Ponds 9, 10 11 and 12. Within each tri-section three ''habitats'' are identified: fill sites, areas that were covered by fill-dirt in 1988 and are now largely vegetated with *Kochia scoparia;* grassland areas covered mainly by salt grass; and ''open'' areas, which consist of regions once occupied by cattails and that were disked in 1988 to eliminate nesting habitat for tri-colored blackbirds. Within each tri-section, six sites of each ''habitat'' type have been chosen for long term monitoring of soils, vegetation, and insects. Soil samples are collected to a depth of 0.15 m with a 2.54 cm (1-inch) diameter push-tube sampler. Samples from 54 sites are collected in this effort during February-March, 1990.

The soil samples are analyzed by LBL to determine total and water-extractable total selenium and selenite concentrations. The objective of this effort is to track changes in the total and water-extractable selenium concentrations in the surface soil over time. The 0.15 m-long samples are homogenized by chopping and seiving them prior to analysis. Total water extractable selenium and selenite were determined using a 5:1 water to dry soil mass ratio following procedures described extensively in previous progress reports (also, see LBL Quality Assurance/Control Plan). Total selenium analyses were performed using x-ray fluorescense (XRF).

6.1. Total and Water Extractable Selenium Concentrations

Histograms showing the concentrations of total selenium, total water-extractable selenium, and water-extractable selenite for each soil/habitat type are shown in Figures 6.1 through 6.3. Plotted values represent the geometric mean concentrations and error bars are one standard deviation from the mean. Analysis of the data sets within each habitat type indicate that the concentration values are described adequately by a log-normal distribution. Data from 1989 and 1990 sample sets are shown. (Note: all concentrations listed here are in units of mg per kg-dry soil).

In 1990, mean values for total selenium concentrations in the fill, grassland, and open areas are <2, 2.8 and 9.3 mg/kg, respectively. Mean values for water-extractable total selenium concentrations in the fill, grassland, and open areas are 0.06, 0.15, and 0.33 mg/kg, respectively. Mean values for water-extractable selenite concentrations in the fill, grassland, and open areas are 0.006, 0.032, and 0.036 mg/kg, respectively. Concentrations measured this year are not significantly different than values measured last year, as clearly indicated by the width of the error bars shown in Figure 6.1. Within any habitat type, concentrations vary dramatically, making generalizations about ''habitat'' types unreliable.

The water-extractable fractions of total selenium for each soil/habitat type are shown in Figure 6.4 for the 1989 and 1990 data sets. In 1990, values were 3.7%, 5.4%, and 3.6% for the fill, grasslands, and open soil/habitat types respectively. These values are not significantly different than those measured in 1989. Values presented for the filled areas are not very reliable due to the large potential errors in the reported total selenium values for samples containing less than 2 mg/kg-soil total selenium (i.e., the detection limit for XRF is about 1 mg/kg-soil).

In 1990, the ratio between selenite and selenate (defined as the total water-extractable minus the selenite) in the water-extracts for the fill, grassland, and open areas are 24%, 28%, and 13%, respectively. These are in general higher than in 1989 (19%, 19%, and 10%), but due to the wide variability it is not possible to conclude that this represents a significant trend.

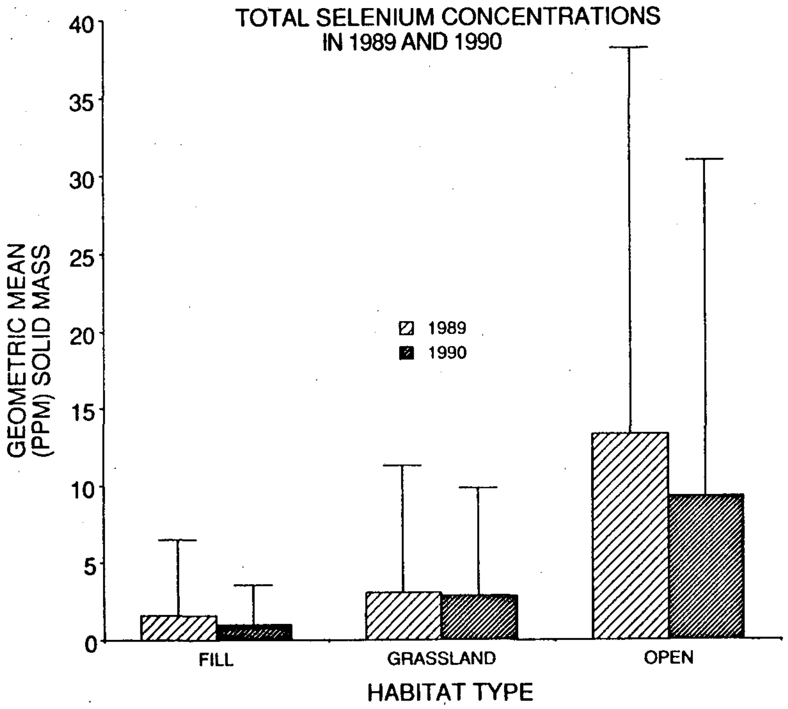

Figure 6.1. Comparison of the distribution of total selenium concentrations for each habitat type (measured by XRF). Each bar represents the geometric mean of 18 samples.

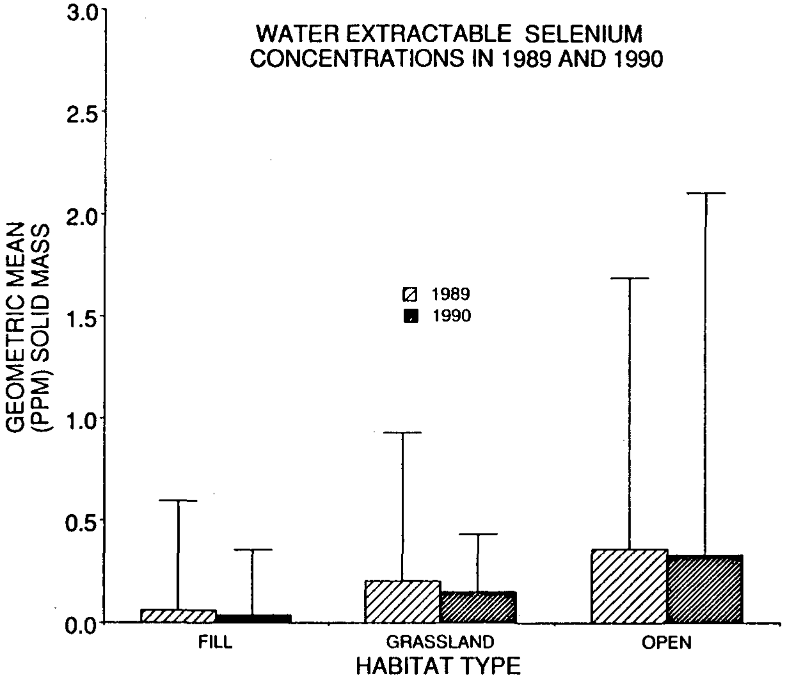

Figure 6.2. Comparison of the distribution of water-extractable total selenium concentrations for each habitat type. Each bar represents the geometric mean of 18 samples.

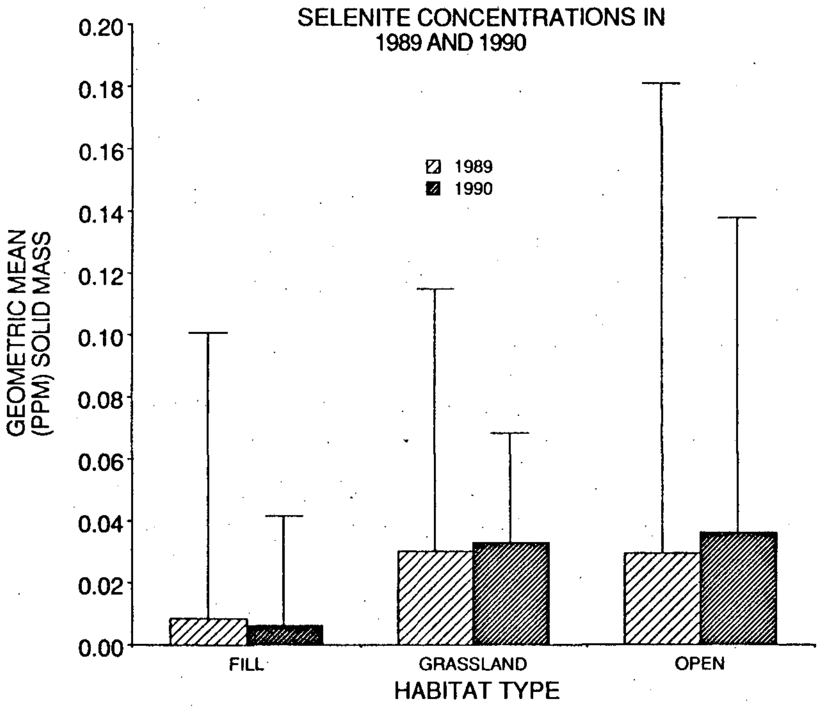

Figure 6.3. Comparison of the distribution of water-extractable selenite concentrations for each habitat type. Each bar represents the geometric mean of 18 samples.

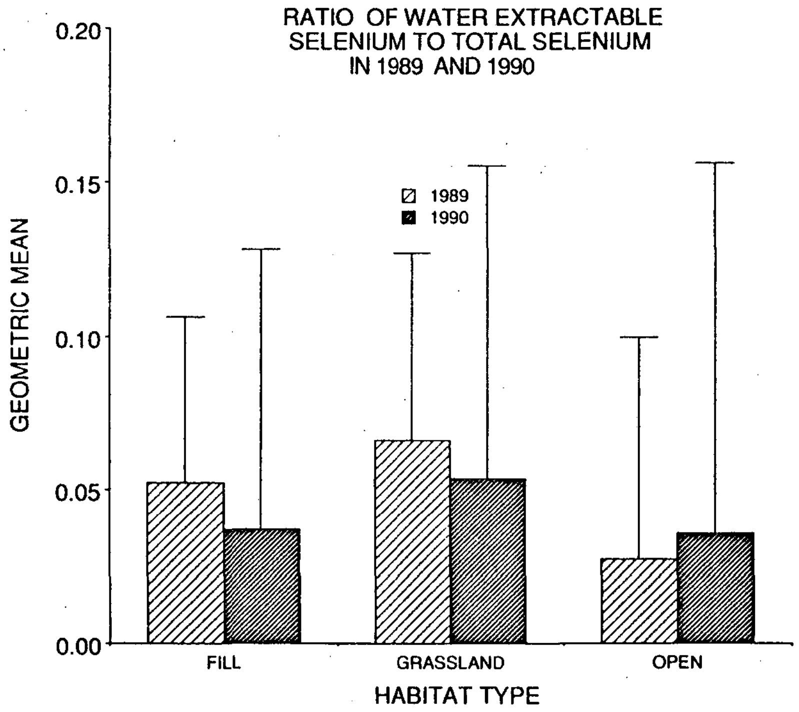

Figure 6.4. Comparison of the ratio between the water-extractable and total selenium concentrations for each habitat type. Each bar represents the geometric mean of 18 samples.

6.2. Discussion of Reservoir-Wide Soil Selenium Data

Several observations can be made from the data presented in Figures 6.1 through 6.4. The include:

- by "habitat", selenium concentrations are greatest in the open areas and least in the filled areas, as would be expected from historical use of the Reservoir and the filling operations;
- within any "habitat" selenium concentrations range over an order of magnitude;
- due to this wide range of values within each habitat and the limited number of samples (18 for each habitat-type) confidence intervals of the mean values are large;
- representative mean values for the total selenium values are <2, 2.8 (± 3.8), and 9.3 (± 11.8) mg/kg-soil in the fill, grassland, and open areas, respectively;
- representative mean values for the water-extractable total selenium values are 0.04 (± 0.14), 0.15 (± 0.15), and 0.33 (± 1.0) mg/kg-soil, in the fill, grassland, and open areas, respectively;
- the fraction of the total selenium inventory in Kesterson soils that is water-extractable is about 5%, indicating that only a limited amount of the selenium is currently mobile and available for plant uptake;
- the ratio of selenite to selenate in the water-extracts is from 10 to 30%;
- accumulation of water-extractable selenium at the top of the fill surface is not yet detectable in this sample set as a whole, however, as described in Section 2.2, this is undoubtably occurring; and
- no significant changes in total or water-extractable selenium concentrations have been observed between the 1989 and 1990 data sets.

7. QUALITY CONTROL AND QUALITY ASSURANCE FOR CHEMICAL ANALYSIS IN THE KESTERSON PROGRAM

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7.1. Introduction

The Geochemistry Group has had a quality assurance program in operation for over three years, covering chemical analysis for selenium, arsenic and boron in samples collected from the Kesterson Reservoir. We now have a large body of statistics and can demonstrate improvement in operation and have increased confidence over time in the selenium measurements made.

7.2. Measurement Statistics

Analytical chemistry has a number of means to judge the quality of the measurements made. Here we are considering the entire measurement process which includes the performance of the analyst and preparation of samples prior to measurement. This means that blind quality control samples must be placed in the sample preparation process. We use standard solutions to gauge accuracy and precision, duplicates to gauge precision with the natural matrix, blanks to gauge contamination and spiked samples or known addition to gauge interference.

7.3. Operations

Selenium analysis is performed by hydride generator AAS. Samples are feed untreated into the instrument to read selenite (SeO_3^{-2}) concentration. Total selenium is analyzed by treating a 5.0 ml sample with 0.2 ml of a 2% w/v solution of ammonium persulfate and 5.0 ml of concentrated HCl before it is fed into the instrument. Our studies indicate that the concentration of organic forms of selenium in water samples is usually not significant. Therefore, the concentration of selenate is often calculated as the difference between the total selenium and the selenite. For selenium analyses it is often necessary, after an initial reading, to dilute samples to bring them into the linear range of reading.

Arsenic analysis is also performed by hydride generator AAS but the processing of samples is different. A 5.0 ml aliquot of sample is mixed with 5.0 ml of concentrated HCl, 0.5 ml of an 80% w/v solution of urea and reduced by adding 0.5 ml of a 40% w/v solution of potassium iodide. Unlike selenium analysis, if a sample requires dilution to bring the concentration into the linear range of the instrument, it must be diluted with a processed blank.

Boron is analyzed by feeding the sample solution directly into the inductively coupled plasma spectrometer. The only pretreatment which may be required is dilution to bring the concentration into the linear range of the instrument and reduce the viscosity of the sample.

For quality controlled analyses of selenium, arsenic and boron the analyst prepares and runs operational control samples consisting of a standard, a blank and a spiked sample for each 10 analytical samples. There is one operational duplicate for each 20 analytical samples. In addition, 15% of the sample load consists of blind quality control samples prepared by the Quality Assurance Manager in containers intended to be indistinguishable from the others. These consist of standards, spiked samples, duplicates and blanks placed in the containers.

Calibration standard solutions with 10 and 20 ppb selenium are prepared fresh daily from a 1000 ppm (as selenite) selenium AAS standard traceable to NIST. Blind standards containing both selenite and selenate are prepared from a stock solution which is itself prepared from a high concentration or ''super'' stock solution, which is itself prepared from dry sodium selenite and sodium selenate. The standard solutions used for blind standards are also used for spiking samples.

7.4. Selenium

7.4.1. Blanks

It is important to distinguish between the instrument limit of detection (ILD) and the method limit of detection (MLD). The ILD is determined by analyzing a series of standards prepared to contain known amounts of the analyte. The MLD is determined by analyzing blanks prepared blind in the same manner as any research sample. The MLDs for selenite and total selenium are 0.10 ppb and 0.63 ppb respectively. The method limits of quantification (MLQ) for selenite and total selenium are 0.31 ppb and 1.89 ppb respectively

7.4.2. Standards

We have established standards with both selenite and selenate because speciation of selenium has been important in many of the studies we have performed. Because selenite solutions with concentrations in the range of 40 ppb or less oxidize rapidly we make up each standard from a concentrated stock. We report statistics on total selenium rather than selenate because it is a direct analytical measurement.

The standard deviation in these measurements includes errors in formulating these standards each time. One identifiable source of error is in the adjustable pipettes used. This is 0.36% relative deviation in the range used.

Statistics on 297 accepted calibration verifications using a 10 ppb calibration standard give a value of 10.01 ppb with a standard deviation of 0.12 ppb or a relative deviation of 1.2%. Statistics on 400 calibration checks using a 20 ppb calibration standard give a value of 20.02 ppb with a 0.10 ppb standard deviation or a relative deviation if 0.5%. The calibration values are well within one standard deviation of the nominal value of standards. These statistics have been accumulated over FY1990 and indicate the maximum drift between calibrations.

Table 7.1 gives the relative deviations of series of repeat measurements of sets of standard solutions run during the last part of fiscal 1989 and the most of fiscal 1990. They were run blind to the analyst and, for total selenium, subject to all sample preparation procedures. They indicate that our precision varies with the concentration of selenium and that we have generally had a slight improvement over time. The smaller number of analyses of selenite is the result of researchers request for analyses of total selenium only. The greater relative differences of total selenium measurements in all standards, in spite of more analyses being performed, is most likely due to divergence generated by sample preparation.

Table 7.1. Selenium standard statistics, 6/26/89 - 3/15/90

label	Se^{+4}				Σ Se			
	conc.	r.d.%	# of analyses	% 95% c.i.	conc.	r.d.%	# of analyses	% 95% c.i.
Se XI a	2.0	20.5	23	42.3	4.6	10.1	42	20.5
Se XI b	4.3	8.1	31	16.5	9.4	8.6	65	17.2
Se XI c	8.3	11.4	30	23.2	18.3	8.6	63	17.1
Se XI d	17.2	7.3	29	15.0	36.4	8.2	70	16.7
Se XII a	47.4	6.3	33	12.9	96.0	6.8	69	13.5
Se XII b	97.7	4.9	32	9.9	192.4	6.2	65	12.4

Table 7.2. Selenium standard statistics, 12/18/89 - 9/21/90

label	Se^{+4}				Σ Se			
	conc.	r.d.%	# of analyses	% 95% c.i.	conc.	r.d.%	# of analyses	% 95% c.i.
Se XIII a	2.3	10.5	32	25.3	5.2	11.8	53	23.6
Se XIII b	4.6	6.5	32	13.3	10.6	10.1	51	20.4
Se XIII c	9.2	6.3	36	12.9	21.1	8.2	55	16.6
Se XIII d	18.2	4.8	31	9.9	40.7	7.6	50	15.3
Se XIV a	54.9	5.6	33	11.5	114.4	7.5	51	15.1
Se XIV b	111.9	5.8	35	11.8	222.5	4.7	51	9.4

r.d.	relative deviation, expressed as percent
c.i.	confidence interval, expressed as percent

7.4.3. Spike Recoveries

A persistent drawback in our spike recovery measurements has been the difficulty in knowing *a priori* what the selenium concentrations of many samples are. Ideally the spike of analyte added is equal to the amount of the original analyte. Spikes less than ¼ or more than 4 of the original analyses are not statistically meaningful. Because of this, of 174 selenite and 299 total selenium spiked sample analyses, only 173 selenite analyses and 269 total selenium analyses were in a statistically meaningful range. Our average recovery for a selenite spike was 87.4% and for a total selenium spike it was 92.7%. Acceptable percentage recovery is 80% – 120%.

7.4.4. Duplicates

Duplicates provide a measure of our analytical precision which includes factors such as foaming, which repeated measurements of standards do not reflect. The average relative difference in 1990 for duplicate selenite analyses was 3.8% and for duplicate total selenium analyses 4.2%. Duplicates for which one of the values were less than the MLQ were discarded, giving 119 selenite and 148 total selenium duplicates used to calculate the averages given above.

7.5. Arsenic

7.5.1. Blanks

The MLD for arsenic is 1.76 ppb and the MLQ is 5.36 These relatively high values are most likely due to the few arsenic blanks analyzed (15), which is in turn due to the few requests for arsenic analysis to date. The consequent lower level of analyst experience may result in more erratic performance.

7.5.2. Standards

Arsenic standards are all prepared from a 1000 ppb standard solution traceable to NIST. The average of 98 accepted calibration verification analyses of a 10 ppb solution was 9.998 ppb with a standard deviation of 0.117 ppb or a relative deviation of 1.2%. For 37 accepted calibration verification analyses of a 5 ppb solution the average was 4.978 with a standard deviation of

0.090 ppb or a relative deviation of 1.8%. Both are well within the standard deviation of the formulated value.

Table 7.3 gives the relative deviations of a series of blind standards over a wide range of arsenic concentrations.

7.5.3. Spike Recoveries

Recovery of arsenic spikes averaged 111.1% for 38 analyses where the spike was between ¼ and 4 times the initial concentration.

7.5.4. Duplicates

The average relative difference for 59 duplicates for which both determinations were above the limit of quantification was 6.8%.

7.6. Boron

7.6.1. Blanks

The MLD for boron is 0.234 ppm and the MLQ is 0.668 ppm. This is based on the analyses of 34 blind blanks.

7.6.2. Standards

Boron calibration standards are prepared from a 1000 ppm AAS standard traceable to NIST. The average value for 69 accepted calibration confirmation analyses of a solution with a formulated value of 10 ppm is 9.8 ppm with a standard deviation of 0.52 ppm or a relative deviation of 5.3%. The average value for 48 accepted calibration confirmation analyses of a solution with a formulated value of 25 ppm is 25.26 ppm with a standard deviation of 1.18 ppm or a relative deviation of 4.7%.

Tables 7.4 and 7.5 give the relative deviations of a series of blind standards. Standards in the B I series were prepared from a stock solution which we formulated from reagent grade sodium tetraborate. The standards in the B II series were prepared from a commercial 1000 ppm AAS standard traceable to NIST.

Table 7.3. Arsenic standard statistics, 10/11/89 - 9/27/90

label	conc.	r.d.%	# of analyses	% 95% c.i.
As I a	9.94	11.3	28	23.2
As I b	19.6	13.3	33	27.1
As I c	39.1	11.5	30	23.4
As I d	78.1	5.6	26	11.5
As I e	161	8.5	27	17.5

Table 7.4. Boron standard statistics, 1/31/90 - 5/23/90

label	conc.	% r.d.	no. of points	% 95% c.i.
B I a	2.34	11.1	59	22.1
B I b	4.74	8.8	62	17.5
B I c	9.26	11.4	59	22.8

Table 7.5. Boron standard statistics, 6/5/90 - 8/14/90

label	conc.	% r.d.	no. of points	% 95% c.i.
B II a	2.55	10.0	10	22.4
B II b	4.42	9.3	10	20.6
B II c	9.32	8.2	11	18.1
B II d	18.8	10.5	11	23.2
B II e	38.6	8.2	10	18.2

7.6.3. Spike Recoveries

The average spike recovery for 80 boron analyses for which the spike concentrations were between ¼ and 4 times the original boron concentrations was 91.6%.

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