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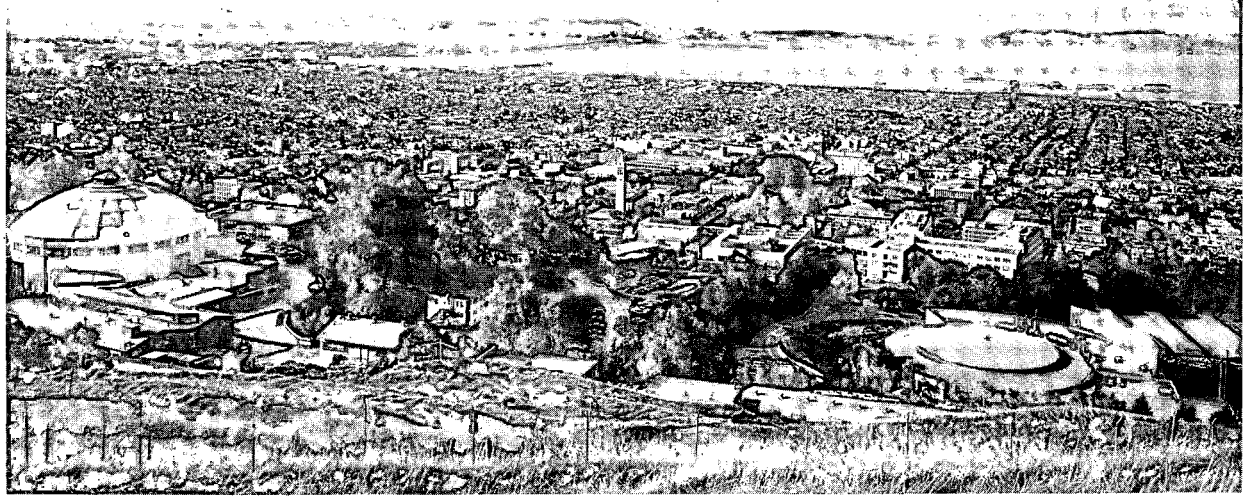

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Hydrological, Geochemical, and Ecological Characterization of Kesterson Reservoir

Annual Report
October 1, 1986 through September 30, 1987

Earth Sciences Division
Lawrence Berkeley Laboratory
University of Calfornia
Berkeley, CA 94720

Sanitary Engineering and
Research Laboratory
Richmond, CA

December 1987

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EXECUTIVE SUMMARY

Over the past two years scientists and engineers at Lawrence Berkeley Laboratory (LBL) and the Sanitary Engineering and Environmental Health Research Laboratory (SEEHRL) have investigated the effects of selenium contamination at Kesterson Reservoir. Selenium was present in food chain items at levels potentially toxic to birds by 1983. Although selenium concentrations have decreased in food chain items since drainage water inflow to the Reservoir ceased in 1986, selenium concentrations remain unacceptably high. Degradation of local groundwater resources, both from selenium contamination and accumulation of salts in near surface soils is also of concern. This report summarizes the results of a multidisciplinary program of research and monitoring activities aimed at providing a technical basis for choosing the best method for remediation of Kesterson Reservoir.

Our early studies at Kesterson Reservoir were guided by the observation that most of the selenium discharged to the Reservoir was concentrated in a layer of organic detritus and mineral soil on the bottom of the disposal ponds. Relevant literature indicated that under chemically reducing conditions, selenium would be converted from the highly soluble selenate species, which predominates in drainage water, to the more insoluble forms such as zero-valent selenium. Field observations confirmed that both the pond bottom soils (when flooded) and native groundwater were chemically reducing, thus explaining the high concentration of practically insoluble selenium in the pond-bottom sediments and the lack of widespread selenium contamination in the underlying aquifer. Motivated by the observation that selenium could be geochemically immobilized (contained) in the pond bottom sediments, we hypothesized that by permanently flooding the Reservoir with a selenium-free water supply, selenium concentrations in food chain items would decline to acceptable levels and the groundwater would remain free of undesirably high concentrations of selenium.

Early data showing the promise of this hypothesis was used as the technical basis for proposing the Flexible Response Plan (FRP) as the preferred method for cleaning up the Reservoir. The FRP required flooding the parts of the Reservoir with the highest

selenium inventories with moderate-salinity, low-selenium well water. The remainder of the Reservoir was to be plowed and disced, to prevent regrowth of potentially contaminated vegetation. In March, 1987, the California State Water Resources Control Board rejected the Flexible Response Plan and requested immediate implementation of the On Site Disposal Plan (ODP). The ODP requires excavating the top 6 inches of soil in Ponds 1, 2, 3, and 4, and the areas in the remaining ponds where the concentration of selenium is greater than or equal to 4 parts-per-million (ppm). These soils, along with contaminated vegetation will be stored in an on-site landfill. Until March 1987, our research efforts focused primarily on evaluating the feasibility of geochemically and biologically immobilizing selenium in the pond bottom sediments. After March 1987, as a result of the Board Order, our emphasis shifted to include evaluation of post-ODP conditions at the Reservoir.

From 1981 to 1986, an estimated 5000 to 8000 acre-feet per year of agricultural drainage water was discharged into Kesterson Reservoir, with an average selenium concentration of 300 parts-per-billion (ppb) and a concentration of total dissolved solids (TDS) of approximately 10,000 ppm. An estimated 50% of the drainage water seeped into the underlying aquifer. The rest evaporated, primarily during the hot summer months, concentrating salts and selenium in the surface waters and sediments. Although the shallow aquifer and soils underlying the Reservoir are naturally saline, the TDS of the drainage water was 2 to 3 times higher than that of the native groundwater.

Kesterson Reservoir overlies a thick sequence of alternating layers of sands, silts, and sandy loams. In general, the top 10 to 20 feet is characterized as a sandy loam. Below this depth, high permeability sands extend to a depth of approximately 80 feet. This unit is underlain by approximately 10 feet of finer grained, relatively low permeability sediments. A sandy unit extends from the bottom of this unit to the top of the Corcoran Clay, which is typically encountered at depths of greater than 200 feet.

The Reservoir is situated in the midst of a seasonal wetland where many duck ponds are intentionally flooded each winter. The 1280 acres comprising the 12 Kesterson Ponds account for approximately 8% of the seasonal wetland within a 124-square-mile

region centered on the Reservoir. Prior to developing the Reservoir, the depth to the water table varied throughout the year and over the Reservoir, ranging from a depth of 10 feet during the dry summer months to above the ground surface in low lying regions of the Reservoir during the winter. The regional hydraulic gradient in the shallow aquifer (above the Corcoran clay) is from the southwest to the northeast, with an average value of approximately $5x10^{-4}$ (feet of water/feet of linear distance). Based on an extensive set of field measured hydraulic conductivities, the average pre-Kesterson groundwater pore velocity is estimated to have ranged from 20 to 30 feet/year. Flooding the Reservoir created a groundwater mound with a height of approximately 3 feet during the winter months, and up to approximately 10 feet during the summer months. Seepage of drainage water created a plume of saline water that migrated laterally away from the Reservoir at an estimated rate of 150 feet per year, and vertically at an estimated rate of 15 feet per year.

Ongoing and extensive groundwater sampling from numerous monitoring wells has demonstrated that for the most part, even though 50% of the drainage water seeped into the underlying groundwater aquifer, selenium concentrations remain below 5 ppb in the shallow groundwater. However, there are several exceptions, mostly in the southern part of the Reservoir, where many wells located on the berms surrounding Ponds 1 and 2 had selenium concentrations in excess of 10 ppb. An extensive program of field sampling demonstrated that the monitoring wells with elevated selenium concentrations were also oxidizing and contained elevated concentrations of nitrate-nitrogen. Conversely, high concentrations of aqueous selenium were nearly always absent under chemically reducing or low-nitrate conditions.

Initially, the elevated concentrations of selenium in some of the monitoring wells located on the berms surrounding Pond 2, suggested that Pond 2, as a whole, might be allowing selenium to enter the upper aquifer. A berm extending into the middle of Pond 2 was constructed so that additional monitoring wells could be installed downgradient of the area where the highest selenium concentrations had been observed. A total of twelve new monitoring wells, with depths ranging from 40 to 100 feet, were drilled along the berm. Subsequent sampling demonstrated that although drainage water had migrated

to depths of over 100 feet, the groundwater was chemically reducing and selenium concentrations were less than 3 ppb.

The lack of elevated concentrations of selenium under the center of Pond 2 indicates that the elevated concentrations of selenium observed in sampling wells along the berms around Ponds 1 and 2 are associated with isolated plumes. The best characterized of these plumes is located at the intersection of Ponds 2, 3, and 4, where during 1984 and 1985, selenium concentrations ranged from 10's to 100's of ppb in several of the monitoring wells. Over the past one and one-half years, more than 30 sampling wells have been installed here and have demonstrated that the plume is limited to an area of less than 500 by 500 feet and a depth of less than 80 feet. Similar or smaller dimensions are expected for the other areas where selenium has migrated into the aquifer, as is indicated by the "patchy" nature of the observed selenium distribution.

The precise mechanism that allows selenium to migrate into the aquifer in some areas and prevents migration in other areas remains uncertain. However, laboratory experiments and field observations indicate that selenium breakthrough is caused by the superposition of several factors, including: higher-than-average seepage rates; elevated concentrations of nitrate; lower-than-average organic content in the detrital layer and/or mineral soils; and lithological composition of the subsurface sediments.

Field and laboratory experiments have demonstrated that the deeper soils and sediments underlying the organic rich surface layer can also immobilize selenium under fully saturated conditions. During late October of 1986, Pond 1 was flooded after it had been allowed to dry out over the summer. Extensive soil water and groundwater sampling prior to and after flooding demonstrated that although the concentrations of soluble selenium in the top four feet of soil were initially in the range of 100's to 1000's of ppb, selenium concentrations declined after flooding and elevated concentrations below 4 feet were only observed at 1 of the 5 sampling sites. Analysis of the temporal and spatial changes in the distribution of dissolved selenium indicates that from 70 to 80% of the soluble selenium in the top 4 feet of the soil column was immobilized within a month after flooding the Pond. The relatively slow seepage velocities (5 to 15 feet/year)

combined with rapid immobilization of soluble selenium explains the lack of widespread elevated concentrations of selenium in the groundwater after the Pond was flooded. Laboratory studies demonstrate similar behavior and indicate that immobilization of selenite is primarily an inorganic process, while selenate requires microbial mediation to undergo such rapid immobilization.

Immobilization of soluble selenium in the native groundwater has also been demonstrated. Field sampling of regions of the shallow aquifer that are not influenced by seepage of drainage water indicate that the shallow groundwater is chemically reducing, presumably, as a result of the mineralogical makeup of the aquifer sediments. A mixture of selenate, selenite, and a non-reactive chemical tracer was injected into the native groundwater. Groundwater samples were extracted weekly for the following month. Both selenate and selenite were unstable. Over the month-long sampling period, the concentration of these two species returned to near-background levels, indicating that they were converted to less soluble forms and incorporated into the soil matrix. The results from this experiment suggest that soluble selenium will not persist in the reducing native groundwater.

By early 1986, drainage water inflows to the Reservoir had nearly ceased. Concerned that the selenium contained in the pond bottom soils would be remobilized when allowed to dry, provisions were made by the U. S. Bureau of Reclamation (USBR) for a local supply of selenium-free (an average value of less than or equal to 1 ppb) water for flooding some of the Ponds in the interim period between cessation of drainage water inflow and implementation of the ODP. With the exception of a short period during July and August 1986, when selenium-laden drainage water was discharged to the Reservoir through the San Luis Drain, Ponds 1, 2, 5 and 7 have received an intermittent supply of selenium-free water for over a year. During interim operations at the Reservoir, water was not applied to the remaining Ponds but many shallow pools (ephemeral pools) formed during the winter as a result of the seasonal water table rise, accumulation of rainfall, and the groundwater mound formed by flooding Ponds 1, 2, 5 and 7.

The LBL/SEEHRL studies have followed the changes in selenium in the surface water and biota as drainage water inflows were replaced with the selenium-free water supply. The entire range of aquatic habitats present at the Reservoir, deep permanent water, shallow permanent waters, and ephemeral pools were sampled. All visible living aquatic organisms, except fish, were collected quantitatively (i.e., numbers or biomass determined from a known area). Quantitative measurements were also made of the microscopic animals and plants which provide the base of the food chain.

Weekly monitoring of surface water concentrations since July of 1986 show that the selenium concentrations in Ponds 1, 2, 5 and 7 have fallen from over 400 ppb down to an average value of 5 ppb (the target clean up goal). The ephemeral pools located in the northern ponds, where no water was applied, had concentrations ranging from 40 to 2500 ppb, with an average value of 373 ppb. The low concentrations observed in the flooded ponds, in comparison to the high concentrations observed in the ephemeral pools, indicates that surface water concentrations can be kept below 5 ppb by permanently flooding the Reservoir with selenium-free water.

Compared to values present before agricultural drainage water was reduced (i.e. 1983-1985) selenium has also declined in the tissues of most aquatic organisms where permanent water has been maintained. The most pronounced and complete decline in tissue selenium was found in the experimental permanent water enclosure (a 1 acre enclosure in Pond 5, called 5E) that began receiving a selenium-free water supply several months before the rest of the Reservoir. Plant tissue selenium in this enclosure has declined by 80-90% during the first complete year of its operation. Declines in the selenium content of aquatic insects have also been considerable (about 80%) and even the slowest-growing animals present (mosquitofish) have declined 64%. Declines have also been observed in the permanent deep-water monitoring site in Pond 5, where selenium in the plant biota has declined by two-thirds since its peak in November, 1986. At the sites that have experienced wetting and drying episodes during the past year, such as the monitoring site in Pond 7, selenium concentrations have declined in some of the organisms and remained the same or increased in others.

The amount of selenium in the biota was controlled by the kind of organism present as well as the selenium in the water or in its food. Longer-lived organisms such as mosquitofish, tabanid and benthic chironomid larvae had the highest concentrations of selenium. Short-lived algae had low concentrations of selenium. Algae also lost and gained selenium more quickly than the longer-lived fish or dragonflies. An important exception was the short-lived brinefly larvae which concentrated selenium to very high levels. Brinefly larvae are characteristically abundant in shallow waters of high salinity, such as pools that are re-wetting or drying. Brinefly larvae were briefly abundant in Pond 5 during the summer of 1986, but did not occur in 1987 when salinities were lower. Apparent rapid changes in animal selenium in spring were caused by the hatching of aquatic insect larvae into aerial adults and their replacement by young larvae with lower selenium.

Analysis of the speciation of selenium in the soils provides insight into the degree to which selenium is dissolved in the surface or soil water and is available for uptake by plants, microorganisms, and invertebrates. Soil samples collected in the permanently flooded areas that were not allowed to dry out before the soluble selenium was extracted from them indicate the presence of very low concentrations of soluble selenium. Typically 50% of the selenium inventory is in the form of zero-valent selenium, which is practically insoluble in water. The remaining selenium in the permanently wet areas consists of organic selenium and selenite sorbed on soil particles.

In the areas that have dried out over the summer (ephemeral pools or intentionally flooded seasonal wetlands), typically 10 to 25% of the selenium reverts to the highly soluble selenate and selenite species. On the soil surface, soluble selenium salts accumulate. Below the soil surface the soluble selenium is dissolved in the pore waters of the partially saturated soil matrix. During the winter months, the water table may rise to the surface, carrying dissolved selenium and dissolving selenium salts on the soil surface. Under natural conditions, immobilization (conversion to insoluble species by chemical and biological processes) begins when the soils are fully saturated, but does not proceed fast enough to prevent high concentrations of selenium in the surface water. Many areas of the Reservoir experienced repeated wetting and drying over the past year as a result

of the intermittent water supply. Pore water sampling from one of these areas indicated that in as little as one week after the soil surface was dried out, immobilized selenium was converted to selenite and selenate, creating pore water concentrations in excess of 1000 ppb. Such rapid changes in the concentration of soluble selenium, and the potential for remobilizing dissolved selenium in the root zone and surface waters where it is available to biota, indicate that rapidly fluctuating water levels are detrimental to *in situ* immobilization of selenium.

Provided that the Ponds are continuously flooded, extrapolation of decline rates of food chain items from Pond 5 and 5E indicates that the selenium levels in most of the food chain items will decline to the target value of 3 ppm by 1990. The longest time period was for tabanid larvae, which is projected to reach the 3 ppm value by 1992. Our 17 month laboratory microcosms and 12 month study at the large field mesocosm at Kesterson also provide experimental evidence that such a clean-up is possible. Nevertheless, it is premature to make definitive conclusions from the Kesterson field studies based on only 9 months of observation since the last selenium-contaminated drainwater was delivered to the Reservoir.

In January, 1987 we began a set of field measurements aimed at assessing post-ODP conditions at the Reservoir. Test plots were installed in Ponds 6, 9, 10 and 11 for determining the effects of removing surface vegetation, excavating the soil surface, and discing the surface-most soil. The plots were instrumented with soil water samplers for determining the distribution and concentration of dissolved selenium and with tensiometers, for determining the direction of soil water movement. Selenium concentrations from initial and repeated sampling of soil waters at 23 sites throughout the Reservoir ranged from 1000's of ppb at 6 inches to 100's of ppb at a depth of 4 feet. Such high concentrations of dissolved selenium, at depths of up to 4 feet were unexpected. Although the quantity of selenium that currently resides at depths of greater than 6 inches is probably less than 25% of the selenium inventory at the Reservoir and selenium concentrations are less than less than the 4 ppm excavation criterion, these high concentrations of soluble selenium raise some questions regarding the effectiveness of the proposed excavation program.

At the present time the primary concern regarding the effectiveness of the ODP for achieving a satisfactory level of cleanup stems from estimates that 460 acres of seasonal wetlands will form on a yearly basis at the Reservoir. In these areas, the seleniferous pore waters, with selenium concentrations ranging from 100's to 1000's of ppb, will rise to the surface and create ephemeral pools with high concentrations of dissolved selenium. Biotic contamination resulting from exposure to seleniferous waters is anticipated.

Additional concerns stem from the continually changing geochemical and biological regimes created by the fluctuating water table. During the summer months when the water table is below the soil surface, selenium will be oxidized to soluble forms. Evaporative fluxes, enhanced by the shallow depth of the water table, will concentrate selenium and salts in the near surface soils. During the winter months when the water table rises above the ground surface, biological uptake and deposition of decaying organic matter on the bottom of the ephemeral pools will also reconcentrate selenium in the near surface soils. At Kesterson, in the absence of applied surface water, the combined effects of evaporative fluxes and biological immobilization result in an environment where natural leaching of selenium and other salts is nearly impossible. This situation has both benefits and drawbacks. On one hand, contamination of the shallow aquifer by virtue of selenium transport from the vadose zone is unlikely due to the prevailing upward flux of soil water and solutes. On the other hand, inventory of soluble selenium currently residing in the vadose zone can be expected to persist and possibly reconcentrate in the surface most soils unless other selenium loss or fixation mechanisms are acting. Consequently, food chain contamination is expected to continue in the ephemeral pools and possibly in the terrestrial food chain if the inventory of selenium in these areas is not decreased or immobilized.

The selenium literature suggests that loss and immobilization mechanisms are strongly tied to biological cycling in soils. Cycling of organic matter converts some fraction of the selenium salts to various volatile forms which can be transported to the atmosphere and converts some to organic and less soluble inorganic forms. Under current conditions at the Reservoir, field measurements demonstrate that volatilization rates are low in the permanently flooded and permanently dry areas. High rates of

selenium volatilization have been observed in the immediate vicinity of wetland vegetation that is allowed to dry out and decay. There are many factors that influence the rate at which selenium can be volatilized and immobilized by biological cycling, including: temperature; moisture content; organic content; soil structure; salinity; season; sunlight; and selenium speciation. A systematic analysis of the influence of these factors has not been undertaken. Nevertheless, volatilization and immobilization are undoubtably some of the mechanisms by which the selenium inventory can be decreased or contained. Field and laboratory experiments (by U.C. Riverside and LBL) are currently underway to assess the degree to which addition of organic matter can enhance volatilization and immobilization of selenium in the Kesterson soils.

The need for careful biological monitoring and perhaps additional remedial measures after implementation of the ODP is apparent. The ephemeral pools that will form each winter are of special concern. Possible remedial measures include but are not limited to i) ground leveling (and filling) to prevent the occurrence of ephemeral pools, ii) winter flooding to lower surface water selenium concentrations, iii) permanent flooding to immobilize residual selenium, iv) volatilization and immobilization of residual selenium by adding organic amendments to the soil, v) groundwater fixation, or vi) excavation to greater depths.

1. INTRODUCTION

This report summarizes the results of the LBL/UCB investigations at Kesterson Reservoir for the period from October of 1986, to September of 1987. The report is divided into 4 sections:

- Surface Water
- Groundwater
- Soils and Sediments
- Ecological Studies

Due to the fundamentally multidisciplinary nature our investigations we attempt to provide cross-referencing between these sections whenever appropriate.

Persons responsible for contributions to this report include, in alphabetical order: Sally Benson, Harry Bowman, Alex Coate, Eugene Duckart, Alex Horne, Robert Long, Joan Oldfather, Lisa Palermo, Jim Roth, Karen Segleman, Ray Solbau, Lynn Suer, Tetsu Tokunaga, Oleh Weres, Art White and Andy Yee.

2. SURFACE WATER

Selenium concentrations in the surface water at Kesterson Reservoir have been monitored on a regular basis since November 1985. Initially samples were collected monthly in Pond 5 and monthly in Ponds 7 and 11 beginning in April 1986 as part of the ecology program. This data is reported in Section 5. The data reported here concerns more extensive and more frequent collections beginning in July 1986 which was before the final cessation of drain water inflows. Water samples were collected from Ponds 1, 2, 5, and 7, which were intentionally flooded during interim operations at the Reservoir. However, the water supply was somewhat intermittent. Consequently, large regions in most of these Ponds may have dried out and re-flooded during the monitoring period. Samples were also collected from the ephemeral pools that formed from rising groundwater and surface accumulation of rainfall in the northern ponds (Ponds 8, 9, 10, and 11). Speciation of selenium in the surface water, particularly with regard to the presence of volatile compounds, has also been investigated.

2.1 Selenium Concentrations in Ponds 1, 2, 5, and 7 (Flooded Areas)

Water samples have been collected on a weekly basis at 25 stations around the Reservoir. The locations of these stations are shown in Figure 2.1. The samples are filtered in the field. Analyses are performed in accordance with the USBR QA/QC procedures. These monitoring stations include 10 wells supplying water to flood the ponds, the inlet from the San Luis Drain into Pond 2, the weirs between the Ponds, and several locations along the berms. The results of this monitoring program are summarized in the figures and text below.

The water supply wells are low in selenium and moderately saline, as was intended. Selenium concentrations are at or below 2 parts-per-billion (ppb), with an average value of less than 1 ppb. Boron concentrations in the water supply wells range from 1 to 12 ppm. These values indicate that seven of the wells are supplying native groundwater and the remaining three are supplying approximately 50% recycled drainage water and

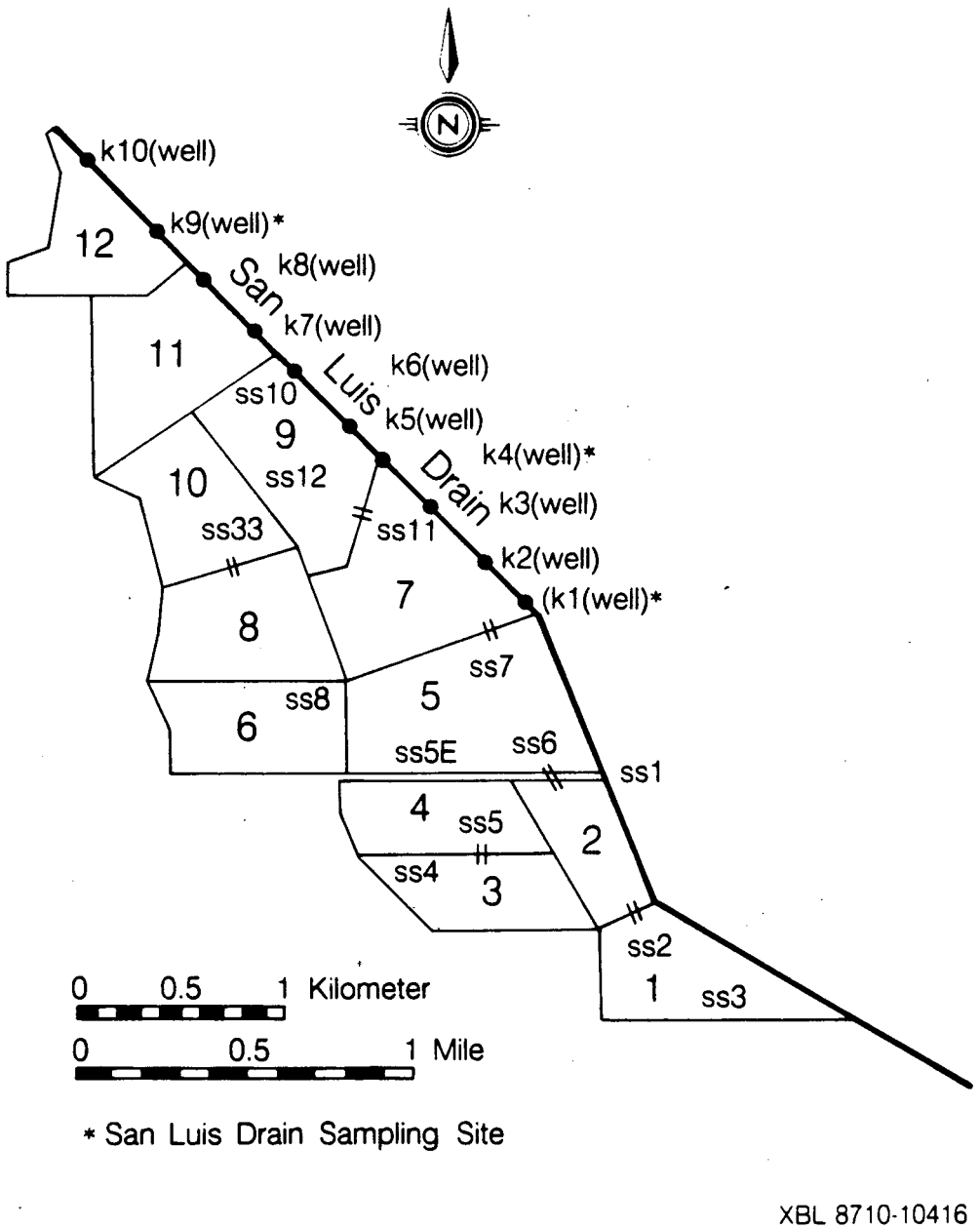

Figure 2.1. Sampling sites for LBL routine surface water collections.

50% native groundwater (the average boron concentration in the shallow wells underlying the Reservoir is approximately 15 ppm (USBR, 1986)). Electrical conductivity (EC) values range from 5,000 to 11,000 μmhos/cm. Over the past 4 months, the average concentration of boron measured at the San Luis Drain/Pond 2 weir ranged from 4 to 6.5 ppm. Over the same time period field measured EC has ranged from 7,800 to 9,000 μmhos/cm. A comparison between the EC and boron concentration of the drainage water and the water supply wells suggests that the water supply is approximately 25% recycled drainage water and 75% native groundwater. As illustrated in Figure 2.2, selenium concentrations at the inlet from the San Luis Drain into Pond 2 (the primary water delivery point for the interim water supply) have fallen from over 400 ppb to less than 2 ppb over the past year. The ability to deliver water at or below 1 to 2 ppb suggests that the selenium contained in the sediments of the San Luis Drain remains immobilized when the sediments are kept submerged.

Graphs of the concentration of selenium in surface waters collected at the weirs between Ponds 1/2, 2/5, and 5/7, are shown in Figures 2.3 through 2.5. Selenium concentrations have declined throughout the nearly one and one-half year monitoring period and are all now at or below 10 ppb. No systematic comparison has been made between the selenium concentrations from samples collected at the weirs and samples collected from the middle of the Ponds. However, comparison between the average selenium concentration of 5 water samples obtained monthly from the center of Pond 1 are typically within 20% of the value reported at the Pond 1/2 weir. Similar spot checks for Pond 7 and the experimental pond, 5E, also suggest that the samples collected from the weirs and berms provide a reliable indicator of the concentrations of selenium in filtered surface water collected from the center of the ponds. A comparison between the recently completed synoptic surveys and the values measured from the LBL surface water sampling program will provide a more meaningful assessment of the degree to which samples collected at the weirs are representative of average pond water selenium concentrations.

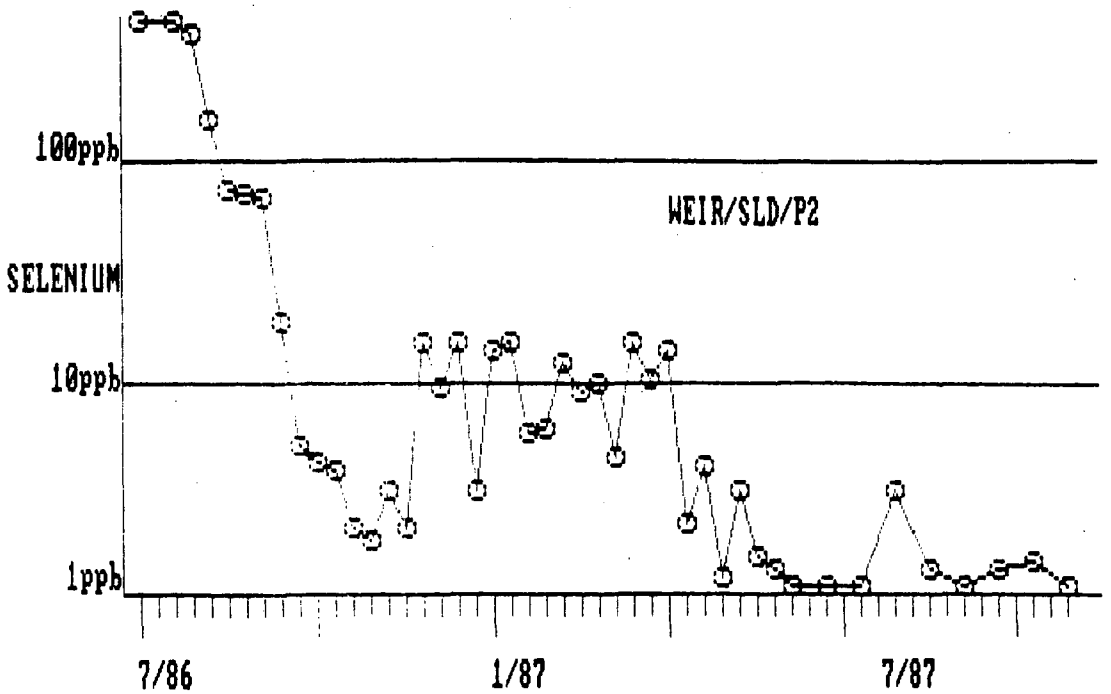

Figure 2.2. Selenium concentration measured at the weir between the San Luis Drain and Pond 2 (SS1). The increase in selenium concentration, up to 10 ppb, observed during the three month period from December of 1986 to March of 1987 was caused by mixing with residual drainage water due to changing water operations.

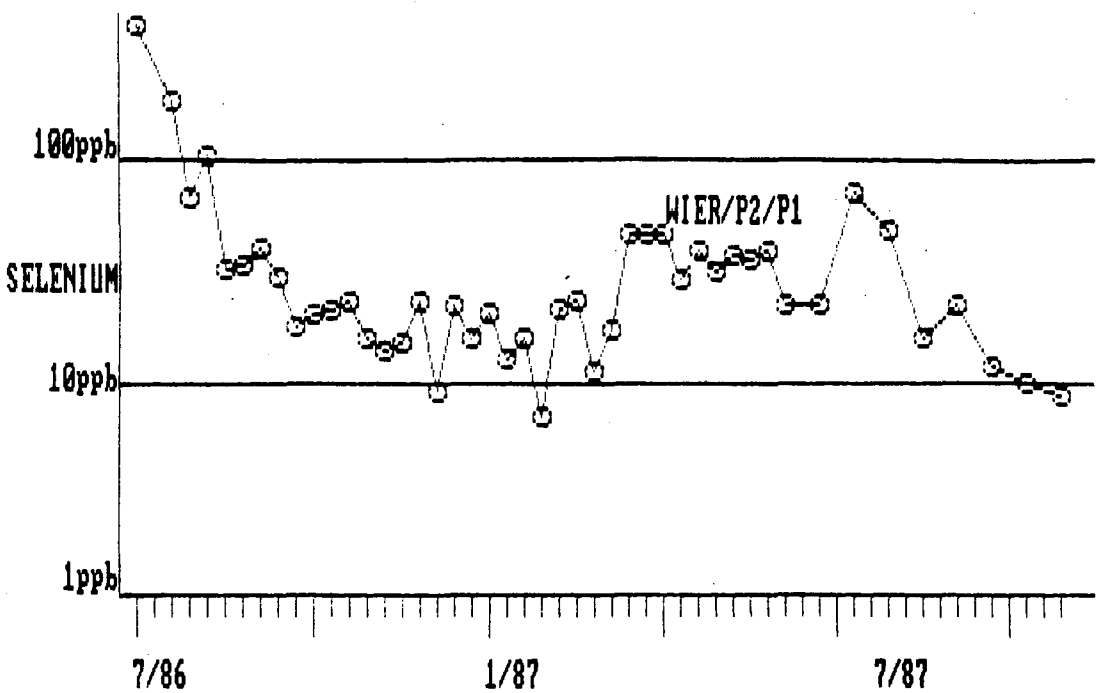

Figure 2.3. Selenium concentration measured at the weir between Pond 1 and Pond 2 (SS2).

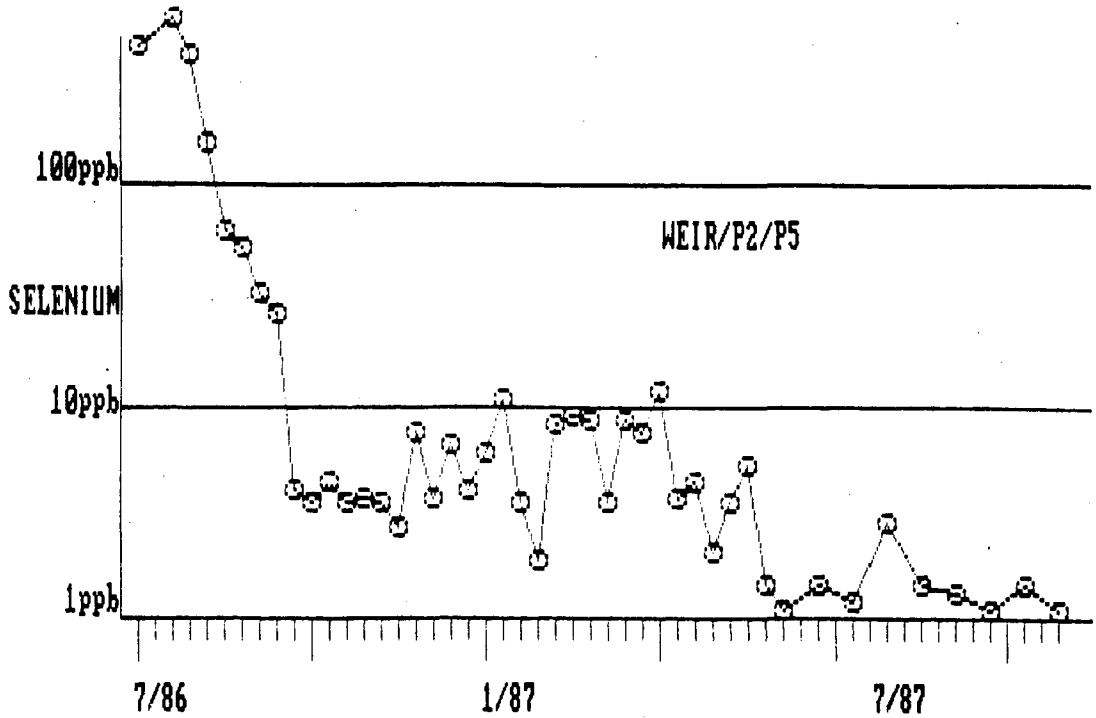

Figure 2.4. Selenium concentration measured at the weir between Pond 2 and Pond 5 (SS6).

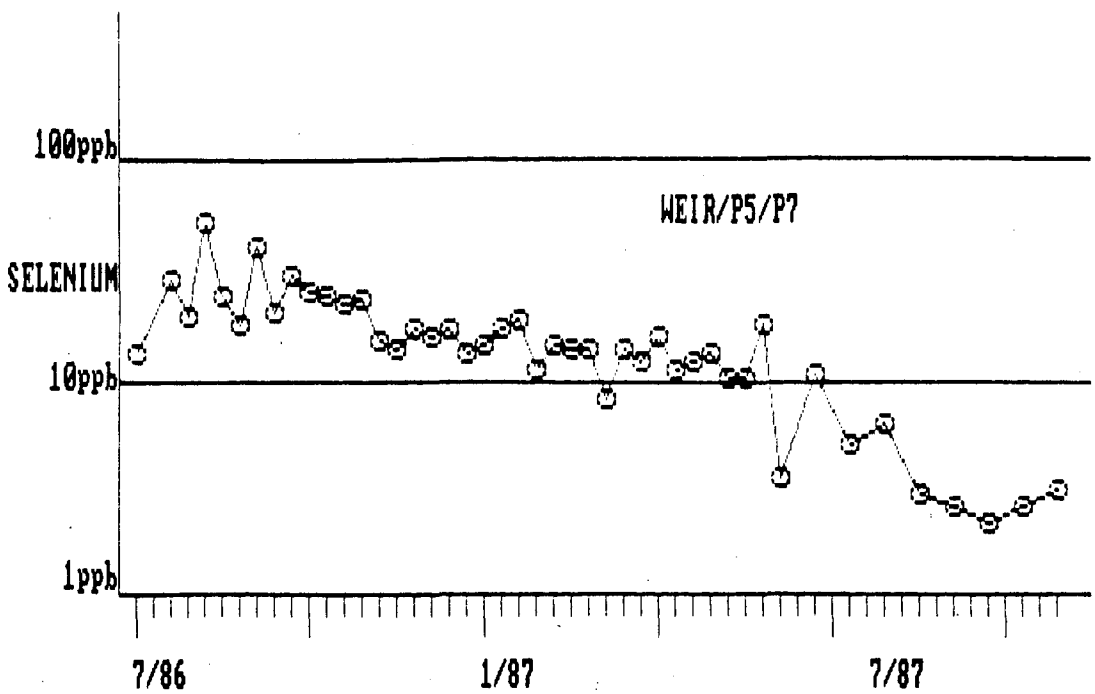

Figure 2.5. Selenium concentration measured at the weir between Pond 5 and Pond 7 (SS7). Note that the slug of drainage water with a high selenium concentration that entered Ponds 2 and 5 (see Figure 2.2, 2.3, and 2.4) was not detected at the Pond 5/7 weir.

The decline in the selenium concentrations in the surface water demonstrates that the selenium contained in the pond bottom sediments is effectively immobilized when kept submerged year-round. An alternative hypothesis is that biological uptake occurs at a rate sufficiently high to keep surface water selenium concentrations low. The low concentrations of selenium in the surface waters also suggest that the transfer of selenium from contaminated biota and sediments to the surface water is small enough to keep surface water selenium concentrations below the target goal of 5 ppb.

2.2. Selenium Concentrations in Ephemeral Pools

During March of 1987, numerous and extensive pools of water were observed in Ponds 6, 8, 9, 10, 11,and 12, none of which were intentionally flooded as part of interim operations at the Reservoir. These pools formed from a combination of factors, including: rising groundwater caused by intentional flooding of the numerous duck clubs located to the west of the Reservoir; accumulation of rainfall in local topographic depressions; and the groundwater mound created by flooding Ponds 1, 2, 5, and 7. The degree to which each of the factors contributed to the formation of the pools observed during 1987 is uncertain. Nevertheless, during the winter and early spring, formation of similar pools covering an estimated 450 acres of the Reservoir, is expected to continue even without the addition of water to the Kesterson Ponds (USBR, 1986).

In late March 1987, 26 surface water samples were collected from ephemeral pools located in Ponds 8 through 12 (see Figure 2.6 for locations and selenium concentrations). A frequency plot showing the distribution of the selenium concentrations observed in these samples is presented in Figure 2.7. The average concentration in 26 samples, collected over a one-week period in March was 373 ppb. The highest concentration was approximately 2500 ppb the lowest concentrations were in the range of 40 ppb (LBL Progress Report 5). Analysis of the data suggests a log-normal distribution, with a geometric mean of 197 ppb.

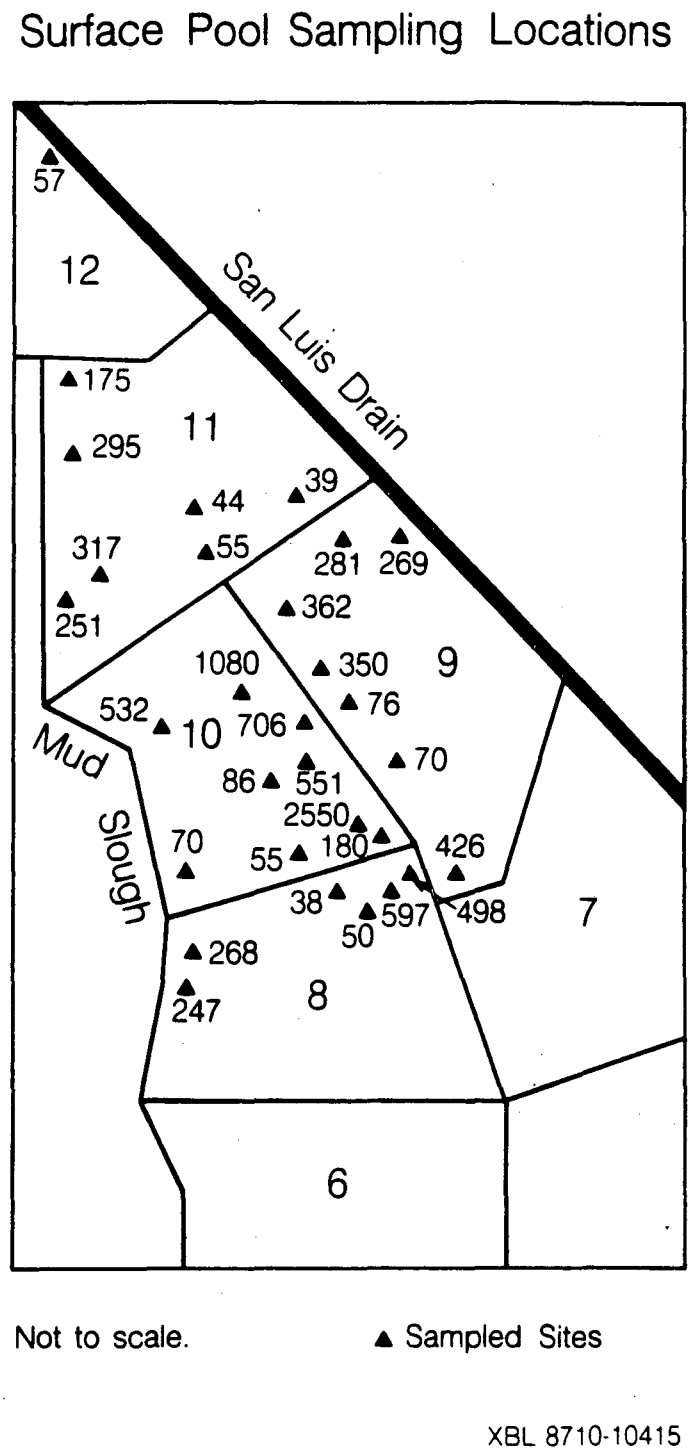

Figure 2.6. Sampling sites for surface water collections from the ephemeral pools located in Pond 8 through 12. Selenium concentrations, reported in parts-per-billion are listed next to the sampling site.

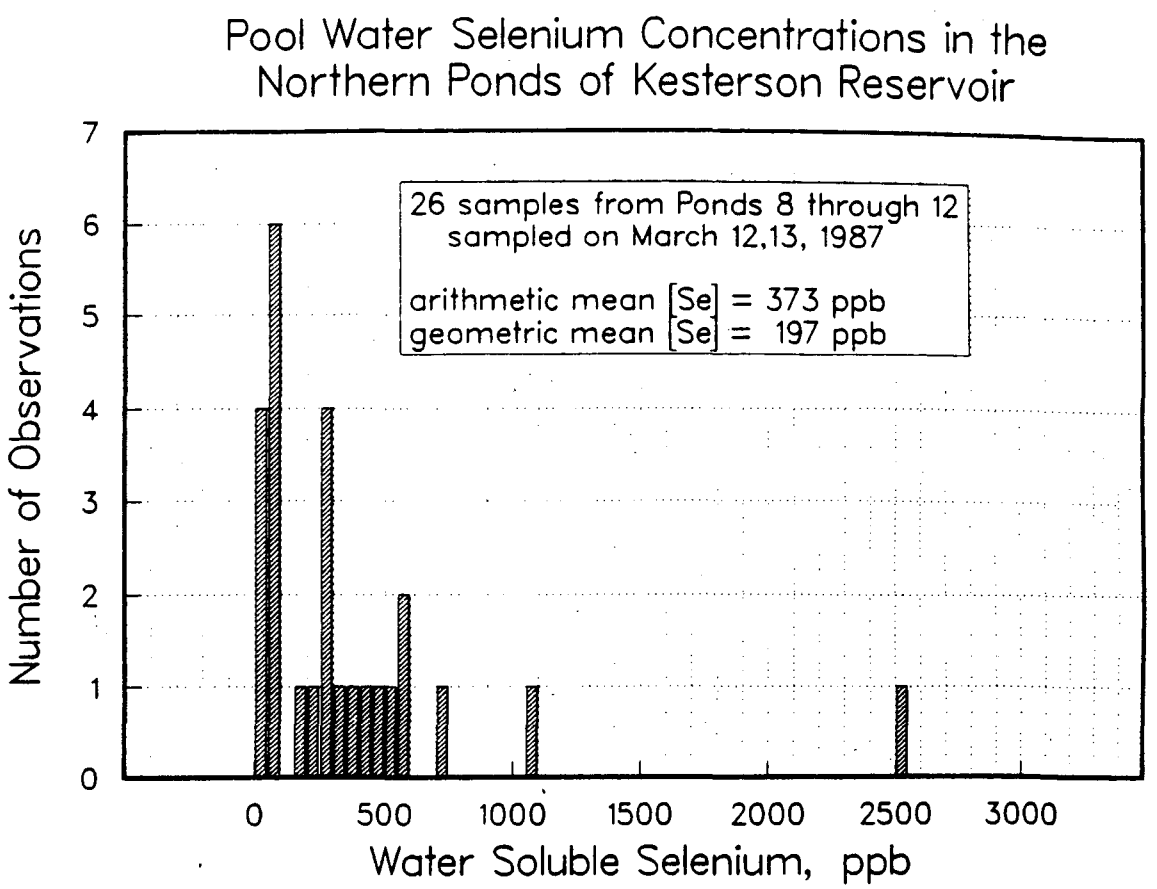

Figure 2.7. Frequency distribution of selenium concentration measured at 26 locations in the ephemeral pools in Ponds 8 through 12.

Elevated selenium concentrations in these pools originate from dissolution of seleniferrous salts, remobilization of biotic selenium contained in the vegetative mats remaining in the bottom of the pools, and upward movement of the selenium laden water that resides in the vadose zone. These factors are discussed further in Sections 3.3.2 and 3.3.3. The degree to which each of these factors contributed to the observed high concentrations of selenium is unknown. Studies are underway to assess the contribution from each of the factors and to evaluate the environmental hazards posed by these pools after implementing the On Site Disposal Plan.

2.3. Selenium Speciation in Water.

Water samples are routinely analyzed to determine the concentration of selenite (Se^{+4}) and total selenium. In addition to these routine measurements, measurements have been made to determine the concentration of volatile selenium compounds in the surface waters. A method for determining volatile selenium in water was devised and described in LBL Progress Report 2. This method has since been standardized and recovers approximately 98% of the dimethylselenide in a water sample. Recovery of other volatile compounds has not been documented.

Analyses of several surface water samples for volatile selenium, Se^{+4}, and total non-volatile selenium are summarized in Table 2.1. Substantial volatile selenium was detected in the first water sample only, which was collected in June 1986 when the water level in Pond 5 was dropping rapidly and a mass of dying, decaying *Chara* (macro algae) was present near the sampling site. The *Chara* at that time and place contained about 60 ppm selenium (dry weight) and the volatile selenium in the water was almost certainly derived from decay of this seleniferous vegetation. All of the other water samples in Table 2.1 were collected under Interim Management conditions, and all contained less than 2 ppb volatile selenium.

Available data suggest that the concentration of organic selenium compounds, vola-

tile or otherwise, are less than 2 ppb in the surface water under interim management conditions. Work is continuing to develop analytical methods for detecting nonvolatile organic selenium compounds in water at concentrations in the parts-per-billion range.

Table 2.1. Speciation of Se in Surface Water.

Date	Pond	Near/Over	Vol. Se (ppb)	Se^{+4} (ppb)	Nonvol. Se (ppb)
6-17-86	5	Dying Chara	16	29	43
6-17-86	1	Ruppia	0.5	17	31
5-28-87	5	Chara	1.4	7.6	10
5-29-87	5	In Chara	1.6	6.7	7.6
5-28-87	5E	Chara	0.8	2.8	3.2
5-29-87	7	Ooze	0.9	27	33
5-29-87	4	Ruppia	1.0	20	24
5-29-87	-	Blank	0.4	0.4	0.8

2.4. Discussion of Surface Water Selenium Concentrations

Comparison between the low selenium concentrations observed in the ponds that have been flooded during the past year and the high concentrations observed in the ephemeral pools clearly demonstrates that permanent flooding with a selenium free water supply is a very effective means of lowering surface water concentrations to the target concentration of 5 ppb. A situation intermediate between these two extremes was investigated by the Pond 1 experiment, where a pond which was dry throughout the summer was flooded in late October, 1986. Within the first few months after flooding, the selenium concentration in the surface water dropped from approximately 45 ppb down to 15 to 20 ppb, where it remained until early summer (LBL Progress Report 6). During June and July the water supply to Pond 1 was erratic, first causing an increase in selenium concentration, and later a decrease, down to approximately 10 ppb.

Comparison between the relatively low selenium concentrations observed in Pond 1 (45 to 10 ppb) and the high values observed in the ephemeral pools (an average of 373 ppb) suggests that seasonal flooding of the areas in which ephemeral pools may form would provide an extra measure of control over surface water selenium concentrations.

In addition to lowering the surface water selenium concentrations, repeated flooding on a yearly basis would tend to decrease the inventory of soluble selenium in the near surface soils by driving soluble selenium deeper into the soil profile (see section 3.4.3). Extensive monitoring of the groundwater under Pond 1 demonstrated that mid-autumn flooding did not create elevated concentrations of soluble selenium in the upper aquifer (see sections 3.4.1 and 3.4.3). The apparently limited potential for groundwater contamination, along with the promise of long-term declines in the near-surface inventory of soluble selenium suggest that seasonal flooding may be another way of minimizing the hazard posed by high surface water selenium concentrations in ephemeral pools. Impacts to wildlife, caused by such a management strategy, would need to be investigated to assess its potential benefits and drawbacks.

3. GROUNDWATER

Over the past year we have studied the groundwater system at Kesterson Reservoir with the objective of:

- understanding and determining the extent of the past influences of operating the Reservoir;
- providing the basic hydrologic and geochemical data needed to design an appropriate clean up plan; and
- predicting the future impacts of implementing a clean-up scheme.

To meet these objectives we have characterized the hydrologic setting, measured hydrologic properties of the pond-bottom soils and upper aquifer, and determined the extent of the drainage water and selenium plumes. In addition, laboratory experiments and computer models have been used to identify the geochemical and/or biological mechanisms that control the mobility of selenium in the various environments. A major part of our efforts has been devoted to field observations and experiments, where we directly observe the behavior of soluble selenium under actual Reservoir conditions. These have been most valuable in improving our understanding of the behavior of selenium at Kesterson Reservoir. A summary of all of these activities is provided below. For the most part, more detailed descriptions of experimental procedures, methodology, and data have been provided in the LBL Quarterly Progress Reports.

For the purposes of this report we include the vadose zone as a sub-category under the general heading "groundwater". We do this because at Kesterson Reservoir, soil water can often be found in different conditions throughout the year. During the dry season, soil water can be characterized as being part of the vadose zone which overlies the shallow aquifer. During the wet season, the shallow water table rises through the soil profile, often up to the soil surface. In this condition, the soil water is in principle groundwater. In low lying regions of the Reservoir, the seasonal rise of the water table can result in surface ponding of displaced soil water.

The intimate relationship between groundwater, the vadose zone, and surface water

in this setting is problematic insofar as it creates continually changing hydrological, geochemical, and biological conditions in the near-surface soils. These changing conditions, in turn, repeatedly alter the chemical state of selenium and the risk it presents to local wildlife and groundwater resources. The reactive nature of selenium, combined with a varied hydrological setting, present a challenge for predicting future impacts of any cleanup scheme in which the natural hydrological cycle is left unchanged.

3.1. Hydrologic Setting*

Kesterson Reservoir is situated in the midst of a seasonal wetland. Within a 124-square-mile region centered on Kesterson Reservoir, approximately 18 percent of the land is seasonally flooded for duck ponds (Mandle and Kontis, 1986). Kesterson Reservoir accounts for approximately 8 percent of the total seasonal wetland within this region. The average depth to the water table ranges from 1.5 in the western part of the region to 10 ft, in the east. Annual fluctuations of approximately 5 feet are caused by flooding nearby duck ponds and winter precipitation.

Under Kesterson Reservoir, the aquifer system can be divided into two distinct units: an unconfined aquifer extending from near the ground surface to a depth of 200 feet (upper unit) and a confined aquifer below the E (Corcoran) clay (Hotchkiss and Balding, 1971). Extensive groundwater monitoring has demonstrated that the influences of Kesterson Reservoir on the groundwater system are confined to the upper unit, henceforth referred to as the upper aquifer. Therefore, our investigations are limited to this unit.

On a regional scale, groundwater movement is from the south and west, to the northeast. A pre-Kesterson survey of the water table elevation in the shallow aquifer reported that the hydraulic gradient in the general vicinity of the Reservoir ranged from

*In the following sections we report data both in English units and in metric units. This ambiguity is deeply imbedded in our measurement and reporting systems.

$5x10^{-4}$ to $9x10^{-4}$ (State of California, 1967). In the immediate vicinity of the Reservoir, in the region between Mud and Salt Sloughs, the average hydraulic gradient was approximately $5x10^{-4}$. Based on the range of hydraulic conductivity values reported in section 3.1.2, pre-Kesterson downgradient groundwater velocities ranged from less than 1 feet/year to approximately 160 feet/year. Assuming that the geometric mean hydraulic conductivity provides a representative average for the upper aquifer (40 ft/day - see section 3.1.2), in the absence of applied surface water, groundwater would migrate downgradient at an average rate of 20 to 30 feet/year.

Seepage from the Kesterson Ponds and migration of selenium are strongly influenced by local variations in the physical properties, chemical composition, and thickness of the fine-grained surface layer, as well as reservoir operations. When drainage water was being delivered to the Reservoir, seasonal variations in the water supply, evaporation rate, and water table elevation resulted in periodic flooding of the different ponds. The terrains resulting from variations in water operations and ground surface topography are discussed in greater detail in section 4.1. However, the terrains can be grouped hydrologically into the broader categories of permanently flooded, seasonally flooded or dry. In the southern part of the Reservoir, the Ponds were for the most part, permanently flooded, and the underlying sediments remained fully saturated; a downward hydraulic gradient persisted throughout the year. Drainage water was discharged to the northern ponds only periodically, primarily during the winter and spring months. Under these ponds, the water table rose to the surface during the wet season, and receded below the surface in the dry season. During the summer and autumn, the hydraulic gradients within the surface soils were primarily in the upward direction (LBL Progress Report 6). In the winter and spring, the gradient was downward (LBL Progress Report 1). In the absence of applied surface water, the hydraulic gradient during winter and early spring may have been upward or downward, depending on the local hydrological conditions and topography (LBL Progress Report 6).

An estimated 50% of the 8000 acre-feet per year of drainage water that was delivered to the Reservoir seeped into the upper aquifer (USBR, 1986). As illustrated in Figure 3.1, surface ponding created a groundwater mound that closely followed the contours of the flooded areas within the Reservoir. Drainage water that seeped into the upper aquifer moved both laterally and vertically into the upper aquifer (see section 3.2.1).

An important hydrologic feature of the Reservoir area is the very shallow depth to the water table. The water table is generally within 10 ft of the soil surface, and in places rises seasonally above the soil surface. The combination of a shallow water table, and the climate at the reservoir in which potential evaporation greatly exceeds annual rainfall is very conducive to high evaporative water losses from soil. As noted as least as early as 1952 (Soil Conservation Service, 1952), soils of the reservoir region are saline. Associations of saline soil profiles with shallow water tables are common, with salinization resulting from high evaporative rates from the water table leaving salt accumulated within the soil profile (e.g. Birkeland, 1974, Bresler et al., 1982). At Kesterson Reservoir, this naturally saline soil environment has received large quantities of additional salts from disposal of high salinity drainage water.

The reservoir water and salt inventories are presently and will continue to be strongly influenced by evaporation and rainfall. As shown in meteorological data from the Reservoir (Figure 3.2), potential evaporation greatly exceeds precipitation. The combined effects of the shallow water table which enhances upward flow of soil water, and the large excess of potential evaporation relative to rainfall result in a soil environment where natural leaching of selenium and other salts is virtually impossible.

3.1.1. Hydrological Properties of the Pond Bottom Soils

During operation of the Reservoir for disposal of agricultural drainage waters, pond soils served as a barrier to rapid leaching of seleniferous, saline water into the shallow aquifer. The extent to which pond soils have impeded downward transport of selenium

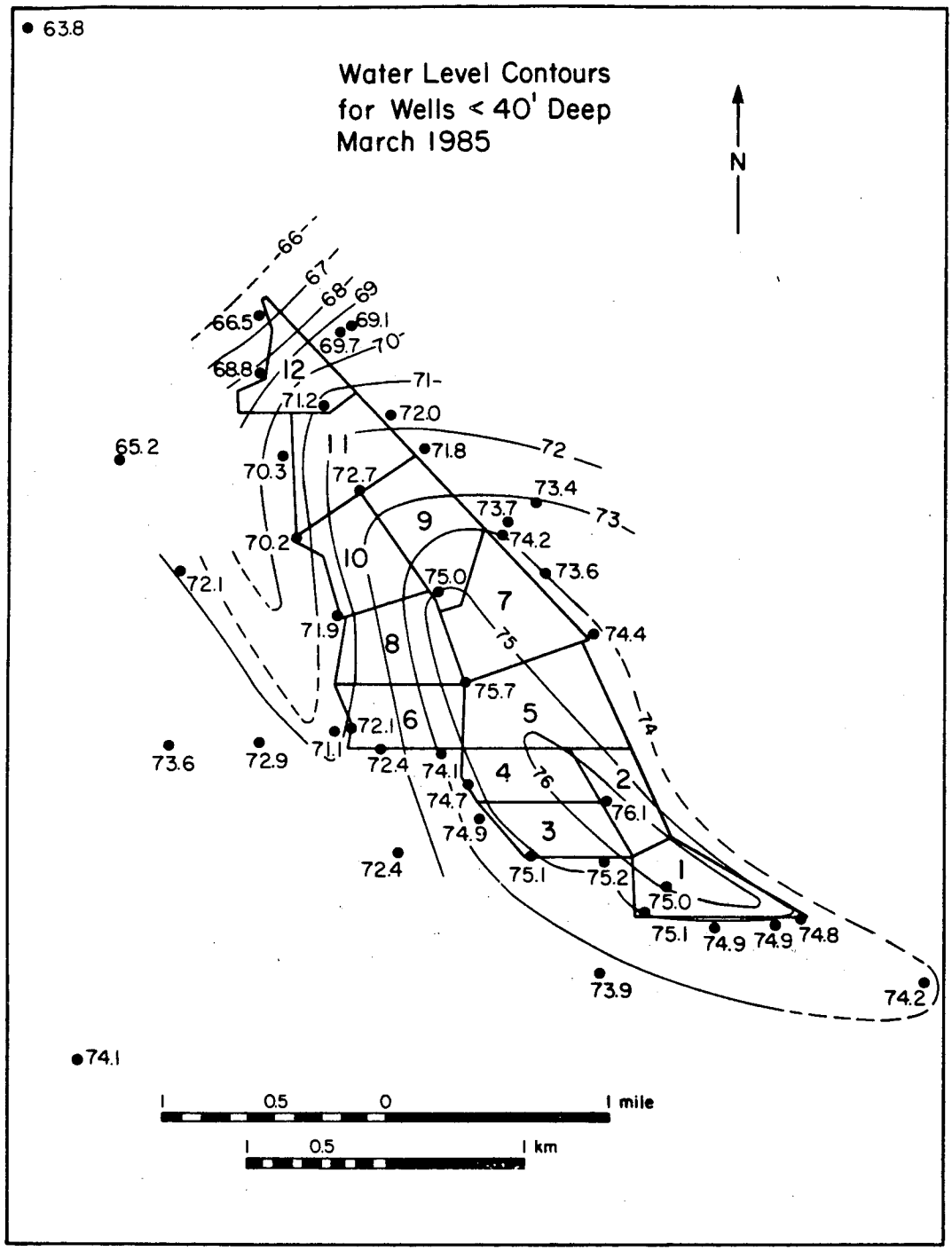

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Figure 3.1. Watertable elevation (measured in feet above mean-sea-level) around Kesterson Reservoir during late-winter of 1985.

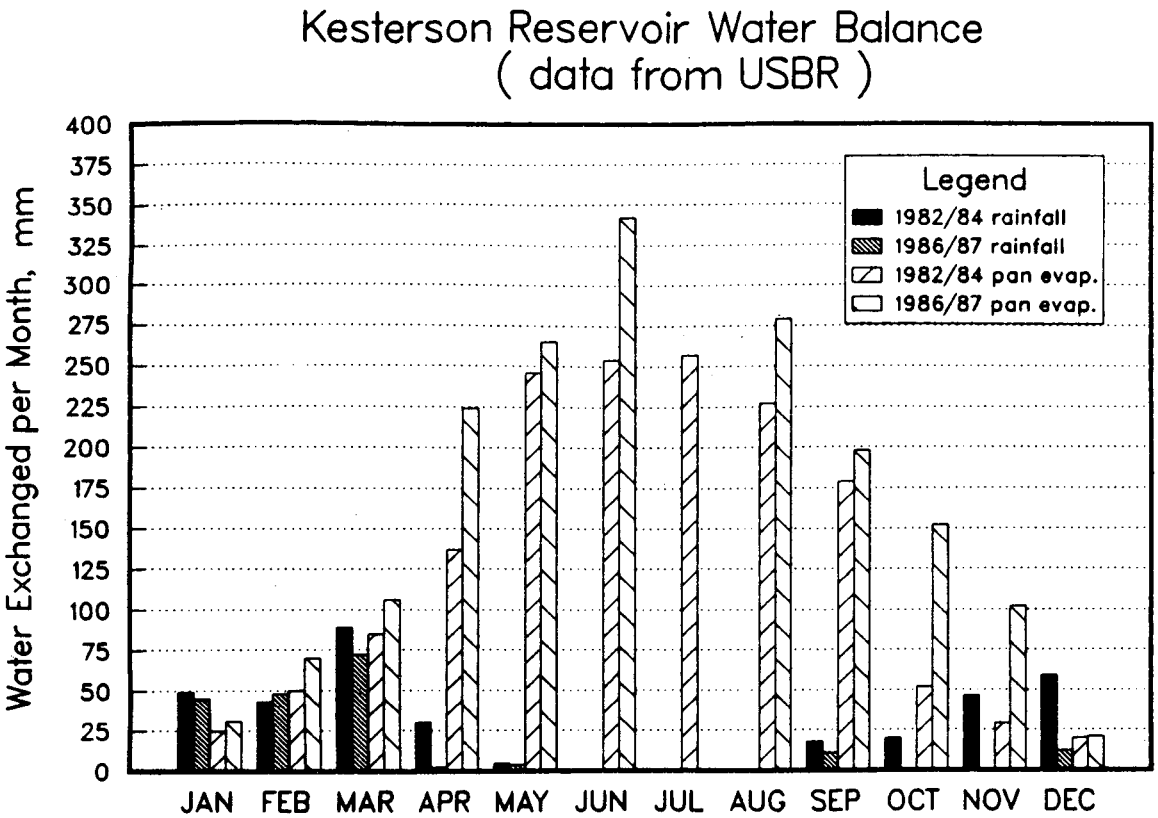


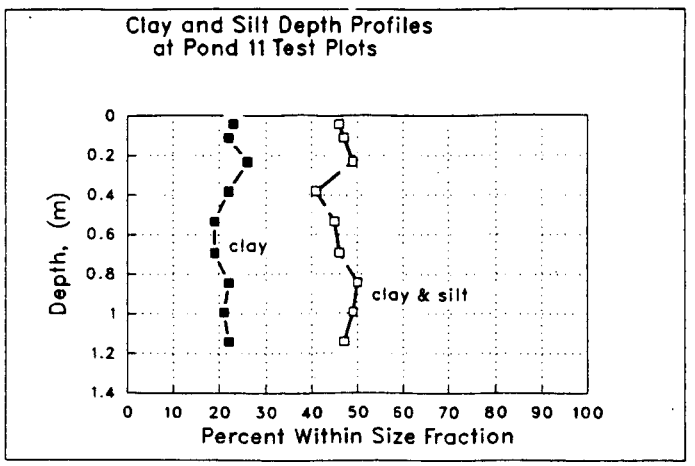
Figure 3.2. Rainfall and pan evaporation at Kesterson Reservoir for the period from 1982 to 1984 and 1986/1987.

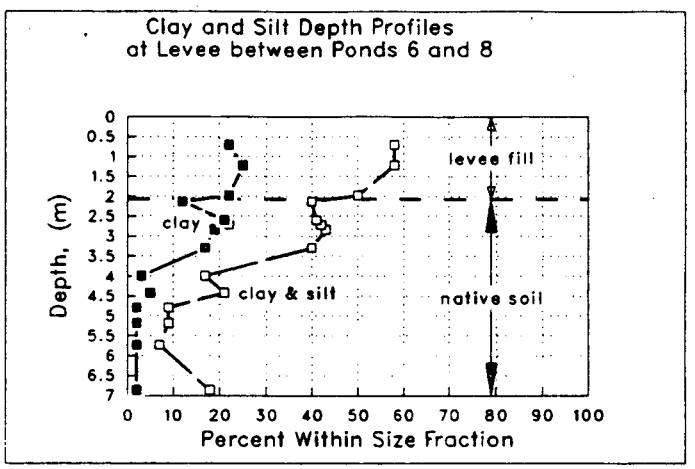
at different locations depends on a range of chemical, biological, and hydraulic influences. Important chemical and biological processes regulating the fate of selenium in pond soils are discussed in sections 3.2, 4.3 and 4.4. In this section, a brief summary of some relevant hydrological observations will be provided.

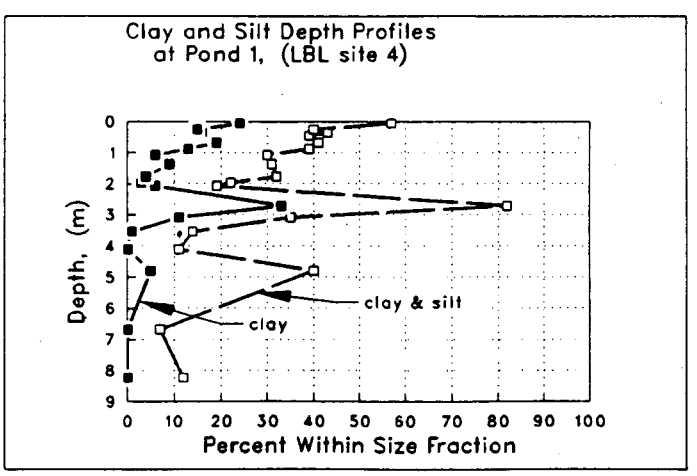
Particle-size distribution data are useful in characterizing heterogeneities within soil profiles (e.g. horizon boundaries), and estimating numerous soil properties including the (water saturation-dependent) hydraulic conductivity, specific surface area, and (when combined with clay mineralogical analyses) ion exchange capacity. Both hydrometer and sieve methods (Gee and Bauder, 1986) were used to determine particle-size distributions. The reported particle-size classes conform with U.S. Dept. of Agriculture conventions (clay $\leq 2\mu$m, silt 2 to 50μm, and sand 50μm to 2mm).

Particle-size analyses from three widely separated locations at the Reservoir are summarized in Figures 3.3a,b,c. (Note that the vertical scale for depth varies among frames.) While the three profiles shown in this figure are indicative of both lateral and vertical variations in reservoir soils, some general observations can be made. The surface 1 to 2 m of the present native soil is generally of finer texture than deeper strata of the shallow aquifer. Clay and silt contents each generally contribute about 20% to the weight of the surface mineral soils. Particle-size distributions of individual surface soil samples exhibited a range in textures from sandy loams to sandy clay loams. These textures as well as other observed profile features such as high salinity and the presence of calcium carbonate agree with descriptions of the Waukena soil series which was used to characterize the Reservoir area in an early soil survey (Soil Conservation Service, 1952). It should be noted that while the profiles shown in Figures 3.3a,b,c are from sites with only moderate amounts of surface organic material, other locations within the reservoir have substantial surface accumulations of organic matter derived from wetland vegetation.

Particle-size distributions of samples taken below about 2 m in native soil profiles







Figures 3.3a,b,c. Profiles of the clay and silt fraction at sites in Pond 11 (3.3a), Pond 6/8 (3.3b), and Pond 1 (3.3c).

tend to be dominated by the sand fraction. This pattern is apparent in Figures 3.3b and 3.3c, and has generally been observed during well drilling at numerous other locations within the reservoir. The substantial particle-size contrast between the finer textured surface soils and the deeper sands indicates that the principle physical and physical-chemical barrier to groundwater contamination by selenium is the surface soil.

The saturated hydraulic conductivity, K_s, of reservoir soils is an important physical parameter in determining the extent of drainwater seepage into the shallow aquifer. While the complex chemistry of selenium precludes directly associating drainwater seepage with selenium transport, pond seepage is a prerequisite for explaining localized observations of shallow aquifer selenium contamination within the short operation period when drainage water was discharged to the Reservoir. The hydraulic conductivity of a soil is a property which is qualitatively related to its particle-size distribution (e.g. Jaynes and Tyler, 1984, Campbell, 1985). Finer textured soils are commonly associated with low permeabilities. However, in field soils this relation is often very weak due to the influences of soil aggregation and macropores (e.g. Beven and Germann, 1982). Thus, the most reliable assessment of K_s for the pond soils comes from direct field measurements.

In a study of the reservoir site prior to its development, Luthin (1966) measured K_s of surface soils with an infiltrometer. A value for K_s of 11 m yr^{-1} (0.10 ft day^{-1}) was reported in that work. During 1986 and 1987, hydraulic conductivity profiles of surface soils at the reservoir were measured at several sites. These measurements employed a constant head, auger hole method (Reynolds et al., 1983, Reynolds and Elrick, 1985) with a Guelph permeameter. Depth profiles of the field-saturated hydraulic conductivity, K_{fs}, were measured to as deep as 1.22 m. Results of measurements at various locations throughout Pond 1, and at test plots in Ponds 9, 10, and 11 are presented in Figure 3.4a,b,c. The high degree of spatial variability in the measured K_{fs} is consistent with thorough studies of this phenomenon by others (e.g. Nielsen et al., 1973, Warrick

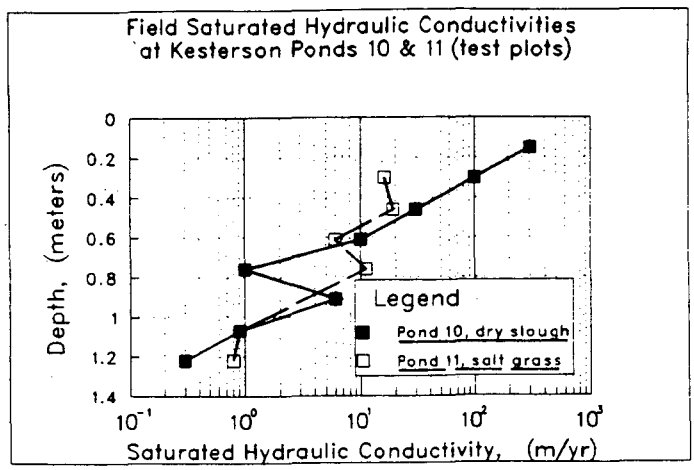
and Nielsen, 1980).

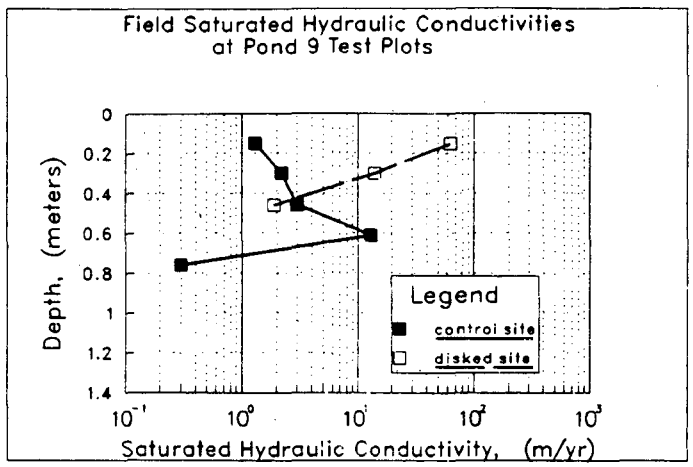
Despite the tremendous variation in K_{fs}, both within and between sites, a few generalizations can be made. The K_{fs} of the uppermost 0.3 m of the soil profiles tend to be quite high. In some profiles, values in excess of 100 m yr^{-1} were measured within 0.2 m of the surface. From field observations, this pattern appears to be due to the predominance of macropores within the upper portions of the soil profiles. Within the first 1 to 2 m of soil, K_{fs} generally decreases with depth. In some cases, this decrease covers two orders of magnitude. K_{fs} values on the order of from 1 to 10 m yr^{-1} were commonly encountered in these subsurface measurements. These data are in reasonable agreement with Luthin's results. From the particle-size analyses of samples from deeper strata, it can be inferred that the permeability increases in the vicinity of 2 m below the surface. Thus the low permeability barrier impeding rapid drainwater percolation appears to generally occur at depths of about 0.3 to 2 m.

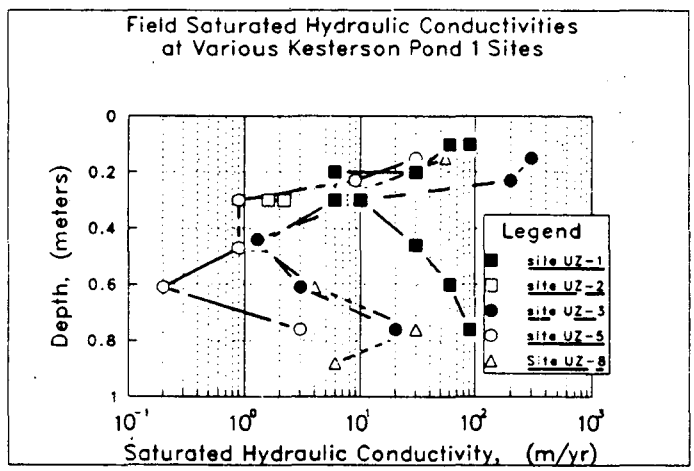
While chemical and biological factors are important in determining the extent of selenium transport and immobilization, as discussed in Section 3.2.2, high seepage rates contribute to the potential for selenium migration into the upper aquifer. The presence of occasional high permeability zones within the otherwise low permeability soils is consistent with the observation that selenium has entered the upper aquifer in limited and isolated areas.

3.1.2. Hydrologic Properties of the Upper Aquifer

After seeping through the layer of fine grained soils underlying the ponds, the rate and direction that the drainage water and selenium plumes migrate are influenced by the hydrologic properties of the upper aquifer. Nine of the sites shown in Figure 3.5, were chosen for investigating the hydrologic properties of the aquifer, to a depth of 100 ft below the ground surface. Numerous boreholes were drilled at each of the sites, providing information on the local geology and hydrologic properties of the upper aquifer.







Figures 3.4a,b,c. Field saturated hydraulic conductivity profiles at sites in Pond 10 and 11 (3.4a), Pond 9 (3.4b), and Pond 1 (3.4c).

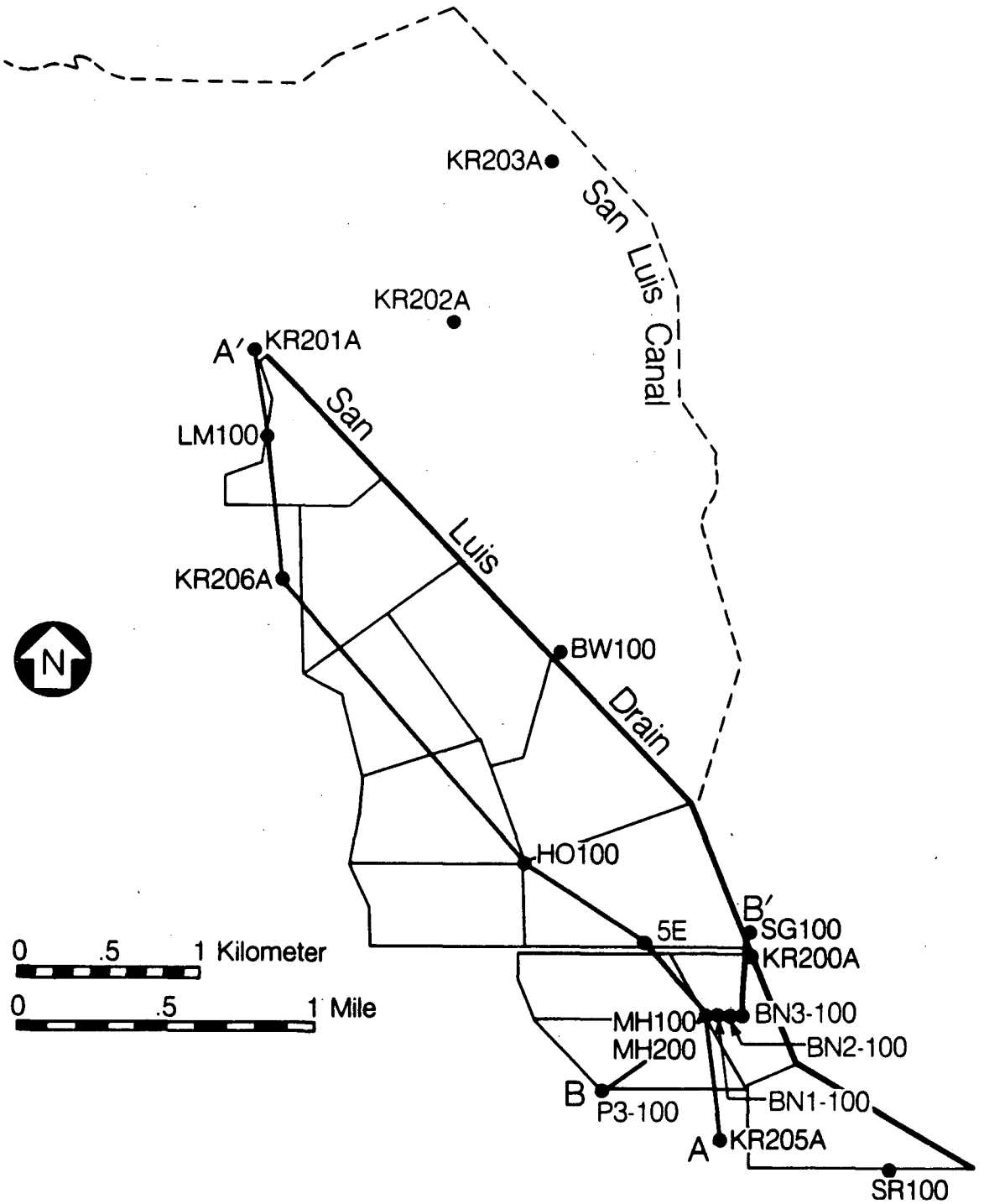


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Figure 3.5. Location of the LBL study sites (LM, MH, SR, SG, BW, HO, BN1, BN2, and BN3), USBR wells with geophysical logs (KR wells), and the cross section A-A prime and B-B prime.

Geophysical logs obtained by the USBR from 8 additional sites within the immediate vicinity of the Reservoir have been included in developing the hydrogeologic model of the area. Investigations at each of the nine sites included:

- lithological evaluation of the sediments (LBL Progress Reports 1, 2,and 6);
- geophysical logging for defining the sub-surface stratigraphy (LBL Progress Reports 2 and 6);
- steady-state and pressure transient pumping tests for evaluating the hydraulic conductivity of the shallow aquifer (LBL Progress Reports 1 and 2); and
- tracer testing for determining the solute transport properties of the upper aquifer (LBL Progress Report 3).

A brief summary of the results of these investigations is provided below.

A typical data set from one of the study sites is illustrated in Figure 3.6 (LBL Progress Report 2). The geophysical logs, particularly the spontaneous potential and natural gamma logs are useful for differentiating layers of finer grained sediments from the sandy units in the lithologic column. In general, the gamma radioactivity and spontaneous potential of the finer grained sediments are higher than those of the sandier units. Pumping test data provide measurements of the hydraulic conductivity as a function of depth below the ground surface. In general, depth intervals with the low hydraulic conductivity values correlate well with the presence of the finer grained sediments identified from analysis of geophysical logs (LBL Progress Report 2).

Correlation of lithologic and geophysical profiles indicate the presense of thick sands, interbedded by three major clay/silt layers (LBL Progress Reports 2 and 6). Two cross sections, one trending approximately North-South, and one trending approximately East-West are illustrated in Figures 3.7a and 3.7b. In general, the top 10-20 ft of soil (C1) is underlain by 60 ft of sand (S1), 10 ft of finer grained sediments (C2), 120-150 ft of sand (S2), and 10-30 ft of clay (C3, probably the E (Corcoran) Clay). Because of its potential importance as an aquitard, the C2 unit has been studied in some detail. Available data suggest that it is essentially continuous in the region under the Reservoir, but

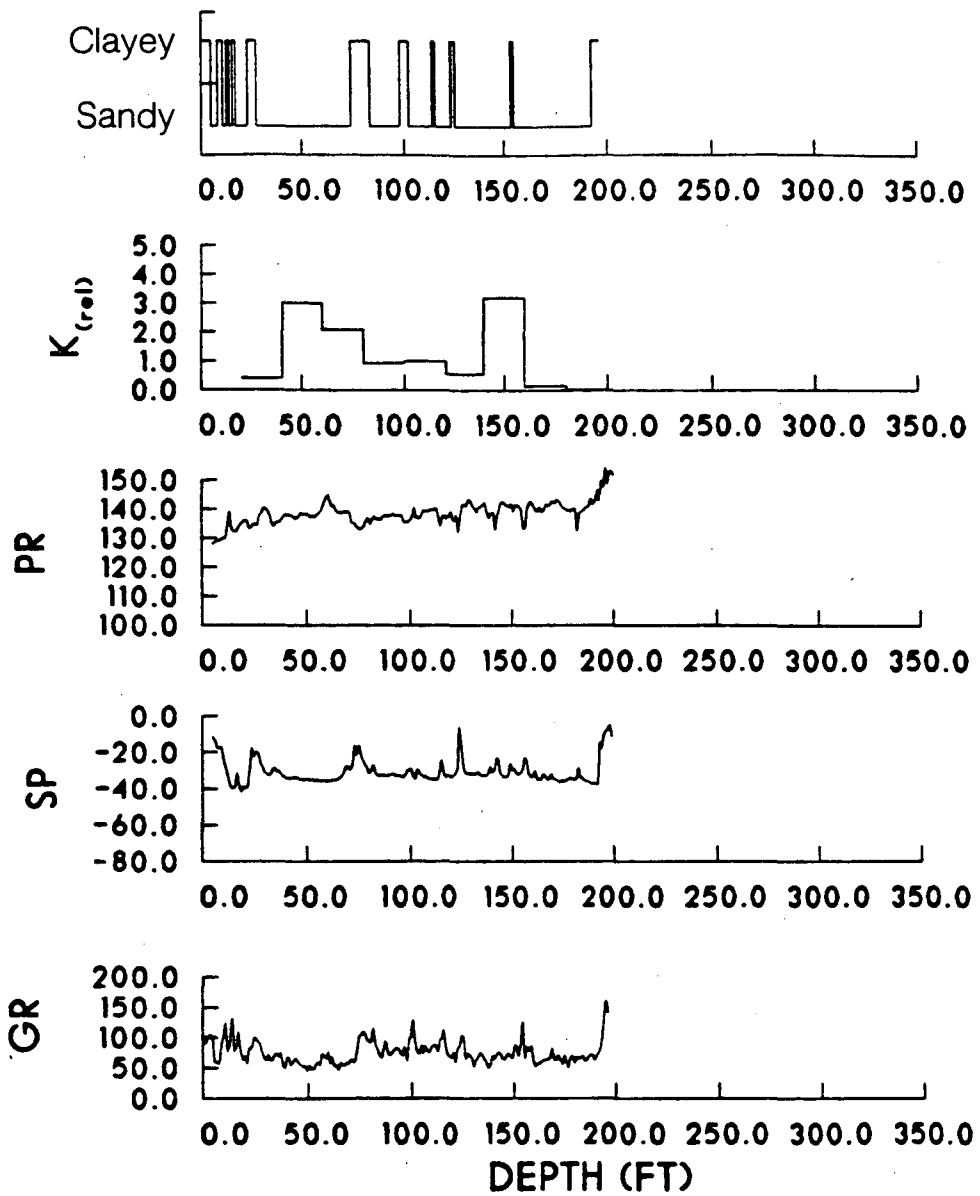


Figure 3.6. Illustration of a typical data set from one of the LBL study sites. Data includes natural gamma logs (GR), spontaneous potential (SP), point resistance (PR), permeability distribution ($K_{(rel)}$), and identification of layers of fine grained sediments. Note that in this graph $K_{(rel)}$ refers to the hydraulic conductivity of the interval divided by the average value measured at Kesterson. The last graph illustrates the location of fine grained sediments in the upper aquifer (left-sandy and right-clayey).

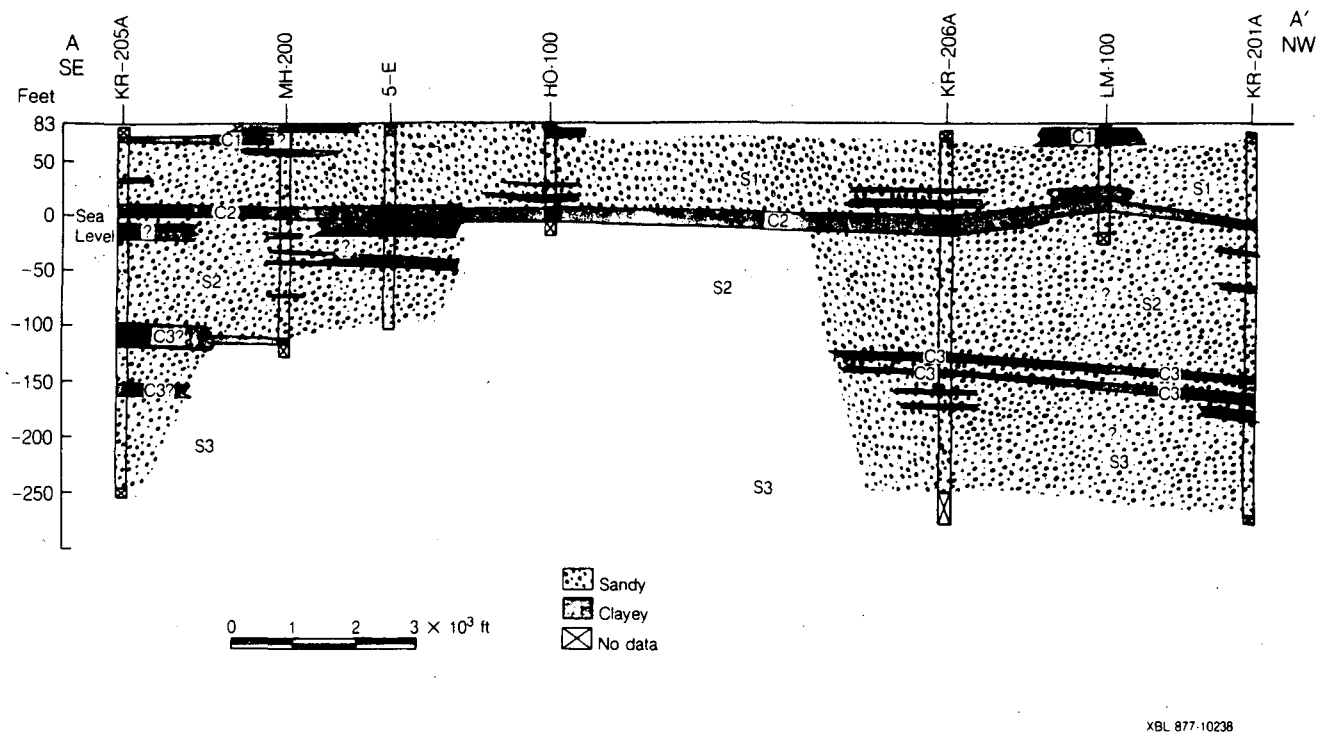


Figure 3.7a. Reconstruction of the subsurface lithology along cross section A-A prime.

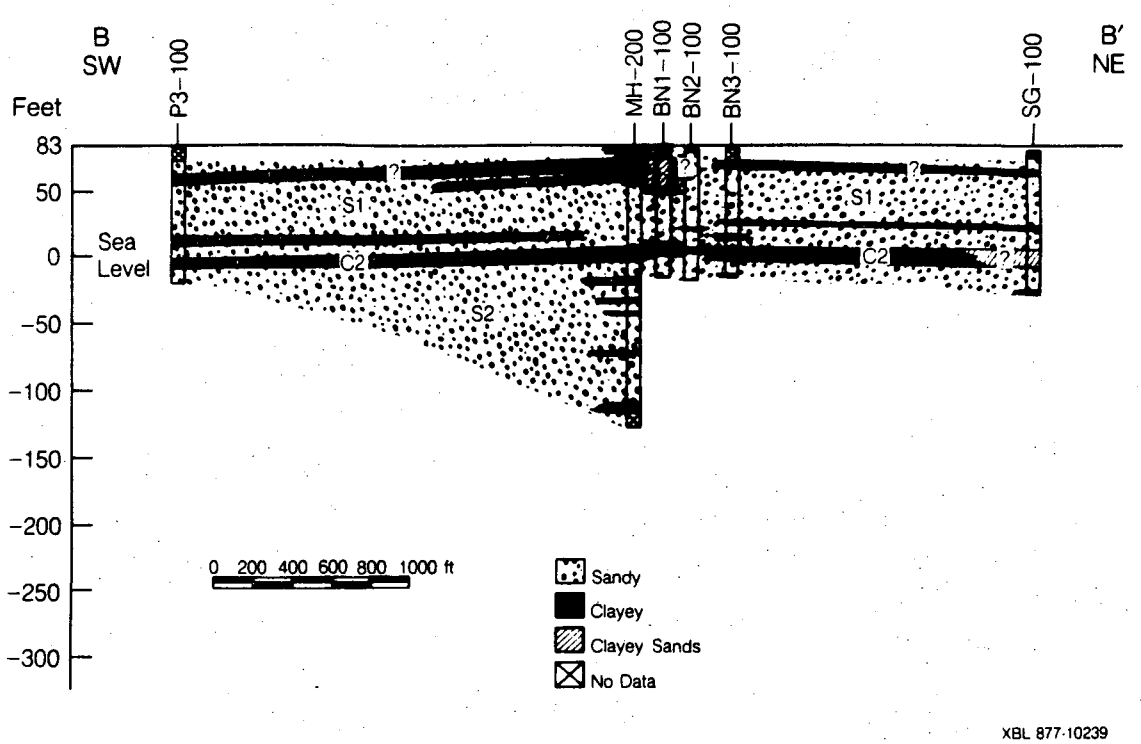


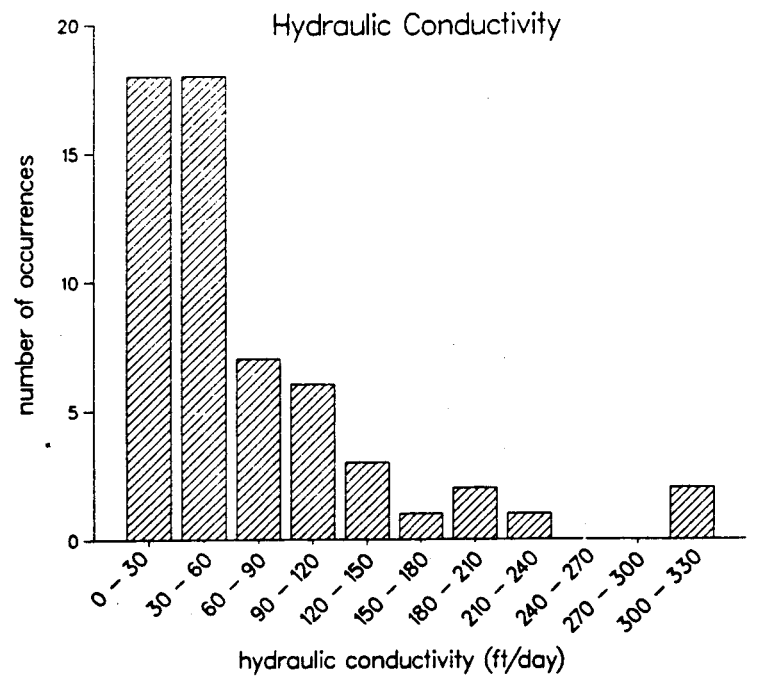
Figure 3.7b. Reconstruction of the subsurface lithology along cross section B-B prime.

in some places, may only be several feet thick. Along the eastern border of the Reservoir, the C2 layer appears to intercalated with sandy sediments. Additional data, to the east of the Reservoir are required to establish the continuity of this layer and develop a geologic model of the subsurface sediments downgradient of the Reservoir.

A total of 57 single well pumping tests were conducted for the purpose of measuring the hydraulic conductivity of the upper aquifer (LBL Progress Reports 1 and 2). The majority of these tests were conducted within the first 100 feet below the ground surface. Of these tests, 36 were conducted in wells with screened intervals of 20 feet, thus providing average values for the twenty foot thick test interval (LBL Progress Report 2). The remaining wells, which were all within the top 40 feet, had 5 feet screens (LBL Progress Report 1). Both steady state and transient testing techniques were used to measure hydraulic conductivity (Earlougher, 1977). The data were analyzed with a procedure described in LBL Progress Report 1 that uses a computer simulator to factor the natural heterogeneity of the upper aquifer and seepage from the ponds into the analysis procedure.

A histogram of the horizontal hydraulic conductivity values is shown in Figure 3.8. The arithmetic mean of these values is 70 ft/day and the geometric mean is 40 ft/day. The maximum hydraulic conductivity is approximately 5 times higher than the arithmetic mean.

Analyses of the chemical composition of the groundwater suggest that the C2 layer impeded the vertical flux of drainage water at depth (LBL Progress Report 2). The horizontal hydraulic conductivity measured in a well that intersects this layer is typically an order of magnitude lower than the average value. However, this measurement does not provide an accurate measure of the vertical hydraulic conductivity of the C2 layer because, other more permeable layers usually intersect the borehole in addition to the C2 layer, thus increasing the measured value, which is an arithmetic average of all the sediments intersecting the borehole. An alternative means of evaluating the vertical



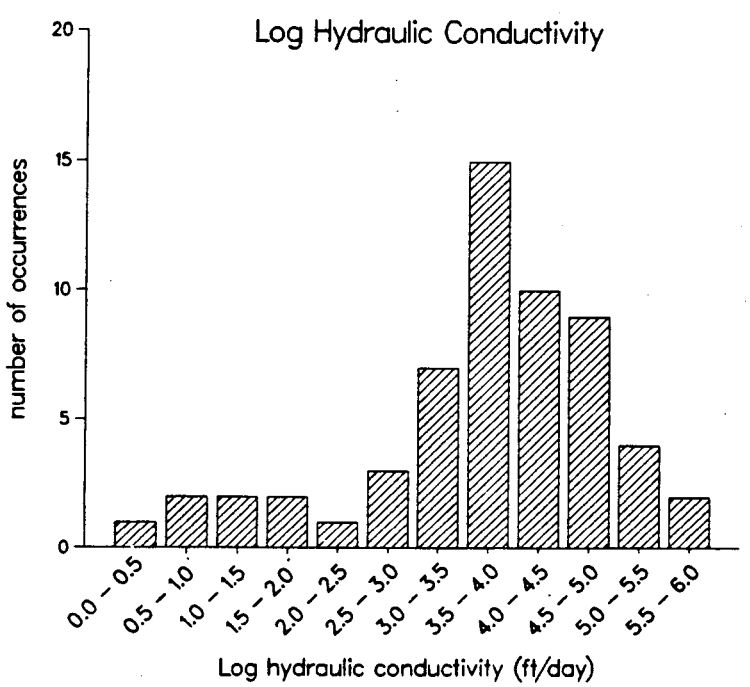


Figure 3.8. Histogram of the hydraulic conductivity values measured in the upper aquifer.

hydraulic conductivity of the C2 layer is provided by vertical interference tests. In these tests, a well above or below the C2 layer is pumped while the pressure drawdown is observed in a well on the opposite side of this layer. One such test, recently completed, indicated that the vertical hydraulic conductivity of the C2 layer is at least 3 orders of magnitude lower than the average hydraulic conductivity of the sandier units above and below it. Since no pressure drawdown was detected in the observation well (a drawdown as little as 1/4 inch (0.01 psi) could have been detected with the measurement device used), we can only place an upper limit on the vertical hydraulic conductivity of the C2 layer.

While hydrological measurements provide information that is useful for predicting the average velocity at which solutes migrate through the groundwater system, they provide little data on the variability of the sediments, which plays a major role in controlling solute transport. A tracer test was conducted for the purpose of directly measuring the transport properties of the sandy upper aquifer (LBL Progress Report 3). The test began by establishing a steady flow field between two wells by pumping water (4.8×10^{-3} m^3/s) from one well, and injecting it into another well located 100 ft away. After 12 hours of pumping/injecting, a steady flow field was established and a one hour slug of a 300 ppm fluorescein solution was injected into the aquifer. Pumping and injection continued for the ten days it took for the tracer to travel from the injection well to the pumping well. Fluid samples from five observation wells (with 5 feet screened intervals), located mid-way between the pumping and injection wells, were collected at regular intervals until the tracer slug passed by the observation wells.

The tracer recovery curve from the one of the observation wells is shown in Figure 3.9. The multiple peak recovery curve indicates that fluid is flowing through several distinct strata, each of different permeability and thickness. As illustrated in Figure 3.10, reconstruction of the hydrologic properties from the tracer data indicates that within this 20 ft section of the aquifer, there are at least 12 distinct strata. The thickness of

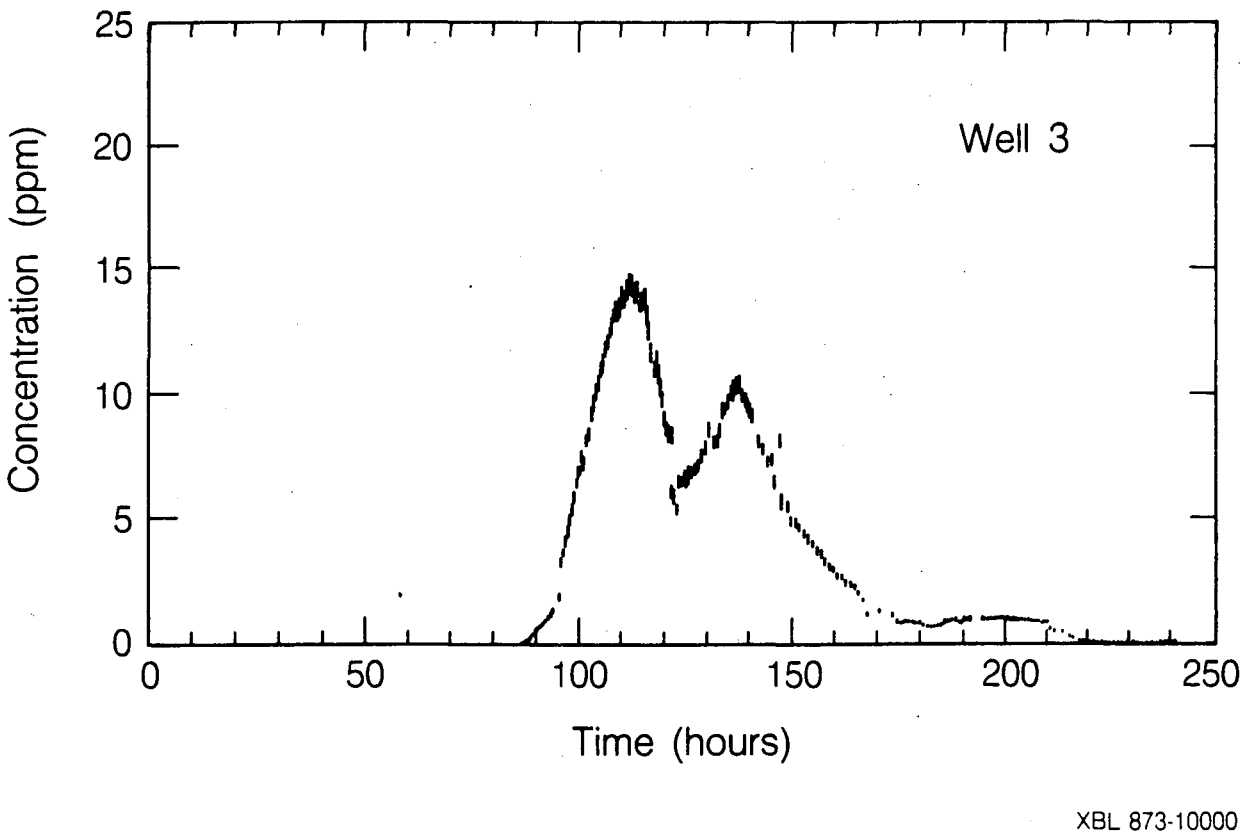


Figure 3.9. Tracer return curve from one of the tracer test monitoring wells. Notice the presence of two peaks, corresponding to solute transport in two distinct channels. Also note that the one-hour injection pulse has spread out to over 100 hours, indicating highly dispersed flow velocities.

the layers range from less than 0.25 feet to approximately 3.0 feet. The highest hydraulic conductivity is approximately 4 times greater than the smallest value and 1.8 times higher than the average value. Data from the test indicate that both hydrodynamic dispersion (due to pore-level mixing), and the effects of geologic heterogeneity are important dispersive mechanisms for chemical transport in this aquifer. However, hydraulic conductivity variations are the dominant dispersive mechanism.

3.2. Plume Investigations

Seepage of drainage water carrying salts and selenium from Kesterson Reservoir into the underlying aquifer is one the the major concerns that arose from operation of the Reservoir. Although the shallow aquifer underlying the Reservoir is naturally high in total dissolved solids (TDS), the TDS of drainage water was typically 2 to 3 times higher and contained high concentrations of selenium and boron. Early observations, based on groundwater quality data obtained from the USBR monitoring program, indicated that for the most part, whereas the drainage water was clearly seeping into the aquifer, elevated concentrations of selenium were not present. Subsequent investigations demonstrated that soluble selenium was bound in the pond bottom sediments by a combination of chemically reducing conditions and/or biological activity (Weres et al., 1985). There were exceptions to the above observations, the largest one being at the intersection of Ponds 2, 3, and 4. A majority of the groundwater sampling wells located along a 250 ft section of the berm centered at the intersection had selenium concentrations in the range of 10's to 200 ppb. Elevated concentrations of selenium were also observed for a short time on the northwestern boundary of Pond 12. Within this general framework we began our investigations of the groundwater system in the vicinity of Kesterson Reservoir. Our investigations have focused on three broad areas:

- obtaining better definition of the extent of the drainage water and selenium plumes;
- identification of the geochemical and/or biological processes that control the mobility of selenium in the upper aquifer; and

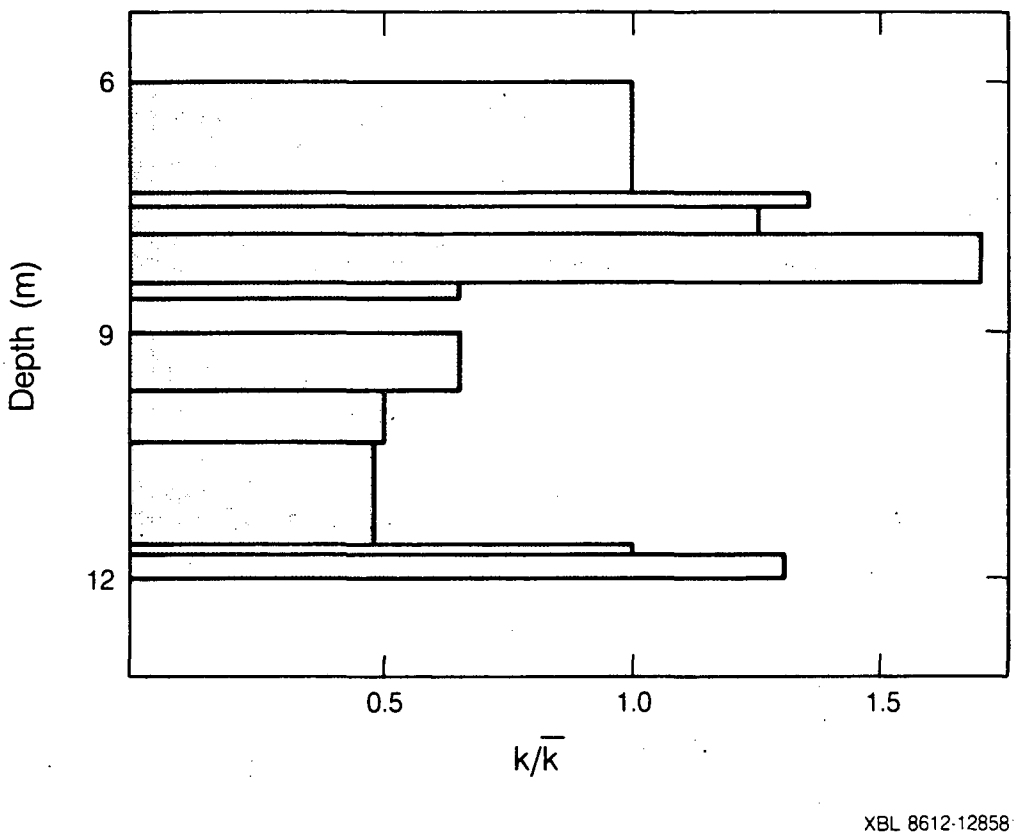


Figure 3.10. Reconstruction of the hydraulic conductivity distribution from the tracer test data.

- prediction of the persistence and migration of the drainage water and selenium plumes in the upper aquifer.

The following sections summarize the results of these investigations. More detailed descriptions of methods, chemical analyses, and experimental results have been provided in LBL Progress Reports 1 through 6.

3.2.1. Extent of Drainage Water and Selenium Plumes

Most of the data available for assessing the extent of the drainage water and selenium plumes are from monitoring wells located along the berms surrounding the Kesterson Ponds. With the exception of the area along the northern half of the east side of the Reservoir (Ponds 7, 9, 11, and 12), Kesterson Reservoir is surrounded by private land where there is only limited access for the purpose of installing monitoring wells. The lack of appropriately located monitoring wells precludes complete definition of the lateral extent and leading edge of the drainage water and selenium plumes. However, based on observations from the Reservoir, detailed analysis of the hydrologic setting, and the results of computer modeling, we can place some bounds on the extent of these plumes.

3.2.1.1. Drainage Water Plume

Extensive groundwater sampling and analyses have demonstrated that the boron present in the drainage water does not react with the pond bottom sediments and is a good indicator of the extent of the drainage water plume. Electrical conductivity (EC), which is primarily influenced by the concentration of salts, is also a useful indicator of drainage water migration. However, due to evaporative accumulation of salts in near surface soils, it may not provide reliable information in some cases. Boron concentrations in excess of 10 parts-per-million (ppm) and electrical conductivities of greater than 10,000 μmhos/cm from monitoring wells directly adjacent to the Ponds indicate that drainage water has migrated to depths ranging from less than 20 feet to nearly 140 feet. The average depth of the plume at the 9 study sites discussed in section 3.1.2 is approximately 70 feet below the ground surface (LBL Progress Reports 2 and 6). Computer

modeling of the groundwater system, supplemented by a limited amount of groundwater sampling data, indicate that drainage water migrated at an average horizontal velocity of approximately 150 feet per year while the Reservoir was in operation (LBL Progress Reports 2 and 3). Assuming that undiluted drainage water was discharged to the Reservoir for the 5.5 year period from 1981 to 1986, the average distance that drainage water has migrated from the edge of the ponds is on the order of 1000 feet.

Pumping test data indicate that locally, hydraulic conductivity values may be up to 5 times greater than the mean value (see section 3.1.2). Consequently, it is conceivable that in isolated flow channels (such as might be formed by a buried remnant slough), drainage water may be migrating at rates that are up to 5 times greater than the average value. The impact of the occurrence of these high conductivity flow channels on the overall migration of the plume is uncertain. Modeling studies indicate that if they are continuously aligned with the hydraulic gradient and if they pass under the Reservoir, solutes will migrate up to 5 times farther than the average distance (LBL Progress Report 6). On the other hand, if the high conductivity channels do not pass under the Reservoir, or are not aligned with the hydraulic gradient, they will have little influence on the rate of migration (LBL Progress Report 6). Only two of 57 pumping tests suggested the presence of such high conductivity sands. Furthermore, it is unlikely that channels filled with high conductivity sands are continuous or are aligned with the hydraulic gradient over thousands of feet. Consequently, although regions with higher-than-average velocities most certainly exist, their overall influence on migration of the plume is moderated by the natural heterogeneity of the hydrologic setting.

3.2.1.2. Selenium Plumes in the Upper Aquifer

To supplement the USBR's data base on selenium migration in the upper aquifer, the boreholes shown in Figure 3.11 were installed for additional monitoring and testing. A detailed water sampling and analysis program using these boreholes confirmed earlier observations that even where drainage water had migrated into the upper aquifer,

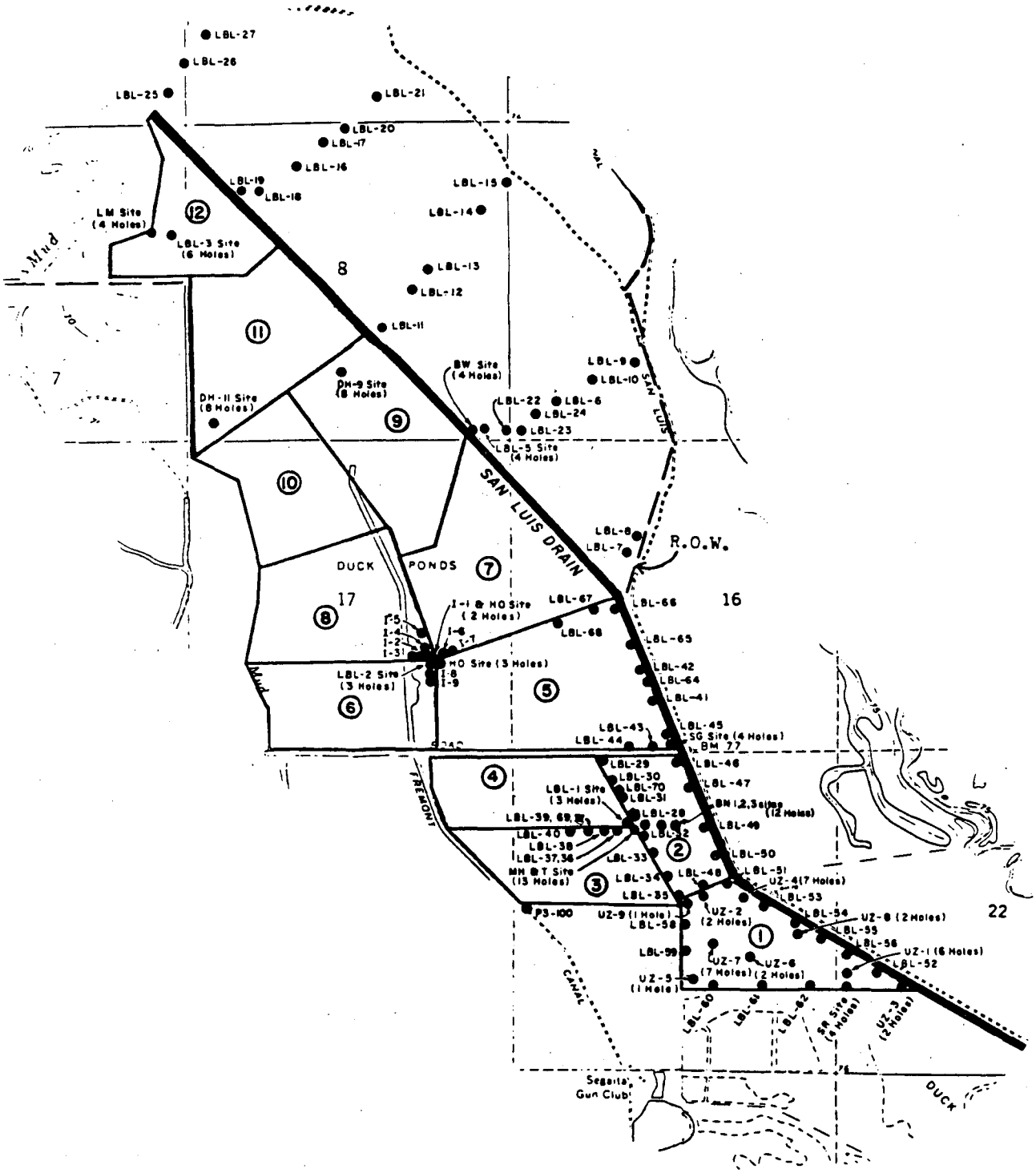


Figure 3.11. Location of LBL groundwater monitoring wells at Kesterson Reservoir.

selenium was rarely present at concentrations exceeding 2 ppb, with the exception of boreholes located near the intersection of Ponds 2, 3, and 4, and at isolated boreholes located along the San Luis Drain, adjacent to Ponds 1, 2 and 5. Elevated concentrations of selenium, ranging from 10 to 200 ppb, were detected in these areas. Elevated concentrations of selenium correlated well with redox potentials exceeding 300 mV, the presence of dissolved oxygen, the lack of dissolved ferrous iron, and the presence of elevated concentrations of nitrate (see sections 3.2.2 and LBL Progress Reports 1 through 5).

The presence of elevated selenium concentrations in many boreholes surrounding Pond 2 suggested that Pond 2, as a whole, might be allowing selenium to enter the upper aquifer. This concern led to the construction of a berm extending into the middle of Pond 2, where additional monitoring boreholes were installed. During July 1987, fluid samples from the new boreholes were collected and analyzed. Whereas elevated boron concentrations indicated that drainage water had migrated to depths of at least 100 ft, selenium concentrations did not exceed 3 ppb in any of the 12 boreholes located on the berm, indicating that seepage from Pond 2, as a whole, was not allowing selenium to enter the upper aquifer. Furthermore, none of the geochemical conditions associated with elevated selenium concentrations, such as redox potentials exceeding 300 mV, oxidizing water or the lack of dissolved ferrous iron were detected in the sampling boreholes on the berm.

Recent sampling of a set of 6 wells located in the northeast corner of Pond 9 indicate the presence of selenium concentrations in the range of 30 to 50 ppb, at depths of 10 to 15 feet (LBL Progress Report 6). Deeper wells (25 to 30 feet) located at the same site have concentrations of less than 3.8 ppb. Elevated selenium concentrations at this location are attributed to discontinuous ponding which impaired (Se) immobilization within the surface soils, and to discharge of selenium-rich drainage water directly into Pond 9 during 1986 (a pump was used to flood Pond 9 directly from the San Luis Drain for several months during the winter of 1985-1986).

The best current understanding of the extent of selenium contamination in the upper aquifer is that selenium has migrated into the upper aquifer in isolated areas, most of which are located adjacent or near to Pond 2. The best characterized and probably largest of these local "plumes" is located at the intersection of Ponds 2, 3 and 4. The horizontal and vertical extents of this local plume are shown in Figures 3.12 and 3.13. This local plume is confined to an area of less than 500 feet by 500 feet and a depth of less than 80 feet. Similar or smaller dimensions are expected for the other apparently smaller plumes detected underneath and downgradient of the Reservoir, as is indicated by the "patchy" nature of the distribution of elevated selenium concentrations along the berm between the Freitas Ranch and the San Luis Drain. Clearly, such isolated occurrences of selenium cannot be attributed to regional scale lithological or hydrological parameters.

While the precise mechanism that allowed selenium to enter the groundwater in these limited areas is imperfectly understood, localized groundwater contamination probably involves the superposition of several contributing factors which will be summarized in Section 3.2.3.

3.2.2. Correlations Between Selenium, Nitrate, and Oxidizing Conditions in the Upper Aquifer

The drainage water which formerly entered Kesterson Reservoir contained a large concentration of nitrate ion, typically 200-300 ppm (as nitrate). Nitrate has a profound effect upon the ability of soil, pond sediment, and anaerobic sludge to remove selenium from water (Section 4.3 and LBL Progress Report 5 and 6). The presence of nitrate in agricultural drain water is recognized as the major obstacle to selenium removal by anaerobic processes, and the concentration of nitrate in the water is the major factor controlling the operation of the water treatment process (Weres et al., 1987).

In an attempt to determine if nitrate was contributing to selenium migration into the upper aquifer, approximately 150 groundwater samples were sent to the Soil and

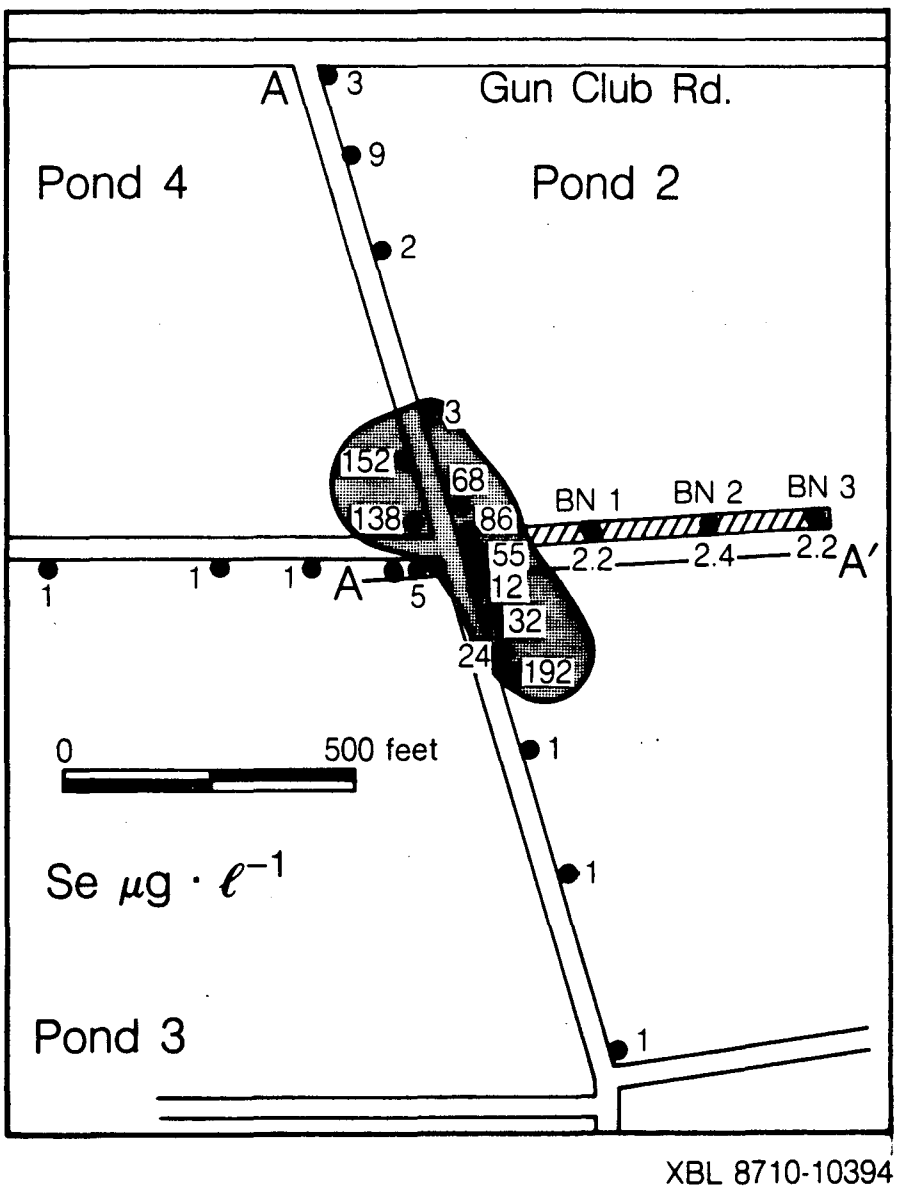


Figure 3.12. Areal extent of the selenium plume at the intersection of Ponds 2, 3, and 4. The shaded area includes wells with selenium concentrations of greater than 10 ppb. Note that the concentrations indicated on the illustration were measured over the period from 1986 to 1987.

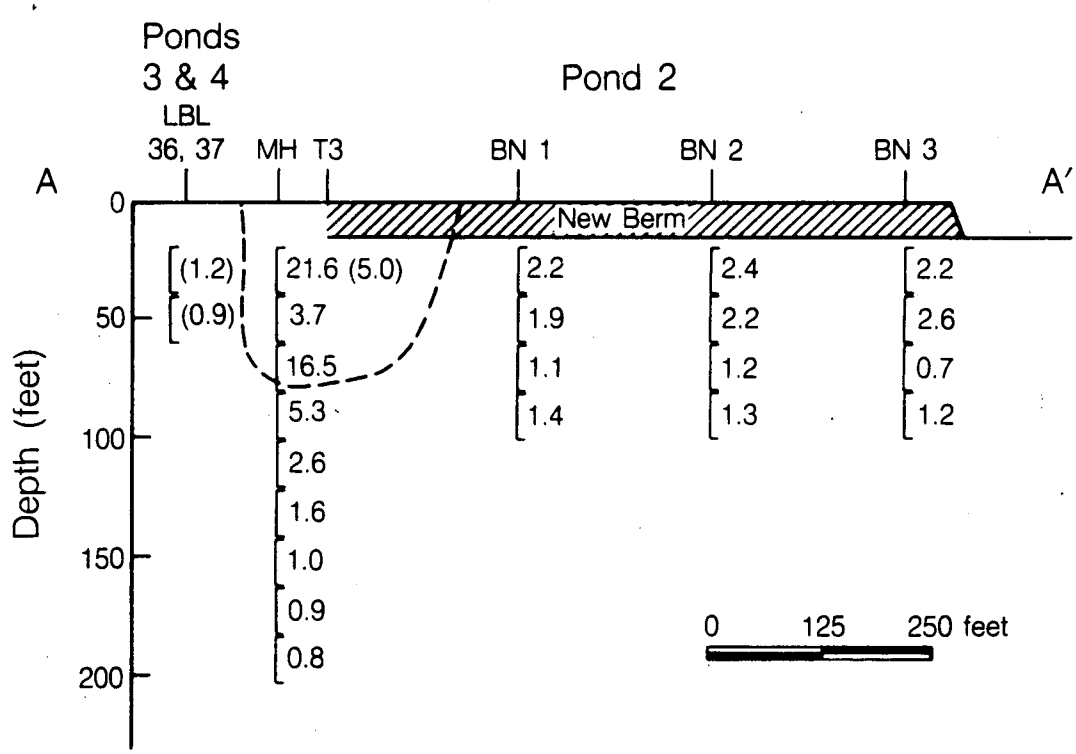


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Figure 3.13. Vertical extent of the selenium plume at the intersection of Ponds 2, 3 and 4. Note that concentrations are listed in parts-per-billion (ppb). Values in parenthesis were measured from sampling during 1986. The rest of the values were obtained from a mid-July sampling in 1987.

Plant Laboratory Inc. in Santa Clara, California for nitrate analyses using the cadmium reduction method. This analytical method does not distinguish nitrate from nitrite, so the values reported here may include some amount of nitrite together with nitrate. Since the samples were stored up to one year prior to analysis, it is possible that some of the nitrate was transformed by microbial action. However, loss of nitrate is unlikely to affect the conclusions of this investigation because nitrate concentrations are in the range of 1 to 200 ppm. Also, since these samples were filtered through 0.45μm filters when collected in the field, most bacteria and colloidal organic matter on which they feed had been removed.

The correlation between total selenium in groundwater and redox potential (Eh) measured in the field is illustrated in Figure 3.14. With few exceptions, Eh values of greater than +300 mV are associated with elevated selenium concentrations (greater than 10 ppb). The correlation between nitrate and total selenium in the water is shown in Figure 3.15. Out of the 25 samples with selenium concentrations greater than 20 ppb, 22 of them contained nitrate concentrations of greater than 1 ppm. Of the 128 samples with selenium less than 10 ppb, only 10 had nitrate concentrations of over 1 ppm.

An association also exists between nitrate and oxidation potential (Figure 3.16). Groundwaters with nitrate concentrations of greater than 20 ppm are all oxidizing with a field-measured Eh of greater than + 300 mV. Among the samples with Eh of less than 300 mV, only a few contained a detectable concentration of nitrate. Figure 3.17 shows that nitrate and ferrous iron are mutually exclusive.

In summary, these data are consistent with the hypothesis that nitrate, when it is present in the groundwater, produces oxidizing conditions which cause ferrous iron to precipitate, but favors the persistence of soluble selenium.

Historically, Pond 2 was the major entry point for drainage water coming from the San Luis Drain into Kesterson Reservoir. Biological uptake in the surface water gradually removed nitrate from the pond water as it moved from Pond 2 to Pond 5, and on to

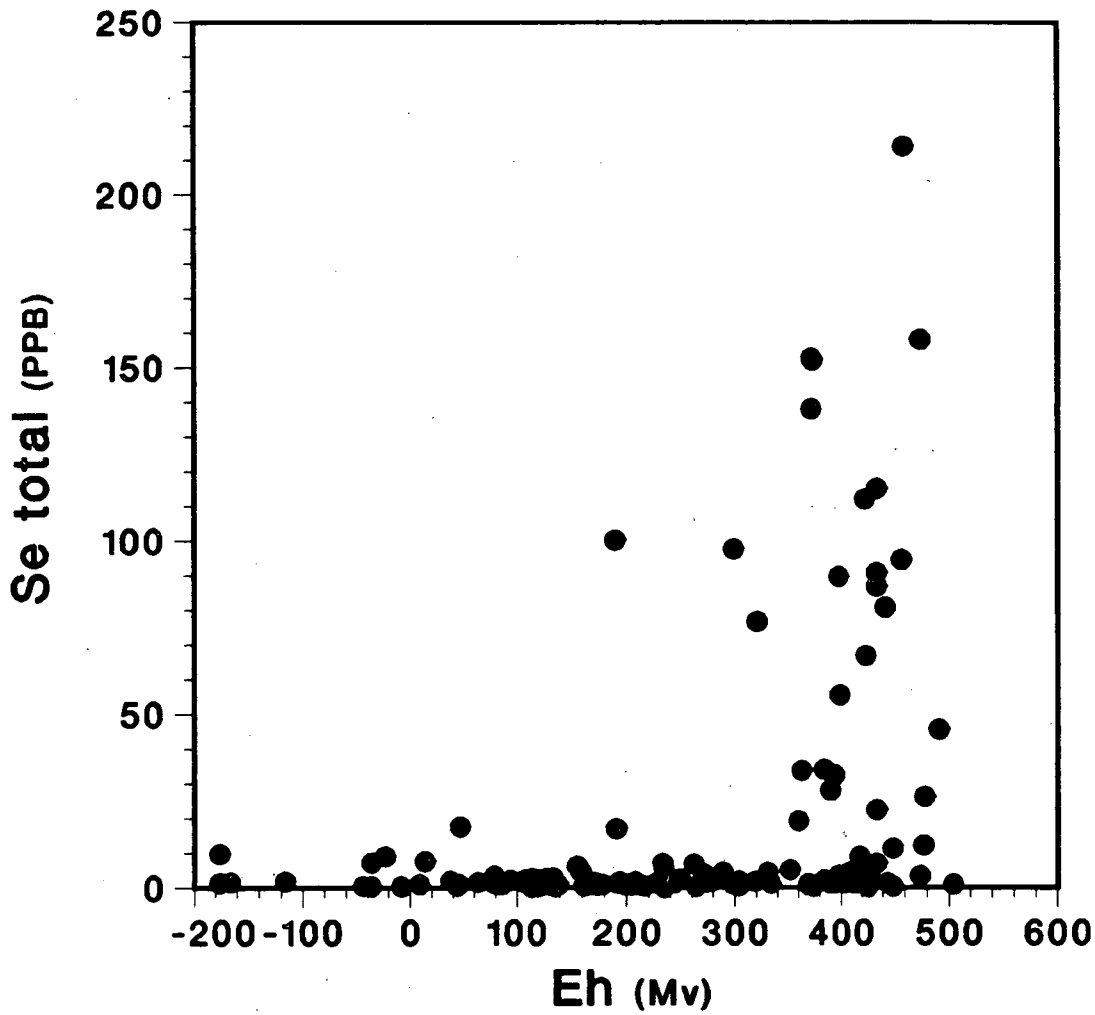


Figure 3.14. Selenium concentration vs. Eh for groundwater samples.

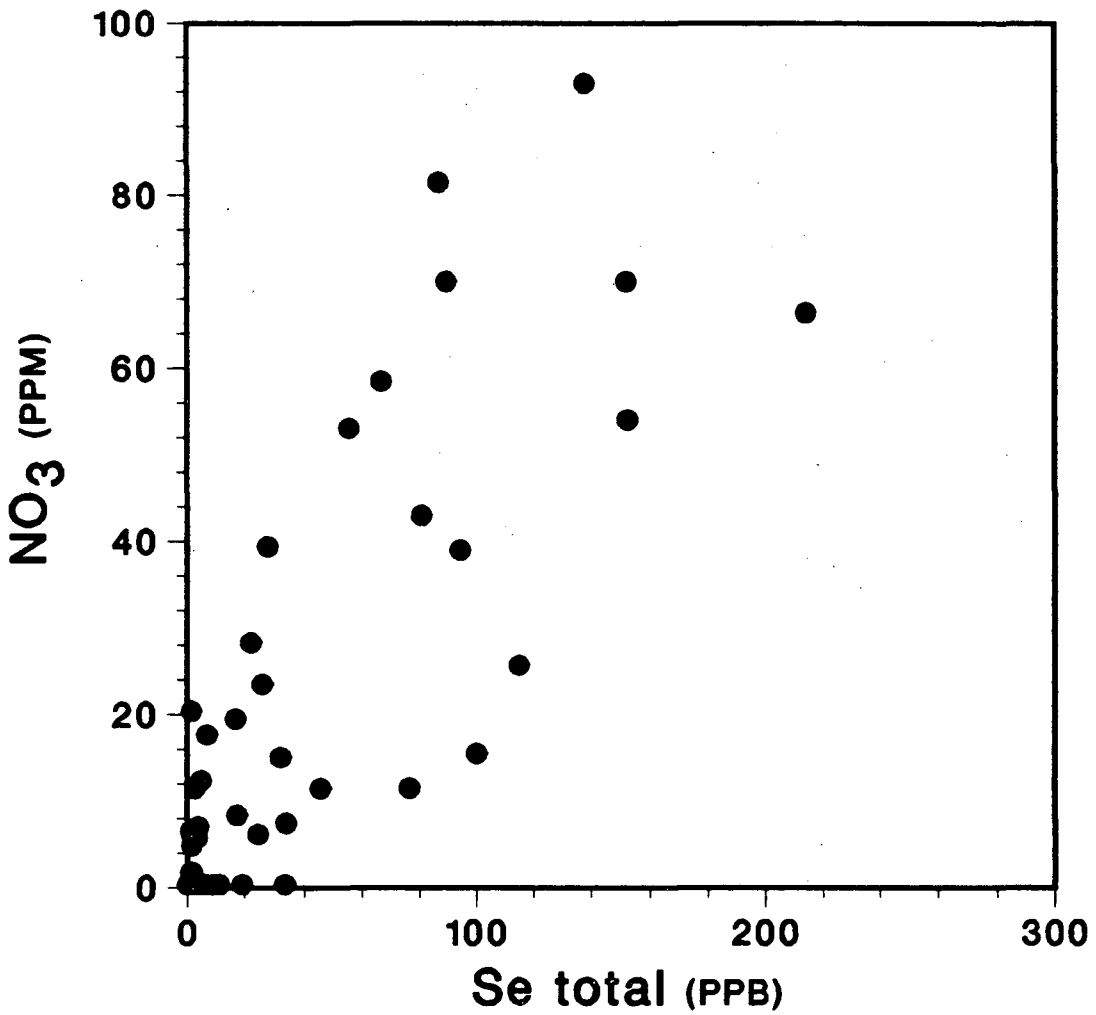


Figure 3.15. Selenium concentration (ppb) vs. nitrate concentration (ppm) for groundwater samples.

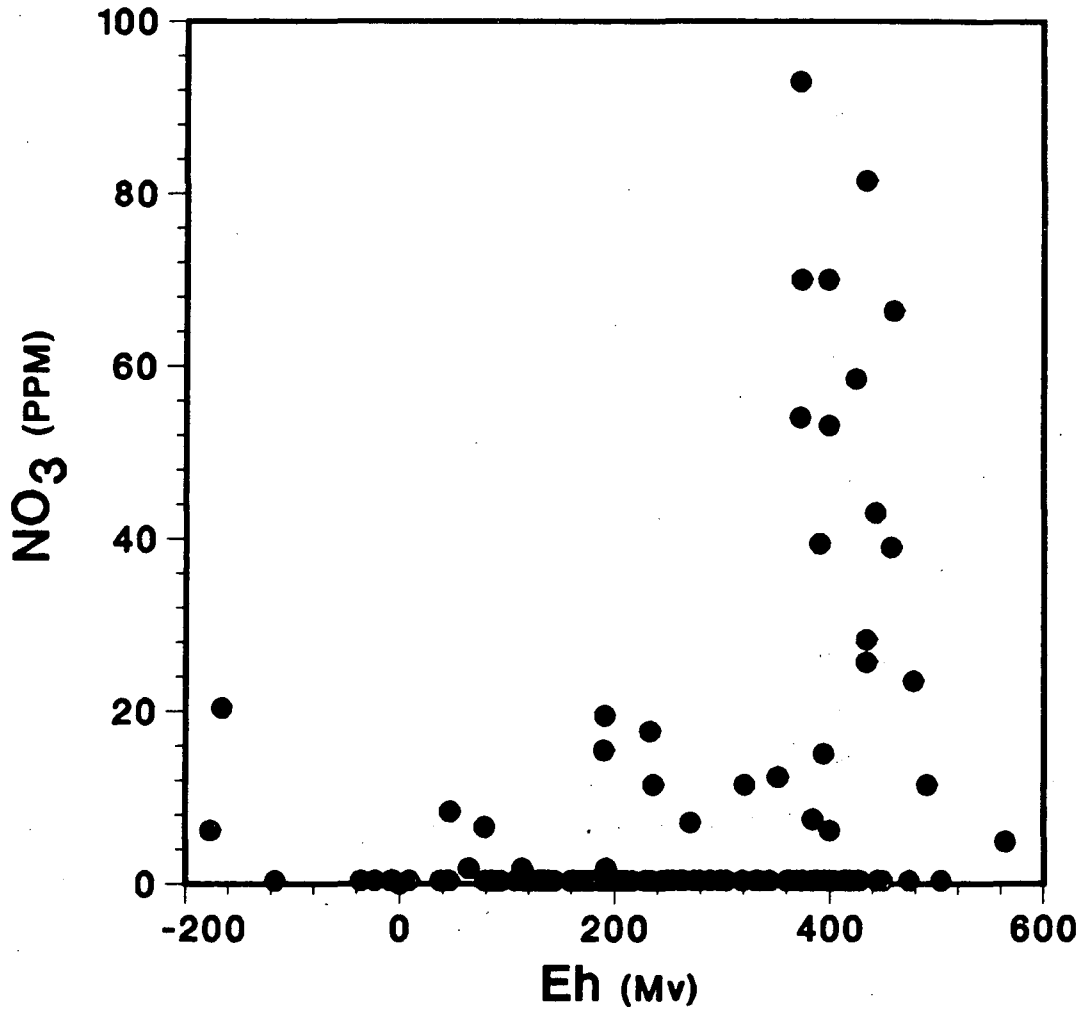


Figure 3.16. Eh vs. nitrate concentration (ppm) for groundwater samples.

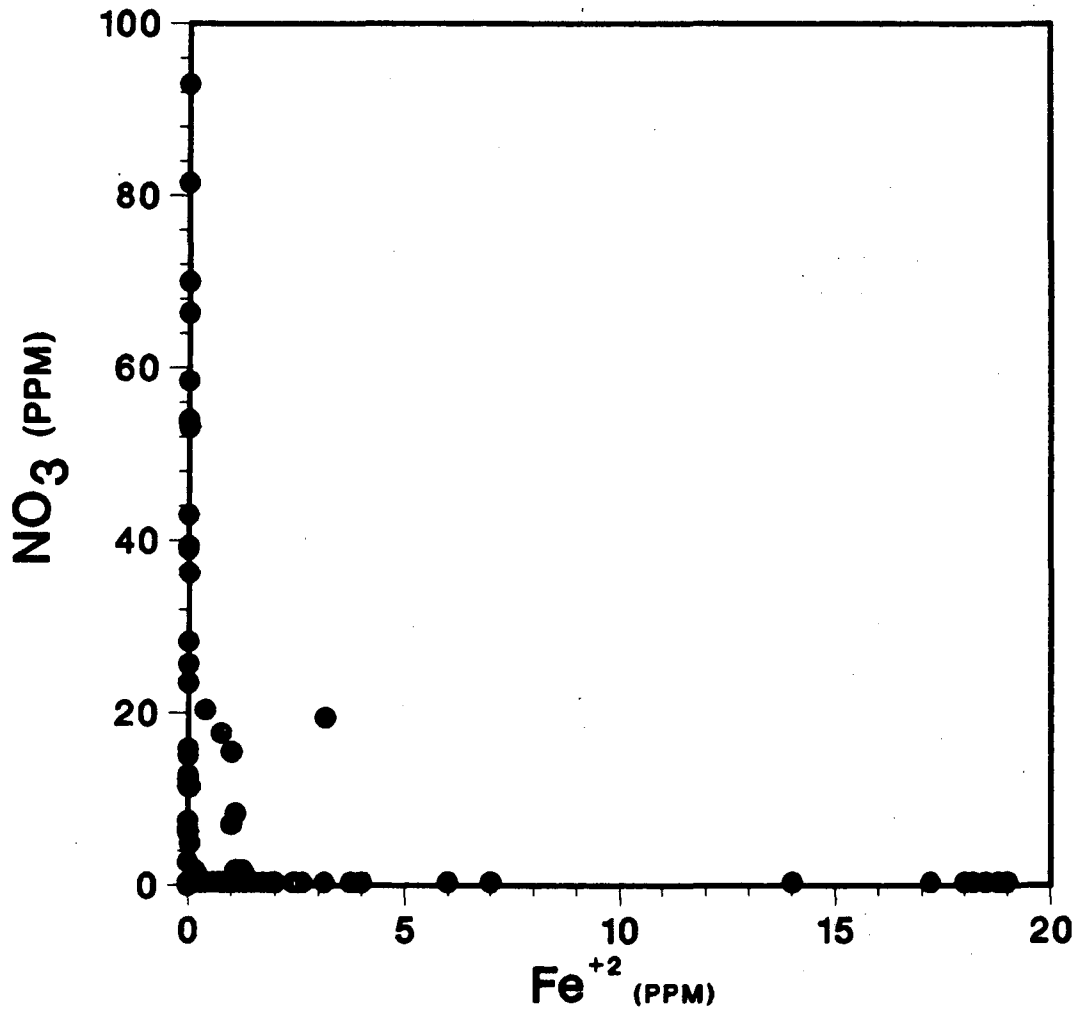


Figure 3.17. Nitrate concentration (ppm) vs. ferrous iron concentration (ppm) for groundwater samples.

Table 3.1. Nitrate in Kesterson Pond Water

Sampling site	Date	Nitrate (ppm)
2/5	5-18-84	248
2/5	6-13-84	175
2/5	7-10-84	195
2/5	8-8-84	195
2/5	9-19-84	177
2/5	10-30-84	168
2/5	12-5-85	82
2/5	2-24-86	168
3	6-13-84	<0.1
3	7-10-84	0.3
3	8-8-84	0.1
3	9-21-84	0.1
3	12-5-85	42
5/6	5-17-84	133
5/6	6-13-84	63
5/7	6-13-84	176
5/7	7-10-84	89
5/7	8-8-84	115
5/7	9-20-84	97
6/8	5-17-84	19
6	6-13-84	0.1
6	7-10-84	0.1
6	8-8-84	0.1
8	5-17-84	9
8	2-24-86	29
9	12-10-85	38
9	2-24-86	84
12	1-12-84	418
12	5-17-84	5

"2/5" = collected at wier connecting ponds 2 and 5,
"3" = sample from pond 3 and so on.
Data provided by J. Esget of USBR

ponds more distant from the entry point. The few nitrate values available for the Kesterson Ponds are assembled in Table 3.1, and summarized in Table 3.2. Most of these data were collected during the summer of 1984 (USBR surface water monitoring program). The expected pattern is evident. Nitrate levels in Ponds 2 and 5 were consistently high. Nitrate levels in Ponds 3 and 6 were generally low, with isolated high values. Only two data points are available for each of Ponds 8, 9, and 12, too few to generalize. The single very high value reported in Pond 12 very likely corresponds to a period when Pond 12 was receiving water directly from the San Luis Drain. The historical distribution of nitrate in surface water suggested by the admittedly scanty data in Tables 3.2 and 3.3 is consistent with the observation that most of the regions where selenium has entered the groundwater are located in the southern part of the Reservoir, where nitrate concentrations were higher.

Table 3.2. Summary of Nitrate in Pond Water

Pond	#	Mean (ppm)	Min. (ppm)	Max. (ppm)
2	8	176	82	8
3	5	8	<0.1	42
5	6	112	63	176
6	4	5	0.1	19
8	2	19	9	29
9	2	61	38	84
12	2	212	5	418

Table 3.2 summarizes data in Table 3.1.
= number of samples from that pond.
"6/8" data combined with "6" data and so on.

3.2.3. Summary of Factors Contributing to Breakthrough of Selenium to the Upper Aquifer

Since widespread elevated concentrations of selenium have not been observed in the groundwater under Pond 2 it is clear that elevated concentrations of nitrate are not in

themselves sufficient to cause selenium migration into the upper aquifer. Related work on water treatment (Weres et al. 1987) suggests that the parameter controlling nitrate breakthrough is the ratio of nitrate entering the sediment with percolating groundwater, to the supply of organic matter available to react with the nitrate and remove it from the water. Based on laboratory work, a relationship describing the conditions for effective selenium removal was developed. Selenium and nitrate are removed from water percolating through the superficial sediment at the bottom of a pond if (Section 4.3, and Weres et al., 1987):

$$U \leq \frac{a\,r\,P}{n}$$

where

n = concentration of nitrate in the pond water (g/L)

a = 0.8, a parameter that is empirically determined by the experiments

r = the fraction of organic matter useful by denitrifying bacteria, estimated as = 0.6

P = annual production rate of dry weight organic matter ($kg/m^2/yr$),

U = the annual average Darcy velocity of water seeping through the bottom of the pond (m/yr).

The equally important variables in this expression are n, P and U. Increased nitrate concentration, increased seepage rate, and decreased supply of organic matter will all favor the breakthrough of selenium and nitrate to the groundwater.

Pond 2 has been kept more-or-less consistently filled with water since water deliveries began in 1978. Therefore, Pond 2 has experienced a consistently high hydraulic gradient, creating a relatively high and steady seepage rate. The seepage rate combined with high nitrate concentration in the pond water increased the tendency for nitrate and selenium to migrate through the superficial sediment into the upper aquifer. Even so, the distribution of selenium and nitrate underneath Pond 2 is confined to several isolated areas, each with an areal extent of less than 500 feet by 500 feet. That contaminated groundwater appears to be limited to the edges of Pond 2 and along the San Luis

Drain suggests an association of contaminated groundwater with the berms that define the Ponds. Scraping away superficial soil in the vicinity of the berms during construction may have contributed to higher-than-average infiltration rates. Also, the slopes of the berms support much less vegetation than the interior of Pond 2. Therefore, the berm slopes accumulate less organic matter than pond bottom soils, favoring localized breakthrough of nitrate and selenium to the deep aquifer.

Local variations of permeability and lithology within the aquifer may also affect the mobility of selenium. Regional studies under irrigated farmlands to the south of Kesterson Reservoir, conducted by the U.S. Geological Survey, indicate lithological controls on both redox potentials and selenium distributions in the deep groundwater in that area. Groundwaters associated with sediments in the Coastal Range are oxidizing and high in selenium, while groundwaters originating from the same source but presently associated with sediments from the Sierra Nevada are reducing and devoid of selenium. These differences are correlated with the presence of minerals containing iron(II) in the sediment; Sierra Nevada granodiorites contain abundant mafic minerals. Recent drilling on the berm in Pond 2 has locally encountered poorly sorted sediments containing clasts of Coast Range provenance. Buried channels containing oxidized Coast Range sediments could serve as conduits where oxidizing water carrying selenium could migrate through the upper aquifer with relatively little chemical retardation.

3.2.4. Selenium Fixation in the Upper Aquifer

Laboratory experiments and field observations have provided insights on the factors that contribute to migration of selenium through the pond bottom sediments. Less is known about the fate of selenium once it has migrated into the upper aquifer. Two field experiments were conducted to evaluate the stability of selenate and selenite in the shallow aquifer system (LBL Progress Report 5). One of these experiments was conducted in a region where the aquifer contained reducing native groundwater. The other was conducted in an oxidizing part of the drainage water plume that had a selenium

concentration of less than 3 ppb.

The experiment in the reducing zone involved injecting approximately 2 cubic meters of a mixture that contained 1 ppm Se^{+6} as sodium selenate, 1 ppm Se^{+4} as sodium selenite, and 1 ppm sodium fluorescein, a strongly fluorescent dye. The injected solution was prepared by mixing groundwater from a nearby well with a concentrated solution of sodium fluorescein, Se^{+4} and Se^{+6}. Extreme care was taken to ensure that the mixture was not contaminated with oxygen. In reducing groundwater fluorescein is a non-reactive tracer that can be used to measure the degree to which the injected solution is being diluted with resident groundwater.

Injection of the test solution took approximately one day. During the injection phase, fluid samples were collected hourly to verify proper formulation of the solution. After injecting the mixture, it was allowed to remain in the aquifer for one week before the withdrawal phase began. Approximately 1/8 of the tracer solution was withdrawn from the well each week and analyzed for Se^{+4}, Se^{+6} (by the difference of Se total and Se^{+4}), and fluorescein.

The data from the native groundwater site (called Redox 3) are plotted in Figure 3.18 (selenite and selenate concentrations are normalized to the input concentration). If no chemical reaction occurs, the Se^{+6}/fluor and Se^{+4}/fluor ratios should be equal to the initial injected concentration; i.e., approximately 1000 ppb/1000 ppb. The data from this site show strong removal of dissolved selenium from the water. Selenite is very unstable in the reducing groundwater. Within ten days of injection, Se^{+4} decreased less than 10 ppb. Selenate decreased more slowly but steadily, dropping to less than 10 ppb 25 days after being introduced into the aquifer. A parallel experiment was conducted by keeping the solution of Se^{+4}, Se^{+6} and flourescein in the air-tight flask. Both Se^{+4} and Se^{+6} remained in solution over a one month period suggesting that reaction between the solution and the sediments was responsible for selenium removal observed in the field experiments.

A similar experiment conducted in an oxidizing region within the drainage water plume underlying Pond 2 indicated that soluble selenium remained in solution over the one month period. By the end of the one month period, as a result of groundwater flow, the injected solution was too diluted with resident groundwater to obtain any additional information. Similar experiments are now being conducted in a reducing region of the drainage water plume.

A large body of evidence exists which indicates that aqueous selenium is removed as groundwater becomes reduced. However, the mechanism by which selenium is actually precipitated or sorbed by the aquifer is still not known. Laboratory experiments reported in Section 4.4 indicate that selenite ion may be removed from water by purely inorganic processes, possibly involving simple sorption upon mineral surfaces. The removal of selenate ion from solution requires microbial or chemical reduction involving some - as yet unknown - reducing agent in the water or sediment. Possible reducing agents include iron(II) or manganese(II) dissolved in the water, small amounts of organic matter in the sediment, or minerals containing iron(II) or manganese(II). Microbial removal of selenate from water in mineral soil thought to resemble the shallow aquifer sediment has been demonstrated in the laboratory (Section 4.4). A slower, purely inorganic reduction mechanism, possibly involving catalysis on mineral surfaces, cannot be excluded, but has not yet been observed in the laboratory.

3.3. Salt and Soluble Selenium Distributions in the Vadose Zone

Recently obtained data from the vadose zone in Pond 1 and the northern Ponds have shown that selenium concentrations in the pore waters are typically in the range of 1000's of ppb in the top 0.2 m inches of the soil profiles and decrease to 100's of ppb at depths of about 1 m (LBL Progress Reports 3 through 6). Concern over such high concentration of soluble selenium in the near-surface soils, led us to re-evaluate the present-day extent of soil contamination. With respect to the reservoir soils, this entails assessing the distribution of selenium and other salts within soil profiles. The inclusion of

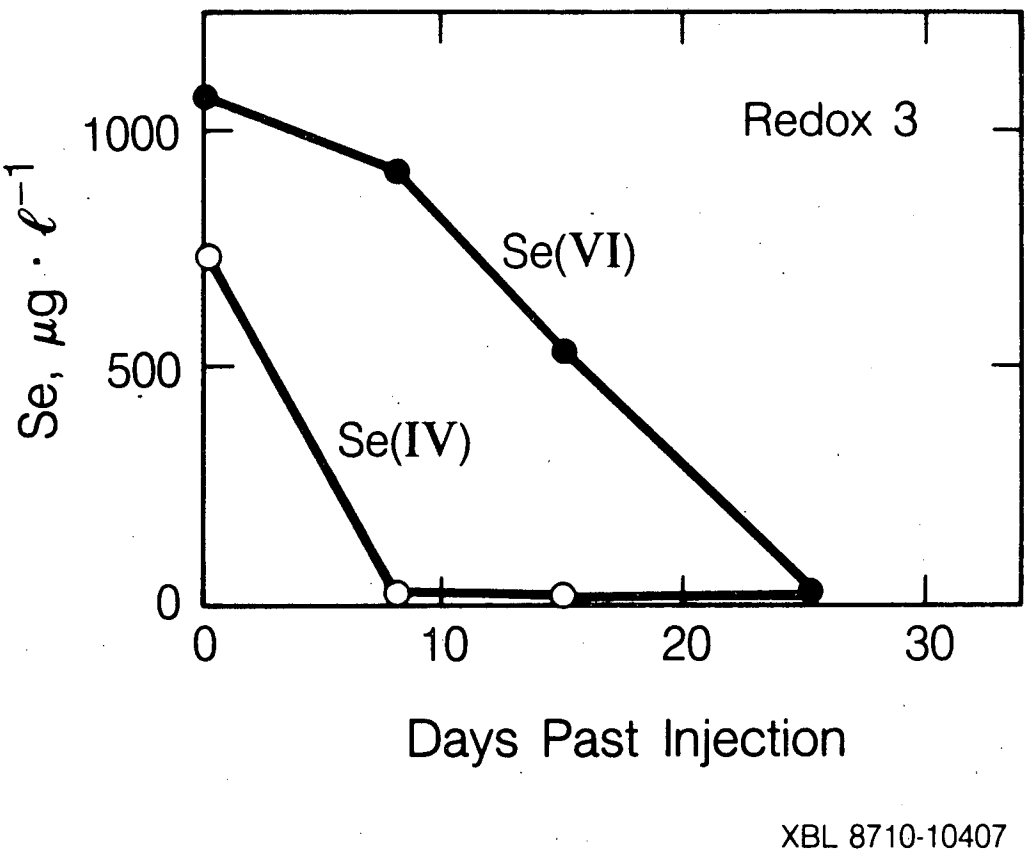


Figure 3.18. Concentration of selenite and selenate in groundwater samples extracted during the selenium injection test at Redox 3 (the native groundwater site).

other salts in this study of reservoir contamination was motivated by two considerations. First, high soil salinity is in itself a form of contamination in that a large variety of plant species will not grow under such conditions. Thus, design of remedial activities must incorporate the interdependence of the desired plant community with the residual soil salinity. Secondly, localized zones of high soil salinity can serve as indicators of likely regions of current or eventual selenium contamination. In a sense, soil salts tend to behave like tracers, moving along flow paths, and accumulating in areas of potential concentration. By combining information on current patterns of selenium and salt distribution with knowledge of the processes which transform and transport selenium, future implications of various management strategies can be evaluated.

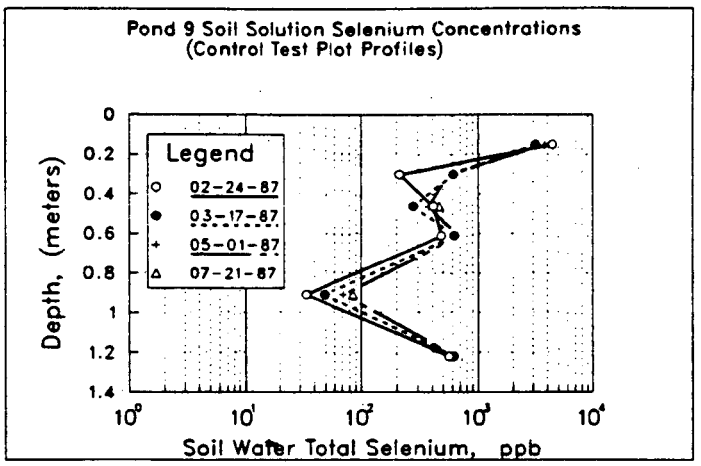
In this section, patterns of salt and water-soluble selenium distribution in several different reservoir soil environments will be described. For this purpose, attention will be focused on individual soil profiles at Ponds 6, 9, and 10, with occasional references to data from other reservoir sites. These soils are chemically very different from those in areas of continuous ponding at the reservoir. Most soil profiles described here are generally under vadose conditions, i.e. presently partially water-saturated and above the water table. Periodic water-saturation has occurred in the past due to both drain water applications and seasonal rises in the water table. Furthermore, future periodic water-saturation of many soils within the reservoir is very likely to occur due to the seasonal rise in the shallow water table. The Pond 9 site will serve to represent pond soils which have received moderate quantities of drain water. For comparison with the Pond 9 case, soils from Ponds 1 and 11 will also be briefly considered since these represent environments which have historically received respectively greater and lesser quantities of drain waters. Pond soils situated in surface depressions are of special concern for several reasons associated with the tendency for accumulating high concentrations of selenium and other salts in such settings. Data from a monitoring site located within a dry slough tributary in Pond 10 will be presented to illustrate some features of these depressions.

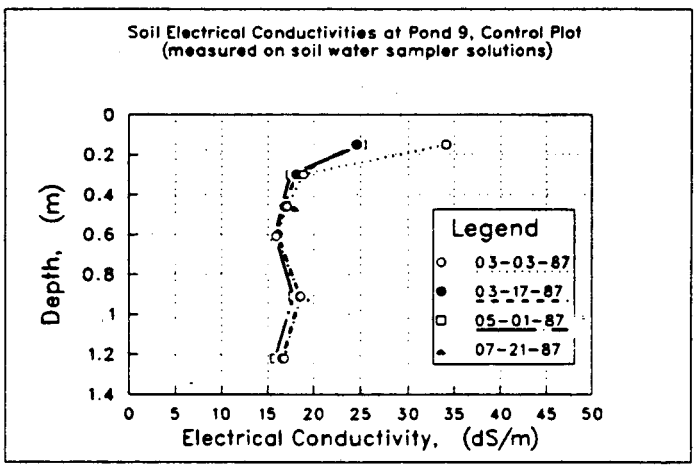
Finally, a site at Pond 6 where 0.5 ft of surface soil has been excavated will be considered. This site, and several similarly excavated test plots have been studied to obtain data relevant to assessing potential impacts of the Onsite Disposal Plan.

3.3.1. Pond 9 Soil Profiles

At several sites within Pond 9, as well as in Ponds 1, 6, 7, 10, and 11, soil water samplers have been installed to permit relatively undisturbed extraction of soil solutions. From these samplers, soluble selenium and salinity of soil pore waters can be measured. At most of these monitoring sites, tensiometers have also been installed to allow measurements of local hydraulic head profiles, from which the direction of water flow can be determined. Pond 9 has historically received an irregular supply of drain water (USBR, 1986). Following seepage of the last application of drainage water, and drying of the northern section of Pond 9, several soil monitoring test plots were selected in late 1986. The sites were instrumented with soil water samplers and tensiometers in February of 1987.

The depth distribution of water-soluble selenium at several times from one of the Pond 9 sites is depicted in Figure 3.19a. The concentrations in this figure are expressed in terms of mass of selenium in the soil solution per unit mass of soil solution. This form of expressing concentrations is directly analogous to other water concentration expressions, such as those used to characterize groundwater and surface water. In other parts of this report, concentrations are referenced to the solid mass of soil, rather than to the mass of solution. Referencing concentrations to the solid phase is more appropriate for expressing total (soluble and insoluble) concentrations, and for observing changes in soluble species when the water content of the reference volume is changing with time. It is with this latter purpose in mind that solid phase referencing of concentrations are used in the description of soluble selenium changes on residual soil surfaces at excavation test plots. Conversions from a solid-referenced concentration to a solution concentration requires multiplication by the mass ratio of solids to solution. The meaningfulness of





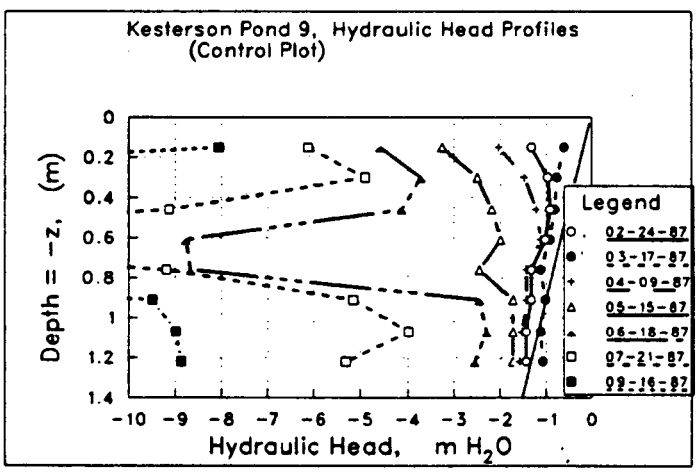


Figure 3.19a,b,c. Selenium concentrations (3.19a), electrical conductivity (3.19b), and hydraulic head profiles (3.19c) at the Pond 9 test plot.

this conversion is limited to water-soluble species.

The depth distribution of water-soluble selenium in the Pond 9 test plot shown in Figure 3.19a is typical of water-soluble selenium distributions measured at most other vadose zone sites. Due to the very low solubility of selenium under reducing conditions (e.g. Geering et al., 1968, Elrashidi et al., 1987), high surface soil selenium levels were probably initially concentrated by precipitation under anoxic conditions established by flooding with drainage waters (Weres et al., 1985). The concentration of dissolved selenium exceeds 1000 ppb in the shallowest sampler. The soluble selenium content generally decreases with depth, with concentrations on the order of 100 ppb typifying the subsurface down to about 1 m. Most of the soluble selenium in this profile is in the form of selenate, SeO_4^{2+}. While most other monitored profiles exhibited lowest soluble selenium concentrations at the deepest sampling point, a local selenium maxima was measured in the bottom sampler at 1.22 m at the Pond 9 site. Samples obtained in even deeper strata from both cores and well water indicate that soluble selenium concentrations decrease gradually with depth at this site (LBL Progress Report 6). Selenium concentrations ranging from 30 to 50 ppb were characteristic of water samples taken at 3.0 to 4.6 m. Samples from the deepest wells had less than 4 ppb at depths of 7.6 to 9.1 m.

Sampling of soil water over a period of 5 months revealed no significant temporal variations in selenium concentrations in soil pore waters. The lack of a temporal variation as shown in Figure 3.19a for the Pond 9 test plot was characteristic of other undisturbed soil profiles (i.e., nonflooded, or non excavated profiles). Sampling at later times will be required to understand the temporal dynamics of soil water selenium. During most of the summer, field soil water samples were not obtained due to desaturation of soil profiles beyond the range where vacuum soil water extraction is possible. A related problem in comparing soil water selenium concentration data at different times involves the effects of changing soil water contents (drying and wetting). Lack of change in soluble selenium per mass of soil solution under drying conditions implies that the actual

soluble selenium content per mass of soil solids is in fact decreasing. Due to lack of simultaneous measurements of soil water contents, actual temporal changes in soluble selenium in these depth profiles can not be precisely determined. However, subsurface soil water content variations over time on other reservoir core samples indicate that maximum fluctuations in water content are in the range of two-fold, when comparing late summer and late winter cores. This variation is small in comparison to the range of measured soluble selenium concentrations. Samples will be collected during the upcoming wet season for direct comparisons with measurements made during the past year.

Despite a history of more regular ponding with seleniferous drain water, Pond 1 soluble selenium profiles during the summer of 1986 were generally similar to those of Pond 9 (LBL Progress Report 3). The soluble selenium contents in Pond 1 profiles below depths of 1 m exhibited more rapid decreases with depth than in Pond 9. This may be due to more effective reductive immobilization of selenium under more continuous ponding.

Soluble selenium profiles in the Pond 11 test plots, while exhibiting the usual trend of generally decreasing concentrations with depth, display a few notable differences from the previous profile descriptions (LBL Progress Reports 3 through 6). This pond has received less seleniferous drain water than other ponds to the south (USBR, 1986). A dense growth of salt grass and alkali weed over much of this pond (USBR, Oct. 1986, table 4-33) probably enhanced evapotranspirative removal of soil water, minimizing deeper leaching into the shallow aquifer. The combination of less drain water application and enhanced evapotranspiration diminishes the ability to sustain anoxic surface conditions associated with efficient selenium immobilization. The resulting soluble selenium profiles at Pond 11 are consistent with all of these factors (LBL, 5th and 6th Progress Reports, 1987). High levels of soluble selenium penetrate relatively deep into the soil profile, with concentrations in the range of 1000 ppb (per mass of soil solution) measured to depths of 0.6 m. This profile is probably due to seepage under predom-

inantly oxidizing conditions. Below 0.6 m, soluble selenium concentrations in the Pond 11 test plots drop off very sharply. This pattern is indicative of either limited drainwater leaching below this depth, or efficient immobilization at depth, or a combination of these factors.

While equilibrium water-solubility of selenium is governed by the redox status of the soil solution (e.g., Geering et al., 1968, Elrashidi et al., 1987), it should be kept in mind that soil environments are generally nonequilibrium systems. Furthermore, coexistence of localized reducing and oxidizing zones at the scale of individual soil aggregates is very commonly observed in both the field and laboratory (e.g. Currie, 1961, Smith, 1977, Leffelaar, 1986). Due to these factors, references to the vadose zone as an oxidizing environment must be regarded as both a relative statement and a description of dominant redox conditions.

Not all observed profiles of soluble selenium were found to generally decrease with depth. A case of extreme depth variation of soluble selenium will be seen in a later section describing an excavation test plot.

Having surveyed the extent of soluble selenium penetration into vadose zone reservoir soils, it has become clear that selenium contamination is not simply a surficial problem. The extent to which the observed high subsurface soluble selenium concentrations will pose a hazard is uncertain. However, in the absence of managed application of surface water, the regional influences of high potential evaporation, shallow water table, and low precipitation will all tend to drive soluble selenium towards the soil surface. Consequently, management practices involving mechanical mixing (i.e. disking) or burial of the surface-most soils will not provide a long term solution for removal of the selenium from the near-surface soils. The discussion of potential reconcentration of subsoil selenium at the surface will be continued in sections on surface depressions and excavation tests.

While high concentrations of selenium are of special concern, the more general problem of very high soil salinity also deserves attention. Well before operation of the reservoir for disposal of drain waters, the soils had already been recognized as being saline (Soil Conservation Service, 1952). Much of the local aquifer waters are also very saline (e.g. Deveral et al., Nov. 1984). During active use of the reservoir, pond soils were leached with very saline drain water. The electrical conductivity (EC) serves as a convenient, qualitative indicator of dissolved salt concentrations (e.g. U.S. Salinity Laboratory, 1954). While the ECs of San Luis Drain water at the reservoir have varied, values in the range of 10 decisiemens m^{-1} (dS m^{-1} = mmho cm^{-1}) have been typical. Salinity of pond waters is further concentrated by evaporation during the summer months. Presently, most measured reservoir soil water EC values are higher than 15 dS m^{-1}, with some field soil water extracts having EC values as high as 70 dS m^{-1} (LBL, 6th Progress Report, 1987). As shown in Figure 3.19b, vadose zone soil water EC values tend to be higher towards the soil surface, characteristic of evaporative salt concentration. Laboratory measurements on saturated paste extracts (Rhoades, 1982) from reservoir soils have consistently resulted in ECs greater than 10 dS m^{-1}. These high saturation paste ECs are well in excess of the traditional criterion of 4 dS m^{-1} used to define saline soils. The extensive nature of high salinity at the reservoir, both historically and currently, precludes non-salt tolerant plant growth under natural conditions. Extensive soil reclamation with high quality water would be required if post-closure management were to include revegetation with nonhalophytes. Due to the high sodium composition of the soil salts, such a reclamation process could be hampered by decreased permeability resulting from dispersion of soil colloids.

By comparing soluble selenium and EC profiles at various sites, it becomes evident that surface accumulations of soluble selenium occur much more effectively than for other salts, (e.g., LBL, 6th Progress report, 1987). The preferential concentration of selenium over other salts within the surface soil reflects the strong redox-dependence of

selenium solubility in contrast to lack of such effects with respect to other common soil salts. Redox-dominated concentration (immobilization) of selenium in surface soils appears to not only have occurred during percolation of seleniferous drainage waters, but also may influence selenium redistribution during ephemeral pool formation under rising water table conditions. Biological uptake subsequent deposition of organic matter on the bottom of these pools is another mechanism contributing to concentration of selenium in the surface-most soils.

The direction of water flow within the vadose zone is discernable from hydraulic head measurements made with tensiometers (e.g., Hillel, 1980). Relative changes in local soil water contents can also be inferred to a limited extent from tensiometer data. A plot of hydraulic head profile variations over time at the Pond 9 monitoring site is presented in Figure 3.19c. As indicated on the graph, the gravitational datum is taken at the soil surface. For purposes of qualitatively interpreting these data, one only needs to know that soil water generally moves from regions of higher hydraulic head toward regions of lower hydraulic head (more negative hydraulic head). With this background, it is evident that soil water was flowing downward throughout the measured profile during March of 1987. Later data in Figure 3.19c are indicative of three mechanisms of soil water loss. Data from the uppermost 0.31 m of the profile reflect evaporative water loss through the soil surface. Data through May 1987 for depths below 1.0 m are indicative of drainage of soil water towards the declining water table. Finally, the large changes in hydraulic head in the central portion of the monitored profile are a result of water uptake by invading plants. The hydraulic head plots can also be used to infer local changes in soil water content. At a given depth, data shifting to the left often imply local decreases in water content, while shifts towards the right often imply rewetting. Quantitative measures of soil water content with tensiometers are precluded due to a lack of a unique correspondence between the matric component of hydraulic head and water content (e.g., Hillel, 1980).

The importance of evaporation, seepage, and especially plant water uptake in removing soil water are very well illustrated in Figure 3.19c, and from tensiometer data at other sites (LBL Progress Report 6). In view of the effectiveness of all three of these pathways for water and solute movement from reservoir soils, it appears prudent that remedial management strategies utilize these pervasive transport mechanisms to assist in efficient decontamination. The mechanisms of evaporation and transpiration can enhance decontamination techniques such as growth of selenium accumulating plants or volatilization (see section 4.5). which require that soil selenium be at or near the surface.

3.3.2. Surface Depression Monitoring at Pond 10

Due to the combination of a shallow water table which seasonally rises, and the existence of regions within the reservoir with elevations lower than the maximum rise of the water table, ephemeral pools form in the Kesterson ponds. These seasonal pools, found in surface depressions, occur even without application of surface water, and even during years of below-average rainfall (e.g., LBL 5th Progress Report, 1987). The water quality of these ephemeral pools was addressed in section 2.2. Here, the distribution of selenium and salts measured within the soil underlying one such ephemeral pond will be described. Some possible mechanisms responsible for development of the observed selenium and salinity profiles in these depressions will be suggested.

A soil profile monitoring site in Pond 10 was selected in what appears to be a remnant tributary to Mud Slough. The site was selected due to previous observations of ephemeral ponding, its relatively undisturbed soil, and its naturally well defined boundaries. Surface ponding in this depression persisted until the end of March 1987. Selenium concentrations of 530 ppb were measured in this surface water in mid March. The site was instrumented at the beginning of June, 1987 with soil water samples and tensiometers as described previously for Pond 9. Soil water-soluble selenium, soil water ECs, and hydraulic head profiles from this site are presented in Figure 3.20a,b,c. The soil solution selenium profile (Figure 3.20a) shows very high concentrations at the surface

(exceeding 3 ppm), which decline nearly 3 orders of magnitude over the measured profile depth of 1.2 m. The EC profile (Figure 3.20b) is indicative of very extensive salt accumulation. The tensiometer data (Figure 3.20c) reflect large evapotranspirative water losses throughout the upper 0.6 m of the soil. The depth of penetration of the drying front is due to water uptake by the roots of a sparse growth of alkali weed.

The observations of both high levels of soil water selenium and other salts at this site are explainable in terms of likely patterns of pond filling during use of the reservoir for disposing of drain water and the nature of evaporation from shallow water tables. It is reasonable to expect that regions of the reservoir at lower surface elevations received, on average, greater portions of drain water. Thus, these surface depressions may have historically received disproportionate amounts of selenium and other salts carried in the drainage water. While downward transport of common salts can continue during ponding until the hydraulic head gradient is dissipated or solubility limits are encountered, deep leaching of selenium through these surface depressions can be substantially hindered due to redox controls on its solubility and biological uptake of selenium. Surface depressions are in some ways ideal environments for development of reducing conditions. The more continuous presence of surface water diminishes oxygen exposure, and also can accelerate accumulation of organic matter vital in selenium immobilization. In addition, biological uptake of soluble selenium will be prolonged in the depressions which remain wet longer than elsewhere.

Evaporation of soil water is very strongly influenced by the proximity of a shallow water table (e.g., Gardner, 1957, Gardner and Fireman, 1958). In local depressions at Kesterson Reservoir, the water table can remain within about 1 m from the surface for prolonged periods, allowing for extensive evaporation relative to surrounding higher soils. Soluble salts, including selenium, are carried in the evaporative flow, and deposited near the soil surface. Thus, both the nature of water deposition and evaporation in low lying areas at the reservoir are conducive to salt and selenium concentration at these soil sur-

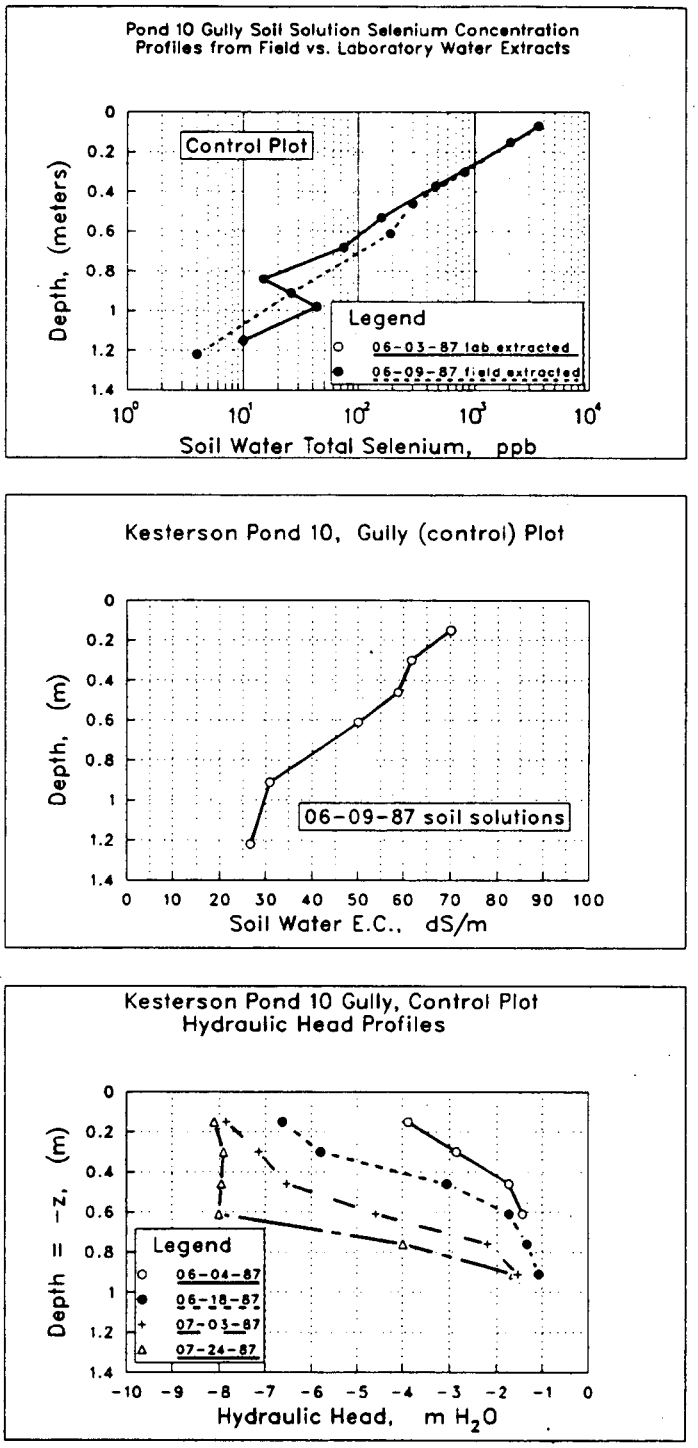


Figure 3.20a,b,c. Selenium concentrations (3.20a), electrical conductivity (3.20b), and hydraulic head profiles (3.20c) at the Pond 10 gully site.

faces. In a following section, the implications of this pattern on water quality in ephemeral ponds will be addressed. As will be seen in the next section, evaporative reconcentration of selenium has immediate relevance to the proposed excavation of surface soil for On Site Disposal Plan (ODP).

3.3.3. Excavation Test Site Observations

The proposed ODP entails excavating 0.15 m (1/2 ft) of the surface mineral soil in areas where its total selenium concentration exceeds 4 ppm (relative to the soil solid mass). This excavation is to be followed by further analyses of the surface 0.15 m of the residual soil. In places where the residual soil still exceeds the 4 ppm target level, further excavation may be required (USBR, 1987). Excavated soil is to be placed in a lined and capped disposal facility at the reservoir. Anticipated problems associated with the ODP include accelerating soil water evaporation rates by lowering the soil surface, consequent reconcentration of selenium and other salts on residual soil surfaces, and seasonal flooding which could release these constituents into ephemeral pond waters.

In view of the State Water Quality Control Board Order to implement the ODP, a series of test plots have been excavated to obtain early data on the impacts of this procedure on residual soils and ephemeral pools. Test plots in Ponds 6, 9, 10, and 11 have been excavated to a depth of 0.15 m. Additional plots in Ponds 6, 9, and 11 have had the surface 0.30 m (1.0 ft) of soil excavated. The plots are nominally 64 m^2 in area, and were excavated by a bulldozer during May 1987. In addition to monitoring with soil water samplers and tensiometers, periodic samples of residual soil surface material are taken for selenium and EC measurements. The residual soil surface is being sampled to address the abovementioned concerns.

Only preliminary data are currently available (LBL, 6th Progress Report, 1987), and the 0.15 m excavation test plot form Pond 6 will be used as an illustrative example here. Data from soil water samplers, tensiometers, and surface soil cores of this site are shown in Figure 3.21a,b,c. The depth profile of soluble selenium at the Pond 6, 0.15 m

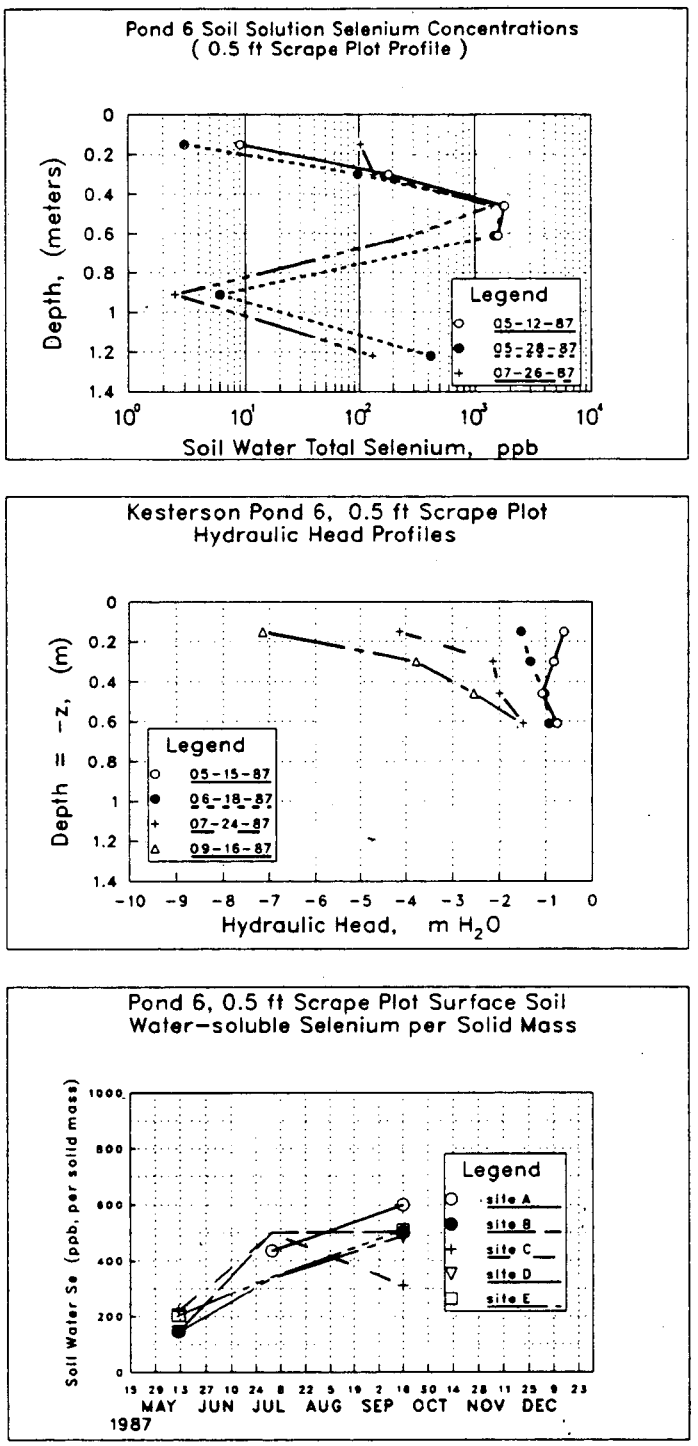


Figure 3.21a,b,c. Selenium concentrations (3.21a) electrical conductivity (3.21b), and hydraulic head profiles (3.21c) at the Pond 6 excavation site.

excavation (Figure 3.21a) clearly illustrates the potentially complex nature of selenium transport. In this profile, aqueous concentrations of selenium oscillate over a thousand-fold range within about 1 m in depth. The fact that the present concentration maxima are located at depths of 0.6 and 1.2 m indicates that surface soil selenium surveys will not always locate regions with large inventories of soluble selenium. Evaporative soil water loss at the excavated site is apparent from the tensiometer measurements of hydraulic head variations (Figure 3.21b). With long term potential evaporation greatly exceeding rainfall, some of the highly concentrated soluble selenium at depth is likely to return to the (excavated) soil surface. This process is evident in the temporal increases in soluble selenium measured in surface soil cores (Figure 3.21c). 0.15 m thick core samples are taken from 5 locations within each excavation plot to provide indications of both variability within plots and general temporal trends. Selenium concentrations of surface cores are reported on a "mass of selenium per mass of soil *solids*" basis to permit best evaluation of changes in a zone which undergoes large water content changes. Increases in surface soluble selenium in excess of 200% have been observed during 4 dry months at the Pond 6, 0.15 m excavation. Salinity measurements on these cores indicate that this soluble selenium increase is largely due to evaporative concentration of subsurface selenium (as opposed to transformation of surface insoluble selenium to soluble forms). The rapid reconcentration of soluble salts including selenium was expected in Pond 6 due to excavation in a region of sustained shallow water table proximity. The water table at this site persists within about 1 m from the surface in part due to continued flooding in the adjacent Pond 5. The excavation process further enhances evaporative concentration of these salts by bringing the evaporating surface into closer proximity to the water table. Excavating the soil will also have the effect of increasing the areal extent of freely evaporating surface depressions. It should be noted that most of the other excavation test plots have not shown such large increases in surface selenium (LBL, 6th Progress Report, 1987). This appears to be due to either lower evaporation

flux through the soil or lower levels of soluble selenium available for upward transport. Nevertheless, evaporative concentration of solutes is expected to be higher in the areas that are excavated, compared to those that are not.

An associated problem of surface salt and selenium accumulation at excavated areas of the reservoir is that of seasonal rewetting and development of ephemeral ponds. Excavation will obviously result in lowering of the soil surface, which in turn will result in more extensive seasonal ponding from the rising shallow water table.

3.4. Selenium Transport due to Seasonal Flooding

During the autumn of 1986 we began a field experiment for evaluating selenium transport due to flooding a pond that had dried out over the summer. The primary goal was to provide data for assessing the Flexible Response Plan (FRP) as a possible remedial action at Kesterson. The FRP was motivated by the observation that selenium is geochemically immobilized under permanently wet and chemically reducing conditions (Weres et al., 1985). Implementation of the FRP called for permanently flooding the ponds with a low-selenium water supply as a means of harnessing the naturally occurring geochemical and biological processes that keep selenium bound to the pond bottom sediments. One of the concerns with this plan was that rewetting a pond, after inadvertent periods of drying, would cause selenium contamination of the upper aquifer. The Pond 1 reflooding experiment was designed to address this concern.

Soil water samplers and tensiometers were installed at nine monitoring sites in Pond 1 during the summer months of 1986, and flooding began in October 1986. Monitoring of soluble selenium concentrations in shallow Pond 1 sediments has taken place on a monthly basis for approximately one year. Refer to LBL Progress Reports 3 through 6 for complete descriptions of monitoring design, performance and results. Observations from this experiment are summarized below.

- Prior to flooding, concentrations of soluble selenium in the vadose zone were typically in the range of 1000's of ppb within a foot of the soil surface (LBL Progress Report 3). Concentrations dropped to 10's of ppb at a depth of 4 feet. Samples collected from shallow groundwater monitoring wells (depths of 6 to 10 feet) had concentrations of less than 10 ppb.

- Intensive monitoring during and after flooding detected rapid mobilization of solutes, including selenium, to depths of at least four feet (LBL Progress Report 4). Concentrations of 1000's of ppb were observed to depths of 4 feet. Solute transport occurred much more quickly than would be predicted based on available saturated hydraulic conductivity (K_s) data and uniform infiltration. Such rapid transport provides strong evidence for the existence of preferential flow paths of water in soil macropores.

- Selenium immobilization by reductive chemical and biological processes began several days after flooding and it appears that only relatively small quantities of selenium actually migrated into the upper aquifer (LBL Progress Report 5).

- Analysis of groundwater samples collected in July and August 1987, from 25 shallow wells (depths ranging from 10 to 40 feet) indicates that reflooding Pond 1 did not create widespread elevated concentrations of selenium in the upper aquifer. Selenium concentrations from all of these wells were less than 4 ppb and the average value was approximately 2 ppb.

This section addresses questions regarding the mobility and transport of soluble selenium in the shallow pond bottom soils.

3.4.1. Selenium Immobilization/Discharge Estimates

In LBL Progress Report 5 we reported on a series of calculations for determining the quantity of selenium that has been immobilized by various chemical and/or biological mechanisms and the quantity that has been transported deeper into the soil profile. In an effort to perform this calculation in a slightly more accurate manner, a new method has been applied to the data sets from the 5 sites that were flooded. (Note that only 5 of the 9 monitoring sites were actually submerged during this experiment. Surface water levels remained below target elevations as a result of a somewhat intermittent water supply.)

A typical data set from one of the monitoring sites is illustrated in Figures 3.22 and 3.23. Pore water samples extracted from the nested soil water samplers were routinely analyzed for selenite and total selenium. Chloride analyses have been obtained from

approximately 1/2 of the flooded sites. Both depth profiles of soluble selenium and temporal changes in the chemical composition of the porewaters have been obtained from the nine sampling sites in Pond 1 (see LBL Progress Reports 3 through 6).

As illustrated in Figures 3.22 and 3.23, selenium and chloride concentrations rose immediately after flooding, primarily due to the dissolution of soluble salts at the soil surface. Since chloride does not react with the other chemicals present in the soil, after dissolution of the surface crust, changes in the chloride concentration take place primarily due to physical transport in water. Therefore changes in the chloride concentration can be used to indicate the rate at which water seeps through the soil profile. On the other hand, selenium at the initiation of flooding, released into solution by dissolution and the oxidation of reduced forms by aerated waters, and is then subject to chemical and/or biological immobilization.

For the purposes of estimating the amount of selenium that is immobilized after flooding, the following simplifying assumptions are invoked. First, we assume that dissolution of selenium and chloride is essentially instantaneous and complete, so that all of the potentially soluble solute are dissolved within a very short time following wetting. The assumption of instantaneous and complete dissolution allows the post-flooding high concentrations to represent the initial inventories of the two solutes. Second, we assume that the soil profile becomes fully water saturated once surface ponding occurs. This assumption is not strictly correct. However, preliminary computer modeling results indicate that at least 90% saturation occurs within the first day after the ground surface is flooded. In the absence of soil saturation measurements, this assumption is necessary for calculating the initial inventories of selenium and chloride in the soil profile.

In order to calculate the rate of seepage from the pond, a simple mass balance is performed on chloride content of the monitoring zone. For instance, the mass of chloride present at any time following flooding ($M_{Cl,t}$) can be represented by the following equation,

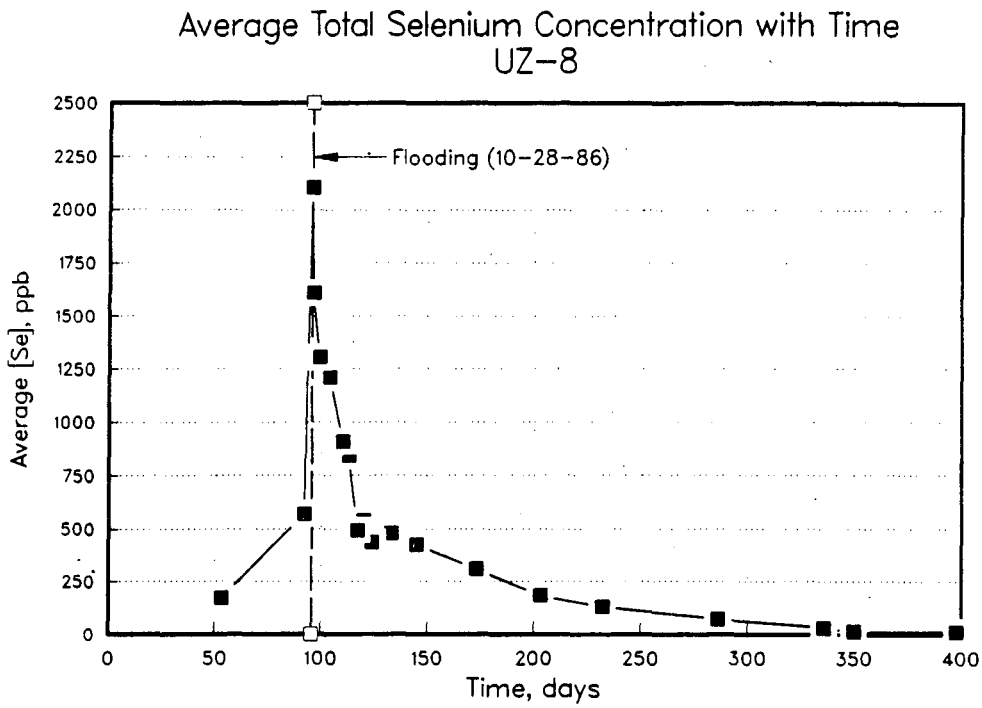


Figure 3.22a. Average concentration of soluble selenium in the top four feet of the soil profile at the UZ-8 monitoring site.

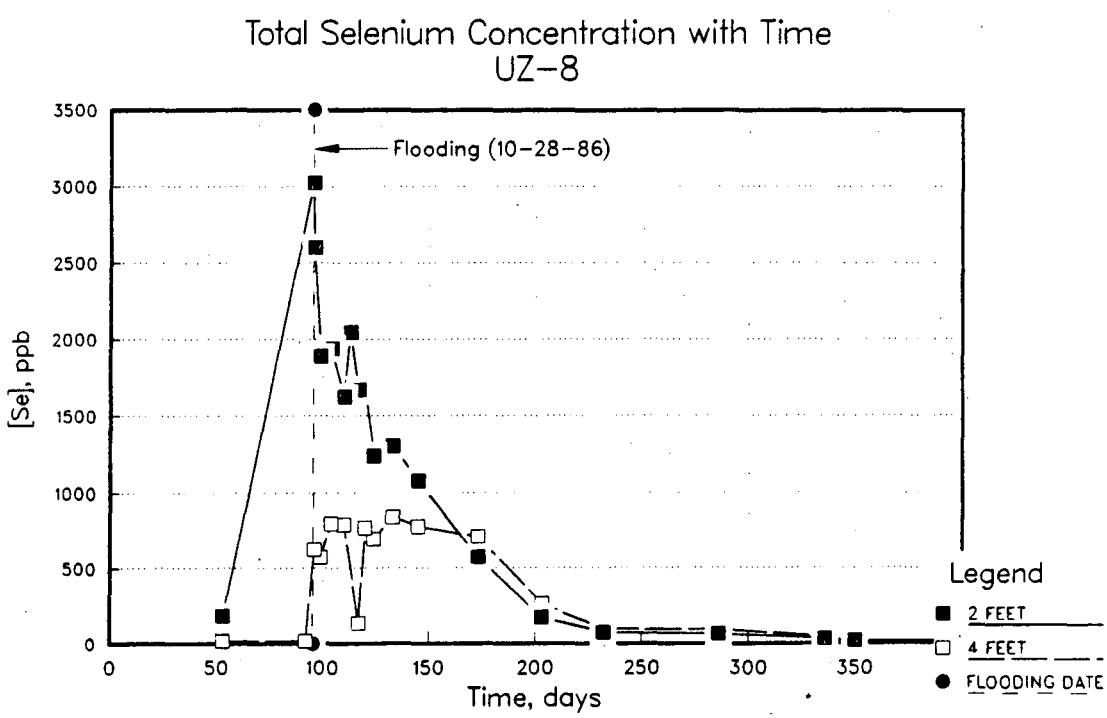


Figure 3.22b. Selenium concentrations at the 2 foot and 4 foot samples at the UZ-8 monitoring site.

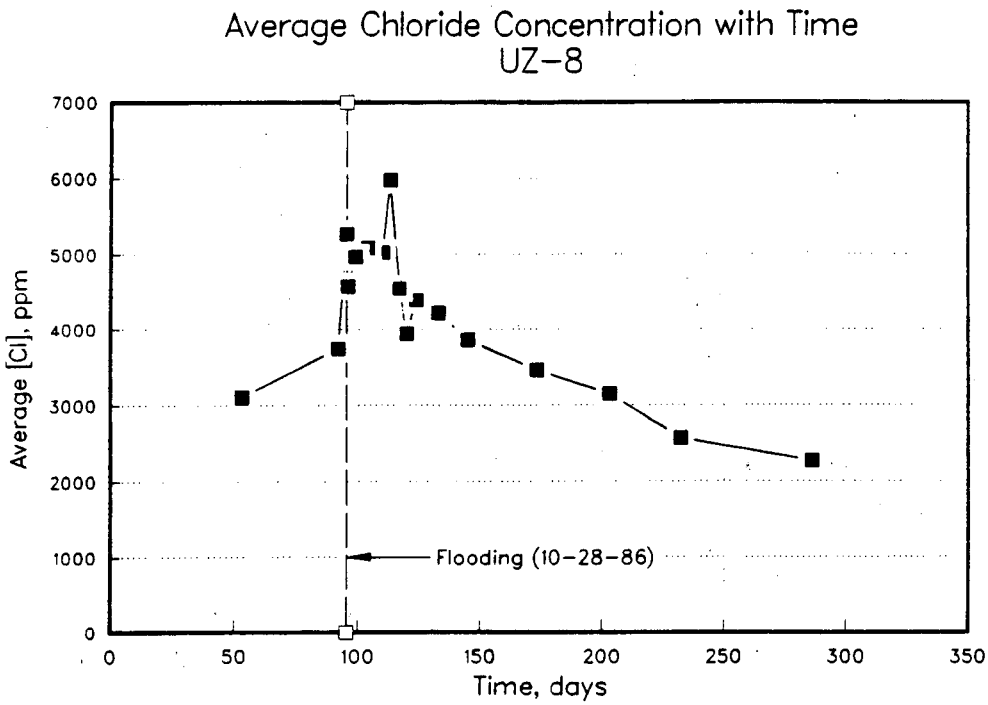


Figure 3.23a. Average concentration of chloride in the top four feet of the soil profile at the UZ-8 monitoring site.

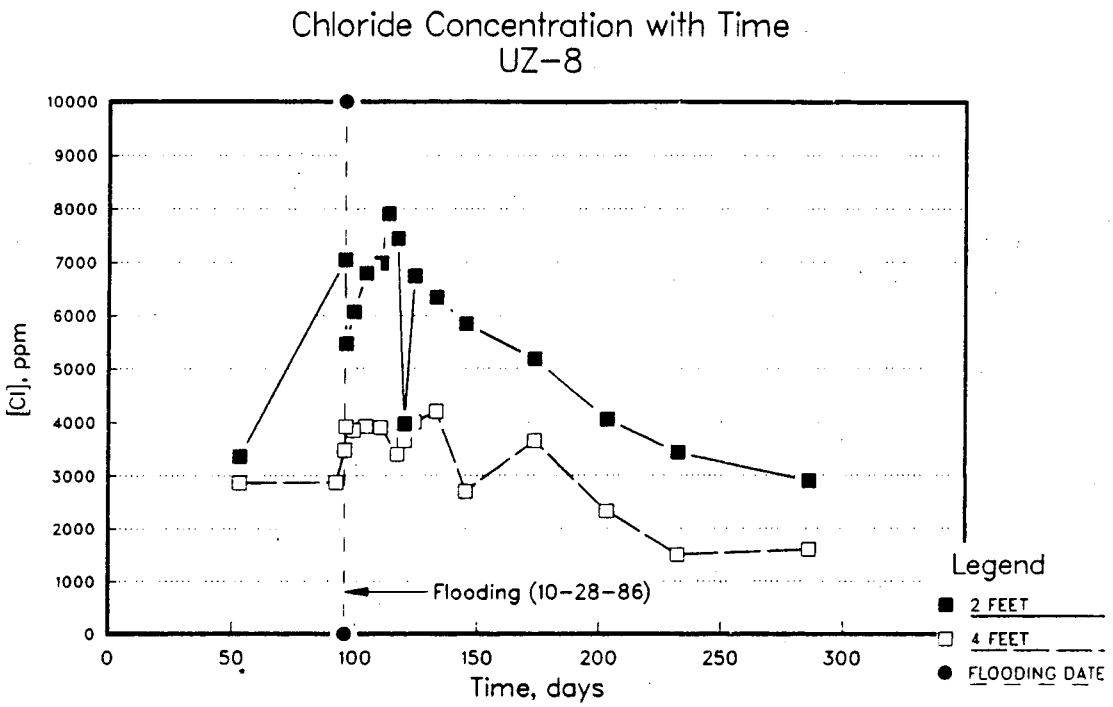


Figure 3.23b. Chloride concentrations at the 2 foot and 4 foot samples at the UZ-8 monitoring site.

$$M_{Cl,t} = M_{Cl,o} + M_{Cl,in} - M_{Cl,out}$$

where $M_{Cl,o}$ is the initial mass in the system (the above mentioned post-flooding high). $M_{Cl,in}$, the cumulative mass that has flowed into the monitoring zone with infiltrating waters since the initiation of flooding, and $M_{Cl,out}$, the cumulative mass outflow that has occurred out of the bottom, are defined in the following manner,

$$M_{Cl,in} = \rho_s \, v \cdot n \cdot A \cdot C_{Cl,in}(t) \cdot t$$
$$M_{Cl,out} = \rho_s \, v \cdot n \cdot A \cdot C_{Cl,out}(t) \cdot t$$

where,

ρ_s = density of the solution
v = average pore water velocity, m/s
n = porosity (= 0.4)
A = cross-sectional area (= 1 m^2)
$C_{Cl,in}$, $C_{Cl,out}$ = Cl concentration of waters entering and exiting the monitoring zone, respectively, ppm
t = the time since flooding began (s).

For the purpose of these estimates, $C_{Cl,out}(t)$ is defined to be the concentration in waters collected from the four foot sampler, and $C_{Cl,in}(t)$ is set equal to pond water chloride concentrations. The only unknown quantity is v, the average pore water velocity, which is assumed to be constant over the monitoring zone and throughout the duration of flooding. By using a trial and error procedure in which the measured chloride content of the monitoring zone is compared to the to the calculated value, the average pore water velocity can be determined.

The assumption that the pore velocity is constant from October of 1986 to June of 1987 is not strictly correct, but was deemed satisfactory for the purposes of these calculations. Throughout this period, pond water and groundwater elevations were measured, allowing for the calculation of gradients across the monitoring zone. Shortly after flooding, gradients and therefore pore water velocities were at a maximum. The gradients stabilized approximately 1 month after flooding and remained essentially constant for the rest of the time. As will be shown below, use of the constant velocity assumption in

the simple predictive model is justified.

For selenium, a mass balance also is performed, however, since soluble selenium is subject to immobilization when the soils are fully saturated an extra term must be added to the mass balance equation. This extra term (M_{imm}) is the mass of selenium that is immobilized and incorporated into the soil matrix. The mass balance equation takes the form,

$$M_{Se,t} = M_{Se,o} + M_{Se,in} - M_{Se,out} - M_{imm}$$

where,

$$M_{Se,in} = \rho_s \, v \cdot n \cdot A \cdot C_{Se,in}(t) \cdot t$$
$$M_{Se,out} = \rho_s \, v \cdot n \cdot A \cdot C_{Se,out}(t) \cdot t$$

and ρ_s, v, n, and A are as above for chloride. $M_{Se,o}$ is the initial mass of soluble selenium in the system and is determined from the maximum post-flooding average soluble selenium concentration. $C_{Se,in}(t)$ is set equal to selenium concentrations measured in infiltrating pond waters and $C_{Se,out}(t)$ to concentrations measured in waters collected from the four foot water sampler. Since the velocity is determined from the analysis of the chloride data and $M_{Se,t}$ is the measured mass of selenium in the system, the only unknown is M_{imm}. The difference between the initial inventory ($M_{Se,o}$) and the sum of the flows across the monitoring zone boundaries is the quantity that has been immobilized (M_{imm}).

Immobilization and migration of the inventory of soluble selenium have been calculated for each of the flooded sites (UZ-1, UZ-3, UZ-5, UZ-6, and UZ-8). Figures 3.24 to 3.27 show plots of selenium immobilization and discharge versus time at four of the wetted sites. The data plots represent the fraction of the initial mass of total selenium present in the system ($M_{Se,o}$,the post-flooding high) that has been immobilized within the top 4 feet and that has migrated below four feet. At this time, chloride analyses have been performed only on samples from three of the wetted sites - UZ-8, -6, and -3.

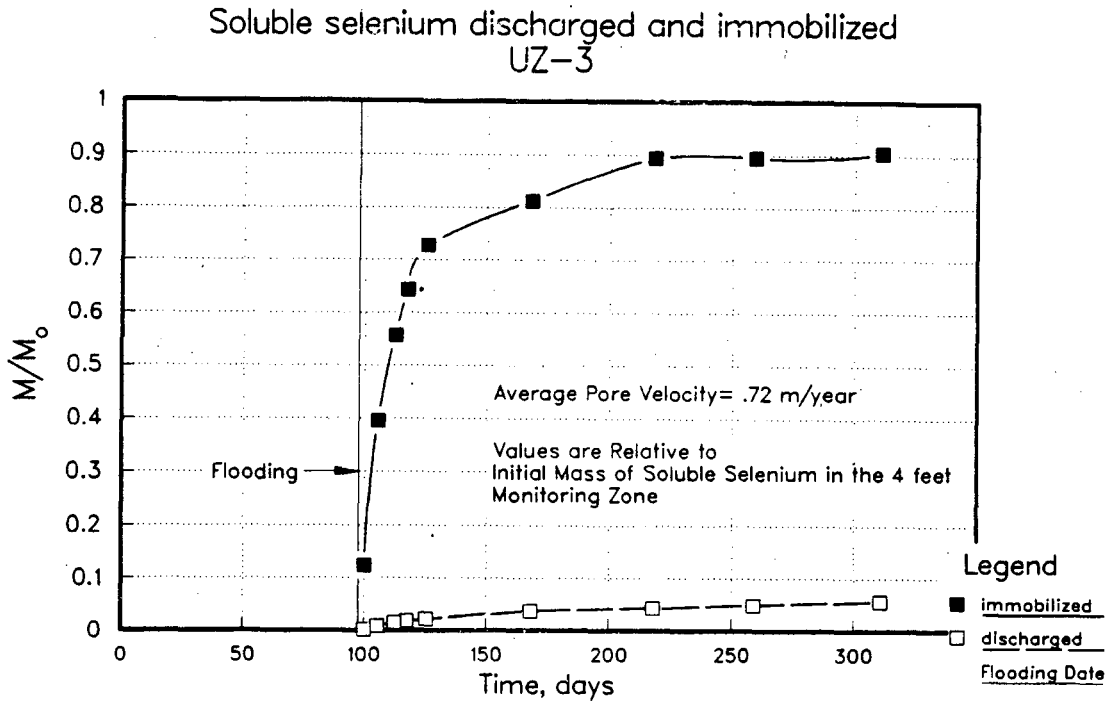


Figure 3.24. Calculated values for the amount of selenium immobilized (incorporated into the soil matrix) and discharged below the sampling interval at the UZ-3 monitoring site.

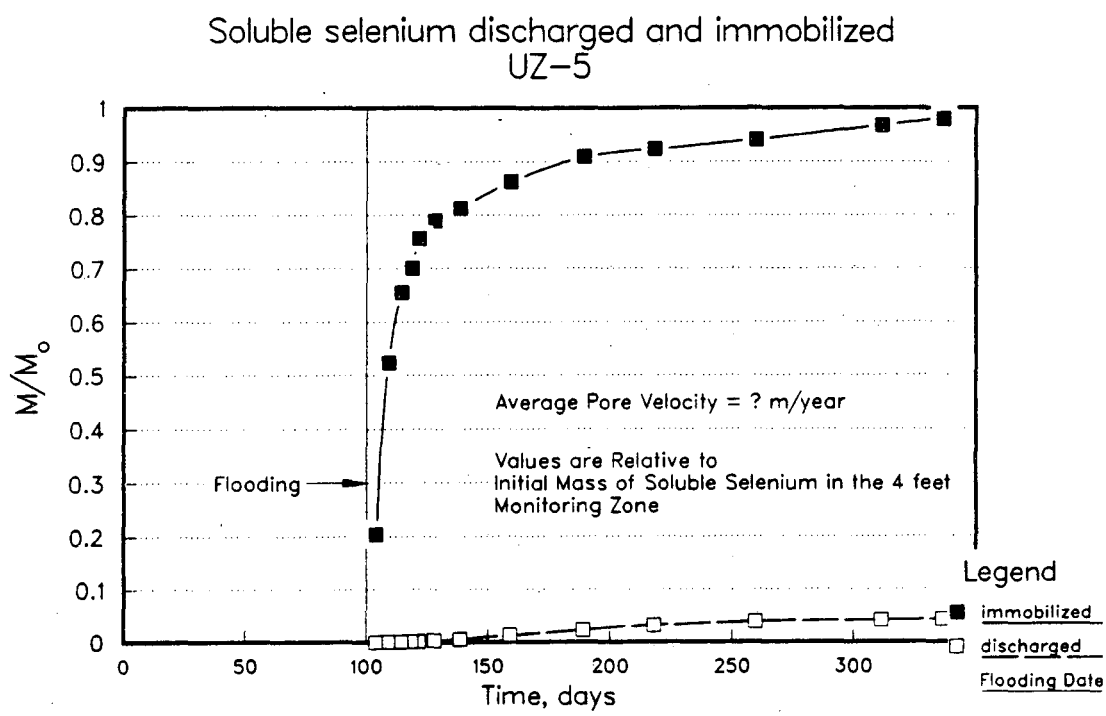


Figure 3.25. Calculated values for the amount of selenium immobilized (incorporated into the soil matrix) and discharged below the sampling interval at the UZ-5 monitoring site.

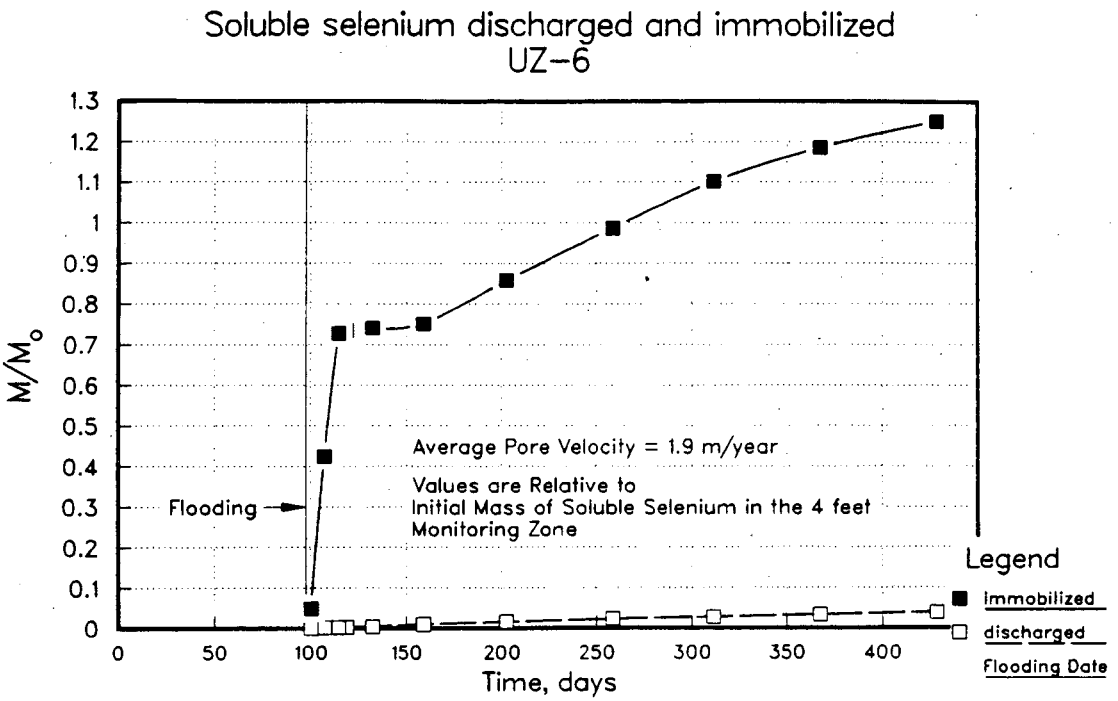


Figure 3.26. Calculated values for the amount of selenium immobilized (incorporated into the soil matrix) and discharged below the sampling interval at the UZ-6 monitoring site.

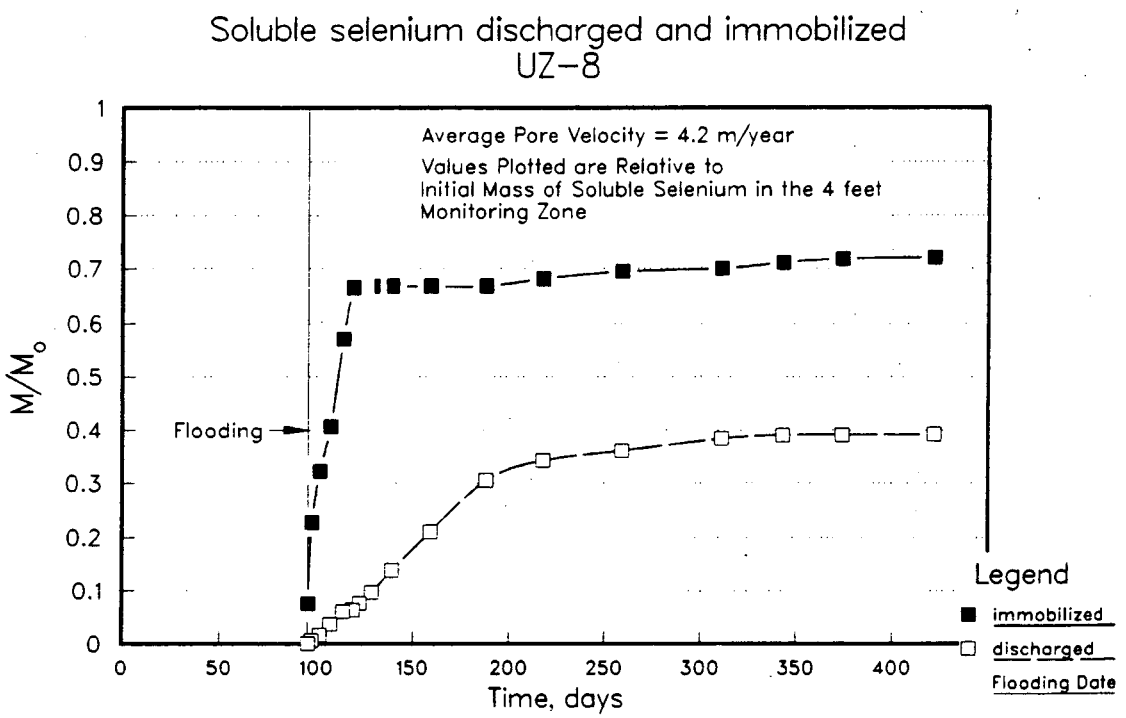


Figure 3.27. Calculated values for the amount of selenium immobilized (incorporated into the soil matrix) and discharged below the sampling interval at the UZ-8 monitoring site.

Therefore, no data are available from UZ-1 and -5 on possible average pore water velocities. However, immobilization/migration estimates at UZ-5 are not very sensitive to average pore water velocity, because the selenium concentration of water leaving at the four feet depth is roughly equal to that of the infiltrating pond water. Therefore, knowledge of the actual pore water velocity at UZ-5 is not necessary for estimating the fraction that was immobilized. It should be noted that it is possible to calculate ratios greater than unity for the normalized-mass of selenium immobilized because selenium is continually added to the soils from infiltrating pond water. These waters are low in total selenium (10-40 ppb),and yet, at sites with low initial soluble Se inventories, this inflow can be significant.

Table 3.3 summarizes the mass balances of soluble selenium in the top 4 feet of soils at each of the five sites as of June 1, 1987. The quantities listed include percentages of the initial selenium inventory that have been immobilized and discharged from the four feet monitoring zone. At UZ-1 a range of values has been calculated based on a reasonable range of pore water velocities.

Table 3.3. Selenium Discharge/Immobilization as of June 1, 1987

Site	Initial mass, g/m^2	Discharged		Immobilized	
		% of Initial Mass	Mass, g/m^2	% of Initial Mass	Mass, g/m^2
UZ-1	0.675	12-72	0.08-0.485	83-70	0.56-0.47
UZ-3	0.88	6	0.05	91	0.80
UZ-5	0.14	4	0.006	97	0.14
UZ-6	0.054	3	0.001	110	0.059
UZ-8	0.984	38	0.38	70	0.69
Average	0.55		0.11*		0.42*

* - averages are arithmetic averages of the mass quantities and do not include data from UZ-1

3.4.2. Migration of Soluble Selenium into the Soil Column

Significant variability exists throughout Pond 1 with regard to selenium inventories in sediments, hydraulic conductivities, clay contents, and other physical properties and conditions that influence the remobilization and subsequent immobilization of selenium. Nevertheless, if we assume that the four data sites can be considered representative of Pond 1 as a whole, we estimate that 42 kg total selenium have been discharged below four feet into underlying materials, and 162 kg have been immobilized within the top four feet of soil.

These estimates of the quantities of selenium that are immobilized are considerably higher than those presented in LBL Progress Report 5. Approximately 2 to 3 times more immobilization is estimated from this most recent set of calculations and one-half the discharge. This recent set of calculations is more accurate than the past set because our analysis incorporated a more realistic model of the physical system. Specifically, more realistic estimates of the fluid velocity were used. One test of the validity of this method is provided by comparing the measured chloride content of the study block to the value predicted by out model. As demonstrated by Figure 3.28 the comparison between the measured and calculated chloride contents for the UZ-8 site is very good. Deviation between the predicted and calculated chloride concentrations does not exceed 7.5% at any of the sites.

The validity of these calculations is also substantiated by the observation that selenium concentrations in excess of 10 ppb were not detected in deeper sampling wells (6 to 40 feet) at 4 of the 5 flooded sites. At UZ-8, concentrations of 200 to 300 ppb were observed at a sampling well screened from a depth of 6 to 8 feet and 8 to 10 feet. This is consistent with our estimate that nearly 40% of the soluble selenium at UZ-8 migrated out of the 4 foot thick monitoring zone. At all of the other sites, where elevated selenium concentrations were not detected, we calculated that less than 10% of the soluble selenium inventory migrated out of the monitoring zone.

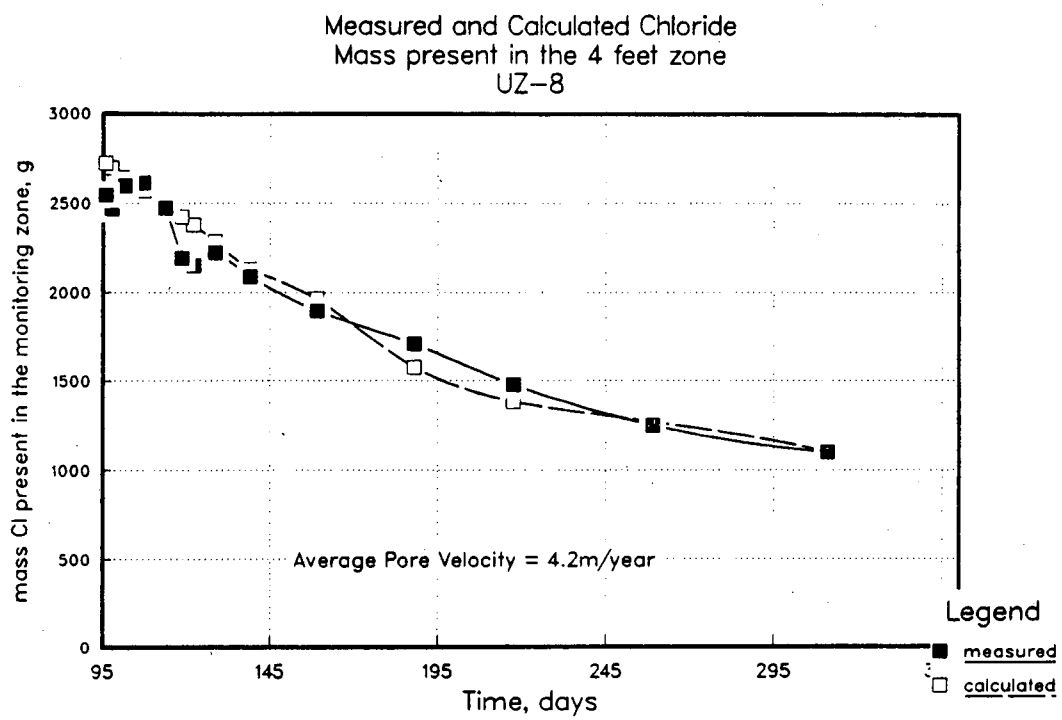


Figure 3.28. Measured and calculated chloride content in the four foot sampling interval at the UZ-8 site.

One of the major sources of uncertainty in predicting solute transport through field soils stems from heterogeneities in their physical structure and hydraulic properties. In general, theories describing miscible fluid displacement in uniform soil, predict the appearance of a non-adsorbed solute at the outflow end of a saturated column after the application of approximately one-pore volume of fluid. Experiments involving the transport of solutes in field situations, however, have often demonstrated quite different behavior. In fact, the preferential movement of solutes through larger soil voids is well documented. Kissel et al. (1973), demonstrated with a solution of chloride and fluorescein dye that relatively large continuous soil cracks were important pathways of transport in saturated swelling clay soils. Fluorescein and chloride were found to move quite rapidly through soil cracks whereas in nearby areas little or no fluorescein was found.

Large pores, channels, or cracks, exist in pond bottom soils at Kesterson, and they are probably the cause for the rapid increase in selenium concentrations at depths of up to 4 feet shortly after flooding. Clay shrinkage during hot summer months and subsequent dessication cracking probably accounts for the majority of these macropores. Remnants of shrinkage cracks resulting from long term dessication cracking may persist as natural fissures in swelling clay soil (e.g. Godfrey, 1964). In an effort to determine if these conduits are major pathways for the downward movement of solutes through Kesterson pond bottoms, we have compared hydraulic conductivity values determined by conventional field measurements (see section 3.1.1) to values indicated from reflooding Pond 1. Conventional field measurements typically provide hydraulic conductivity values that are representative of a relatively small volume of soil. As a result, depending on the location of the measurement, the effects of macropores may be missed entirely. The values determined from the Pond 1 experiment average a greater volume, depending on the depth interval over which the hydraulic gradient is measured. Therefore, if macropores are the major pathways for migration through the surface soils, their presence should be reflected in higher hydraulic conductivity values compared to conven-

tional field measurements. With these thoughts in mind and using pore velocities calculated above and measured gradients, effective hydraulic conductivities have been calculated. Table 3.4 lists the effective K_s determined in this manner, as well as the measured gradients and average pore water velocities calculated based on the chloride data.

Table 3.4. Fluid Flow in Flooded Pond 1 Sediments

Site	Average Pore Water Velocity, m/y	gradient, i	effective K_s, m/y	harmonic mean* K_{fs} m/y
UZ-8	4.2	.076	21.9	$\approx$ 4 m/yr
UZ-6	1.9	.023	32.7	-
UZ-3	0.7	.25	1.2	$\approx$ 4 m/yr

* calculated from data reported in section 3.1.1

Effective K_s measurements performed by this method agree within an order of magnitude with values of effective K_s calculated from field measurements presented in section 3.1.1 and are within range of Luthin's (1966) predictions.

There was no systematic relationship between the hydraulic conductivity values measured by these two methods. At one of the sites it was lower, and at the other two they were higher. This suggests that in some areas macropore flow may provide a significant contribution to pond seepage, allowing solutes to migrate into the upper aquifer at rates significantly greater than the average values presented above. However, general agreement between the hydraulic conductivity values calculated with this method, and the values previously reported indicate that matrix flow governs seepage through the pond bottoms. Even in regions where the macropores create locally high seepage velocities, selenium migration into the upper aquifer is inhibited by the rapid immobilization that follows resaturation.

3.4.3. Discussion of the Pond 1 Reflooding Experiment

Observations from the Pond 1 experiment indicate that selenium immobilization is most rapid shortly after flooding, and thereafter proceeds at a slower rate. Gunnison et al. (1985) describe how flooding can lead to very rapid geochemical and biological changes in an initially well-aerated soil. Upon submergence, air in the pore space is quickly displaced by water. In a matter of several days, available oxygen can be exhausted by aerobic microbes through the decomposition of organic matter. Microbial activity shifts to the anaerobic variety, and alternate inorganic terminal electron acceptors are utilized. Reduction of inorganic compounds locally proceeds in a thermodynamically determined step-wise manner mediated by anaerobic microorganisms. The data observed from Pond 1 are consistent with such a model.

Several investigators have studied the solubility dependence of selenium on oxidation-reduction potential (e.g., Lakin (1961), Geering et al. (1968), and Elrashidi et al. (1987)). An important result of these investigations has been the determination that at high redox, selenate (SeO_4^{2-}) is the dominant species present in solution, whereas under conditions of moderate to low redox, more reduced forms persist which have lower solubilities. These reduced forms include selenite (SeO_3^{2-} or $HSeO_3^-$) and selenide (HSe^-). Weres et al. (1985) as well as earlier LBL Progress Reports have discussed the decreased solubility of selenium in its lower oxidation states. Data presented here, indicating selenium immobilization, are suggestive of such chemical processes and lend support to a description of a system whereby rapidly developing reducing conditions in the newly flooded soils lead to the microbially mediated reduction of selenate to less soluble forms (see section 4.4).

As of July, 1987 soluble selenium concentrations in the pore waters at the permanently wet sites in Pond 1 were low in comparison to the areas where the water table is below the ground surface (see section 3.3.1). All available data suggest that they would remain low if they were continually flooded with a low-nitrate water supply. Dur-

ing June and July 1987, much of Pond 1 dried out due to the lack of an adequate water supply. Soluble selenium concentrations quickly rose at the monitoring sites in the areas that dried out, due to oxidation of reduced forms through atmospheric exposure and upward evaporative fluxes. At sites UZ-3 and -4 selenium concentrations exceeding 1 ppm occurred in a period of a few weeks.

Inflows to Pond 1 were terminated in early August when it became clear that the existing water supply at the Reservoir was not sufficient to keep Ponds 1, 2, 5, and 7 flooded. Monitoring is continuing through this period, as it will when the pond is reflooded.

4. SOILS AND SEDIMENTS

4.1. The Terrains of Kesterson Reservoir

The selenium in sediments at Kesterson Reservoir is strongly associated with organic matter. The nature and amount of organic matter in the sediment is in turn determined by the local *depositional environment.* There are four major terrains within Kesterson Reservoir, which correspond to four distinct depositional environments and sediment profiles. The distribution of these terrains is governed by water levels as illustrated in Figure 4.1, and the distribution of terrains will change if water levels change. The relatively dry northern ponds contain large areas covered by salt grass (*Distichalis*) mixed with alkali weed (*Cressa*). Except during very wet years, these areas are above water year-round. Along the berms and where the salt grass borders playa, relatively small strips and patches containing many different species are present; e.g. gumplants and other members of the sunflower family. The extensive "playa" areas are completely flooded in winter and spring and completely dry in summer and fall. In late summer and fall the playas are covered with a salt crust, resembling alkali salt flats. They flood in December, and about March the water plant *Ruppia* grows very rapidly and fills in the flooded playas. The *Ruppia* becomes overgrown by filamentous algae. In early summer the playas dry out again, and the *Ruppia* and algae biomass decomposes, leaving only some fibrous detritus mixed with and underlying the salt crust. The *Ruppia* survives the summer as dormant tubers and seeds, which sprout the following winter and spring. Areas which are flooded during the winter and remain damp during the summer and fall are dominated by cattails, and smaller stands of alkali bullrush and similar plants border the cattails in some areas. Areas that are permanently flooded are dominated by the large alga *Chara* which is overgrown by diatoms and other algae that are attached to it. *Chara* grows rapidly during the spring, then dies back during the fall, when water levels drop, and in winter, when the temperature is lowest. Areas with not quite enough water to support *Chara* are dominated by diatoms and bacteria.

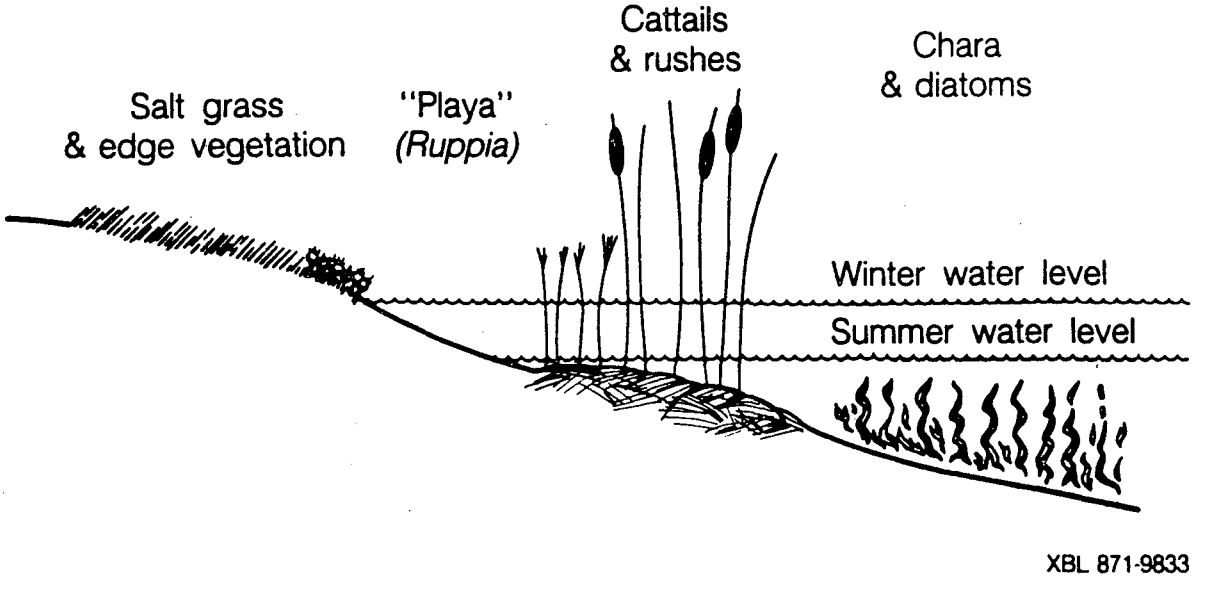


Figure 4.1. The four major terrains of Kesterson Reservoir.

The water level and vegetation control the deposition of organic matter. In the salt grass areas the soil is relatively dry, and little organic matter accumulates, because organic matter quickly decays in the presence of air. Much biomass produced by *Ruppia* and algae in the playa areas decomposes during the summer, and little or no organic matter accumulates from year to year. Loose deposits of peat-like material accumulate in the cattail areas. When compressed in a coring tube, the total thickness of this material is typically one inch, but may reach four inches in some areas. The *Chara* areas deposit a characteristic, strongly sulfidic "algal ooze", which is typically one inch thick, but may be several inches or more thick in areas where wind and currents cause organic detritus to accumulate; e.g. the southern parts of Ponds 4 and 5. The historical distribution of the four terrains within Kesterson Reservoir is summarized in Table 4.1.

Table 4.1. Historical distribution of terrains in Kesterson Reservoir

Pond	Terrains	Classification
1	Playa, CT	Wet
2	CT, Water	Wet
3	Playa, CT, SG	Wet
4	CT, Playa, Water	Wet
5	Water, CT	Wet
6	Playa, CT, SG	Wet
7	Playa, CT, Water	Wet
8	Playa, CT, SG	Wet
9	Playa, SG, CT	Dry
10	SG, Playa	Dry
11	SG, Playa	Dry
12	SG, Playa	Dry

Notes:

Water = Permanently flooded.

CT = Cattails and similar emergent vegetation.

Playa = Areas flooded in winter, dry and barren in summer.

SG = Areas dominated by salt-grass and other terrestrial vegetation.

4.2. Concentration and Speciation of Selenium in Sediment Cores

Analytical methods for determining concentrations of different chemical species of selenium in sediment samples have been reported in LBL Progress Reports Nos. 2 and 4. A variety of sediment and soil samples collected in various terrains of Kesterson Reservoir have been analyzed using these methods. Selected data of this kind are presented here, mostly relating to playa areas and cattail areas. Additional sediment samples are being analyzed to establish time trends, seasonal changes, and to characterize selenium distribution and speciation in salt grass and *Chara* dominated areas.

Typical sediment data are presented in Tables 4.2 to 4.5, and summarized in Table 4.6. All of the analyses reported here are of sediment samples that were dried and pulverized. This processing has little effect upon speciation in sediment or soil that was already field dry when collected. However, drying sediments that were collected wet inevitably oxidizes some fraction of the selenium and converts it into soluble form. For this reason soluble selenium is not determined in dried samples of initially wet sediment. Soluble selenium in wet sediment may be estimated by washing the material with a suitable brine without drying it. These data (not presented here) indicate that the soluble selenium content of sediments collected in wet areas is usually much less than 1 ppm selenium relative to the dry weight of the sample. The only exceptions to this rule are encountered with loose peat floating at the surface of shallow, well-aerated water, and with peat or algae deposits that are wet but exposed to the atmosphere, with no water standing over them.

"Insoluble Se^{+4}" is the fraction of Se^{+4} that is very tightly bound to the sediment, and requires molten KOH to extract it. Organic matter interferes with the determination of insoluble Se^{+4}. Reliable determination of insoluble Se^{+4} requires that a spiked sample be run in parallel to document good recovery. In practice, it is found that insoluble Se^{+4} cannot be determined in sediments collected from wet areas, nor in the organic-rich superficial section of cores collected in dry areas. Accordingly, insoluble Se^{+4} is

determined and reported only for the deeper portion of cores collected in dry areas.

"Se^0" is zero-valent selenium which is preferentially extracted by sodium sulfide or sodium cyanide. Se^0 includes elemental selenium, but also zero valent selenium atoms in polysulfide molecules or bound to organic matter.

In these Tables "Selenium - Other" was determined by subtracting values for Se^0, Se^{+4} and Se^{+6} from the total selenium concentration. The species included under the rubric "Selenium - Other" will depend on what species were explicitly analyzed for. At a minimum, "Selenium - Other" will include organic selenium compounds and selenium in sulfide or selenide minerals, if these species are present. Where insoluble Se^{+4} is not reported, "Selenium - other" may include this species. "Total Se^{+4}" includes the soluble and insoluble subspecies, and is reported only for samples where soluble selenium and insoluble Se^{+4} have been determined. "Soluble Selenium" is the sum of Se^{+6}, soluble Se^{+4} and any water soluble organic selenium compounds that may be present. In practice, "soluble Se" and soluble Se^{+4} are actually determined, and Se^{+6} is calculated as the difference between these values. Therefore, the value reported for Se^{+6} will include soluble organic selenium compounds if these are present.

Table 4.2 depicts a sample collected at site UZ-7 in Pond 1, which is located in a (winter) edgewater area transitional from playa to saltgrass. Here "Selenium-other" and Se^0 are the major species, and there is less soluble selenium or insoluble Se^{+4} than in the other playa sites.

Table 4.3 depicts a sample collected in a small area of open water in the middle of Pond 2, where filamentous algae and bacteria predominate. This core is representative of the areas where selenium is effectively removed from solution within the upper few inches of the pond bottom soil.

Table 4.4 depicts a sample collected in dense cattails in Pond 2. The first four inches (samples 32-1 and 32-2) are peat-like material obviously derived from decomposed cattail leaves. Despite its stringy texture and obvious origin, this material contains only

Table 4.2. Selenium Speciation in an 8-Inch Core (KC-21) from Pond 1

Sample	Inches	Se Total	Se^0	Se^{+6}	Se^{+4}			Se Other	Sol. Se	C (%)	N (%)
					Sol.	Insol.	Total				
21-1	0-1	29.0	9.3	1.71	1.34			16.65	3.05		
21-2	1-2	10.2	3.5	0.63	0.56	1.02	1.58	4.49	1.19		
21-3	2-3	1.6	0.2	0.27	0.09	0.28	0.37	0.84	0.28		
21-4	3-4		0.5	0.14	0.04	0.15	0.19		0.18		
21-5	4-6		0.1	0.07	0.02	0.19	0.21		0.09		
21-6	6-8		0.0	0.09	0.05	0.12	0.17		0.14		

Core designation: KC-21
Date collected: 10-10-86
Site collected: UZ-7, NE Pond 1
Description: Site transitional from playa to saltgrass.
Comments: Toward upper edge of the playa zone.

Table 4.3. Selenium Speciation in an 18-Inch Core (KC-31) from Pond 2

Sample	Inches	Se Total	Se^0	Se^{+6}	Se^{+4}			Se Other	Sol. Se	C (%)	N (%)
					Sol.	Insol.	Total				
31-1	0-1	63.1	26.8							3.87	0.35
31-2	1-2	6.1	0.0							0.99	0.11
31-3	2-3	3.7								1.02	0.11
31-4	3-5	2.3								1.01	0.09
31-9	8-9	0.3								0.44	0.03
31-13	12-13	0.3								0.43	0.02
31-18	17-18	0.2								0.05	0.03

Core designation: KC-31
Date collected: 1-22-87
Site collected: Pond 2, end of berm
Description: Open water 8" deep, mucky bottom, no Nitella.
Comments: Collected before the fire.

6% carbon (dry weight). The water content of this material is very high, 77% after the free liquid water had been squeezed from a sample by hand. Probably, this "peat" has a large content of silica fibers inherited from the vegetation, and also contains hydrophyllic organic polymers that are residues of microbial reworking of the organic material. In the area from which this core sample was collected, the peat forms a very loose and porous deposit up to one foot thick at the base of the living cattail leaves. This thick but very loose deposit is compressed into a dense mat one to four inches thick in the course of collecting and extruding the core, and this "core thickness" is reported here. On a dry weight basis, the selenium content of the peat is very high, and Se^0 predominates. The concentration of selenium below the peat in the interval 4-14 inches is moderately elevated. The concentration of selenium in the peat is large because the peat contains selenium inherited from the cattail leaves that it is derived from. Anaerobic conditions probably do not exist within the loose peat deposit, and the peat does not remove more than a fraction of the selenium from the water. Most of the selenium is removed from the percolating water by the mineral soil underneath the peat. Within the mineral soil the decline of selenium concentration with depth is quite slow, suggesting a relatively slow and perhaps imperfect selenium fixation process.

Table 4.5 depicts a core collected in very dry cattails in Pond 1. The peat layer has dried and decomposed down to about 1 inch thickness and the density has increased to near that of the underlying mineral soil. Se^0 and organic selenium predominate, with a subordinate but substantial amount of soluble selenium also present. A substantial amount of selenium is present all the way down to 10 inches depth. Both total selenium and soluble selenium increase in the deepest sample (34-1), indicating substantial migration of soluble selenium through the profile.

The data in Tables 4.2 to 4.5 are summarized in Table 4.6 together with other data that were presented in LBL Progress Report No. 5. The data here are aggregated in different ways to emphasize different points. The "amount" of selenium in a given inter-

Table 4.4. Selenium Speciation in a 14-Inch Core (KC-32) from Pond 2

Sample	Inches	Se Total	Se^0	Se^{+6}	Se^{+4}			Se Other	Sol. Se	C (%)	N (%)
					Sol.	Insol.	Total				
32-1	0-2	232	160					72		6.27	0.45
32-2	2-4	192	133					59		5.68	0.39
32-3	4-6	13.2	5.9					7.3		0.67	0.06
32-4	6-8	11.3	5.0					6.3		0.56	0.06
32-5	8-10	8.6								0.36	0.04
32-6	10-12	7.0								0.25	0.03
32-7	12-14	5.2								0.16	0.04

Core designation: KC-32
Date collected: 1-22-87
Site collected: Pond 2, S. side of berm near end.
Description: Dense cat-tails, about 15" water.
Comments: Collected before the fire.

Table 4.5. Selenium Speciation in a 10-Inch Core (KC-34) from Pond 1

Sample	Inches	Se Total	Se^0	Se^{+6}	Se^{+4}			Se Other	Sol. Se	C (%)	N (%)
					Sol.	Insol.	Total				
34-8	0-1	119.0	66.1	9.00	1.95			41.9	10.95	3.82	0.30
34-7	1-2	15.6	3.9	4.22	0.80			6.7	5.02	1.25	0.07
34-6	3-4	32.9	12.2	2.62	0.99			17.1	3.61	2.62	0.13
34-5	4-5	6.3	1.4	1.75	0.85	1.55	2.40	0.8	2.60	0.43	0.02
34-4	6-7	2.0		0.88	0.06	0.31	0.37	0.75	0.94	0.32	0.02
34-3	7-8	1.8		0.63	0.07	0.33	0.40	0.77	0.70	0.24	0.02
34-2	8-9	1.1		0.62	0.05	0.28	0.33	0.15	0.67	0.09	0.01
34-1	9-10	3.2		2.42	0.07	0.28	0.35	0.43	2.49	0.16	0.02

Core designation: KC-34
Date collected: 10-24-86
Site collected: UZ-8 in Pond 1
Description: Very dry cat-tails.
Comments: This is what you get when a cat-tail area is thoroughly dried out.

val is calculated from the average concentration assuming that the bulk density of the dried sediment is 1.30 (relative to the density of water). Bulk density = 0.23 is assumed for the dried peat in inches 0-4 of core KC-34. The 0-1 inch layer usually but not always contains much more selenium than deeper strata. Substantial amounts of soluble selenium are present in all dry area cores, and the percentage of soluble selenium compared to the total selenium increases with depth. The 0-4 or 0-5 inch interval in dry area cores usually contains well above 1ppm soluble selenium. In deeper dry area sediments where insoluble Se^{+4} may be determined without interference from organic matter, this species always represents a substantial fraction of the total selenium present.

Se^0 is practically ubiquitous in the shallow samples, and most appear to contain some organic selenium as well. The proportion of Se^0 is particularly high in samples associated with cattails (KC-32 and 34). Selenium inventories are generally higher in cattail areas than in playa areas, but the amount of selenium in playa core KC-33 is quite high, and the selenium content at this site appears to have increased with time.

Cores KC-32 and 34 have practically the same selenium inventory, and were collected in basically similar cattail beds, except that KC-32 was wet and KC-34 was very dry at the time of collection. The drying process severely decomposed the peat at KC-34 (UZ-8 in Pond 1), and dramatically altered the speciation of selenium, producing a substantial amount of soluble selenium.

4.2.1. Practical Implications of Selenium Speciation in Kesterson Soils

The data presented herein illustrate the effect of water upon the speciation of selenium in sediment and soil at Kesterson Reservoir. In continuously wet areas, relatively little soluble selenium is present in the sediment, and the concentration of selenium in the surface water can achieve quite low levels. In dry areas, typically 10 to 25% of the selenium is present in water soluble form. Due to near-drought conditions and a restricted water supply, in 1987 wide areas of the Reservoir, including historical

Table 4.6. Summary of Selenium Distribution in Cores

Core	Date	Site	Depth (inch)	Tot.Se (ppm)	Sol.Se (ppm)	Sol.Se (%)	Se^0 (%)	Ins.Se^{+4} (%)	Amount g/m^2
KC-2	8-??-85	UZ-1,dry playa,P1	0-4	6.9	2.5	36	25		0.91
			0-1	23.2	7.7	33	25		0.76
			1-4	1.4	0.7	51		21	0.14
KC-11	12-13-85	Recently flooded playa,P1	0-4	11.0			38		1.45
			0-1	34.6			46		1.14
			1-4	3.1				24	0.31
KC-14	2-28-86	Flooded playa, near KC-11	0-4	22.4			18		2.96
			0-1	70.6			19		2.33
			1-4	6.4					0.63
KC-33	10-24-86	Dry playa,P1, near KC-11	0-5	34.2	6.1	18			5.64
			5-10		0.6				
			0-1	111	15.1	14			3.66
			4-5	1.6	0.9	54		44	
KC-21	10-10-86	Dry upper playa, P1,UZ-7	0-3	13.6	1.5	11	32		1.35
			0-1	29.0	3.0	10	32		0.96
			2-3	1.6	0.3	18		18	
KC-31	1-22-87	P2,8" water,mucky bottom	0-5	15.5			35		2.56
			0-1	63.1			42		2.08
KC-32	1-22-87	P2 cattails before fire	0-14						7.9
			0-4	212.			69		4.9
			4-10	11.0			48		2.18
			10-14	6.1					0.80
KC-34	10-24-86	V.dry cattails, P1,UZ-8	0-10	21.0	3.3	16			6.94
			0-5	39.6	5.3	13	46		6.53
			5-10	2.5	1.3	53		17	0.41
			0-1	119.	11.	9	56		3.93

cattail and water-covered terrains, have been much drier than in the past. A substantial fraction of the selenium inventory within these dry areas has been converted to soluble form.

The distribution of the four terrains depicted in Figure 4.1 is governed by water levels within Kesterson reservoir and their variation over the course of the year. Implementation of the On-Site Disposal Plan will convert practically the entire area of Kesterson Reservoir to salt grass and playa terrains, wherein soluble selenium constitutes a significant fraction of the total selenium inventory. While the total inventory of selenium remaining within Kesterson Reservoir after implementation of ODP will be smaller than it is today, a significant fraction of what remains will be in water soluble form, and thereby capable of contaminating seasonal bodies of surface water and entering the food chain.

The soluble fraction of the residual selenium post ODP may or may not be in the 10-25% range typical of dry area samples collected in 1985 to 1987 and reported here. It is well established that the insoluble fraction of selenium includes different chemical species. These species may have different susceptibility to oxidation, and those more easily oxidized to soluble form will be depleted with the passage of time, leaving a less reactive inventory of selenium in the soil. The total amount of selenium in the soil will gradually decrease as selenium is removed by volatilization. In principle, this process should decrease the residual selenium inventory and especially its soluble fraction with time. The rate of this process is unknown, but experiments and field measurements are underway to measure them. The depletion of residual selenium inventory by volatilization may be amenable to artificial acceleration. Similarly, the inventory of soluble selenium in the near surface soils may be reduced by an appropriately designed flooding and drying scheme. Appropriate field tests by UCR and LBL are under way. These techniques should be particularly effective in removing the water soluble selenium from superficial soil, and a large fraction of water soluble selenium is conducive to their suc-

cessful application.

4.3. Nitrate, Organic Matter and the Fixation of Selenium in Pond Bottom Sediments

That microbial reactions efficiently remove selenium from water percolating through pond bottom sediments at Kesterson Reservoir is strongly suggested by the large concentration of selenium in superficial sediments and its near absence from deeper groundwater. This process has been simulated in the laboratory, and the roles of nitrate and organic matter have been explored. The following paragraphs and Figure 4.2 (taken from Weres et al. 1987) elaborate on the effect of nitrate and organic matter upon the removal of selenium from water.

A black, organic matter-rich sediment derived from *Chara* and *aufwuchs* and collected at the southern edge of Pond 5 was used in these experiments. Selenium-bearing brine was passed through 5.3 cm I.D. glass columns containing approximately 15 cm of this sediment. The flow rate corresponded to roughly 1 pore volume per day.

Column No.7 received San Luis Drain water containing approximately 290 ppb total selenium (predominantly Se^{+6}) and 240 ppm nitrate. More selenium came out of this column than went in, and a substantial fraction of the selenium in the water was converted to selenite Se^{+4}. The sediment in the column initially was black. Over the course of the experiment the entire volume of sediment was bleached to a pale grey-green color, and coarse gas bubbles appeared throughout the sediment, probably nitrogen and other gases produced by denitrifying bacteria. Column No. 9 received a brine compounded to resemble the San Luis Drain water (including 290 ppb Se^{+6}), but containing no nitrate. After a settling-in period (days 1-6) the column removed about 80% of the selenium from the water percolating through it. Air dissolved in the brine slowly bleached the sediment without formation of gas bubbles.

Column No. 8 received San Luis Drain water which contained selenium and nitrate

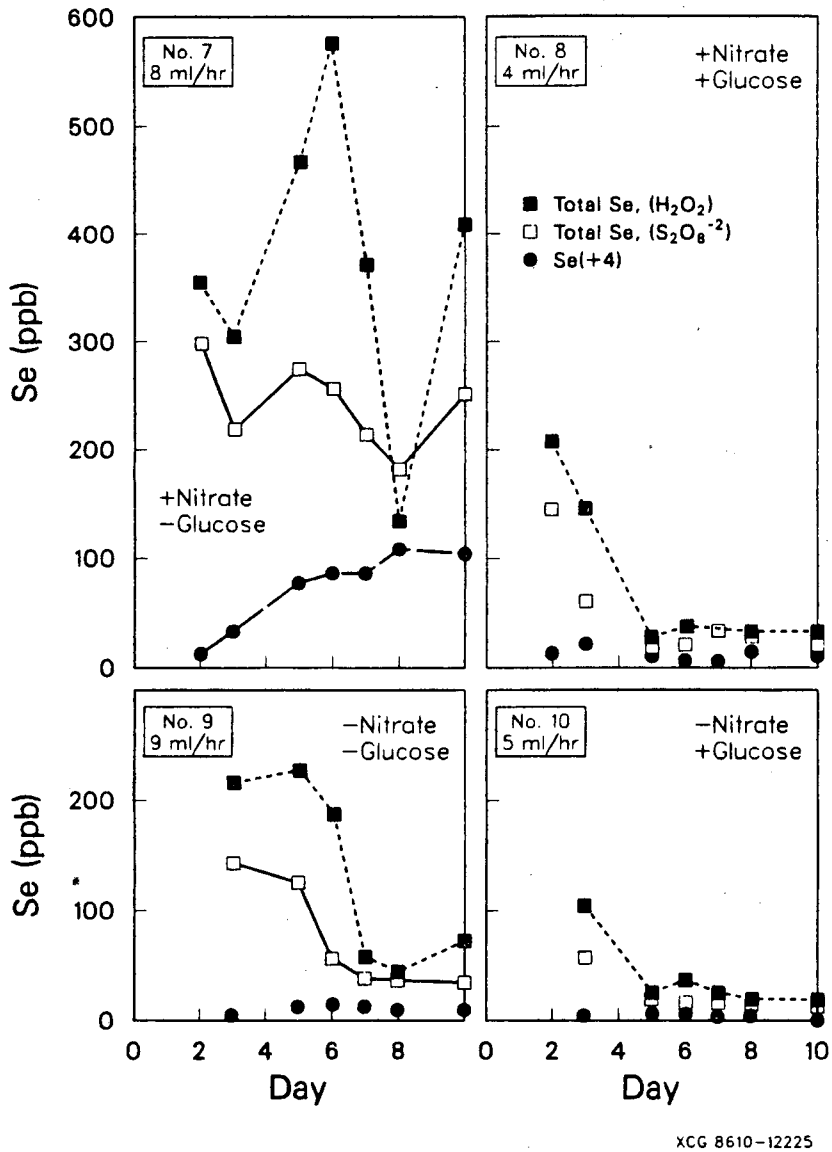


Figure 4.2. The effect of nitrate and organic matter upon removal of selenium from water. Figures 4.2, 3, and 4 reproduced from Weres et al. (1987).

and 1000 ppm glucose added to it. The added glucose maintained a black sediment with excellent selenium-removal capability. Bleaching was restricted to a superficial layer where many gas bubbles were produced. Evidently, denitrification was completed in this superficial layer, and the deeper sediment was protected from oxidation. Column No. 10 received synthetic brine without nitrate, but with glucose added. The sediment in this column remained black with no bleached zone evident, and selenium removal was excellent.

Evidently, denitrifying microbes catalyze the reaction of nitrate in the water with organic matter in the sediment. Eventually the sediment is bleached and loses its ability to sequester selenium, and may actually release selenium to the water. Providing an external supply of organic matter to the denitrifying organisms protects the sediment from oxidation and preserves its ability to sequester selenium. Further experiments established that much smaller concentrations of glucose are able to protect the sediment from bleaching by nitrate; for example, 50 ppm glucose will reduce 36 ppm nitrate.

Incidental to work on water treatment for selenium removal, the nitrate mediated breakthrough of selenium to groundwater was modeled in a pilot plant. Figure 4.3 depicts a small pilot plant used in the water treatment research described by Weres et al. (1987). Essentially, the large tank contains an ecological and geochemical model of the deep water, *Chara* vegetated areas of Kesterson Reservoir. The pilot plant was installed on a sunny roof-top at LBL. A six inch layer of black sediment taken from a deep water area of Kesterson Pond 4 (when it was still wet) was placed at the bottom of the tank, on top of the layers of sand and gravel. The tank was filled with agricultural drain water. A Kesterson-like ecosystem of *Chara*, diatoms, zooplankton and mosquito fish was maintained in the tank. Water slowly percolated down through the mud layer and treated water was removed from the bottom of the tank. Additional water was pumped into the tank from the make-up barrel as needed to maintain a constant water level. These experiments were conducted in the fall of 1986.

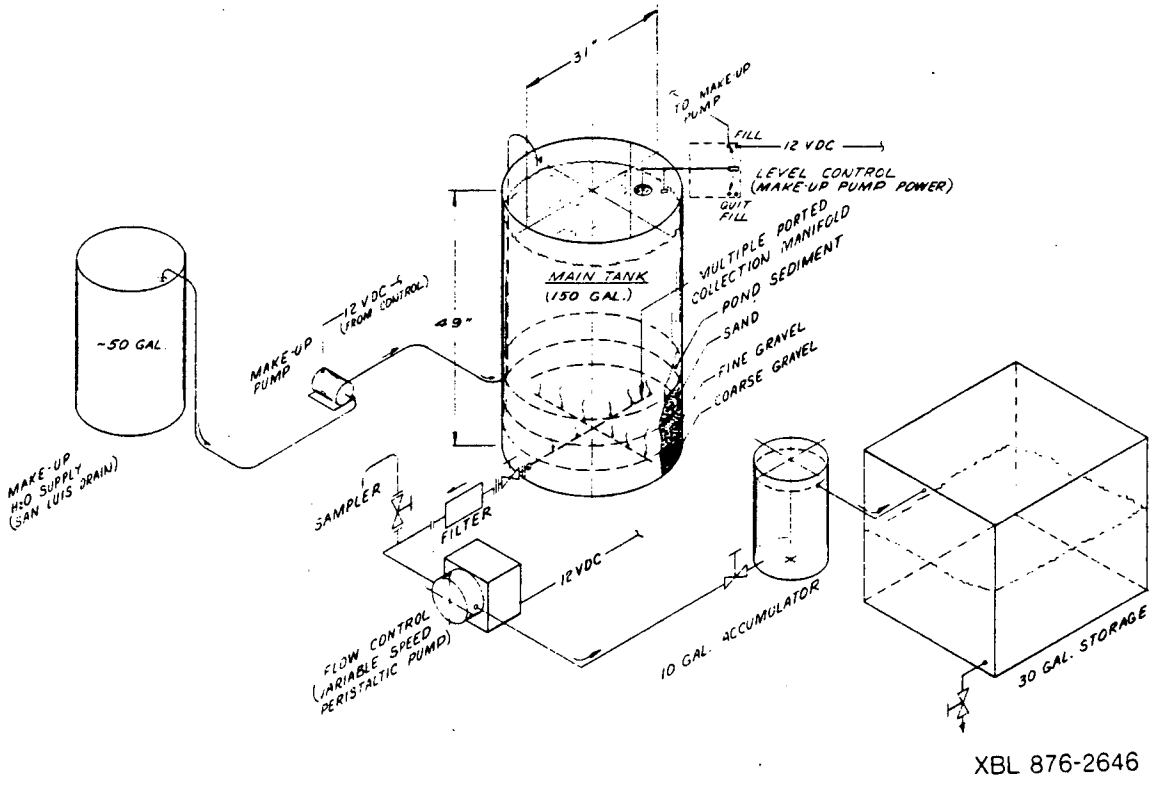


Figure 4.3. A pilot plant for removing nitrate and selenium from water.

After six weeks of successfully treating water averaging about 150 ppm nitrate the system was put on a high nitrate water feed, containing about 560 ppm nitrate and 400 ppm selenium. As expected, the high nitrate concentration destroyed the ability of the sediment to remove selenium from the water. The resulting breakthrough of selenium and nitrate is shown in Figure 4.4. The cluster near 0 ppm nitrate, 8-15 ppb selenium includes 8 closely spaced points collected through November 4. Selenium and nitrate break through from November 11 on. As in the groundwater data reviewed in Section 3.2.2, a strong association of selenium with nitrate is evident; low selenium is associated with low nitrate and vice-versa.

4.4. Laboratory Demonstration of Selenium Fixation in Mineral Soil from Kesterson Reservoir

The experiments described in the preceding Section dealt with selenium removal in superficial, organic matter-rich pond bottom sediments. These deposits are typically 1-2" thick, and rarely more than 6" thick. They are underlain by mineral soil which contains very little organic matter, and consists of clay, silt and sand mixed in varying proportions. The black color of dispersed pyrite extends from one inch to one foot below the organic-rich sediments into the mineral soil, indicating downward migration of hydrogen sulfide and perhaps other reducing agents. Below that the mineral soil is gray or yellowish-gray indicating the absence of sulfides.

In salt grass and playa areas seasonal drying causes oxidation and decomposition of organic matter, and prevents its accumulation. The soil in these areas contains a modest amount of organic matter in the first inch, and much less below that. None-the-less, the deep groundwater underlying areas of playa and saltgrass is nearly everywhere free of selenium or nitrate, indicating that effective selenium and nitrate removal mechanisms function here as well, without a superficial, organic-rich layer. Evidently the mineral soil is also able to take selenium and nitrate from the water percolating through it. The results of the Pond 1 experiment, described in Section 3.4 of this report, are consistent

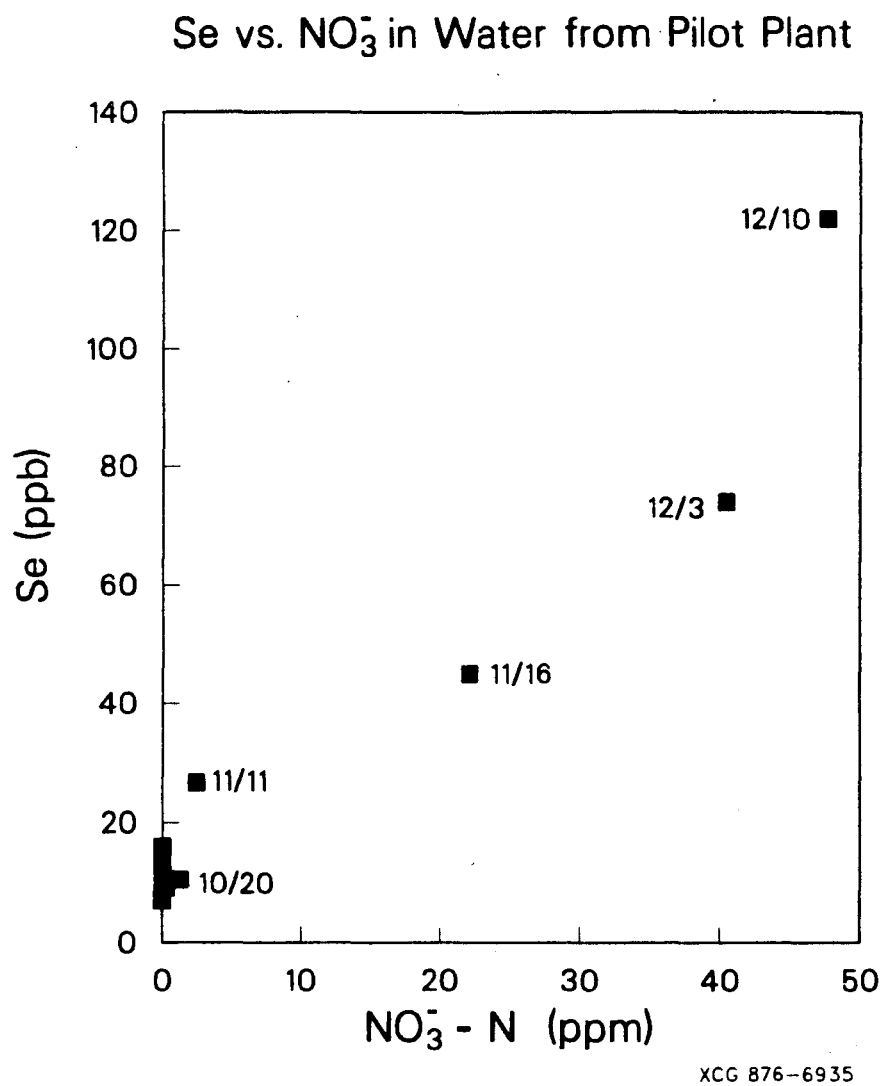


Figure 4.4. Selenium and nitrate concentration exiting the water treatment pilot plant. Each point is labeled with the corresponding date in 1986.

with this conclusion.

We have demonstrated that nitrate may cause selenium to enter the groundwater, but the evidence presented above has no bearing on the question of how far the selenium will get once in the groundwater. The fate of the plume, including how far it travels before it disappears, will be determined by the chemical interaction of selenium and nitrate in the contaminated groundwater with mineral soil deep in the aquifer. A series of laboratory experiments were conducted to explore these questions.

Glass columns 1" diameter by 6" high were used (Biorad Econocolumns). The bottom of the column is fitted with a porous disk which supports the weight of the sediment, and a plastic cap with a Luer fitting. The column was filled with a sediment slurry dispersed in simulated SLD brine without selenium or nitrate. The slurry was allowed to settle for one or more days, ultimately producing a sediment column approximately 4 inches high. The top of the column was closed-off using a Bio-Rad flow adapter, a device which provides an air-tight connection from a porous disk held flush against the top of the sediment in the column to a 1/16" plastic tube. There was no air space at the top of the column. A collapsible intravenuous fluid bottle suspended 0.5 to 1.5 meters above the top of the column was used as the brine reservoir. The brine was deaerated and transferred to the bottle with nitrogen pressure without exposure to air. This arrangement allowed deaerated solutions to be provided to the column. Flow rate was adjusted by adjusting the elevation of the reservoir bottle. In most cases the flow rate allowed approximately 30-40 hours residence time in the sediment (about 15-20ml/day $\approx$ 0.6-0.8 pore volumes/day). The brine going in and out of the columns was analyzed for selenium and nitrate.

Nitrate was determined by the UV absorption method. Total selenium and Se^{+4} were determined by AAS as with other water samples.

Initial experiments were performed using mineral soil collected in Pond 1 at site UZ-1 from the depth interval 13 to 26" in May 1987, when the site had been flooded for

several months. This soil is a clay loam with no visible organic matter and yellowish gray in color. In this area, sulfidic streaks never extend more than about 4" below the surface. The hydraulic conductivity of this soil estimated in our experiments was roughly 1 meter/year. While this soil is quite shallow, it resembles the mineral soil deeper in the aquifer closely, and has no apparent resemblance at all to the superficial black sediment found elsewhere in the Reservoir.

Figure 4.5 illustrates the removal of Se^{+6} from deaerated brine which contained 100 ppb Se^{+6} and no nitrate; approximately 96% of the selenium was removed with a residence time of approximately 30 hours. In a parallel experiment using an identical column Se^{+4} was removed equally well (not shown).

An identical column was provided with brine that contained approximately 115 ppb Se^{+6} and 50 ppm nitrate (Figure 4.6). Passing this solution through the sediment decreased the total concentration of selenium only by about 25 ppb, to 90 ppb. An additional 8 ppb was converted to Se^{+4}. Thus, nitrate greatly diminished the ability of the mineral soil to remove selenium from the water but did not stop the reaction completely. After two weeks the brine was changed to 120 ppb Se^{+6} without nitrate (Figure 4.7). The concentration of selenium in the effluent decreased very rapidly, dropping to about 2 ppb after two weeks. Therefore, the inhibiting effect of nitrate is completely reversible, if nitrate exposure is of limited duration. This observation indicates that the effect of nitrate is not limited to oxidizing the sediment and exhausting whatever reducing agent may be present. Apart from oxidizing the sediment, nitrate also directly inhibits the selenium reduction mechanism in a reversible manner.

A third identical column (C) was provided with brine that contained 100 ppb Se^{+4} and 50 ppm nitrate. The Se^{+4} was removed from the water as in the absence of nitrate, with only 4 ppb coming through the column. Part of the nitrate was removed from solution, and the concentration of nitrate in the effluent steadily declined, dropping below 1 ppm after about 20 days. After four weeks the brine was modified to contain

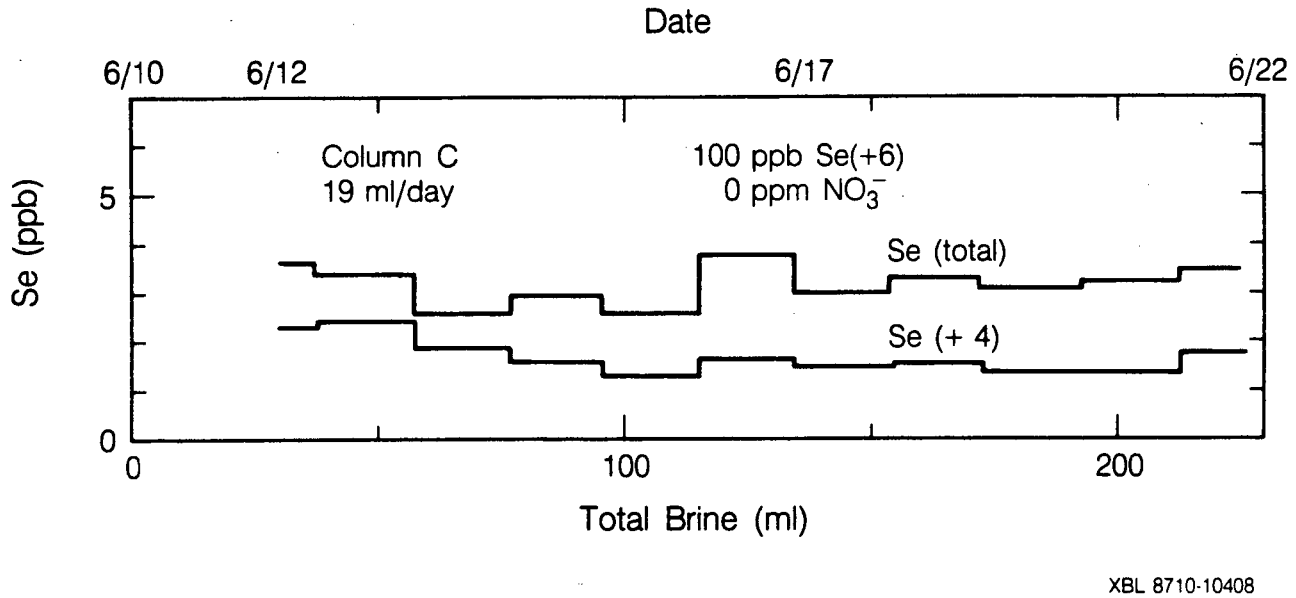


Figure 4.5. Selenium concentrations coming out of a soil-filled column. Brine entering the column contains 100 ppb Se^{+6} and no nitrate.

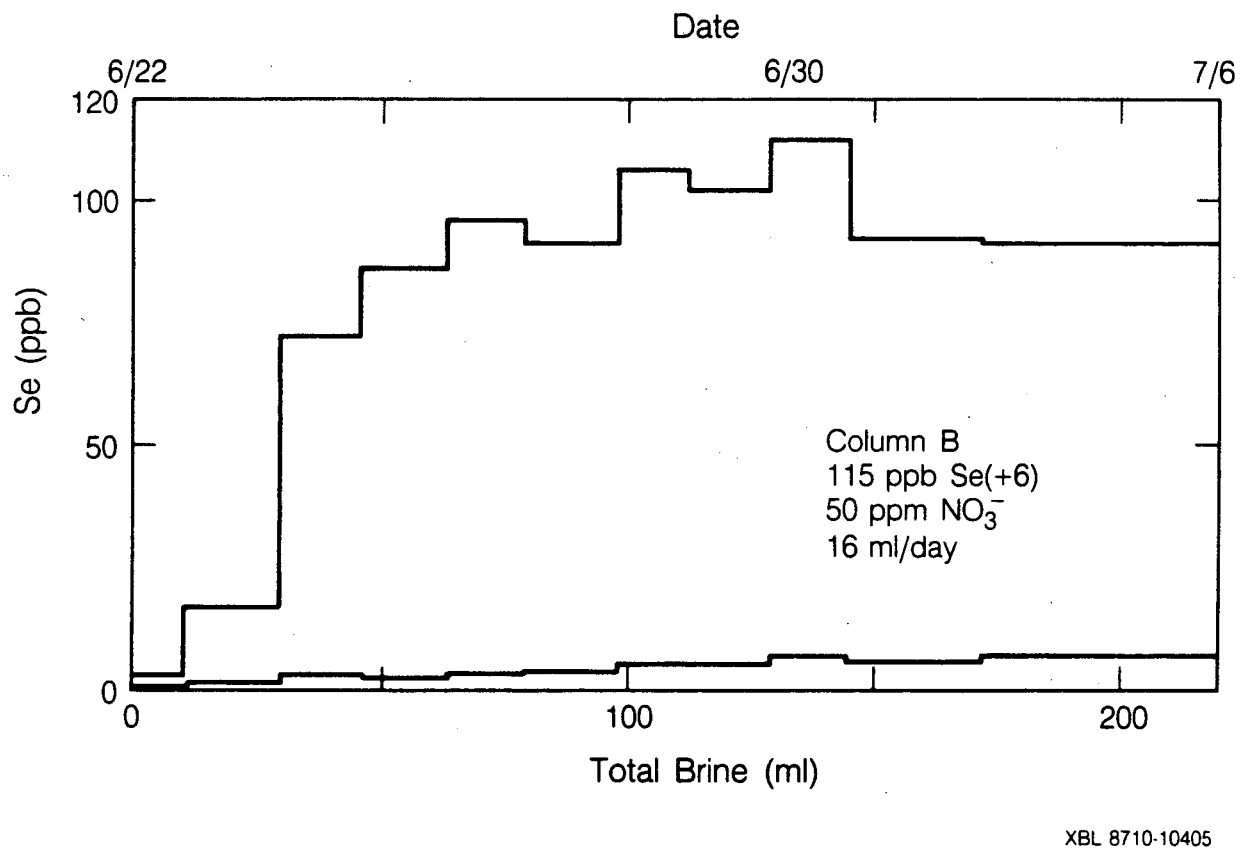


Figure 4.6. Selenium concentrations coming out of a soil-filled column. Brine entering the column contains 115 ppb Se^{+6} and 50 ppm nitrate.

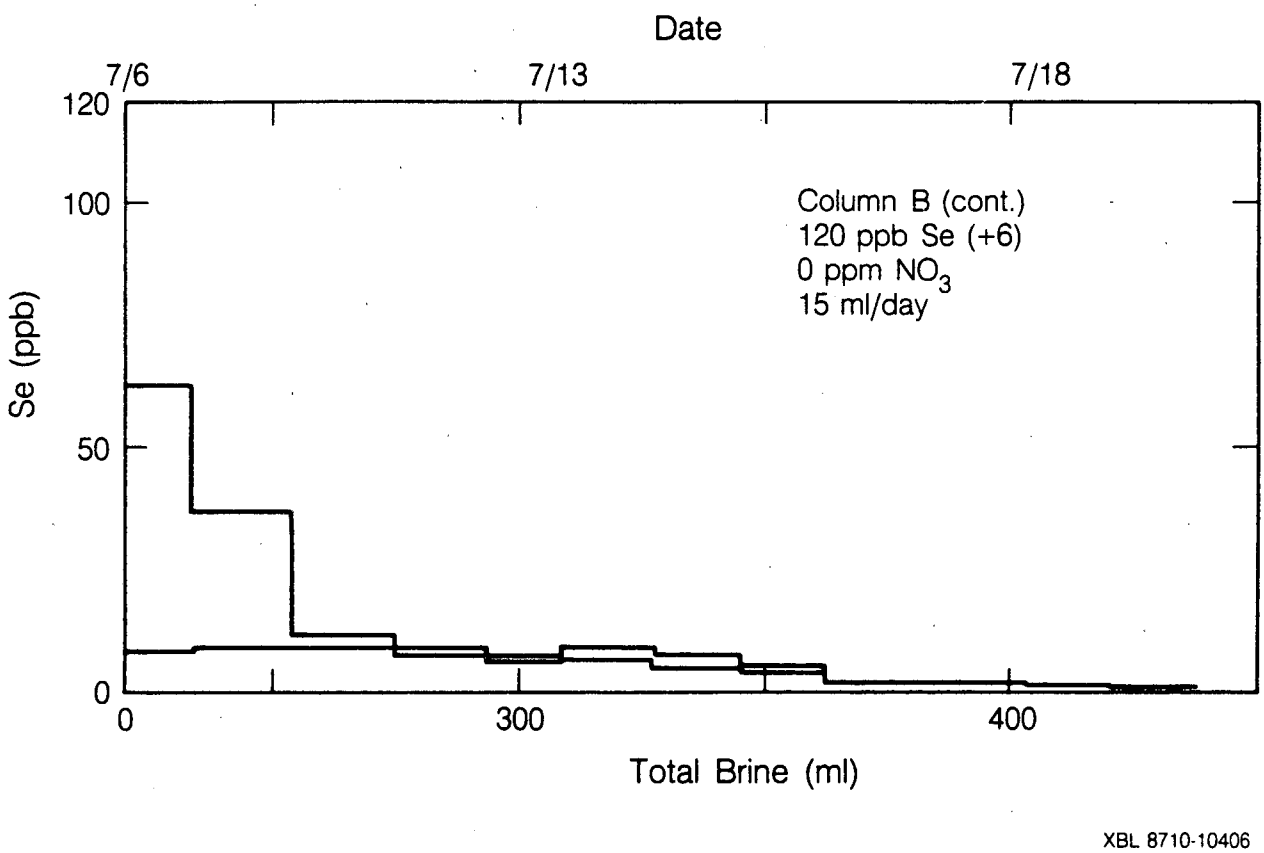


Figure 4.7. Selenium concentrations coming out of a soil-filled column after nitrate was removed from the brine entering the column.

100 ppb Se^{+4} plus 100 ppm nitrate and the experiment was continued for another four weeks. With this nitrate concentration, total selenium in the effluent brine increased to about 7 ppb, including about 2 ppb of Se^{+6}. About one-third of the nitrate was removed from the brine. Alltold, this column received 65 mg of nitrate over an eight week period, and removed about 25 mg of nitrate from the brine, which corresponds to 0.5 kg nitrate removed per m^3 sediment volume. Finally, the column was provided with brine containing 100 ppb Se^{+6} and no nitrate. Removing nitrate partially restored the sediment's ability to remove selenium from the water, with 10 to 90 ppb total selenium in the effluent brine.

Another column (D; not shown) was filled with sediment from the same source which had been heat sterilized as a slurry in an autoclave for about 4 hours at 150 °C. The heat sterilized sediment removed Se^{+4} from the water as well as the unsterilized sediment (3-5 ppb Se(tot) in the effluent), but completely lost its ability to remove Se^{+6}. This result suggests that Se^{+4} is removed by an inorganic process - very likely adsorption upon oxides and other minerals - while Se^{+6} is removed by a microbially mediated process. Alternatively, microbes may convert Se^{+6} to Se^{+4}, which is then removed from the brine by inorganic reactions; our results are consistent with this interpretation.

The ability of severely dried mineral soil to take selenium from water was tested using an archived sample collected in the same place and depth in August 1985, when the site was very dry. This soil had been dried throughly, and was crushed and sieved to 30 mesh or finer before use. Brine containing 100 ppb Se^{+6} and no nitrate was passed through a column of this soil for 11 days with no removal of selenium from solution evident (not shown).

The ability of organic matter to "rejuvenate" oxidized sediment was tested. The column was flushed with a brine containing 1000 ppb Se^{+6}, 0.1% sucrose, and 55 ppm fertilizer (mostly ammonium sulfate), and then allowed to stand for three weeks with that solution in it. Some diffuse black zones developed in the sediment during that time,

indicating reduction of sulfate to sulfide. At the end of that time brine containing 100 ppb Se^{+6} but no nitrate or sucrose was provided to the column. The selenium in the first effluent was about 12 ppb, and rapidly dropped to 2 ppb and remained at that level through the end of the experiment three weeks later. The initial 1000 ppb Se^{+6} had been almost completely removed from solution, and the sediment demonstrated its ability to remove nearly all Se^{+6} from additional brine. This result may be compared to the results of the Pond 1 experiment, where the dessicated soil regained its ability to remove selenium from the water, albeit slowly and incompletely, about six weeks after the Pond was refilled with water. Adding sucrose obviously accelerated and enhanced "rejuvenation" of the selenium sorbing properties of the sediment.

In summary:

1. Removal of Se^{+4} from the water is an inorganic process, which is affected little by the presence of nitrate.
2. In these experiments removal of Se^{+6} was shown to be a microbially mediated process. A parallel, strictly inorganic selenium removal process cannot be excluded, but if present, it is very much slower than the microbial process, at least in this particular soil sample.
3. Nitrate is a specific inhibitor for removal of Se^{+6}. This effect is completely reversible after a brief interval of nitrate exposure.
4. The sediment is able to remove a substantial amount of nitrate from the water as well. The denitrification process has an induction period of several days.
5. Severely drying the sediment destroys its ability to remove Se^{+6}. The damage caused by drying is readily reversed by rewetting the sediment and exposing it to sucrose.

Some of these experiments will be repeated using freshly collected soil samples from deeper strata of the upper aquifer, to determine if these conclusions are also valid for the upper aquifer.

4.5. Volatilization of Selenium from Northern Pond Soils

Early criticism of the "Dry-Flex" component of the Flexible Response Plan (USBR, 1986) focused on the perception that the total mass of selenium in the near-surface soils

would not be decreased and that soluble selenium could contaminate the ephemeral pools that would form during the winter months. In May of 1987, we began a series of laboratory experiments designed to address these concerns and assist in developing a plan for managing the inventory of selenium in the northern pond soils. A review of possible management options indicated that enhanced biological cycling of organic matter in the northern pond soils offered the possibility of decreasing the selenium burden of the area by selenium volatilization while simultaneously decreasing the amount of soluble selenium in seasonal ponds. Review articles (Alexander, 1973; Wood, 1974) point to the importance of microorganisms in the effective recycling of several naturally occuring toxic elements, and suggest that attending to the biological cycles of these elements can provide means for regulating both their toxicity and their distribution.

Enhanced biological cycling of organic matter in moist or moistened northern pond soils can be achieved by addition of organic amendment and nitrogen fertilizer, thus increasing the biomass of soil microorganisms (bacteria, actinomycetes, fungi, etc.) and increasing the rate of biological selenium cycling (Doran, 1982). The biological selenium cycle is tied to the biological cycles of carbon, nitrogen, and sulfur, and the rate of cycling of these elements is proportional to the level of microbial activity in soils.

The idea of accelerating selenium volatilization from Kesterson soils by amendments that stimulate the activity of soil microorganisms was suggested early this year by U. Karlson and W. T. Frankenberger of the University of California at Riverside. Their laboratory data demonstrated that with the addition of various carbon amendments and moisture, volatilization rates could be measureably enhanced (Karlson and Frankenberger, 1987). The climate and geography of Kesterson are favorable for decreasing its selenium burden by biological cycling. Its almost level terrain, high mean annual temperature, proximity to sources of irrigation water, and long growing season for plants are all positive factors for this management option.

4.5.1. Experimental Design and Results

The laboratory experiment on selenium volatilization from Pond 9 soil with 6.6 μg/g total selenium began on May 16, with the dual purpose of using a Kesterson soil to confirm the results of Karlson and Frankenberber (1987) and of providing guidelines for field experiments at Kesterson.

Eight duplicate treatments, shown in Table 4.7, were set up in diffusion flasks (Figure 4.8). The "Control" flasks received no organic amendment but water was added to keep the soil moist (each flask contained 250 g of soil and 50 g of water). The amended flasks received, in addition, 4% of organic amendment in the form of salt grass (Distichlis) clippings, aerated sewage sludge, or sucrose. The organic amendment contained approximately 3 g of organic carbon. In order to test the effect of fertilizer nitrogen on selenium chemistry, half of the flasks were fertilized with 0.71 g of ammonium sulfate containing 0.15 g of nitrogen. The resulting carbon to nitrogen ratio in these flasks was approximately 20:1. All of the flasks were incubated at room temperature (26-28 $^\circ$ C).

At approximately one month intervals the activated carbon was removed from half of the flasks and the volatilized selenium was washed off the filters with water. The concentration of selenium in the wash water was measured using AAS and the amount of selenium volatilized was calculated from the measured selenium concentration and the volume of wash water. This analytical method has not undergone QA/QC testing and documentation, but preliminary tests suggest that recovery of volatile selenium using this wash method is in the range of 50 to 60%. Consequently, the volatilization rates reported here are lower than the actual value by a factor of nearly 2. A detailed description of experimental methods is given in the 6th Progress Report (LBL, 1987), with results of the experiment to the 87th day of incubation.

New data from this experiment are shown in Table 4.7 with associated Figures 4.9a,b and in Table 4.8 with associated Figures 4.10a,b.

Table 4.7. Volatile selenium collected from all flasks on the 105th day.

Flask	Amendment	0-105th Day Total ng Se	Day of Incubation			
			105th day**		130th Day	
			ng Se	rate*	ng Se	rate*
1	Control	3258	0	0	8183	1.64
2	Control	4352	0	0	6548	1.31
3	Straw	9463	238	0.05	29704	5.94
4	Straw	9633	0	0	17266	3.45
5	Sludge	4296	0	0	2786	0.56
6	Sludge	4531	0	0	3226	0.65
7	Sucrose	27220	8849	1.77	8922	1.78
8	Sucrose	23917	1316	0.26	5717	1.14
9	Control	21798	5807	1.16	4287	0.86
10	Control	22712	2012	0.4	6207	1.24
11	Straw	31638	2767	0.55	28583	5.72
12	Straw	37658	0	0	29612	5.92
13	Sludge	9707	2807	0.56	2572	0.51
14	Sludge	8317	0	0	2099	0.42
15	Sucrose	45653	20821	4.16	2900	0.58
16	Sucrose	54234	10634	2.13	30502	6.1

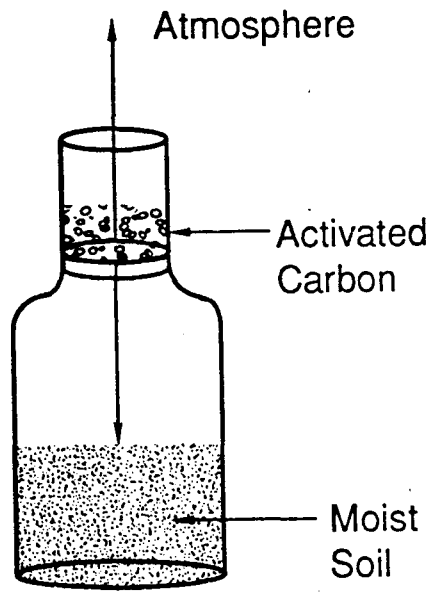
* ng se/g soil/day

** The 105th day data are for the period from 60 to 105 day for the odd number flasks and for the period from 87 to 105 days for the even numbered flasks.

Table 4.8. Trends in Laboratory Selenium Volatilization Rates from Pond 9 Soil. New amendment and/or fertilizer added at 105 days

Flask #	Period Duration / Treatment	Days						
		0-25	0-38	25-60	38-87	60-105	87-105	105-130
		25	38	35	49	45	18	25
		ng se/g soil/day						Odd/even mean
1,2	Control	**0.57**	0.52	**0.06**	0.04	**0**	0	1.48
3,4	Straw	**1.74**	1.22	**0.08**	0.04	**0.03**	0	4.7
5,6	Sludge	**0.59**	0.55	**0.19**	0.04	**0**	0	0.61
7,8	Sucrose	**1.75**	1.99	**1.38**	0.76	**0.98**	0.37	1.46
9,10	Cont.+N	**1.67**	1.68	**1.1**	0.81	**0.65**	0.56	1.05
11,12	Str.+N	**3.92**	4.21	**1.32**	0.58	**0.31**	0	5.82
13,14	Slud.+N	**0.43**	0.5	**0.68**	0.46	**0.31**	0	0.47
15,16	Sucr.+N	**0.97**	1.18	**2.94**	3.63	**2**	2.13	3.34

Data for odd numbered flasks are shown in bold face type.



XBL 8711-10458

Figure 4.8. Diffusion flask with activated charcoal vapor trap.

The "0-105 day total" column of Table 4.7 shows the amount of volatile selenium collected from each flask during the first 105 days of incubation. Comparison of quantity of selenium volatilized in duplicate treatment flasks indicates an overall random error of 12%, with a standard deviation of 8%.

The data reported under the heading "105th day" reflect a 45 day incubation period for odd numbered flasks and an 18 day incubation period for even numbered flasks. Therefore, they are not directly comparable but both of them demonstrate that volatilization rates were low at the end of the 105 day incubation period. The data reported under the heading "130th day" reflect the effects of adding a new round of amendments and fertilizer to each of the flasks.

The average value of the quantity of selenium volatilized for the data presented in Table 4.7 indicate an overall threefold increase in selenium volatilization due to fertiliza-

tion with ammonium sulfate (10,800 ng of selenium without nitrogen fertilizer and 29,000 ng of selenium with nitrogen fertilizer). Fertilized straw and sucrose treatments volatilized the most selenium, and the fertilized sucrose treatment surpassed the fertilized straw treatment by a factor of 1.4.

Figure 4.9a shows final volatilization rates for the first round of incubation that ended on the 105th day. On the 105th day a second round of amendments and fertilizer was applied, repeating the initial treatments, but with two kinds of fertilizer. This time ammonium sulfate was added to all of the odd numbered flasks, while an N-P-K fertilizer (nitrogen-phosphorus-potassium 15-30-15) was applied to all of the even numbered flasks. After an additional 25 days of incubation, volatilized selenium was extracted from the activated carbon traps and measured by AAS. Figure 4.9b shows the volatilization rates from the first 25 days of this second round incubation of amended and fertilized Pond 9 soil.

All of this data has been collated and summarized in Table 4.8 and Figures 4.10a and 4.10b, which show volatilization trends for the whole incubation period. Fertilization with ammonium sulfate generally gave higher selenium volatilization rates and sustained volatilization for a longer period of time, compared to samples incubated without fertilizer.

Straw (salt grass clippings) and sucrose were both effective in stimulating volatilization. Straw acted more quickly and resulted in granular soil structure. Soil structure is an important factor for field experiments because it affects tilling, aeration, permeability, and many other factors related to biological activity in the soil. In this laboratory experiment both straw and sewage sludge amendments appeared to favor granular structure in the soil samples. Sucrose amendment created balls about 1 cm in diameter that were, nevertheless, able to volatilize selenium.

Volatilization rates, with the exception of rates for sucrose-amended and fertilized samples, had generally decreased to low levels before 105 days, as easily metabolized

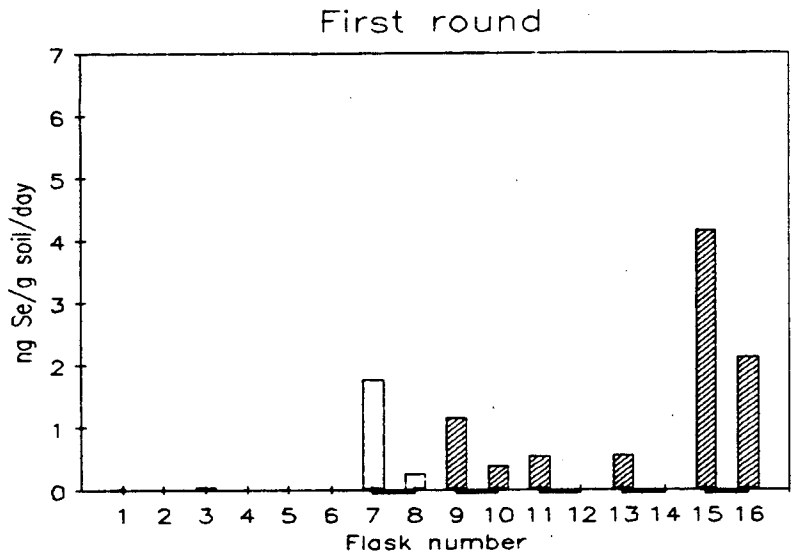


Figure 4.9a. Selenium volatilization rates from Pond 9 soil after 105 days of incubation. Flasks 1-8 received no fertilizer (white bars). Flasks 9-16 received ammonium sulfate (shaded bars). Treatments are shown in Table 4.7. Water lost by evaporation during incubation was periodically replaced with distilled water. Soil in the flasks was stirred to distribute the moisture evenly.

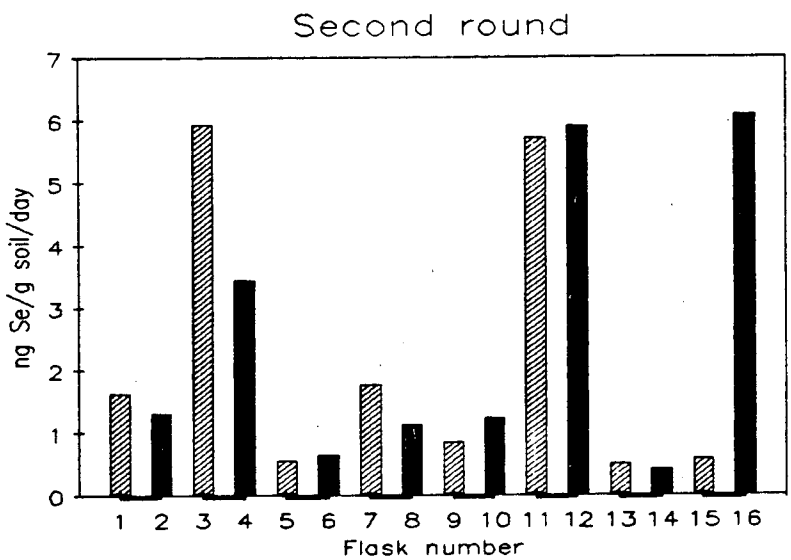


Figure 4.9b. Selenium volatilization rates from Pond 9 soil 25 days after adding a new set of carbon amendments and nitrogen fertilizer (130 total days of incubation from the beginning of the experiment). Odd numbered flasks received ammonium sulfate, NPK 21-0-0 (shaded bars). Even numbered flasks received NPK 15-30-15 (solid bars). All flasks received the same amount of nitrogen (0.15 g).

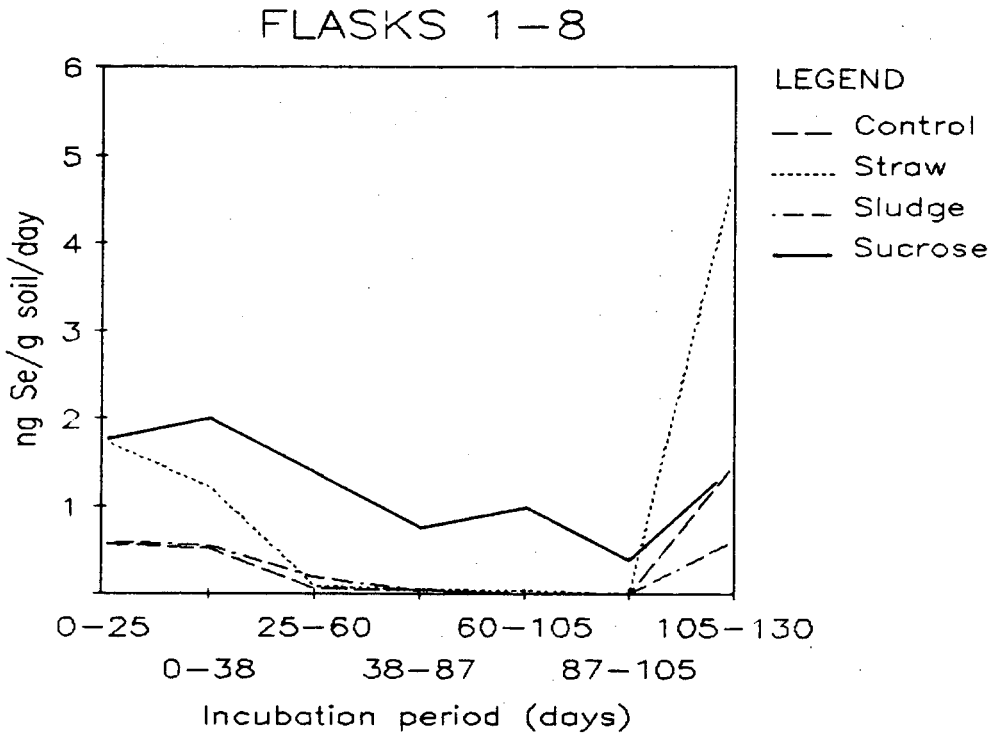


Figure 410a. Selenium volatilization rates from Pond 9 soil during the 130 day test period for the flasks incubated without nitrogen fertilizer.

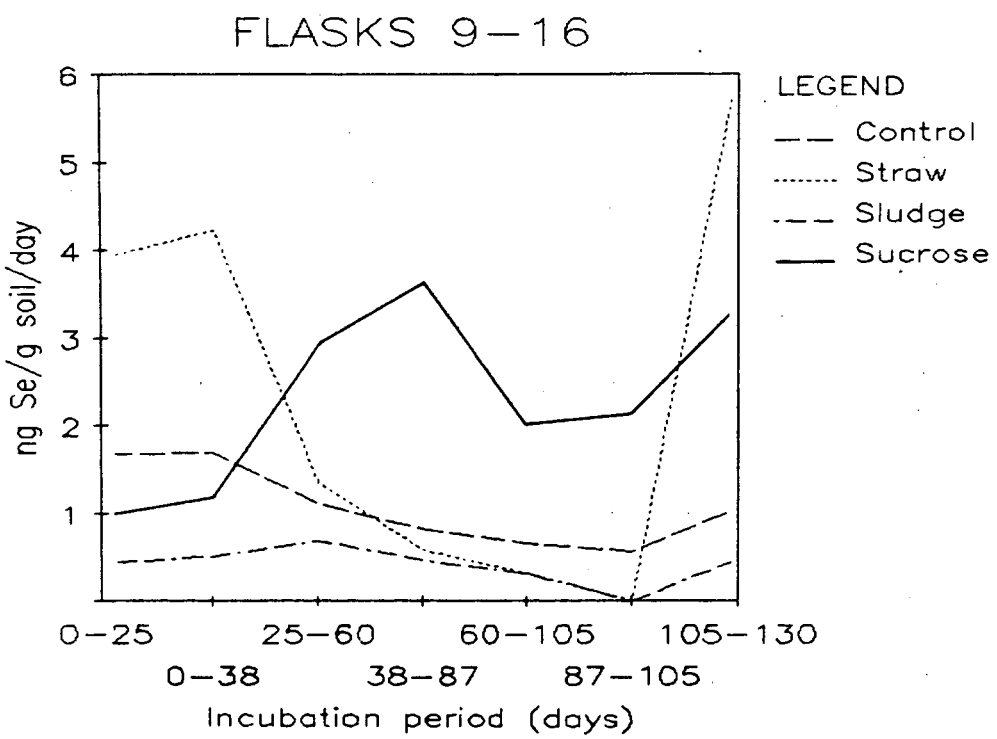


Figure 4.10b. Selenium volatilization rates from Pond 9 soil during the 130 day test period for the flasks incubated with nitrogen fertilizer.

selenium was depleted, or as the soil microorganisms ran out of carbon and nitrogen substrate.

The data show relatively high volatilization rates resulting from the second round of amendments. These second round volatilization rates suggest that enhanced selenium volatilization from soil can persist if the soil microorganisms are maintained with carbon substrate, nitrogen fertilizer, and the conditions of warmth, aeration, and moisture that were provided in the laboratory.

Two possible explanations for the rehabilitated second round volatilization rates can be offered. Firstly, mineralization (release of substrate) and immobilization (sequestration of substrate) can proceed simultaneously where soil microorganisms are active, and a dynamic balance is maintained that allows diffusive losses of volatile selenium metabolites from the soil. Secondly, the conditions that enhance biological cycling are favorable for selenium oxidizers (Janzen and Bettany; 1987a, 1987b; by sulfur:selenium analogy) as well as for selenium reducers so that a dynamic balance is maintained that prevents rapid accumulation of insoluble forms of selenium. This analogy between sulfur oxidation and selenium oxidation is proposed cautiously as a possible explanation because no extensive studies of selenium oxidation have been done (Doran, 1982).

4.5.2. Estimate of Selenium Removal by Volatilization

There are many factors that influence the rate at which selenium can be volatilized from the soil (e.g., temperature, moisture content, salinity, season, selenium speciation, etc.) that have not yet been systematically investigated. A review of available literature, as well as data from preliminary laboratory and field measurements (LBL Progress Report 6) indicate that all of these factors have a large effect on volatilization rates. Nevertheless, some simple calculations can provide an indication, exclusively for the purpose of discussion, of the degree to which selenium volatilization could contribute to the reduction of the near-surface selenium inventory.

For this purpose let us assume that 100 ng Se per gram of soil was lost by volatilization during 25 days of incubation. With this volatilization rate, assuming first order kinetics, the time required to reduce by half the amount of selenium in our sample of Pond 9 soil, with a total selenium concentration of 6.6 μg/g, would be 3 years. In the following 3 years the total selenium concentration would be diminished from 3.3 μg/g to 1.7 μg/g, and so on. These estimates assume that the volatilization rate reported here can be maintained for an extended period in the field, which can only be verified by field experiments. Extrapolation of laboratory data to field conditions is complicated because both positive and negative factors for selenium volatilization will be encountered in the field. For example, reduced night and winter temperatures will tend to decrease volatilization rates, but wetting and drying of soils will tend to increase the rates (Sharma and Singh, 1983). Furthermore, the relationship between total selenium concentration and selenium volatilization rates has not yet been studied systematically. Field conditions could yield rates either faster or slower than rates indicated by our assumption of first-order kinetics.

The literature on selenium cycling in nature, the laboratory data of Karlson and Frankenberger (1987), the experimental data presented here, the field measurements and laboratory experiments presented in LBL Progress Report 6, all indicate that volatilization of selenium from the Kesterson soils will gradually reduce the selenium inventory. These experiments also demonstrate that volatilization rates can be enhanced if suitable organic matter, fertilizer, and water are periodically added to the soils. At the present time, insufficient data are available to determine the length of time needed to "clean-up" soil in this way, or to properly evaluate the practical feasibility of stimulated volatilization as a clean-up option. The field and laboratory experiments currently being conducted by various research groups will help resolve these questions.

5. ECOLOGICAL STUDIES

5.1. Introduction and Rationale

This report is a summary of the ecological research carried out at Kesterson Reservoir since October 1985, but it principally focuses on the spring 1986 - summer 1987 period. Most of the data has been reported in 6 quarterly reports.

The ecological studies were designed to provide a scientific basis for the decisions to be made by the USBR on the management of the Reservoir. We have assumed that selenium was the cause of deaths, deformities, and poor nesting success of water birds at Kesterson Reservoir. Our studies have focused on the pathways by which selenium passed from its origin in the agricultural drain water to the plant and animal food consumed by birds at the Reservoir.

By the time our main studies were commenced (spring, 1986) the supply of agricultural drainwater had been terminated and low-selenium water was being used as a water source. The exception was in July and August 1986 when high-selenium water remaining in the San Luis Drain was disposed of into the Reservoir. Thus, for all but a brief interval we measured the effects of a continually declining external loading of soluble selenium.

5.2. Brief Literature Review

We have reviewed about 100 formal publications on the ecotoxicological effects of selenium. They ranged from brief notes to complete books. Most reported studies in North America but some European data was surveyed. Where possible we also reviewed publications submitted, but not yet published, agency reports, and a few masters and doctorate theses. As might be expected the general thrust of these documents varied; some were concerned with selenium toxicity, some with selenium as an antitoxicant to mercury poisoning, some with detailed laboratory studies of toxicity at the sub-cellular level, and some with ecosystem-level data. This review will focus on those publications

most relevant to the situation at Kesterson Reservoir.

Early toxicity studies at Kesterson Reservoir by the USFWS concerned the discovery, extent, and probable causes of reproductive failures in waterbirds. In 1983 32% of the eared grebe embryos, 15% of coot embryos, and 3-6% of stilt and duck embryos were dead in the egg (Ohlendorf et al., 1986). Expected values for coot were given as 0.1-2%. Other measures of toxic effect included abnormal embryos in the egg (6% grebe, 9% coot, 7% stilt, and 4% ducks). The percentage of nests containing dead or deformed embryos ranged from 17-60%. This toxicity together with few sightings of young birds suggested almost complete nesting failure for "resident" birds (grebe and coot) which were reported as feeding almost entirely at Kesterson. Ducks and stilts which reportedly fed both at Kesterson and elsewhere (Ohlendorf et al., 1986) were more successful in breeding despite the presence of selenium in the food web. Where comparable, selenium levels in the livers and eggs of birds collected at Kesterson were about seven times higher than those collected at nearby Volta Reserve. The USFWS concluded that the higher selenium levels were the probable cause of reproductive failures at Kesterson.

Measurements of selenium in the lower trophic levels of aquatic organisms in Kesterson Reservoir were initiated by the USFWS in May and August, 1983 (Saiki and Low, 1986) and were extended to include biomass estimates in May, August, and December 1984 (Schuler, 1987). Selenium levels and some other elements including boron, arsenic, and cadmium were also measured on some samples (Schuler and Antony, 1987). These data form the baseline for selenium contamination levels up to the period immediately prior to cessation of regular drainwater flows in winter 1985-6 when the USFWS surveys reported selenium values as high as 370 ppm in mosquitofish and 310 ppm in *Ruppia* (widgeon grass) at Kesterson with generally elevated levels throughout the entire ecosystem as compared with Volta. Biomass and species diversity were similar between the two sites and, of the differences, most were accounted for by the saltier water at Kesterson.

In general, higher salinity decreases the species diversity in aquatic environments (Goldman and Horne, 1983 pp. 381-383). Even in the absence of selenium Kesterson Reservoir would always have been a greatly reduced habitat for many waterbirds due to greater water depths, high salt levels, lower invertebrate biomass, and overall poor water quality (Schuler, 1987).

Much laboratory and field mesocosm research on selenium dynamics has been carried out using the gamma-ray emitting radioisotope of selenium (^{75}Se). These studies do not measure the absolute quantity of selenium but rather the proportions of the added isotope in each ecosystem compartment. Early laboratory studies (Sandholm et al., 1973) indicated that the major uptake pathway of inorganic selenium in zooplankton and fish was through the food chain i.e. via algal uptake and not by direct uptake through the body or the gills. Extensive studies with ^{75}Se in mesocosms situated in a lake in Canada (Turner and Rudd, 1983; Rudd and Turner, 1983) found that most added selenium had reached the vegetation 60 days after addition and did not appear to recycle after that. In a related paper Klaverkamp et al. (1983) added six radioisotopes, including ^{75}Se, to a whole lake in the Experimental Lakes Area in Canada. They also concluded that direct uptake from soluble substances (including selenium), is not the main pathway for fish indicating a pathway via algal uptake. This conclusion was arrived at because although much selenium was present in organic form in the epilimniom of the lake, the patterns of body uptake of ^{75}Se did not follow those of the water. A plateau of selenium in fish was reached in 15 days for guts and, in 50 days for gills, blood, kidney, liver, and spleen concentrations. Hasslein et al. (1980) using the same experiment found that absorption and settling were the main selenium removal processes and there was no evidence of major redistribution of isotope by resuspension or settling over a year.

Many studies reported on the ecotoxicology of contamination by selenium, primarily from power station fly-ash disposal (Rogers et al., 1978; Babcock et al., 1983; Sorenson et al., 1984; Lemly, 1985), industrialization (May and McKinney, 1981), smelt-

ing (Burton and Phillips, 1981; Robberech et al., 1983; Wren, 1984), mining (Speyer, 1980), sewage effluent (Furr et al., 1981), and leaching of natural selenium deposits (Lowe et al., 1985). Most studies report concentration of selenium in some organisms but not many are of long enough duration to discover long-term effects.

Studies which report changes over time can be compared to changes seen at Kesterson Reservoir since 1983. Sorenson et al., (1984) showed that selenium declined from 13 to 8 ppb in the water of Belews Lake between 1976 and 1981 but predicts that the recovery of fish from previous selenium toxicity will not be as rapid. Structural components and organs with low-turnover of selenium may be the most affected. Lowe et al., (1985), reviewing national trends in fish selenium levels and other recent trends in the nation's rivers report no statistically significant changes over the last decade.

Detailed studies on the toxicity of various selenium compounds to a variety of aquatic biota are too numerous to review in detail here. Studies encompassed several trophic levels (Halter et al., 1980), several selenium compounds including organics (Palmer et al., 1973), several types of toxicity measurement (Hudson, et al., 1980), tests of natural communities in mesocosms (Salki et al., 1985), and more conventional pure culture laboratory bioassays (Glickstein, 1978; Dunbar et al., 1983; Reading and Buikema, 1983). However, it is not clear if these data can be used directly for predictions of effects in Kesterson. For example, the "safe concentration" of soluble selenium calculated by Reading and Buikema (1983) for the zooplankter, *Daphnia* was 200-400 ppb. For any depression of growth or mortality 800 ppb was required. These concentrations would agree with the UCB/LBL findings that *Daphnia* is sometimes superabundant in seasonal ponds in Kesterson where soluble selenium averaged as high as 250 ppb in spring 1987 (see above, Figure 2.6). However, Brooks et al., (pers. comm.) reported detrimental effects on *Daphnia* reproduction at less than 50 ppb. In contrast, Halter et al., (1980) showed that 160-280 ppb tripled the number of young *Daphnia*. Extensive whole community investigations by Salki et al. (1985) in Canada indicated that even 100 ppb of

soluble selenium had no effect on seasonal dynamics of planktonic crustacea (which included *Daphnia*. These investigators concluded that predation was the major influence in these mesocosm experiments.

Safe food-chain levels of selenium are unknown, but probably vary with the kind of organism of interest. The USFWS has selected 5 ppb dry weight as the safe selenium level for Kesterson food-chain organisms leading to fish, and 3 ppb for the bird food chain.

5.3. Methods

5.3.1. Experimental Approach

Three approaches were used in the ecological study:

1. Long and short term experimental treatments using Kesterson biota but in controlled laboratory conditions at SEEHRL.
2. Long-term experiments at the Reservoir comparing changes in selenium in a 1-acre enclosure isolated from selenium inputs (Pond 5E) and the surrounding area (Pond 5) into which a pulse of selenium was introduced in August, 1986.
3. Long-term comparisons between three disparate index sites in the Reservoir. Sites represented:
   - (i) permanently wet (deep) areas, Pond 5 index site
   - (ii) shallow areas which would have been wet only seasonally but which were kept continuously flooded for most of 1986-1987, Pond 7 index site
   - (iii) ephemerally wet (very shallow) pools with no augmented water supply, Pond 11 index site.

Seasonally wet habitats range from ephemeral pools to wetlands which contain water for much of the year. In this case we wished to distinguish between those habitats which would be used by shore birds (several inches deep water) and those which would not (over one foot deep). Many species of aquatic organism eaten by Kesterson shore

birds, such as soldierfly larvae, are only common in ephemeral pools, which exist for a few weeks or months. Ephemeral pools are thus defined here as a sub-set of seasonal wetlands. Although arbitrary, the distinction is very obvious ecologically. Ephemeral pools not only have an animal biota with species not found in seasonal wetlands, but also lack some biota typical of seasonal wetlands. For example, ephermeral pools do not have rooted plants such as *Ruppia,* which are abundant in seasonal wetlands.

Our studies in the field and in the laboratory reported here were concentrated in four areas. These were:

1. The measurement of selenium levels in the aquatic animals and plants.
2. The identification of as many as possible of the aquatic animals and plants.
3. The description of feeding habits of the more common aquatic animals.
4. The measurement of limnological parameters, such as temperature, salinity, dissolved oxygen, and some nutrients.

5.3.2. Site Selection

The sites selected for long-term study were chosen in spring 1986 in cooperation with USFWS to encompass the majority of habitat types present in the Kesterson Reservoir ecosystem. It is vital to remember that Kesterson Reservoir is better described as a marsh. This is an important distinction since the high degree of heterogeneity in marshes makes it much more difficult to obtain representative samples than in most other common aquatic ecosystems. The Kesterson system is divided by earthen berms into 12 zones that have been called "ponds," although not all of them contain water. The three index sites chosen represent permanent (deep) water (Pond 5), seasonal (shallow) wetlands now kept permanently wet (Pond 7), and ephemeral (very shallow) pools (Pond 11). In some ponds at Kesterson all three of these habitats are present in the same pond, but in general there has been more and deeper water in the southern, lower numbered ponds than in the northern ones. In addition, there is generally a higher selenium inven-

tory in the lower ponds because drain water was normally admitted via the lower ponds.

Pond 5 was chosen because it is the largest pond in the Reservoir and has a high selenium inventory in the sediments. The site in Pond 7 was chosen because it had an area of high sediment selenium underlaying vegetation typical of that in the shallow seasonal wetlands (most of which have lower selenium inventories). We intended to keep the Pond 7 index site flooded continuously, in order to determine the role of rooted plants in food chain selenium cycling. When the original site began to dry out due to low water supplies, an adjacent, wetter area was sampled, beginning in March, 1987. The site in Pond 11 was chosen because it was a very shallow pool system rich in insect larvae which formed the most popular food of shore birds at Kesterson.

The index sites (Figure 5.1) were sampled approximately monthly (while ponds remained wet) from spring 1986 through June 1987. On most occasions on each visit, triplicate quantitative samples of vegetation, aufwuchs, epifaunal invertebrates, and benthic invertebrates were collected from Pond 5 according to a stratified random design. Qualitative samples of fish and emergent vegetation were also obtained. A detailed statement of methods was given in the third progress report (LBL, 1986).

5.4. Results

5.4.1. Laboratory Microcosms

In order to learn about selenium depuration from contaminated Kesterson biota, we isolated specific components (usually exposed to selenium-contaminated sediments and low-selenium water) under laboratory conditions. These studies have enabled us to predict properties of selenium depuration before it occurs in the Reservoir because laboratory conditions of light and temperature largely eliminate seasonal effects.

Long-term 20-liter microcosm studies in the SEEHRL environmental chambers have now been run continuously for 17 months (February 1986 to July 1987) with sampling at approximately monthly intervals. Samples of the macroalga *Chara* (called *Nitella* in ear-

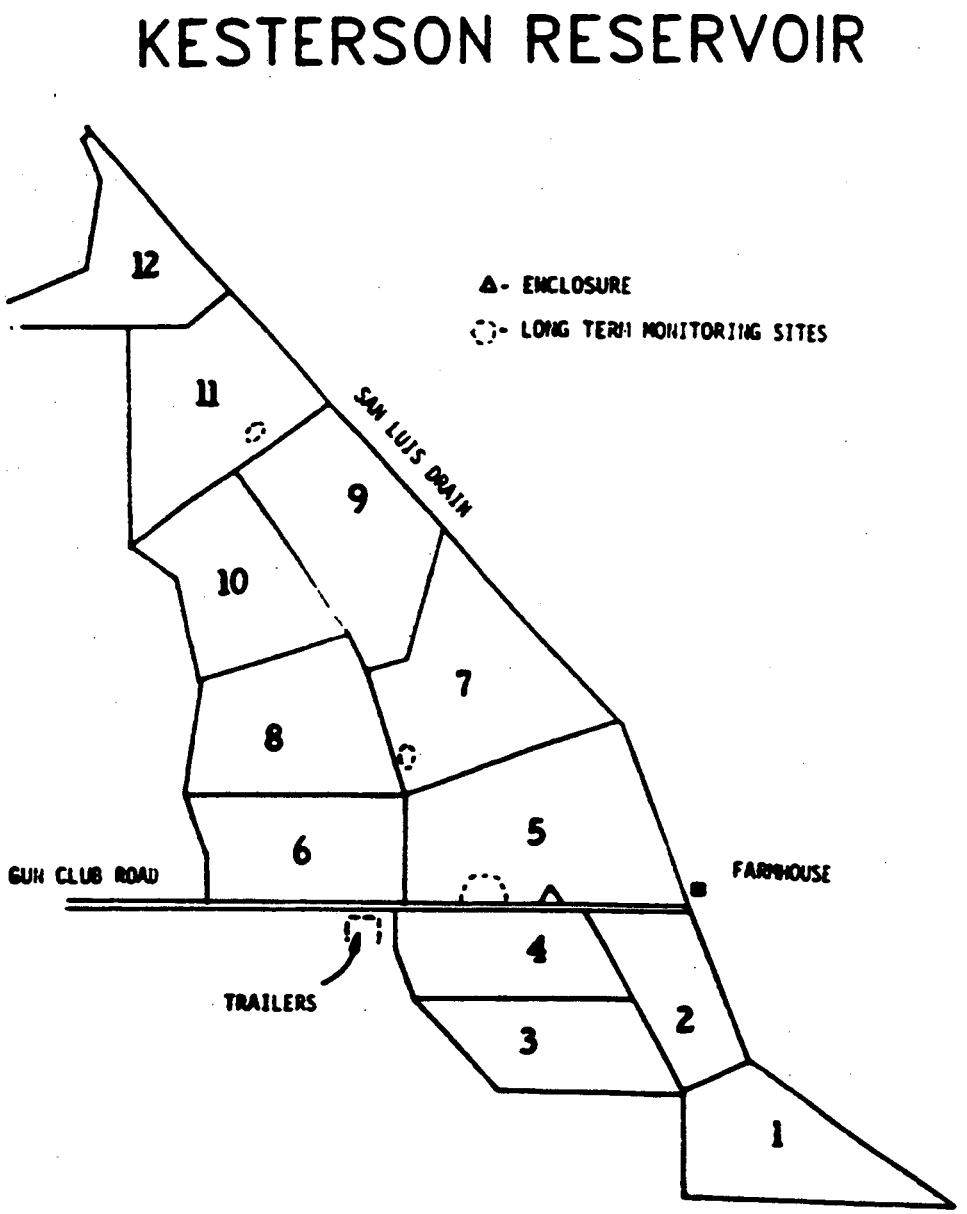
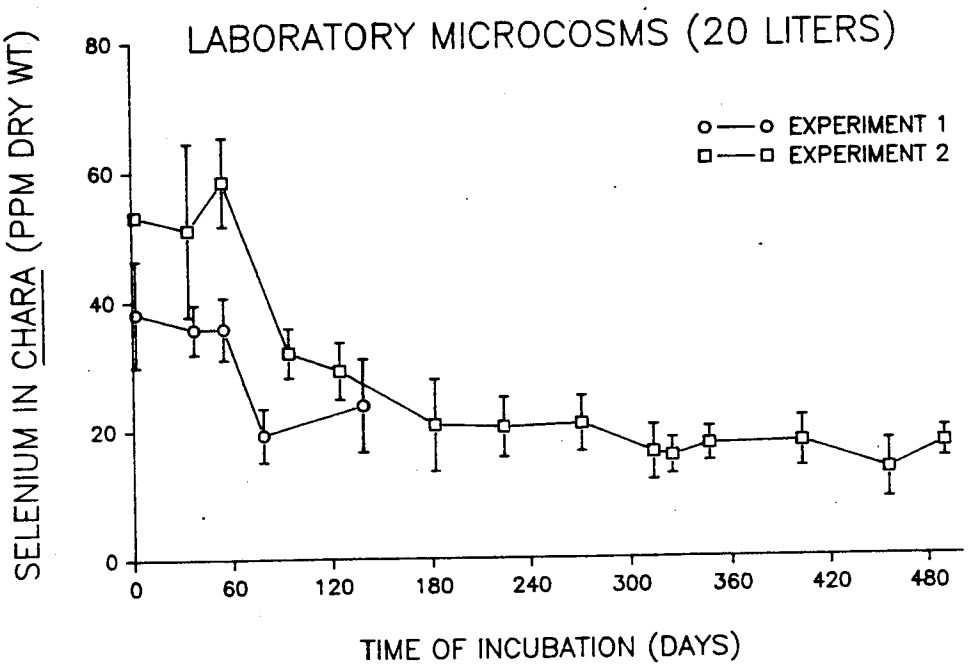


Figure 5.1. Sketch of Kesterson Reservoir showing the location of index sites where periodic biological samples have been collected. At each site triplicate samples were collected using a stratified random design.

lier reports) were collected at approximately monthly intervals. *Chara* stands up to 3 feet high and is the most common submerged plant in the soft-bottomed permanent water at Kesterson. It also provides habitat on and in which most of the aquatic animals and small plants reside. Samples of this plant have shown a large decline in selenium (Figure 5.2). After 17 months tissue selenium had dropped from 53.2 to 17.5 ppm. This represents a loss of 67% of the original load of selenium. The rate of decrease slowed as the lower concentrations were reached and now appears to be reaching a plateau at 13-20 ppm (dry wt selenium). Even though the precision of our measurements is high, there has been no significant decline over the last 100 days (Figure 5.2). Further declines are unlikely since the concentration of "soluble" selenium in the microcosms has also been stable at 10-15 ppb. This concentration is much higher than is now present in most of the Reservoir and is most likely an artifact of the laboratory conditions. Microscopic algae, which remove selenium from water in nature, do not grow well in the microcosms. Furthermore, there is no seepage out of the system, which helps to decrease the overall selenium inventory. Attempts to more closely replicate the selenium levels found in the Reservoir are in progress with these microcosms.

5.4.2. Kesterson Mesocosm (one acre enclosure)

A large-scale field experiment was begun in May 1986 to provide an estimate of the efficacy of addition of low selenium water in an ecologically more realistic system than the laboratory microcosms. A one-acre area (Pond 5E) of Pond 5 including both open water and cattails was enclosed by an earthen berm. Its water was replaced by low selenium ground water pumped from 40 ft beneath the pond. The timing of the closure of Pond 5E proved to be fortuitous, since the enclosure was isolated from the large pulse of high selenium water that entered the Reservoir when the San Luis Drain was flushed in July and August 1986. The enclosure thus provided an illustration of the time course of selenium cycling through the marsh food chain in the absence of new selenium inputs.



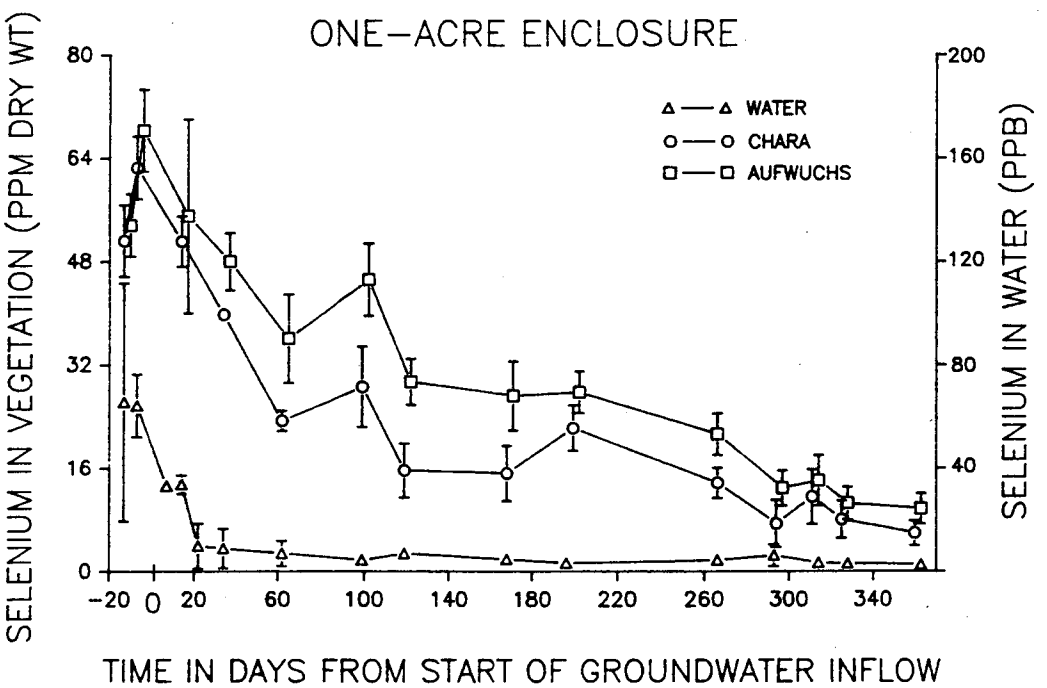
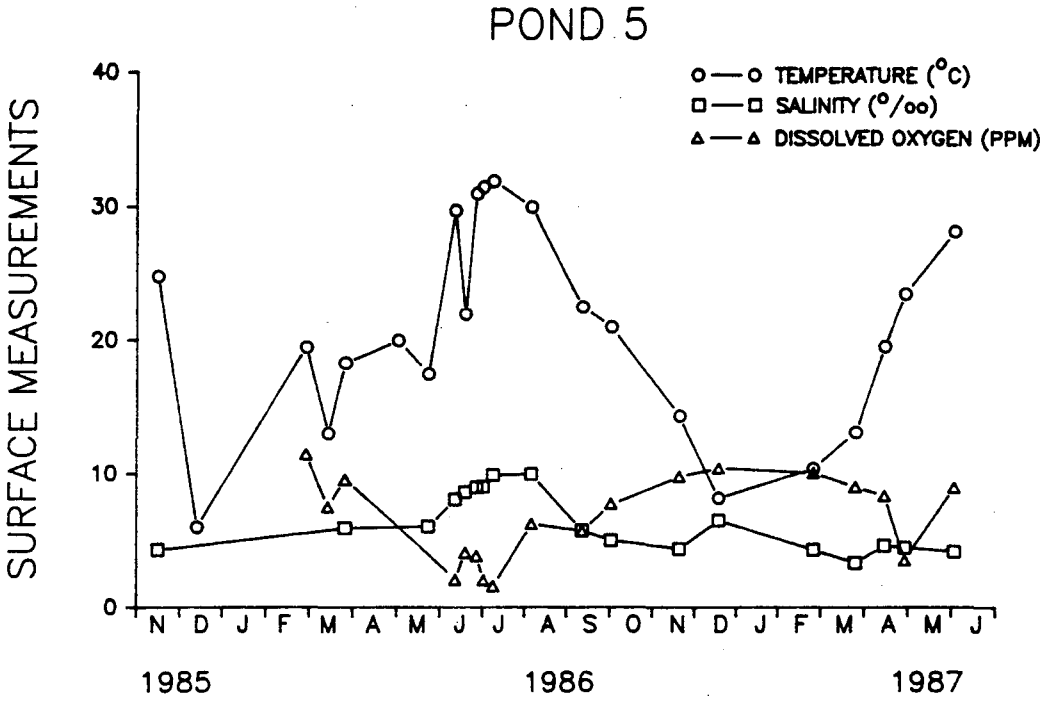


Figure 5.2. Above: Decline of selenium in the macroalga *Chara* in laboratory microcosms. Below: Declines of selenium in water, *Chara*, and aufwuchs in a one-acre experimental enclosure (Pond 5E) of Kesterson Pond 5 during the first year of its operation.

The limnological characteristics of Pond 5E have been similar to those of Pond 5. In both ponds mean water temperatures rose during spring 1986 to reach peaks exceeding 30° C during mid summer, fell to about 10° C in December 1986, then rose again to values exceeding 25° C by spring 1987 (Figure 5.3). Mean salinities within Ponds 5 and 5E ranged from about 4 - 10 o/oo, achieving the highest values in June-July 1986. Mean values for dissolved oxygen ranged from about 3 - 11 ppm in both ponds with the lowest values occurring during summer and the highest values occurring during the winter (Figure 5.3).

The species composition in Pond 5E has also been similar to that of Pond 5. With the exception of soldierfly and brinefly larvae, all aquatic species sampled from Pond 5 have also been sampled from Pond 5E.

Within a few weeks of application of low-selenium (ca. 1 ppb) groundwater, the dissolved selenium in Pond 5E dropped to less than 3 ppb (Figure 5.2). Some of the water in Pond 5E was released through a gate valve into Pond 5 during pumping episodes in the first few days of operation of the enclosure. It is doubtful that such releases did much to flush the Pond 5E water volume; such flushing need not be invoked to explain rapid dissolved selenium declines, since this same phenomenon has repeatedly been observed in replicated laboratory microcosms during the first few days of their isolation from a source of new selenium. The selenium content of the organisms at the base of the food chain also began to decline within a few weeks. The selenium content of the macroalga *Chara* fell from 51.2 to 5.9 ppm (a decline of 88%) between May, 1986 and early June, 1987. Selenium in the aufwuchs community (diatoms, algae, detritus and multitudes of small animals which live attached to *Chara*) fell from 53.6 to 9.7 ppm (a decline of 82%) in the same period (Figure 5.2). After about one year the selenium levels of all organisms, for which sufficient data were available, had fallen substantially (Figure 5.4 - 5.5). In almost every species, selenium concentrations in Pond 5E were less than in Pond 5 (Figures 5.6 - 5.11), which was re-contaminated with selenium in July and



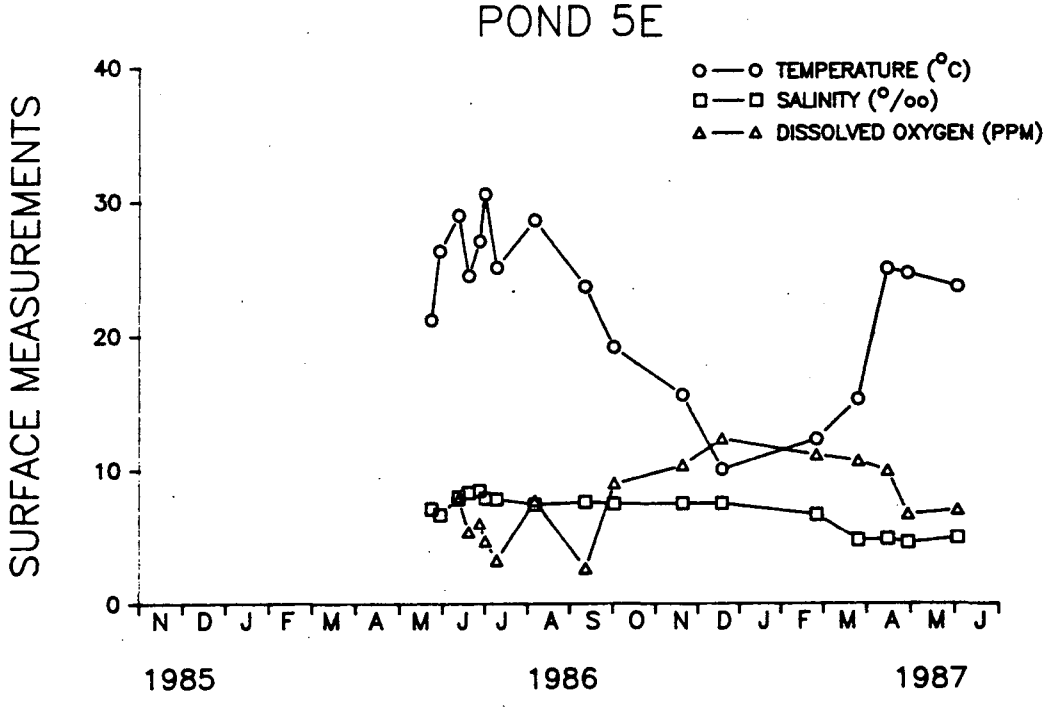


Figure 5.3. Surface temperature, salinity, and dissolved oxygen of Pond 5 (above) and the enclosure (Pond 5E, below).

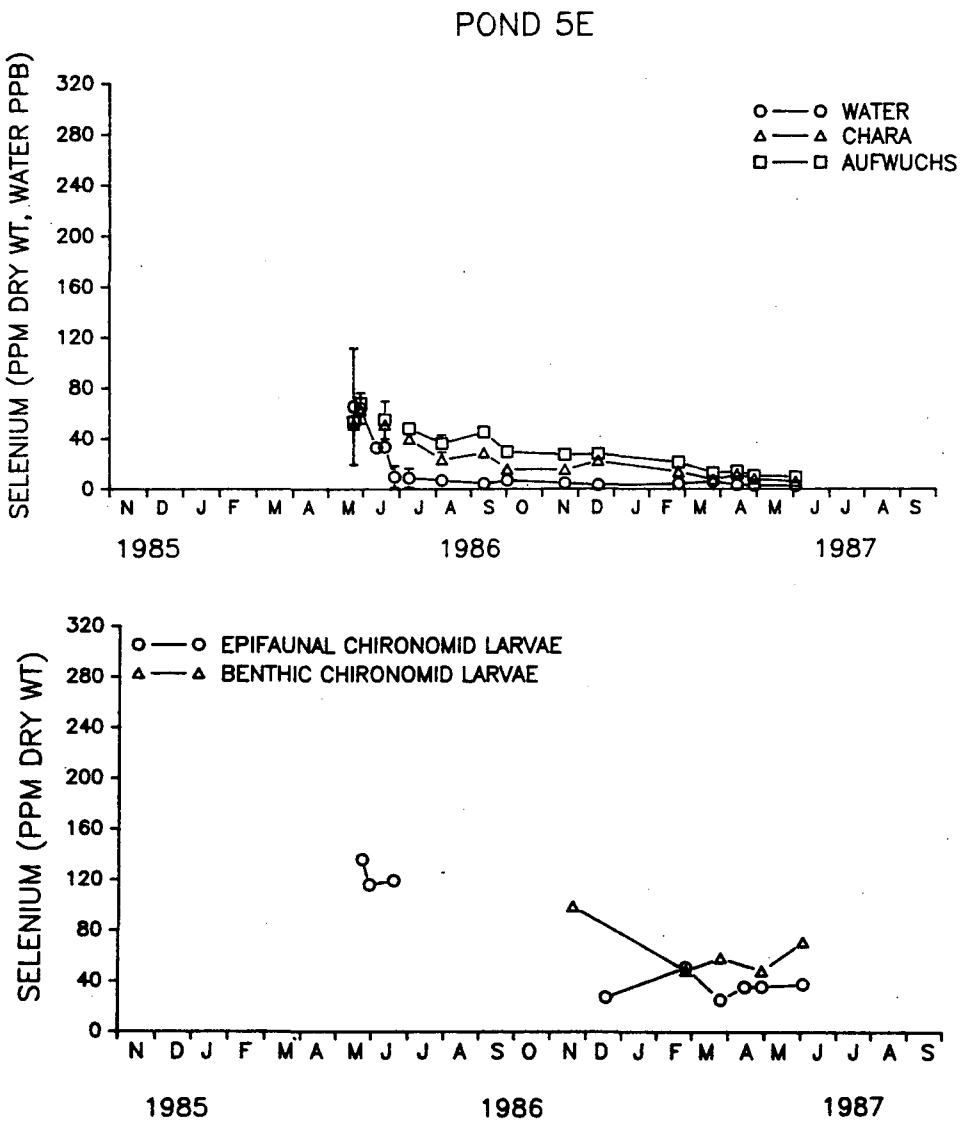


Figure 5.4. Above: Declines of selenium in water, *Chara*, and aufwuchs in a one-acre experimental enclosure (Pond 5E) of Kesterson Pond 5 during the first year of its operation. This is the same data which is shown in the lower panel of Figure 5.2, but is here plotted on the same scale used in the following series of graphs. Below: Selenium concentrations in Chironomid larvae from Pond 5E.

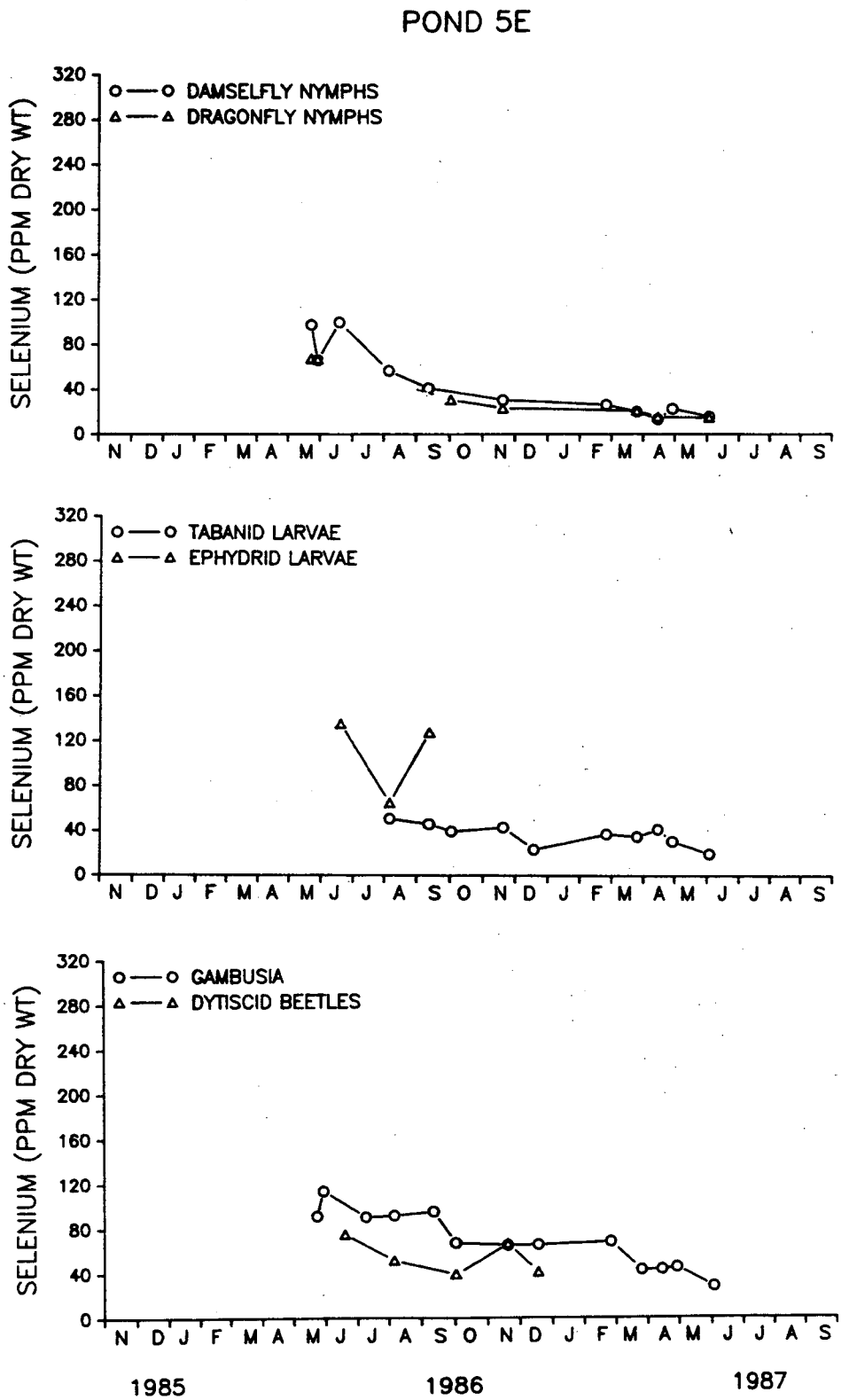
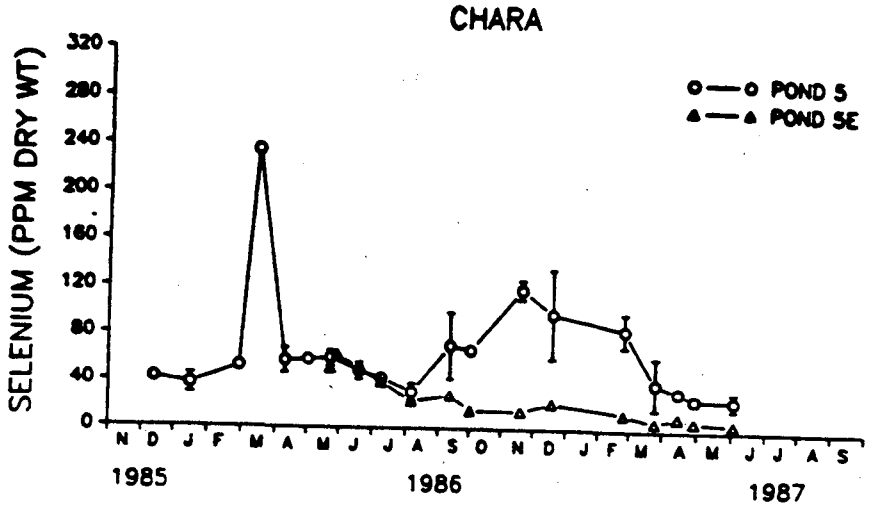
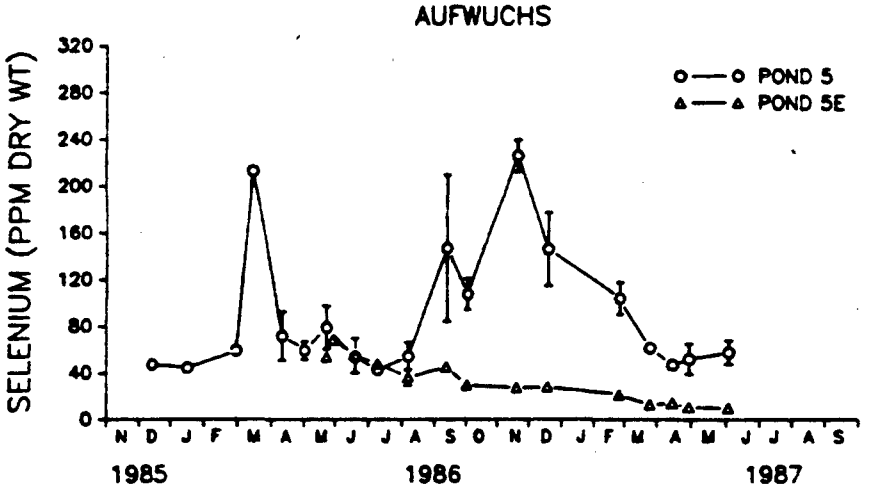
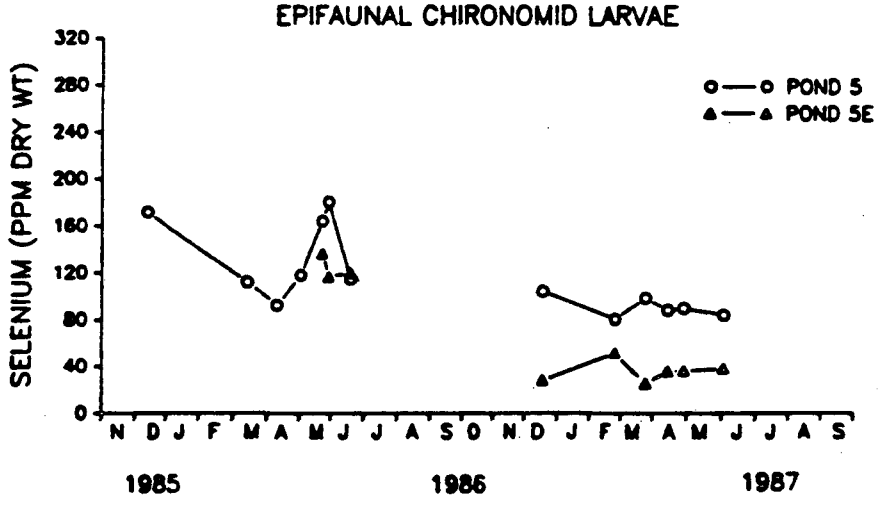


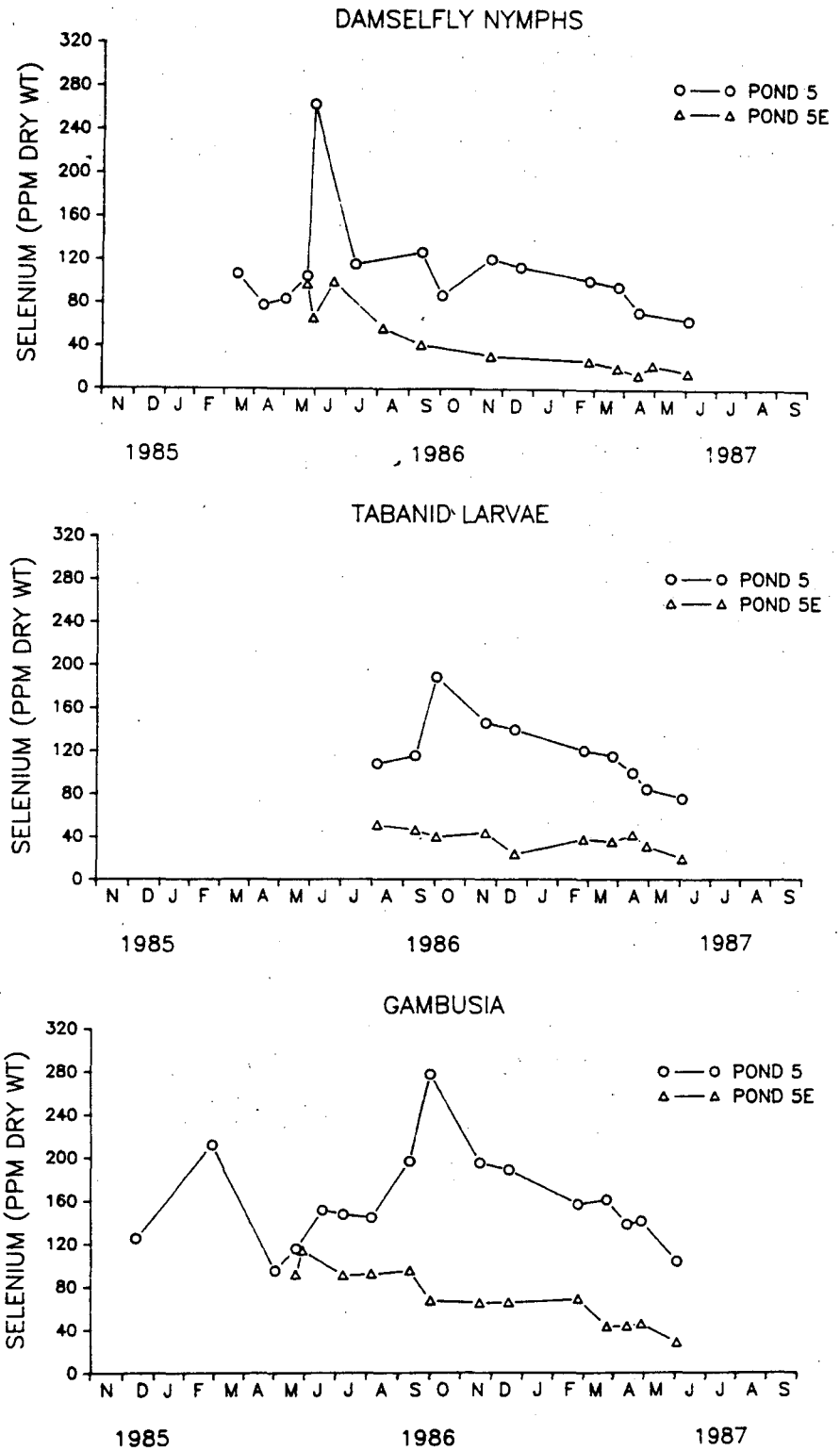
Figure 5.5. Selenium concentrations in damselfly and dragonfly nymphs (upper panel), tabanid and ephydrid larvae (middle panel), and mosquitofish and dytiscid beetles (lower panel) from Pond 5E.







Figures 5.6-5.8. Selenium concentrations in Pond 5 compared with those in Pond 5E, for *Chara* (Figure 5.6, upper panel), aufwuchs (Figure 5.7, middle panel), and epifaunal chironomid larvae (Figure 5.8, lower panel).



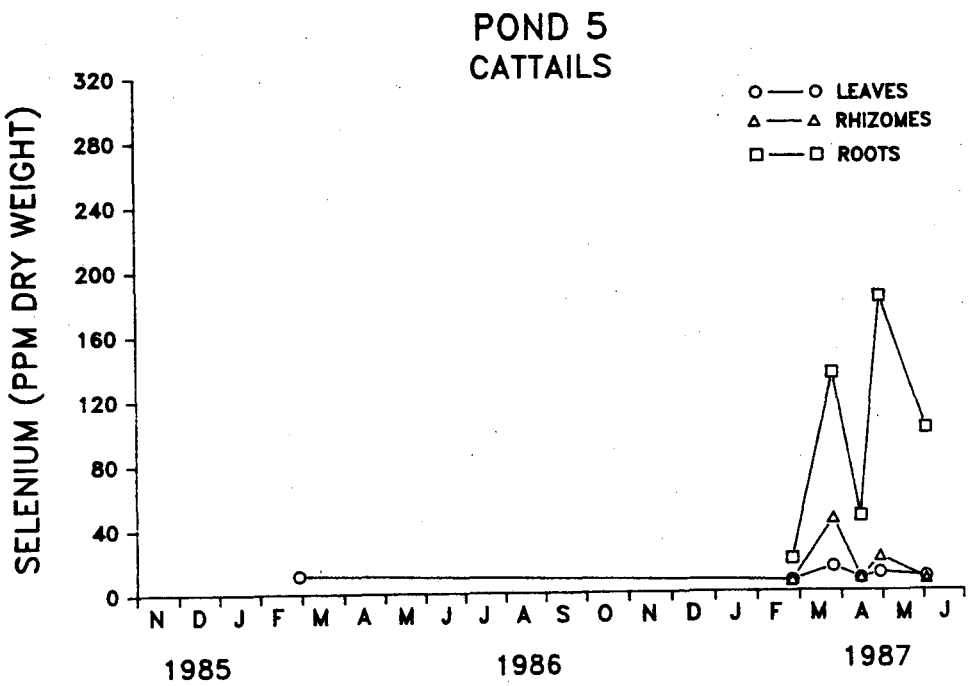
Figures 5.9-5.11. Selenium concentrations in Pond 5 compared with those in Pond 5E, for damselfly nymphs (Figure 5.9, upper panel), tabanid larvae (Figure 5.10, middle panel), and mosquitofish (Figure 5.11, lower panel).

August 1986. Of particular interest was the decline in selenium in the predatory damselfly nymphs (Figure 5.8). These organisms are a food source for many waterbirds and are common and widespread at Kesterson. Over the last year selenium in Pond 5E damselfly nymphs has fallen by 84%, from 97.5 to less than 15.8 ppm (dry wt.). This decline was comparable to that found for organisms at the base of the food chain (Figures 5.4 and 5.6).

The dominant visual feature of the wetter areas of Kesterson Reservoir are cattails, large, rooted emergent plants. Although too tough and undigestible for most marsh dwellers (including bacteria) the extensive cattail stands serve as areas for nesting and winter roosting for blackbirds. Both the common form and tricolored blackbirds--candidates for rare and endangered species status--are present in large numbers, even in 1987. Large declines in the selenium content of cattails were also recorded in the mesocosm, despite the presence of roots down to several inches into the still selenium-rich sediments. Declines between May, 1986 and June, 1987 in cattail leaves, roots, and rhizomes were 87, 60, and 94%, respectively (Figure 12). Cattail roots were high in selenium concentration relative to leaves and rhizomes. The selenium concentrations of roots were, however, lower in Pond 5E than in Pond 5 (Figure 5.12).

Mosquitofish (*Gambusia affinis*) are one of the few vertebrate species which can tolerate very high selenium levels. Mosquitofish are present in many permanent water marshes and reservoirs contaminated with selenium, including fly-ash disposal ponds. Certainly they have sustained great abundances in both the contaminated marsh and the San Luis Drain. Selenium levels in mosquitofish fell more slowly than levels in invertebrates, as might be expected due to the relatively long life-span of the fish (up to 15 months). Nevertheless, a decrease of 69% (91.3 to 28.1 ppm) was recorded over 12 months between May 1986 and June 1987 (Figures 5.5, 5.11).

It is important to note that selenium concentrations in Pond 5E surficial sediments did not decline during the study period (Figure 5.13). The sediment data were based on



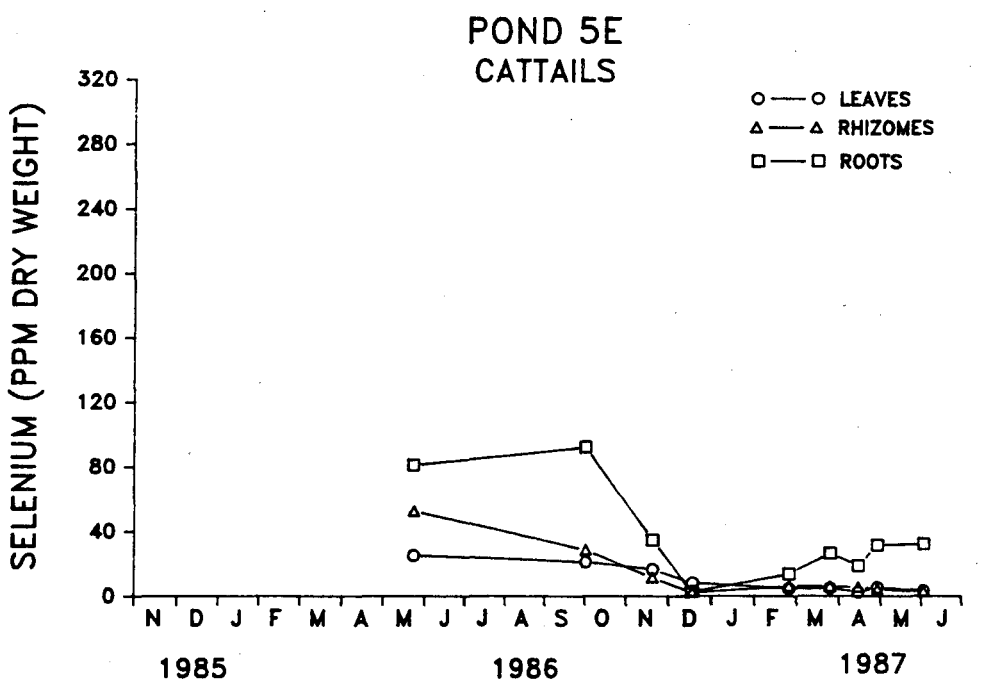


Figure 5.12. Selenium concentration in cattails in Pond 5 (above) and Pond 5E (below).

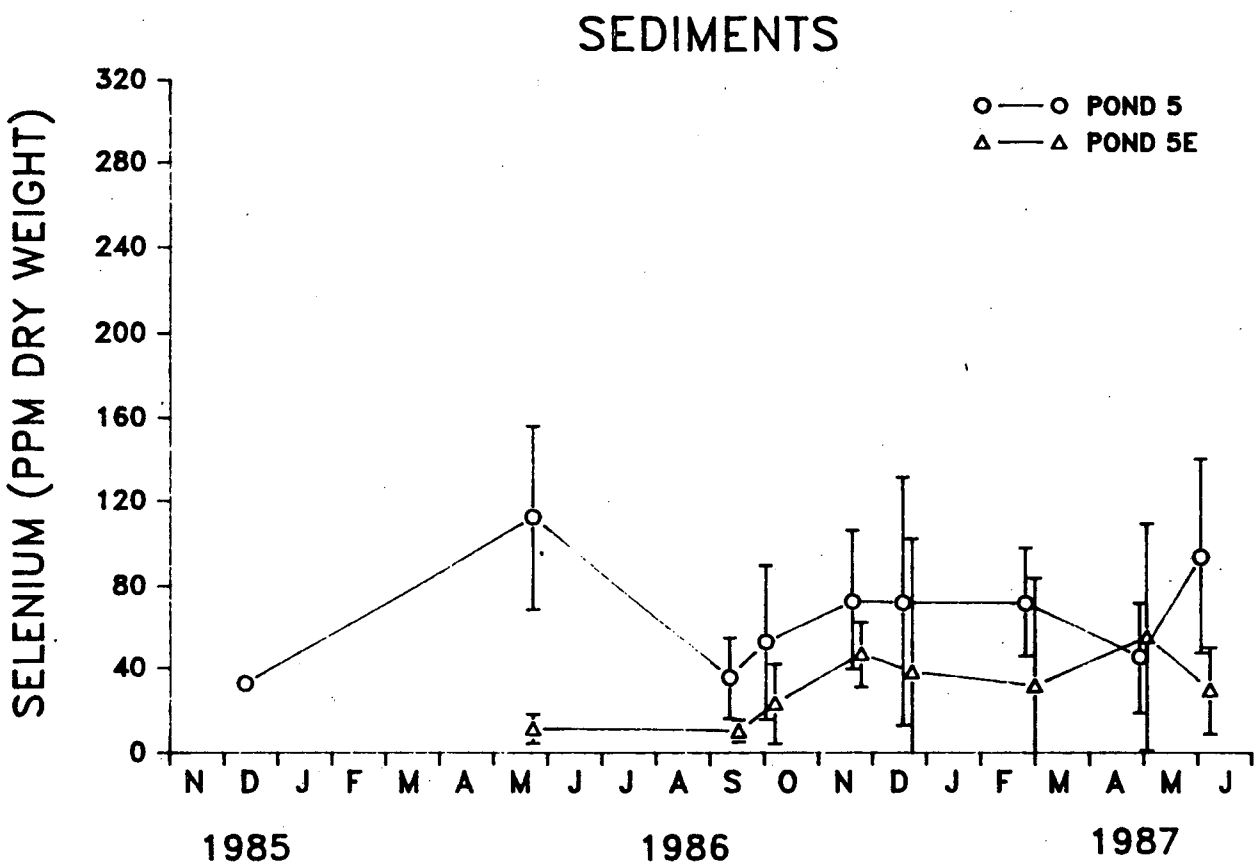


Figure 5.13. Selenium concentrations in surficial sediments of Pond 5 and Pond 5E (below). (Means +- 2se).

samples collected with a ponar grab, from which benthic animals were obtained. Sediment selenium data collected in this manner is subject not only to variability due to horizontal patchiness within each index sampling area, but also to differences in the sediment depth from which the sample is taken.

5.4.3. Field Collections: Reservoir-wide

5.4.3.1. Permanent Deep Water; Pond 5 Index Site.

Table 5.1 compares selenium levels at Kesterson Reservoir during May 1983 and May 1984, before the cessation of agricultural drainwater inputs, with June 1987 levels. The 1987 data are presented as geometric mean values, since these were presented by earlier USFWS investigators (Schuler and Antony, 1987: Saiki and Lowe, 1986). Our Pond 5 data are compared with USFWS data from Pond 2, which was representative of permanently wet ponds in 1983-84. There is a decrease in almost every compartment between 1983 and 1987. Biotic selenium concentrations in 1987 were 36-70% of 1983-84 levels. Sediment selenium showed no such decrease (it was actually higher in 1987, but

Table 5.1. Comparison of selenium concentrations of water, sediments and organisms sampled from permanently wet ponds during 1983, 1984, and 1987. Values represent geometric mean selenium concentrations (ppm d.w. for organisms and sediments; ppb for water).

	May 1983[1] Pond 2	May 1984[2] Pond 2	June 1987[3] Pond 5	% Change 1983 to 1987	% Change 1984 to 1987
Water	78	90	7.7	-90	-91
Sediment	62		88	+42	
Algae	59		38	-36	
Corixids		20	8.1	-59	
Damselfly nymphs	213	138	64	-70	-54
Dragonfly nymphs	155	110	59	-62	-46
Chironomids	200		84	-58	
Mixed insects	180		101	-44	

[1]Saiki and Lowe, 1986
[2]Schuler and Antony, 1987
[3]UCB/LBL

this difference is probably more a reflection of spatial differences in selenium inventory rather than temporal changes).

The decline of soluble selenium, which began after routine drain water supplies were gradually reduced in 1985, was interrupted by the disposal of highly-contaminated water from the San Luis Drain in July and August, 1986. This resulted in a return to historically high levels of soluble selenium (Figure 5.14). In a few weeks the selenium content of *Chara* and aufwuchs rose, indicating rapid uptake, and reached a peak in selenium concentrations in November, 1986. At the same time, the soluble selenium levels fell, suggesting that the supply of new selenium was exhausted.

Selenium concentrations of predatory mosquitofish and tabanid larvae and dytiscids increased after the disposal of drainwater and peaked in October, 1986 (Figures 5.15). Selenium concentrations of the herbivorous brinefly larvae increased to 591 ppm in October 1986 (5.15). Damselfly nymph selenium concentrations did not increase significantly when compared with a previous increase that occurred between May and June 1986 (Figure 5.15); dragonfly nymphs and chironomid larvae were not exposed to the high soluble selenium concentrations, as most had emerged as adults prior to August.

Since November, 1986, Pond 5 plants have shown the rapid declines in selenium which we have found in both laboratory and field tests. About two-thirds of the selenium present has been lost from *Chara*, the dominant submerged plant, in 6 months. Similar losses have occurred in the aufwuchs community, the main food supply. Comparing selenium levels in November, 1986 with the most recent available data (June, 1987), *Chara* selenium has decreased by 78% (119 to 26 ppm) and selenium in aufwuchs by 74% (226 to 57.7 ppm) (Figure 5.14). Comparisons with the USBR biological monitoring in February and May 1987 show that the Pond 5 site provides an accurate estimate of selenium concentrations throughout the entire pond for most species. Due to their longer life cycles, animals showed a less rapid decline in body selenium, but the downward trend is evident (Figure 5.15). Mean selenium concentrations of damselfly nymphs

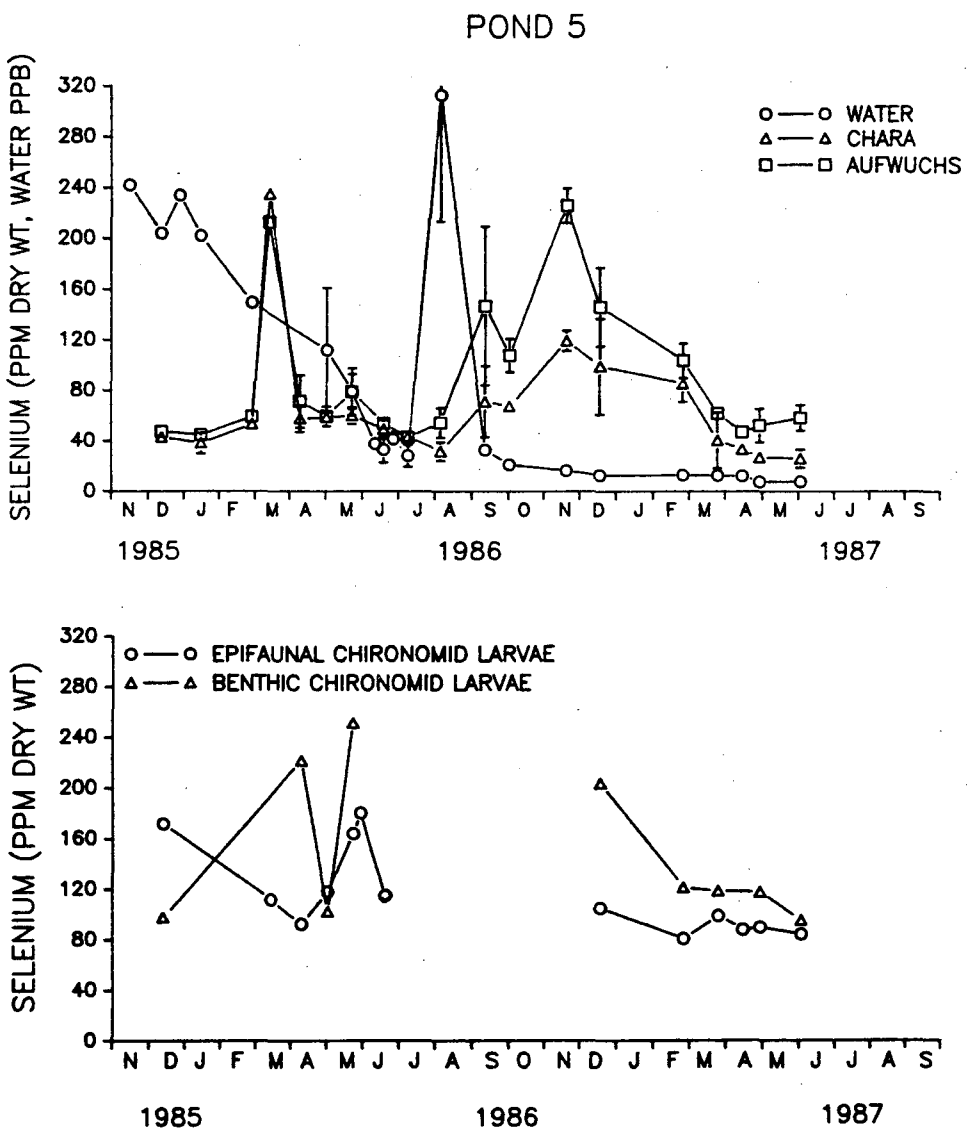


Figure 5.14. Above: Selenium concentrations in water, *Chara*, and aufwuchs from Pond 5. Below: Selenium concentrations in chironomid larvae from Pond 5.

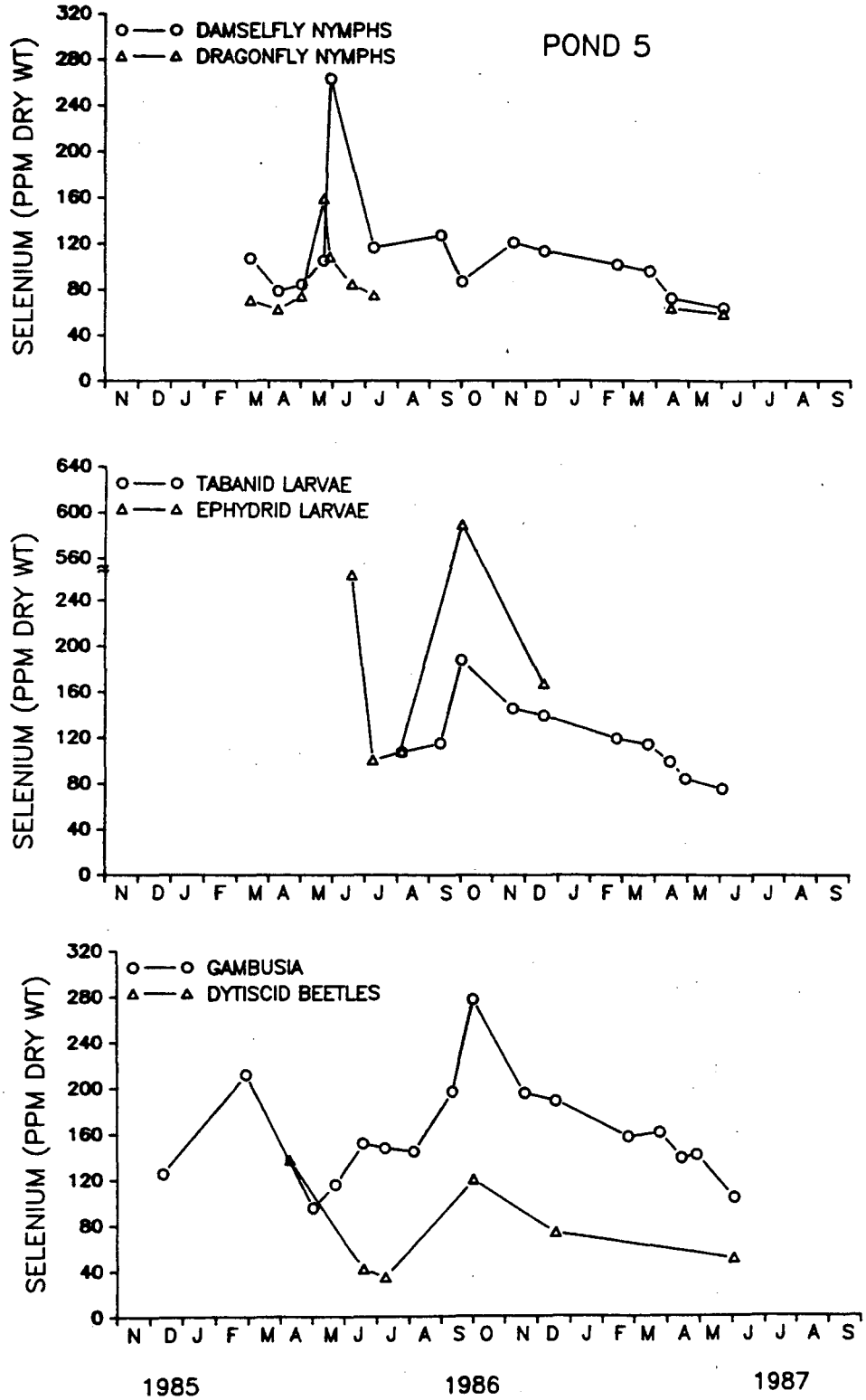


Figure 5.15. Selenium concentrations in damselfly and dragonfly nymphs (upper panel), tabanid and ephydrid larvae (middle panel), and mosquitofish and dytiscid beetles (lower panel). Note the scale break in the middle panel where ephydrid larvae contained nearly 600 ppm in October 1986.

decreased from 121 to 63.8 ppm (47%, see Figure 5.15) between November 1986 and June, 1987. Mean selenium concentrations in mosquitofish declined from 195 to 103 ppm (47%) between the October 1986 peak and June, 1987; selenium concentrations of tabanid larvae decreased from 187.6 to 75.5 (58%) during this same time period.

When selenium concentrations of Pond 5 *Chara* and aufwuchs between the November 1986 peak and June 1987 are fitted to an exponential decay function, the projected times for reaching selenium concentrations less than 3 ppm in Pond 5 are 8 and 11 months, respectively (Table 5.2). When the mean selenium concentrations of mosquitofish and tabanid larvae between October 1986 and June 1987 are fitted to an exponential decay function, the projected times for reaching selenium concentrations less than 3 ppm in Pond 5 are 37 months and 31 months, respectively. However, these projections are probably unrealistically short, as they are based on observed declines in selenium concentrations of biota that was highly contaminated by the July-August 1986 disposal of drainwater. A more realistic prediction of the future behavior of Pond 5 after June 2, 1987 is based on observed rates of decline in selenium concentrations of Pond 5E

Table 5.2. Exponential functions ($y = ae^{bx}$) and projected times to reach 3 ppm based on mean selenium concentrations for Pond 5 from October 1986 (*Gambusia* and tabanid larvae) and from November 1986 (*Chara* and aufwuchs) to June 1987 (all 4 taxa).

	Pond 5			
	Chara	Aufwuchs	*Gambusia*	Tabanid Larvae
slope (b) per day	-.0087	-.0080	-.0033	-.0035
2 s.e. (slope)	.0025	.0024	.00084	.00058
r^2	.906	.885	.909	.954
Time to reach 3 ppm	8 mos.	11 mos.	37 mos.	31 mos.
Projected date to reach 3 ppm	February 1988	May 1988	July 1990	January 1990

biota, since their initial March 1986 concentrations (the starting point for computing the Pond 5E exponential decay function) were lower than the concentrations of Pond 5 biota in November 1986 (the starting point for computing the Pond 5 exponential decay function). These functions and projections are presented in Table 5.3. Figures 5.16 and 5.17 superimpose negative decay functions computed for Ponds 5 and 5E for each of four taxa (*Chara*, aufwuchs, tabanid larvae and mosquitofish). The Pond 5E curves have been plotted so that they intersect with the Pond 5 curves on June 2, 1987, the last date for which selenium values are available. Thus, each plot provides two projections for the clean-up of Pond 5 biota. In every case, the projection based on Pond 5E data is more conservative (predicts a lengthier clean-up time) than the projections based on Pond 5 data. The conservative estimates predict clean-up data of June 1988 for *Chara*, December 1988 for aufwuchs, September 1990 for mosquitofish and June 1992 for tabanid larvae. Projections for other organisms are presented in Table 5.3. These projections may still not accurately predict clean-up times, as the rates of decline may change as biotic concentrations decrease further. So far the net movement of selenium has been from the biota into the sediments (or atmosphere). It is reasonable to suppose that eventually the rate of transfer of selenium from food chain to sediments would be balanced by transfer from sediments to food chain. However these data support the conclusion that this equilibrium point will occur at food chain selenium levels less than 3 ppm.

5.4.3.2. Shallow Wetlands Kept Continuously Flooded: Pond 7 Index Site

Prior to 1987, shallow seasonal waters of Kesterson Reservoir were replete with stands of the submerged rooted aquatic plant *Ruppia* (Widgeon or ditch grass) during spring and summer. Also present were a few patches of a similar plant, *Zanichellia* (horned pondweed). *Ruppia* is of concern at Kesterson for two reasons. First, it is a rooted plant and has potential access to the sub-surface sediments containing selenium. Second, it is reportedly a favored food for many waterbirds, although it is not certain if the plant or more digestible small animals and plants (aufwuchs) attached to it are actu-

Table 5.3. Exponential functions and projected times to reach 3 ppm based on mean selenium concentrations in Pond 5E Biota. Regressions based on May 1986 through June 1987 data. The "combined analysis" estimates clean-up time for Pond 5 Biota by intersecting the Pond 5E regression line with the Pond 5 line on June 2, 1987. This gives a more conservative estimate of clean-up time because it reflects the slower rate of decrease as safe levels are approached.

Pond 5E	*Chara*	Aufwuchs	*Gambusia*	Tabanid Larvae	Epifaunal Chironomid Larvae	Benthic Chironomid Larvae	*Berosus* Larvae	Damselfly Nymphs	Dragonfly Nymphs
slope (b) per day	-.0054	-.0049	-.0031	-.0018	-.0036	-.0023	-.0039	-.0045	-.0039
2 s.e. (slope)	.0012	.00068	.00076	.0016	.0018	.0039	.0017	.0011	.0012
r^2	.8810	.9500	.8660	.3950	.7210	.3150	.7850	.8970	.9150
Time to reach 3 ppm	4.8 mon	8.4 mon	27.3 mon	40.7 mon	20.7 mon	41.4 mon	22.0 mon	9.7 mon	13.1 mon
Projected Date to reach 3 ppm	October 1987	February 1988	September 1989	October 1990	February 1989	November 1990	April 1989	March 1988	July 1988
Combined analysis									
Time for Pond 5 using 5E slope	12.8 mon	18.0 mon	39.7 mon	60.4 mon		-	-	-	-
Projected date for Pond 5 using 5E slope	June 1988	December 1988	September 1990	June 1992	-	-	-	-	

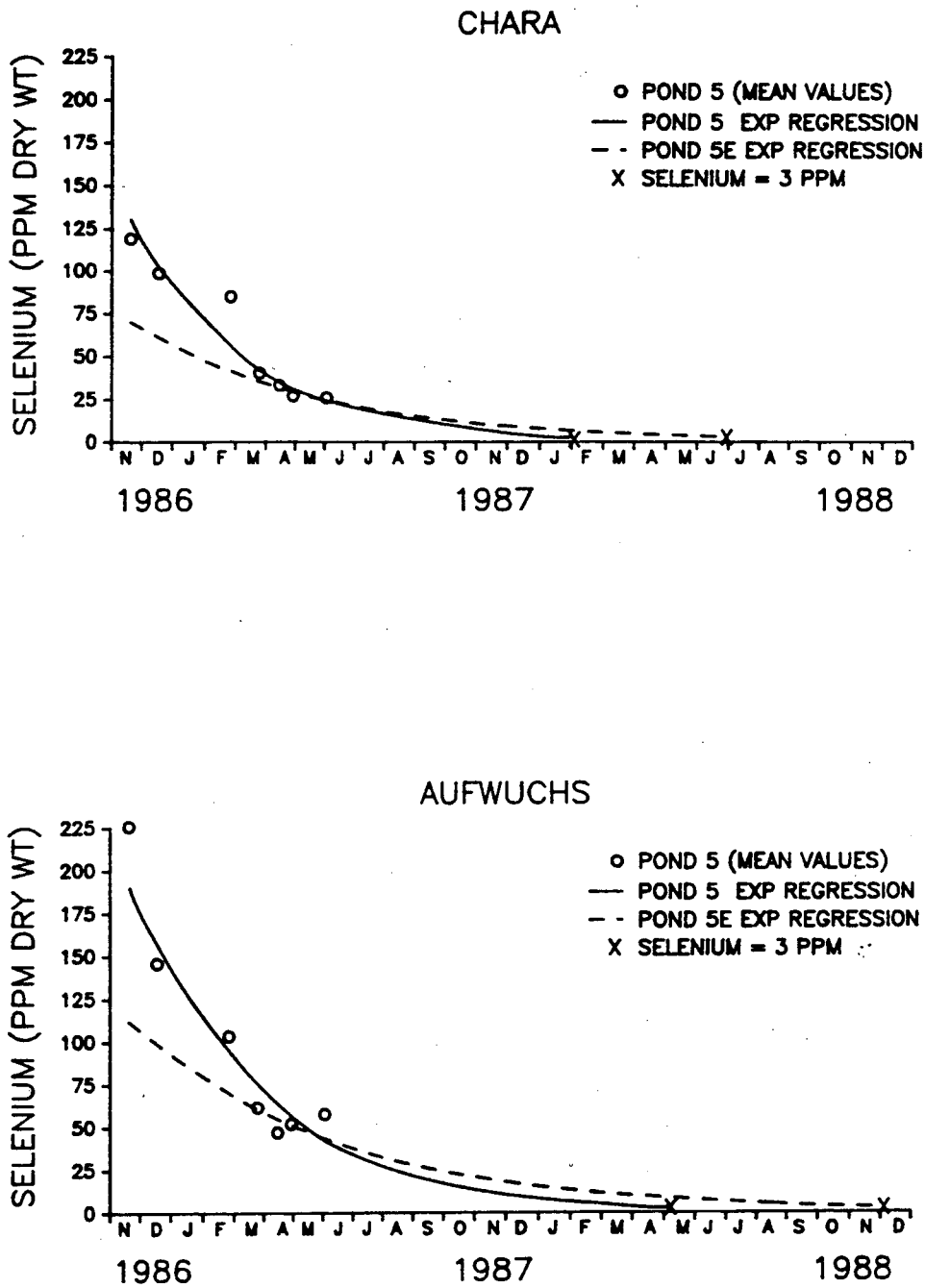


Figure 5.16. Estimated time to reach 3 ppm selenium in *Chara* (upper panel) and aufwuchs (lower panel) from Pond 5, based on exponential regressions using the Pond 5 data (solid lines), and superimposing the 5E regressions (dotted lines) so that the two curves intersect in June 1987. The regression coefficients are given in Tables 5.2 ands 5.3.

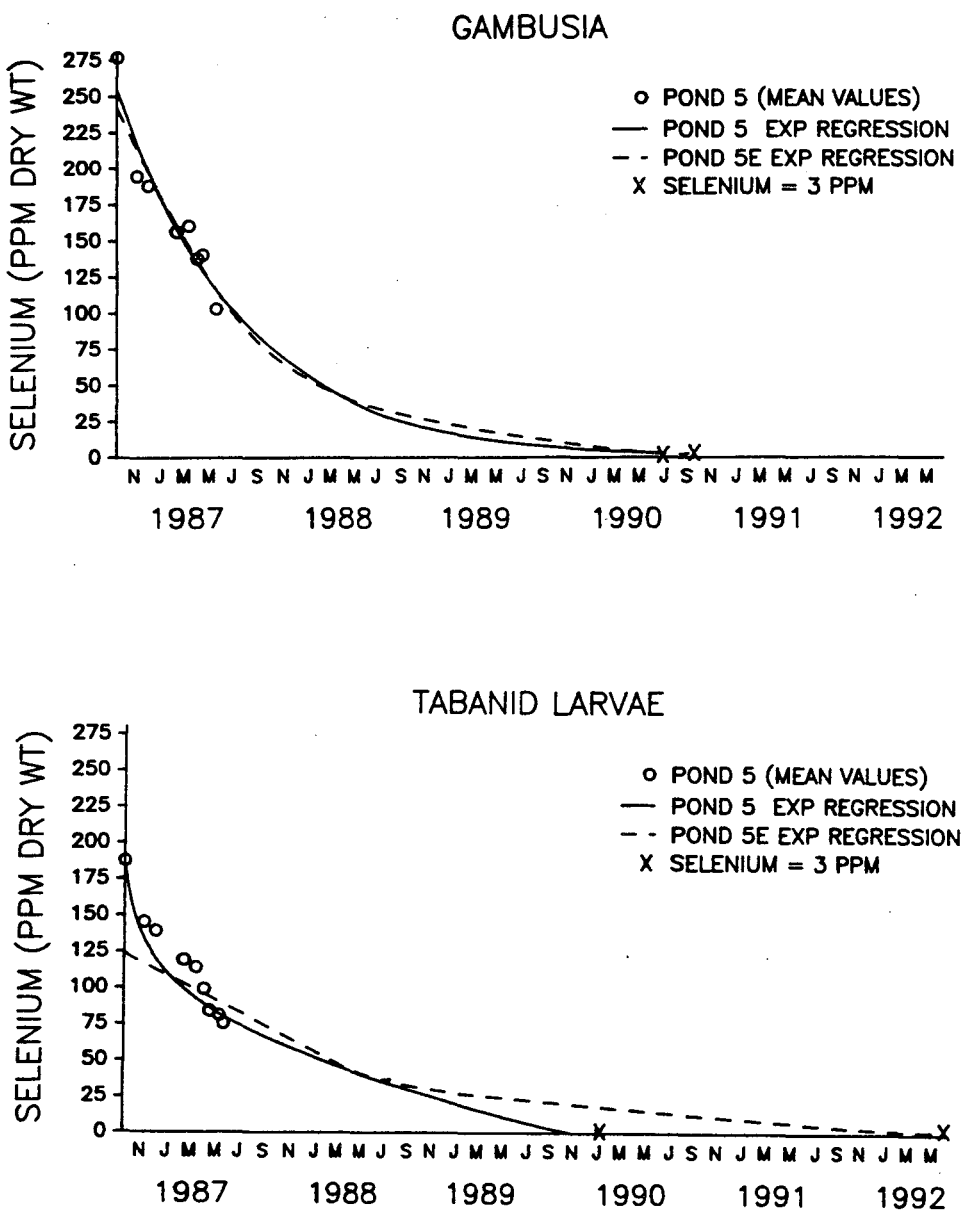


Figure 5.17. Estimated time to reach 3 ppm selenium in mosquitofish (upper panel) and tabanid larvae (lower panel) from Pond 5 based on exponential regressions as in Figure 5.16.

ally digested and assimilated. This plant, which can range from a few inches to a few feet in height, grew in large patches separated from other stands by bare expanses of microalgae-covered mud. By fall 1986 the areas were usually baked dry and the *Ruppia* had formed a matted dry crust over large areas of the pond. In winter the crust was flooded but little growth occurred until spring when light once again became adequate for growth. During fall and winter, *Ruppia* seeds from the previous year's plants may remain; these are potential bird food. In spring 1987 the generally lower water depths produced smaller plants which persisted for a shorter time than the previous year.

The Pond 7 site was to be maintained in a permanently wet condition, to a depth of about 1 foot, from summer-fall, 1986 through spring 1987. However, lower levels occurred due to water shortages, so an adjacent area was sampled beginning in March 1987. *Ruppia* at these sites was present as over-wintering stems in the early spring of 1987. Growth was slow and the plants were covered all winter and spring with a heavy coating of aufwuchs. The brilliant green dense stands found at the index site in spring 1986 were not present in spring 1987, although they occurred elsewhere in the Reservoir. The species is probably not a good competitor under permanent water situations and may soon be replaced by *Chara*, cattails, alkali bulrush, or algae mats.

Table 5.4 compares March 1987 selenium levels at the Pond 7 site with May 1983-84 selenium levels in Ponds 8 and 7. Selenium concentrations of water, damselfly and dragonfly nymphs were lower during 1987 in the Pond 7 site than during 1983-84 in Ponds 7 and 8. Selenium concentrations of sediment and *Distichlis* were higher; and *Gambusia*, *Ruppia*, and algae were not much different.

Table 5.5 compares March 1987 selenium levels at the Pond 7 site with February and May 1987 selenium levels at seasonal sites sampled during synoptic surveys (USBR biological monitoring). These latter sites were not kept in a permanently wet condition. The water selenium concentration at our Pond 7 site was within 2 standard errors of the mean value for all seasonal sites, sampled during February and May. In 10 of 16 possible

Table 5.4. Comparison of selenium concentrations of water, sediment, and organisms sampled from seasonal wetland areas during 1983, 1984, with those from the Pond index site in March 1987. Values are geometric mean concentrations (ppm d.w. for organisms and sediments; ppb for water).

	May 1983[1] Pond 8	May 1984[2] Pond 7	March 1987[3] Pond 7 Index Site	% Change 1983 to 1987	% Change 1984 to 1987
Water	100	120	20	-80	-83
Sediment	3		38	+1,166	
Algae	59		67	+14	
Ruppia	59		51	-14	
Distichlis leaves		1.3	11		+1,100
Damselfly nymphs	120	92	27	-213	-71
Dragonfly nymphs	96	62	42	-56	-32
Gambusia	164		130	-21	

[1]Saiki and Lowe, 1986
[2]Schuler and Antony, 1987
[3]UCB/LBL

Table 5.5. Comparison of selenium concentrations at Pond 7 UCB/LBL index site with concentrations for all seasonal wetland sites sampled during the 1987 USBR Habitat Surveys. Values are arithmetic mean concentrations (ppb for water and ppm dry weight for organisms ± 2 s.e.). ND indicates no significant difference in values (within 2 standard errors of the mean); + indicates a higher value at Pond 7 site; - indicates a lower value at Pond 7 site.

	All Seasonal Sites February[1]	All Seasonal Sites May[1]	Pond 7 Site Index March[2]	Pond 7 vs. Feb. Seasonal Site	Pond 7 vs. March Seasonal Sites
Water	57±27	22±10	20±4	ND	ND
Ruppia	53±36	36±8	54±25	ND	ND
Ruppia Aufwuchs	92±36		70±25	ND	
Distichlis leaves		26±25	11		ND
Typha leaves		5±5	8		ND
Typha rhizomes		26±25	12		ND
Typha roots		113±72	90		ND
Chironomid larvae	74±20	8	53±5	ND	+
Damselfly nymphs	65±15		27	-	
Dragonfly nymphs	48±11	31±3	42±1	ND	+
Mayfly nymphs	42±6	33	78	+	+
Gambusia	170±20	98±48	130	-	ND

[1]Data from USBR biological monitoring
[2]Data from UCB/LBL research program

comparisons, the biotic concentrations (or mean concentrations + 2 S.E.) at our Pond 7 site fell within 2 standard errors of the mean values for seasonal wetlands. In 4 cases selenium concentrations at the Pond 7 site were higher than at seasonal wetlands sampled during the USBR monitoring (February and May mayfly nymphs, May chironomid larvae and dragonfly nymphs); in 2 cases concentrations were lower than at seasonal wetlands sampled during the USBR monitoring (February damselfly nymphs and mosquitofish). Pond 7 sediment selenium was higher at the index site in 1987 than the earlier data from Pond 8 in 1983 and other Pond 7 sites in 1984. This is to be expected, since the index site was chosen in an area of high selenium inventory.

One of the most abundant plants in seasonal wetlands was the submerged species, *Ruppia*, which increased in selenium concentration after May 1986, then returned to May 1986 levels by June, 1987 (Figure 5.18). This may demonstrate a seasonal trend. *Ruppia* did not grow well while the Pond 7 sites were kept continuously wet in 1986-7 and would probably be replaced by other organisms over the next few years, if these sites were to be kept wet.

5.4.3.3. Ephemeral (very shallow) Pools: Pond 11

Ephemeral, very shallow waters, are a characteristic of much of California. In wet years ephemeral pools may last for months and in dry years not exist at all. Usually, their annual existence is a matter of weeks. Ephemeral pools have a biota which is specifically adapted to short, irregular wet periods but, since common predators are often absent, the biomass of some species can be high.

In Kesterson Reservoir in spring 1986 many seasonal pools were crowded with insect larvae--in particular the conspicuous black maggots of the soldierfly *Odontomyia* sp. (Stratiomyidae). This slow-moving maggot was the main item in the diet of the common wading birds (avocets, stilts etc.) in the USFWS bird gut content study in 1983, and we observed numerous wading birds feeding there in 1986. For this reason, seasonal pools were selected for long-term study.

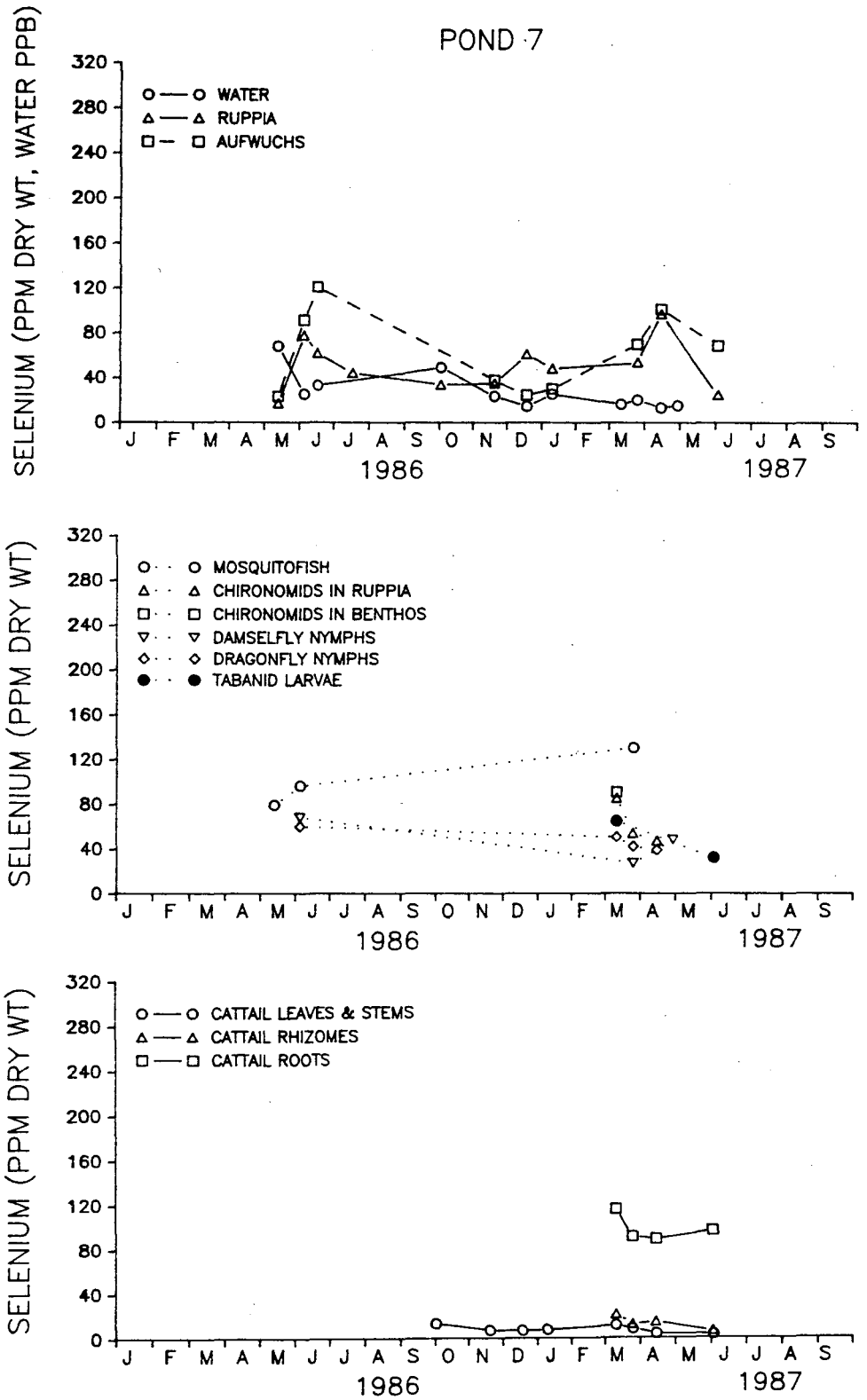


Figure 5.18. Selenium concentrations in water, *Ruppia*, and aufwuchs (upper panel), various animals (middle panel), and cattails (lower panel) from Pond 7 during 1986-1987.

In the dry winter of 1986-1987 water was never present at the Pond 11 site, so between-year comparisons of selenium concentrations of aquatic invertebrates cannot be made. Samples were collected throughout the year from the terrestrial vegetation which grows in these areas during dry years. These plants presumably serve as part of the detrital food supply during subsequent wet years. Plants such as *Distichlis* and *Cressa* had low selenium levels, ranging from 0.3 to 2.4 ppm and from 0.8 to 9.1 ppm, respectively (Table 5.6).

A small amount of water was present in a nearby old slough in Pond 11, but only for a few weeks. The water was very saline (>40 o/oo), and contained relatively high dissolved selenium, (ca. 140 ppb). This site is classed as a seasonal wetland, not an ephemeral pool, and contained Ruppia in 1986. In 1987 the selenium concentrations of the few Ruppia plants that had time to grow was about 40 ppm, less than selenium concentrations of Ruppia at the Pond 7 site during the previous year, when it was a comparable seasonal wetland.

Table 5.6. Pond 11 selenium concentrations (ppm dry weight) of aquatic invertebrates (April-May 1986) and terrestrial plants (April 1986 to June 1987).

	1986						1987		
	Apr.	May	June	Oct.	Nov.	Dec.	Mar.	Apr.	Jun.
Distichlis	-	-	2.3	2.2	1.1	1.3	2.4	1.4	0.3
Cressa	3.6	-	-	-	-	2.7	9.1	3.1	0.8
Damselfly nymphs	-	-	32						
Stratiomyid larvae	-	31	36						
Notonectids	-	47	-						
Corixids	-	14	31						
Beetles	-	55	37						
Brinefly larvae	-	-	34						

5.4.4. Food-chain Study

5.4.4.1. Taxonomy of Pond 5 and 5E Aquatic Invertebrates

All species sampled from the *Chara* communities and shoreline ooze areas of Ponds 5 and 5E (Table 5.7) have widespread distributions, at least within western North America. Several of them have been previously found in saline pools and/or hot springs.

5.4.4.2. Structure of the Food Web

The food web structure shown in Figure 5.19 is based upon:

1. gut content analyses,
2. composition of the aufwuchs, and
3. published information on food habits of individual species or taxa.

Based on gut content analyses, the trophic base of the floating *Chara* community in Pond 5 and 5e consisted primarily of diatoms (especially *Gyrosigma*) and aufwuchs detritus (Table 5.8, 5.9). Only a few herbivores (hydrophilid species) fed on living *Chara*. Aufwuchs detritus, presumably formed from decomposing tissues of *Chara* and aufwuchs organisms, consisted of very fine, unidentifiable, particulate material within a clear, sticky matrix. This substrate was colonized by bacteria (e.g., pink, sulfur-fixing bacteria) (Table 5.10). Other components of the aufwuchs, such as living green algae, blue-green algal filaments and microinvertebrates never, as a group, exceeded 10.8% of the total aufwuchs biomass (Table 5.10) and were relatively uncommon within the guts of herbivores (Table 5.8). The primary consumer trophic level in Ponds 5 and 5e included herbivorous dipteran and mayfly larvae, detritivorous soldierfly larvae, the herbivorous larvae and adults of hydrophilid beetles, and an assemblage of microinvertebrates. Secondary consumers (predators) within the *Chara*/aufwuchs community included odonate nymphs, mosquitofish, tabanid and dytiscid larvae, and dytiscid adults. Corixids were probably omnivorous, as guts of individuals sampled from Ponds 5 and 5e contained diatoms and detritus, yet the species examined (*Corisella inscripta*) has been categorized as

Table 5.7. Species list of Pond 5 and 5e aquatic invertebrates sampled from *Chara* beds.

Common Name	Taxon	Species	Life History Stages	Distribution	Notes
	Odonata				
Dragonfly	Libellulidae	*Tarnetrum corruptum*	N,A	Widespread	most common dragonfly in CA
	Aeshnidae	*Anax walsinghami*	N	Widespread	largest dragonfly in N.A.
Damselfly	Coenagrionidae	*Ischnura barberi*	N,A*	Widespread	
	Ephemeroptera				
Mayfly	Baetidae	*Callibaetis montanus*	N,A	Calif. (Sacramento Valley) and SW U.S.	nymphs have wide pH and temp. tolerances
	Hemiptera				
Water boatman	Corixidae	*Corisella inscripta*	N,A	Western U.S.	tolerant of saline water, has been found in sewage oxidation ponds in Concord, CA
Backswimmer	Notonectidae	*Notonecta unifasciata*	N,A	Western N.A.	found in saline pools and hot spring
Velvet water bug	Hebridae	*Merragata hebroides*	A		
	Coleoptera				
Predaceous diving beetles	Dytiscidae	*Hygrotus sp.*	L,A	Nearctic	genus found in saline pools
		Rhantus anisonychus	A		
Water scavenger beetles	Hydrophilidae	*Berosus fraternus*	L,A	Widespread	
		Enochrus diffusus	L,A	Widespread	
		Enochrus conjunctus	L,A	Widespread	
	Diptera				
Biting midges	Ceratopogonidae		L,P,A	Widespread	
Midges	Chironomidae	*Chironomus attenuatus*	L,P,A*	Widespread	most common species of the genus; tolerant of fluctuations in salinity and temp.; in sewage oxidation ponds near Concord, CA; abundant in silty ooze of CA rice fields
		Eukieffierella sp.	L,P,A*	Widespread	
Soldierfly	Stratiomyidae	*Odontomyia sp.*	L	Widespread	
Horsefly	Tabanidae	*Tabanus punctifer*	L,P,A*	Western U.S.	unusual for adults to bite humans
Flowerfly/Rattail maggot	Syrphidae	*Eristalis aenea*	L,P,A	Widespread	
Brinefly	Ephydridae	*Ephydra packardi*	L,P,A*	Widespread	tolerant of wide ranges in salinity from 1-8 $^{o}/oo$, with an optimum in range of 4-5 $^{o}/oo$; most widespread fly associated with relict waters of moderate salinity (e.g. Salton Sea).

*adults reared in the laboratory from immature stages obtained from field samples.

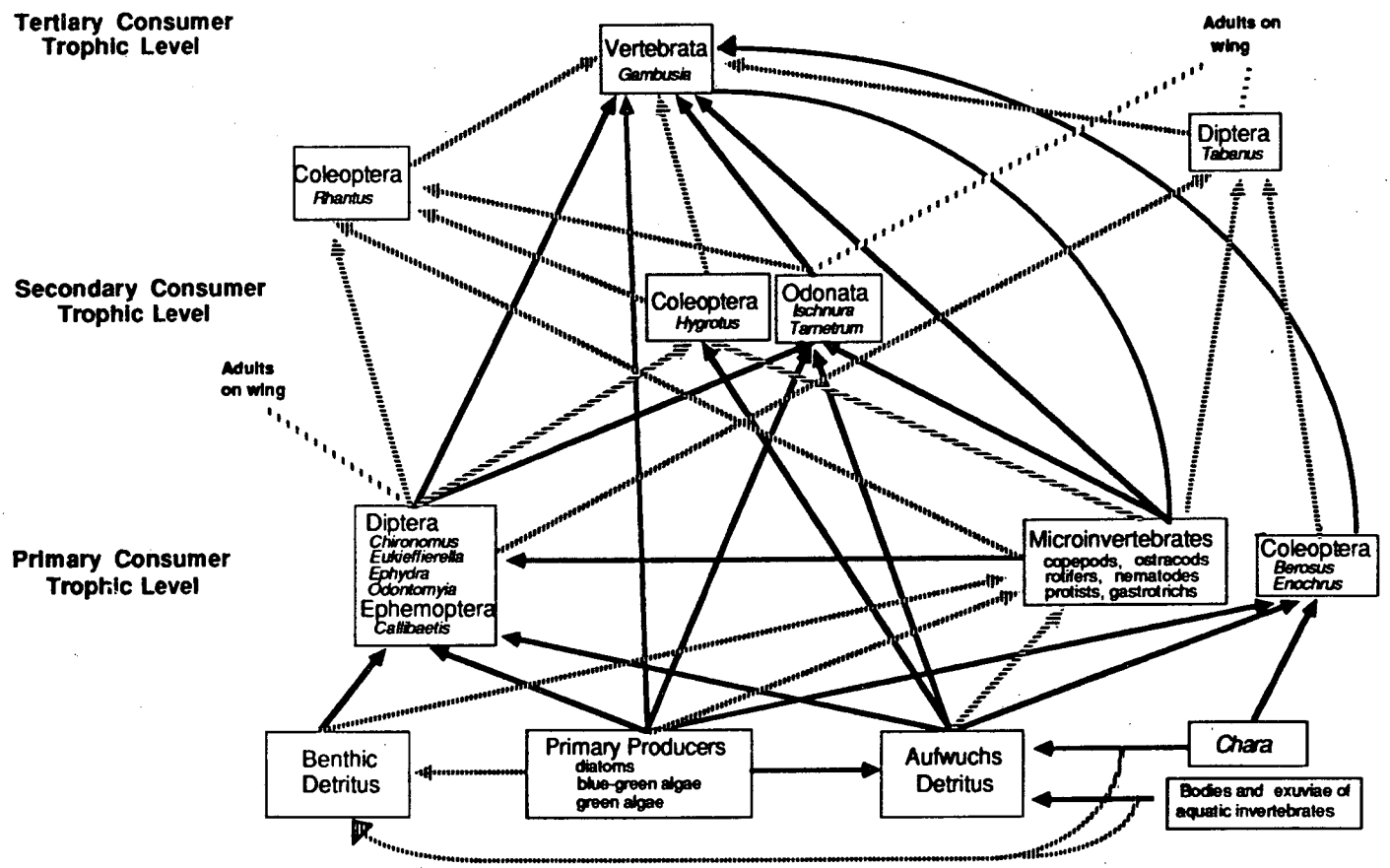


Figure 5.19. Food web of the *Chara* community and benthos in Pond 5 at Kesterson Reservoir. Solid lines with arrows indicate food pathways established by gut content analyses. Dotted lines with arrows indicate hypothetical pathways based upon published information. Dotted lines without arrows indicate emergence of aerial adults from aquatic larvae.

Table 5.8. Seasonal summary of gut contents of Pond 5 aquatic invertebrates. The total number of guts with contents (N) and the number empty (E) are indicated for each season. NP indicates that the species was not present in field samples. ++ indicates that the frequency of the item, relative to N, was >0.5. + indicates a frequency < 0.5.

SPECIES AND DATE	(N/E)	GUT CONTENTS* "Plants"			Crustaceans			Insects					Others		
		diat	bl-grn	grn	ostr	cope	clad	chiro	cer	ephy	dyt	uni	rot	det	sed
Odonata															
Tarnetrum corruptum															
Sept - Nov '86	(1/0)										+				
Dec '86 - Feb '87	(NP)														
Mar - May '86, '87	(9/4)	+			++	++	+	+			+	++	+		
June - Aug '86, '87	(1/0)	+		+				+				+			
Ischnura barberi															
Sept - Nov '86	(7/0)	++			++	+		+	+					+	+
Dec '86 - Feb '87	(1/3)	+						+						+	
Mar - May '86, '87	(10/3)	+			+	+	+	++				+	+	+	
June - Aug '86, '87	(3/0)	++			+			++		+				++	
Ephemoptera															
Callibaetis montanus															
Sept - Nov '86	(NP)														
Dec '86 - Feb '87	(3/1)	++												++	++
Mar - May '86, '87	(1/0)	+		+										+	+
June - Aug '86, '87	(NP)														
Hemiptera															
Corisella inscripta															
Sept - Nov '86	(NP)														
Dec '86 - Feb '87	(0)														
Mar - May '86, '87	(1/8)	+												+	
June - Aug '86, '87	(1/1)													**	

* bl-grn = blue-green algae, cer = ceratopogonid larvae, chiro = chironomid larvae, clad = cladocerans, cope = copepods, det = detritus, diat = diatoms, dyt = dytiscid larvae, ephy = ephydrid larvae, grn = green algae, ostr = ostracods, rot = rotifers, sed = sediment grains, uni = unidentified arthropod parts, ** = amorphous granular material, distinct from detritus

TABLE 5.8 (cont.)

GUT CONTENTS *

SPECIES AND DATE	(N/E)	"Plants"			Crustaceans			Insects					Others		
		diat	un-par	grn	ostr	cope	clad	chiro	cer	ephy	dyt	uni	rot	det	sed
Coleoptera															
Dytiscidae															
Hygrotus sp.															
larvae															
Sept '86 - Feb '87	(0)														
Mar - May '87	(0/9)														
June - Aug '87	(0)														
adults															
Sept - Nov '86	(1/2)											+			
Dec '86 - Feb '87	(0)														
Mar - May '87	(0/2)														
June - Aug '87	(0)														
Hydrophilidae															
Berosus fraternus															
larvae															
Sept '86 - Feb '87	(0)														
Mar - May '87	(2/3)			++											
June - Aug '87	(2/1)	+		++											
adult															
Sept '86 - Feb '87	(0)														
Mar - May '87	(0/1)														
June - Aug '87	(2/0)	+												++	
Enochrus spp.															
larva															
Sept - Nov '86	(0/2)														
Dec '86 - May '87	(0)														
June - Aug '87	(2/6)													**	

* bl-grn = blue-green algae, cer = ceratopogonid larvae, chiro = chironomid larvae, clad = cladocerans, cope = copepods, det = detritus, diat = diatoms, dyt = dytiscid larvae, ephy = ephydrid larvae, grn = green algae, ostr = ostracods, rot = rotifers, sed = sediment grains, uni = unidentified arthropod parts, ** = amorphous granular material, distinct from detritus.

TABLE 5.8. (cont.)

GUT CONTENTS*

SPECIES AND DATE	(N/E)	"Plants"			Crustaceans			Insects					Others		
		diat	bl-grn	grn	ostr	cope	clad	chiro	cer	ephy	dyt	uni	rot	det	sed
Coleoptera															
Hydrophilidae															
adults															
Sept - Nov '86	(0/4)														
Dec '86 - Feb '87	(0)														
Mar - May '87	(1/1)	+	+	+								+		+	
June - Aug '87	(6/1)	++		++										++	+
Diptera															
Chironomidae															
Chironomus attenuatus															
Sept - Nov '86	(1/0)	+		+										+	+
Dec - Feb '87	(11/2)	++	++	++	+	+						+	+	++	+
Mar - May '86,'87	(8/0)	++	+	++	+									++	+
June - Aug '87															
Eukieffierella sp.															
Dec '86 - Feb '87	(2/0)	++													
Mar - May '87	(5/0)	++		++								+		++	++
June - Aug '87															
Stratiomyidae															
Odontomyia sp.															
Sept - Nov '86	(1/0)	+													
Dec '86 - Feb '87	(NP)														
Mar - May '87	(1/1)	+	+	+										+	
June - Aug '86,'87	(0/1)														
Tabanidae															
Tabanus punctifer															
Sept '86 - Aug '87	(2/0)													**	
June - Aug '87	(1/0)													*	
Syrphidae															
Eristalis aenea															
Sept - Nov '86	(1/0)	+	+	+										+	+
Dec '86 - Feb '87	(0)														
Mar - May '87	(2/2)	++	+	+										++	+

* bl-grn = blue-green algae, cer = ceratopogonid larvae, chiro = chironomid larvae, clad = cladocerans, cope = copepods, det = detritus, diat = diatoms, dyt = dytiscid larvae, ephy = ephydrid larvae, grn = green algae, ostr = ostracods, rot = rotifers, sed = sediment grains, uni = unidentified arthropod parts, ** = amorphous granular material, distinct from detritus.

TABLE 5.9. Seasonal summary of gut contents of Pond 5 mosquitofish (Gambusia). The total number of specimens with contents in guts (N) and the number with empty guts (E) are indicated for each season. ++ indicates that the frequency of the item, relative to N, was > 0.5. N. + indicates a frequency < 0.5.

			GUT CONTENTS*														
DATE	N/E	F	"Plants"		Crustaceans			Insects							Others	
			diat	bl-grn	ost	cop	clad	chir	cer	ephy	hemi	syr	col	uni	nem	det
Pond 5																
August '86	3/0	3.0							++		+	++				
Sept - Nov '86	7/0	3.3	+		+	++	++	++	+				+		+	+
Pond 5e																
August '86	3/0	3.3	+	++				+								
Sept - Nov '86	11/1	2.8	++		+	+	+	+	+	+			+	+		++

* bl-grn = blue-green algae, cer = ceratopogonid larvae or adults, chiro = chironomid larvae or adults, clad = cladocerans, col = coleoptera, cope = copepods, det = detritus, diat = diatoms, ephy = ephydrid larvae, hemi = hemipterans, nem = nematodes, ost = ostracods, syr = rat-tail maggots, uni = unidentified insects,

Table 5.10 Composition of Chara aufwuchs.

	POND 5 MEAN PERCENTAGE (± s.d.)(n=3)				
Items	24 Mar	14 Apr	28 Apr	2 June	21 July
Living Diatoms					
Gyrosigma sp.	17.1 ±18.0	21.2 ± 10.5	31.0 ± 3.0	61.9 ± 16.6	12.6 ± 10.2
Navicula	5.5 ± 3.2	7.5 ± 5.0	5.9 ± 8.4	2.5 ± 1.4	5.1 ± 8.0
Synedra	7.6 ± 11.4	3.7 ± 3.2	1.2 ± 1.4	0.3 ± 0.5	0.3 ± 0.5
Coscinodiscus	0	0	0	0.9 ± 0.9	1.6 ± 1.5
Total living diatoms	30.2 ±32.6	32.4 ± 18.7	38.1 ± 12.8	65.6 ± 19.4	19.6 ± 20.2
Dead Diatoms (frustules)					
Gyrosigma sp.	22.2 ± 7.3	23.1 ± 8.8	19.4 ± 9.0	10.6 ± 1.1	37.2 ± 11.1
Navicula	2.3 ± 2.5	1.8 ± 1.9	0	0	1.8 ± 2.4
Synedra	5.7 ± 9.6	2.9 ± 2.5	0	0	0
Total dead diatoms	30.2 ±19.4	27.8 ±13.2	19.4 ± 9.0	10.6 ± 1.1	39.0 ± 13.5
Detritus	35.8 ±10.6	33.1 ± 6.8	35.2 ± 23.6	22.9 ± 17.4	30.6 ± 18.1
Green Algae	1.6 ± 1.4	1.1 ± 0.9	2.1 ± 3.0	0	1.9 ± 1.7
Blue-green filaments	0	2.6 ± 2.4	2.1 ± 3.7	0	0
Sediment grains	1.9 ± 1.7	3.0 ± 3.6	2.2 ± 3.8	0.9 ± 0.9	6.2 ± 9.1
Other	0.3 ± 0.5	0	0.9 ± 0.7	0	2.7 ± 2.6
	POND 5e				
Living Diatoms					
Gyrosigma	14.1 ± 0.4	28.2 ± 15.8	13.0 ± 3.4	62.8 ±19.2	19.1 ± 11.2
Navicula	4.2 ± 0.6	6.4 ± 4.1	2.9 ± 2.1	4.7 ± 3.4	1.1 ± 1.2
Synedra	0	5.8 ± 8.9	0	0	0.7 ± 0.6
Coscinodiscus	0	1.9 ± 2.2	1.4 ± 1.0	0	13.2 ± 17.2
Total living diatoms	18.3 ± 1.0	42.3 ±31.0	17.3 ± 6.5	67.5 ± 22.6	34.1 ± 30.2
Dead Diatoms (frustules)					
Gyrosigma	31.2 ± 8.7	13.1 ± 12.1	36.0 ± 4.3	11.0 ± 0.7	11.8 ± 6.2
Navicula	1.3 ± 0.6	0.7 ± 1.2	0	0.3 ± 0.5	0.3 ± 0.5
Syndera	0	5.8 ± 8.9	0	0	0
Coscinodiscus	0.3 ± 0.6	1.1 ± 0.6	0	0	7.0 ± 7.7
Total dead diatoms	32.8 ± 9.9	20.7 ± 22.8	36.0 ± 4.3	11.3 ± 1.2	19.1 ± 14.4
Detritus	45.1 ± 8.0	30.8 ±12.8	38.0 ± 6.4	20.4 ±14.9	43.2 ± 17.8
Green Algae	0	0.5 ± 0.4	6.3 ± 5.8	0	1.2 ± 1.3
Blue-green filaments	0	0	0	0	0
Sediment grains	1.8 ± 2.4	1.8 ± 0.9	0.9 ± 0.9	0.9 ± 1.4	2.2 ± 3.1
Other	1.6 ± 1.2	3.9 ± 4.1	1.3 ± 1.3	0	0.2 ± 0.5

a piercing carnivore in the literature. Tertiary consumers included mosquitofish, tabanid larvae, and large dytiscid adults.

Gut content analyses revealed that the trophic base of the benthic and shoreline "ooze" environments in Ponds 5 and 5E was detritus and diatoms. However, it was not possible to determine if the diatoms within the guts of organisms sampled from these environments were alive or dead when ingested. The benthic "ooze" environment was inhabited primarily by chironomid larvae, (primarily *Chironomus attenuatus*, the same species which occupied *Chara* beds) and their gut contents were indistinguishable from those of epifaunal chironomids (Table 5.11). Inorganic sediment particles were rarely present within the guts of either epifaunal or benthic chironomids.

The shoreline "ooze" environment was not sampled quantitatively. However, qualitative collections included rat-tailed maggots, soldierfly larvae, brinefly larvae or tabanid larvae, depending upon the season. Gut contents rat-tailed maggots and soldierfly larvae consisted primarily of highly decomposed, particulate matter (detritus).

Table 5.11. Gut contents of *Chironomus attenuatus* sampled from the benthic ooze (**B**) vs. floating *Chara*/aufwuchs (**C**). N = number of specimens with gut contents; **E** = number with empty guts. All values for gut contents represent mean percentage biomass (± s.d.).

Date	Habitat	N/E	Gut Contents			
			Diatoms	Detritus	Other*	Sediment Grains
25 Feb '87	B	7/0	20.0±12.2	71.7±13.7	0.3±0.5	7.9±4.9
"	C	7/0	34.1±17.9	59.3±16.7	6.0±4.4	0.7±0.7
24 Mar '87	B	4/0	30.7±11.4	68.6±13.1	4.1±2.2	3.0±2.7
"	C	3/0	27.7±17.1	67.7±16.0	1.8±0.9	2.9±3.5
28 Apr '87	B	3/0	13.1±11.2	75.0±12.4	2.2±1.2	9.7±2.2
"	C	3/0	15.8±17.6	69.2±9.1	11.7±7.8	3.3±1.4

*Other includes green algae, blue-green filaments, ostracod valves, and unidentified arthropod parts.

5.5. Discussion

The concentrations of selenium in the biota at Kesterson Reservoir have been much higher than are reported elsewhere in the literature. With the exception of bird livers, which seem to be high in selenium (>20 ppm dry wt.) in sites as disparate as San Francisco Bay and the estuaries of the Netherlands, few sites show biota values of 100-200 ppm in whole bodies of aquatic animals or soluble/suspended selenium levels of 200-400 ppb. Most previous research, therefore, has focused on the effect of selenium at very low levels in water and in the food chain, or with the accumulation and toxicity of selenium, not its loss or deaccumulation. In contrast, our research has concentrated on the loss of selenium from highly contaminated biota. Many of our conclusions, though applicable to Kesterson Reservoir, await confirmation as to their applicability in other areas contaminated by selenium.

Selenium levels in most of the aquatic biota in the deeper permanently wet site (Pond 5) declined soon after ambient soluble selenium (all chemical species) fell below 20 ppb. In Pond 5 these low levels of soluble selenium were reached in November 1987, several months after the discharge of highly contaminated drainwater into the Reservoir in July and August 1987. In Pond 5E, soluble selenium fell below 5 ppb within weeks of pumping uncontaminated groundwater into the enclosure in March 1986. Exponential decay functions fit to selenium concentrations of *Chara*, aufwuchs, tabanid larvae and mosquitofish in Pond 5E provide a basis for predicting when Pond 5 organisms will fall below 3 ppm in Pond 5. According to these predictions, *Chara* will reach this level by June 1988, aufwuchs by December 1988, mosquitofish by September 1990, and tabanid larvae by June 1992. Although these predictions are conservative relative to those based on Pond 5 rates of selenium decline, they may still underestimate rates of decline when biotic concentrations approach soluble selenium levels.

At the Pond 7 index site soluble selenium concentrations have fluctuated near 20-30 ppb since November 1986. Although biotic selenium concentrations have not declined as

rapidly as in Pond 5, they were not as high as Pond 5 biotic selenium concentrations following the discharge of drainwater into that pond. Biotic concentrations of similar organisms sampled from Ponds 5 and 7 index sites in March 1987 were similar in value. These observations indicate that keeping deep water ponds flooded year round is effective in reducing food chain selenium levels, but that maintaining shallow water in formerly seasonal wetlands is less effective, at least in the first year. Unfortunately, the water supply to the Pond 7 index site was discontinued in early 1987, and the pond dried up in May 1987. Observations during the preceding year suggest that such shallow sites were to be kept wet continuously for several years, the kinds of organisms present would change, with *Ruppia* probably becoming replaced by *Chara* or other algae.

The discharge of drainwater into the Reservoir in July-August 1987 provided an opportunity to monitor the responses of biota to a spike of soluble selenium. Selenium concentrations of the herbivorous brinefly larvae and predatory tabanid larvae, dytiscid adults and mosquitofish peaked in October, prior to a November peak in selenium values of the primary producers, *Chara* and aufwuchs. One or more factors may have contributed to rapid increases of biotic selenium, including direct uptake from water, migration of contaminated mosquitofish from the drain, or transfer of selenium through the food chain.

Peaks in the biomass of ephydrid (brinefly) larvae occurred during August and October 1987, and the mean selenium concentration of this herbivorous species exceeded 560 ppm in October. Gut content analyses revealed that mosquitofish in Pond 5 were eating brinefly larvae in October and that other potential prey, such as odonate nymphs and chironomid larvae were not present at that time of year. Hence, it is possible that brinefly larvae that rapidly concentrated selenium, either directly from the water or via the food chain, were a major prey item of tabanid larvae and mosquitofish, and were a primary pathway for the transfer of selenium.

These observations support the idea that the potential for clean-up is greater in

permanently wet ponds than in seasonal ponds. First, brinefly larvae seem to respond rapidly to spikes of soluble selenium. These spikes occur repeatedly in seasonal ponds that dry and are then re-wetted with contaminated, rising groundwater (Figure 2.6). Finally, brinefly are more frequently found in seasonal vs. permanent wetlands at Kesterson Reservoir (USBR, 1987), perhaps because competitors and predators of brinefly larvae are relatively scarce in these habitats.

5.6. Summary

Providing that the ponds are continuously flooded, our data indicate that the selenium levels in most elements of the the Kesterson food chain could reach environmentally acceptable levels in 1990 (i.e 4 years after the last addition of selenium-rich drainwater). Some food chain elements (e.g., tabanid larvae) could take until 1992. It is yet not possible to be absolutely certain if permanent flooding will totally protect all possible bird and animal life at Kesterson. Our 17 month laboratory microcosms and 12 month study at the large field mesocosm at Kesterson provide experimental evidence that such a clean-up is possible. To date the short period of field observations indicates that clean-up is generally working in the permanently wet areas and not in the seasonal wetlands or ephemeral pools. Keeping seasonal wetlands covered with shallow water year round showed no clear advantage in the first year. It would be premature to conclude definitive results from the Kesterson field studies based on only 9 months of observation after the last selenium-contaminated drainwater was delivered.

Selenium in Kesterson Reservoir biota was present at levels potentially toxic to birds by 1983 and, while levels fluctuated, biotic selenium concentrations remained fairly constant until 1986. Although named a Reservoir, the area is best considered as a marsh since it is very shallow and choked with aquatic vegetation. In summer 1985 reductions began in the output of selenium from the irrigated farmland, incrementally decreasing the mass loading of selenium. By late spring 1986 selenium concentrations in the Reservoir water had declined to a quarter of that present 6 months earlier. The final delivery

to Kesterson was in August 1986. The UC Berkeley ecological studies followed the subsequent changes in selenium in the biota in the Reservoir. The entire range of aquatic habitats, deep permanent water, shallow permanent waters, and ephemeral pools were sampled monthly. All visible living aquatic organisms, except fish, were collected quantitatively (i.e. numbers or biomass determined from a known area). Quantitative measurements were also made of the microscopic animals and plants which provide the base of the food chain.

Compared to values present before agricultural drainwater was reduced (i.e. 1983-1985) selenium has declined greatly in the water and in tissues of most aquatic organisms at Kesterson marsh where permanent water has been maintained. Such a rapid decline was not predicted, given the short time (9 months) since cessation of selenium input. The major exception was the submerged plant Ruppia which showed no consistent trend over time.

Increases as well as decreases in biotic selenium were quite rapid. A short-lived increase in soluble selenium occurred in August 1986 when high-selenium drain water was added. Four out of five of the most abundant organisms at the permanent (deep) water index site at Pond 5 increased tissue selenium within two months of this addition. Increases and decreases in biotic selenium since autumn 1985 were best explained by changes in soluble selenium, indicating a dominant role for soluble rather than sediment selenium in this system up to now. This finding agrees with other published studies using radioisotope additions to mesocosms and whole lakes. Sediment selenium in the permanent waters remained high and changes in sediment selenium levels are best explained by changes in biotic selenium which, when dead, falls to the bottom.

These findings indicate that, at the range of concentrations found in permanent waters at Kesterson, recycling or remobilizing processes were mostly unidirectional. Soluble selenium moved from the water to the biota and then to the sediments. This conclusion was well supported in the deeper permanent water but less well supported where

shallow was maintained over what would have been seasonal wetlands. It was not the case for the ephemeral pools (seasonal wetlands) where rewetting in winter produced soluble selenium levels averaging over 200 ppb and some aquatic biota with increased in selenium concentrations.

More time than the nine months since the last selenium delivery in August 1986 is required to determine if the declines and increases in selenium in the various organisms found at Kesterson are permanent trends. Studies over at least two years are required to make reliable decisions in field ecology. Management strategies such as keeping permanent water in formerly seasonally dry areas will, over a few years, change the biota present and thus the selenium content.

The amount of selenium in the biota was controlled by the kind of organism present as well as the selenium in the water or in its food. Longer-lived organisms such as mosquitofish, tabanid and benthic chironomid larvae had the highest concentrations of selenium. An important exception were short-lived brinefly larvae which concentrated very high levels of selenium. Brinefly larvae are characteristically abundant in shallow waters of high salinity, such as ponds which are drying out or just re-wetting. They were briefly abundant in Pond 5 in the summer of 1986 but did not occur there in 1987 when salinities were lower. Short-lived algae had low concentrations of selenium. Algae also lost and gained selenium more quickly than the longer-lived fish or dragonflies. Apparent rapid changes in animal selenium in spring were caused by the hatching of aquatic insect larvae into aerial adults and their replacement by young larvae with lower selenium.

The most pronounced and complete decline in tissue selenium was found in the experimental permanent water enclosure (1 acre. 4,000 m-3 mesocosm). Plant tissue selenium in this enclosure has declined by 80-90% during the first complete year of its operation. Declines in the selenium content of aquatic insects have also been considerable (about 80%) and even the slowest-growing animals present (mosquitofish) have declined 64%. These results are similar to the declines found earlier in laboratory microcosms.

As of June, 1987 selenium in the plant biota at the permanent water index site in Pond 5 had declined by two-thirds since its peak in November, 1986. Present values are roughly where they were prior to the August 1986 San Luis Drain disposal indicating that the majority of plant selenium is lost within a year once low-selenium water is applied. This observation is important because the ground elevation in Pond 5 is not level and there are areas which dried and rewetted due to an inadequate water supply in 1987. Drying and rewetting can remobilize soluble selenium and should be better controlled in future permanent water operations.

Studies in ephemeral pools (seasonal wetland index site in Pond 11) were hampered by the dry year. The ephemeral pools at the Pond 11 site, which were full of insect larvae last spring, did not rewet in 1987. Selenium in the terrestrial vegetation growing on the site in 1987 was low.

The Pond 7 site (seasonal wetland) would have become completely dry in summer 1986 but was maintained wet from fall 1985 until spring 1987. Selenium in biota from this site in early June 1987 can be compared with that from similar organisms in seasonal wetlands in previous years. Out of 8 biotic comparisons, 4 at the Pond 7 site showed declines, one showed an increase, and 3 remained about the same as were found in similar sites in past years. The Pond 7 site can be also compared to similar sites which remained as seasonal wetlands and were measured in February and May 1987 as part of the USBR habitat survey USBR, 1987). Most comparisons showed no significant difference between the studies; in a few cases (e.g., mayfly and dragonfly nymphs, chironomid larvae) data collected at the Pond 7 site in March showed higher values than the synoptic seasonal sites; and in a few cases (damselfly nymphs, brinefly larvae, mosquitofish) the March data were lower. One of the most abundant plants in seasonal wetlands is the submerged species, *Ruppia*, which did not show a decline either over time or when seasonal wetlands were converted to permanent waters (i.e. the Pond 7 site). This species did not grow well in permanent water and will probably be replaced by

other organisms over the next few years. Common species present in seasonal wetlands which did decline in selenium when converted to permanent water were saltgrass, algae, and chironomids.

Detailed food chain studies were made by examination of the gut contents of the aquatic insects present at Kesterson. The purpose was to determine on what the most common species fed. An outstanding feature of Kesterson Reservoir is the enormous amounts of aufwuchs (microscopic algae, bacteria and tiny animals growing on underwater plants). Aufwuchs may outweigh the larger vegetation on which it is growing.

Gut content analyses revealed that living diatoms and aufwuchs detritus, formed from the decaying tissues of *Chara* and aufwuchs organisms, were the principal components at the base of the food chain in Ponds 5 and 5e. It is likely that the base of the food chain in Pond 7 was formed from the same components, although the specific composition of the aufwuchs and aufwuchs detritus probably differed, since *Ruppia*, rather than *Chara*, contributed to the detrital base. Herbivores within Ponds 5 and 5e included dipteran larvae, mayfly larvae, and an assemblage of microinvertebrates within the aufwuchs. Predators included odonate nymphs, tabanid larvae, dytiscid larvae and adults and mosquitofish. All aquatic species identified from Ponds 5 and 5e have been sampled from Pond 7, as well.

Although the bird population at Kesterson was evidently affected by the selenium present in the diet, previous studies by USFWS in 1984 and our own investigations found no direct evidence that the present populations of fish or aquatic animals and plants are being similarly affected. The abundance and diversity (a common measure of biological health) of these species was about what would be expected in a saline marsh. Conditions at Kesterson are severe. Water temperatures and salinity are high in summer, dissolved oxygen is often low, and frequent drying out of many areas makes it difficult for most fish to survive.

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