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Anticipated Soil Selenium Concentrations at Kesterson Reservoir

S.M. Benson, T.K. Tokunaga, and P. Zawislanski

October 1992

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Anticipated Soil Selenium Concentrations at Kesterson Reservoir

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Abstract

Temporal trends from soil monitoring data collected at Kesterson Reservoir have been reviewed to shed light on anticipated concentrations of total and water-extractable selenium in surface and subsurface soils. Based on these data, a mass balance model for selenium has been developed and employed to evaluate the rate of leaching, remobilization and volatilization that has occurred since the Reservoir was dried out in 1987. Results from a series of calibration runs were then extrapolated 25 years in the future to forecast the evolution and redistribution of selenium within the soil profile. Projected water-extractable selenium concentrations within the 0.15 to 1 m depth interval were then used to drive a food-chain based risk-assessment model described in a separate report (CH2M Hill, 1992). Inventories of water-extractable selenium in the root zone increased in 4 of the 5 scenarios investigated. However, predicted values for the average concentration of water-extractable selenium in the root zone fall within the range of values observed at Kesterson today. Consequences of these projected increases on wildlife residing in and around Kesterson are addressed in CH2M Hill (1992).

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Introduction

The work described herein was carried out at the request of the United States Bureau of Reclamation to assist in evaluating alternatives for continued management of the former Kesterson Reservoir, Merced County, California. From 1978 to 1986, Kesterson Reservoir was used for disposal of selenium-contaminated subsurface drainage water. The estimated 9000 kg of selenium delivered to Kesterson during this period accumulated largely in the surface-most 0.15 m of pond bottom sediments (Weres et al., 1989). By 1988, the Reservoir was dried out and the low-lying areas were filled with imported and local fill (soils and sediments). About 50% of the Reservoir was filled with an average thickness of 25 cm of fill. Since 1987, the inventory and distribution of the inventory within the soil profile[1] has been monitored. Today, as in 1987, the majority of the inventory is largely insoluble and concentrated in a thin detrital layer and the surface-most 0.15 m of soil. However, detailed monitoring of the distribution and speciation of the selenium inventory deeper in the soil profile indicates that a growing fraction of water-extractable selenium is potentially available for uptake into plants and the food chain .

Concern about the long-term evolution of the selenium inventory and effects on biological exposure prompted this effort to predict trends in soil-selenium concentrations in areas not covered with fill material over the next 20 years. These projections are then used to drive a biological risk assessment model over the same 20 year period. This report describes the data base available to support these projections, the methodology used to predict time trends, the results of the predictions and finally, how these predictions have been incorporated into the biological risk assessment. The biological risk assessment was carried out by CH2M Hill and is described in a separate report (CH2M Hill, 1992).

There remains much to be learned before we can predict, from first principles, the behavior of selenium in Kesterson soils. A complex interplay of seasonally variable physical, chemical and biological processes cyclically transform selenium from one form to another, transport the soluble and gaseous forms within the soil profile and gradually dissipate the

[1] Henceforth the term soil profile is used to represent the top 2 m of Kesterson soils.

selenium inventory. Comprehensive understanding of the individual processes, rates and interplay between them is beyond the present understanding of the scientific community. For example, in spite of the intensive research carried out to date at Kesterson, even such information so basic as "What are the different forms of selenium present in the soil?" have only been answered partially.

Nevertheless, building on a foundation of information on biogeochemical cycling of selenium, we have learned much about how selenium behaves in the Kesterson environment and have developed a substantial data base from which we may extrapolate the time trends observed from 1987 to 1991, into the future. From intensive monitoring data, supported by laboratory and theoretical studies conducted by others and ourselves, we have identified three "phenomena" that appear to control the inventory and redistribution of selenium within the soil profile. These include 1) remobilization of insoluble selenium, 2) leaching of selenium from surface soils to deeper in the soil profile and 3) volatilization, which converts selenium to gaseous forms that are dissipated in the atmosphere. Undoubtedly these phenomena involve a whole suite of chemical, physical and biological processes that interact to produce the phenomena we are able to observe through monitoring the inventory and distribution of selenium within the soil profile. In spite of the inherent complexity, and for lack of a more rigorous framework for embarking on this endeavor, we build upon the monitoring data at hand to project the effects of these processes into the future.

Objectives

The objectives of this effort include the following:

- Synthesize data gathered from ongoing monitoring and research efforts at Kesterson regarding evolution of the selenium inventory;

- Develop a mass balance model for selenium in the grassland[2] and open[3] habitats that can be used to extrapolate observed 1987-92 time-trends into the future;
- Predict the average evolution of the current inventory and distribution of soil selenium in the grassland and open habitats over a 25-year period, beginning in 1987; and
- Through the above exercise, identify gaps in existing knowledge so as to prioritize future research efforts.

Soil Selenium Data Base from Kesterson Reservoir

Since 1987, intensive collection of soil and soil-water samples to determine selenium concentrations has taken place as part of a variety of monitoring and research activities at Kesterson Reservoir. These include the following:

- Soil selenium fractionation and speciation studies;
- Long-term soil and soil-water selenium monitoring in former Ponds 5, 6, 7, 8, 9, 10 and 11;
- Annual synoptic sampling of soil selenium at Kesterson;
- Volatilization experiments in former Ponds 2, 4 and 11; and
- Soil-Water-Vegetation management experiments in former Ponds 2, 5 and 7.

A description of relevant data collected during each of these activities and how they were used in this study is provided in the following sections of the report.

---

[2] The grassland habitat is one of three major habitatats remaining at Kesterson following draining and filling the low-lying areas of the former Reservoir. Now, as in the past, the grassland habitat is vegetated with a combination of annual and perennial grasses (CH2M Hill, 1992).

[3] The open habitat is another of three major habitatats remaining at Kesterson following draining and filling the low-lying areas of the former Reservoir. Historically, the open habitat was vegetated with cattials. After the Reservoir was drained the cattials were disked into the soil. The open habitat is slowly being re-vegetated with a variey of annual and perenial plant species (CH2M Hill, 1992).

Soil Selenium Fractionation and Speciation Studies

As early as 1985 it was clear that most of the selenium delivered to Kesterson was converted from selenate to sparingly-soluble forms by microbial activity in the pond bottom sediments and uptake by aquatic flora (Weres et al., 1985). Since then several research efforts have attempted to identify the predominant species of selenium present in the soils (Weres et al., 1989; Tokunaga et al., 1991; Zawislanski, 1990). From these investigations, selenate, selenite and elemental selenium have been proposed as the major species of selenium present in the surface soils. In addition, selective extractions indicate that unidentified species of organically associated and organically bound forms may also form a significant fraction of the inventory. Information regarding each of the predominant forms of selenium in the soils is summarized briefly below.

The selective extraction techniques used for this investigation are described in Tokunaga et al. (1991) and Weres et al. (1989). Five major pools of selenium are identified with these extraction techniques, including: water extractable selenate; water extractable selenite; adsorbed selenium; organically-associated selenium, and; refractory[4] selenium. Note that the selective extraction techniques employed to fractionate selenium into the pools defined below are not mutually exclusive and as such, there remains significant uncertainty with regards to the forms of selenium present. Nevertheless, the following summarizes our best understanding of the nature and distribution of selenium in Kesterson soils.

Selenate occurs predominantly in forms that are readily extracted from the soil with a 1:5 mass ratio of soil-to-water solution (henceforth referred to as water-extractable selenium). Comparisons between soil extracts and soil water solutions collected in situ

[4] Note that the term "refractory" is operationally defined in tbis context as selenium that could not be extracted from the soils using the extaction methods that remove the other 4 fractions identified. Evidence from numerous sources suggest that this pool is largely elemental selenium (Weres et al., 1989; Oremland etal., 1989; and Tokunaga et al., 1991). Under the present conditions, this pool is nearly insoluble and under geochemically reducing conditions this pool may remain in its current form. However, under the oxiding conditions in the vadose zone at Kesterson, this pool is expected to slowly oxidize and become mobile and available for transport and plant uptake. Hence, the name "refractory" is used in the context of its current status rather than an indication of its future behavior.

with suction samplers suggest that nearly all the selenate is dissolved and freely transported within the soil profile and is available for plant uptake. Selenate comprises typically about 90% of the selenium in soil-water solutions. Minor amounts of selenate may also be present in adsorbed forms or co-precipitated with carbonate minerals in surface soils, organic detritus and salt crusts (Tokunaga et al., 1991; Zawislanski, 1990).

Selenite in Kesterson soils occurs in water-extractable, adsorbed and co-precipitated forms (Tokunaga et al., 1991; Zawislanski, 1990). Selenite typically comprises about 10% of the water-extractable fraction. However, the majority of selenite appears to be associated with adsorbed or co-precipitated phases that limit the mobility and availability of selenite (Weres et al, 1989; Tokunaga et al, 1991). In addition, a significant fraction of the organically associated selenium may occur as selenite adsorbed or otherwise incorporated with soil organic matter.

Elemental selenium is also believed to comprise a significant fraction of the selenium inventory in Kesterson soils. Elemental selenium is formed by microbial reduction of selenate or selenite (Geering et al., 1968; Doran, 1982; Oremland et al., 1989). A significant fraction of organically-associated selenium may be in the elemental form (Tokunaga et al., 1991). Elemental selenium is nearly insoluble in Kesterson soils and as such has extremely limited availability for plant uptake or transport.

Figures 1a, 1 b and 1c provide illustrative examples of the distribution of the various forms of selenium in Kesterson soils in 1990. Data presented represent conditions at Kesterson ranging from the cattail-habitat of former Pond 2 (open habitat), to the re-vegetated playa-habitat in Pond 9 (now considered grass-land habitat) to the grassland-habitat of Pond 11. In each case, fractionation data from two depth intervals are provided, the surface ten centimeters (0 - 0.1 m) and from 0.45 to 0.55 m.

While there is a wide range of variability in soil selenium concentrations and speciation in Kesterson soils, the following generalizations can be made. In the open and grassland habitats, the surface-most interval contains typically greater than 50% "refractory" selenium. In this same interval, the water-extractable pool comprises from 2

to 5% of the total selenium inventory, most of which is selenate. The remainder of the selenium inventory in this interval is distributed between adsorbed and organically-associated forms.

Deeper in the soil profile, a much larger fraction of the total inventory is in water-extractable forms. For the three samples shown in Figure 1, from 40 to 60% of the selenium is present as water-extractable selenate. The remainder of the selenium is distributed amongst the adsorbed, organically-associated, and "refractory" pools, with large site-to-site variability.

These data also illustrate that the concentration of selenium in the 0.45 to 0.55 m depth interval is typically less than 1/10 the concentration in the surface ten centimeters. However, such large contrasts are not present in the water-extractable inventory. For example, as shown in both Figures 1b and 1c, water-extractable concentrations are nearly equal in these two depth intervals. In the open habitat, however, as illustrated by the sample shown in Figure 1a, the amount of water-extractable selenium in the surface-most 10 cm may be an order of magnitude greater than deeper in the soil profile.

The data provided in Figures 1a-1c, as well as data from previous studies (Weres et al., 1989; and Tokunaga et al., 1991) suggest that within the surface 10 cm there is a large pool of selenium that is currently in insoluble or immobile forms. Thermodynamic considerations indicate that selenate is the stable form of selenium in this environment and that eventually the speciation will shift in this direction (Geering et al., 1966; Doran, 1982; Elrashidi et al., 1987; and Weres et al., 1989; and Tokunaga et al., 1991). Specifically, we expect that some fractions, such as adsorbed selenite and organically associated selenium will be oxidized or mineralized and released into the soil water. Less is known about the stability of elemental selenium in this environment. From thermodynamic considerations, we expect that elemental selenium will eventually be transformed to selenite or selenate. However, the rate and mechanisms of these transformations remain uncertain. Bacteria capable of oxidizing elemental selenium have been identified (Saratchandra and Watkinson, 1981), but these specific bacteria have not been identified in Kesterson soils, nor is it

certain that others may not act in a similar capacity. Slow abiological mechanisms of transformation may also be effective in long-term transformations. The complexity of the system is compounded by seasonal variations in redox conditions, populations of soil microorganisms, and soil moisture which act to periodically shift the thermodynamic status of the soil system towards more reducing conditions (Zawislanski, 1989; Ita and Benson, 1992).

Experiments are underway to accelerate the rate of transformations within Kesterson soils to determine the relative rate at which the presently immobile pools are oxidized to more mobile and avaliable forms of selenium (Weres et al., 1989; Yee, 1990; Zawislanski and Zavarin, 1992). Results from these suggest that all fractions are potentially labile to varying degrees. Oxidation or volatilization of all soil selenium fractions have been observed when soils have been provided with adequate moisture, aeration and a plentiful population of soil microorganisms. "Refractory fractions" in general are oxidized or volatilized at low rates compared to the other soil fractions. However, recent experiments conducted at slightly elevated temperatures (35°C) have demonstrated oxidation of the "refractory" fraction from 12 to 22% over a 3-month period. Together, these data and previous investigations suggest that a large fraction of the selenium inventory at Kesterson is susceptible at times to oxidation and remobilization. Only through detailed monitoring of soil-selenium concentrations will site-specific mechanisms and rate constants be obtained.

In the following sections, ongoing soil-selenium monitoring data will be described briefly and discussed in the context of how they are used in the current effort to extrapolate observed trends into the future.

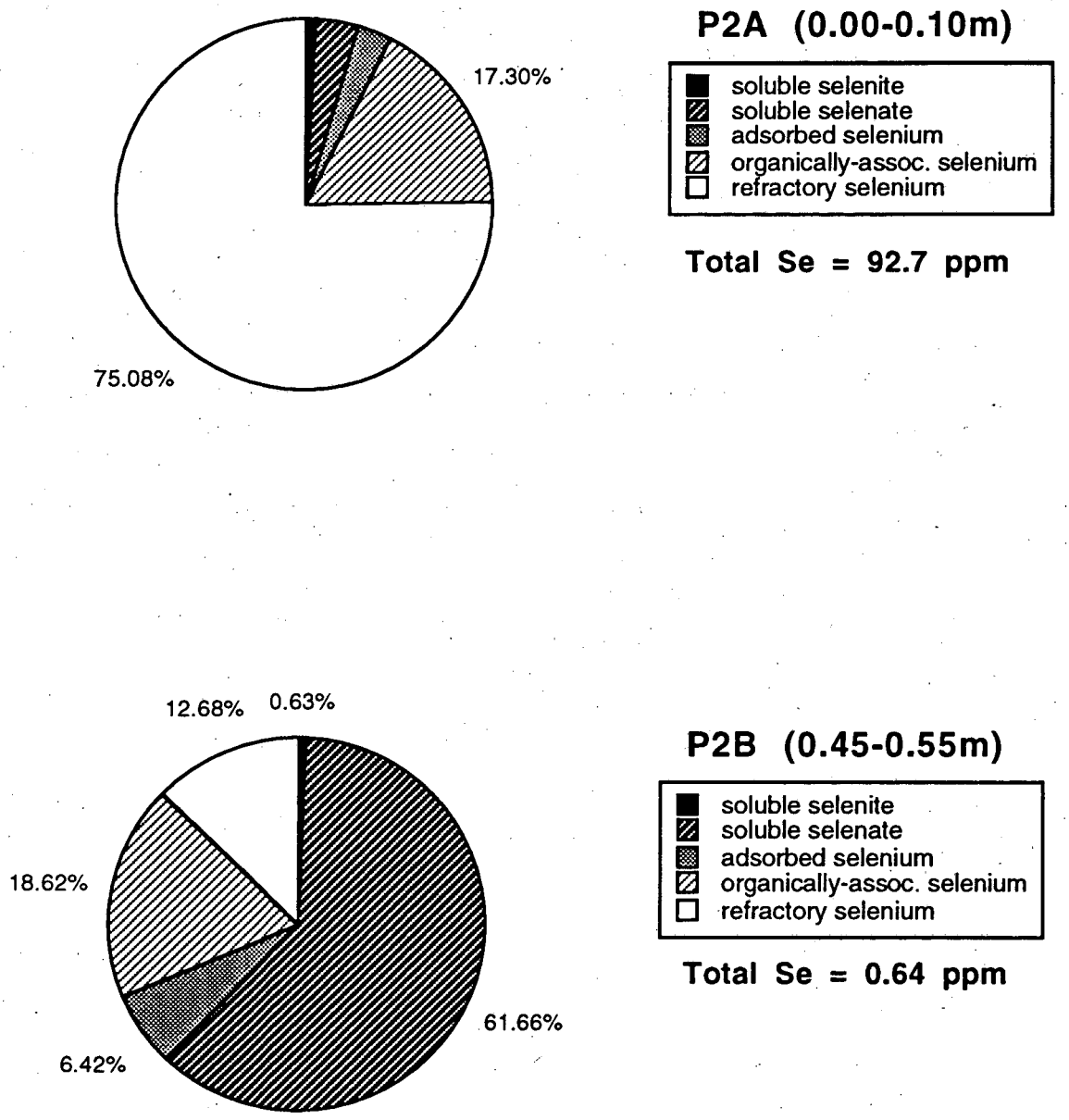
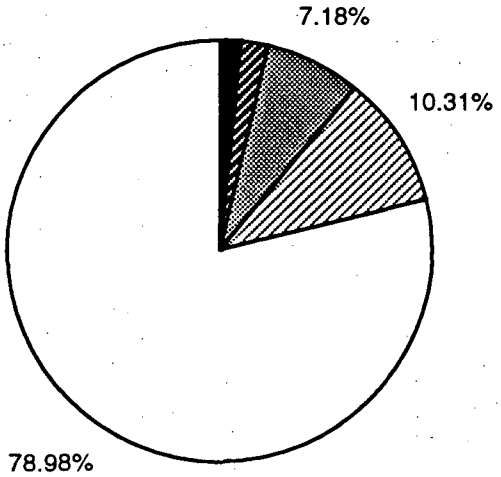


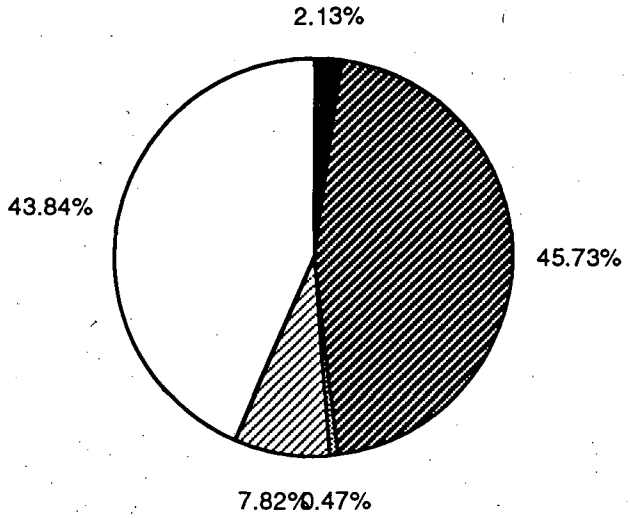
Figure 1a. Illustrative example showing the dominant forms of selenium in two Kesterson soils. These data were collected from former cattail habitat in Pond 2 (now open habitat) in November, 1990. Data illustrated in the top panel are from the surface soil (0 -0.10 m) and the lower panel from a sub-soil (0.45 - 0.5 m).



P9A (0.00-0.10m)

- soluble selenite
- soluble selenate
- adsorbed selenium
- organically assoc. selenium
- refractory selenium

Total Se = 4.22 ppm

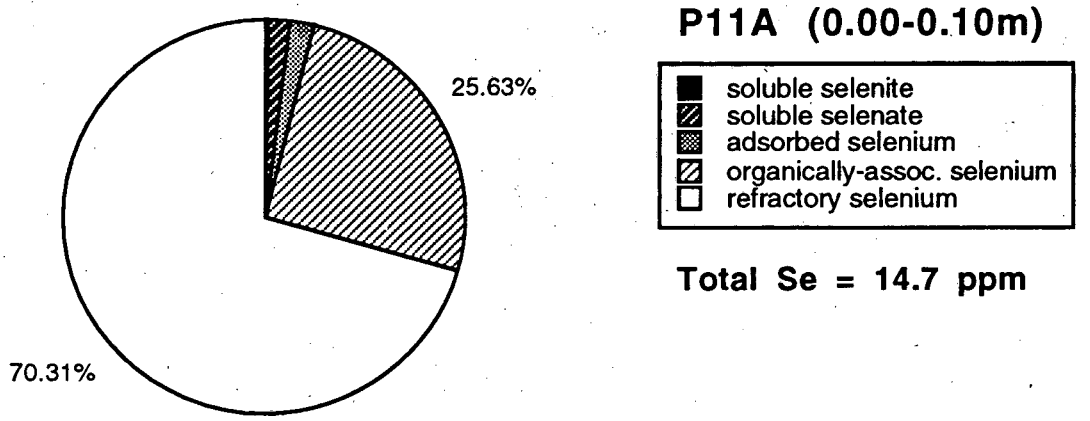


P9B (0.45-0.55m)

- soluble selenite
- soluble selenate
- adsorbed selenium
- organically-assoc. selenium
- refractory selenium

Total Se = 0.42 ppm

Figure 1b. Illustrative example showing the dominant forms of selenium in two Kesterson soils. These data were collected from re-vegetated playa habitat in Pond 9 (now grassland habitat) in November, 1990. Data illustrated in the top panel are from the surface soil (0 -0.10 m) and the lower panel from a sub-soil (0.45 - 0.5 m).



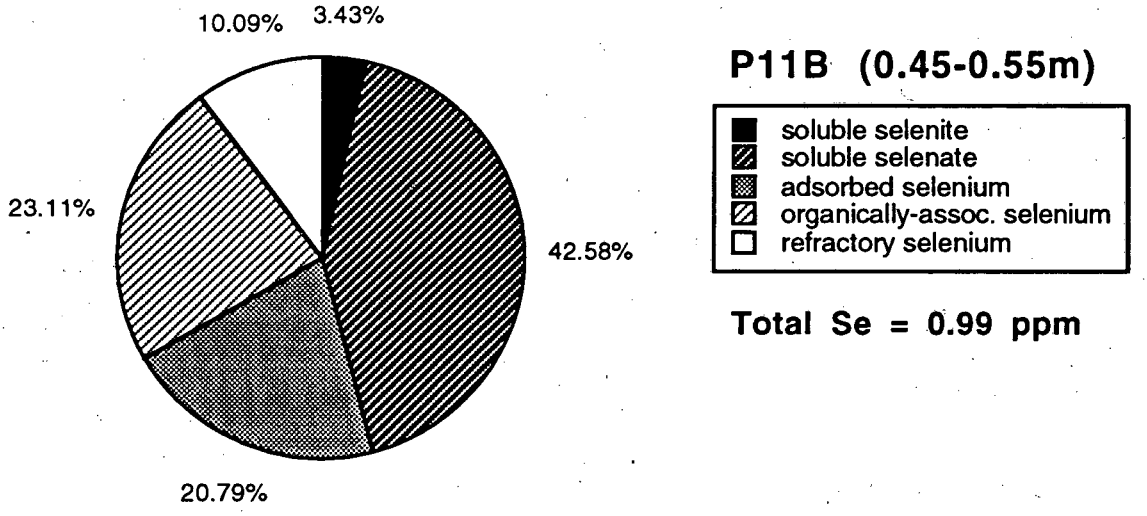


Figure 1c. Illustrative example showing the dominant forms of selenium in two Kesterson soils. These data were collected from grassland habitat in Pond 11 in November, 1990. Data illustrated in the top panel are from the surface soil (0 -0.10 m) and the lower panel from a sub-soil (0.45 - 0.5 m).

Long Term Soil and Soil-Water Selenium Monitoring

Beginning in 1987 several grassland and playa sites within Kesterson were instrumented with soil-water samplers, tensiometers and neutron probe access holes for monitoring selenium transport in the vadose zone (Long, 1988; LBL, 1988; 1990a,b). Soil water samples and extracts of soil cores from these plots have been obtained at regular intervals since this time. These sites have provided the foundation for our understanding of the physical and chemical "processes" taking place within the top 2 m of Kesterson soils. Monitoring sites have been established in former Ponds 1, 2, 3, 5, 6, 7, 8, 9, 10, and 11. Data sets collected from two sites with the longest and most complete records are described below.

Pond 11

The test plot 11C is located in the south west corner of Pond 11 in an area covered with a dense and stable growth of salt grass (*Distichlis spicata*) and that had been subject to seasonal flooding with incoming San Luis Drain water. The depth of the water table at the 11C test plot varies sesaonally from a summer low of about 3 m to about 1.5 m in mid-winter. Detailed descriptions of all the monitoring data are provided in LBL (1988; 1990a; and 1990b) and Tokunaga et al. (1991). Two methods for tracking changes in the inventory and distribution of water-extractable selenium have been used in the 11C test plot 1) soil solution sampling with permanently installed vacuum extraction cups and 2) water-extracts from soil cores. Each method has its own particular set of advantages and disadvantages but together they provide a convincing record of the evolution of the selenium inventory at this site.

Electrical conductivities and selenium concentrations of pore waters collected from 1989 to 1991 with the vacuum-cup extraction system are shown in Figure 2a and 2b. These data illustrate two trends. First, overall concentrations of selenium and major ions (chloride, sulfate and sodium) have increased in the soil solution. Second, their distribution in the soil profile has shifted from being highest near the soil

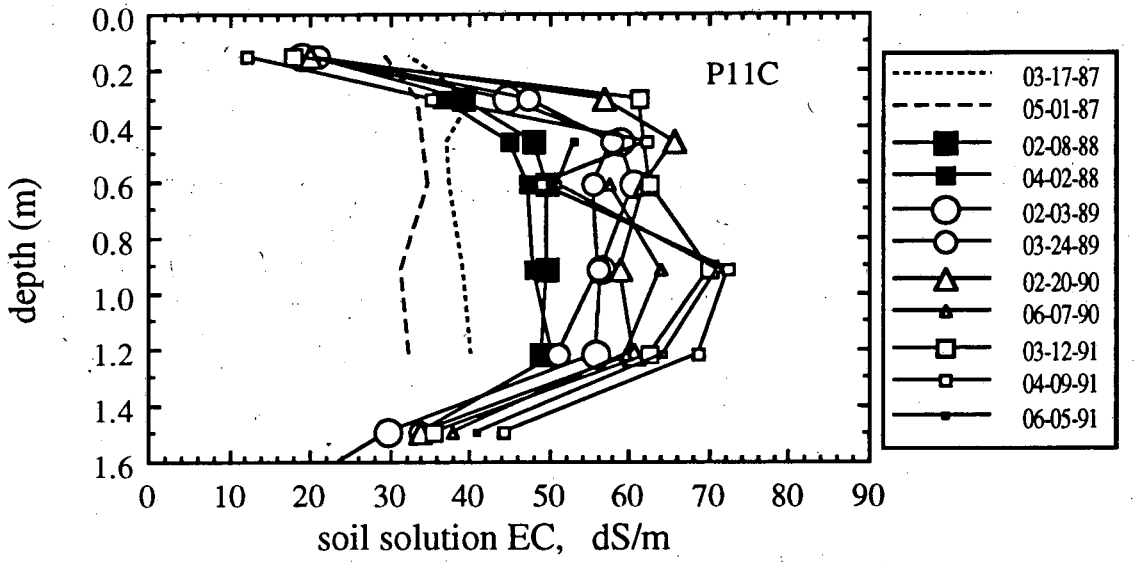


Figure 2a. Time trends in electrical conductivity (EC) of the soil solution at experimental plot 11C in the southwest corner of former Pond 11.

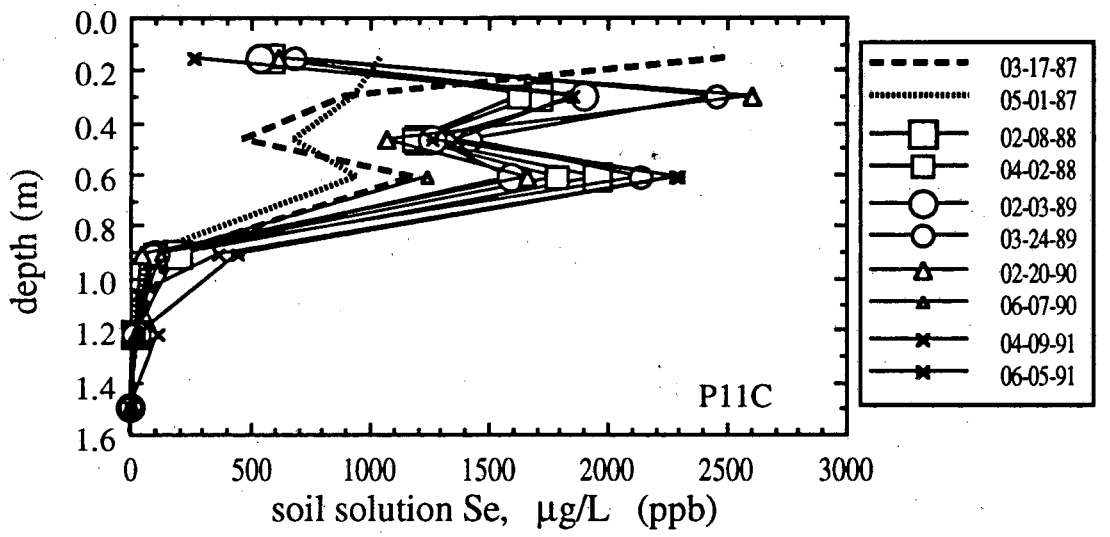
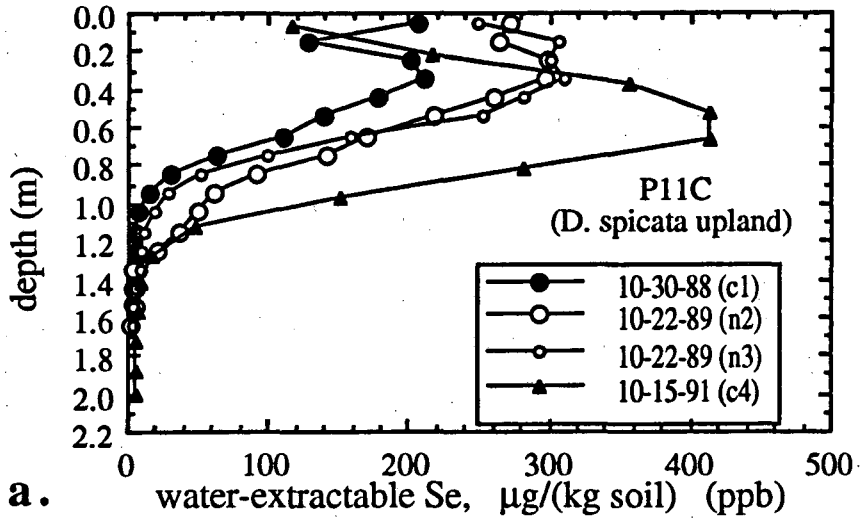


Figure 2b. Time trends in soil solution selenium concentrations at experimental plot 11C in the southwest corner of former Pond 11.



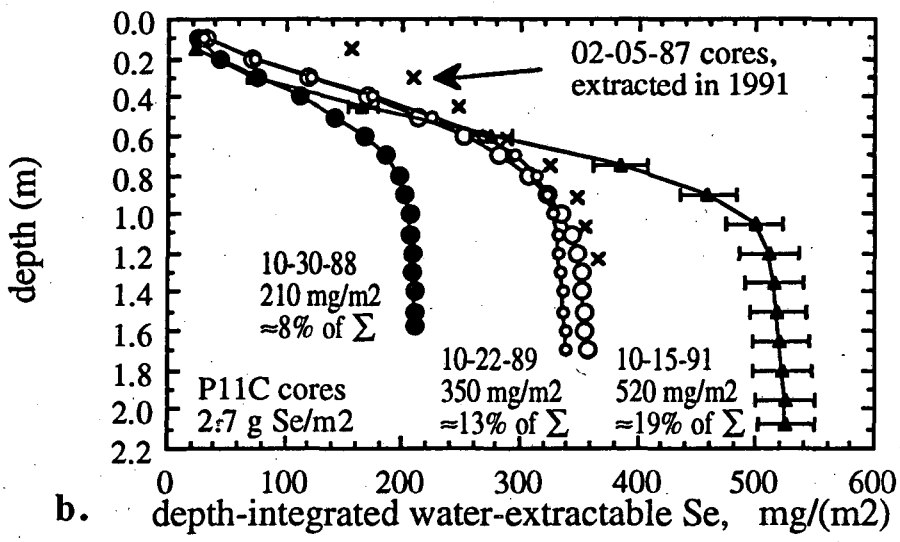


Figure 3a and 3b. Time trends in water-extractable selenium concentrations at experimental plot 11C in the southwest corner of former Pond 11. (a) water-extracted Se [mg/(kg-dry soil)] and (b) depth integrated water-extractable Se (mg/m^2).

surface to being highest at about 1 m depth. These changes can be attributed to the following three processes: leaching of dissolved salts and selenium due to winter rains; evaporative and transpirative fluxes of chloride- and sulfate-rich groundwater into the root zone and; remobilization of the selenium inventory.

Similar information is available from the soil water extracts shown in Figures 3a and 3b. In 1988, water-extractable selenium concentrations were highest in the top 0.5 m of the soil profile. By the next year, water-extractable selenium concentrations nearly doubled in the upper 0.5 m and increased in the depth interval from 0.5 to 1 m. By 1991, surficial inventories declined to pre-1988 levels. This decrease was accompanied by a large increase in water-extractable selenium concentrations in soils from 0.5 to 1 m depth. Since there is little selenium in the groundwater, these changes must be caused by remobilization and leaching of the resident selenium inventory.

The extent of remobilization can be determined from the depth-integrated inventory of water-extractable selenium shown in Figure 3b. In 1988, the total inventory of water-extractable selenium was about 200 mg/m^2. By 1991, it more than doubled, increasing to about 500 mg/m^2. Figure 3b also illustrates that most of water-extractable selenium is located in the top meter of the soil profile and that the largest increases also occurred here.

Pond 8EP

In mid 1988 an experimental plot was developed in former Pond 8 (Plot 8EP) to evaluate the magnitude of evaporative fluxes of solutes in Kesterson soils. The Pond 8 test plot is located in a former playa that was frequently flooded with up to 50 cm of San Luis Drain water. Over the monitoring period, the plot was revegetated with *Bassia hyssopifolia,* a deep rooted annual. The test plot is located in the center of Pond 8 and detailed descriptions of the monitoring data are provided in LBL (1988; 1990a; 1990b) and in Zawislanski (1989).

Chloride and water-extractable selenium concentrations from a series of shallow soil samples (0 - 9 cm) are given in Figures 4a and 4b. These data illustrate the results of two important processes: 1) evaporative accumulation of salts and selenium during the summer months and 2) leaching during the winter rainy season. The net effect of these seasonal transport processes over the 3 1/2 year period is to reduce the chloride concentration by about 75% and the selenium content by 50%. Differences in the relative declines in chloride and selenium can be explained by remobilization of a fraction of the immobile selenium in the surface soils.

Depth profiles of water-extractable selenium concentrations over this same time period are provided in Figure 5. From 1988 to 1990, rapid increases in the inventory of water-extractable selenium are apparent, similar to those observed in the Pond 11 test plot. However, from 1990 to 1991 a different pattern emerges. Significant declines are observed from 0 to 20 cm and from 1.2 to 2 m. These can be attributed to a reduction of selenate to less mobile forms of selenium, presumably by creating reducing conditions due to water table rise and seasonal rainfall infiltration in the fine-textured soils present at this site. Although water-extractable selenium inventories remain higher than 1988 values, these data illustrate the importance of periods with wetter-than-average soil conditions on the behavior of the selenium inventory at Kesterson.

These data suggest that evolution of the selenium inventory will not take place in a monotonic fashion. Instead, year-to-year variations in leaching and remobilization rates are expected to occur due to external influences such as intensity and timing of winter rains, patterns of vegetation growth and succession, and diversity and abundance of soil microorganisms. The net effect of the interplay between these processes will become clearer as our window of observation increases.

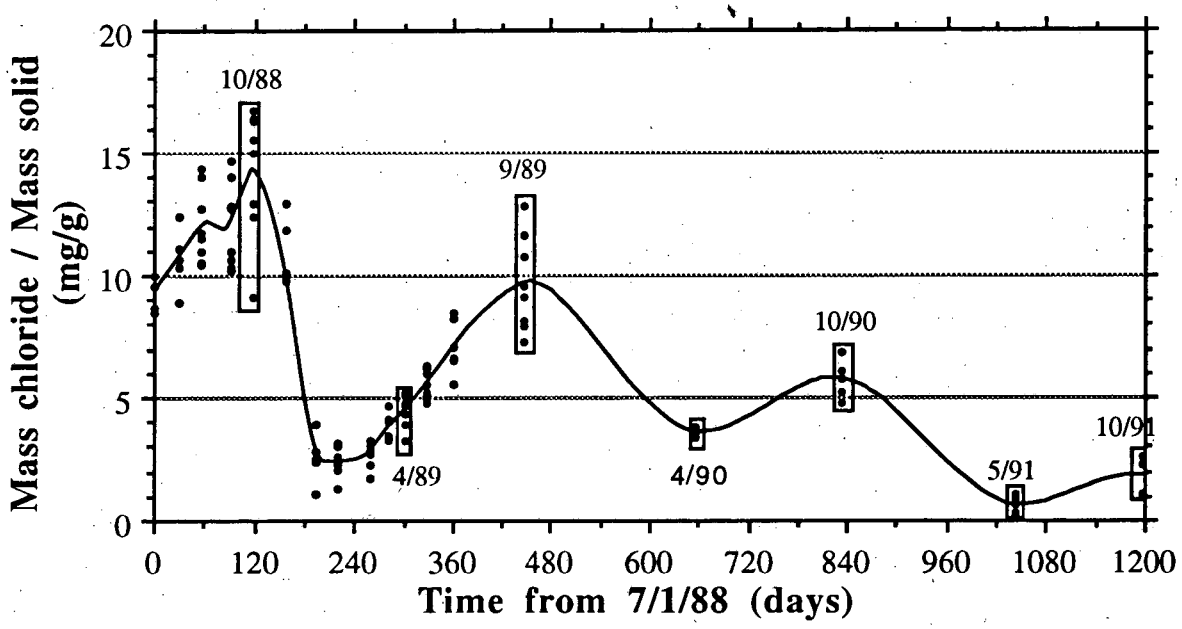


Figure 4a. Time trends in water-extractable chloride concentrations in the top 9 cm at experimental plot 8EP in the north east corner of former Pond 8.

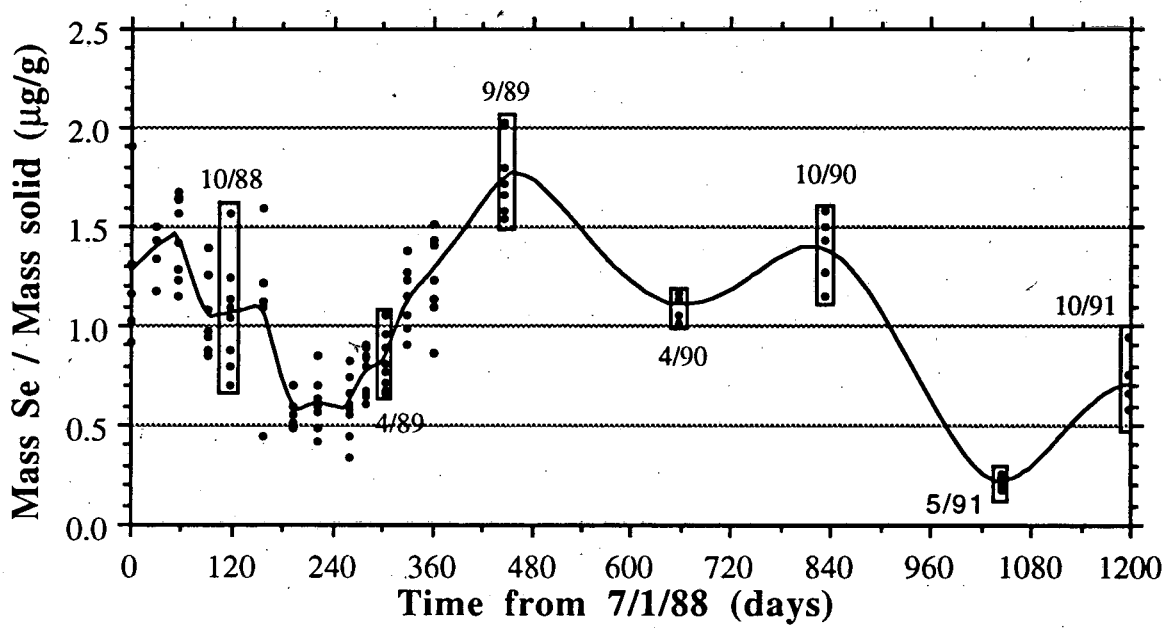


Figure 4b. Time trends in water-extractable selenium concentrations in the top 9 cm at experimental plot 8EP in the north east corner of former Pond 8.

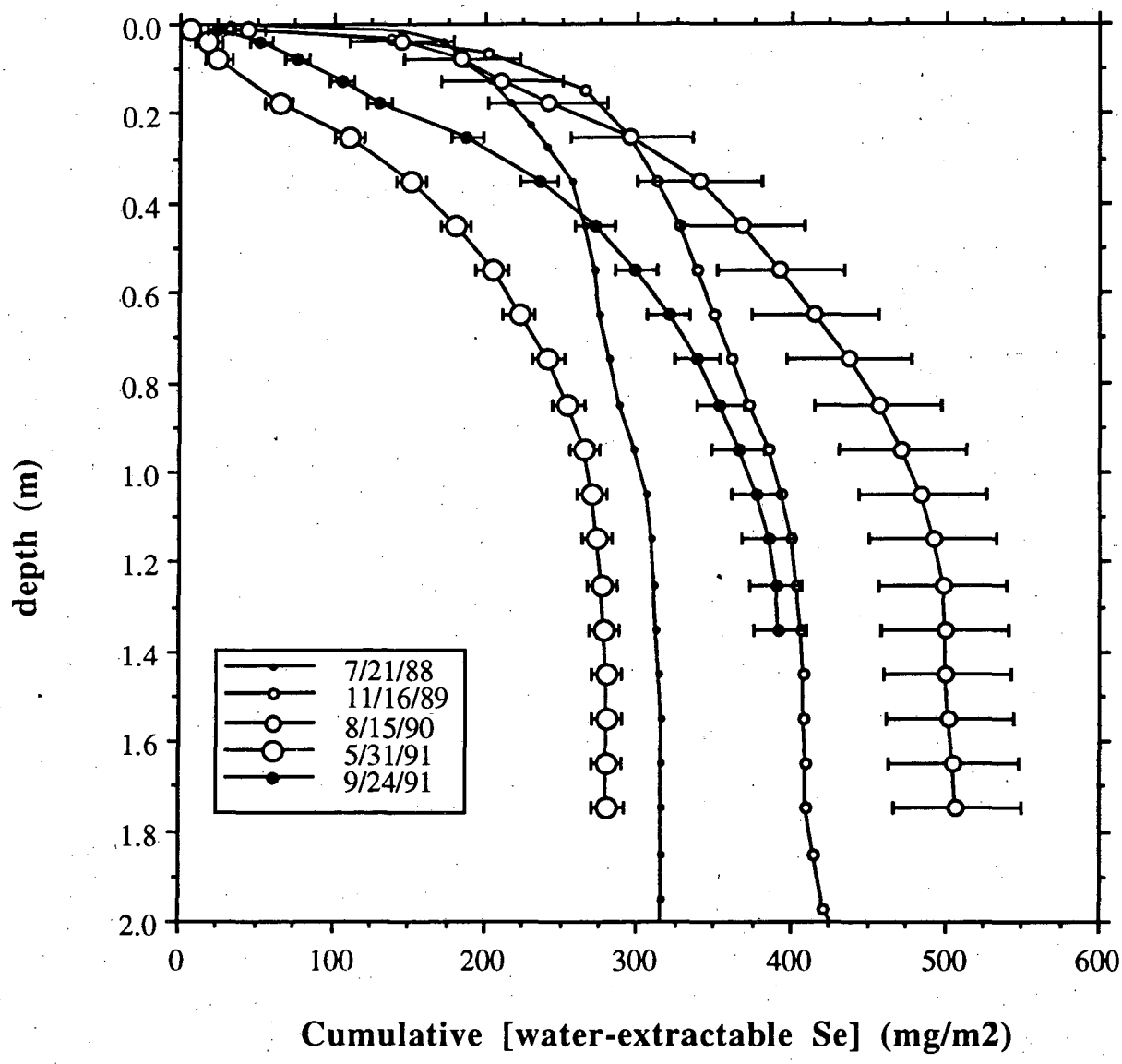


Figure 5. Time trends in water-extractable selenium concentrations at experimental plot 8EP in the north east corner of former Pond 8. Error bars represent cumulative error from three replicates to a depth of 1 m. No replicates are available below this depth.

Annual Synoptic Sampling of Soil Selenium at Kesterson Reservoir

Each year samples of the top 15 cm of soil are collected from 54 locations throughout Kesterson as a component of the ongoing biological monitoring program (LBL 1990a; 1990b). For sampling purposes, Kesterson is divided into three trisections: Trisection 1 includes all the former Ponds below Gun Club Road; Trisection 2 includes former Ponds 5, 6, 7 and 8; and Trisection 3 includes former ponds 9, 10, 11 and 12. Within each trisection, 6 samples are collected within each of the three habitats described previously (e.g., Fill, Grassland and Open).

Samples are analyzed for total selenium, water-extractable selenium, sulfate and chloride. Analysis of variance (ANOVA) was used to identify temporal trends in soil selenium concentrations[5]. Because the samples are collected in the late-winter and early-spring, influences of seasonal leaching of salts and water-extractable selenium may be reflected in the data, as well as long term trends. Results from the sampling program are summarized in Table 1 and in Figures 6 through 8. Geometric mean concentrations are provided for each year's entire sample set. Similar trends are observed when the data is evaluated on a Triesction-by Trisection basis or on a habitat-by-habitat basis. For a detailed discussion of these data see Wahl (1992).

As shown in Table 1 and Figures 6, 7 and 8, statistically significant reservoir-wide changes have not occurred in the total and water-extractable inventories of selenium in the top 15 cm of soil over the three year monitoring period. Significant changes have, however, been observed in the ratio of water-extractable to total selenium, sulfate and chloride concentrations. These changes reflect the same processes observed in the more detailed long-term and process-oriented monitoring described previously.

The increase from 1989 to 1991 in the ratio of water-extractable to total selenium indicates a gradual remobilization of the selenium inventory. Significant year-to-year

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[5] Fisher's PSLD method was used to determine ignificant differences in concentrations within year, tri-section and habitat ($P < 0.05$) (Mead, 1988). Log-transformed concentrations where used for ANOVA on all but the sulfate data because the concentration data were found to be log-normally distributed. Sulfate data were normally distributed and ANOVA was performed on the data as collected.

changes in sulfate and chloride concentrations are a reflection of seasonal leaching by infiltrating rainwater. While sulfate concentrations decline monotonically over the monitoring period, chloride concentrations decline from 1989 to 1990 and then increase from 1990 to 1991. Differences in temporal trends between sulfate and chloride can be explained by limits on the solubility of sulfate salts (e.g. gypsum and thenardite). Once transported deeper into the profile, sulfates may precipitate due to transpirative concentration of solutes in the root zone. Due to the much higher solubility limits, chloride salts will remain mobile and may be transported back to the soil surface by evaporation at the onset of the hot summer months.

Year	Total Selenium (mg/kg-soil)	Water Extractable Selenium (mg/kg-soil)	Ratio of Water Ext. to Total Selenium	Sulfate (mg/kg-soil)	Chloride (mg/kg-soil)
1989	3.9 A	0.17 A	0.05 A	2120 A	545 A
1990	2.7 A	0.12 A	0.04 A	1800 AB	220B
1991	2.9 A	0.19 A	0.07B	1380 B	500 A

Table 1. Geometric mean concentrations of total selenium,water-extractable selenium, sulfate and chloride in the top 0.15 m of soil from 54 samples collected annually as part of the bioogical monitoring program. Within a column, values sharing the same letters are not significantly different at the 95% confidence level.

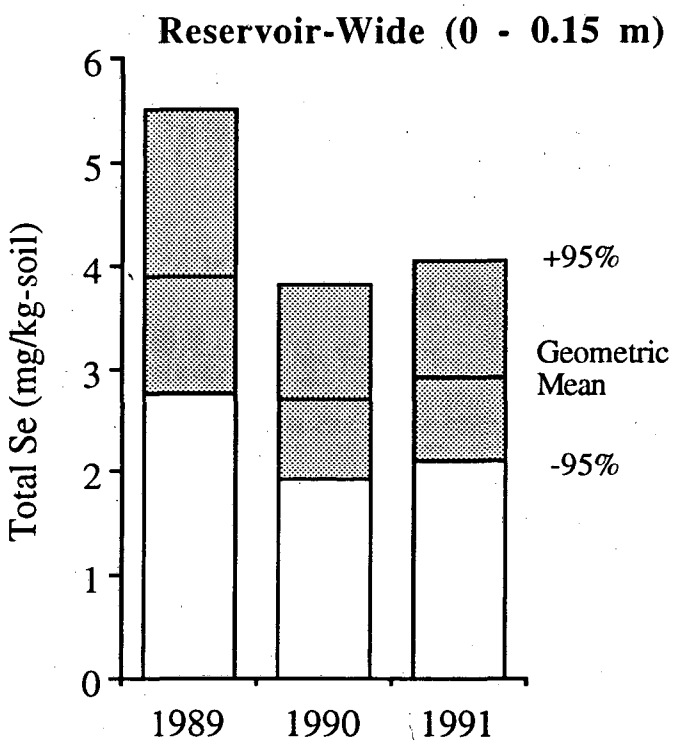

Figure 6. Geometric mean total selenium concentrations in the top 0.15 m of soil from 54 samples collected as part of the synoptic sampling for 1989, 1990 and 1991. Note that no significant changes in the inventory of total selenium in the top 0.15 m have been observed over this period.

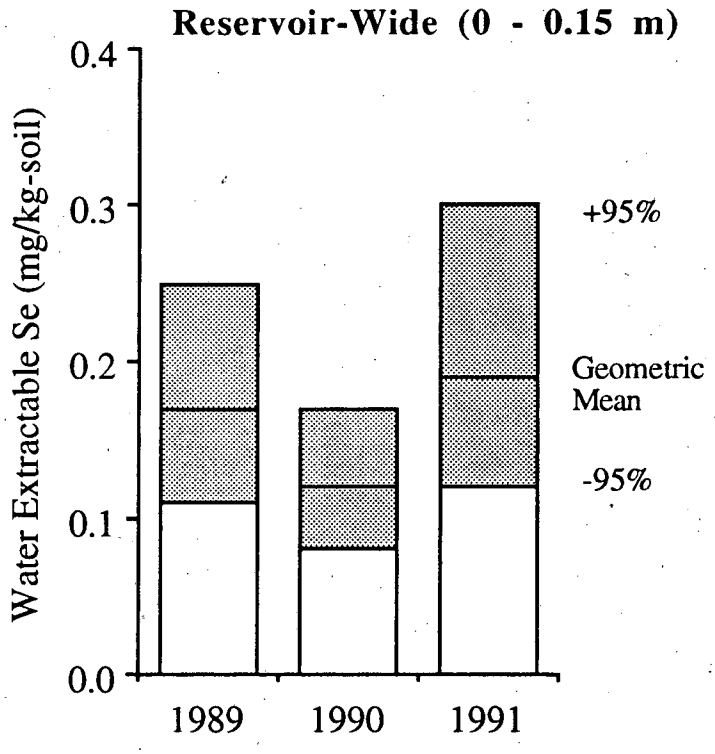

Figure 7. Geometric mean water-extractable selenium concentrations in the top 0.15 m of soil from 54 samples collected as part of the synoptic sampling for 1989, 1990 and 1991. Note that no significant changes in the reservoir-wide water-extractable selenium has been observed over this period.

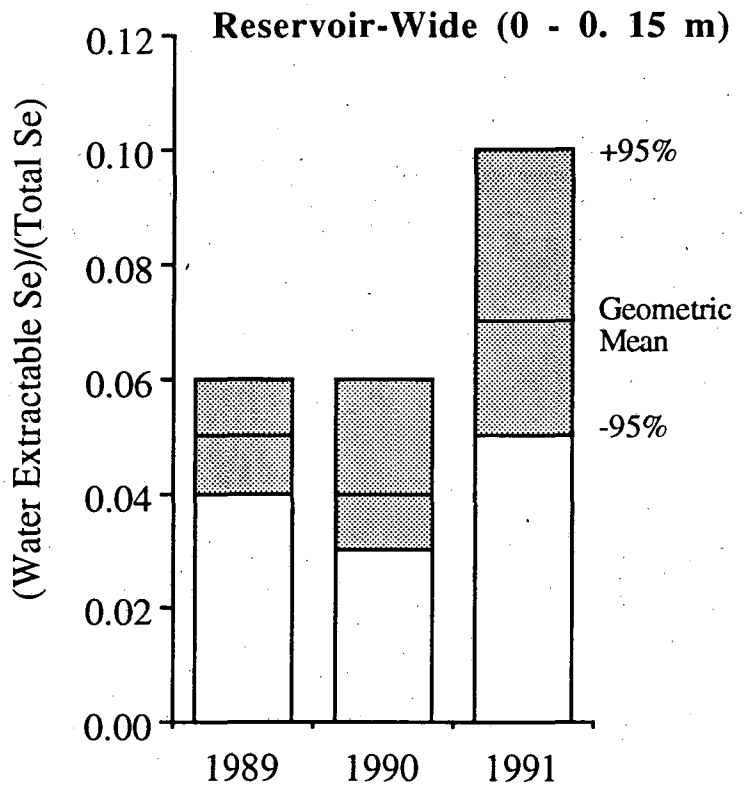

Figure 8. Geometric mean value for the ratio of water-extractable to total selenium concentrations in the top 0.15 m of soil from 54 samples collected as part of the synoptic sampling for 1989, 1990 and 1991. Note that a significant increase in this ratio was observed from 1989 to 1991 and from 1990 to 1991.

Field-Measured Selenium Volatilization Rates at Kesterson Reservoir

Selenium may be transformed from aqueous inorganic and organic forms to gaseous forms (largely dimethylselenide) through microbial activity and plant transpiration (Doran, 1982; Frankenberger and Karlson, 1988; Frankenberger, 1990). In soils, fungi appear to have the greatest capacity to volatilize selenium and do so as a detoxification mechanism. Whereas fungal volatilization of selenium may occur throughout the profile, it is most effective as a dissipation mechanism near the soil surface, where dimethylselenide can be transported to the atmosphere before it partitions into the soil-water or onto the surface of soil particles (Goldhammer and Alemi, 1990; Tokunaga, 1990). Plants may also contribute to selenium volatilization and may be comparatively effective for removing selenium from deeper in the soil profile (Terry et al., 1990; Biggar et al., 1990; ANR, 1992).

Although laboratory experiments demonstrate that microorganisms all of the selenium fractions identified in Kesterson soils may volatilize, volatilization rates of elemental selenium are comparatively low (Yee, 1990; Doran and Alexander, 1977). In particular, we have demonstrated that in Kesterson soils where the water-extractable selenium has been removed, selenium is volatilized as effectively as in native, unaltered soils (Yee, 1990). However, recent data from volatilization experiments in former Pond 4 and with San Luis Drain sediments suggest that approximately 50 to 75% of the selenium is relatively resistant to rapid (< 5 years) volatilization through microbial processes (W.T. Frankenberger, personal communication, 1992).

Rates of selenium volatilization have been measured as part of ongoing experiments aimed at stimulating volatilization rates through adding moisture and organic amendments to Kesterson soils. In each case, these experiments have been accompanied by measurement of volatilization rates in a nearby control plot where the soils have not been treated to stimulate volatilization rates. A summary of the field-measured volatilization rates from the control plots at these sites is provided in Table 2. In addition, volatilization data provided by Weres et al. (1989) are included in the table.

As shown, annually-averaged emission rates measured at Kesterson range from 0.4 to 3.5 $\mu g\ m^{-2}\ h^{-1}$. When normalized to the concentration of total selenium in the soils, volatilization rates fall in the range of 0.07 to 0.25 ($\mu g\ m^{-2}\ h^{-1}$)/(mg-Se/kg-soil). The corresponding annual depletion rates fall in the range of 0.3 to 1.0% of the total selenium inventory per year, with an average value of 0.6% per year. These low rates indicate that changes in the total inventory attributable to volatilization will be slow.

Table 2. Summary of field-measured selenium volatilization rates from untreated soils at Kesterson Reservoir.

Location	Annually-averaged Emission Rate ($\mu g\ m^{-2}\ h^{-1}$)	Soil Selenium Concentration (mg/kg-soil)	Volatilization Rate Per Unit Soil Se Concentration ($\mu g\ m^{-2}\ h^{-1}$)/(mg/kg)	Corresponding Annual Depletion Rate (%/year)***
Pond 4 Test Plot[1]	3.5	39*	0.09	0.4
Pond 4 Test Plot[2]	2.6	39*	0.07	0.3
Pond 11 Test Plot[1]	0.8	3.7*	0.2	0.9
Pond 11 Test Plot[2]	0.4	3.7*	0.1	0.5
Pond 2 Test Plot[3]	4**	48.3	0.08	0.3
Reservoir Wide[4]	2	8.5	0.25	1.0
Average Value			0.13	0.6

* Median of initial values from the test plots (0 - 0.15 m depth interval).
** Estimated from measurements collected during August - October, 1991.
*** Based on an estimated bulk density for surface soils of 1400 kg/m^3.
1 Frankenberger and Karlson, 1988.
2 Frankenberger, 1990.
3. ANR, 1992.
4. Weres et al., 1989.

Expected Trends in Soil Selenium At Kesterson Reservoir

The combination of remobilization, leaching and volatilization are expected to create the following changes in the inventory and distribution of selenium in Kesterson soils over the next several decades:

- the total inventory of selenium in Kesterson soils will decline at an annual rate of approximately 1% of the remaining inventory;
- water-extractable selenium in surface soils (0 -0.15 m depth) will be leached to deeper levels in the soil profile;
- water-extractable selenium inventories will most likely increase in the root zone in response to oxidation of selenium within this zone, as well as due to leaching of selenium from surface soils;
- the distribution of total selenium within the profile will change from being strongly concentrated near the soil surface to more evenly distributed within the upper 2 meters of soil;
- as a result of redistribution, total selenium concentrations will decline in the 0 -0.15 m depth interval and gradually increase at greater depths; total selenium concentrations are never expected to exceed the largest values heretofore observed at Kesterson;
- significant quantities of selenium will not be transported below 2 meters due to the chemically reducing conditions below the water table that favor immobile forms of selenium.

A schematic illustrating the net effect of the changes on the water-extractable selenium concentrations is presented in Figure 9. In the following section, the methodology for attempting to quantify the rate and extent to which these processes occur is described.

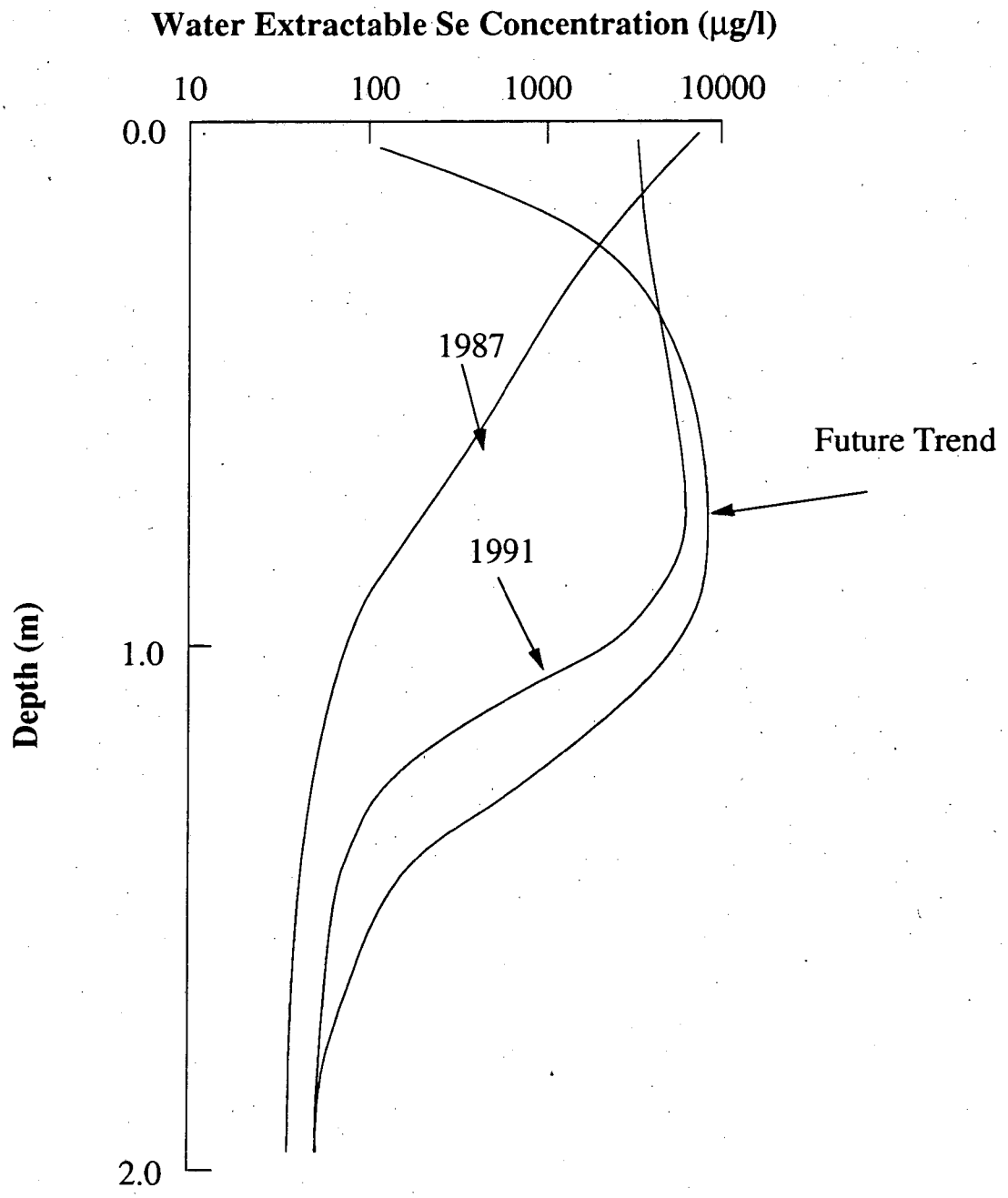

Figure 9. Schematic illustrating the distribution of water-extractable selenium concentrations in 1987, 1991 and under predicted future conditions.

Predicted Changes in the Selenium Inventory and Distribution

To provide a more quantitative assessment of observed changes in the inventory and distribution of selenium in the soil profile over the past 5 years and to predict how these changes will continue into the future, a simple mathematical model has been developed and applied to the soil selenium data. The model tracks total and water-extractable selenium inventories in the top 2 m of soil and has been used to interpret existing data as well as to predict the range of possible future conditions. A detailed description of the approach, calibration and application of this model follows.

Approach and Model Description

As illustrated in Figure 10, the top 2 m section is subdivided into three units for the purposes of tracking changes in the inventory: 1) from the soil surface to a depth of 0.15 m, 2) from 0.15 to 1 m and 3) from 1 to 2 m. Dividing the system into these three units was done primarily because:

- a relatively large data base is available to track changes in selenium concentrations in the top 0.15 m of soil;
- compared to deeper levels in the soil profile, the top 0.15 m of soil is most strongly influenced by microbial volatilization of selenium;
- concentrations of selenium in the top 0.15 m change dramatically in response to seasonal leaching and bare-soil evaporation (Ita and Benson, 1992);
- root uptake of soil moisture appears to be greatest in the depth interval from 0.15 to 1 m (LBL, 1988; 1990a, 1990b);
- below a depth of 1 m the soils are less affected by seasonal cycles in soil moisture content and by transport of solutes from surface soils, and consequently, are not expected to undergo rapid changes in selenium concentrations; and

- at Kesterson, the seasonal maximum depth to the water table, which occurs in the early fall, averages about 2.5 m below the ground surface.

The three "processes" that have been incorporated into the model are shown in Figure 11. These include selenium volatilization, leaching, and remobilization. As described earlier, these processes encompass a far more complicated interplay of physical, chemical and microbial processes that vary in importance throughout the year. Nevertheless, as a first approximation, these three processes can be used to describe the overall behavior of the system. As included in the model, the role of each of them is as follows.

Volatilization will transfer to the atmosphere a fraction of the selenium inventory from subunits within the system. For example, microbial volatilization is expected to remove selenium from the surface-most unit and plant volatilization from the root zone. The rate of volatilization is expressed in terms of the fraction of the total selenium inventory that is removed from each subunit per year. The quantity volatilized within a given year is calculated from

$$VOLI = VI*TII$$

where VOLI is the mass of selenium volatilized from unit I, VI is the volatilization rate for unit I and TII is the total inventory of selenium in unit I. Rate constants may be different for each subunit.

Leaching provides the mechanism for transporting selenium from one unit to another within the system. As currently included, leaching can only transport selenium deeper into the soil profile. This is in keeping with observations that rainfall infiltration transports selenium from the surface soils to depth. Very slow transport from unit 2 to unit 3 and from unit 3 to the groundwater system by molecular diffusion may also be mimicked by slow leaching rates. The leaching rate is expressed in terms of the percent of the water-extractable selenium inventory that is transported from one subunit to another over a 1 year period. Note that this is the net leaching that occurs over a one year period, not the

maximum leaching that is observed immediately following the rainy season. The mass of selenium transported from unit I to unit J in a given year (LEACHIJ) is calculated by

$$LEACHIJ = LIJ*EII$$

where, LIJ is the leaching rate from unit I to unit J, and EII is the inventory of water-extractable selenium in unit I. Rate constants may be different for each subunit.

It should be noted that the net transfer selenium from Unit 2 to Unit 1 is considered to be insignificant in this model. While this is a reasonable assumption as long as the inventory of selenium is greater in Unit 1 than in Unit 2, eventually, counter-diffusion of water-extractable selenium from deeper in the soil profile towards the soil surface may become significant. For the calculations described in this report, total selenium concentrations remain higher in Unit 1 than in the deeper units. Consequently, the assumption of no net transfer of selenium from Unit 2 to Unit 1 is a reasonable one.

The remobilization term accounts for increases in water-extractable selenium that occur due to oxidation or desorption of reduced forms of selenium, dissolution of selenium-bearing salts and decomposition of organic-matter-associated forms of selenium. Again, over the seasonal cycle, simultaneous or cyclical oxidation and reduction of selenium is expected to occur. Therefore, as with the leaching component, the rate constant associated with this "process" reflects the net effect of these competing processes over a year. The quantity remobilized within a given year is given by

$$REMOBI = RI*TII$$

where, REMOBI is the mass of selenium remobilized from unit I, RI is the remobilization rate for unit I and TII is the total inventory of selenium in unit I. Rate constants may be different for each subunit.

Rate constants for each of these processes were determined by calibrating the model with data from the long-term monitoring sites described above. Calibration, details of which are provided below, involved trial-and-error adjustment of remobilization and leaching rates from the subunits until the model results compared favorably with the mea-

sured data. Volatilization rates for units 1 and 2 (V1 and V2) were assigned a value of 1% per year, in keeping with field measured volatilization rates. Decreases in the inventory attributable to this small volatilization rate are not expected to be detectable for the 5 year period for which data are available. It was assumed that volatilization from unit 3 is negligible (e.g. V3=0).

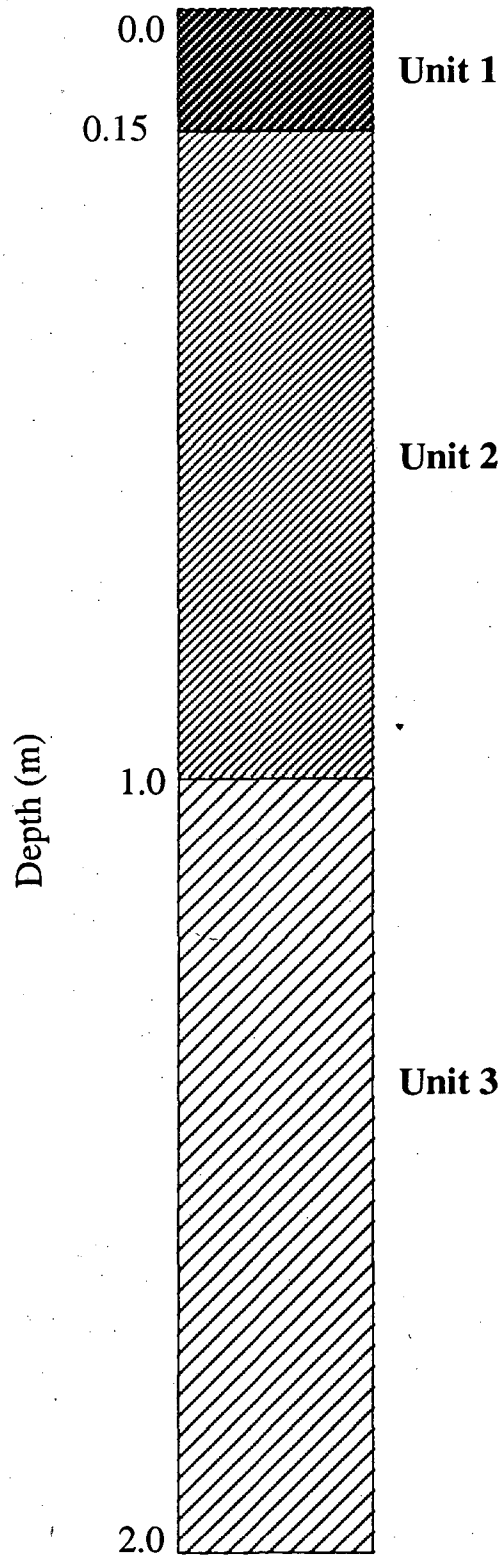

Figure 10. Illustration of the three subunits that the top 2 m of Kesterson soils have been divided into for model calibration and prediction.

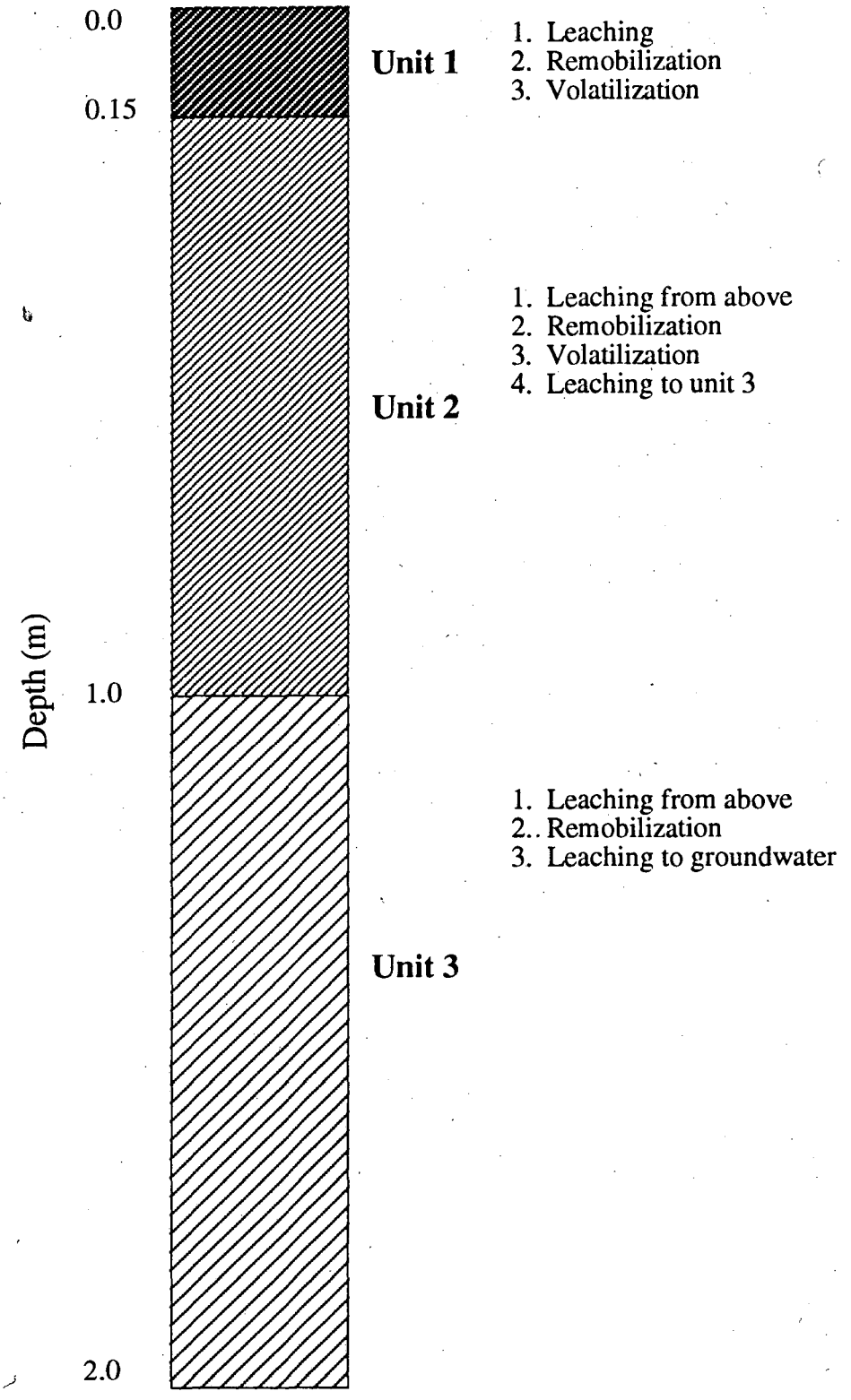

Figure 11. Illustration indicating the dominant processes affecting the selenium inventory within each of the three subunits of the model.

Computational Procedure

The model uses an explicit time-stepping procedure to calculate yearly changes in the selenium distribution and inventory in the soil profile. A flow chart for the initialization and calculation procedure used by the model are provided in Figures 12 and 13. Model inputs include initial concentrations of total and water-extractable selenium and volatilization, leaching and remobilization rate constants for each unit. Model outputs include inventories and concentrations of water-extractable and total selenium for each subunit over time.

As shown in Figures 12 and 13, starting with the initial inventory of selenium, the model calculates the amount of selenium volatilized, leached and remobilized within each unit over a one-year period. After completing these calculations (see Figure 13), the model updates the inventories of water-extractable and total selenium in the subunits. Having updated the inventories, the model repeats these calculations for the desired number of yearly intervals.

The computer program employed to carry out these calculations was written in the context of the EXCEL® spreadsheet environment.

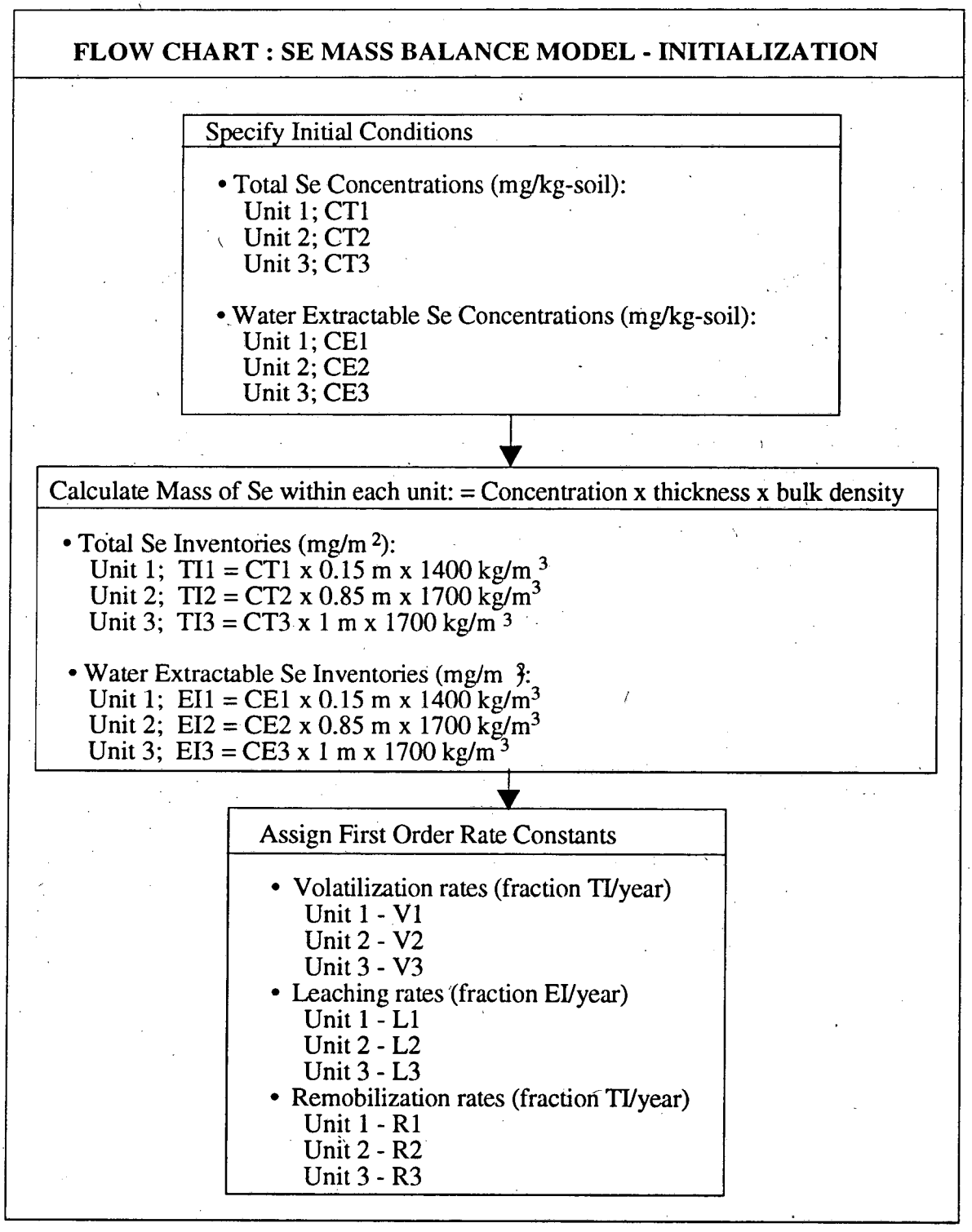

Figure 12. Flow chart for the mass balance model used to calibrate and predict the future behavior of selenium in Kesterson soils: data input and program initialization.

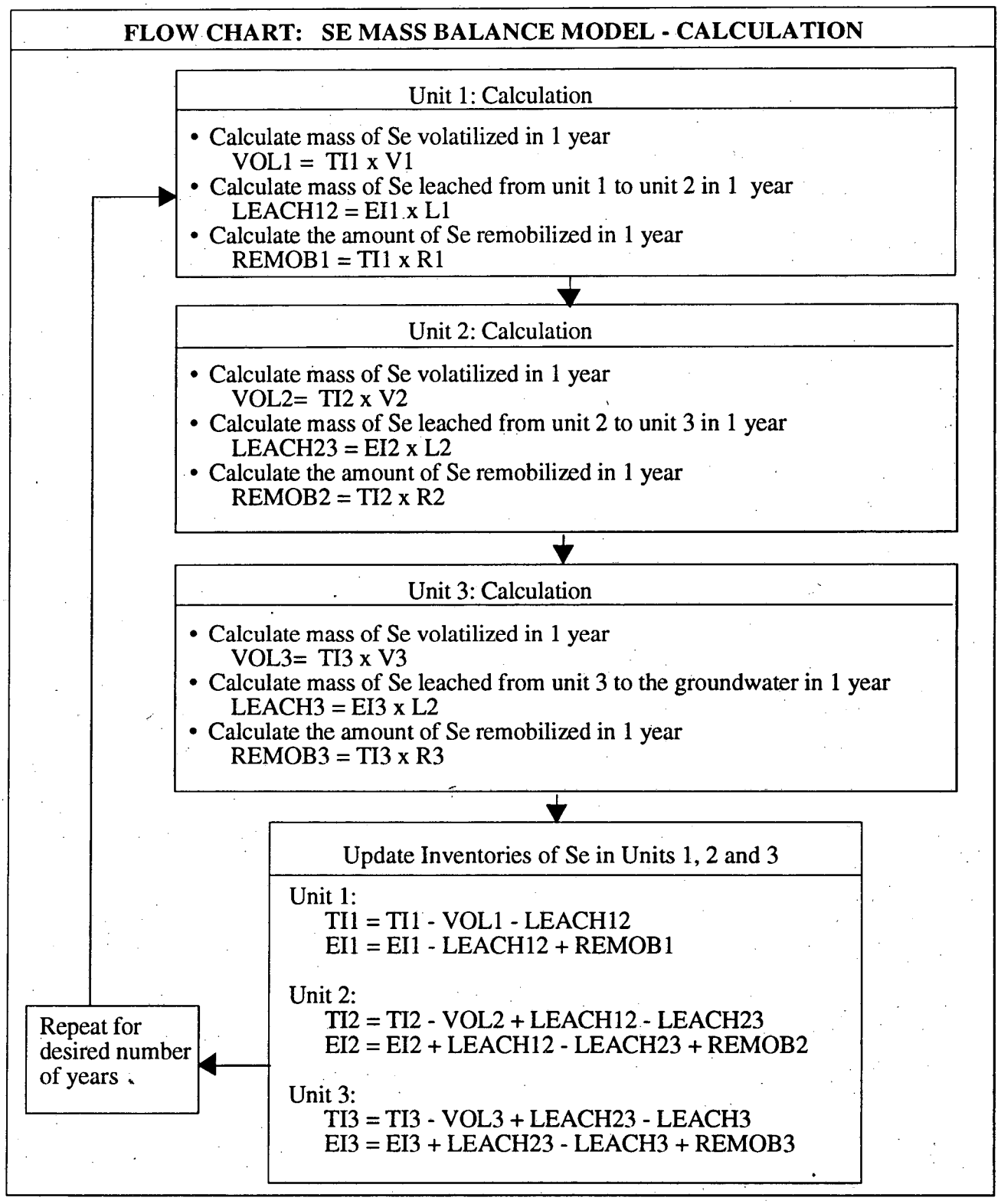

Figure 13. Flow chart for the mass balance model used to calibrate and predict the future behavior of selenium in Kesterson soils: calculation algorithm.

Model Calibration Procedure

As described previously, there are several detailed data sets from which estimates of the rate constants can be obtained and consequently, the model calibrated. For the purpose of these calculations, initial conditions were assigned beginning with 1987 or 1988, depending on the availability of data. Specific pieces of information used for this purpose include the following:

- initial concentrations of total and water-extractable selenium and for the depth intervals from 0 to 0.15 m, 0.15 to 1 m, and 1 to 2 m;
- soil-solution selenium concentrations; and
- depth-integrated inventories of water-extractable selenium within each of the subunits and over the entire soil profile.

In calibrating the model the following procedure was used to establish a consistent method for obtaining rate constants. First, a lower limit for the leaching rate from the first to the second unit was determined by matching the rate of depletion of chloride from the surface-most unit. During this step, all other rate constants were set to zero. Having determined the leaching rate for unit 1, the remobilization rate for that unit was then determined by increasing the rate from zero to the value required to approximately match the observed changes in its water-extractable inventory. Next, the remobilization rate for Unit 2 was increased until calculated and measured concentrations of water-extractable selenium were in reasonable agreement. If Unit 3 was only partially saturated for a majority of the year, its remobilization rate was increased up to a maximum of the value determined for Unit 2. If the calculated and measured values for water-extractable selenium for Unit 3 did not match well, the leaching rate from Unit 2 to Unit 3 was increased until the match was satisfactory. In general, because of the low concentrations of selenium in the 1 to 2 m interval, values for the leaching and remobilization rate constants for Unit 3 did not have a great influence on the rate constants for Units 1 and 2.

Due to the relatively slow rate constants and small percentage of the selenium inventory initially in extractable forms, changes in total selenium concentrations within the profile are not large enough to be quantified over the monitoring period and consequently were not used in the calibration procedure.

Detailed description of the calibration data from two sites are provided below.

Plot 8EP

Initial and subsequent concentrations of selenium over the period from 1988 to 1991 in plot 8EP are provided in Table 3. These were used to determine a set of leaching and remobilization rate constants that were consistent with the observed data. Rate constants were obtained by the calibration procedure described above and are summarized in Table 4. Matches between observed and calculated concentrations of water-extractable selenium for the three subunits are shown in Figures 14, 15 and 16. As indicated in Table 4, annual remobilization rates in all surface-most units were on the order of 7% of the immobile inventory. Remobilization rate constants for Units 2 and 3 are zero, indicating that over the 3 year monitoring period no significant remobilization has occurred at depth in the soil profile. Examination of Figure 14 suggests that the low remobilization rate is attributable to a large amount of reduction that occurred during the 1990-1991winter. This is consistent with the heavy rains that occurred during this period, the fine-textured nature of the 8EP soils and the relatively sparse growth of vegetation in this plot.

The leaching rate of 40% of the water-extractable inventory per year from layer 1 to layer 2 indicates that rainfall infiltration plays a major role in redistributing selenium within the soil profile. Only a small amount of leaching from unit 2 to 3 appears to occur. This is consistent with field observations that leaching appears to be confined largely to the upper meter of the soil profile.

Matches between observed and calculated concentrations in Plot 8EP indicate that the major trends observed are represented reasonably well with the model. However, year to

year variations are not reproduced accurately. This indicates that the rate constants, as implemented in the model are not constant over the three-year period. This can be explained in part by variations in quantity, intensity and timing of the rainy season, particularly for Unit 1. During 1989, the major rains occurred in mid-winter when the soils were nearly saturated from regional water-table increases. The combination of the high water saturation and a high water-table limits the effectiveness of leaching. In contrast, during 1990, the total rainfall was greater and perhaps more significantly, a series of large rainfall events occurred in mid-May, when the soils were drier and significant leaching was more likely to occur. As mentioned above, a sequence of heavy rains occurred in March 1991, leading to wetter-than-average soil moisture conditions.

The role of vegetation on the soil-moisture regime and transport of solutes may also contribute to annual variations in the rate constants. During the summer of 1989, no vegetation was allowed to grow in Plot 8EP. Thus, compared to the summer of 1990 when *Bassia* invaded the plot and transpired a large fraction of the soil moisture, the soil was relatively moist. Similarly, in 1991, the plot was only sparsely vegetated. Higher moisture contents tends to maintain the reducing conditions that favors immobilization of selenium and limits the effectiveness of leaching.

Unit	Depth (m)	1988 Total Se (mg/kg-soil)	1988 Water-Extractable Se (mg/kg-soil)	1989 Water-Extractable Se (mg/kg-soil)	1990 Water-Extractable Se (mg/kg-soil)	1991 Water-Extractable Se (mg/kg-soil)
1	0.0 - 0.15	6.60	0.82	0.94	0.63	0.98
2	0.15 - 1	0.30	0.06	0.10	0.18	0.07
3	1 - 2	0.05	0.01	0.02	0.02	0.007

Table 3. Summary of soil selenium concentrations in Plot 8EP from 1988 to 1991.

Depth Interval (m)	Leaching rate (fraction of water-extractable /year)	Remobilization rate (fraction of immobile/year)	Volatilization rate (fraction of total Se/year)
Plot 8EP			
0.0 - 0.15	0.4	0.07	0.01
0.15 - 1	0.04	0	0.01
1 - 2	0.01	0	0
Plot 11C			
0.0 - 0.15	0.5	0.03	0.01
0.15 - 1	0.02	0.09	0.01
1 - 2	0.01	0.09	0

Table 4. Summary of leaching and remobilization rate constants determined from Plot 8EP and 11C.

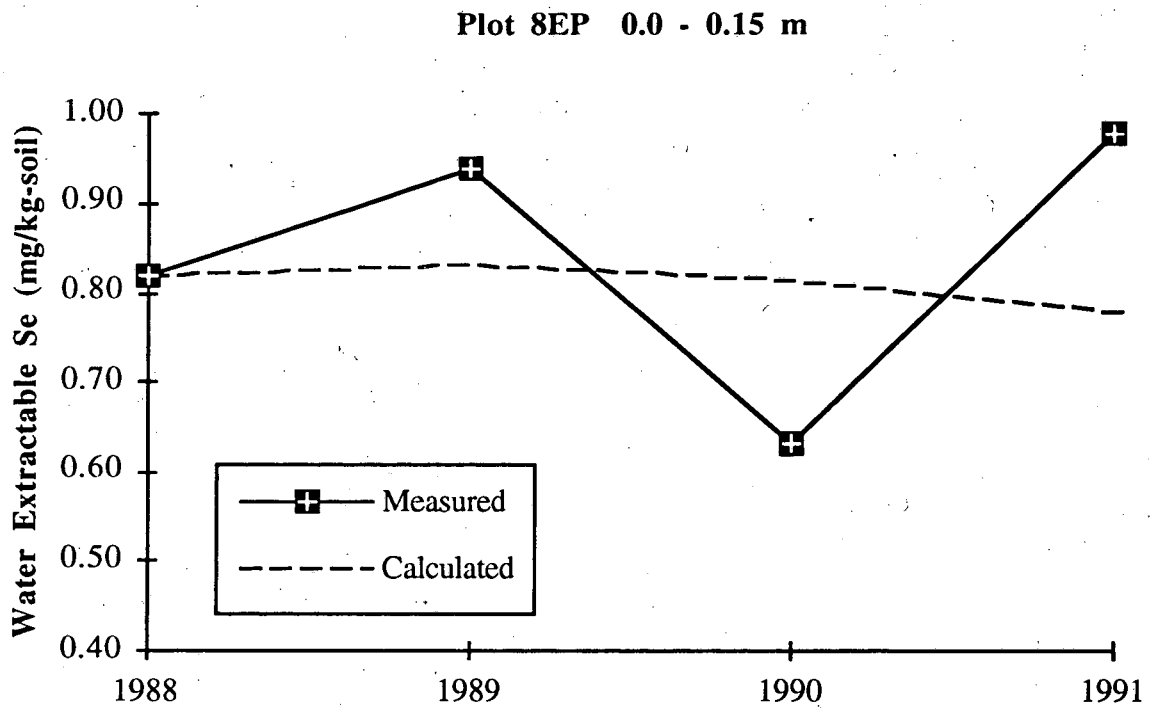

Figure 14. Comparison between measured and calculated water-extractable selenium concentrations in the top 0.15 m of soil at Plot 8EP.

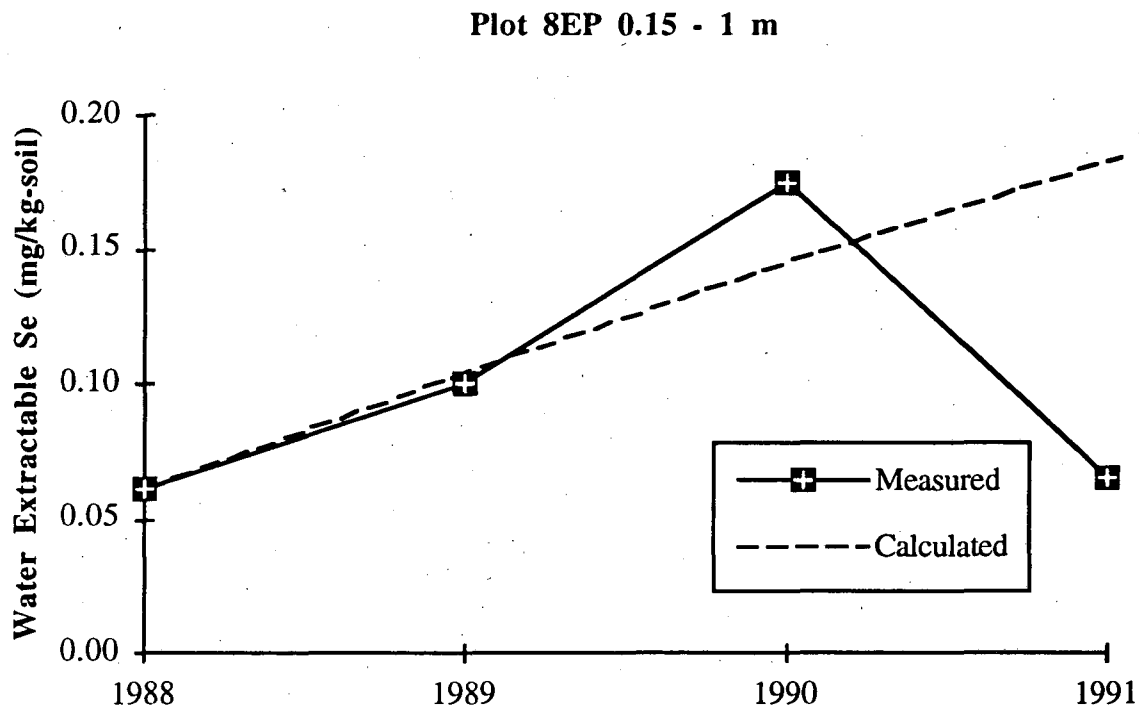

Figure 15. Comparison between measured and calculated water-extractable selenium concentrations in the depth interval of 0.15 to 1 m of soil at Plot 8EP.

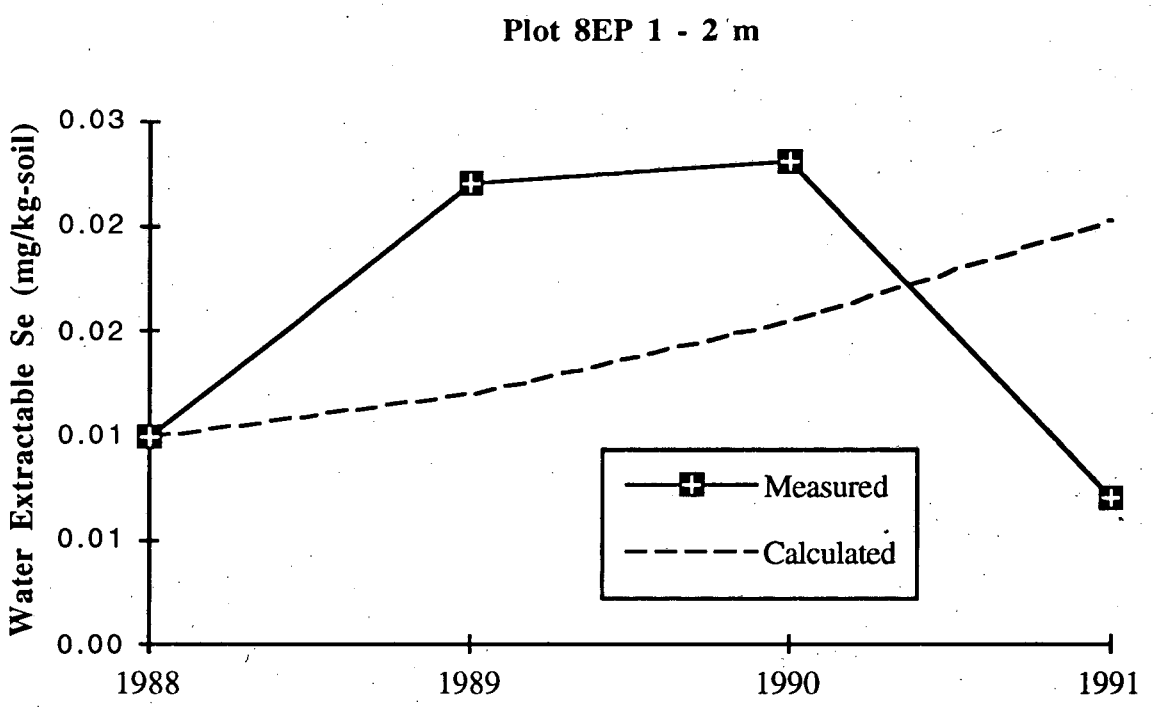

Figure 16. Comparison between measured and calculated water-extractable selenium concentrations in the depth interval of 1 to 2 m of soil at Plot 8EP.

Plot 11C

Initial and subsequent concentrations of selenium over the period from 1988 to 1991 in Plot 11C are given in Table 5. These were used to determine a set of leaching and remobilization rate constants that were consistent with the observed data. Rate constants were chosen by the calibration procedure described above and summarized in Table 4. Matches between observed and calculated concentrations of water-extractable selenium are shown in Figures 17, 18 and 19 for the three subunits. In addition, Figure 20 shows the match between the total inventory of water-extractable selenium in the top 2 m of soil. As indicated in Table 4, remobilization rates in all three units are on the order of 3 to 9% of the immobile inventory per year. The annual leaching rate of 50% of the water-extractable inventory per year from Unit 1 to Unit 2 again indicates that rainfall infiltration plays a major role in redistributing selenium within the soil profile.

In general, the matches between calculated and measured concentrations of selenium shown in Figures 17 through 20 are better for Plot 11C than they are for Plot 8EP. These good matches suggest that the rate constants determined by the calibration procedure are nearly constant over the 3-year period. This may be explained in part by the presence of a dense and stable growth of salt grass (*D. spicata*) in the test plot that persisted over the entire monitoring period.

Depth (m)	1988 Total Se (mg/kg-soil)	1988 Water-Extractable Se (mg/kg-soil)	1989 Water-Extractable Se (mg/kg-soil)	1990 Water-Extractable Se (mg/kg-soil)	1991 Water-Extractable Se (mg/kg-soil)
0.0 - 0.15	5	0.20	0.25	NA	0.11
0.15 - 1	0.9	0.11	0.19	NA	0.32
1 - 2	0.05	0.00	0.01	NA	0.02

NA - not available

Table 5. Summary of soil selenium concentrations in Plot 11C from 1988 to 1991.

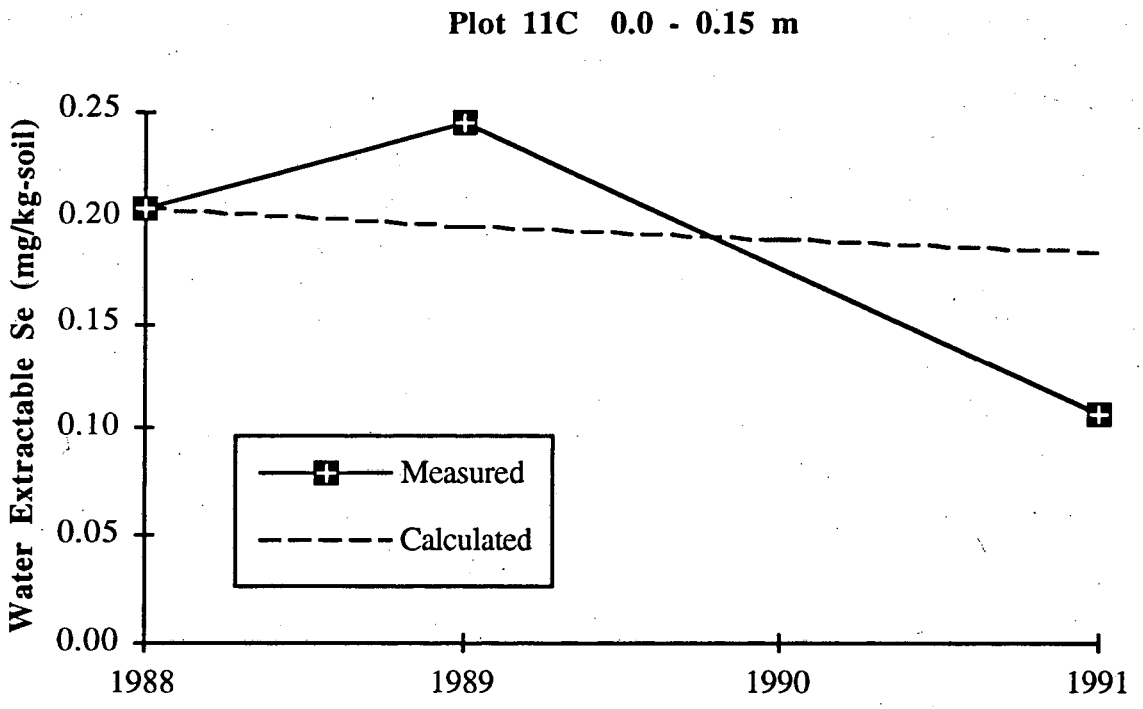

Figure 17. Comparison between measured and calculated water-extractable selenium concentrations in the top 0.15 m of soil at Plot 11C.

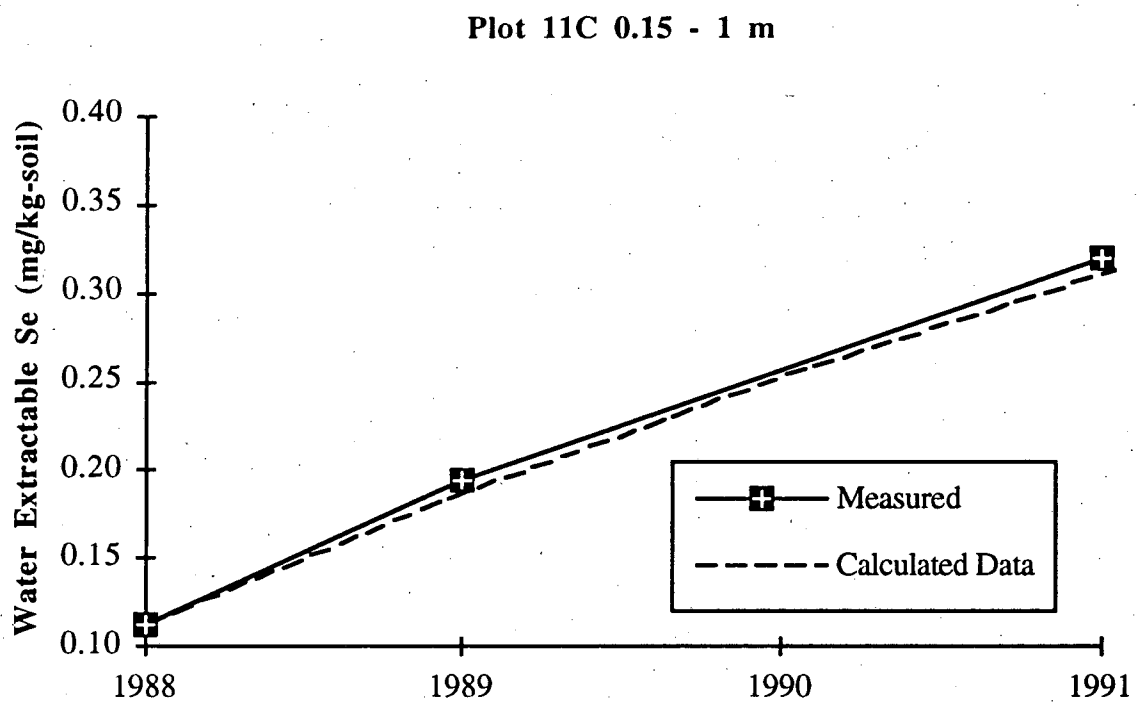

Figure 18. Comparison between measured and calculated water-extractable selenium concentrations in the depth interval of 0.15 to 1 m of soil at Plot 11C.

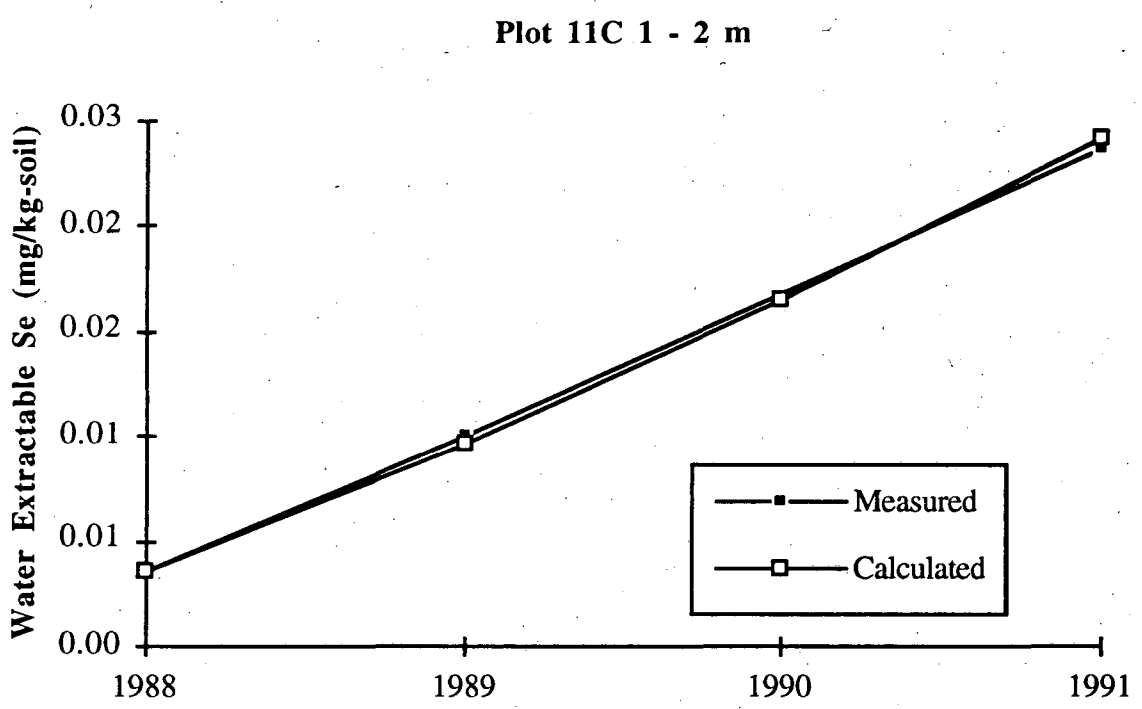

Figure 19. Comparison between measured and calculated water-extractable selenium concentrations in the depth interval of 1 to 2 m of soil at Plot 11C.

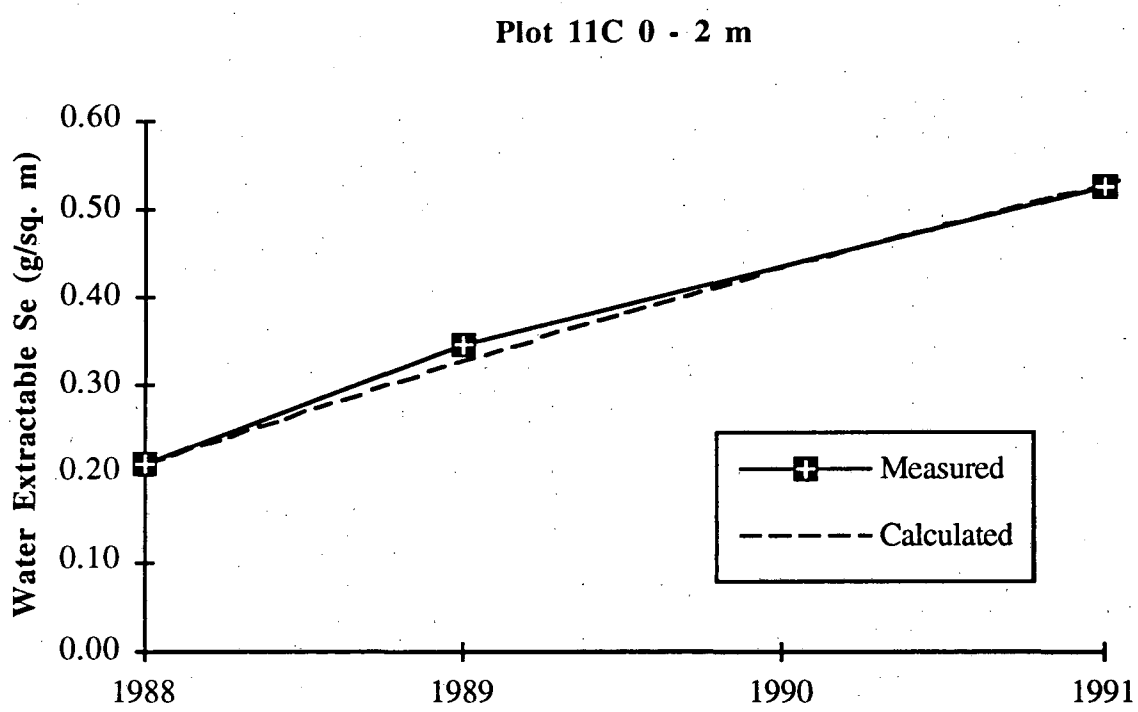

Figure 20. Comparison between measured and calculated inventories of water-extractable selenium in the top 2 m of soil in Plot 11C (note that inventories are expressed as grams of Se per m^2).

Prediction of Soil Selenium Concentrations for a Twenty-five Year Period

Using a range of rate constants determined from the calibration exercise described above, the model was used to forecast soil-selenium concentrations over a twenty-five year period beginning in 1987. Following a discussion of the initial conditions used in the model, calculated concentrations of water-extractable and total selenium are presented for 5 cases spanning the range of observed leaching, remobilization and volatilization rates.

Initial conditions listed in Table 6 are established based on the results of the Reservoir-wide sampling program described previously and from supplemental information gathered elsewhere at the Reservoir. For Unit 1, values for total and water-extractable selenium were taken directly from the 1989 Reservoir-wide sampling data (values were rounded to the nearest significant figure). It is assumed that these values remained essentially unchanged from 1987 to 1989. This assumption is consistent with the Reservoir-wide and profile monitoring investigations described previously.

For Units 2 and 3, initial conditions are estimated based on profile sampling described by Long et al.(1990), Weres et al. (1989), Zawislanski (1990) and Tokunaga et al. (1991). An estimated 20% (1800 kg) of the 9000 kg of selenium delivered to Kesterson from 1981 to 1986 is located in the depth interval of 0.15 to 1 m. If this inventory is distributed uniformly over this interval, the average selenium concentration will be approximately 0.25 mg/(kg-soil). Limited information is available for assessing the fraction of this inventory that was water-extractable prior to 1989. However, recent data indicate that about 50% is presently in water-extractable form (see Figures 1a to 1c). Observations of increasing concentration of water-extractable selenium in this depth interval over the past 4 years, combined with information provided in Tables 2 and 3, indicate that it is reasonable to assume that approximately 20% of this inventory was water-extractable in 1987, the first year that most of the Reservoir was dried out. The total and water-extractable selenium concentrations in Unit 3 were assumed to be 20% of the values assigned to Unit 2.

The calibration data presented in this report and additional unpublished calibration runs indicate that leaching and remobilization rates may vary over a wide range and from year to year. Given the range of soil properties, hydrologic parameters, depth to water table and vegetative cover, this is not surprising. No one set of conditions will be representative of the Reservoir as a whole. Also, in light of the short duration over which conditions have been monitored compared to the forecasting horizon, it is prudent to consider a range of likely scenarios. The five cases presented in this report are listed in Table 7 and were chosen to cover the spectrum of possible conditions. This list is by no means exhaustive, but results from these calculations span the range of a much larger set of cases that were investigated. Volatilization rates for Units 1 and 2 range from 0.001 to 0.02, leaching rates from 0.01 to 0.35 and remobilization rates from 0.01 to 0.10. Because of the small inventory of selenium in Unit 3, and slow leaching rate from Unit 2 into Unit 3, the results of the calculations are not very sensitive to the rate constants for Unit 3. For this reason, the rate constants for Unit 3 were held constant at the following values: V3 = 0, L3= 0.01 and R3 = 0.

For the 5 cases listed in Table 7, predicted concentrations of water-extractable selenium in the top 0.15 m of soil are illustrated in Figure 21. As shown, temporal trends vary from monotonic decreases over the 25-year period (Case 4) to remaining nearly constant (Case 2), to increasing for a 4 to 10-year period before declining (Cases1, 3 and 5). Most likely, there will be individual sites at Kesterson that will follow each of these trends.

Unit	Depth (m)	Total Se (mg/kg-soil)	Water-Extractable Se (mg/kg-soil)
1	0 - 0.15	4	0.2
2	0.15 - 1	0.25	0.05
3	1 - 2	0.05	0.01

Table 6. Initial conditions used to compute future trends in soil-selenium concentrations at Kesterson Reservoir.

Case	Unit	VI (fraction of total inventory volatilized per year)	LI (fraction of water-extractable inventory leached per year)	RI (fraction of immobile inventory remobilized per year)
1	1	0.01	0.35	0.05
1	2	0.01	0.01	0.1
1	3	0	0.01	0
2	1	0.01	0.15	0.02
2	2	0.01	0.01	0.02
2	3	0	0.01	0
3	1	0.001	0.15	0.05
3	2	0.001	0.01	0.05
3	3	0	0.01	0
4	1	0.01	0.15	0.01
4	2	0.01	0.01	0.01
4	3	0	0.01	0
5	1	0.02	0.15	0.05
5	2	0.02	0.01	0.05
5	3	0	0.01	0

Table 7. Initial conditions and rate constants used to compute changes in soil-selenium concentrations.

The ratio between the leaching and remobilization rates (LIJ*EII/RI*TII) is the primary factor governing temporal trends. Where this ratio is high, water-extractable selenium concentrations will remain the same or decrease over time (Case 4). Where this ratio is low, water-extractable selenium concentrations will increase until the inventory of total selenium is decreased substantially (Case 3). The reservoir-wide monitoring data of the top 0.15 m of soil presented previously, suggest that on-average, the concentration of water-extractable selenium has remained nearly constant over this period (see Table 1), thus indicating that the rate of selenium remobilization is nearly balanced by the rate of leaching.

For the 5 cases listed in Table 7, predicted concentrations of water-extractable selenium in soils from 0.15 to 1 m deep are given in Figure 22. Except for Case 4, water-extractable selenium concentrations increase over the entire 25 year period. The combination of leaching from Unit 1 and remobilization within Unit 2 governs the rate at which selenium concentrations increase within this unit. Note that although these calculations predict a significant increase in water-extractable selenium concentrations, even the maximum concentrations are less than, or equal to, concentrations presently observed at some Kesterson locations (for example, see Figures 1a and 1c).

Tracking the inventory of water-extractable selenium within the top 2 m of soil is another way of evaluating these calculations. As shown in Figure 23, except for Case 4, the inventory of water-extractable selenium in the top 2 m increases over the entire 25-year period. Increases in water-extractable selenium inventories are governed solely by remobilization rates. As indicated in Table 7, the range of remobilization rates within Units 1 and 2 span the range of values determined from the calibration procedure described previously. Ultimately, remobilization rates in Unit 1 will dominate the overall response because the majority of selenium resides within this unit.

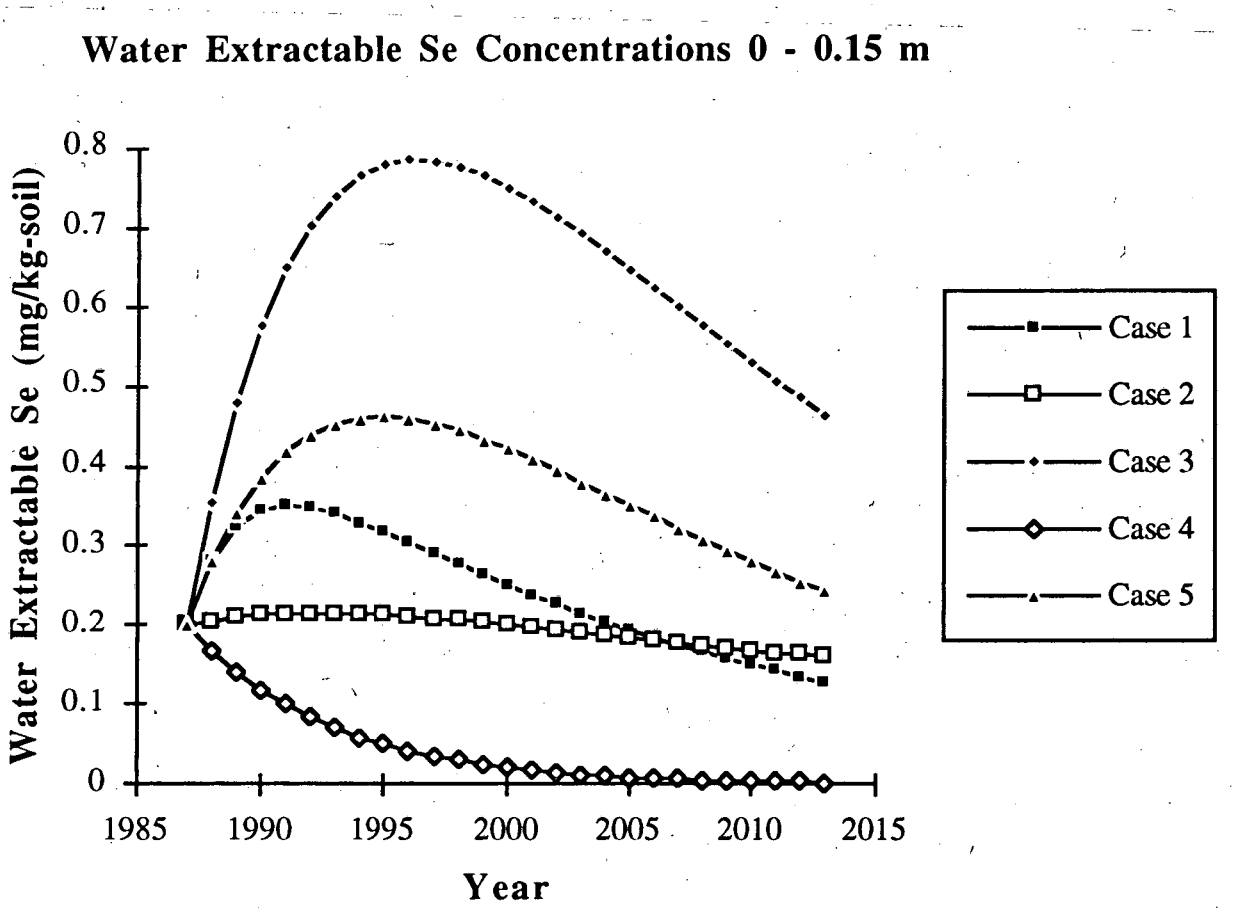

Figure 21. Predicted concentrations of water-extractable selenium in the top 0.15 m of soil at Kesterson Reservoir for the cases listed in Table 5.

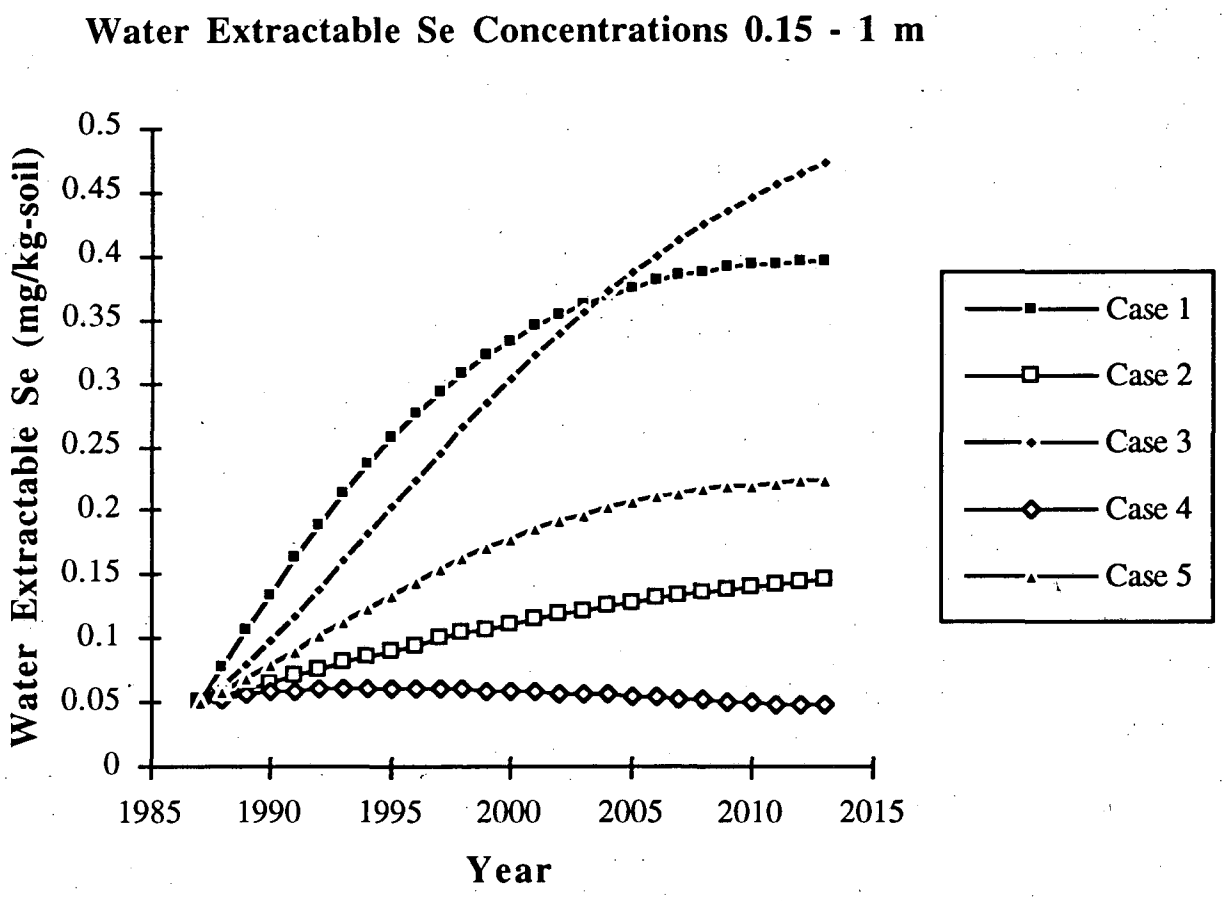

Figure 22. Predicted concentrations of water-extractable selenium in the depth interval from 0.15 to 1 m at Kesterson Reservoir for the cases listed in Table 5.

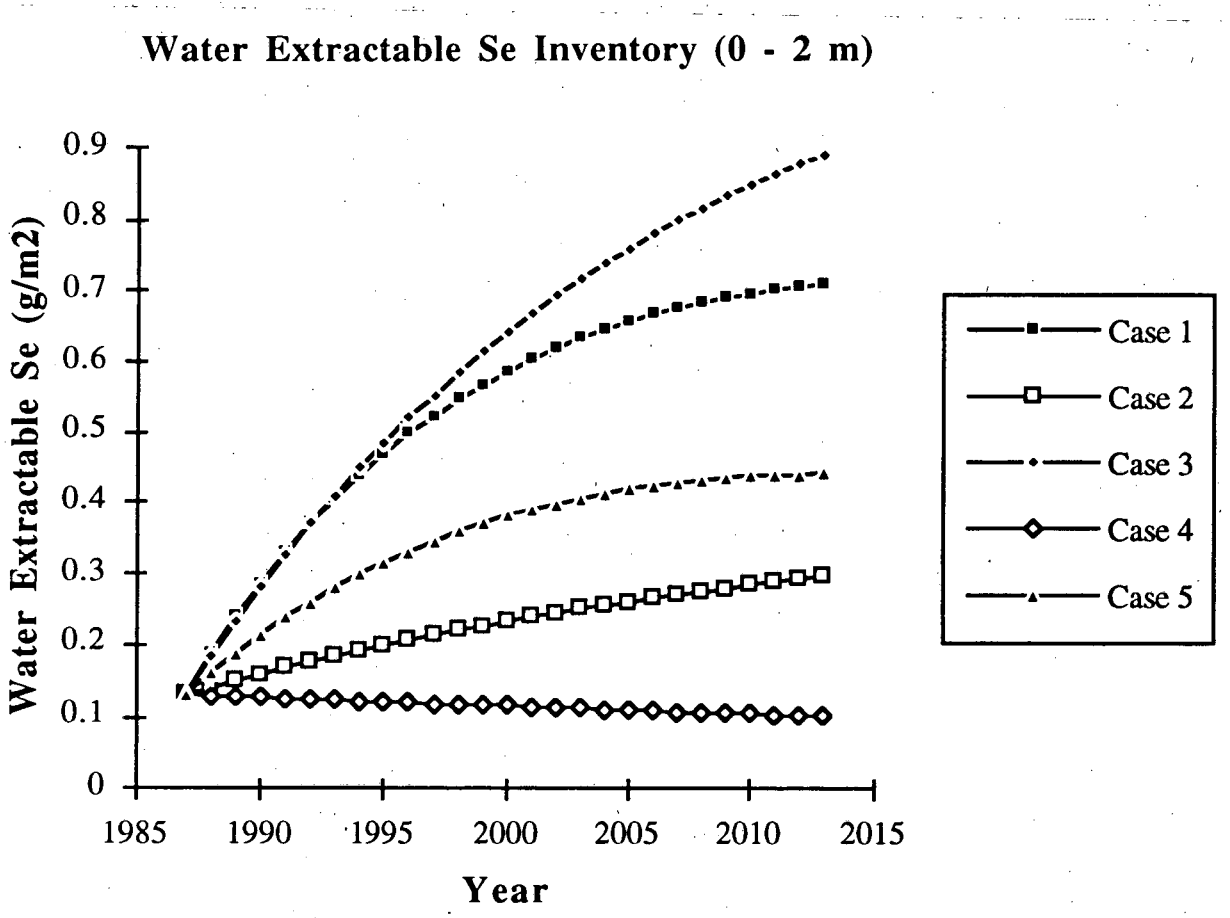

Figure 23. Predicted inventories of water-extractable selenium in the top 2 m of soil at Kesterson Reservoir for the cases listed in Table 5.

Total selenium concentrations are also calculated by the model. Temporal trends for total selenium in Units 1 and 2 are given in Figures 24 and 25. As shown, concentrations in the surface-most 0.15 m are expected to decline gradually over the entire period due to a combination of leaching, remobilization and volatilization. Total selenium concentration will decline most rapidly in locations with high leaching and remobilization rate constants (such as Cases 1, 3 and 5). Volatilization will only slowly contribute to depletion of the selenium inventory. Slow to moderate rates of depletion of the surficial inventory are consistent with the limited observations obtained during the Reservoir-wide monitoring program.

While total selenium concentrations decline in the upper unit of the soil profile, concentrations in the 0.15 to 1 m depth interval will remain the same or increase gradually (see Figure 25). High remobilization and leaching rates in Unit 1 cause the largest increases in selenium concentrations to occur in Unit 2 (Cases 1 and 3). Again, note that although significant increases are predicted, values still fall within the range of concentrations presently observed in some locations at Kesterson (see Figures 1a through 1c).

Comparison between Figures 22 and 25 indicates that where remobilization rates are high (Cases 1, 3 and 5), within the next few years the majority of selenium in the 0.15 to 1 m depth interval will be in water-extractable forms. This suggests that the pool of selenium readily available for plant uptake will increase in the coming years. Implications of this prediction have been explored through the use of a computer model simulating the Kesterson food chain (CH2M Hill, 1992).

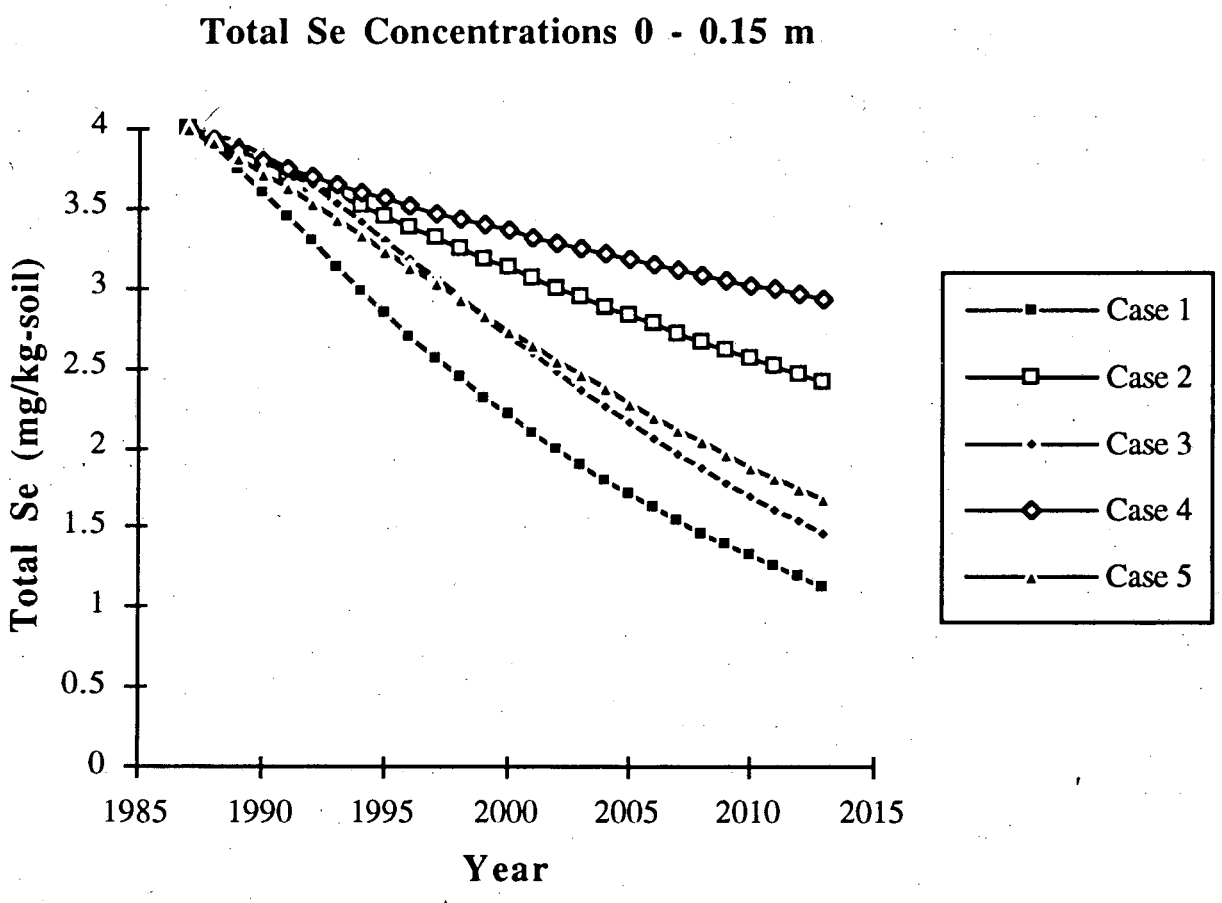

Figure 24. Predicted concentrations of total selenium in the top 0.15 m of soil at Kesterson Reservoir for the initial conditions and cases listed in Tables 6 and Table 7, respectively.

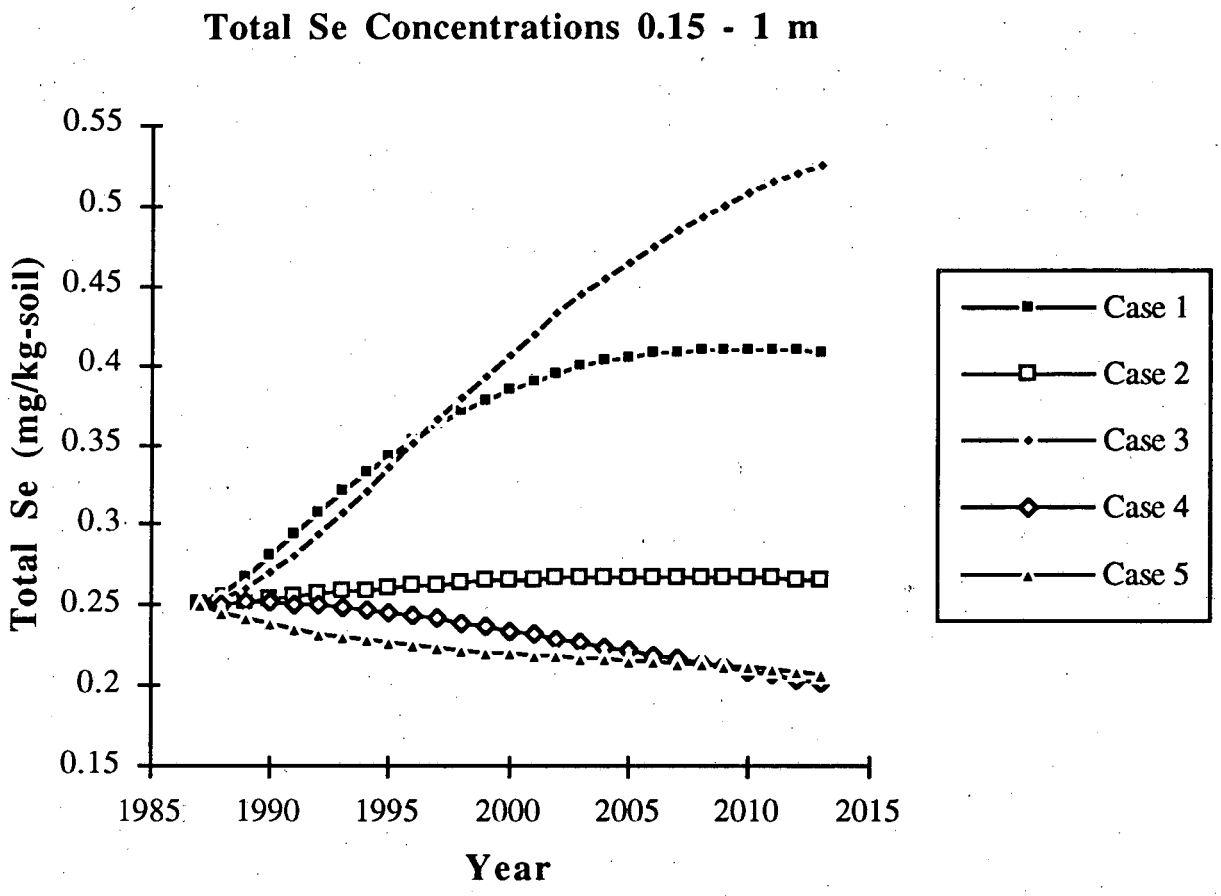

Figure 25. Predicted concentrations of total selenium in the 0.15 to 1 m depth interval at Kesterson Reservoir for the initial conditions and cases listed in Tables 6 and Table 7, respectively.

Use of Model Predictions for Biological Risk Assessment

Predicted water-extractable selenium concentrations in the 0.15 to 1 m depth interval were used to drive a food-chain-based biological risk assessment model (CH2M Hill, 1992). Motivation for choosing this depth interval, compared to the others, is based on observations from tensiometers and neutron-probe soil moisture measurements which indicate that *D. spicata* and *B. hyssopifolia* extract water most vigorously from this interval (LBL, 1988; 1990a; and 1990b). Unfortunately, there are limited Kesterson data providing correlations between concentrations of selenium in plant tissue and water-extractable selenium concentrations in this depth interval (Wu et al., 1990). Because of this deficiency, available data on correlations between water-extractable selenium in the 0 to 0.15 m depth interval and plant tissue selenium concentrations were adjusted to reflect sub-soil selenium concentrations. The adjustment involved assuming that sub-soil (0.15 to 1 m) concentrations of water-extractable selenium were on the order of 20% of those in the 0 to 0.15 m depth interval. Whereas this is a reasonable assumption shortly after Kesterson was dried out (Long et al., 1988), as time progresses, selenium concentrations in the sub-soil may increase towards or exceed surface soil concentrations. For this reason, we recommend that deeper soil samples be collected to improve these correlations and the rigor of this analysis.

A limited subset of the 5 cses presented here were used in the risk-assessment model, including Case 1, Case 4 and Case 5. As illustrated in Figure 22, these 3 cases span the range of possible concentrations in this depth interval and as such, are considered to be representative of expected temporal trends.

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