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The Pond 2 Selenium Volatilization Study: A Synthesis of Five Years of Experimental Results, 1990–1995

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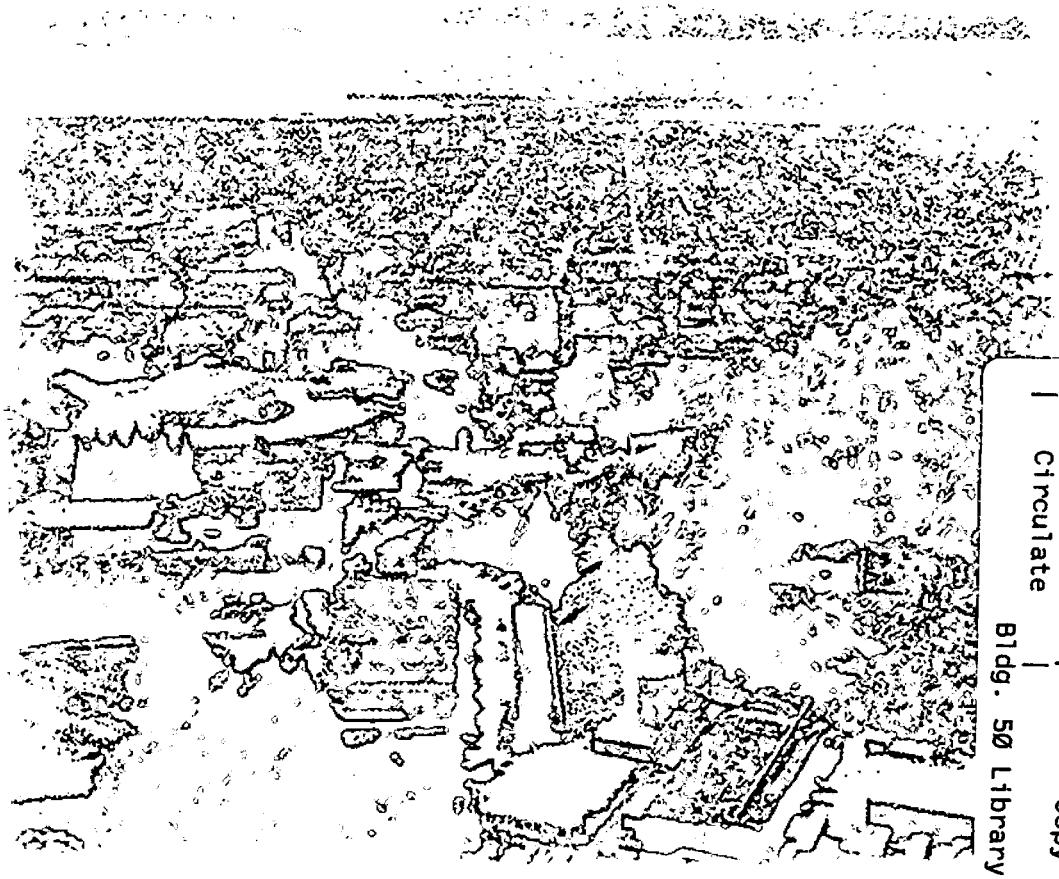
Earth Sciences Division

February 1996



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The Pond 2 Selenium Volatilization Study: A Synthesis of Five Years of Experimental Results, 1990-1995

A Joint Report to the U.S. Bureau of Reclamation

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1.0 INTRODUCTION

Microbial volatilization is a potential remedial measure to decrease the selenium inventory in Kesterson Reservoir soils. Past studies in both the field and the laboratory suggest that a significant percentage of the selenium inventory may be removed in this fashion. The objectives of this study include the quantification of selenium losses and a test of a pilot-scale design which in the future may be used in other parts of the Reservoir.

1.1 Background and Impetus

Small-scale field and laboratory experiments carried out from 1987 to 1990 indicated that microbial volatilization may be an effective means of dissipating selenium from Kesterson Reservoir soils. However, comparison of soil depletion data with measured gaseous emissions suggested that only part of the Se decline may be due to volatilization while the remainder may be attributed to leaching of dissolved Se. Discrepancies could not be resolved because those early experiments were not designed to account for solute displacement. Furthermore, the small-scale experiments generally involved intensive management, such as frequent irrigation, artificial temperature control, and organic supplements, all designed to increase microbial activity. Such management is not possible on the scale of 1,200 acres that is the Kesterson Reservoir. Therefore, a pilot-scale field study was designed to test the effectiveness of several lower intensity management strategies. These strategies included combinations of weekly irrigation, bi-weekly disking, and vegetation. This report summarizes efforts of a research team consisting of scientists from Lawrence Berkeley National Laboratory, University of California-Davis, and University of California-Riverside. Within, a synthesis of data collected over a five-year-long experiment, is analyzed with the intent of evaluating the effectiveness of this low-cost soil management method as a means of Se bioremediation.

1.2 Field Experiment Design

In 1989, the site for this study was chosen in the northern end of Pond 2 (Figure 1.1), an area which was very frequently flooded during the operation of the Reservoir and supported primarily cattail vegetation. Selenium concentrations here are amongst the highest in the Reservoir. Preliminary soil sampling in this plot in November 1989

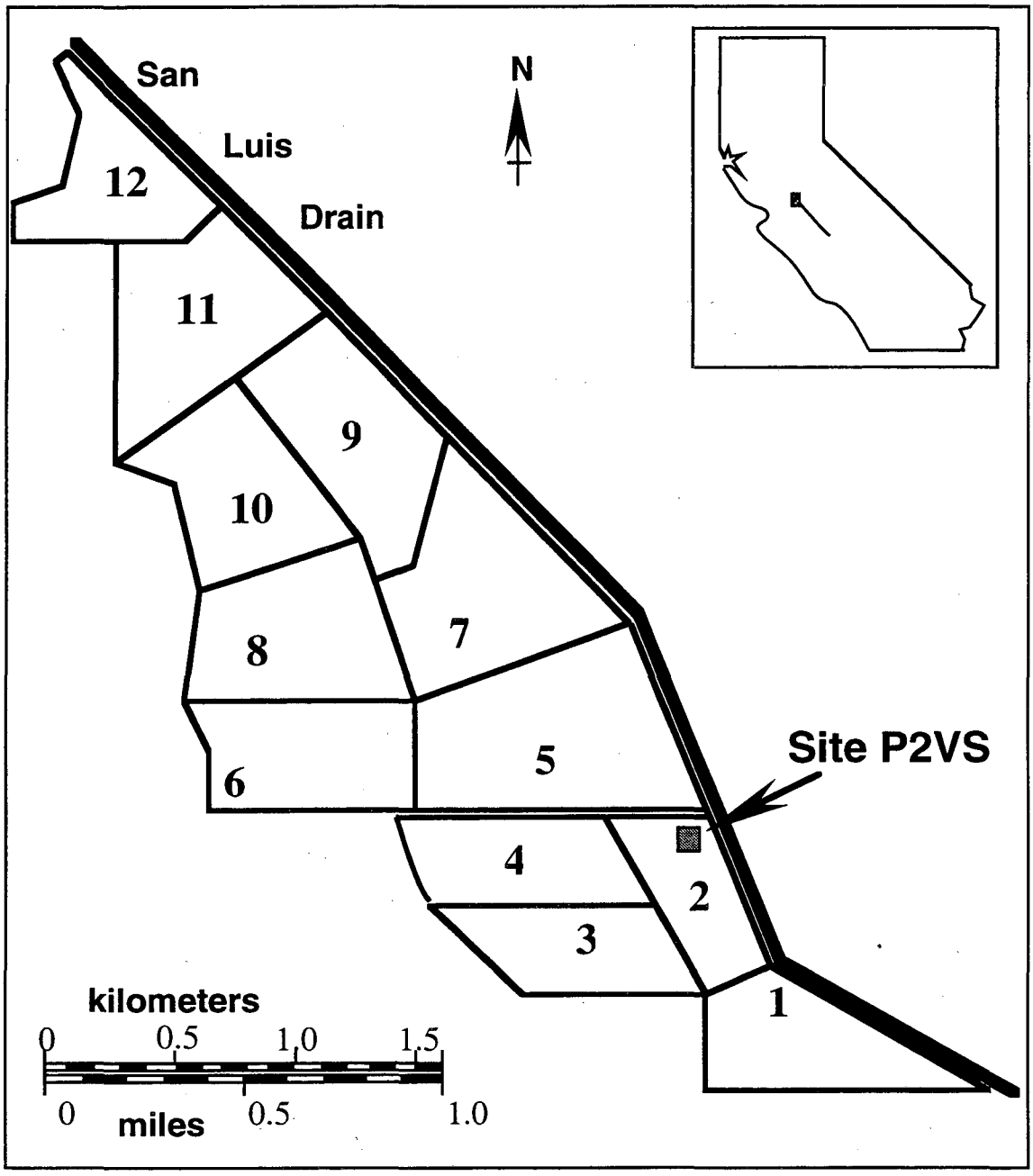

Figure 1.1 Location of experimental site within Kesterson Reservoir.

indicated that the mean [Se] in the top 15 cm (5 samples) was 291 ppm; in the 15 to 30 cm interval it was 27.3 ppm. (Much more intensive subsequent sampling of this area showed the near-surface concentrations to more commonly be in range of 25 to 100 ppm). Furthermore, the same soil intervals were found to be less saline than average (1:10

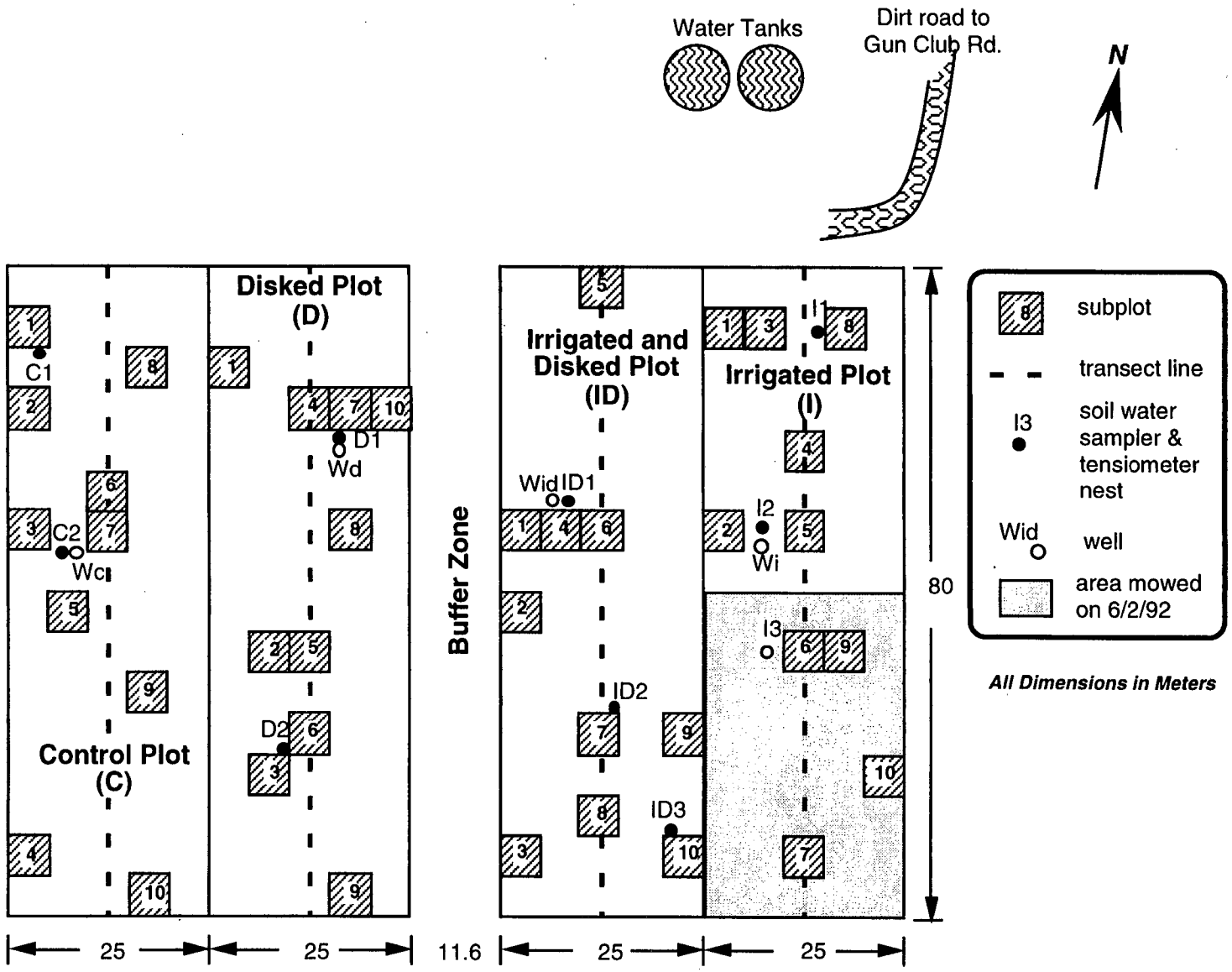

Figure 1.2 Site layout.

soil:water extract electrical conductivity normalized to field water content ranged from 23 dS/m to 69 dS/m). In preparing this plot for the study, cattail residues on the soil surface were incorporated in 1990 into the top 20 cm of soil by repeated disking and rototilling. This was done to homogenize the surface soils and improve the availability of cattails as a carbon source. Such "pre-disking" would also help minimize the chances for soil Se dilution through rototilling, because subsequent rototilling was only done to a 10 cm to 15 cm depth. The plot was then divided into four subplots, each being reserved for a particular treatment: irrigation only ("I"), irrigation and disking (rototilling) ("ID"), disking (rototilling) only ("D"), and control or no action ("C") (Fig. 1.2). An 11.6 meter buffer zone was set up between the irrigated and non-irrigated plots in order to prevent irrigation water from falling onto the disked plot. The irrigated plots are watered once a week for approximately 1 hour using a stationary sprinkler system designed by Dr. W. Wallender of U.C. Davis, resulting in a single application of approximately 10 mm of water. The "disked" plots are rototilled once every 2 weeks using a small tractor-mounted tiller. The plots are not tilled during the wetter parts of the winter because the soil is too wet, clogs up the machinery and is difficult to impossible to drive over.

Losses of selenium in the soil are monitored by annual sampling along selected transects and in randomly selected subplots as well as by direct measurement through charcoal trapping of dimethylselenide (DMSE). Monitoring of the vadose zone for potential short-term and long-term leaching of selenium deeper into the profile is being conducted using tensiometers, soil water samplers and core sampling. In order to determine the amount of near-surface selenium lost to volatilization, selenium displaced by infiltrating water must be quantified. These efforts aid in constructing a selenium mass balance in the vadose zone and estimating selenium losses due to volatilization.

2.0 MOISTURE CONDITIONS

The control and monitoring of moisture conditions within the experimental plot are important in that Se volatilization, reduction/oxidation, and leaching are all influenced by moisture contents and hydraulic gradients in the soil profile.

2.1 Irrigation, Rainfall, Groundwater, and Ponding

Moisture is important in promoting microbial activity. Both laboratory and field tests have shown a positive correlation between moisture content and selenium volatilization rates. Irrigation and rainfall are the main sources of moisture to the soil profile. Seasonal groundwater fluctuations also result in wetting up of the profile, but have little effect on the moisture content of the surface layer, the layer which is subject to microbial volatilization. It is important to note here that because of slight variations in surface elevation and a regional groundwater gradient, the depth to the water table varies in the experimental plot. As seen in Figure 2.1, the water table is shallowest in the control treatment. After normalization for ground surface elevation, water table elevations relative to sea level are roughly equal throughout the plot, except for the end of the summer, when water levels drop further in treatments D, I and ID, than in C (Fig. 2.2).

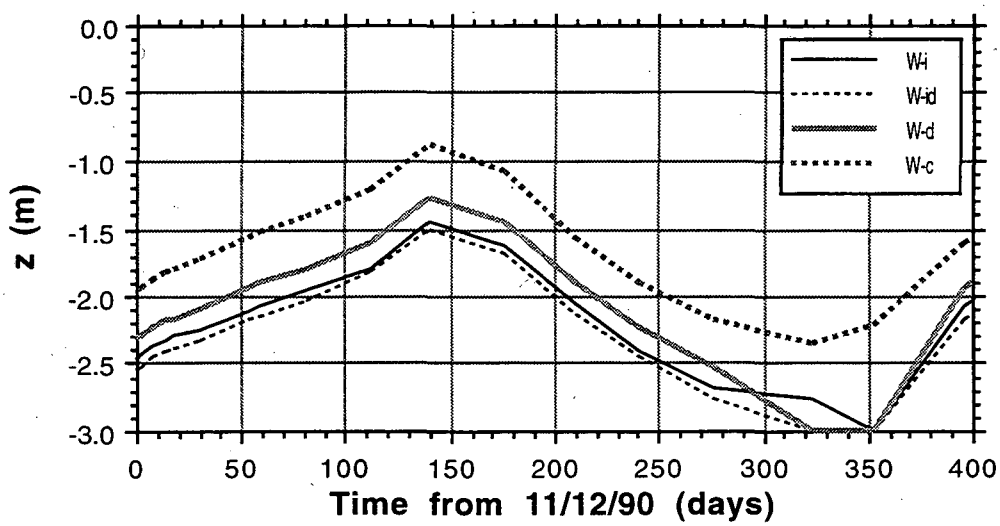

Figure 2.1 Depths to the water table relative to soil surface, as measured in 1990/1991.

The I and ID treatments are irrigated every week during the spring, summer, and fall months and every two weeks in the winter when rainfall is less than 10 mm during a 2-week period. Due to low evaporation rates during the winter, less frequent irrigation suffices to maintain the surface soils moist. The onlyinflux of water to treatments D and C comes from rainfall, most of which is restricted to a 3-month period between December and March (Figure 2.3). Over the first year of the experiment, for example, the total water influx into the irrigated treatments was roughly 2.5 times greater than into the non-irrigated treatments. However, during warm and hot months, when selenium volatilization is likely to be the highest, the non-irrigated treatments receive almost no water, except for the occasional spring shower. On the other hand, the influx due to rainfall is often much greater than that due to irrigation. The irrigation amount was designed to only wet the top few centimeters of soil, but not to cause leaching. The lack of leaching caused by irrigation has been confirmed using tensiometers and neutron probes (see Section 2.2). There is, of course, no way to control leaching from rainfall infiltration. On occasion, winter storms may deposit nearly 100 mm of water in one day (see inset in Fig. 2.3). Furthermore, this generally occurs during the coldest months, when evapotranspiration is minimal. Therefore, the chances of creating steep hydraulic potential gradients and resultant downward leaching of solutes are greatly increased. These gradients are identified and explored further in Section 2.2.

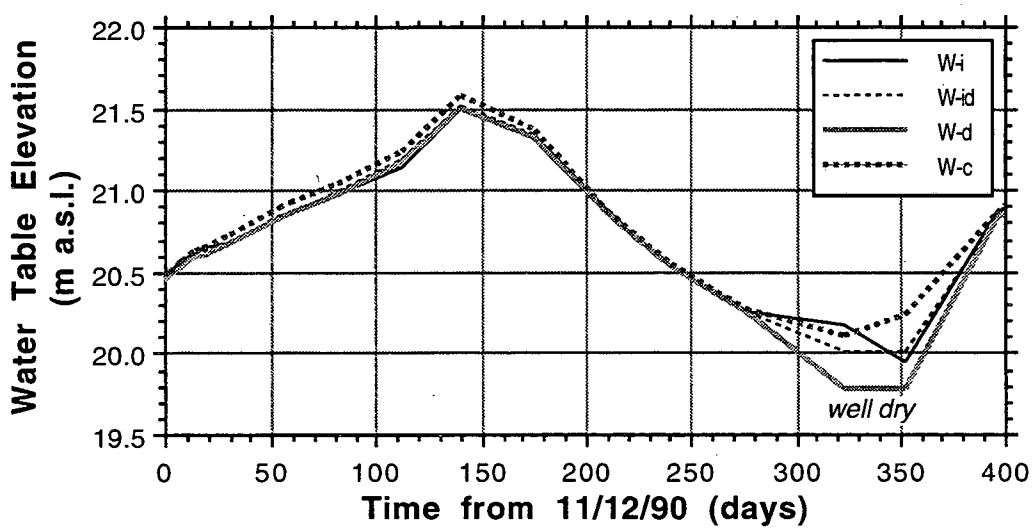

Figure 2.2 Water table elevation relative to mean sea level in wells W-i, W-id, W-d, W-c.

The kind of intense rainfall as shown in the inset of Fig. 2.3, often leads to ponding of water in the eastern parts of the experimental plot. Although temporary ponding may occur

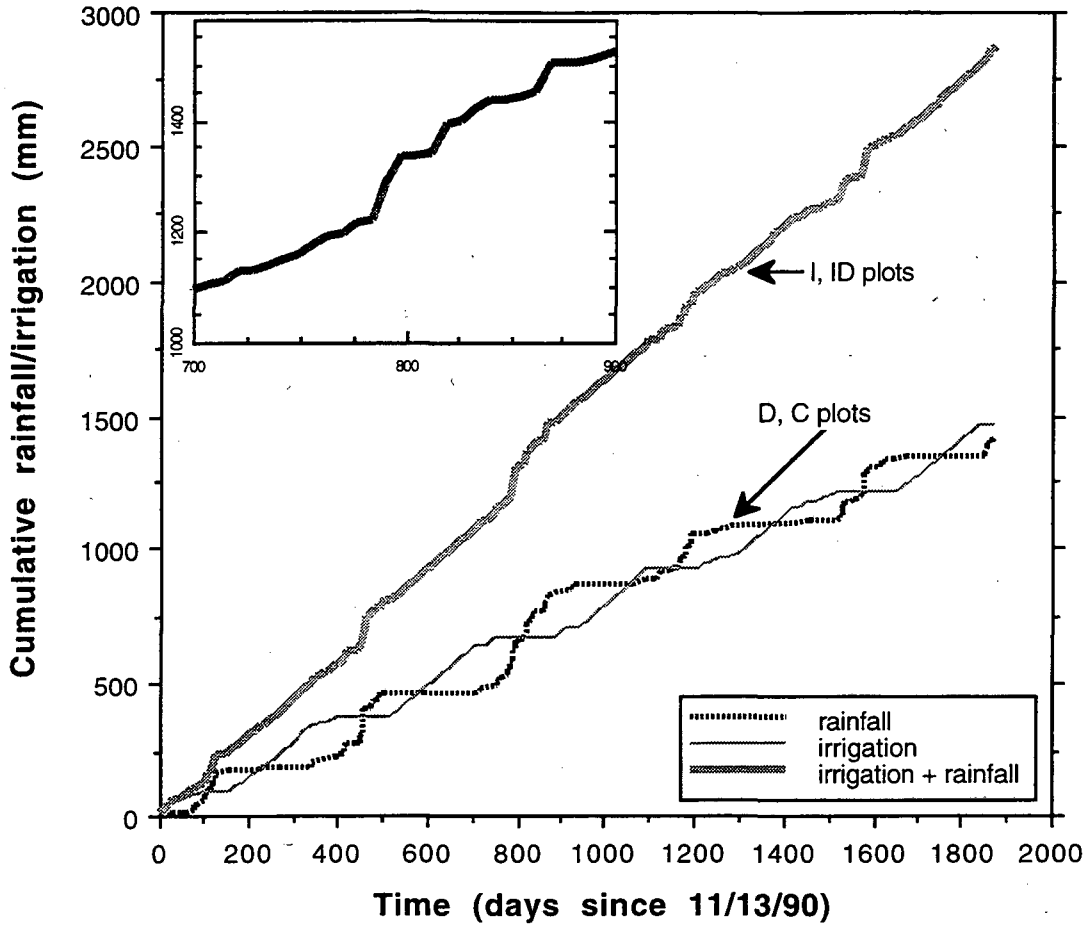

Figure 2.3 Irrigation and rainfall in experimental plot between 11/90 and 12/95.

anywhere in the plot, ponding which lasts for more than several days is found only in the northern half of the control plot and the northern third of the disked plot. This can be related to the topography of the site (Fig. 2.4). (In Chapter 4, the correlation of total Se concentrations with topography will be discussed.) During periods of flooding, the entire profile of many low-lying areas, especially in treatments C and D, is completely water-saturated. This results in significant soluble Se reduction, presumably to selenite which is subsequently sorbed and/or precipitated (Section 2.3), and elemental Se.

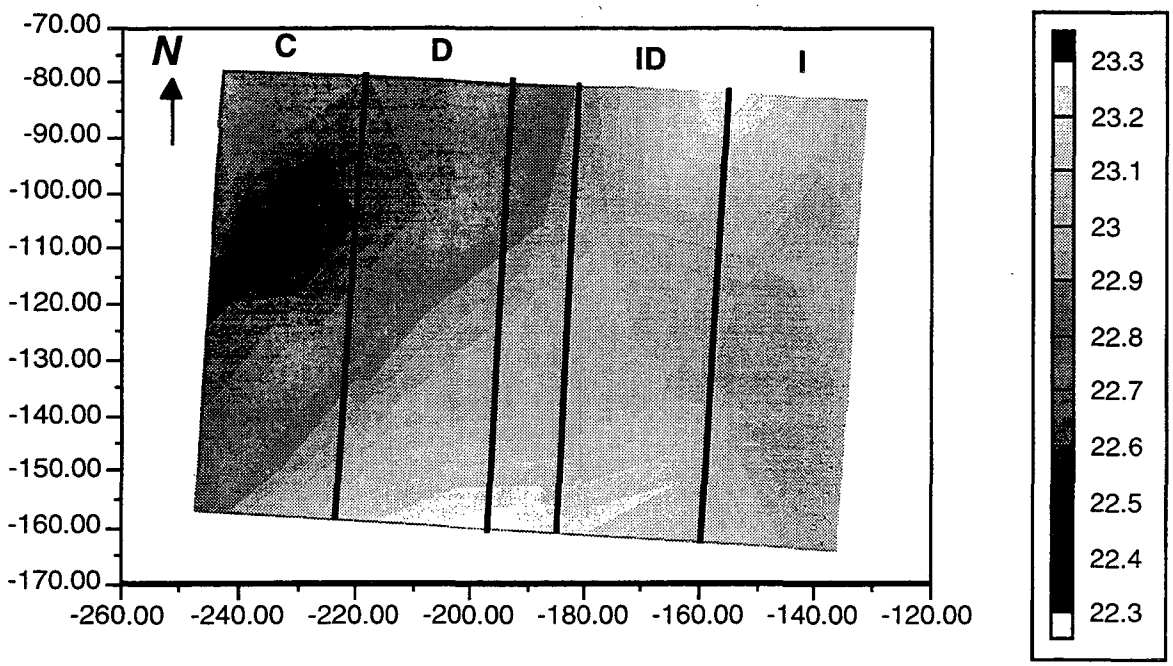

Figure 2.4 Topography of experimental plot, all scales in meters. Elevation relative to mean sea level.

2.2 Soil Moisture Monitoring

The vadose zone monitoring system was installed in July 1990. In total there are 10 nests of tensiometers and soil water samplers, three in each of the irrigated plots and two in each of the non-irrigated plots. The locations of these devices were chosen to coincide with locations of both soil and gas sampling (see Fig. 1.2). Soil water samples and tensiometer readings are taken on a monthly basis. In addition, readings are taken following irrigation and rainfall events. Each nest consists of 4 tensiometers and 4 soil water samplers with porous cups at the following depths: 0.425 m, 0.60 m, 0.80 m, and 1.00 m. All of the instruments are buried at least 30 cm below the soil surface in order to allow disking machinery to pass over the soil. Tubing is routed 1 meter away from the tensiometers and soil water samplers to a common standpipe through which the samplers are sampled and the tensiometers are read. There are 4 wells, one in each treatment. These penetrate to an average depth of 2.8 m. Wells are sampled on a quarterly basis. They are also used as neutron probe access holes. Neutron probe readings are taken at monthly intervals.

2.2.1 Soil matric potential measurements

Tensiometer data reveal seasonal changes in matric potential strongly influenced by plant roots. In non-disked treatments, the soil profile dries out significantly in the summer due to plant transpiration, as indicated by very negative matric potentials (Fig. 2.5 and Fig. 2.8). All plots are affected by winter rains, as seen by near unit gradient in hydraulic head in early March of 1991 (as an example, data from 1990 through 1991 is shown in Figures 2.5 to 2.8). The significance of these observations is that during summer months there is a large hydraulic gradient toward the root zone of plots I and C. However, due to the low moisture content, solute transport is relatively slow. More importantly, the reversal of hydraulic gradient during winter months suggests a high likelihood of solute movement from the surface toward the water table. The effects of storms and infiltration on solute movement is further explored in subsequent sections.

Irrigation does not significantly affect the hydraulic gradients, which indicates that irrigation water does not infiltrate to the 0.425 m depth (Fig. 2.5 to 2.8).

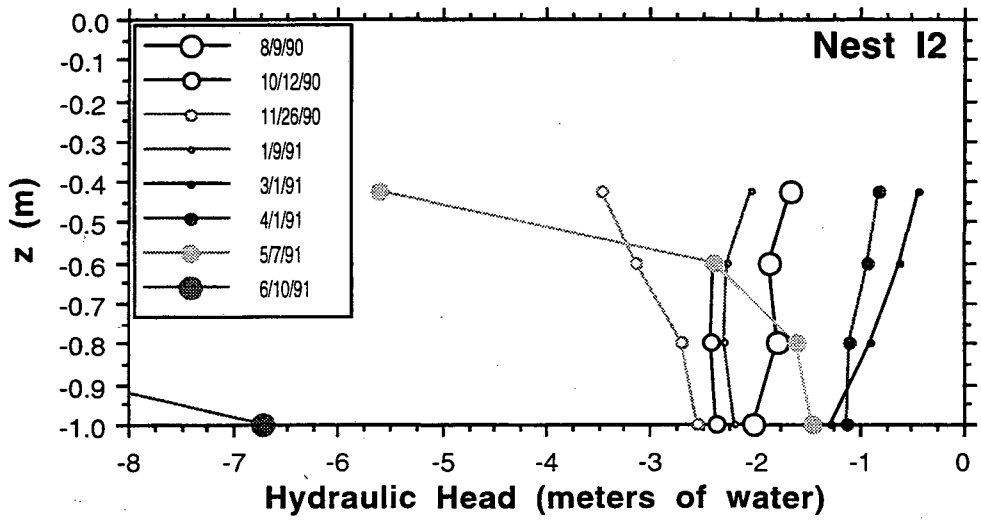

Figure 2.5 Hydraulic head distributions in the irrigated treatment. Hydraulic head was beyond the measurable range for the remainder of 1991.

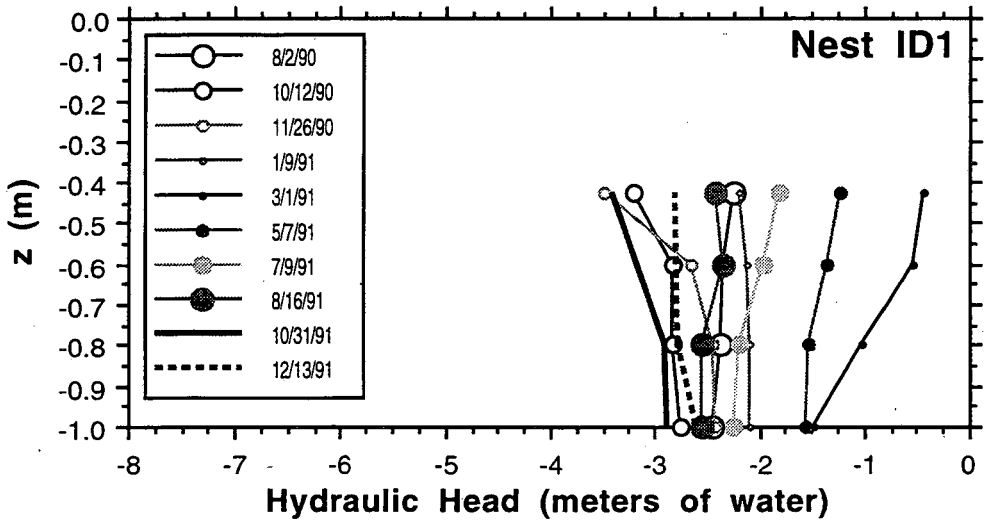

Figure 2.6 Hydraulic head distributions in the irrigated/disked treatment.

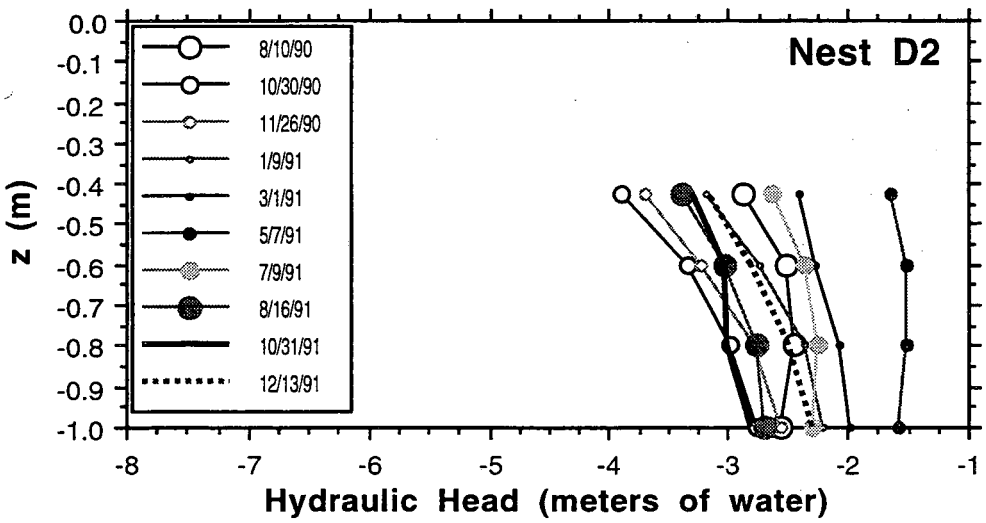

Figure 2.7 Hydraulic head distributions in the disked treatment.

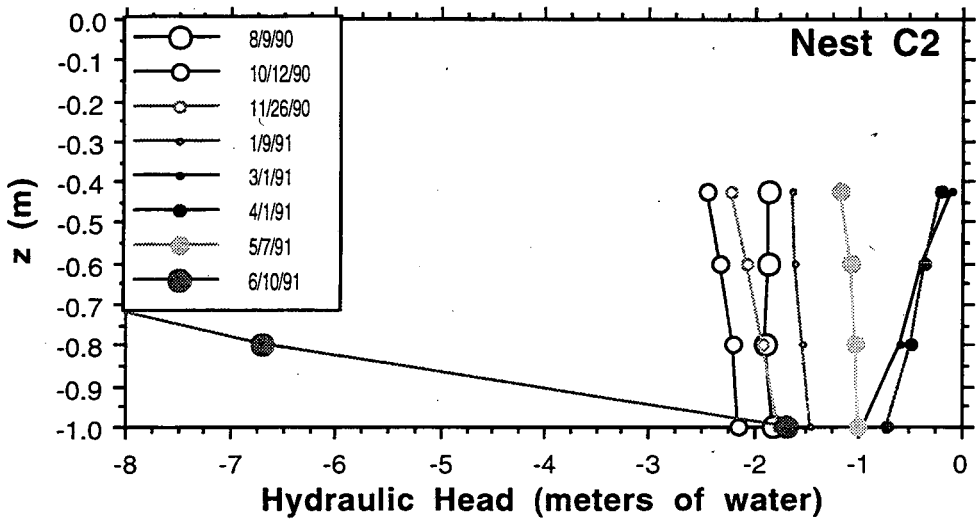

Figure 2.8 Hydraulic head distributions in the control treatment. Hydraulic head was beyond the measurable range for the remainder of 1991.

2.2.2 Moisture content measurements using neutron probe

The trends described above were also observed in soil moisture content as determined via neutron probe measurements. The instrument used was an Am-241/Be-source HydroProbe, manufactured by CPN Corp. (Model 503 DR). The probe was lowered into PVC wells, one in each treatment; readings were taken at 15 cm intervals, down to the water table. From direct counts of backscattered thermalized neutrons, slowed via collisions with hydrogen atoms, volumetric moisture content was estimated using a regression based on an "average" Kesterson soil. Therefore, moisture content values should be considered as reference values for the observation of moisture changes.

Moisture content is inversely proportional to the degree of vegetation within the plot (Fig. 2.9 and 2.10). As there is no vegetation in the rototilled treatments (ID and D), and the soil is mulched through this process, evapotranspiration is minimized and the soil profile retains moisture throughout the year. Conversely, plants in the non-rototilled treatments remove water via transpiration, resulting in a very dry soil profile throughout most of the year. All treatments are affected by winter and spring rainfall, which in the case of treatment I can result in as much as a tripling of moisture content. The vast and rapid changes in moisture content following major rainfall events have great significance in terms of solute transport into the soil profile. Changes can occur over relatively short

periods of time. For example, moisture content before and after the major storms of 1991 and 1992 is shown in Fig. 2.11 through 2.14. Clearly, the greatest changes occurred in treatment I (as represented by nest I2). Not only did the moisture content increase most significantly in this treatment, but rainwater infiltrated *as deep as 1.6 m* in March of 1992.

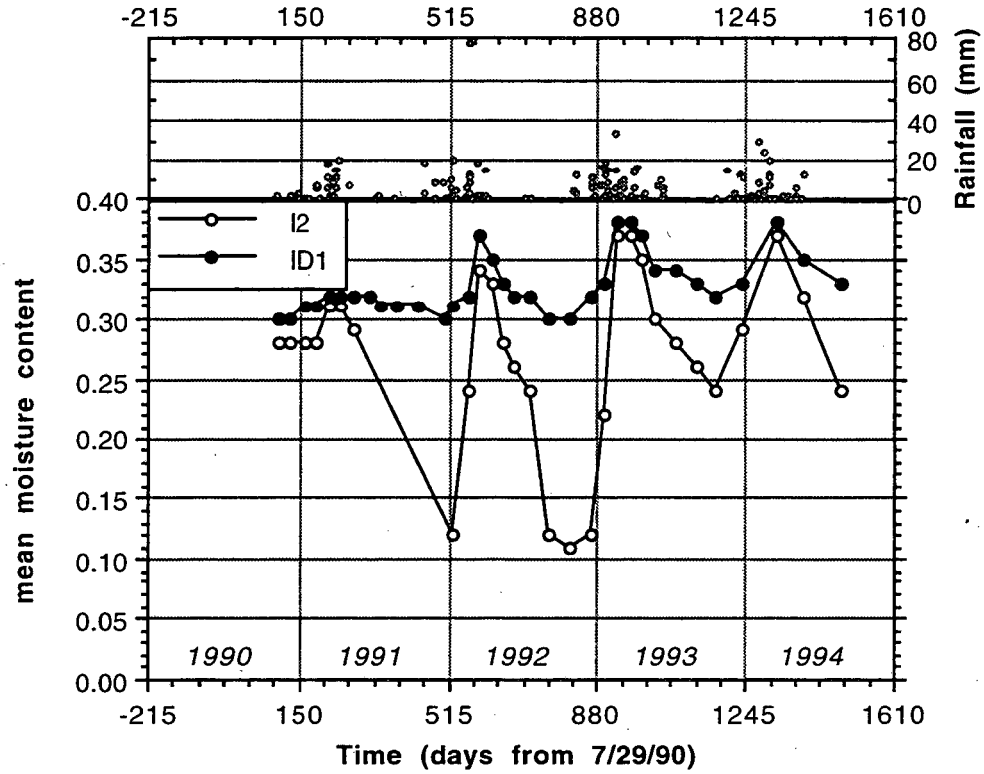

Figure 2.9 Changes in mean moisture content over the top 2.1 m of soil in treatments I and ID, as estimated from neutron probe readings.

Conversely, increases in moisture content in treatment ID and D were much smaller and limited to the top 1 m or less in depth. Although moisture content increased significantly in treatment C in March of 1992, because of the relative high position of the water table (about 1 m below the surface), infiltration was limited to the top 1 m. The significance of these findings is that there is potential for transporting soluble Se below the depth to which the soil is sampled, especially in treatment I.

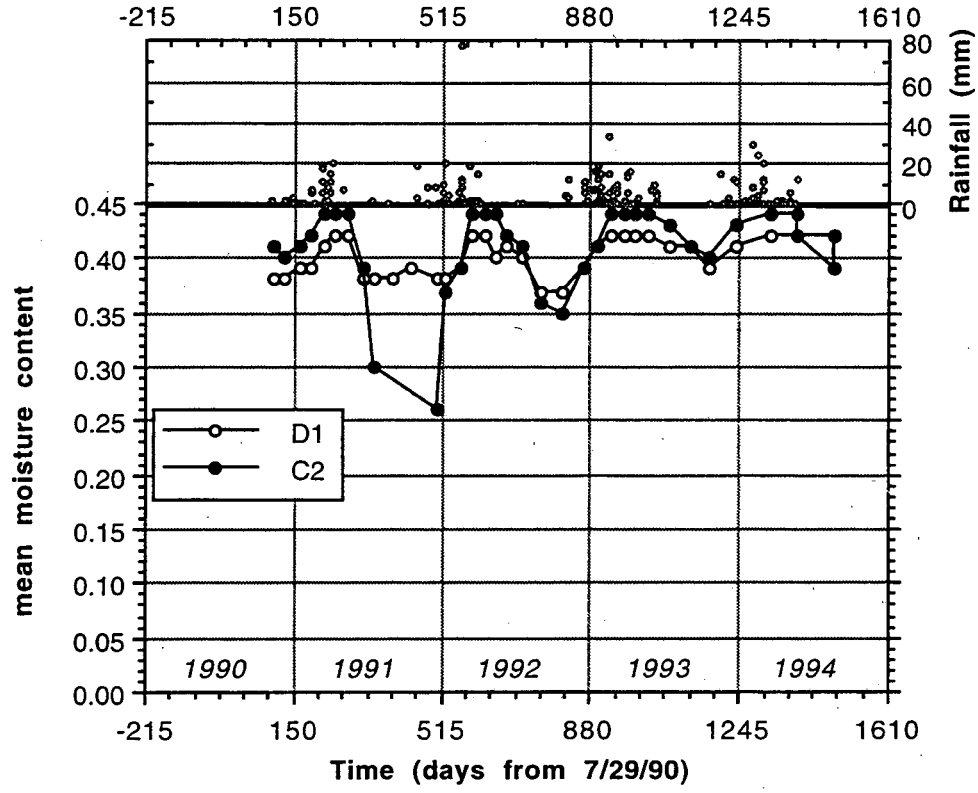

Figure 2.10 Changes in mean moisture content over the top 2.1 m of soil in treatments D and C, as estimated from neutron probe readings.

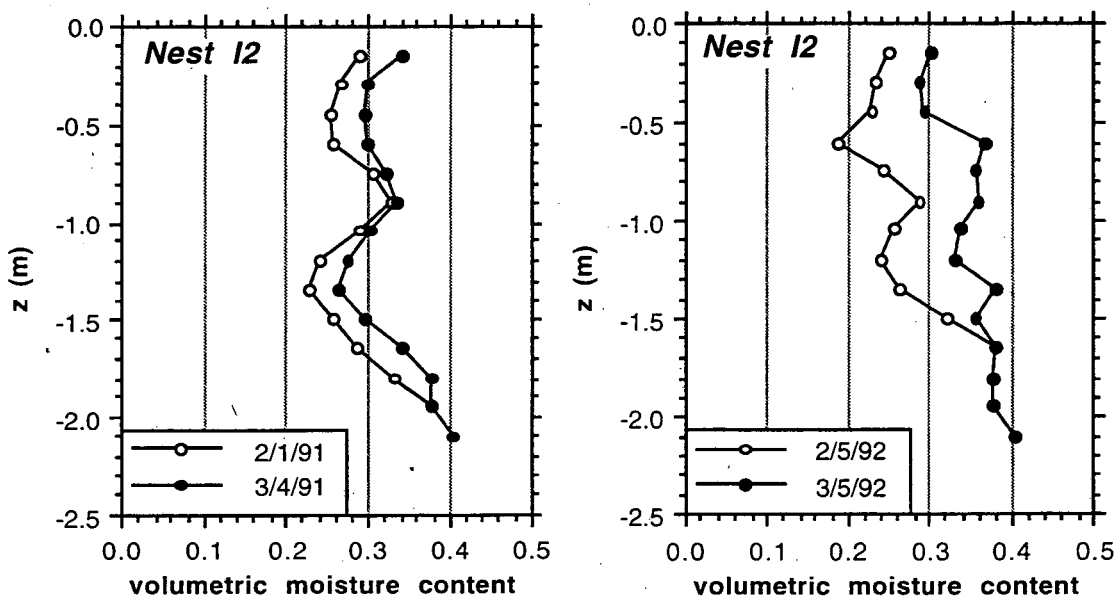

Figure 2.11 Changes in moisture content in treatment I, due to heavy rains over periods of roughly 1 month, as estimated from neutron probe readings.

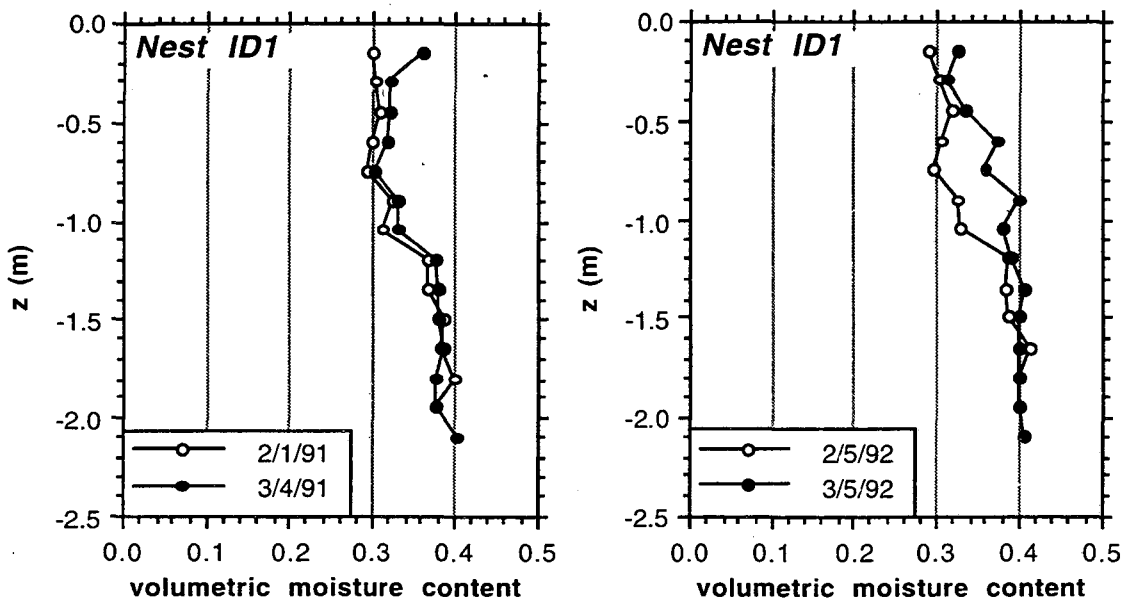

Figure 2.12 Changes in moisture content in treatment ID, due to heavy rains over periods of roughly 1 month, as estimated from neutron probe readings.

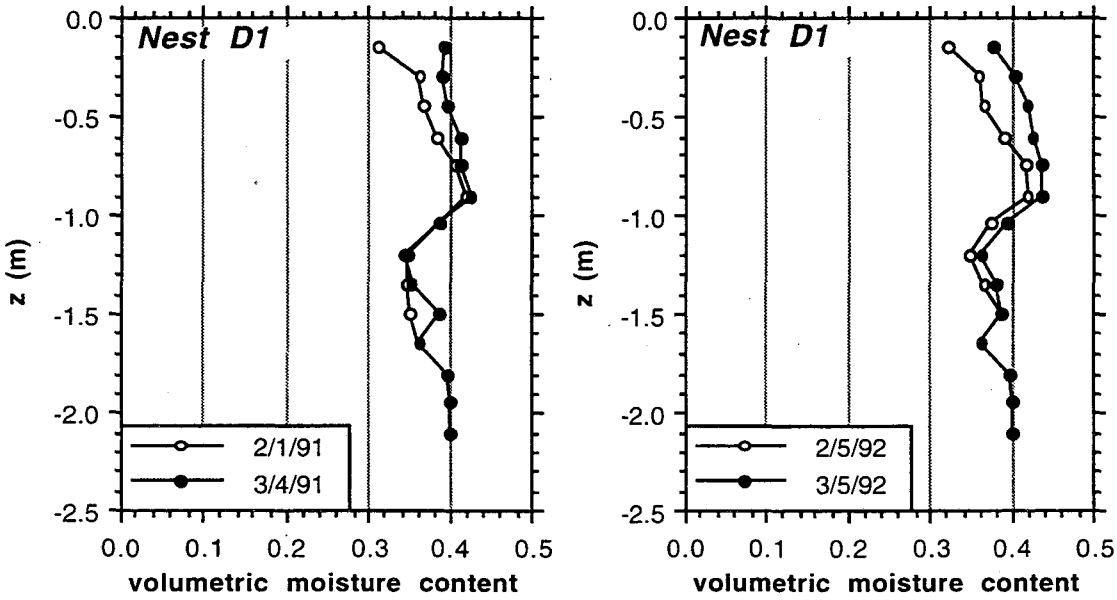

Figure 2.13 Changes in moisture content in treatment D, due to heavy rains over periods of roughly 1 month, as estimated from neutron probe readings.

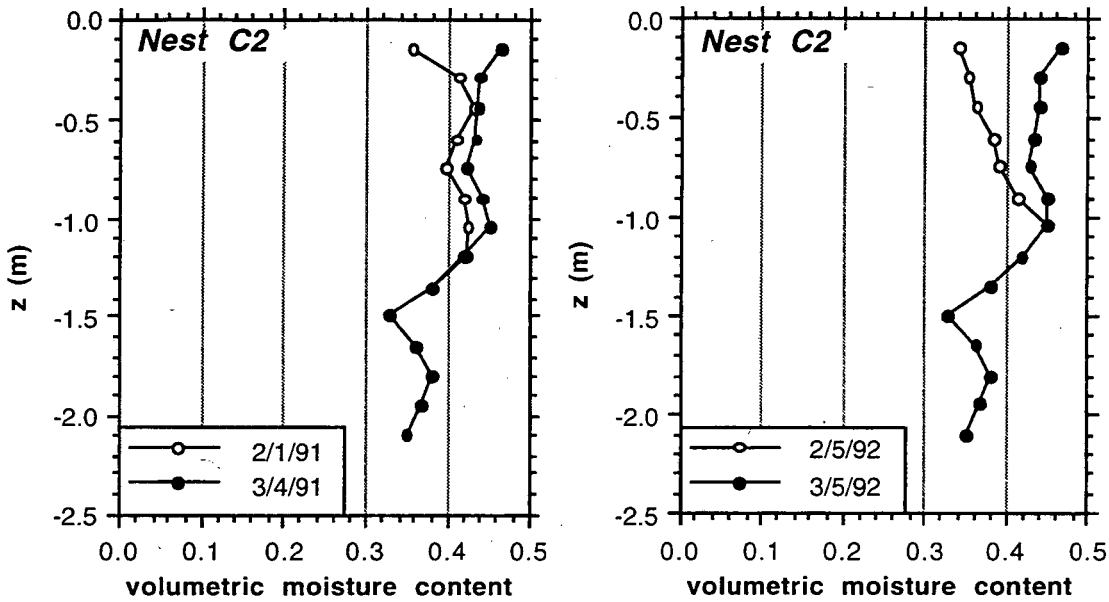

Figure 2.14 Changes in moisture content in treatment C, due to heavy rains over periods of roughly 1 month, as estimated from neutron probe readings.

2.3 Solute Dynamics

The degree to which solute movement is affected by rainfall infiltration is confirmed by changes in soil-water Se and Cl concentrations. These data, which are depth-integrated between 0.425 and 1.00 m, are shown in Fig. 2.15 through 2.18 and are expressed as mass per m^2 in order to be comparable with soil Se data, presented in a subsequent subsection. In response to rainfall-induced infiltration, pulses of Se equivalent to as much as 2 g m^{-2} and of Cl equivalent to as much as 1500 g m^{-2} have been observed. Generally, Cl concentrations do not vary as much because the Cl depth-gradient in most cases is rather flat, i.e., Cl concentrations are usually within one order of magnitude within a soil profile. The Se pulses are equivalent to as much as 25% of the Se in the top 0.60 m of the soil profile and are evidence of Se displacement. Two caveats need to be placed on this argument. Firstly, soil water samplers are generally biased to collecting sample from macropores when macropores are water-saturated. As this is likely the case following rainstorms, solute concentrations observed in this manner may not be representative of the bulk solution and may lead to an overestimation of the net mass of solute being displaced. Secondly, some percentage of solute being displaced downward in the winter will be

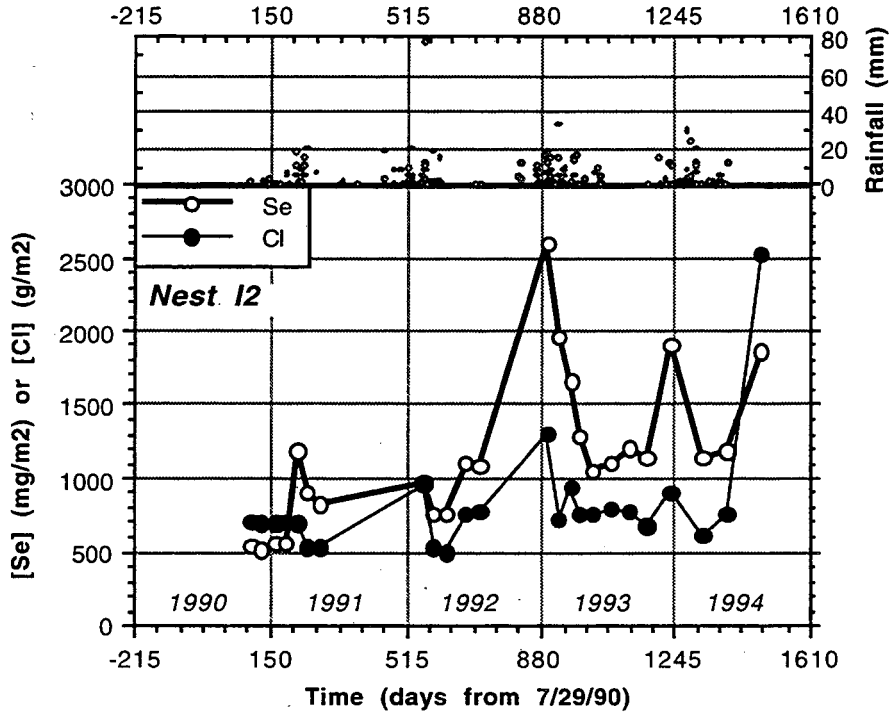

Figure 2.15 Mass of Se and Cl over the depth of 0.4 m to 1.0 m in treatment I, based on data from soil water samplers and neutron probe measurements at nest I2.

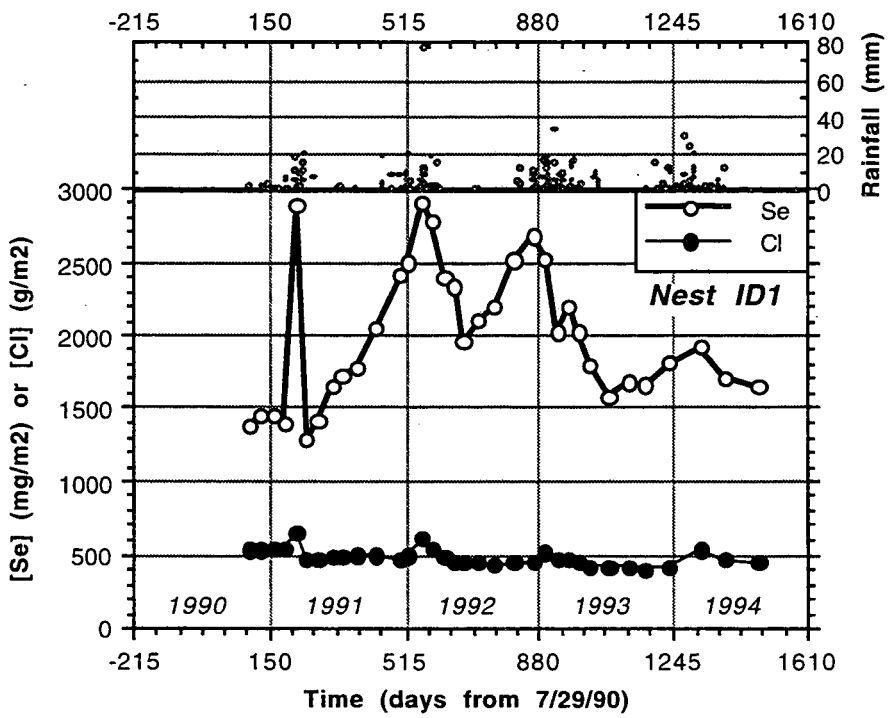

Figure 2.16 Mass of Se and Cl over the depth of 0.4 m to 1.0 m in treatment ID, based on data from soil water samplers and neutron probe measurements at nest ID1.

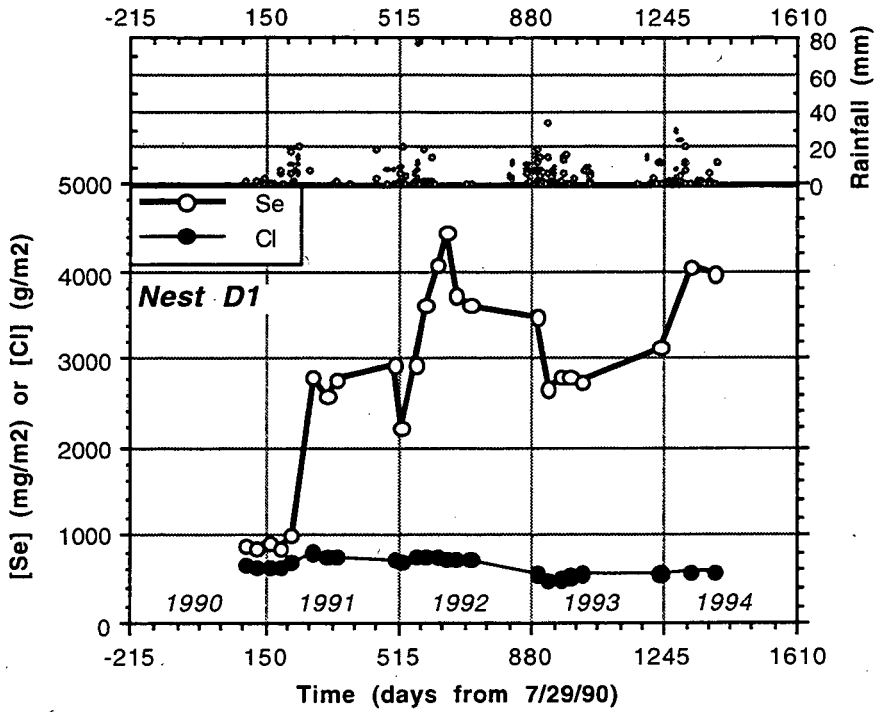

Figure 2.17 Mass of Se and Cl over the depth of 0.4 m to 1.0 m in treatment D, based on data from soil water samplers and neutron probe measurements at nest D1.

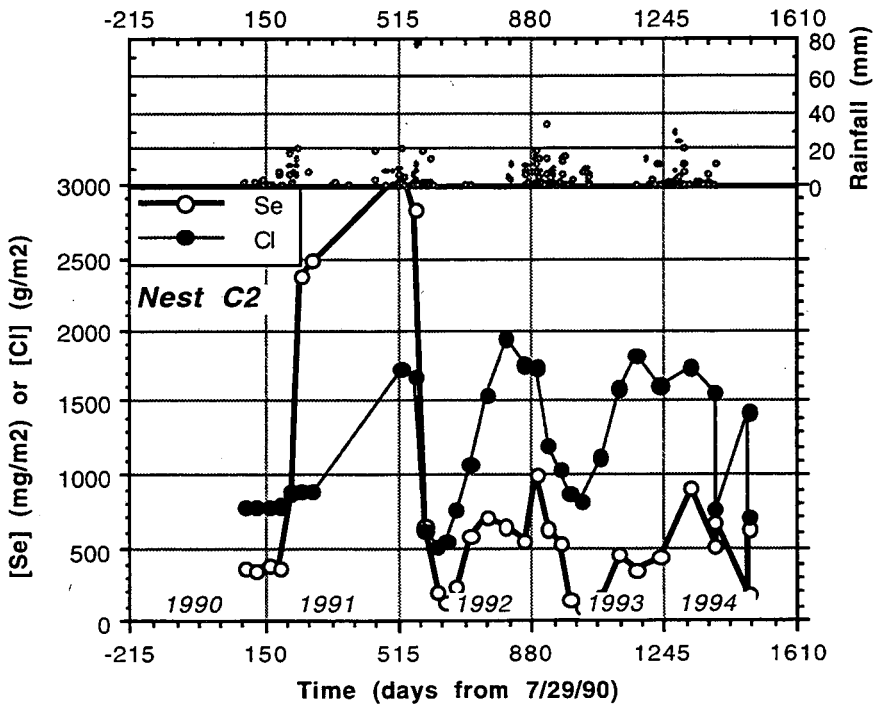

Figure 2.18 Mass of Se and Cl over the depth of 0.4 m to 1.00 m in treatment C, based on data from soil water samplers and neutron probe measurements at nest C2.

transported upward during the summer and fall due to evapotranspiration. There may be more of a movement toward the root zone than toward the surface in vegetated plots, such as in treatment I. Nevertheless, the net loss of solutes from the top 0.60 m may be high enough to be detected in the analysis of annually collected soil samples.

3.0 DIRECT MEASUREMENT OF DMSE EMISSIONS

Since volatilization is a microbially mediated aerobic process, proper amounts and proportions of moisture, aeration, temperature and carbon source are important in optimizing Se emissions from seleniferous dry sediments. The large scale study in Pond 2 is designed to address the means of manipulating these factors to develop a low cost management plan for Kesterson Reservoir.

3.1 Selenium Volatilization: Background

Microbial volatilization permanently removes selenium (Se) from the soil and dissipates it into a gaseous form where it is dispersed and diluted into the atmosphere (Frankenberger and Karlson, 1994). Volatilization of Se is an important transformation in the biogeochemical cycling of Se and the remediation of seleniferous soils. The biogenic contribution of Se in the atmosphere represents approximately 25% of the total atmospheric input (MacKenzie, 1979) which includes both vegetation and microbial contributions. Volatile methylated Se species detected in the atmosphere include DMSe $(CH_3)_2Se$, DMDSe $(CH_3)_2Se_2$, dimethyl selenone $[(CH_3)_2SeO_2]$ and possibly dimethyl selenoxide $[(CH_3)_2SeO]$. DMSe is the primary Se species produced from both soil and water. DMDSe is usually only produced at high inorganic Se levels (i.e., >100 mg kg^{-1} soil). Both $(CH_3)_2SeO_2$ and $(CH_3)_2SeO$ are reaction products of oxidation reactions in the atmosphere (Rael et al., 1995). Once Se is methylated into a volatile species, it is released into the atmosphere, diluted and dispersed by air currents away from the contaminated soils. DMSe reacts with OH and NO_3 radicals and ozone (O_3) within a few hours to yield products as yet unknown (Atkinson et al., 1990). However, it is likely that these oxidized products may be scavenged onto aerosols or sorbed onto particulates that have a relatively long residence time (7-9 days) in the atmosphere and can travel considerable distances (MacKenzie et al., 1979).

There is a diverse group of microorganisms in soils, sediments and water capable of reducing and methylating Se. Fungi appear to be quite active in soils and dewatered sediments. We recently isolated three genera of fungi (*Acremonium falciforme, Penicillium citrinum* and *Ulacladium tuberculatum*) capable of volatilizing inorganic ^{75}Se (Karlson and Frankenberger, 1989). Bacteria including *Aeromonas* sp., *Flavobacterium* sp. and

Pseudomonas sp. are known to methylate Se(IV) under aerobic conditions in lake sediments (Chau et al., 1976).

Soil-Se consists of both a soluble and insoluble fraction. It is believed that the soluble Se fraction is readily available for volatilization but the insoluble Se fraction must be converted into a soluble form or mineralized to be volatilized. Factors such as temperature, microbial diversity, aeration, and organic materials acting as priming substances are all important in transforming the residual Se into a readily available form for uptake by the methylating microorganisms. Previous work has shown that there is an interaction between the cumulative soluble Se collected upon leaching and cumulative Se volatilization potential upon amendment of organic materials (Calderone et al., 1990). As more soluble Se is leached, the Se volatilization potential decreases, indicating that the soluble Se pool serves as a substrate for methylation. Zieve and Petersen (1981) demonstrated that there was a relationship between the evolution of gaseous Se and the decrease in the water soluble Se content.

Volatilization tends to be highly dependent on the Se species and concentration. Without carbon amendments, volatilization of Se is up to an order of magnitude greater with Se(IV) than Se(VI). The reduction step from Se(VI) to Se(IV), is most likely the rate-limiting step in the methylation reaction. Elemental Se is not readily subject to methylation because of its insolubility. The Se ion is subject to volatilization at a wide range of concentration of 0.01 to 250 mg kg^{-1} soil. Even at extremely low Se levels (0.01 to 25 mg kg^{-1} soil) both Se(IV) and Se(VI) are readily converted into volatile methylated Se species. The optimum Se concentration range for methylation is 0.1 to 25 mg kg^{-1} for Se(IV) and 0.04 to 1 mg kg^{-1} for Se(VI) (Karlson and Frankenberger, 1989).

Upon carbon amendments (e.g., galacturonic acid), as much as 23 to 34% of $^{75}Se(IV)$ was removed via volatilization after 37 days of incubation (Karlson and Frankenberger, 1988). Among the carbon sources known to promote volatilization of Se, pectin and proteins are the most stimulatory. Pectin addition increased Se volatilization up to 130-fold and canceled the preference of Se(IV) over Se(VI) in the methylation reaction (Karlson and Frankenberger, 1988). With three pectin amendments over a period of 118 days, approximately 50% of the added Se was volatilized. Pectin is a complex carbohydrate consisting of a polymer of galacturonic acid units bound to one another. The carboxyl

group of galacturonic acid building blocks may be partially or completely esterified with methyl groups, possibly serving as methyl donors.

Protein sources such as casein, albumin and gluten enhanced gaseous Se production 19-fold over unamended seleniferous soils (Frankenberger and Karlson, 1989). Crude casein and its components δ-, β-, and K-casein were equally stimulatory in pond water producing a >50-fold enhancement in DMSe yield (Thompson-Eagle and Frankenberger, 1990). Dialysis studies indicated that the active ingredient of casein was likely a peptide or peptide mixture rather than N-, amino acid- or carbon-limited.

Kesterson dewatered sediments containing 61 mg Se kg^{-1} soil were incubated for 273 days in closed systems located in a greenhouse (Karlson and Frankenberger, 1990). Volatile Se was collected from a continuous air exchange stream using activated carbon. Various economical and readily available organic and inorganic amendments were tested for their capacity to enhance microbial volatilization of Se. The highest Se removal (44%) resulted from the combined application of orange peel and $ZnSO_4$ as a micronutrient, followed by citrus peel alone (40%), cattle manure (19.5%), pectin (16.4%) and straw plus N (8.8%). Without the carbon amendments, the cumulative Se volatilization was 6.1% of the initial Se inventory. This bench-scale study confirms that volatilization of Se is an effective means to dissipate and remove Se from seleniferous soils and sediments. Subsequent field experiments have shown similar observations.

Field Studies

In monitoring Se depletion over time, experiments were carried out in Pond 4 at Kesterson Reservoir. Approximately 40 to 65% of the Se inventory at Pond 4 were removed under optimum conditions in 2 years. In addition, San Luis Drain (SLD) sediments were monitored for gaseous production of alkylselenides as well as depletion of Se in the dewatered sediment itself. Unfortunately, the winter rains wash out the SLD experiment providing only preliminary results with approximately 25% Se removal in 12 months. The data obtained for both seleniferous sediments indicate that depletion of Se is dependent upon a first-order reaction, where volatilization is directly proportional to the substrate concentration. At a high Se concentration, one would expect greater volatilization rates. With declining Se concentrations, volatilization rates also decline. High volatilization rates of Se would be expected to occur at concentrations greater than 25 mg kg^{-1} of total Se and during the initiation of the management program.

Two separate field experiments are being carried out in Pond 2. Direct measurements of DMSe emission are being made in the 2-acre plot in order to compare changes in soil-Se concentrations with Se emissions. Such direct measurement is important in arriving at a total mass balance of Se in soils. Another experiment is being conducted in soils collected from the 2-acre plot, but contained in wooden boxes. This study was conducted to eliminate the leaching component and dilution effect as a result of deep tillage in reducing the Se inventory in soil. Thus, the only mechanism for loss of Se in the seleniferous sediment would be via volatilization.

3.2 Selenium Volatilization in the 2-acre Plot

3.2.1 Methodology

Seven sub-plots were randomly selected from each treatment (irrigated, irrigated/disked, disked and control), to collect data in the volatilization experiments. The following data were obtained.

Volatile Se: Used volatilization chambers (Biggar and Jayaweera, 1993) to collect volatile Se. Volatile Se collected on activated carbon was extracted (Jayaweera and Biggar, 1992) and analyzed for Se. In each treatment, a control chamber was used to measure background atmospheric Se concentrations.

Soil Se: Collected 4 sub-samples at 0-10 cm depth around the volatilization chamber and made into one bulk sample for Se analysis. Selenium was extracted in 1:5, soil: water ratio and analyzed for selenite, selenate, other Se forms and total Se (Fio and Fuji, 1990). The soil was analyzed for total soil Se by acid digestion, once a year.

Gravimetric Moisture Content: As described previously, a bulk soil sample was collected at 0-10 cm depth into moisture cans and gravimetric moisture content was measured in the lab.

pH and Electrical Conductivity (EC): pH and EC were measured in 1:5, soil: water extract.

3.2.2 Research Report for 1993

Research included the temporal measurements of Se volatilization and its associated soil and moisture measurements in Pond 2 long-term field experiment.

3.2.2.1 Temporal Dynamics of Se Volatilization

During the period of June to December, the Se volatilization measurements were conducted seven times in all four treatments. All measurements were performed the day following an irrigation event. In the disked/irrigated treatment, disking was done prior to irrigation.

The irrigated treatment, followed by irrigated/disked treatment had relatively high volatilization rates except in November and December. During November, control and disked treatments had relatively high volatilization rates, but in December all four treatments had very similar and very low volatilization rates (Fig. 3.1). Cumulative Se losses in 1993 showed that irrigated treatment had the highest Se volatilization followed by irrigated/disked, control and disked (Fig. 3.2). The irrigated treatment had the highest and the disked treatment had lowest Se volatilization in 1991 and 1992 as well. However, in 1991 and 1992, the control treatment had the second highest cumulative Se losses, unlike in 1993.

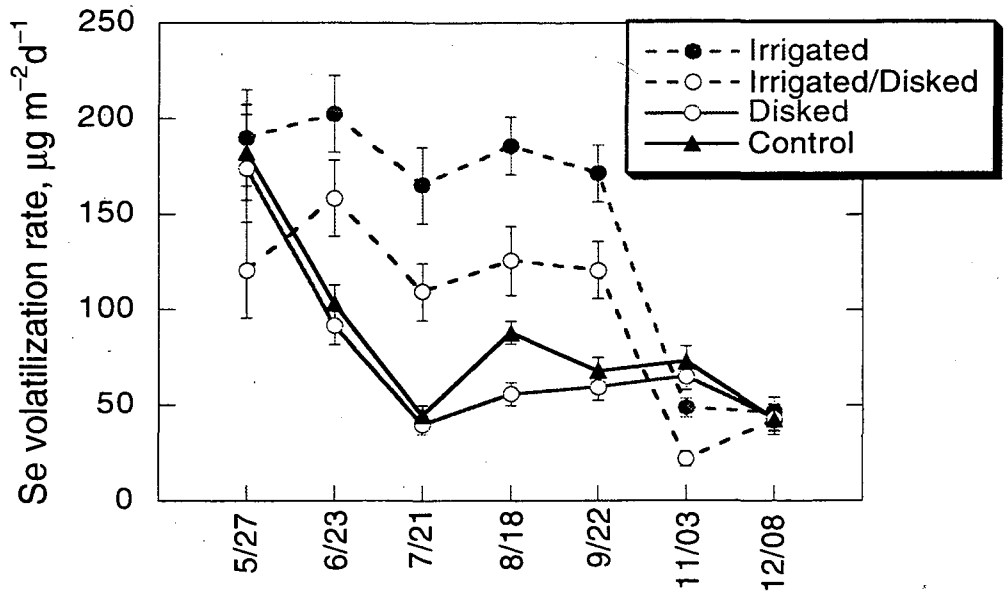

Fig. 3.1 Temporal measurements of Se volatilization rates in 1993.

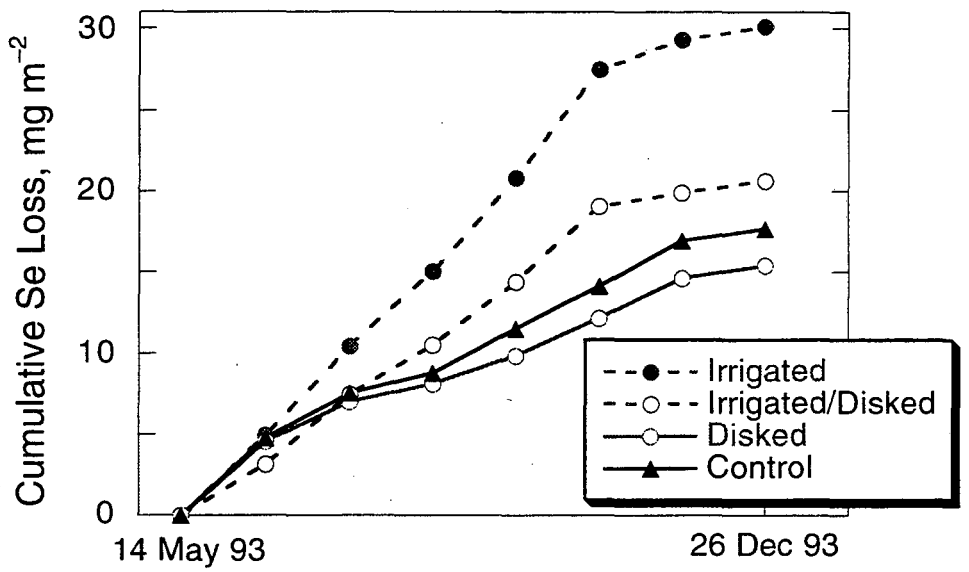

Fig. 3.2 Cumulative Se loss in 1993.

Temporal changes of gravimetric moisture content are shown in Fig. 3.3. Both irrigated treatments – irrigated and irrigated/disked, had the highest moisture content whereas disked and control treatments had the lowest. In all treatments, however, in May and December, the moisture content was higher than during other times. There was a markedly larger decline in moisture content in the non-irrigated plots during the late spring as a result of the cessation of seasonal rains.

The relationship between Se volatilization and moisture content in the treatments is shown in Fig. 3.4 and 3.5. As shown in Fig. 3.4, the irrigated treatment had high gravimetric moisture content as well as high volatilization rates, over the irrigated/disked treatment. In non-irrigated treatments, the moisture contents and Se volatilization were relatively lower than the irrigated treatments. In general, the rate of volatilization followed the changes in moisture content until September. In November and December, the increase in moisture content was associated with a decrease in Se volatilization rates. This is likely due to low temperatures during winter months controlling the rate of volatilization although other factors may be important. High soil moisture may reduce the gaseous flow path from the soil to the atmosphere due to water filled pore spaces, and volatile Se may dissolve in pore water making it unavailable for gaseous transfer.

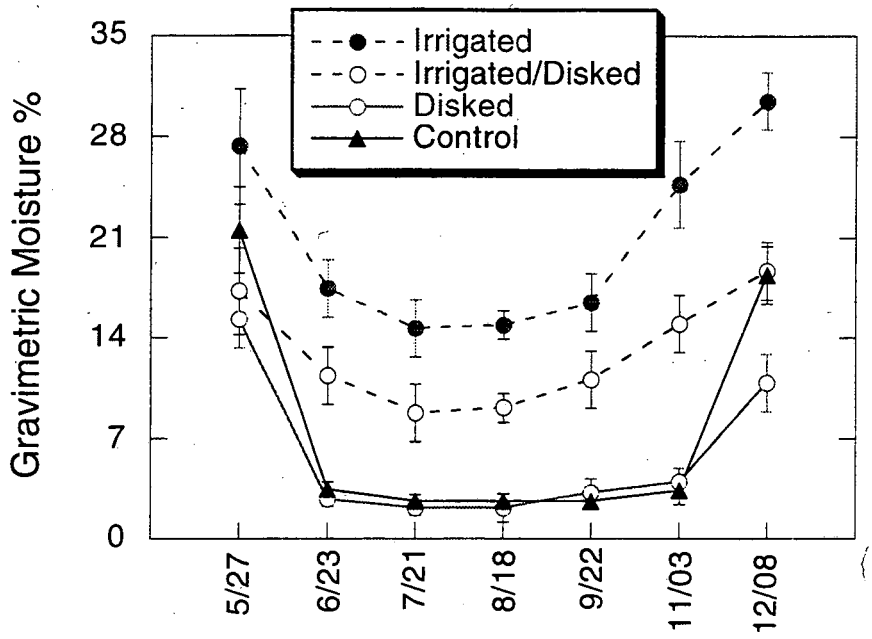

Fig. 3.3 Temporal measurements of moisture content in 1993.

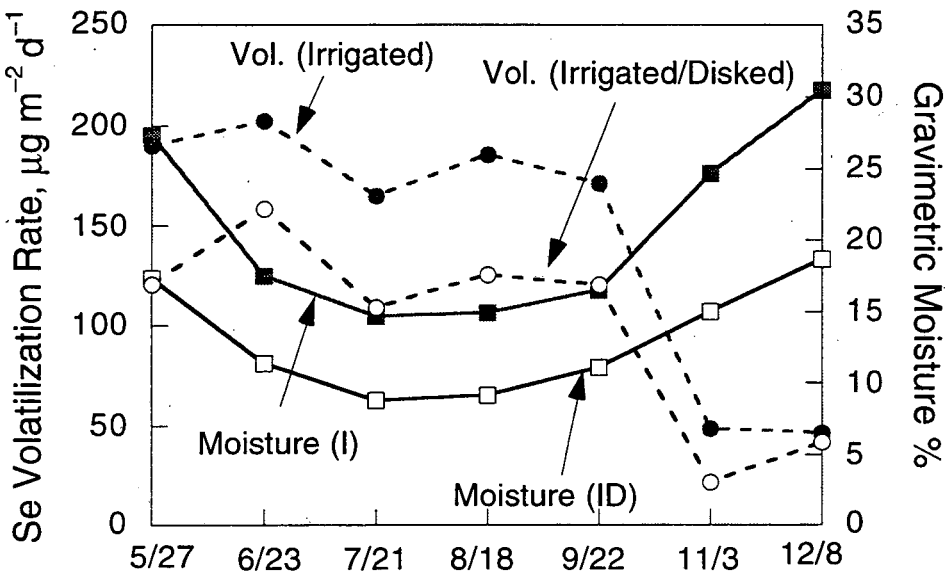

Fig. 3.4 Se volatilization rate and moisture content in irrigated plots (1993).

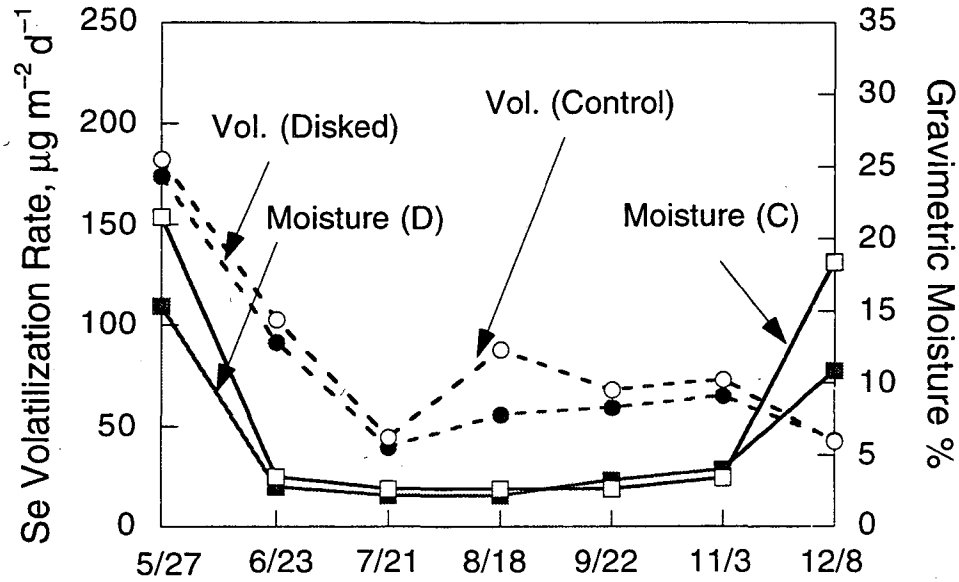

Fig. 3.5 Se volatilization rate and moisture content in non-irrigated plots (1993).

3.2.2.2 Temporal Dynamics of Soil Se

Total water soluble Se

During the period of June to December, total water soluble Se was highest in the disked treatment. Water soluble Se in the other three treatments was 2 to 5 times lower than in the disked treatment (Fig. 3.6). These dynamics showed a very close resemblance to the temporal dynamics in 1992 (Biggar and Jayaweera, 1992). Soil in the disked treatment is most aerated due to disking, the absence of plants, and lowest moisture content (Fig. 3.6). Such conditions can result in Se oxidation and solubilization.

Soluble selenite

Soluble selenite concentration in 1993 showed a decreasing, albeit noisy trend over time in all treatments. The highest selenite concentrations were seen in the irrigated treatment (Fig. 3.7). The irrigated treatment also had the highest water content (Fig. 3.3). Therefore, this treatment may have undergone the highest degree of reduction which is shown by the highest selenite concentration. The lowest selenite concentrations were found in irrigated/disked treatment. This may be due to lower Se reduction rates because of aeration provided by disking operation. It is interesting to note that in December, except

for the disked treatment, all other treatments had very similar selenite concentrations (Fig. 3.7).

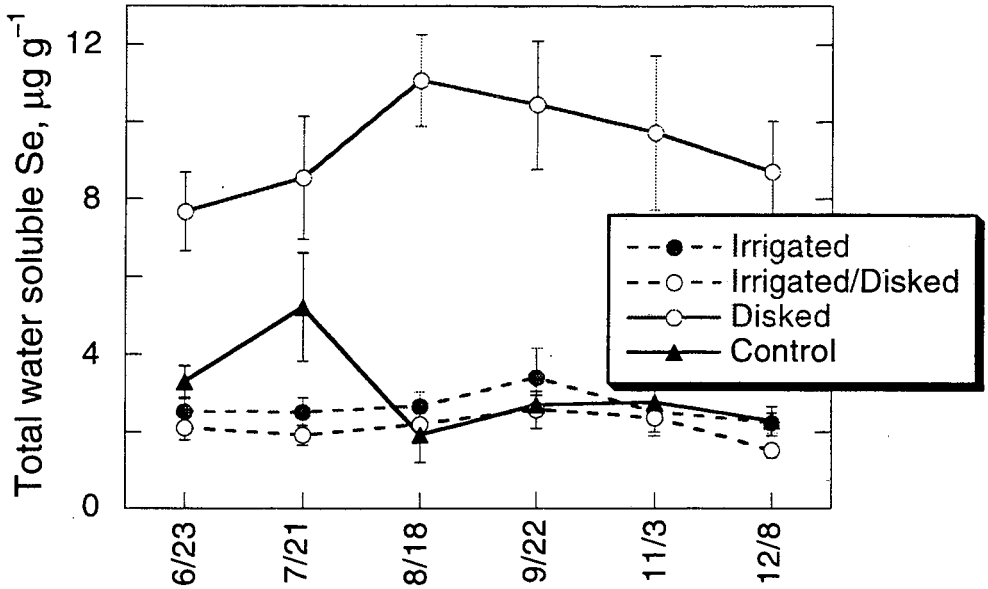

Fig. 3.6 Temporal changes in water soluble Se (0-10 cm depth) (1993).

Selenite/soluble Se ratio

The highest selenite/soluble Se ratio was found in the irrigated treatment, followed by irrigated/disked treatment, control and the disked treatment (Fig. 3.8). Irrigated treatment also had the highest water content (Fig. 3.3). Irrigated/disked treatment had the next highest water content and also the next highest selenite/soluble Se ratio. It is interesting to note that the control and disked treatments had very similar water contents, but selenite/soluble Se ratio was exceptionally low in disked treatment. This shows that disking may aerate the soil to yield low selenite concentrations, thus giving low selenite/soluble Se ratios.

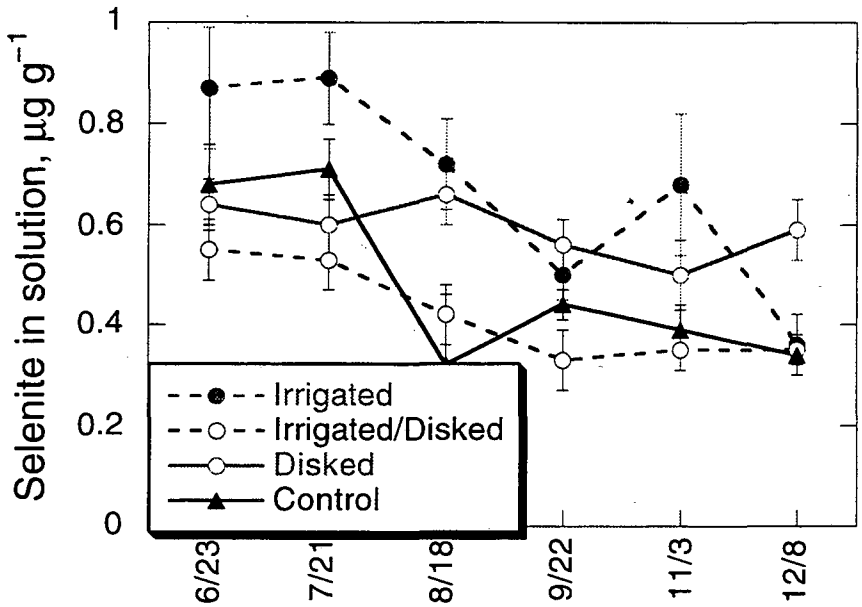

Figure 3.7. Temporal changes in soluble selenite (0-10 cm) in 1993.

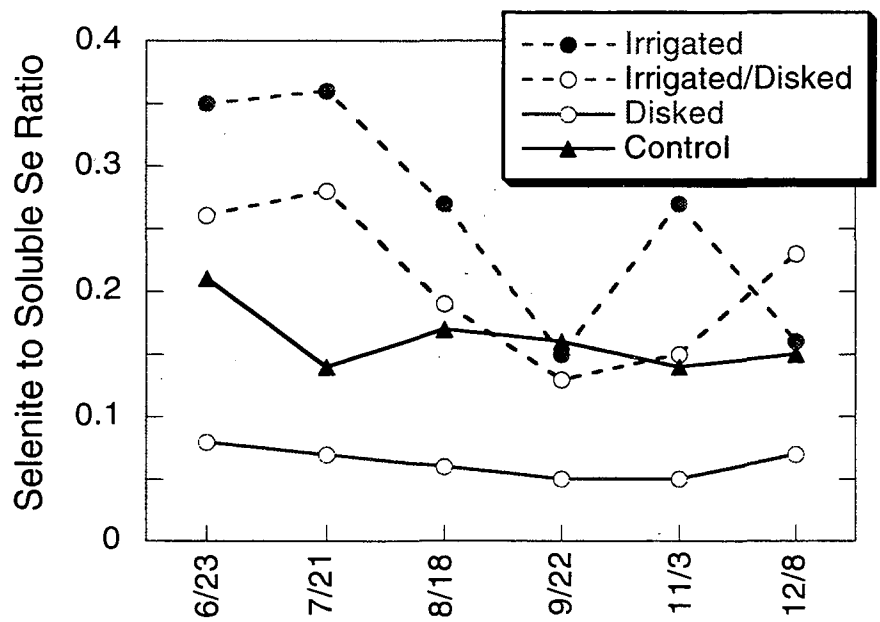

Figure 3.8. Temporal changes in the selenite to soluble Se ratio (0-10 cm) in 1993.

3.2.3 Research Report for 1994-95

Research included the following:

(i) Temporal dynamics of Se volatilization;
(ii) Temporal dynamics of various soil Se forms;
(iii) Temporal dynamics of other chemical properties.

3.2.3.1 Temporal Dynamics of Se Volatilization

In 1994 we conducted Se volatilization measurements seven times between January and October. Se volatilization rates and cumulative losses were highest in the control plot followed by irrigated, disked and irrigated/disked (Figures 3.9, 3.10). The pattern of Se volatilization was quite different in 1994 than in previous years. Until 1994, the highest cumulative Se volatilization was seen in irrigated followed by irrigated/disked, control and disked treatment. Furthermore, with the exception of the control treatment, volatilization rates dropped significantly from previous years. For example, the cumulative Se loss in the irrigated treatment in 1993 was about 30 mg m^{-2} (Fig. 3.3); in 1994 it was only around 16 mg m^{-2} (Fig. 3.10).

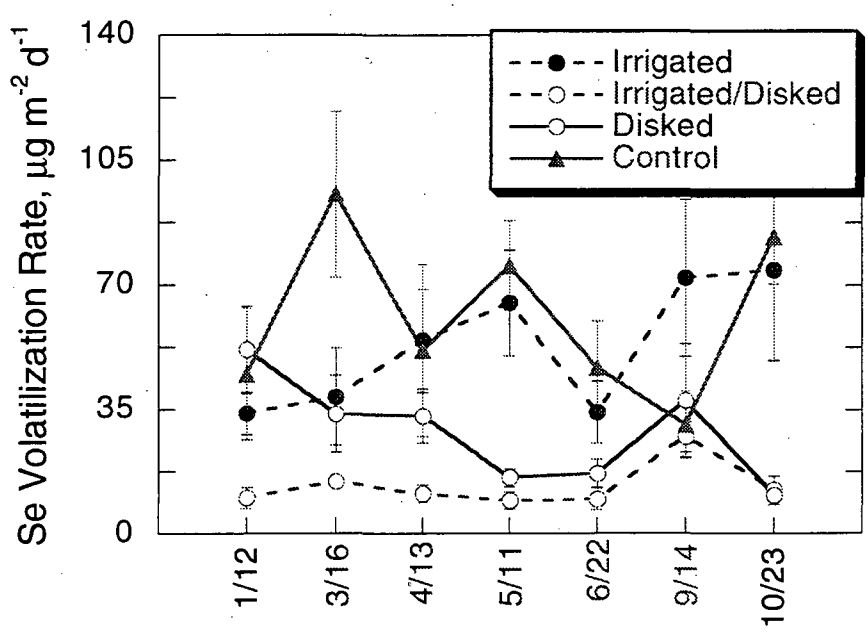

Figure 3.9 Temporal measurements of Se volatilization rates in 1994.

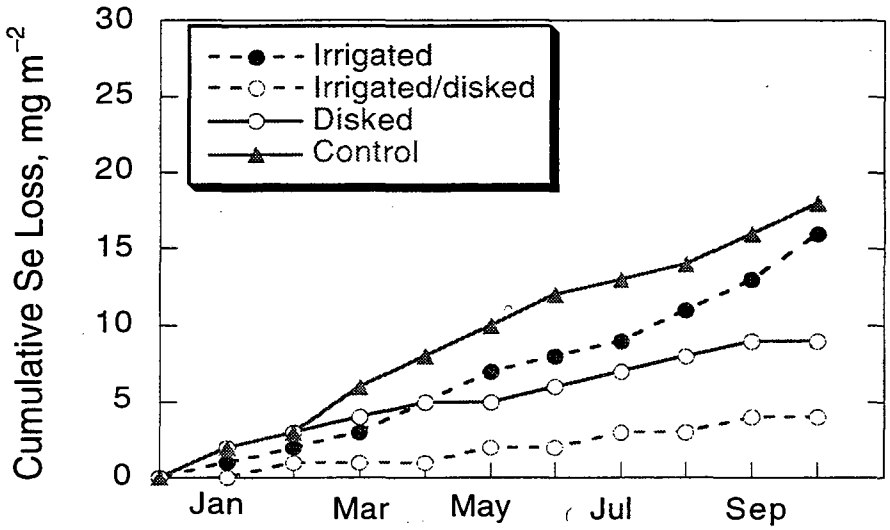

Figure 3.10 Cumulative Se loss in 1994.

The gravimetric moisture content in various treatments may be responsible for trends in Se volatilization in 1994. In 1994, the gravimetric moisture content was different than in previous years. As shown in Fig. 3.11, unlike in previous years, the control treatment had the highest moisture content until June, followed by irrigated, disked and irrigated/disked. However, in September and October irrigated and irrigated/disked treatments had slightly higher moisture content. However, overall moisture content in the irrigated plots was more or less the same as in 1993.

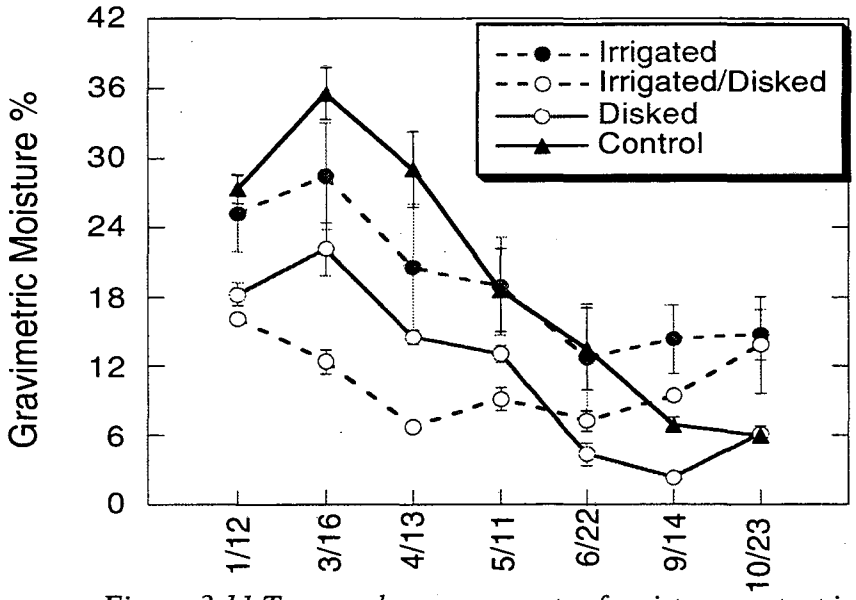

Figure 3.11 Temporal measurements of moisture content in 1994.

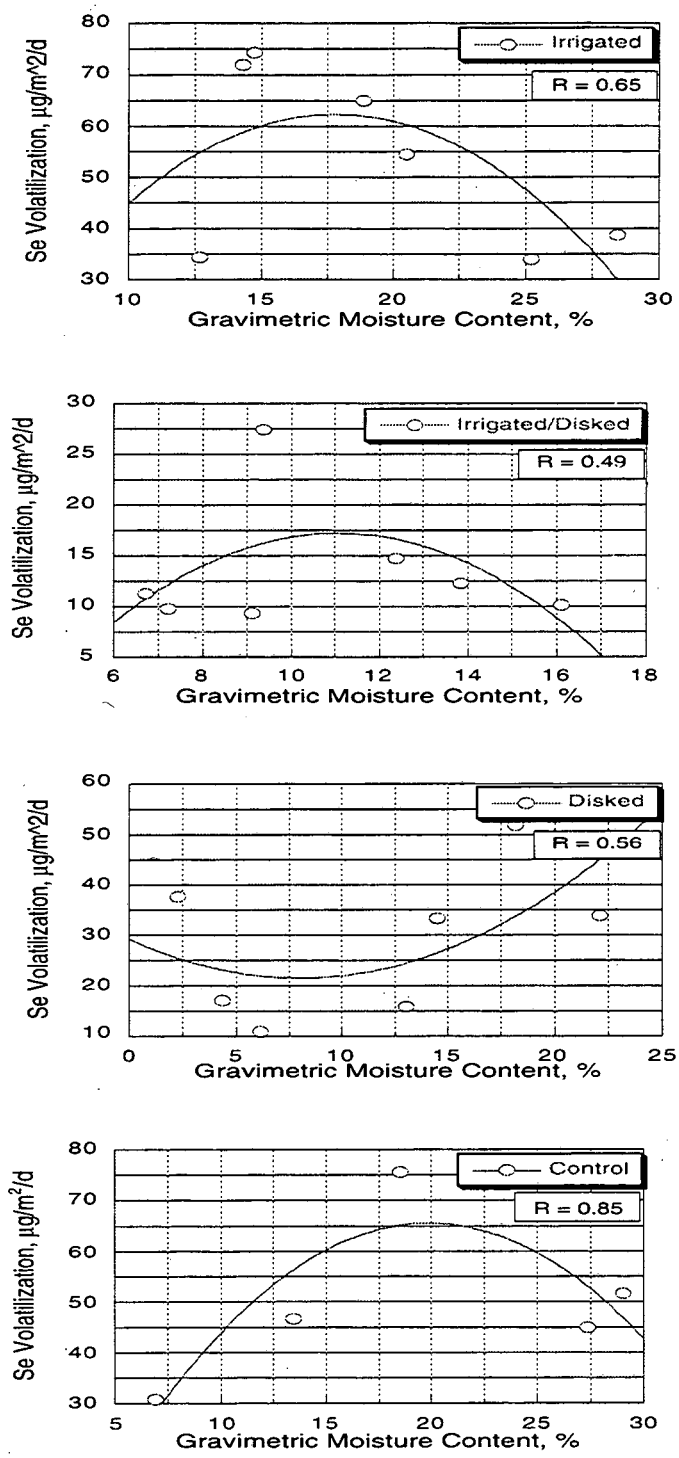

Figure 3.12 Second order polynomial fit - Se volatilization and soil moisture.

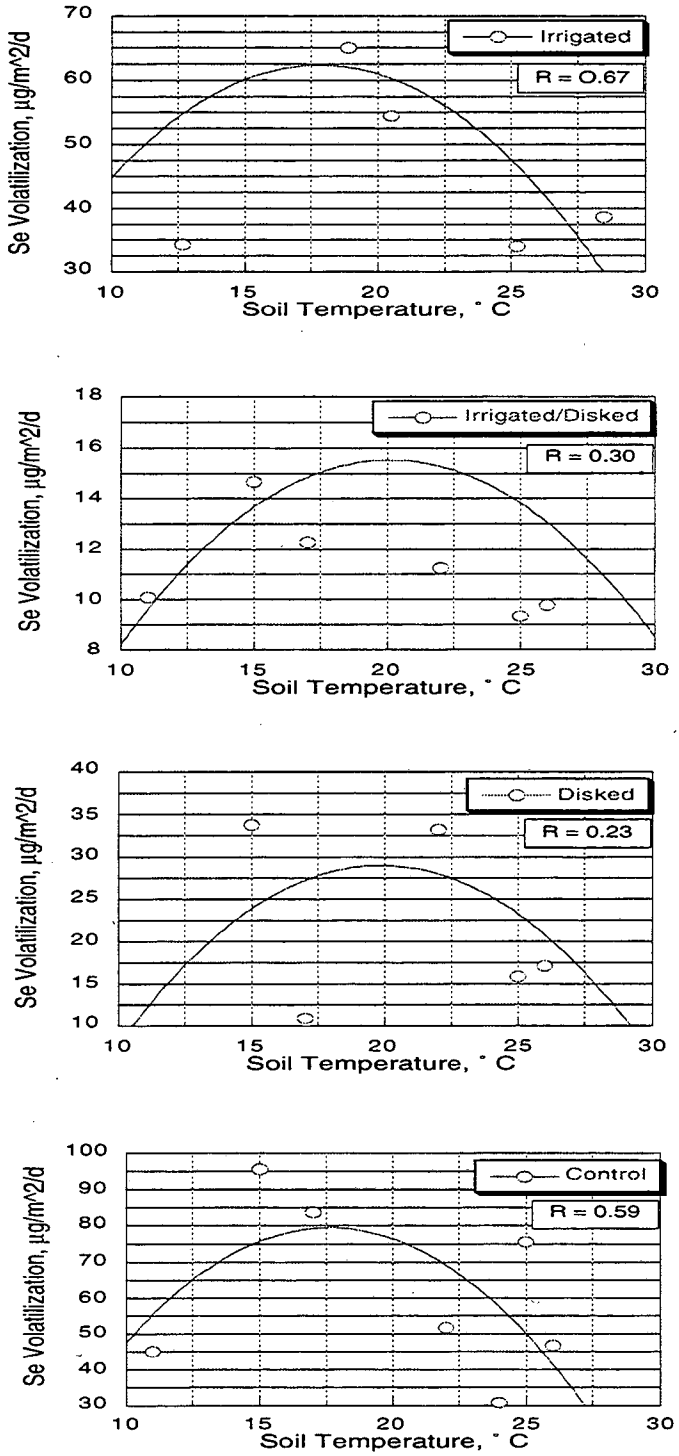

Figure 3.13 Second order polynomial fit - Se volatilization and soil temperature.

The relationship between Se volatilization and moisture content for each treatment is shown in Fig. 3.12. In all four treatments, second order polynomial had a reasonably good fit. Each data point used in this correlation is the average of seven replicates. In irrigated, irrigated/disked and control treatments, there was an optimum moisture content for Se volatilization. In irrigated treatment and in the control the optimum moisture content is around 18-20% and in irrigated/disked treatment optimum is around 11%. This difference may be accounted for the presence of plants and consequent high organic C in irrigated treatment and control and the absence of plants in irrigated/disked treatment. In the disked treatment, however, an entirely different trend was observed, with a minimum in Se volatilization at around 8% gravimetric moisture content.

The relationship between Se volatilization and the soil temperature for the four treatments is expressed by a second order polynomial fit (Fig. 3.13). Similar to the moisture correlation, each data point is the average of seven replicates. The irrigated treatment and the control showed the best fit whereas the irrigated/disked and disked treatments showed fairly a poor fit. In all four treatments the optimum temperature for Se volatilization is around 20° C. This is lower than has been observed in laboratory experiments, probably because other variables are not controlled, e.g. moisture content, and also because of sparseness of data at higher temperatures.

3.2.3.2 Temporal Dynamics of Soil Se

Total Soluble Se

Temporal changes in total water soluble Se are shown in Fig. 3.14. The disked treatment had the highest water soluble Se. The other treatments had very similar concentrations until May. Starting in June, the soluble Se in the control and irrigated treatments increased above that in the irrigated/disked treatment. The dynamics of soluble Se in 1993 showed similar behavior (Fig. 3.6).

Soluble Selenite

The dynamics of soluble selenite in 1994 are shown in Fig. 3.15. The irrigated treatment had the highest soluble selenite and irrigated/disked had the lowest. The high selenite in irrigated treatment can be explained by more reduced conditions in this plot. The lowest selenite concentration in irrigated/disked treatment may be due to the aeration of the

soil system due to disking. Soluble selenite concentrations in 1994 seems to decrease slightly from January to October. A similar trend has also seen in 1993, but not in 1992.

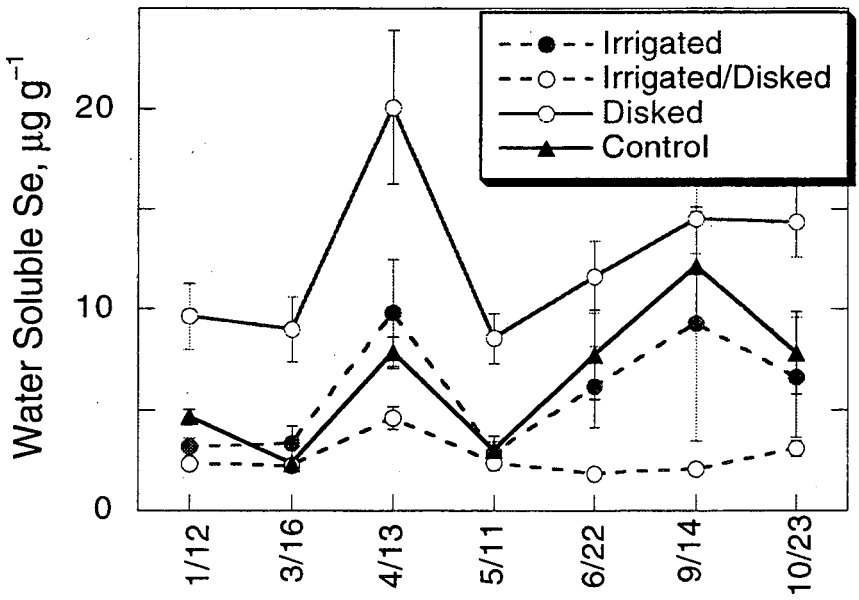

Figure 3.14 Temporal changes in water soluble Se (0-10 cm) in 1994.

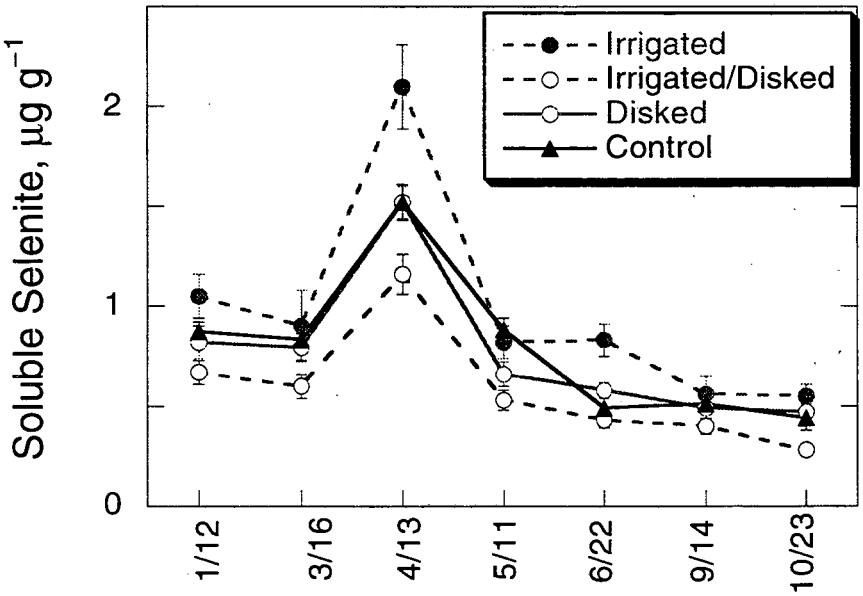

Figure 3.15 Temporal changes in soluble selenite (0-10 cm) in 1994.

Selenite/Water Soluble Se Ratio

The disked plots had the lowest selenite to total water soluble Se ratio (Fig. 3.16). This is very similar to the behavior in 1993 and 1992. The disked plot may be more aerobic than all other plots, which would lead to selenite oxidation. The highest ratio of selenite to water soluble Se was shown by irrigated plots. The control had the intermediate selenite to water soluble ratio. In all four treatments, the ratio of selenite to water soluble Se showed a linear relationship with gravimetric moisture content (Fig. 3.17). In other words, more moisture means more selenite in the system which indicates more reduction of Se.

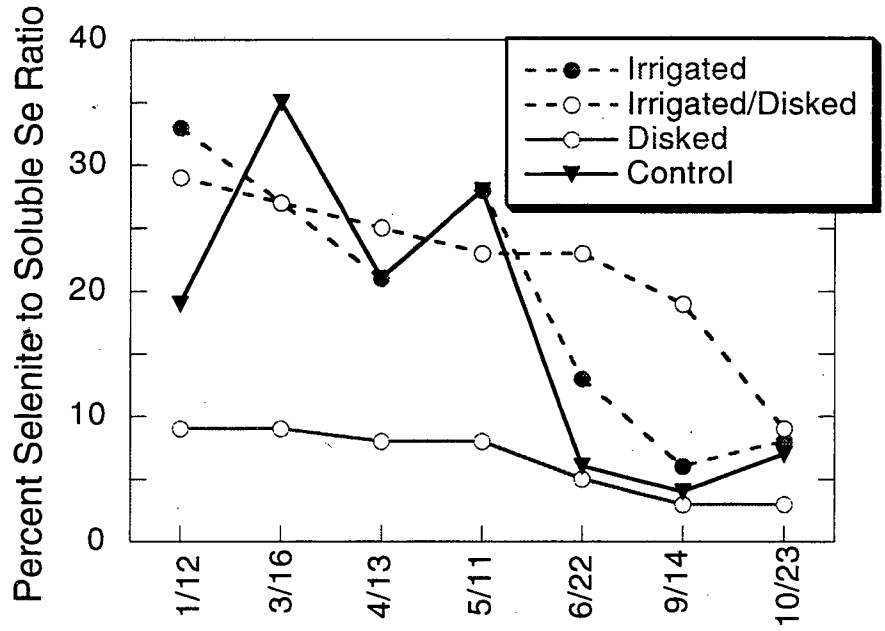

Figure 3.16 Temporal changes in the selenite to water soluble Se ratio (0-10 cm) in 1994.

3.2.3.3 Temporal Dynamics of Selected Chemical Properties

Temporal Measurements of pH

The dynamics of pH in the Pond 2 experiment are shown in Fig. 3.18. The irrigated/disked treatment had the highest pH and it ranged from 7.78 to 7.98. The irrigated/disked, disked and control had very similar pH values. It is interesting to note that over time, the pH did not show any significant changes.

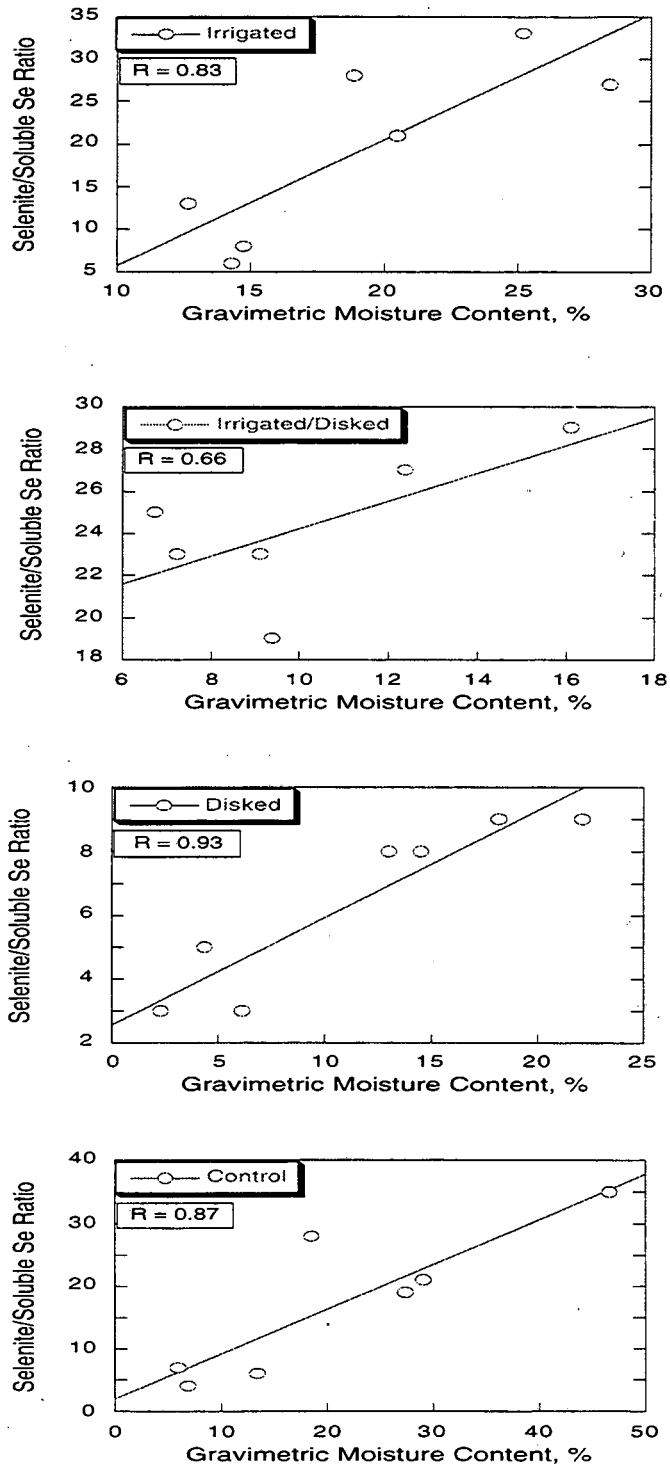

Figure 3.17 Linear fit - selenite to soluble Se ratio and soil moisture.

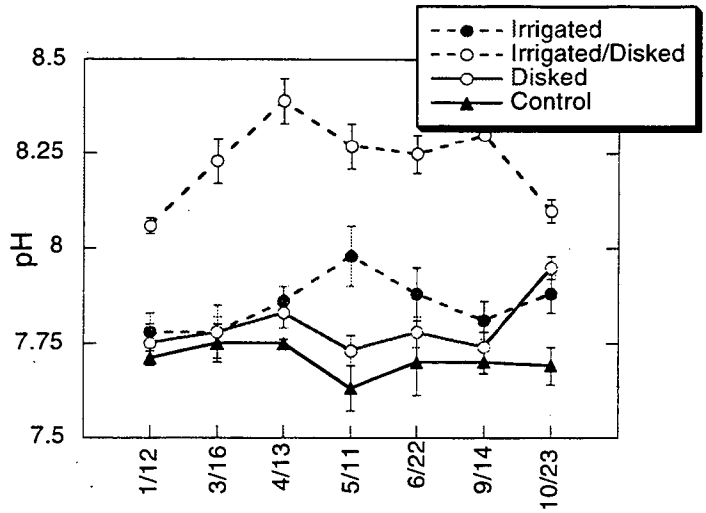

Figure 3.18 Temporal measurements of pH in 1994.

Temporal Measurements of EC

Both non-irrigated treatments (disked and control) seems to have high EC values (Fig. 3.19), whereas both irrigated treatments (irrigated and irrigated/disked) have low values. In all four treatments, however, there is an increasing trend in EC during the latter part of the year, and the highest increase is shown by the control. This may be attributed to the high evapotranspiration in the control during summer months. Although the irrigated treatment was also vegetated, this effect may have not been as important because of irrigation.

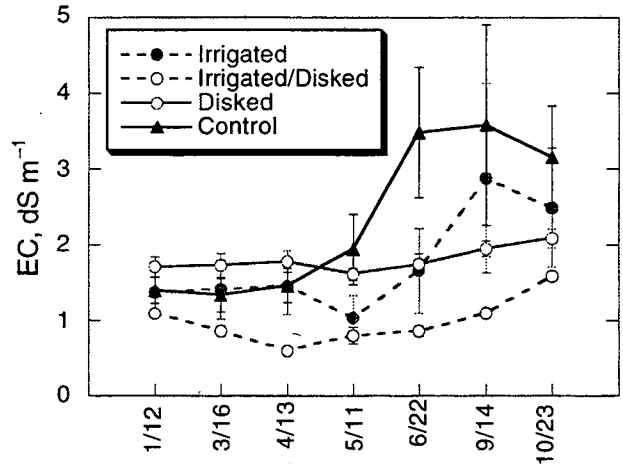

Figure 3.19 Temporal measurements of EC in 1994.

3.3 Selenium Dissipation in Contained Soils

3.3.1 Methodology

3.3.1.1 Field Conditions

As a supplement to the 2-acre field plot established in Pond 2, soil from this plot was collected in October 1990, homogenized and placed in three wooden boxes (5 x 10 feet) to monitor the loss of Se inventory in contained systems under field conditions. A plastic liner (0.4 mil) was placed on the bottom of the boxes and soil consisted of a 5-6 inch lift (depth). The soil contained some vegetative tissues (cattail roots) at the initiation of the project, but was not amended with any carbon source thereafter. The seleniferous soil from Pond 2 was mixed every other week and maintained under field-moist conditions throughout most of the year.

In most cases, soil samples were taken monthly during good weather conditions, beginning in October 1990, on a five-point pattern to study Se depletion. The five samples taken from each box were composited and Se concentrations were determined from this bulk sample.

3.3.1.2 Measurements of Volatile Selenium Emission

The apparatus used for in-field measurements of alkylselenide production consisted of an inverted galvanized steel box, 22"x22"x4" with a brass tube connector at the top center. The apparatus included a compressor vacuum pump, 250 ml gas washing bottles (40-60 μm porosity), 6-place manifold, 1/4" ID vinyl tubing and surgical tubing. The agents used for the scrubbing solution were hydrogen peroxide (30%) and 0.05 N sodium hydroxide. The purpose of the H_2O_2 was to oxidize the volatile Se into the Se(VI) species.

The flux chambers were pushed approximately 2" into the soil. The vacuum pump was connected to an electrical supply near Pond 2. The manifold was then connected to the pump with vinyl tubing. A trap was inserted between the manifold and pump to prevent the scrubbing solution from being drawn into the pump in case the gas washing bottle was tipped or blown over by the wind. From the manifold, 6-20 foot sections of vinyl tubing were connected to the sampling boxes. The scrubbing solution consisted of 80 mL of 0.05 N NaOH (pre-measured) plus 20 mL H_2O_2 (30%) (final = 6%) which was kept cold in an ice chest until used. After H_2O_2 was added and all the tubes were connected, the pump was started. The flow rate of the manifold was adjusted at the port of each chamber with a flow gauge to 2 L/min. The flow rate was monitored in the field throughout the day during

sampling. The duration of the measurements was one hour, with the starting and finishing times being recorded. In most cases, measurements were made at mid-day.

At the end of the sampling period, the pump was turned off. The washing bottle was opened and the alkali peroxide solution was poured off directly into a 125 mL polyethylene bottle and placed in an ice chest packed in blue ice. The washing bottled were then rinsed twice with deionized water and filled with 80 mL of 0.05 N NaOH to be used for the next sampling. The alkali peroxide sample was boiled to drive off the residual H_2O_2. Each sample was boiled for 15 minutes, allowed to cool and brought to volume (100 mL) and poured into 125 mL polyethylene bottles. All samples were refrigerated (4°C) overnight before shipping. Solutions were analyzed for total Se at the University of California, Riverside.

3.3.1.3 Chemical Analyses of Soil Se

Dried and ground soil samples were digested on a heating block with a sequential digestion procedure of nitric acid, hydrogen peroxide and hydrochloric acid, as described below. A soil sample of 0.25 g was treated with 2.5 mL deionized water and 2.5 mL concentrated HNO_3, and digested at 85°C for at least 12 h. Hydrogen peroxide (1.5 mL of 30% peroxide) was then added, and the sample was heated at 85°C for an additional 4-6 h. Concentrated HCl (18 mL) was added and the mixture heated for a minimum of 12 h at 80°C. The samples were allowed to cool, diluted to 50 mL with deionized water, and stored at 4°C for analysis. Selenium was analyzed using atomic absorption spectrometry with hydride generation. The instrument used was a Varian Spectra AA-10 Atomic Absorption Spectrometer (Mulgrade, Victoria, Australia) with a BGA-76 Vapor Generator Assembly. The operational conditions were the same as described by EPA test methods for evaluating solid waste, method 3050 (U.S. Environmental Protection Agency, 1994). Recovery of the procedure measured with spike samples ranged from 80-120%.

3.3.2 Results and Discussion

3.3.2.1 Volatile Emission Rates

It is evident that at the beginning of this project (9/91), high rates of volatile Se emission were detected within all three subplots (Figure 3.20) with an average of 60 $\mu g\ m^{-2}\ h^{-1}$ (1400 $\mu g\ m^{-2}\ d^{-1}$). A relatively high rate was also monitored in October 1991 (average = 25 $\mu g\ m^{-2}\ h^{-1}$, or 600 $\mu g\ m^{-2}\ d^{-1}$). During the winter season of 1991-92, emanation of volatile Se dropped considerably to within the 1-3 $\mu g\ m^{-2}\ h^{-1}$ range. In the spring of 1992,

the rates began to increase with an average reading of 13 μg m^{-2} h^{-1} in April, 23 in May, 29 in July, 18 in August, and 15 μg m^{-2} h^{-1} in September of 1992. Again, as the temperatures began to cool off in October 1992, the rates of volatile Se emission were also reduced, particularly during the winter season of 1992-93. It is evident that in the summer of 1993, emanation of volatile Se again increased up to 13 μg m^{-2} h^{-1} in August of 1993, with a proportional decrease with cooler temperatures in the fall and winter of 1993.

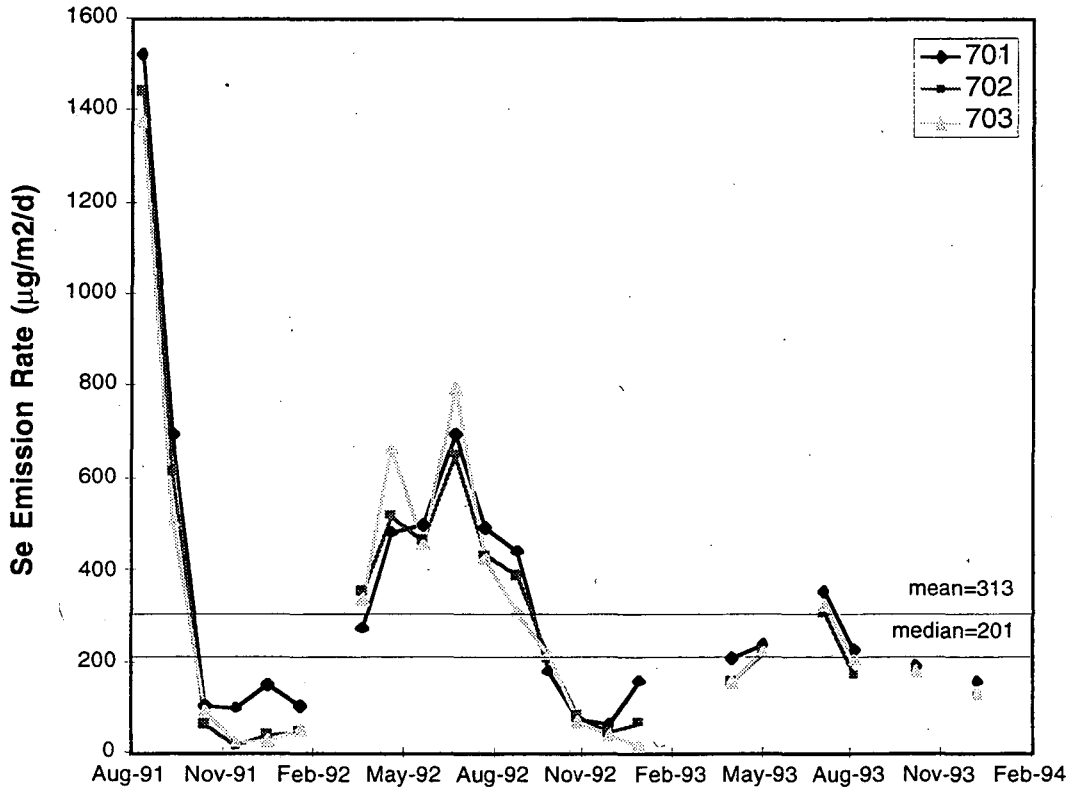

Figure 3.20 Volatile Se emissions as measured in boxes 701, 702, and 703 over the period of 9/91 through 12/93.

Overall, the greatest emission was recorded at the onset of this investigation. It is speculated that a substantial percentage of Se was in the water-soluble form at this time, readily available for microbial methylation and volatilization. It is evident that there is a seasonal variation in microbial Se volatilization with the greatest emission of gaseous Se released in the summer months during the year. Less volatile Se was produced in the fall and winter months. One must keep in mind that these subplots were non-amended with carbon sources and thus the availability of methyl donors is probably a limiting factor to promote volatilization of Se. There is no vegetation grown in these subplots and because

of a lack of carbon as a source of building blocks and energy, C is most likely limiting microbial methylation of Se. Further studies would be worthwhile to add a carbon source to stimulate the mineralization of unavailable Se into a microbially-available form for enhanced uptake and subsequent volatilization. Carbon sources known to promote volatilization of Se include protein sources as well as complex carbohydrates such as pectin. These specific carbon sources are known to stimulate methylating microorganisms in soil capable of transforming inorganic as well as organic Se into volatile methylated species.

3.3.2.2 Losses of Se in Soil

Fig. 3.21 shows the Se concentration of the soil in the contained boxes from October 1990 to November 1994. It is evident by examining this data that the variance of Se concentrations decreased with time. After approximately 10 months of mixing and aeration, the variance was reduced roughly by 50%. The temporal data shows a decrease in Se concentration with two phases of depletion. Phase 2 resulted from changing the plastic liner at the interface between the soil and the wooden box, thus resulting in more complete soil turnover. During phase 1 (October 1990 to December 1993), approximately 30% of the Se inventory was lost over 38 months of study. In phase 2 (January 1994 to November 1994), approximately 20% of the Se inventory was lost after 10 months.

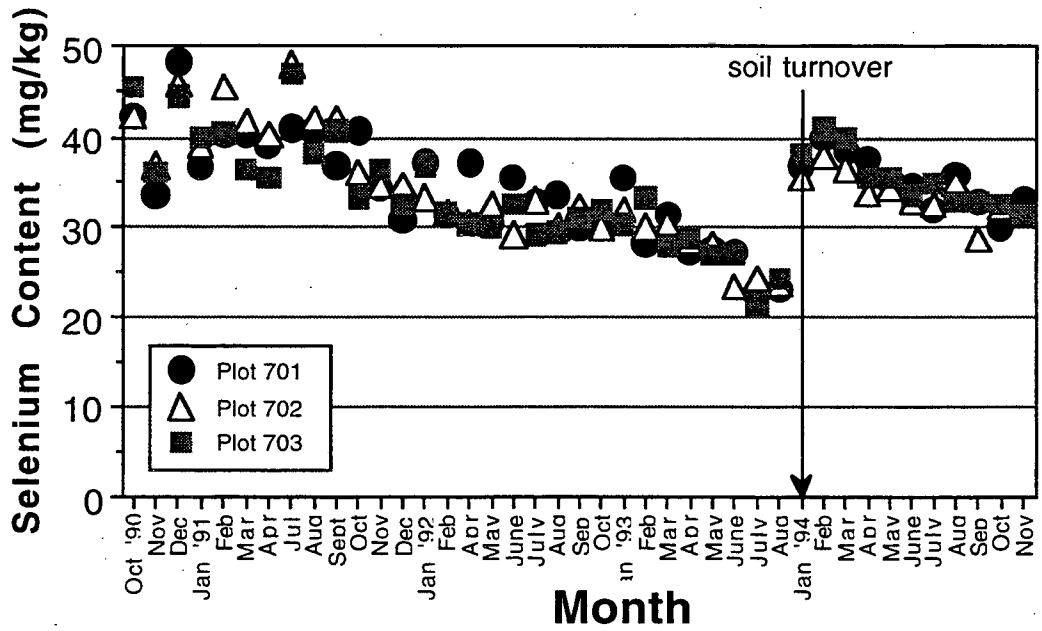

Figure 3.21 Changes in selenium concentration in contained Pond 2 soils.

In previous experiments in determining *in situ* Se volatilization at Kesterson Reservoir (Pond 4), it was evident that Se depletion from the soil was dependent upon a first-order reaction (Flury et al, 1995). However, it has also been suggested that depletion of Se in these experiments may partially be due to deeper cuts with tillage of the dewatered sediments providing a dilution effect in the Se inventory and possibly due to leaching the soluble Se fraction deep into the subsurface. Experiments with Pond 2 dewatered sediments show that high rates of depletion can occur in contained systems. While the mixing effect influenced the soil Se values to converge to their sample mean, reduction in the mean can be attributed to the loss of Se due to microbially mediated volatilization.

3.3.3 Discussion

Volatilization of Se may contribute to a considerable loss of the Se inventory in seleniferous soils. This field experiment was carried out to assess microbial volatilization of Se as a bioremediation approach to dissipate Se. By working with contained systems, we have eliminated the contribution of dilution as a result of deeper tillage with each pass. Also, we have eliminated the leaching component in removing the soluble Se from the bioactive zone in which microorganisms methylate and subsequently volatilize Se. This study has unequivocally demonstrated that Se depletion in the contained boxes is a result of volatilization. This study demonstrates a range of Se depletion from 20 to 30% over 10-38 months. However, it is not known whether depletion rates would appear to be the same if the soil were perfectly mixed, i.e. turned over on a regular basis. There appears to be a relationship between soil temperature and the rate of depletion with a rapid decrease in the Se inventory in each of the plots during the late spring and summer months.

Selenium volatilization is temperature dependent. A temperature study revealed that Se leached and Se volatilized both increased in response to increasing temperatures, possibly by promoting Se mineralization and increasing the soluble Se fraction available for methylation (Calderone et al., 1990). In field measurements, volatilization of Se fluctuates seasonally with rates being greater in the spring and summer, when compared to fall and winter months. There is also a diurnal peak of volatile Se emission from mid-day to mid-afternoon that correlates with soil and atmospheric temperature. During the winter season, both the cold temperature and high moisture content reduced the rate of Se volatilization. Previous studies have shown that maximum Se volatilization from seleniferous dewatered sediments occurs at 70% of the water holding capacity (field-moist soil); whereas, in a heavy clay soil, between 18% and 25% moisture is optimal (Abu-Eirreish et al., 1968). In a loam soil, Zieve and Peterson (1981) found that 28% was optimal for volatilization while

16% and 40% moisture regimes gave rise to considerably less volatile Se. There are some indications that fluctuations in the soil water content can stimulate the Se volatilization because sequential drying and re-wetting cycles promote microbial activity. Irrigation with wetting and drying cycles release organic-bound Se to the methylating organisms.

4.0 SOIL SELENIUM DYNAMICS

Direct observation of total and soluble selenium in soils gives spatial and temporal distribution within the test plot. Changes in Se concentrations in soil are the ultimate measure of the success of methylation at reducing the Se inventory. Although microbial volatilization effectively occurs only near the soil surface, monitoring of deeper soils accounts for Se leaching due to water infiltration.

4.1 Sampling Methodology

Two types of soil samples are taken. An annual north-south transect is taken through the middle of each treatment in July (see Fig. 1.2). Soil samples are collected using a tractor-mounted Giddings rig, except the 1990 transect, which was collected using a hand-auger. Samples are taken every 3 m along these lines and down to the depth of 0.60 m, in 0.15 m increments. Soil from the transects is extracted using a 1:5 soil:water extract and extracts are analyzed for total soluble selenium via HGAAS. Also, in September/October 1990, 1991, and 1992 and April 1991, 10 subplots within each treatment were sampled. Soil was cored to 0.60 m in 0.15 m increments, except for 30% of the subplots in which an additional two increments, 0.60-0.90 m and 0.90-1.20 m, are taken. Five such cores are taken in each subplot and composited by depth. All soil samples are extracted for total Se using an acid digest and analyzed via HGAAS.

4.2. Plot-wide Soil-Se Distribution Based on Subplot Data

Data collected from subplots in September 1990 was compiled to generate spatial distribution maps of total Se which are shown in Figures 4.1 through 4.4. In the 0-15 cm interval there are four major "features" in the total Se distribution: three "highs," one in the middle of the irrigated treatment, one in the northeast corner of the disked treatment, and one on the northwest edge of treatment C and a "low ridge" which runs roughly SW-NE throughout the entire plot. These features correlate well with the topographic contours of the plot (Figure 2.4), that is, areas of higher Se usually correspond to lower elevation and vice versa. This can be explained by the fact that the lower areas would have been ponded over longer periods of time than the topographic highs. Another interesting feature is the very good correlation between high selenium in the 45-60 cm interval in the central portion of the C treatment and by far the lowest elevation in the entire plot. This suggests that past ponding in this region, whether due to flooding or rainfall, resulted in the flushing of high concentrations of Se deep in the profile.

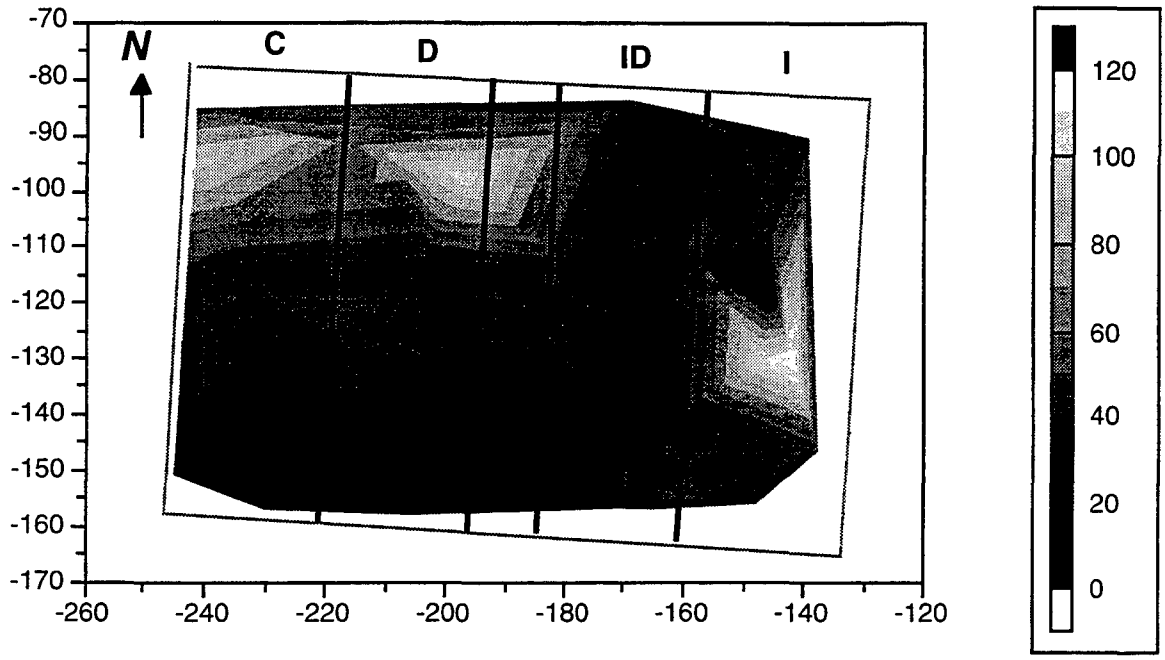

Figure 4.1 Total Se in top 15 cm of soil in plot P2VS, based on subplot data from 9/90. [Se] in ppm. Grid in meters.

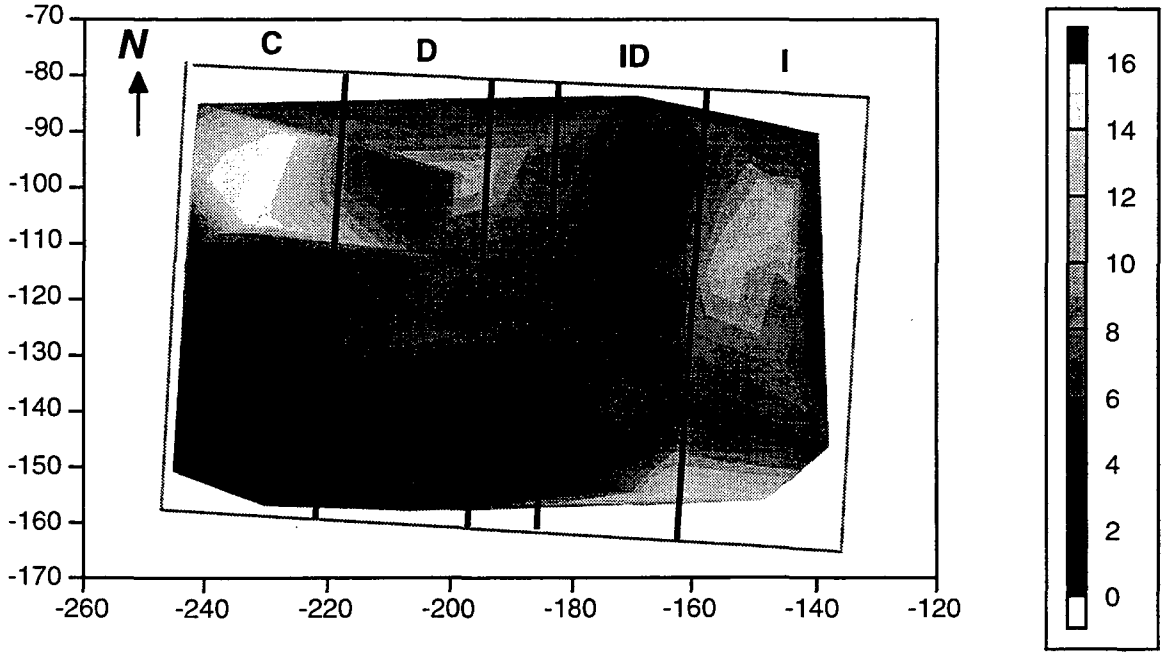

Figure 4.2 Total Se in the 15-30 cm interval of soil in plot P2VS, based on subplot data from 9/90. [Se] in ppm. Grid in meters.

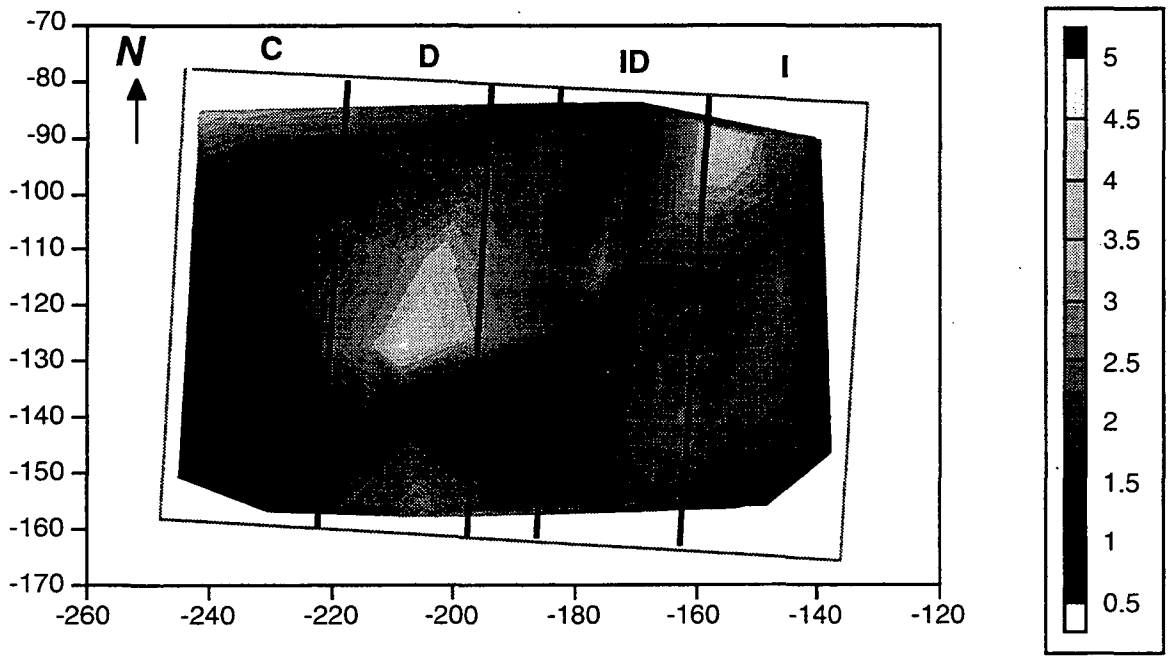

Figure 4.3 Total Se in the 30-45 cm interval of soil in plot P2VS, based on subplot data from 9/90. [Se] in ppm. Grid in meters.

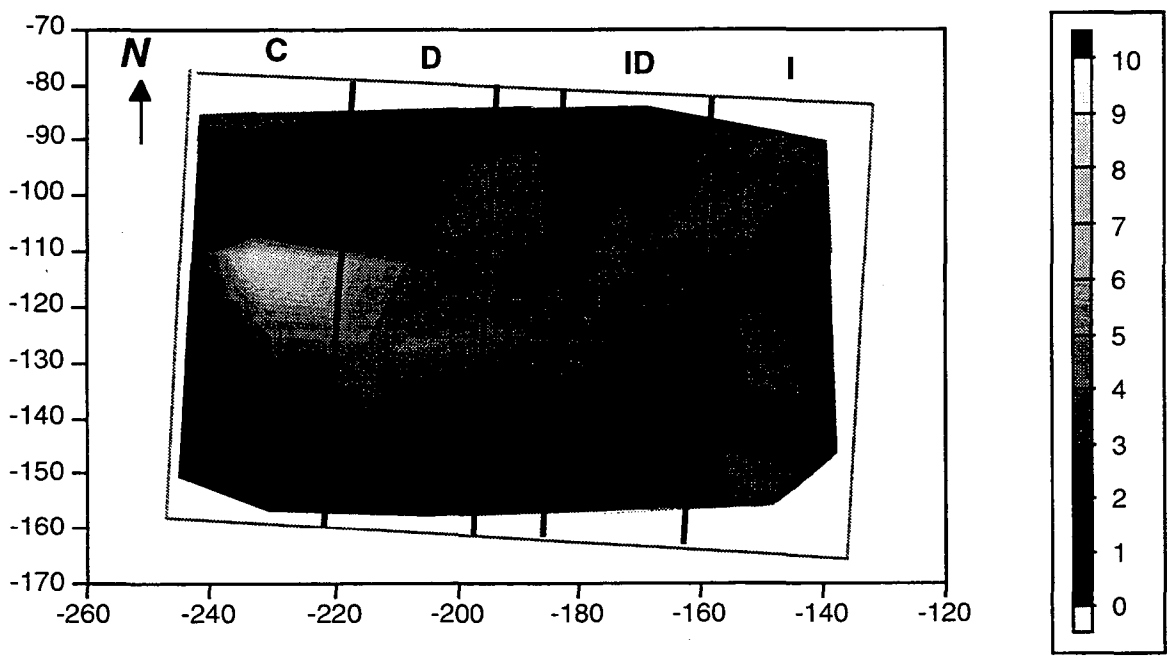

Figure 4.4 Total Se in the 45-60 cm interval of soil in plot P2VS, based on subplot data from 9/90. [Se] in ppm. Grid in meters.

4.2 Soil-Se and Salinity Along N-S Transects

Data from the 1990, 1991, 1992, 1993, and 1994 transects are presented herein. Samples were also collected in 1995, but as of yet have not been analyzed. Total Se distributions along each transect in the 0-0.15 m interval are shown in Fig. 4.5-4.8. This is the depth interval of nominally the greatest interest because of the highest Se concentrations and the favorable conditions for fungal growth. Within this interval, the average plot-wide total Se concentration was 50 ppm, with transect soils from the I treatment being high above that average at 97.8 ppm in July 1990.

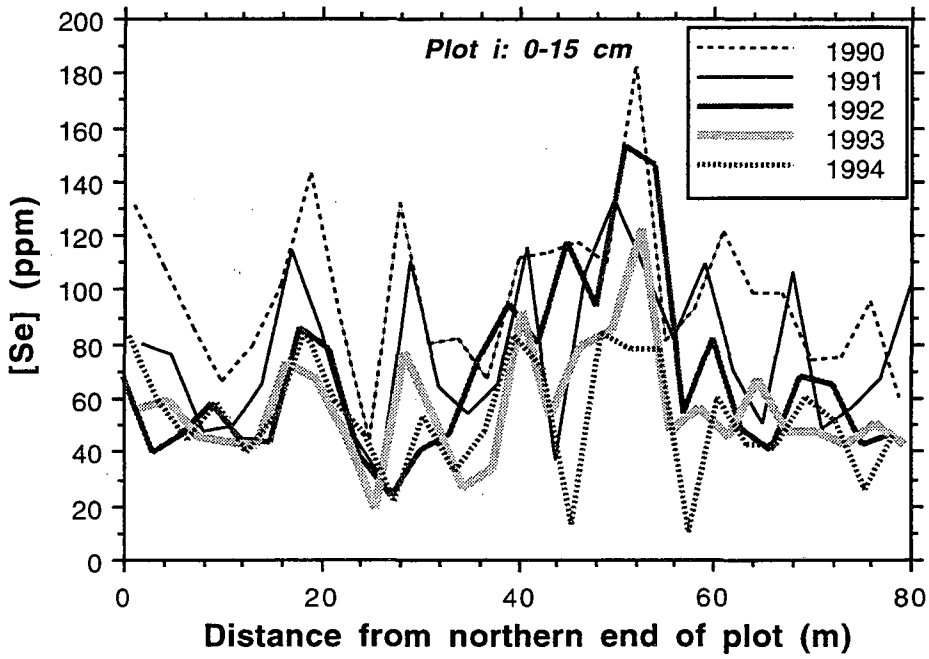

Figure 4.5 Total Se in the top 15 cm of the soil profile along the N-S transect of plot I.

The variability of near-surface Se concentrations is evident from these figures. For example, total Se in the ID treatment declines by a factor of 5 between the northern end and the southern end of the plot. Such differences can be explained to a large degree by comparing Se spatial distribution with site topography (Fig. 2.4). Although it is clear that declines in total Se were observed in treatments I and ID and to a lesser extent D and C, they are difficult to quantify from these figures due to the large spatial variability. Mean transect Se concentrations, expressed as mass per area, are shown in Fig. 4.9-4.12. Here the year-to-year changes in Se concentrations are more readily discerned. The largest and most consistent declines in total Se were observed in the irrigated treatment (Fig. 4.9). An

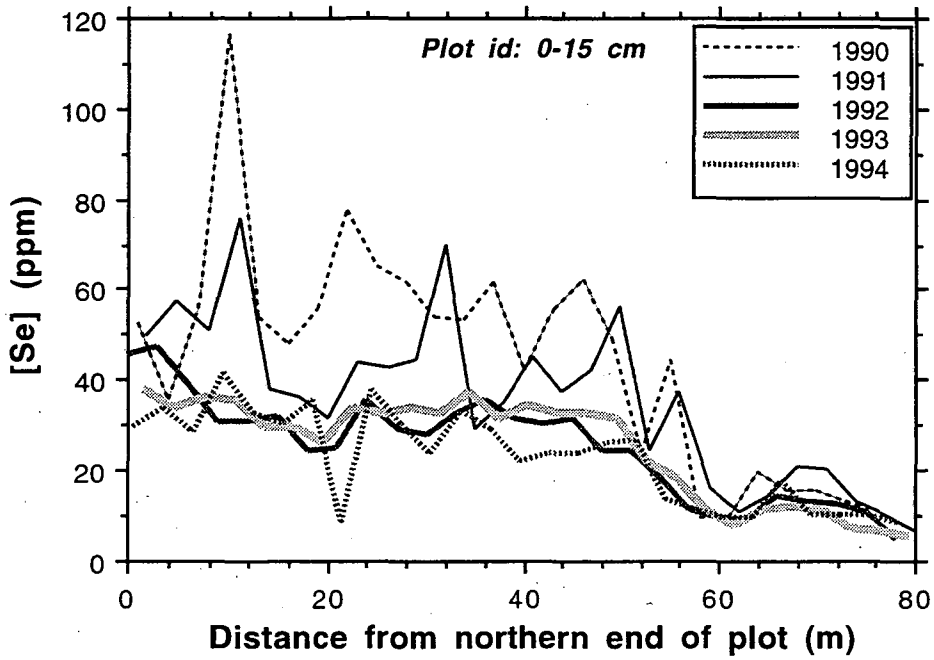

Figure 4.6 Total Se in the top 15 cm of the soil profile along the N-S transect of plot ID.

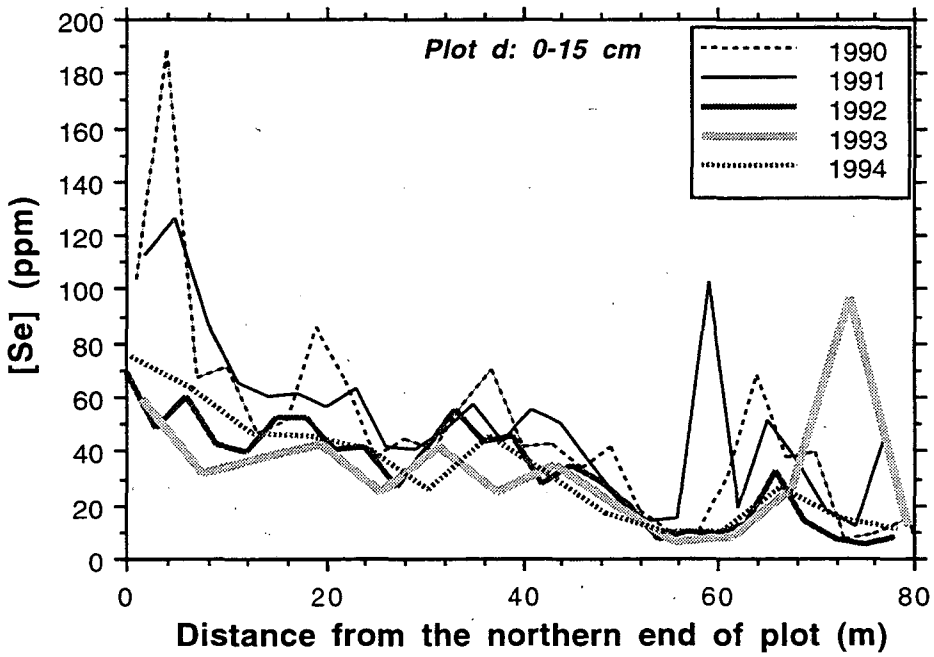

Figure 4.7 Total Se in the top 15 cm of the soil profile along the N-S transect of plot D.

average of roughly 2 g m^{-2} of Se was lost from the top interval per year, except between 1993 and 1994, when little change was observed. However, as mentioned above, Se

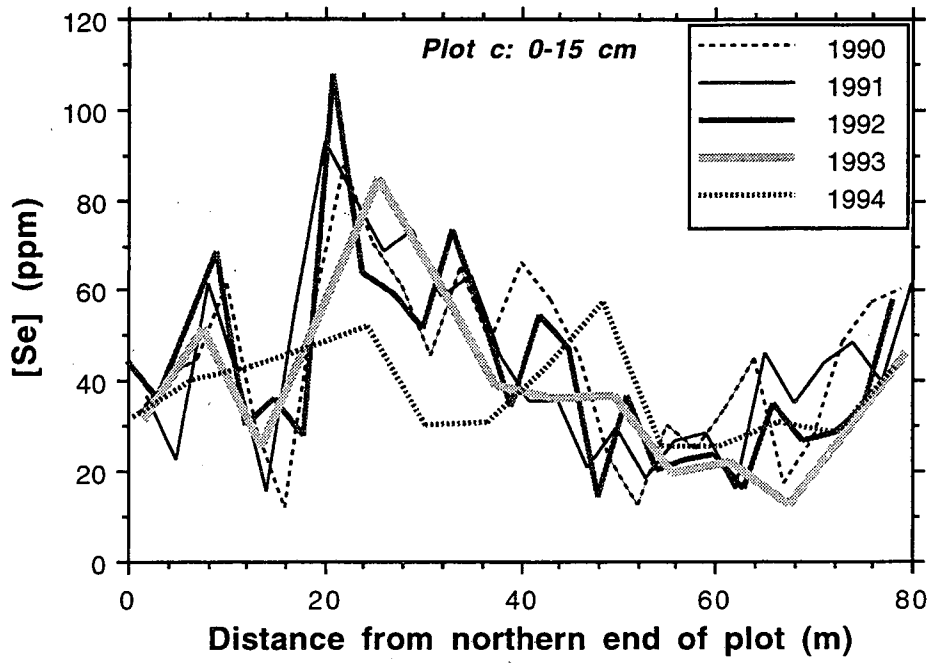

Figure 4.8 Total Se in the top 15 cm of the soil profile along the N-S transect of plot C.

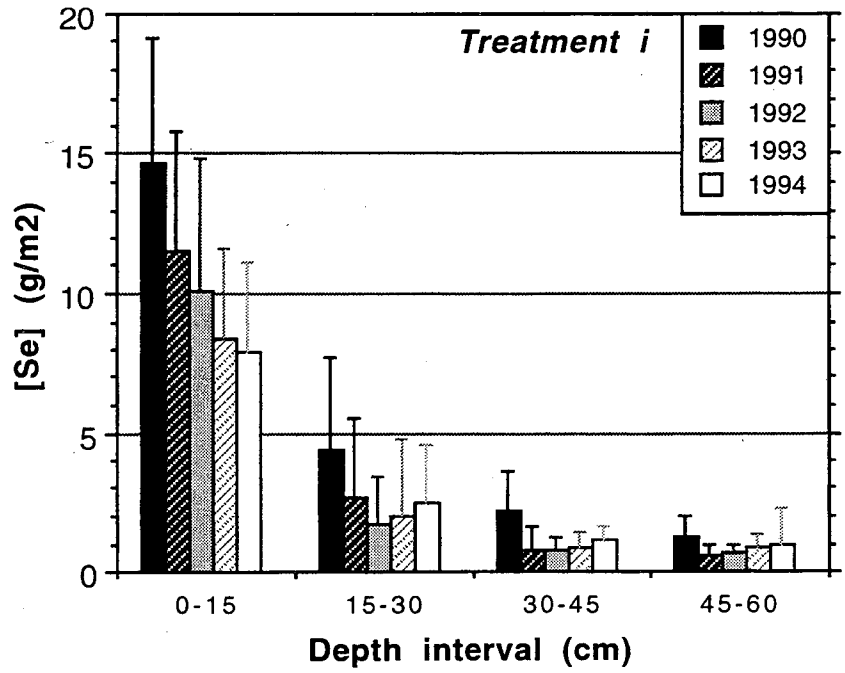

Figure 4.9 Total Se mass, normalized to area, in the soil profile along the N-S transect of treatment I.

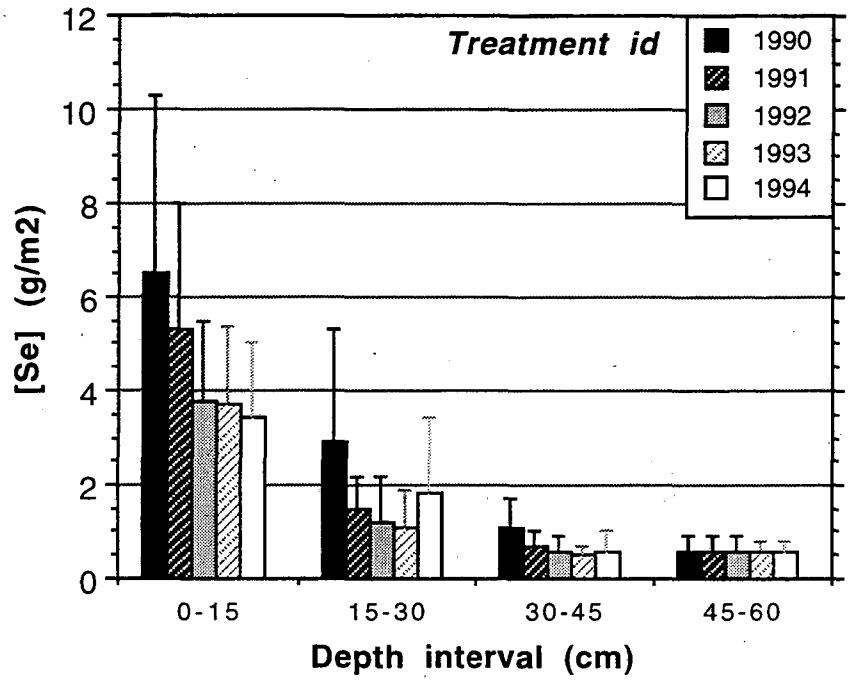

Figure 4.10 Total Se mass, normalized to area, in the soil profile along the N-S transect of treatment ID.

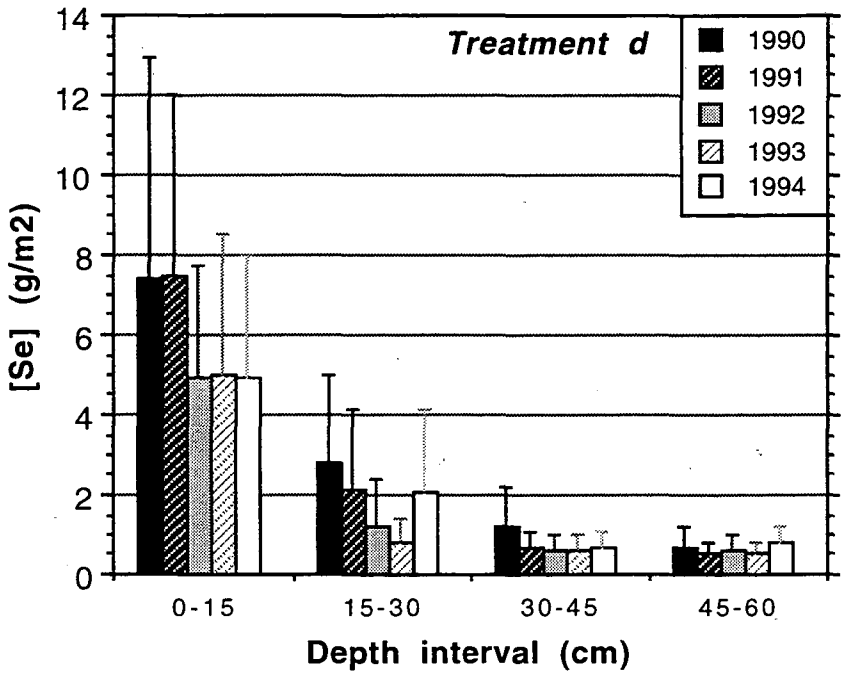

Figure 4.11 Total Se mass, normalized to area, in the soil profile along the N-S transect of treatment D.

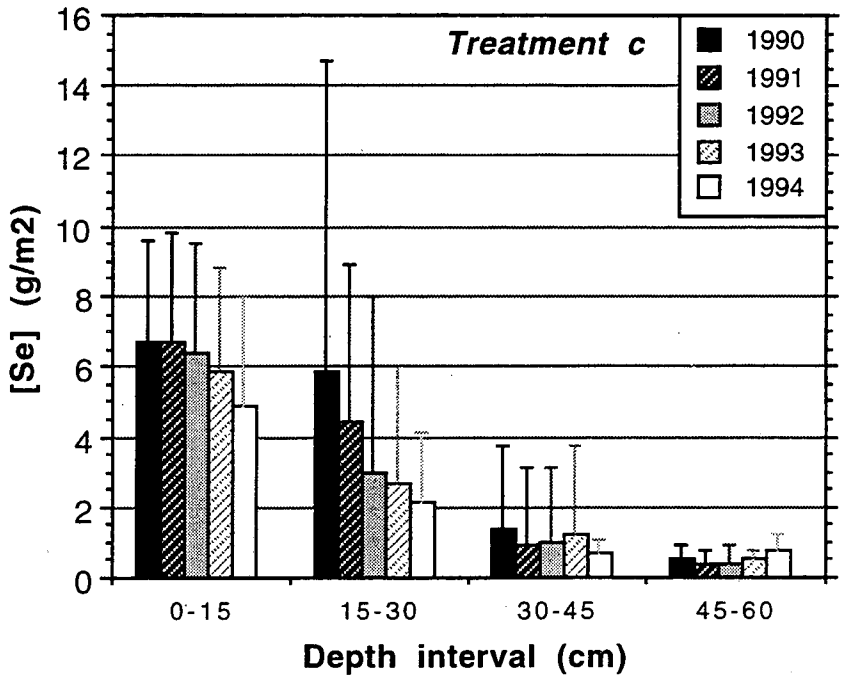

Figure 4.12 Total Se mass, normalized to area, in the soil profile along the N-S transect of treatment C.

concentrations in this treatment were anomalously high in 1990. In fact, 1990 Se concentrations were distinctly higher in all intervals, whereas there were no significant changes subsequent to 1991 below 0.15 m. It is possible that this is a result of the different sampling technique used in 1990. By using a hand auger, which can only sample 10 to 15 cm of soil at a time, it is possible that the top portion of each interval was preferentially sampled, because of incomplete recovery. Since Se concentrations decrease with depth, this would result in apparently higher concentrations in each of the intervals sampled. There were declines in Se in the top 0.15 m of treatments ID and D from 1990 to 1991 and from 1991 to 1992, but no changes were observed between 1992 and 1993, or between 1993 and 1994. The observed declines are on the order of 1 g m^{-2} per year. In treatment D, only between 1991 and 1992 was there a significant decline observed in the top 0.15 m interval, a decrease on the order of 2 g m^{-2}. However, year to year decreases were observed in the 0.15 to 0.30 m interval, except for 1993 to 1994, when an increase was observed. No significant changes in total Se concentrations in the top interval of treatment C were observed, but much like in treatment D, declines in the 0.15 to 0.30 m interval were observed, primarily between 1990 and 1991, and 1991 and 1992.

There are two mechanisms which can be invoked to explain the observed patterns: microbial volatilization and physical redistribution of Se with moisture fluxes. Generally, the first mechanism applies to the 0 to 0.15 m interval only, whereas transport of Se by infiltrating rainwater can affect the entire soil profile. As noted in a previous section, vertical displacement of Se on the order of 1 to 2 g m^{-2} has been commonly observed following rainstorms. Since these changes are on the order of the net changes observed in total Se decrease, potential losses of Se via volatilization are difficult to quantify, but appear to be on the order of 0.5 g m^{-2} yr^{-1} or less. This rate by far exceeds Se methylation rates commonly measured at Kesterson Reservoir (Frankenberger and Karlson, 1988).

The amount of Se which can be vertically displaced may be estimated from the water-extractable Se in the top 0.15 m of soil. This data for treatment I is shown in Fig. 4.13 and represents the results of analysis of 1:5 soil:water extracts, normalized to soil mass.

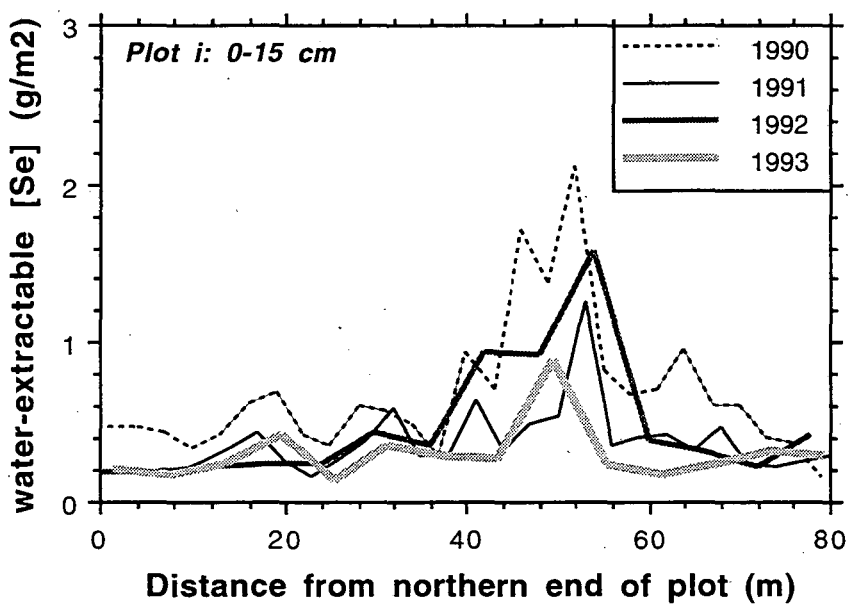

Figure 4.13 Water-extractable Se in the top 0.15 m of the soil profile along the N-S transect of treatment I (1994 data currently unavailable).

Once again, 0.5 to 2 g m^{-2} of Se is in a water-soluble form and could potentially be leached. Furthermore, soluble Se concentrations do not vary significantly from year to year, suggesting a re-oxidation of selenite, elemental Se, or organic Se over the summer period. Rates required to replenish such quantities of soluble Se are within the ranges observed in laboratory and other field experiments (Tokunaga et. al., 1991; Zawislanski

and Zavarin, in press). Electrical conductivity (EC) measured in the same extracts is also an indicator of downward displacement of solutes. This data for treatment I is shown in Fig.4.14 and is indicative of very significant net downward movement of solutes as salinity in this interval was at times reduced by as much as 75%. Unlike Se, salts are not subject to immobilization due to chemical reduction. Therefore, EC increases at times due to evapotranspirative-induced flow.

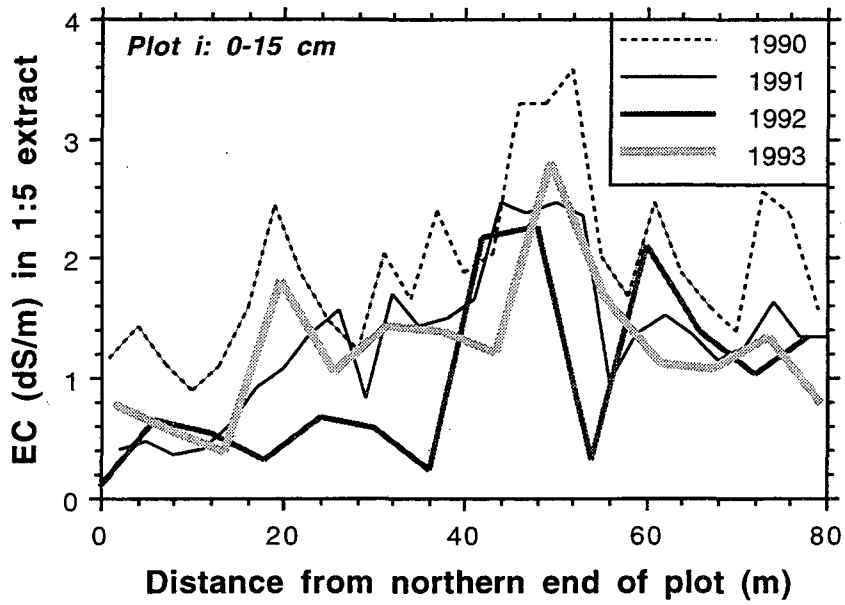

Figure 4.14 Electrical conductivity in a 1:5 water extract in the top 0.15 m of the soil profile along the N-S transect of treatment I.

It is worth noting that the largest decrease in total Se in treatment I was observed between 45 and 60 m along the transect (Fig. 4.5). This corresponds perfectly with the region of highest soluble Se (Fig. 4.13).

4.3 Soil-Se in 5 by 5 m Subplots

Soil samples were collected from 5 by 5 m subplots (see Fig. 1.2 for locations) in September of 1990, October of 1991 and 1992, and April 1991. Total Se concentrations, expressed in terms of mass per m^2 are shown in Fig. 4.15 through 4.18. These data do not show the same trends as N-S transect data. Specifically, there appear to be no consistent declines in total Se concentrations, except in the 0-0.15 m interval of treatment D. There are no easy explanations for this disparity. One possibility is Se re-distribution

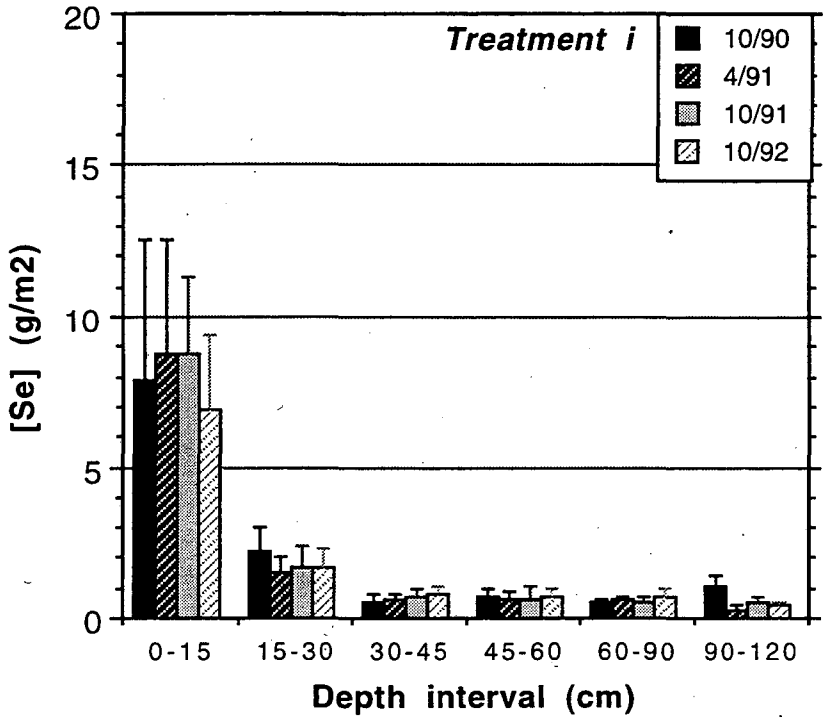

Figure 4.15 Total Se in soil from subplots from treatment I.

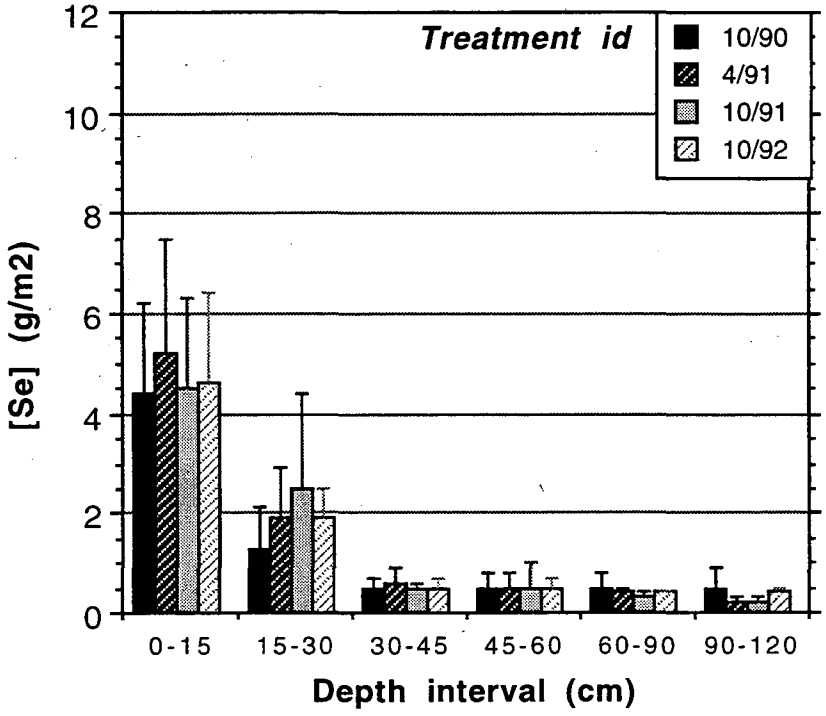

Figure 4.16 Total Se in soil from subplots from treatment ID.

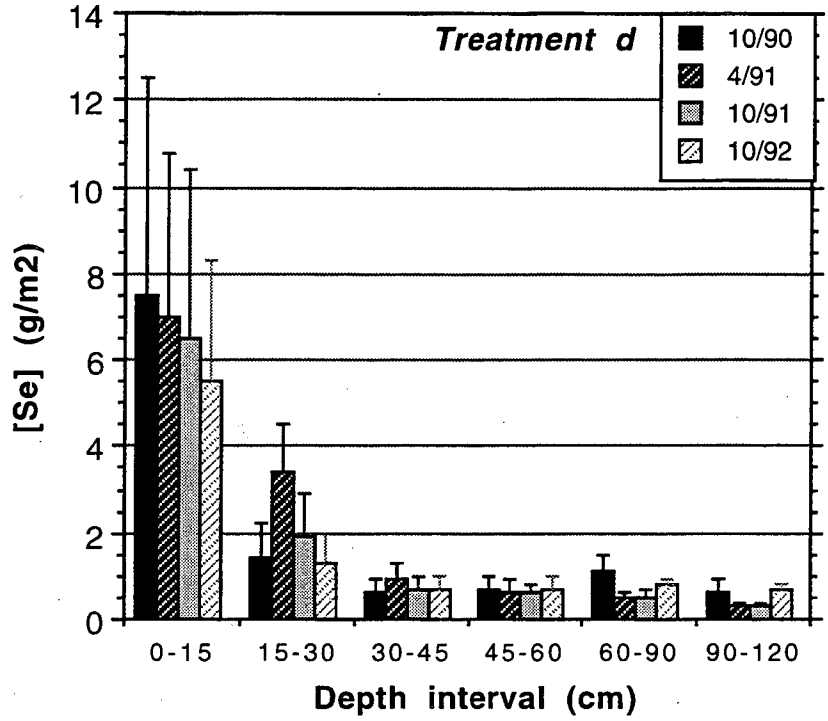

Figure 4.17 Total Se in soil from subplots from treatment D.

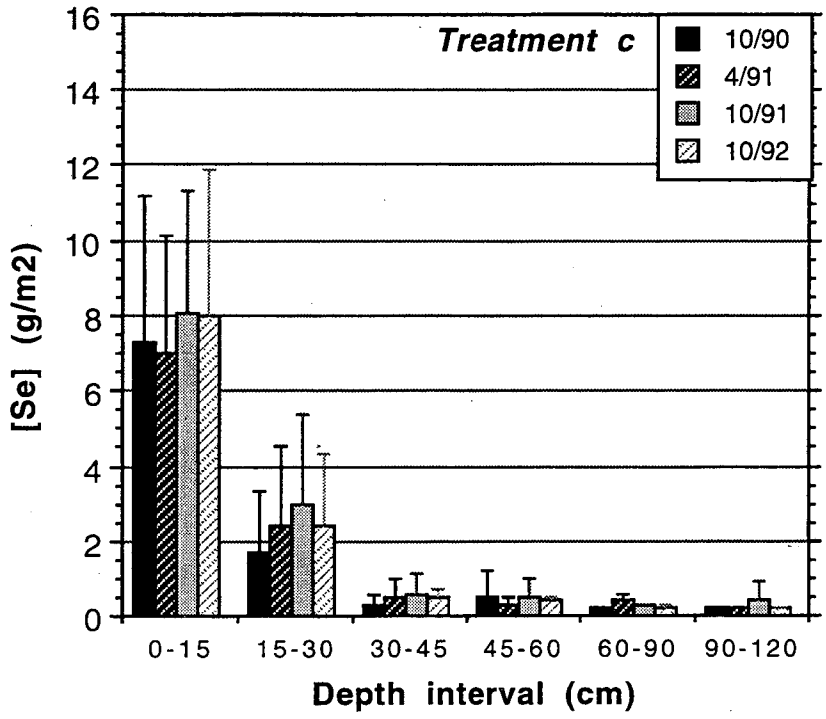

Figure 4.18 Total Se in soil from subplots from treatment C.

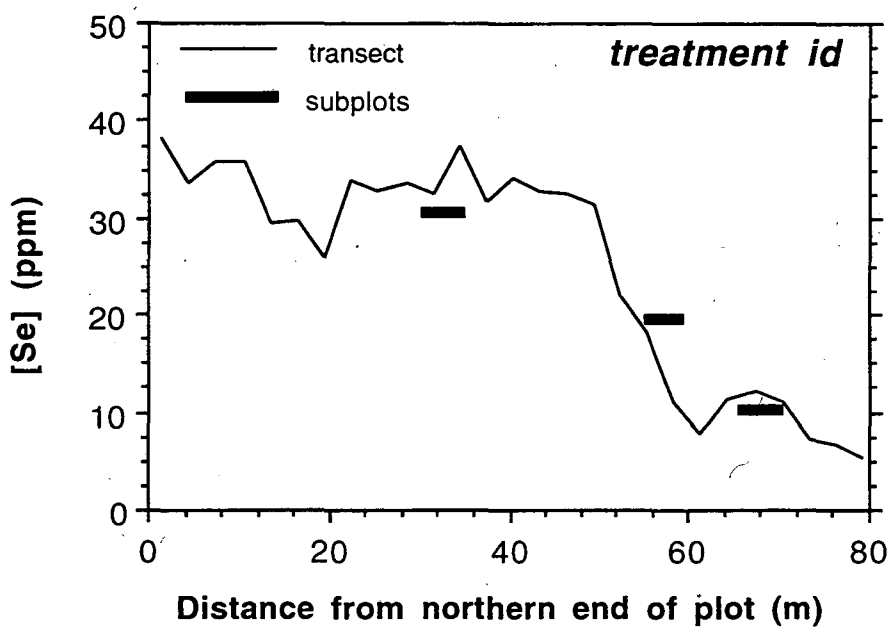

Figure 4.19 Total Se in the top 0.15 m of soil from the 1993 transect subplots from treatment ID as compared with data from concurrently sampled subplots.

over the period of July to October. Also, subplot data are derived from samples composited from five cores and therefore may better represent the sampled area. During the July 1993 collection of transect soils, selected subplots (I4, 6; ID6, 7, 8; D4; and C6) were sampled for the purpose of comparison. As seen in Fig. 4.19, these results were fairly close to data from nearby transect samples, suggesting that the two sampling approaches are consistent with each other and that changes observed between transect data collected in July and subplots in October are not a function of sampling approach, but rather actual temporal changes and differences in spatial distribution of Se concentrations.

4.4 Synthesis of Soil-Se Data

All currently available soil Se data from transect and subplot soils was integrated over the sampled depth of 0.0 to 0.60 m (Fig. 4.20 through 4.23). This representation accounts for Se which may have been flushed out of the top 0.15 m but was not displaced below 0.60 m. With the exception of the July 1990 sample in treatments I, ID, and C, and declines from 1991 to 1993 in treatment D, there are no consistent trends in total Se concentrations. One needs to note that the spatial variability of the July 1990 sample in treatment ID is significantly greater than in subsequent data sets, likely a result of soil homogenization with bi-weekly rototilling. Also, spatial variability is generally smaller in

the subplot data sets than in transects, which is especially apparent in the I treatment. This is a function of the composite nature of the subplot samples.

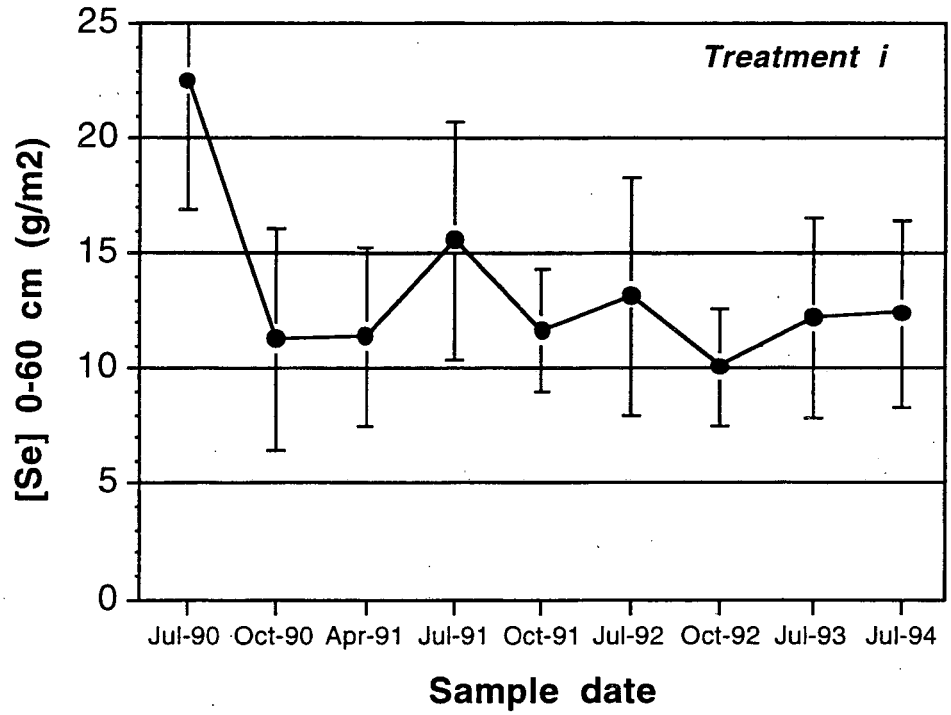

Figure 4.20 Cumulative total Se in soil from transects and subplots from treatment I.

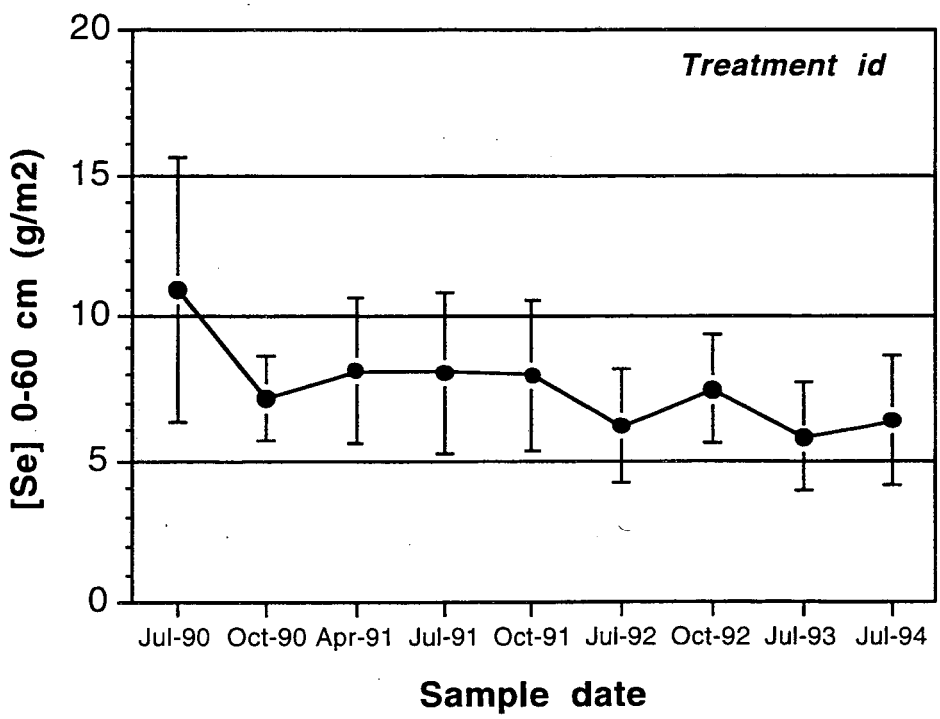

Figure 4.21 Cumulative total Se in soil from transects and subplots from treatment ID.

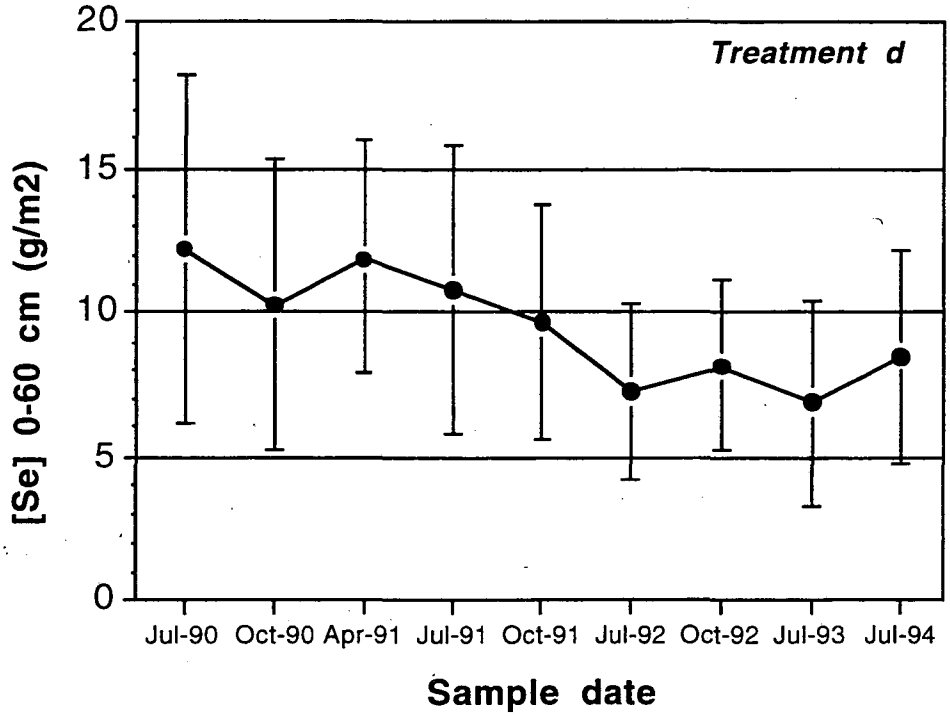

Figure 4.22 Cumulative total Se in soil from transects and subplots from treatment D.

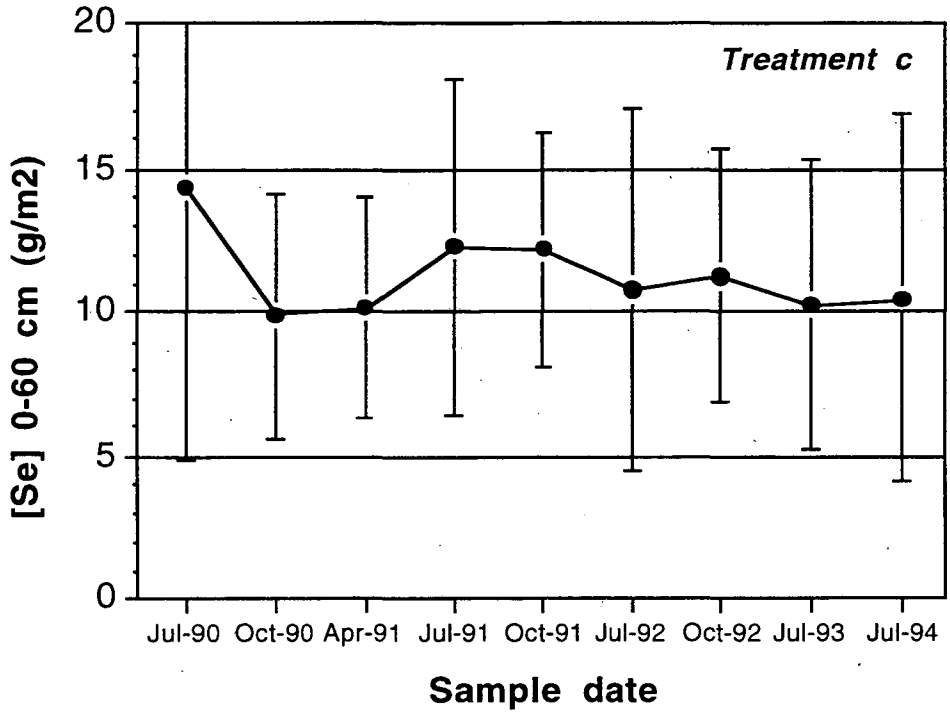

Figure 4.23 Cumulative total Se in soil from transects and subplots from treatment C.

5.0 PLANT-SE: UPTAKE BY NATURALLY ESTABLISHED SPECIES

Uptake of soluble Se by plants affects both the distribution and concentration of Se in soil. By removing soluble Se from the root zone and distributing it to above-ground parts, plants bring Se to the soil surface and make it more available to methylation. Subsequently, dead plant tissue contributes to the litter layer which, when incorporated into the soil, serves as a source of organic carbon. Se bound in plants in the experimental plot needs to be accounted for in order to complete the Se mass balance and estimate the potential for removing Se from the soil via plant management.

5.1 Previous Work

Previous investigations by Wu et al. (1993; 1994) into the effects of irrigation and tillage on the soil-plant relationship and dissipation at Kesterson indicated that species richness, biomass and Se accumulation on naturally established annual herbaceous species were positively affected by irrigation. Average Se accumulation by the plants of the nonirrigated field plots ranged from 13 to 15 mg Se m^{-2} while the irrigated plots ranged from 45 to 60 mg Se m^{-2}. The degree and direction of the irrigation effects were found to be species dependent (Wu et al., 1993, 1994). The greatest response to irrigation both in terms of biomass production and tissue Se accumulation was shown by the annual legume species *Melilotus indica* (Melilotus or sour clover). This species appears to have the ability to accumulate selenium even when grown in soils containing high levels of organic matter and soil sulfate. Tillage had the opposite effect on vegetative biomass, in that it prevented the establishment of vegetation on the two-acre field plot.

Monitoring of soil Se conditions showed that the total soil Se concentrations in the top 15 cm of soil were found to be in the range of 40 to 70 mg Kg^{-1} dry weight. Soil Se concentrations below 25 cm soil depth were much lower and were within a range of only 2 to 4 mg Kg^{-1}. The distribution of the total soil Se concentration in the top soil horizon did not change significantly over the period from 1991 to 1993 despite the irrigation and tillage treatments and heavy winter rains. Only 5 to 10% of the total soil Se inventory in the top 15 cm soil was water extractable. The concentration of water extractable Se in the soil was significantly reduced in the 1993 soil survey (Wu et al., 1993, 1994). A possible explanation for this finding was that the water soluble portion of the selenium inventory was leached down by winter rains (see Chapter 4).

5.2 Methods

Oven dried leaves from several individuals composed each plant sample, which were ground into a powder to insure sample homogenization. A total of 7 ml concentrated HNO_3 and 2 ml $HClO_4$ were added to 50 mg of dry plant material in a 75 ml volumetric digestion tube and allowed to digest for at least 12 hours at room temperature. Further digestion was performed from between 100 to 210° C using a heating block (scientific AD-40 block digester). After cooling of the sample, reduction of the plant digestion extract was made by adding 3 ml of 6 N HCl and heating for 10 minutes at 150° C. Samples were brought to a final volume of 75 ml using 4 N HCl. Selenium and arsenic concentrations were determined by hydride generation flame atomic absorption spectrophotometry with a heated quartz cell, using argon as the carrier gas.

Soils were air dried for a minimum of three weeks at room temperature and screened through a 1 mm sieve and thoroughly mixed. Soil-water mixtures (1:2 w/v) were shaken slowly for 12 hours in 500 ml acid washed polyethylene flasks. Clear soil extracts were collected by centrifugation and filtration through #1 Whatman filter paper. Water extracts were stored at 10 °C in acid washed polyethylene flasks. Water extracts and leachate were measured for pH, electrical conductivity (EC). The barium sulfate turbidimetric method (Chesnin and Yien, 1950) was used for determining soil sulfate concentrations.

Selenite concentrations of soil water extracts or leachates were determined by hydride generation flame atomic absorption of undigested samples without reduction. Selenate concentrations were determined using hydride generation flame atomic absorption on samples reduced by adding 3 ml of 6 N HCl to 5 ml of soil extract and heating for 10 minutes at 150 °C, and brought to a final volume of 10 ml using 4 N HCl. For total soil extract or leachate selenium and arsenic levels, 5 ml of sample was digested with 5 ml concentrated HNO_3 and 2 ml $HClO_4$ in a 75 ml volumetric digestion tube and allowed to digest for at least 12 hours at room temperature. Further digestion was performed from between 100 to 210° C using a heating block (scientific AD-40 block digester). After cooling of the sample, reduction of the digestion extract was made by adding 3 ml of 6 N HCl and heating for 10 minutes at 150 °C. Soil extract samples were brought to a final volume of 75 ml using 4 N HCl. For total soil selenium and arsenic analysis 1 g of soil was digested with 7 ml concentrated HNO_3 and 2 ml $HClO_4$. Samples were then analyzed

using hydride generation flame atomic absorption spectrophotometry with a heated quartz cell, using argon as the carrier gas. All samples were analyzed at the Department of Environmental Horticulture, University of California, Davis. Accuracy and precision of laboratory analysis was checked using blanks, and spikes made from Na_2SeO_3 (sodium selenite) or National Bureau of Standards' tomato leaf reference material for arsenic.

5.3 Results

5.3.1 Plant-Se

Table 5.1 shows the biomass, tissue Se concentration, and Se accumulation per square meter for the two-acre field plots including the tilled-irrigated (ID), tilled not-irrigated (D), not-tilled irrigated (I), and not-tilled not-irrigated (C) field plots. More than 10 different herbaceous plant species were found. *Polypogon monspeliensis* had the highest biomass in all the irrigation-tillage treatments. Its dry weight ranged from 551 g m^{-2} of the D plot to 184 g m^{-2} of the ID plot. *Bromus hordeaceus, Polypogon monspeliensis, and Melilotus indica* were the most widely spread species and were found in all the field plots. Eight species including *Conyza coulter, Cirsium vulgare, Epilobium ciliatum, Lactuca serriola, Melilotus indica, spergularia marina,* and *Sisymbrium irro* had tissue Se concentrations over 30 μg g^{-1} dry weight. *Melilotus indica* again had its highest tissue Se concentration over 77 μg g^{-1}, and *S. irro* had its tissue Se concentration over 127 μg g^{-1}. Biomass of a species attributed significantly to Se accumulation. In the I treatment, *A. patula* had a Se accumulation over 20 mg Se m^{-2}, and *P. monspeliensis* had more than 14 μg g^{-1} in the control plot. The nontilled plots had a higher average Se accumulation of 2.19 and 3.22 mg m^{-2} than the D plot which only had 0.86 and 1.21 mg m^{-2}.

5.3.2 Soil-Se

The soil chemical characters of the two-acre field plots are presented in Table 5.2. The soils were slightly basic, saline and contained high concentrations of sulfate. The water extractable Se detected in the top 15 cm soil ranging from 0.55 to 5.68 mg kg^{-1} represented approximately only one tenth of the total soil Se inventory of the top soil horizon ranging from 16 to 21 mg Kg^{-1}. The water extractable Se below 15 cm soil ranged from 0.9 to 2.8 mg kg^{-1} and the total soil Se ranged for 1.4 to 4.7 mg kg^{-1}. Tillage had no measurable

Table 5.1 Plant species, dry weight, tissue selenium concentration, and selenium accumulation measured for the two-acre field plots managed under four different tillage-irrigation combination treatments in 1994 and samples were taken in May 1995.

Treatment Species	Plant shoot dry weight (g)	Tissue Se concentration ($\mu g\ g^{-1}$)	Se accumulation mg Se m^{-2}	Average Se accumulation mg m^{-2}
Irrigated/Disked				
Atriplex patula	15.3 ± 15.6	24.19 ± 9.21	0.46 ± 0.54	
Bromus hordeaceus	14.6 ± 0.0	16.33 ± 0.00	0.24 ± 0.00	
Epilobium ciliatum	1.6 ± 0.9	23.85 ± 14.30	0.04 ± 0.02	1.21 ± 0.83
Frankenia salina	60.8 ± 76.2	13.91 ± 8.62	0.84 ± 0.91	
Lactuca serriola	13.5 ± 0.0	13.63 ± 0.00	0.18 ± 0.00	
Melilotus indica	27.8 ± 26.5	58.15 ± 43.60	1.11 ± 0.82	
Polypogon monspeliensis	184.7 ± 54.6	28.37 ± 17.93	5.32 ± 3.24	
Spergularia marina	41.3 ± 33.1	37.82 ± 3.51	1.51 ± 1.18	
Disked				
Bromus hordeaceus	24.3‡ ± 39.8	9.32 ± 2.46	0.23 ± 0.37	
Bromus diadrus	3.2 ± 0.00	4.18 ± 0.00	0.01 ± 0.00	
Bromus rubens	4.0 ± 0.6	7.09 ± 0.99	0.03 ± 0.00	
Cirsium vulgare	41.2 ± 38.4	8.37 ± 4.54	0.44 ± 0.58	
Epilobium ciliatum	2.1 ± 0.0	12.43 ± 0.00	0.03 ± 0.00	0.86 ± 1.08
Hordeum murinum	18.1 ± 0.0	6.76 ± 0.00	0.12 ± 0.00	
Lactuca serriola	19.7 ± 23.1	12.37 ± 3.53	0.27 ± 0.39	
Melilotus indica	8.4 ± 3.3	77.64 ± 94.00	0.50 ± 0.54	
Polypogon monspeliensis	551.6 ± 135.8	13.87 ± 17.34	7.76 ± 9.95	
Sonchus asper	4.0 ± 0.0	11.36 ± 0.00	0.04 ± 0.00	
Vulpia microstachys	12.0 ± 15.7	6.98 ± 1.83	0.07 ± 0.07	
Irrigated				
Atriplex patula	517.6 ± 0.0	39.48 ±0.00	20.44 ± 0.00	
Bromus hordeaceus	157.4 ± 194.8	11.04 ± 2.98	1.79 ± 2.57	
Bromus rubens	8.9 ± 13.1	8.60 ± 1.53	0.07 ± 0.09	
Cirsium vulgare	3.5 ± 0.0	32.62 ± 0.00	0.11 ± 0.00	3.22 ± 0.76
Conyza coulteri	8.4 ± 0.0	46.86 ± 0.00	0.39 ± 0.00	
Epilobium ciliatum	2.2 ± 0.0	5.50 ± 0.00	0.01 ± 0.00	
Melilotus indica	31.5 ± 20.3	25.01 ± 30.99	0.67 ± 0.70	
Polypogon monspeliensis	415.8 ± 274.7	14.78 ± 7.80	5.79 ± 4.25	
Sisymbrium irro	18.4 ± 0.0	127.02 ± 0.00	2.34 ± 0.00	
Vulpia microstachys	59.1 ± 0.0	10.66 ± 0.00	0.63 ± 0.00	
Control				
Atriplex patula	21.9 ± 0.0	17.81 ± 0.00	0.39 ± 0.00	
Bromus hordeaceus	9.1 ± 6.2	12.05 ± 0.00	0.11 ± 0.07	
Erodium moshatum	17.7 ± 0.0	16.62 ± 0.00	0.29 ± 0.00	2.19 ± 2.28
Lactuca serriola	12.1 ± 1.3	27.9 ± 12.18	0.11 ± 0.02	
Melilotus indica	33.2 ± 28.5	50.69 ± 27.42	1.76 ± 1.12	
Polypogon monspeliensis	275.4 ± 94.4	48.29 ± 25.97	14.45±11.66	
Spergularia marina	14.1 ± 4.9	31.29 ± 10.89	0.41 ± 0.00	

‡ mean ± one standard deviation.

effect on total soil Se distribution (Table 5.3). There was a significant interaction for the of water extractable Se affected by tillage and soil depth. In general disking and irrigation tended to reduce levels of water extractable Se in the top 15 cm of soil.

Table 5.2. Soil chemical characters of the two-acre field soil under different irrigation and tillage management conditions.

Treatment	Soil depth (cm)	pH	EC ($dS\ m^{-2}$)	Sulfate ($mg\ Kg^{-1}$)	Water extractable Se ($mg\ kg^{-1}$)	Total soil Se ($mg\ kg^{-1}$)
ID	0-15	7.44±0.18 †	2.51±1.46	865±409	1.32±0.74	15.90±6.50
	30-45	7.49±0.29	3.77±1.72	1330± 705	1.16±0.62	2.12±1.45
D	0-15	7.44±0.12	5.59±2.13	2235±574	5.68±3.33*	17.37±5.40
	30-45	7.39±0.30	3.68±0.65	1425±354	1.54±0.62	1.68±0.62
I	0-15	7.43±0.13	4.55±2.63	1820±764	0.96±0.84	21.51±17.88
	30-45	7.20±0.27	5.76±2.40	1925±758	0.90±0.62	1.47±0.75
C	0-15	7.46±0.19	6.62±1.55	2745±593	0.55±0.35	16.83±13.32
	30-45	7.46±0.30	10.24±5.34	2915±1065	2.84±3.12	4.73±4.35

† Mean ± one standard deviation, sample size = 10 .

Table 5.3 Analysis of variance performed on the water-extractable and total Se detected for soil samples collected at two depths from the 2-acre plot in May, 1995.

Source of variance	Water extractable soil-Se ($mg\ kg^{-1}$)	Total soil Se ($mg\ kg^{-1}$)
Tillage	NS	NS
Irrigation	***	NS
Soil depth	NS	***
Tillage*Irrigation	NS	NS
Tillage*Soil depth	***	NS
Irrigation*Soil depth	NS	NS

Note: All tests performed using Box-Cox transformed data
*** Significant at the 0.01 level. NS not significant.

There was essentially no difference in the vegetation in any of the treatment combinations of disking and irrigation in the two-acre plot. The rains in the spring of 1995 were heavy to prevent equipment going into the study area, so even the areas which were normally tilled contained dense vegetation. Again, the heavy rains canceled out any irrigation effects on the vegetation. Natural vegetation found in the two-acre treatment sub-plots consistently had higher total Se accumulation per square meter field than either the Tall fescue and Melilotus plots. Again, this is primarily due to a difference in biomass production, not selenium bioextractive abilities of the respective plant communities.

5.3.3 Conclusions

There are many possible explanations concerning the lack of detectable reduction of total soil Se concentrations. The presence of high soil sulfate has been cited as a significant problem in the removal of Se by plants. While soil sulfate levels are high, plants still accumulated significant amounts of selenium but with large variation in the amount of Se accumulation in the field obscured the effectiveness of Se dissipation by plants. Another explanation is that the poor establishment of the planted species reduced the efficiency of the Se bioextractive abilities of these plants. However, there were areas containing native vegetation which had species with both high tissue Se and biomass which still had no detectable effect on reduction of total soil Se. Finally, the amount of bioavailable Se (i.e. the water extractable fraction) was only a small fraction of the total soil Se. This low availability tends to obscure any detection of changes in the pool of total soil Se.

6.0 SUMMARY OF FINDINGS

The effects of microbial volatilization on soil-Se concentrations can only be evaluated by accounting for other Se losses in the system. Along with the loss of DMSE to the atmosphere, Se can be taken up by plants, as well as leached below the monitored interval. In the following sections, an attempt is made to reconcile results of direct emission measurements with soil, plant and soil water data.

6.1 Se Mass Balance

As described in Chapter 4, net annual losses of Se were observed from the 0-15 cm interval of each treatment. In most cases, these declines were small, well within a half a standard deviation from the mean value of the previous year. Nonetheless, the decreases were consistent and given the length of this field experiment, they reflect real physical processes and are not a result of sampling biases. An exception is the large difference observed between the 1990 and 1991 transect samples (e.g. Fig. 4.9), probably as a result of a change in sampling technique. The mean mass contributions of the processes involved are summarized in Tables 6.1 through 6.4. The goal of presenting data in this fashion is to elucidate whether or not the measured and estimated fluxes can account for the observed changes in total Se inventory in the 0-60 cm soil interval. Both low and high estimates of volatilization rate and plant uptake are presented, thereby allowing for a realistic range of rates. Se volatilization rates were not measured all year (cf. Fig. 3.2), so some extrapolation of the measured rates needed to be made. Plant uptake is rather variable depending on the environment, season, and moisture content of the soil (cf. Table 5.1).

Table 6.1 Year-to-year losses of Se fractions in the 0-60 cm interval of soil in treatment I and estimate of soluble Se available for leaching.

Period (July to July)	Change in total Se (g/m2)	Se volatilized low est. (g/m2)	Se volatilized high est. (g/m2)	Se accumulated in plants low est. (g/m2)	Se accumulated in plants high est. (g/m2)	Se required to be flushed low est. (g/m2)	Se required to be flushed high est. (g/m2)	Soluble Se (g/m2)
1990-1991	-6.9	0.09	0.27	0.005	0.05	*6.81*	*6.58*	***2.06***
1991-1992	-2.4	0.09	0.135	0.005	0.05	*2.31*	*2.22*	***1.56***
1992-1993	-1	0.034	0.051	0.005	0.05	*0.96*	*0.90*	***2.30***
1993-1994	0.2	0.03	0.03	0.005	0.05	*-0.24*	*-0.28*	***1.72***

Therefore, a wide range of values was assumed. The second to last column shows the amount of Se which is not accounted for after volatilization and plant accumulation are considered and which would need to be leached out of the 0-60 cm interval in order to reconcile the mass balance. The last column shows the amount of soluble Se potentially available for leaching by infiltrating rainwater.

Table 6.2 Year-to-year losses of Se fractions in the 0-60 cm interval of soil in treatment ID and estimate of soluble Se available for leaching.

Period (July to July)	Change in total Se (g/m2)	Se volatilized low est. (g/m2)	Se volatilized high est. (g/m2)	Se accumulated in plants low est. (g/m2)	Se accumulated in plants high est. (g/m2)	Se required to be flushed low est. (g/m2)	Se required to be flushed high est. (g/m2)	Soluble Se (g/m2)
1990-1991	-2.9	0.038	0.114	0.005	0.05	*2.86*	*2.74*	***1.45***
1991-1992	-1.9	0.038	0.057	0.005	0.05	*1.86*	*1.79*	***1.74***
1992-1993	-0.4	0.017	0.0255	0.005	0.05	*0.38*	*0.32*	***1.57***
1993-1994	0.6	0.02	0.02	0.005	0.05	*-0.63*	*-0.67*	***1.14***

Table 6.3 Year-to-year losses of Se fractions in the 0-60 cm interval of soil in treatment D and estimate of soluble Se available for leaching.

Period (July to July)	Change in total Se (g/m2)	Se volatilized low est. (g/m2)	Se volatilized high est. (g/m2)	Se accumulated in plants low est. (g/m2)	Se accumulated in plants high est. (g/m2)	Se required to be flushed low est. (g/m2)	Se required to be flushed high est. (g/m2)	Soluble Se (g/m2)
1990-1991	-1.4	0.024	0.072	0.005	0.05	*1.37*	*1.28*	***1.99***
1991-1992	-3.5	0.024	0.036	0.005	0.05	*3.47*	*3.41*	***2.03***
1992-1993	-0.4	0.018	0.027	0.005	0.05	*0.38*	*0.32*	***2.57***
1993-1994	1.6	0.017	0.017	0.005	0.05	*-1.62*	*-1.67*	***1.95***

It is evident that by accounting only for DMSE emissions and plant uptake, the Se mass balance is, in most cases, incomplete. With the exception of the 1990 to 1991 decreases in total Se observed in treatments I and ID and the 1991-1992 decreases in treatment D, soluble Se in the 0-60 cm interval is of sufficient concentrations to complete the mass balance, if most of it were leached below the monitored interval. Based on the amount of rainfall, as measured by the CIMIS weather station, infiltration to below 60 cm most

certainly did occur during winter periods. This was observed in pore water as collected by water samplers and moisture increases down to 1 m depth were observed via neutron probe monitoring (Chapter 2). The exact mass of Se which was transported in soluble form is difficult to quantify, because of the significance of macropore flow early on in the infiltration process into relatively dry soils. However, there is no doubt that very large fluxes of soluble Se were observed and are evidence of the leaching of Se from surface soils. The comparison of leachable Se with Se lost from the system does not imply that *all* soluble Se was flushed out, only to show that a large fraction of the Se lost *could have been* leached. The relative importance of soluble Se as compared with the other Se pools is shown in Tables 6.5 through 6.8. It is evident that the leaching of soluble Se out of this

Table 6.4 Year-to-year losses of Se fractions in the 0-60 cm interval of soil in treatment C and estimate of soluble Se available for leaching.

Period (July to July)	Change in total Se (g/m2)	Se volatilized low est. (g/m2)	Se volatilized high est. (g/m2)	Se accumulated in plants low est. (g/m2)	Se accumulated in plants high est. (g/m2)	Se required to be flushed low est. (g/m2)	Se required to be flushed high est. (g/m2)	Soluble Se (g/m2)
1990-1991	-2.1	0.066	0.198	0.005	0.05	*2.03*	*1.85*	***1.59***
1991-1992	-1.5	0.066	0.099	0.005	0.05	*1.43*	*1.35*	***1.81***
1992-1993	-0.5	0.034	0.051	0.005	0.05	*0.46*	*0.40*	***2.08***
1993-1994	0.2	0.025	0.025	0.005	0.05	*-0.23*	*-0.28*	***1.62***

Table 6.5 Relative contribution of Se pools to total Se inventory in the 0-60 cm interval in treatment I.

Period (July to July)	Total Se (% of total)	Volatilized Se low estimate (% of total)	Volatilized Se high estimate (% of total)	Plant Se low estimate (% of total)	Plant Se high estimate (% of total)	Soluble Se (% of total)
1990-1991	100	0.58	1.73	0.03	0.32	**13.21**
1991-1992	100	0.68	1.02	0.04	0.38	**11.82**
1992-1993	100	0.28	0.42	0.04	0.41	**18.85**
1993-1994	100	0.24	0.24	0.04	0.40	**13.87**

interval could result in a 10% to 20% and greater loss relative to the total Se inventory. On the other hand, even very liberal estimates of Se volatilization rates translate to a potential loss of 0.5% to 2% per year. Probably an estimate of a 1% loss per year is more reasonable. Plant uptake of Se is very low. Even a very high estimate translates to an annual soil depletion of less than 1%.

Table 6.6 Relative contribution of Se pools to total Se inventory in the 0-60 cm interval in treatment ID.

Period (July to July)	Total Se	Volatilized Se		Plant Se		Soluble Se
		low estimate	high estimate	low estimate	high estimate	
	(% of total)	(% of total)	(% of total)	(% of total)	(% of total)	(% of total)
1990-1991	100	0.47	1.41	0.06	0.62	**17.90**
1991-1992	100	0.61	0.92	0.08	0.81	**28.06**
1992-1993	100	0.29	0.44	0.09	0.86	**27.07**
1993-1994	100	0.31	0.31	0.08	0.78	**17.81**

Table 6.7 Relative contribution of Se pools to total Se inventory in the 0-60 cm interval in treatment D.

Period (July to July)	Total Se	Volatilized Se		Plant Se		Soluble Se
		low estimate	high estimate	low estimate	high estimate	
	(% of total)	(% of total)	(% of total)	(% of total)	(% of total)	(% of total)
1990-1991	100	0.22	0.67	0.05	0.46	**18.43**
1991-1992	100	0.33	0.49	0.07	0.68	**27.81**
1992-1993	100	0.26	0.39	0.07	0.72	**37.25**
1993-1994	100	0.20	0.20	0.06	0.59	**22.94**

Table 6.8 Relative contribution of Se pools to total Se inventory in the 0-60 cm interval in treatment C.

Period (July to July)	Total Se (% of total)	Volatilized Se low estimate (% of total)	Volatilized Se high estimate (% of total)	Plant Se low estimate (% of total)	Plant Se high estimate (% of total)	Soluble Se (% of total)
1990-1991	100	0.54	1.61	0.04	0.41	**12.93**
1991-1992	100	0.61	0.92	0.05	0.46	**16.76**
1992-1993	100	0.33	0.50	0.05	0.49	**20.19**
1993-1994	100	0.24	0.24	0.05	0.48	**15.43**

Several statements can be made about the rates of selenium volatilization measured in the 2-acre plot:

- Cumulative Se losses from 1991 to 1994 from four different treatments in decreasing order were as follows:

  1991: Irrigated > Control > Irrigated/disked > Disked

  1992: Irrigated > Control > Disked > Irrigated/disked

  1993: Irrigated > Irrigated/disked >Control > Disked

  1994: Control > Irrigated > Disked >Irrigated/disked

- In all four years, the irrigation treatment had relatively high volatilization rates except in 1994. In 1994, the control plot had the highest Se volatilization that may be attributed to the unusually wet winter in 1994.

- Generally the disked and the irrigated/disked plots had the lowest Se volatilization. Both these treatments differed from irrigated and control treatments by not having any plants. Therefore, it is reasonable to conclude that plant presence has some beneficial effect on Se volatilization. This may be an indirect effect due to contribution of organic C by plants.

- During the fall season, the control and disked treatments had the highest Se volatilization rates in all four years. This may be due to increased moisture content in these non-irrigated plots. During the winter season, all four treatments had low and

similar Se volatilization rates. This is due to the limiting effect of temperature on Se volatilization.

- A second order polynomial fit in irrigated and control plots showed that the optimum gravimetric moisture content for Se volatilization is around 18-20%. Both these treatments had fairly good plant growth. In the irrigated/disked treatment, where there is no plant growth, the optimum gravimetric moisture content is around 8%. This may be due to some other limiting factor, such as lack of organic C.

- In all four treatments, Se volatilization had a fair second order polynomial fit with soil temperature. The optimum temperature for Se volatilization seems to be around 20°C, although this trend is obscured by a number of other variables which cannot be controlled in a field setting.

Experiments carried out in enclosed boxes (Section 3.3) gave somewhat different results. According to the direct emission measurements in the boxes, the net mass of Se volatilized over the period of the experiment (Oct. 1990 through Nov. 1994) would have been around 0.45 g m^{-2}. This is a higher net volatilization than found in most cases in the 2-acre plot, where the total losses were between 0.24 and 0.49 g m^{-2} in treatment I, 0.11 and 0.22 g m^{-2} in treatment ID, 0.083 and 0.15 g m^{-2} in treatment D, and 0.19 and 0.37 g m^{-2} in treatment C. The higher rates in the boxes are probably a result of a thinner layer of soil and better aeration. Also, since soluble selenium was not flushed out, more of it was available for methylation. Nonetheless, the measured total Se loss from the enclosed boxes is equivalent to no more than 5% of the soil inventory. In contrast, soil-Se measurements (Fig. 3.21) show a net loss of around 20%. There is no easy explanation for this discrepancy.

6.2 Conclusions

Elucidating the effectiveness of microbial volatilization on Se dissipation was the primary goal of this field project. Although Se losses from the 0 to 15 cm interval and the 15 to 60 cm interval were observed, only a fraction of this loss can be attributed to methylation. The remainder is likely a result of Se displacement with infiltrating rainwater. The management of moisture conditions in a field setting is difficult in the winter and the vertical displacement of soluble Se is inevitable. The degree to which this happened was

unexpected. Two factors contributed to this situation: a very high proportion of soluble Se and relatively permeable, sandy loam soils.

Once 0-60 cm Se data is integrated (Figures 4.20-23), it is apparent that with the exception of the differences between 1990 and 1991 in treatments I and ID, and 1991 and 1992 in treatment D, few consistent long-term trends were observed. Physical and chemical processes notwithstanding, the largest decrease in this interval between 1990 and 1994 occurred in treatment I (45%; 20% between 1991 and 1994), followed by ID (42%; 21% between 1991 and 1994), then D (30%; 21% between 1991 and 1994), and finally C (27%; 15% between 1991 and 1994). This is in contrast to the order of highest measured volatilization rates (I>C>ID≥D). The reason why actual losses of soil-Se were lowest in treatment C is the relatively shallow water table. During winter periods, even before major rains and ponding, the water table rises above 1 m depth, thereby wetting up the profile and limiting the extent of Se leaching (cf. Fig. 2.11). Interestingly enough, the relative decline in soil-Se between 1991 and 1994 was more or less the same for all treatments (15 to 21%), despite widely varying measured volatilization rates (Fig. 3.2 and 3.10).

Although the direct emission measurements in the enclosed boxes gave showed similar rates to measurements made in the irrigated plots, the net loss of soil-Se in the enclosed boxes was around 20%, which is much less than in the 2-acre pond, most likely because leaching of Se was limited. The isolation of a limited volume of soil and the mode of management may have contributed to higher volatilization rates and is an indication that the low-intensity management scheme is not sufficient to significantly boost volatilization rates. As seen in both the contained soils and the 2-acre plot, measured volatilization rates were both temperature and moisture sensitive, but generally declined with time, likely as a result of progressively lower organic C. This again points to the need for organic amendment to boost Se methylation rates.

If optimum conditions are maintained, which would require the addition of organic C sources, microbial volatilization of Se could continue at a rate equivalent to between 1 and 5 % of the total Se inventory, in the 0-60 cm interval, per year. Because of the leaching of soluble Se into the profile, actual rates will probably be much lower as less soluble Se would be available to the microbial community. Given these uncertainties, if one assumes a methylation rate of 1% of the existing inventory per year, and that rate could be maintained, half of the inventory would be removed in 69 years. If the methylation rate could be maintained at a very high 5% per year, the Se inventory "half-life" would be 14

years. To obtain and maintain the higher methylation rate, very intensive management techniques would need to be employed. In order to bring the soil-Se to 4 ppm, the lower rate would have to be maintained for approximately 230 years; the higher rate for 46 years.

Disking and rototilling, which serve to aerate the soil, and thereby increase volatilization rates, also result in solubilization of Se and an increase in leachability. This in turn results in vertical displacement of Se. Leaching of Se into the soil profile and immobilization at depth, is a process which cannot be prevented. Nonetheless, it is a process which results in a net reduction of Se near the soil surface and reduction of its bio-availability. Se re-oxidation and upward redistribution are much slower than leaching and chemical reduction. Although some Se will be brought back up to the surface, evaporation rates from a low bulk density surface are low. If the present pattern of wet winters continues, significant declines in near-surface soil-Se inventories will be observed throughout the Reservoir.

The future employment of similar management schemes in an attempt to reduce Se concentrations in surface soils should be considered, although since roughly equal losses were observed in all treatments, it seems that these types of treatments are probably not sufficient to significantly increase volatilization rates beyond natural levels. Given the amount of investment into the experimental field plot, it is recommended that the experiment be continued, but at much reduced intensity. A subset of transect samples should be collected once a year, and a complete set every two years. The samples should be analyzed for total and water-soluble Se. Direct measurements of volatile emissions should be made monthly on days on which the temperature is typical for the month. The enclosed boxes should be sampled on a quarterly basis and analyzed for both total and soluble Se. Sparser but longer term measurements will provide a unique data set which will, if nothing else, be an excellent assessment of Se levels on this scale.

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