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IN SITU MICROBIAL VOLATILIZATION OF SELENIUM IN SOILS: A CASE HISTORY

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ABSTRACT: A pilot-scale field experiment has been conducted since 1990 to test the effectiveness of microbial volatilization in removing selenium (Se) from soils contaminated with agricultural drainage water. The experiment, in which only irrigation and aeration were employed to enhance microbial processes, was designed to measure all major Se fluxes, including not only selenium loss via volatilization, but also advection with infiltrating rainwater, evapotranspirative transport, and plant uptake. The goal was to account for the total Se mass balance and address questions as to the significance of microbial volatilization relative to other fluxes. Although data collected from 1990 to 1994 showed decreases of Se concentrations in the top soil, subsequent data demonstrated that advective Se fluxes due to rainwater infiltration and evapotranspiration are largely responsible for the observed changes. Se volatilization was measured to account for an annual loss of only about 1%, with volatilization rates decreasing significantly with time, presumably due to the depletion of soil organic carbon. The integrated results of this project demonstrate the advantages and even necessity of an inter-disciplinary and multi-phase approach to evaluating the effectiveness of bioremediation strategies. Extreme caution needs to be taken in interpreting early results; long-term data collection and follow-up are indispensable.

INTRODUCTION

The delivery of high concentrations of selenium (Se) in agricultural wastewater to Kesterson Reservoir, CA, during the late 1970's and early 1980's resulted in one of the most prominent cases of ecosystem-scale trace element contamination of soil, water, and biota (Benson et al., 1990). 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 soils (Karlson and Frankenberger, 1990). However, measured gaseous Se emissions could not account for observed Se depletion in the soil, suggesting that only part of the Se decline could be due to volatilization. Discrepancies could not be resolved because the early experiments were not designed to account for solute displacement. Furthermore, small-scale experiments generally involved intensive management, such as frequent irrigation, temperature control, and organic supplements, all designed to increase microbial activity. Such management is not feasible on the scale of the 500 acre Kesterson Reservoir. Therefore, a pilot-scale field study was carried out to test the effectiveness of low-intensity management strategies, including combinations of irrigation, disking, and vegetation. A synthesis of data collected over an eight-year-long experiment is analyzed with the intent of evaluating the effectiveness of low-cost soil management as a means of Se bioremediation.

MATERIALS AND METHODS

Site Layout. A 2-acre site was selected in an area which was very frequently flooded during the operation of the Reservoir and supported primarily cattail (*Typha*) vegetation. Se concentrations in this area (up to 100 $\mu g\ g^{-1}$) were amongst

the highest in the Reservoir. Cattail residues on the soil surface were incorporated into the top 20 cm of soil by repeated disking and rototilling, in order to homogenize the surface soils and improve the availability of cattail litter as a carbon source. The plot was then divided into four subplots, each being reserved for a particular treatment: irrigation only ("I"), irrigation and disking ("ID"), disking only ("D"), and control or no action ("C") (Fig. 1). The irrigated plots were watered once a week with 10 mm of water. The disked plots were rototilled every 2 weeks, except during the rainy season. After July 1996, the treatments were terminated.

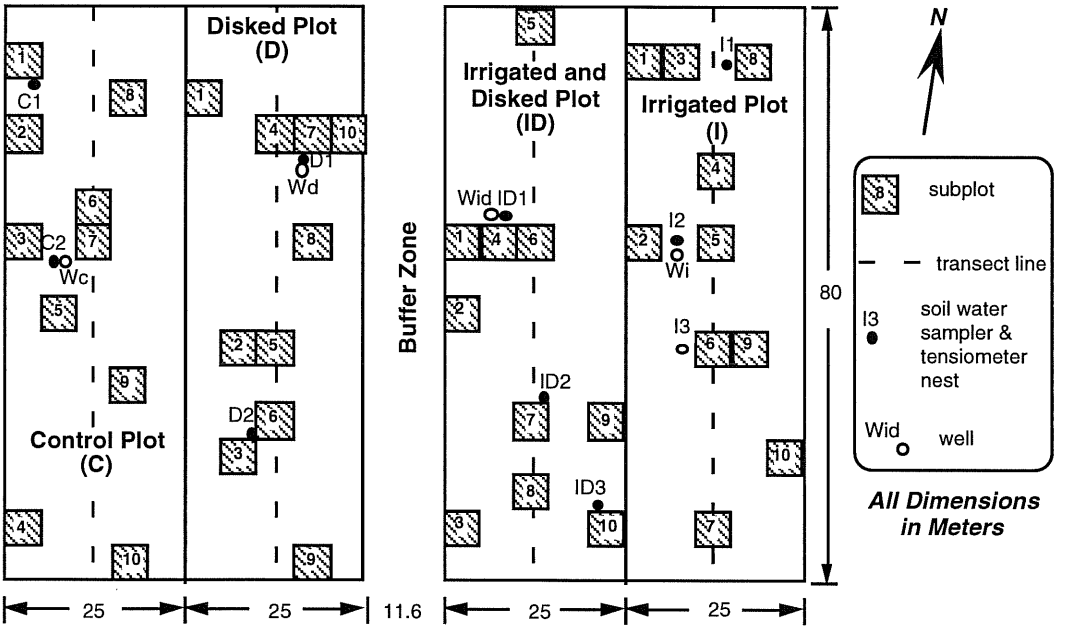

FIGURE 1. Layout of pilot-scale experimental site.

Soil Sampling and Analysis. An annual north-south transect was taken through the middle of each treatment in July from 1990 to 1996. Follow-up sampling took place in treatments I and ID in August 1998. Samples were obtained down to the depth of 0.60 m, in 0.15 m increments. Soil samples were extracted for total Se using an acid digest (Tokunaga et al., 1994) and analyzed via hydride-generation atomic absorption spectroscopy HGAAS (Weres et al., 1989). Soils were also extracted using a 1:5 soil:water extract and analyzed for total soluble Se via HGAAS (Tokunaga et al., 1994).

Direct Measurements of Volatile Se Emissions. Seven 5 m by 5 m sub-plots were randomly selected from each treatment to measure in-situ volatile Se emissions, using volatilization chambers (Biggar and Jayaweera, 1993). Measurements were made on a monthly basis during the spring, summer, and fall. Rates were not measured in the winter due to inclement weather conditions, but past experience showed very low volatilization rates during that time. Measurements were taken over an area of 0.25 m^2 for 24 hours, thereby accounting for diurnal temperature fluctuations. Volatile Se collected on activated carbon was extracted and analyzed using HGAAS.

Uptake of Se by Plants. Measurements of biomass and plant tissue-Se (Wu et al., 1993) were performed on plants at the field site on an annual basis.

Moisture and Solute Monitoring. Ten vadose zone monitoring nests, each consisting of four tensiometers and four soil water samplers, were installed down to a depth of 1 m (Fig. 1). All of the instruments were buried at least 30 cm below the soil surface in order to allow disking machinery to pass over the soil. Soil water samples and tensiometer readings were taken on a monthly basis from 1990 through 1994 and quarterly through 1996. Soil water was analyzed for total dissolved Se using HGAAS. Four wells were sampled on a quarterly basis. Neutron probe readings were taken in these well casings at monthly intervals.

RESULTS AND DISCUSSION

Soil-Se and Salinity Levels. Selenium concentrations in the top 0.60 m of soil in the irrigated treatment are shown in Fig. 2. Based on these data, and similar trends from the irrigated/disked and disked plots, it appeared that there were significant decreases in Se concentrations in the top 0.15 m interval, but slight increases in Se in the deeper intervals of the treated plots from 1990 to 1994. From 1994 to 1996, Se concentrations in the top 0.15 m of all plots, including the control treatment, increased. When differences in bulk density of the soils are considered and the mass of Se in the top 0.60 m is integrated (Fig. 3), the early decreases in Se appear much less significant. Dates listed in each column represent the years from which the given year was statistically different (95% confidence level). This shows that following the initial decline from 1990 to 1991, very few significant differences were observed. The follow-up sampling in 1998 showed a decrease in Se and salinity (Fig. 4; expressed as electrical conductivity of soil:water extracts) in the irrigated treatment, but no change in the irrigated/disked treatment. The overall similarity in inter-treatment Se trends, as well as matching changes in salinity, suggest processes unrelated to microbial volatilization are responsible for Se fluxes.

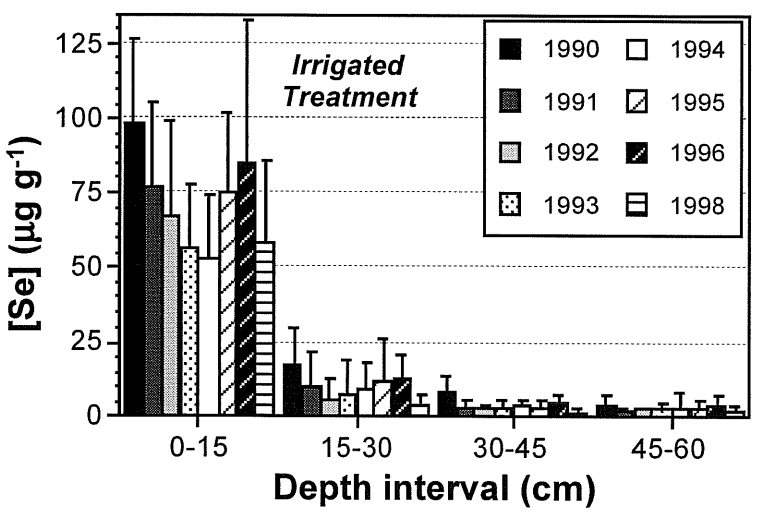

FIGURE 2. Concentrations of Se in the irrigated treatment.

Volatile Se Emissions. Cumulative Se volatilization, as measured during 1993, is shown in Fig. 5. Se losses, expressed as mass per area, can be compared with data in Fig. 3. Annual Se emissions, measured using this method, are two to three orders of magnitude lower than the total Se inventory, and therefore cannot account for the decreases in Se in the top 0.15 m as shown in Fig. 1. Although seasonal and spatial variability was observed, in none of the treatments did volatile emissions amount to more than 1% of the Se inventory in the 0-60 cm interval.

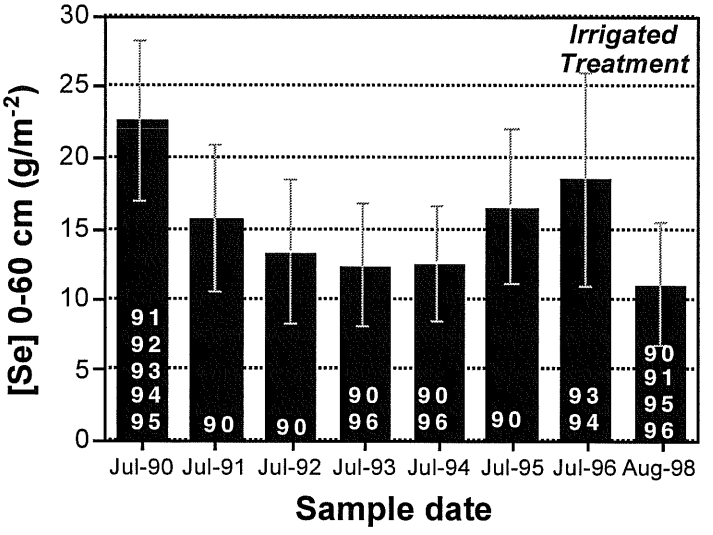

FIGURE 3. Cumulative total Se mass, normalized to area, in the 0-60 cm depth interval in the irrigated treatment.

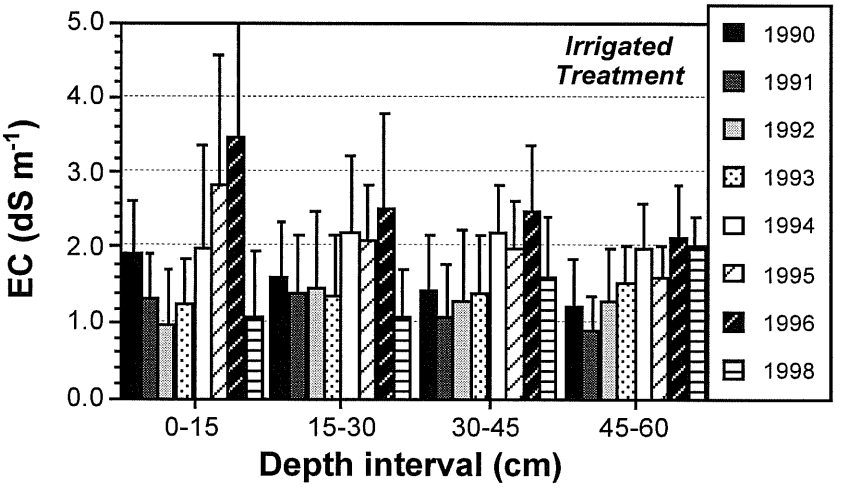

FIGURE 4. Electrical conductivity of soil:water extracts from the irrigated treatment.

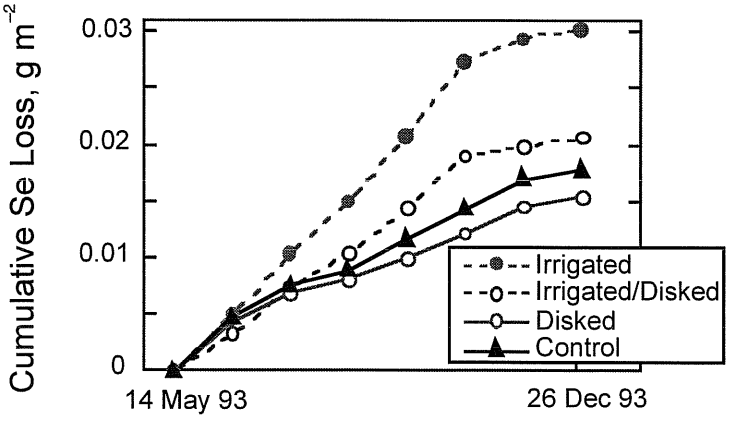

FIGURE 5. Cumulative volatile Se emissions in 1993.

Uptake of Se by Plants. The presence of plants has a profound effect on the soil-water regime by redistributing solutes along rhizosphere-directed hydraulic potential gradients. In addition, plants take up solutes in soil water, including Se. Plants in treatment I accumulated the highest Se mass (3.22 mg Se m^{-2} yr^{-1}). A comparison of the Se flux into plant tissue (1 to 3 mg Se m^{-2} yr^{-1}) with the total Se inventory in the soil (Fig. 3), indicates that plants remove less than 0.05% of the total Se per year.

Transport of Se in the Aqueous Phase. All treatments were affected by winter and spring rainfall, which in the case of the vegetated treatments resulted in as much as a tripling of moisture content. The vast and rapid changes in moisture content following major rainfall events strongly influence solute transport into the soil profile. Changes can occur over relatively short periods of time. For example, during one storm in March 1992, rainwater infiltrated *as deep as 1.6 m*. Such deep infiltration results in the displacement of Se-rich pore-waters, as seen in Fig. 6, where as much as 2 g of Se per m^2 has been displaced in the aqueous phase.

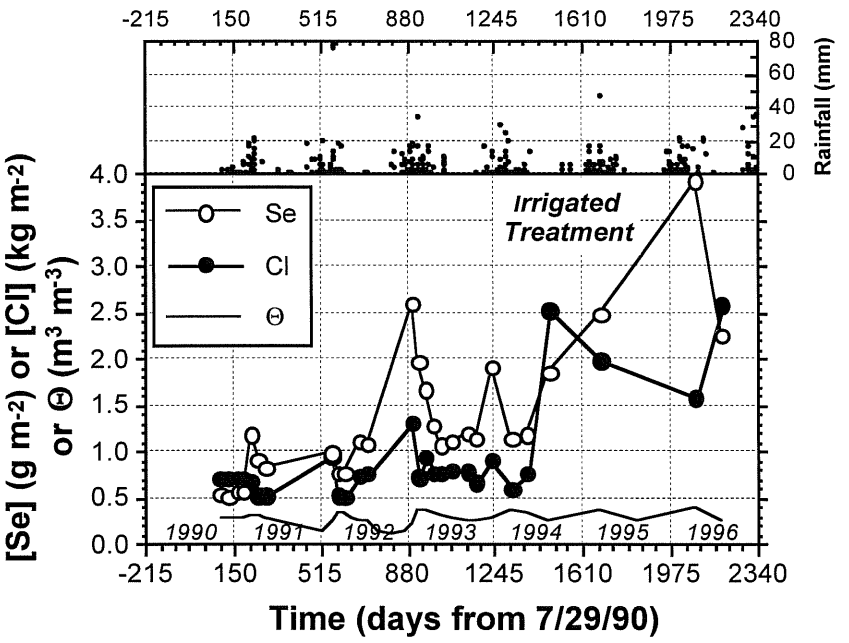

FIGURE 6. Mass of Se and Cl, and moisture content (Θ) over the depth of 0.4 m to 1.0 m in treatment I.

Data Synthesis. The mean mass contributions of the processes involved are summarized in Table 1 for the irrigated treatment. 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. 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. This analysis is conservative in that it does not consider the possibility of in-situ Se solubilization (Tokunaga et al., 1994). From this presentation it is clear that the mass of soluble Se is the same order of magnitude as the mass required to complete the Se mass balance. It is also apparent that Se

volatilization and plant uptake are very small fluxes compared to vertical fluxes of aqueous Se.

Table 1. Annual losses of Se fractions in the 0-60 cm soil interval in treatment I and estimates of soluble Se available for leaching.

Period	Δ in total Se	Se volatilized		Se accumulated in plants		Se required to be flushed		Soluble Se
		low est	high est	low est.	high est.	low est.	high est.	
	(g/m2)	(g/m2)	(g/m2)	(g/m2)	(g/m2)	(g/m2)	(g/m2)	(g/m2)
1990-91	-6.9	0.09	0.27	0.005	0.05	*6.81*	*6.58*	***2.06***
1991-92	-2.4	0.09	0.135	0.005	0.05	*2.31*	*2.22*	***1.56***
1992-93	-1	0.034	0.051	0.005	0.05	*0.96*	*0.90*	***2.30***
1993-94	0.2	0.03	0.03	0.005	0.05	*-0.24*	*-0.28*	***1.72***

CONCLUSION

It is apparent that by accounting only for volatile Se emissions and plant uptake, the Se mass balance is, in most cases, incomplete. The displacement of soluble Se is the most reasonable explanation for the observed fluctuations in Se concentrations and distribution in the top 60 cm of the soil profile. Increases in concentrations in 1995 and 1996 further confirm this mechanism. The sharp decrease in Se concentrations in the irrigated plot in 1998 is likely in response to the very wet El Niño winter, which resulted in the flushing of solutes out of near-surface soils. Direct measurements of volatile Se flux show losses no greater than 1% per annum, a change that is difficult to discern from soil data alone. Long-term monitoring and consideration of all fluxes of Se are evidently necessary in order to assess the effectiveness of bioremediation in field-scale trials.

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