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June 1989

DISCLAIMER

Selenium Immobilization in a Pond Sediment
at Kesterson Reservoir

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Abstract

Kesterson Reservoir, Merced County, CA, a disposal facility for agricultural drain water, became the object of intense scientific investigation following discovery in 1983 that Se-laden agricultural drain water was having serious effects on the reproductive success of waterfowl. A remedial measure involving permanent flooding with low-Se water, aimed at taking advantage of low Se solubility under reducing conditions, was proposed as a means of limiting Se movement into groundwater and biota. A field experiment was undertaken to evaluate the feasibility of the proposed remedial measure, its impact on the quality of shallow groundwater and for quantifying Se immobilization and transport through a newly-flooded pond bottom soil. Extensive soil water and groundwater sampling demonstrated that although initial soluble Se concentrations in the top 1.22 m (4 ft) of soil typically ranged from approximately 1000 to 3000 $\mu g \, L^{-1}$, Se concentrations declined dramatically after flooding and elevated concentrations below 1.22 m were observed at only one of five sampling sites. Analysis of the temporal and spatial changes in the distribution of dissolved Se and Cl^- indicated that 66 to 108% of the initial soluble Se present in the top 1.22 m was immobilized shortly after flooding. These estimates were consistent with the low Se concentrations observed in shallow monitoring wells. The extent to which Se immobilization occurred correlated inversely with average pore water velocity. Data presented suggest that reducing conditions in the newly flooded soils lead to the microbially mediated transformation of selenate to less soluble or mobile forms.

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INTRODUCTION

Kesterson Reservoir, a 520-ha agricultural drain water disposal facility located along the western side of the San Joaquin Valley in Merced County, CA, is operated by the U.S. Bureau of Reclamation (USBR) and is fed by the San Luis Drain (SLD), a 137-km-long concrete-lined canal that extends from the Five Points area in Fresno County. Agricultural drain water that originated in subsurface tile drains installed in irrigated fields of some low-lying areas of the western San Joaquin Valley began flowing into the Reservoir in 1978. In 1983 impaired reproductive success and birth deformities were observed in waterfowl living at the Reservoir, which occupies a portion of the 2387-ha Kesterson National Wildlife Refuge. It was later determined that high concentrations of Se ($\approx 300 \ \mu g \ L^{-1}$) in agricultural drain water had entered into food chains and lead to the observed mortality rates in waterfowl (Ohlendorf et al., 1986). In 1984 studies indicated that Se was entering into local groundwaters in limited areas and that soil and vegetation at the Reservoir were contaminated with Se. Leaching of valley farm soils by percolating irrigation water is the source of Se in drain water, which was carried to the Reservoir via the SLD.

The annual inflow to Kesterson Reservoir ranged from approximately 600 to 1000 ha m year^{-1} over the period 1981 to 1984. After measuring inflows and calculating evaporation losses, it was estimated that approximately 50% of the water that had been delivered to the Reservoir had percolated down through the bottom sediments into the shallow aquifer (USBR, 1986). Even though Se concentrations in SLD water typically were 200 to 300 $\mu g \ L^{-1}$, Se concentrations in groundwater samples, in general, were low and remained below 5 $\mu g \ L^{-1}$. However, the presence of other trace elements such as boron indicated that drainage water had migrated up to 35 m into the underlying aquifer (Lawrence Berkeley Laboratory, 1985). In the few isolated areas where Se did migrate into the groundwater, the vertical distribution of Se did

not correlate with the maximum vertical penetration of pond water, however, it did correspond to the depth at which the groundwater became chemically reducing (Lawrence Berkeley Laboratory, 1986).

Observations as to the distribution of Se throughout soils at Kesterson revealed that a large majority of the total Se inventory is confined to a thin layer of organic detritus and mineral soil on the bottom of the the disposal ponds, suggesting a mechanism that preferentially removes Se from infiltrating pond water and precipitates it in shallow soils. Further observations indicated that both the flooded shallow pond sediments and native groundwater were chemically reducing and that soluble Se is not found under mildly-reducing conditions. Reducing conditions in the shallow soils are controlled by the presence of H_2S produced through anaerobic activity. Soluble Se has been shown to be absent in the presence of either H_2S or Fe^{+2}. The primary removal mechanism has been proposed to be the reduction of Se species by bacterial activity to elemental and organic forms, which are generally insoluble (Weres et al., 1985).

Our understanding of the various factors that control the solubility and speciation of Se is incomplete. However, the importance of the soils oxidation-reduction potential has been identified as a dominant factor in determining the presence or absence of soluble Se. The various oxidation states of Se that can exist in soils include selenide(-II), elemental Se(O), selenite(IV), selenate(VI), and various ill-defined organic Se compounds (Rosenfeld and Beath, 1964). Inorganic Se is most mobile in the Se(IV) and Se(VI) forms (Adriano, 1986). Lakin (1961) and Geering et al. (1968) examined the conditions under which Se may assume either higher or lower oxidation states. Both of these investigators determined that the redox potential (pe + pH) may indicate what to expect regarding the valence state of Se in soil. Elrashidi et al. (1987) used thermodynamic data in a theoretical study to develop equilibrium reactions and constants for Se minerals and solution species that relate to soils and determined that the redox potential of soil is the major factor controlling the speciation of Se in solution. The study determined that at high redox (pe + pH > 15.0) Se(VI) is the major species in solution, whereas in the medium range (pe + pH > 7.5 - 15.0) Se(IV) is dominant. At low redox (pe + pH < 7.5) Se(-II) and Se(O) are the

major species, particularly in alkaline environments. Solubility of selenate minerals is very high, and adsorption is only on the order of several percent (Alemi et. al., 1988a). Selenite minerals are also highly soluble, however, adsorption onto soil particles can be extensive and has been reported to be the primary factor controlling Se(IV) entry into the soil solution (Hingston, 1981; Neal et. al., 1987). In general, Se(-II) minerals and Se(O) appear to be extremely insoluble under reducing conditions and act as major inert sinks for Se present in the system. The presence of Se(-II) minerals, however, is speculative and based on theoretical calculations only. At Kesterson Reservoir, Se(O) is the major species under reducing conditions (Lawrence Berkeley Laboratory, 1987b).

Several investigators have examined the effects of ponding on the geochemical state in soils. Ponnamperuma (1965) observed that reduction of the soil is the single most significant chemical change brought about by flooding and that it results directly from the exclusion of oxygen and its rapid consumption by microorganisms in the utilization of organic matter. The demand for oxygen easily outpaces the supply, which requires diffusion from the overlying soil and water column. Depletion of oxygen and the establishment of anaerobic conditions can occur within 24-48 hours (Takai, 1956; Yamane and Sato, 1968). During anaerobic respiration, inorganic compounds are utilized as electron receptors (they are reduced) in order to release the energy in organic matter through oxidation. Upon the exhaustion of available oxygen, anaerobic bacteria utilize in a step-wise manner, and in accordance with thermodynamic predictions, nitrate, manganese, ferric iron, followed by sulfate and then carbon dioxide. The soils redox potential decreases. Reduced species accumulate either as soluble components or as precipitated compounds within the soil matrix (Gunnison et al., 1985). Alemi et. al. (1988b), in column experiments involving undisturbed and air-dried sediments from Kesterson Reservoir, reported that microbial processes played an important role in the immobilization of Se through the maintenance of reducing conditions.

Observations made at Kesterson regarding the distribution of Se throughout soil and water and the theoretical treatments of Se chemistry in the literature had important implications in the

consideration of possible remedial strategies at the Reservoir. It appeared that by permanent flooding and the resulting establishment of chemically reducing conditions Se could be geochemically contained within the shallow sediments of the Reservoir and that exposure to wildlife through food chains could therefore be minimized. Eventually this idea was formally proposed as one of several possible remedial action plans.

The subject of this paper is an experiment performed principally as a means of evaluating the effectiveness and risk-potential of one of the proposed remedial action plans for Kesterson Reservoir cleanup. Maintaining the Reservoir in a permanently flooded condition would involve an initial flooding period, followed at instances in the future by additional periods of Reservoir re-flooding due to potentially unavoidable or inadvertent periods of drying. There was some concern, based on the highly soluble and mobile nature of Se(VI), that the flooding of aerated pond bottom soils could drive unacceptably high concentrations of Se downward to shallow water-bearing units. This experiment, therefore, was designed to monitor, during controlled re-flooding of one of the shallow ponds of the Reservoir, Se fluxes through the near-surface sediments and into the underlying groundwater aquifer. Important questions to be addressed included: (1) would the geochemical conditions of the shallow sediments promote Se immobilization; (2) to what extent would Se immobilization occur and at what rate; (3) would Se immobilization be sufficiently effective to prevent contamination of groundwater; (4) and what are the physical parameters that either enhance or inhibit Se removal.

MATERIALS AND METHODS

Soil Properties

Kesterson Reservoir rests within a Quaternary flood plain terrace west of the San Joaquin River. Underlying the Reservoir, basin-fill deposits extend to depths of 61.0 to 91.4 m (200 to 300 ft), where the Corcoran Clay is encountered, and consist of alternating layers of sands, clays, and silts. Silty to clean sand predominates with lesser amounts of clay and silt arranged in lenses.

Units above the Corcoran Clay to the ground surface comprise the shallow aquifer (Hotchkiss and Balding, 1971). An early survey of the Reservoir area classified the soils as belonging to the Waukena soil series (Soil Conservation Service, 1952). The surface 1 to 2 m of the pond soils are generally of finer texture than than deeper materials. Clay and silt sized material each make up approximately 20 to 30% of the surface mineral soils. Individual surface samples can be classified in a range of textures from sandy loams to clay loams. Samples collected below 2 m tend to be dominated by the sand fraction.

Monitoring Equipment

Monitoring packages that included eight tensiometers and eight soil water samplers installed to depths of 0.15 m to 1.22 m (0.5 ft to 4.0 ft) at 0.15-m depth increments were constructed at nine sites (UZ-1 to UZ-9) throughout a 38.6-ha pond of the Reservoir (Figure 1). Shallow groundwater monitoring wells were installed at each site for the collection of water samples from discrete intervals in the shallow aquifer. Each site was equipped with one well screened in the 1.8 to 3.0-m interval. At three sites, deeper nested wells were completed covering the interval from 3.0 m to 12.2 m. These nests consist of six wells, screened from 3.0-4.6 m, 4.6-6.1 m, 6.1-7.6 m, 7.6-9.1 m, 9.1-10.7 m, and 10.7-12.2 m. The wells were installed with the use of hollow stem auger drilling equipment and consisted of machine-slotted 0.05-m diameter PVC back-filled with pea gravel and sealed with a bentonite slurry.

Experimental Procedures

Prior to flooding, monitoring packages collected base-line water quality and soil water hydraulic potential data in the unsaturated pond bottom sediments. Flooding was accomplished through the opening of a culvert directly connecting the SLD with the pond and utilized local groundwater pumped from wells located in the northern portion of the Reservoir. Samples collected from the SLD throughout the experiment contained Se at concentrations usually much lower than $5 \mu g L^{-1}$. Electrical conductivity (EC) of the Drain water ranged from 0.4 to 1.4 $S m^{-1}$. Five of the nine sites (UZ-1, -3, -5, -6, and -8) were flooded over a four to five day period

0.15 m
0.76 m
1.2 m
0.76 m
0.15 m
.30 m
0.91 m
0.91 m typical
0.91 m
0.30 m
1.07 m
.46 m
1.22 m
0.46 m
1.07 m
.61 m
1.22 m
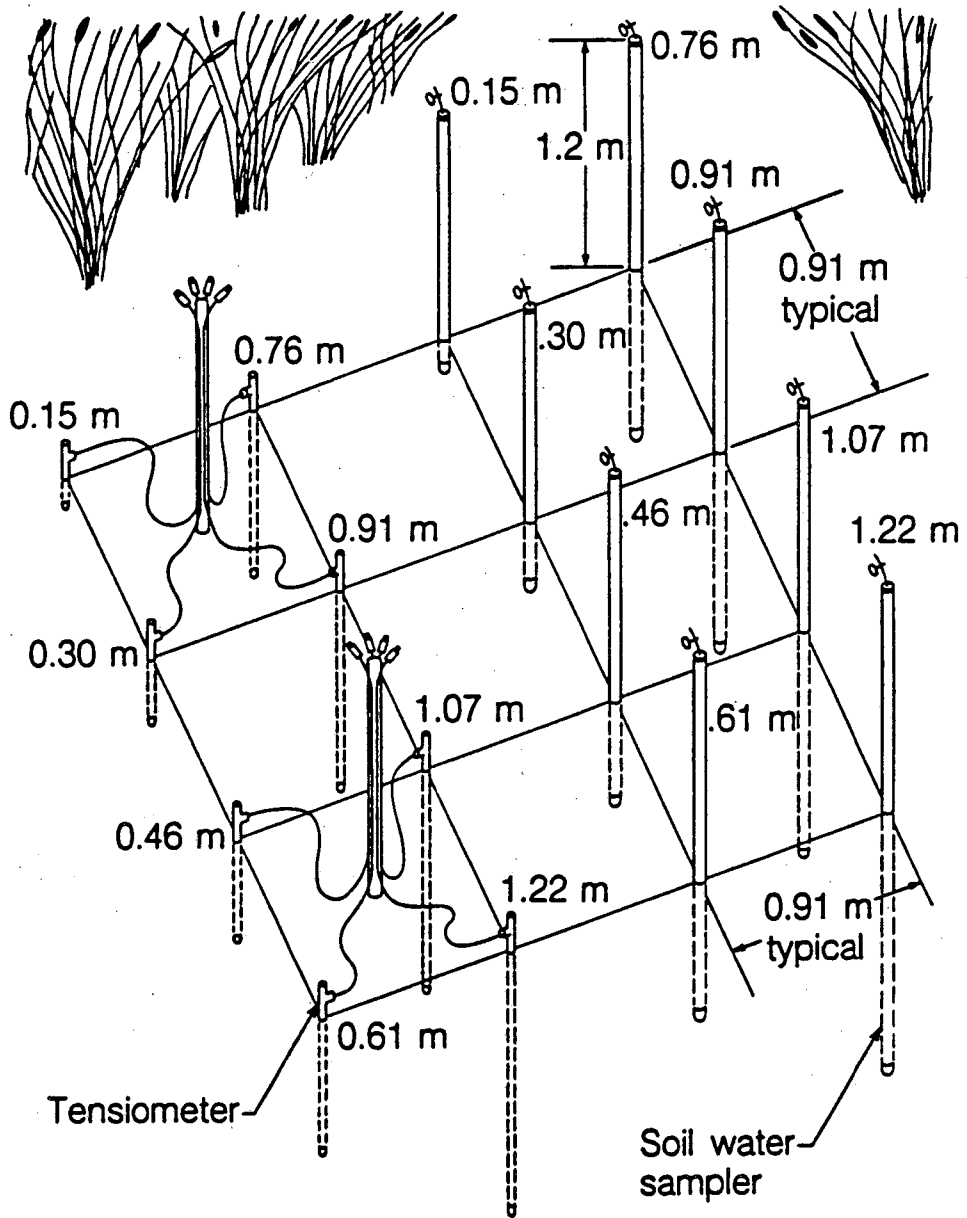0.91 m typical
0.61 m
Tensiometer
Soil water sampler

Figure 1. Plan view of a typical monitoring site.

following the introduction of water into the pond. Within the first week water ponded to depths of 0.1 to 0.5 m, depending on the elevation of each site, eventually stabilizing between 0.2 and 0.6 m. After a period of approximately eight months, due to increased evaporation in the late spring and summer, the drying of adjacent duck ponds, and insufficient water supply, large areas of the pond began to dry out. The discussion and analysis presented here are restricted to data collected from these five wetted sites and only during the portions of the experiment involving the initial flooding episode and ponding. Overall, ponded conditions ranged from approximately 200 to 300 days, depending on the site.

Pore-water Sampling

An intensive sampling program was undertaken during and after flooding. Samples of soil water and pond water were collected at flooded sites at intervals of a few days to a week immediately following their submergence. Sample intervals were then gradually reduced to two weeks and finally one month as conditions became less transient. Samples of groundwater were collected from wells roughly every three to six months.

During unsaturated conditions, suctions of 0.03 to 0.08 MPa were applied to soil water samplers, depending on the moisture conditions (depth), and time periods of two days to two weeks were required to collect sufficient sample volume. During ponding, there was no need to apply a vacuum to the sampler. In either case, after sufficient water for chemical analysis had collected in the sampler, the sampler was completely emptied and a small sub-sample saved for analytical purposes.

Analytical Methods

Chloride was determined by titration with silver nitrate (Mohr Titration). Selenium concentrations were measured at an in-house laboratory using hydride generation (Varian Autohydride Generation Model VGA76) followed by atomic absorption spectroscopy (Perkin Elmer Model 3030). All samples were analyzed for Se(IV) and total Se. Selenite was measured directly from the soil water sample without any pre-treatment. Total Se was measured after an

oxidation/reduction process that converts all of the selenium to the Se(IV) form. The conversion process involved boiling a mixture of 5 ml of the sample with 5 ml 12 M HCL and 0.2 ml 2% ammonium persulfate for 10 minutes. The limits of detection for Se(IV) and total Se are 1 μg L^{-1} and 2 μg L^{-1}, respectively. An established QA/QC program with duplicates, spikes, standards, and blanks was used to monitor the accuracy of the analyses. One blind QA/QC sample was submitted for every 7 field samples. The analytical performance was judged to be satisfactory if duplicates were within ±20%, spikes within 80 to 120% recovery, and standards within ±5%. Critical samples within batches where these criteria were not met were reanalyzed.

Following the experiment, additional speciation studies were undertaken to assess the fraction of Se associated with dissolved organic compounds in the pore water samples. Attempts were made to isolate organo-Se compounds from representative samples at 3 sites of the test plots. Using a modification of the procedure described by Fio and Fujii (1988), 5 ml of acidified field sample (pH 2.2) was passed through a 2-cm long XAD-8 resin column to separate hydrophobic, neutral organo-Se compounds. The sample was followed by 5 ml of 0.1 M HCL as the eluate. The columns were then washed with 0.2 M NaOH to desorb the organic-Se. The eluates were collected and analyzed using the method described above for total Se. In addition to the separation using the XAD-8 resin column, cation-exchange resin columns were used to isolate Se associated with amino acids, proteins, and peptides (Moore and Stein, 1951). The cation-exchange resin (AG50X2) in the hydrogen form was packed in 0.6 by 9-cm columns. The separation procedure was identical to the one used with the XAD-8 column. The results of the separations are provided in Table 1.

The results listed in Table 1 indicate that organo-Se compounds are not present at concentrations greater than several percent in the pore water samples collected from Pond 1. Total Se concentrations in the eluates from both the XAD-8 and ion-exchange columns were within the analytical precision of the measurement techniques, and analysis of the NaOH washes indicated low recovery. This observation is consistent with recent results reported by Fio and Fujii (1988), who reported that organo-Se compounds composed only a small fraction of the total water

extractable Se in selected San Joaquin Valley soils. The lack of appreciable organo-Se compounds present in the pore water samples from Pond 1 suggests that the vast majority of the difference between the total Se and the Se(IV), as determined by the methods described above, is in the Se(VI) form.

Table 1. Separation of organo-Se compounds with XAD-8 and ion-exchange columns.

Sample Number	Total Se ($\mu g\,L^{-1}$)	After XAD-8 ($\mu g\,L^{-1}$)	NaOH wash ($\mu g\,L^{-1}$)	After Ion-exchange ($\mu g\,L^{-1}$)	NaOH wash ($\mu g\,L^{-1}$)
1	1030 1140 1062	1067	5	1082 1140	0 8
2	902 956 956	886	2	994 1072	0 12
3	1302 1396 1384	1315	1	1408 1474	0 0.5

FIELD DATA

Se and Cl⁻ Distributions under Vadose Conditions

Soil water samplers and tensiometers installed prior to flooding provided baseline information under vadose zone conditions on the distribution of solutes and hydraulic head throughout the soil profile. Figure 2 is a profile of Se and Cl⁻ concentrations observed at site UZ-8 before the pond was flooded. Concentrations of soluble Se approached 2500 $\mu g\,L^{-1}$ near the surface dropping to approximately 15 $\mu g\,L^{-1}$ at a depth of 1.22 m. Chloride concentrations ranged from approximately 6.5 g L^{-1} near the surface to 3.0 g L^{-1} at a depth of 1.22 m. Samples of groundwater collected in wells screened in the 1.8 to 12.2-m zone commonly were below 10 $\mu g\,L^{-1}$ of Se.
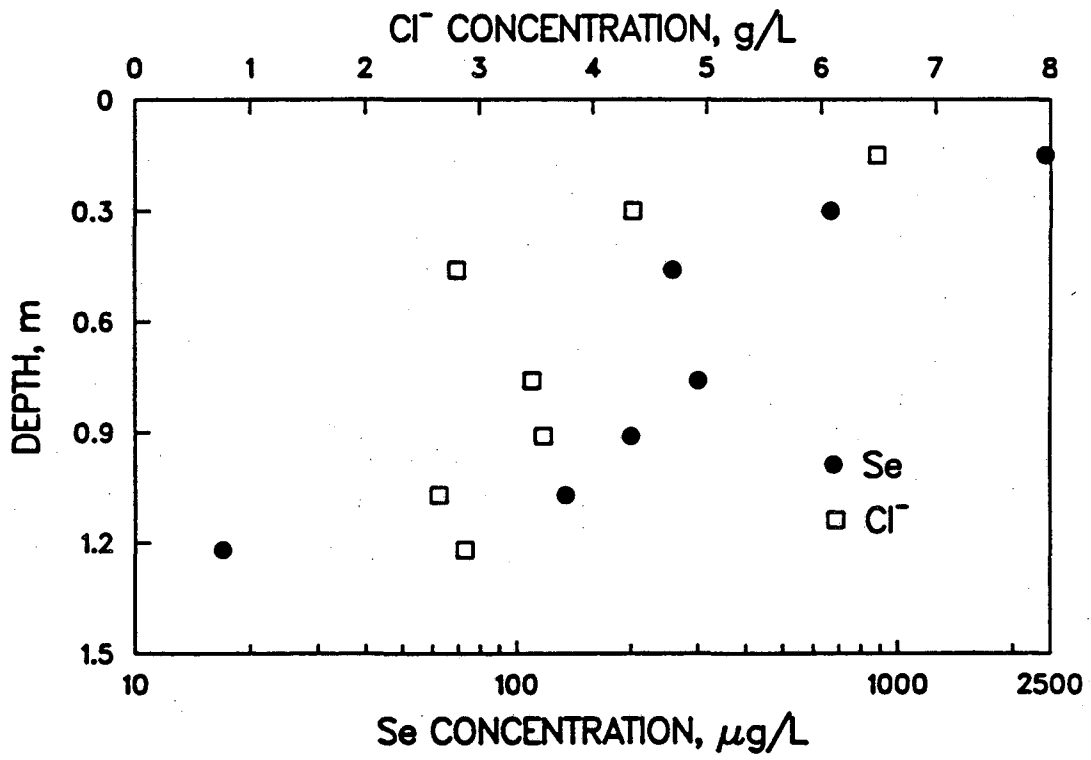
Figure 2. Pre-flooding total Se and Cl⁻ profiles at site UZ-8.

The Movement of Se and Cl⁻ due to Pond Flooding

Figure 3 includes plots of solute breakthrough curves following pond flooding observed at four of eight depth locations within site UZ-8 as well as concentrations in the pond water. Data are presented for Cl⁻ and total Se. Pond water total Se concentrations generally remained below 100 µg L⁻¹ while pond water Cl⁻ levels were fairly constant within the 1.0 to 2.0 g L⁻¹ range. These levels of Cl⁻ in pond water reflect the relatively high salinity of groundwater pumped into the SLD that was utilized in pond flooding. Soil water total Se concentrations increased dramatically within many soil water samplers immediately after the flooding episode, commonly by a factor of two and in some cases by an order of magnitude or more. Chloride levels also increased due to flooding, however, not to the extent that was observed with total Se. Chloride increases in individual soil water samplers were generally less than a factor of two.

Analysis of groundwater samples collected periodically over the approximately one-year-long experiment indicated that flooding did not create widespread elevated concentrations of Se in the shallow aquifer. Concentrations of total Se and Cl⁻ in shallow groundwater monitoring wells are illustrated in Figure 4. Prior to flooding, levels in groundwater were generally less than 10 µg L⁻¹. At one site, UZ-8, an increase in total Se was observed to 322 µg L⁻¹ some four and one-half months after flooding before returning to 16 µg L⁻¹ approximately eight months later. Groundwater at UZ-1 reached a high of 20 µg L⁻¹ prior to returning to < 5 µg L⁻¹. Samples collected at the remaining three sites never exceeded 5 µg L⁻¹.

ANALYSIS

Qualitative Discussion of Se Distributions

The observed solute concentration increases following flooding resulted largely from the downward movement of highly concentrated ore waters near the surface and from the dissolution of Se(VI) and Cl⁻ mineral phases contained in a surficial evaporite mineral crust. Another possibility for Se includes the oxidation and subsequent dissolution of reduced Se mineral phases. In
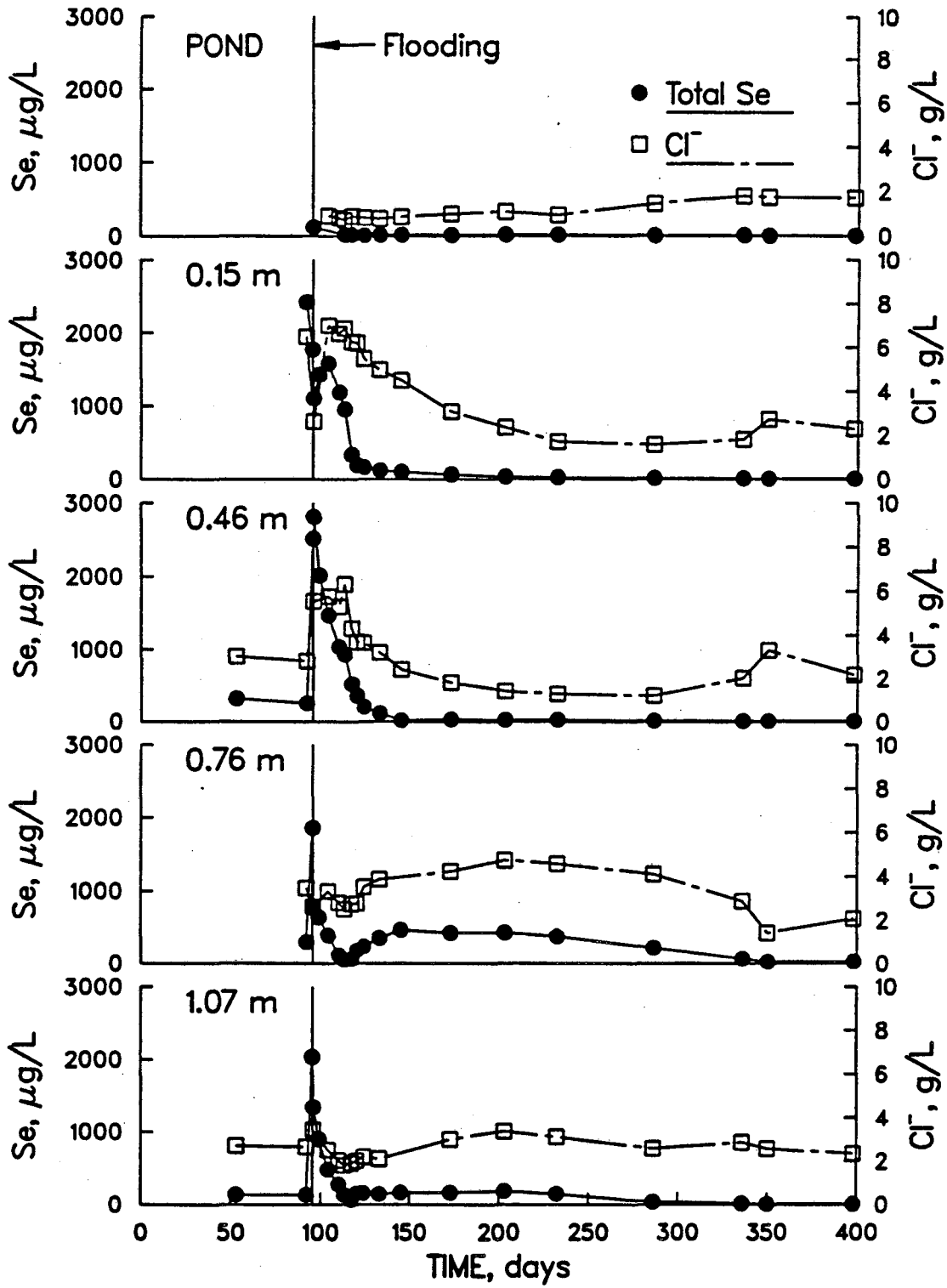
Figure 3. Total Se and Cl⁻ concentrations of four of eight soil water samples collected throughout the experiment time period at site UZ-8.
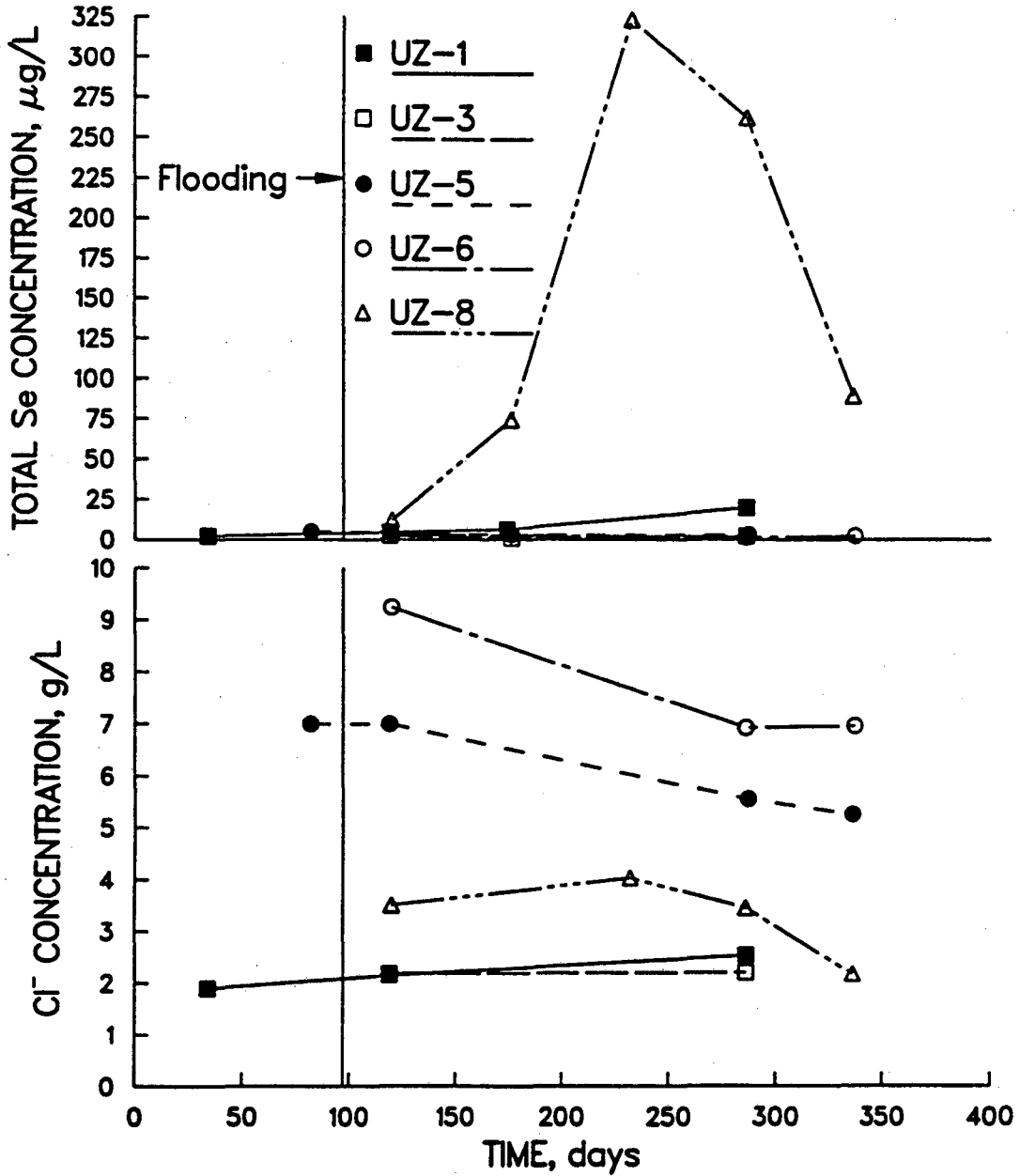
Figure 4. Total Se and Cl⁻ concentrations vs. time in shallow groundwater samples collected throughout the experiment at the five flooded sites.

Figure 5 curves are plotted of average total Se and average Cl^- observed in the eight soil water samplers at the five wetted sites. These data represent estimates of the temporal variation of total mass of the particular solute within the 1.22-m-thick study zone. Total Se and Cl^- concentrations measured just after flooding represent maximum levels observed throughout the experiment. Following the sudden rise, Se concentrations declined rapidly and at a rate much more rapid than in the case of Cl^-. For site UZ-3, for example, we see that roughly 50 days following flooding the average Se concentration in the study block had been reduced from an initial value, Se_o, of 1700 $\mu g \cdot L^{-1}$ to only 250 $\mu g \cdot L^{-1}$ ($Se/Se_o = 0.15$) while the average Cl^- concentration varied only from $Cl_o = 3.7 \ g \ L^{-1}$ to 3.4 $g \ L^{-1}$ ($Cl/Cl_o = 0.92$). If Cl^- can be assumed to behave conservatively, Se therefore appears to have undergone a rapid chemical transformation that selectively removed it from solution.

In Figure 6 Se(VI) to Se(IV) concentration ratios have been plotted for four of eight depths at site UZ-8. Reflecting the predominantly oxidizing conditions that existed in the pond sediment under unsaturated conditions, Se(VI) to Se(IV) ratios prior to flooding were typically much greater than unity. In the the deeper samples ratios were generally in the range of 1 to 10 while near the surface ratios of from 10 to 100 or greater were more typical. At sites UZ-5 and UZ-6, however, ratios as low as 0.02 were observed in deeper soil water, indicating a possible lack of atmospheric oxygen at depth. At nearly all of the soil water sampler locations, the flooding episode led to an increase in the Se(VI) to Se(IV) ratio, indicating that Se was remobilized preferentially in the form of Se(VI) by the oxidizing pond waters. Ratios increased immediately with flooding and by factors from approximately 2 to 30. Even in the shallow soil water (0.15-m and 0.30-m depths), already characterized by relatively high ratios, increases were observed. The increase often was very short-lived, especially in the shallow soil water. Selenate to selenite ratios quickly dropped in only a few days after flooding, as immobilization occurred, eventually stabilizing at values less than one. The large apparent Se immobilization, therefore, occurred primarily with the Se(VI) oxidation state. Pond water ratios remained nearly constant over time in the approximate range of 0.5 to 3.5. *In situ* monitoring of Eh performed in a similar experiment

- 15 -

Figure 5. Average Se and Cl⁻ concentrations of the eight soil water samplers vs. time for the five flooded sites.
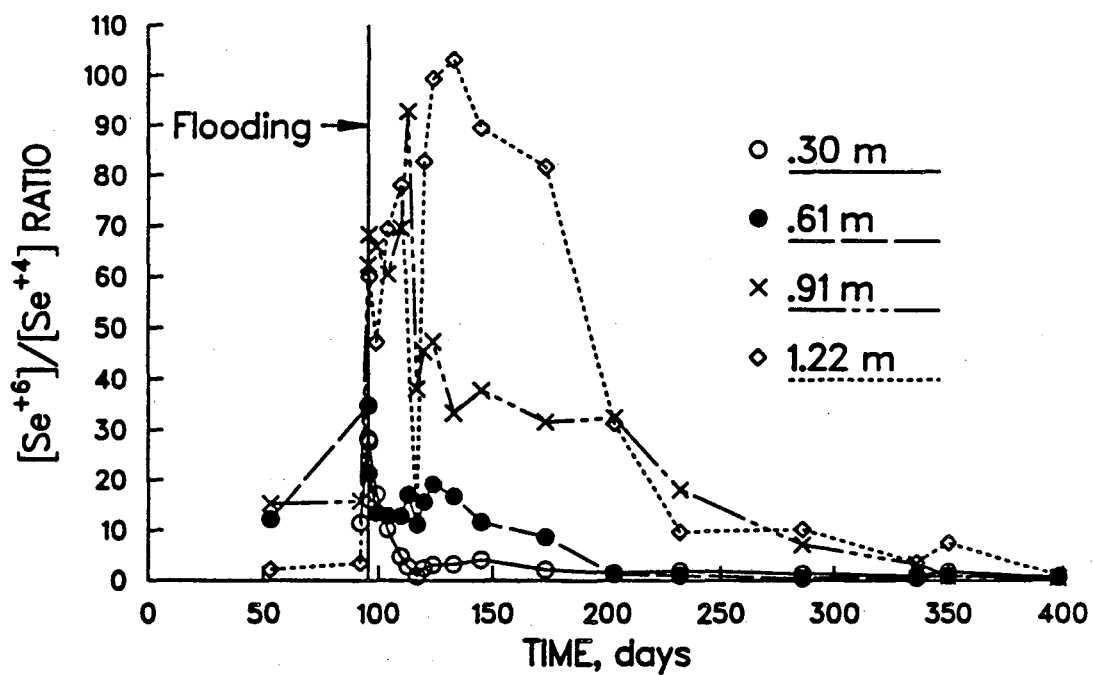
Figure 6. Se(VI) to SE(IV) ratios of samples collected throughout flooding at UZ-8.

reported in Long (1988) suggested that reducing conditions were established in approximately the same time frame as those observed to have resulted in Se immobilization. With the onset of flooding, Eh decreases of approximately 200 mV were typically observed within the first few days in the uppermost 0.61 m of pond sediment.

Selenium Immobilization Estimates

The primary goals of this experiment were to evaluate the effect of flooding on soluble Se concentrations in shallow soil water and groundwater underneath the Reservoir and to determine the extent and rate to which Se immobilization would occur under ponded conditions. A series of calculations have therefore been performed utilizing the average Cl^- concentration data and the concept of mass balance in a practical effort to quantitatively determine Se transport out of the study zone and the degree to which Se was removed from solution. The method normalizes variations in average Se to that of a non-reactive solute in a relatively simple and unencumbered approach. All results and calculations presented pertain only to the 1.22-m-thick monitoring zone. The immobilization calculations include the following series of assumptions:

(1) Transport is purely by advection; diffusion and dispersion are ignored as a first approximation.

(2) Chloride behaves in a conservative manner.

(3) The dissolution of Se and Cl^- mineral phases is essentially instantaneous and complete during flooding, so that all of the potentially available solute enters into solution within a very short time following wetting - possibly within a few hours. Therefore, solutes are not being introduced into the study block, after the initial flooding episode, other than by migration of infiltrating waters.

(4) The diffusion of solutes from within the interior of soil aggregates or other regions of immobile water to the soil water sampler cup surface is negligible. The observed Cl^- response therefore does not reflect the existence of a Cl^- source.

(5) Saturation of the system is 100% at the time that the mass balance calculations com-

mence. The calculations are initiated at the time of the maximum post-flooding average solute concentrations and not necessarily from the first post-flooding sampling event. The maximum values were observed from one-half day to eight days following actual flooding, depending on the site. Initial inventory quantities of Se and Cl⁻ are determined from these post-flooding maxima, and immobilization quantities are normalized to the initial Se inventory.

(6) The porosity of the saturated medium, ϕ, is constant throughout the 1.22-m-thick monitoring zone and does not vary in time.

(7) The average pore water velocity of fluid that infiltrated through the 1.22-m-thick study block throughout the duration of flooding is treated as a constant in the calculation procedure.

With these assumptions, therefore, the average Cl⁻ concentration can be directly equated with the total mass of Cl⁻ present in the study block, M_{Cl}, by the equation:

$$M_{Cl} = \phi V C_{Cl,ave} \tag{1}$$

where $C_{Cl,ave}$ represents the average Cl⁻ concentration of soil water collected in the eight soil water samplers and V is the bulk volume of the 1.22-m-deep soil column (assume a unit surface area in plan view). The temporal variation in $C_{Cl,ave}$ (Fig. 5) can therefore be used as an indication of the rate at which water seeps through the soil profile.

In order to calculate the rate of seepage from the pond, a simple mass balance is performed on Cl⁻ within the study block. The mass of Cl⁻ present in the study block with time, $M(t)_{Cl}$, can be represented by the following equation:

$$M(t)_{Cl} = M_{Cl,o} + M_{Cl,in} - M_{Cl,out} \tag{2}$$

where $M_{Cl,o}$, the initial mass in the system, is the above mentioned post-flooding maximum. $M_{Cl,o}$ occurs at time T_o. $M_{Cl,in}$ is the cumulative mass that has flowed into the study block with infiltrating waters since T_o, and $M_{Cl,out}$ is the cumulative mass outflow that has occurred out of the bottom since T_o. These quantities are defined as follows:

$$M_{Cl,in} = v\phi A \int_{T_o}^{t} C(t)_{Cl,in} dt \qquad [3]$$

$$M_{Cl,out} = v\phi A \int_{T_o}^{t} C(t)_{Cl,out} dt \qquad [4]$$

where, ϕ is as above, v is average pore velocity, A is cross-sectional area, and $C(t)_{Cl,in}$ and $C(t)_{Cl,out}$ represent time-varying, known Cl^- concentrations of waters entering and exiting the monitoring zone, respectively. The integration is performed in a step-wise manner with $C(t)_{Cl,in}$ and $C(t)_{Cl,out}$ assuming constant values within each time-step. For the purposes of the estimates, $C(t)_{Cl,out}$ is set equal to the Cl^- concentration of waters collected from the sampler at the 1.22-m depth, and $C(t)_{Cl,in}$ is set equal to pond water Cl^- concentrations. The observed value of Cl^- in the study block with time, $M(t)_{Cl}$, is determined simply by multiplying the observed average Cl^- concentration by the total volume of water present in the 1.22-m zone. A porosity of 0.4, an area of 1 m^2, and a depth of 1.295 m are assumed for these calculations at each of the sites. The only unknown quantity in Eq. [2-4] is v, the average pore water velocity, which is determined in the following manner. A trial and error procedure is undertaken that produces estimates of study block Cl^- content versus time, based on Equation [2-4], utilizing arbitrarily chosen values of v. For each increment in time, a percent difference is determined between the calculated and the observed Cl^- contents. For each choice of v, these percent differences are averaged. The choice of v that produces a minimum average percent difference is selected as the best estimate of the average pore water velocity.

In Figure 7 we see the observed and calculated Cl^- contents for one of the sites based on the optimized value of average pore water velocity. The percentage deviation between the calculated and observed values was determined for each time step (sampling interval) at each site. Four of the sites possessed average deviations ≤ 7% with a maximum average deviation of 20% (UZ-1). Average pore water velocities varied between sites from a low of 0.44 to a maximum of 4.1 m year^{-1}.

For Se, a similar mass balance procedure is performed, however, an extra term, M_{Imm}, is added to the mass balance equation, Equation [2], to account for the transformation and immobil-
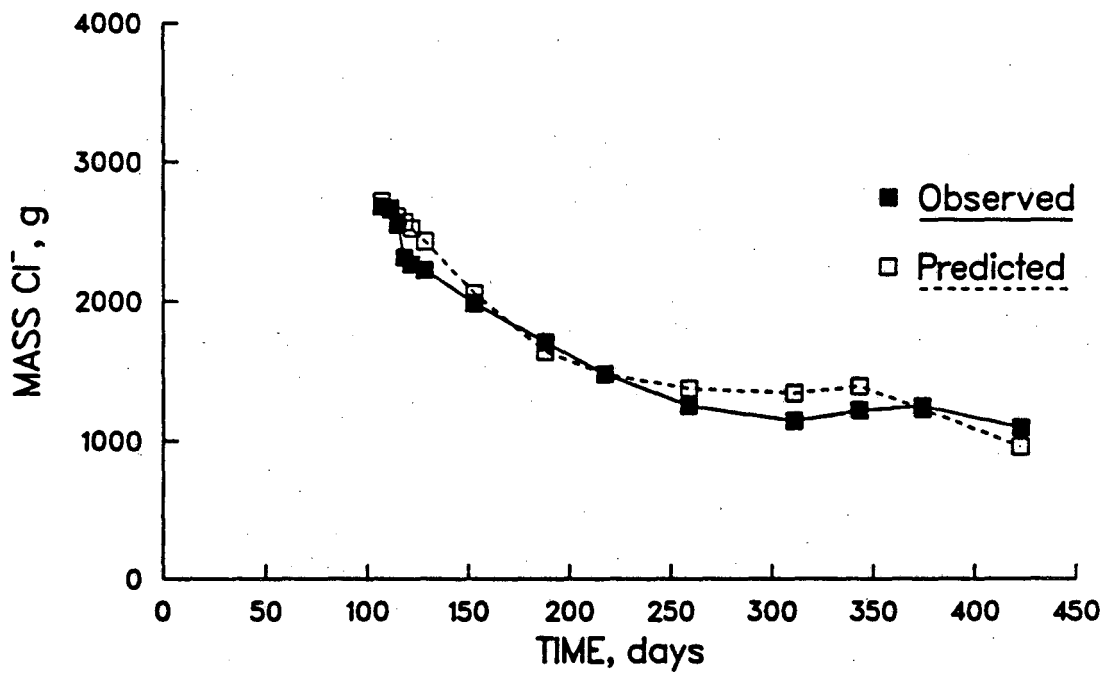
Figure 7. Predicted and observed study block Cl^- content at UZ-8 based on the optimized average pore water velocity ($v = 4.1$ m year^{-1}).

ization of Se from solution. The mass balance equation takes the form,

$$M(t)_{Se} = M_{Se,o} + M_{Se,in} - M_{Se,out} - M_{imm} \qquad [5]$$

where,

$$M_{Se,in} = v\phi A \int_{T_o}^{t} C(t)_{Se,in} dt \qquad [6]$$

$$M_{Se,out} = v\phi A \int_{T_o}^{t} C(t)_{Se,out} dt \qquad [7]$$

and v, ϕ, and A are as above for Cl^-. $M_{Se,o}$ is the initial mass of Se in the system and is determined from the post-flooding maximum average Se concentration. $C(t)_{Se,in}$ is set equal to the Se concentrations measured in infiltrating pond waters and $C(t)_{Se,out}$ to concentrations measured in waters collected from the 1.22-m soil water sampler. Since the velocity is determined from the analysis of the Cl^- data, and $M(t)_{Se}$ is the observed mass of Se in the system, the only unknown in Eq. [5-7] is M_{imm}. The difference between the initial inventory ($M_{Se,o}$) and the sum of the fluxes crossing the monitoring zone boundaries is the quantity that has been immobilized (M_{imm}).

Immobilization and migration of the inventory of soluble Se have been calculated for each of the flooded sites. Refer to Figure 8 for plots of the quantity of Se that was immobilized or discharged during the flooded portion of the experiment. The data plotted have been normalized to the initial mass of total Se present in the system, $M_{Se,o}$ - the post-flooding maximum. It should be noted that it was possible to calculate ratios greater than unity since some Se was added to the system with infiltrating pond water. This water, however, was low in total Se (10-40 $\mu g\ L^{-1}$), and yet, at sites with low initial inventories, the mass of Se inflow could be significant.

Table 2 summarizes the results of the soluble Se mass balance calculations in the 1.22-m zone at each of the five sites. The calculations were performed for the period that began with flooding and ended, for each site, when ponded water was no longer present. The quantities listed include percentages of the initial Se inventory that were immobilized in and discharged below the 1.22-m zone based on average pore water velocities determined in the Cl^- mass balances. We see that immobilization quantities ranged from 66 to 108%, whereas estimates of the mass of Se

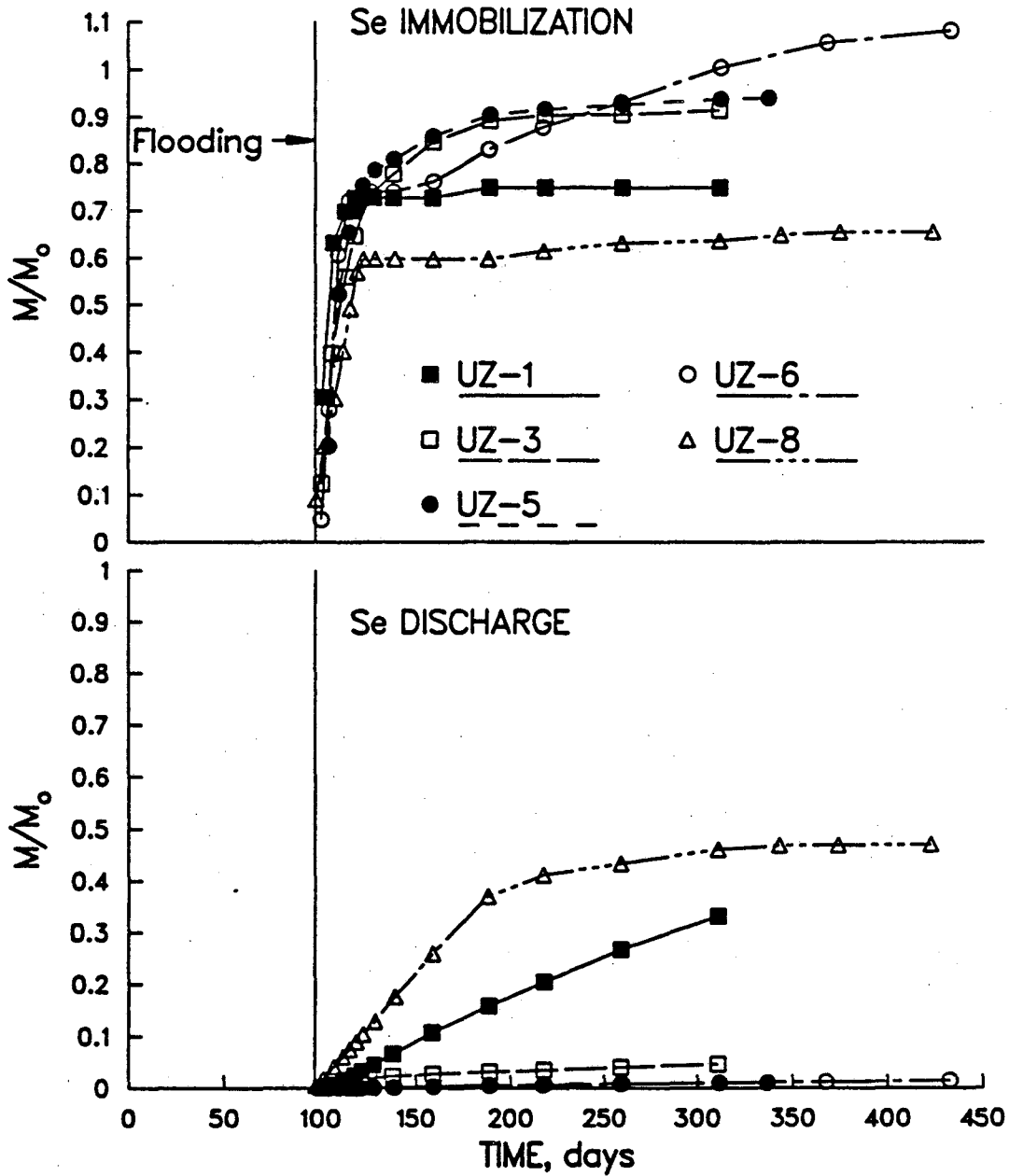Figure 8. Results of the Se immobilization calculations at the five sites. Quantities plotted are normalized to the initial inventory of soluble Se, M_o, in the 1.22-m thick study block.

discharged ranged from 1 to 47%.

Table 2. Se discharge/immobilization during flooding

Site	Averge Pore Water Velocity, m year^{-1}	Initial Mass of Soluble Se g m^{-2}	Discharged		Immobilized	
			% of Initial Mass	Mass, g m^{-2}	% of Initial Mass	Mass, g m^{-2}
UZ-1	1.9	.67	33	.22	75	.51
UZ-3	.64	.88	5	0.46	91	.80
UZ-5	.44	.14	1	.001	94	.13
UZ-6	.76	.05	1.5	.001	110	0.58
UZ-8	4.1	.83	47	.39	66	.55
Average		.52		.13		.41

DISCUSSION OF IMMOBILIZATION ESTIMATES

The approach utilized above in the analysis of Se immobilization rests on several simplifying assumptions with regards to such issues as the use of Cl^- as a tracer, the possibility of kinetically limited dissolution of Cl^-, the contribution of diffusive solute fluxes from zones of immobile water into the advective stream, the extent of study block saturation at the initiation of the calculation procedure, and the degree of temporal and spatial variation in the porosity and average pore water velocity. Clearly, there is a level of uncertainty associated with these assumptions. However, for the purposes of these calculations they were deemed satisfactory. Chloride has been used extensively in the determination of groundwater and soil water velocity in tracer tests (Biggar and Nielsen, 1962; Miller et al., 1965; Kissel et al., 1973) due to its ease of analysis, high water solubility, mobility, low cost, and invulnerability to chemical transformations. At Kesterson, halite has been identified as the dominant Cl^- bearing mineral, and concentrations of Cl^- in soil water suggest that halite is found only in the surficial evaporite mineral crust. Jurinak et al. (1977), in batch experiments examining dissolution kinetics of various salts with a shale-derived saline soil, observed that highly soluble salts such as halite were quickly dissolved

within the initial 0.5 minutes of contact with water and, in columns, moved through the soil profile in an early, initial pulse. For already solubilized Cl^- within regions of immobile water to be transport limited by slow diffusion to the soil water sampler cup surface, a Cl^- concentration gradient is required between soil water within the immobile zone and soil water at the cup surface. The pre-flooding Cl^- levels give an indication of the approximate Cl^- concentrations of soil water within aggregates. Examination of Cl^- breakthrough data in individual soil water samplers (Figure 3) reveals that, after the post-flooding maximums, Cl^- levels did not decline very rapidly and did not vary to a large extent from the preflooding levels. It does not appear that the Cl^- concentration at aggregate surfaces (or at least at sampler cup surfaces) was appreciably different from that within aggregates, and that therefore, diffusive fluxes out of aggregates would have been small.

Initial inventory quantities of Cl^- and Se in the study block were calculated from post-flooding maximum concentrations which occurred from one to eight days following flooding, depending on the site. Complete saturation was assumed in the calculation of these quantities. Computer modeling of the infiltration process indicates that the minimum saturation is at least 90% within the first day of flooding, and tensiometer data confirm that the wetting front quickly passed through the whole extent of the monitoring zone. The assumption of constant porosity throughout the fully-saturated soil profile and throughout time makes consideration of changes in study block water volume unnecessary in the mass balance procedure. Temporal variations in porosity are not expected to be significant. And finally, with regards to the pore water velocity assumption, it is not the intent to imply that the average pore water velocities determined depict actual fluid velocities but that they represent spatially and temporally averaged values. Fluid potential gradients measured between the pond surface and shallow monitoring wells suggest that fluid velocities varied by up to a factor of two over the analysis period.

An independent analysis of the seepage rates has been performed in Long et al. (1988) through one-dimensional numerical modeling of the observed Cl^- breakthrough data at each of the five wetted sites. The maximum deviation in the pore water velocity estimates between the

two methods at any particular site on a percentage basis is 60% with three of the five sites differing by < 33%. This degree of agreement is considered reassuring and is taken as a positive indicator of the soundness of the mass balance procedure. In order to examine any potential effect of this suggested level of fluid velocity uncertainty on the Se immobilization estimates, sensitivity studies performed in Long (1988) repeated the above immobilization calculations using a range of ± 50% of the average pore water velocities presented above in Table 2. The difference in immobilization quantities was greatest at sites UZ-1 and UZ-8 where the Se concentration of water exiting the study block (the concentration observed in the deepest soil water sampler) was appreciably different than that of water entering the study block (pond water). The greatest difference in immobilization quantities occurred at site UZ-8 where 57% and 79% of the initial Se inventory in the aqueous phase was estimated to have been removed from solution based on the upper and lower velocity values, respectively. At site UZ-5, where the inflow and outflow concentrations were roughly equal, the variation in velocity had virtually no effect. Regardless of some degree of uncertainty in the pore water velocity estimates, therefore, extensive Se immobilization definitely occurred within the shallow pond sediments during flooding.

Additional evidence is provided in support of the immobilization calculations in observations of soluble Se concentrations in shallow groundwater monitoring wells. Elevated Se concentrations were detected at only two of the five sites, UZ-1 and UZ-8. Groundwater total Se concentrations at UZ-1 rose only very slightly to nearly 20 μg L^{-1}, however, in Fig. 4 we see that at UZ-8, in a well screened from 2.4 to 3.0 m, a concentration of 322 μg L^{-1} was observed. These observations are consistent with the estimates above that 0.22 and 0.39 g m^{-2} migrated out of the 1.22-m-thick monitoring zone below sites UZ-1 and UZ-8, respectively. This corresponds to 33 and 47% of the initial quantity of soluble Se at each of the two sites. At each of the other sites, where elevated levels of Se were not detected in groundwater, less than 0.05 g m^{-2} of soluble Se was estimated to have migrated out of the monitoring zone. Based on a discharge quantity nearly equal to that of UZ-8, it may seem reasonable to expect the the Se level in groundwater at UZ-1 could have been higher, however, the shallow well at UZ-1 is at 3.0 to 4.6 m while the well at

UZ-8 is only at 2.4 to 3.0 m. It should be kept in mind that the processes that lead to immobilization in the shallow zone can continue to take place below the 1.22-m depth.

In Figure 9 the average pore water velocities from Table 2 have been plotted vs. the corresponding percent discharged and percent immobilized quantities for each site. At sites with relatively low pore water velocities, the greatest degree of immobilization has occurred while the least amount of Se migrated out of the study block. On the other hand, the highest quantity of Se discharge and lowest of removal are associated with the site possessing the maximum average pore water velocity. A correlation is suggested between the effectiveness of the Se removal mechanism and fluid velocity. Soil leaching experiments reported in Lawrence Berkeley Laboratory (1987a) demonstrated that in 0.1-m-long columns Darcy flow rates over the range of 0.91 to 7.0 m year^{-1} exerted a significant effect on Se mobilization, suggesting a time-dependent Se immobilization process. Columns characterized by higher flow rates produced higher total Se concentrations in outflow solutions over the course of the experiments. Regions in the Kesterson pond bottoms where the thin veneer of fine-grained material is absent or meager may have sustained sufficiently high average pore water velocities during past Reservoir operation to allow infiltrating pond water to pass through the reducing layer without the necessary residence time to allow for effective Se removal.

CONCLUSIONS

Observations from the experiment at Kesterson Reservoir indicate that following the establishment of ponded conditions, Se in pore waters contained within shallow pond sediments underwent a rapid chemical transformation that lead to selective removal from solution and immobilization within the near-surface profile. Even though Se concentrations in soil water of near-surface sediments typically exceeded 1000 μg L^{-1} prior to and immediately after flooding, Se concentrations in groundwater sampled in the 1.8 to 12.2 m-depth interval remained below 20 μg L^{-1} at four of five monitored sites, and it is anticipated that levels in groundwater will continue to decline as the immobilization process continues. A comparative analysis of the temporal
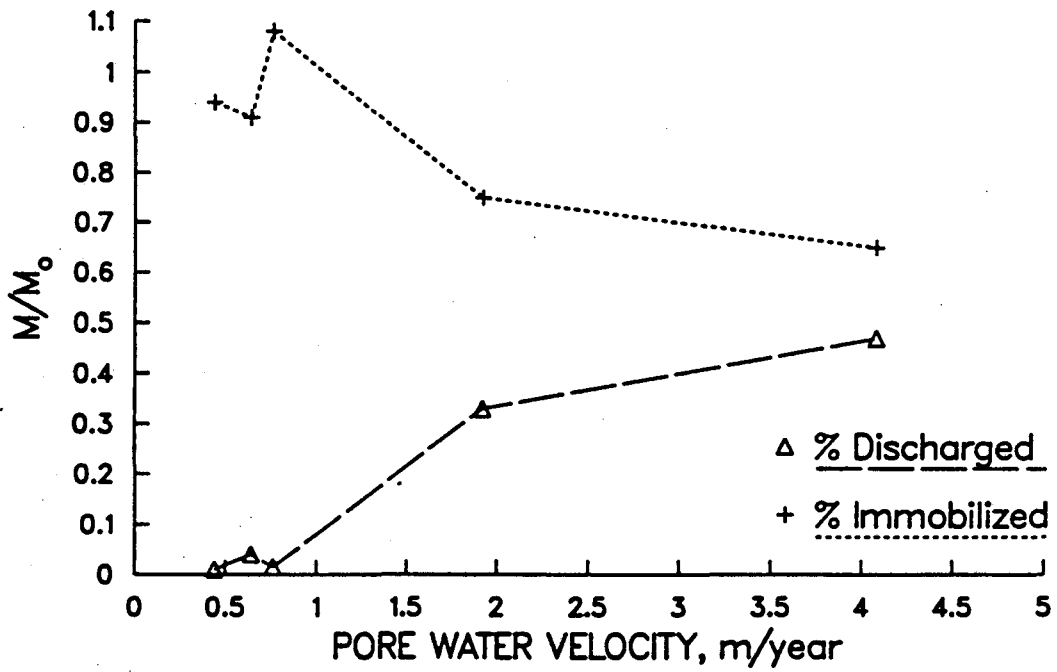
Figure 9. The relationship observed between average pore water velocity and the degree of Se immobilization and discharge.

variation of dissolved Se and a conservative solute, Cl^-, indicated that roughly 60 to 80% of the initial inventory of soluble Se was immobilized in the top 1.22 m of the soil profile within a month of pond flooding, and over the total monitoring period of 7 to 10 months, immobilization ranged from 66 to 108% of the initial Se inventory. Selenium levels in soil water sampled from the 1.22-m-thick study block, after an initial increase after flooding, declined rapidly and continued to fall as long as the pond remained flooded.

An important result of previous investigations of the geochemical behavior of Se has been the determination that under conditions of high redox, Se(VI) is the dominant species in solution, whereas under conditions of moderate to low redox, more reduced species persist including Se(IV), Se(-II), and Se(O), which have lower solubilities. Data presented here, indicating Se immobilization, are consistent with such descriptions and with descriptions of the effect of ponding on the geochemical state in soils. Support is given to a system model whereby rapidly developing reducing conditions in the newly flooded soils lead to the microbially mediated reduction of Se(VI) to less soluble or mobile forms.

Various physical factors have been identified by others that promote the migration of soluble Se through the pond bottoms and into groundwater, including in general, the absence of reducing conditions and, more specifically, the presence of nitrate (Lawrence Berkeley Laboratory, 1987b). In the present study, the average pore water velocity has been shown to influence the degree to which Se remains mobile in soil water and groundwater systems. Relatively higher seepage rates resulted in less Se immobilization and contributed to the contamination of shallow groundwater. At sites where v exceeded 0.76 m year^{-1} the quantity of Se that was transported below the top 1.22 m of soil was equal to or in excess of 33% of the initial Se inventory whereas at sites with lower average pore water velocities discharge percentages remained below 5%. These facts suggest that the Se removal mechanism is subject to kinetic restraints and that average pore water velocity effects Se removal through variations in the residence time of infiltrating pore fluids as they pass through zones characterized by anaerobic bacterial activity and reducing conditions.

ACKNOWLEDGEMENT

REFERENCES

Alemi, M. H., D. A. Goldhamer, and D. R. Nielsen. 1988. Selenate transport in steady state, water-saturated soil columns. *J. Environ. Qual.* 17:608-613.

Alemi, M. H., D. A. Goldhamer, M. E. Grismer, and D. R. Nielsen. 1988. Elution of selenium from contaminated evaporation pond sediments. *J. Environ. Qual.* 17:613-618.

Adriano, D. C. 1986. *Trace elements in the terrestrial environment.* Springer-Verlag, New York, NY.

Biggar, J. W., and D. R. Nielsen. 1962. Miscible displacement: II. Behavior of tracers. *Soil Sci. Soc. Am. Proc.* 26:125-128.

Elrashidi, M. A., D. C. Adriano, S. M. Workman, and W. L. Lindsay. 1987. Chemical equilibria of Se in soils: A theoretical development. *Soil Sci.* 144:141-152.

Fio, J. L., and R. Fujii. 1988. Comparison of methods to determine selenium species in saturation extracts of soils from the western San Joaquin Valley, California. U. S. Geol. Surv. Open File Report 88-458. Sacramento, CA.

Geering, H. R., E. E. Cary, L. H. Jones, and W. H. Allaway. 1968. Solubility and redox criteria for the possible forms of selenium in soils. *Soil Sci. Soc. Am. Proc.* 32:35-40.

Gunnison, D., R. M. Engler, and W. H. Patrick. 1985. Chemistry and microbiology of newly flooded soils: Relationship to reservoir water quality. p. 39-57. *In* D. Gunnison (ed.) Micro-bial processes in reservoirs, Dr. W. Junk Publishers, Boston, MA.

Hingston, F. J. 1981. A review of anion adsorption. p. 51-90. *In* M.A. Anderson and A.J. Rubin (ed.) Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science. Ann Arbor, Mi.

Hotchkiss, W. R., and G. O. Balding. 1971. Geology, hydrology, and water quality of the Tracy-Dos Palos area, San Joaquin Valley, CA. U.S. Geol. Surv. Open File Report.

Jurinak, J. J., J. C. Whitmore, and R. J. Wagenet. 1977. Kinetics of salt release from a saline soil. *Soil Sci. Soc. Am. J.* 41:721-724.

Kissel, D. E., J. T. Ritchie, and E. Burnett. 1973. Cl^- movement in undisturbed swelling clay soil. *Soil Sci. Soc. Am. Proc.* 37:21-24.

Lakin, W. H. 1961. Geochemistry of Se in relation to agriculture. p. 3-12. *In* M.S. Anderson et al. (ed.) Selenium in agriculture. USDA Agric. Handb. No. 200. U.S. Gov. Print. Office, Washington,D.C.

Lawrence Berkeley Laboratory. 1985. Hydrological, geochemical and ecological characteriza-tion of Kesterson Reservoir. Progress Report 1. LBID-1101. Berkeley, CA.

Lawrence Berkeley Laboratory. 1986. Hydrological, geochemical and ecological characteriza-tion of Kesterson Reservoir. Progress Report 2. LBID-1188. Berkeley, CA.

Lawrence Berkeley Laboratory. 1987. Hydrological, geochemical and ecological characteriza-tion of Kesterson Reservoir. Progress Report 5. LBID-1291. Berkeley, CA.

Lawrence Berkeley Laboratory. 1987. Hydrological, geochemical and ecological characteriza-tion of Kesterson Reservoir. Annual Report. LBL-24250. Berkeley, CA.

Long, R.H. 1988. Analysis of selenium and chloride movement through a shallow pond sediment at Kesterson Reservoir. Master's Thesis. University of California, Berkeley.

Long, R. H., S. M. Benson, M. Alavi, and T. N. Narasimhan. 1988. Transport of a conservative solute through a shallow pond bottom. p. 13-31. *In* H.J. Morel-Seytoux and D.G. Decoursey (ed.) Proc. Eight Annual AGU Front Range Branch Hydrology Days Conf., Fort Collins, CO. 19-21 Apr. 1988.

Miller, R.J., J.W. Biggar, and D.R. Nielsen. 1965. Cl^- displacement in Panoche clay loam in relation to water movement and distribution. *Water Resour. Res.* 1:63-73.

Moore, S., and W. H. Stein. 1951. Chromatography of amino acids on sulfonated polystyrene resins. *J. Biol. Chem.* 192:663-681.

Neal, R. H., G. Sposito, K. M. Holtzclaw, and S. J. Traina. 1987. Selenite adsorption on alluvial soils: I. Soil composition and pH effects. *Soil Sci. Soc. Am. J.* 51:1161-1165.

Ohlendorf, H. M., R. L. Hothem, C. M. Bunck, T. W. Aldrich, and J. F. Moore. 1986. Relationships between Se concentrations and avian reproduction. *In* 51st Annual Wildlife and Natural Resources Conf., Wildlife Management Institute, Reno, NV.

Ponnamperuma, F. N. 1965. Dynamic aspects of flooded soils and the nutrition of the rice plant. p. 295-328. *In* Proc. Symposium Mineral Nutrition of the Rice Plant, 1964. The Johns Hopkins Press, Baltimore, MD.

Rosenfeld, I., and O. A. Beath. 1964. Se geobotany, biochemistry, toxicity, and nutrition. Academic Press, New York, NY.

Soil Conservation Service. 1952. Soil survey of the Los Baños area, CA, series 1939, (12). USDA, Washington, D.C.

Takai, Y., T. Koyama, and T. Kamura. 1956. Microbial metabolism in reduction processes of paddy soils: I. *Soil Science and Plant Nutrition* 2:63-66.

U.S. Bureau of Reclamation. 1986. Final environmental impact statement, volume 2, Kesterson Program. Sacramento, CA.

Weres, O., A. F. White, H. A. Wollenberg, and A. Yee. 1985. Geochemistry of Se at Kesterson Reservoir: Possible remedial measures. Lawrence Berkeley Laboratory, Earth Sciences v8 no. 3, Berkeley, CA.

Yamane, I., and K. Sato. 1968. Initial rapid drop of oxidation-reduction potential in submerged air-dried soils. *Soil Science and Plant Nutrition* 14:68-72.