REPORT OF PHASES I AND II
and ADDENDUM

STUDY OF

ATTENUATION OF SELENIUM DRAINING FROM
IRRIGATED SELENIFEROUS AGRICULTURAL SOILS

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The San Joaquin Valley Drainage Program was established in mid-1984 as a cooperative effort of the U.S. Bureau of Reclamation, U.S. Fish and Wildlife Service, U.S. Geological Survey, California Department of Fish and Game, and California Department of Water Resources. The purposes of the Program are to investigate the problems associated with the drainage of irrigated agricultural lands in the San Joaquin Valley and to formulate, evaluate, and recommend alternatives for the immediate and long-term management of those problems. Consistent with these purposes, Program objectives address the following key areas: (1) Public health, (2) surface- and ground-water resources, (3) agricultural productivity, and (4) fish and wildlife resources.

Inquiries concerning the San Joaquin Valley Drainage Program may be directed to:

San Joaquin Valley Drainage Program
2800 Cottage Way, Room W-2143
Sacramento, California 95825-1898

ATTENUATION OF SELENIUM DRAINING FROM IRRIGATED SELENIFEROUS AGRICULTURAL SOILS

Volume 1
Report

By
Rosemary H. Neal and Garrison Sposito

Department of Soil and Environmental Sciences
University of California, Riverside

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EXECUTIVE SUMMARY

The behavior of selenium in irrigated agricultural soils is dependent on a number of environmental factors, some of which may be controlled to a certain extent by managerial practices at the farm level. From a chemical viewpoint, the interactions between the aqueous species of selenium present in soils, and surfaces which may exist in the latter, provide a means by which the movement of selenium in an irrigated soil profile might be attenuated.

The purpose of this study is two-fold. The primary motivation was to identify the variables within an irrigated soil system which play an important role in the transport and transformation of selenium, in order to implement managerial conditions which could control the eventual fate of this element in the San Joaquin Valley. A second, but no less important priority was to increase current understanding of the chemical nature of this element, and by experimental investigation provide hitherto undocumented information concerning its chemistry of transformation, surface interaction and speciation. Such information could then be used to further understanding of this element, and others of similar chemical nature.

In order to obtain the necessary information pertaining to Se behavior in soils, a series of laboratory experiments had to be carried out before any large scale field experiments could be conducted. This report summarizes the experiments carried out during Phases I and II of this project, which have involved both column and laboratory batch experiments. Since this Project is only partially completed, some experiments are currently in progress, and, for this reason, only incomplete data are available for them at this time.

Initial laboratory experiments were designed to investigate the interactions between the two inorganic oxyanions of selenium, selenite and selenate, which predominate in the aqueous phase of soils, and the solid surfaces of the soil itself. The data obtained have revealed that of these two species, selenate is the least interactive and therefore the most mobile. Under the oxic alkaline conditions of the western San Joaquin Valley selenate is the predominant inorganic species, and thus is rapidly leached through soils and into drainage waters. If conditions were more acid, selenite would predominate, and would largely be adsorbed to solid surfaces in the soil.

In response to this finding, a series of experiments, utilizing columns of soil maintained under glasshouse conditions, were conducted to monitor the movement of selenium within the soil profile. Soils were collected to a depth of 2m from both the Panhill and Panoche soil series, and the passage of selenium through the profiles investigated. In order to understand more of the chemistry involved, input waters of differing solution composition were used, with the intention of increasing selenium attenuation in the soil. Both long- and short- term irrigation regimes were investigated, together with the effect of additional organic matter, soluble iron complexes, and the presence of nitrates. Data from the short - term irrigation regimes have been collected and processed, and these indicated that both nitrate and soluble organic material played a significant role in the mobility and speciation of selenium in the soil columns. The presence of significant quantities of organic-selenium associations indicates the importance of this largely ignored aspect of selenium chemistry.

Little is known about its conformation, indeed whether it is a species or series of species, or merely a surface phenomenon involving soluble organic materials. However, its presence necessitates further investigation of its behavior in soils.

The data obtained from the short-term column experiments were used in the design of subsequent long-term irrigation experiments, which are currently in the completion and analysis stage. It is anticipated that the data obtained will give a clearer indication of the chemical processes active in the irrigated profile, and enable recommendations as to the formulation of suitable managerial practices.

The need for a greater understanding of selenium chemistry in soils also has been addressed in the form of laboratory experiments which have been designed to investigate the kinetics of transformation of selenium as a function of oxidation-reduction conditions. These experiments are ongoing, and are not reported at this time.

From the evidence collected to date, it appears that a greater understanding of selenium chemistry in soils is required before any recommendations can be made. However, it is apparent that the soil is a useful tool which can be manipulated to elicit a desired response. Such manipulations may not be desirable under normal agricultural conditions, but could be of significant importance when considering, say, the attenuation of selenium in waste effluent at a location set aside for such a purpose.

CHAPTER 1

STUDY OBJECTIVES

The following objectives were designed to address the question concerning the chemical behavior of selenium in the alkaline irrigated agricultural soils of the Western San Joaquin Valley.

    i. To compare the surface chemistry of the two selenium oxyanions, selenate and selenite, as a function of soil and solution composition, and with respect to the behavior of other anions, including sulfate and nitrate.

    ii. To design glasshouse experiments utilizing columns of Panhill and Panoche soils which would investigate the effect of varying chemical composition on the transport and transformation of selenium in drainage water.

    iii. To investigate the redox kinetics of aqueous selenium species under soil conditions emulating those found typically in the Western San Joaquin Valley.

    iv. To use the results of the experiments outlined in objectives 1 and 2 to design and execute a comprehensive field demonstration at a suitable location in the Western San Joaquin Valley. The results of the field demonstration would be used to aid in the optimization of managerial practices which would lead to a reduction in the transport of selenium in the soil profile.

The behavior of selenium in soils and waters cannot be well understood without a fundamental knowledge of the chemical interactions which affect it. If measures to manipulate this element in irrigated agriculture are to be employed, then the full extent of the impact on the surrounding environment must be evaluated. The overall purpose of this study is to further current understanding of the chemistry of selenium, and provide information which may be utilized in improving the results of anthropogenic impact on the soils and waters of not only the San Joaquin Valley, but wherever selenium toxicity occurs in soils.

This report is presented in six chapters. Chapter 2 addresses the behavior of selenate and selenite in soils, illustrating the importance of differentiating between these two anions, and explaining why selenate predominates in the alkaline conditions of the San Joaquin Valley soils. The data presented in Chapter 3 were collected from a series of preliminary soil column experiments which were designed to investigate the effect of drainage water composition on selenium speciation and mobility. These data were used in the design of subsequent experiments which are described in Chapter 4. Chapters 5 and 6 summarize the current status of the Project and discuss the planned research for the remaining phases.

CHAPTER 2

SELENATE ADSORPTION ON ALLUVIAL SOILS OF THE WESTERN SAN JOAQUIN VALLEY

2.1 Introduction

Selenium in aqueous systems is most mobile in the Se(IV) and Se(VI) oxidation states, and is found predominantly as the anions, SeO_3^{2-}, $HSeO_3^-$ or SeO_4^{2-}, under the pH and redox conditions prevalent in the soils of the San Joaquin Valley (Neal et al., 1987a). It is well known that selenate (SeO_4) predominates in alkaline, oxidized soils and waters. A balance among the three anion species may be ultimately responsible for the effective pollutant load of Se in soils and waters. Studies concerning the sorption of selenate under alkaline, oxidized conditions by soils and soil constituents have given rise to wide ranging results in the literature, the most prominent variation being the extent to which selenate is adsorbed onto solid surfaces. A series of experiments were designed to study the adsorption of selenate on two soils from the Western San Joaquin Valley as a function of pH in order to establish the importance of surface phenomena in the transportation processes of an irrigated profile.

Besides the need to investigate the behavior of selenate in soil systems as a function of pH, the effect of varying solution composition on selenate adsorption was considered. Benjamin (1983) incorporated four cations, including cupric ions (Cu^{2+}), in adsorption experiments to investigate the adsorption of selenate on amorphous iron oxyhydroxide. He reported a significant increase in the amount of selenate sorbed above pH 5.5 when cupric ions were present. Neal et al. (1987b) reported similar findings for selenite adsorption in soil systems to which calcium had been added.

Anion competition with selenate is not widely reported in the literature. Singh et al. (1981) showed that selenate was more effectively desorbed from soils by phosphate than by sulfate, which is in accordance with the more recent findings of Ryden et al. (1987), who ranked a number of anions according to their adsorptive behavior with hydrous Fe oxide gel. The extent of adsorption of these anions ranked selenate seventh out of nine, below sulfate and above chloride, although the authors reported that essentially the same amount of SeO_4^{2-} and SO_4^{2-} were adsorbed. Phosphate and selenite were shown to adsorb much more strongly than selenate. Davis and Leckie (1980) also found the uptake of sulfate and selenate by amorphous iron oxyhydroxide to be essentially equivalent. Selenate transport in soil columns of Panoche loam was found by Goldhamer et al. (1986) to be retarded by the presence of Cl^-, which the authors interpreted to be indicative of specific adsorption of the selenate compared to Cl^-. It may be pertinent to note that Cl^- and SO_4^{2-} anions were added in the form of Ca salts, which may affect SeO_4 behavior through the synergistic effect described earlier.

The objectives of this part of the study were to investigate the adsorption of selenate on weathered alluvial soils from the western San Joaquin Valley at concentrations comparable to those encountered in the field, and compare the behavior with other anions, including selenite, under identical experimental conditions. It was from these data that experiments pertaining to the movement of selenium in the soil profile were designed.

2.2 Material and Methods

2.2.1 Soil Samples and Preparation

The soil samples used in this study and their preparation for sorption experiments have been described in detail by Neal et al. (1987a). In brief, the air-dried <2mm fraction of each soil was washed four times with NaCl solutions, with a final ionic strength of 50 mol m^{-3}. Soil pastes were prepared immediately prior to each experiment, so that storage time was minimized. The electrode potential (redox) of each paste was determined using a platinum electrode together with a calomel reference electrode. It was measured after paste preparation before starting the experiments and at predetermined times throughout the experimental procedure. The moisture content of each paste was determined for each sorption experiment performed, and the quantity of soil and solution varied to obtain a solid:solution ratio of 1:25 w/w.

2.2.2 Sorption Studies

Sorption studies were carried out under the same experimental regime as used by Neal et al. (1987a,b). Additional experiments were performed using soil pastes prepared in 50 mol m^{-3} NaClO$_4$ in order to ascertain the extent of Cl$^-$ exclusion by the soils used. Selenate sorption in 50 mol m^{-3} NaClO$_4$ background was also investigated for comparative purposes. Paste samples containing 1.000g (± 0.05%) oven-dry soil were mixed with 50 mol m^{-3} NaCl or NaClO$_4$ in screw-capped Teflon® centrifuge tubes. The electrode potential was measured prior to, and after adjustments of pH. The latter were made using NaOH and HCl for the selenate and sulfate experiments, and NaOH and HClO$_4$ for those experiments carried out to determine Cl$^-$ exclusion, or selenate sorption in a ClO$_4^-$ background. The initial selenate and sulfate concentrations were 5.3 ± 0.4 mmol SeO$_4^{2-}$ m^{-3} as Na$_2$SeO$_4$, and 0.47 mol SO$_4^{2-}$ m^{-3} as Na$_2$SO$_4$, respectively. Analysis of the Na$_2$SeO$_4$ solution showed >98% Se was present as the selenate species. The samples were equilibrated for 2h in a thermostatically controlled waterbath (298K ± 0.5K). Carbon dioxide-free air (medical grade) was introduced into each sample through a manifold of Teflon® tubing, both to act as a solution agitator and as a means of maintaining the necessary electrode potential to prevent the reduction of selenate to selenite (Neal et al.,1987a). After the equilibration period, the solutions were removed from the waterbath, centrifuged at 12000 RCF, and their electrode potential measured immediately. The samples were then filtered (Nucleopore 0.2μm polycarbonate), and pH was determined using a Ross micro-combination pH electrode.

The collected supernatant solution containing selenate was divided into two portions immediately upon completion of the sorption experiment. One portion was acidified with Instra-analyzed grade concentrated HCl to an appropriate dilution and final concentration of 6M HCl, and frozen. This portion was later analyzed using hydride-generated inductively-coupled plasma spectroscopy to determine the amount of selenite-Se in each sample. The second portion placed in a glass test-tube and acidified with Instra-analyzed HCl to a final concentration of 6M. The samples were heated in containers of boiling water for 0.6h in order to facilitate the reduction of selenate to selenite. Upon completion of the reduction step, the sample was cooled, and then frozen until analysis using hydride generated ICP and/or the colorimetric method of Holtzclaw et al. (1987).

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The effect of Ca^{2+} on selenate sorption was investigated. A final concentration of 50 mol Ca^{2+} m^{-3} was attained by adding $CaCl_2$ simultaneously with selenate. All other steps of the procedure above remained unchanged.

Adsorption experiments designed to compare chloride or sulfate adsorption with the behavior of selenate in soil samples taken from the surface horizons of the Panoche and Panhill soils were carried out on $NaClO_4$ - or NaCl - saturated pastes, respectively. Two other soils from the western San Joaquin Valley were used for comparison. Initial concentrations of 50 mmol Cl^- m^{-3} and 0.47 mol SO_4^{2-} m^{-3} were used. The conditions of these experiments were identical to those described above, with the exception of the analytical determinations. Chloride was determined using a Haake-Büchler digital chloridometer. Sulfate determinations were made using Technicon Autoanalyzer II.

2.3 Results and Discussion

The adsorption of selenate, sulfate and chloride was expressed quantitatively as the percentage of the initial anion concentration lost from solution during the equilibration period of the experiments.

Within the precision of the experimental method, no net loss of selenate from solution was detected at any pH value in systems containing soil pastes prepared in 50 mol m^{-3} NaCl background solution (Fig. 1). The response for all soils was similar, indicating that the existence of soil compositional differences which may exist - and indeed were important in the case of selenite adsorption (Neal et al. 1987a) - had a negligible effect on the sorptive behavior of selenate under the experimental conditions.

Although the Eh values obtained would seem to suggest the possible existence of selenite in systems below pH 7.3, the apparent lack of this species at equilibrium may be explained by one or both of the following hypotheses. Firstly, although precision was less than 5%, the accuracy of the Eh measurements maybe insufficient to compare the values obtained with thermodynamically derived data to the level of detail suggested, namely the distribution of species in a system. Secondly, the equilibration time of the experiments was significantly less than would be expected necessary for a redox conversion between selenate and selenite to occur. Page et al. (1986) reported the transformation of selenate to selenite under flooded conditions occurred after "a few days", which is appreciably longer than the time period in the present experiments.

Figure 2 illustrates an example of the relative sorptive behavior of four oxyanions, selenate, selenite, sulfate and chloride. The anions were equilibrated with the soil, and the amount of anion attenuated was expressed as a percentage of its initial concentration. Sorption of SeO_4^{2-}, SeO_3^{2-} (Neal et al.,1987) and SO_4^{2-} were observed in a background of 50 mol m^{-3} NaCl. Chloride sorption was investigated in $NaClO_4$ electrolyte. (A comparative investigation of SeO_4^{2-} and SeO_3^{2-} sorption on $NaClO_4$-saturated pastes revealed that the amount of Se sorbed was unaffected by the nature of the background electrolyte). Selenite exhibited positive attenuation, especially at lower pH values, whereas, as previously discussed, negligible attenuation of SeO_4^{2-} was observed. The behavior of SO_4^{2-} was found to be almost identical to that of SeO_4^{2-} under the conditions imposed, indicating a similarity in behavior between these two anions as suggested by Ryden et al. (1987). Although the Cl data were of poorer quality than shown by the other anions, the phenomenon of anion exclusion was exhibited as expected. These data suggest a difference
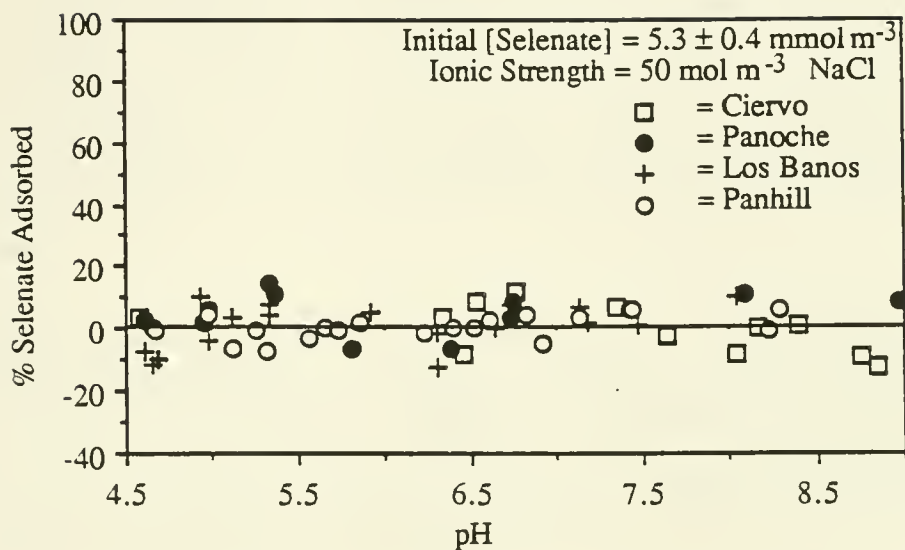
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Figure 1. Adsorption of selenate by four alluvial soils from the western San Joaquin Valley
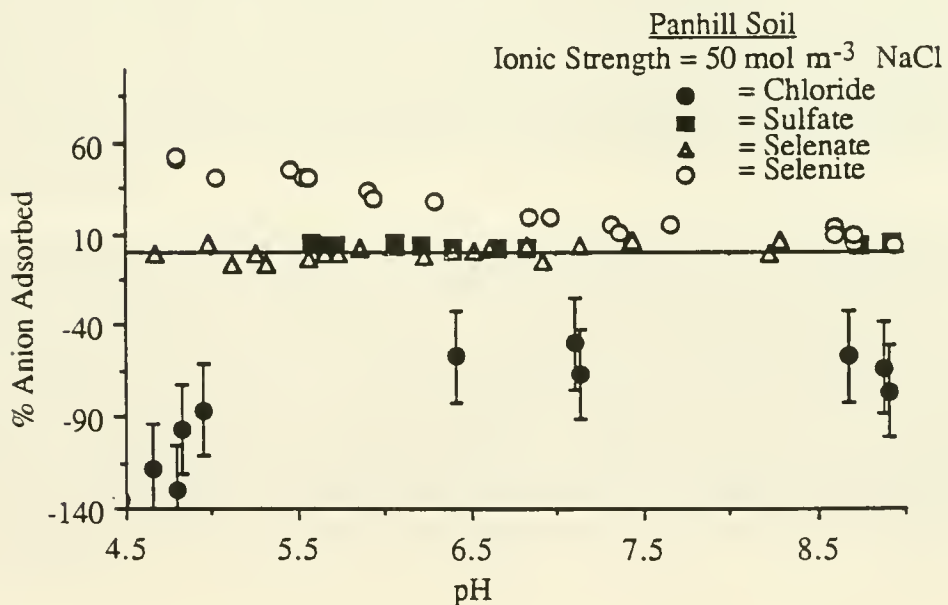

Figure 2. Adsorption of four anions on Panhill soil. Initial anion concentrations were 50 mmol Cl⁻ m⁻³, 5.2 ± 0.2 mmol SeO4²⁻ m⁻³, 1.90 mmol SeO3²⁻ m⁻³, 0.47 mmol SO4²⁻ m⁻³

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in the surface behavior of anions such as SeO_4^{2-} and SO_4^{2-} as compared with Cl^- and, by association, NO_3^-.

The recent findings of Hayes et al.(1987), who utilized extended X-ray absorption fine structure (EXFAS) measurements to provide structural information concerning ions sorbed at the goethite-water interface, further substantiate these results. These authors showed that selenate forms a weakly bonded, outer-sphere surface complex, in contrast to the strongly bonded inner-sphere surface complex formed by selenite. The data presented here would seem to indicate that selenate, and probably sulfate, retain a hydration shell when sorbed, and thus are not as "strongly" attracted to solid surfaces as selenite which was shown to be sorbed directly onto a goethite surface. These relative distances also have been suggested by Sposito (1984, Chap.5) in a schematic portrayal of an inorganic hydroxyl surface.

In light of the findings reported by Benjamin (1983) that selenate adsorption on amorphous iron oxyhydroxide was positively affected by the addition of divalent cations such as Cu^{2+}, and the response of selenite to the addition of Ca^{2+} reported by Neal et al. (1987b), selenate sorption was investigated in the presence of 50 mol $CaCl_2$ m^{-3}. The absence of any significant difference between the systems comprising either 50 mol m^{-3} Na or 50 mol m^{-3} Na/Ca (data not shown), indicated that a mechanism similar to that involving selenite (Neal et al, 1987b) and selenate (Benjamin, 1983), does not seem to play a significant role in the behavior of selenate in soils.

2.4 Conclusions

From the data reported in section 2.3 it was concluded that of the two inorganic species of selenium which predominate in soil systems, selenate, the most prevalent ion in oxic alkaline systems, was the least reactive towards soil surfaces, and thus potentially the most mobile. The behavior of selenate under the conditions described is though to most closely resemble that of sulfate, and therefore would be displaced easily from soil surfaces by more specifically adsorbed anions such as phosphate, selenite etc. Synergistic effects reported for selenite with calcium (Neal et al. 1987b) and selenate with copper (Benjamin, 1983), were not detected for selenate with calcium in these experiments, indicating the absence of a controlling mechanism which might be associated with precipitation and/or increased surface attraction.

These findings were considered in addressing the problem of increasing the attenuation of selenium in soils. Since the attenuation of selenite may be greatly enhanced through the addition of calcium to a system, such a control on the movement of selenate could be facilitated through the reduction of the more oxidized species to this form. Few sources in the literature report kinetic data for such transformations, either between selenate and selenite or between these species and organic forms. Little evidence is cited for the interaction between these oxyanions and soluble organic material, which may also play a major role in the behavior of selenium. Column experiments were designed to address some of these aspects, and, latterly, a series of laboratory experiments have been instigated with the intention of increasing our knowledge pertaining to the chemistry of this element in soil systems.

CHAPTER 3

TRANSFORMATION AND MOBILITY OF SELENIUM IN THE SOIL PROFILE

3.1 Soils

3.1.1. Collection of Soil samples

Soil samples were collected on February 3 & 4 1988, from two locations in West Fresno County. Soil from the Panhill soil series was collected from a site at T13 R12 s17, and soil from the Panoche soil series was collected from a site at T15 R13 s22.

The soil was removed in 0.5m sections down to a depth of 2m using a hydraulically operated stainless steel 4" soil corer. A random pattern of collection points within a marked location was established. Samples taken at each point were divided into the appropriate 0.5m depth portion and placed in 20 gal. containers lined with plastic bags. This resulted in the collection of four bulk samples at each site. Sub-samples to determine the field moisture content at each depth were taken at each sampling point using pre-weighed cans. These cans were sealed and stored until the return to UC Riverside on February 5. Immediately upon return the sub-samples were weighed and dried in a thermostatically controlled oven at 110°C for 48 h.

The soils from each fraction collected in the 20 gal. cans, were homogenized using a concrete mixer. These were then stored in the plastic-lined cans until required. A subsample was taken after homogenization to be used for chemical and physical laboratory determinations. Subsequent portions of the soil have been air-dried, passed through a 2mm screen and used in a series of glasshouse column experiments.

3.1.2. Physical and Chemical Properties of the Soils

3.1.2.1. Particle Size Analysis

Particle size analysis was performed using the Pipette Method (Gee and Bauder, 1986). The mineral fraction was partitioned into three size fractions; clay, ($<2\mu m$) , silt, ($>2\mu m$ $<53\mu m$) , and sand, ($>53\mu m$). Figure 3 illustrates the variation in the amount of these particle size fractions within the two soil profiles. Perhaps the most noteworthy feature is the presence of increased amounts of sand in the 0.5 - 1.0 m section of the Panoche soil. This would appear indicative of a sand "stringer", and may be an important consideration for selenium transport. Data reported in Table 1 revealed an average of ~ 10% of the whole soil fraction may be attributed to organic material, soluble salts, carbonates and iron oxides, which are all removed during particle size analysis.
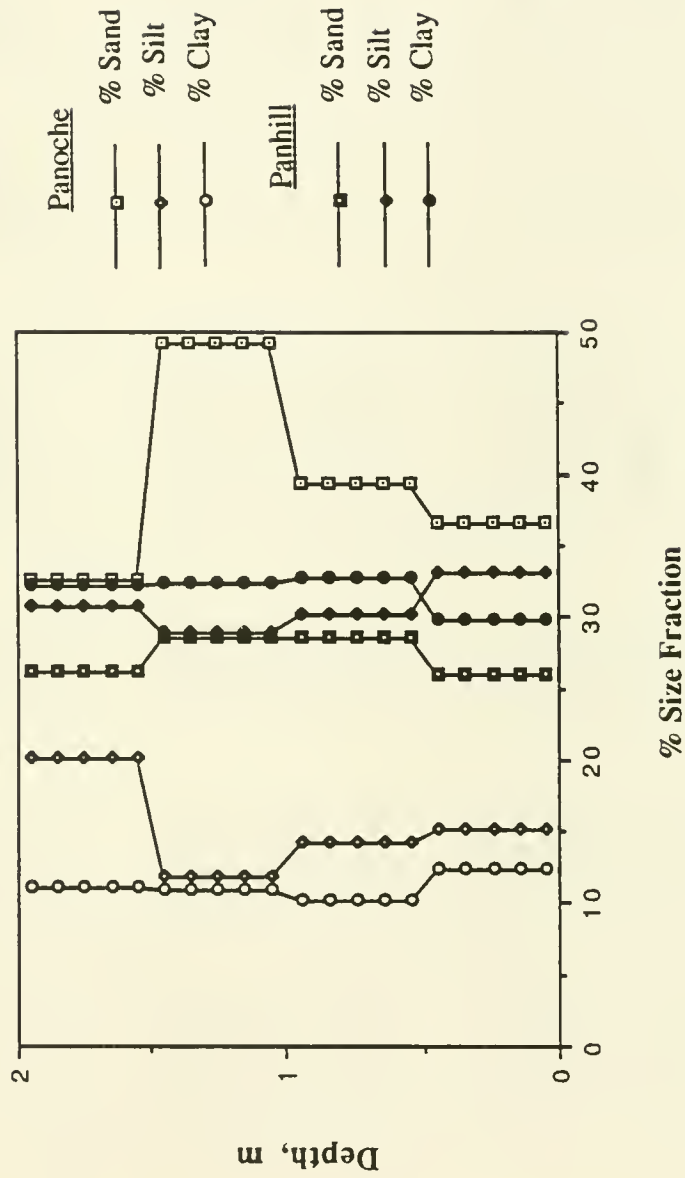
Figure 3. Distribution of sand, silt and clay in Panoche and Panhill soil profiles

Table 1. Selected Physical Characteritics of the Panhill and Panoche Soils.

Soil / Depth m	Particle size analysis			Predominant Clay Minerals †	% Kaolinite §	Total Carbon Content %
	% Sand	% Silt	% Clay			
Panhill						
0 - 0.5	26.3	30.8	32.3	S, V, M, K	17.77	7.1 ± 0.3
0.5 - 1.0	28.6	29.0	32.4	S, V, K, M	16.22	7.09 ± 0.02
1.0 - 1.5	28.6	30.2	32.8	S, V, K, M	18.62	6.9 ± 0.2
1.5 - 2.0	26.0	33.1	29.8	S, V, K, M	14.81	7.1 ± 0.2
Panoche						
0 - 0.5	32.6	20.2	36.1	S, K, V, M	21.46	7.32 ± 0.06
0.5 - 1.0	49.3	11.8	27.9	S, K, V, M	20.91	7.13 ± 0.09
1.0 - 1.5	39.4	14.4	36.0	S, K, V, M	21.00	7.09 ± 0.06
1.5 - 2.0	36.6	15.2	35.8	S, K, V, M	27.94	7.01 ± 0.05

† Clay Minerals are presented in order of relative quantity. S = smectites, K = kaolinites, V = vermiculites, M = micas.

§ % kaolinite = the percentage of the total clay minerals present as kaolinite, as determined by Thermographic analysis

3.1.2.2. Carbon Content

Total Carbon was determined using a Dohrmann Carbon Analyzer. The data shown in Table 1 reveal little variation in the amount of carbon present in both the two soils and throughout the soil profiles.

3.1.2.3. Characterization of Clays

The predominant clay minerals present in the soil samples were identified using a Siemens X-ray Diffractometer. Samples were prepared according to the method of Jackson (1979). Montmorillonite was found to predominate in these soils, and was present together with traces of vermiculite, kaolinite and mica. The amount of kaolinite present in the clay fractions was quantified thermographically, and found to be slightly higher in the Panoche soil. (Table 1)

3.1.2.4. Oxide Determination

Iron, manganese, and aluminum oxide contents were quantified using ammonium oxalate extraction and citrate-bicarbonate-ditionite (CBD) extraction techniques as described by Jackson et al. (1986). Ammonium oxalate was used to determine the quantity of noncrystalline aluminosilicates and hydrous oxides, and CBD for determining free iron-aluminum oxides and hydroxides. The data obtained are illustrated in Table 2b.

In general, the quantities of amorphous and crystalline oxides recovered were low, with little evidence for change with depth in either profile. With the exception of amorphous iron, the Panhill soil had slightly greater oxide content than the Panoche soil, irrespective of profile depth.

The slightly lower concentrations of both iron and aluminum CBD-extractable oxides in the 0.5 - 1.0m section of the Panoche profile may be correlated with the elevated amount of sand and the proportionately lower percentage of the silt fraction found at this depth (section 3.1.2.1).

3.1.2.5. Saturation Extracts

Saturation extracts were made from each soil sample according to the method of Chapman and Pratt (1978). The cation composition of the extracts was determined using Inductively Coupled Plasma spectroscopy (ICP). Concentrations for selenium, calcium and manganese are reported in Table 2a. Selenium was not detected in the extracts from the Panhill soil. Selenium concentrations in extracts from the Panoche soil were low (<0.75 μmol kg^{-1}), and present as the selenite species.

Values for pH showed some variation with depth. The pH of Panhill soil ranged between 8.03 ± 0.05 and 7.64 ± 0.02, with the highest pH occurring between 0.5 and 1.0 m depth. Less variation was apparent for the Panoche soil where the pH ranged between 7.84 ± 0.01 and 7.71 ± 0.05.

The oxidation - reduction potential (Eh) also indicated greater variation in the Panhill soil, where a value of 548 ± 5 mV was determined for the surface section. The redox of the deeper sections was found to be significantly lower. Redox measurements of the Panoche soil extracts showed no significant difference as a function of soil depth, and were lower in value than those found for the Panhill soil.

Table 2a. Selected Chemical Characteristics of Saturation Extracts Taken From the Panhill and Panoche Soils.

Soil/depth m	pH	Eh (mV)	EC dS m⁻¹	Se µmol kg⁻¹	Ca mmol kg⁻¹	Mn µmol kg⁻¹
Panhill						
0 - 0.5	7.88 ± 0.09	548 ± 5	1.69 ± 0.17	ND	2.07 ± 0.03	0.08 ± 0.01
0.5 - 1.0	8.03 ± 0.05	496 ± 7	1.32 ± 0.15	ND	1.52 ± 0.01	0.07 ± 0.02
1.0 - 1.5	7.69 ± 0.04	484 ± 5	2.64 ± 0.0	ND	11.0 ± 0.1	0.2 ± 0.1
1.5 - 2.0	7.63 ± 0.02	479 ± 2	2.66 ± 0.05	ND	5.90 ± 0.02	0.07 ± 0.02
Panoche						
0 - 0.5	7.84 ± 0.01	478 ± 4	2.99 ± 0.05	0.04 ± 0.03	7.6 ± 0.2	0.12 ± 0.01
0.5 - 1.0	7.71 ± 0.05	475 ± 1	4.52 ± 0.16	0.11 ± 0.10	6.3 ± 0.1	0.07 ± 0.01
1.0 - 1.5	7.78 ± 0.02	472 ± 7	6.93 ± 0.07	0.45 ± 0.10	6.53 ± 0.03	0.09 ± 0.01
1.5 - 2.0	7.76 ± 0.03	465 ± 4	8.59 ± 0.04	0.75 ± 0.05	6.61 ± 0.09	0.06 ± 0.01

ND - not detected

Table 2b. The Distribution of Noncrystalline Aluminosilicates and Hydrous Oxides, and Free Iron-Aluminum Oxides and Hydroxides as Determined by Selective Dissolution

Soil and Depth in meters	Ammonium Oxalate Extractable			Citrate-bicarbonate-dithionite Extractable		
	Fe	Mn	Al	Fe	Mn	Al
	----------g/kg oven dry soil----------			----------g/kg oven dry soil----------		
Panhill						
0 - 0.5	0.44 ± 0.00	0.22 ± 0.03	0.57 ± 0.02	14.66 ± 0.00	0.27 ± 0.00	0.88 ± 0.00
0.5 - 1.0	0.43 ± 0.02	0.25 ± 0.01	0.54 ± 0.01	14.52 ± 0.00	0.33 ± 0.00	0.83 ± 0.03
1.0 - 1.5	0.44 ± 0.00	0.26 ± 0.03	0.50 ± 0.01	14.74 ± 0.08	0.27 ± 0.00	0.80 ± 0.00
1.5 - 2.0	0.41 ± 0.04	0.23 ± 0.03	0.46 ± 0.05	14.31 ± 0.08	0.29 ± 0.01	0.81 ± 0.00
Panoche						
0 - 0.5	0.53 ± 0.02	0.14 ± 0.00	0.46 ± 0.01	12.49 ± 0.19	0.26 ± 0.00	0.69 ± 0.00
0.5 - 1.0	0.55 ± 0.04	0.15 ± 0.01	0.40 ± 0.06	10.59 ± 0.04	0.27 ± 0.03	0.52 ± 0.00
1.0 - 1.5	0.67 ± 0.02	0.15 ± 0.00	0.43 ± 0.00	12.26 ± 0.15	0.25 ± 0.01	0.60 ± 0.00
1.5 - 2.0	0.56 ± 0.05	0.14 ± 0.01	0.43 ± 0.00	12.30 ± 0.38	0.24 ± 0.00	0.62 ± 0.02

Electrical conductivity was determined using a dipping cell (cell constant 1.00) in connection with a conductivity meter. The EC for the Panoche soil was significantly higher than the Panhill soil, reaching a value of 8.59 ± 0.04 dS m^{-1} between a depth of 1.5 and 2 m. In both soils, EC increased with increasing depth, although much greater values were recorded for the Panoche soil throughout the whole profile.

3.2 Glasshouse Soil Column Studies - Phase 1

A series of Glasshouse soil column studies have been carried out under various environmental conditions. Experiments 1, 2, and 3 have been completed, and the results will be described in this chapter. Experiments 4,5,6, and 7 were completed in September, and preliminary findings will be discussed in Chapter 4.

3.2.1. Experiments 1,2 and 3

3.2.1.1. Objectives

The objectives of the first three experiments were to investigate the following:

> A. the effect of differing soil compositional effects on the behavior of selenate in drainage water.

> B. the effect on selenate mobility of the redox potential of the soil system as a function of solution composition.

3.2.1.2. Experimental Design

Air-dried 2mm soil was packed into 5.5 x 60 cm plastic irrigation pipe to a depth of 50.0 cm. The soil was supported in the column by a perforated plastic plate, a piece of nylon mesh, and a thin pad of fiberglass. Synthetic drainage water, containing selenate (350 ppb) and of a composition suggested by the San Joaquin Valley Drainage Program (as indicated by the attached document), was applied to the top of each column in three 150 mL increments. These increments were applied six times over a 14 day period. The soil surface was covered by a circle of filter paper to minimized surface disturbance during application. The top of each column was covered with film to prevent the introduction of extraneous material and moisture.

The columns were exposed to three experimental conditions. These were in the form of differing input water composition. Table 3 illustrates the constituents of each input water. Experiment 1 was designed to represent a controlled system with which the results of Experiments 2 and 3 were compared. Experiment 2 was designed to investigate the effect of nitrate on selenium behavior in the columns, and so nitrate salts were omitted from the input water. The conditions of Experiment 3 were similar to those of the Experiment 1 with the exception of the addition of an organic source in the form of glucose.

Leachate emerged from the bottom of each column after the third application of water. The leachate was collected using plastic funnels mounted at the base of each column, which directed the solution into sealed polyethylene bottles. Three fractions were collected following the application of the drainage water, and their volume determined. On the 14th day after the first irrigation the columns were dismantled. The soil was sectioned into

Table 3. Composition of Input Water for Experiments 1 to 3

Constituents	Expt.1	Expt.2	Expt.3
	------------------mmol L^{-1} ----------------		
$CaSO_4.2H_2O$	12.5	12.5	12.5
$Na_2SO_4.10H_2O$	32.3	32.3	32.3
$NaHCO_3$	4.91	4.91	4.91
KCl	0.13	0.13	0.13
$MgCl_2.6H_2O$	12.3	12.3	12.3
$NaNO_3$	2.14	-----	2.14
NaCl	31.6	33.74	31.6
H_3BO_3	1.2	1.2	1.2
Na_2SeO_4 *	0.004	0.004	0.004
Glucose	-----	-----	6.6 g/L

* 0.004 mmol Na_2SeO_4 L^{-1} ¡ 0.315 mgSe L^{-1}

10 cm portions as measured from the base of each column. The moisture content of each portion was determined immediately. The remaining soil was mixed with deionized water until the consistency of a saturated paste was reached. The pastes were left to equilibrate for 16 h, at which time the aqueous portion was extracted by vacuum filtration.

A portion of the extracted liquid was analyzed immediately for total selenium and a suite of other elements using Inductively Coupled Plasma spectroscopy (ICP). Two additional portions of each extractant were acidified immediately with HCl (6N) and stored at 4°C, in preparation for the determination of selenite and selenate using Hydride Generated Atomic Absorption Spectrophotometry (HGAAS). The remaining portions of extractants were used for the determination of the redox potential (Eh), pH, electrical conductivity, and nitrate and chloride ion content.

3.2.1.3. Results and Discussion

Data generated from these experiments are expressed as a function of the whole profile depth. The results obtained enable differences in soil composition which may occur within the profiles to be identified.

3.2.1.3.1. Composition of Leachates

The volume of leachate collected from each column is presented diagrammatically in Figure 4. In most instances leachate was collected from all columns with the exception of the 1.5 - 2.0 m Panhill section and corresponding Panoche section in Experiment 2 and the 0 - 0.5 m and 1.5 - 2.0 m sections of the Panoche soil in Experiment 3. No leachate from these columns had appeared by the designated collection time. The data indicate the 0-0.5m section of the Panhill profile to be the least water retentive section of this soil, whereas no significant trend was found for the Panoche soil in spite of the elevated amount of sand present in the 0.5 - 1.0m section of the latter.

The speciation of selenium in the leachates collected from the columns are shown in Figures 5 and 6. Columns for which no data are presented are due either to the the absence of leachate, as outlined in the previous paragraph, or through loss of sample. A number of important features are immediately apparent. Firstly, that the speciation of the leachate was dependent on the chemical composition of the input water. Although the overall composition of the leachate varied with both profile depth and leachate chronology, in most instances selenate contributed a significant portion in the leachates collected from Experiment 1. Both organic selenium species and traces of selenite were also present, most especially in the first leachate fraction, although the amount of organic selenium decreased to below detection with each subsequent fraction. In contrast, the leachates recovered from the second experiment were comprised almost entirely of selenate, with the exception of the 0.5 - 1.0 m portion of the Panoche soil, where a significant portion of organic selenium was detected in both the first and second leachate samples. It is possible that this anomaly may be correlated with the increased amount of sand in this section of the profile, which may not attenuate organic selenium as well as the other more finely textured sections.

The conditions imposed in Experiment 2 were investigated in response to recent findings that the presence of nitrate in waters produces oxidizing conditions, thus causing selenium to remain soluble (Weres 1988, pers. comm.). Current opinion hypothesizes that the subsequent reduction of nitrate promotes reducing conditions, and thus enhances selenium reduction through microbiological processes (Fraley et al. 1987). From the data
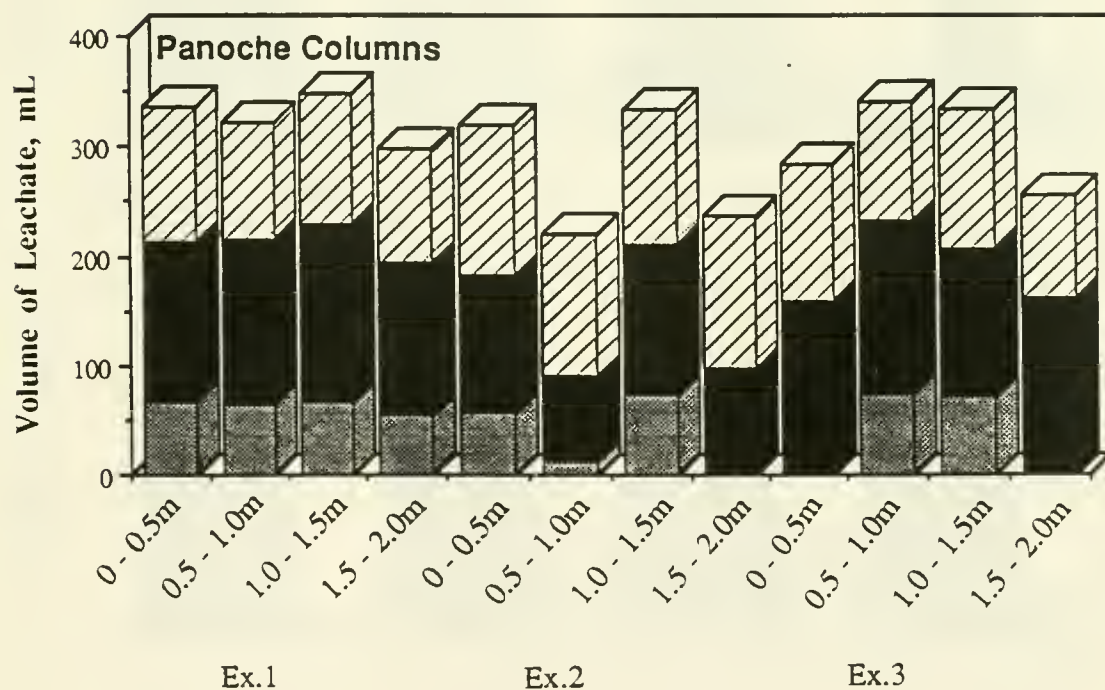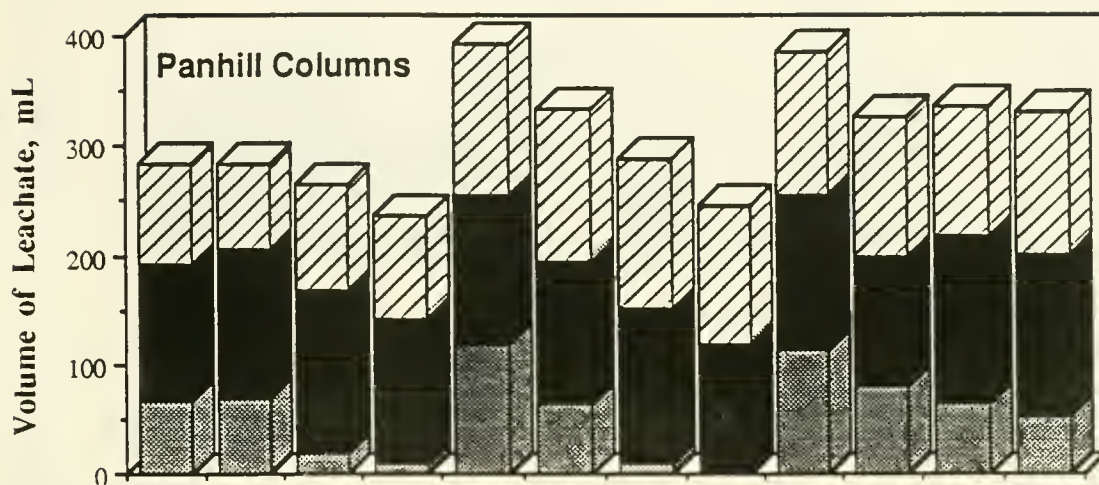
Figure 4. Volume of leachate eluted from the soil columns in Experiments 1 to 3
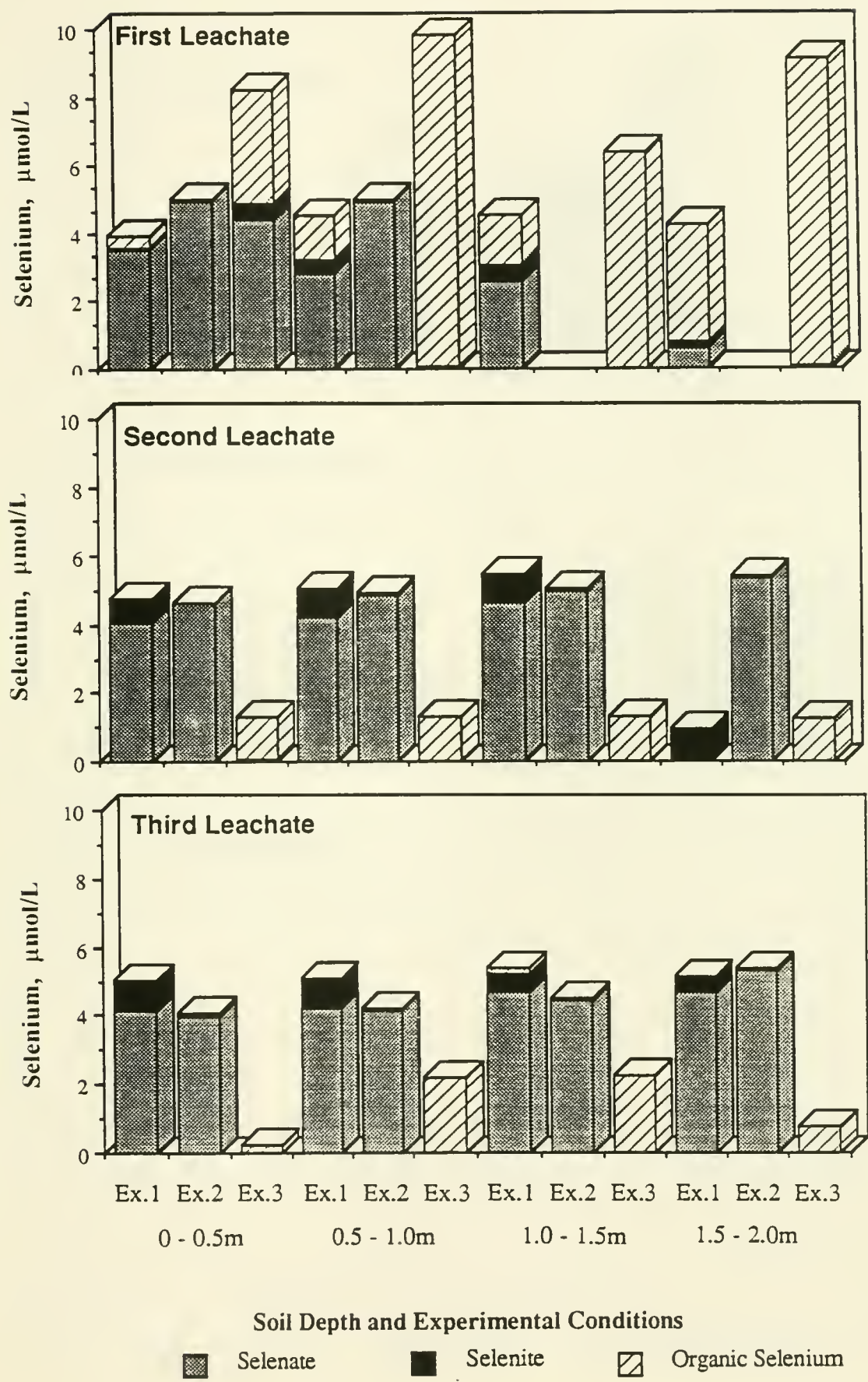
Figure 5. Selenium speciation in the leachates collected from the Panhill soil columns
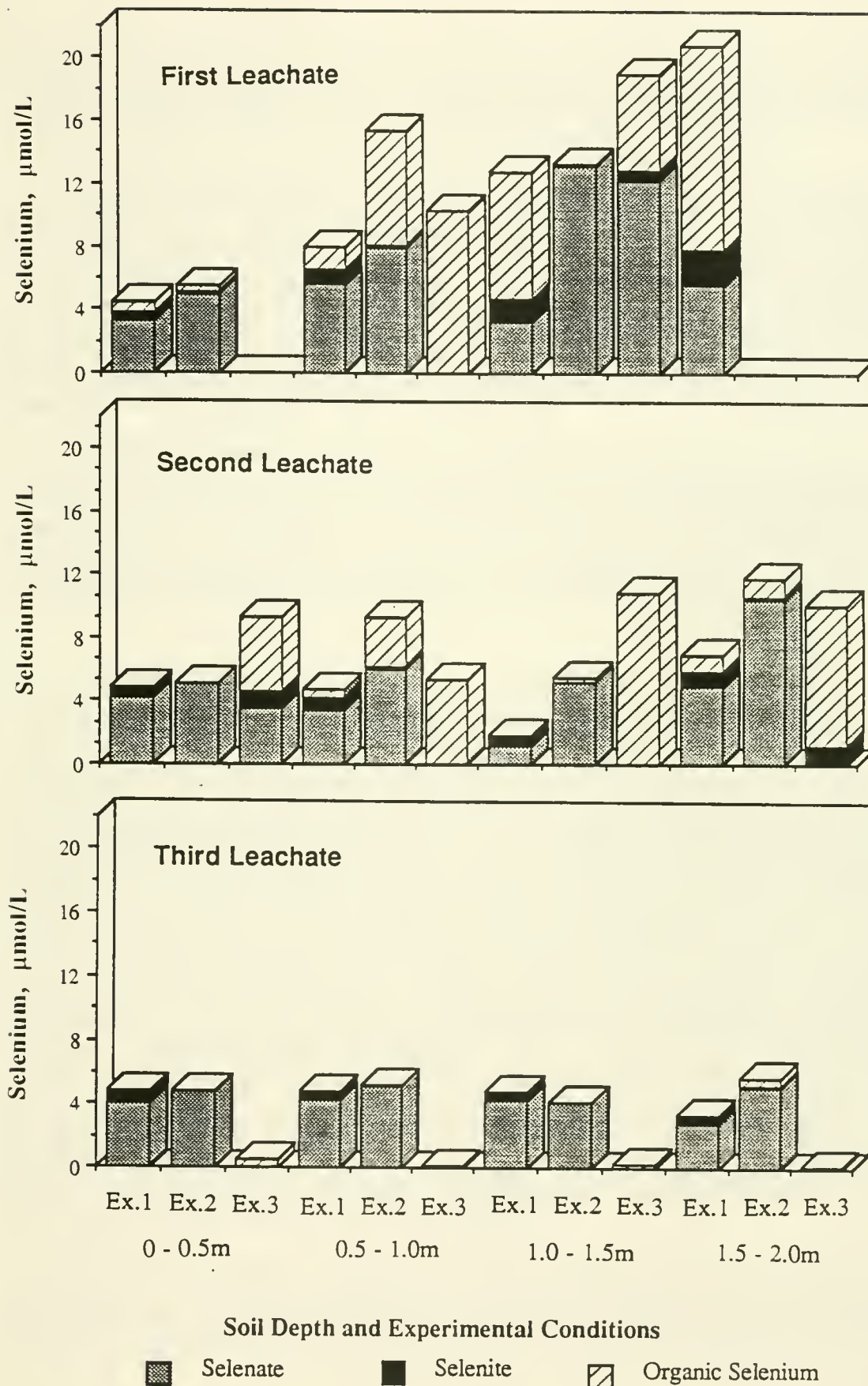
Figure 6. Selenium speciation in the leachates collected from the Panoche soil columns

presented in this section it would appear that the absence of nitrate in the input water resulted in negligible transformation of selenate in the soil profile. The presence of trace amounts of organic selenium in the columns of Experiment 1 indicate that under the conditions of these experiments some transformation of selenate was occurring.

Input water for the third experiment included a carbon source, in the form of glucose, with the objective of increasing microbial activity within the soil profile. The concentration and speciation of selenium leached from these columns were quite dissimilar to those previously discussed. Concentrations of soluble selenium in the first fraction of Experiment 3 were in general greater than those determined in Experiments 1 and 2, but this decreased significantly in the second and third fractions. Indeed, the amount of soluble selenium eluted in the third fraction was significantly smaller than those of Experiments 1 and 2. Chemical speciation of the leachates indicated that in most instances the selenium was predominantly in an organic form, or associated with soluble organic material, since negligible quantities of selenate or selenite were detected.

Very little information is available at the present time as to the nature of the organic selenium association. That such large quantities were eluted during the first leachate collection period would seem to indicate a behavioral pattern not dissimilar to negative adsorption such as that exhibited by chloride ions. This phenomenon would explain the much lower concentrations of this "species" in the later leachate fractions. Clearly more information pertaining to this seemingly important association is necessary if the transport and transformation mechanisms of selenium are to be better understood.

3.2.1.3.2. Distribution of Soluble Selenium in Soil Columns

The distribution of total soluble selenium entrained within the soil columns upon conclusion of these experiments is illustrated in Figures 7 and 8. The data for Experiment 1 revealed a reasonably consistent distribution of approximately $3\mu mol\ kg^{-1}$ soluble selenium throughout the soil profiles of both soil types (calculated as concentration per kg soil solution present at completion of each experiment). Speciation analyses revealed that approximately 30% of the soluble selenium was present as selenate, and that the remainder was probably present as currently unidentified organic forms. Concentrations of selenite were negligible. The distribution between the species was found consistent throughout the column irrespective of soil composition. These findings indicate that under the control conditions imposed in Experiment 1, selenium mobility was evident, and that this may be attributed to the selenate species. The presence of a significant amount of organically associated selenium in the soil profile, which was correspondingly less evident in the leachates, would seem to indicate that given a sufficient residence time, selenate may either be transformed into an organic species, or may be attenuated through an interactive process with organic materials. The behavior of the organic species is as yet unknown, especially in the area of surface interactive phenomena. The absence of any significant amounts of selenite may be indicative of the absence of a reduction transformation to this species, or that, if present, this species was 'irreversibly' sorbed to the soil surfaces as defined by the experimental procedures outlined in section 3.2.1.2. Concentrations of soluble manganese, which may be used as an indicator of redox potential, were $< 1\ \mu mol\ kg^{-1}$, and measured Eh ranged between 460 and 590 mV.

The absence of nitrate from the input water used in Experiment 2 had a marked effect on the distribution of selenium within the soil columns. Total selenium analyses showed similar amounts of soluble selenium were present in the columns as were in those of Experiment 1. However, subsequent speciation of these solutions revealed that in most
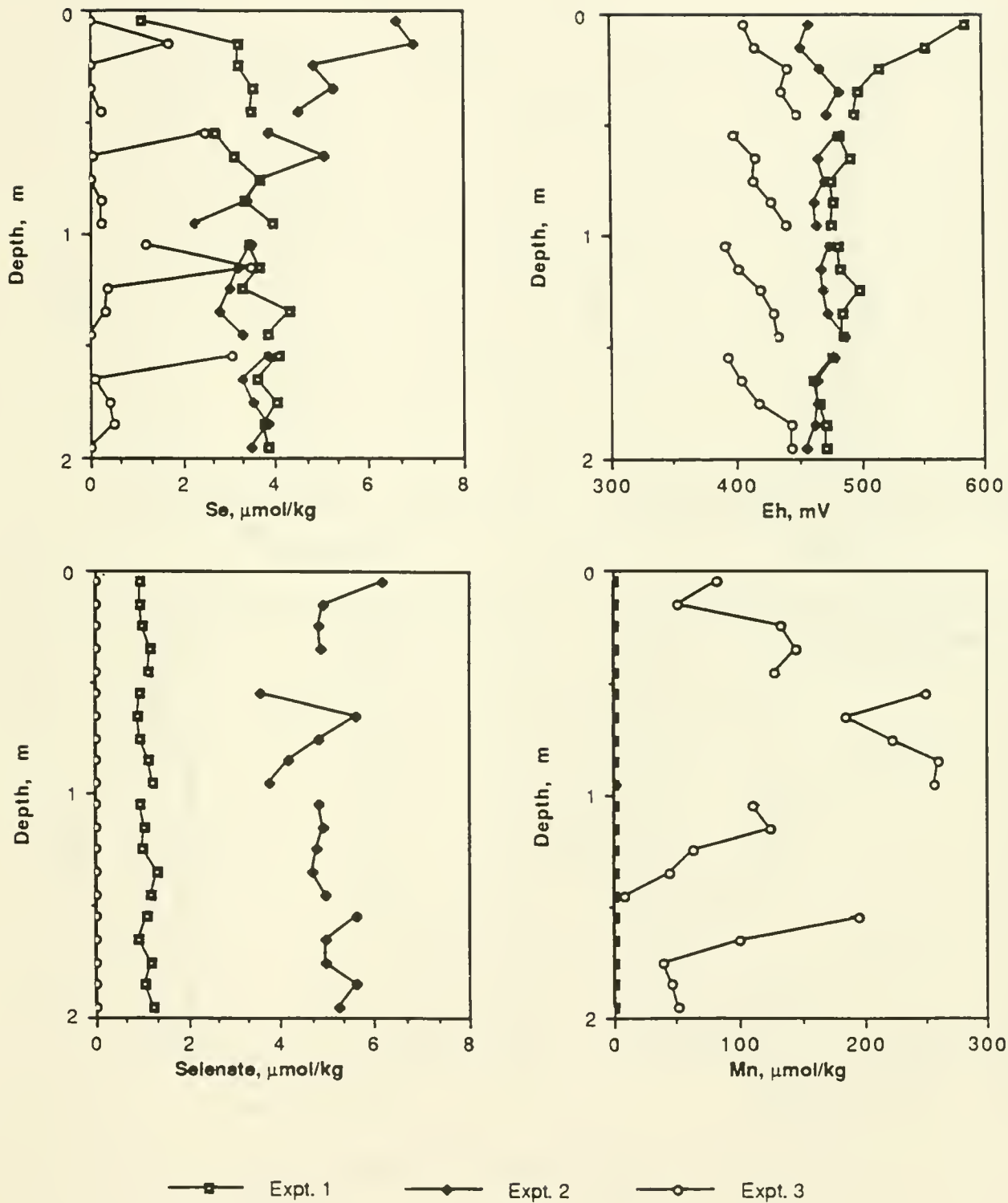
Figure 7. Variations in the concentration of soluble selenium, selenate, and manganese, and the redox potential with depth in the Panhill soil columns as a function of experimental conditions.
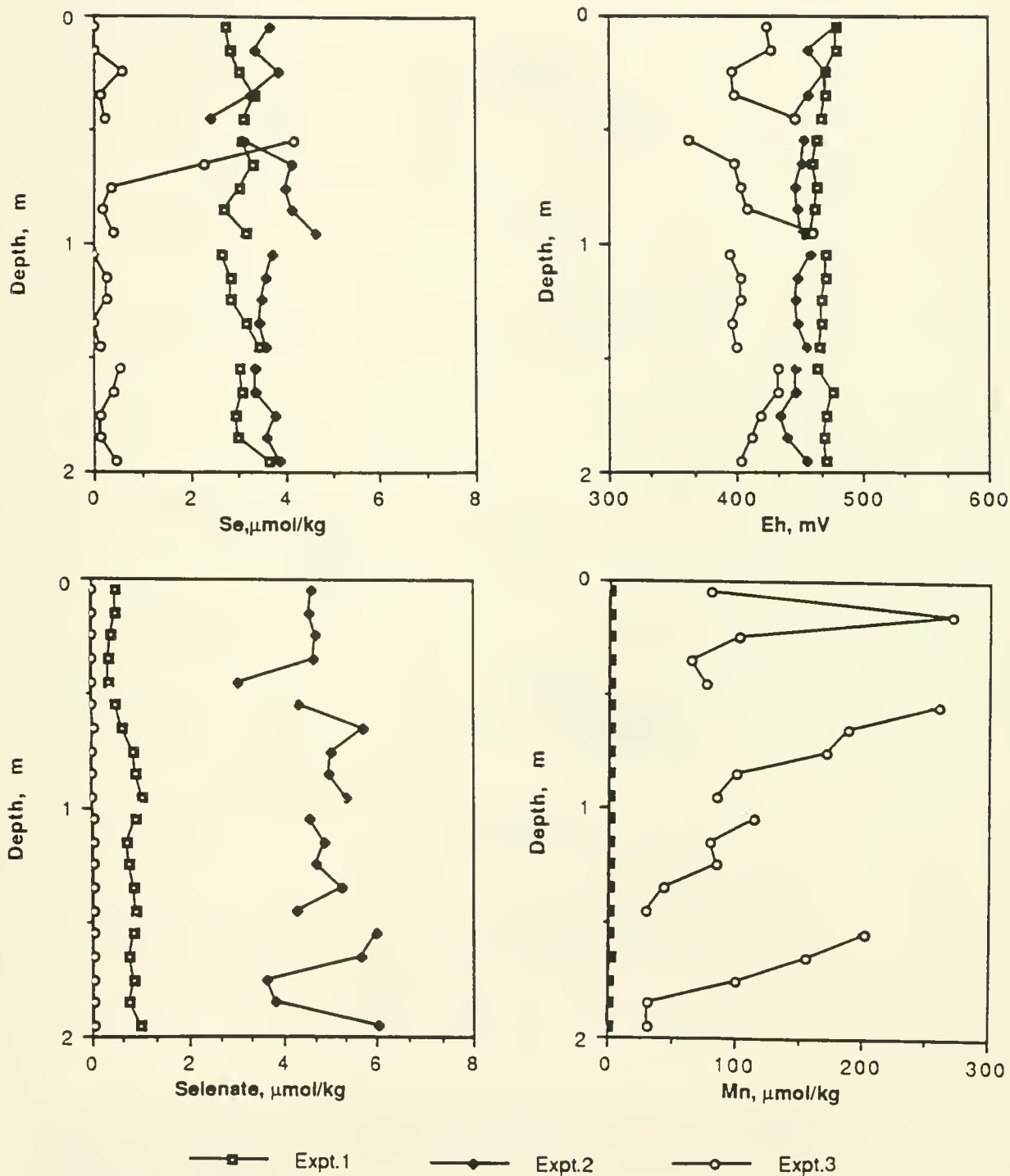
Figure 8. Variations in the concentration of soluble selenium, selenate, and manganese, and the redox potential with depth in the Panoche soil columns as a function of experimental conditions.
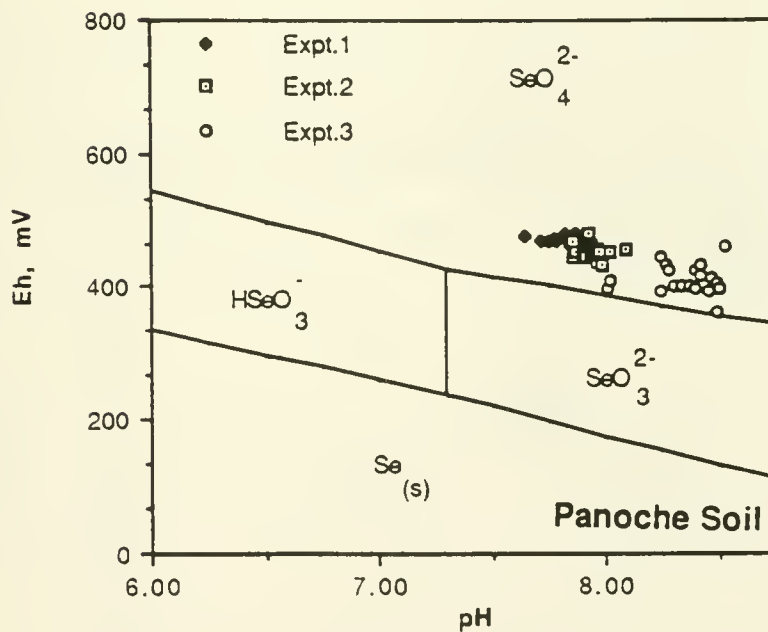
Figure 9. Redox potential vs. pH of soil solution in Panhill and Panoche soils superimposed on Se thermodynamic data and plotted as a function of experimental conditions
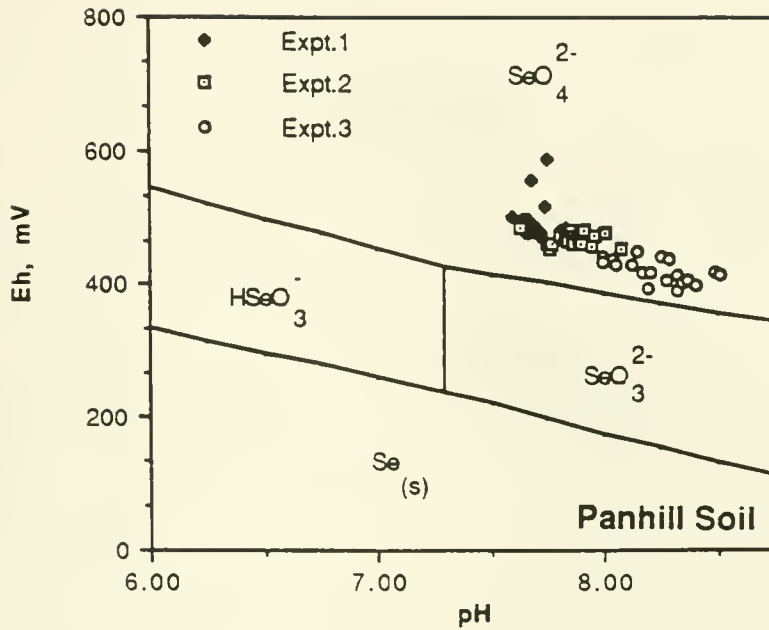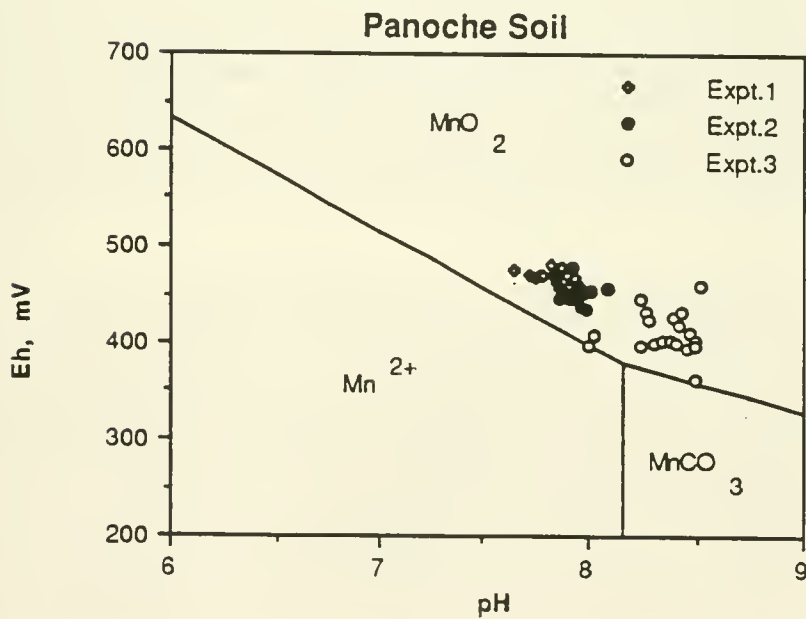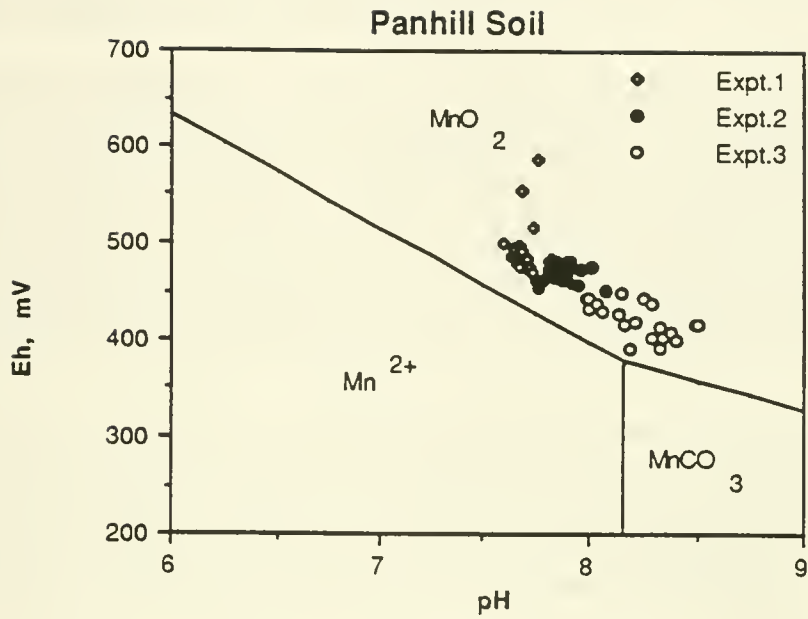
Figure 10. Redox potential vs. pH of soil solution in Panhill and Panoche soils superimposed on Mn thermodynamic data and plotted as a function of experimental conditions

instances > 97 % of the soluble selenium was in the selenate form, with traces of selenite. The distinct absence of organically associated selenium would suggest that the formation of such species may well be microbially mediated, and such a mechanism may require the presence of nitrate. The Eh status and soluble manganese concentrations were not significantly different from those in Experiment 1.

The addition of glucose to the input water used in Experiment 3, elicited dramatically different responses compared with those of Experiments 1 and 2. Concentrations of soluble selenium in the soil profiles were significantly reduced in comparison with the control conditions, and little selenate or selenite was detected in any of the solutions. Since negligible quantities of inorganic selenium were detected, the increased concentrations of soluble selenium present in the upper portions of each of the Panhill soil columns, and to a much lesser extent the Panoche soil columns, may be attributable to organic associations, and would suggest that attenuation processes may be occurring. Elevated selenium concentrations in the 0.50-0.70m sections of the Panoche soil corresponded to the increased sand content found at this depth, as illustrated in Figure 8.

The redox status of both soils was affected by the addition of glucose. Redox values in Experiment 3 were lower than for both Experiments 1 and 2, and appeared to increase slightly with the depth of each individual column. Values for pH were slightly higher than had been recorded for the previous experiments and exhibited a slight decrease with depth. Redox and pH values for all three experiments have been plotted together with theoretical thermodynamic data for aqueous inorganic selenium species in figure 9.

It is important to consider two points at this stage of the discussion. Firstly, Eh measurements were made on the saturation extracts and not on the soils themselves and may, therefore, not present a true representation of the actual redox status of the columns. Secondly, the superimposition of experimental data pertaining to soils upon thermodynamically calculated data from so called 'pure systems' has its limitations, and this fact should be recognized in the interpretation of the data. The inclusion of glucose in the input water of Experiment 3 resulted in increased pH values, and a slight decrease in the redox potential. Although this appears negligible compared to the changes that appear to be required if organic selenium species were present, assuming the valence of selenium in these species to be less than 4. Such a discrepancy raises questions concerning the speciation of selenium under these conditions, and will require a more detailed investigation.

A final point to note is the dramatic increase in soluble manganese that resulted from the addition of glucose (approx. 100-200 times) as shown in figures 7 and 8. It may be postulated that a decrease in the redox potential may have lead to the transformation between a solid phase, such as MnO_2 and soluble Mn^{2+} ions. Values for Eh and pH have been plotted together with thermodynamic data for the manganese species discussed above, in figure 10. Although it appears that the points lie within the MnO_2 phase, the coordinates used to predict the phase boundaries would be most probably displaced in environmental samples, and these points may actually lie in the Mn^{2+} area. At this time it is uncertain as to whether manganese may be controlling the Eh of the system, although it appears that the reduction of selenate to selenite and more reduced species may be associated with the reduction of manganese. Clearly, this phenomenon requires additional investigation in order to clarify this point.

The distribution of nitrates in the soil columns is presented in Figure 11. Data from Experiment 1 show evidence for leaching, with increasing nitrate concentrations with depth. The concentration of nitrate in Experiment 2 reflects inherent concentrations within the soil since none was added with the input water, and values do not exceed 0.5 mM. A

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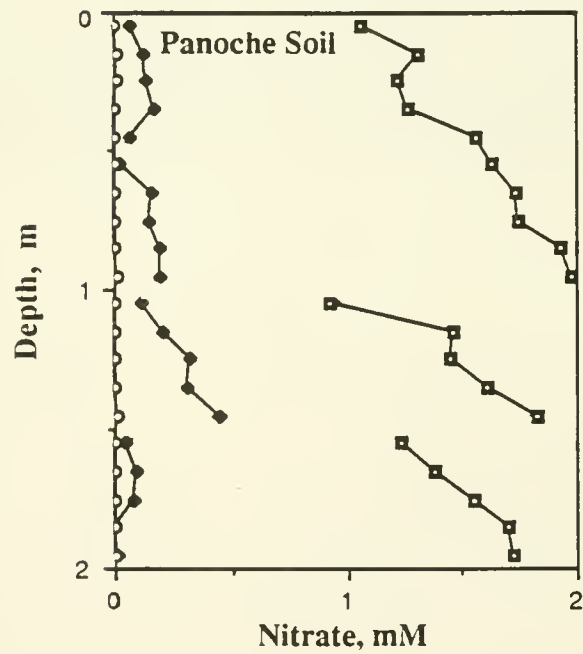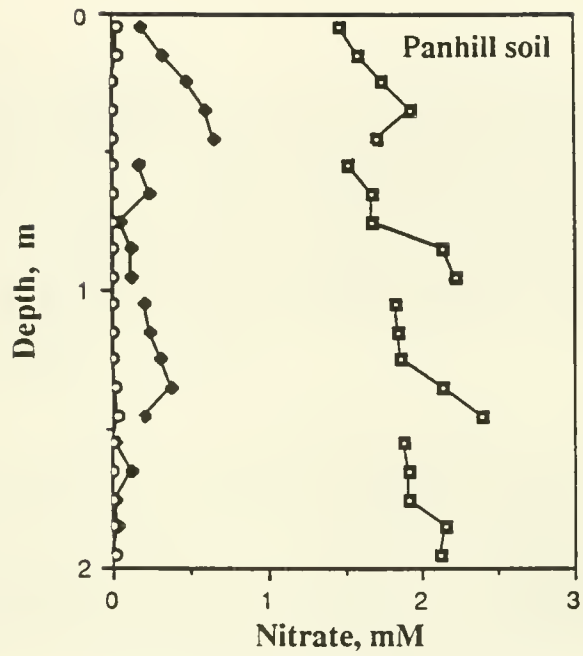
Figure 11. The distribution of soluble nitrates in Panhill and Panoche soil profiles

Concentration of 2.14 mM nitrate was included in the input water of Experiment 3, however, although little remained within the soil columns. The inclusion of the carbon source sufficiently enhanced microbial activity and the transformation of nitrate into a unidentified form.

3.2.1.4. Conclusions

The data obtained from Experiments 1 - 3 have provided important information which may be used to understand the behavior of selenium in soils. With respect to selenate, the predominant form of selenium in drainage waters, the presence of nitrate, a carbon source, and possibly manganese oxides have a measurable impact on both the transformation and transportation of selenium in the soil profile. It is apparent that a threshold level of nitrate is required in order for transformations between selenium species to occur. This was evidenced by the lack of organic selenium found in either leachate of soil waters of Experiment 2. Similarly, the activity of microbiological flora may be enhanced through the addition of a carbon source, with the result of some transformation between selenate and the unidentified organic selenium association.

These findings also have revealed certain gaps in the current understanding of selenium chemistry in soils. The behavior of the organic selenium association is not well known, and from the data presented in this report appears contradictory. Whilst increased selenium concentrations were eluted from the columns in Experiment 3, apparent retention occurred at the upper levels of each soil column, particularly in the Panhill soil. Perhaps, and it seems most likely, more than one "species" is involved in these processes, and thus new areas which require immediate experimentation have opened up, and must be investigated if we are to address the problems of selenium in the San Joaquin Valley with any confidence.

In partial response to these findings a second set of column experiments were set up and will be completed by the end of the fiscal year. Information concerning these experiments is presented in Chapter 4.

CHAPTER 4

WORK IN PROGRESS

4.1 Column Studies

4.1.1. Experimental Conditions

The data obtained from Experiments 1,2 and 3 have shown that the attenuation of selenium in alkaline irrigated soils may be influenced by a number of factors, not the least of which appears to be the redox potential of the system. The presence of currently unidentified selenium compounds, which are probably organic or associated with colloidal organic material, in the leachate and solution waters of both the control and glucose amended columns indicates a considerable gap in our knowledge of both the speciation and kinetics of this element. Experiments 4,5,6 and 7 have been designed with the objective of increasing our understanding of the chemistry of selenium under the conditions imposed by irrigated agriculture.

Soil column experiments have been set up under glasshouse conditions, including only soil collected to a depth of 1.5m. Each soil profile has been packed within 5.5 x 175 cm plastic irrigation pipe, and supported vertically. Each experiment was run for a 9 week period, during which time each column received 7 applications of 180mL synthetic selenium - containing drainage water every 10 days. The drainage water composition was consistents with the attached copy of specifications (see appendix). The concentration of selenium in the input waters was 2.5 μmol L^{-1} (~200 μg L^{-1}). These experiments were dismantled in September 1988, and the process of soil and leachate analysis is currently underway as described in Experiments 1 - 3.

The composition of input water to each experiment was varied as a described in Table 4, which will enable a comparison in the behavior of selenium under the control conditions of Experiment 4 with those arising from the addition of an organic source (Expt.5), the inclusion of a soluble iron compound (Expt.6), and the absence of nitrate (Expt.7).

4.1.2. Preliminary Data

A number of data have been collected from Experiments 4 - 7. These data are, as yet, incomplete but are included to illustrate the behavior of selenium in these longer-term column experiments.

Three leachate fractions were collected from each experiment. Leachate emerged after the fifth application of water, yielding between 30 and 160 mL per fraction. One noteworthy feature was that the leachate collected from the Panoche soil had a yellow coloration, indicating the presence of organic material, whist the Panhill leachates were almost colorless. The EC of the leachate collected from the Panoche soil was generally much higher than fro Panhill soil, reaching values > 40 dSm^{-1} for the first fraction collected from Experiments 4 and 6. EC decreased with increasing leachate volume until final values < 10 40 dSm^{-1} were recorded for both soils. The selenium content of the leachates were markedly different for the two soil types. Total soluble selenium concentrations for the first leachate collected from the Panoche soil was ~12 μmol L^{-1} (1 mg L^{-1}) irrespective of experimental conditions, whilst only ~ 1.2 μmol L^{-1} (100 μg L^{-1}) was detected in the leachates collected from the Panhill soil. Data shown in Table 2a indicate a higher inherent

Table 4. Composition of Input Water for Experiments 4 to 7

Constituents	Expt.4	Expt.5	Expt.6	Expt.7
	---------------------------mmol L^{-1}------------------------			
$CaCl_2.2H_2O$	12.48	12.48	12.48	12.48
Na_2SO_4	44.76	44.76	44.76	44.76
$NaHCO_3$	4.91	4.91	4.91	4.91
KCl	0.128	0.128	0.128	0.128
$MgCl_2.6H_2O$	12.34	12.34	12.34	12.34
$NaNO_3$	2.14	2.14	2.14	-
NaCl	12.17	12.17	12.17	12.17
H_3BO_4	1.2	1.2	1.2	1.2
Na_2SeO_4 *	0.0025	0.0025	0.0025	0.0025
Yeast Extract	-	3g/L	-	-
$FeSO_4.7H_2O$	-	-	100 mg Fe/L	-

* 0.0025 mmol Na_2SeO_4 L^{-1} i 0.197 mg Se L^{-1}

Se concentration in the Panoche soil which would account for this phenomenon, and indicate the extent of selenium mobility under irrigation conditions such as those used in these experiments. That little selenium emerged from the Panhill soil columns would seem to indicate that some degree of attenuation of the selenium that was introduced in the irrigation water may have occurred, and that only a small percentage, if any at all, may have been eluted from the Panoche soil.

The soil column experiments were run for four nine-week overlapping time periods. Data is currently available for only the first of these experiments. Under the control conditions of Experiment 4, selenium was leached to a depth of 0.8m in the Panhill soil but was detected only in the upper 0.3m of the Panoche soil. The data indicate that selenium is more mobile in the Panhill soil, and this may be attributed to clay swelling and moisture retention in the Panoche soil which inhibited the flow of selenium-bearing water through the soil profile. Soluble selenite was present in significant amounts in the upper portions of the columns (~ 0.25 μmol L^{-1}) but to a lesser extent than selenate (~1.65 μmol L^{-1}). Traces of organic selenium were determined also (~ 0.25 μmol L^{-1}). The proportionate distribution of these species were found to vary with both soil type and profile depth.

## 4.2 Laboratory Studies of Redox Kinetics

4.2.1 Objectives

Increasing awareness of the lack of information concerning the kinetic behavior of the various redox species of selenium that occur in natural systems has led to the design of the following experiments.

The primary objective is to investigate experimentally the oxidation-reduction transformations of selenium species in representative San Joaquin Valley soils under varying pH, O_2 concentration, and adsorption conditions. From the data obtained kinetic equations will be developed that will describe quantitatively the rates of the transformations investigated under experimental conditions. Finally, the information obtained will be applied to the behavior of selenium in irrigated agricultural soils, with an emphasis on modelling selenium transformations in soil profiles.

4.2.2. Experimental Design

The rate of transformation between selenium species will be investigated as a function of pH and redox conditions (dissolved O_2). The reactions considered will be primarily:

$$SeO_4{}^{2-} + 2e + 2H^+ = SeO_3{}^{2-} + 2H_2O \text{ (1)}$$
$$SeO_3{}^{2-} + 4e + 6H^+ = Se(c) + 3H_2O \text{ (1)}$$
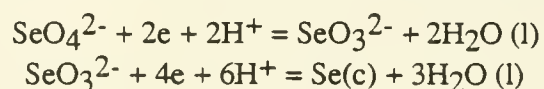
however, in view of the importance of organic-selenium associations, the role of these species will be considered. Initial experiments will investigate these reactions in a synthetic sterile soil solution whose composition will emulate that of a pore waters of the soils to be used. This medium will simulate an abiotic environment under which rate constants for the various processes involved can be established. The experiments will be carried out in a NaCl electrolyte solution, and effects of changes in ionic strength, pH, O_2 concentration, and the presence of other ions, such as Fe, Mn, Ca, NO_3 and SO_4, will be investigated for their affect upon selenium behavior. Transformations will be monitored through a regular

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sampling program to determine concentrations of Fe, Mn, Ca, NO3, SO4, and selenium species, together with the measurement of pH and redox potential.

Once transformation rates have been established under synthetic conditions, subsequent experiments will be carried out in sterile and non-sterile soil saturated paste extracts in order to determine the effect of naturally occurring organic materials, and of microbial intervention on oxidation-reduction transformations, respectively. Finally, wet soil will be included to examine the role played by adsorbing surfaces. The soils used in this study will be Panoche (fine-loamy mixed, calcareous, thermic Typic Torriorthents) and Panhill (fine-loamy mixed, thermic, Typic Haplargids) (Neal et al.,1987a,1987b,1988).

Concentrations of selenium and other ions in these studies will reflect the actual concentrations present in soil, irrigation and drainage waters of the Western San Joaqion Valley. Experiments will be carried out in an incubation system which has been adapted from designs by Turner and Patrick (1968). The apparatus holds approximately 300mL of solution, portions of which will be removed by suction into a sealed container as the experiments progress. Redox will be monitored using two platinum wires which have been sealed into the bottom of the glass container and connected to a calomel reference electrode inserted into the top of the reaction chamber. The electrodes are monitored continuously using a chart recorder with a FSD of 500 mV. Solutions and/or soil will be circulated in an enclosed container using a magnetic stirrer and a a flow of air. The oxygen content of the air will be used to control the redox potential of the system. The effect of changes in pH and O_2 concentration on the reduction of NO_3^- and selenium, ferrous iron production, and the transformation of Mn from an easily reducible form to the exchangeable form, will be monitored. This information will be used to determine transformation rate constants for selenium, and compare its behavior with other reducible ions in soil systems.

CHAPTER 5

RESEARCH REQUIREMENTS ARISING FROM CURRENT PROGRESS

5.1 Laboratory work

An number of unanswered questions have arisen from the data presented in Chapters 3 and 4. These should be addressed as follows:

1. <u>Redox kinetic studies as described in Chapter 4.</u> The data obtained will enhance our understanding of the fundamental behavior of selenium in soil systems, especially under conditions arising from irrigation practices. Without this information complete comprehension of selenium chemistry cannot be attained, and thus an insight into the long-term effects of anthropogenic influence on selenium in soils will be limited.

2. <u>Additional glasshouse column studies to encompass further experimental requirements.</u> Questions concerning selenium manipulation by chemical means must be further examined. An example of this would be to investigate the use of the soil as a natural filter, which could be used to reduce the level of selenium in wastewater treatment effluent. A considerable proportion of the selenium in such effluent is though to be in organic forms, and thus further experimentation as to the behavior of organic selenium, and of selenium interaction with organic materials would be required. These studies should be in the form of laboratory experiments, column investigations and, finally, implementation in field experiments.

5.2 Field Studies

Field experiments whose design would be based on the data obtained from the soil column studies, and may be carried out in cooperation with other SJVDP projects. The exact design of the filed experiments would depend on the findings of Project Phases I and II, and the resultant direction of the project based on these findings. It is anticipated that experimental conditions similar to those obtained under glasshouse conditions would be set up, and a large scale investigation of Se behavior in the soil profile examined. The latter would include a Se monitoring program both in the soil profile and from sub-surface collector drains. Speciation studies of the collected material would be necessary in order to establish the distribution of selenium between both inorganic and organic forms. Data collected from the field would be used together with those arising from the redox chamber experiments in order to construct a predictive model for selenium movement in the soil profile. Given the necessary data it is probable that such a model could be applied to other anions prevalent in irrigated soils.

CHAPTER 6

SUMMARY AND CONCLUSIONS

Information gathered during Phases I and II of this project has led to the following conclusions.

Firstly, that the chemistry of selenium is dependent on the form in which the selenium exists in the aqueous phase. If, as in the soils of the western San Joaquin Valley, selenate predominates, then surface attenuation phenomena will not play a role in attenuating its mobility in the soil profile. However, the presence of organic-selenium associations, attenuation may play an important role in selenium mobility through the soil profile. Since little information pertaining to the chemistry and environmental impact of these species currently exists, additional laboratory experiments are required to identify and characterize these associations, and to assess their behavior in irrigated agricultural soil systems.

Secondly, that the chemistry of selenium in soils and waters is still not well understood, especially under conditions imposed by agricultural management schemes. Further investigations concerning the kinetics of transformation between the predominant selenium species, and the impact of other soil constituents and microbial activity on these transformations, need to be examined before final recommendations concerning the manipulation of selenium in the environment can be made. Indeed, long-term studies of the effect of certain types of in-situ treatments require further investigation in order to assess the impact of such manipulations on the environment as a whole.

Thirdly, data from column studies indicate that the movement of selenium in the soil profile is affected by the inclusion of amendments. Data from Experiments 4 - 7 will provide further information to substantiate these findings, and assist in the design of future field trials aimed at incorporating these findings into managerial practices. Ideally, in order to transform selenate to a less mobile form, a lowering of the redox potential would seem necessary. The inclusion of a carbon source to stimulate microbial reduction and/or volatalization of selenate seems an appropriate course of action, but this would require the incorporation of large quantities of organic material, and as such would give rise to other problems associated with contamination from excess amounts of organic matter in soils and waters of the western San Joaquin Valley. In addition, this process gives rise to the formation of unknown organic selenium associations, the impact of which are, similarly, unknown, and thus may provide greater hazard than selenate itself. This suggests that the use of other materials and/or treatments may be more realistic and should be considered.

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APPENDIX

SYNTHETIC DRAIN WATER

ATE CF CALIFORNIA-RESOURCES AGENCY

GEORGE DEUKMEJIAN, Governor

EPARTMENT OF WATER RESOURCES
NTRAL DISTRICT
O. BOX 160088
CRAMENTO
95816

September 19, 1985

SEP 24 1985

Mr. Ed Lee
U. S. Bureau of Reclamation
2800 Cottage Way
Sacramento, CA 95825

Dear Ed:

The Estuarine Biology Committee has been working on an assignment to develop
recommendations as to the quality of subsurface agricultrual drainage and
dilution water to be used in laboratory toxicity testing. This memo conveys
recommendations for three representative water qualities and three dilution
water qualities.

For drainage, we chose water from the San Luis service area, the present
San Luis Drain and the Northern service area. A worst case test would involve
the use of San Luis drain water whereas a more representative case might be
to use water from the San Luis service area.

The dilution waters recommended can be used to evaluate the effects of
increasing levels of minerals on the toxicity of drainage water components.
The values suggested represent freshwater, brackish water and ocean water in
general. Chemical data available from the San Joaquin River and Suisun Bay
have been used to establish the general chemical composition of the drainage
waters.

Before presenting the recommended values, there are a few assumptions we used
in developing the estimates which must be kept in mind. These assumptions are
also important when interpreting test data from laboratory studies in which the
waters were used.

1. The approach used by the Bureau to develop drainage estimates may not be
    suitable for our use. The Bureau estimates include assumptions about rates
    at which farmers may hook up to a collector system or install new drains,
    and changes in quality with time due to leaching, water management, etc.
    We believe that not enough data are available to validate these
    assumptions.

2. There are data available on the quality of certain agricultural drains,
    collector drains and observation wells which were developed using suitable
    field and laboratory techniques (1984-85 data). An approach using
    frequency distribution for the observed constituents seemed reasonable.
    This approach works best for trace element data. For common chemicals,
    relation between the constituents and total dissolved solids were developed
    using data from the Bureau and Water Resources collected from the Central
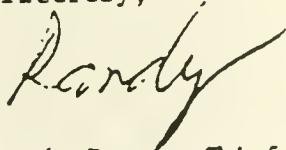   portion of the west side of the San Joaquin Valley.

3. The recommended qualities will be used to evaluate the toxicity of drainage
    to selected laboratory plants and animals in laboratory systems. The
    information gathered from the studies will only be a portion of the
    information needed to protect the quality of surface waters which might be
    exposed to subsurface agricultural drainage. Other studies will provide
    information on dispersion, sources and sinks, temporal changes in receiving
    water quality, etc.

4. The laboratory studies will concentrate on processes (mode of uptake, fat
    in the tissues, bioaccumulation, physiological and behavorial responses,
    antagonism and synergism) involved in the toxicological effects of the
    water and its components.

5. An effluent criteria related to drainage water will probably be based on
    individual elements. Under this assumption, the "safe" level of an element
    would be derived by diluting the original concentrate to a level where the
    adverse environmental impact of concern was not observed. Whether the
    original level was 200 or 400 ug/L should be of little consequence.

6. There will be some parallel tests using actual drainage water and dilution
    waters.

This material was discussed by the Estuarine Biology Committee and there was
general agreement on the approach used. I am sending them copies at this time
and any comments will be provided to their representatives on the ITCC. After
all comments are considered, the recommendations as to representative drainage
water can be forwarded to laboratories needing these data. Using the above
assumptions, the qualities are listed below. If you have any questions, please
call me at (916) 322-7165.

Sincerely,

Randy Brown, Chief
Bay-Delta Ecological Studies Section
Bay-Delta Studies Branch

Enclosure

NOTICE: IF YOU DETACH
ENCLOSURE PLEASE INSERT

CODE NO._____
INITIAL_____
DATE_____

Drainage

Common Chemicals - All Waters

Constituent	Factor x TDS	Example at TDS = 10,000 mg/L
Calcium	0.05	500
Magnesium	0.03	300
Sodium	0.25	2,500
Potassium	0.0005	5
Bicarbonate	0.03	300
Sulfate	0.43	4,300
Chloride	0.20	2,000
NO_3-N	0.003	30
PO_4-P		0.3 [1]
pH		7.2 [1]

[1] All drainage waters regardless of TDS.

Trace Elements and Specific Conductance

Constituent	San Luis Service Area[1]	San Luis Drain[2/4]	Northern Area[3]
Specific Conductance, μS ug/L	6,500[5]	10,600	3,800
Arsenic, ug/L	2	1.2	1.6
Boron, ug/L	8,000	13,000	2.4
Cadmium, ug/L	<1	1	<1
Chromium, ug/L	30	35	10
Copper. ug/L	7	5	3
Iron, ug/L	90	100	100
Lead. ug/L	2	2	<5
Manganese, ug/L	20	20	100
Mercury. ug/L	>0.1	0.16	0.1
Molybdenum, ug/L	30	75	10
Nickel. ug/L	20	20	15
Selenium, ug/L	100	350	3
Silver, ug/L	>1	1	<1
Zinc, ug/L	10	15	10

[1] All Bureau stations south of Kesterson including collector drains.
[2] Flow weighted from present collector drains going to San Luis Drains.
[3] All Bureau stations north of Kesterson.
[4] For San Luis Drain average values were calculated using the limit of detection for those values reported as less than the limit of detection.
[5] The average of the upper 80% of the values tested.

Dilution Waters

Freshwater	Relationship Used
TDS = 350 mg/L	TDS = simple average — S.J.R. @ Vernalis
TH = 140 mg/L	TH = 0.42 TDS − 7.71 r = 0.96
SO_4 = 64 mg/L	SO_4 = 0.14 TDS + 14.74 r = 0.64
Ca = 32 mg/L	Ca = 0.09 TDS + 0.71 r = 0.93
Mg = 16 mg/L	Mg = 0.05 TDS − 1.75 r = 0.96
HCO_3 = 100 mg/L	None found — simple average.

NOTE: For both fresh and brackish waters, alkalinity reported as $CaCO_3$.

Brackish Water – From Chipps Island and S.J.R. @ Antioch—average values

TDS	— mg/L =	1200
Hardness	— mg/L =	200
SO_4	— mg/L =	120
Ca	— mg/L =	50
Mg	— mg/L =	60

NOTE: For both fresh and brackish waters, pH is generally such less than 8.3, thus alkalinity will be due to biocarbonate.

Ocean Water

Instant Ocean @ 33,000 mg/L TDS

ACKNOWLEDGEMENTS

ADDENDUM

ATTENUATION OF SELENIUM DRAINING FROM IRRIGATED SELENIFEROUS AGRICULTURAL SOILS

Volume 1
Addendum

Prepared for the
San Joaquin Valley Drainage Program
2800 Cottage Way, Room W-2143
Sacramento, CA 95825-1898

Under
U. S. Bureau of Reclamation
Contract No. 7-FC-20-05250

By
Rosemary H. Neal and Garrison Sposito

Department of Soil and Environmental Sciences
University of California, Riverside

December 1988

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TRANSFORMATION AND MOBILITY OF SELENIUM IN THE SOIL PROFILE: LONG TERM EXPERIMENTS

A1. Long-Term Column Studies

A1.1. Objectives

The data obtained from Experiments 1,2 and 3, in which Se-bearing water was passed through 0.5m columns of soil over a 14-day period, indicated the attenuation of selenium in alkaline irrigated soils to be influenced by a number of factors, both inherent and imposed, and including the redox potential of the system. The presence of uncharacterized selenium compounds in leachate and solution waters, which were probably organic in nature or associated with colloidal organic material, indicated a considerable gap in the knowledge of both the aqueous speciation and kinetic behavior of this element. The conditions implemented in Experiments 4,5,6 and 7 were designed with the objective of simulating the behavior of selenium in the soil, using columns containing material from various depths in the soil profile under a cyclic water application regime. Thus it was hoped to further current understanding of selenium chemistry under the conditions similar to those imposed by irrigated agriculture. The use of a saline input water was considered a suitable medium in providing an extreme environment which might provoke the greatest response, and could be usefully extrapolated for consideration of the leaching behavior of drainage water contained in evaporation ponds.

In addition, recent investigations by a number of researchers prompted the use of the following amendments:

(1) Karlson and Frankenberger (1989) emphasized the importance of adding a C-source to soils to enhance microbial activity and increase ensuing Se-volatalization processes and hence reducing toxic concentrations in soils and waters. However, currently there is no information as to the effect of such amendments on the leaching behavior of selenium, and hence its behavior at depth in the soil profile. Data from Experiments 1-3 would seem to imply considerable influence from such amendments, and so before such treatments are applied on a large scale, these factors require consideration.

(2) The interaction of nitrate with Se in soils and waters has been recognized by Weres (1988). Current opinion hypothesizes that the presence of nitrate in soils and waters reflects redox conditions which favor the existence of selenate, and that an oxidation-reduction potential sufficiently low for selenate reduction to a less mobile form will not occur if nitrate is present. The equilibrium potential for the oxidation-reduction reaction of NO_3^- /NO_2^- is given as 0.54V (pH 7) (Bohn et al. 1985), whereas SeO_4^{2-}/SeO_3^{2-} has an equilibrium potential of 0.44V under the same conditions (Sposito et al. 1986). It is pertinent to note that the oxidation-reduction equilibrium potential for MnO_2/Mn^{2+} is very close to that of selenate having a theoretical value of 0.40V (Bohn et al., 1985), and that the occurrence of Mn^{2+} in the soil system would probably be indicative of selenate reduction.

(3) A recent study by Murphy (1988) indicated selenate could be reduced effectively to elemental selenium through interaction with ferrous hydroxide under alkaline conditions.

Although the author indicated that the reaction rate was very slow below pH 8, no evidence exists to suggest that such a mechanism could, or could not, be induced in soils. Ferrous hydroxide, such as that used by Murphy (1988), may be formed from ferrous sulfate and sodium hydroxide in stoichiometric amounts. Whilst it is not feasible to include the latter compound in input water since it would affect pH, ferrous sulfate was added to see if such a simple approach might impose suitable conditions in the soil columns as to induce changes in Se speciation.

A2. Experimental Conditions

Soil columns, including only soil which had been collected from the profile between the surface and a depth of 1.5m, were set up under glasshouse conditions. Each soil profile was packed within 0.055 x 1.75 m plastic irrigation pipes, which were aligned vertically using a suitable levelling device. Experimental conditions were imposed for 9 weeks, during which time each column received a total of 7 applications of water every 10 days. Each application consisted of 180mL (0.075m) synthetic selenium - containing drainage water. The drainage water composition was consistent with the attached copy of specifications (see appendix). A fresh stock solution of sodium selenate was made prior to each irrigation, and was added to the input waters to a final concentration of 2.5 μmol SeO_4^{2-} L^{-1} (~200 μg L^{-1}), thus ensuring the application of selenate-Se. Upon conclusion, the experiments were dismantled (September 1988) and the composition of both soil solution and leachate determined as described for Experiments 1 - 3. in Chapter 3

The composition of input water to each experiment was varied as indicated in Table 4.(Chapter 4). Experimental data collected from the first three short-term experiments indicated the importance of modifying the chemical composition of the system, and so a comparison between the behavior of selenium under control conditions (Expt. 4) and those resulting from the addition of an organic source (Expt.5), the inclusion of a soluble iron compound (Expt.6), and the absence of nitrate (Expt.7) were investigated.

A3 Results

A3.1. Leachate Composition

The emergent leachate was collected in three discrete fractions from each soil column. In each experiment leachate emerged after the fifth application of water had been added (900mL), and were then collected at the time a new irrigation was applied. Yields were between 30 and 160 mL per fraction, and were dependent primarily on total input volume, soil type, and column packing density. One noteworthy feature, however, was that the leachate collected from the Panoche soil had a distinct yellow coloration, indicating the presence of soluble organic material, whilst the Panhill leachates were almost colorless by comparison.

The EC of the leachate collected from the Panoche soil was generally much higher than from Panhill soil columns, reaching values > 40 dSm^{-1} for the first fraction collected from Experiments 4 and 6. These data reflect the higher inherent EC value of the Panoche soil, as was indicated in Table 2a in Chapter 3. The leachate EC decreased with each leachate fraction collected until final values of < 10 dSm^{-1} were recorded for the last eluent collected from both soils.

The selenium content of the leachates was markedly different for the two soil types also. Total soluble selenium concentrations for the first leachate fraction collected from the Panoche soil columns ranged between 2.4 and 5.36 μmol L^{-1}, with the highest concentrations eluted from columns under control conditions and conditions of added iron (Fig.A1). Leachate collected from the Panhill soil columns did not exceed 0.4 μmol Se L^{-1} in the first fraction, and dropped to below detection under all experimental conditions by the time the final leachate was collected. Data in Table 2a (Chapter 3) indicated a higher inherent Se concentration in the Panoche soil than in the Panhill soil, with concentrations ranging between 0.04 μmol kg^{-1} in the upper 0.5m to 0.45 μmol kg^{-1} in the 1.0 to 1.5m section, and such values would account for these differences. Since concentrations of Se in the leachate decreased with each leachate fraction, it may be presumed that the Se added in the input water did not reach further than a depth of 1.5m during the 9 week period of investigation.

Nitrate concentrations of the leachates were determined to evaluate differences between the two soil types and the experimental conditions. Within the limits of experimental error, concentrations of nitrate eluted form both soil columns were in agreement for each experiment indicating that differences arising from differences in soil column packing density were very small (Table A1).

A3.2. The Distribution of Soluble Se in the Irrigated Profile

The distribution of soluble selenium within each of the soil columns was evaluated upon completion of each experiment. Data have been calculated based on the amount of soil present in each 0.1m section, the moisture content of each 0.10m fraction at the time of sampling, and the concentration of soluble selenium found in replicate samples of solution extract. The data are presented in Figure A2.

Distinctly different patterns of Se distribution within the soil columns under the differing experimental conditions were revealed. Under control conditions, ie. those of Experiment 4, Se was detected only to a depth of 0.6m in the Panhill soil, and below this depth the concentration of soluble Se dropped below detection levels. In the Panoche soil soluble Se was detected only above a depth of 0.3m under these same conditions. These findings indicate that Se mobility in the Panoche soil was attenuated with respect to the Panhill soil. This substantiates the claim that, in both instances, the elution of Se from the bottom of the columns, especially that from the Panoche soil, may only be attributed to Se inherently present within the soil.

The inclusion of iron sulfate in the input water (Expt.6) resulted in apparently enhanced mobility of Se, since soluble Se was detected in significant quantities below 1.25m in both soils.

In Experiment 7, in which nitrate had been excluded from the input water, a similar pattern was observed, with significantly enhanced Se concentrations in the lower levels of both soil type columns. One might speculate that the reduced concentrations of soluble Se in the leachates from these columns may have been affected by the absence of nitrate, suggesting a relationship between nitrate concentrations and Se mobility.

In the columns to which the carbon source had been added (Expt.5), however, Se concentrations throughout the Panhill soil were significantly depleted. In the case of the

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Table A1. Selenium and Nitrate Concentrations in Leachates Collected from Panhill and Panoche Soil Columns During the Four Long-Term Experiments

	Panhill Soil		Panoche Soil	
Expt.#/ Fraction#	Se μmol L^{-1}	NO3 mmol L^{-1}	Se μmol L^{-1}	NO3 mmol L^{-1}
4	0.22	23.16	5.36	19.22
	0.11	0.72	1.43	0.62
	nd	0.48	0.25	nd
5	0.37	32.09	3.45	37.44
	0.18	8.55	0.20	6.35
	nd	0.53	nd	nd
6	0.35	24.63	5.24	23.88
	0.14	0.75	1.87	0.76
	nd	0.67	0.19	nd
7	0.16	18.23	2.40	28.69
	0.14	7.33	nd	nd
	nd	nd	nd	nd

nd= none detected
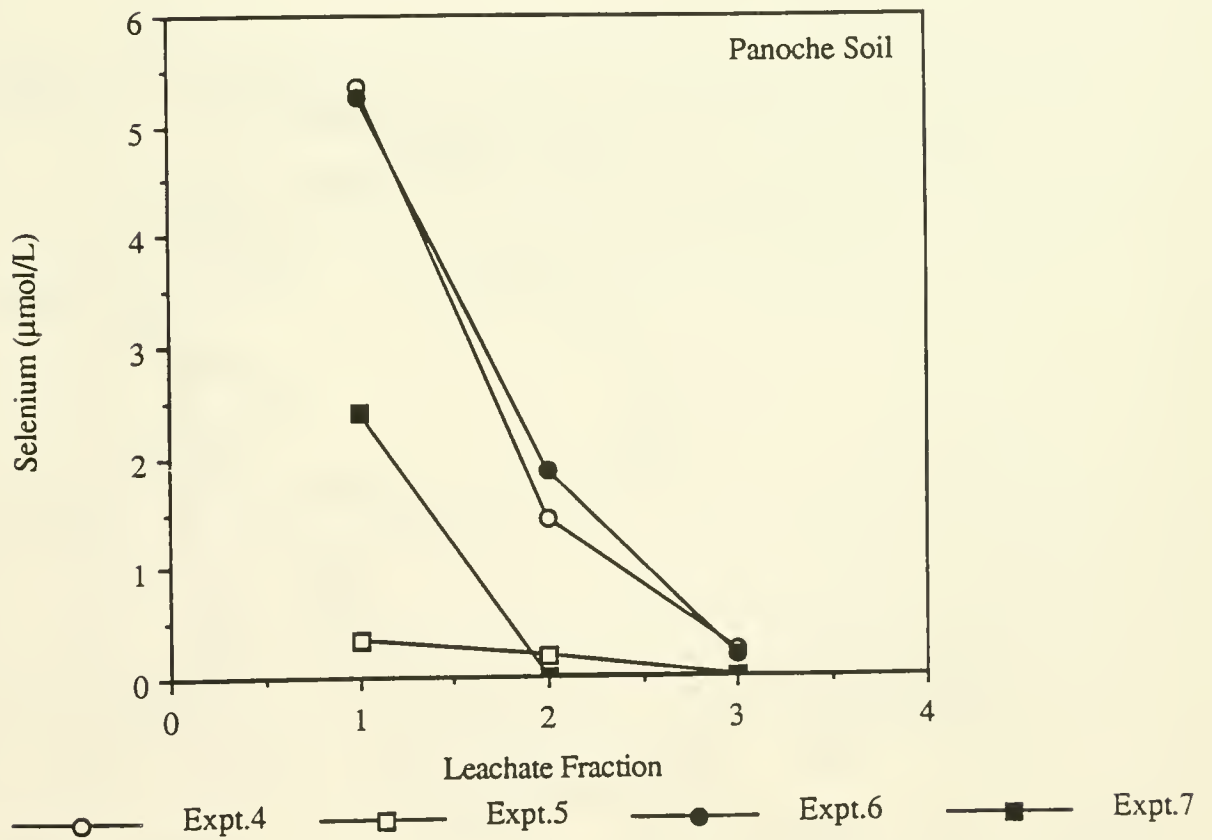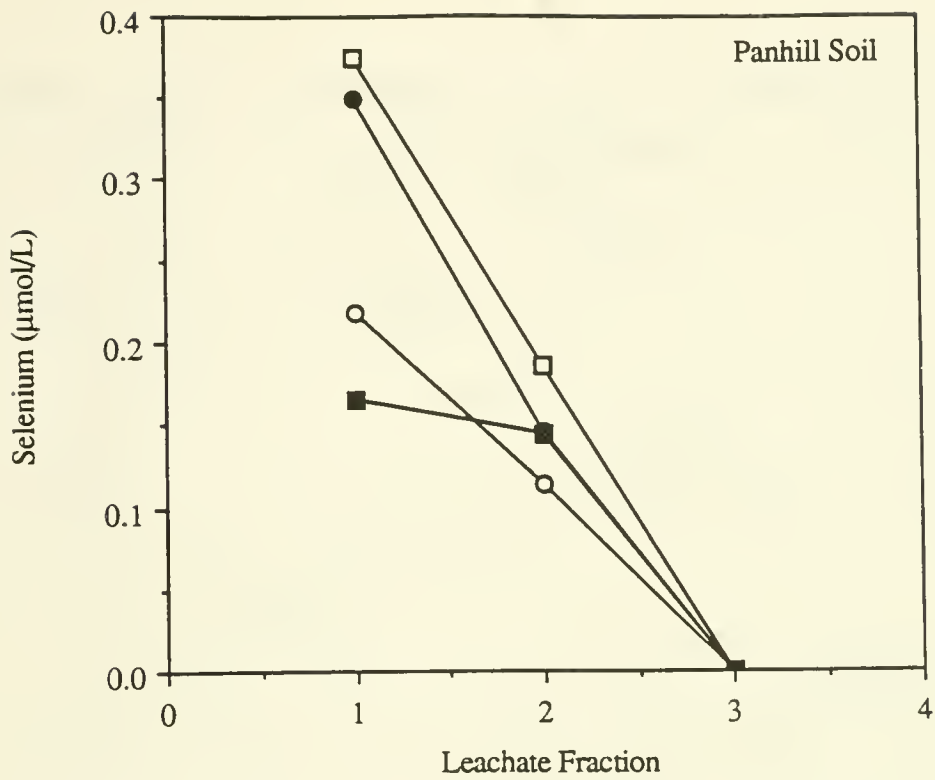
Fig. A1 Soluble Selenium Eluted from Soil Columns as a Function of Experimental Conditions
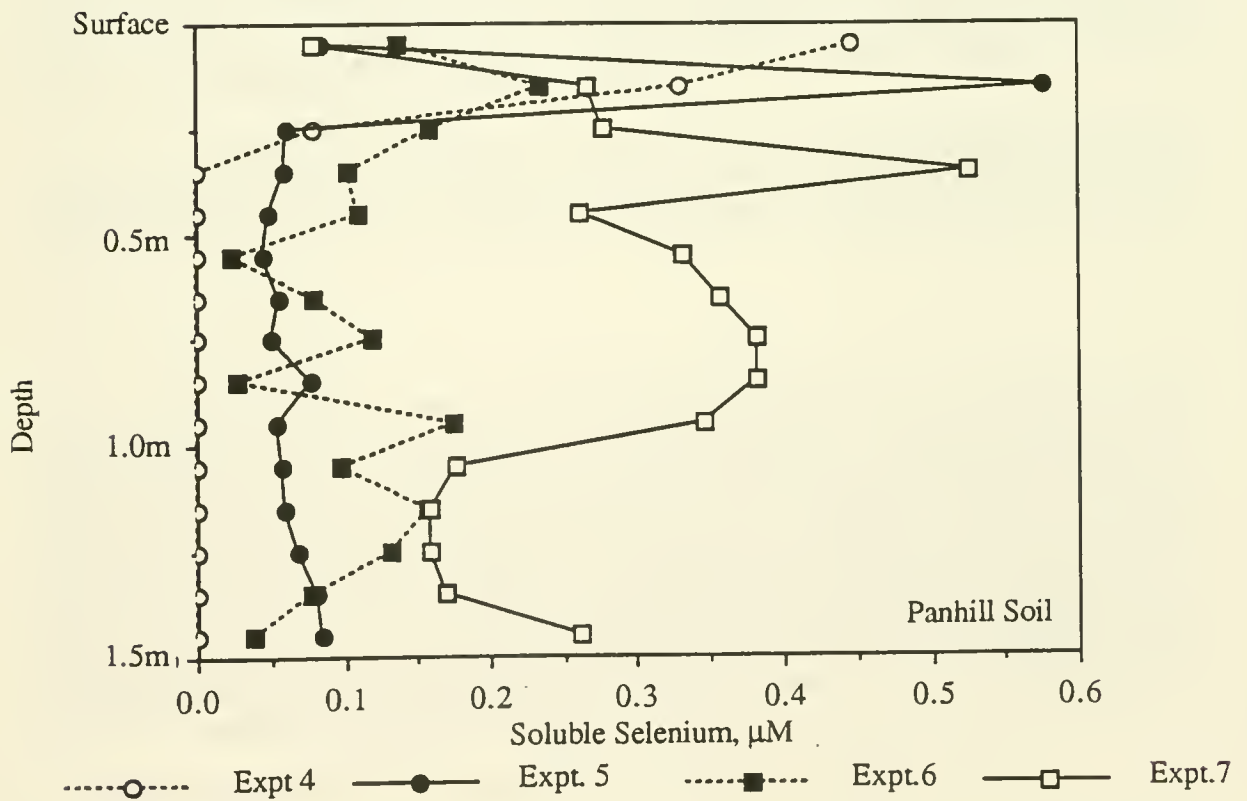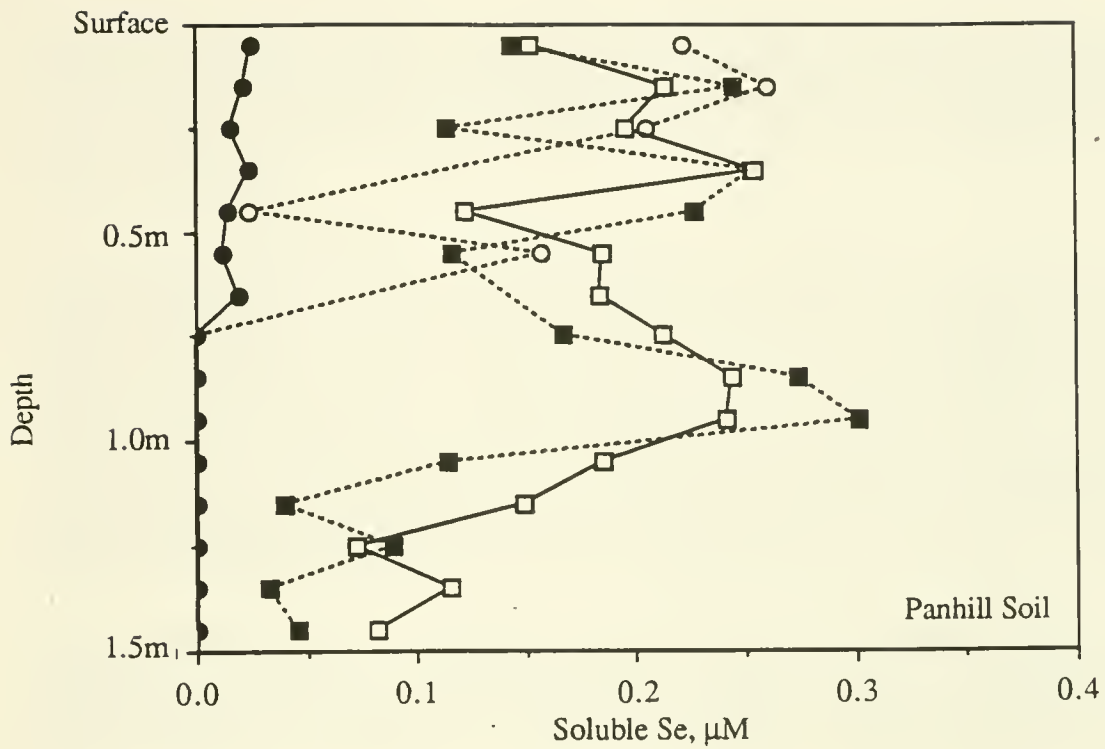
Fig. A2 Distribution of Soluble Selenium as a Function of Experimental Conditions

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latter, soluble Se concentrations in the upper 0.6m were very low compared with those of the control conditions, whereas in the Panoche soil, concentrations were elevated compared to those observed in Experiment 4. These data suggest the addition of a carbon source may have influenced the behavior of the inherent Se in the Panoche soil, particularly since the amount of Se leached form Panoche soil under these conditions was reduced compared to control conditions.

By observing the distribution of soluble selenium in the soil columns, one may draw the following conclusions from these experiments. Firstly, that under the control conditions of Experiment 4, Se was leached no further than half way down the soil columns, and in the case of the Panoche soil, an even lesser distance. This indicated that under such conditions there exist mechanisms which may be responsible for the attenuation of selenate Se. These include: adsorption processes, which have been shown only to be effective for selenite, although there is no evidence to date to suggest whether or not organically associated Se is attenuated by similar mechanisms; microbial transformations, which are extremely likely under aerobic conditions such as these, and may transform selenate to both to volatile and non-volatile species; and reduction processes, whether chemically or microbially mediated, which transform selenate to more reactive, less mobile species.

When no additional nitrate was added to the columns (Expt.7), the depth to which Se was carried was much greater. This change alludes to the importance of a relationship between this anion and Se compounds in soil systems. The presence of nitrate is though to inhibit the transformation of selenate to less mobile species (Weres, 1988), thus conflicting with the information presented in Fig A2, when Se is considered as a single entity.

Similarly, a change resulted from the addition of a soluble organic compound to the input water. In the case of the Panhill soil, soluble Se concentrations were reduced to very low concentrations ($<0.05\mu M$), whereas in the Panoche soil, soluble Se concentrations actually increased relative to the control conditions, with an especially pronounced peak in the upper 0.3m. As previously mentioned, these elevated concentrations could be the result of interactions with the inherent Se in the Panoche soil.

Why any of these responses were seen may not be completely explained by simply observing the concentration of soluble Se, since this gives no insight into the inter-species relationships that may exist within the system. Hence, Se speciation for each of the experiments was determined.

A3.3. Selenium Speciation

Three soluble Se species were determined, selenate, selenite, and Se associated with soluble organic complexes. Analytical techniques to determine the exact nature of Se-organic associations are in their infancy, and were not used to identify these species. However, Se associated with organic complexes was determined by difference, and since identification of complexes was possible, this fraction was referred to as organic-Se Of these three fractions, selenate is considered the most mobile and least reactive, and the form most commonly present in the soils and surface waters of the western San Joaquin Valley. Selenite, which may be sorbed to a greater extent than selenate, is favored by slightly lower redox conditions than those of selenate, although the data from Expts. 1-3 suggest these two species.may coexist. Little information is available pertaining to either the mobility or reactivity of organically associated Se species.

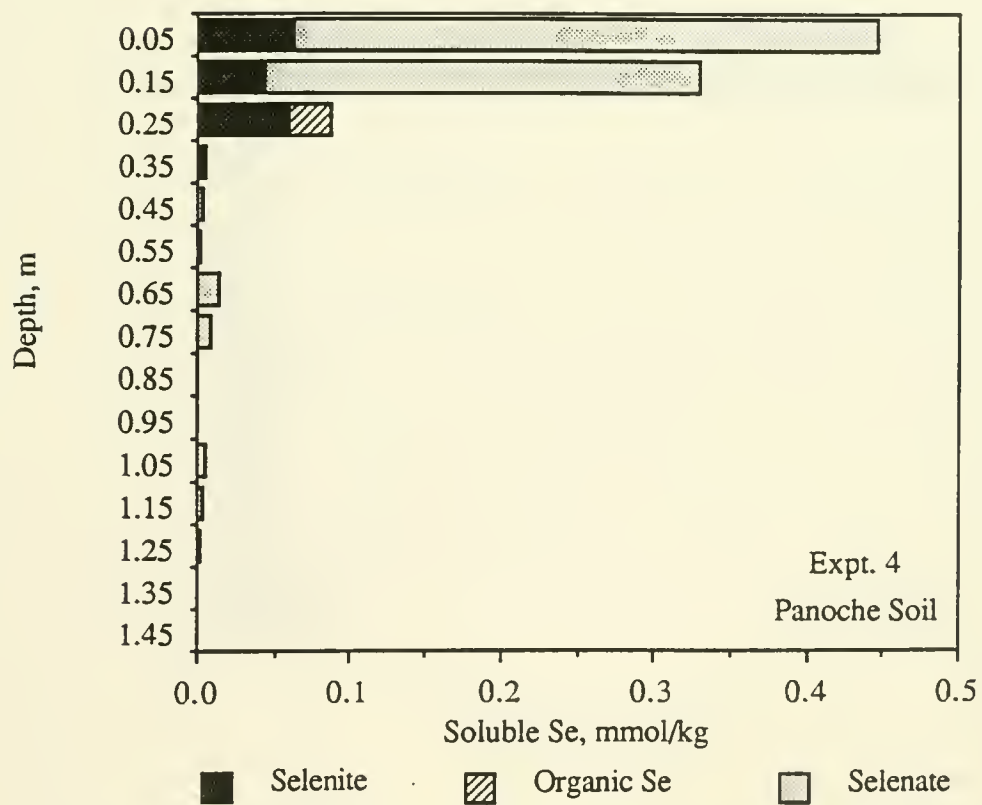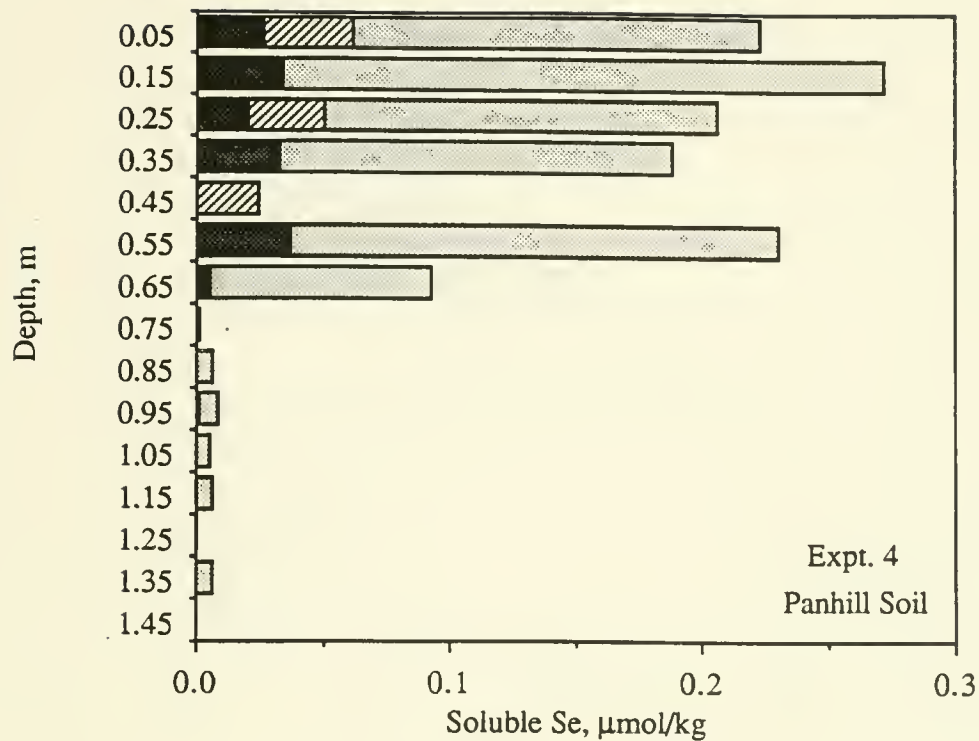The speciation data for all four experiments are presented in Figures A3 - A6.

Fig.A3 Speciation of Soluble Selenium under Control Experimental Conditions
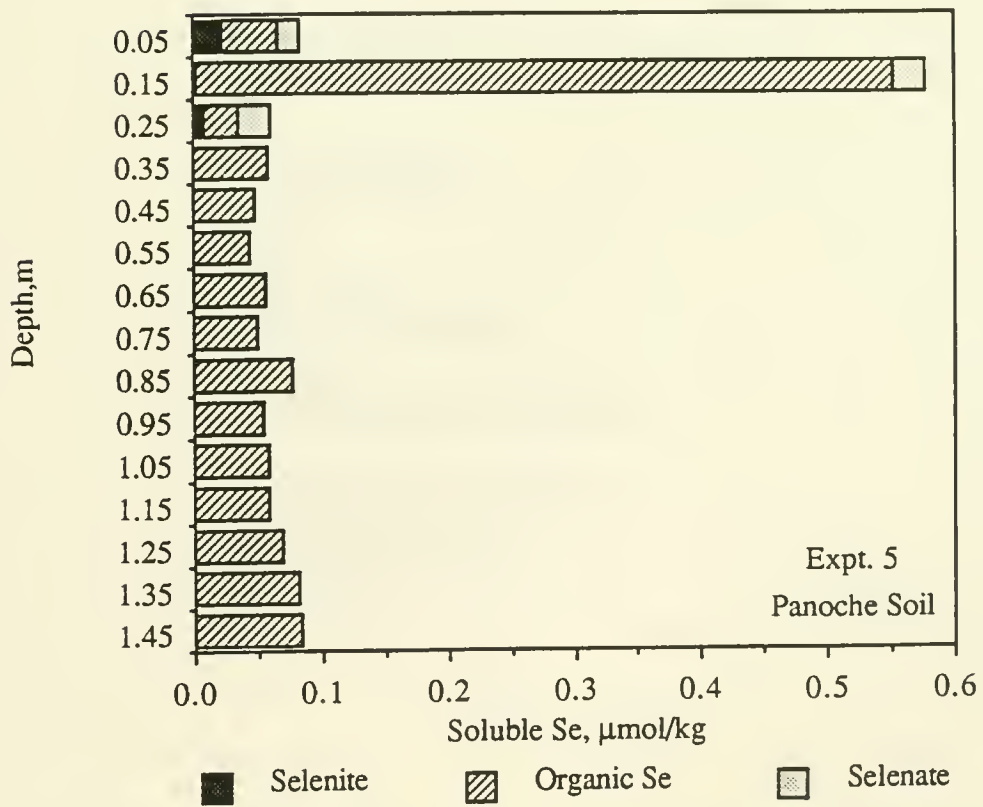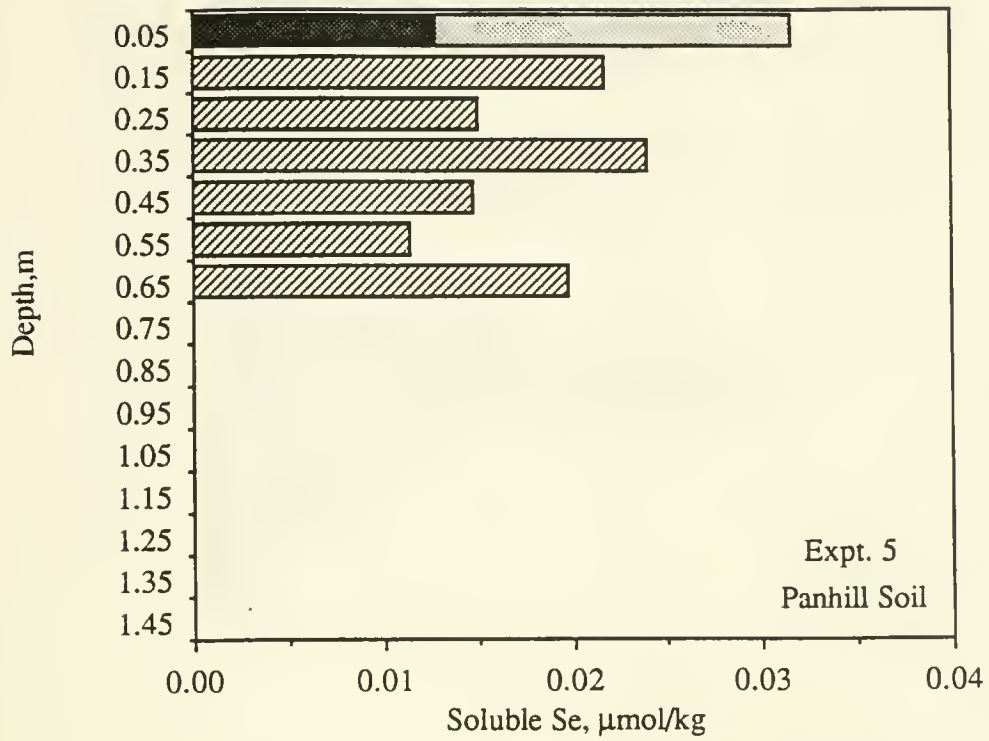
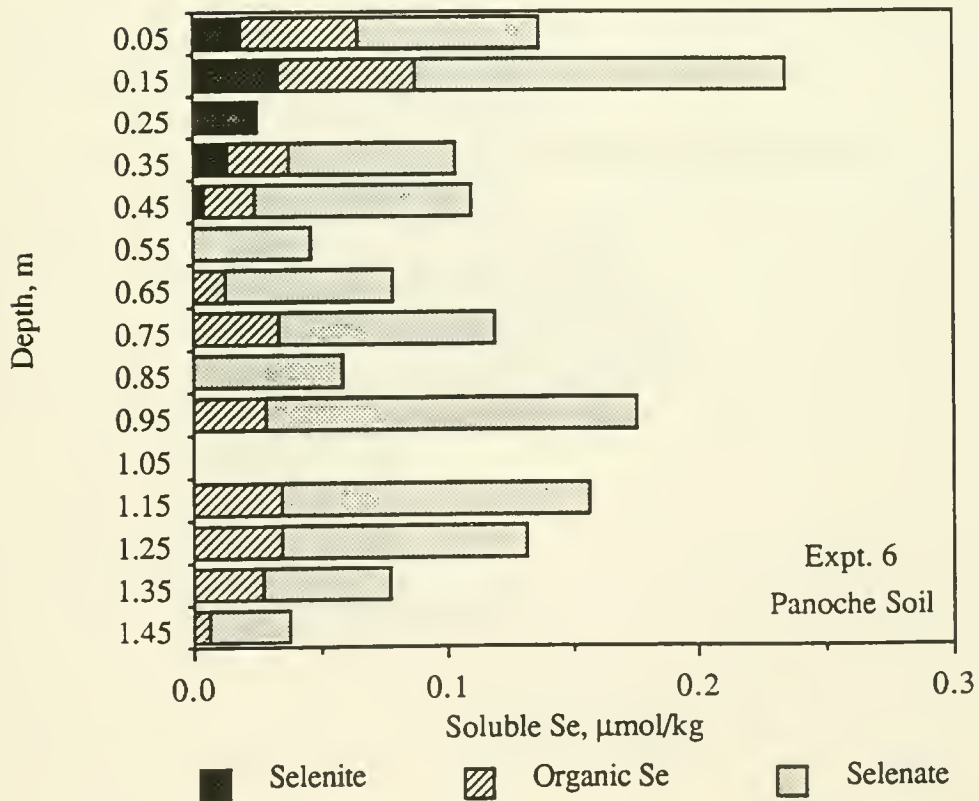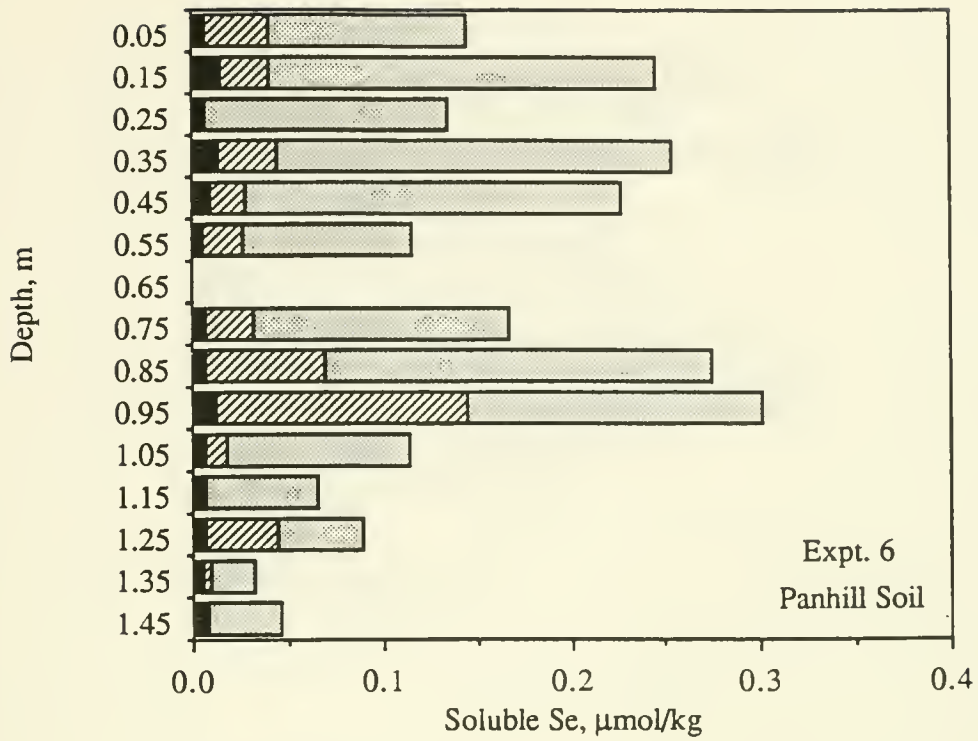Fig.A4 Speciation of Soluble Selenium under Added Carbon Experimental Conditions

Fig. A5 Speciation of Soluble Selenium under Added Iron Experimental Conditions
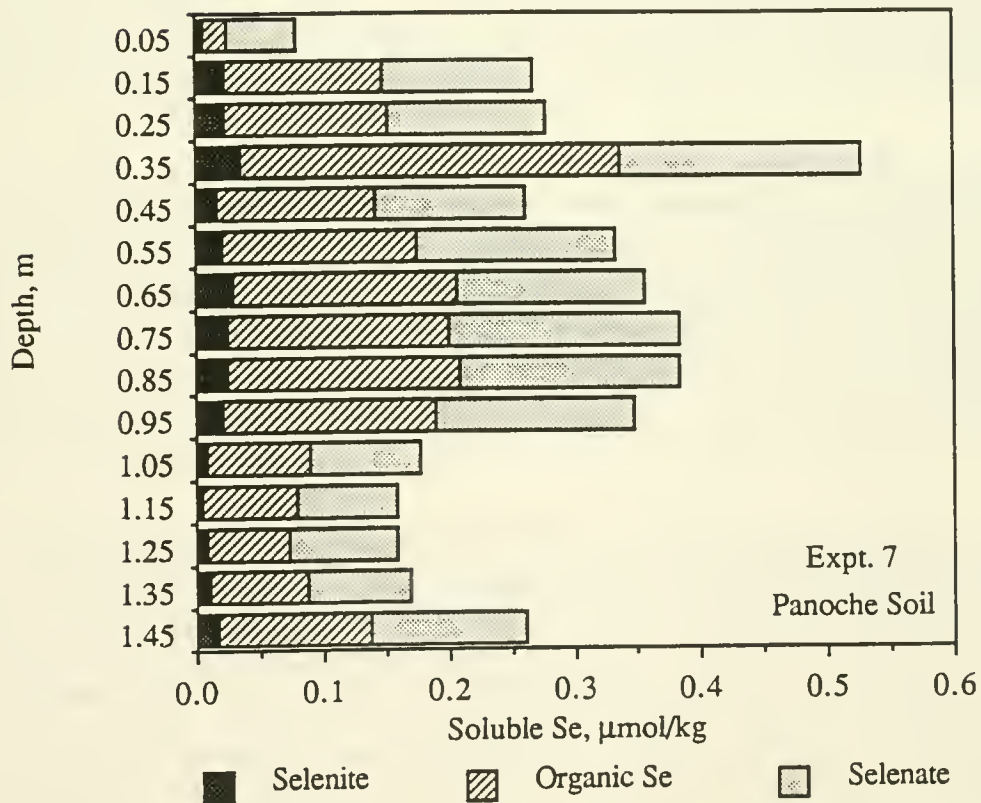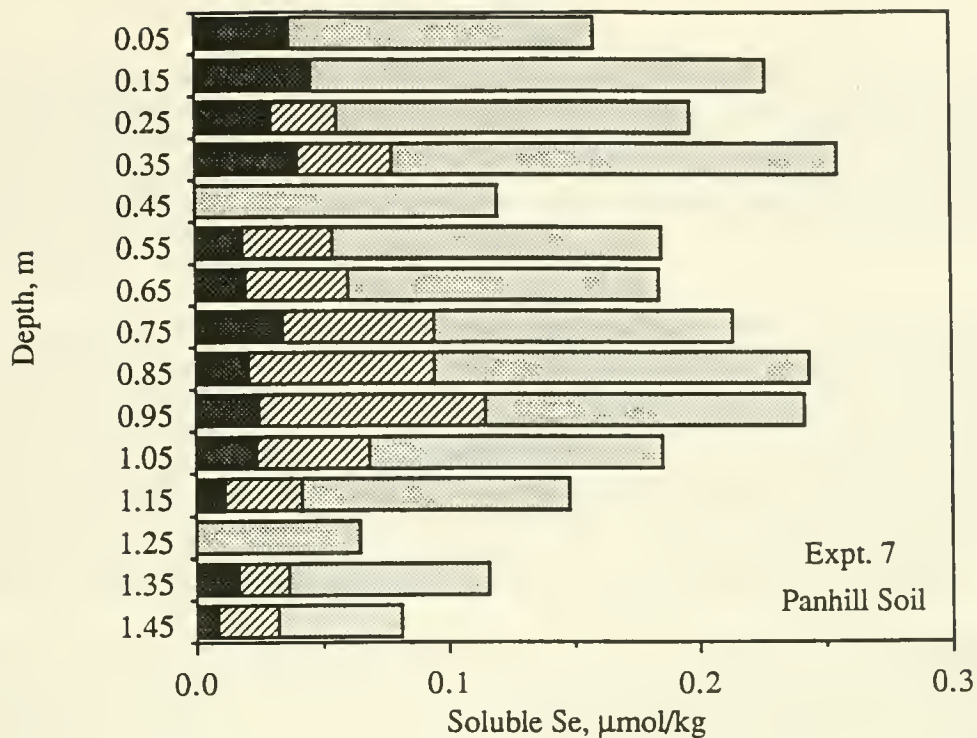
Fig. A6   Speciation of Soluble Selenium under Non-Supplemented Nitrate Experimental Conditions

Under control conditions, nearly all the soluble Se was present as selenate, with some selenite and organic Se detected in the upper 0.5m of the columns of both soil types (Fig. A3). Significant concentrations of soluble selenite were detected in both soil types, indicating some transformation (10-20%) from selenate to this more reduced species may have occurred. These so-called control conditions serve as a basis for comparison with the other experiments, and show that the mobility and transformation of Se under these conditions was limited.

Transformation of selenate to other Se species was most evident in Experiment 5, where organically associated Se was the predominant species below a depth of 0.10m. In the Panhill soil columns, Se was detected to a depth of 0.7m, with concentrations ranging between 0 and 0.025 μmol kg^{-1}. This depth of leaching is comparable with that reached under control conditions of Experiment 4 (Fig. A3). In the Panoche soil columns, however, organically associated Se was detected throughout the entire depth, and at significantly higher concentrations than in the Panhill soil (~0.075μmol kg^{-1}). Thus, in the case of the Panoche soil it would appear that under conditions of added organic carbon, Se either became more mobile, or the organic compound solubilized the inherent Se.

Both the mobility and transformation of Se were influenced by the conditions of Experiments 6 and 7. In the columns to which iron had been added (Expt.6), selenium was leached to 1.45m, and selenate was the predominant species present. In the absence of added nitrate (Expt.7) organic Se comprised a significant portion of the soluble Se, especially in the Panoche soil where the concentrations of selenate and organic Se were near parity. Soluble selenite was also present in significant concentrations in these columns (Expt.7), especially in the Panhill soil. It is possible that the presence of soluble iron in Experiment 6 may have served to maintain higher redox conditions that those found in the controlled environment of Expt. 4, so that selenate was mobilized over a greater distance. In Expt.7, however, the absence of nitrate, as postulated by Weres (1988), appears to have resulted in increased concentrations of the more reduced Se species, possibly due to favorable changes in the redox potential.

In an attempt to understand further the mechanisms which might be controlling distribution and speciation of Se in these soil column experiments, concentrations of nitrate and soluble Mn were determined. Nitrate and manganese are known to be affected by changes in the redox potential of a system. The reduction of nitrate to nitrite is thought to affect the reduction of selenate to selenite and possibly organic selenium compounds, and since the presence of nitrate indicates a redox potential higher than that theoretically required for the existence of selenite, its formation may be prevented. The dissolution of MnO_2, as indicated by increased concentrations of Mn^{2+}, however, would seem to suggest lowered redox conditions, and would be indicative of more favorable conditions for selenate reduction to selenite.

Under conditions of depleted nitrate, and those of added Fe, no soluble Mn was detected in either the Panhill or Panoche soil columns (Fig. A7). Under these conditions, significant amounts of selenite and organic Se were detected, indicating a lowering of redox potential, that was not associated with Mn. However, soluble Mn was detected in columns where, (i) the soils had been treated with a soluble organic compound, and (ii) under control conditions. In both these instances Mn solubilization was not apparent below a depth of 0.5m, and no differences due to soil type was noted. From this data it may be postulated that suitable conditions for the reduction of MnO_2 to Mn^{2+} existed, and would, therefore, be favorable for the reduction of selenate to selenite or, possibly, organic Se species. Such organic associations were evident under these conditions, but the data is not sufficient to
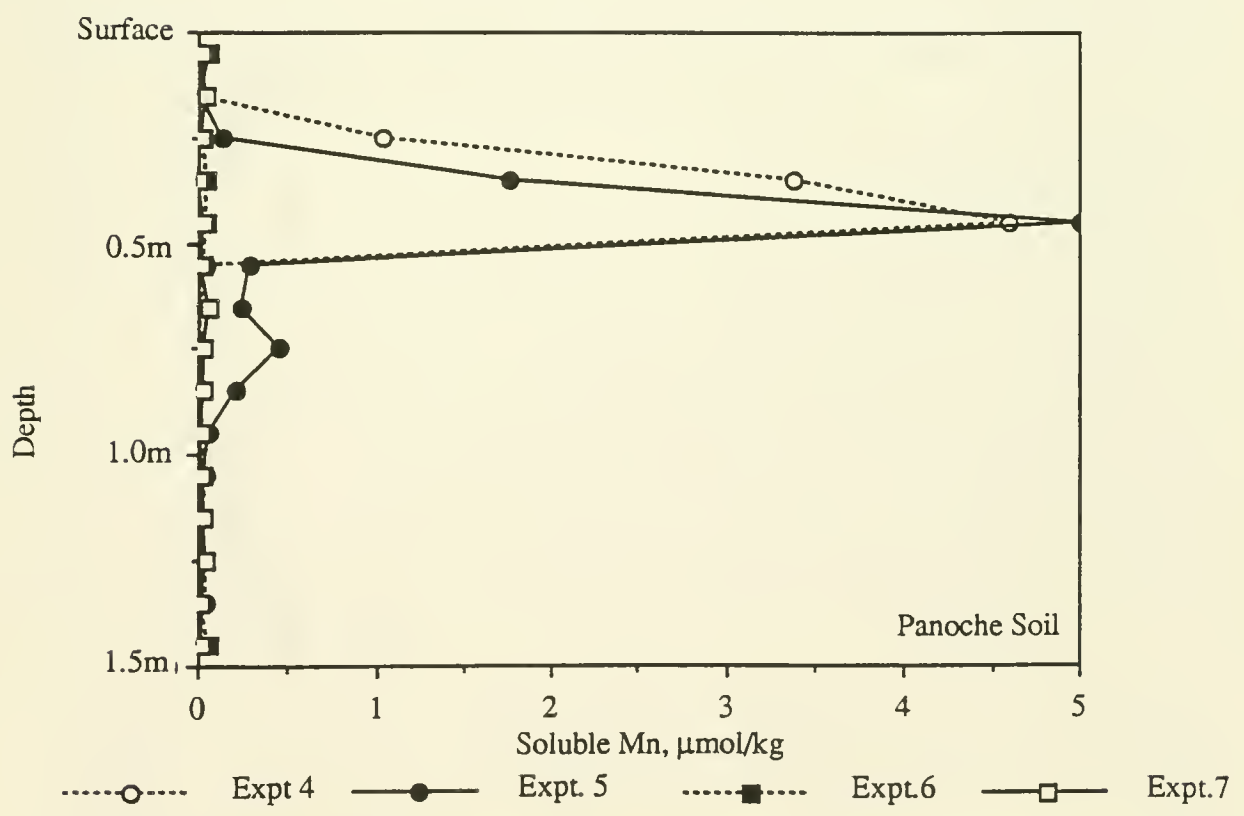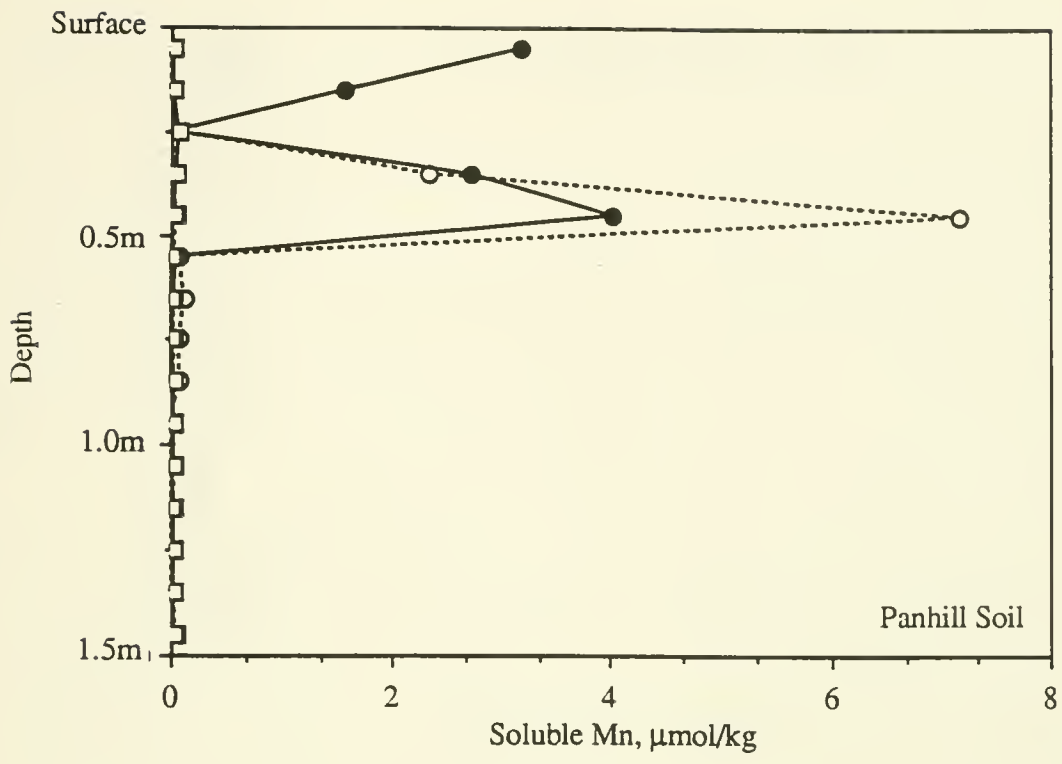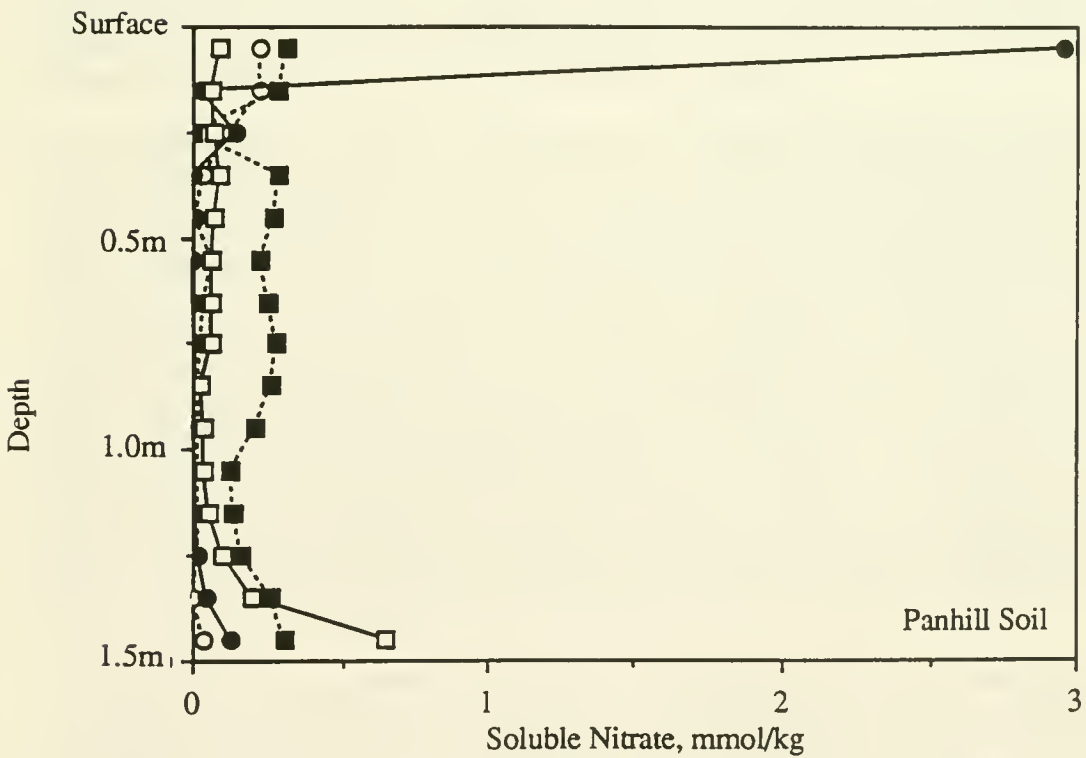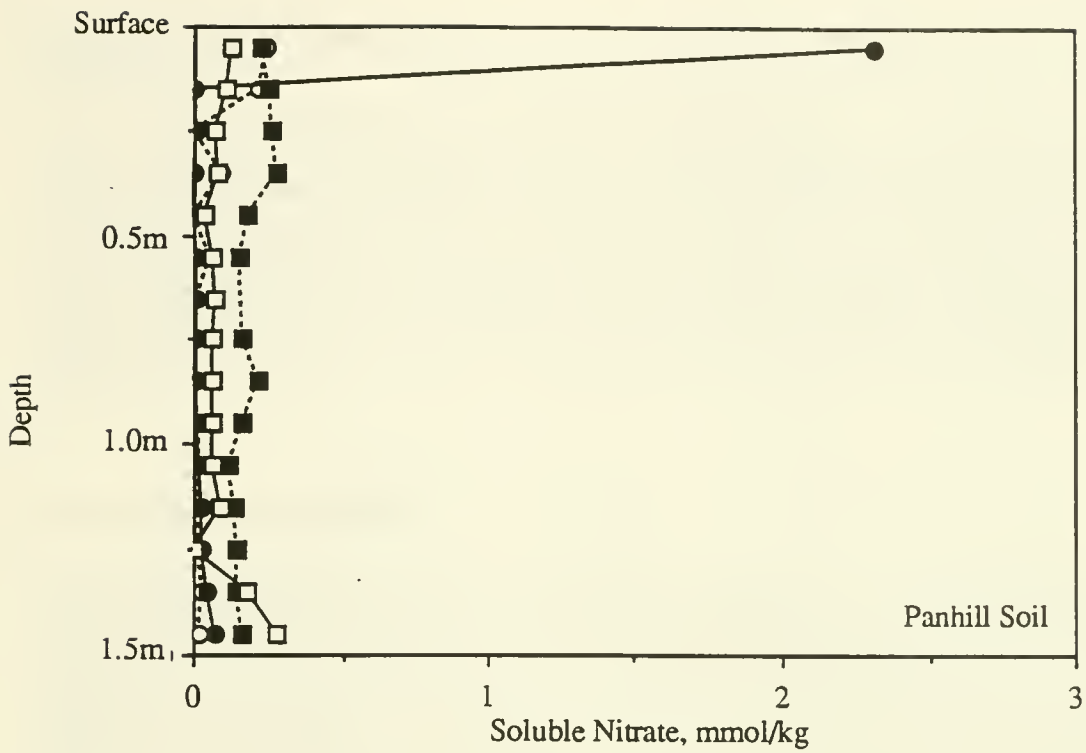
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Fig. A7 Distribution of Soluble Manganese as a Function of Experimental Conditions

Fig. A8 Distribution of Soluble Nitrate as a Function of Experimental Conditions

determine whether such species exist, or whether this phenomenon is merely an association.

Concentrations of soluble nitrate in the soil columns followed a predictable pattern (Fig. A8). Concentrations were highest in the columns treated with Fe, supporting the hypothesis that the presence of Fe maintained a higher redox potential. This may be compared with the data from Expt. 4, where control conditions were imposed, and nitrate concentrations were lower than those of Expt.6. The inclusion of an organic source significantly enhanced the concentration of nitrate found in the upper 10 cm of columns of both soil types, but dropped to below detection below this depth. The absence of nitrate suggests the existence of lowered redox conditions below the upper surface of the columns.

A4. Recovery Calculations

An estimate of the Se budget for the long-term experiments was calculated from the following information: the amount of Se leached from the soil columns, and the amount determined to be soluble within the soil profile. The difference between the sum of these values and the amount of Se added to each column, may be attributed either to sorption phenomena, or to microbial mechanisms of removal. The native concentration of Se in the Panhill soil was negligible, and therefore any difference between the amount of Se added to columns containing this soil type and the Se recovered (Fig. A9), may be attributed to loss either as a result of microbial volatalization, or sorption onto soil. Soluble Se was detected in the Panoche soil, however (Table 2a), with concentrations ranging from 0.04 μmol kg^{-1} in the upper 0.5m to 0.45 μmol kg^{-1} between 1.0- and 1.5m. This inherent Se may be responsible for the significant amount of soluble Se leached from, and retained by, the Panoche soil columns, and would affect the recovery calculations by underestimating the amount of added Se which was lost from these soil columns.

In attributing the most likely mechanism(s) which would be responsible for the loss of Se from the soil columns, the behavior of both Se species and soil components must be considered. The greatest amount of Se was lost under control conditions and conditions of added organic material (Expts. 4 & 5). In these instances the predominant soluble species were selenate and organic Se, respectively. From data discussed in Chapter 2 of this report, selenate is not expected to be sorbed on to soil, but a significant portion of selenite may be. No information exists pertaining to the sorptive properties of organic Se, and so no assumptions as to its behavior can be made at this time. However, the presence of all three species in the soil columns indicates that transformations of selenate occurred, and that sorption may play a role in attenuating Se movement through the profile. In the columns of Expt.6, organic Se was the predominant species, and significant concentrations of soluble Mn were observed, indicating lowered redox conditions. It is most probable that microbial volatalization played a significant role in removing Se under these conditions, since the addition of an organic source would serve to increase the efficiency of microbial flora. However, the occurrence of organic Se within the profiles suggests that some non-volatile products are made, and these may not be sorbed effectively by the soil matrix.

Much less Se was lost under the conditions of Experiments 6 and 7. If the addition of Fe maintained a higher redox potential, then the predominance of selenate would not favor sorption as a method of Se attenuation. The presence of selenite and organic Se in the soil columns indicates that some transformation occurred, and that any loss may be primarily attributed to sorption mechanisms. In Expt.7, the absence of added nitrate appeared to
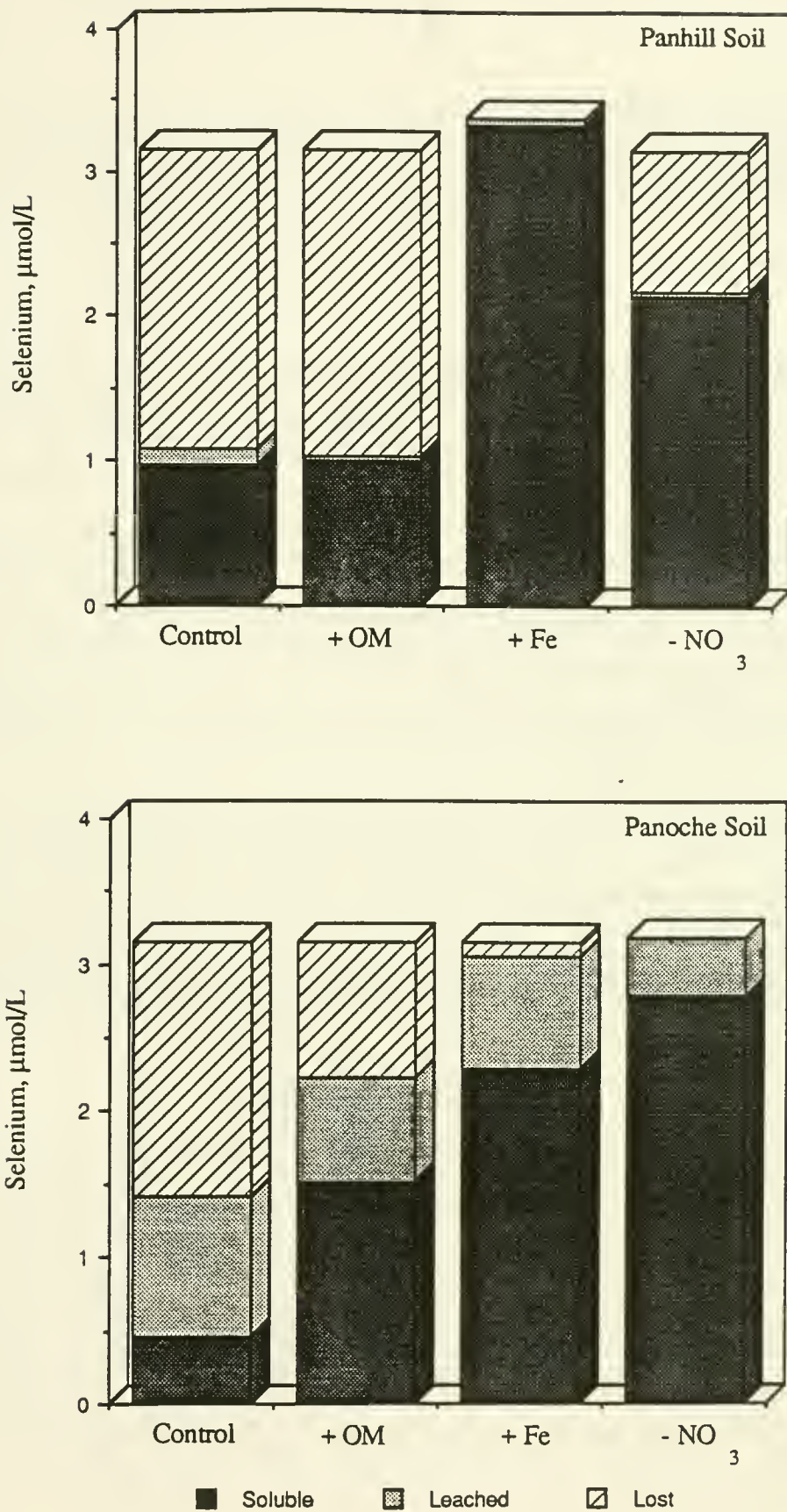
Fig. A9 Estimated Selenium Recovery from Soil Columns as a Function of Experimental Conditions

enhance transformations to the more reduced Se species, although this was not reflected by levels of soluble Mn. As in the case of Expt.6, losses were probably due to sorption phenomena, although as in all cases, microbial volatalization probably accounted for some loss. The latter is highly dependent on a number of factors, not the least of which is the availability of a suitable carbon source, as indicated in Expt.5.

A5. Summary and Conclusions

The movement of Se in soils is affected significantly by the chemical environment. Under the conditions described, in which simulated drainage water was used to generate the chemical environment of a soil at depth in the soil profile, Se movement appeared restricted, and was probably controlled through sorption processes and microbial transformations.

The existence of more than one Se species together, may be the result of kinetic phenomena, rather than the observance of strict oxidation-reduction potentials. Redox transformations may be slow, thus allowing for the coexistence of various species.Currently, there is no information pertaining to the kinetic behavior of Se in the soil environment, and so the results from these column experiments are open to considerable speculation. In addition, it may be argued that, whilst these experiments were only able to identify trends on a macro scale, i.e. the Se composition of 0.1m sections of soil, the existence of micro-environments in the soil, in which differing redox conditions may exist, are extremely likely, and may account for the diversity in speciation that was seen.

Selenium movement was affected by the inclusion of solution amendments, which may be responsible for maintaining a chemical environment favorable to a particular species. Amendments which create environments favor the existence of selenate will enhance Se mobility in the soil profile, whilst those resulting in Se transformation to more reduced species will increase attenuation. It would seem, however, that the inclusion of organic amendments, result not only in the production of volatile organic species, but also produce uncharacterized non-volatile species, whose role in the environment is relatively unknown. The use of such amendments may exacerbate the problem of Se toxicity in the soil profile.

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