LBL-26438 c.2

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAY 1 8 1989

LIBRARY AND
DOCUMENTS SECTION

Hydrological, Geochemical, and Ecological Characterization of Kesterson Reservoir: Annual Report, October 1, 1987– September 30, 1988

October 1988

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.

LBL-26438 c.2

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-26438

Hydrological, Geochemical, and Ecological Characterization of Kesterson Reservoir

Annual Report
October 1, 1987 through September 30, 1988

Earth Sciences Division
Lawrence Berkeley Laboratory
University of Calfornia
Berkeley, CA 94720

Sanitary Engineering and
Research Laboratory
Richmond, CA

October 1988

This work was supported by the U.S. Bureau of Reclamation, under U.S. Department of Interior Interagency Agreement 8-AA-20-06330, through U.S. Department of Energy Contract DE-AC03-76SF00098.

Table of Contents

List of Figures vii

List of Tables xiii

1. INTRODUCTION 1

2. ECOLOGICAL STUDIES 3

2.1. Summary 3
2.2. Controlled Continuous Flooding (Pond 5E) Update 4
2.2.1. Description of Pond 5E during 1988 4
2.2.2. Selenium content of water and biota 5
2.3. Terrestrial Ecology Study 15
2.3.1. Introduction 15
2.3.2. Methods 16
2.3.2.1. Quantitative Sampling 16
2.3.2.2. Qualitative Sampling 16
2.3.2.3. Laboratory Procedures 17
2.3.2.4. Synoptic Survey 17
2.3.3. Results 18
2.3.3.1. Qualitative Samples 18
2.3.3.2. Quantitative Samples 21
2.3.3.3. Synoptic Survey 25
2.3.4. Discussion 29

3. VADOSE ZONE MONITORING 31

3.1. Introduction 31
3.2. 1.0 Ft Excavation Test Plot at Pond 6 32
3.3. Pond 9 Soil Monitoring 38
3.4. Pond 11 Saltgrass Soil Monitoring Sites 44
3.5. Ephemeral Pools 49
3.6. Accumulation of Salts and Trace Elements through Evaporative Flow at and near the Soil Surface 52
3.6.1. Measuring Evaporation Rates from Bare Soils 52

3.6.2. Monitoring Changes in Salt and Trace Element Concentrations 54
3.6.3. Estimating Evaporative Flux of Salts and Selenium towards Soil Surface 59
3.6.4. The Effects of Evaporative Transport on the Whole of Kesterson Reservoir 67

4. GROUNDWATER 69

4.1 Introduction 69
4.2 Multiwell Tracer Experiment 69
4.2.1. Experimental Design 72
4.2.1.1. Test Site Configuration 72
4.2.1.2. Tracer Sampling Method and Frequency 76
4.2.1.3. Description: Tracer Experiment 2 - 1988 76
4.2.2. Analysis Method 90
4.2.2.1. Conceptual Model 90
4.2.2.2. Mathematical Model 92
4.2.3. Tracer Data Analysis - Experiment No. 2 95
4.2.3.1. Tracer Recovery Calculations 96
4.2.3.2. Analysis of Tracer Breakthrough Curves from Individual Wells 98
4.2.4. Discussion - Tracer Experiment No. 2 102
4.2.4.1. Structure, Velocity Distribution and Dispersivity Values 102
4.2.4.2. First Order Decay Constants for Nitrate 104
4.2.4.3. First Order Decay Constants for Selenate 105
4.3. Geophysical Investigations for Plume Monitoring 108
4.3.1. Geophysical Methods 108
4.3.2. Results 110
4.4. Pond 1 Reflooding Experiment 110

5. SELENIUM CHEMISTRY 115
5.1. Reduced Sulfur Compounds and the Soil Chemistry of Selenium 115
5.1.1. Introduction 115
5.1.2. Experimental 118
5.1.2.1. Total dissolved selenium - Method I 118
5.1.2.2. Total dissolved selenium - Method II 119
5.1.2.3. Total dissolved selenium - Method III 119
5.1.2.4. Solubility of selenium compounds in hydrogen sulfide solutions 119

5.1.2.5. Estimation of polysulfide-bound selenium in sulfidic pore water 120
5.1.2.6. Solubility of selenium in the presence of sulfur compounds 121
5.1.2.7. Speciation of selenium in sulfidic water 121
5.1.2.8. Effect of sulfulr compounds upon volatilization of Se 122
5.1.2.9. Analytical method for Se^0 123
5.1.3. Results 125
5.1.4. Discussion 132
5.2 Analytical Methods for Biological Samples and Sediments 134
5.2.1. Introduction 134
5.2.2. Control of blank readings 136
5.2.3. Study design 137
5.2.4. Results 152
5.2.5. Conclusions and recommendations 153

6. REFERENCES 157

6.1. LBL Reports 157
6.2. Vadoze Zone References 157
6.3. Groundwater References 157
6.4. Selenium References 159

APPENDICES 161

Appendix A: 163
Appendix B: 207
Appendix C: X-Ray Fluoresscence Analysis 215
Appendix D: Magnesium Nitrate Decomposition 217
Appendix E: Sodium Peroxide Decomposition Method 223
Appendix F: Carbonate-Nitrate Decomposition Method 226

List of Figures

		Page
Figure 2-1.	Selenium concentrations in water, Chara, and aufwuchs in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond. Error bars represent ± 2 standard errors.	6
Figure 2-2.	Selenium concentrations in epifaunal and benthic chironomid larvae in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	8
Figure 2-3.	Selenium concentrations in dragonfly and damselfly nymphs in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	9
Figure 2-4.	Selenium concentrations in Gambusia (mosquitofish), tabanid (horsefly) larvae, and Physa (pond snails), in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	10
Figure 2-5.	Selenium concentrations in dytiscid beetle adults and Berosus (hydrophilid beetle) larvae in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	11
Figure 2-6.	Selenium concentrations in surficial sediments in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond. Error bars represent ± 2 standard errors.	12
Figure 2-7.	Selenium concentrations in cattails (Typha) in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	13
Figure 2-8.	Selenium concentrations in alkali bullrush (Scirpus) in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.	14
Figure 2-9.	Seasonal variation in mean selenium concentration in components of quantitative plant samples at the Pond 11 index site. Error bars represent ± 2 standard errors.	22

Figure 2-10.	Seasonal variation in mean biomass of components of quantitative plant samples at the Pond 11 index site. Error bars represent ± 2 standard errors.	23
Figure 2-11.	Seasonal variation in means of biomass, numbers, and selenium concentration of arthropods at the Pond 11 index site. Error bars represent ± 2 standard errors.	24
Figure 2-12.	Mean biomass of *Distichlis* and *Cressa* Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.	26
Figure 2-13.	Means of biomass, numbers, and selenium concentration of grasshoppers, Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.	27
Figure 2-14.	Mean selenium concentration in soils, Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.	28
Figure 3-1.	Depth-distribution of soil water selenium from various monitoring sites at Kesterson Reservoir. Data are from Ponds 1, 6, 7, 8, 9, 10, and 11.	33
Figure 3-2a,b.	(a) Pond 6, 1 ft excavation test plot time trend of surface soil salinity obtained through electrical conductivity measurements. (b) Pond 6, 1 ft excavation test plot time trend of surface soil water-soluble selenium.	35
Figure 3-3a,b.	Ephemeral pool water quality over Pond 6, 1 ft excavation test plot.	37
Figure 3-4a,b,c.	Pond 9 "playa" monitoring site soils; soluble Se profiles, 1987 and 1988.	39
Figure 3-5a,b,c,d.	Pond 9 soil profile soluble sodium, calcium, magnesium, and sulfate. Comparisons of field vacuum extracts and laboratory extracts.	40
Figure 3-6a,b.	Pond 9 soil profile soluble boron and arsenic. Comparisons of field and laboratory extracts.	42
Figure 3-7a,b.	Pond 9 soils. Comparison of 1988 drying cycle hydraulic head responses in vegetated (a), and unvegetated (b) test plots.	43
Figure 3-8a,b,c.	Pond 11 saltgrass monitoring site soils; soluble selenium profiles, 1987 and 1988.	45
Figure 3-9a,b.	Pond 11 soils; (a) comparison of soluble Se from field versus laboratory extracts. (b) comparison of electrical conductivity in field versus laboratory extracts soil water samples.	47

Figure 3-10a,b,c.	Pond 11 soils; field soil water electrical conductivity profiles, 1987 and 1988.	48
Figure 3-11a,b.	Ephemeral pool water quality; (a) surface water source in Pond 7, (b) water table source in Pond 6.	51
Figure 3-12a.	Bare soil evaporation rates at Pond 8EP (a) and Pond 9BE (b) as a function of the saturation of the top 10 cm of soil.	55
Figure 3-13a,b.	The relationship between bare soil evaporation rates and water table depth at Pond 8 plot EP, (a) Depth to water table vs. time, (b) Bare soil evaporation as a function of the depth to the groundwater table.	56
Figure 3-14.	Hydraulic head profiles at Pond 8, plot EP (a) and Pond 9, plot BE (b).	57
Figure 3-15.	Electrical conductivity of soil water in the top 10 cm of soil at Pond 8, plot EP (a), and Pond 9 plot BE (b) from July to September, 1988.	58
Figure 3-16a,b	Mass of total "dissolved" solids in the top 10 cm of soil in Pond 8 plot EP, normalized to field water content (a) and normalized to mass ot soil (b) July-August 1988.	60
Figure 3-17a,b,c.	Mass of water soluble selenium (a) and boron (b) and arsenic (c) in the top 10 cm of soil in Pond 8, plot EP, normalized to mass of soil, July-August 1988.	61
Figure 3-18a,b,c,d.	Concentration profiles in Pond 8, plot EP soil of total "dissolved" solids (a), sodium (b), major cations (c) and boron (d). Note variation in concentration (horizontal) scale.	63
Figure 3-19a,b,c,d.	Concentration profiles in Pond 8, plot EP soil of water-soluble selenium (a), water-soluble selenite (b), water-soluble arsenic (c), and clay content profiles with depth (d).	65
Figure 3-20a,b,c,d.	Concentration profiles in Pond 9, plot BE soil of total "dissolved" solids (a), boron (b), water-soluble selenium (c), and water-soluble arsenic (d).	66
Figure 3-21a,b.	General theoretical relationships between bare soil evaporation rate and water table depth (a) and soil texture (b). Both figures from Hillel, 1980.	68
Figure 4-1.	Schematic of the flow field between production/injection well pair.	71
Figure 4-2.	Plan view of the pumping, injection, and monitoring wells used for the tracer experiment.	73

Figure 4-3.	Cross sectional view of the wells used for the 1988 tracer experiment.	74
Figure 4-4.	Schematic of the sampling and mixing unit used to collect fluid samples during the tracer experiment.	77
Figure 4-5.	Fluorescein breakthrough curves for monitoring well 1.	79
Figure 4-6.	Fluorescein breakthrough curves for monitoring well 2.	79
Figure 4-7.	Fluorescein breakthrough curves for monitoring well 3.	80
Figure 4-8.	Fluorescein breakthrough curves for monitoring well 4.	80
Figure 4-9.	Fluorescein breakthrough curves for monitoring well 5.	81
Figure 4-10.	Fluorescein breakthrough curves for monitoring well 7.	81
Figure 4-11.	Fluorescein breakthrough curves for monitoring well 8.	82
Figure 4-12a,b.	Selenate and nitrate breakthrough curves for monitoring well 1.	83
Figure 4-13a,b.	Selenate and nitrate breakthrough curves for monitoring well 2.	84
Figure 4-14a,b.	Selenate and nitrate breakthrough curves for monitoring well 3.	85
Figure 4-15a,b.	Selenate and nitrate breakthrough curves for monitoring well 4.	86
Figure 4-16a,b.	Selenate and nitrate breakthrough curves for monitoring well 5.	87
Figure 4-17a,b.	Selenate and nitrate breakthrough curves for monitoring well 7.	88
Figure 4-18a,b.	Selenate and nitrate breakthrough curves for monitoring well 8.	89
Figure 4-19a,b.	Schematic of a multiple flow path aquifer (4-19a) that would create the tracer breakthrough curve shown by the bottom curve.	91
Figure 4-20a,b,c.	History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 2.	99
Figure 4-21.	Comparison between the selenate breakthrough curve for well 2 and the theoretical curve generated using the transport parameters determined from the fluorescein analysis.	101

Figure 4-22.	Comparison between the selenate breakthrough curve for well 2 and the theoretical breakthrough curve using the velocity distribution listed in Table 4-3. (Note: no decay term was included in these calculations.)	103
Figure 4-23.	Comparison between nitrate and selenate first-order decay coefficients for the individual flow paths identified from these tracer experiments.	107
Figure 4-24.	Location map of the area investigated during the 1987 geophysical survey.	109
Figure 4-25.	Interpretive map showing the inferred locations of the drainage water plume and the areas of nearsurface salinization.	111
Figure 5-1.	Selenium profiles in Kesterson Reservoir Pond 2. Dry weight selenium in soil (ppm) vs. depth in inches. The superficial material is peat of relatively low density but very high selenium content.	117
Figure 5-2.	Solubility of selenium in the presence of sulfur compounds vs. pH. Each solution consisted of deaerated Na_2SO_4/NaCl brine with 2.5mM sulfur compound and citrate/phosphate buffer with pH adjusted to value desired. Solution deaerated and sealed with small amount of gray Se under vacuum in glass ampoule, and placed on shaker table. Total dissolved Se concentration determined after four days.	128

List of Tables

		Page
Table 2-1.	Scientific and common names of terrestrial plants found in Kesterson Reservoir.	19
Table 2-2.	Seasonal variation in selenium concentration (mean ppm) in terrestrial plants (qualitative samples), 1988.	20
Table 3-1.	Change in salt content in surface soil cores at Pond 8EP.	62
Table 3.2.	Salt accumulation rates for Pond 8EP and 9BE based on soil evaporation rates.	64
Table 4.1	Depth, casing size, slotted interval and local coordinates for the withdrawal, injection and monitoring boreholes used for the multiwell tracer experiments.	75
Table 4.2	Summary of the values for $1/C_o\int Cdt$ for fluorescein, selenate, and nitrate during Experiment No. 2.	97
Table 4.3	Summary of the data analyses of the tracer breakthrough curves from individual weeks during tracer Experiment No. 2.	100
Table 5-1.	Sulfide increases the solubility of selenium.	126
Table 5-2.	Speciation of selenium in peat water.	126
Table 5-3.	Speciation of Se in sulfidic water.	129
Table 5-4.	S-Compounds and volatilization of Se.	131
Table 5-5.	Origin and description of samples analyzed.	139
Table 5-6.	Repeated analyses of sediment samples using carbonate/nitrate	141
Table 5-7.	Six simultaneous analyses of sediment samples using carbonate/nitrate decomposition accompanied by six blanks.	142

Table 5-8.	Repeated analyses of sediment samples using sodium peroxide decomposition.	143
Table 5-9.	Six simultaneous analyses of sediment samples using sodium peroxide decomposition with corresponding blanks.	144
Table 5-10.	Summary of results for sediment samples.	145
Table 5-11.	Repeated analyses of biological samples using magnesium nitrate decomposition.	146
Table 5-12.	Six simultaneous analyses of biological samples using magnesium nitrate decomposition.	147
Table 5-13.	Repeated analyses of biological samples using carbonate/nitrate.	148
Table 5-14.	Six simultaneous analyses of biological samples using carbonate/nitrate decomposition method.	149
Table 5-15.	Summary of results for biological samples.	150
Table 5-16.	Comparison of powder XRF and magnesium nitrate/AAS results in routine analytical work.	154

1. INTRODUCTION

This report summarizes the results of the LBL/UCB investigations at Kesterson Reservoir for the period from October, 1987 to September 1988. The report is divided into four sections

- Ecological Studies
- Vadose Zone Monitoring and Research
- Ground Water Investigations
- Selenium Chemistry

Due to the fundamentally multidisciplinary nature of these investigations, topics within each one of the broad categories overlap, and where appropriate, we cross-reference to appropriate sections.

During the past year the results of these investigations have also been reported in LBL Progress Reports No. 7 and No. 8. In addition, several topical reports describing the results of these investigations have also been prepared. These include three papers on the Pond 1 reflooding experiment (Long et al., 1988a, 1988b, and 1988c) and two papers on the results of the off-site geophysical investigations (Goldstein et al., 1987, 1988).

2. ECOLOGICAL STUDIES

2.1 SUMMARY

Over the last year the ecological studies have focussed on two areas, the wet and dry zones. Much of our work was devoted to the provision of data for the May, 1988 SWRCB hearings on the on-site disposal option. These data are available in previous reports. The studies reported here are the latest results from the Pond 5E experiment, which has now been terminated, and the terrestrial food chain study, which has also been terminated. Although most of the data for these two projects have been collected and analyzed, there remain the last collections (September) to be fully analyzed.

Tentative conclusions from the Pond 5E experiment indicate that the decline in selenium has continued for most biota. The decline, which commenced soon after the introduction of low-selenium water, has not been a smooth decline. The initial logarithmic decline has shown a definite seasonal cycling with the winter values being higher than those of summer. Most species are still apparently not in equilibrium with the selenium in their environment. The sources of selenium in Pond 5E are new (from the approximately 1.0 ppb in the groundwater supply) or recycled selenium (from excretion of plants and animals). Thus a continued declining trend is apparent for most, but not all, species. The final data points will allow calculation of the depuration kinetics for the final stages.

For the terrestrial food chain, tentative conclusions can also be made. The predominant terrestrial vegetation (saltgrass, alkali weed) is low in selenium (2-5 ppm) but is underlain by a large detritus pool which is rich in selenium (averaging about 63 ppm). It is not clear if this detritus pool is slowly decaying or is being continually replaced, but future studies could clarify this aspect. Food chain insects, some of which are heavily contaminated with selenium, but most of which are not, may reflect the selenium in the detritus pool as well as that in seeds and fresh material.

2.2. CONTROLLED CONTINUOUS FLOODING (POND 5E) UPDATE

Field sampling of Pond 5E--the last remaining wet pond at Kesterson--has continued with regular monthly sampling visits through September 1988. The pond was sampled twice in June. Results of selenium analyses are now available for samples collected up to the second June sampling, and in many cases (particularly invertebrates) July data are now available as well. The latest available data are presented in updated versions of Figures 2-1 through 2-7. Appendix Table 1 contains the detailed numerical data.

2.2.1. Description of Pond 5E during 1988

Since its isolation from the remainder of Pond 5 in May 1986, Pond 5E has been continuously flooded with low-selenium and relatively fresh water pumped from the shallow groundwater beneath the pond. During this time the biota of the pond have gradually adapted to the permanently wet conditions in ways that have been described in previous reports in this series. For example, invertebrate species such as brinefly larvae and rattail maggots formerly occurred in Pond 5E during the summer when temperature and salinity rose, and dissolved oxygen fell. These species did not occur in the second year, when the pond never experienced these environmental extremes. In their place other forms more typical of a freshwater pond (principally beetles) have increased in numbers. Typical Pond 5E insects such as chironomid larvae and odonate nymphs were more perennial in the second year. We have also shown that selenium has been steadily declining in most components of the biota during the first two years.

Pond 5E continues to evolve. Pond snails (Physa)--totally absent in 1986 and 1987--were first observed in January 1988; by midsummer Physa dominated the invertebrate biomass in the pond. The number of coots feeding and roosting in Pond 5E began to increase in March 1988 as Pond 5 began to dry out. During the summer of 1988 at least 3 dozen coots appeared to be resident in Pond 5E, although they were evidently not nesting (G. Santolo, pers. comm.). Pond 5E water during the first two years was clear and contained little suspended algae (phytoplankton). Underwater Chara stands were perennial, subsurface light being available for photosynthesis. In contrast, during the spring and summer of 1988, Pond 5E water was murky with suspended algae,

and Chara totally disappeared from the pond in early June. Increased plant nutrients from coot droppings may have been the cause of the increased planktonic microalgal growth.

Chara began to grow later in June, either from sexual reproduction or from germination of bulbils. The new growth sprouted from the substrate through root-like holdfasts, the rhizoids. This was in contrast to Chara growth in the two previous years, which consisted of vegetative growth from branchlet tips, remote from the sediments. Rhizoids from which the original growth began had earlier decayed as layer upon layer of Chara growth shaded out the epibenthic zone. Chara rhizoids are not true roots, but are known to be capable of absorption of nutrients from soils and transportation of such nutrients to the rest of the plant.

Ruppia maritima, widgeongrass--a seed plant with true roots--began to colonize Pond 5E during the summer of 1988. Ruppia has not yet become abundant, but appears to be persisting in the pond.

Pond 5E water levels were inadvertently allowed to drop during August 1988, which dried the nearshore sediments, killing the aquatic vegetation there (Chara and Ruppia).

2.2.2. Selenium content of water and biota

With two major exceptions (new-growth Chara and benthic chironomid larvae, both discussed in more detail below) the biota of Pond 5E has continued to decline in selenium content since the last report. Dissolved selenium remains at less than 4 ppb, as it has for the last year (Figure 2-1). Chara remaining in May and early June declined in selenium to ca. 10 ppm dry weight (Figure 2-1). In contrast, new-growth Chara (arising from rhizoids, see above) was in most cases much higher when sampled in late June (Figure 2-1). Five samples collected from various parts of the pond on June 22 had selenium concentrations of 11.4, 27.4, 55.2, 58.5, and 128.5. The increased selenium may have come from the sediments through rhizoid transport, since selenium in near-surface sediments of pond 5E is known to be high and extremely patchy (Appendix Table 1, Figure 2-6). Interestingly, Ruppia collected from Pond 5E in early June contained only 15 ppm (mean of analyses by two methods). Ruppia roots could be less effective than

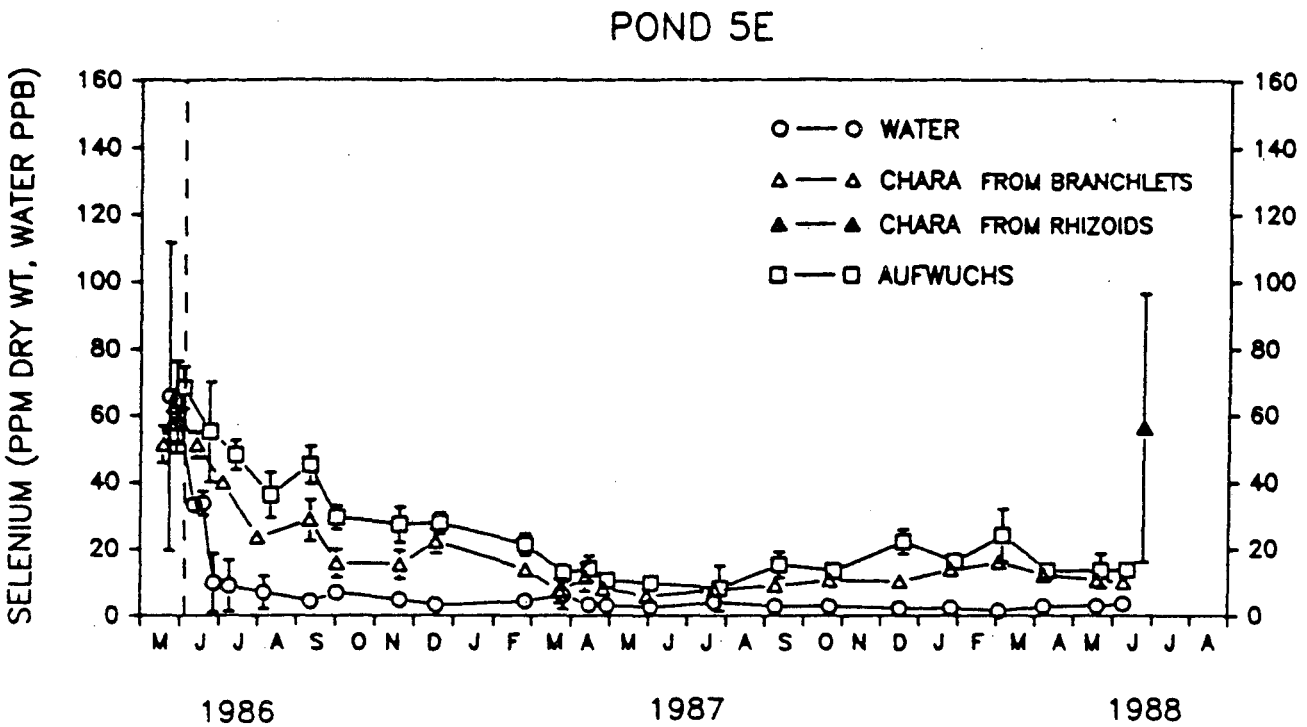


Figure 2-1. Selenium concentrations in water, Chara, and aufwuchs in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond. Error bars represent ± 2 standard errors.

Chara rhizoids at transporting sediment selenium upward, but more samples would be needed to evaluate the importance of sediment patchiness on Ruppia selenium in Pond 5E. Aufwuchs (attached growths) on Chara in May and early June remained less than 14 ppm. New Chara collected in late June had not yet supported enough aufwuchs for selenium analysis.

Most invertebrates continued to decline in selenium content, although in general insect biomass was low in summer. Epifaunal chironomid larvae declined to 22.7 ppm by late July (Figure 2-2), but benthic chironomid larvae were over twice as contaminated in July as in early June (Figure 2-2), for unknown reasons. Odonate nymphs showed little change since the last report; dragonflies (Anisoptera) had 15.2 ppm in late June, and damselflies (Zygoptera) 14.5 ppm in July (Figure 2-3).

Mosquitofish continued to decline in selenium, having 25.2 ppm in July (Figure 2-4), the lowest level yet seen in the pond. Tabanid larvae increased slightly in selenium (39.8 ppm in late June, up from 33.7 ppm in October 1987, Figure 2-4), but such larvae are very rare now. Significantly, Physa, the pond snail which dominated the invertebrate biomass in summer 1988, has very low selenium, less than 10 ppm dry weight (Figure 2-4).

Larvae of Berosus (Coleoptera: Hydrophilidae) declined moderately in selenium, to 27.2 ppm in July (Figure 2-5), but selenium in small dytiscid beetle adults increased from 13.3 ppm in April to 34.3 ppm in July (Figure 2-5).

Above-sediment cattail (Typha) parts remain low (less than 4 ppm, see Figure 2-7). Cattail roots increased in May, to nearly 60 ppm, but declined to ca. 30 ppm by July 1988. Alkali bullrushes (Scirpus) continued to have less than 2 ppm selenium in leaves, stems, seeds, and rhizomes; and Scirpus roots decreased to ca. 10 ppm in July 1988, comparable to 1987 minima, although Scirpus roots were much higher in selenium in June. (Figure 2-8, Appendix Table 1).

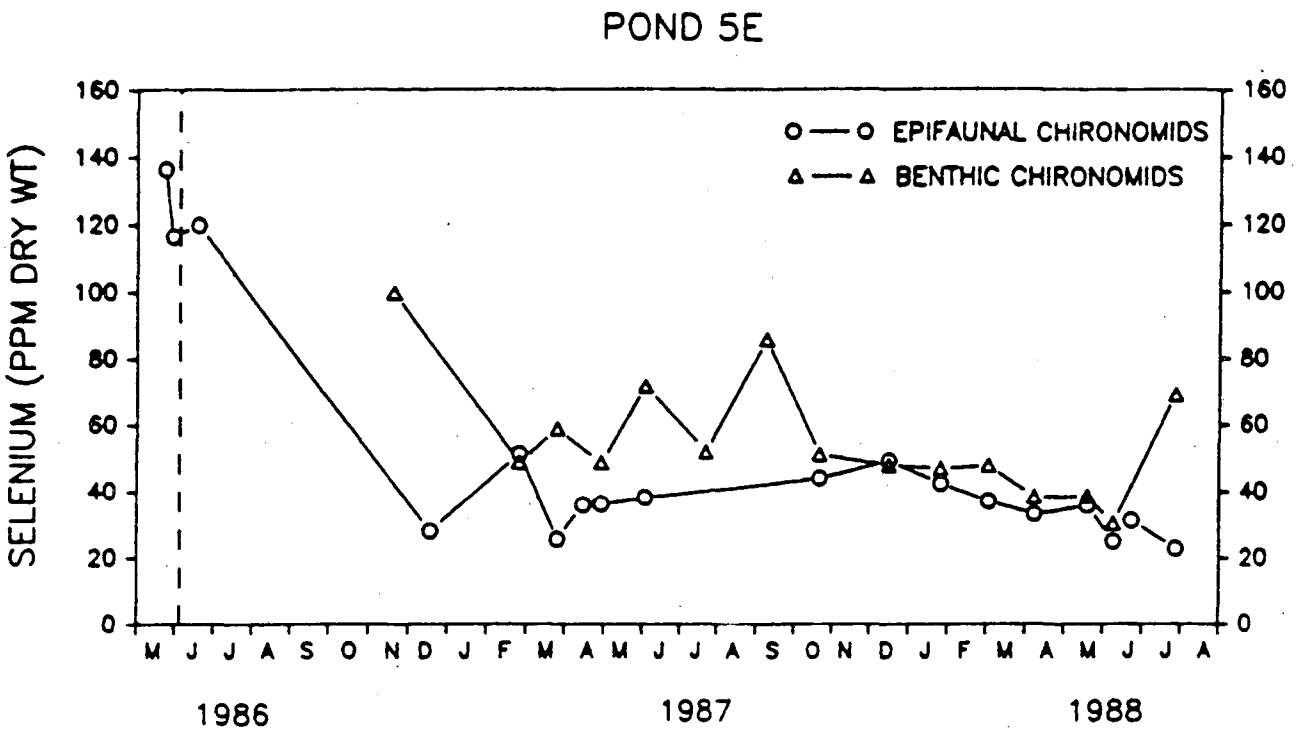


Figure 2-2. Selenium concentrations in epifaunal and benthic chironomid larvae in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

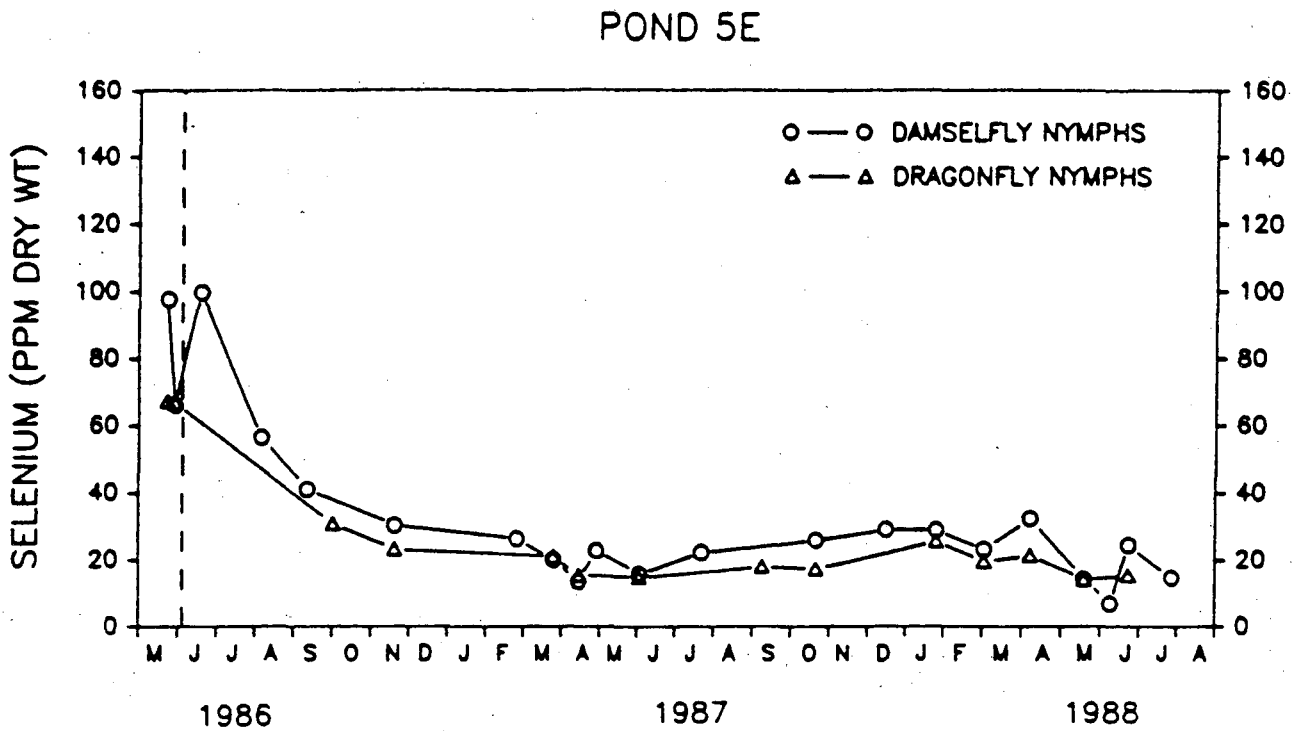


Figure 2-3. Selenium concentrations in dragonfly and damselfly nymphs in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

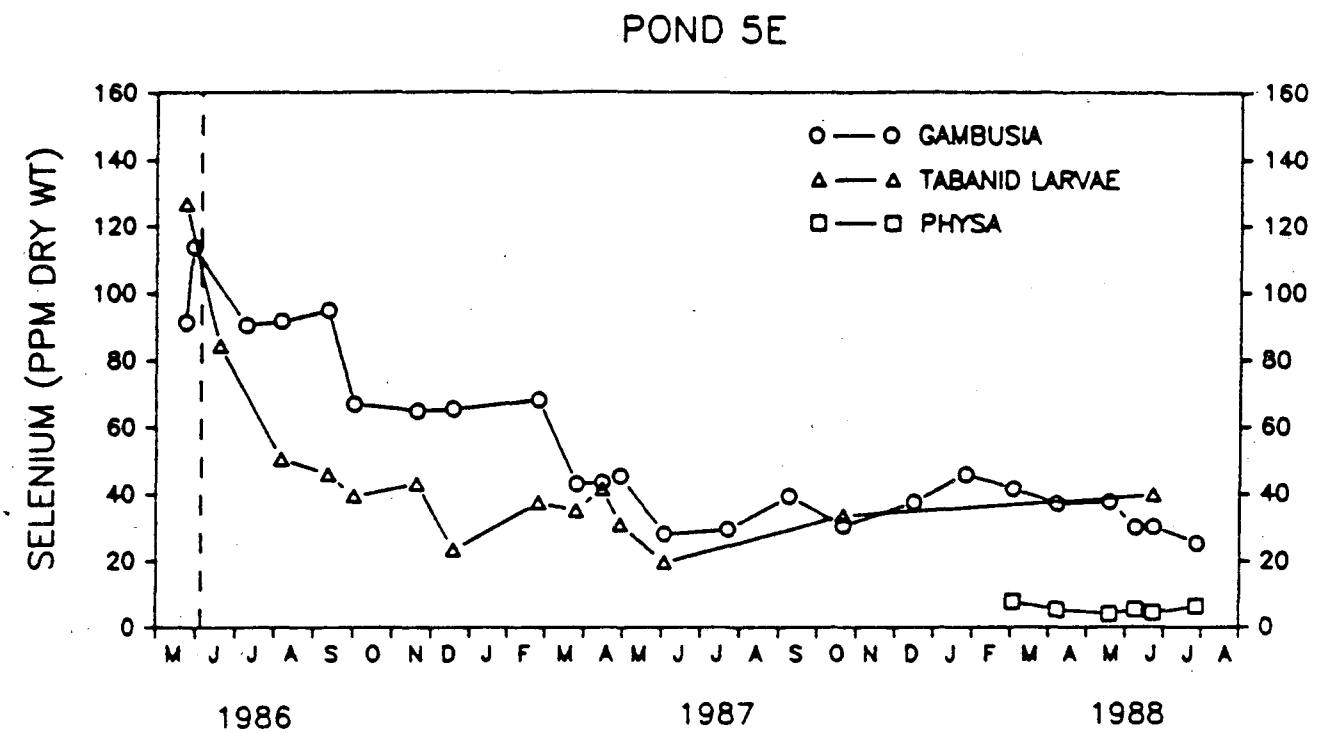


Figure 2-4. Selenium concentrations in Gambusia (mosquitofish), tabanid (horsefly) larvae, and Physa (pond snails), in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

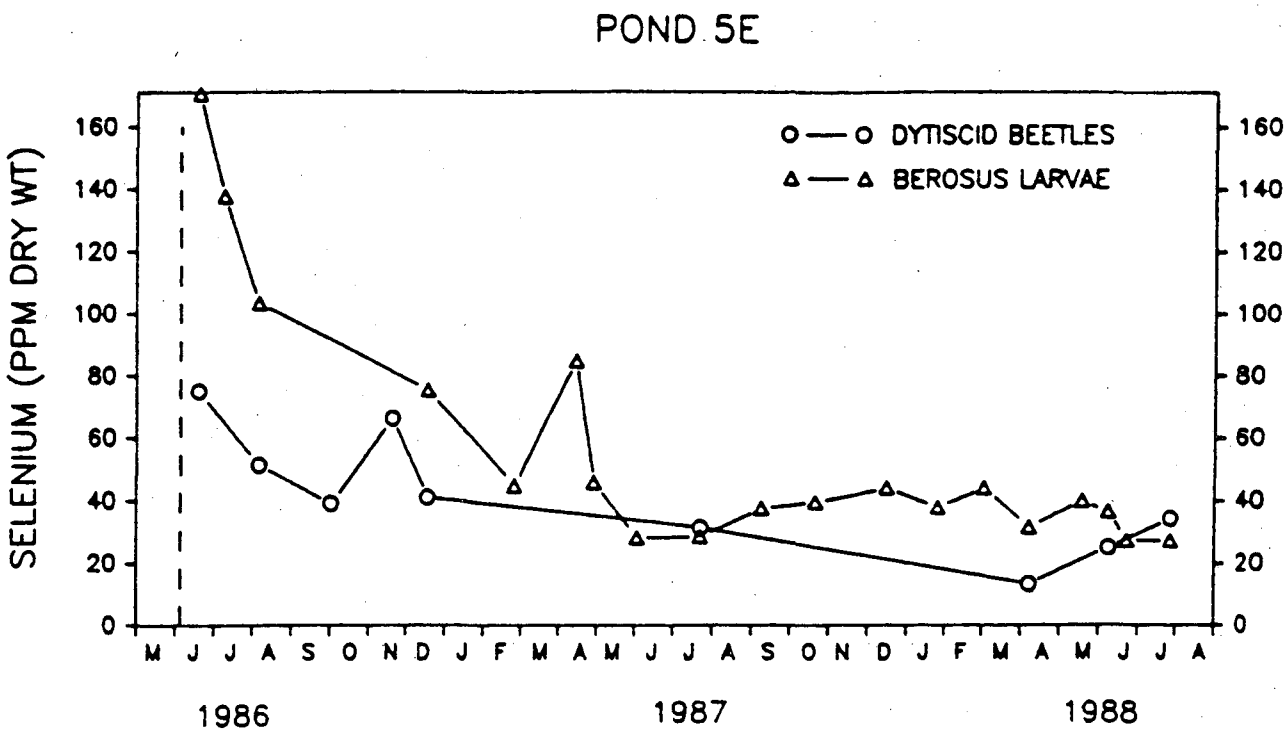


Figure 2-5. Selenium concentrations in dytiscid beetle adults and Berosus (hydrophilid beetle) larvae in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

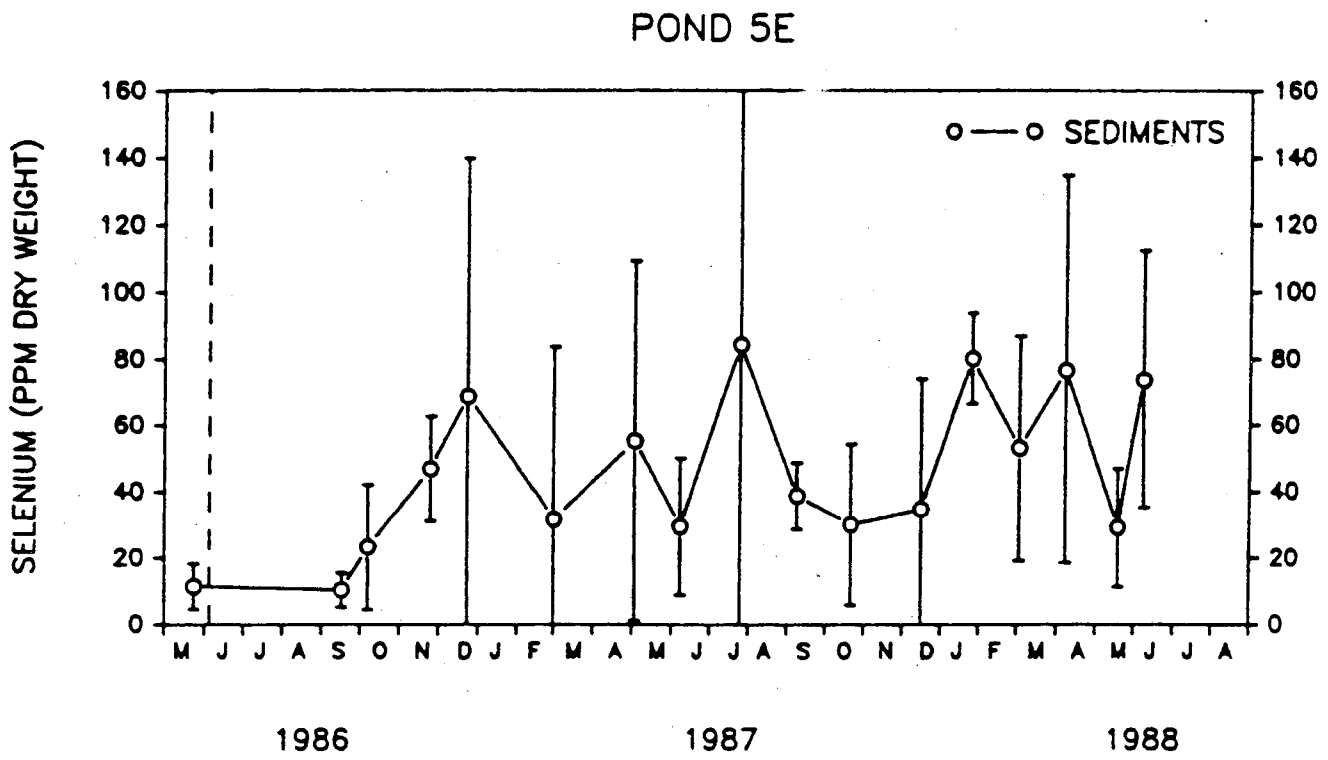


Figure 2-6. Selenium concentrations in surficial sediments in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond. Error bars represent ± 2 standard errors.

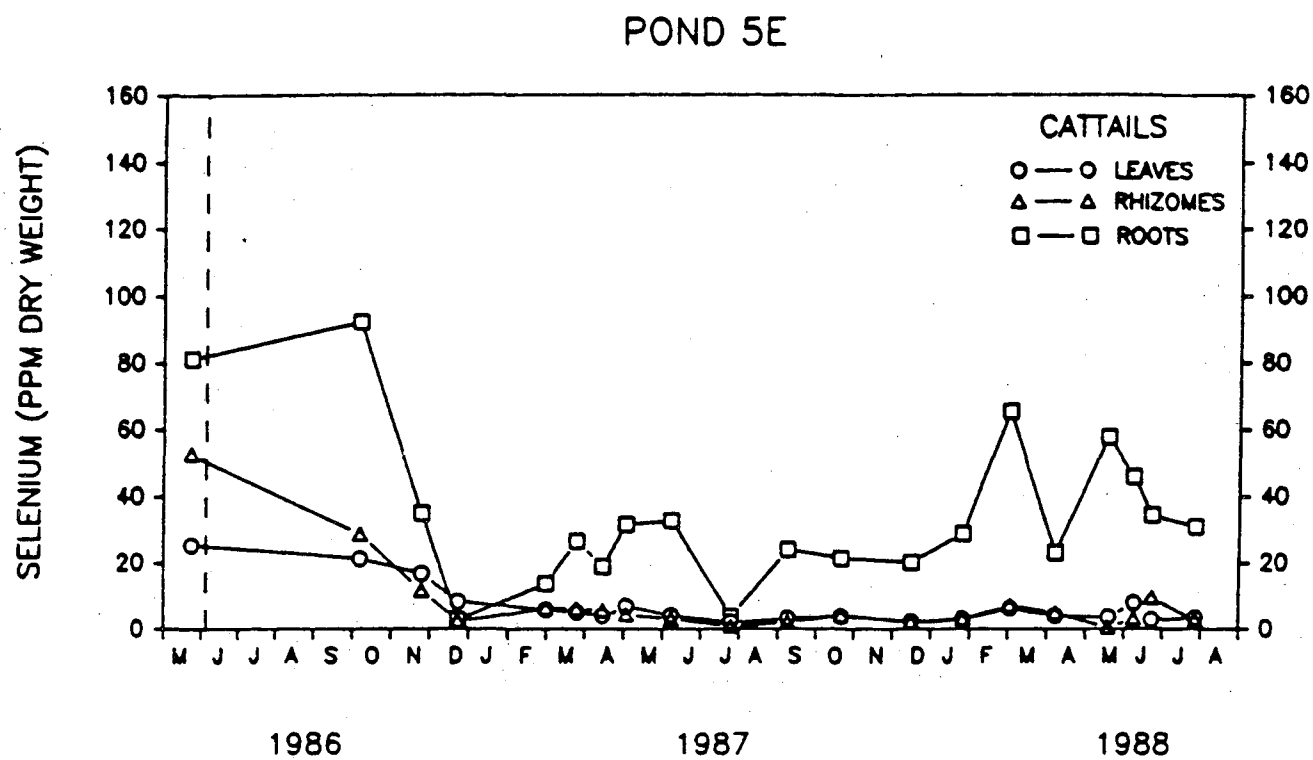


Figure 2-7. Selenium concentrations in cattails (Typha) in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

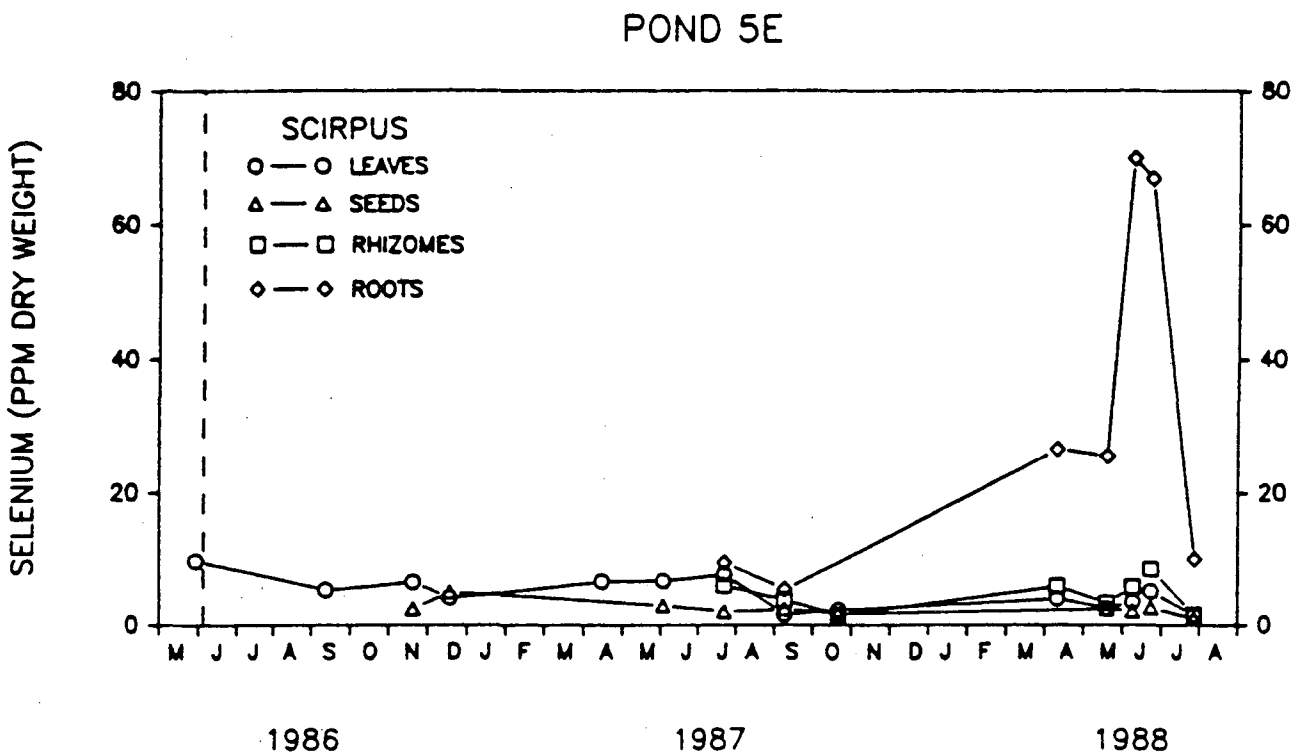


Figure 2-8. Selenium concentrations in alkali bullrush (Scirpus) in Pond 5E, 1986-1988. The vertical dashed line indicates when the pond was first isolated from the main pond.

2.3. TERRESTRIAL ECOLOGY STUDY

2.3.1. Introduction

The terrestrial ecology study was begun in March, 1988 to provide some basic data needed to understand selenium dynamics and effects of selenium contamination in upland areas, and to evaluate the effectiveness of proposed and on-going experimental techniques for decontaminating dry areas. The approach parallels that used successfully in the aquatic ecology studies, i.e., identifying key components of the food chain, and then monitoring seasonal and long-term changes in population parameters and selenium levels, and determining how selenium moves through the food chain.

The study was intended to provide the following:

(1) Baseline data on population dynamics (abundance, growth rate, standing-crop biomass, timing of reproduction, etc.) and selenium levels of key species in a "no-action" treatment, contaminated dry area, so that the effectiveness of various experimental ecological modification and volatilization treatments now being implemented, may be independently evaluated;

(2) Information and experience that would be useful to CH2M Hill in designing a long-term monitoring program; and

(3) General information on selenium dynamics in upland areas that would be applicable to contamination problems in other areas of the Central Valley.

An area of Pond 11 was selected as the "no-action" dry index site, and a synoptic survey encompassing most of the reservoir was conducted to verify the representativeness of the index site. Most of the upland area of the reservoir is dominated by stands of salt grass (*Distichlis spicata*), in which are mixed smaller patches or isolated individuals of other plant species. Most of the work reported here was conducted within these meadows of salt grass. The basic program consisted of monthly quantitative sampling of vegetation, roots, surface soil, and insects at the index site, plus a monthly qualitative survey in Pond 11 of plant phenology and community development, and of selenium levels in approximately 30 species of plants collected in a transect

from one side of the pond to the other. Details of the methods employed are described below.

2.3.2. Methods

2.3.2.1. Quantitative Sampling

Quantitative plant samples were collected monthly at the dry index site in Pond 11, within 4-5 m of a wooden stake installed there. The index site is located at the southern end of the pond, near the intersection of the pond's boundary road with the road bisecting Ponds 9 and 10.

The sampling unit was a 1/64th m^2 area, within which all vegetation, detritus, roots and soil down to 5 cm below the ground surface were collected. A 1/4 m^2 iron quadrat frame, divided by strings into 16 1/64 m^2 units was placed on the ground, and three of the 1/64 m^2 units were chosen at random for sampling. Above-ground vegetation was clipped off at ground level with pruning scissors and placed in a plastic bag. Next, loose surface detritus and seeds were collected by hand and placed in a second bag. Finally, a sharp trowel was used to dig out a square-sided sample of soil and roots down to 5 cm depth. Thus, three samples consisting of three bags each, were collected on each sampling day. In addition, three samples of insects were taken by means of 100 rapid sweeps of a 40 cm diameter heavy sweep net, in three parallel transects separated by several meters, and always taken by walking upwind from the plant sampling site while sweeping.

2.3.2.2. Qualitative Sampling

On each visit to the reservoir, after the quantitative sampling was completed, a transect was walked from the dry index site to the northern edge of the pond, following the same route each time. Along the way, samples of each plant species sighted were taken for selenium analysis and for developing a voucher collection. Identifications were made by staff of the U. C. Berkeley Herbarium, especially Barbara Ertter. Notes were made of observed changes in growth, reproductive condition, etc., since the previous visit. Plants obtained in special areas, e.g., formerly wet depressions, were bagged and analyzed separately.

2.3.2.3. Laboratory Procedures

Plant samples from the field were refrigerated overnight, and insects were frozen. Quantitative plant samples were sorted into live vs. dead vegetation. The live vegetation was separated by species before drying, weighing, and preparing for selenium analysis. Dead vegetation was dried, weighed, and prepared for selenium analysis without attempting to sort it by species. Detritus samples were sorted into seeds, occasional insects, and detritus before drying and weighing. Roots were extracted from soil by sieving with a 4 mm mesh screen. Roots were washed with tap water before drying and weighing.

After freezing, insect samples were sorted into species or lowest recognizable taxon before drying and weighing. For selenium analysis, some combinations of taxa among replicates and of different but related taxa (e.g., all flies) had to be made to provide sufficient material for analysis.

Qualitative samples were sorted into piles of different species. Specimens representing different stages of development were dried and pressed for the voucher collection. Others were cut into pieces of stem, leaves, and roots, which were combined for selenium analysis. On some occasions seeds or flowering tops of some species were analyzed separately.

2.3.2.4. Synoptic Survey

A synoptic survey of salt grass meadows in the reservoir was conducted on 6 July 1988. A total of 28 stations from Ponds 4 through 12 were sampled. A stake was installed at each station, and crews collected three samples of soil and above-ground vegetation within a meter of each stake. The sampling unit was the rim of a plastic 5 gal bucket (269 mm diameter, area = 568 cm^2). Vegetation was quantitatively sampled by clipping with scissors, and a non-quantitative sample of surface soil was then taken with a trowel from each clipped area. In addition, three 50-sweep samples of insects were collected at each station. Laboratory procedures were the same as for the regular monthly collections, except that detritus and roots were not collected in the synoptic survey.

2.3.3. Results

2.3.3.1. Qualitative Samples

To date, 28 species of plants have been identified from Pond 11; these are listed in Table 2-1. Several species are small annuals which were seen in the first couple of months of the study and then died as summer progressed. Others such as *Cressa truxillensis* had not yet germinated in March, but became abundant later on. *Cressa* became a dominant plant in *Distichlis* meadows throughout the reservoir, as well as in dry, formerly wet playa areas. *Cressa* seeds from 1987 or earlier years were abundant in the surface debris throughout Pond 11 and comprised nearly all the seeds found in the quantitative samples. As summer progressed, the number of Cressa seeds visible on the ground declined dramatically, and their biomass in the quantitative samples also declined (see below). Since the decline occurred long after the germination period, we assume that the loss was mainly due to seed-eating animals.

Most plants appeared to be growing rapidly in March and April. *Distichlis* was in bloom by mid-April in the center of Pond 11. *Cressa, Atriplex, Sonchus,* and other plants bloomed in May, and by mid-June many of the larger plants such as thistles and mustard were drying up and dying. Burning bush (*Kochia scoparia*), the dominant plant in dry playa areas as well as disturbed areas that had been experimentally disced or scraped, was still growing and had not yet bloomed in August, at the time of our last visit. *Distichlis, Frankenia,* and *Cressa* were still green in August, although the *Cressa* were turning brown and dropping seeds.

Mean selenium concentrations in qualitative plant samples taken in March-June are shown in Table 2-2 (no qualitative collections were made in July or August). Complete selenium data for qualitative samples are provided in Appendix Table 2. The main apparent trend in Table 2-2 is that a number of species had higher concentrations of selenium in March, at which time the plants were small, shallowly rooted shoots, than later in the summer. This trend may be related to the fact that the upper, organic layer of soil has generally a much higher concentration of selenium than deeper layers. As the plants grow, their roots penetrate deeper into the soil, so they would then be extracting water and nutrients from soil with lower levels of selenium. A decline

Table 2-1. Scientific and common names of terrestrial plants found in Kesterson Reservoir.

Amsinckia sp.	fiddleneck
Atriplex sp. 1	saltbush
Atriplex sp. 2	saltbush
Bromus sp. 1	brome, chess, cheatgrass
Bromus sp. 2 (japonicus-mollis group)	brome, chess, cheatgrass
Centaurea solstitialis	star thistle
Cirsium sp.	thistle
Cotula coronopifolia	brass buttons
Cressa truxillensis	alkali weed
Cuscuta salina	salt marsh dodder
Distichlis spicata	salt grass
Erodium cicutarium	filaree
Frankenia grandifolia	alkali heath
Heliotropum curassavicum	seaside heliotrope
Hordeum sp.	foxtail barley
Kochina scoparia	burning bush
Lactuca sp.	lettuce
Lasthenia sp.	composite--no common name
Lupinus biocolor	lupine
Medicago sp.	alfalfa
Melilotus indica	sweet clover
Rumex sp.	dock
Senecio vulgaris	common groundsel
Sesuvium sessile	sea purselane
Sida leprosa	alkali mallow
Sisymbrium sp.	mustard
Sonchus sp.	sow thistle
Scirpus sp.	bulrush

Table 2-2. Seasonal variation in selenium concentration (mean ppm) in terrestrial plants (qualitative samples), 1988.

Species	Pond 11				Pond 12
	March	April	May	June	March
Amsinckia	0.9		8.2		0.8
Atriplex 1	2.5	2.6	1.9	0.6	2.6
Atriplex 2				0.0	
Bromus 1	1.2	2.7	2.2		
Bromus 2		2.9	3.7		
Centaurea				6.3	
Cirsium		2.0			5.9
Cotula					5.8
Cressa		2.1	1.3	1.5	
Cuscuta				0.5	
Distichlis	1.6	0.5	1.1	1.4	3.5
Erodium	3.9	3.0	4.1		4.8
Frankenia	3.7	4.0	3.4	2.1	3.3
Heliotropum	4.5				
Hordeum		1.3			6.8
Kochina	7.4	1.9	1.6	1.5	7.8
Lactuca	7.4				
Lasthenia	2.9				3.2
Lupinus					3.7
Medicago	6.9	1.4			4.4
Rumex					4.9
Senecio	5.3	1.2			5.6
Sesuvium	4.2				2.5
Sida	39.8	1.9	3.1	9.8	4.6
Sisymbrium sp.	7.6				
Sonchus	2.7	5.8	4.0	5.6	6.4
plant 34				5.0	

in soil selenium concentration during the summer is an unlikely explanation, as the surface soil concentration measured at the dry index site did not change during the six months of sampling (Figure 2-9).

2.3.3.2. Quantitative Samples

Mean biomass values for different components of the quantitative samples are plotted in Figure 2-10. Complete results are provided in Appendix Table 3. The upper part of Figure 2-10 reflects the increasing biomass of *Distichlis* and *Cressa* as the growing season proceeds. The lower portion shows the decreasing biomass of seeds (*Cressa*) mentioned earlier. Considerable variation is evident in the early phase of sampling, suggesting that the sampling technique became more refined with practice.

Mean selenium levels in different components of the quantitative plant samples are shown in Figure 2-9. Data for August are incomplete. There was little change in concentration in live, above-ground *Distichlis* and *Cressa* during the summer (upper portion of Figure 2-9), both averaging about 2 ppm. *Distichlis* roots, however, showed high levels of selenium, averaging about 32 ppm (lower portion of Figure 2-9---"roots" were essentially 100% *Distichlis*). The surface detritus averaged about 63 ppm and surface soil 20 ppm.

Mean biomass and numbers of insects and other arthropods are plotted in Figure 2-11; complete data are provided in Appendix Table 4. Sweep net sampling was not begun until May. The increasing biomass of arthropods as summer progressed was due almost entirely to grasshoppers, which increased in both number and body size through July. Selenium levels in arthropods are shown in Figure 2-11 and Appendix Table 5, except for July and August, for which the laboratory results are not yet available. No conclusions may be drawn from the data available to date, but we note a few instances of high selenium levels (e.g., one sample of a fly identified as Species B (67 ppm), and a sample of sowbugs collected by hand in March (44.3 ppm, Appendix Table 5)).

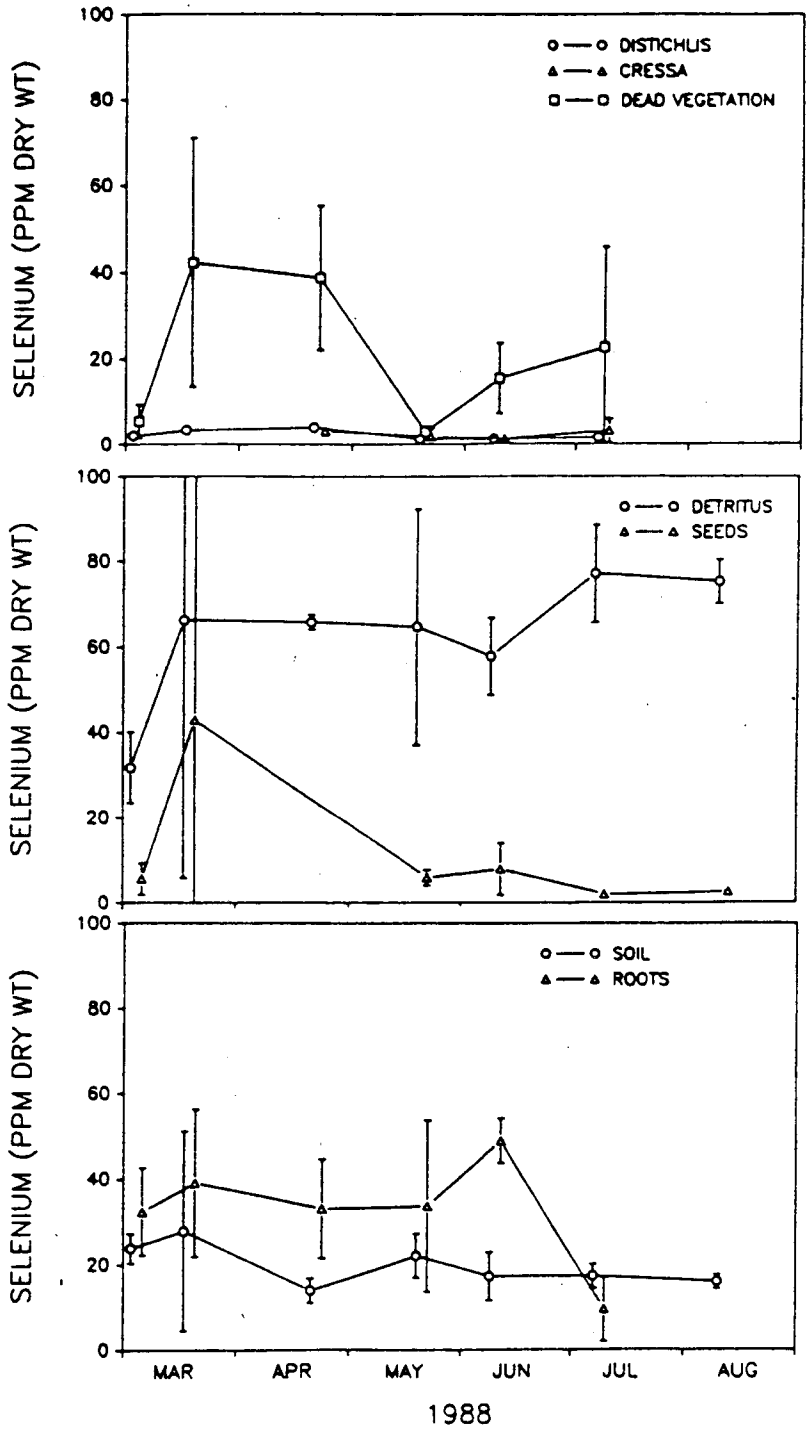


Figure 2-9. Seasonal variation in mean selenium concentration in components of quantitative plant samples at the Pond 11 index site. Error bars represent ± 2 standard errors.

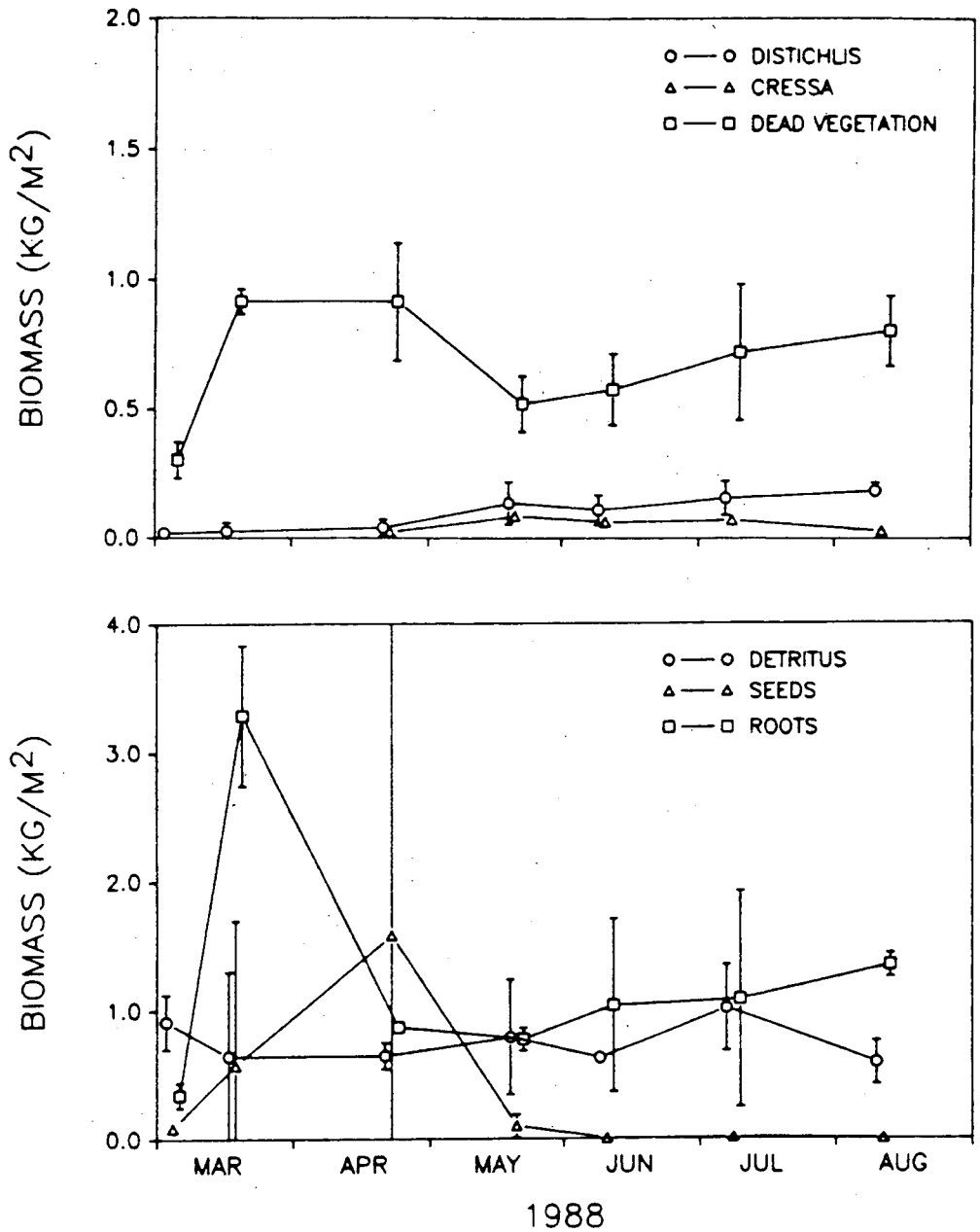


Figure 2-10. Seasonal variation in mean biomass of components of quantitative plant samples at the Pond 11 index site. Error bars represent ± 2 standard errors.

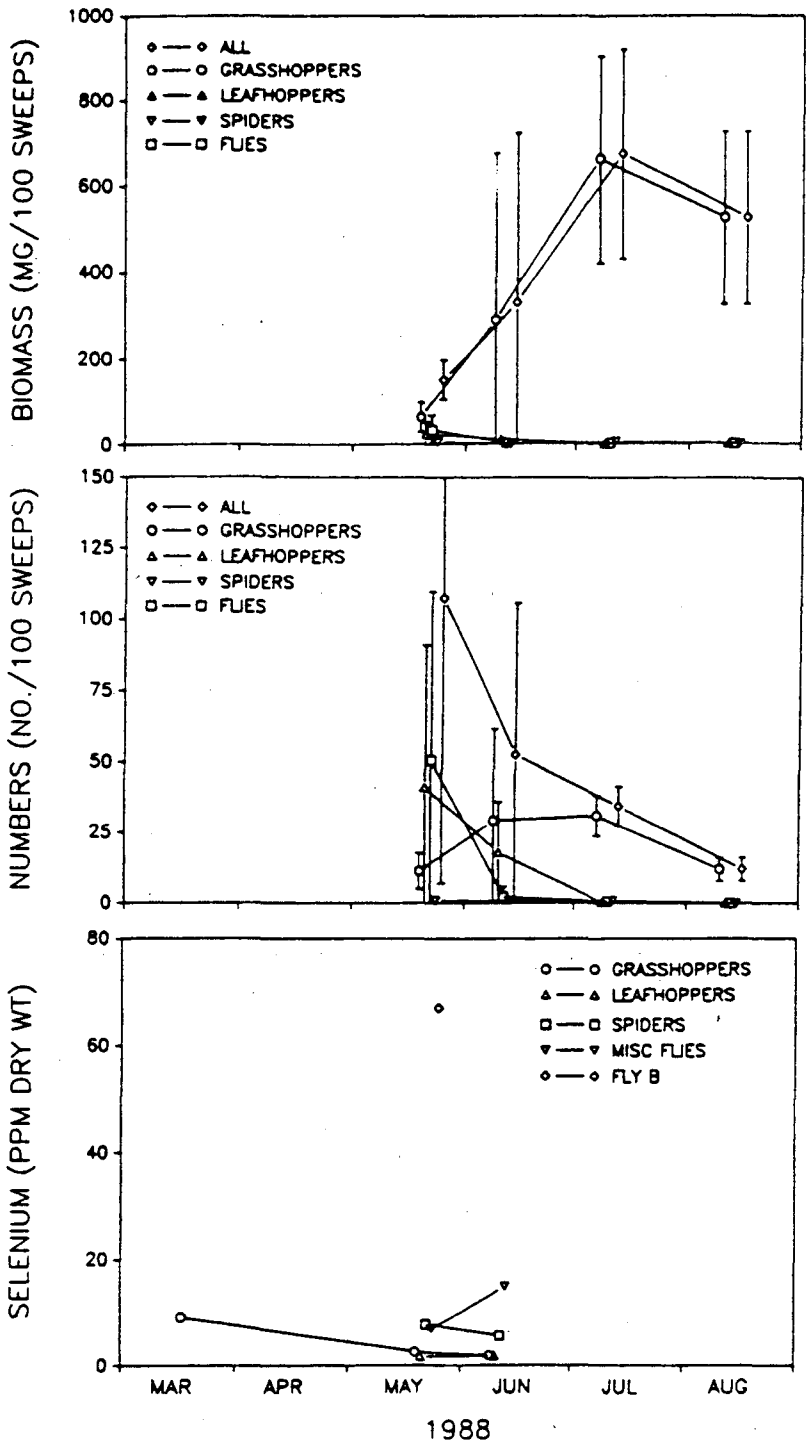


Figure 2-11. Seasonal variation in means of biomass, numbers, and selenium concentration of arthropods at the Pond 11 index site. Error bars represent ± 2 standard errors.

2.3.3.3. Synoptic Survey

Mean biomass per pond for the dominant plants *Distichlis* and *Cressa* are shown in Figure 2-12. Complete data and means per pond and per station are provided in Appendix Tables 6 through 8. Figure 2-12 shows that Pond 11 is at the low end of the scale in terms of *Distichlis* biomass, and intermediate for *Cressa*. Mean values for these species at the index site in July (Figure 2-10) are typical of Pond 11.

Selenium analyses for plants in the synoptic survey are incomplete at this time, except for the 10 stations in Pond 11 (Appendix Tables 9-11). Mean selenium concentrations for *Distichlis* and *Cressa* in Pond 11 are 1.4 and 2.0 ppm, respectively, compared to 1.6 and 3.2 ppm at the index site on the same day (Figure 2-9).

Grasshoppers and leafhoppers were sorted from the synoptic sweep net samples (remaining insects are still frozen). Complete data on numbers, biomass, and selenium levels are provided in Appendix Tables 12 through 15. Leafhoppers had declined greatly by July as their plant resources died, so that they were found at only a few stations in the synoptic survey. Grasshoppers were still abundant, and mean numbers, biomass, and selenium levels per pond are shown in Figure 2-13. Biomass means ranged from 5.3 (Pond 5) to 353.8 mg per 50 sweeps, with Pond 11 at an intermediate level of 205.3 mg/50 sweeps. At the dry index site mean biomass on the same day was 662 mg/100 sweeps, or about 330/50 sweeps.

Mean selenium levels in grasshoppers ranged from 2.5 ppm in Pond 11 to 5.9 ppm in Pond 7 (Figure 2-13). Selenium analyses for insects collected in July and August at the index site have not been completed.

Mean selenium concentrations in surface soils in Ponds 4 through 12 are shown in Figure 2-14. Means per station and complete data are provided in Appendix Tables 16 and 17. A generally higher level of contamination in southern pond soils is evident in Figure 2-14, as expected from historical considerations. Pond 11 is intermediate in selenium concentration among northern pond soils, and examination of Figure 2-9 indicates that soils at our index site are typical of Pond 11.

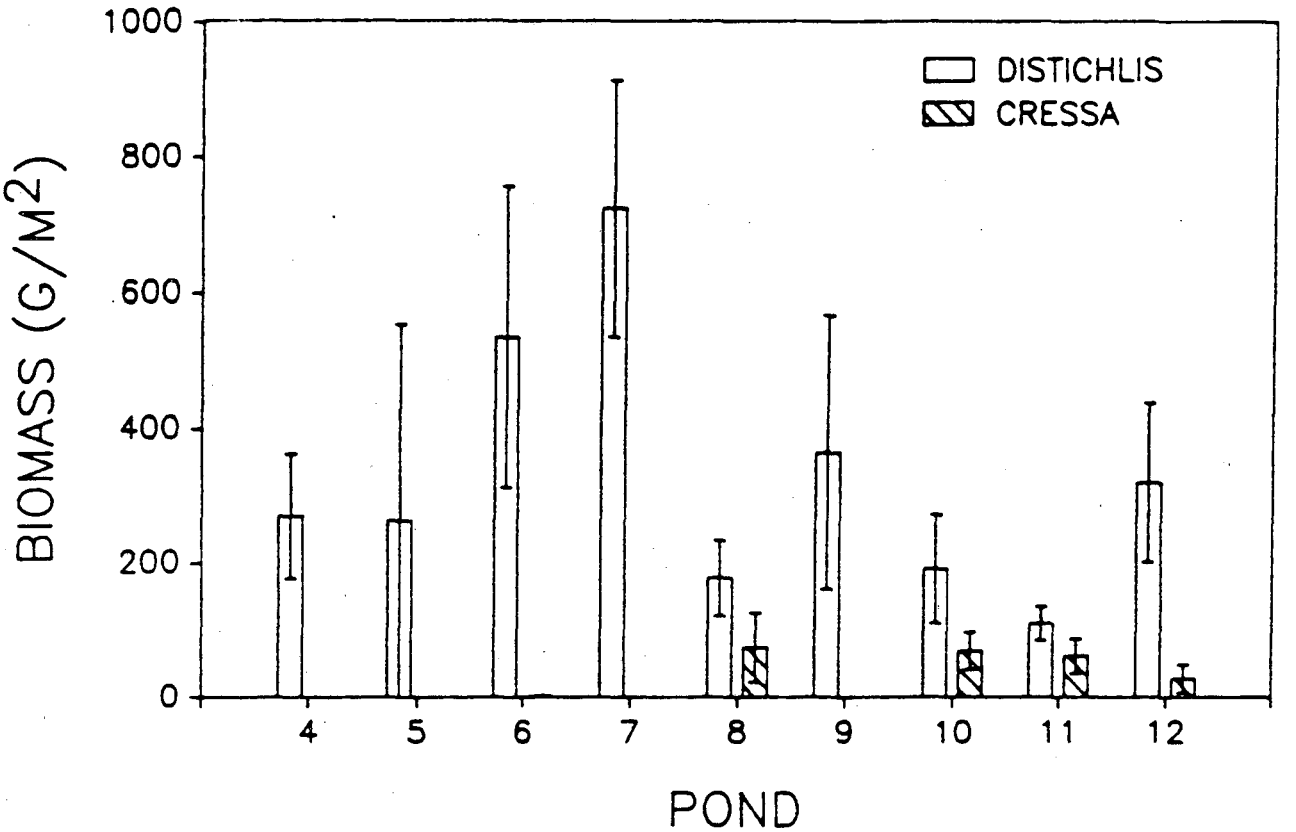


Figure 2-12. Mean biomass of *Distichlis* and *Cressa* Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.

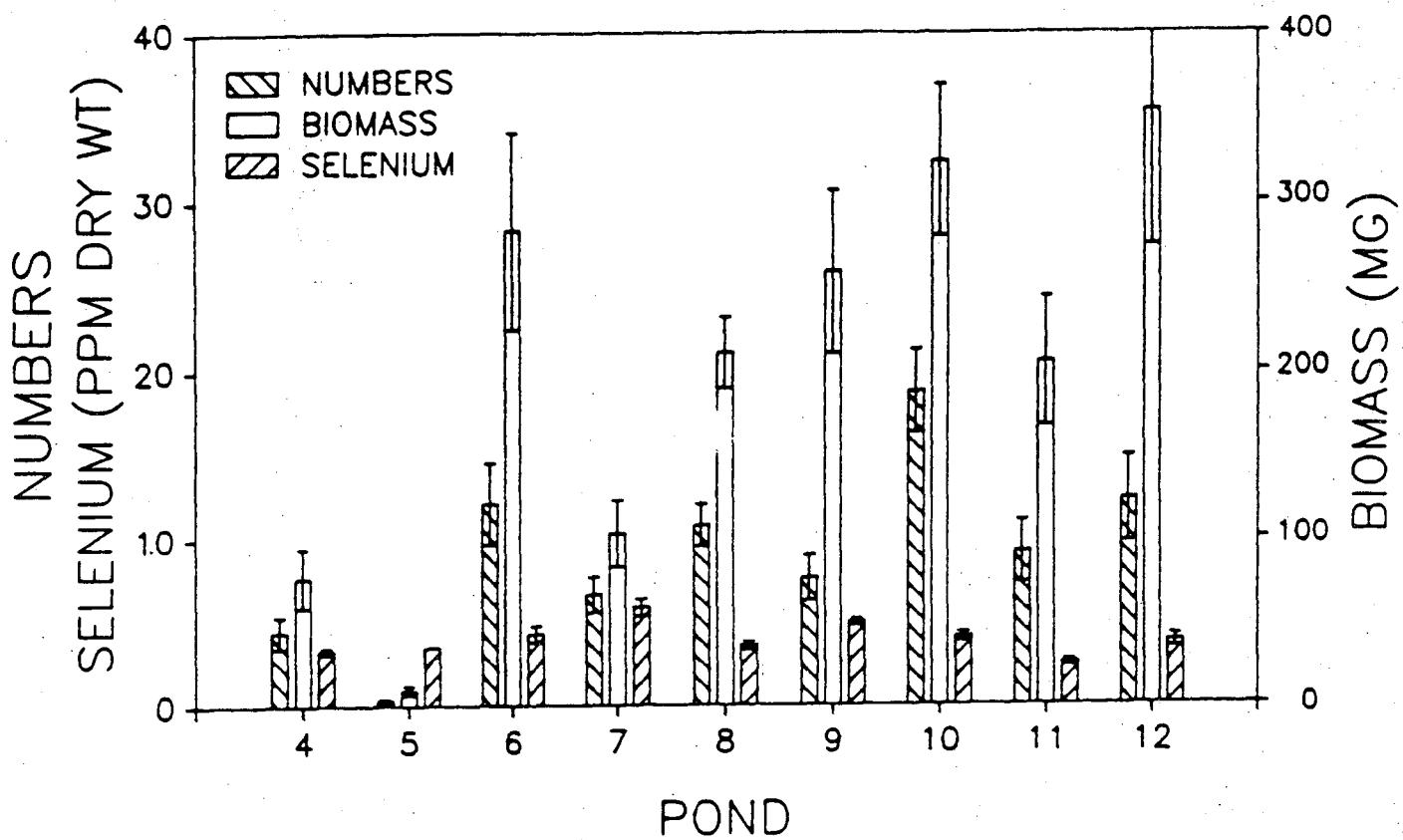


Figure 2-13. Means of biomass, numbers, and selenium concentration of grasshoppers, Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.

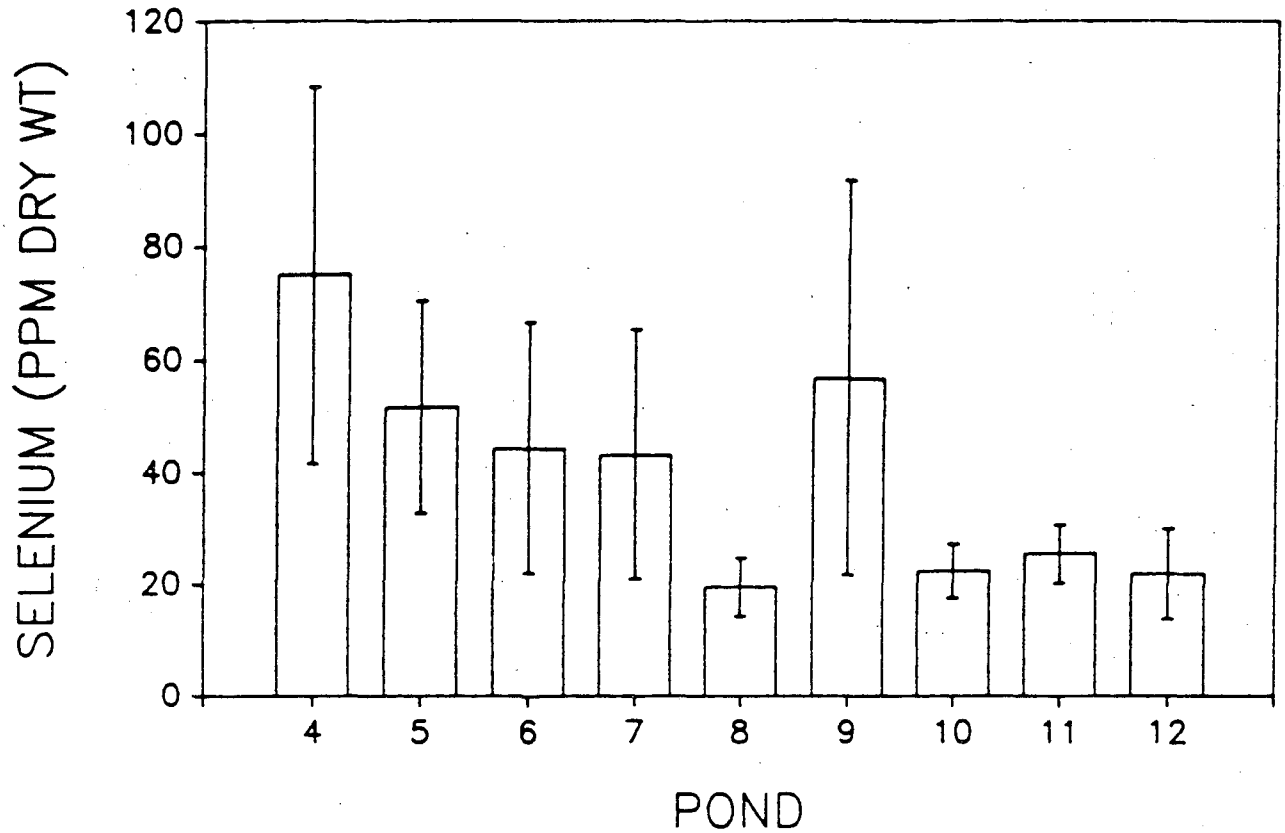


Figure 2-14. Mean selenium concentration in soils, Synoptic survey, 6 July 1988. Error bars represent ± 2 standard errors.

2.3.4. Discussion

The major purpose of the terrestrial component of the U. C. Berkeley (LBL-SEEHRL) ecology research program was to determine the biomass and selenium contamination levels in food-chain organisms in areas which had been exposed to seleniferous drainage water. In particular, a base line for a "no action" and possible ecological modification actions must be provided at the level where selenium enters the food web (i.e. at the lowest trophic levels). As in the aquatic ecosystem, there is little bioconcentration of selenium in mammals and birds in the terrestrial system. These higher trophic levels tend to have a selenium contamination similar to their prey. This contrasts with the plants and bacteria which provide the big step up from parts-per-billion in the water to parts-per-million in the living organisms.

The above objective has been only partially-fulfilled because the quantitative lower trophic level sampling has only taken place over the past 6 months. At the time of writing (September, 1988), not all samples have been analyzed for selenium, and some minor identification and literature work remains to be accomplished. However, sufficient data have been gathered to indicate that the spring-summer dynamics of the terrestrial community are of concern and should be fully analyzed in conjunction with the on-going qualitative monitoring projects (US FWS, CH2M-Hill, Inc.). For this purpose we have provided a complete data appendix in this report.

If compared with samples taken at similar times, our results can be used as a comparison with future samples in dry areas anywhere in the Reservoir. They can also be compared with those from the experimental plots. Our reservoir-wide synoptic survey in the summer of 1988 provided both the qualitative and quantitative information needed for a risk analysis of the same type that was previously carried out in 1986 for wet-management options.

3. VADOSE ZONE MONITORING

3.1. INTRODUCTION

Various studies concerned with soil water and ephemeral pools at the Reservoir have been outlined in previous reports (e.g. 1987 Annual Report). These activities focused on monitoring of excavated test plots, playa and saltgrass soil environments, and ephemeral pools. Along with the continuation of these works which will be updated in following sections, several related studies have more recently been initiated. These studies include the determination of bare soil evaporation rates and the characterization of distributions of select major ions and trace elements at new monitoring sites in Ponds 8 and 9. Summaries of all of the abovementioned studies are provided in the following sections.

A review of several important hydrological influences on the Kesterson Reservoir soil environment is useful in understanding the physical context in which the various soil processes to be described take place. As noted in an early (1939) soil survey, soils of this area have been saline long before operation of the Reservoir (Soil Conservation Service, 1952). The formation of saline soils is commonly observed in regions characterized by low rainfall, high evaporation, and a shallow depth to the water table (U.S. Salinity Laboratory, 1954). All of these factors are characteristic of Kesterson Reservoir and its surroundings. Annual rainfall at the Reservoir has ranged from around 200 to 360 mm, while annual pan evaporation has ranged from around 1500 to 2200 mm (1984-1988, USBR personal communication). The shallow water table fluctuates within 3 m of the soil surface, with seasonal maximum elevations commonly occurring within 1 m from the soil surface. In some areas, this seasonal rise extends above the soil surface creating ephemeral pools. The depth of the shallow water table strongly influences evaporation from bare soils (e.g. Moore, 1939, Gardner and Fireman, 1957). In this environment where evaporative soil water losses exceed rainfall leaching, accumulation of salts within the soil profile results. This

process of evaporative salt concentration must be considered in assessing any method for management of the Reservoir. As will be discussed in sections 3.2 and 3.6, for unvegetated soils, the soluble forms of selenium will concentrate near the soil surface with other soluble salts. As shown in section 3.4, soluble selenium and salt concentration occurs within the root zone in soils vegetated with saltgrass.

3.2. 1.0 FT EXCAVATION TEST PLOT AT POND 6

As described in previous reports (6th Progress Report, 1987 Annual Report, 7th Progress Report), excavations of surface soils to depths of 0.5 and 1.0 ft have been performed to assess the effects of the ODP on residual soils. The effectiveness of the ODP in the Kesterson Reservoir environment appeared questionable due to three basic principles. These include the pervasive occurrence of high concentrations of soluble selenium to depths of about 1 m (Figure 3-1), the enhanced tendency for capillary rise of soluble salts (including selenium) to the soil surface, and the enhanced tendency for formation of ephemeral pools due to the increased areal extent of topographically low regions. As noted previously, the combined effects of a shallow water table, low rainfall, and high potential evaporation have long been recognized in the process of soil salinization through evaporative concentration of salts. Excavation results in closer proximity of the water table to the soil surface, and higher rates of evaporatively driven "capillary" flow to the surface. The effect of evaporative transport of solutes to the soil surface exacerbates the ephemeral pool problem due to dissolution of these soil salts at potentially high concentrations in surface waters.

One method of quantifying temporal trends in surface soil salinity and selenium content is through periodic analyses of surface soil samples. As described in previous reports, 0.15 m deep core samples are periodically taken in the residual soil surface of the excavation test plots. Water-soluble soil constituents are extracted in the laboratory from 5:1 ratios of water to soil which have been continuously stirred for 1 hr, centrifuged, and filtered (0.45 μm). The extracted solution is then analyzed for electrical conductivity, selenite, and total selenium, (EC). Occa-

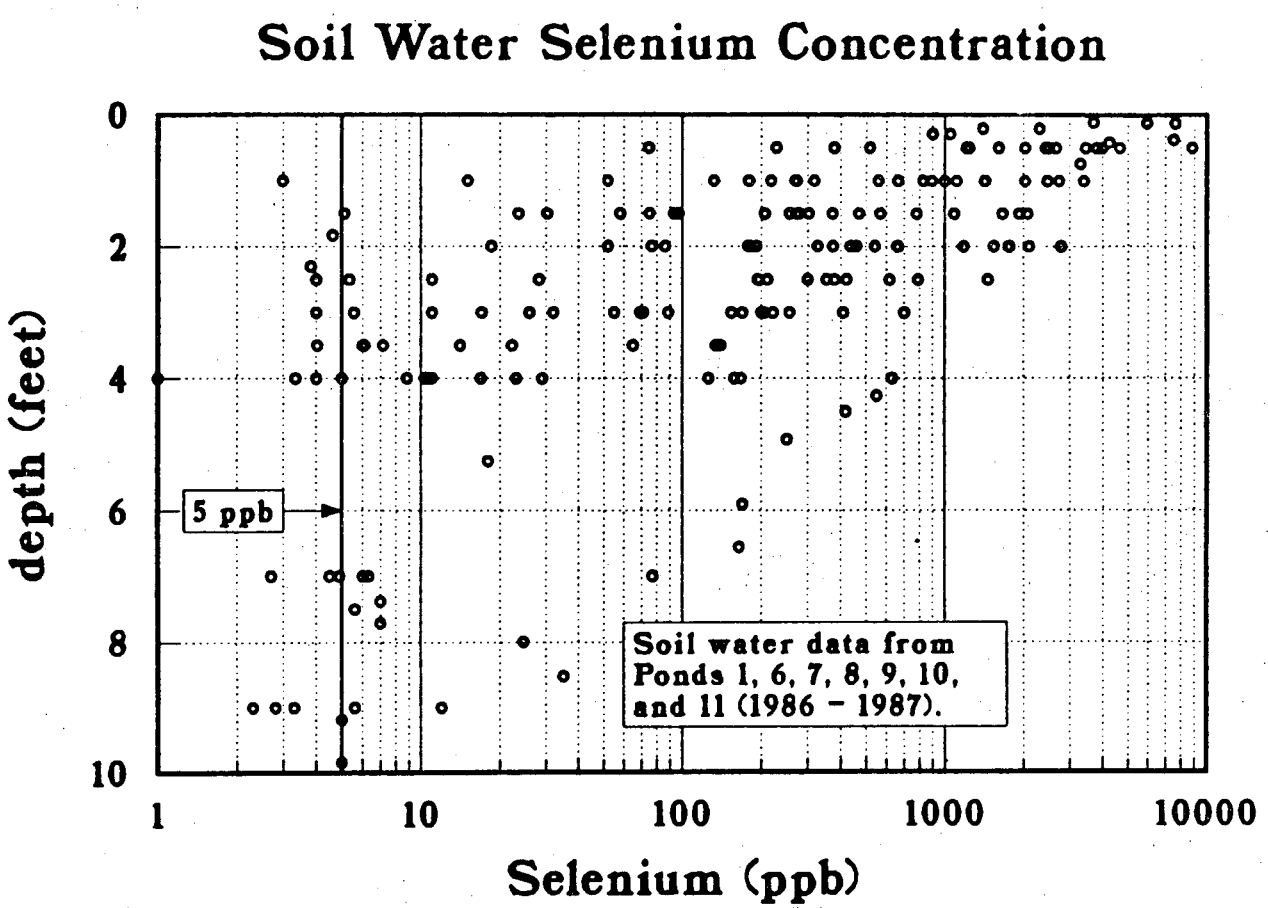
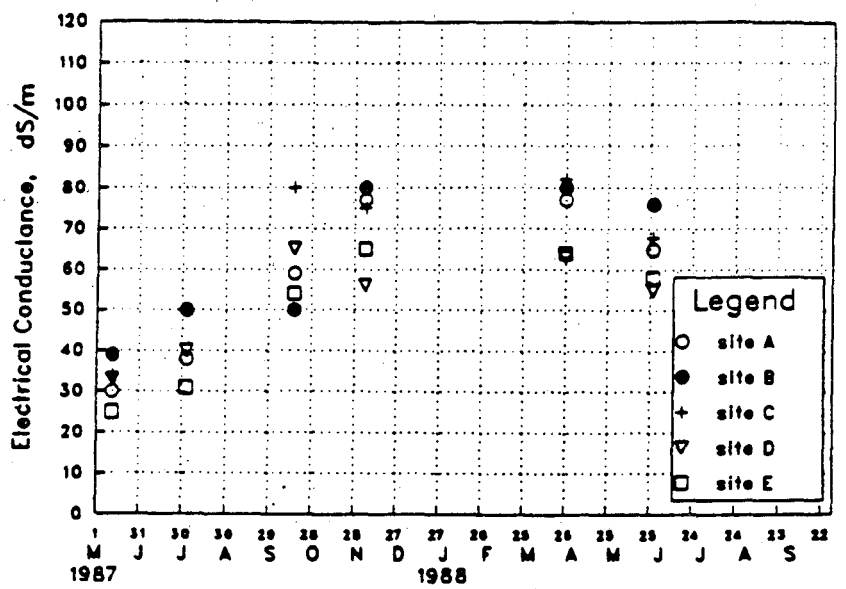


Figure 3-1. Depth-distribution of soil water selenium from various monitoring sites at Kesterson Reservoir. Data are from Ponds 1, 6, 7, 8, 9, 10, and 11.

sional analyses are also performed for major ions and trace elements. EC time trend data from cores taken in the 1.0 ft excavation test plot in Pond 6 are shown in Figure 3-2a. The EC data are all normalized to soil water contents corresponding to a water:soil mass ratio of 0.20 which typifies excavated soil surfaces near saturation. The approximately two-fold increase in ECs during 1987 corresponds to an upward evaporative soil water flux of about 0.2 m/yr. While more recent sets of samples for the present year have yet to be processed, the mean value of 64 dS/m for the May 1988 ECs are twice as high as the mean of ECs at the beginning of the experiment in May 1987 which was 32 dS/m (coefficients of variation are ≤ 16%).

Soluble selenium analyses of the surface core samples from the Pond 6, 1.0 ft excavation test plot are shown in Figure 3-2b. While a slight increase in surface soil soluble selenium concentrations was observed during 1987, the limited 1988 data show no trend. Unlike simpler soluble salts, the soluble selenium concentration is not simply governed by soil water flow, evaporation, and precipitation. More complex transformations of selenium including strong redox-dependent solubility, adsorption, and volatilization can result in large spatial and temporal variations in the soluble selenium inventory. These complexities may require longer observation intervals to discern significant patterns. These data nevertheless demonstrate that even with a 1.0 ft deep excavation, high concentrations of soluble selenium will persist in the residual surface soils.

At the 1.0 ft excavation test plot in Pond 6, the seasonal rise in the shallow water table displaced soil pore waters upwards, and resulted in ponding at the surface from mid-November 1987 to late March 1988. This surface water was regularly sampled at 3 sites, and analyzed for soluble selenium and EC. Surface water samples were collected from interior regions of cylindrical rings inserted into the soil. The protruding upper end walls of the rings isolated interior waters from possible lateral contamination during the initial stages of ponding. Consistent differences in water levels inside the rings versus outside the rings indicated that the rings effectively prevented lateral surface water contamination. While mixing of surface waters was prevented, it should be noted that the extent of water table rise in the Pond 6 excavation test plots was enhanced by the



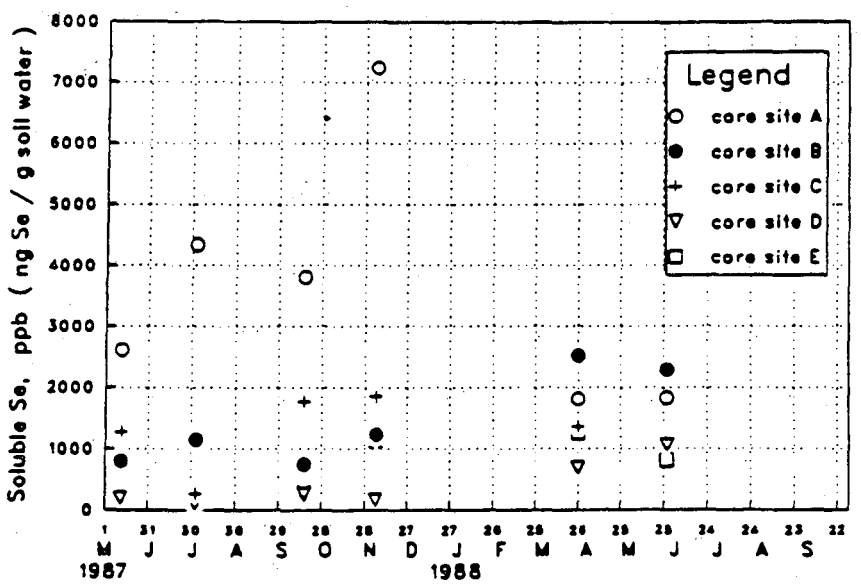
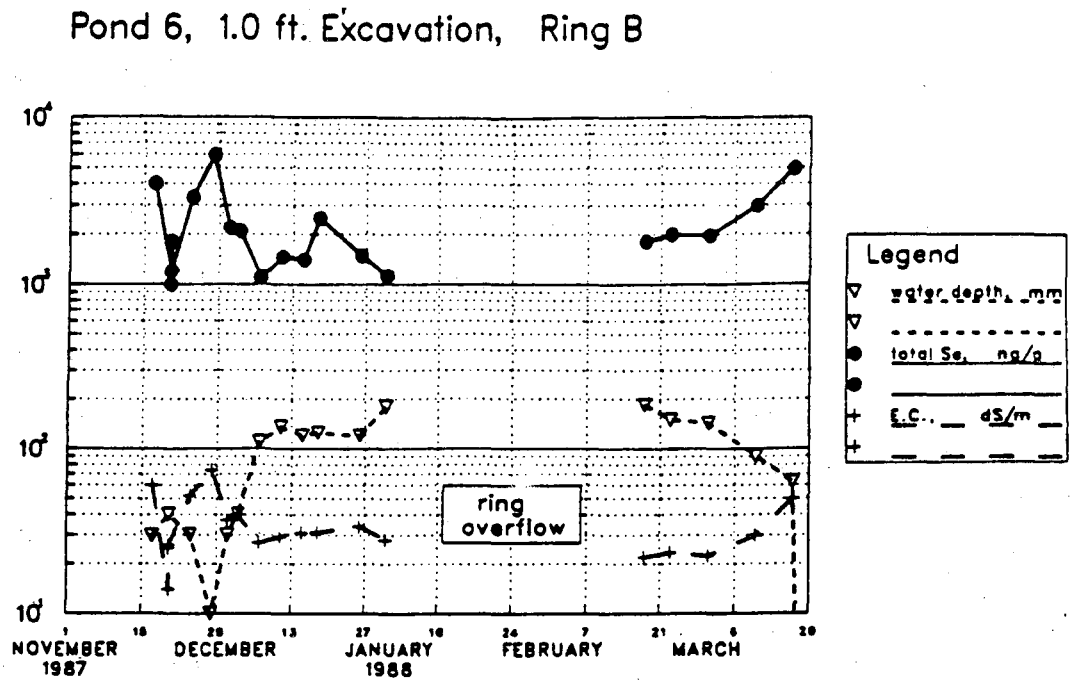


Figure 3-2a,b. (a) Pond 6, 1 ft excavation test plot time trend of surface soil salinity obtained through electrical conductivity measurements. (b) Pond 6, 1 ft excavation test plot time trend of surface soil water-soluble selenium.

proximity of the adjacent flooded Pond 5. Data from two sampling rings in this test plot are presented in Figure 3-3a and 3-3b. Soluble selenium concentrations in the surface water are extremely high, and generally exceed 1000 ppb. Selenate generally accounts for at least 90% of the soluble selenium from these waters. Concentrations of other dissolved salts are also high, as indicated by the ECs which are generally in excess of 30 dS/m. Occasional sampling of surface waters outside of the rings yielded selenium concentrations and ECs comparable to values for ring interiors. Temporal fluctuations in both soluble selenium and ECs are partially accounted for by rainfall and evaporation. During the period of November 1987 through March 1988, 155 mm of rainfall and 437 mm of net pan evaporation were recorded by the USBR (J. Esget, personal communication).

Since the surface water at this excavation site primarily originates from pore waters, correlation between surface and pore water quality is expected. General agreement between surface soil water quality and surface water quality data is apparent upon comparing Figures 3-2a,b and 3-3a,b. The time trend in Figure 3-2a shows a pattern of increasing salinization of the surface soil as reflected in soil water EC data. Based on the soil core EC data from Nov. 5, 1987, an EC for surfacing water (in the absence of rainfall dilution) of 71±20 dS/m was projected. This salinized soil water was eventually displaced to the surface on Nov. 17, 1987, yielding the initially extremely saline surface waters with a measured EC of 60 dS/m (Figure 3-3a). A similar, though much less distinct time trend is observed for soluble selenium in pore waters. From the soil core data, surface water selenium concentrations in excess of 1000 ppb were projected. The large scatter in the data, and small sample number of 5 cores precluded more definitive predictions. The selenium concentrations in surface waters sampled at this site ranged from 700 to 6000 ppb.

Results of this experiment clearly demonstrate that the ODP would not have significantly lowered selenium concentrations in surface water. The selenium concentrations in the excavation test plot surface waters were several times higher than the concentrations measured in the ponds during active disposal of drainage waters into the Reservoir (≈300 ppb). Excavation to depths in excess of 1 m would probably be needed before a low selenium environment could be



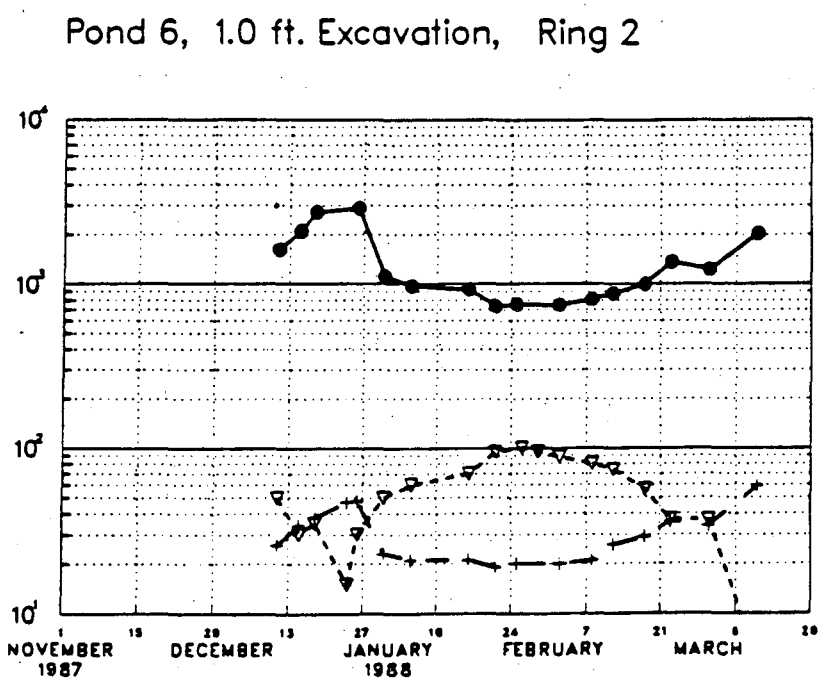


Figure 3-3a,b. Ephemeral pool water quality over Pond 6, 1 ft excavation test plot.

assured (see Figure 3-1 for the depth distribution of soluble selenium). *Any* excavation will contribute to accelerated salt (and selenium) accumulation in residual soil surfaces, and simultaneously increase the probability of ephemeral pool formation.

3.3. POND 9 SOIL MONITORING

Soils in the playa environment of the northern portion of Pond 9 have been monitored for nearly 2 years. During this period, no surface waters were introduced. With the absence of periodic flooding, terrestrial vegetation has become established during the spring in both 1987 and 1988. A dense growth of *Kochia Scoparia* dominated the Pond 9 test plot plant community in 1988, while a more sparse mixture of annual shrubs was observed in 1987. Soluble selenium depth profiles from field soil water samples exhibited considerable fluctuations during this period. Both increases and decreases as large as five-fold have been measured in soil water selenium concentrations within particular soil-water samplers (Figure 3-4a,b,c). However, no distinct time trends in whole profile soluble selenium inventories are presently evident. Soil water concentrations in excess of 1000 parts-per-billion selenium commonly persist in the upper portions of the profiles. These high selenium levels give way to concentrations in the range of tens and hundreds of parts-per-billion at greater depths.

Water-soluble constituents in Reservoir soil profiles are also commonly extracted in the laboratory from core samples. As noted in previous work (1987 Annual Report), soluble selenium extracted by this laboratory method has been found to agree well with analyses of direct vacuum-extracted field samples in aerated *vadose zone* soils. Further comparisons of these two methods of soil solution sampling are presented in the discussion of Pond 11 soils. While measurements of soluble selenium concentrations in vadose soils at the Reservoir are essentially equivalent in field and laboratory extractions, such agreement can not be expected for components which have been adsorbed or have precipitated due to reaching solubility limits under field conditions. The addition of distilled water to soils in laboratory extracts shifts equilibria to favor desorption and dissolution which result in higher recoveries of susceptible species. This effect on the major ions Na^+, Ca^{2+}, and SO_4^{2-} is shown in Figure 3-5a,b, and c respectively.

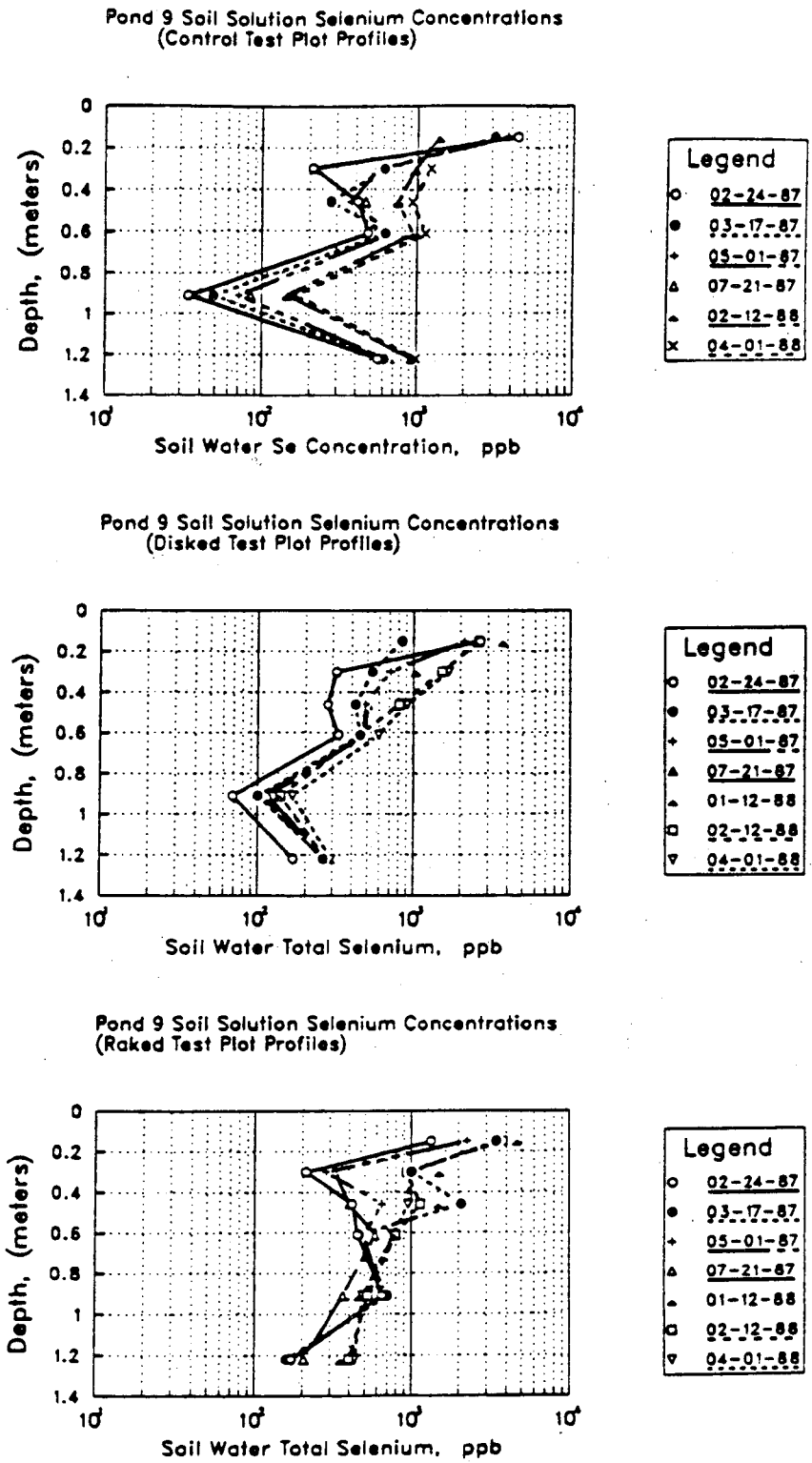


Figure 3-4a,b,c. Pond 9 ''playa'' monitoring site soils; soluble selenium profiles, 1987 and 1988.

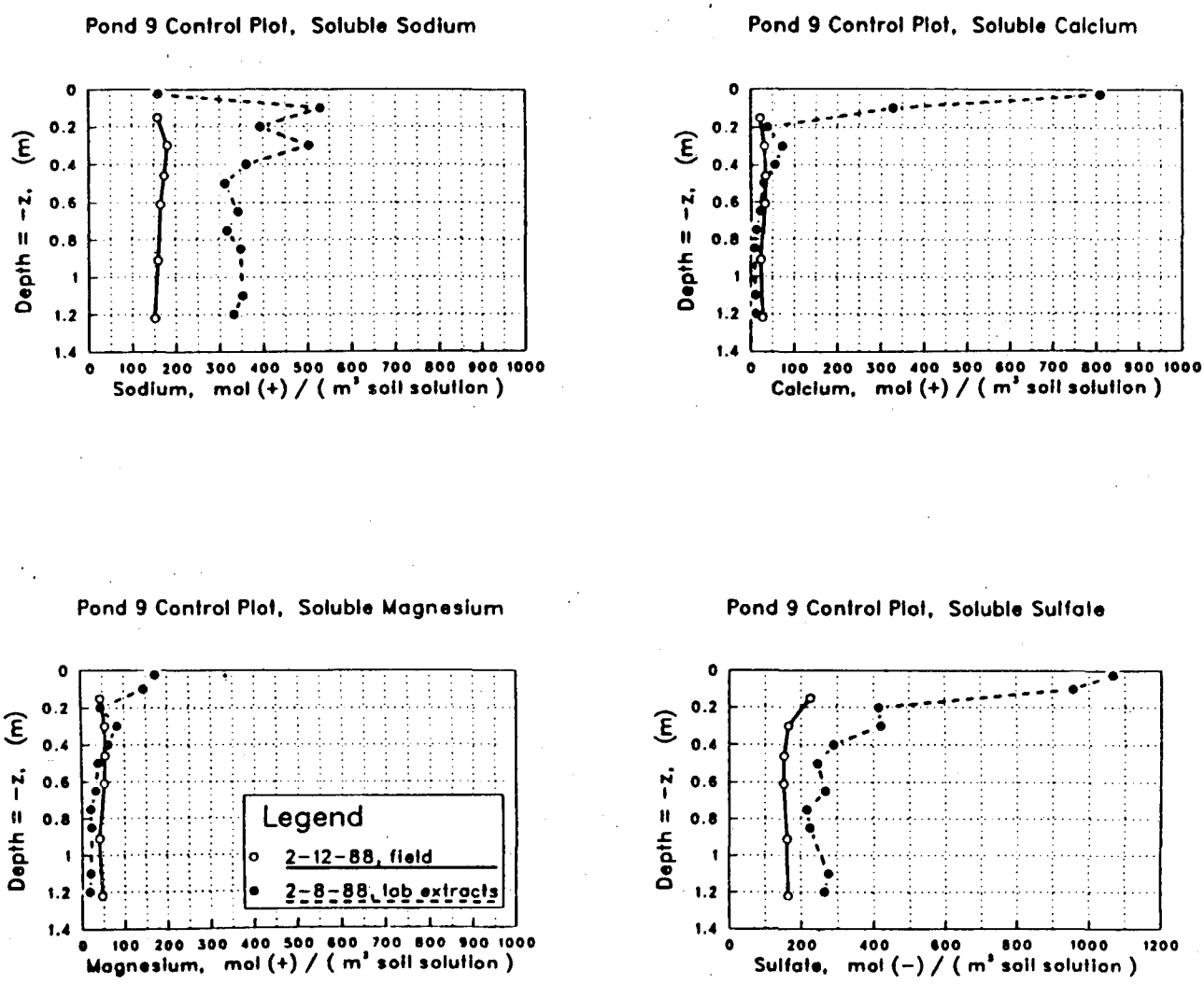
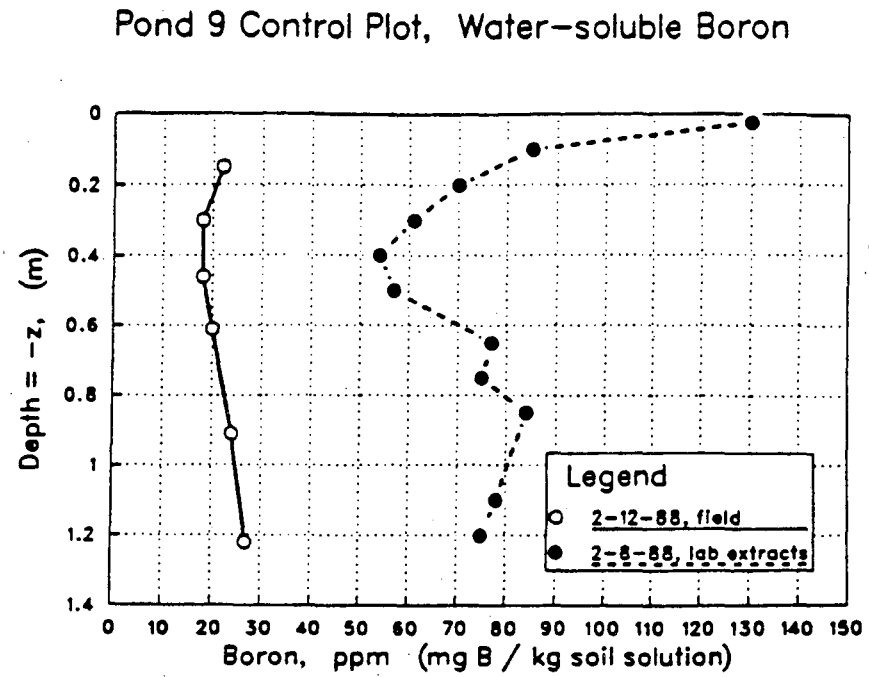


Figure 3-5a,b,c,d. Pond 9 soil profile soluble sodium, calcium, magnesium, and sulfate. Comparisons of field vacuum extracts and laboratory extracts.

Concentrations of the 5:1 laboratory extracts have been normalized to the original field water contents to allow comparisons with direct field vacuum extracts of soil solutions. The discrepancies between field and laboratory extracts of Na^+ and SO_4^{2-} demonstrate that precipitates of these ions are pervasive throughout the soil profile. The maxima for Ca^{2+} and SO_4^{2-} at the soil surface are consistent with independent x-ray diffraction studies which show that gypsum ($CaSO_4 \cdot 2H_2O$) is the dominant evaporite mineral in this zone. The agreement between field and laboratory extracts for Ca^{2+} and Mg^{2+} (Figure 3-5d) indicate that these species are largely in solution at depths below 0.30 m at this site. Comparisons of water extraction methods for the trace elements boron and arsenic are shown in Figure 3-6a and 6b respectively. It is emphasized that the field extracts represent concentrations in actual soil solutions, and that the laboratory extracts represent the sum of currently and potentially soluble quantities. In both the boron and arsenic profiles, the major portion of the potentially water-soluble inventories are in adsorbed or precipitated forms under field conditions at this site. Similar observations have been noted in other soils of Pond 8 (Figure 3-19c), and Pond 9 (Figure 3-20d), for arsenic, and Pond 11 soils for both boron and arsenic (data not shown). It should be noted that concentrations from laboratory extracts do not provide absolute measures of potentially soluble species due to limited mixing times and low solubilities of certain minerals (most commonly gypsum and calcite). Longer mixing times and larger water:soil ratios would generally yield higher quantities of dissolved species.

While the Pond 9 monitoring site has largely become revegetated during the past two years, one test strip at the site has been maintained as a bare soil environment through periodic (manual) weeding. Comparison of the hydrological differences between vegetated and non-vegetated Pond 9 test plots are provided in hydraulic head profiles Figure 3-7a,b. The tensiometer data demonstrate that plant root uptake of soil water in the control plot is effectively dewatering the upper 1.5 m of soil (Figure 3-7a). In contrast, the unvegetated soil profile loses water only through evaporation at the soil surface and to drainage towards the declining water table (Figure 3-7b). An estimated 0.15 to 0.2 m more water has been extracted in the vegetated soil compared to the unvegetated soil. In an environment where formation of ephemeral pools is of



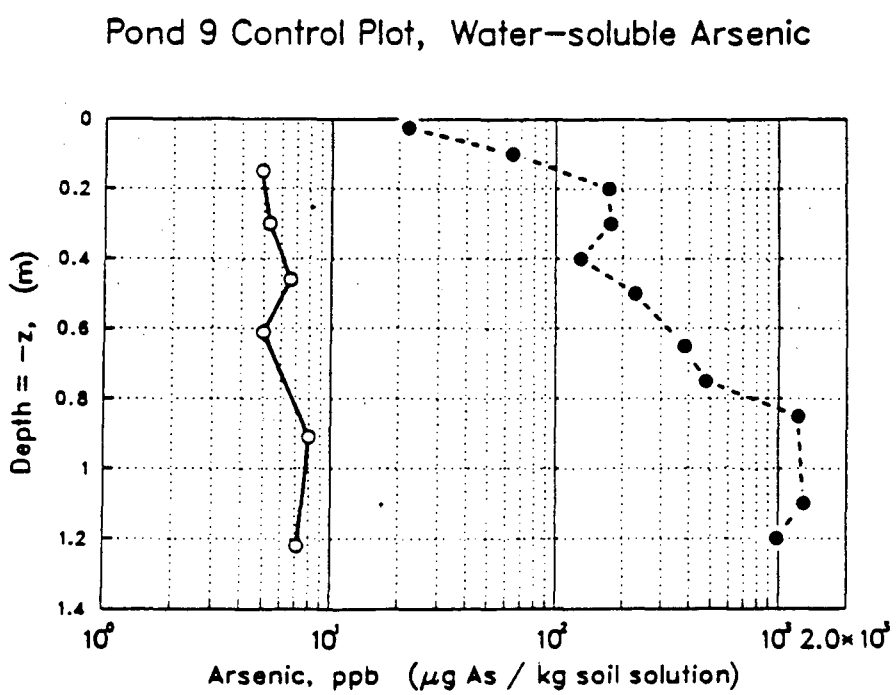
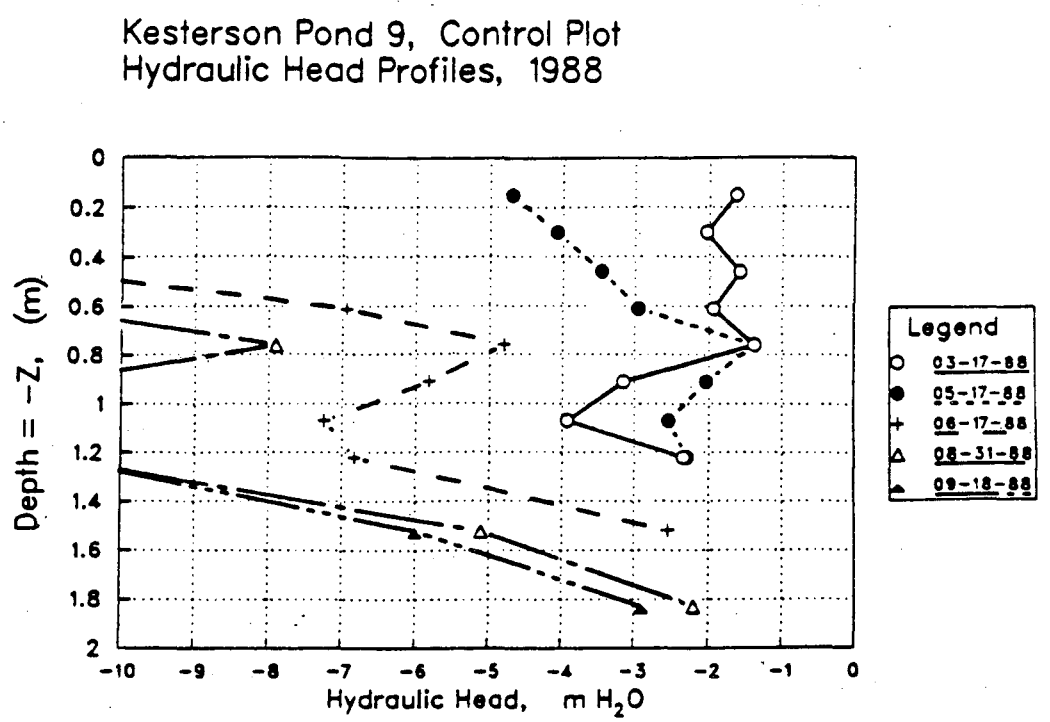


Figure 3-6a,b. Pond 9 soil profile soluble boron and arsenic. Comparisons of field and laboratory extracts.



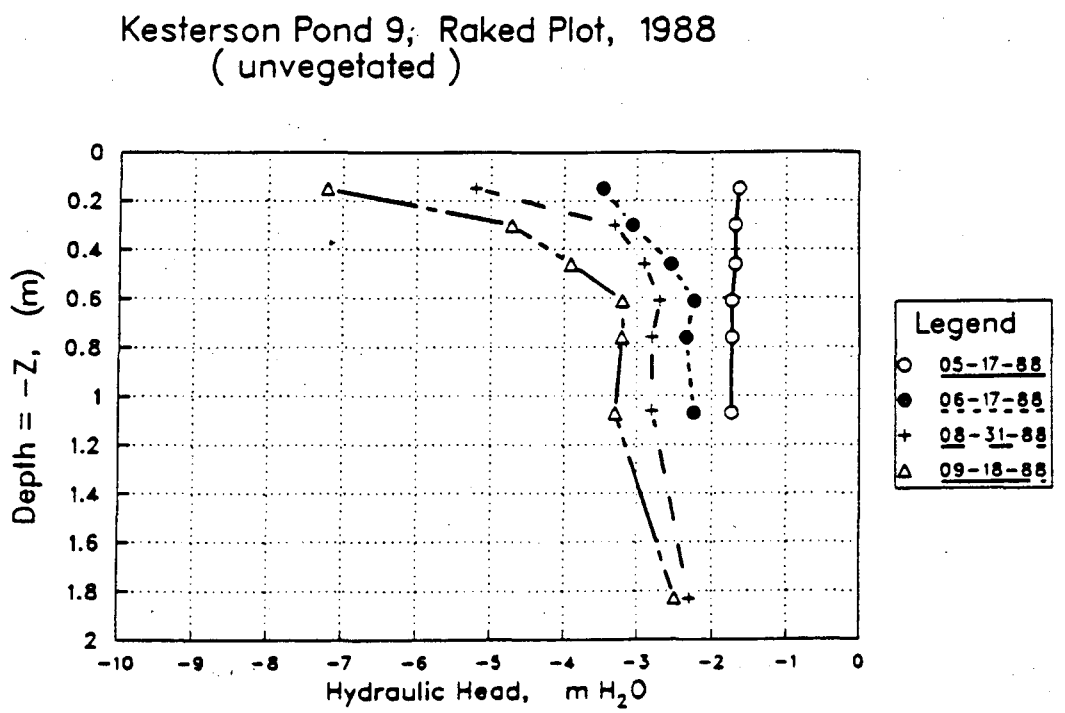


Figure 3-7a,b. Pond 9 soils. Comparison of 1988 drying cycle hydraulic head responses in vegetated (a), and unvegetated (b) test plots.

concern, plant growth on Reservoir soils can significantly assist in delaying pool formation through dewatering of the soil profile. As will be noted in discussions of Pond 11 soils, vegetation also assists in minimizing surface accumulations of salts.

3.4. POND 11 SALTGRASS SOIL MONITORING SITES

Monitoring of the densely vegetated, and infrequently flooded upland saltgrass environment in Pond 11 is continuing. Due to the infrequency of flooding with drain waters, and to transpirative removal of soil water through plant roots, the region of salt accumulation is observed within the rooted zone. This is in sharp contrast to salt distributions in bare soil profiles at the Reservoir where accumulation occurs largely at the surface. In the Pond 11 saltgrass soils, soluble selenium is also distributed considerably more uniformly throughout the upper meter of soil. With nearly two years of soil water data from the Pond 11 saltgrass sites, time trends in soluble selenium inventories, soil salinity, and vitality of the plant community are becoming apparent. General increases in the soluble selenium profiles in the Pond 11 sites suggest that remobilization of selenium from insoluble to soluble forms has taken place (Figure 3-8a,b,c). The early (Nov. 1986) surficial treatment of the three sites (control, disked, harvested saltgrass) have not persisted. The initially rapid saltgrass regrowth has obscured differences between the various Pond 11 test plots so that the three monitored plots can be treated as replicates. Depth-averaged soluble selenium inventories at these sites under comparable late winter and early spring conditions show increases in the range of about 50%. Uncertainty in the percentage increase for selenium in solution is largely due to uncertainties in the soil water content profiles. An insufficient amount of soil water content data at these sites precludes quantitative evaluation of the influence of differences in soil water contents. Evapotranspirative drying of the soil profile will generally yield more concentrated soil solutions simply due to the selective removal of water, without actual increases in solute content. However, it is unlikely that lower soil water contents could account for most of the apparent increase in selenium in solution for several reasons. First, tensiometer data during the periods in question are comparable, indicative of comparable soil water contents. Second, the measured rainfall during the 1987/1988 season at Kesterson Reservoir of

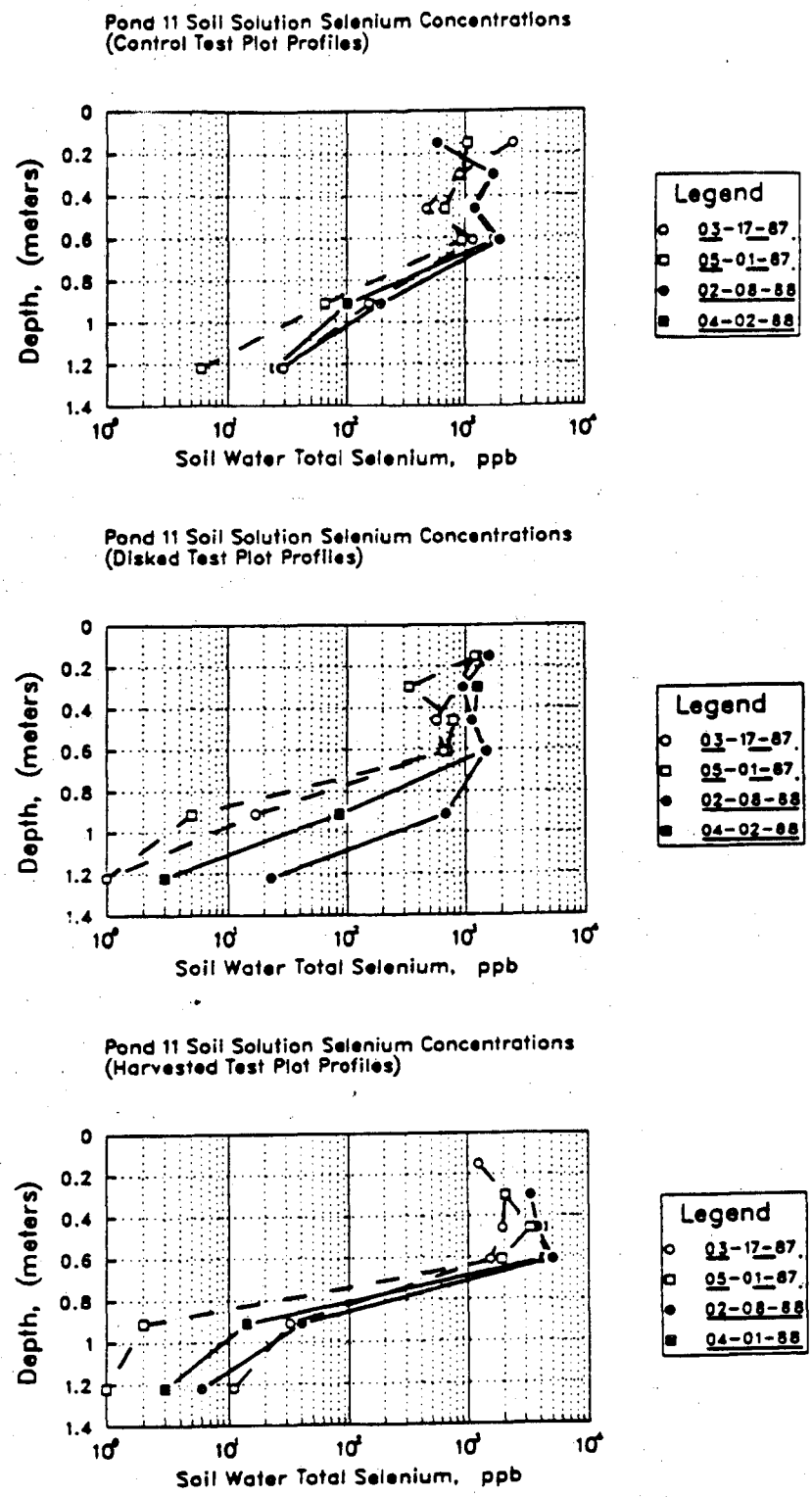
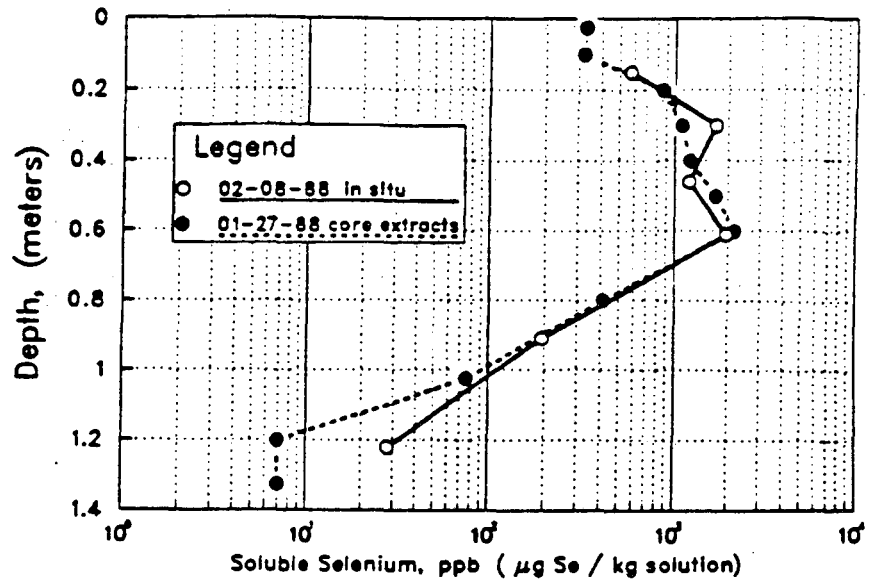


Figure 3-8a,b,c. Pond 11 saltgrass monitoring site soils; soluble selenium profiles, 1987 and 1988.

229 mm is slightly greater than that of the 1986/1987 season (195 mm). Third, during both periods, water table rise in the Pond 11 test site was nearly identical, with maxima at 0.98±0.01 m below the soil surface. A minor mechanism for soluble selenium increases in the lower portions of the Pond 11 profiles is that of upward movement of selenium from below the monitored depth (1.2 m). This upwards flow is due to saltgrass and alkali weed uptake of soil water, and is clearly indicated by tensiometer data (not shown), and temporal changes in EC profiles. Due to the measured low selenium concentrations at the deepest soil water samplers, upward flow of selenium from below 1.2 m is expected to result in only minor contributions to the soil selenium inventory. All of these abovementioned considerations indicate that formerly immobile selenium in the Pond 11 soils is moving into solution. Among the possible mechanisms for this increase in selenium in solution is that of oxidation of adsorbed selenite. Experiments directed at measuring the adsorbed selenite inventory in various Reservoir soils are currently being pursued.

The previously mentioned comparisons between field and laboratory extractions of soil solutions have also been performed on Pond 11 soils. As shown in Figure 3-9a, 5:1 water:soil laboratory extracts provide reliable indications of selenium in solution under vadose conditions. The water extraction procedure does not readily oxidize or desorb selenium. As previously noted, the laboratory water extraction does dissolve and desorb numerous other species (major ions and other trace elements). This is reflected in the discrepancies in EC profiles obtained from field and laboratory water extractions (Figure 3-9b). The major ions which contribute most to the higher laboratory extract ECs are Na^+, Ca^{2+}, and SO_4^{2-}. Significant quantities of boron and arsenic are also solubilized in the water extraction process.

Soil water EC data are indicative of increased salinization of the Pond 11 soil profiles (Figure 3-10a,b,c). Comparison of early spring data from 1987 and 1988 show profile-averaged increases in soil water ECs of 8 dS/m. This increase could be attributed to a combination of a drier soil profile in 1988 and plant root uptake of deeper saline soil waters into the monitored profile. As previously mentioned, tensiometer data indicate that the soil water content profiles were comparable during the two periods in question. This leaves inflow of salts from below the



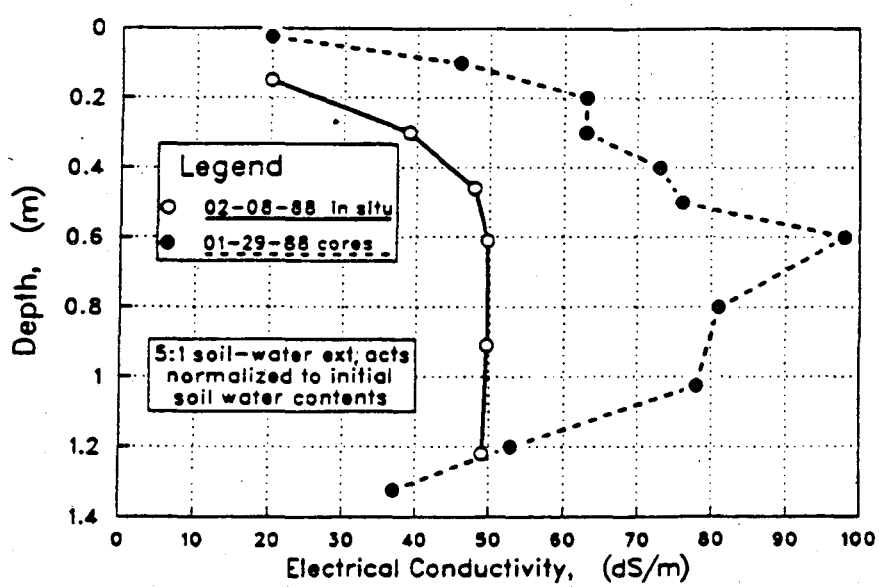


Figure 3-9a,b. Pond 11 soils; (a) comparison of soluble selenium from field versus laboratory extracts. (b) comparison of electrical conductivity in field versus laboratory extracts soil water samples.

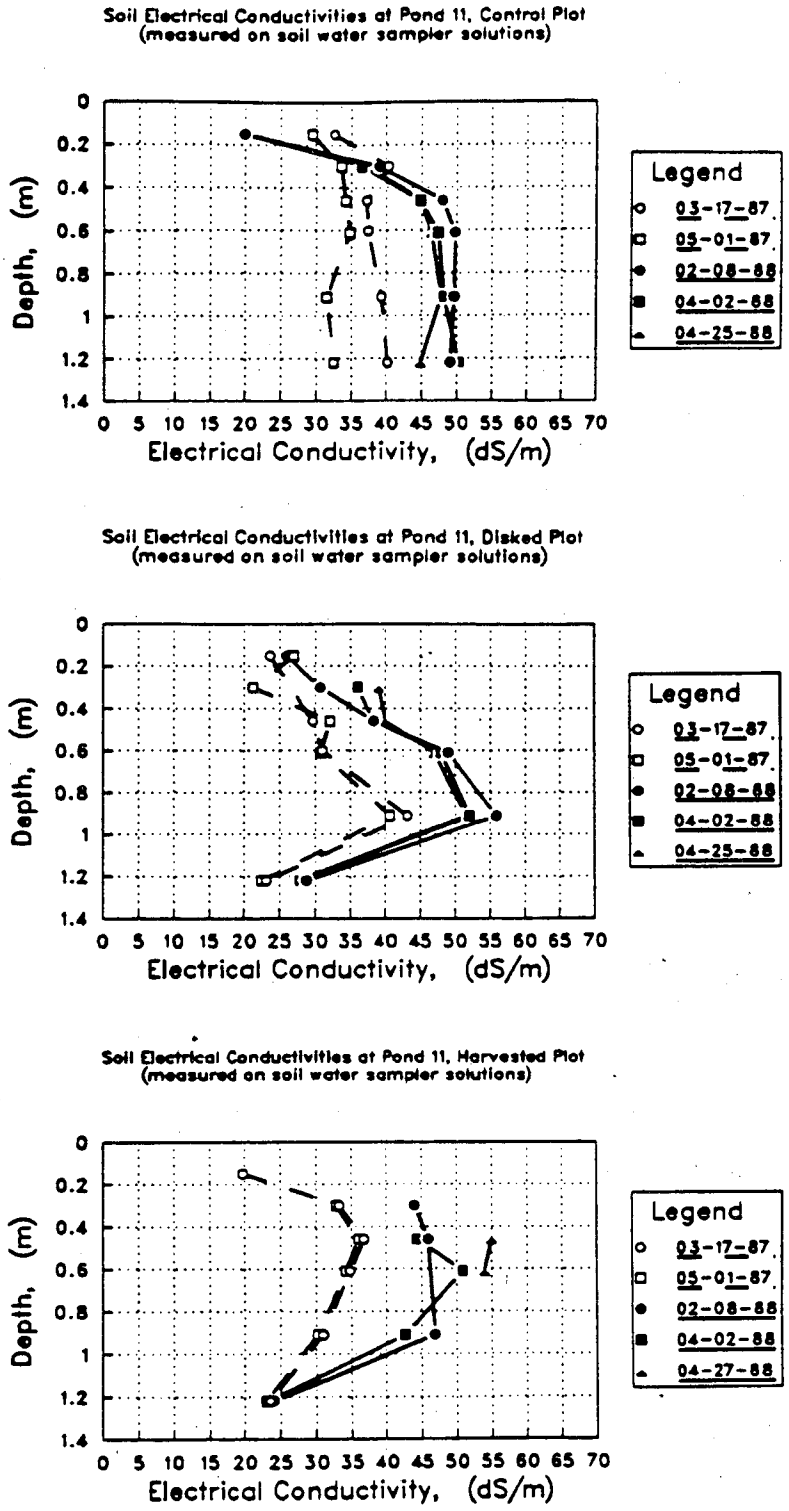


Figure 3-10a,b,c. Pond 11 soils; field soil water electrical conductivity profiles, 1987 and 1988.

monitored zone as the only explanation for the observed EC increases. Assuming upward flow of deeper soil water having an EC of 20 dS/m resulted in increased salinization of soils with an average volumetric water content of 0.30, a calculated upward flow of 0.16 m of water is obtained. Use of a higher inflow EC of 40 ds/m results in an estimated upwards flow of 0.08 m. The reasonableness of the selected range of inflow water ECs is based on ECs measured in the deepest (1.22 m) soil water samplers.

Increased salinization of the soil profile will result in a generally less favorable plant and microbial environment through decreasing the soil water potential. The previously mentioned EC increase of 8 dS/m corresponds to about a -300 J/kg (-3 bar) decrease in the soil water potential. Increased salinization of the Pond 11 soils may already be adversely affecting growth of the saltgrass. Comparisons of tensiometer data from late spring and summer of 1987 and 1988 indicate that transpirative removal of soil water in the 0.46 to 1.22 m depth interval was slower and less complete during the current year. The lack of sufficient leaching of these soil profiles will result in further salinization, which will further constrain plant growth.

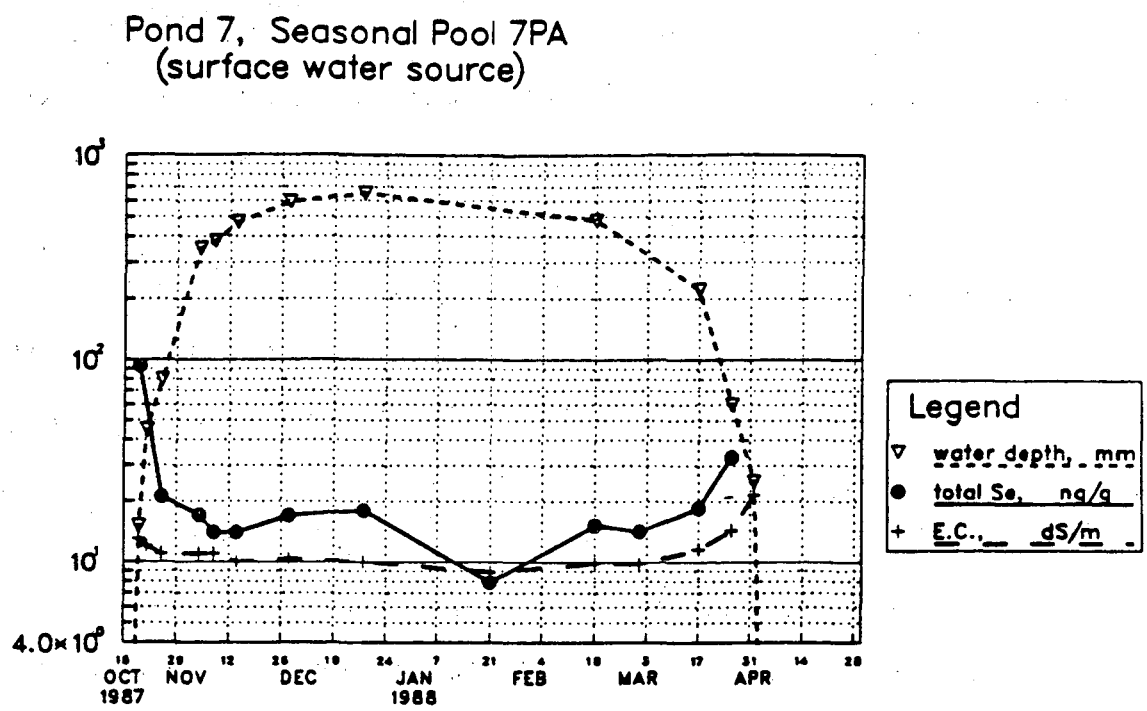
3.5. EPHEMERAL POOLS

Ephemeral pools at Kesterson Reservoir form as a result of several factors. These sources for surface water formation are (1) runoff from adjacent (intentionally) flooded areas, (2) soil water displaced upwards by the seasonally rising water table, and (3) rainfall. In many pools, all three of these factors contribute simultaneously. From extensive field monitoring during the 1987/1988 wet season, it has been observed that the majority of ephemeral pools formed as a result of runoff/leakage from adjacent flooded ponds. Due to below average precipitation during the recent wet season, the contribution of rainfall to ephemeral pool formation was below average this season. While a small fraction of the pools were formed solely by the rising water table, this seasonal phenomenon will always contribute to the tendency for ephemeral pool formation through diminishing the hydraulic potential gradient which drives infiltration, and thereby decreasing seepage rates. Again, it should be noted that most ephemeral pools at Kesterson Reservoir form as a result of a combination of the abovementioned factors.

In the interest of highlighting differences in ephemeral pool water quality associated with different dominant water sources, two of the monitored sites will be described. The first of these sites formed as a result of overflow from intentional water applications in Pond 7. The second site (in Pond 6) formed as a result of water table rise and rainfall.

The Pond 7 ephemeral pool site "7PA" is located in an elevated region adjacent to Pond 8. Due to continued flooding of Pond 7 with local well water, site 7PA was reflooded in October 1987. Time trends for pool water depth, soluble selenium concentration, and EC at this site are shown in Figure 3-11a. Dissolution of surface salts, including selenium salts, at the inception of flooding contributes to high initial concentrations of these solutes. Soluble selenium concentrations were initially in excess of 300 ppb. The initially high pool water selenium concentrations are rapidly diminished, primarily as a result of dilution with waters with low selenium concentrations, and also due to displacement into the soil. Similar, though less pronounced time trends were observed for salinity, as indicated by EC trends. An approximately steady-state, with respect to soluble selenium concentration and salinity, was observed for about 5 months. During this time, selenium concentrations remained less than 20 ppb, and ECs were about 10 dS/m. In preparation for implementing the ODP, dewatering of the reservoir began on January 24, 1988. The water level in pool 7PA began receding in late March 1988, and was accompanied by increases in both soluble selenium concentrations and salinity. Increases in selenium concentrations are probably due to mixing of the remaining surface waters with remobilized selenium from exposed surface sediments, as well as from evaporative concentration. Salinity increases are due to evaporative concentration.

A very different set of water quality data were obtained in ephemeral pools formed from rising groundwater and rainfall, in the absence of overflow waters from intentional flooding. Ephemeral pool site 6PC, near the east edge of Pond 6, developed under these conditions. This pool emerged in late November of 1987, and persisted through early March, 1988. This pool persisted with a fairly stable depth of about 0.2 m, during a relatively dry rainy season. (The recorded total rainfall at Kesterson Reservoir from October 1987 to January 31, 1988 was 155



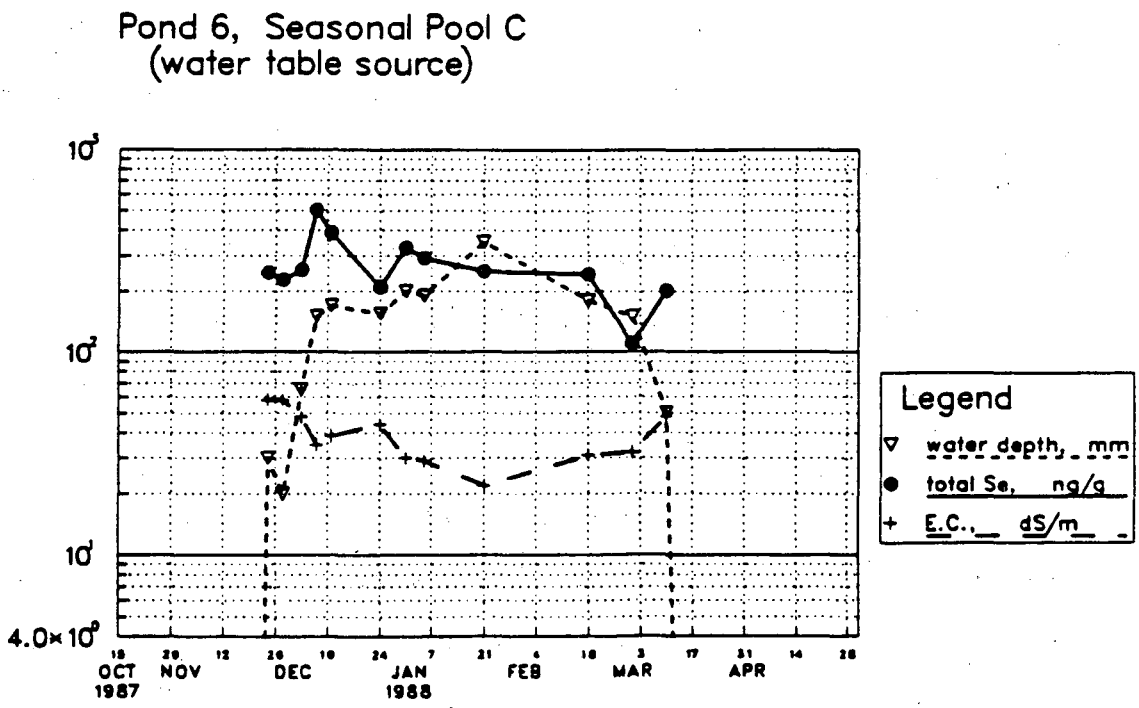


Figure 3-11a,b. Ephemeral pool water quality; (a) surface water source in Pond 7, (b) water table source in Pond 6.

mm. Pan evaporation during this same period amounted to 437 mm.) Due to the persistence of this pool, as well as to observed rises in its water level even in the absence of rainfall, it can be concluded that the principle cause of this pool was the rising water table. As in the case of the Pond 6, 1.0 ft excavation test plot however, the extent of water table rise at site 6PC was enhanced by its proximity to the flooded Pond 5. Time trends for ponding depth, selenium concentrations, and ECs at site 6PC are summarized in Figure 3-11b. Soluble selenium concentrations persist in the range of the initial high levels of about 300 ppb throughout most of the ponded period. High ECs in the range of 20 to 60 dS/m persisted throughout this period as well. These phenomena can generally be expected when rising groundwater displaces saline soil pore waters containing high selenium concentrations up to the surface. A number of ephemeral pools of this type were observed during the recent wet season, as well as during the previous year (LBL 5th Progress Report, March 1987; LBL 1987 Annual Report, Dec. 1987). Direct comparisons of water quality data between ephemeral pool site 6PC and the Pond 6, 1.0 ft excavation site are not justified since their soil environments are not comparable. The pool at site 6PC formed over a small "playa" region, while the nearby 1.0 ft excavated site was originally vegetated with cattails.

3.6. ACCUMULATION OF SALTS AND TRACE ELEMENTS THROUGH EVAPORATIVE FLOW AT AND NEAR THE SOIL SURFACE

Due to the proximity of the water table to the soil surface and high pan evaporation rates during most of the year, evaporative flow is an important mechanism in the redistribution and concentration of soluble salts and trace elements near and at the soil surface. Drying of the soil surface creates a substantial upward soil water potential gradient, the shape of which is governed by the potential evaporation, soil characteristics, and the depth to the groundwater table. The need for estimating soil evaporation rates became apparent when a rise in the concentrations of salts and selenium was observed over a period of approximately one year, even though no drain water was applied. Salinization of soils due to evaporative flow from a saline aquifer is a common problem. The problem is compounded when the soils are fine-textured, since they have a

relatively high unsaturated hydraulic conductivity (Hillel, 1980). The accumulation of salts at the soil surface will be accompanied by an accumulation of selenium and other trace elements.

3.6.1. Measuring Evaporation Rates from Bare Soils

The microlysimeter method was used to measure evaporation rates from Kesterson soils. (Methods of Soil Analysis, C.A. Black, Chief Ed., American Society of Agronomy, 1965). This procedure involves the placing of a small plastic (or metal) tube in the ground, removing it with the soil intact, sealing the bottom of the tube, weighing the tube with the soil core and bottom cap, and placing it back in the soil, such that the surface of the soil in the tube is level with the surrounding soil. After a certain period of time, preferably in multiples of 24 hours and not more than a few days, the tube with the soil is removed from the ground and weighed. The difference in weight is due to the loss of water through evaporation, since the bottom of the tube is sealed off from the environment.

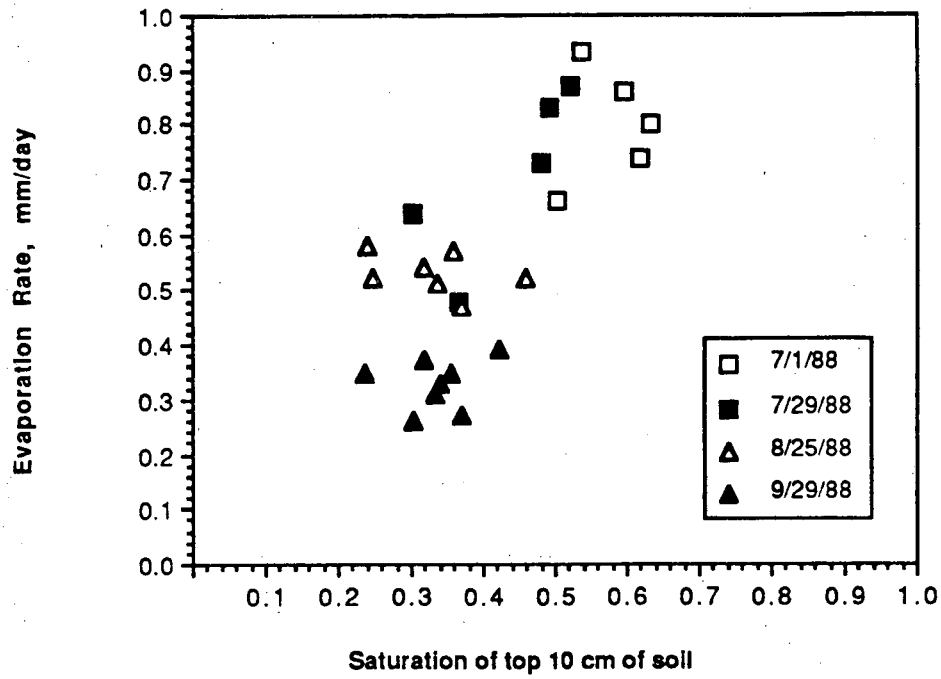
Measurements of bare soil evaporation rates commenced in late June 1988. At that time, the surface soil in most parts of the Reservoir was very dry. This made it difficult to take surface soil cores without a mechanical tool, e.g. auger. Since a plastic microlysimeter is preferred over a metal one, because of the tendency of metal to create an unnatural thermal environment inside the tube, microlysimeters for this project were made out of PVC pipe. The tubes have an inside diameter of approximately 5.1 cm and are approximately 10 cm long. The walls are 5 mm thick. The bottom 1.5 to 2.0 cm on the outside of the tube were bevelled to make the bottom edge sharp. While in many ways desirable, these were not sturdy enough to be pounded into very dry soil. Therefore, several attempts at measuring evaporation rates in Pond 6 failed. Because of the substantial depth to the groundwater table at the raked and control plots in Pond 9, the soil evaporation rates in those plots were found to be between 0.1 and 0.2 mm/day. These rates were low enough to be very close to the range of error for this method. Since the rates were expected to fall even more during the summer as the water table declined further, monitoring bare soil evaporation in these plots was abandoned.

Bare soil evaporation rates have been monitored during the months of July, August, September, and early October in Pond 8 (plot EP, a centrally located playa) and Pond 9 (plot BE, located just north-east of the junction of Ponds 8, 9, and 10). Soils in both of these plots, especially plot 8EP, contain high concentrations of salts and selenium. Since they are both topographically low, the depth to the groundwater table is relatively small and the surface soil was moist enough to insert and remove microlysimeters. After the 24-hour measurement period, the microlysimeters were removed, sealed on top, and taken to the laboratory. The soil was then homogenized and the following soil properties and moisture characteristics were determined: bulk density, solid density, porosity, gravimetric moisture content, volumetric moisture content, and relative saturation. Over the months of July, August, and September, bare soil evaporation rates ranged from 0.25 mm/day to 0.95 mm/day at Pond 8EP and from 0.3 mm/day to 1.4 mm/day at Pond 90E.

Measured evaporation rates, plotted as a function of the saturation in the soil, are shown in Figures 3-12a and b. The decline in the groundwater table during the time is shown in Figure 3-13a for plot 8EP. Figure 3-13b relates the measured evaporation rates to the depth to the water table. Even though the trends in these figures are clear, the evaporation rates are quite variable. During any given sampling period, variability of evaporation rates can, at least in part, be attributed to the spatial variability of soil properties. Otherwise, the limitations of this method for estimating bare soil evaporation in the field must be invoked to account for scatter in the data. The progressive drying of the soil profile at plots 8EP and 9BE is illustrated by the changes in soil water potential as shown in Figure 3-14.

3.6.2. Monitoring Changes in Salt and Trace Element Concentrations

Soil water extracts were also made with the soils collected for the evaporation rate measurements. The procedure for making such extracts is described in Section 3.1. In contrast to those procedures, extracts were made using a 10 to 1 mass ratio of water to soil and the solution was stirred for two hours instead of one hour. The higher water to soil ratio was used in an attempt to dissolve as close to 100% of precipitated salts as possible. The electrical conductivities of the extracts were measured and normalized to the actual field water content (Figure 3-15).



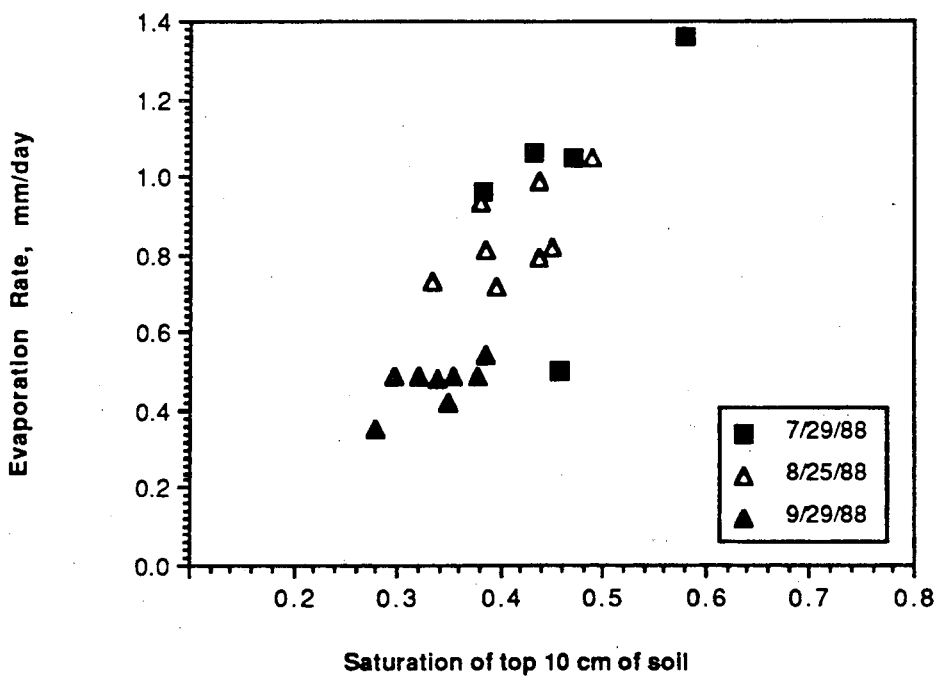
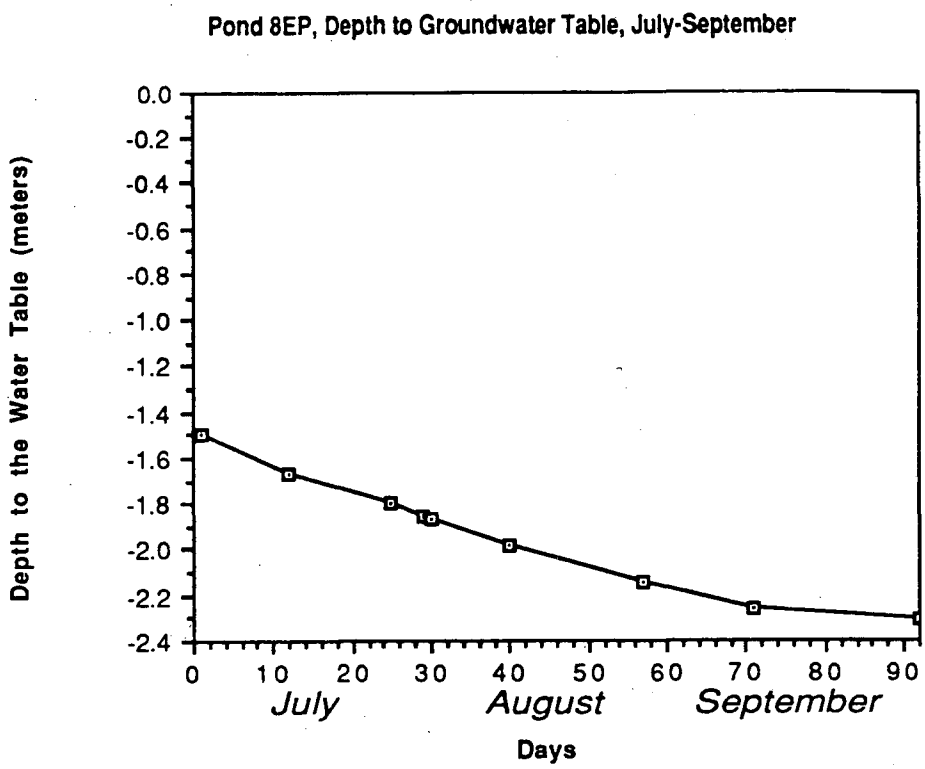


Figure 3-12a. Bare soil evaporation rates at Pond 8EP (a) and Pond 9BE (b) as a function of the saturation of the top 10 cm of soil.



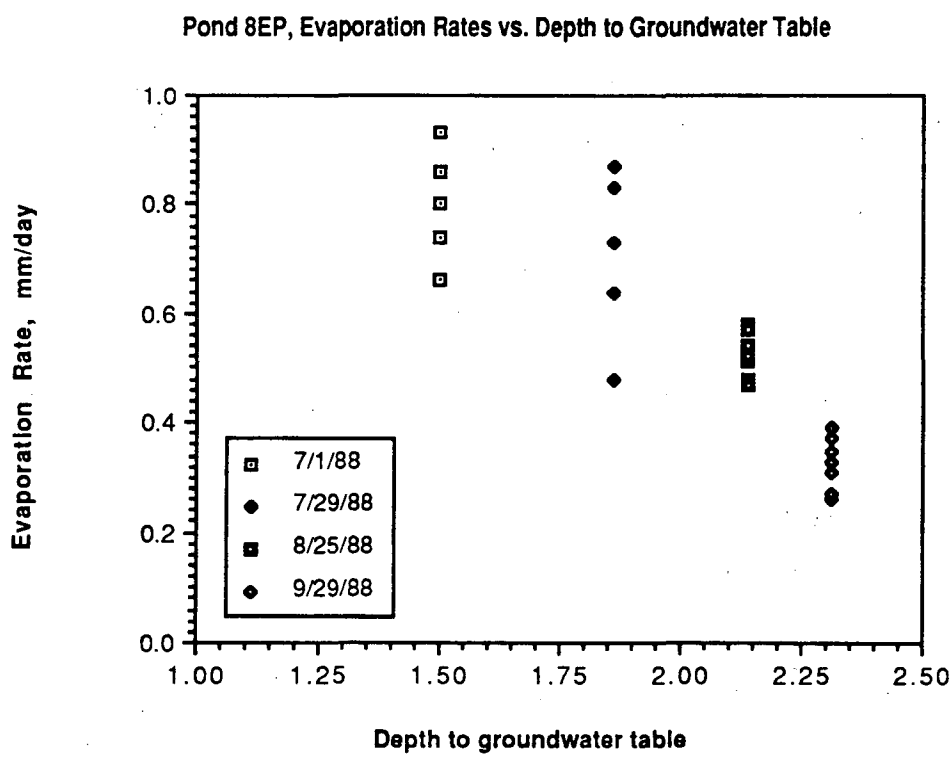
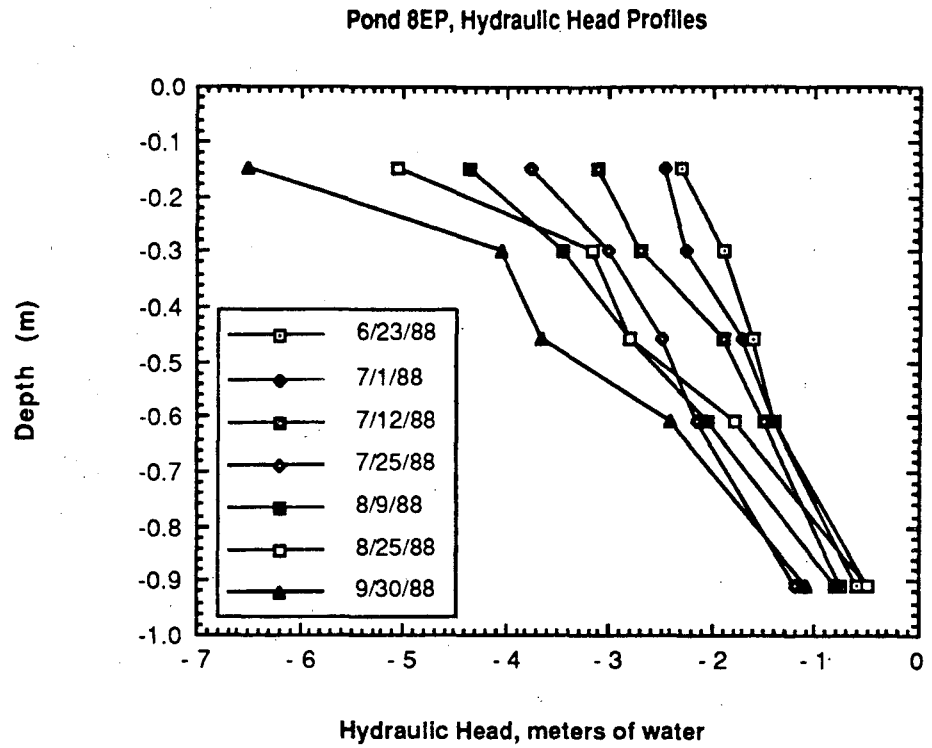


Figure 3-13a,b. The relationship between bare soil evaporation rates and water table depth at Pond 8, plot EP. (a) Depth to water table vs. time, (b) Bare soil evaporation as a function of the depth to the groundwater table.



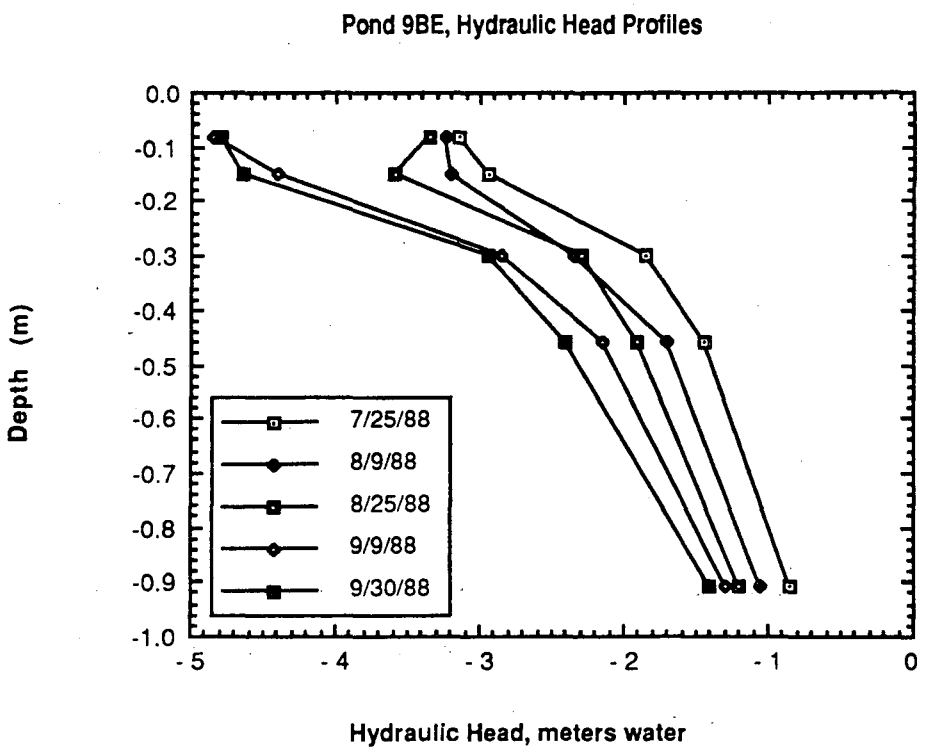
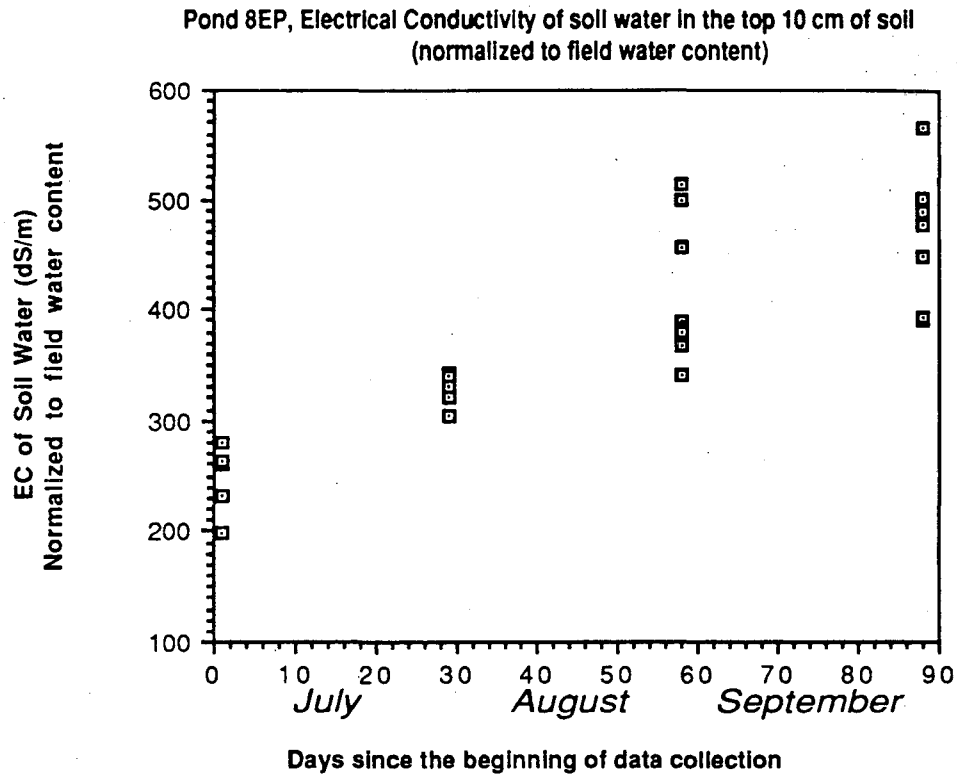


Figure 3-14. Hydraulic head profiles at Pond 8, plot EP (a) and Pond 9, plot BE (b).



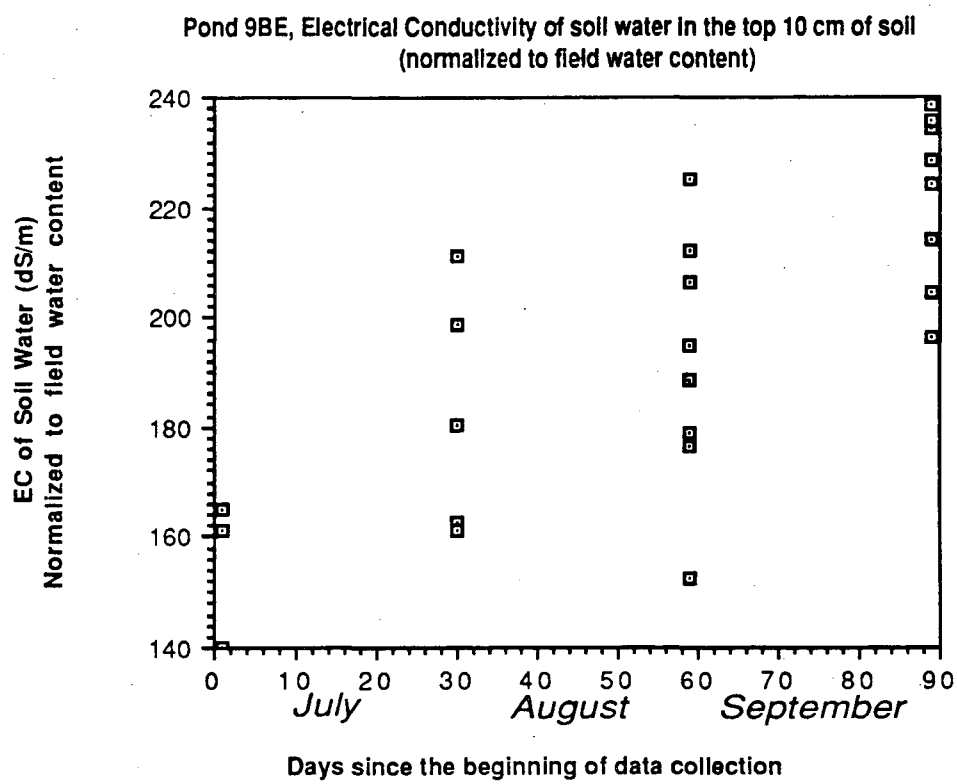
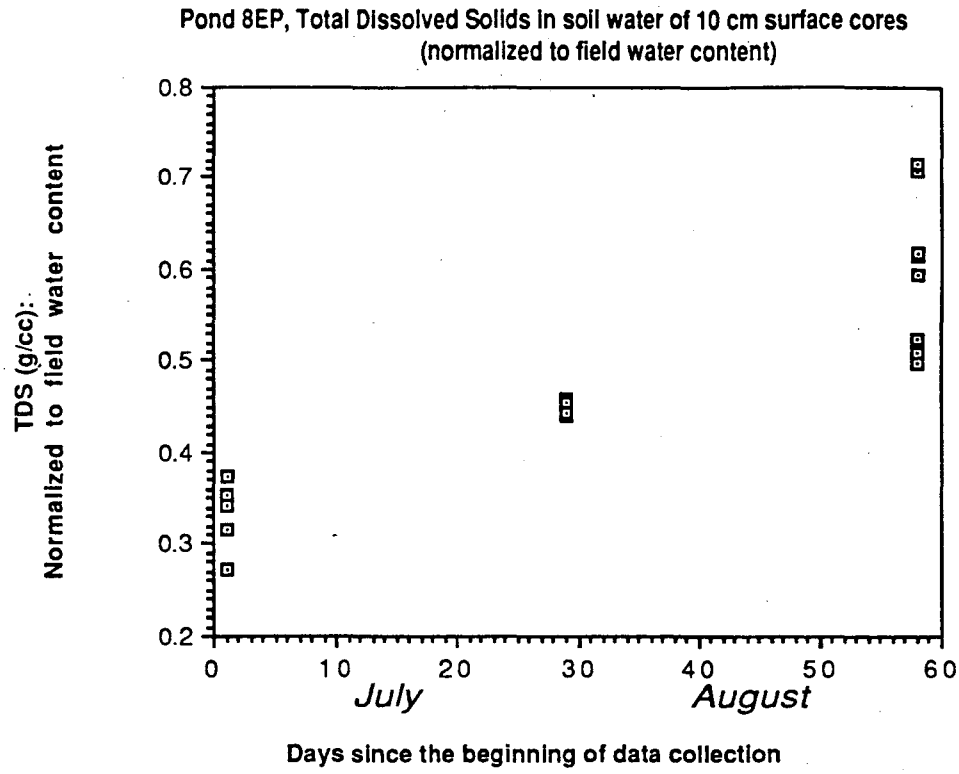


Figure 3-15. Electrical conductivity of soil water in the top 10 cm of soil at Pond 8, plot EP (a), and Pond 9 plot BE (b) from July to September, 1988.

In spite of the large variability in the electrical conductivity data, it is still clear that a large increase in salt concentration has occurred over the three months of July, August, and September. The trend seen in Figures 3-15a and 3-15b is due to two separate factors: the reduction in the volume of water in the top 10 cm of soil and the transport of salts towards the soil surface. In order to separate these two effects, the concentration of dissolved solids needs to be normalized to the mass of soil in each microlysimeter. At the time of writing, complete chemical analyses of the soil samples from the microlysimeters in plot 9BE were not available. The concentrations of total dissolved solids in extracts from surface soil in plot 8EP, normalized to field water content, are shown in Figure 3-16a. The same concentrations, but normalized to the mass of soil, are shown in Figure 3-16b. From the latter figure an increase in salt mass near the soil surface is apparent. Once more, there is substantial variability in the data: this does not mean that salt concentrations in certain spots are not changing or even decreasing. It is simply related to the fact that there is substantial variability of salt concentrations at the soil surface even on the scale of 1 m^2. Even greater variability is seen in the total water-soluble selenium concentrations (Figure 3-17a), boron concentrations (Figure 3-17b), and arsenic concentrations (Figure 3-17c). Nevertheless, net increases in these concentrations over a two-month period are observed. Due to the great variability in trace element concentrations, a statistically large number of samples needs to be taken to determine, from field data, the rates of trace element accumulation at the surface. Because periodic collection of such a large data set is not feasible with our present level of effort, laboratory column experiments will be used to determine the rate at which trace elements accumulate under controlled conditions.

3.6.3. Estimating Evaporative Flux of Salts and Selenium Toward Soil Surface

Evaporative transport of salts and selenium may be estimated in two ways: (i) by looking at changes in mean values of salt concentrations for each sampling period, and (ii) by estimating a concentration of salts and selenium in soil water entering the top 10 cm of the soil surface, based on measured evaporation rates. The first method is quite straightforward: mean values of salt concentrations in plot 8EP soils may be estimated from the data presented in Figure 3-16b. Table



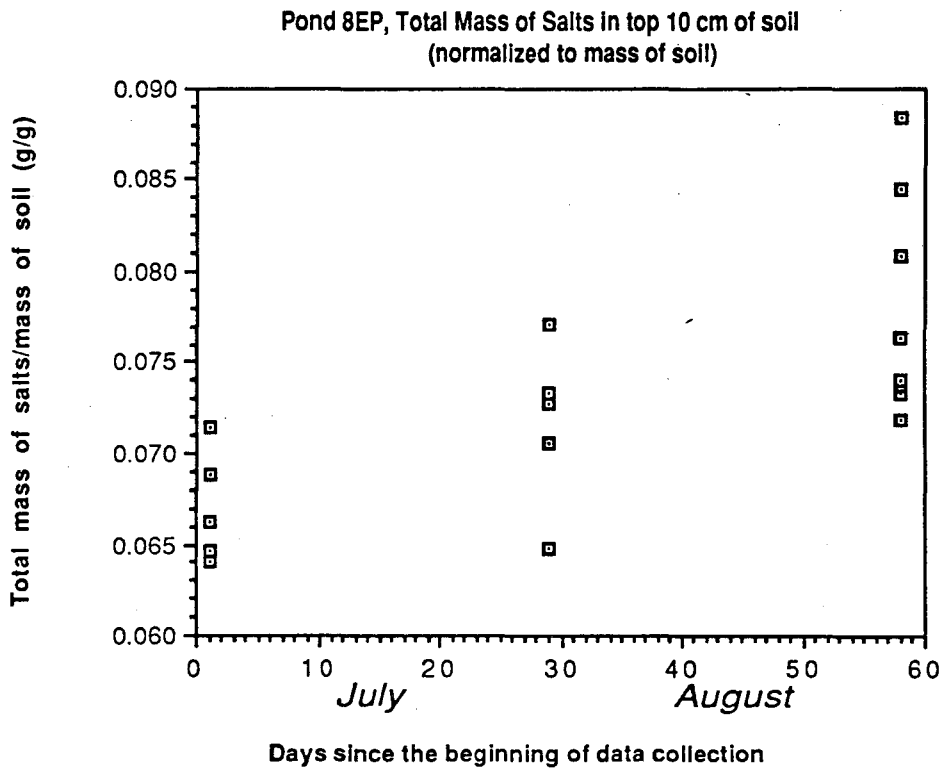
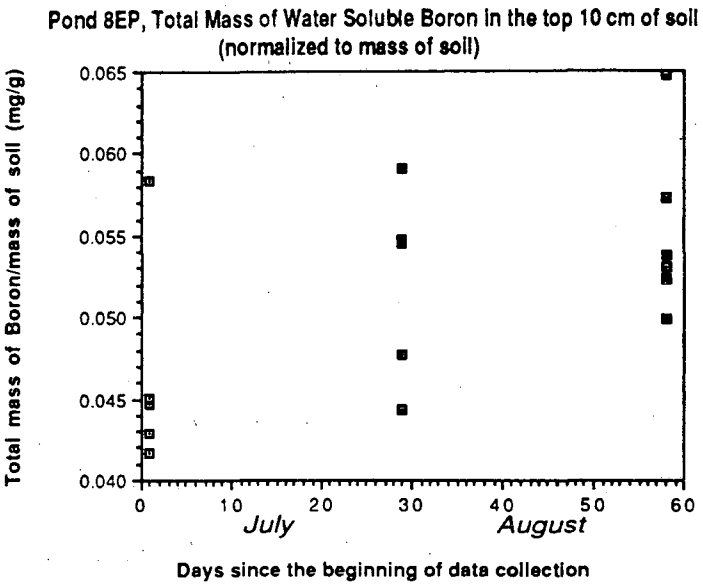
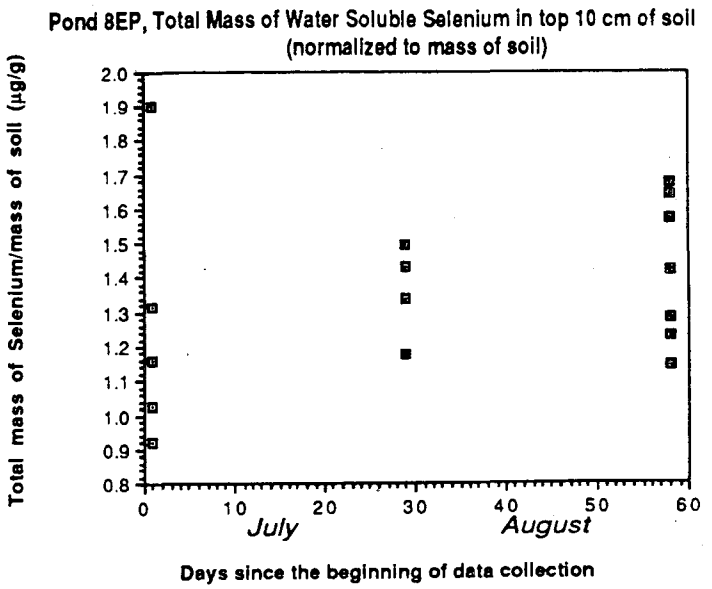


Figure 3-16a,b. Mass of total "dissolved" solids in the top 10 cm of soil in Pond 8 plot EP, normalized to field water content (a) and normalized to mass of soil (b), July-August 1988.





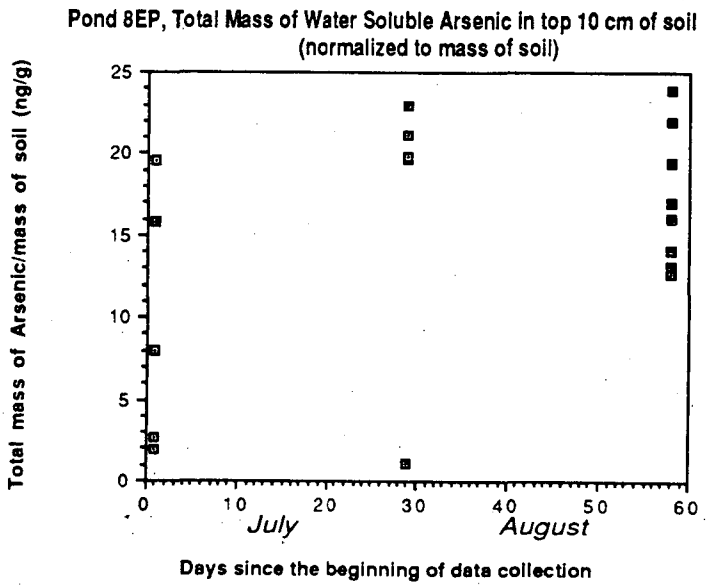


Figure 3-17a,b,c. Mass of water soluble selenium (a) and boron (b), and arsenic (c) in the top 10 cm of soil in Pond 8, plot EP, normalized to mass of soil, July- August 1988.

3.1 summarizes changes in salt content over the months of July and August.

Table 3.1. Change in salt content in surface soil cores at Pond 8EP.

Sampling date	Mean salt mass/soil mass ratio	Mean mass of salts
7/1/88	0.06704 g/g	16.5 g
7/29/88	0.07170 g/g	17.7 g
8/25/88	0.07789 g/g	19.2 g

The mean mass of salts is calculated using a mean soil mass of 246.3 g. Thus, the mass of salts in the top 10 cm of soil had increased by 1.2 g over the month of July and an additional 1.5 g during the month of August. The soil in the microlysimeter tubes has a surface area of approximately 20.26 cm^2, which means that the accumulation rate of salts in the surface 10 cm of plot 8EP soils was on the order of 0.0024 $g/cm^2/day$, or 24 $g/m^2/day$. Over the period of July and August, the total mass of salts in this depth interval increased by approximately 1.4 kg/m^2 (16%). The chemical analyses of soils from plot 9BE were not complete at the time of writing and thus a similar estimation of salt flux for that plot cannot be made yet.

The second method requires the knowledge of salt concentrations in soil water at depth. This information has been collected for several months at plot 8EP through soil water samplers. In addition, complete soil cores have been collected from both plots 8EP and 9BE. The samples were taken from the soil surface to below the water table in 10 cm intervals, with the exception of the soil in the top 30 cm which was sampled on a finer scale. These soils were homogenized within each interval in the laboratory and water extracts were made of each interval. The results of some of the chemical analyses performed on this material are shown in Figures 3-18, 3-19, and 3-20. Total soluble species are those which were measured in the soil extracts. Dissolved species are those which were measured in water from soil-water samplers. The distinction between the two gives an estimate of the precipitated or adsorbed mass of each species. It is quite apparent, for example, from Figure 3-18b, the sodium profile, that at a depth of 20 cm approximately 50% of the sodium inventory is not dissolved in the soil water. On the other hand, most of the water-

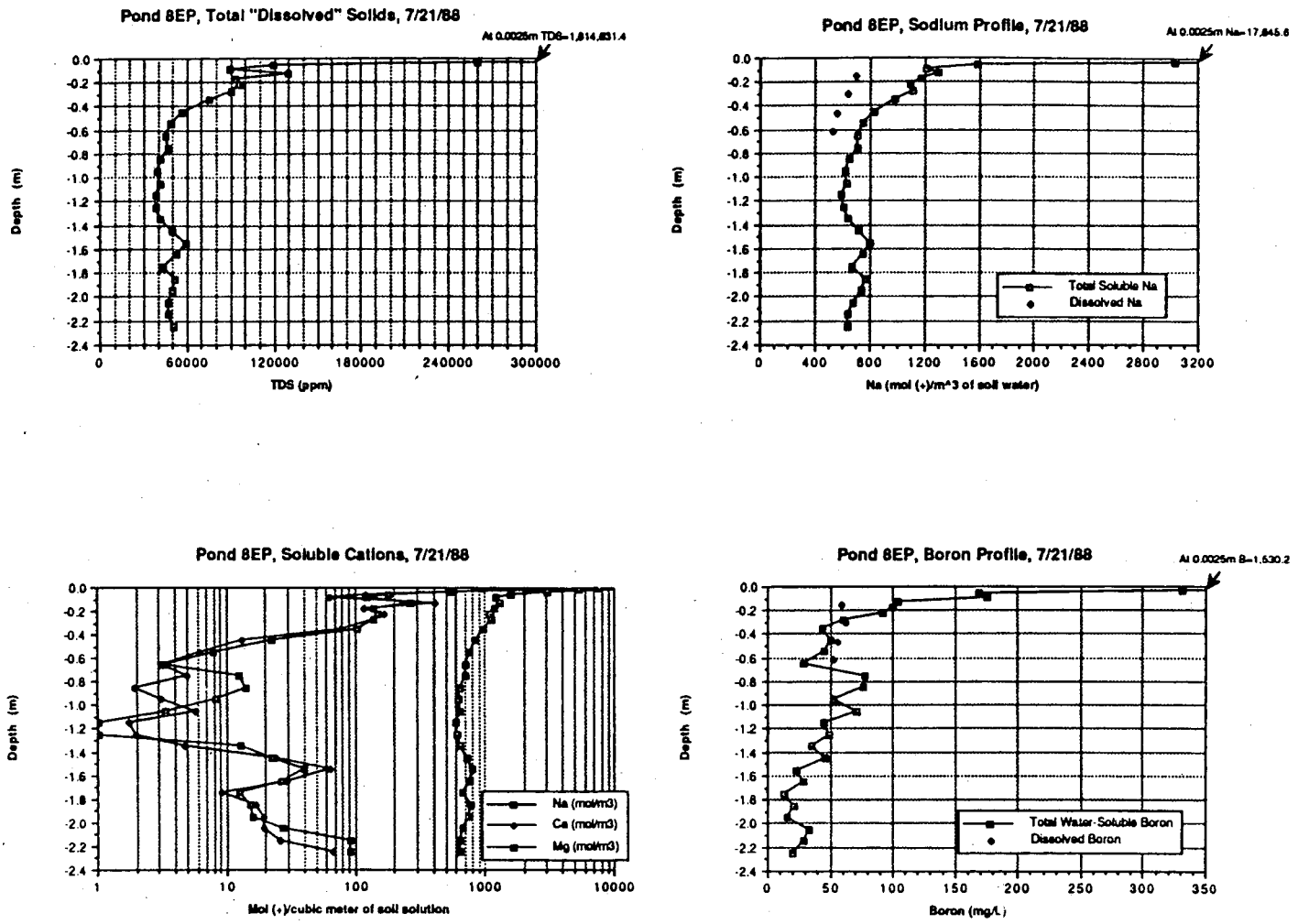


Figure 3-18a,b,c,d. Concentration profiles in Pond 8, plot EP soil of total "dissolved" solids (a), sodium (b), major cations (c) and boron (d). Note variation in concentration (horizontal) scale.

soluble selenium at that depth is dissolved in the soil water (Figure 3-19a). A very different pattern is exhibited by the arsenic profile at plot 8EP. The arsenic dissolved in the soil water represents only a minor fraction of the total arsenic inventory which appears to be in a sorbed phase. This is supported by the fact that the peak in the arsenic profile coincides with the peak in relative clay content of the soil (Figure 3-19). (Soil-water samplers have only recently been installed at plot 9BE and have not yielded any data yet.)

Using an estimate of total dissolved solids concentrations in soil water at depth, the mass of salts moving upward due to an evaporative flux may be calculated by multiplying the evaporation rate by the concentration of salts dissolved in the pore water. The values calculated with this method are summarized in Table 3.2.

Table 3.2. Salt accumulation rates for Pond 8EP and 9BE based on soil evaporation rates

Plot	Concentration of salts in soil water	Mean evaporation rate	Accumulation rate of salts at surface
8EP	50,000 mg/l	0.65 $l/m^2/day$	32.5 $g/m^2/day$
9BE	30,000 mg/l	0.90 $l/m^2/day$	27.0 $g/m^2/day$

The value of accumulation rate obtained for plot 8EP soils using the above method agrees well with the same value obtained through direct measurement (32.5 vs. 24 $g/m^2/day$). The difference between these two values is probably within the range of field variability and is also the result of an approximation of salt concentration in soil water. The accumulation rate in plot 9BE cannot be confirmed yet for reasons already mentioned. Data presented in Figure 3-16b give a clue as to the relative increase of salt mass over the two month period. It appears that the total mass of salts in the top 10 cm of soil at plot 8EP increased by 16% from July 1st to August 25th.

A similar comparison may be made for selenium and boron, although spatial variability makes quantitative evaluation more difficult. The total mass of water-soluble selenium in the top 10 cm of soil increased by 15% over the two month period, while the total mass of boron

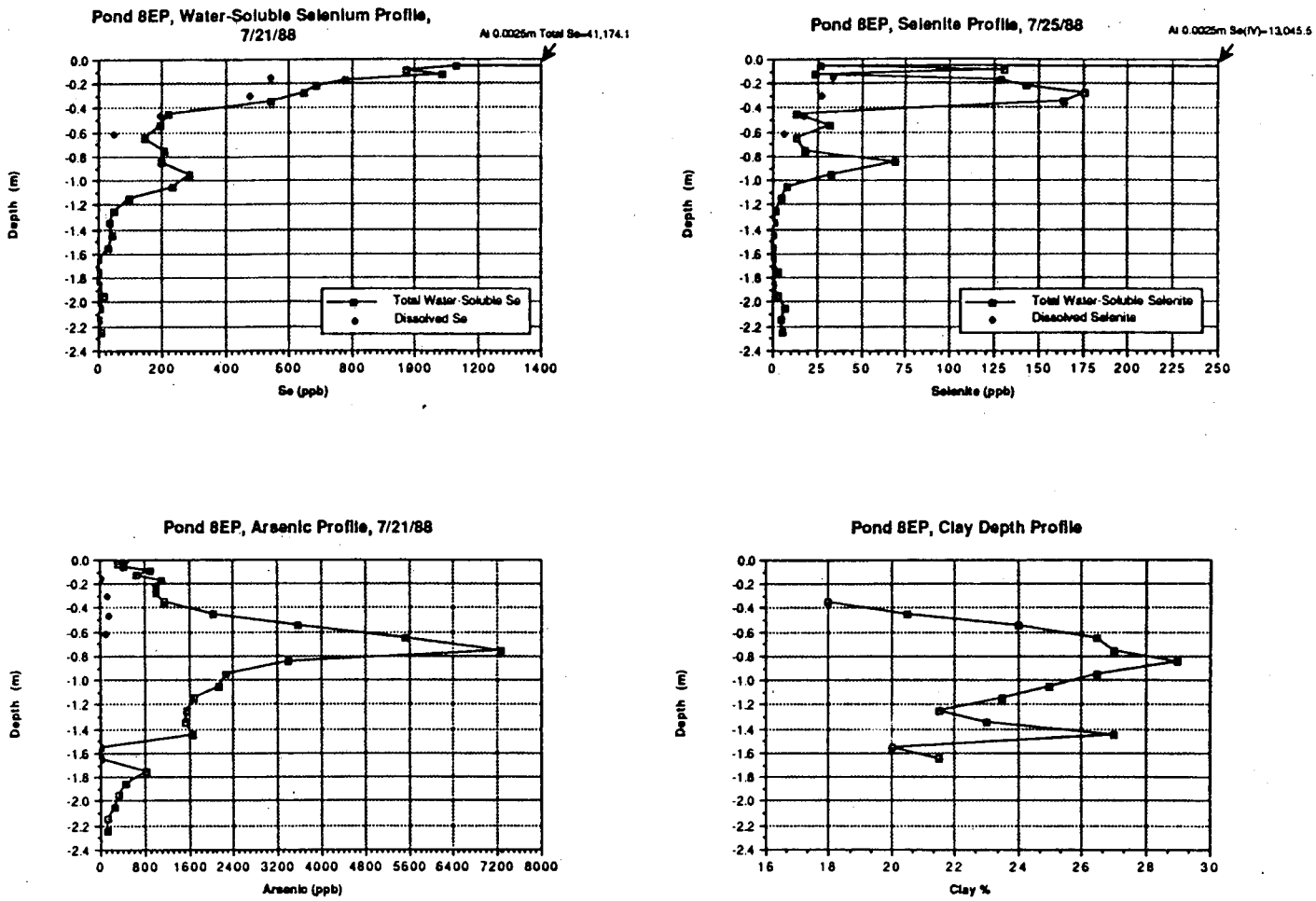


Figure 3-19a,b,c,d. Concentration profiles in Pond 8, plot EP soil of water-soluble selenium (a), water-soluble selenite (b), water-soluble arsenic (c), and clay content profiles with depth (d).

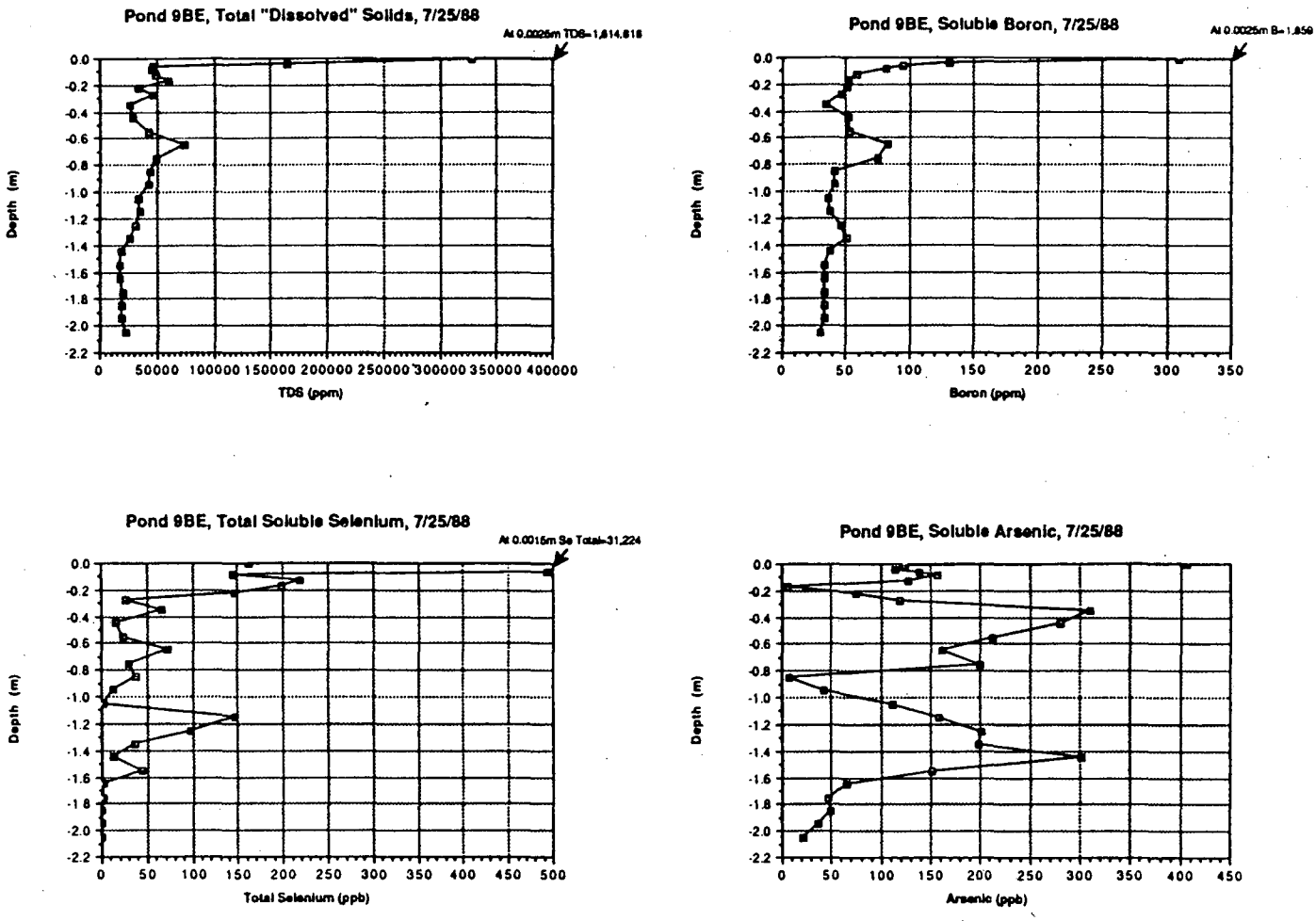
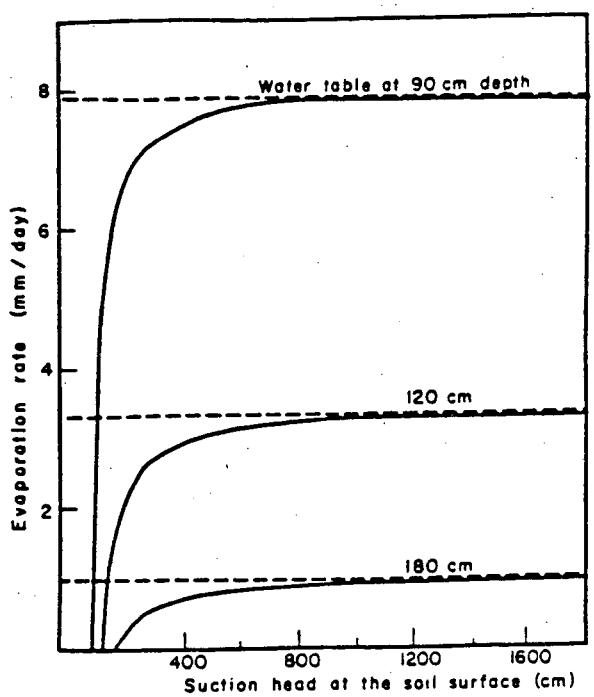


Figure 3-20a,b,c,d. Concentration profiles in Pond 9, plot BE soil of total "dissolved" solids (a), boron (b), water-soluble selenium (c), and water-soluble arsenic (d).

increased by 17% over the same period. It needs to be emphasized that an increase of 15% in the soluble inventory does not imply an increase of 15% of the total selenium inventory because much of the selenium is presently in insoluble forms.

3.6.4. The Effects of Evaporative Transport on the Whole of Kesterson Reservoir

The rate at which salts and trace elements will accumulate at the soil surface depends on two factors: (i) the bare soil evaporation rate, and (ii) the current concentration of salts and selenium in the soil water. From that standpoint, the data obtained in plots 8EP and 9BE will be two points in a large spectrum of evaporative flux values. On one hand, the concentrations in soil water at these two sites are quite high. On the other hand, while pan evaporation rates are highest during the summer months, as shown in Figure 3-21, bare soil evaporation rates are more dependent on the position of the groundwater table and soil characteristics. While potential evaporation affects the bare-soil evaporation rates, it is the depth to the groundwater table and the unsaturated permeability of the soil which limit bare soil evaporation rates (Gardner, 1958). Therefore, as the water table rises, bare soil evaporation rates are expected to increase over the next few months. As more data are collected, better estimates of bare soil evaporation rates and correlation with water table fluctuations and soil properties will be possible. Since 50% of the Reservoir has been filled with heterogeneous, yet mostly coarse-textured, non-native soil, bare soil evaporation rates will be, on the average, reduced in the filled areas due to the increased distance between the soil surface and the water table. In vegetated parts of the Reservoir, transpiration through plants will tend to concentrate salts and selenium in the root zone. A study of the affect of transpiration on the selenium inventory is now underway in both the laboratory and at Kesterson Reservoir.



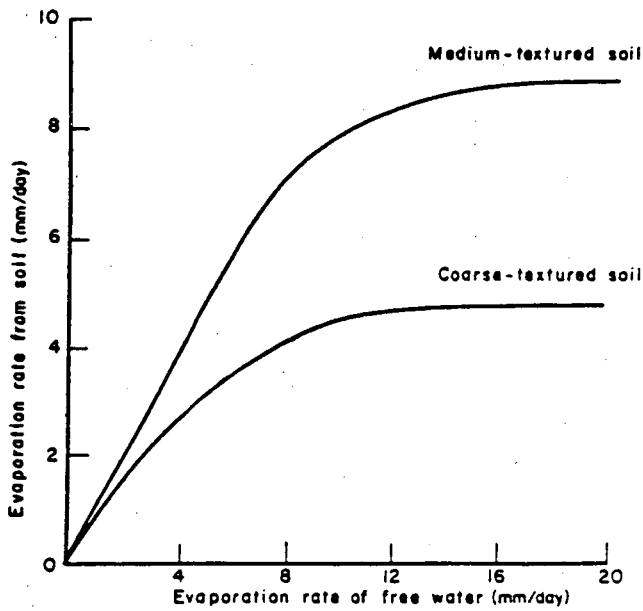


Figure 3-21a,b. General theoretical relationships between bare soil evaporation rate and water table depth (a) and soil texture (b). Both figures from Hillel, 1980.

4. GROUNDWATER INVESTIGATIONS

4.1 INTRODUCTION

As a result of groundwater investigations conducted during 1986, and 1987, we concluded that selenium would not persist in a soluble form in the aquifer underlying the Reservoir unless nitrate-nitrogen was also present (LBL Annual Report, 1987). This conclusion was supported by a series of field and laboratory experiments, as well as USBR monitoring data that indicated both nitrate and selenium concentrations in the shallow aquifer were declining rapidly. During this past year we have continued our investigations to provide additional information pertinent to evaluating the effects of Kesterson Reservoir operations on the underlying aquifer. Specifically, we have focussed our efforts on four areas;

- quantifying the parameters and processes that disperse solutes as they migrate through the aquifer;
- developing a better understanding of the factors that allow the small plumes of selenium to persist in the groundwater;
- using non-instrusive geophysical methods for locating the plume of saline drainage water that seeped into the aquifer and migrated to the east of the Reservoir; and
- quantifying the rate at which the reducing conditions and selenium immobilization occur after fully saturated conditions are established.

A summary of these investigations is provided below.

4.2. MULTIWELL TRACER EXPERIMENTS

The multiwell tracer experiments conducted at Kesterson Reservoir were designed for two primary purposes. The first objective was to evaluate the factors controlling transport of non-reactive chemical species in the shallow aquifer underlying Kesterson Reservoir. Specifically,

the experiments were intended to:

- provide information about the micro-scale (0.1 to 1 m) structure of the sediments;
- measure the longitudinal dispersivity of the individual flow paths within the aquifer; and
- identify the major dispersive mechanisms in the aquifer.

This information, when integrated with larger scale geological and hydrological information constitutes the data base for predicting the rate at which the saline drainwater plume will migrate downgradient.

The second objective of these tracer experiments was to provide information on the interaction between selenate, nitrate, and the aquifer sediments. Specifically, they provided information about:

- the rate at which selenate is removed from solution by interaction with the aquifer sediments in the presence of nitrate;
- the rate of denitrification in the aquifer;
- retardation of selenate, nitrate, and fluorescein by reversible sorptive mechanisms.

To meet these objectives, two tracer experiments have been conducted. For both experiments, an injection/withdrawal well pair was used to create a controlled flow field. A schematic of the flow field generated by the injection/withdrawal well pair is shown in Figure 4-1. After a steady flow field was established, a short pulse of tracer was injected along with the flow stream into the injection well. Tracer breakthrough curves were monitored at several passive observation boreholes located midway between the injection and withdrawal wells. Injection/withdrawal continued until complete tracer breakthrough curves were obtained for all of the observation wells.

The first experiment, which was conducted during July 1986, was designed to investigate only the non-reactive transport properties of the aquifer. Fluorescein dye, a relatively non-reactive and weakly sorbed tracer was used during this experiment (Gaspar, 1987; Smart and

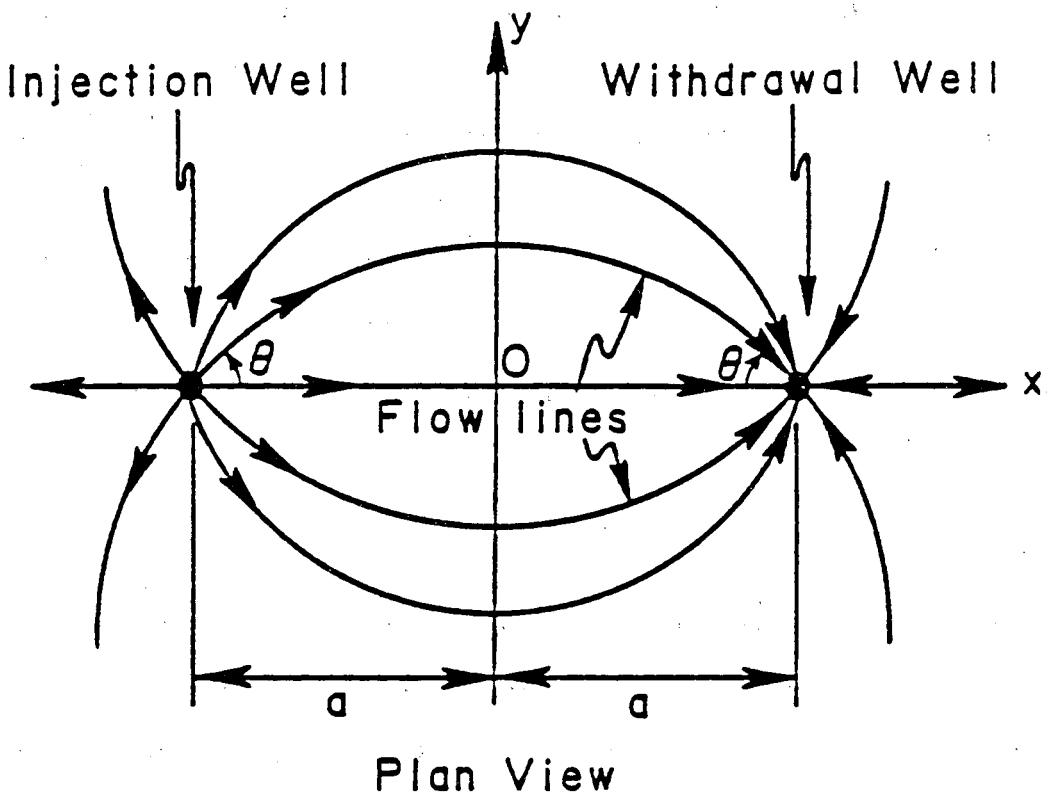


Figure 4-1. Schematic of the flow field between production/injection well pair.

Laidlaw, 1977). Preliminary results of this experiment were reported in LBL Progress Report No. 3. Results from this experiment will not be repeated here. See Benson (1988) for a comprehensive discussion of this experiment.

The second experiment, which was conducted during April, 1988, was designed to investigate further the transport properties of the aquifer and to provide information on reactive transport of selenium and nitrate in the shallow aquifer. This experiment was carried out in two phases and took approximately three weeks. During the first phase, fluorescein dye was used as a non-reactive tracer. This phase of the experiment was similar to the 1986 experiment, except that the injection/withdrawal wells were located in such a way that the flow field was rotated 90° with respect to the flow field generated during the first experiment. During the second phase of the experiment, a mixture of sodium selenate and sodium nitrate was introduced into the injection stream. The experiment continued until breakthrough curves were obtained for selenate and nitrate. This report discusses the results from phase 1 and phase 2 of Experiment No. 2.

4.2.1. Experimental Design

4.2.1.1. Test Site Configuration

A plan view of the pumping/injection wells and the monitoring boreholes is illustrated in Figure 4-2. A cross-sectional view of these wells and monitoring boreholes is shown in Figure 4-3. Well depths, casing sizes, slotted intervals and local coordinates are provided in Table 4-1. Wells I2 and I6 were used for the first experiment as the pumping/injection pair. Wells I4 and I8A were the injection/withdrawal pair for the second experiment. The monitoring boreholes, named well 1 through well 8 were constructed to sample fluids from several different depths within the flow field created by the pumping and injection well. A schematic of the different sampling intervals and their relation to the pumping and injection wells is illustrated in Figure 4-3. The monitoring boreholes consisted of 2 inch diameter (0.051 m) PVC casing with a 1.52 m slotted interval at the bottom of the casing.

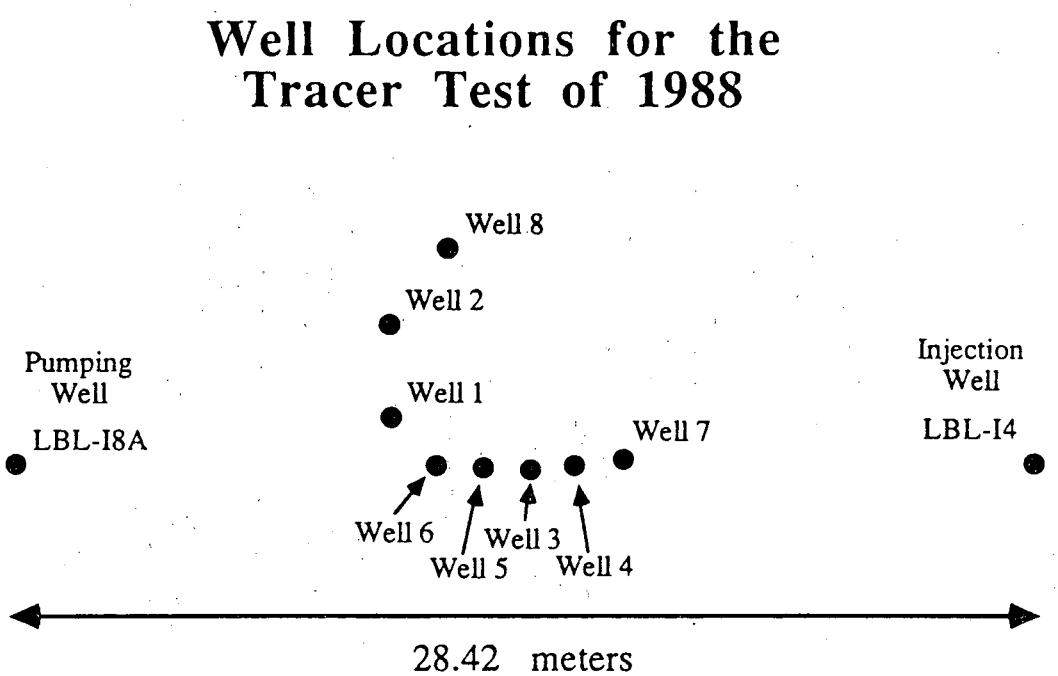


Figure 4-2. Plan view of the pumping, injection, and monitoring wells used for the tracer experiment.

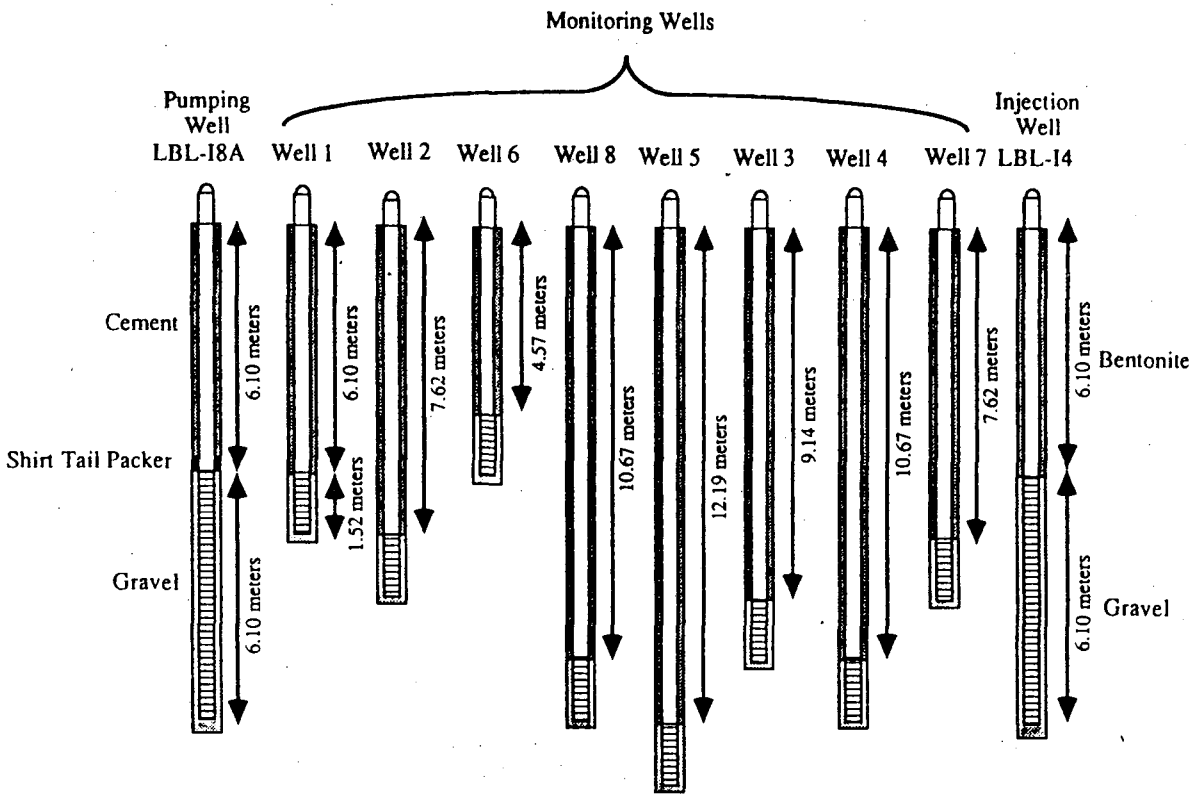


Figure 4-3. Cross sectional view of the wells used for the 1988 tracer experiment.

Table 4.1. Depth, casing size, slotted interval and local coordinates for the withdrawal, injection and monitoring boreholes used for the multiwell tracer experiments.

Borehole	Use	Depth (m)	Slotted interval (m)	Casing diameter (m)	x coordinate (m)	y coordinate (m)
LBL-I2	Injection	12.19	6.10-12.19	0.10	-0.48	16.11
LBL-I4	Injection	12.19	6.10-12.19	0.10	14.21	0.0
LBL-I6	Withdrawal	12.19	6.10-12.19	0.10	-3.40	-13.87
LBL-I8a	Withdrawal	12.19	6.10-12.19	0.10	-14.21	0.0
Well 1	Observation	7.62	6.10- 7.62	0.05	-3.38	-0.96
Well 2	Observation	9.14	7.62- 9.14	0.05	-3.44	3.37
Well 3	Observation	10.67	9.14-10.67	0.05	-0.65	-0.05
Well 4	Observation	12.19	10.67-12.19	0.05	0.09	0.0
Well 5	Observation	13.72	12.19-13.72	0.05	-1.36	-0.03
Well 6	Observation	6.10	4.57- 6.10	0.05	-2.17	0.0
Well 7	Observation	9.14	7.62- 9.14	0.05	0.91	0.1
Well 8	Observation	12.19	10.67-12.19	0.05	-1.83	5.63
LBL-I1	Observation	12.19	6.10-12.19	0.10	-0.75	3.28

4.2.1.2. Tracer Sampling Method and Frequency

The tracer sampling installation was designed to create a well-mixed fluid volume within the slotted interval of the borehole and to collect periodic samples of the borehole fluids from each of the monitoring wells. A schematic of the sampling unit and borehole installation is illustrated in Figure 4-4. A similar apparatus has been used by Grisak et al., 1977, for point dilution experiments.

The samples were collected automatically with a computer-controlled, solenoid-activated valve system. All of the monitoring wells were attached to the same sampling unit, to ensure uniformity in sample collection procedures and timing. The samples were collected in 100 ml polyethylene bottles with polypropylene caps. Bottles were capped within a short time after collection; however, during the night, some samples remained open for up to 8 hours. All of the samples were protected from direct exposure to sunlight due to concerns regarding degradation of the fluorescein dye.

Samples were collected hourly for the first part of the experiment. After the tracer returns were observed at all of the monitoring wells, the sampling rate was lowered to once every 2 hours. Fluorescein analyses were made using a spectrofluorometer (model Kontron Spectrofluorometer SFM-23). Selenite and total selenium concentrations were measured using the procedures described in Section 5. Nitrate analyses were performed by Soil and Plant Labs, Inc., using the cadmium reduction method.

4.2.1.3. Description: Tracer Experiment 2 - 1988

This experiment was conducted in two phases. During the first phase of the experiment, fluorescein dye was used as the tracer to identify flow paths, fluid velocities and dispersivity of the individual flow paths. During the second phase of the experiment, a mixture of sodium selenate and sodium nitrate was injected into the aquifer to establish rates of immobilization and the extent to which nitrate interfered with transformation and immobilization of selenate. The two experiments were not conducted simultaneously because several single well tracer experiments

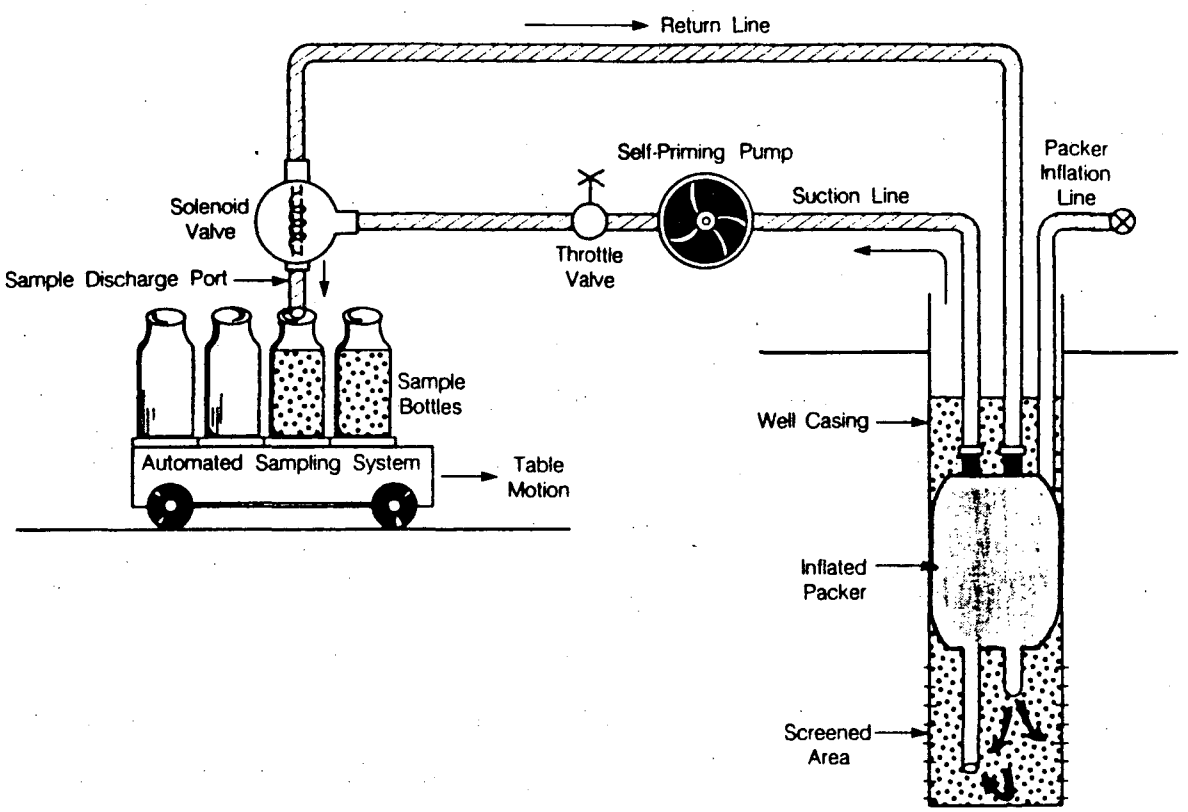


Figure 4-4. Schematic of the sampling and mixing unit used to collect fluid samples during the tracer experiment.

conducted earlier had indicated that nitrate may interfere with measuring fluorescein concentrations. To avoid analysis problems created by mixing fluorescein and nitrate, the experiment was conducted sequentially.

Prior to the first phase of the experiment, the injection/withdrawal system was operated for 24 hours to create a steady flow field. During this time and throughout phase 1 and phase 2 we maintained a steady pumping rate of 5.05×10^{-3} m^3/s (80 gpm).

On April 19 a 3825 s (63.75 minute) pulse with 140 ppm fluorescein was injected into well LBL-I4. The tracer solution was introduced into the flow stream by pumping 3.3×10^{-6} m^3/s (0.2 l/minute) of a highly concentrated fluorescein solution into the injection stream.

Fluid samples were collected at 3600 s (1 hour) intervals from the monitoring boreholes during phase 1. Approximately 1500 samples were collected and analyzed.

Fluorescein breakthrough curves for the monitoring wells 1, 2, 3, 4, 5, 7 and 8 are shown in Figures 4-5 through 4-11. The data presented in Figures 4-5 through 4-11 are normalized to the average input concentration of 140 ppm. No tracer returns were observed in observation well 6, which was slotted in the 1.52 m interval above the slotted interval of the injection well. As illustrated in these figures, the tracer returns consisted of a set of distinct peaks, superimposed on one another. The fastest tracer returns arrived in observation well 3 at around 1.5×10^5 (55 hours) after the tracer slug was injected into the aquifer. Tracer returns typically continued for several days after the first arrivals. Fluorescein concentrations were measured for $\approx 7 \times 10^5$ (8 days) after the injection pulse.

Phase 2 began on April 25, 5.2×10^5 (6 days) after the fluorescein slug was injected into the aquifer. A mixture of 301 ppb selenate (Se^{+6}) and 41.8 ppm nitrate (NO_3^-) was introduced with the injection stream for 20160 s (5.6 hours). Pumping and injection were not interrupted during the transition from phase 1 to phase 2, to prevent any disturbance to the steady flow field generated by the doublet. Fluid samples were collected at hourly intervals for the first 3 days after the selenate/nitrate mixture was injected. Thereafter, samples were collected every two hours.

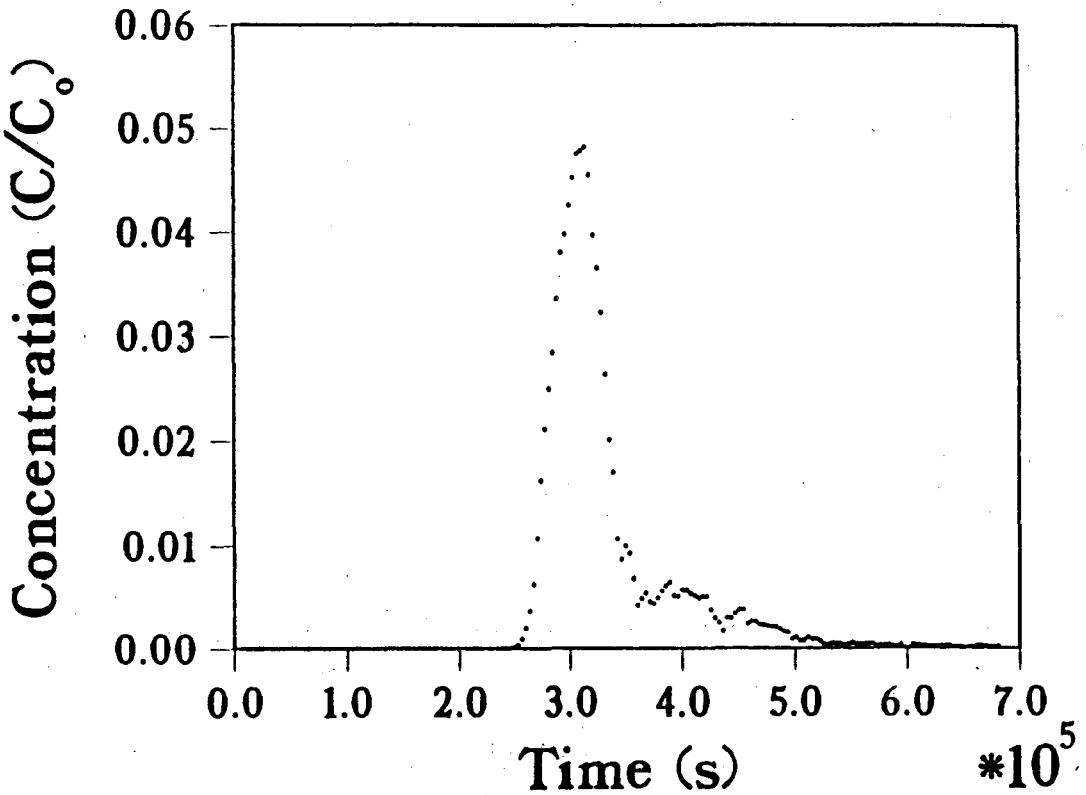


Figure 4-5. Fluorescein breakthrough curves for monitoring well 1.

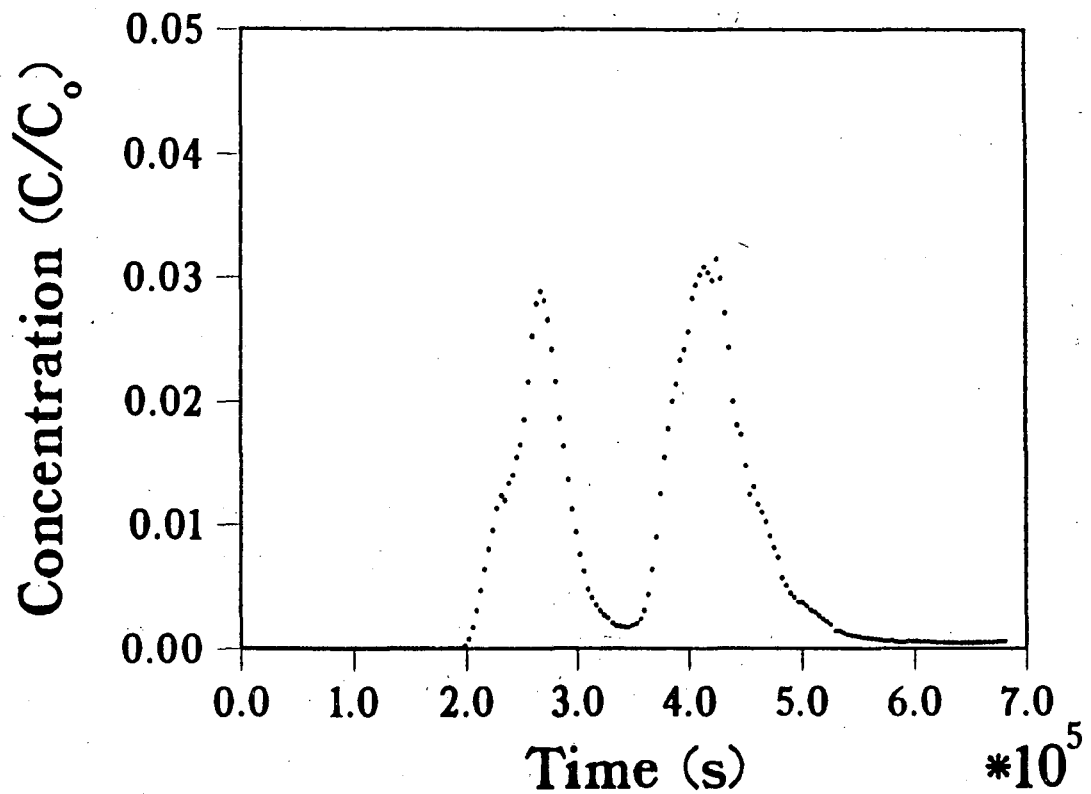


Figure 4-6. Fluorescein breakthrough curves for monitoring well 2.

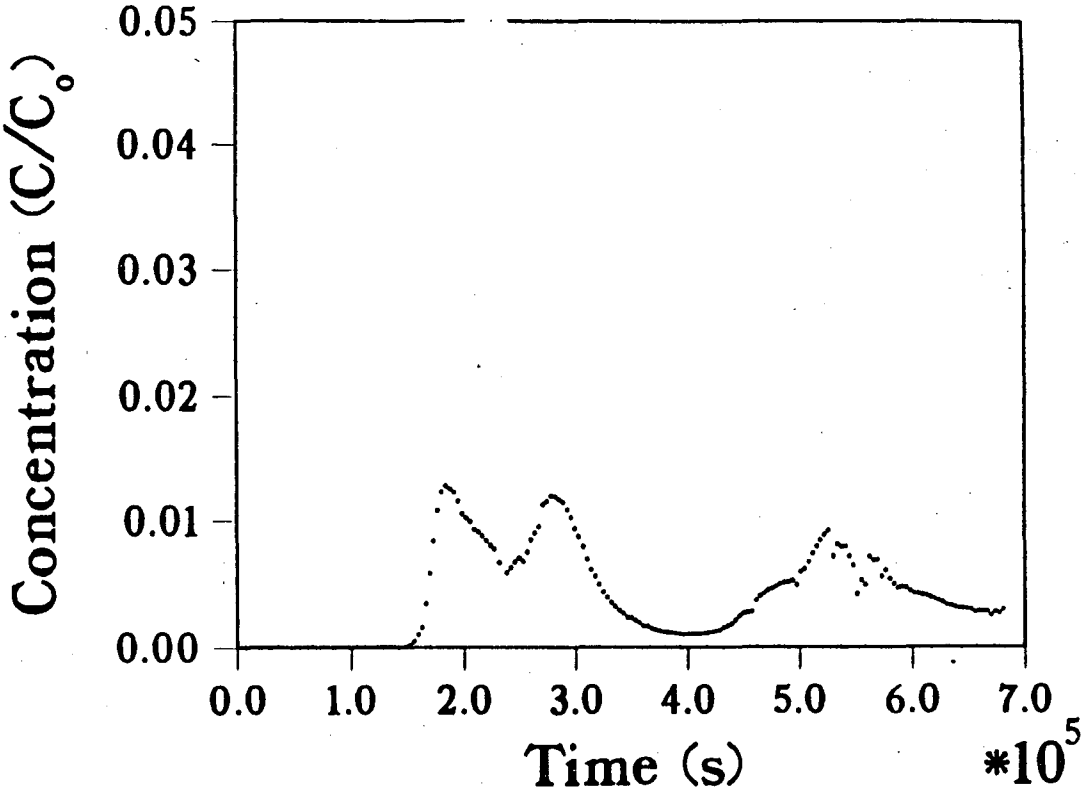


Figure 4-7. Fluorescein breakthrough curves for monitoring well 3.

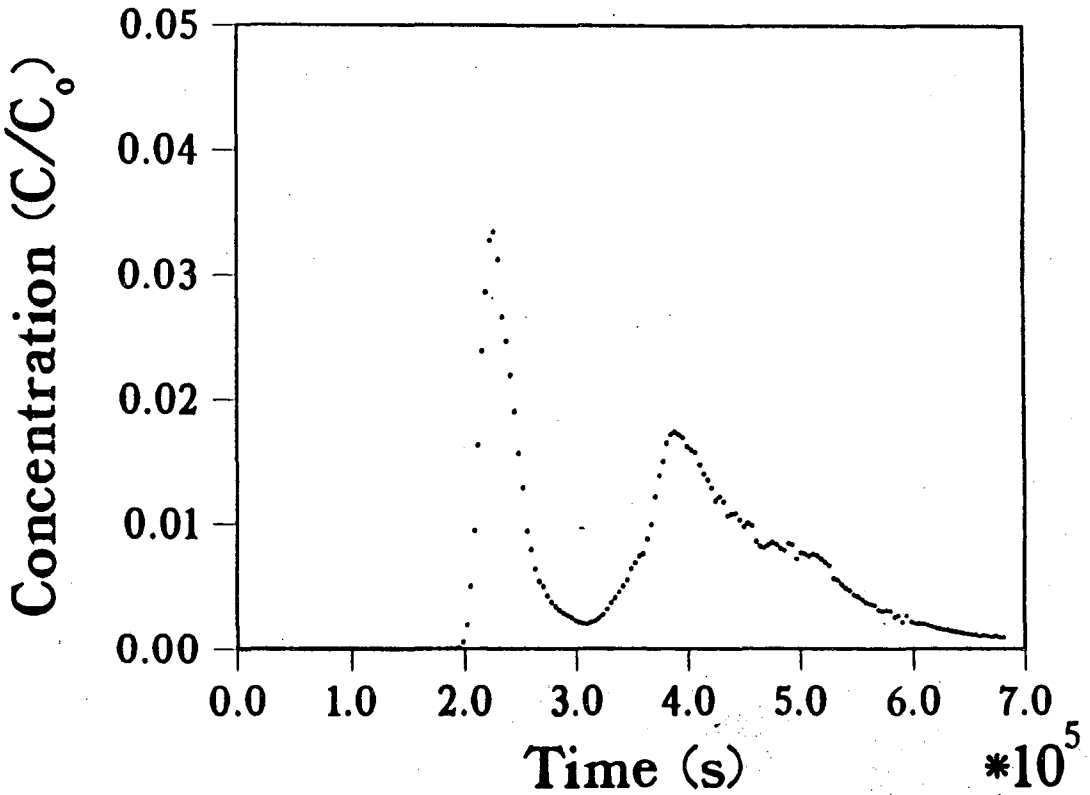


Figure 4-8. Fluorescein breakthrough curves for monitoring well 4.

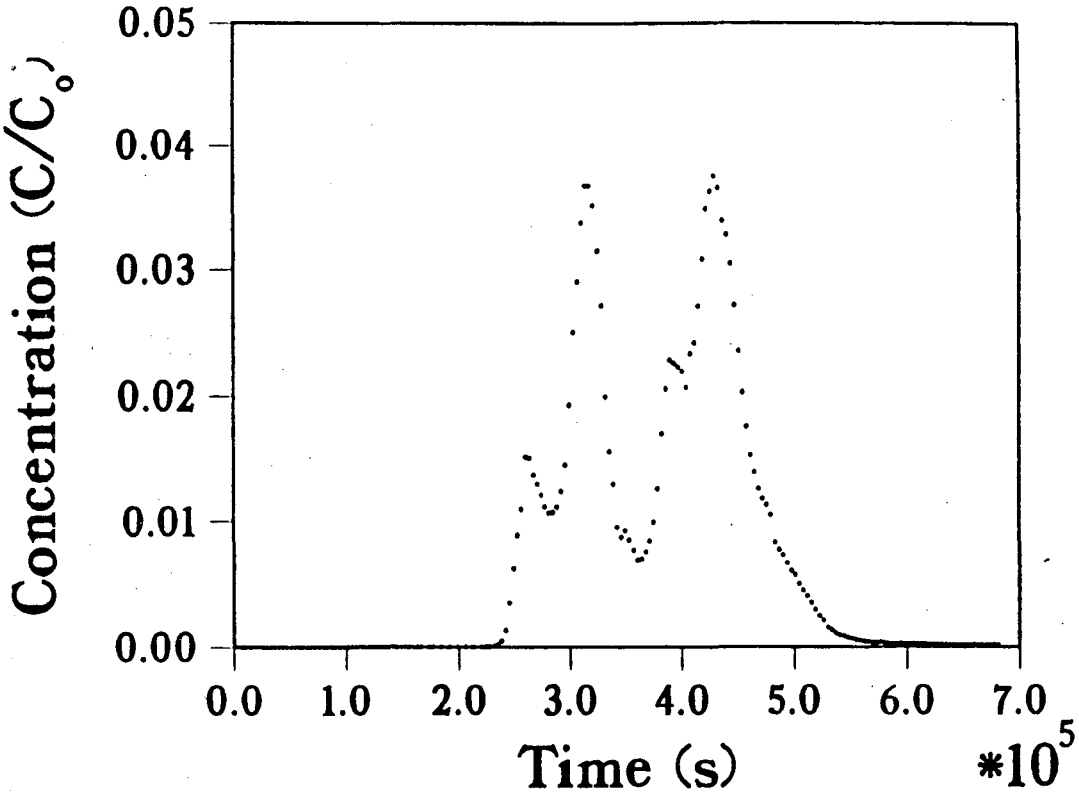


Figure 4-9. Fluorescein breakthrough curves for monitoring well 5.

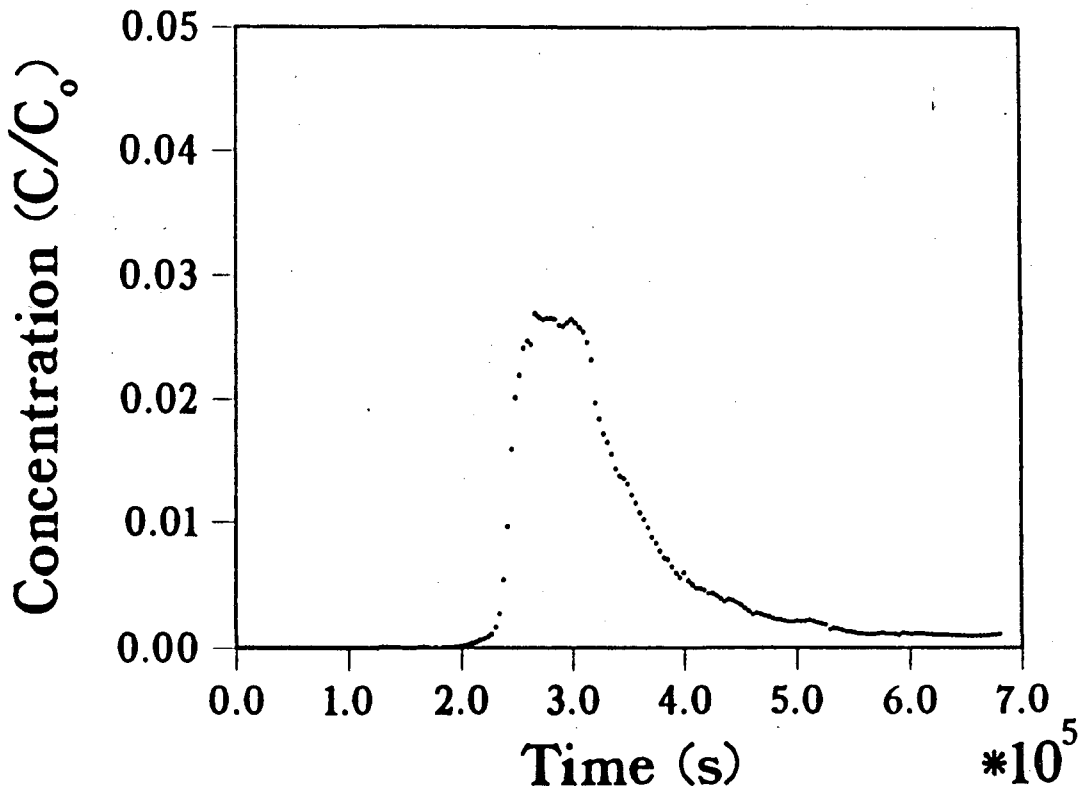


Figure 4-10. Fluorescein breakthrough curves for monitoring well 7.

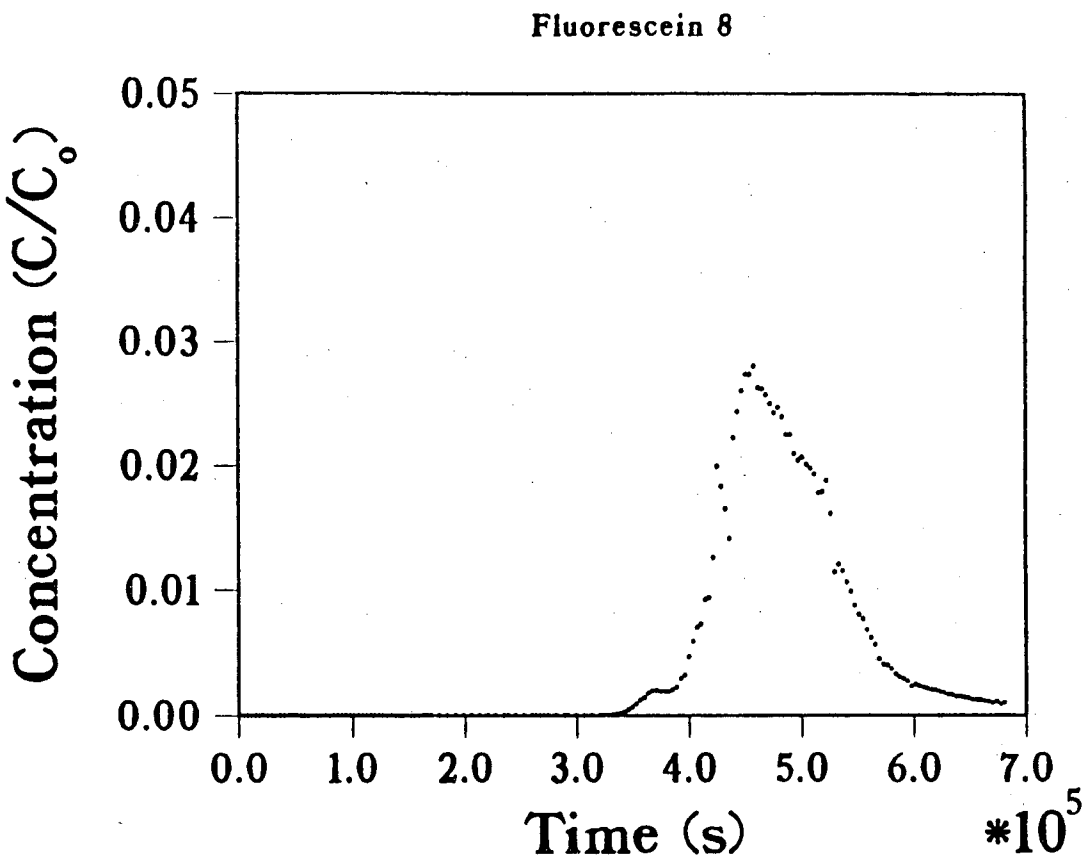


Figure 4-11. Fluorescein breakthrough curves for monitoring well 8.

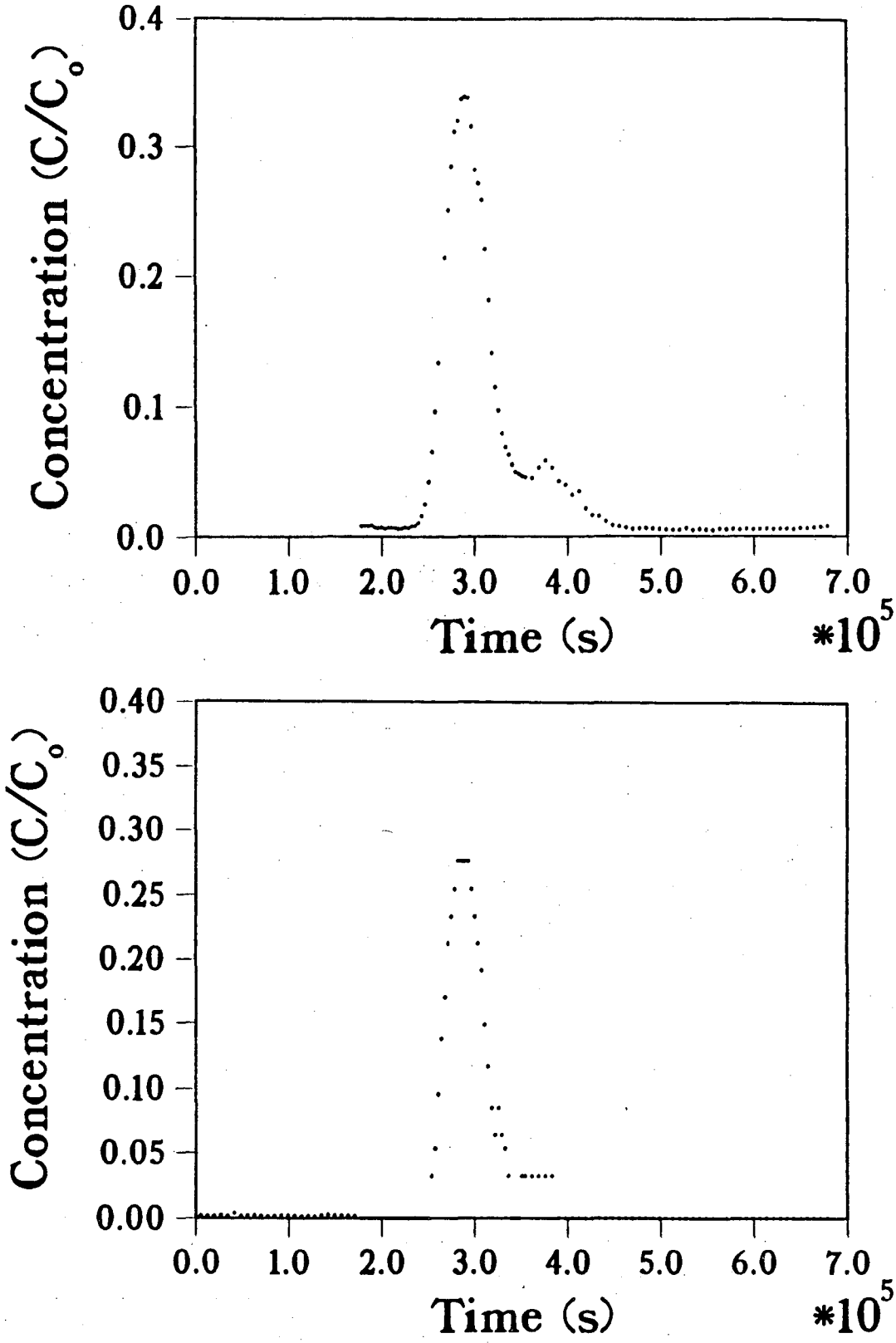
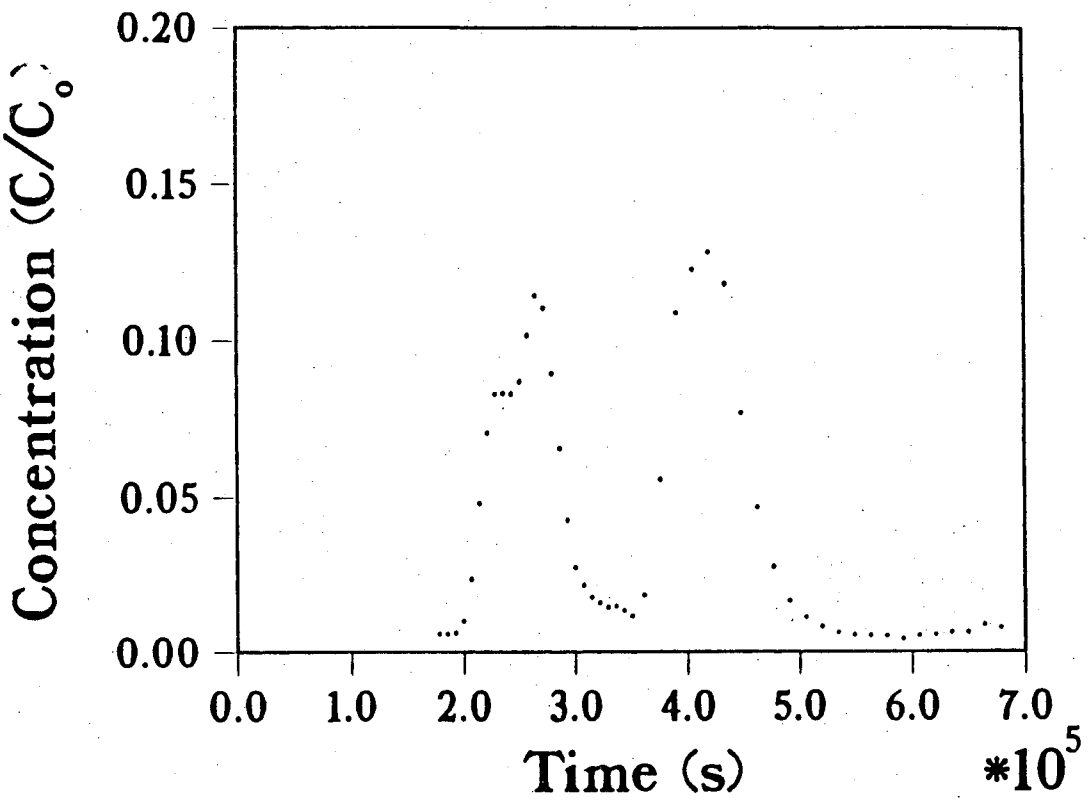


Figure 4-12a,b. Selenate and nitrate breakthrough curves for monitoring well 1.



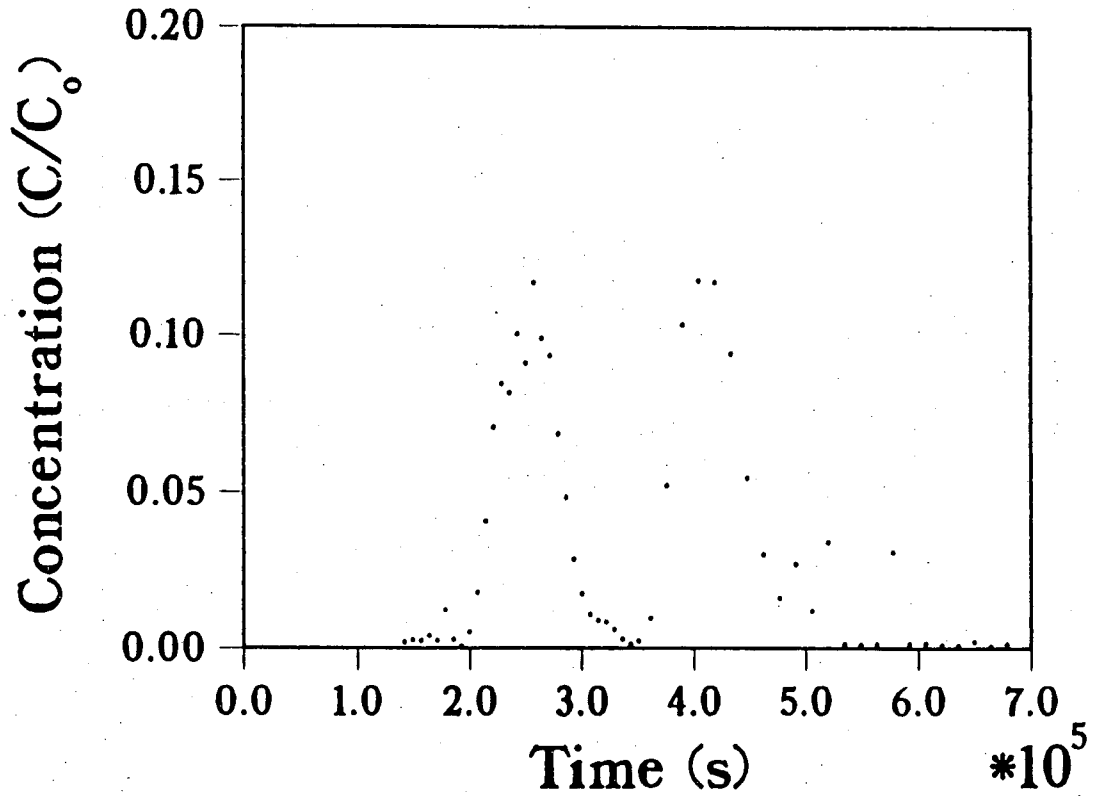
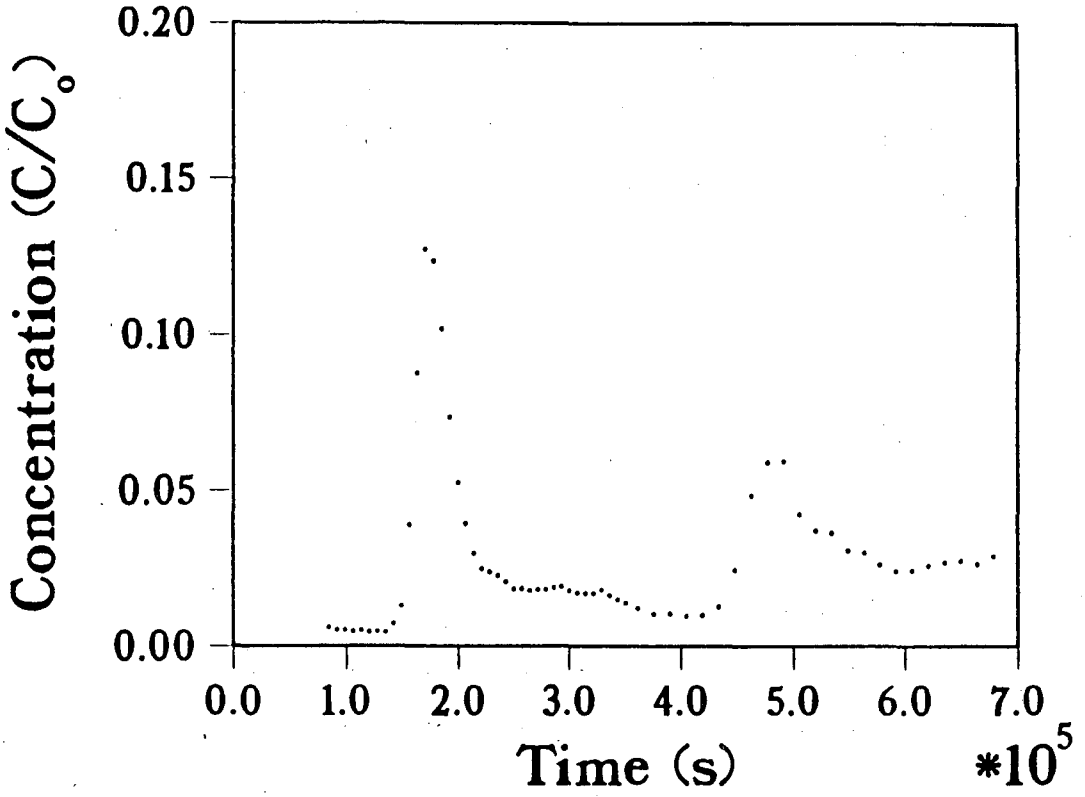


Figure 4-13a,b. Selenate and nitrate breakthrough curves for monitoring well 2.



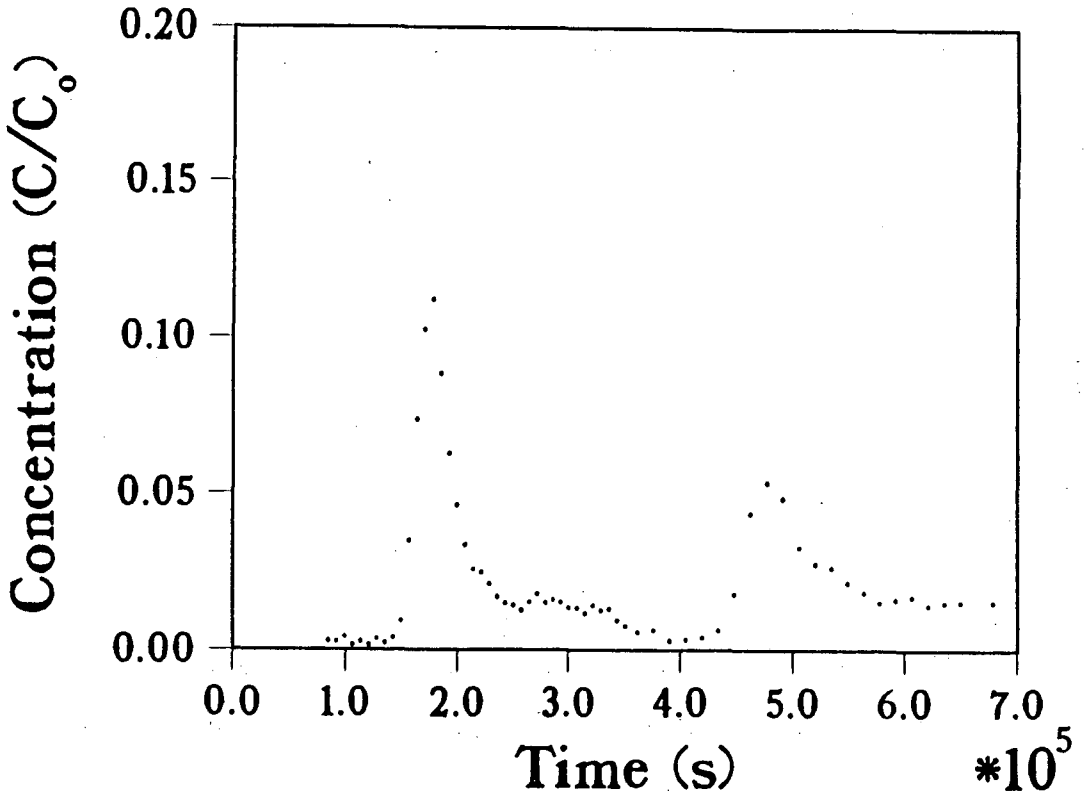
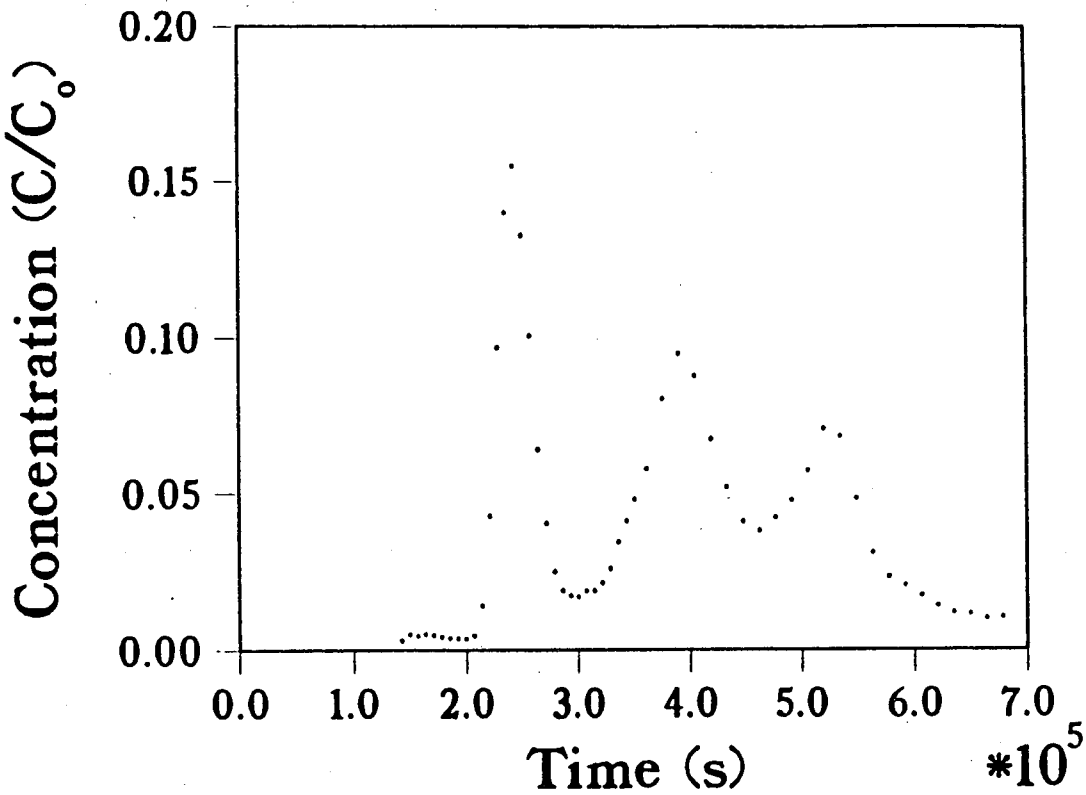


Figure 4-14a,b. Selenate and nitrate breakthrough curves for monitoring well 3.



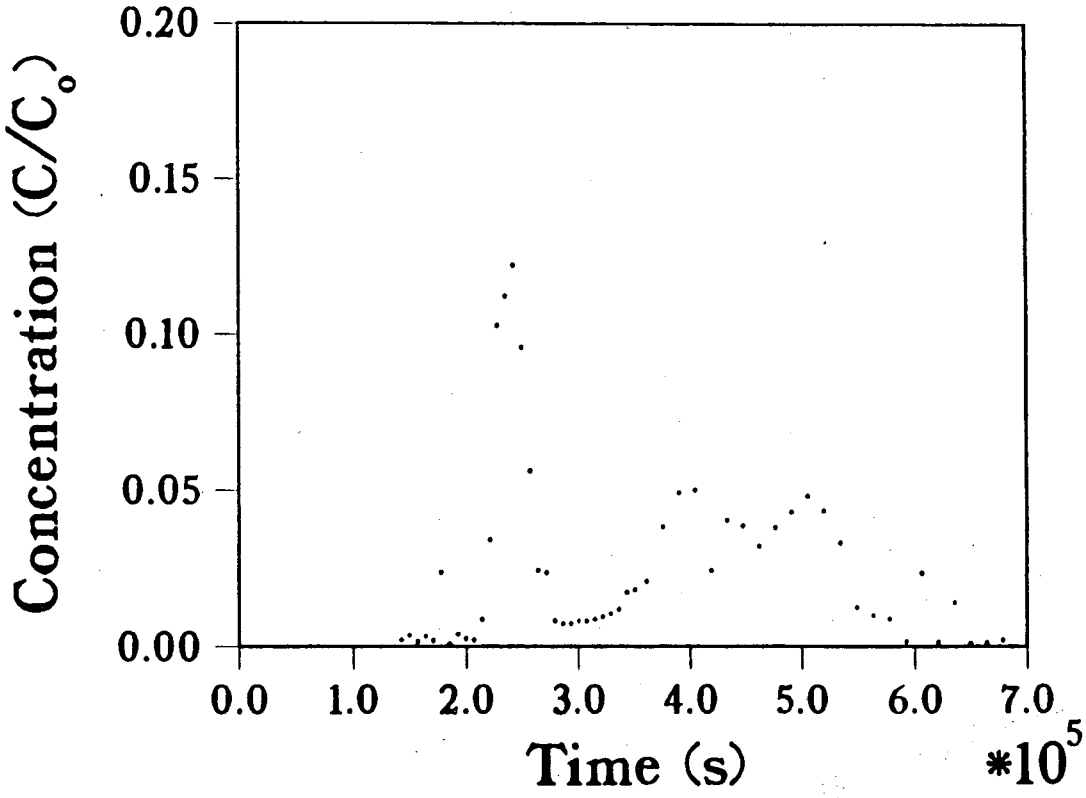
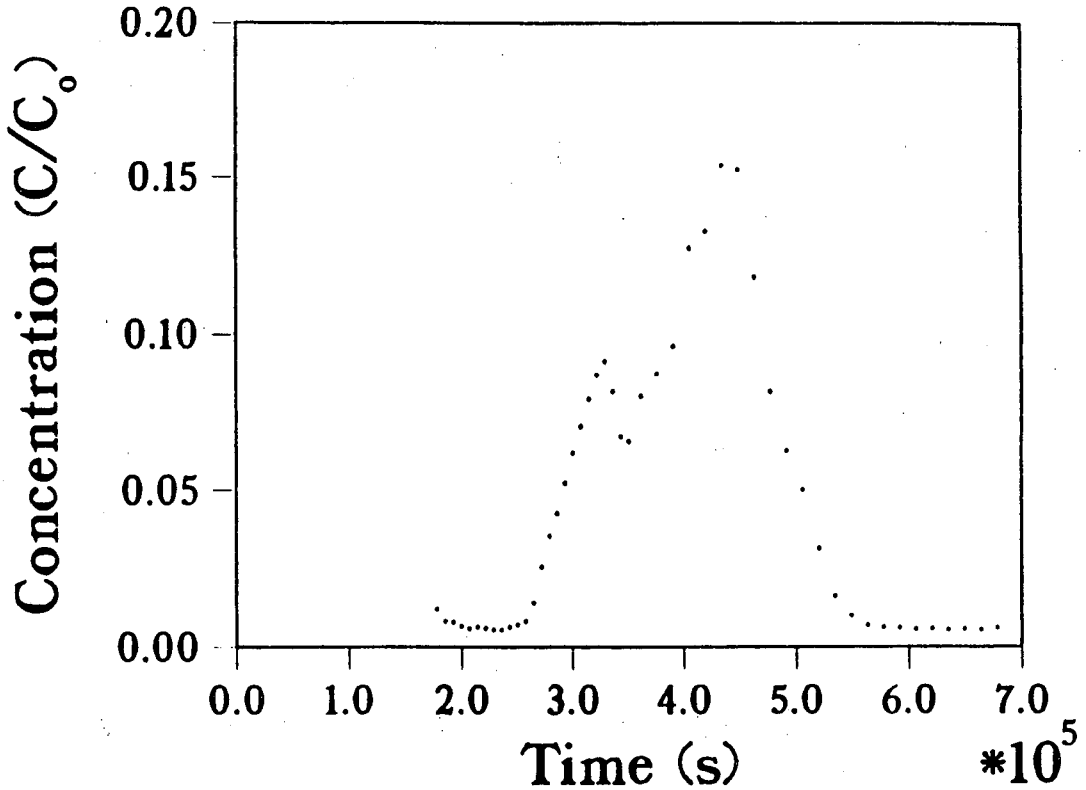


Figure 4-15a,b. Selenate and nitrate breakthrough curves for monitoring well 4.



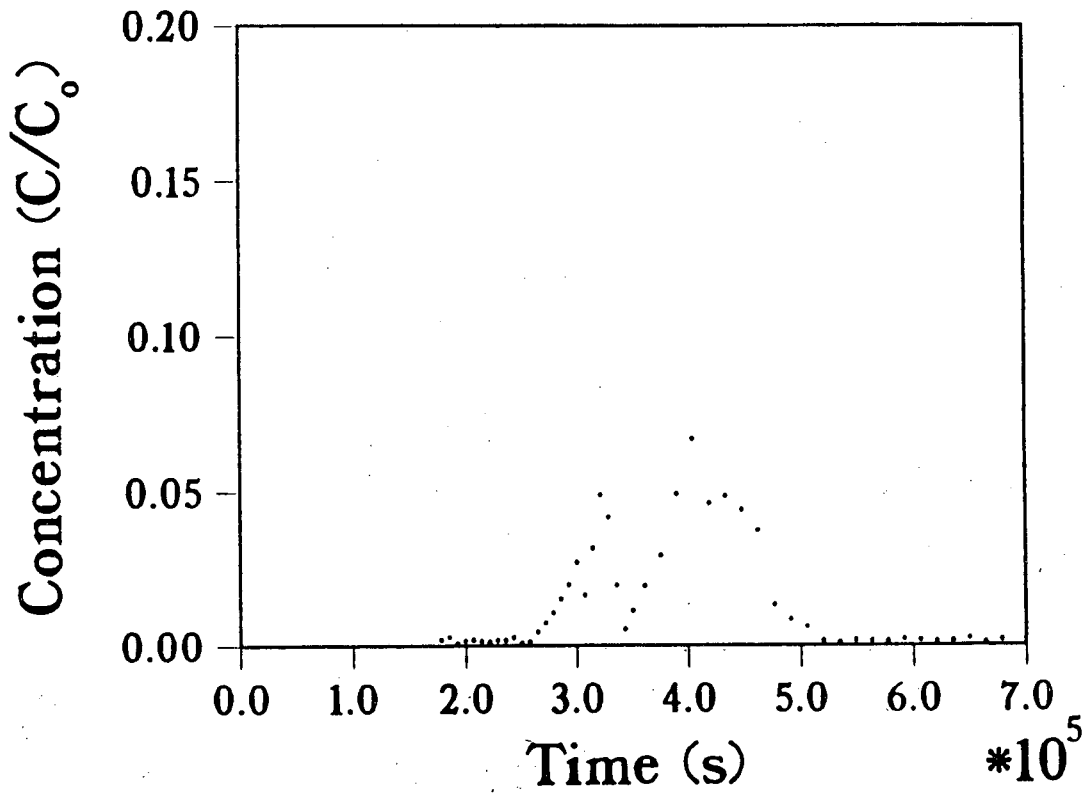
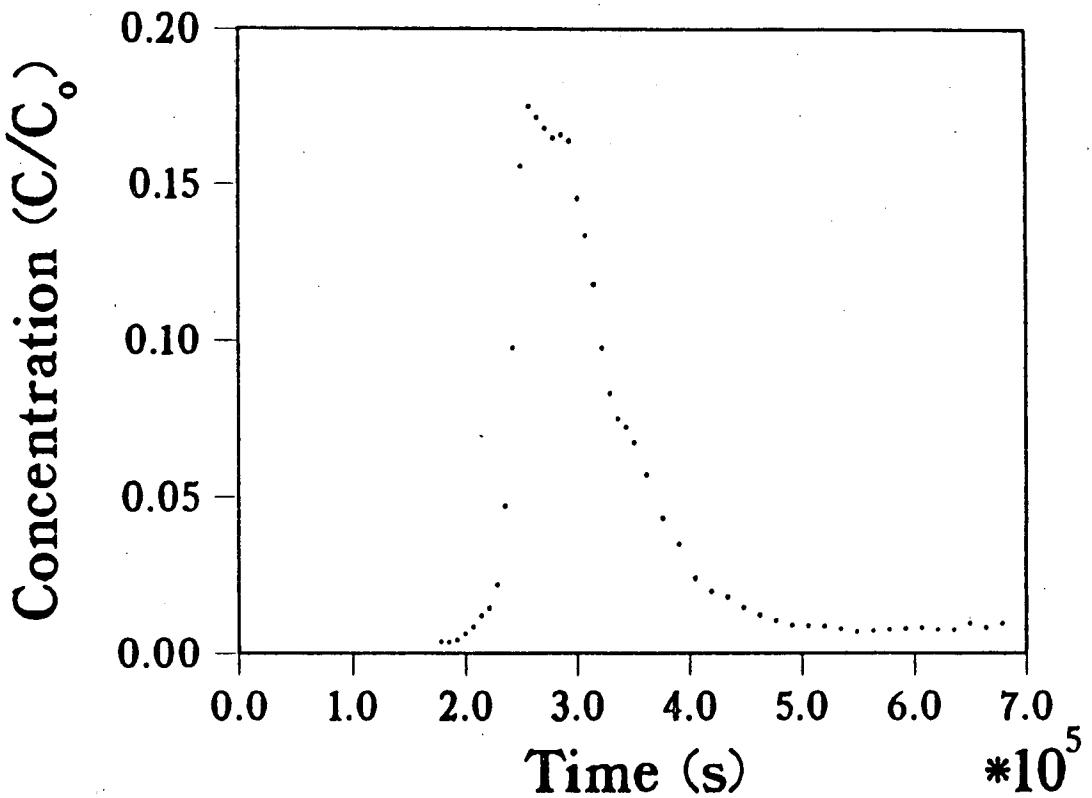


Figure 4-16a,b. Selenate and nitrate breakthrough curves for monitoring well 5.



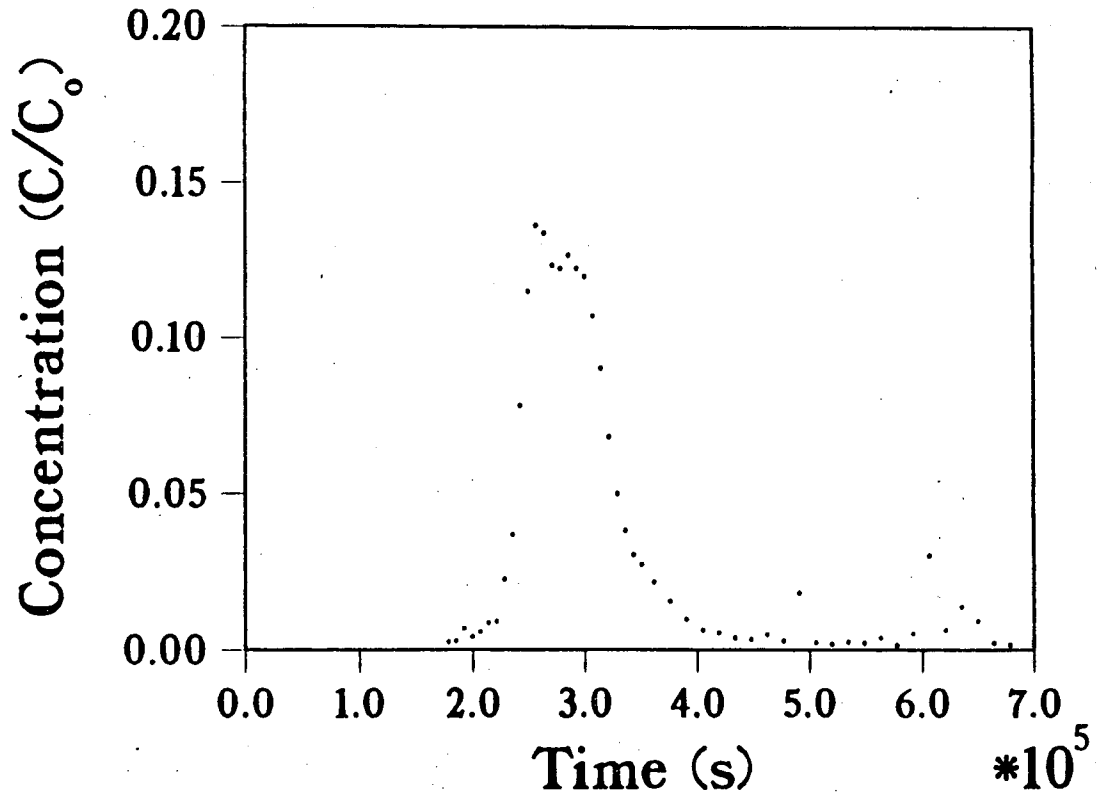
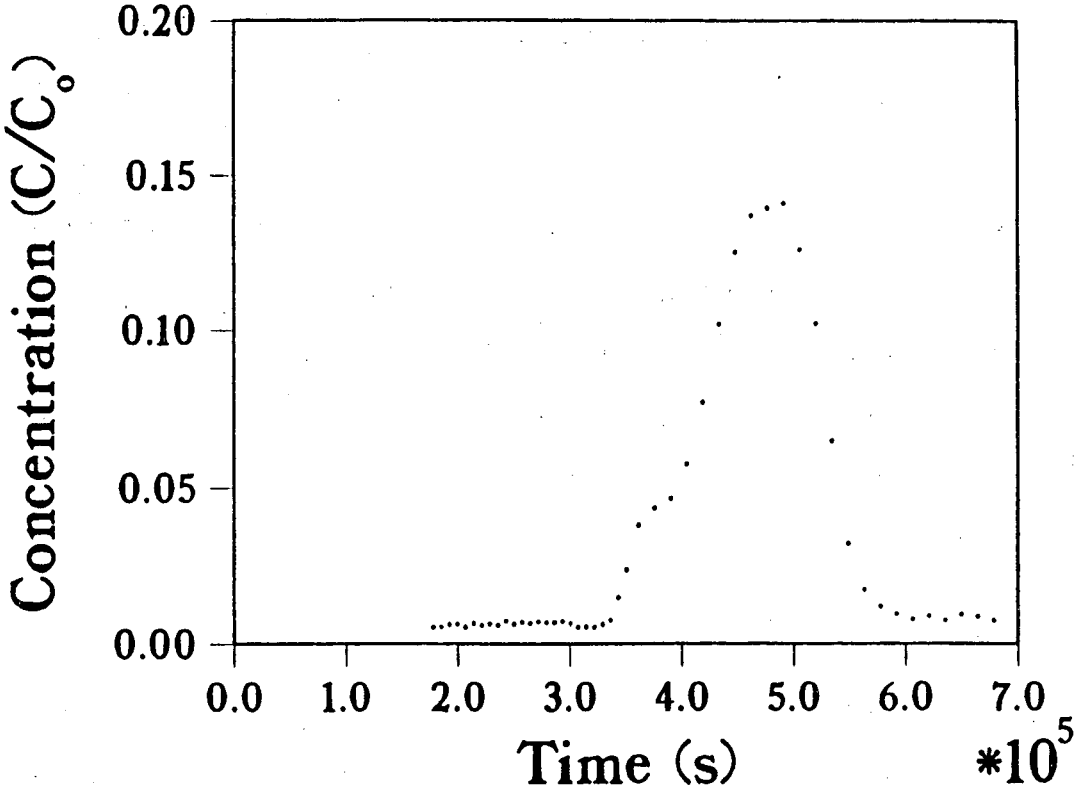


Figure 4-17a,b. Selenate and nitrate breakthrough curves for monitoring well 7.



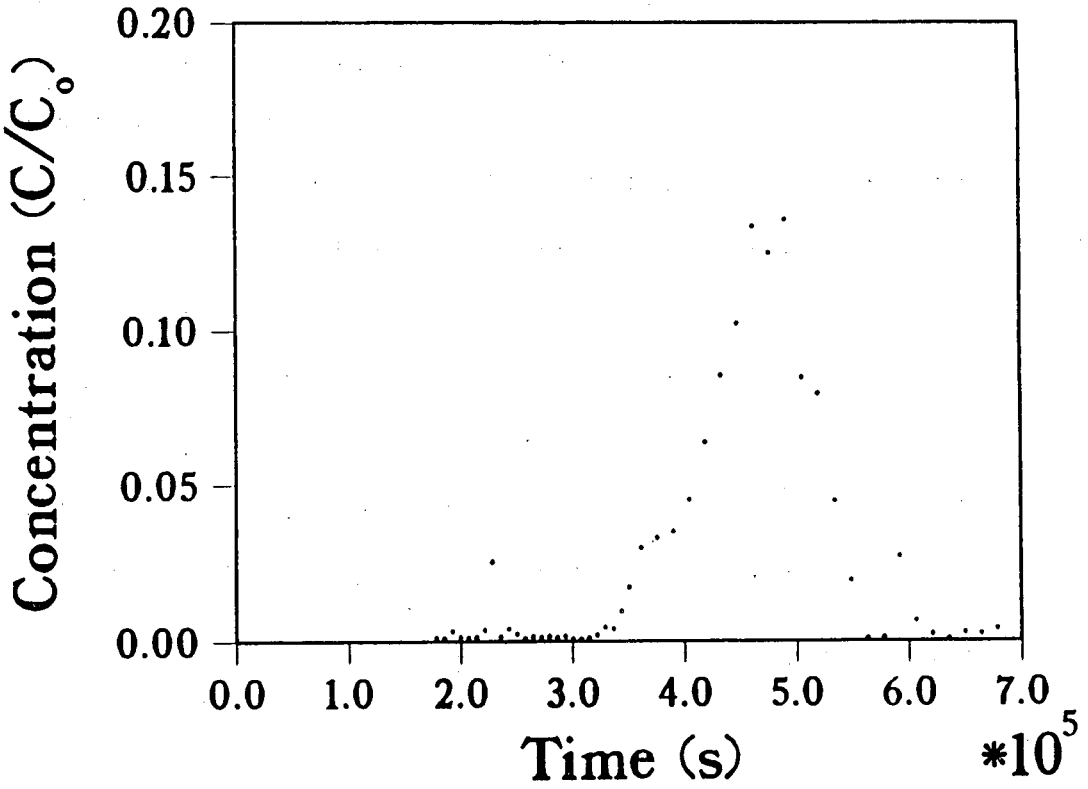


Figure 4-18a,b. Selenate and nitrate breakthrough curves for monitoring well 8.

Selenium and nitrate (NO_3^-) returns from observation wells 1, 2, 3, 4, 5, 7, and 8 are shown in Figures 4-12a,b through 4.18a,b. Concentrations are normalized to the input concentration of 301 ppb, and 41.8 ppm, for selenium and nitrate, respectively. Peak concentrations reached approximately 15% of the input concentrations. The character of the breakthrough curves are similar to those observed for the fluorescein tracer. In general the number of peaks and arrival times are roughly comparable, showing a consistency between the two phases of the experiment. Note that the maximum concentration of selenate and nitrate exceeds maximum fluorescein concentrations because a nearly six hour input pulse was used for phase 2, in comparison to a 1 hour pulse for phase 1.

4.2.2. Analysis Method

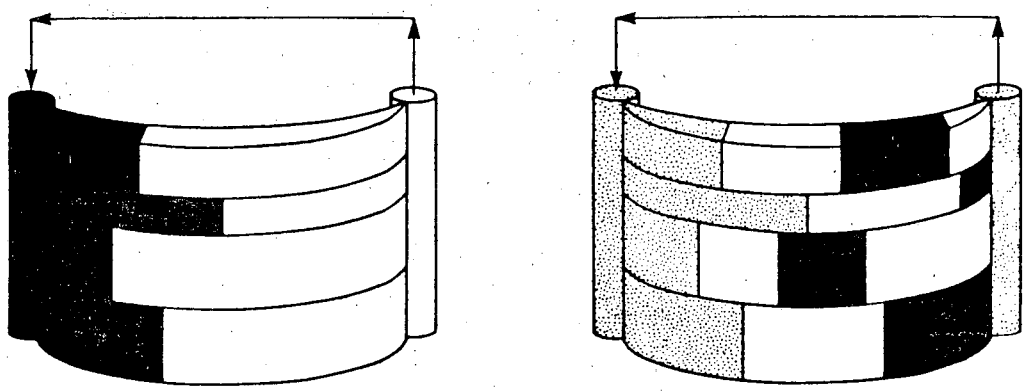
4.2.2.1. Conceptual Model

The tracer breakthrough curves (Figures 4-5 to 4-11, 4-12a,b to 4-18a,b) consist of a series of peaks, superimposed on one another. The shapes of these breakthrough curves are indicative of the presence of multiple flow paths, each with a different average fluid velocity. The breakthrough curves can be viewed as a signature of sediments through which the tracer traveled on its way to the monitoring borehole. The more permeable the pathway, the faster the fluid velocity. The objective of this analysis procedure is to gain information about the structure and transport properties of aquifer sediments by deciphering the tracer signature.

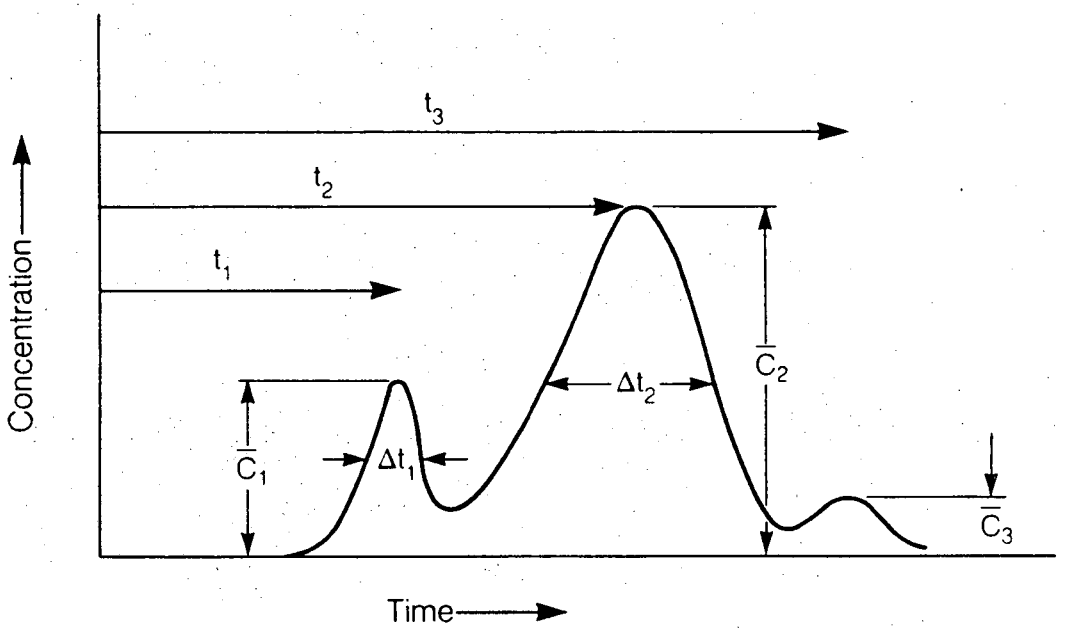
A simplified schematic showing how a two well tracer test in a purely stratified aquifer could result in tracer breakthrough curves like the ones observed during these experiments is illustrated in Figure 4-19a. While the tracer pulse is injected, the tracer migrates away from the borehole at a rate that is proportional to the permeability distribution, according to the following relationship (Russell and Prats, 1967).

$$\frac{v_i}{v} \propto \frac{k_i}{k} \tag{4.1}$$

where v_i is the velocity in layer i, v is the average velocity, k is the permeability of layer i and k is the average permeability. After the pulse of tracer is injected, the tracer continues to travel



XBL 8612-12780



XBL 8612-12783

Figure 4-19a,b. Schematic of a multiple flow path aquifer (4-19a) that would create the tracer breakthrough curve shown by the bottom curve.

towards the withdrawal well, at a velocity that is governed by Equation 4.1. Within each layer, the tracer pulse maintains its integrity, except for small amount of dispersion created by pore-level mixing (Molz et al., 1986). The tracer may also be retarded or transformed by interaction with the aquifer sediments. For a monitoring well located midway between injection and withdrawal wells, the pulses would pass by, in succession, creating the type of signature shown in Figure 4-19b.

4.2.2.2. Mathematical Model

The following assumptions were employed in developing the analysis procedure for interpreting these data.

- The fluids were completely mixed in the wellbore at all times during the tracer experiments. This assumption requires essentially instantaneous mixing of fluids that enter the borehole with the fluids in the remainder of the borehole.
- Flow into the wellbore occurs in well-defined discrete layers, with thickness h_n, velocity v_n, and concentration of $C_n(t)$. The number of flow paths, thickness of each flow path, and velocity are not restricted by the model.
- Flow out of the wellbore occurs in well defined discrete flow paths, each with the same thickness and flow velocity as the flow paths that enter the wellbore. Flow out of the wellbore occurs at the mixed concentration $\bar{C}(t)$ in the wellbore.
- The cross sectional area across which fluids enter and leave the wellbore is equal to the area that the wellbore projects on a plane normal to the direction of flow. Accordingly, the area for each flow path is equal to $2rh_n$; where r is the radius of the wellbore.
- The volume in which the fluids are mixed is equal to the sum of two volumes; the volume between the bottom of the packer and the bottom of the wellbore ($\pi r^2 h$) and the volume of the surface plumbing of the sampling unit.
- The length of the flow path is independent of the heterogeneity of the aquifer and is determined only by the geometry of the doublet flow system. For some highly complex

aquifers this assumption may appear to be overly restrictive. However, it does not seem unreasonable for the shallow aquifer underlying Kesterson because of the limited presence of very low permeability sediments amidst the higher permeability sands and the flat-lying nature of the sandy layers.

- Transverse dispersion is neglected.
- Within a flow path, flow of non-reactive solutes is governed by the one-dimensional advection-dispersion equation

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \tag{4.2}$$

where C is the tracer concentration, D_l is the longitudinal dispersion coefficient, v is the fluid velocity, t is time and x is the distance along the flow path.

- Flow of reactive solutes is governed by the one-dimensional advection-dispersion equation with first order-decay of the solutes given by

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \tag{4.3}$$

where λ is the first order decay coefficient and the other terms are defined as before.

The validity of the last two assumptions is addressed by Benson (1988).

With these assumptions, the mass balance for the tracer in the aquifer/well system is developed as follows:

$$\Delta M_t = \int_o^h \left[\frac{\partial}{\partial z} (M_{ti} - M_{to}) \right] dz \tag{4.4}$$

where ΔM_t is the change in the mass of the tracer in the borehole in the time interval Δt, M_{ti} is the time-averaged (over Δt) mass of tracer that flows into the wellbore in the interval dz, M_{to} is the time-averaged mass of tracer that flows out of the wellbore in the interval dz, and h is the thickness of the slotted interval. Assuming that the interval h is divided into a set of discrete layers, each with thickness h_n, Equation 4.4 can be written as

$$\Delta M_t = \sum_{n=1}^{\text{No. of layers}} M_{ti_n} - M_{to_n} \tag{4.5}$$

The mass of tracer entering from each layer can be written

$$M_{ti_n} = \rho_n v_n A_n C_n(t)\Delta t \tag{4.6}$$

where $A_n = h_n\ 2r_w$, v_n is the average fluid velocity in layer n, ρ_n is the fluid density, and $C_n(t)$ is the average concentration of tracer in layer n over the time period Δt. The mass of tracer that flows out of each layer is given by

$$M_{to_n} = \rho_n\ v_n\ A_n\ \bar{C}(t)\ \Delta t \tag{4.7}$$

where $\bar{C}(t)$ is the concentration of the tracer in the wellbore. Combining Equations 4.5 and 4.6, the mass balance can be written

$$\frac{\Delta M_t}{\Delta t} = 2r_w \sum_{n=1}^{\text{No. of layers}} \rho_n\ v_n h_n (C_n(t) - \bar{C}(t)) \tag{4.8}$$

The appropriate expression for the left hand side of the equation includes the mass of tracer in both the slotted interval of the well and in the volume of the sampling unit. In the most general form the mass of tracer in these two volumes is given by

$$M_t = \rho V_p C_p(t) + \rho V_w \bar{C}(t) \tag{4.9}$$

where the V_p and V_w are the volumes of the sampler plumbing and packed off interval of the wellbore, respectively, and $C_p(t)$ is the concentration of tracer in the plumbing volume of the sampling unit. The concentration of solute is nearly the same in the wellbore and surface plumbing, therefore

$$M_t = (V_w + V_p)\ \bar{C}(t)\rho \tag{4.10}$$

and

$$\frac{\Delta \bar{C}(t)}{\Delta t} = \frac{2r_w}{V_w + V_p} \sum_{n=1}^{\text{No. of layers}} v_n h_n (C_n(t) - \bar{C}(t)) \tag{4.11}$$

In order to evaluate $C_n(t)$, the one dimensional solution to the advective-dispersion (Eq. 4.2) was used. For a pulse input of duration t_o, the concentration at any point along the flow path can be evaluated from

$$C_n(x,t) = \frac{C_o}{2}\left[\operatorname{erfc}\left[\frac{x-vt}{2(D_l t)^{1/2}}\right] + e^{vx/D_l}\operatorname{erfc}\left[\frac{x+vt}{2(D_l t)^{1/2}}\right]\right]$$
$$-\frac{C_o}{2}\left[\operatorname{erfc}\left[\frac{x-v(t-t_o)}{2(D_l(t-t_o))^{1/2}}\right] + e^{vx/D_l}\operatorname{erfc}\left[\frac{x+v(t-t_o)}{2(D_l(t-t_o))^{1/2}}\right]\right] \tag{4.12}$$

for $t > t_o$ (Ogata and Banks, 1961).

For the case where a solute is removed from solution by a first order chemical reaction, the solution is given by

$$C(x,t) = \frac{C_o}{2} e^{\frac{(v-u)x}{2D_l}} \operatorname{erfc}\left[\frac{x-ut}{2(D_l t)^{1/2}}\right] + \frac{C_o}{2} e^{\frac{(v+u)x}{2D_l}} \operatorname{erfc}\left[\frac{x+ut}{2(D_l t)^{1/2}}\right]$$
$$- \frac{C_o}{2} e^{\frac{(v-u)x}{2D_l}} \operatorname{erfc}\left[\frac{x-u(t-t_o)}{2(D_l(t-t_o))^{1/2}}\right] - \frac{C_o}{2} e^{\frac{(v+u)x}{2D_l}} \operatorname{erfc}\left[\frac{(x+u(t-t_o))}{2(D_l(t-t_o))^{1/2}}\right] \quad (4.13)$$

where

$$u = v\left[1 + \frac{4\lambda D_l}{v^2}\right]^{1/2}$$

(van Genuchten and Alves, 1982).

A computer program was written to solve Equations 4.11, 4.12 and 4.13 for the purpose of calculating the tracer concentration at the monitoring wells. A complete description of the computer program is available in Benson (1988).

A history matching procedure was used to interpret the test data. Comparison between the fluorescein, selenate, and nitrate breakthrough curves was used as the basis for assessing the extent to which selenate and nitrate were being removed from solution by interaction with the sediments.

4.2.3. Tracer Data Analysis - Experiment No. 2

The results of phase 1 and phase 2 of the experiment are described together because consideration of each of the three solutes together provided better resolution of the structure of the sediments and degree to which denitrification or selenate immobilization occurred. When necessary, the following principles were applied to achieve an integrated analysis of the tracer breakthrough data from the three solutes.

- The structure of the flow paths was identical for each of the solutes (i.e., n and h_n were identical).

- The value of the longitudinal dispersivity was the same for each of the solutes.
- The flow velocity may be different for each of the solutes. In practice, fluorescein and selenate velocities were within ± 5% of each other. Nitrate was transported at essentially the same rate that selenate was. These small differences between the velocity of selenate and fluorescein can be attributed to retardation of the fluorescein ($R \approx 1.05$) or anion exclusion of selenate (Smart and Laidlaw, 1977; Gaspar, 1987; Goldhamer et al., 1986).
- A first order decay term was introduced when adjustment of these parameters, within the confines of the above-mentioned stipulations, did not result in a satisfactory match between the predicted and actual tracer breakthrough curves.

By using these principles it was nearly always possible to achieve an excellent match between the predicted and observed tracer breakthrough curves for fluorescein, selenate, and nitrate.

4.2.3.1. Tracer Recovery Calculations

The amount of tracer sampled by each well was evaluated by numerically integrating the concentration versus time curve. Values are listed in Table 4-2 for fluorescein, selenate, and nitrate. Expected values for fluorescein, selenate and nitrates are 3825 s, 20160 s, and 20160 s, respectively. The different values for fluorescein and selenate (nitrate) are due to the different duration of the tracer pulses for Phase 1 and Phase 2 of the experiment. The percentage of the ideal response is also listed for each of the solutes in Table 4-2. For fluorescein, values range from 73% to 125%, with an average value of 96%. For selenate, values range from 91% to 112%, with an average value of 98%. Nitrate values are significantly lower, with values ranging from 34 to 84%, and an average value of 64%.

A single explanation for the wide range of tracer recovery values for the fluorescein tracer is not available at this time. For some of the observation wells, such as well 3 and well 8, it can be explained by the presence of flow paths with velocities too slow for the tracer to have reached the monitoring wells, and is indicated by the non-zero tracer concentration at the end of the mon-

Table 4.2. Summary of the values for $1/C_o \int Cdt$ for fluorescein, selenate, and nitrate during Experiment No. 2.

Observation Well	Fluorescein		Selenate		Nitrate	
	$\frac{1}{C_o}\int_0^{600,000\,s} Cdt$ (s)	% Ideal Response	$\frac{1}{C_o}\int_0^{600,000\,s} Cdt$ (s)	% Ideal Response	$\frac{1}{C_o}\int_0^{600,000\,s} Cdt$ (s)	% Ideal Response
Well 1	3180	83%	22190	110%	14980	74%
Well 2	4207	110%	18790	93%	16940	84%
Well 3	2799	73%	16190	80%	11850	59%
Well 4	3769	99%	21840	108%	12560	62%
Well 5	4791	125%	22660	112%	6802	34%
Well 7	3444	99%	18830	93%	12580	62%
Well 8	3174	83%	18420	91%	15300	76%
Average		$\frac{1}{n}\sum = 96\%$		$\frac{1}{n}\sum = 98\%$		$\frac{1}{n}\sum = 64\%$

itoring period. Two of the wells, well 2 and well 5 have recovery values in excess of 100%. This could be the result of 3 factors, including: analytical errors; transverse mixing between flow paths; or incomplete mixing in the borehole. Without additional information, which one or combination of the factors is responsible for the field observations can not be resolved.

Selenate recovery ranged from 80% to 112%. Values of less than 100% recovery are indicative of removal of the solute from solution and/or slow flow paths. Resolution of these two possibilities is made possible by detailed history matching of the breakthrough curves. This is discussed in greater detail in the well-by-well analysis. Recovery values in excess of 100% indicate one or more of the following: analytical errors; remobilization of selenium already sequestered in these sediments; transverse mixing between the flow paths; and/or incomplete wellbore mixing.

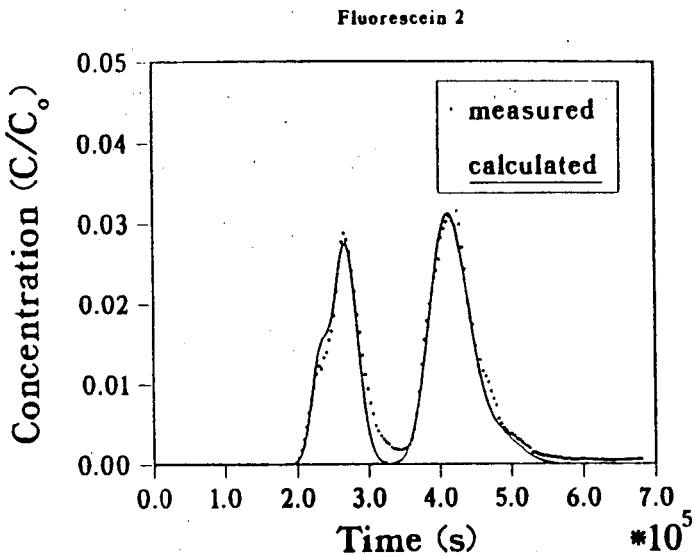
Nitrate recoveries, ranging from 34% to 84% indicate clearly that nitrate was being removed from solution during this experiment. On average, 32% of the nitrate was consumed during the 8 day monitoring period.

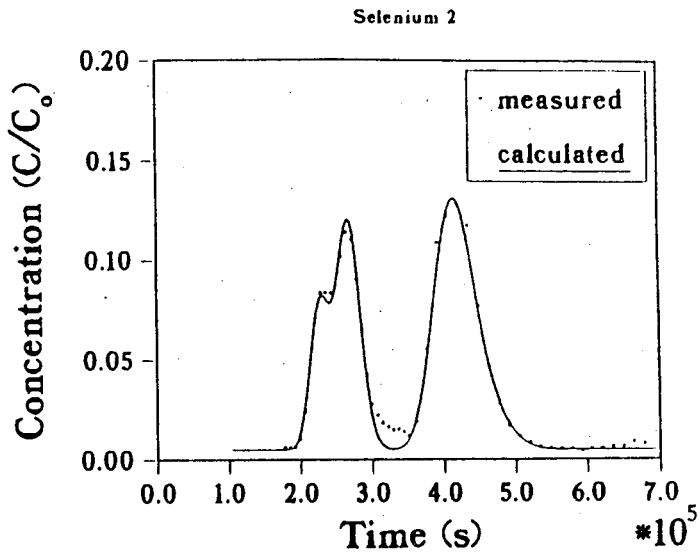
4.2.3.2. Analysis of Tracer Breakthrough Curves from Individual Wells

A detailed description of the analysis procedure is provided using the data from monitoring well 2 as an example. More complete discussion of the analysis of each of the wells is provided in Benson (1988).

Tracer breakthrough curves for fluorescein, selenate, and nitrate for well 2 are shown in Figures 4-6 and 4-13a,b. All three of the breakthrough curves have similar features, two large peaks, which upon closer examination reveal that they are each composed of the superposition of two flow paths.

The data from well 2 provide excellent examples of two common differences between the fluorescein and selenate breakthrough curves, including; different flow velocities and immobilization of selenate. The history match of the fluorescein breakthrough curve is shown by the solid line in Figure 4-20a. The parameters used to generate this match are listed in Table 4-3. If these





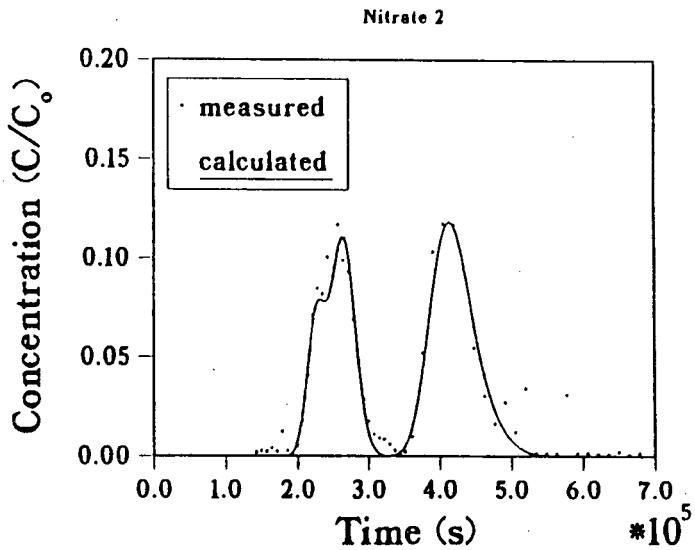


Figure 4-20a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 2.

Table 4.3. Summary of the data analyses of the tracer breakthrough curves from individual weeks during tracer Experiment No. 2.

Observation Well	Flow Path	Thickness h(m)	Longitudinal Dispersivity α_{L_n}(m)	Fluorescein Velocity v_n(m/s x 10^{-5})	Selenate		Nitrate	
					Velocity v_n(m/s x 10^{-5})	Decay Coefficient λ(s^{-1} x 10^6)	Velocity v_n(m/s x10^5)	Decay Coefficient λ(s^{-1} x 10^6)
1	1-1	0.3	0.035	6.19	6.39	-	6.34	0.75
1	1-2	0.8	0.03	5.68	6.26	-	6.26	0.75
1	1-3	0.22	0.04	4.52	5.03	-	5.03	0.75
1	1-4	0.20	0.035	3.87	4.45	-	4.45	0.75
2	2-1	0.12	0.03	7.87	8.39	-	8.39	-
2	2-2	0.31	0.03	6.83	7.09	0.75	7.15	1.0
2	2-3	0.51	0.03	4.55	4.46	0.6	4.64	0.75
2	2-4	0.46	0.03	4.29	4.36	0.6	4.36	0.75
2	2-5	0.12	0.03	3.77	3.97	0.6	3.97	0.75
3	3-1	0.06	0.035	8.05	8.92	-	8.92	0.4
3	3-2	0.04	0.035	6.89	8.92	-	8.92	0.4
3	3-3	0.18	0.08	5.34	5.95	2.75	5.95	2.75
3	3-4	0.10	0.03	3.19	3.19	0.5	3.19	0.5
3	3-5	0.24	0.025	2.81	3.19	0.5	3.19	0.5
3	3-6	0.20	0.05	2.47	2.76	-	2.76	0.5
3	3-7	0.70	0.2*	1.74	2.03	-	2.03	0.5
4	4-1	0.32	0.035	6.22	6.22	-	6.22	1.25
4	4-2	0.15	0.03	3.87	3.87	-	3.87	1.25
4	4-3	0.36	0.027	3.58	3.65	-	3.58	1.25
4	4-4	0.33	0.03	3.13	2.76	-	2.83	1.25
4	4-5	0.36	0.04	2.68	2.76	-	2.83	1.25
5	5-1	0.11	0.02	5.92	5.62	1.0	5.60	5.0
5	5-2	0.38	0.018	4.92	4.92	1.0	4.92	3.5
5	5-3	0.08	0.03	4.30	4.30	-	4.30	3.0
5	5-4	0.19	0.01	4.02	4.02	-	4.02	0.25
5	5-5	0.39	0.01	3.62	3.65	-	3.65	3.0
5	5-6	0.26	0.06	3.53	3.44	-	3.44	2.0
5	5-7	0.11	0.03	3.24	3.31	-	3.31	2.0
7	7-1	0.33	0.025	5.13	5.35	-	5.35	1.0
7	7-2	0.37	0.025	4.44	4.7	-	4.7	1.0
7	7-3	0.25	0.04	3.83	4.05	-	4.05	2.0
7	7-4	0.29	0.2*	3.21*	3.53	-	3.53	2.0*
7	7-5	0.28	0.2*	1.99*	2.19	-	2.19	2.0*
8	8-1	0.03	0.028	4.71	4.71	-	4.71	0.75
8	8-2	0.10	0.028	3.86	4.71	-	4.71	0.75
8	8-3	0.63	0.04	3.86	3.92	-	3.92	0.30
8	8-4	0.50	0.04	3.37	3.50	-	3.50	0.30
8	8-5	0.26	0.3*	2.12*	2.26	-	2.26	0.3

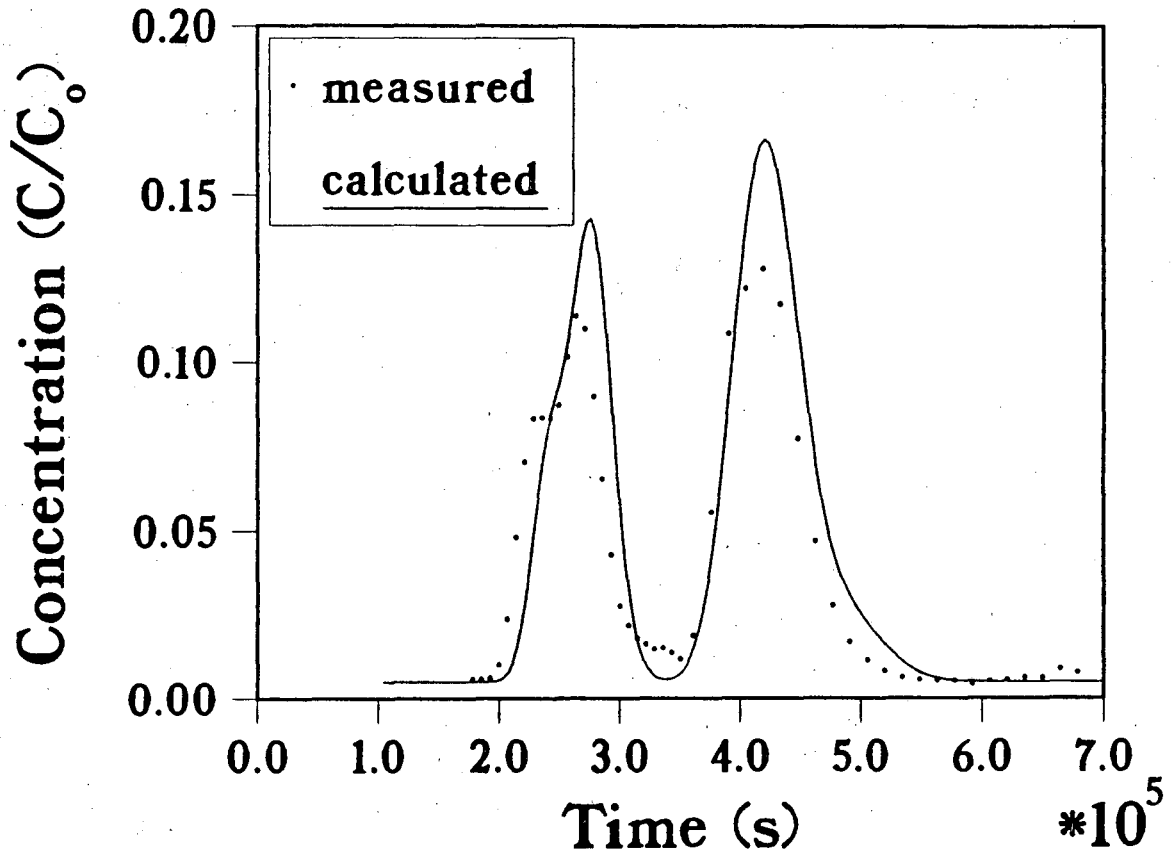


Figure 4-21. Comparison between the selenate breakthrough curve for well 2 and the theoretical curve generated using the transport parameters determined from the fluorescein analysis.

parameters are used to generate a breakthrough curve for selenate, during Phase 2 of the experiment, the curve shown by the solid line in Figure 4-21 is obtained. For comparison, Figure 4-21 also shows the measured breakthrough curve for selenate. As demonstrated, the predicted peaks are both too high and the arrival times are too slow. By adjusting the velocities of the individual flow paths to the values listed in Table 4-3, the match between the calculated and observed data shown in Figure 4-22 is obtained. Here the velocity of the flow paths matches the observed arrival times but, the tracer peaks are too high. To lower them to match the observed data, the first order decay coefficients (λ) listed on Table 4-3 had to be introduced. The final history match for selenate is shown in Figure 4-20b. The history match for nitrate is shown in Figure 4-20c.

A summary of the analyses from all of the wells is provided in Table 4-3. Figures showing the match between the calculated and observed concentration for all of the wells are provided in Appendix B.

4.2.4. Discussion - Tracer Experiment No. 2

The results of tracer Experiment No. 2 are reviewed to assess the information obtained about

- the structure and velocity distribution of the flowpaths,
- the longitudinal dispersivity values measured in the individual flow paths, and
- the first order decay constants for nitrate and selenate.

4.2.4.1. Structure, Velocity Distribution and Dispersivity Values

The results from this experiment confirm the structural complexity of these sediments that was previously identified from Experiment No. 1 (LBL Progress Report No. 3). Thirty eight individual flow paths were identified within the 7.62 m thick interval of the aquifer tested during this experiment. The thickness of the flow paths ranged from 0.03 to 0.7 m, with an average thickness of 0.28 m (s.d. = 0.19 m).

Flow velocities (normalized to the expected velocity for location of each monitoring well)

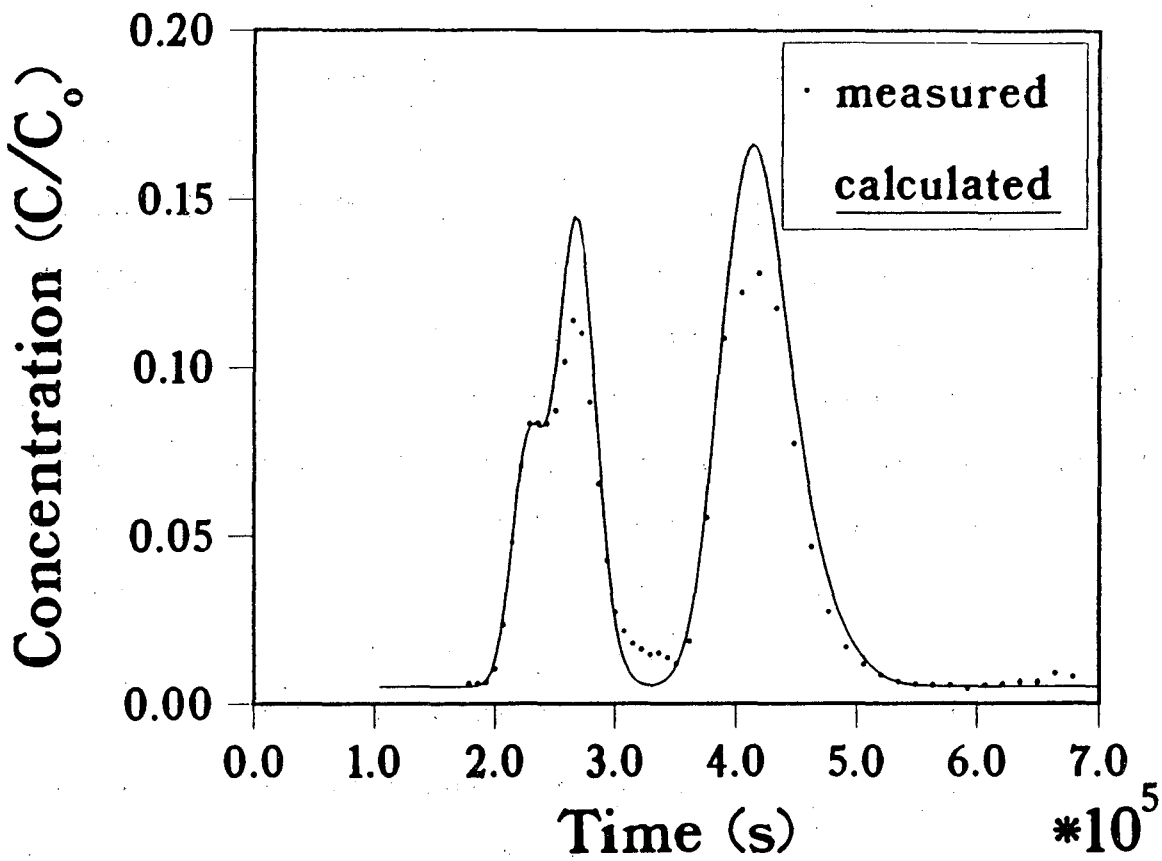


Figure 4-22. Comparison between the selenate breakthrough curve for well 2 and the theoretical breakthrough curve using the velocity distribution listed in Table 4-3. (Note: no decay term was included in these calculations.)

ranged from 0.26 to 1.19 times the expected value, indicating a wide range of flow velocities and the heterogeneity of the sediments. The average normalized flow velocity was 0.67 times the expected value (s.d.= 0.24).

Dispersivity values for individual flow paths ranged from 0.01 m to 0.08 m (note that the values listed in Table 4-3 that are asterisked are not included in this range). The average value was 0.032 m (s.d. = 0.01).

4.2.4.2. First Order Decay Constants for Nitrate

As indicated in Table 4-3, in all but one flow path, nitrate was removed from solution as it was transported from the injection well to the monitoring wells. Denitrification is caused by chemical and biochemical processes that reduce nitrate to NO_2 or N_2 (Freeze and Cherry, 1979). In an ideal system described by reversible thermodynamics, denitrification would be expected to occur in 25° C water with a pH of 7 at redox potentials of less than +250 mv (Freeze and Cherry, 1979). Redox potentials ranging from 126 to 266 mv (and pH of 6.5 to 6.7) have been measured at the experimental site (LBL Progress Report No. 2), indicating that the extensive denitrification observed during this experiment is not unexpected. Although denitrification has been observed extensively in near surface soils, little is known about the processes that control denitrification within an aquifer. In the limited literature on denitrification in aquifers, biological processes have been cited as the controlling factor (Edmunds, 1973; Gillham and Cherry, 1978).

As mentioned earlier, an average of 32% of the nitrate was not recovered from the monitoring wells during the eight day monitoring period. Detailed history matching of the breakthrough curves yielded first order decay constants for nitrate ranging from 0 to 5×10^{-6} s^{-1}. The average value for the 38 flow paths was 1.24×10^{-6} s^{-1} (s.d. = 0.9×10^{-6} s^{-1}). In general, there was a slight trend towards increasing decay coefficients, with greater depth below the ground surface. This is consistent with an oxidation-reduction controlled process where the redox potential decreases at greater depths in the aquifer. Field measured redox potentials in the aquifer under Kesterson Reservoir follow this general trend (LBL Progress Report No. 2).

The wide range of first order decay coefficients measured at all depths within the 7.62 m thick section of the aquifer suggest that denitrification rates are strongly dependent on the mineralogical and biological makeup of the sediments. This conclusion is supported further by the lack of correlation between the decay rates and any of the other transport parameters (Benson, 1988).

4.2.4.3. First Order Decay Constants for Selenate

Like nitrate, the speciation and mobility of selenium are strongly controlled by the redox potential (Geering et al., 1968; Sharma and Singh, 1983; LBL, 1986; and Elrashidi, et al., 1987). Selenate (Se^{+6}) is the thermodynamically stable form of selenium under strongly oxidizing conditions. Selenite (Se^{+4}) is the stable form under mildly oxidizing conditions. Both of these species are highly soluble but selenite is more strongly adsorbed than selenate. Selenite adsorption is influenced by the organic content of the soil, clay content, competing anions, and pH (Balistrieri and Chao, 1987; Singh et al, 1981; and Neal et al, 1987). Compared to selenite, selenate is weakly adsorbed at pH's in excess of 6 (Balistrieri and Chao, 1987). Under reducing conditions, elemental selenium (Se) and selenide (Se^{2-}), which are both extremely insoluble, are the stable forms of selenium (Geering et al, 1968; Elrashidi, 1987).

In the aquifer underlying Kesterson Reservoir, the redox measurements fall in the stability field of selenite and elemental selenium. Therefore, there are two potential immobilization mechanisms for removing selenate from solution. Selenate can be reduced to selenite and then adsorbed on the mineral grains or it can be transformed to the highly insoluble elemental selenium. The precise mechanisms by which the transformations take place remains uncertain. Possibilities include both biological and inorganic processes.

In an effort to elucidate the primary immobilization mechanism, both selenite and total selenium (essentially selenate plus selenite) concentrations were measured in the fluid samples collected from the monitoring wells. Without exception, selenite concentrations remained at background concentrations throughout the experiment ($\approx$ 1 ppb). However, the lack of elevated selenite concentrations does not in itself provide insight into which of the two primary

mechanisms was responsible for immobilizing selenium. If the primary mechanism for immobilization involves transformation of selenate to selenite, followed by adsorption of selenite, the lack of selenite in the fluid samples would only indicate that adsorption quickly follows the transformation. Balistrieri and Chao (1987) demonstrated that equilibrium conditions for selenite adsorption on goethite were reached in less than 2 hours. This reaction time is significantly faster than the time scale of the tracer experiment, suggesting that rapid adsorption of selenite may account for the lack of elevated selenite concentrations in the fluid samples. Alternatively, the lack of selenite may indicate that the transformation of selenate involves biological reduction to elemental selenium.

The single well selenium injection/withdrawal experiments conducted during FY87 showed that in the reducing native groundwater and in the reducing areas of the drainage water plume both selenate and selenite were quickly immobilized (LBL Annual Report, 1987). Groundwater quality data from Kesterson indicate that high concentrations of nitrate contribute to creating oxidizing conditions in isolated areas of the Reservoir (LBL Progress Report No. 5; LBL Progress Report No. 7) 1987). During this experiment, nitrate was introduced with selenate to allow us to measure the rate of selenium immobilization under the artificially high redox potentials created by the presense of nitrate.

As indicated by the results of the detailed history matching of the breakthrough curves listed in Table 4-3, clear evidence for transformation and immobilization of selenate was present only in 3 of the 8 monitoring wells. Within these wells, only 8 of 19 flowpaths indicated a significant degree of immobilization. First order decay constants for these flow paths ranged from 0.5×10^{-6} to 2.75×10^{-6} s^{-1}.

One of the objectives of this experiment was to determine the correlation between selenate and nitrate decay rates. Figure 4-23 shows the decay rate for nitrate plotted as a function of the selenate decay rate, measured from individual flow paths. Two general observations can be made from this graph. First, the decay constants for selenate never exceeded the decay constants for nitrate (as is indicated by the data points that fall on or above the solid line shown in Figure 4-

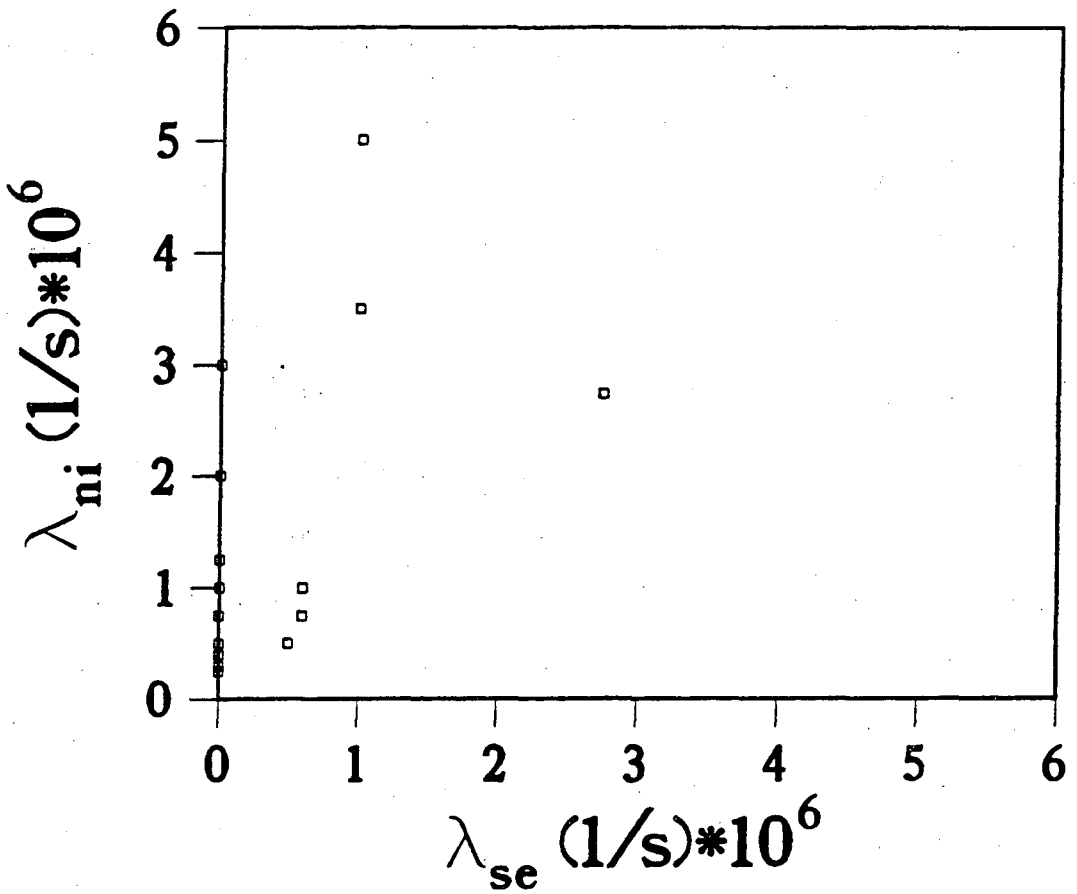


Figure 4-23. Comparison between nitrate and selenate first-order decay coefficients for the individual flow paths identified from these tracer experiments.

23). Second, when the decay constant for nitrate was greater than $3 \times 10^{-6}\ s^{-1}$, selenate decay constants were greater than zero. Due to the limited extent of selenate immobilization that was observed during this experiment, it is difficult to draw additional conclusions regarding correlations between the decay constants for nitrate and selenate in this environment. Nevertheless, it is clear that the presence of nitrate inhibits selenium immobilization. This is particularly evident when the results of the single well tracer experiments are compared to this experiment. A decay constant of approximately $5 \times 10^{-6}\ s^{-1}$ was measured during the single well injection/withdrawal experiment conducted at this location. This is about 2 times larger than the fastest rate observed for selenate during this experiment. This large difference, along with the majority of observations indicating a complete lack of immobilization, strongly support the conclusion that the presence of nitrate strongly inhibits transformation and immobilization of selenate in the shallow aquifer.

4.3. GEOPHYSICAL INVESTIGATIONS FOR PLUME MONITORING

A reconnaissance ground conductivity survey was conducted in October, 1987 in an attempt to locate the plume of saline drainage water that seeped from the Reservoir into the underlying shallow aquifer. The survey was conducted on the Freitas Ranch property, adjacent to Kesterson Ponds 1, 2, and 5, where lateral migration of the plume had been anticipated but no groundwater samples have been collected (LBL Progress Report No. 2). The results of this survey have been described in detail by Goldstein et al (1988a,b). Only a brief summary of the results of this investigation will be provided here.

4.3.1. Geophysical Methods

A location map showing the survey lines is provided in Figure 4-24. The purposes of the survey were to determine the background electrical conductivity of the near-surface soils and to identify anomalies that could be attributed to migration of the drainage water plume. Two instruments were used to conduct the survey, the Geonics EM31 and the EM34-3. Both of these instruments consist of a transmitter that produces a time-varying magnetic field and a receiver

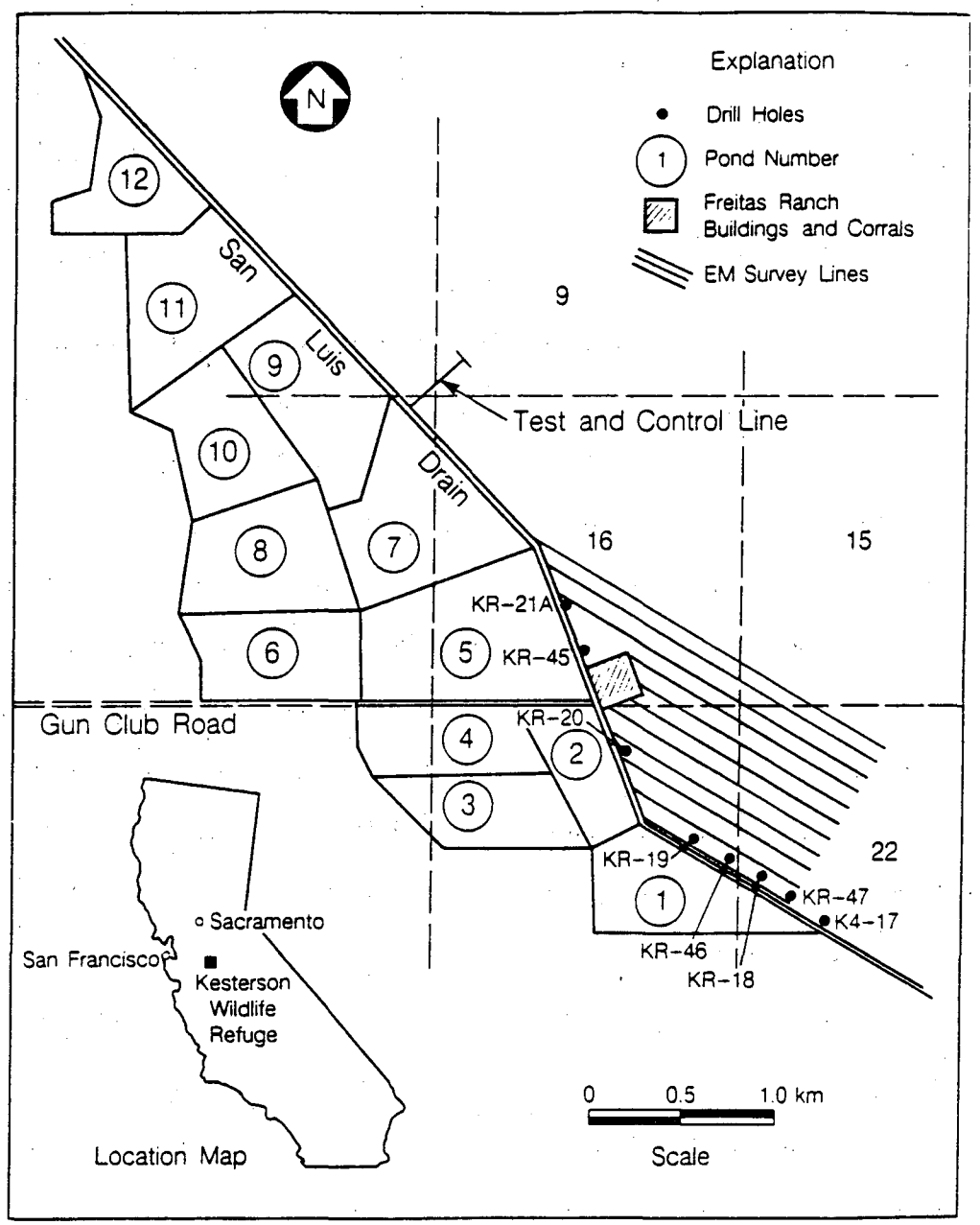


Figure 4-24. Location map of the area investigated during the 1987 geophysical survey.

that detects the signal from the transmitter after it has traveled through the ground. The spacing between the transmitter and receiver controls the depth of investigation for these measurements. Three different spacings were used, to achieve depths of investigation of 7, 15, and 30 m. Based on the water quality data obtained under the Reservoir, this range of depths should be adequate to detect the presence of the drainage water plume.

4.3.2 Results

Background soil conductivities are in the range 150 mS/m everywhere in the survey area. Similar values have been measured in the Mendota area by Hanson and Grismer (1987). Several individual anomalies of 300 to 400 mS/m were mapped within the survey area. The conductivity anomalies can be grouped into two categories, shallow anomalies that are not attributed to migration of the drainage water plume and deeper anomalies that are attributed to migration of the plume. Deeper anomalies were indicated when elevated conductivities were measured at all three depths of investigation. Shallow conductivity anomalies are attributed to salinization of the near surface soils due to evaporative accumulation of salts in shallow depressions. There is no indication that these shallow salinization features are related to operation of Kesterson Reservoir. However, in the region immediately adjacent to The Reservoir, we expect that the artificially elevated water table created by flooding the ponds would contribute to an accelerated rate of evapotranspiration accumulation of salts. A map showing the location of these anomalies is provided in Figure 4-25.

As shown in Figure 4-25, there is an elongated region adjacent to the Reservoir where the ground conductivity measurements indicate the presence of a deep conductivity anomaly. The leading edge of this conductivity anomaly (defined as the point where conductivity measurements deviate from the background levels) appears to extend approximately 350 m from the edge of the Reservoir. The lateral extent of the deep conductivity is consistent with the predicted extent of the drainage water plume (LBL Progress Report 3, 1986). In the absence of water quality data from this area it is not possible to determine conclusively the extent to which the drainage water plume has migrated. However, the ground conductivity measurements indicate

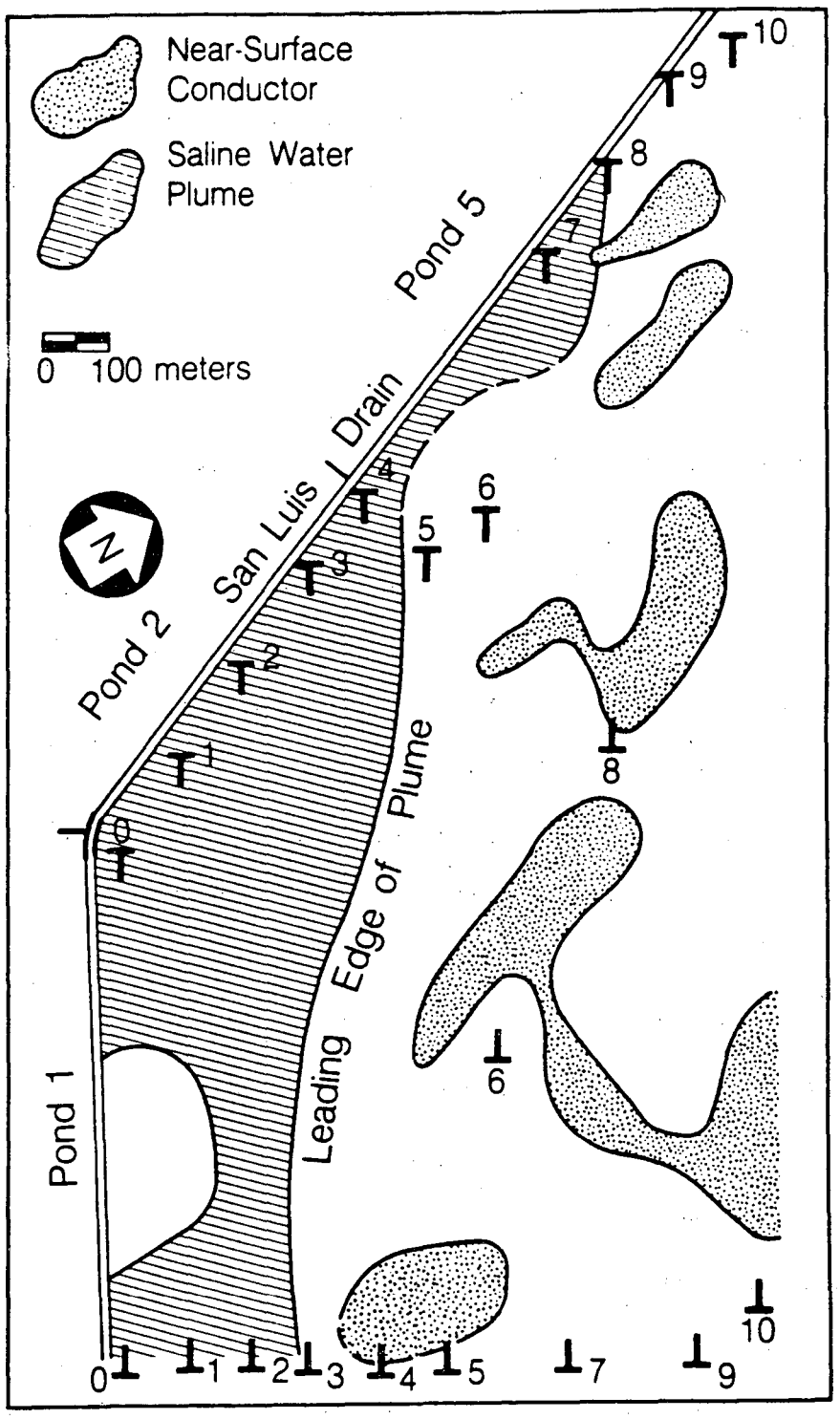


Figure 4.25. Interpretive map showing the inferred locations of the drainage water plume and the areas of nearsurface salinization.

that the maximum probable distance that the drainage water plume has migrated is 350 m from the edge of the Reservoir.

The ground conductivity survey is being repeated during October of 1988 in an attempt to map migration of the drainage water plume and to detect changes in the conductivity of the near-surface soils.

4.4. POND 1 REFLOODING EXPERIMENT

In the summer of 1986 we began an experiment designed to evaluate the potential for creating unacceptably high concentrations of selenium in the groundwater when a dry pond was reflooded. This experiment is now complete and several reports provide detailed descriptions of the experiment, the analysis method used to interpret the data, and the results of this analysis (Long, 1988; Long et al, 1988a,b). This experiment has also been described in detail in LBL Progress Reports 4 through 8, and the 1987 Annual Report. A brief summary of the major findings of this experiment are listed below.

- Prior to reflooding Pond 1, selenium concentrations in vadose zone soil water ranged from 1000's of parts-per-billion in the top 0.3 m down to 10's of parts-per-billion at a depth of 1.2 m.
- Several months after flooding the Pond, the total quantity of soluble selenium in the top 1.2 m of soil had dropped to an average value of less than 15% of the initial post-flooding inventory.
- *In situ* redox measurements obtained during the 1987-1988 phase of the reflooding experiment showed that reducing conditions were established within several days to several months after flooding.
- Chloride concentrations in the pore water changed slowly, indicating that rapid seepage could not account for the observed decline in the concentration of soluble selenium. Detailed advective-dispersive modeling of the migration of chloride indicated that the mean seepage velocity (pore velocity) was 1.13 m/year (coefficient of variation ≈

300%).

- When the pond was allowed to dry out the concentrations of soluble selenium increased to pre-flooding values within weeks after unsaturated conditions were established.
- Consideration of the facts indicates that, following flooding, soluble selenium is quickly transformed to insoluble or readily adsorbed species and immobilized in the soil profile. Mass balance calculations indicate that between 60 to 80% of the initial inventory was immobilized in the top 1.2 m of soil in the first month after flooding. Over the following months the immobilization rate decreased but, overall, between 66 and 100% of the soluble inventory was immobilized within 7 months.
- The above conclusion is supported by the lack of widespread elevated levels of selenium in groundwater monitoring wells in and around Pond 1.

5. SELENIUM CHEMISTRY

5.1. REDUCED SULFUR COMPOUNDS AND THE SOIL CHEMISTRY OF SELENIUM

It is demonstrated that zero-valent selenium becomes soluble under strongly reducing conditions by reacting with hydrogen sulfide, and this process explains downward migration of selenium below portions of Pond 2. Organic sulfur compounds also increase the solubility of selenium, and this reaction is an important link in the microbial cycling of selenium in soil. Adding organic sulfur compounds to soil strongly increases the rate of selenium volatilization. The solubility of selenium with organic sulfur compounds depends strongly on pH, and acid conditions block the reaction, decreasing the solubility and biological availability of selenium.

Several methods for determining total selenium in sediments and biological materials have been tested and compared. X-ray fluorescence is the preferred analytical method for samples containing greater than 3 ppm selenium. If atomic absorption spectroscopy is used, magnesium nitrate decomposition is very convenient and precise, although it under estimates the true concentration with certain sample matrices. Sodium peroxide decomposition is preferred for sediment samples. None of these methods involve the extremely hazardous reagents perchloric acid or hydrofluoric acid.

5.1.1 Introduction

In the absence of nitrate and oxygen, selenate and selenite are quickly removed from porewater by microbial reactions and selenite adsorption. These processes account for the absence of selenium from the groundwater underneath Kesterson Reservoir. In the past, very strongly reducing conditions existed underneath thick deposits of peat or algal ooze in permanently wet terrains. In some historically wet areas of Kesterson Reservoir with thick organic deposits and

strongly reducing conditions - notably in the interior of Pond 2 - penetration of substantial amounts of selenium up to two feet deep has been observed (see Figure 5-1, note that spatial variability precludes quantitative assessment of the extent of downward migration). These concentration profiles strongly suggest that selenium regains at least limited mobility under strongly reducing conditions.

Above pH 7 elemental sulfur will react with H_2S to form polysulfide anions; e.g.:

$$S_8(s) + 2\ HS^- + 2\ OH^- \rightarrow 2\ S_5^=(aq) + 2\ H_2O \qquad (1)$$

This reaction is used in the commercial production of polysulfide compounds, and the presence of polysulfides in mildly alkaline, sulfidic pore waters in nature has been convincingly documented (Boulegue and Michard, 1979). Because selenium is very similar to sulfur in its chemistry, an analogous reaction of selenium is to be expected:

$$Se_n + HS^- + OH^- \rightarrow Se_{n-1} + SeS^= + H_2O \qquad (2)$$

In fact, elemental selenium readily dissolves in a solution of sodium sulfide to form a dark red solution. This reaction is routinely used in the determination of Se^0, and it increases the solubility and mobility of Se^0 in nature as well. In sulfidic waters in nature the dominant species of dissolved selenium will probably be selenium substituted polysulfide anions; that is, $S_mSeS_n^=$ where m+n+1 = 2 to 6.

The symbol Se^0 is used to represent zero-valent selenium, a category which includes elemental selenium but also other compounds where a formally zero-valent selenium atom is bonded to one or more selenium or sulfur atoms; e.g. SeS_2, $(C_6H_5Se)_2$ or aminoacid dimers bridged by the group -SSeS- (Ganther, 1968). In analytical work, Se^0 is operationally defined as selenium which is preferentially extracted by thiophyllic reagents; e.g. Na_2S, NaCN, Na_2SO_3 all of which dissolve elemental sulfur as well (Davis, 1968, Weres and Tsao, 1983).

This laboratory has extensive experience with H_2S and polysulfides (Weres, et al., 1985) and the chemistry of polysulfides and related compounds has been reviewed elsewhere (Weres and Tsao, 1983). Polysulfide anions are intensely colored, and even dilute solutions are bright

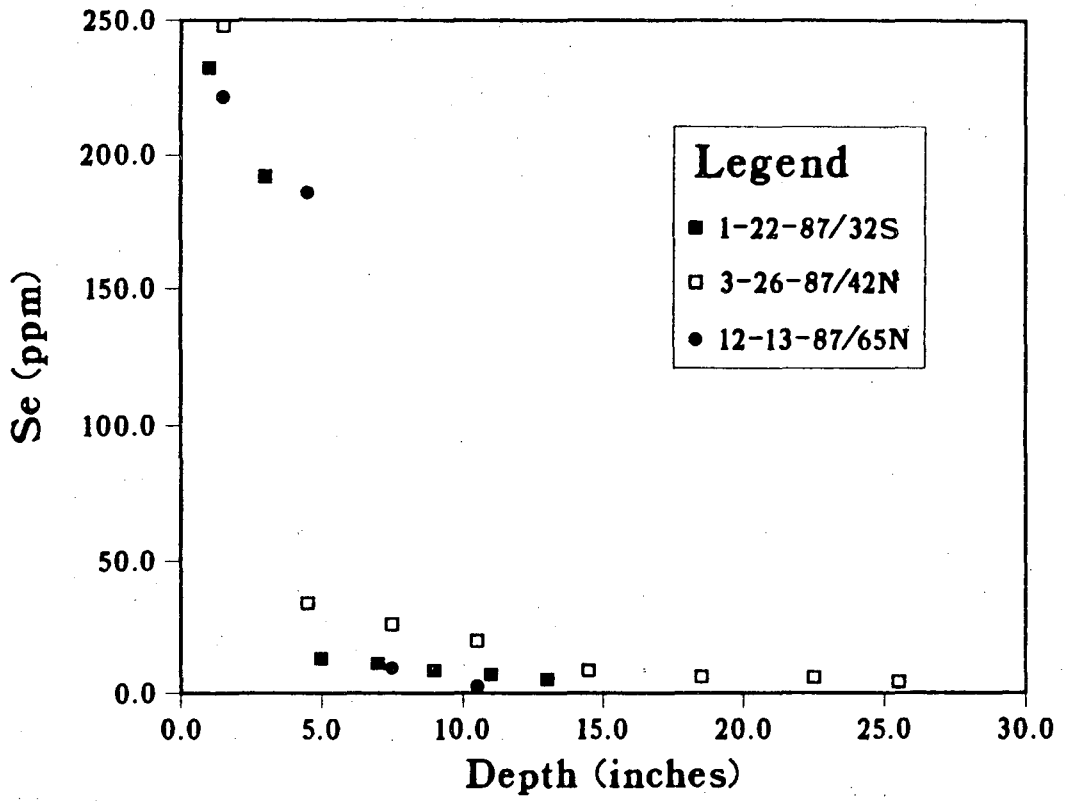


Figure 5-1. Selenium profiles in Kesterson Reservoir Pond 2. Dry weight selenium in soil (ppm) vs. depth in inches. The superficial material is peat of relatively low density but very high selenium content.

yellow. Acidifying the solution decomposes the polysulfides releasing H_2S and precipitating colloidal sulfur:

$$S_n^{=} + 2\,H^+ \rightarrow H_2S + S_{n-1}^0(\text{ppt}) \qquad (3)$$

The acidified solution loses most of its yellow color, and develops a bluish white haze of colloidal sulfur which may be removed by filtering the solution through a 0.22 or 0.45 μm filter. This reaction allows polysulfide-bound selenium to be easily estimated as described below.

While H_2S and polysulfides are the most abundant reduced sulfur compounds in sulfidic water, organic sulfur compounds may also be present. A variety of thiols, including cysteine, glutathione, mercaptoacetic acid and both isomers of mercaptopropionic acid have recently been identified in water extracted from mildly sulfidic ocean bottom sediments (Shea and MacCrehan, 1988). Thiols possess the weakly acidic -HS group, which will react with Se^0 as does H_2S, forming a selenium containing organic anion; in the case of 3-mercaptopropionate ion:

$$HSCH_2CH_2COO^- + Se_n + OH^- \rightarrow {}^-SeSCH_2CH_2COO^- + H_2O + Se_{n-1} \qquad (4)$$

Because thiols that contain oxygen or nitrogen will be less susceptible to oxidation than HS^-, they may exist and influence the chemistry of selenium over a wider range of conditions.

Selenium associated with aminoacids and peptides has been reported in ocean water (Cutter, 1982). The tripeptide glutathione (glutamic acid, cysteine, glycine) is of particular interest. Glutathione is an important cofactor in the metabolism of selenium (Garberg and Hogberg, 1986). Like other thiols, glutathione reacts with selenite to form a dimer bridged by the selenotrisulfide group -SSeS- (Ganther, 1968). This reaction is believed to be the first step in biochemical assimilation of selenite ion (Garberg and Hogberg, 1986).

5.1.2. Experimental

Many of the experiments described in this section involve air sensitive reagents and solutions. Air sensitive solutions of Na_2S, Na_2SO_3, organic sulfur compounds, H_2S and Na_2S_4 were prepared just before starting the experiment. Procedures with air sensitive samples were executed as quickly as possible.

5.1.2.1. Total dissolved selenium - Method I

If presence of organic selenium compounds is expected, the sample is digested with an excess of H_2O_2 to convert all of the selenium to selenate.

To 25 ml water sample add 1 ml 1N NaOH and 1 ml 30% H_2O_2, heat to decompose H_2O_2 (that is, until fine oxygen bubbles are gone), add 1 ml 1.5 N HCl, restore volume to 25 ml, combine 5 ml of this solution with 5 ml 12 N HCl, heat in a tighly sealed container at 100°C for 20 minutes, analyze by hydride generator AAS.

5.1.2.2. Total dissolved selenium - Method II

Polysulfides and polyselenides are relatively resistant to oxidation. In this method, the sodium sulfide opens up any polysulfide or polyselenide species that may be present, ensuring complete oxidation of selenium by H_2O_2.

Prepare Na_2S/NaOH reagent immediately before use: 1M Na_2S plus 1M NaOH. Filter 3 ml of sample into a screw cap culture tube, add 1 ml Na_2S/NaOH reagent, then add 1 ml 30% H_2O_2, heat at 100°C to decompose H_2O_2, add 5 ml 12N HCl, heat 20 minutes at 100°, then analyze using hydride generator AAS.

5.1.2.3. Total dissolved selenium - Method III

As in Method II, but use 1 N NaOH in place of the Na_2S/NaOH reagent. Method III is a streamlined version of Method I.

5.1.2.4. Solubility of selenium compounds in hydrogen sulfide solutions.

A brine was prepared with major ion composition similar to San Luis Drain water but without selenium or nitrate. A portion of the brine was deaerated and the right amounts of Na_2S solution and HCl were added without exposure to air to produce a solution containing 100 ppm total sulfide with pH 7.4. The selenium compounds tested were elemental Se, SeS_2, and diphenyldiselenide $(C_6H_5Se)_2$. About 15 mg of the given compound was placed in a 15 ml plastic centrifuge tube, the tube was filled with the sulfide solution, then capped and alternatively

shaken and sonicated for about 20 minutes. Then the tube was centrifuged and opened. The liquid phase was carefully removed and filtered through a 0.22 μm filter, then analyzed for total Se using Method II above. In each case a parallel test was run using the brine without H_2S to determine the extent of contamination by solid particles of selenium which may be carried over.

5.1.2.5. Estimation of polysulfide-bound selenium in sulfidic pore water

Acidifying a sample of sulfidic water will decompose polysulfides producing filterable colloidal sulfur particles which will contain any polysulfide-bound selenium initially present.

Black, very sulfidic peat and pond-bottom muck were collected at Kesterson Reservoir and stored in air-tight containers. The oxidized superficial material was removed and only water-saturated material was taken for analysis, as contact with air will precipitate polysulfides by oxidizing them to sulfur. About 100 g of slurry with associated water was scooped into each of two 8 oz. centrifuge bottles, and centrifuged for about 10 minutes to press sulfidic water out of the slurry. Prolonged centrifugation was avoided to avoid excessive contact with air. The bottles were removed from the centrifuge, and the water decanted and immediately filtered through paper to remove coarse particles. Then about 50 ml of water was filtered through 0.22 μm membrane filters, producing a clear, yellow, foul smelling water sample.

An aliquot was immediately removed for determination of total selenium using Method II above. The remaining water was acidified by adding 0.2 ml 6N HCl, stripped with N_2 for a few minutes, then filtered again (0.22 μm) and analyzed for total Se by Method II. The difference between the two values approximates the initial concentration of polysulfide bound selenium initially present in the water.

To confirm that the selenium removed by the second filtration is associated with colloidal sulfur particles, the filter was extracted by forcing through it 10 ml of freshly prepared 0.5 M Na_2SO_3 solution with pH adjusted to about 7.7. Sulfite is also a thiophyllic reagent capable of dissolving colloidal sulfur and Se^0. Selenium in the sulfite extract was determined by Method II.

5.1.2.6. Solubility of selenium in the presence of sulfur compounds

Solubility values were determined by reacting elemental Se with a buffered solution of the given compound for four days, and determining selenium dissolved in the resulting solution. Test solutions were prepared by adding 2.5 mM sulfur compound to a deaerated buffered brine containing 0.04 M Na_2SO_4, 0.03 M NaCl, 5 mM citric acid, 5 mM disodium phosphate, and 5 mM boric acid. The initial pH was near 3.5, and pH was progressively increased by adding NaOH to the solution while maintaining it anoxic by continually bubbling nitrogen through it. 5 ml aliquots were removed as needed for tests at different pH values, and pipetted into 10 ml glass ampoules. A small amount of powdered glass was added to the ampuole to nucleate smooth gas release, the ampoule was briefly evacuated, about 20 mg of gray Se (325 mesh) was added, vacuum was reapplied, and the ampoule sealed using a torch while still under vacuum.

The ampoules were placed upon a shaker table. After four days of shaking the ampoules were removed and opened, the liquid was carefully removed using a plastic syringe and blunted 17.5 gauge needle, and selenium particles were removed by filtering it through a 0.45 μm syringe filter. The filtered solution was immediately analyzed for total selenium using Method III above.

5.1.2.7. Speciation of selenium in sulfidic water

The method described for estimating polysulfidic selenium was later modified to allow two classes of organic selenium compounds to be estimated as well. Samples were obtained by centrifuging sulfidic materials collected at Kesterson Reservoir and filtering the supernatant through 0.45 μm membrane filters just prior to use. Reference solutions of selenium/sulfur compounds were prepared by reacting a deaerated 4 mM solution of the given sulfur compound in water with powdered Se in ampoules for three days or longer. The following sulfur compounds were used to prepare the standards: reduced glutathione, 3-mercaptopropionic acid, and sodium tetrasulfide (Na_2S_4). Solutions of the two organic compounds were adjusted to near pH 8.1, but the polysulfide solution was used at its initial pH (near 10). Immediately before use, the ampoule was opened, part of the solution was extracted and filtered to remove selenium particles (0.45 μm) and then diluted 2 ml into 50 of deaerated Na_2SO_4/NaCl brine (0.04M/0.03M). This dilute

solution was then analyzed in parallel with the actual sulfidic water samples.

Sodium tetrasulfide was prepared immediately before use by dissolving 0.96 g of S_8 in 50 ml of 0.2 M Na_2S in a 50 ml screw-cap culture tube at 100°C. The reaction typically requires one hour and is helped by occasionally shaking or sonicating the tube. The resulting solution nominally contained 0.2 M Na_2S_4. It was cooled to room temperature and filtered 0.45 μm before use.

The experiment was performed four times with minor variations. In the final run, three preparations were made from each sample:

- The sample was analyzed for total Se using Method II.
- 2.5 ml of 0.2M Na_2S_4 was added to 10 ml sample, allowed to stand for about 2 minutes, then acidified by adding 1 ml 6N HCl. After about two minutes of blowing N_2 through it to remove H_2S, the sample was filtered (0.45 μm), and filtered a second time a few minutes later to remove the secondary colloidal sulfur haze which sometimes formed. The final filtrate was analyzed for total selenium by Method II.
- 0.5 ml of 6N HCl was added to approximately 30 ml of sample remaining from previous tests. The sample was allowed to stand for 1 to 3 minutes, then filtered (0.45 μm) and analyzed for total Se by Method II.

Increasing reaction time has little effect on the amount of Se precipitated; nor does heating the sample mixed with Na_2S_4 (B) have much effect.

5.1.2.8. Effect of sulfur compounds upon volatilization of Se

Starting material was surface soil collected in May 1987 from the waste pile at the 0.5 ft scrape plot near the SW corner of Pond 11 in Kesterson Reservoir. The soil was crushed and sieved 30 mesh. Twelve tests were run simultaneously in open 250 ml wide-mouth plastic bottles in an open box at room temperature. In each test, 25 g of soil was wetted with 5 ml of a solution of glucose plus $NaNO_3$ in water (5% plus 0.75%; C/N = 16). In tests 11, 15, 16 and 18, 200 ppm penicillin-G and 200 ppm streptomycin added to glucose/nitrate solution. This combination of

antibiotics controls both gram positive and negative bacteria, and the concentrations were respectively triple and double those typically used in biomedical research. Test compounds were added as 2% solution in water adjusted to pH 7.5 - 8.0, 1 ml at start, and 1 ml seven times during the experiment, plus distilled water as needed to replace water lost by evaporation. Glucose/nitrate solution was used in place of test solution in control experiments.

After five weeks, soluble selenium was extracted with Na_2SO_4/NaCl brine (0.04 M/0.03 M), the residue was dried to constant weight, crushed, and analyzed for total Se and Se^0. Soluble selenium in the Na_2SO_4/NaCl brine extract was determined using Method I above. Total selenium values were determined by X-ray fluorescence, corrected for soluble selenium extracted; statistical uncertainty in individual total Se values was approximately ±0.6 ppm.

5.1.2.9. Analytical method for Se^0

Equipment and supplies. Full facilities for analyzing selenium in water using AAS with hydride generation. A fume hood. Pipettors and tips, 0.2 ml, 1 ml, and 5 ml. Screw-capped 50 ml centrifuge tubes. Centrifuge with appropriate rotor. Spatula. Laboratory balance. Shaker table with attachments needed to hold centrifuge tubes. 100 ml stopped cylinders. 100 ml beakers. Funnels. Filter paper. Screw-capped glass culture tubes. Hot-plate. Large beaker.

Reagents. Concentrated hydrogen peroxide (30%). 0.3 M Na_2S, prepared daily from $Na_2S{\cdot}9H_2O$. 1N NaOH. 6N HCl. Concentrated HCl (12N). 'Caustic brine C'', containing 0.16 M NaOH, 0.16 M NaCl, 0.14 M Na_2SO_4.

Procedure. Parallel extractions are performed, one using sodium sulfide, the other using caustic brine C. Sodium sulfide extracts Se^0, but Se^{+6}, Se^{+4}, and organic Se may interfere. The caustic brine matches the pH and ionic strength of the sodium sulfide reagent, and will extract Se^{+6}, Se^{+4}, and organic Se to the same extent, but it will not touch Se^0. Therefore, the difference between the two determinations corresponds to the amount of Se^0 present.

Caution. Na_2S is toxic and releases highly toxic H_2S if mixed with acid. All steps of the procedure involving the Na_2S reagent in open containers should be performed inside the fume

hood. Destroy unused sulfide reagent by adding an excess of c. H_2O_2, or by adding a soluble iron salt and bubbling air through it for several hours.

Weigh identical 0.200 g aliquots of dry, pulverized sediment into two labeled centrifuge tubes. Add 5 ml of Na_2S reagent to one tube, and 5 ml caustic C to the other tube. Cap tubes securely and shake 10 minutes. Put 0.2 ml 1N NaOH into each of two labeled beakers. Centrifuge and decant liquids into separate beakers. Add another 5 ml of the appropriate solution to each tube, resuspend sediment, centrifuge again, add supernatants to the beakers. While swirling, add 2 ml c. H_2O_2 to beaker with Na_2S extract. Immediately cool down the beaker by placing it in a container with cold tap water after first and second portion of H_2O_2. Similarly add 1 ml c. H_2O_2 to beaker with caustic brine extract.

Under the fume hood, add 1 ml 6N HCl to each beaker. Place funnels with filter paper in 25 ml cylinders. Pour liquids from beakers into the funnels. Rinse beakers into the funnels with a small amount of water. Rinse beakers under running tap water. After liquid has drained from funnels, rinse filter paper with a small amount of water. Remove funnels, make up total volume in each cylinder to 25 ml. Pour liquids back into the beakers. Add 5 ml of c. HCl to each of two labeled culture tubes. Pipette 5 ml of liquid from each beaker into the corresponding culture tube. Cap culture tubes loosely. Bring half of a large beaker-full of water to a boil on the hot plate. Place culture tubes in boiling water. Wait until characteristic bubbles from decomposition of H_2O_2 subside. Keep tubes in boiling water for additional 10 minutes. Remove tubes from water, allow to cool, tighten caps. Analyze for total selenium by AAS. The difference between the two readings will correspond to Se^0 in the sediment. One ppb difference corresponds to 1 ppm Se^0 in the sediment.

Explanation. The hydrogen peroxide oxidizes the extracted selenium to selenate and destroys excess sulfide. The small amount of NaOH added ensures that the solution will remain alkaline; otherwise some colloidal sulfur will be produced and may entrap part of the selenium. Less H_2O_2 suffices for the caustic brine extract which contains no sulfide. Acidifying the extract after oxidizing it serves to precipitate organic colloids, which are then removed by filtering the

extract. If no precipitate forms and the extract remains clear, the filtration step may be eliminated.

Because the result is calculated as the difference of two numbers, the effective Limit of Quantification (LOQ) will depend more on their relative value than on the theoretical LOQ for the separate readings, which is 1 ppm. Ten percent of the larger reading is a fair estimate of actual LOQ. When samples low in total selenium are to be analyzed (e.g. playa sediments) theoretical sensitivity may be increased by using 25 or 50 ml graduated cylinders, thereby reducing the dilution factor.

5.1.3. Results

The effect of hydrogen sulfide upon the solubility of selenium is illustrated in Table 5-1. Several compounds of Se^0 were contacted with a 3mM solution of H_2S at pH 7.4 for 20 minutes. Parallel experiments using brine without sulfide allowed the maximum interference by selenium particles carried-over to be estimated; it is small. Clearly, H_2S markedly enhances the solubility of Se^0; these values are low estimates because of the short reaction time.

Table 5-2 illustrates the effect of acidifying sulfidic water upon its selenium content. The water used in the experiment was centrifuged from Pond 2 peat which had been allowed to stand water-logged in a sealed jar for several weeks prior to the experiment. The original filtrate (a) was clear, bright yellow and had a sulfidic smell. The acidified filtrate had a bluish white haze. The refiltered acidified brine (b) was clear with a very faint yellow color. This procedure removed 114 ppb Se from the water, corresponding to 58% of that initially present. There was no visible discoloration of the filter membrane, suggesting that precipitation of humic acid is not a factor here. The selenium recovered from the filter by extracting with sodium sulfite corresponds to 96 ppb in the initial brine sample, or 84% of that removed from the brine by acid. A parallel analysis demonstrated that volatile compounds represented only 4 ppb of the selenium in the water. Four determinations on four separate water samples centrifuged from peat gave an average of 160 ppb Se precipitated by acid, corresponding to an average of 60% of the total dissolved selenium.

Table 5-1. Sulfide increases the solubility of selenium.

Solute pH	Apparent solubility (ppb Se)	
	Brine with NaSH 7.4	Brine
Se^0(black)	1391	89
SeS_2	1481	10
$(C_6H_5Se)_2$	3050	12

Table 5-2. Speciation of selenium in peat water.

Sample	Se (ppb)
(a) Raw filtrate	198
(b) Acidified and refiltered	84
(a) - (b) = polysulfidic Se	114
(c) Recovered for filter	96
(d) Volatile Se recovered	4

The solubility of selenium in the presence of sulfur compounds is illustrated in Figure 5-2. The three thiols (cysteine, 3-mercaptopropionic acid, and glutathione) dramatically increase the solubility of selenium, particularly above pH 7. Increasing reaction time with cysteine from 4 to 7 days had little effect, indicating that chemical equilibrium had been closely approached. At pH 9.1, the extent of reaction is 4-8%; that is, 4-8% of the sulfur compound has reacted with the excess of selenium. The pH dependence of the equilibrium is consistent with reaction (4); because the reaction requires hydroxide ion, increasing pH favors it. The solubility of selenium drops-off rapidly with decreasing pH. In the case of mercaptopropionic acid the curve flattens out below pH 6, as increasing protonation of the carboxylic group decreases the average negative charge of the molecule, favoring formation of the negatively charged $-SSe^-$ group. The effects of the aminoacids serine (the oxygen analog of cysteine) and methionine are practically indistinguishable from the control, i.e., buffered brine with no compounds added. While methionine is a sulfur compound, the sulfur atom is methylated, and there is no thiol group.

Polysulfidic selenium produced by dissolving the element in sodium tetrasulfide solution is quantitatively precipitated by acid (Table 5-3). Roughly half of the selenium dissolved in the glutathione solution is also precipitated by acid, but acid has no effect upon selenium dissolved by reaction with 3-mercaptopropionic acid. Adding a large excess of Na_2S_4 to the solution quantitatively converts the selenium from thiol-bound to polysulfidic. Practically all of the selenium dissolved by glutathione or 3-mercaptopropionic acid is precipitated by acid after reaction with Na_2S_4 solution. The small "B" value in this case probably represents a reagent blank.

These data suggest a simple analytical procedure to estimate three chemical classes of water soluble selenium under reducing conditions. The selenium precipitated by acid alone corresponds to polysulfidic Se plus some fraction of thiol-bound Se. The additional selenium precipitated by Na_2S_4 plus acid corresponds to the bulk of the thiol-bound Se. The selenium which cannot be precipitated either way corresponds to still other species, where the selenium is not associated with thiol groups.

Five samples of sulfidic and/or organic rich water squeezed from Kesterson sediments were

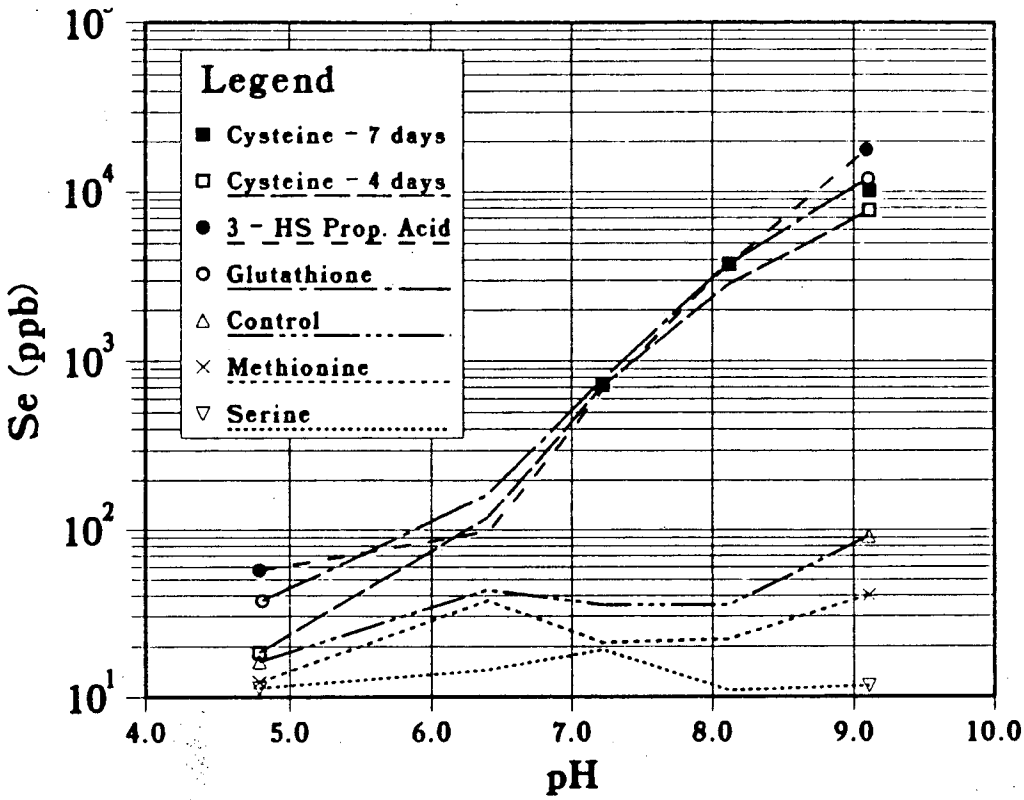


Figure 5-2. Solubility of selenium in the presence of sulfur compounds vs pH. Each solution consisted of deaerated Na_2SO_4/NaCl brine with 2.5mM sulfur compound and citrate/ phosphate buffer with pH adjusted to value desired. Solution deaerated and sealed with small amount of gray Se under vacuum in glass ampoule, and placed on shaker table. Total dissolved Se concentration determined after four days.

Table 5-3. Speciation of Se in Sulfidic Water

Sample	Day	A	B	C	A-C	C-B	%A-C ≈ Poly SSe	%C-B ≈ ppt OrgSe	%B non-pptSe
Na_2S_4 + Se	1	992	6	6	986	0	99	0	1
	2	591	24	5	586	–	99	–	4
Glutathione	1	174	5	81	93	76	53	44	3
	2	170	8	104	66	96	39	56	5
	3	202	8	76	126	68	62	34	4
3-HS Prop.Acid	2	183	9	190	–	181	–	99	5
	3	256	7	328	–	321	–	125	3
	4	135	6	147	–	141	–	104	4
Pond 5 muck	1	267	66	89	178	23	67	9	25
Pond 2 mud	3	218	86	102	116	16	53	7	39
	3	226	86	111	115	25	51	11	38
Peat slurry	3	183	117	126	57	9	31	5	64
	3	170	98	136	34	38	20	22	58
Oxid. P2 peat	4	162	117	158	4	41	2	25	72
	4	180	120	177	3	57	2	32	66
Oxid. P5 muck	4	176	72	181	–	109	–	62	41
	4	177	66	177	0	111	0	63	37

analyzed in this way. The "Pond 5 muck" and "Pond 2 mud" were strongly sulfidic materials easily maintained in that condition by prolonged storage in a water-logged state in a closed jar. In either case, polysulfidic selenium was the major dissolved species, followed by non-precipitable Se and a much smaller amount of thiol-bound Se. The "peat slurry" was less strongly reducing, having stood in a bottle for nearly a year, and the fraction of polysulfidic Se was smaller. The "oxidized P2 peat" had been stored in a partially saturated state for several weeks with limited air contact. In that sample, non-precipitable Se predominated, with a lesser amount of thiol-bound Se but practically no polysulfidic Se. Finally, "oxidized P5 muck" had been exposed to air to the point of changing color from black to grey-green. Here thiol-bound Se predominated, with a lesser amount of non-precipitable Se also present. This sample probably had the largest and most active population of microbes, aggressively decomposing the organic matter in the sediment. It most closely resembles an aerated peat soil. Note, however, that in the absence of H_2S, selenite and methane selenium acid may also be present and will also register as part of ''C-B'' together with thiol bound Se.

The volatilization of selenium from soil provides a convenient assay of the bioavailability of selenium (Table 5-4). In most cases slightly more selenium was volatilized with antibiotics added, but the difference was not statistically significant. This observation suggests that bacteria are not the organisms responsible for volatilization and, indeed, suppressing the growth of bacteria might enhance volatilization by favoring competing microorganisms. Results with and without antibiotics were combined in analyzing the data.

Results with serine or glutamic acid added were not significantly different from the control experiments. All four sulfur compounds dramatically increased the amount of selenium lost to the atmosphere, averaging 29% of the total inventory in just five weeks, or roughly four times more than in the control. While the percentage lost in control experiments is scarcely greater than the experimental uncertainty, the percentage lost with sulfur compounds added is much larger than the uncertainty, and so is the increase caused by adding sulfur compounds. The amount of Se^0 decreased by 26% in the control experiments, and 50% with sulfur compounds

Table 5-4. S-Compounds and volatilization of Se.

Experiment	Test	N Anal.	Tot.Se (ppm)	Average (ppm)	%Se gone	Soluble Se(ppm)	Se^0 (ppm)	Average (ppm)	%Se^0 gone
Start	-	3		**7.30**±0.35	-			**3.26**±0.34	-
Control	1	1	7.23				2.41		
	8	1	6.64				2.36		
	11	1	7.10				2.28		
	18	1	6.20	6.80±0.30	7	0.12±0.01	2.25	2.32±0.04	26
Serine	2	3		6.80±0.35	7	0.20		2.66	18
Glutamic Acid	3	2		6.67±0.42	9	0.17		2.29	30
Average				**6.76**±0.21	**7**±6	0.16±0.02		2.42±0.12	**26**±11
Methionine	4	3		4.99±0.29	32	0.42		1.55	52
3-HSProp.Acid	5	1	5.58				1.79		
	15	1	5.12	5.35±0.35	27	0.30±0.08	1.65	1.72±0.07	47
Cysteine	6	1	5.64				1.56		
	16	1	4.68	5.16±0.35	29	0.21±0.03	1.53	1.54±0.02	53
Glutathione	7	2		5.15±0.35	29	0.15		1.66	49
Average				**5.16**±0.17	**29**±5	0.27±0.06		1.62±0.05	**50**±10
Difference				**1.60**±0.27	**22**±4	-0.11±0.06		0.80±0.13	**24**±4

Notes to Table 4:

- Starting material saline surface soil collected in Kesterson Reservoir pond 11, crushed and seived 30 mesh.
- In tests 11, 15, 16 and 18, 200 ppm penicillin-G and 200 ppm streptomycin added to glucose/nitrate solution.
- First average includes values for control, serine, glutamic acid. Second average includes values for four sulfur compounds, and "difference" is between the two averages.
- Soluble selenium values determined by analyzing Na_2SO_4/NaCl brine extracts made at end of the experiments. Total selenium values by X-ray fluorescence, corrected for soluble selenium extracted; statistical uncertainty in individual total Se values approximately ±0.6 ppm, decreased by averaging repeat analyses and grouped tests. Se^0 values by preferential extraction in 0.3 M Na_2S.

added. While some of the Se^0 may have been converted to other species rather than volatilized, Se^0 is clearly reactive under these conditions, and adding sulfur compounds increases its reactivity. As expected, adding sulfur compounds increased the amount of soluble selenium in the soil.

5.1.4. Discussion

The ability of reduced sulfur compounds to solubilize Se^0 and increase its biological availability has been amply demonstrated. A substantial concentration of dissolved selenium may be present in the pore water of organic-rich sediments under reducing conditions. Very strongly reducing, sulfidic conditions favor selenium substituted polysulfide ions as the major species. Polysulfidic selenium probably is responsible for the limited downward migration of selenium observed underneath parts of Pond 2. Polysulfidic Se does not represent a threat to groundwater, because polysulfides exist only in the presence of H_2S, which is rapidly removed from water by reaction with iron oxides in carbon-poor mineral soil.

In less reducing, but still organic-rich environments polysulfidic Se disappears and selenium associated with organic compounds predominates. While the speciation shifts dramatically, the total amount of selenium present remains roughly constant. Thiol-bound selenium (operationally defined as Se precipitated by Na_2S_4 and acid, but not by acid alone) and nonprecipitable Se are present in subequal amounts. Selenite and methane seleninic acid may also be present under these conditions and will interfere with the determination of thiol bound Se. This residual category of "nonprecipitable Se" (B in Table 5-3) will include selenoethers (e.g. selenomethionine) and, in oxidizing environments, selenate ion. Many other compounds of selenium and sulfur may be present where oxygen and organic matter coexist, and many of them will fall into this category.

The dramatic, pH-dependent effect of organic thiols upon solubility of selenium assures an important role in soil chemistry of selenium. While it is not necessarily a unique explanation, the ability of thiols to solubilize selenium does explain the ability of microorganisms to oxidize Se^0 (Sarathchandra and Watkinson, 1981) and to volatilize it. Selenoglutathione was reported as a

major species of selenium in pore water extracted from selenium-poor peat soil (van Dorst and Peterson, 1984). Extracts were made of soil spiked with Se^{75} and analyzed using high voltage electrophoresis (Peterson and Butler, 1962), a technique which is unable to resolve corresponding sulfur and selenium aminoacids (Ibid.). It is very possible that the Se-glutathione complex containing the group $-SSe^-$, was misidentified as selenoglutathione, containing the group $-Se^-$. Since the ability of glutathione to form selenium complexes is central to the intracellular biochemistry of selenium (Garberg and Hogberg, 1986), it is entirely likely that microbes use glutathione or related thiols to mobilize Se^0 in the extracellular environment as well. The large effect of sulfur compounds upon the volatilization of selenium, including Se^0, supports the role of thiols in making selenium biologically available.

It is noteworthy that methionine, which has no effect upon the solubility of selenium, stimulates volatilization as do the other sulfur compounds, which dissolve Se^0. The volatile species of selenium produced is probably dimethylselenide, formed by methylating selenium. Methionine is the major source of methyl groups for biochemical transmethylation reactions, and thereby may directly stimulate the volatilization process. The product of demethylating methionine is the thiol homocysteine. Despite its inability to solubilize selenium microorganisms convert methionine to a thiol which does have that ability.

The increment in total selenium volatilized in the presence of sulfur compounds was twice the increment of additional Se^0 removed. Evidently, thiols indirectly stimulate the bioavailability of other species of selenium in soil as well.

The large effect of pH upon selenium solubility with thiols explains the large decrease of soluble selenium in soil with decreasing pH (van Dorst and Peterson, 1984). An analogous effect has been reported in aquatic ecosystems (Cherry, et al., 1979); decreasing the pH of water in a pond decreases the selenium content of invertebrates living in the pond. These observations suggest that dissolution of Se^0 by reaction with thiols is a critical step in the geochemical cycling of selenium, one which may be blocked by simply decreasing pH. It is likely that the small but continuous recycling of selenium from sediment to surface water and biota under Wet-Flex condi-

tions involves formation of soluble organic selenium compounds. Knowing the role of thiols and the large effect of pH upon the solubility and bioavailability of selenium *in vitro*, in soil, and in aquatic ecosystems, we now realize that the relatively high pH of Kesterson water favored recycling of selenium to the surface water and biota. With lower pH, particularly with more acidic pond-bottom sediment, the recycling of selenium would have been smaller. Low salinity water, and particularly water low in sulfate, would enhance the immobilization of selenium in pond-bottom sediment by favoring the rapid deposition of organic-rich, acid sediment, and not allowing the production of H_2S. This observation may find practical application in the control of selenium toxicity in freshwater bodies contaminated with selenium, e.g. from fly ash.

While enhanced volatilization of selenium in the presence of sulfur compounds does not necessarily translate into a practical soil clean-up process, it does provide a critical insight into the geochemical cycling of selenium in soil, and suggests how these processes may be controlled. The application of thiophyllic reagents and their precursors to removing selenium from San Luis Drain sediments will be investigated in the coming months.

5.2 Analytical Methods for Biological Samples and Sediments

5.2.1. Introduction

Over the past three years the Kesterson project at LBL has required the chemical analysis of several thousand samples of biological material and sediment or soil for selenium. Several analytical procedures have been developed or modified in the course of this work. Over the past year these procedures have been formally tested and documented. The results of the test work are summarized here.

- X-Ray fluorescence

  Sediments and biological materials are routinely analyzed using X-ray fluorescence spectroscopy if sufficient sample material is available, and the concentration of selenium in the dried material is > 3 ppm. Approximately 2 g of sediment is required for analysis, or 0.2 g dry biological material. The sediment is pulverized in a ball mill and pressed

into a pellet for analysis. Dried biological samples are crushed, if that is sufficient to allow representative subdivision and a coarsely uniform sample texture, or else pulverized. The detailed XRF procedure is described in Appendix C.

Samples too small for XRF analysis or containing < 3 ppm Se are analyzed by Atomic Absorption Spectroscopy (AAS) with Hydride Generation. The major step in preparing solid samples for analysis by AAS is the decomposition reaction. An oxidizing liquid or melt is used to completely oxidize selenium and organic matter in the sample, converting the selenium to selenate ion dissolved in water. Ultimately this extract is diluted up to a standard volume and reacted with HCl to convert the selenium in it to selenious acid which is determined using the hydride generator/AA. Three decomposition methods have been developed or modified at LBL, and are presently used. None of these methods require perchloric acid or HF, and were developed in part to eliminate the need for these extremely hazardous reagents. Nor do they require overnight digestion.

The decomposition methods reported here are:

- Magnesium nitrate decomposition

  Magnesium nitrate decomposition used with biological samples is described in Appendix D. This is a well-established, widely used technique (Ref. 1, and references therein) which we modified to perform all operations within a single test-tube, making it more reliable and quite fast. Our version allows biological samples as small as 3 mg to be analyzed. Practically all biological samples smaller than 0.2 g grams were analyzed by AAS preceded by magnesium nitrate decomposition.

- Sodium peroxide decomposition

  Sodium peroxide decomposition used with sediment samples, is described in Appendix E. This technique has good sensitivity and a relatively low blank, and is the preferred decomposition method for sediment samples.

- Carbonate/nitrate decomposition

Carbonate/nitrate decomposition described in Appendix F, may be used for either biological samples or sediments. While it is quite reliable, it is also relatively laborious and suffers from a relatively high blank value with biological samples.

The descriptions of the decomposition methods presented in the appendices are taken directly from our updated laboratory standard operationg procedures manual and are complete and accurate.

5.2.2. Control of blank readings

The bulk of the work in this laboratory involved numerous samples containing > 3 ppm Se, and methods were chosen accordingly. Under these circumstances moderately elevated blank readings are to be expected, but for the most part are also acceptable. Several sources of contamination contribute to blank readings with AAS analysis.

Selenium in the reagents makes a small contribution to the blank. Analyses of the reagent chemicals indicated that reagents contribute roughly 0.01 ppm and 0.03 ppm to the blank with the Na_2O_2 and carbonate/nitrate decomposition methods, respectively.

After some months of heavy use, the box furnace required by all methods may become contaminated with selenium, sometimes causing large, erratic blank readings. This source of contamination is minimized by using a large enough box furnace and occasionally burning-off accumulated selenium oxides by increasing temperature to 1100°C for one hour with the furnace empty.

Cross-contamination of the glass culture tubes is a problem with all decomposition methods reported here, but especially with magnesium nitrate decomposition, where the entire reaction takes place inside the tube. Careful cleaning of the tubes as described in Appendix D will eliminate most of this problem. Using clean tubes and discarding them after one analysis would in principle eliminate this source of contamination completely. Segregating tubes used for the magnesium nitrate procedure would eliminate carry-over of selenium from this procedure to the other procedures.

The Na_2O_2 and carbonate/nitrate decomposition reactions are carried out inside of metal tubes (zirconium and Inconel, respectively) which are coated with an oxide layer that adsorbs some amount of selenium. Here as well, proper cleaning as described in Appendices D and E is very effective in reducing the blank value. The problem is particularly acute with samples of low selenium content, and may be controlled by designating "clean" tubes for low Se samples, and "dirty" tubes for high Se samples. This was done during the present study.

With the sodium peroxide decomposition method, "clean" tubes were used with samples and controls containing < 3 ppm and associated blanks, and dirty tubes were used with samples and controls containing > 3 ppm Se.

With the carbonate/nitrate method applied to sediments no distinction was made between clean and dirty tubes; the tubes used for production samples and blanks were interchanged after every run.

Because of the much larger reducing power of biological samples, the carbonate/nitrate method had to be modified as described at the end of Appendix F. The nitrate content of the flux was increased, and the sample size was decreased from 0.2 g to 0.05 g. Because biological samples were frequently high in selenium, sensitivity was not a problem, but high blank readings were encountered. This problem was controlled by designating "clean" Inconel tubes used only with samples containing < 10 ppm Se, and "dirty" tubes used only with samples containing > 10 ppm Se.

5.2.3. Study design.

A variety of reference materials were used as test samples, most of them from Kesterson Reservoir, plus some certified reference materials. These are described in Table 5-5. Both LBL internal references and reference materials provided by the US Bureau of Reclamation were used. The reference materials were selected to cover a variety of matrices (sediment, aquatic vegetation, terrestrial vegetation and fish) and a range of concentrations from low to high.

Most of the samples were analyzed by XRF in triplicate and average values reported. The

biological samples were analyzed by XRF in two different ways: the powder method used in routine work, plus the more accurate (and laborious) pelletized method (Appendix C).

Sediment samples were analyzed by AAS using two decomposition methods: Na_2O_2 and carbonate/nitrate. Biological samples were analyzed by AAS using two decomposition methods: $Mg(NO_3)_2$ and carbonate/nitrate. The study design was basically similar in all four cases. Two series of runs were made for each case.

In the first series (Tables 5-6, 5-8, 5-11 and 5-13), the same samples were analyzed six times in six separate runs together with corresponding blanks and controls, and the results were averaged. In some cases the same reference materials were used for controls as for samples. In these cases, "controls" and "production samples" were designated beforehand. While all analytical values are reported here, the results for the control samples and blanks were used only to determine whether to accept or reject a particular set of data, as they would be in routine analytical work. Only the results of the "production" samples were carried forward to the summary Tables 5-10 and 5-15. These series of analyses most closely reproduced routine laboratory practice; indeed, in the case of the magnesium nitrate decomposition tests, samples for this study were combined in sets together with samples routinely being analysed for SEEHRL. These series accurately reflect the entire variance in the analytical results, including interset variance.

In the second series, a sample was analyzed several times (usually 6) in a single run together with 6 blanks (Tables 5-7, 5-9, 5-12 and 5-14). These series provide an estimate of the intraset variance for the various analytical methods.

Spiked samples were not run. The central problem is to eliminate the effects of matrix and selenium speciation upon the result. If one adds a spike of, say, sodium selenite, the chemical form of the selenium added will be so different from most of the natural selenium that the analytical results may be meaningless or even dangerously misleading. Therefore, we instead chose to rely on reference materials and an absolute and highly reliable method (pelletized XRF) to document accuracy.

Table 5-5. Origin and description of samples analyzed.

Sediments:	
KC9-1	LBL internal reference material. Deep Chara ooze, S. edge Kesterson Pond 4, flooded, December 1985.
KS1-S	USBR supplied reference material; aka SJVDP6876. Soil, S. edge of Kesterson Pond 1.
1633a	US-NBS Standard Reference Material 1633a - Coal Fly Ash. Certificate of analysis dated 4-18-1975, revised 1-5-1985.
KC2-2	LBL internal reference material. Dry soil from playa area S. edge Kesterson pond 1, 1-2 inches depth; collected August 1985.
KS12-E	USBR supplied reference material, soil from E. edge of Kesterson pond 12.
PACS-1	National Research Council (Canada), Division of Chemistry, Marine Analytical Chemistry Standards Program - Marine Sediment Reference Material PACS-1; certificate of analysis dated January 1981, revised October 1987.
Biological materials:	
S4/Gambusia	LBL internal reference material. Mosquito fish collected alive at Kesterson pond 8, July 1986; oven dried and pulverized.
DOLT-1	National Research Council (Canada), Division of Chemistry, Marine Analytical Chemistry Standards Program - Dogfish material DOLT-1; certificate of analysis dated December 1986.
RM-50/Tuna	NBS Reference Material RM-50 - Albacore Tuna; aka SJVDP6877.
S1/Algae	LBL internal reference material. Mixture of Chara and aufwuchs collected alive at southern edge of Kesterson pond 5, summer 1986; oven dried and pulverized.
S2/Typha	LBL internal reference material. Live cattail leaves collected 1986 at Kesterson Reservoir; oven dried and pulverized.
S3/Scirpus	LBL internal reference standard. Bullrush seeds collected at Kesterson Reservoir summer 1986. Separated from chaff, oven dried and pulverized.

KV101/Algae	USBR supplied reference material aka SJVDP6879 aka S8/Algae; similar to LBL S1/Algae.
KV102/Cressa	USBR supplied reference material - alkali weed; aka S7/Cressa.
KV103/Dist.	USBR supplied reference material - saltgrass; aka S5/Distichalis.
KV104/Frank.	USBR supplied reference material - alkali heath; aka S6/Frankenia.
KV105/Scirpus.	USBR supplied reference material - bullrush; aka S9/Scirpus.
KV106/Typha	USBR supplied reference material aka SJVDP6878 aka S10/Typha. Cattails; emergent part.

Table 5-6. Repeated analyses of sediment samples using carbonate/nitrate decomposition.

Run Date Sample	1 5/18/88	2 5/20/88	3 5/23/88	4 5/24/88	5 5/25/88	6 5/26/88	Mean	S.D.
Samples								
KC9-1	65.39	59.70	61.69	62.94	57.53	62.55	61.63	2.73
KS1-S	62.12	55.11	54.59	57.68	62.03	57.53	58.18	3.27
1633a	9.45	9.65	8.88	10.11	10.32	10.57	9.83	0.62
KC2-2	2.77	2.62	2.26	2.57	2.86	3.03	2.69	0.27
KS12-E	3.08	3.35	2.88	3.42	3.79	3.58	3.35	0.32
PACS-1	0.95	1.10	0.84	1.25	1.07	1.26	1.08	0.17
Controls								
KC9-1	64.08	–	57.28	–	–	60.28	60.55	3.41
KS1-S	–	55.94	–	57.99	62.42	–	58.78	3.31
1633a	–	–	–	10.22	–	10.32	10.27	0.07
KC2-2	2.78	–	–	2.63	–	2.85	2.75	0.11
KS12-E	–	–	2.90	–	3.67	–	3.29	0.54
1633a	–	1.05	1.01	–	–	–	1.03	0.03
Blanks								
B-1	0.86	0.30	0.28	0.38	0.32	0.26	0.40	0.23
B-2	0.64	0.35	0.44	0.30	0.52	0.22	0.41	0.15
B-3	–	–	0.61	0.50	0.79	lost	0.63	0.15

Each run included 10 to 12 tubes consisting of 6 production samples, 2 or 3 controls, and 2 or 3 blanks. No distinction was made between "clean" and "dirty" tubes. Blank values were averaged and subtracted from values < 12 ppm Se.

Table 5-7. Six simultaneous analyses of sediment samples using carbonate/nitrate decomposition accompanied by six blanks.

Sample	Accompanying blank Se(ppm)	Se conc. (ppm)
PACS-1	0.14 ± 0.08	1.17 ± 0.08
1633a	0.07 ± 0.05	10.54 ± 0.12
KC9-1	–	67.68 ± 0.43

Three samples were chosen at random and processed in three separate runs, each consisting of 6 blanks and 6 analyses of the same sample. Blank values were subtracted from values < 12 ppm Se.

Table 5-8. Repeated analyses of sediment samples using sodium peroxide decomposition.

Run Date Sample	1 7/15/88	2 7/18/88	3 7/19/88	4 7/20/88	5 7/20/88	6 7/21/88	6 runs Mean	 S.D.
Samples								
KC9-1	63.24	58.47	60.13	64.59	lost	70.38	63.36	4.61
KS1-S	61.16	lost	58.16	60.36	65.33	68.56	62.71	4.17
1633a	10.40	11.03	10.76	11.93	12.56	14.00	11.78	1.35
KC2-2	2.62	2.51	2.63	2.46	2.88	2.91	2.67	0.19
KS12-E	2.92	3.08	3.10	3.01	3.11	3.82	3.17	0.32
PACS-1	1.03	1.06	1.08	1.23	1.27	1.26	1.16	0.11
Controls								
KC9-1	64.64	59.75	59.04	–	–	70.80	63.56	5.43
KS1-S	–	–	58.10	62.94	64.80	70.14	64.00	4.98
1633a	10.29	11.51	–	11.92	12.70	–	11.61	1.01
KC2-2	2.54	2.97	2.35	–	lost	2.54	2.60	0.26
KS12-E	–	3.00	–	3.18	–	–	3.09	0.13
PACS-1	1.04	–	1.01	1.22	–	–	1.09	0.11
Blanks (1-12)								
B-1	0.09	0.36	0.23	0.16	0.18	0.21	0.21	0.09
B-2	0.13	0.52	0.16	0.18	0.14	0.23	0.23	0.15
Blanks (1-12)								
B-3	0.11	0.04	0.15	0.08	0.09	0.17	0.11	0.05
B-4	0.13	0.07	0.14	0.11	0.12	0.10	0.11	0.02

Each run of 14 tubes included 6 samples, 2 controls with Se > 3 ppm, 2 controls with Se ≤ 3 ppm, 2 blanks in "clean" tubes, and 2 blanks in "dirty" tubes. Blanks were subtracted from values < 8 ppm Se.

Table 5-9. Six simultaneous analyses of sediment samples using sodium peroxide decomposition with corresponding blanks.

Sample	Blank Se(ppm)	Se conc. (ppm)
KC9-1	0.13 ± 0.05	59.58 ± 0.83
KS1-S	–	56.60 ± 0.65
1633a	–	10.69 ± 0.19
KC2-2	0.05 ± 0.01	2.36 ± 0.03
KS12-E	–	2.97 ± 0.17
PACS-1	–	1.17 ± 0.05

Data from four runs of twelve tubes each are compiled here. Two runs included six analyses of a single sample and six blanks, and two runs included six analyses of two samples only. Two of the runs were in "clean" tubes, and two in "dirty" tubes.

Table 5-10. Summary of results for sediment samples.

Sample	Na_2O_2 oxidation method		Carbonate/ nitrate oxidation method		XRF		Other laboratories	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
KC9-1	63.36	4.61	61.63	2.73	62.2	0.9	–	–
KS1-S	62.71	4.17	58.18	3.27	58.5	0.8	63.0[a]	5.9
1633a	11.78	1.35	9.83	0.62	–	–	10.3[b]	0.6
KC2-2	2.64	0.22	2.69	0.27	2.75	0.48	–	–
KS12-E	3.17	0.32	3.35	0.32	3.5	0.6	2.5[a]	0.09
PACS-1	1.16	0.11	1.08	0.17	1.37	0.52	1.09[c]	0.11

a. XRF value from USGS Denver (2).
b. From US-NBS certificate of analysis.
c. From National Research Council (Canada) certificate of analysis.

Table 5-11. Repeated analyses of biological samples using magnesium nitrate decomposition.

Run Date Sample	1 6/10/88	2 6/13/88	3 6/14/88	4 6/14/88	5 6/15/88	6 6/16/88	Mean	S.D.
Samples								
S4/Gambusia	90.97	78.10	105.48	98.78	88.82	95.51	92.94	9.37
DOLT-1/Dogfish	5.62	4.64	6.08	5.78	5.93	4.63	5.44	0.65
Sl/Algae	54.19	59.15	53.57	63.21	51.34	51.80	55.54	4.67
KV106/Typha	29.92	35.36	36.16	35.51	35.27	33.02	34.21	2.36
Controls								
S2/Typha	48.27	45.49	48.46	49.91	45.09	43.82	46.84	2.37
KV102/Cressa	–	–	22.82	24.45	21.73	lost	23.00	1.37
KV106/Typha	34.18	32.53	–	–	–	–	33.36	1.17
Blanks								
B1	0.24	0.22	0.23	0.32	0.36	0.17	0.26	0.07
B2	0.19	0.16	0.25	0.30	0.46	0.09	0.24	0.13

Data from 6 runs of 16 tubes are summarized here. Each run included 4 samples reported here, 2 controls, 2 blanks, and 8 routine production samples of biological material. In all respects, these were handled as routine production runs.

Blank values were subtracted from values < 10 ppm Se. Se concentrations were corrected for the blank in the liquid extracts, before Se concentrations in the solid samples were calculated. Blank readings in the liquid extracts were converted to reported ppm Se in the solid by assuming sample weight = 70 mg.

Table 5-12. Six simultaneous analyses of biological samples using magnesium nitrate decomposition.

Set No.	Sample	No. of analyses	Se(ppm) Mean ± S.D.
1	S4/Gambusia	5	96.10 ± 2.77
	DOLT-1/Tuna	6	6.49 ± 0.33
	Blank	5	0.30 ± 0.10
2	S1/Algae	6	52.59 ± 1.62
	KV106/Typha	6	33.78 ± 1.38
	Blank	3	0.37 ± 0.22

Data from two additional sets of analyses are summarized here. The values determined for sample DOLT-1 were corrected for the blank by using the average of blank readings in that set. Values determined for the other samples were not corrected for the blank. Otherwise blanks handled as described beneath Table 5-11.

Table 5-13. Repeated analyses of biological samples using carbonate/nitrate decomposition.

Set Set	Run Date Sample	1 9/22/88	2 9/22/88	3 9/23/88	4* 9/26/88	5* 9/26/88	6 9/27/88	Mean Mean	S.D. S.D.
1	**Samples**								
	S4/Gambusia	77.97	75.53	66.71	56.79	75.15	75.64	70.43	8.73
	Sl/Algae	67.32	64.75	61.57	56.43	56.67	63.53	61.71	4.41
	KV106/Typha	29.02	27.75	25.77	28.84	28.97	35.30	29.28	3.20
	Controls								
	S2/Typha	40.29	40.80	41.00	46.56	46.37	51.16	44.42	4.41
	KV101/Algae	95.23	98.41	93.64	85.43	84.09	90.33	91.19	5.64
	Blanks								
	B1	2.67	2.53	1.77	2.14	2.62	1.49	2.20	0.49
	B2	–	–	1.48	2.75	2.48	2.53	2.31	0.57
2	**Sample**								
	DOLT-1	6.05	6.79	5.20	5.42	lost	6.01	5.89	0.62
	Controls								
	S3/Scirpus	3.70	2.46	1.97	3.30	2.22	2.45	2.68	0.67
	Blank								
	B1	0.91	1.03	1.08	1.05	1.64	2.46	1.36	0.60
	B2	1.05	1.13	1.21	1.33	1.24	1.65	1.27	0.21

*Extracts reheated and reanalyzed.

Six sets of 10 or 11 tubes are summarized here. Each set included 1 or 2 blanks, 3 samples and 2 controls with Se > 10 ppm in the dirty tubes, plus 2 blanks, 1 sample and 1 control with Se < 10 ppm in the clean tubes. Values of Se < 40 ppm were corrected by subtracting the corresponding averaged blank.

Table 5-14. Six simultaneous analyses of biological samples using carbonate/nitrate decomposition method.

Sample	Mean	S.D.
S4/Gambusia	70.71	3.60
DOLT-1/Dogfish	5.28	0.50
S1/Algae	56.98	2.02
KV106/Typha	30.58	2.99
Blanks set 1	1.80	0.27
Blanks set 2	1.06	0.08

Six blanks were simultaneously run in "clean" tubes, and 6 in "dirty" tubes. Then each sample was analyzed 6 times in a single run using the corresponding tubes. The blank values were subtracted from values < 40 ppm Se.

Table 5-15. Summary of results for biological samples.

Sample	$Mg(NO_3)_2$ oxidation method		carbonate/ nitrate oxidation method		XRF (LBL) "Routine" powder method		XRF (LBL) pelletized method		Other laboratories	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
S4/Gambusia	92.94	9.37	70.43	8.73	108	2	116	1	–	–
DOLT-1/Dogfish	5.44	0.65	5.89	0.62	7.1	0.5	–	–	7.34[a]	0.42
RM-50/Tuna	–	–	–	–	3.7	0.4	4.3	0.1	–	–
"	4.43	0.23	–	–	–	–	–	–	3.6[b]	0.4
Sl/Algae	55.54	4.67	61.71	4.41	67.0	1.2	71.3	0.7	–	–
KV101/Algae	–	–	91.19	5.64	97	2	104	2	–	–
"	77.08	3.80	–	–	–	–	–	–	78.5[c]	19.6
"	76.38	3.89	–	–	–	–	–	–	–	–
KV102/Cressa	–	–	–	–	23.2	0.4	24.7	1.2	–	–
"	23.30	0.53	–	–	–	–	–	–	–	–
KV103/Dist.	–	–	–	–	54.3	2.4	54.8	2.9	–	–
"	47.82	2.91	–	–	–	–	–	–	–	–
KV104/Frank.	–	–	–	–	24.4	0.5	23.4	1.2	–	–
"	20.62	1.23	–	–	–	–	–	–	–	–
KV105/Scirpus	–	–	–	–	51.2	2.2	48.1	0.7	–	–
"	45.98	2.06	–	–	–	–	–	–	–	–
KV106/Typha	34.21	2.36	29.28	3.20	37.6	0.2	34.8	0.6	–	–
"	34.22	0.78	–	–	–	–	–	–	35.9[d]	3.56
"	33.17	1.68	–	–	–	–	–	–	–	–

a. National Research Council (Canada) certificate of analysis.

b. NBS Certificate of Analysis quoted in Ref. 2.

c. Ref. 2; average of hydride generator AAS values only; average of all values is 86.7ppm.

d. Ref. 2; average of all analyses reported.

For each sample in the Table, the first line contains values generated or compiled in the course of the present study; following lines contain values generated during earlier method testing work.

The QA/QC protocol employed was basically the same for all AAS work, and can be summarized as follows:

1. The blank values were checked for each set, and were considered acceptable if below a specified limit. This limit varied with the decomposition method and sample:

   a. Na_2O_2 method (sediments only):

      1. Acceptable blank < 0.4 ppm for samples containing > 3 ppm Se.

      2. Acceptable blank < 0.2 ppm for samples containing < 3 ppm Se.

   b. $Mg(NO_3)_2$ method (biological only):

      Acceptable blank < 0.5 ppm for all samples. Sample aliquots of variable size are analyzed using this method, and the blank values reported in the Tables were calculated assuming a typical sample size for the given set, usually 70 mg.

   c. Carbonate/nitrate method for sediments:

      Acceptable blank < 0.75 ppm for all samples.

   d. Carbonate/nitrate method for biological materials:

      1. Acceptable blank < 2.5 ppm for samples containing > 10 ppm Se.

      2. Acceptable blank < 1.5 ppm for samples containing < 10 ppm Se.

      During the present study no data were rejected for high blank readings.

2. The values determined for both control samples were required to be within 20% of established values for those samples. If not, the HCl extract was again heated at 100°C for 20 minutes and reanalyzed. If that did not correct the problem, the entire run was rejected and the analysis repeated from scratch. In practice, reheating usually corrected the problem, and complete reanalysis is rarely called for. During the present study, only two sets of tubes required reheating (both in Table 5-13) and no complete reanalyses were required.

5.2.4. Results

While some inconsistencies remain to be explained, the pelletized XRF values for all samples with > 3 ppm Se are believed to be the most reliable, and the AAS results will be compared with them.

Results for sediment samples are presented in Tables 5-6 through 5-9 and summarized in Table 5-10. With both decomposition methods intraset variance is much smaller than interset variance. The Na_2O_2 decomposition gives lower blank readings, but moderately higher variance for samples with > 9 ppm than does the carbonate/nitrate method. The coal ash reference material (1633a) could not be reliably analyzed by XRF because it contains a substantial amount of germanium, which interferes with determination of selenium. Below about 3 ppm XRF runs out of sensitivity and becomes unreliable.

Test results for biological samples are presented in Tables 5-11 to 5-14. As with sediments, interset variance is greater than intraset variance, particularly with magnesium nitrate decomposition. Test results for biological samples are summarized in Table 5-15. This Table also includes summary results from earlier method validation studies, including the results of an interlaboratory round-robin.

With biological samples the different methods *do* give moderately different results. With terrestrial vegetation the divergence is small: the two XRF methods agree within 10%, and the magnesium nitrate/AAS results are 0-15% lower.

Matters are more complex with fish tissue and aquatic vegetation; both samples of "algae" are a mixture of *Chara* and *aufwuchs*, and contain a substantial amount of calcium which increases the X-ray density of the sample and interferes with XRF analysis. For fish and aquatic vegetation, powder XRF gives values that are consistently a few percent lower than from pelletized XRF. For the sample RM-50/Tuna magnesium nitrate/AAS agreed well with pelletized XRF, but for S4/Gambusia and the two algae samples, the magnesium nitrate/AAS values were lower by 20-25%. In all three cases the variance of the magnesium nitrate value was considerably smaller than the discrepancy, indicating a bias rather than a random error. The

carbonate/nitrate method gave higher values for the two algae samples than magnesium nitrate, but a lower value with S4/Gambusia. The Gambusia reference material is rather greasy, and probably exceeds the oxidizing power of the carbonate/nitrate flux mixture.

It is noteworthy that the average of values for KV101/Algae reported by several laboratories is practically equal to our result using the magnesium nitrate method. This suggests that the problem is more a generic one affecting hydride generator AAS than one specific to our magnesium nitrate decomposition method.

While the magnesium nitrate method gives readings that are moderately but consistently low with some samples, it is quite precise; for example, samples KV101/Algae and KV106/Typha were analyzed in two or three method validation studies spanning a period of over a year but produced very consistent results.

Finally, Table 5-16 compares results obtained using powder XRF with results obtained using magnesium nitrate/AAS for a series of biological samples. These data were extracted from routine production data over a period of several weeks. The magnesium nitrate method - particularly applied to vegetation samples - gives results that are, on the average, slightly lower than from powder XRF.

5.2.5. Conclusions and recommendations

Overall, XRF is the best analytical method for samples that contain > 3 ppm Se, whether biological or sediment. Powder XRF is adequate for routine biological work, but at least initially it should be validated against pelletized XRF or neutron activation analysis to test for possible matrix effects.

In the near future several of our test samples will be analyzed by neutron activation to finally resolve lingering inconsistencies between the XRF results and AAS results for biological materials.

For sediment samples containing < 3 ppm Se, Na_2O_2 decomposition/AAS is preferred. With all of the AAS methods LOD and LOQ are limited by the blank reading; with the lowest

Table 5-16. Comparison of powder XRF and magnesium nitrate/AAS results in routine analytical work.

Sample #	Sample Type	Se(ppm) XRF	Se(ppm) $Mg(NO_3)_2$	Ratio $\frac{Mg(NO_3)_2}{XRF}$
	Animals			
3064	Gambusia	35.9 ± 2.9	33.7	0.94
3065	Gambusia	24.2 ± 1.9	25.0	1.03
3067	Berosus larvae	38.5 ± 3.1	38.8	1.01
3141	Grasshoppers	1.9 ± 0.2	1.9	1.00
3150	Grasshoppers	2.0 ± 0.8	2.3	1.15
3155	Tabanid larvae	41.1 ± 3.3	38.5	0.94
3157	Anax nymphs	18.5 ± 1.5	11.9	0.64
3159	Gambusia	38.8 ± 3.1	37.5	0.97
3161	Gambusia	22.7 ± 1.8	24.0	1.06
	Plants			
3054	Typha rhizomes	3.2 ± 0.8	3.0	0.94
3057	Scripus seeds	2.4 ± .7	1.7	0.71
3082	Aufwuchs	15.1 ± 1.4	12.5	0.83
3083	Ruppia	16.9 ± 1.4	13.2	0.78
3110	Dist. Roots	56.7 ± 4.5	50.2	0.89
3134	Sida	8.2 ± 1.0	11.4	1.39
3308	Dist. Roots	18.4 ± 1.5	15.31	0.83
Geometric mean - animals				0.96 ± 0.16
Geometric mean - plants				0.89 ± 0.20
Geometric mean - all samples				0.93 ± 0.18

blank, the Na_2O_2 is very attractive for work below 3 ppm. Both the Na_2O_2 method and the carbonate/nitrate method are reliable in the sense that one does not seem to encounter samples that refuse to give anything like the correct result, something that other laboratories using mixed acid digestion methods have encountered. This reliability must be balanced against the problem of the blank and the relatively more laborious procedure, particular complaints in the case of the carbonate/nitrate method.

Magnesium nitrate is the preferred decomposition method for AAS analysis of biological samples. While the magnesium nitrate method gives moderately low results with certain matrices, the precision is good. The variant used in our laboratory allows very small samples to be routinely analyzed (of particular importance with insects), and it is very quick and convenient.

The carbonate/nitrate method will rarely be the method of choice, but it provides a useful alternative to compare other methods against. It is unique among the decomposition methods in allowing either sediments or biological samples to be processed with minor change in procedure, and the only known matrix effect is the low reading obtained with exceptionally greasy animal tissue. For this reason, it can be very useful if matrix effects are suspected, and neither XRF or NAA is available.

6. REFERENCES

6.1. GENERAL REFERENCES

Lawrence Berkeley Laboratory Progress Report 1, 1985, LBID-1101, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 2, 1986, LBID-1188, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 3, 1986, LBID-1213, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 4, 1986, LBID-1250, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 5, 1987, LBID-1291, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 6, 1987, LBID-1312, Berkeley, CA.

Lawrence Berkeley Laboratory Annual Report, 1987, LBL-24250, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 7, 1988, LBID 1404, Berkeley, CA.

Lawrence Berkeley Laboratory Progress Report 8, 1988 LBID-1420, Berkeley, CA.

6.2. VADOSE ZONE

Gardner, W. R., and M. Fireman, 1958. Laboratory Studies of Evaporation from Soil Columns in the Presence of a Water Table. *Soil Sci., 85,* 228-232.

Hillel, D., 1980. *Fundamentals of Soil Physics.* Academic Press, New York.

Moore, R. E., 1939. Water Conduction from Shallow Water Tables. *Hilgardia, 12,* 383-426.

Soil Conservation Service, U.S. Dept. of Agriculture, 1952. Soil Survey of the Los Banos Area, California. Series 1939 (12).

U. S. Salinity Laboratory Staff, Feb. 1954. Diagnosis and Improvement of Saline and Alkaline Soils. L.A. Richards, editor, Agricultural Handbook No. 60. U. S. Department of Agriculture. U. S. Government Printing Office, Washington, D.C.

6.3 GROUNDWATER

Balistieri, L. S., and T. T. Chao, 1987. Selenium Adsorption by Goethite. *Soil Science Society of America Journal, 51,* 1145-1151.

Bar-Yosef, B., and D. Meek, 1987. Selenium Sorption by Kaolinite and Montmorillonite. *Soil Science, 144* (1), 11-19.

Benson, S. M., 1988. Characterization of the Hydrogeologic and Transport Properties of the Shallow Aquifer Under Kesterson Reservoir. Ph.D. Dissertation, University of California, Berkeley.

Edmunds, W. M., 1973. Trace Element Variations Across an Oxidation-Reduction Barrier in a Limestone Aquifer. Proceedings, Symposium on Hydrogeochemistry and Biochemistry, Tokyo, Japan, 1970. The Clarke Company, Washington, D.C.

Elrashidi M. A., D. C. Adriano, S. M. Workman, and W. L. Lindsay, 1987. Chemical Equilibria of Selenium in Soils: A Theoretical Development. *Soil Science, 144,* (2) 141-152.

Freeze, R. A., and J. A. Cherry, 1979. *Groundwater.* Prentis-Hall, Englewood Cliffs, New Jersey.

Gaspar, E, 1987. *Modern Trends in Tracer Hydrology.* Volume I. CRC Press, Inc. Boca Raton, Florida.

Geering, H. R, E. E. Cary, L. H. P. Jones, and W. H. Allaway, 1968. Solubility and Redox Criteria for the Possible Forms of Selenium in Soils. *Soil Science Society of America Proceedings, 32* 35-40.

Gillham, R. W., and J. A. Cherry, 1978. Field Evidence of Denitrification in Shallow Groundwater Systems. Proceedings, 13th Canadian Symposium on Water Pollution Research, McMaster University, Hamilton, Ontario.

Goldhamer, D. A., M. Grismer, D. Nielsen, and J. W. Biggar, 1968. Transport of Selenium in San Joaquin Soils: Influence of Soil and Water Physical and Chemical Properties. In 1985-1986 Technical Progress Report. UC Salinity/Drainage Task Force Division of Agriculture and Natural Resources, University of California.

Goldstein, N. E., D. Alumbaugh, and S. M. Benson, 1988. Final Report - Ground Conductivity Measurements Adjacent to Kesterson Ponds 1, 2, and 5. Lawrence Berkeley Laboratory Report, LBL-24657, Berkeley, California.

Goldstein, N. E., D. Alumbaugh, and S. M. Benson, 1989. Saline Groundwater Plume Mapping with Electromagnetics. Special Publication on Environmental Geophysics, (editor S. Ward) Society for Exploration Geophysics, (in press).

Grisak, G. E., W. F. Merritt, and D. W. Williams, 1977. A Fluoride Borehole Dilution Apparatus for Groundwater Velocity Measurements. *Canadian Geotechnical Journal, 14,* 554-561.

Guven, O., R. W. Falta, F. J. Molz and J. G. Melville, 1986. A Simplified Analysis of Two-Well Tracer Tests in Stratified Aquifers. *Groundwater, 24* (1) 63-71.

Hoopes, J. A., and D. R. F. Harleman, 1967. Waste Water Recharge and Dispersion in Porous Media. *Journal of the Hydraulics Division,* American Society of Civil Engineers, Sept., 56-70.

Long, R. H., 1988. Analysis of Selenium and Chloride Movement through a Shallow Pond Sediment at Kesterson Reservoir. Master's Thesis, University of California, Berkeley.

Long, R. H., S. M. Benson, M. Alavi, and T. N. Narasimhan, 1988. Transport of a Conservative Solute through a Shallow Pond Bottom. Proceedings, Eighth Annual American Geophysical Union Range Front Branch Hydrology Days, April 19-21, Fort Collins, Colorado. Also Lawrence Berkeley Laboratory Report LBL-25217, Berkeley, California.

Long, R. H., S. M. Benson, and T. Tokunaga, 1988. Selenium Immobilization in a Pond Sediment at Kesterson Reservoir. Submitted for publication by the *Soil Science Society of America,*

Molz, F.J., O. Guven, J. G. Melville, R. D. Crocker, and K. T. Matteson, 1986. Performance, Analysis, and Simulation of a Two-Well Tracer Test as the Mobile Site. *Water Resources Research, 22* (7), 1031-1037.

Neal, R. H., G. Sposito, K. M. Holtzclaw, and S. J. Traina, 1987. Selenite Adsorption on Alluvial Soils: I. Soil Composition and pH Effects. *Soil Science Society of America, 51,* 1161-1168.

Russel, D. G., and M. Prats, 1967. Performance of Layered Reservoirs with Crossflow. *Journal of Petroleum Technology,* March, 53-67.

Singh, M., N. Singh, and P. S. Relan, 1981. Adsorption and Desorption of Selenite and Selenate Selenium on Different Soils. *Soil Sciences, 132,* (2) 134-141.

Sharma, S. and R. Singh, 1983. Selenium in Soil, Plant, and Animal Systems. *CRC Critical Reviews in Environmental Control, 13,* (1) 23-46.

Smart, P. L., and I. M. S. Laidlaw, 1977. An Evaluation of Some Fluorescent Dyes for Water Tracing. *Water Resources Research, 13* (1) 15-33.

van Genuchten, M. Th, and W. J. Alves, 1982. Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation. United States Department of Agriculture Technical Bulletin 1661. Washington, D. C.

6.4. SELENIUM REFERENCES

J. Boulegue and G. Michard, 1979. Sulfur Speciation and Redox Processes in Reducing Environments, E. A. Jenne, (editor) *Chemical Modeling in Aqueous Systems, Speciation, Sorption, Solubility, and Kinetics, ACS Symposium, 93*, 25.

D. S. Cherry, R. K. Guthrie, S. R. Larrick, and F. F. Sherberger, 1979. The Influence of Coal Ash and Thermal Discharges upon the Distribution and Bioaccumulation of Aquatic Invertebrates. *Hydrobiologia, 362*, 257-267.

G. A. Cutter, 1982. Selenium in Reducing Waters. *Science, 217*, 829.

R. E. Davis, 1968. Mechanisms of Sulphur Reactions. G. Nickless (editor), *Inorganic Sulphur Chemistry*, 85-136, Elsevier (Amsterdam).

H. E. Ganther, 1968. Selenotrisulfides. Formation by the Reaction of Thiols with Selenious Acid. *Biochemistry, 7*, 2898.

P. Garberg and J. Hogberg, 1986. The Role of Selenium-Oxygen Interactions in Selenium Metabolism. *Ambio 15*, 354.

R. D. Giauque, R. B. Garrett, and L. Y. Goda, 1977. Energy Dispersive X-ray Fluorescence Spectrometry for Determination of Twenty-Six Trace and Two Major Elements in Geochemical Specimens. *Anal. Chem., 49*, 62.

R. D. Giauque, R. B. Garrett, and L. Y. Goda, 1979. Determination of Trace Elements in Light Element Matrices by X-ray Fluorescence Spectrometry with Incoherent Scattered Radiation as an Internal Standard. *Anal. Chem., 51*, 511.

R. D. Giauque, F. S. Goulding, J. M. Jaklevic, and R. H. Pehl, 1973. Trace Element Determination with Semiconductor Detector X-ray Spectrometers. *Anal. Chem., 45*, 671.

P. J. Peterson and G. W. Butler, 1962. Paper Chromatographic and Electropyhoretic Systems for the Identification of Sulphur and Selenium Amino Acids. *J. Chromat. 8*, 70.

D. C. Reamer and C. Veillon, 1981. Preparation of Biological Materials for Determination of Selenium by Hydride Generation - Atomic Absorption Spectrometry. *Anal. Chem., 53* (8), 1192-1195.

S. U. Sarathchandra and J. H. Watkinson, 1981. Oxidation of Elemental Selenium to Selenite by *Bacillus Megaterium, Science, 211*, 600.

D. Shea and W.A. MacCrehan, 1988. Determination of Hydrophilic Thiols in Sediment Porewater Using Ion-Pair Liquid Chromatography Coupled with Electrochemical Detection. *Anal. Chem. 60*, 1449.

S. H. van Dorst and P. J. Peterson, 1984. Selenium Speciation in the Soil Solution and its Relevance to Plant Uptake. *J. Sci. Food Agric. 35*, 601.

W. J. Walker, R. G. Bureau, D. Silberman and A. Jacobson, 1988. The San Joaquin Valley Drainage Program Selenium Round-Robin: Final Report. May 1988. Department of Land, Air and Water Resources, University of California, Davis, CA 95616.

O. Weres and L. Tsao, 1983. Reaction of Hydrogen Sulfide with Oxygen in the Presence of Sulfite. Report LBL-11377. Lawrence Berkeley Laboratory, January. Chapter 2.

O. Weres, L. Tsao and R. M. Chatre, 1985. Catalytic Oxidation of Aqueous Hydrogen Sulfide in the Presence of Sulfite. *Corrosion, 41* (6), 307-316.

APPENDICES

APPENDIX A.

Appendix Table 1. Total selenium concentrations (mean, n, sd) in water (ppb), biota, and sediments (both ppm dry weight) in the 0.8-acre enclosure (Pond 5E) from its formation in May 1986 to July 1988.

	Water*			*Chara*			Aufwuchs			Sediments		
22 May 86	65.6,	2	32.6,	51.2,	3	4.8,	53.6,	3	4.2,	11.4,	3	5.9,
28 May 86	64.2,	3	10.5,	62.5,	3	4.2,	68.3,	3	5.5,			
11 Jun 86	33.1,	3	1.8,									
18 Jun 86	33.6,	3	3.2,	51.1,	3	3.4,	55.0,	3	13.0,			
26 Jun 86	9.8,	3	7.6,									
8 Jul 86	8.9,	3	6.7,	39.8,	3	1.1,	48.0,	3	3.9,			
5 Aug 86	6.9,	3	4.3,	23.3,	3	1.4,	36.1,	3	6.0,			
11 Sep 86	4.4,	3	2.1,	28.6,	3	5.4,	45.2,	3	4.9,	10.3,	3	4.5,
1 Oct 86	6.9,	3	0.3,	15.6,	3	3.7,	29.4,	3	3.1,	23.2,	3	16.3,
19 Nov 86	4.7,	3	0.3,	15.2,	3	3.7,	27.2,	3	4.7,	46.9,	3	13.7,
17 Dec 86	[illegible]2,	3	0.1,	22.2,	3	3.1,	27.8,	3	2.8,	68.6,	3	61.6,
25 Feb 87	[illegible]4,	3	0.4,	13.7,	3	2.1,	21.2,	3	2.8,	31.6,	3	45.2,
24 Mar 87	6.2,	3	3.6,	7.4,	3	3.2,	12.9,	3	2.4,			
14 Apr 87	3.3,	3	0.0,	11.6,	3	3.7,	14.1,	3	3.4,			
28 Apr 87	3.1,	3	0.4,	8.0,	3	2.5,	10.5,	3	2.2,	55.3,	2	38.3,
2 Jun 87	2.6,	3	0.2,	5.9,	3	1.7,	9.7,	3	2.1,	29.5,	3	17.9,
21 Jul 87	4.1,	3	0.7,	7.7,	3	1.2,	8.2,	3	5.9,	84.4,	3	95.1,
8 Sep 87	2.9,	3	0.8,	9.1,	3	1.5,	15.3,	3	3.3,	38.7,	3	8.7,
20 Oct 87	2.9,	3	0.1,	10.6,	3	1.9,	13.5,	3	1.2,	30.1,	4	24.3,
14 Dec 87	2.2,	3	0.1,	10.4,	3	1.5,	22.3,	3	1.5,	34.8,	3	34.2,
25 Jan 88	2.3,	3	0.0,	13.8,	3	1.2,	16.2,	3	1.3,	80.3,	3	11.9,
2 Mar 88	1.5,	3	0.2,	16.0,	3	0.9,	24.1	3,	6.9,	53.1,	3	29.5,
7 Apr 88	2.9,	3	0.5,	12.2,	3	0.3,	13.5	3,	0.3,	76.7,	3	50.4,
18 May 88	3.0,	3	0.7,	10.7,	3	2.1,	13.6	3,	4.5,	29.2,	3	15.5,
8 Jun 88	3.6,	3	0.6,	10.0,	4	1.2,	13.8	1,		73.8,	4	38.6,
22 Jun 88				56.2,	5,	44.9,						
26 Jul 88												

* 22 May - 26 June 1986 unfiltered water; rest filtered

Appendix Table 1 (continued). Pond 5E selenium.

	Gambusia			Tabanid larvae & pupae			Tabanid adults	
22 May 86	91.3,	2	11.7,	126.8,	1			
28 May 86	113.7,	2	1.1,					
18 Jun 86				84.3,	1			
8 Jul 86	90.4,	2	0.6,					
5 Aug 86	91.7,	2	4.5,	50.6,	2	0.6,		
11 Sep 86	94.9,	3	23.3,	45.9,	2	6.8,		
1 Oct 86	66.9,	3	30.0,	39.4,	3	6.7,		
19 Nov 86	64.8,	6	12.8,	43.1,	3	3.9,		
17 Dec 86	65.5,	1		23.3,	1			
25 Feb 87	68.2,	3	17.5,	37.3,	2	3.6,		
24 Mar 87	43.1,	4	10.1,	35.1,	1			
14 Apr 87	43.6,	3	18.8,	41.6,	1			
28 Apr 87	45.5,	2	3.3,	30.9,	1			
28 May 87								
2 Jun 87	28.1,	7	9.5,	19.5,	1			
21 Jul 87	29.4,	3	5.9,					
8 Sep 87	39.4,	4	3.5,					
20 Oct 87	30.5,	2		33.7,	1			
14 Dec 87	37.7,	2	0.9,					
25 Jan 88	46.0,	3	9.0,					
2 Mar 88	41.6,	2	4.5,					
7 Apr 88	37.2,	4	5.0,					
18 May 88	37.7,	3	3.8,					
8 Jun 88	30.0,	3	5.1,				7.5,	1
22 Jun 88	30.1,	5	6.2,	39.8,	1			
26 Jul 88	25.2,	7	8.5					

Appendix Table 1 (continued). Pond 5E selenium.

	Chironomid larvae & pupae (epifaunal)			Chironomid larvae & pupae (benthic)			Chironomid adults	
22 May 86	136.2,	1						
28 May 86	116.3,	1						
18 Jun 86	119.6,	1						
8 Jul 86								
5 Aug 86								
11 Sep 86								
1 Oct 86								
19 Nov 86				99.6,	1			
17 Dec 86	28.0,	1						
25 Feb 87	51.3,	5	7.1,	48.6,	1		123.0,	1
24 Mar 87	25.6,	4	4.0,	58.8,	1			
14 Apr 87	35.9,	1						
28 Apr 87	36.2,	2	1.7,	48.5,	1			
28 May 87				25.5,	1			
2 Jun 87	38.1,	1		71.5,	5	13.8,		
21 Jul 87				51.7,	1			
8 Sep 87				85.6,	1			
20 Oct 87	44.1,	1		51.0,	1			
14 Dec 87	49.3,	1		47.8,	2	6.1,		
25 Jan 88	42.4,	2	10.3,	46.9,	1			
2 Mar 88	37.1,	4	4.9,	47.8,	3	14.3,		
7 Apr 88	33.2,	4	5.7,	38.3,	3	12.2,		
18 May 88	35.8,	1		38.5,	3	7.9,		
8 Jun 88	24.9,	1		30.3,	1			
22 Jun 88	31.3,	2	2.0,					
26 Jul 88	22.7,	1		69.0,	2	18.5		

Appendix Table 1 (continued). Pond 5E selenium.

	Zygopteran nymphs	Zygopteran adults	Anisopteran nymphs	Anisopteran adults
22 May 86	97.5, 6 31.9,		67.2, 1	
28 May 86	66.0, 2 2.3,	106.0, 1	66.6, 2 10.0,	72.7, 1
18 Jun 86	99.6, 1			
8 Jul 86				
5 Aug 86	56.4, 1			
11 Sep 86	40.9, 1			
1 Oct 86			30.6, 1	
19 Nov 86	30.4, 2 5.2,		23.1, 1	
17 Dec 86				
25 Feb 87	26.2, 2 10.5,			
24 Mar 87	20.0, 1		20.9, 1	
14 Apr 87	13.4, 1		15.3, 1	
28 Apr 87	22.8, 2 0.9,	50.2, 1		
28 May 87				
2 Jun 87	15.8, 1		14.7, 1	
21 Jul 87	22.2, 1			
8 Sep 87		36.8, 1	18.0, 1	
20 Oct 87	25.8, 1		17.3, 1	5.1, 1
14 Dec 87	29.1, 1			
25 Jan 88	28.9, 2 3.2,		25.6, 1	
2 Mar 88	23.1, 3 2.6,		19.5, 2 7.1,	
7 Apr 88	32.3, 1		21.3, 3 5.0,	
18 May 88	14.4, 2 4.2,		14.2, 2 4.5,	
8 Jun 88	6.8, 1			
22 Jun 88	24.4, 1		15.2, 1	
26 Jul 88	14.5, 2 0.7,	18.5, 2 19.4		

Appendix Table 1 (continued). Pond 5E selenium.

	Ephydrid larvae & pupae	Ephydrid adults	Stratiomyid larvae	Syrphid larvae & pupae
22 May 86				
28 May 86				
18 Jun 86	135.0, 1			63.9, 2 37.9,
8 Jul 86				
5 Aug 86	64.6, 1			
11 Sep 86	127.3, 1			
1 Oct 86				
19 Nov 86				
17 Dec 86				
25 Feb 87				
24 Mar 87				
14 Apr 87				
28 Apr 87				
28 May 87				
2 Jun 87				
21 Jul 87				
8 Sep 87				
20 Oct 87				
14 Dec 87				
25 Jan 88				
2 Mar 88				
7 Apr 88				
18 May 88				
8 Jun 88				
22 Jun 88				
26 Jul 88				

Appendix Table 1 (continued). Pond 5E selenium.

	Corixid adults & nymphs	Ephemeroptera nymphs	*Physa*	Plankton
22 May 86				
28 May 86				
18 Jun 86				
8 Jul 86				
5 Aug 86				
11 Sep 86				
1 Oct 86				
19 Nov 86				
17 Dec 86				
25 Feb 87		19.9, 1		
24 Mar 87				
14 Apr 87				
28 Apr 87				
28 May 87				
2 Jun 87				
21 Jul 87				
8 Sep 87				
20 Oct 87				
14 Dec 87	4.7, 1			
25 Jan 88				
2 Mar 88			7.7, 1	
7 Apr 88		16.1, 1	5.3, 1	
18 May 88		17.4, 1	4.0, 2 0.8,	
8 Jun 88			5.4, 2 1.6,	
22 Jun 88			4.4, 1	11.8, 1
26 Jul 88			6.4, 3 1.0,	

Appendix Table 1 (continued). Pond 5E selenium.

	Notonectid adults & nymphs	Isopods	Bees
22 May 86			
28 May 86			
18 Jun 86			
8 Jul 86			
5 Aug 86			
11 Sep 86			
1 Oct 86			
19 Nov 86			
17 Dec 86			
25 Feb 87			
24 Mar 87			
14 Apr 87			
28 Apr 87			
28 May 87			
2 Jun 87			
21 Jul 87			
8 Sep 87			
20 Oct 87			
14 Dec 87			
25 Jan 88			
2 Mar 88			
7 Apr 88			
18 May 88			
8 Jun 88			
22 Jun 88	5.8, 1	39.6, 1	
26 Jul 88			7.3, 1

Appendix Table 1 (continued). Pond 5E selenium.

	Dytiscid larvae	Dytiscid adults	Colepteran larvae	Coleopteran adults
22 May 86				
28 May 86	83.4, 1			
18 Jun 86		74.9, 1		
8 Jul 86				
5 Aug 86		51.3, 1		
11 Sep 86				49.0, 2
1 Oct 86		39.1, 2 14.1,		
19 Nov 86		66.3, 2 27.6,		
17 Dec 86		41.0, 1		20.3, 1
25 Feb 87				
24 Mar 87	14.0, 1			
14 Apr 87	17.2, 1			
28 Apr 87	17.8, 3 1.5,			
28 May 87				
2 Jun 87	11.6, 1			
21 Jul 87		31.3, 1		
8 Sep 87			22.0, 1	
20 Oct 87				
14 Dec 87				
25 Jan 88				
2 Mar 88				
7 Apr 88	17.2, 1	13.3, 1		40.0, 1
18 May 88	16.9, 1			
8 Jun 88		25.3, 1		
22 Jun 88				
26 Jul 88		34.3, 3 23.3		

Appendix Table 1 (continued). Pond 5E selenium.

	Berosus larvae			*Berosus* adults			Hydrophilid larvae		Hydrophilid adults		
22 May 86											
28 May 86											
18 Jun 86	170.4,	1									
8 Jul 86	137.6,	1									
5 Aug 86	103.4,	1							41.8,	1	
11 Sep 86											
1 Oct 86											
19 Nov 86				22.1,	1				16.5,	1	
17 Dec 86	75.2,	1									
25 Feb 87	44.6,	1									
24 Mar 87											
14 Apr 87	84.8,	1									
28 Apr 87	45.7,	1							43.0,	1	
28 May 87											
2 Jun 87	28.1,	1							26.0,	1	
21 Jul 87	28.5,	1									
8 Sep 87	37.5,	1									
20 Oct 87	39.5,	1					20.1,	1	24.1,	2	3.8,
14 Dec 87	44.1,	1									
25 Jan 88	37.8,	2	3.5,								
2 Mar 88	44.0,	3	7.0,								
7 Apr 88	31.5,	2	13.4,						30.6,	1	
18 May 88	40.0,	2	0.8,	50.3,	1						
8 Jun 88	36.5,	2	3.1,	30.9,	1				4.1,	1	
22 Jun 88	27.3,	2	5.4,								
26 Jul 88	27.2,	4	3.9,	20.9,	2	21.0			7.7,	1	

Appendix Table 1 (continued). Pond 5E selenium.

	Typha leaves			*Typha* stems			*Typha* rizomes			*Typha* roots		
22 May 86	25.2,	1					52.6,	1		81.1,	1	
28 May 86												
18 Jun 86												
8 Jul 86												
5 Aug 86												
11 Sep 86												
1 Oct 86				21.1,	2	6.1,	28.5,	1		92.2,	1	
19 Nov 86				16.7,	1		11.5,	1		34.8,	1	
17 Dec 86	8.2,	1					2.3,	1		2.7,	1	
25 Feb 87	5.8,	1		3.6,	1		6.2,	1		13.8,	1	
24 Mar 87	5.0,	1					6.0,	1		26.5,	1	
14 Apr 87	3.9,	1		1.0,	1		5.5,	1		18.8,	1	
28 Apr 87	6.9,	1		3.9,	1		4.3,	1		31.6,	1	
28 May 87												
2 Jun 87	4.1,	2	0.3,	2.7,	2	1.9,	3.0,	3	0.5,	32.8,	2	2.8,
21 Jul 87	2.1,	1		0.2,	1		0.8,	2	0.1,	3.7,	1	
8 Sep 87	3.3,	2	1.3,	1.2,	2		2.1,	3	0.3,	24.0,	2	5.7,
20 Oct 87	3.8,	2	0.7,	1.6,	2	1.3,	4.1,	2	0.1,	21.4,	2	5.8,
14 Dec 87	2.3,	1		1.4,	1		2.0,	1		20.2,	1	
25 Jan 88	3.1,	1		1.2,	1		3.0,	1		28.9,	1	
2 Mar 88	6.2,	1		2.6,	1		7.1,	1		65.6,	1	
7 Apr 88	3.9,	2	1.9,	1.0,	2	0.1,	4.8,	2	0.7,	23.0,	2	15.4,
18 May 88	3.6,	1		0.5,	1		0.4,	1		57.8,	1	
8 Jun 88	7.9,	1		1.7,	1		3.1,	1		45.9,	1	
22 Jun 88	2.8,	1		0.9,	1		9.5,	1		34.4,	1	
26 Jul 88	3.5,	1		0.4,	1		2.6,	1		30.9,	1	

Appendix Table 1 (continued). Pond 5E selenium.

	Scirpus leaves & stems		*Scirpus* seeds			*Scirpus* rhizomes		*Scirpus* roots	
22 May 86									
28 May 86	9.7, 1								
18 Jun 86									
8 Jul 86									
5 Aug 86									
11 Sep 86	5.3, 2	2.1,							
1 Oct 86									
19 Nov 86	6.5, 1		2.4, 1						
17 Dec 86	4.1, 1		5.0, 1						
25 Feb 87									
24 Mar 87									
14 Apr 87	6.6, 1								
28 Apr 87									
28 May 87									
2 Jun 87	6.7, 2	5.6,	2.9, 2		0.1,				
21 Jul 87	7.7, 1		2.0, 1			6.0, 1			
8 Sep 87	1.6, 2	0.2,	2.4, 1			3.8, 1		9.5, 1	
20 Oct 87	2.3, 2	0.5,	1.7, 1			1.5, 1		5.4, 1	
14 Dec 87									
25 Jan 88									
2 Mar 88									
7 Apr 88	4.0, 2	1.1,				5.9, 1		26.6, 1	
18 May 88	2.5, 2	1.2,	2.4, 1			3.3, 1		25.5, 1	
8 Jun 88	3.5, 2	3.3,	2.1, 1			5.8, 1		69.9, 1	
22 Jun 88	5.1, 2	4.8,	2.6, 1			8.5, 1		66.8, 1	
26 Jul 88	1.5, 2	0.1,	1.0, 1			1.6, 1		10.1, 1	

Appendix Table 2. Selenium concentration (ppm dry wt), qualitative plant samples, Ponds 11 and 12.

Pond	Date	Location	Spp #	Species	Wt (g)	Se1	Se2	Se3	Mean
11	03/02/88	Mound	10	Amsinckia	1.35	0.9			0.9
11	03/02/88	Mound	11	Distichlis	2.00	1.3			1.3
11	03/02/88	Dry index site A	2	Erodium	0.10	2.5			2.5
11	03/02/88	Mound	2	Erodium	0.97	1.8			1.8
11	03/02/88	Dry index site A	6	Frankenia	2.04	4.3			4.3
11	03/02/88	Mound	6	Frankenia	4.38	1.1			1.1
11	03/02/88	Central site	13	Heliotropum	0.80	4.5			4.5
11	03/02/88	Dry index site A	5	Lactuca	1.04	8.2			8.2
11	03/02/88	Mound	5	Lactuca	3.02	2.2			2.2
11	03/02/88	Dry index site A	3	Medicago	2.02	14.9	12.7		13.8
11	03/02/88	Mound	3	Medicago	1.68	2.7	2.7		2.7
11	03/02/88	Mound	8	plant spp 8	1.60	4.0			4.0
11	03/02/88	Dry index site A	7	Senecio	1.35	6.1	5.1	4.8	5.3
11	03/02/88	Mound	7	Senecio	0.12	1.6			1.6
11	03/02/88	Central site	7	Senecio	0.86	5.9			5.9
11	03/02/88	Central site	12	Sesuvium	3.47	4.2			4.2
11	03/02/88	North site	1	Sisymbrium	3.13	11.0			11.0
11	03/02/88	Mound	9	Sisymbrium	2.95	1.7			1.7
11	03/02/88	Central site	14	Sisymbrium	1.47	4.7			4.7
11	03/16/88	Transect	21	Atriplex 1	0.48	2.5			2.5
11	03/16/88	Transect	28	Bromus 1	1.84	1.2			1.2
11	03/16/88	Depression 1	11	Distichlis	2.37	1.9			1.9
11	03/16/88	Transect	2	Erodium	1.84	7.5			7.5
11	03/16/88	Depression 1	6	Frankenia	2.74	5.1			5.1
11	03/16/88	Transect	6	Frankenia	6.47	4.1			4.1
11	03/16/88	North edge	26	Kochia	0.97	8.4	6.7		7.6
11	03/16/88	Depression 1	26	Kochia	1.94	7.8	6.7		7.3
11	03/16/88	North edge	5	Lactuca	0.50	9.2			9.2
11	03/16/88	Depression 1	5	Lactuca	2.07	10.9	9.4		10.2
11	03/16/88	Transect	19	Lasthenia	0.26	2.9			2.9
11	03/16/88	Transect	3	Medicago	5.59	4.3			4.3
11	03/16/88	Depression 1	7	Senecio	0.80	10.8	9.3		10.1
11	03/16/88	Transect	7	Senecio	3.30	3.4			3.4
11	03/16/88	North edge	25	Sida	0.55	41.0	38.6		39.8
11	03/16/88	North edge	1	Sisymbrium	2.99	12.8			12.8
11	03/16/88	Transect	24	Sonchus	4.87	2.7			2.7
11	04/20/88	Transect	21	Atriplex 1	0.92	4.8			4.8
11	04/20/88	Depression 1	21	Atriplex 1	3.46	0.3			0.3
11	04/20/88	Depression 1	31	Atriplex 1	5.33	2.6			2.6
11	04/20/88	Transect	28	Bromus 1	2.47	2.0	3.3		2.7
11	04/20/88	Transect	30	Bromus 2	2.09	2.9			2.9
11	04/20/88	Transect	16	Cirsium	2.23	2.0			2.0
11	04/20/88	Transect	27	Cressa	3.95	0.9			0.9
11	04/20/88	Depression 1	27	Cressa	3.83	2.0			2.0
11	04/20/88	Depression 1	27	Cressa	4.05	3.5			3.5
11	04/20/88	Depression 1	11	Distichlis	2.44	0.5			0.5
11	04/20/88	Transect	2	Erodium	2.73	3.0			3.0
11	04/20/88	Transect	6	Frankenia	5.73	2.8			2.8
11	04/20/88	Depression 1	6	Frankenia	4.01	5.2			5.2
11	04/20/88	Transect	18	Hordeum	3.28	1.0			1.0

Appendix Table 2 (continued). Selenium, qualitative plant samples, pond 11 and 12.

Pond	Date	Location	Spp #	Species	Wt (g)	Se1	Se2	Se3	Mean
11	04/20/88	Depression 1	26	Kochia	2.89	1.9			1.9
11	04/20/88	Transect	3	Medicago	3.13	1.4			1.4
11	04/20/88	Transect	7	Senecio	1.81	1.2			1.2
11	04/20/88	Transect	25	Sida	1.47	1.9			1.9
11	04/20/88	Transect	4	Sonchus	1.92	5.0	6.5		5.8
11	05/18/88	Transect	10	Amsinckia	1.20	8.2			8.2
11	05/18/88	Depression 1	31	Atriplex 1	1.81	2.2			2.2
11	05/18/88	Depression 1	21	Atriplex 1	2.03	0.0			0.0
11	05/18/88	Transect	21	Atriplex 1	1.61	3.6			3.6
11	05/18/88	Transect	28	Bromus 1	0.17	2.4	2.2		2.3
11	05/18/88	Transect	30	Bromus 2	0.54	3.7			3.7
11	05/18/88	Depression 1	27	Cressa	1.57	1.6			1.6
11	05/18/88	Transect	27	Cressa	0.82	1.0			1.0
11	05/18/88	North site	11	Distichlis	0.32	1.1	0.6		0.9
11	05/18/88	North site	11	Distichlis	1.16	1.3			1.3
11	05/18/88	Transect	2	Erodium	0.89	4.1			4.1
11	05/18/88	Depression 1	6	Frankenia	2.25	3.9	4.0		4.0
11	05/18/88	Transect	6	Frankenia	1.96	2.8			2.8
11	05/18/88	Depression 1	26	Kochia	2.63	1.6			1.6
11	05/18/88	Transect	25	Sida	1.47	3.1			3.1
11	05/18/88	Transect	4	Sonchus	0.94	4.0			4.0
11	06/08/88	North edge	21	Atriplex 1	3.97	0.5			0.5
11	06/08/88	Transect	21	Atriplex 1	4.99	1.2			1.2
11	06/08/88	Depression 1	21	Atriplex 1	7.72	0.0			0.0
11	06/08/88	Transect	21a	Atriplex 2	7.64	0.0	0.0		0.0
11	06/08/88	Transect	33	Centaurea	7.01	7.5	5.0		6.3
11	06/08/88	Wet index site	27	Cressa	6.60	2.8			2.8
11	06/08/88	North edge	27	Cressa	3.66	0.4	1.5		1.0
11	06/08/88	Transect	27	Cressa	4.98	2.1			2.1
11	06/08/88	Depression 1	27	Cressa	6.54	0.3			0.3
11	06/08/88	Dry index site A	32	Cuscuta	4.40	0.5			0.5
11	06/08/88	Wet index site	11	Distichlis	6.68	0.9			0.9
11	06/08/88	North edge	11	Distichlis	1.47	1.0			1.0
11	06/08/88	Transect	11	Distichlis	1.11	0.4			0.4
11	06/08/88	Transect	11	Distichlis	2.68	1.9			1.9
11	06/08/88	Transect	11	Distichlis	0.45	3.7	1.8		2.8
11	06/08/88	North edge	6	Frankenia	3.06	2.1			2.1
11	06/08/88	Transect	6	Frankenia	5.61	2.3			2.3
11	06/08/88	Depression 1	6	Frankenia	7.81	2.0			2.0
11	06/08/88	Wet index site	26	Kochia	6.15	0.8			0.8
11	06/08/88	Depression 1	26	Kochia	7.49	2.2			2.2
11	06/08/88	Transect	34	plant spp 34	4.78	5.0			5.0
11	06/08/88	Transect	25	Sida	5.13	8.2	11.4		9.8
11	06/08/88	Transect	4	Sonchus	9.60	6.8			6.8
11	06/08/88	Transect	4	Sonchus	5.10	4.4			4.4
11	07/06/88	Frankenberger site 8		Citrus	93.25	6.1	6.9		6.5
11	07/06/88	Frankenberger site 26		Manure	74.80	4.5			4.5
11	07/06/88	Frankenberger site 5		Straw	93.98	4.8			4.8
12	03/02/88		10	Amsinckia	2.37	0.8			0.8
12	03/02/88		21	Atriplex 1	0.35	2.6			2.6
12	03/02/88		16	Cirsium	0.07	5.9			5.9
12	03/02/88		15	Cotula	2.41	5.8			5.8
12	03/02/88		11	Distichlis	1.63	3.5			3.5

Appendix Table 2 (continued). Selenium, qualitative plant samples, pond 11 and 12.

Pond	Date	Location	Spp #	Species	Wt (g)	Se1	Se2	Se3	Mean
12	03/02/88		2	Erodium	1.14	2.6	2.0		2.3
12	03/02/88		20	Erodium	1.66	8.4			8.4
12	03/02/88		2	Erodium	1.35	3.8			3.8
12	03/02/88		6	Frankenia	1.44	3.3			3.3
12	03/02/88		18	Hordeum	1.07	6.8			6.8
12	03/02/88		26	Kochia	1.64	7.8			7.8
12	03/02/88		19	Lasthenia	0.69	3.2			3.2
12	03/02/88		22	Lupinus	0.32	3.7			3.7
12	03/02/88		3	Medicago	3.22	4.4			4.4
12	03/02/88		17	Rumex	1.38	6.0			6.0
12	03/02/88		23	Rumex	1.25	3.4	4.2		3.8
12	03/02/88		7	Senecio	3.09	5.6			5.6
12	03/02/88		12	Sesuvium	3.95	2.5			2.5
12	03/02/88		25	Sida	0.73	4.6			4.6
12	03/02/88		24	Sonchus	1.42	6.4			6.4

Appendix Table 3. Biomass (g) and selenium concentration (ppm dry wt), quantitative plant samples, Pond 11.

Pond	Date	Location	Repl	Sample type	Wt (g)	Se1	Se2	Mean
11	03/02/88	Dry index site a	1	Distichlis	0.27	1.8	1.8	1.8
11	03/02/88	Dry index site a	2	Distichlis	0.13	2.3		2.3
11	03/02/88	Dry index site a	3	Distichlis	0.47	1.9	1.9	1.9
11	03/02/88	Dry index site a	1	dead vegetation	4.11	3.1		3.1
11	03/02/88	Dry index site a	2	dead vegetation	4.22	9.3		9.3
11	03/02/88	Dry index site a	3	dead vegetation	5.82	3.8		3.8
11	03/02/88	Dry index site a	1	Cressa seeds	1.68	2.4		2.4
11	03/02/88	Dry index site a	2	Cressa seeds	0.97	8.8		8.8
11	03/02/88	Dry index site a	3	Cressa seeds	1.39	5.6		5.6
11	03/02/88	Dry index site a	1	detritus	10.92	24.1	24.2	24.2
11	03/02/88	Dry index site a	2	detritus	16.20	38.5		38.5
11	03/02/88	Dry index site a	3	detritus	15.61	32.8		32.8
11	03/02/88	Dry index site a	1	roots	3.83	26.0		26.0
11	03/02/88	Dry index site a	2	roots	5.88	28.7		28.7
11	03/02/88	Dry index site a	3	roots	6.32	42.5		42.5
11	03/02/88	Dry index site a	1	soil	293.18	27.3		27.3
11	03/02/88	Dry index site a	2	soil	212.92	21.6		21.6
11	03/02/88	Dry index site a	3	soil	271.96	22.6		22.6
11	03/02/88	Dry index site a		sweep seeds	5.66	2.0		2.0
11	03/02/88	Dry index site a		sweep seeds	10.79	1.0		1.0
11	03/16/88	Dry index site a	1	Distichlis	0.04	4.5	4.2	4.4
11	03/16/88	Dry index site a	2	Distichlis	0.26	2.9	2.7	2.8
11	03/16/88	Dry index site a	3	Distichlis	0.92	2.8		2.8
11	03/16/88	Dry index site a	1	dead vegetation	14.74	27.5		27.5
11	03/16/88	Dry index site a	2	dead vegetation	13.51	71.0		71.0
11	03/16/88	Dry index site a	3	dead vegetation	14.60	28.1		28.1
11	03/16/88	Dry index site a	1	Cressa seeds	0.24	5.1		5.1
11	03/16/88	Dry index site a	2	Cressa seeds	26.52	120.0		120.0
11	03/16/88	Dry index site a	3	Cressa seeds	0.04	3.7		3.7
11	03/16/88	Dry index site a	1	detritus	17.32	109.0		109.0
11	03/16/88	Dry index site a	2	detritus	0.09	7.9		7.9
11	03/16/88	Dry index site a	3	detritus	12.65	81.6		81.6
11	03/16/88	Dry index site a	1	roots	52.33	24.8	25.1	25.0
11	03/16/88	Dry index site a	2	roots	43.58	37.6		37.6
11	03/16/88	Dry index site a	3	roots	58.27	54.7		54.7
11	03/16/88	Dry index site a	1	soil	483.46	18.5		18.5
11	03/16/88	Dry index site a	2	soil	413.72	14.1		14.1
11	03/16/88	Dry index site a	3	soil	177.34	51.1		51.1
11	04/20/88	Dry index site a	1	Cressa	0.29	3.2		3.2
11	04/20/88	Dry index site a	2	Cressa	0.34	2.5		2.5
11	04/20/88	Dry index site a	3	Cressa	0.24	4.2		4.2
11	04/20/88	Dry index site a	4	Cressa	0.57	2.0		2.0
11	04/20/88	Dry index site a	5	Cressa	0.23	3.1		3.1
11	04/20/88	Dry index site a	6	Cressa	0.67	2.7	4.2	3.5
11	04/20/88	Dry index site a	1	Distichlis	0.62	3.1		3.1
11	04/20/88	Dry index site a	2	Distichlis	0.08	4.6		4.6
11	04/20/88	Dry index site a	3	Distichlis	0.75	4.9		4.9
11	04/20/88	Dry index site a	4	Distichlis	0.03	3.8		3.8
11	04/20/88	Dry index site a	5	Distichlis	0.65	4.8		4.8
11	04/20/88	Dry index site a	6	Distichlis	1.72	2.9		2.9

Appendix Table 3 (continued). Quantitative plant samples, Pond 11.

Pond	Date	Location	Repl	Sample type	Wt (g)	Se1	Se2	Mean
11	04/20/88	Dry index site a	1	dead vegetation	11.43	50.6		50.6
11	04/20/88	Dry index site a	2	dead vegetation	8.21	63.2		63.2
11	04/20/88	Dry index site a	3	dead vegetation	13.63	18.5	19.6	19.1
11	04/20/88	Dry index site a	4	dead vegetation	14.42	9.3		9.3
11	04/20/88	Dry index site a	5	dead vegetation	17.14	48.2		48.2
11	04/20/88	Dry index site a	6	dead vegetation	20.70	42.0		42.0
11	04/20/88	Dry index site a	1	Cressa seeds	0.06	4.0		4.0
11	04/20/88	Dry index site a	2	Cressa seeds	0.06	7.4		7.4
11	04/20/88	Dry index site a	3	Cressa seeds	74.12			
11	04/20/88	Dry index site a	1	detritus	8.72	64.5	63.4	64.0
11	04/20/88	Dry index site a	2	detritus	10.09	66.4		66.4
11	04/20/88	Dry index site a	3	detritus	11.50	66.7		66.7
11	04/20/88	Dry index site a	1	roots	14.06	37.5		37.5
11	04/20/88	Dry index site a	2	roots	13.84	21.6		21.6
11	04/20/88	Dry index site a	3	roots	12.75	40.2		40.2
11	04/20/88	Dry index site a	1	soil	413.43	16.8		16.8
11	04/20/88	Dry index site a	2	soil	478.35	12.5		12.5
11	04/20/88	Dry index site a	3	soil	413.90	12.3		12.3
11	05/18/88	Dry index site a	1	Cressa	0.92	0.0		0.0
11	05/18/88	Dry index site a	2	Cressa	1.35	3.5		3.5
11	05/18/88	Dry index site a	3	Cressa	1.73	1.8		1.8
11	05/18/88	Dry index site a	1	Distichlis	3.28	1.1		1.1
11	05/18/88	Dry index site a	2	Distichlis	1.08	1.2		1.2
11	05/18/88	Dry index site a	3	Distichlis	2.02	1.2		1.2
11	05/18/88	Dry index site a	1	dead vegetation	8.18	2.8		2.8
11	05/18/88	Dry index site a	2	dead vegetation	6.61	2.7		2.7
11	05/18/88	Dry index site a	3	dead vegetation	9.52	3.5		3.5
11	05/18/88	Dry index site a	1	Cressa seeds	0.70	4.2		4.2
11	05/18/88	Dry index site a	2	Cressa seeds	1.05	6.0		6.0
11	05/18/88	Dry index site a	3	Cressa seeds	2.96	7.4		7.4
11	05/18/88	Dry index site a	1	detritus	7.19	37.1		37.1
11	05/18/88	Dry index site a	2	detritus	10.86	76.8		76.8
11	05/18/88	Dry index site a	3	detritus	19.02	80.2		80.2
11	05/18/88	Dry index site a	1	roots	13.49	51.1	51.7	51.4
11	05/18/88	Dry index site a	2	roots	11.32	16.7		16.7
11	05/18/88	Dry index site a	3	roots	11.44	32.9		32.9
11	05/18/88	Dry index site a	1	soil	393.14	21.4		21.4
11	05/18/88	Dry index site a	2	soil	392.08	17.9		17.9
11	05/18/88	Dry index site a	3	soil	318.67	27.1	26.6	26.9
11	06/08/88	Dry index site a	1	Cressa	1.08	1.2		1.2
11	06/08/88	Dry index site a	2	Cressa	1.00	1.5		1.5
11	06/08/88	Dry index site a	3	Cressa	0.86	1.3		1.3
11	06/08/88	Dry index site a	1	Distichlis	0.90	2.1	1.4	1.8
11	06/08/88	Dry index site a	2	Distichlis	2.44	0.9		0.9
11	06/08/88	Dry index site a	3	Distichlis	1.78	0.9		0.9
11	06/08/88	Dry index site a	1	Frankenia	0.26	3.9		3.9
11	06/08/88	Dry index site a	2	Frankenia	0.38	2.5		2.5
11	06/08/88	Dry index site a	3	Frankenia	0.00			
11	06/08/88	Dry index site a	1	dead vegetation	6.81	19.9		19.9
11	06/08/88	Dry index site a	2	dead vegetation	9.93	7.2		7.2
11	06/08/88	Dry index site a	3	dead vegetation	10.14	19.1		19.1
11	06/08/88	Dry index site a	1	Cressa seeds	0.15	9.7		9.7
11	06/08/88	Dry index site a	3	Cressa seeds	0.06	2.0		2.0
11	06/08/88	Dry index site a	2	Cressa seeds	0.00	12.1		12.1

Appendix Table 3 (continued). Quantitative plant samples, Pond 11.

Pond	Date	Location	Repl	Sample type	Wt (g)	Se1	Se2	Mean
11	06/08/88	Dry index site a	1	detritus	10.64	48.8		48.8
11	06/08/88	Dry index site a	3	detritus	9.85	62.9	62.4	62.7
11	06/08/88	Dry index site a	2	detritus	9.02	62.0		62.0
11	06/08/88	Dry index site a	1	roots	8.14	49.0		49.0
11	06/08/88	Dry index site a	2	roots	26.10	56.7	50.2	53.5
11	06/08/88	Dry index site a	3	roots	14.45	44.3		44.3
11	06/08/88	Dry index site a	1	soil	303.47	21.0	22.5	21.8
11	06/08/88	Dry index site a	2	soil	306.42	17.8		17.8
11	06/08/88	Dry index site a	3	soil	269.41	11.9		11.9
11	07/06/88	Dry index site a	1	Cressa	0.97	1.5		1.5
11	07/06/88	Dry index site a	2	Cressa	1.40	2.1		2.1
11	07/06/88	Dry index site a	3	Cressa	0.96	6.0		6.0
11	07/06/88	Dry index site a	1	Distichlis	3.43	1.7	2.1	1.9
11	07/06/88	Dry index site a	2	Distichlis	2.15	1.4		1.4
11	07/06/88	Dry index site a	3	Distichlis	1.73	1.6		1.6
11	07/06/88	Dry index site a	1	Frankenia	0.00			
11	07/06/88	Dry index site a	2	Frankenia	0.00			
11	07/06/88	Dry index site a	3	Frankenia	0.51	1.9		1.9
11	07/06/88	Dry index site a	1	dead vegetation	14.39	3.7		3.7
11	07/06/88	Dry index site a	2	dead vegetation	11.91	20.2	20.5	20.4
11	07/06/88	Dry index site a	3	dead vegetation	7.40	43.8		43.8
11	07/06/88	Dry index site a	1	Cressa seeds	0.28	1.5	1.4	1.5
11	07/06/88	Dry index site a	2	Cressa seeds	0.23	2.1		2.1
11	07/06/88	Dry index site a	3	Cressa seeds	0.07	2.4		2.4
11	07/06/88	Dry index site a	1	detritus	11.08	82.7		82.7
11	07/06/88	Dry index site a	2	detritus	20.06	64.2	67.2	65.7
11	07/06/88	Dry index site a	3	detritus	16.53	82.9		82.9
11	07/06/88	Dry index site a	1	roots	29.70	4.4		4.4
11	07/06/88	Dry index site a	2	roots	13.24	18.4	15.3	16.9
11	07/06/88	Dry index site a	3	roots	7.93	7.2		7.2
11	07/06/88	Dry index site a	1	soil	300.78	15.7		15.7
11	07/06/88	Dry index site a	2	soil	296.36	16.0		16.0
11	07/06/88	Dry index site a	3	soil	240.87	20.1		20.1
11	07/06/88	Dry index site a		sweep seeds	0.43			
11	07/06/88	Dry index site a		sweep seeds	0.33			
11	08/09/88	Dry index site a	1	Cressa	0.58			
11	08/09/88	Dry index site a	2	Cressa	0.26			
11	08/09/88	Dry index site a	3	Cressa	0.55			
11	08/09/88	Dry index site a	1	Distichlis	2.98			
11	08/09/88	Dry index site a	2	Distichlis	2.41			
11	08/09/88	Dry index site a	3	Distichlis	3.25			
11	08/09/88	Dry index site a	1	Frankenia	0.00			
11	08/09/88	Dry index site a	2	Frankenia	1.40			
11	08/09/88	Dry index site a	3	Frankenia	0.52			
11	08/09/88	Dry index site a	1	dead vegetation	10.41			
11	08/09/88	Dry index site a	2	dead vegetation	13.60			
11	08/09/88	Dry index site a	3	dead vegetation	13.53			
11	08/09/88	Dry index site a	1	Cressa seeds	0.08	3.4		3.4
11	08/09/88	Dry index site a	2	Cressa seeds	0.03	2.8		2.8
11	08/09/88	Dry index site a	3	Cressa seeds	0.07	1.7		1.7
11	08/09/88	Dry index site a	1	detritus	11.28	79.8		79.8
11	08/09/88	Dry index site a	2	detritus	9.73	70.9		70.9
11	08/09/88	Dry index site a	3	detritus	6.75	74.8		74.8
11	08/09/88	Dry index site a	1	roots	19.76			

Appendix Table 3 (continued). Quantitative plant samples, Pond 11.

Pond	Date	Location	Repl	Sample type	Wt (g)	Se1	Se2	Mean
11	08/09/88	Dry index site a	2	roots	21.20			
11	08/09/88	Dry index site a	3	roots	22.29			
11	08/09/88	Dry index site a	.	soil	433.42	16.2		16.2
11	08/09/88	Dry index site a	2	soil	359.66	14.5		14.5
11	08/09/88	Dry index site a	3	soil	425.70	17.4		17.4

Appendix Table 4. Arthropod biomass (mg) and numbers (100 sweeps), Pond 11.

Pond	Date	Location	Repl	Species	N	Wt (mg)
11	05/18/88	Dry index site a	1	Ant	4	3
11	05/18/88	Dry index site a	2	Ant	0	0
11	05/18/88	Dry index site a	3	Ant	0	0
11	05/18/88	Dry index site a	1	Beetle	0	0
11	05/18/88	Dry index site a	2	Beetle	0	0
11	05/18/88	Dry index site a	3	Beetle	0	0
11	05/18/88	Dry index site a	1	Caterpiller	1	5
11	05/18/88	Dry index site a	2	Caterpiller	0	0
11	05/18/88	Dry index site a	3	Caterpiller	0	0
11	05/18/88	Dry index site a	1	Damselfly	0	0
11	05/18/88	Dry index site a	2	Damselfly	0	0
11	05/18/88	Dry index site a	3	Damselfly	0	0
11	05/18/88	Dry index site a	1	Earwig	0	0
11	05/18/88	Dry index site a	2	Earwig	0	0
11	05/18/88	Dry index site a	3	Earwig	0	0
11	05/18/88	Dry index site a	1	Fly	14	11
11	05/18/88	Dry index site a	2	Fly	29	21
11	05/18/88	Dry index site a	3	Fly	109	68
11	05/18/88	Dry index site a	1	Grasshopper	11	95
11	05/18/88	Dry index site a	2	Grasshopper	17	61
11	05/18/88	Dry index site a	3	Grasshopper	6	35
11	05/18/88	Dry index site a	1	Hemiptera	0	0
11	05/18/88	Dry index site a	2	Hemiptera	3	3
11	05/18/88	Dry index site a	3	Hemiptera	0	0
11	05/18/88	Dry index site a	1	Leafhopper	17	10
11	05/18/88	Dry index site a	2	Leafhopper	15	7
11	05/18/88	Dry index site a	3	Leafhopper	91	52
11	05/18/88	Dry index site a	1	Sowbug	0	0
11	05/18/88	Dry index site a	2	Sowbug	0	0
11	05/18/88	Dry index site a	3	Sowbug	0	0
11	05/18/88	Dry index site a	1	Spider	0	0
11	05/18/88	Dry index site a	2	Spider	3	16
11	05/18/88	Dry index site a	3	Spider	0	0
11	05/18/88	Dry index site a	1	Weevil	1	2
11	05/18/88	Dry index site a	2	Weevil	0	0
11	05/18/88	Dry index site a	3	Weevil	1	1
11	06/08/88	Dry index site a	1	Ant	0	0
11	06/08/88	Dry index site a	2	Ant	0	0
11	06/08/88	Dry index site a	3	Ant	0	0
11	06/08/88	Dry index site a	1	Beetle	0	0
11	06/08/88	Dry index site a	2	Beetle	0	0
11	06/08/88	Dry index site a	3	Beetle	0	0
11	06/08/88	Dry index site a	1	Caterpiller	0	0
11	06/08/88	Dry index site a	2	Caterpiller	0	0
11	06/08/88	Dry index site a	3	Caterpiller	0	0
11	06/08/88	Dry index site a	1	Damselfly	0	0
11	06/08/88	Dry index site a	2	Damselfly	5	71
11	06/08/88	Dry index site a	3	Damselfly	0	0
11	06/08/88	Dry index site a	1	Earwig	0	0
11	06/08/88	Dry index site a	2	Earwig	0	0

Appendix Table 4 (continued). Arthropod biomass and numbers, Pond 11.

Pond	Date	Location	Repl	Species	N	Wt (mg)
11	06/08/88	Dry index site a	3	Earwig	0	0
11	06/08/88	Dry index site a	1	Fly	1	1
11	06/08/88	Dry index site a	2	Fly	6	8
11	06/08/88	Dry index site a	3	Fly	0	0
11	06/08/88	Dry index site a	1	Grasshopper	56	657
11	06/08/88	Dry index site a	2	Grasshopper	32	214
11	06/08/88	Dry index site a	3	Grasshopper	0	0
11	06/08/88	Dry index site a	1	Hemiptera	0	0
11	06/08/88	Dry index site a	2	Hemiptera	1	1
11	06/08/88	Dry index site a	3	Hemiptera	0	0
11	06/08/88	Dry index site a	1	Leafhopper	27	20
11	06/08/88	Dry index site a	2	Leafhopper	27	17
11	06/08/88	Dry index site a	3	Leafhopper	0	0
11	06/08/88	Dry index site a	1	Sowbug	0	0
11	06/08/88	Dry index site a	2	Sowbug	0	0
11	06/08/88	Dry index site a	3	Sowbug	0	0
11	06/08/88	Dry index site a	1	Spider	1	1
11	06/08/88	Dry index site a	2	Spider	2	2
11	06/08/88	Dry index site a	3	Spider	0	0
11	06/08/88	Dry index site a	1	Weevil	0	0
11	06/08/88	Dry index site a	2	Weevil	0	0
11	06/08/88	Dry index site a	3	Weevil	0	0
11	07/06/88	Dry index site a	1	Ant	2	3
11	07/06/88	Dry index site a	2	Ant	0	0
11	07/06/88	Dry index site a	3	Ant	1	1
11	07/06/88	Dry index site a	1	Fly	0	0
11	07/06/88	Dry index site a	2	Fly	0	0
11	07/06/88	Dry index site a	3	Fly	2	4
11	07/06/88	Dry index site a	1	Grasshopper	24	434
11	07/06/88	Dry index site a	2	Grasshopper	33	702
11	07/06/88	Dry index site a	3	Grasshopper	36	850
11	07/06/88	Dry index site a	1	Hemiptera	0	0
11	07/06/88	Dry index site a	2	Hemiptera	0	0
11	07/06/88	Dry index site a	3	Hemiptera	1	12
11	07/06/88	Dry index site a	1	Leafhopper	1	2
11	07/06/88	Dry index site a	2	Leafhopper	0	0
11	07/06/88	Dry index site a	3	Leafhopper	0	0
11	07/06/88	Dry index site a	1	Spider	2	10
11	07/06/88	Dry index site a	2	Spider	0	0
11	07/06/88	Dry index site a	3	Spider	1	6
11	08/08/88	Dry index site a	1	Grasshopper	13	576
11	08/08/88	Dry index site a	2	Grasshopper	8	331
11	08/08/88	Dry index site a	3	Grasshopper	15	668

Appendix Table 5. Arthropod selenium concentration (ppm dry wt), Pond 11.

Pond	Date	Location	Repl	Species	N	Wt (g)	Se1	Se2	Mean
11	03/16/88	Upland site		Earwig	1	0.011	9.9		9.9
11	03/16/88	Upland site		Grasshopper	2	0.304	9.2		9.2
11	03/16/88	Upland site		Sowbug	5	0.036	44.3		44.3
11	05/18/88	Dry index site a	1	Ants	4	0.003	9.1		9.1
11	05/18/88	Dry index site a	1	Caterillar (green)	1	0.005	4.1		4.1
11	05/18/88	Dry index site a	1	Fly spp a	42	0.055	6.1		6.1
11	05/18/88	Dry index site a	1	Fly spp b	86	0.037	67.0		67.0
11	05/18/88	Dry index site a	1	Fly spp c & d	20	0.005	8.0		8.0
11	05/18/88	dry index site a	1	Grasshopper	34	0.191	2.6		2.6
11	05/18/88	Dry index site a	2	Hemiptera	2	0.003	4.3		4.3
11	05/18/88	Dry index site a	1	Leafhopper	121	0.068	1.6	1.8	1.7
11	05/18/88	Dry index site a	2	Spiders	3	0.016	7.9		7.9
11	05/18/88	Dry index site a	1	Weevil	2	0.003	4.2		4.2
11	06/08/88	Dry index site a	3	Beetles	3	0.004	1.5		1.5
11	06/08/88	Dry index site a	2	Damselfly	5	0.071	4.3		4.3
11	06/08/88	Dry index site a	2	Fly	4	0.005	1.8		1.8
11	06/08/88	Dry index site a	3	Fly	1	0.001	2.8		2.8
11	06/08/88	Dry index site a	2	Fly spp a	2	0.002	23.3		23.3
11	06/08/88	Dry index site a	3	Fly spp a	5	0.008	6.7		6.7
11	06/08/88	Dry index site a	1	Grasshopper	56	0.657	1.9	1.9	1.9
11	06/08/88	Dry index site a	2	Grasshopper	32	0.214	1.6		1.6
11	06/08/88	Dry index site a	3	Grasshopper	38	0.411	2.0	2.3	2.2
11	06/08/88	Dry index site a	2	Hemiptera	1	0.001	9.6		9.6
11	06/08/88	Dry index site a	1	Leafhopper	27	0.020	2.0		2.0
11	06/08/88	Dry index site a	2	Leafhopper	27	0.017	1.6		1.6
11	06/08/88	Dry index site a	3	Leafhopper	27	0.021	1.9		1.9
11	06/08/88	Dry index site a	2	Spiders	2	0.002	5.7		5.7
11	07/06/88	Dry index site a	1	Spiders	3	0.016			
11	07/06/88	Dry index site a	1	Grasshopper spp 1	22	0.377			
11	07/06/88	Dry index site a	1	Grasshopper spp 2	1	0.047			
11	07/06/88	Dry index site a	1	Grasshopper spp 3	1	0.050			
11	07/06/88	Dry index site a	2	Grasshopper spp 1	32	0.665			
11	07/06/88	Dry index site a	2	Grasshopper spp 2	2	0.041			
11	07/06/88	Dry index site a	3	Grasshopper spp 1	35	0.846			
11	07/06/88	Dry index site a	3	Hemiptera	1	0.012			
11	08/08/88	Dry index site a	1	Grasshopper spp 1	13	0.576			
11	08/08/88	Dry index site a	2	Grasshopper spp 1	8	0.331			
11	08/08/88	Dry index site a	3	Grasshopper spp 1	15	0.668			

Appendix Table 6. Synoptic survey, mean plant biomass (g/m^2) per pond, (6 July 88).

	Distichlis				Cressa				Frankenia			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
4	270.1	7	122.7	46.4	0.0	7	0.0	0.0	0.0	7	0.0	0.0
5	263.4	3	251.3	145.1	0.0	3	0.0	0.0	0.0	3	0.0	0.0
6	534.8	9	332.9	111.0	1.3	9	2.6	0.9	13.5	9	21.0	7.0
7	724.5	9	284.3	94.8	0.0	9	0.0	0.0	0.0	9	0.0	0.0
8	178.3	6	68.8	28.1	74.8	6	63.2	25.8	0.0	6	0.0	0.0
9	364.0	3	175.5	101.3	0.0	3	0.0	0.0	0.0	3	0.0	0.0
10	191.9	9	121.5	40.5	70.0	9	41.8	13.9	6.6	9	15.4	5.1
11	110.2	33	72.4	12.6	62.2	33	73.7	12.8	4.4	33	11.0	1.9
12	319.2	9	177.3	59.1	28.4	9	31.9	10.6	0.0	9	0.0	0.0

	Atriplix (21a)				Sida				Sonchus				Sesuvium			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
4	0.0	7	0.0	0.0	0.0	7	0.0	0.0	0.0	7	0.0	0.0	0.0	7	0.0	0.0
5	65.4	3	103.3	59.7	0.0	3	0.0	0.0	0.0	3	0.0	0.0	0.0	3	0.0	0.0
6	0.0	9	0.0	0.0	0.0	9	0.0	0.0	1.82	9	5.46	1.8	0.959	9	2.876	0.959
7	1.0	9	2.4	0.8	0.27	9	0.82	0.3	0.0	9	0.0	0.0	0.0	9	0.0	0.0
8	5.9	6	14.5	5.9	0.0	6	0.0	0.0	0.0	6	0.0	0.0	0.0	6	0.0	0.0
9	0.0	3	0.0	0.0	0.0	3	0.0	0.0	0.0	3	0.0	0.0	0.0	3	0.0	0.0
10	0.0	9	0.0	0.0	0.0	9	0.0	0.0	0.0	9	0.0	0.0	0.0	9	0.0	0.0
11	0.0	33	0.0	0.0	0.0	33	0.0	0.0	0.0	33	0.0	0.0	0.0	33	0.0	0.0
12	0.0	9	0.0	0.0	0.25	9	0.76	0.3	0.0	9	0.0	0.0	0.0	9	0.0	0.0

Appendix Table 7. Synoptic survey, mean plant biomass (g/m^2) per station, (6 July 1988).

	Distichlis				Cressa				Frankenia			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
p4-27	344.2	3	68.9	39.8	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p4-28	214.5	4	131.7	65.9	0.0	4	0.0	0.0	0.0	4	0.0	0.0
p5-26	263.4	3	251.3	145.1	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p6-23	734.2	3	263.7	152.2	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p6-24	742.1	3	35.3	20.4	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p6-25	128.2	3	22.4	12.9	3.9	3	3.4	1.9	40.4	3	11.7	6.8
p7-18	907.7	3	217.2	125.4	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p7-19	524.9	3	33.9	19.6	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p7-20	740.9	3	405.5	234.1	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p8-21	155.0	3	54.8	31.6	19.2	3	18.8	10.9	0.0	3	0.0	0.0
p8-22	201.5	3	85.0	49.1	130.3	3	18.9	10.9	0.0	3	0.0	0.0
p9-14	364.0	3	175.5	101.3	0.0	3	0.0	0.0	0.0	3	0.0	0.0
p10-15	334.2	3	63.0	36.4	65.6	3	47.3	27.3	0.0	3	0.0	0.0
p10-16	122.9	3	55.0	31.7	104.6	3	32.0	18.5	19.8	3	23.5	13.6
p10-17	118.5	3	80.5	46.5	39.9	3	23.1	13.3	0.0	3	0.0	0.0
p11-1	144.8	3	26.7	15.4	99.1	3	39.0	22.5	8.8	3	15.2	8.8
p11-2	44.3	3	18.5	10.7	119.1	3	70.7	40.8	14.7	3	25.5	14.7
p11-3	99.4	3	51.7	29.9	75.2	3	23.2	13.4	0.0	3	0.0	0.0
p11-4	221.8	3	56.4	32.6	189.7	3	124.8	72.0	0.0	3	0.0	0.0
p11-4a	16.8	3	29.2	16.8	132.1	3	23.1	13.3	0.0	3	0.0	0.0
p11-5	104.3	3	16.7	9.6	0.0	3	0.0	0.0	8.5	3	14.7	8.5
p11-6	198.9	3	87.9	50.8	0.0	3	0.0	0.0	2.5	3	4.3	2.5
p11-7	108.2	3	4.8	2.8	14.4	3	11.8	6.8	10.8	3	18.7	10.8
p11-8	36.0	3	20.0	11.5	10.5	3	11.8	6.8	0.0	3	0.0	0.0
p11-9	102.5	3	54.7	31.6	9.7	3	4.3	2.5	2.7	3	4.7	2.7
p11-10	135.5	3	57.0	32.9	34.3	3	15.4	8.9	0.0	3	0.0	0.0
p12-11	445.8	3	101.3	58.5	54.9	3	20.8	12.0	0.0	3	0.0	0.0
p12-12	309.3	3	217.8	125.7	29.2	3	38.4	22.2	0.0	3	0.0	0.0
p12-13	202.3	3	152.6	88.1	1.3	3	2.2	1.3	0.0	3	0.0	0.0

Appendix Table 7 (continued). Synoptic survey, mean plant biomass (g/m^2) per station, (6 July 1988).

	Atriplix (21a)				Sida				Sonchus				Sesuvium			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
p4-27	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p4-28	0.0	4	0.0	0.0	0.000	4	0.000	0.000	0.00	4	0.00	0.00	0.00	4	0.00	0.00
p5-26	65.4	3	103.3	59.7	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p6-23	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p6-24	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p6-25	0.0	3	0.0	0.0	0.000	3	0.000	0.000	5.46	3	9.45	5.46	2.88	3	4.98	2.88
p7-18	0.6	3	1.1	0.6	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p7-19	2.4	3	4.2	2.4	0.822	3	1.423	0.822	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p7-20	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p8-21	11.9	3	20.5	11.9	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p8-22	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p9-14	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p10-15	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p10-16	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p10-17	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-1	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-2	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-3	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-4	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-4a	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-5	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-6	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-7	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-8	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-9	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p11-10	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p12-11	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p12-12	0.0	3	0.0	0.0	0.000	3	0.000	0.000	0.00	3	0.00	0.00	0.00	3	0.00	0.00
p12-13	0.0	3	0.0	0.0	0.763	3	1.321	0.763	0.00	3	0.00	0.00	0.00	3	0.00	0.00

Appendix Table 8. Synoptic survey, plant biomass (g) and selenium concentration (ppm dry wt).

Date	Station	Repl	Spp #	Species	Wt (g)	Se11	Se12	Mean
07/06/88	p6-23	1	4	Sonchus	0.00			
07/06/88	p6-23	2	4	Sonchus	0.00			
07/06/88	p6-23	3	4	Sonchus	0.00			
07/06/88	p6-24	1	4	Sonchus	0.00			
07/06/88	p6-24	2	4	Sonchus	0.00			
07/06/88	p6-24	3	4	Sonchus	0.00			
07/06/88	p6-25	1	4	Sonchus	0.00			
07/06/88	p6-25	2	4	Sonchus	0.00			
07/06/88	p6-25	3	4	Sonchus	0.93	3.5		3.5
07/06/88	p6-23	1	6	Frankenia	0.00			
07/06/88	p6-23	2	6	Frankenia	0.00			
07/06/88	p6-23	3	6	Frankenia	0.00			
07/06/88	p6-24	1	6	Frankenia	0.00			
07/06/88	p6-24	2	6	Frankenia	0.00			
07/06/88	p6-24	3	6	Frankenia	0.00			
07/06/88	p6-25	1	6	Frankenia	2.93			
07/06/88	p6-25	2	6	Frankenia	1.60			
07/06/88	p6-25	3	6	Frankenia	2.35			
07/06/88	p10-15	1	6	Frankenia	0.00			
07/06/88	p10-15	2	6	Frankenia	0.00			
07/06/88	p10-15	3	6	Frankenia	0.00			
07/06/88	p10-16	1	6	Frankenia	0.77			
07/06/88	p10-16	2	6	Frankenia	0.00			
07/06/88	p10-16	3	6	Frankenia	2.60			
07/06/88	p10-17	1	6	Frankenia	0.00			
07/06/88	p10-17	2	6	Frankenia	0.00			
07/06/88	p10-17	3	6	Frankenia	0.00			
07/06/88	p11-1	1	6	Frankenia	1.50	5.2	4.9	5.1
07/06/88	p11-1	2	6	Frankenia	0.00			
07/06/88	p11-1	3	6	Frankenia	0.00			
07/06/88	p11-2	1	6	Frankenia	0.00			
07/06/88	p11-2	1	6	Frankenia	2.51	3.0		3.0
07/06/88	p11-2	3	6	Frankenia	0.00			
07/06/88	p11-3	1	6	Frankenia	0.00			
07/06/88	p11-3	2	6	Frankenia	0.00			
07/06/88	p11-3	3	6	Frankenia	0.00			
07/06/88	p11-4	1	6	Frankenia	0.00			
07/06/88	p11-4	2	6	Frankenia	0.00			
07/06/88	p11-4	3	6	Frankenia	0.00			
07/06/88	p11-4a	1	6	Frankenia	0.00			
07/06/88	p11-4a	2	6	Frankenia	0.00			
07/06/88	p11-4a	3	6	Frankenia	0.00			
07/06/88	p11-5	1	6	Frankenia	1.45	1.4		1.4
07/06/88	p11-5	2	6	Frankenia	0.00			
07/06/88	p11-5	3	6	Frankenia	0.00			
07/06/88	p11-6	1	6	Frankenia	0.00			
07/06/88	p11-6	2	6	Frankenia	0.00			
07/06/88	p11-6	3	6	Frankenia	0.42	1.3	1.2	1.3
07/06/88	p11-7	1	6	Frankenia	1.84	1.1		1.1
07/06/88	p11-7	2	6	Frankenia	0.00			

Appendix Table 8 (continued). Synoptic survey, plants.

Date	Station	Repl	Spp #	Species	Wt (g)	Sel1	Sel2	Mean
07/06/88	p11-7	3	6	Frankenia	0.00			
07/06/88	p11-8	1	6	Frankenia	0.00			
07/06/88	p11-8	2	6	Frankenia	0.00			
07/06/88	p11-8	3	6	Frankenia	0.00			
07/06/88	p11-9	1	6	Frankenia	0.46	2.7		2.7
07/06/88	p11-9	2	6	Frankenia	0.00			
07/06/88	p11-9	3	6	Frankenia	0.00			
07/06/88	p11-10	1	6	Frankenia	0.00			
07/06/88	p11-10	2	6	Frankenia	0.00			
07/06/88	p11-10	3	6	Frankenia	0.00			
07/06/88	p4-27	1	11	Distichlis	18.82			
07/06/88	p4-27	2	11	Distichlis	23.78			
07/06/88	p4-27	3	11	Distichlis	16.06			
07/06/88	p4-28	1	11	Distichlis	6.95			
07/06/88	p4-28	2	11	Distichlis	5.83			
07/06/88	p4-28	3	11	Distichlis	13.91			
07/06/88	p4-28	4	11	Distichlis	22.04			
07/06/88	p5-26	1	11	Distichlis	31.44			
07/06/88	p5-26	2	11	Distichlis	6.92			
07/06/88	p5-26	3	11	Distichlis	6.52			
07/06/88	p6-23	1	11	Distichlis	34.29			
07/06/88	p6-23	2	11	Distichlis	58.94			
07/06/88	p6-23	3	11	Distichlis	31.88			
07/06/88	p6-24	1	11	Distichlis	44.19			
07/06/88	p6-24	2	11	Distichlis	40.18			
07/06/88	p6-24	3	11	Distichlis	42.08			
07/06/88	p6-25	1	11	Distichlis	5.81			
07/06/88	p6-25	2	11	Distichlis	8.06			
07/06/88	p6-25	3	11	Distichlis	7.97			
07/06/88	p7-18	1	11	Distichlis	57.30			
07/06/88	p7-18	2	11	Distichlis	59.98			
07/06/88	p7-18	3	11	Distichlis	37.40			
07/06/88	p7-19	1	11	Distichlis	30.55			
07/06/88	p7-19	2	11	Distichlis	31.26			
07/06/88	p7-19	3	11	Distichlis	27.63			
07/06/88	p7-20	1	11	Distichlis	66.02			
07/06/88	p7-20	2	11	Distichlis	20.08			
07/06/88	p7-20	3	11	Distichlis	40.15			
07/06/88	p8-21	1	11	Distichlis	12.14			
07/06/88	p8-21	2	11	Distichlis	5.98			
07/06/88	p8-21	3	11	Distichlis	8.30			
07/06/88	p8-22	1	11	Distichlis	16.32			
07/06/88	p8-22	2	11	Distichlis	11.34			
07/06/88	p8-22	3	11	Distichlis	6.67			
07/06/88	p9-14	1	11	Distichlis	27.68			
07/06/88	p9-14	2	11	Distichlis	9.26			
07/06/88	p9-14	3	11	Distichlis	25.08			
07/06/88	p10-15	1	11	Distichlis	17.44			
07/06/88	p10-15	2	11	Distichlis	16.43			
07/06/88	p10-15	3	11	Distichlis	23.07			
07/06/88	p10-16	1	11	Distichlis	10.46			
07/06/88	p10-16	2	11	Distichlis	6.07			
07/06/88	p10-16	3	11	Distichlis	4.42			
07/06/88	p10-17	1	11	Distichlis	11.26			

Appendix Table 8 (continued). Synoptic survey, plants.

Date	Station	Repl	Spp #	Species	Wt (g)	Sel1	Sel2	Mean
07/06/88	p10-17	2	11	Distichlis	2.12			
07/06/88	p10-17	3	11	Distichlis	6.81			
07/06/88	p11-1	1	11	Distichlis	6.47	2.4		2.4
07/06/88	p11-1	2	11	Distichlis	9.09	2.6	2.1	2.4
07/06/88	p11-1	3	11	Distichlis	9.11			
07/06/88	p11-2	1	11	Distichlis	2.38	1.8		1.8
07/06/88	p11-2	2	11	Distichlis	3.63	2.7		2.7
07/06/88	p11-2	3	11	Distichlis	1.54	4.1	3.6	3.9
07/06/88	p11-3	1	11	Distichlis	6.81	1.5		1.5
07/06/88	p11-3	2	11	Distichlis	7.82	2.4		2.4
07/06/88	p11-3	3	11	Distichlis	2.30	1.6		1.6
07/06/88	p11-4	1	11	Distichlis	8.93	2.2		2.2
07/06/88	p11-4	2	11	Distichlis	14.03	1.4		1.4
07/06/88	p11-4	3	11	Distichlis	14.84	1.6		1.6
07/06/88	p11-4a	1	11	Distichlis	0.00			
07/06/88	p11-4a	2	11	Distichlis	0.00			
07/06/88	p11-4a	3	11	Distichlis	2.87	0.8	0.4	0.6
07/06/88	p11-5	1	11	Distichlis	6.73	0.8		0.8
07/06/88	p11-5	2	11	Distichlis	6.17	1.3		1.3
07/06/88	p11-5	3	11	Distichlis	4.88	0.8	0.1	0.5
07/06/88	p11-6	1	11	Distichlis	16.84	1.1		1.1
07/06/88	p11-6	2	11	Distichlis	7.14	1.0		1.0
07/06/88	p11-6	3	11	Distichlis	9.92	1.2		1.2
07/06/88	p11-7	1	11	Distichlis	5.83	0.4		0.4
07/06/88	p11-7	2	11	Distichlis	6.29	0.9		0.9
07/06/88	p11-7	3	11	Distichlis	6.32	0.8		0.8
07/06/88	p11-8	1	11	Distichlis	2.39	0.8		0.8
07/06/88	p11-8	2	11	Distichlis	0.78	0.8		0.8
07/06/88	p11-8	3	11	Distichlis	2.97	0.7		0.7
07/06/88	p11-9	1	11	Distichlis	4.19	1.1		1.1
07/06/88	p11-9	2	11	Distichlis	9.40	1.5		1.5
07/06/88	p11-9	3	11	Distichlis	3.87	1.1		1.1
07/06/88	p11-10	1	11	Distichlis	4.18	0.7		0.7
07/06/88	p11-10	2	11	Distichlis	10.55	1.0		1.0
07/06/88	p11-10	3	11	Distichlis	8.36	1.2		1.2
07/06/88	p12-11	1	11	Distichlis	31.32			
07/06/88	p12-11	2	11	Distichlis	19.85			
07/06/88	p12-11	3	11	Distichlis	24.80			
07/06/88	p12-12	1	11	Distichlis	27.77			
07/06/88	p12-12	2	11	Distichlis	21.13			
07/06/88	p12-12	3	11	Distichlis	3.81			
07/06/88	p12-13	1	11	Distichlis	4.72	3.2		3.2
07/06/88	p12-13	2	11	Distichlis	8.49			
07/06/88	p12-13	3	11	Distichlis	21.26			
07/06/88	p6-23	1	12	Sesuvium	0.00			
07/06/88	p6-23	2	12	Sesuvium	0.00			
07/06/88	p6-23	3	12	Sesuvium	0.00			
07/06/88	p6-24	1	12	Sesuvium	0.00			
07/06/88	p6-24	2	12	Sesuvium	0.00			
07/06/88	p6-24	3	12	Sesuvium	0.00			
07/06/88	p6-25	1	12	Sesuvium	0.00			
07/06/88	p6-25	2	12	Sesuvium	0.49	7.1		7.1
07/06/88	p6-25	3	12	Sesuvium	0.00			
07/06/88	p5-26	1	21a	Atriplex2	0.00			

Appendix Table 8 (continued). Synoptic survey, plants.

Date	Station	Repl	Spp #	Species	Wt (g)	Sel1	Sel2	Mean
07/06/88	p5-26	2	21a	Atriplex2	0.66	9.0		9.0
07/06/88	p5-26	3	21a	Atriplex2	10.48	7.0		7.0
07/06/88	p7-18	1	21a	Atriplex2	0.00			
07/06/88	p7-18	2	21a	Atriplex2	0.00			
07/06/88	p7-18	3	21a	Atriplex2	0.11	9.3		9.3
07/06/88	p7-19	1	21a	Atriplex2	0.00			
07/06/88	p7-19	2	21a	Atriplex2	0.41	11.6	11.1	11.4
07/06/88	p7-19	3	21a	Atriplex2	0.00			
07/06/88	p7-20	1	21a	Atriplex2	0.00			
07/06/88	p7-20	2	21a	Atriplex2	0.00			
07/06/88	p7-20	3	21a	Atriplex2	0.00			
07/06/88	p8-21	1	21a	Atriplex2	2.02	1.3		1.3
07/06/88	p8-21	2	21a	Atriplex2	0.00			
07/06/88	p8-21	3	21a	Atriplex2	0.00			
07/06/88	p8-22	1	21a	Atriplex2	0.00			
07/06/88	p8-22	2	21a	Atriplex2	0.00			
07/06/88	p8-22	3	21a	Atriplex2	0.00			
07/06/88	p7-18	1	25	Sida	0.00			
07/06/88	p7-18	2	25	Sida	0.00			
07/06/88	p7-18	3	25	Sida	0.00			
07/06/88	p7-19	1	25	Sida	0.00			
07/06/88	p7-19	2	25	Sida	0.14	20.2		20.2
07/06/88	p7-19	3	25	Sida	0.00			
07/06/88	p7-20	1	25	Sida	0.00			
07/06/88	p7-20	2	25	Sida	0.00			
07/06/88	p7-20	3	25	Sida	0.00			
07/06/88	p12-11	1	25	Sida	0.00			
07/06/88	p12-11	2	25	Sida	0.00			
07/06/88	p12-11	3	25	Sida	0.00			
07/06/88	p12-12	1	25	Sida	0.00			
07/06/88	p12-12	2	25	Sida	0.00			
07/06/88	p12-12	3	25	Sida	0.00			
07/06/88	p12-13	1	25	Sida	0.00			
07/06/88	p12-13	2	25	Sida	0.13	19.2		19.2
07/06/88	p12-13	3	25	Sida	0.00			
07/06/88	p6-23	1	27	Cressa	0.00			
07/06/88	p6-23	2	27	Cressa	0.00			
07/06/88	p6-23	3	27	Cressa	0.00			
07/06/88	p6-24	1	27	Cressa	0.00			
07/06/88	p6-24	2	27	Cressa	0.00			
07/06/88	p6-24	3	27	Cressa	0.00			
07/06/88	p6-25	1	27	Cressa	0.00			
07/06/88	p6-25	2	27	Cressa	0.35			
07/06/88	p6-25	3	27	Cressa	0.31			
07/06/88	p8-21	1	27	Cressa	1.13			
07/06/88	p8-21	2	27	Cressa	0.00			
07/06/88	p8-21	3	27	Cressa	2.14			
07/06/88	p8-22	1	27	Cressa	6.19			
07/06/88	p8-22	2	27	Cressa	8.23			
07/06/88	p8-22	3	27	Cressa	7.79			
07/06/88	p10-15	1	27	Cressa	2.70			
07/06/88	p10-15	2	27	Cressa	6.77			
07/06/88	p10-15	3	27	Cressa	1.70			
07/06/88	p10-16	1	27	Cressa	3.92			

Appendix Table 8 (continued). Synoptic survey, plants.

Date	Station	Repl	Spp #	Species	Wt (g)	Sel1	Sel2	Mean
07/06/88	p10-16	2	27	Cressa	7.43			
07/06/88	p10-16	3	27	Cressa	6.48			
07/06/88	p10-17	1	27	Cressa	1.54			
07/06/88	p10-17	2	27	Cressa	3.78			
07/06/88	p10-17	3	27	Cressa	1.48			
07/06/88	p11-1	1	27	Cressa	8.16	3.1		3.1
07/06/88	p11-1	2	27	Cressa	4.67	3.2		3.2
07/06/88	p11-1	3	27	Cressa	4.05	2.6		2.6
07/06/88	p11-2	1	27	Cressa	11.13	2.7		2.7
07/06/88	p11-2	2	27	Cressa	3.22	5.0		5.0
07/06/88	p11-2	3	27	Cressa	5.95	4.2		4.2
07/06/88	p11-3	1	27	Cressa	5.79	1.9		1.9
07/06/88	p11-3	2	27	Cressa	3.56	2.4		2.4
07/06/88	p11-3	3	27	Cressa	3.46	2.0	2.0	2.0
07/06/88	p11-4	1	27	Cressa	3.63	3.3		3.3
07/06/88	p11-4	2	27	Cressa	17.80	3.1		3.1
07/06/88	p11-4	3	27	Cressa	10.90	2.3		2.3
07/06/88	p11-4a	1	27	Cressa	8.62	0.9		0.9
07/06/88	p11-4a	2	27	Cressa	7.83	1.3		1.3
07/06/88	p11-4a	3	27	Cressa	6.06	0.8		0.8
07/06/88	p11-5	1	27	Cressa	0.00			
07/06/88	p11-5	2	27	Cressa	0.00			
07/06/88	p11-5	3	27	Cressa	0.00			
07/06/88	p11-6	1	27	Cressa	0.00			
07/06/88	p11-6	2	27	Cressa	0.00			
07/06/88	p11-6	3	27	Cressa	0.00			
07/06/88	p11-7	1	27	Cressa	0.23	0.5		0.5
07/06/88	p11-7	2	27	Cressa	1.55	0.6		0.6
07/06/88	p11-7	3	27	Cressa	0.68	0.3		0.3
07/06/88	p11-8	1	27	Cressa	1.32	0.5	0.5	0.5
07/06/88	p11-8	2	27	Cressa	0.47	0.5		0.5
07/06/88	p11-8	3	27	Cressa	0.00			
07/06/88	p11-9	1	27	Cressa	0.32	2.3		2.3
07/06/88	p11-9	2	27	Cressa	0.53	3.1		3.1
07/06/88	p11-9	3	27	Cressa	0.81	1.8		1.8
07/06/88	p11-10	1	27	Cressa	2.48	1.1		1.1
07/06/88	p11-10	2	27	Cressa	0.94	1.9		1.9
07/06/88	p11-10	3	27	Cressa	2.43	1.0		1.0
07/06/88	p12-11	1	27	Cressa	2.47			
07/06/88	p12-11	2	27	Cressa	2.40			
07/06/88	p12-11	3	27	Cressa	4.48			
07/06/88	p12-12	1	27	Cressa	0.84			
07/06/88	p12-12	2	27	Cressa	0.00			
07/06/88	p12-12	3	27	Cressa	4.13			
07/06/88	p12-13	1	27	Cressa	0.22	12.4		12.4
07/06/88	p12-13	2	27	Cressa	0.00			
07/06/88	p12-13	3	27	Cressa	0.00			

Appendix Table 9. Synoptic survey, mean plant selenium concentration (ppm dry wt) per pond, partial data (6 July 1988).

	Distichlis				Cressa				Frankenia			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
4		0				0				0		
5		0				0				0		
6		0				0				0		
7		0				0				0		
8		0				0				0		
9		0				0				0		
10		0				0				0		
11	1.4	30	0.77	0.14	2.0	26	1.24	0.24	2.4	6	1.52	0.62
12	3.2	1			12.4	1				0		

	Atriplix (21a)				Sida				Sonchus				Sesuvium			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
4		0				0				0				0		
5	8.0	2	1.41	1.00		0				0				0		
6		0				0			3.5	1			7.1	1		
7	10.3	2	1.45	1.02	20.2	1				0				0		
8	1.3	1				0				0				0		
9		0				0				0				0		
10		0				0				0				0		
11		0				0				0				0		
12		0			19.2	1				0				0		

Appendix Table 10. Synoptic survey, mean plant selenium concentration (ppm dry wt) per station, portion data (6 July 1988).

	Distichlis				Cressa				Frankenia			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
p4-27		0				0				0		
p4-28		0				0				0		
p5-26		0				0				0		
p6-23		0				0				0		
p6-24		0				0				0		
p6-25		0				0				0		
p7-18		0				0				0		
p7-19		0				0				0		
p7-20		0				0				0		
p8-21		0				0				0		
p8-22		0				0				0		
p9-14		0				0				0		
p10-15		0				0				0		
p10-16		0				0				0		
p10-17		0				0				0		
p11-1	2.4	2	0.04	0.03	3.0	3	0.32	0.19	5.1	1		
p11-2	2.8	3	1.03	0.59	4.0	3	1.17	0.67	3.0	1		
p11-3	1.8	3	0.49	0.28	2.1	3	0.26	0.15		0		
p11-4	1.7	3	0.42	0.24	2.9	3	0.53	0.31		0		
p11-4a	0.6	1			1.0	3	0.26	0.15		0		
p11-5	0.9	3	0.43	0.25		0			1.4	1		
p11-6	1.1	3	0.10	0.06		0			1.3	1		
p11-7	0.7	3	0.26	0.15	0.5	3	0.15	0.09	1.1	1		
p11-8	0.8	3	0.06	0.03	0.5	2	0.00	0.00		0		
p11-9	1.2	3	0.23	0.13	2.4	3	0.66	0.38	2.7	1		
p11-10	1.0	3	0.25	0.15	1.3	3	0.49	0.28		0		
p12-11		0				0				0		
p12-12		0				0				0		
p12-13	3.2	1			12.4	1				0		

Appendix Table 10 (continued). Synoptic survey, mean plant selenium concentration (ppm dry wt) per station, (6 July 1988).

	Atriplix (21a)				Sida				Sonchus				Sesuvium			
Pond	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE	Mean	N	SD	SE
p4-27		0				0				0				0		
p4-28		0				0				0				0		
p5-26	8.0	2	1.41	1.00		0				0				0		
p6-23		0				0				0				0		
p6-24		0				0				0				0		
p6-25		0				0			3.5	1			7.1	1		
p7-18	9.3	1				0				0				0		
p7-19	11.4	1			20.2	1				0				0		
p7-20		0				0				0				0		
p8-21	1.3	1				0				0				0		
p8-22		0				0				0				0		
p9-14		0				0				0				0		
p10-15		0				0				0				0		
p10-16		0				0				0				0		
p10-17		0				0				0				0		
p11-1		0				0				0				0		
p11-2		0				0				0				0		
p11-3		0				0				0				0		
p11-4		0				0				0				0		
p11-4a		0				0				0				0		
p11-5		0				0				0				0		
p11-6		0				0				0				0		
p11-7		0				0				0				0		
p11-8		0				0				0				0		
p11-9		0				0				0				0		
p11-10		0				0				0				0		
p12-11		0				0				0				0		
p12-12		0				0				0				0		
p12-13		0			19.2	1				0				0		

Appendix Table 11. Synoptic survey, mean insect numbers per station and pond (50 sweeps).

	Mean		N		SD	
Station	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
p4-27	2.3	0.0	3	3	0.6	0.0
p4-28	6.0	0.0	4	4	6.3	0.0
p5-26	0.3	0.0	3	3	0.6	0.0
p6-23	3.3	0.0	3	3	4.2	0.0
p6-24	5.7	0.0	3	3	1.2	0.0
p6-25	27.3	0.0	3	3	8.3	0.0
p7-18	11.3	0.0	3	3	2.1	0.0
p7-19	6.0	19.3	3	3	7.2	5.9
p7-20	2.7	17.0	3	3	2.5	16.5
p8-21	16.3	0.0	3	3	3.8	0.0
p8-22	5.3	0.0	3	3	1.5	0.0
p9-14	7.7	0.0	3	3	8.1	0.0
p10-15	22.7	0.0	3	3	8.6	0.0
p10-16	4.7	0.0	3	3	0.6	0.0
p10-17	29.0	0.0	3	3	8.7	0.0
p11-1	14.7	0.0	3	3	10.1	0.0
p11-2	11.0	0.0	3	3	2.6	0.0
p11-3	28.7	0.0	3	3	5.5	0.0
p11-4	6.3	7.0	3	3	3.5	2.6
p11-4a	3.7	0.0	3	3	2.9	0.0
p11-5	6.3	0.0	3	3	3.5	0.0
p11-6	0.7	13.0	3	3	1.2	16.8
p11-7	1.7	0.0	3	3	1.5	0.0
p11-8	2.3	4.7	3	3	1.5	2.1
p11-9	12.0	0.0	3	3	2.6	0.0
p11-10	14.0	0.0	3	3	10.5	0.0
p12-11	2.0	0.0	3	3	1.0	0.0
p12-12	8.3	0.0	3	3	5.1	0.0
p12-13	26.7	0.0	3	3	12.1	0.0

	Mean		N		SD	
Pond	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
4	4.43	0.00	7	7	1.25	0.00
5	0.33	0.00	3	3	0.09	0.00
6	12.11	0.00	9	9	3.65	0.00
7	6.67	12.11	9	9	1.62	3.73
8	10.83	0.00	6	6	1.53	0.00
9	7.67	0.00	3	3	1.20	0.00
10	18.78	0.00	9	9	3.69	0.00
11	9.21	2.24	33	33	5.31	3.52
12	12.33	0.00	9	9	3.80	0.00

Appendix Table 12. Synoptic survey, mean insect biomass (mg) per station and pond (50 sweeps).

	Mean		N		SD	
Station	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
p4-27	34.0	0.0	3	3	12.5	0.0
p4-28	109.3	0.0	4	4	116.4	0.0
p5-26	9.3	0.0	3	3	16.2	0.0
p6-23	71.7	0.0	3	3	104.8	0.0
p6-24	155.7	0.0	3	3	50.8	0.0
p6-25	621.7	0.0	3	3	271.5	0.0
p7-18	141.7	0.0	3	3	58.6	0.0
p7-19	124.3	15.3	3	3	163.8	6.8
p7-20	44.0	16.3	3	3	39.4	14.4
p8-21	308.3	0.0	3	3	43.1	0.0
p8-22	113.7	0.0	3	3	10.1	0.0
p9-14	258.7	0.0	3	3	283.9	0.0
p10-15	380.7	0.0	3	3	207.7	0.0
p10-16	82.3	0.0	3	3	15.9	0.0
p10-17	510.3	0.0	3	3	148.4	0.0
p11-1	288.0	0.0	3	3	162.5	0.0
p11-2	270.0	0.0	3	3	66.0	0.0
p11-3	500.3	0.0	3	3	60.3	0.0
p11-4	102.7	3.0	3	3	36.9	1.0
p11-4a	79.7	0.0	3	3	75.7	0.0
p11-5	221.3	0.0	3	3	72.0	0.0
p11-6	17.3	10.0	3	3	30.0	12.5
p11-7	24.0	0.0	3	3	25.6	0.0
p11-8	22.7	3.0	3	3	13.6	1.0
p11-9	456.3	0.0	3	3	218.5	0.0
p11-10	275.7	0.0	3	3	133.9	0.0
p12-11	72.3	0.0	3	3	62.8	0.0
p12-12	203.7	0.0	3	3	254.3	0.0
p12-13	785.3	0.0	3	3	407.2	0.0

	Mean		N		SD	
Pond	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
4	77.0	0.0	7	7	23.5	0.0
5	9.3	0.0	3	3	2.4	0.0
6	283.0	0.0	9	9	87.3	0.0
7	103.3	10.6	9	9	29.5	3.3
8	211.0	0.0	6	6	25.7	0.0
9	258.7	0.0	3	3	41.9	0.0
10	324.4	0.0	9	9	67.5	0.0
11	205.3	1.5	33	33	109.9	2.6
12	353.8	0.0	9	9	120.4	0.0

Appendix Table 13. Synoptic survey, mean insect selenium concentration (ppm dry wt) per station and pond (50 sweeps).

	Mean		N		SD	
Station	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
p4-27	3.7		3	0	1.01	
p4-28	2.9		3	0	0.42	
p5-26	3.5		1	0		
p6-23	3.2		2	0	0.14	
p6-24	2.7		3	0	0.40	
p6-25	6.6		3	0	0.95	
p7-18	6.4		3	0	0.78	
p7-19	7.5	5.6	2	3	3.18	0.15
p7-20	3.6	2.8	2	2	0.57	
p8-21	3.1		3	0	0.95	
p8-22	4.0		3	0	1.00	
p9-14	5.0		3	0	0.86	
p10-15	5.1		3	0	0.69	
p10-16	2.9		3	0	0.57	
p10-17	4.5		3	0	0.50	
p11-1	2.1		3	0	0.61	
p11-2	3.2		3	0	0.40	
p11-3	2.0		3	0	0.35	
p11-4	2.8	3.0	3	1	0.40	
p11-4a	2.5		3	0	0.66	
p11-5	3.3		3	0	0.68	
p11-6	2.3	1.9	1	2		0.28
p11-7	1.9		2	0	0.07	
p11-8	1.8	1.7	3	1	0.12	
p11-9	3.5		3	0	0.40	
p11-10	1.8		3	0	0.51	
p12-11	2.7		3	0	0.21	
p12-12	2.9		3	0	0.81	
p12-13	5.8		3	0	0.26	

	Mean		N		SD	
Pond	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers	Grasshopper	Leafhoppers
4	3.3		6	0	0.24	
5	3.5		1	0	0.00	
6	4.3		8	0	0.69	
7	5.9	4.5	7	5	0.68	0.40
8	3.6		6	0	0.29	
9	5.0		3	0	0.16	
10	4.1		9	0	0.40	
11	2.5	2.1	30	4	0.52	0.14
12	3.8		9	0	0.57	

Appendix Table 14. Synoptic survey, insect numbers, biomass (g), and selenium concentration (ppm dry wt).

Date	Station	Repl	Sample	N	Wt (g)	Se1	Se2	Mean
07/06/88	p4-27	1	Grasshopper	2	0.030	4.6		4.6
07/06/88	p4-27	2	Grasshopper	2	0.024	2.6		2.6
07/06/88	p4-27	3	Grasshopper	3	0.048	3.8		3.8
07/06/88	p4-28	1	Grasshopper	14	0.263	3.0		3.0
07/06/88	p4-28	2	Grasshopper	8	0.132	3.2		3.2
07/06/88	p4-28	3	Grasshopper	2	0.042	2.4		2.4
07/06/88	p4-28	4	Grasshopper	0	0.000			
07/06/88	p5-26	1	Grasshopper	0	0.000			
07/06/88	p5-26	2	Grasshopper	0	0.000			
07/06/88	p5-26	3	Grasshopper	1	0.028	3.5		3.5
07/06/88	p6-23	1	Grasshopper	2	0.023	3.3		3.3
07/06/88	p6-23	2	Grasshopper	0	0.000			
07/06/88	p6-23	3	Grasshopper	8	0.192	3.1		3.1
07/06/88	p6-24	1	Grasshopper	5	0.214	2.9		2.9
07/06/88	p6-24	2	Grasshopper	5	0.121	2.9		2.9
07/06/88	p6-24	3	Grasshopper	7	0.132	2.2		2.2
07/06/88	p6-25	1	Grasshopper	18	0.310	6.0	6.5	6.3
07/06/88	p6-25	2	Grasshopper	30	0.748	7.7		7.7
07/06/88	p6-25	3	Grasshopper	34	0.807	5.9		5.9
07/06/88	p7-18	1	Grasshopper	13	0.120	6.9		6.9
07/06/88	p7-18	2	Grasshopper	9	0.097	5.5		5.5
07/06/88	p7-18	3	Grasshopper	12	0.208	6.8		6.8
07/06/88	p7-19	1	Grasshopper	0	0.000			
07/06/88	p7-19	2	Grasshopper	4	0.063	5.2		5.2
07/06/88	p7-19	3	Grasshopper	14	0.310	9.7		9.7
07/06/88	p7-20	1	Grasshopper	0	0.000			
07/06/88	p7-20	2	Grasshopper	5	0.076	4.0		4.0
07/06/88	p7-20	3	Grasshopper	3	0.056	3.2		3.2
07/06/88	p7-18	1	Leafhoppers	0	0.000			
07/06/88	p7-18	2	Leafhoppers	0	0.000			
07/06/88	p7-18	3	Leafhoppers	0	0.000			
07/06/88	p7-19	1	Leafhoppers	26	0.023	5.8		5.8
07/06/88	p7-19	2	Leafhoppers	17	0.013	5.6		5.6
07/06/88	p7-19	3	Leafhoppers	15	0.010	5.5		5.5
07/06/88	p7-20	1	Leafhoppers	0	0.000			
07/06/88	p7-20	2	Leafhoppers	18	0.022	2.8		2.8
07/06/88	p7-20	3	Leafhoppers	33	0.027	2.8		2.8
07/06/88	p8-21	1	Grasshopper	19	0.356	2.6		2.6
07/06/88	p8-21	2	Grasshopper	18	0.297	2.5		2.5
07/06/88	p8-21	3	Grasshopper	12	0.272	4.2		4.2
07/06/88	p8-22	1	Grasshopper	4	0.123	5.0		5.0
07/06/88	p8-22	2	Grasshopper	7	0.115	3.0		3.0
07/06/88	p8-22	3	Grasshopper	5	0.103	4.1		4.1
07/06/88	p9-14	1	Grasshopper	4	0.154	4.1		4.1
07/06/88	p9-14	2	Grasshopper	17	0.580	5.2		5.2
07/06/88	p9-14	3	Grasshopper	2	0.042	5.8		5.8
07/06/88	p10-15	1	Grasshopper	32	0.616	4.9		4.9
07/06/88	p10-15	2	Grasshopper	21	0.303	4.2	4.7	4.5
07/06/88	p10-15	3	Grasshopper	15	0.223	5.8		5.8
07/06/88	p10-16	1	Grasshopper	4	0.064	3.5		3.5

Appendix Table 14 (continued). Synoptic survey, insects.

Date	Station	Repl	Sample	N	Wt (g)	Se1	Se2	Mean
07/06/88	p10-16	2	Grasshopper	5	0.092	2.7		2.7
07/06/88	p10-16	3	Grasshopper	5	0.091	2.4		2.4
07/06/88	p10-17	1	Grasshopper	24	0.342	4.0		4.0
07/06/88	p10-17	2	Grasshopper	24	0.567	4.5		4.5
07/06/88	p10-17	3	Grasshopper	39	0.622	5.0		5.0
07/06/88	p11-1	1	Grasshopper	20	0.424	1.4		1.4
07/06/88	p11-1	2	Grasshopper	3	0.108	2.2		2.2
07/06/88	p11-1	3	Grasshopper	21	0.332	2.6		2.6
07/06/88	p11-2	1	Grasshopper	9	0.221	3.3		3.3
07/06/88	p11-2	2	Grasshopper	14	0.244	2.8		2.8
07/06/88	p11-2	3	Grasshopper	10	0.345	3.6		3.6
07/06/88	p11-3	1	Grasshopper	34	0.493	2.2		2.2
07/06/88	p11-3	2	Grasshopper	29	0.564	2.5	1.9	2.2
07/06/88	p11-3	3	Grasshopper	23	0.444	1.6		1.6
07/06/88	p11-4	1	Grasshopper	10	0.134	2.6		2.6
07/06/88	p11-4	2	Grasshopper	3	0.112	2.6		2.6
07/06/88	p11-4	3	Grasshopper	6	0.062	3.3		3.3
07/06/88	p11-4a	1	Grasshopper	2	0.034	3.1		3.1
07/06/88	p11-4a	2	Grasshopper	2	0.038	1.8		1.8
07/06/88	p11-4a	3	Grasshopper	7	0.167	2.6		2.6
07/06/88	p11-5	1	Grasshopper	3	0.220	3.8		3.8
07/06/88	p11-5	2	Grasshopper	10	0.294	3.5		3.5
07/06/88	p11-5	3	Grasshopper	6	0.150	2.5		2.5
07/06/88	p11-6	1	Grasshopper	2	0.052	2.3		2.3
07/06/88	p11-6	2	Grasshopper	0	0.000			
07/06/88	p11-6	3	Grasshopper	0	0.000			
07/06/88	p11-7	1	Grasshopper	0	0.000			
07/06/88	p11-7	2	Grasshopper	2	0.021	1.9		1.9
07/06/88	p11-7	3	Grasshopper	3	0.051	1.8		1.8
07/06/88	p11-8	1	Grasshopper	4	0.037	1.7		1.7
07/06/88	p11-8	2	Grasshopper	2	0.021	1.9		1.9
07/06/88	p11-8	3	Grasshopper	1	0.010	1.9		1.9
07/06/88	p11-9	1	Grasshopper	9	0.227	3.1		3.1
07/06/88	p11-9	2	Grasshopper	13	0.662	3.6		3.6
07/06/88	p11-9	3	Grasshopper	14	0.480	3.9		3.9
07/06/88	p11-10	1	Grasshopper	25	0.381	1.2		1.2
07/06/88	p11-10	2	Grasshopper	13	0.321	2.2		2.2
07/06/88	p11-10	3	Grasshopper	4	0.125	1.9		1.9
07/06/88	p11-1	1	Leafhoppers	0	0.000			
07/06/88	p11-1	2	Leafhoppers	0	0.000			
07/06/88	p11-1	3	Leafhoppers	0	0.000			
07/06/88	p11-2	1	Leafhoppers	0	0.000			
07/06/88	p11-2	2	Leafhoppers	0	0.000			
07/06/88	p11-2	3	Leafhoppers	0	0.000			
07/06/88	p11-3	1	Leafhoppers	0	0.000			
07/06/88	p11-3	2	Leafhoppers	0	0.000			
07/06/88	p11-3	3	Leafhoppers	0	0.000			
07/06/88	p11-4	1	Leafhoppers	9	0.003	3.0		3.0
07/06/88	p11-4	2	Leafhoppers	8	0.004			
07/06/88	p11-4	3	Leafhoppers	4	0.002			
07/06/88	p11-4a	1	Leafhoppers	0	0.000			
07/06/88	p11-4a	2	Leafhoppers	0	0.000			
07/06/88	p11-4a	3	Leafhoppers	0	0.000			
07/06/88	p11-5	1	Leafhoppers	0	0.000			

Appendix Table 14 (continued). Synoptic survey, insects.

Date	Station	Repl	Sample	N	Wt (g)	Se1	Se2	Mean
07/06/88	p11-5	2	Leafhoppers	0	0.000			
07/06/88	p11-5	3	Leafhoppers	0	0.000			
07/06/88	p11-6	1	Leafhoppers	0	0.000			
07/06/88	p11-6	2	Leafhoppers	32	0.024	1.7		1.7
07/06/88	p11-6	3	Leafhoppers	7	0.006	2.1		2.1
07/06/88	p11-7	1	Leafhoppers	0	0.000			
07/06/88	p11-7	2	Leafhoppers	0	0.000			
07/06/88	p11-7	3	Leafhoppers	0	0.000			
07/06/88	p11-8	1	Leafhoppers	4	0.003	1.7		1.7
07/06/88	p11-8	2	Leafhoppers	7	0.004			
07/06/88	p11-8	3	Leafhoppers	3	0.002			
07/06/88	p11-9	1	Leafhoppers	0	0.000			
07/06/88	p11-9	2	Leafhoppers	0	0.000			
07/06/88	p11-9	3	Leafhoppers	0	0.000			
07/06/88	p11-10	1	Leafhoppers	0	0.000			
07/06/88	p11-10	2	Leafhoppers	0	0.000			
07/06/88	p11-10	3	Leafhoppers	0	0.000			
07/06/88	p12-11	1	Grasshopper	3	0.140	2.9		2.9
07/06/88	p12-11	2	Grasshopper	2	0.016	2.5		2.5
07/06/88	p12-11	3	Grasshopper	1	0.061	2.8		2.8
07/06/88	p12-12	1	Grasshopper	4	0.026	2.0		2.0
07/06/88	p12-12	2	Grasshopper	7	0.090	3.4		3.4
07/06/88	p12-12	3	Grasshopper	14	0.495	3.4		3.4
07/06/88	p12-13	1	Grasshopper	14	0.318	5.7		5.7
07/06/88	p12-13	2	Grasshopper	38	1.064	6.1		6.1
07/06/88	p12-13	3	Grasshopper	28	0.974	5.6		5.6

Appendix Table 15. Synoptic survey, mean soil selenium concentration (ppm dry wt) per pond and station (6 July 1988).

Pond	Mean	N	SD	2SE
4	75.1	7	44.10	33.34
5	51.7	3	16.31	18.84
6	44.4	9	33.56	22.37
7	43.3	9	33.37	22.24
8	19.6	6	6.40	5.22
9	56.8	3	30.31	35.00
10	22.4	9	7.20	4.80
11	25.5	33	15.17	5.28
12	21.9	9	12.17	8.11

Station	Mean	N	SD	2SE
p4-27	30.7	3	13.25	15.30
p4-28	108.5	4	17.60	17.60
p5-26	51.7	3	16.31	18.84
p6-23	36.0	3	5.80	6.70
p6-24	71.3	3	52.50	60.63
p6-25	25.9	3	3.17	3.66
p7-18	35.2	3	23.98	27.69
p7-19	77.0	3	32.88	37.96
p7-20	17.7	3	3.35	3.87
p8-21	14.8	3	3.23	3.74
p8-22	24.5	3	4.61	5.32
p9-14	56.8	3	30.31	35.00
p10-15	17.7	3	6.10	7.04
p10-16	19.7	3	1.62	1.87
p10-17	29.7	3	6.47	7.48
p11-1	41.7	3	8.01	9.25
p11-2	20.9	3	4.63	5.35
p11-3	50.2	3	19.32	22.30
p11-4	40.8	3	12.75	14.72
p11-4a	11.0	3	5.30	6.12
p11-5	26.0	3	5.31	6.13
p11-6	17.3	3	6.91	7.97
p11-7	12.8	3	4.92	5.68
p11-8	8.9	3	5.82	6.72
p11-9	31.1	3	0.86	1.00
p11-10	19.5	3	6.00	6.93
p12-11	36.2	3	7.38	8.52
p12-12	18.0	3	6.43	7.42
p12-13	11.5	3	1.78	2.05

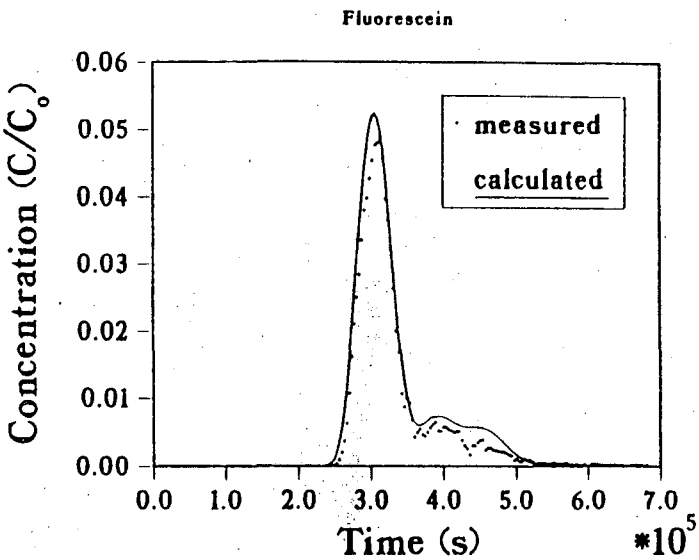
Appendix Table 16. Synoptic survey, soil selenium concentration (ppm dry wt).

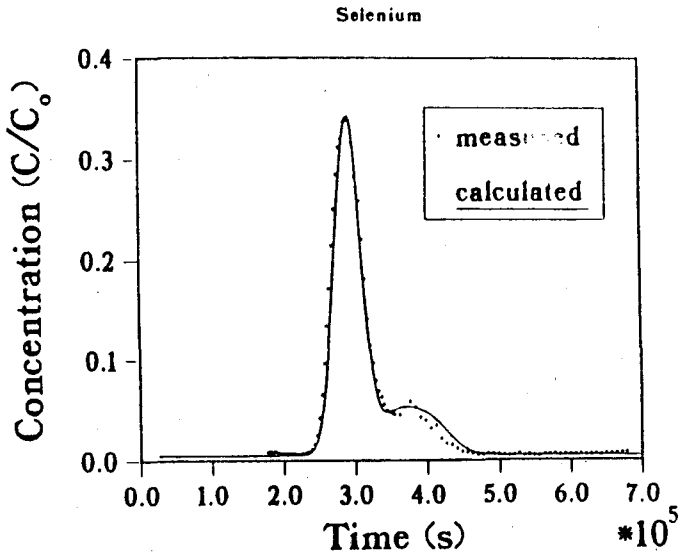
Date	Station	Repl	Sample	Se11	Se12	Mean
07/06/88	p4-27	1	Soil	27.3	27.0	27.2
07/06/88	p4-27	2	Soil	19.5		19.5
07/06/88	p4-27	3	Soil	45.3		45.3
07/06/88	p4-28	1	Soil	107.0		107.0
07/06/88	p4-28	2	Soil	130.0		130.0
07/06/88	p4-28	3	Soil	87.0		87.0
07/06/88	p4-28	4	Soil	110.0		110.0
07/06/88	p5-26	1	Soil	59.4		59.4
07/06/88	p5-26	2	Soil	33.0		33.0
07/06/88	p5-26	3	Soil	62.8		62.8
07/06/88	p6-23	1	Soil	30.6	28.2	29.4
07/06/88	p6-23	2	Soil	40.3		40.3
07/06/88	p6-23	3	Soil	38.3		38.3
07/06/88	p6-24	1	Soil	50.8		50.8
07/06/88	p6-24	2	Soil	32.2		32.2
07/06/88	p6-24	3	Soil	131.0		131.0
07/06/88	p6-25	1	Soil	22.6		22.6
07/06/88	p6-25	2	Soil	26.3		26.3
07/06/88	p6-25	3	Soil	28.9		28.9
07/06/88	p7-18	1	Soil	12.6		12.6
07/06/88	p7-18	2	Soil	61.0	59.7	60.4
07/06/88	p7-18	3	Soil	32.6		32.6
07/06/88	p7-19	1	Soil	99.5		99.5
07/06/88	p7-19	2	Soil	39.3		39.3
07/06/88	p7-19	3	Soil	92.3		92.3
07/06/88	p7-20	1	Soil	17.9		17.9
07/06/88	p7-20	2	Soil	21.0		21.0
07/06/88	p7-20	3	Soil	14.3		14.3
07/06/88	p8-21	1	Soil	13.0		13.0
07/06/88	p8-21	2	Soil	12.8		12.8
07/06/88	p8-21	3	Soil	18.5		18.5
07/06/88	p8-22	1	Soil	21.0		21.0
07/06/88	p8-22	2	Soil	29.7		29.7
07/06/88	p8-22	3	Soil	22.7		22.7
07/06/88	p9-14	1	Soil	63.5		63.5
07/06/88	p9-14	2	Soil	83.2		83.2
07/06/88	p9-14	3	Soil	23.7		23.7
07/06/88	p10-15	1	Soil	24.8	24.6	24.7
07/06/88	p10-15	2	Soil	13.9		13.9
07/06/88	p10-15	3	Soil	14.4		14.4
07/06/88	p10-16	1	Soil	20.6		20.6
07/06/88	p10-16	2	Soil	20.6		20.6
07/06/88	p10-16	3	Soil	17.8		17.8
07/06/88	p10-17	1	Soil	28.6		28.6
07/06/88	p10-17	2	Soil	23.9		23.9
07/06/88	p10-17	3	Soil	36.7		36.7
07/06/88	p11-1	1	Soil	40.6		40.6
07/06/88	p11-1	2	Soil	49.5	50.9	50.2
07/06/88	p11-1	3	Soil	34.3		34.3
07/06/88	p11-2	1	Soil	19.6		19.6

Appendix Table 16 (continued). Synoptic survey, soil selenium.

Date	Station	Repl	Sample	Se11	Se12	Mean
07/06/88	p11-2	2	Soil	26.0		26.0
07/06/88	p11-2	3	Soil	17.0		17.0
07/06/88	p11-3	1	Soil	38.7		38.7
07/06/88	p11-3	2	Soil	39.4		39.4
07/06/88	p11-3	3	Soil	72.5		72.5
07/06/88	p11-4	1	Soil	36.5		36.5
07/06/88	p11-4	2	Soil	55.1		55.1
07/06/88	p11-4	3	Soil	30.7		30.7
07/06/88	p11-4a	1	Soil	9.6		9.6
07/06/88	p11-4a	2	Soil	6.6		6.6
07/06/88	p11-4a	3	Soil	16.9		16.9
07/06/88	p11-5	1	Soil	32.1		32.1
07/06/88	p11-5	2	Soil	22.9		22.9
07/06/88	p11-5	3	Soil	22.9		22.9
07/06/88	p11-6	1	Soil	24.4		24.4
07/06/88	p11-6	2	Soil	10.6		10.6
07/06/88	p11-6	3	Soil	17.0		17.0
07/06/88	p11-7	1	Soil	10.6		10.6
07/06/88	p11-7	2	Soil	18.4		18.4
07/06/88	p11-7	3	Soil	9.5	9.1	9.3
07/06/88	p11-8	1	Soil	6.0		6.0
07/06/88	p11-8	2	Soil	5.1		5.1
07/06/88	p11-8	3	Soil	15.6		15.6
07/06/88	p11-9	1	Soil	31.9		31.9
07/06/88	p11-9	2	Soil	30.2		30.2
07/06/88	p11-9	3	Soil	31.3		31.3
07/06/88	p11-10	1	Soil	21.1		21.1
07/06/88	p11-10	2	Soil	25.4	23.5	24.5
07/06/88	p11-10	3	Soil	12.8		12.8
07/06/88	p12-11	1	Soil	27.7	27.8	27.8
07/06/88	p12-11	2	Soil	41.3		41.3
07/06/88	p12-11	3	Soil	39.6		39.6
07/06/88	p12-12	1	Soil	11.1		11.1
07/06/88	p12-12	2	Soil	23.8		23.8
07/06/88	p12-12	3	Soil	19.2		19.2
07/06/88	p12-13	1	Soil	13.5		13.5
07/06/88	p12-13	2	Soil	10.7		10.7
07/06/88	p12-13	3	Soil	10.2		10.2

APPENDIX B.





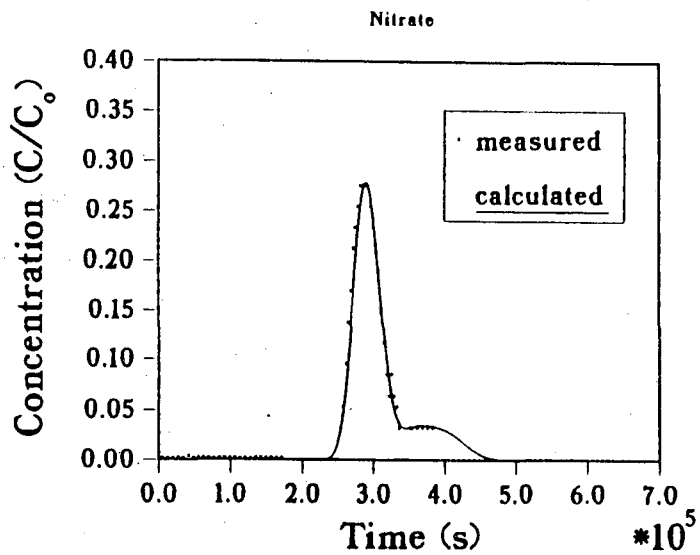
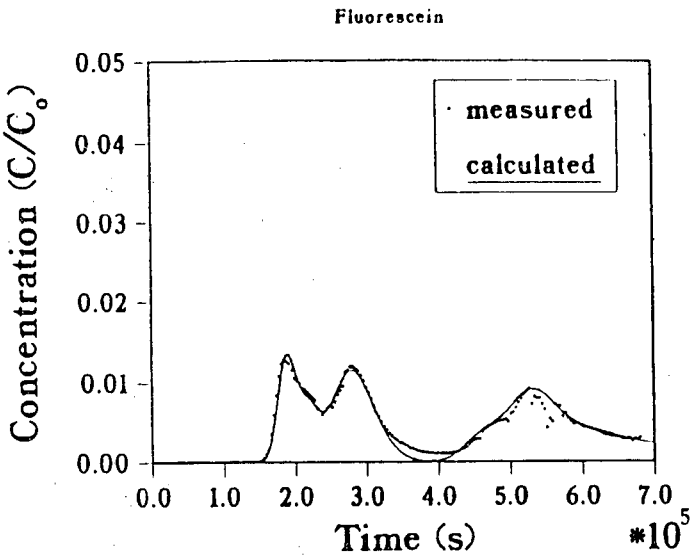
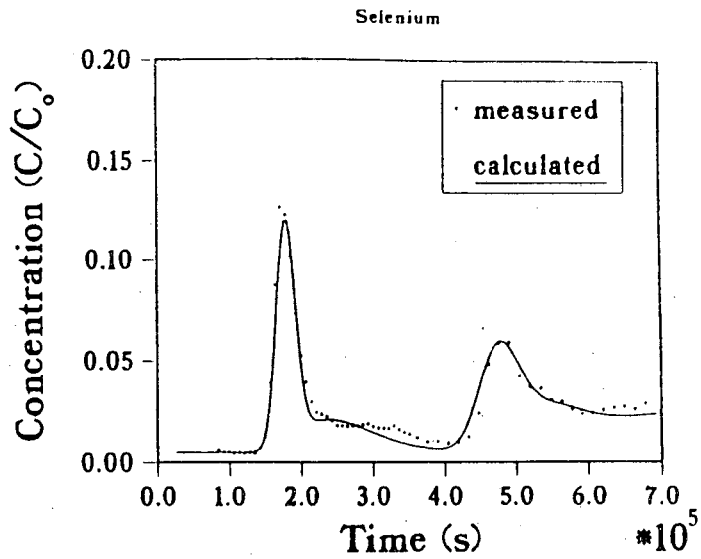


Figure B-1a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 1.





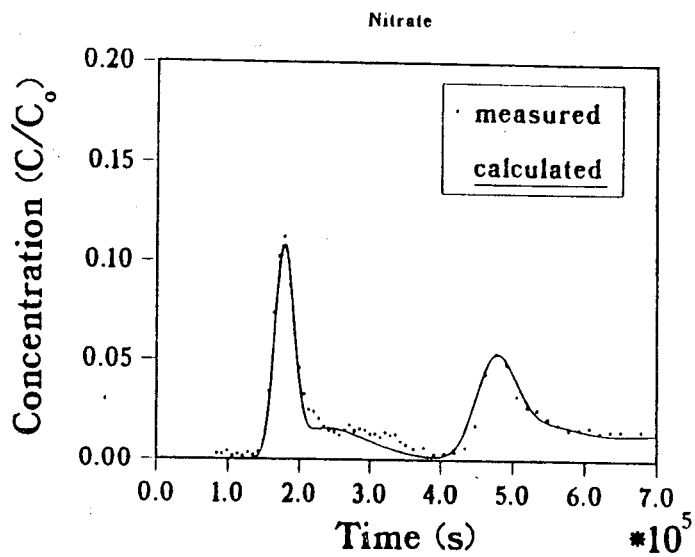
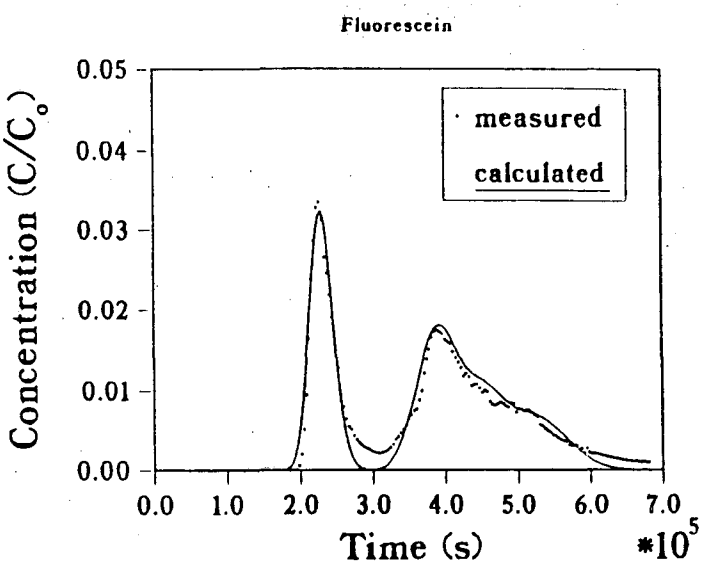
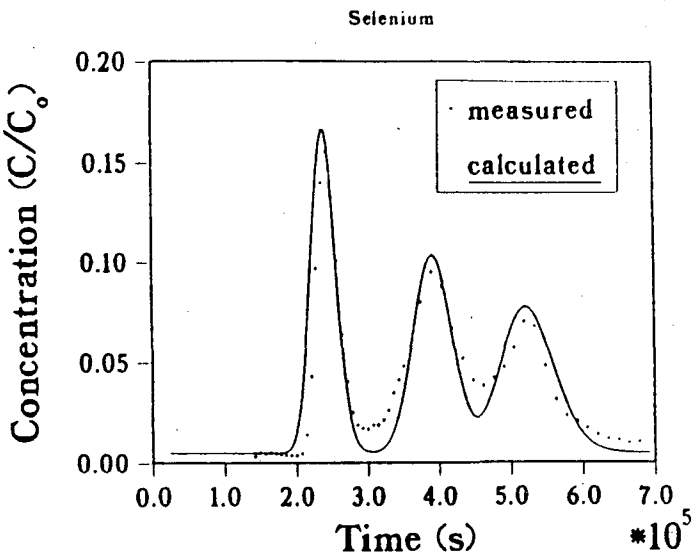


Figure B-2a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 3.





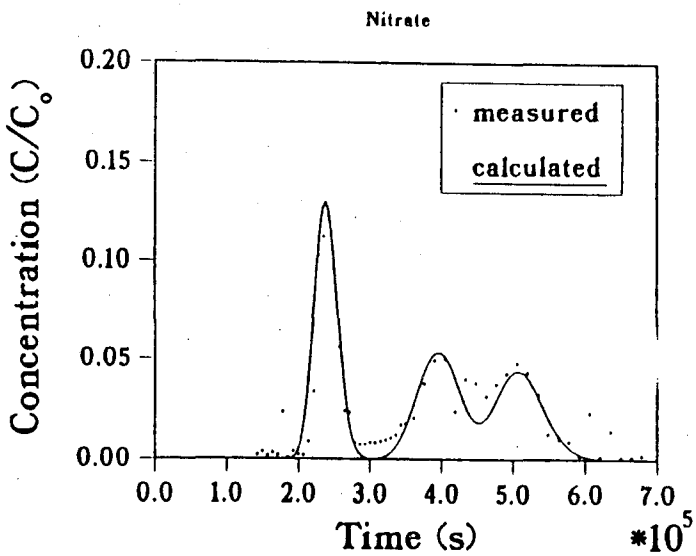
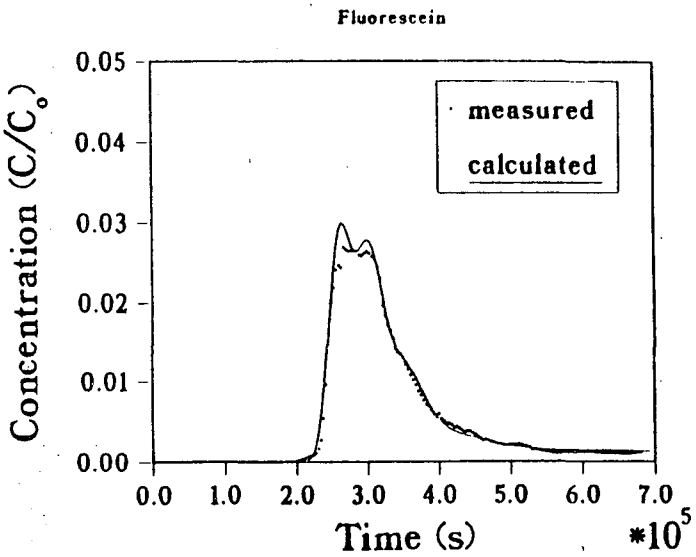
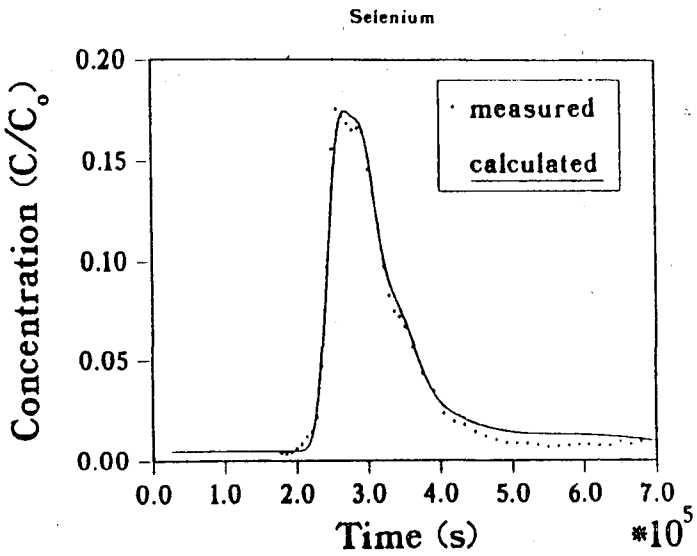


Figure B-3a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 4.





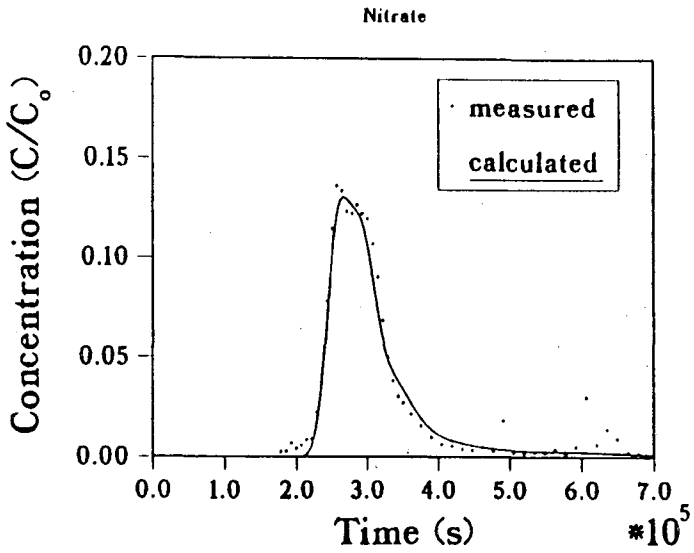


Figure B-4a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 7.

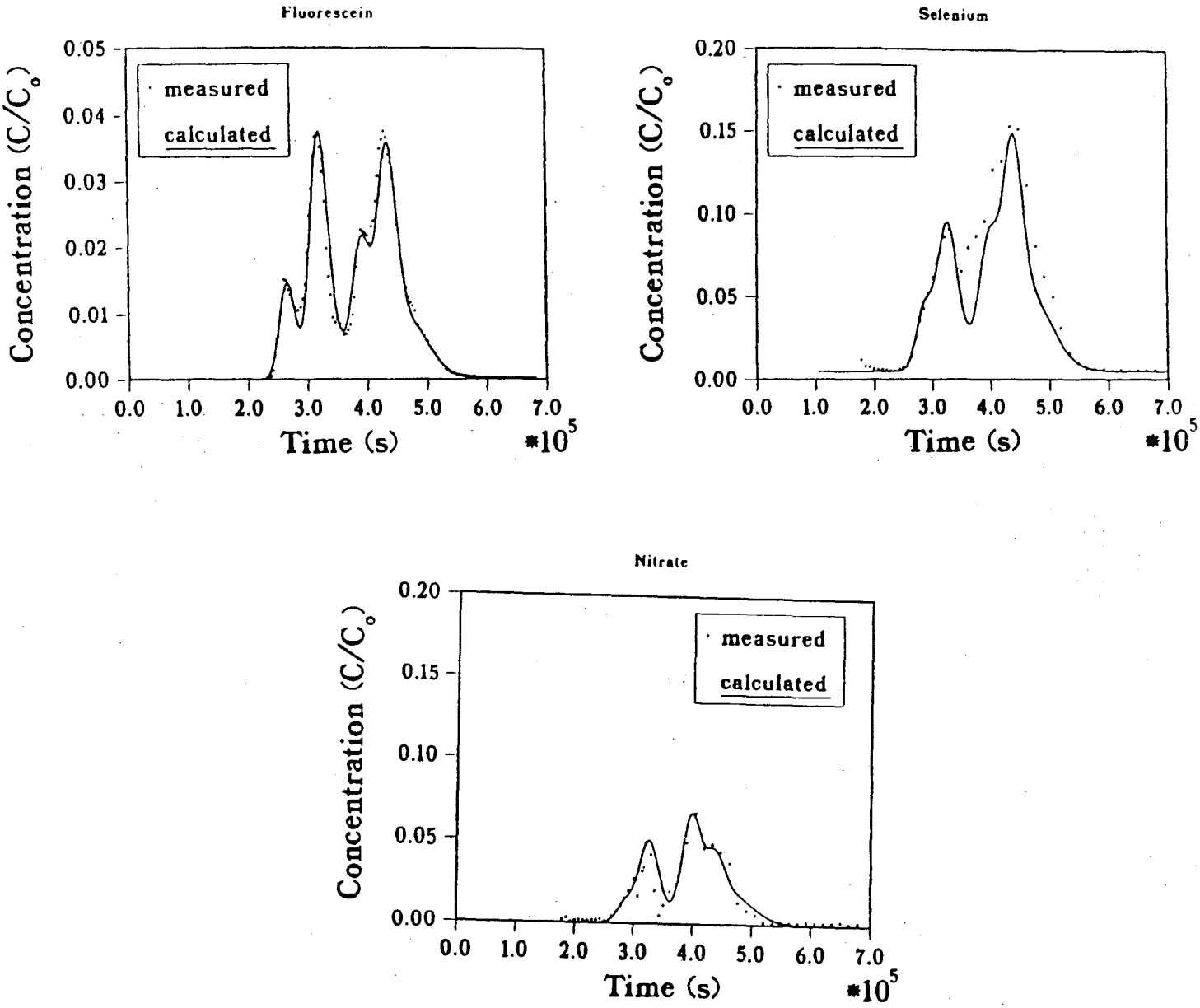
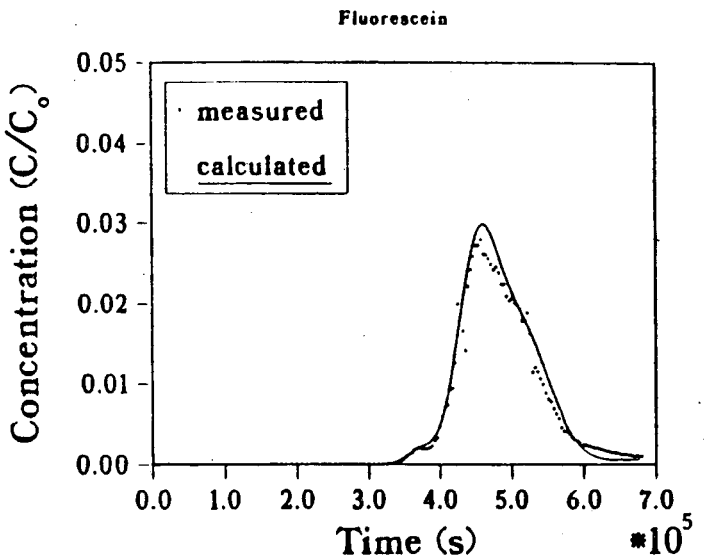
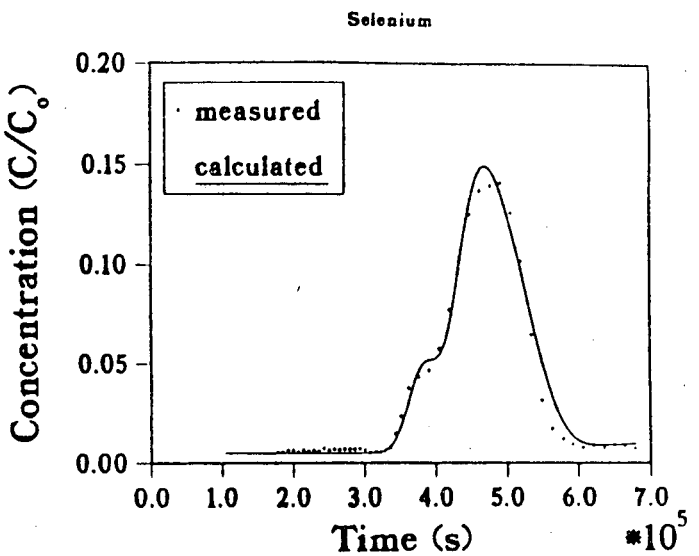


Figure B-4a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 5.





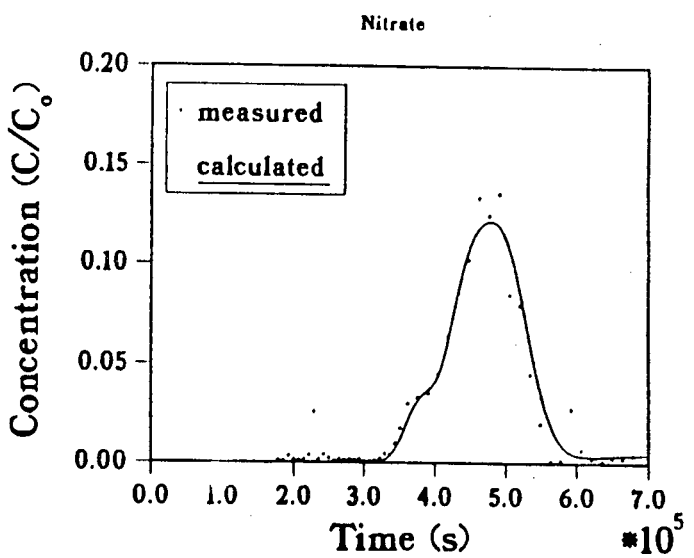


Figure B-5a,b,c. History matches of tracer breakthrough curves for fluorescein, selenate and nitrate for well 8.

APPENDIX C. X-RAY FLUORESCENCE ANALYSIS

The Kesterson project has required determination of selenium in very many samples of sediment and biological material, frequently with little time allowed.

For the purpose of expediting the Se determinations of the routine biological samples, a technique was used that would in most cases yield results that could be low in the range of 1 - 10% of the amount present. The method applied and the calibration procedures used have been reported elsewhere (Davis, 1968). The biological samples were spread as very thin layers and as uniformly as possible on 0.2 mil thick polypropylene film stretched taught in plastic snap ring holders. The typical mass thickness of the samples was in the range of 10 - 20 mg/cm^2. Molybdenum K excitation radiation was used for the x-ray fluorescence determinations. A semiconductor detector was employed to measure the fluorescence radiation intensities. The intensity of backscattered Mo K radiation served as a measure of the amount of sample in the X-ray beam path. This was possible since the incoherent mass scattering coefficients typically do not vary by more than a few percent for most light elements to be expected in biological samples (Davis, 1968). The intensity of the Se K alpha radiation was a measure of the quantity of the selenium in the x-ray beam path. For the routine samples, no matrix absorption corrections were made. The potential errors associated with sample heterogeneity probably were much larger in some cases.

A different method was used to accurately determine the selenium in the biological reference samples (Weres and Tsao, 1983). Sample pellets of mass thickness 40 mg/cm^2 were prepared, and X-ray transmission measurements were made to correct for matrix absorption effects.

The sediment samples were prepared in an entirely different manner. Several grams of finely pulverized samples were pressed in Lucite cells that had Mylar tape windows. The

samples prepared were of infinite thickness for all radiations of interest. The method utilized has been reported (Weres et al., 1985). USGS Geochemical Reference Materials were used to calibrate the spectrometer for the determinations.

For the results reported here, triplicate samples were prepared for the XRF selenium determinations.

APPENDIX D. MAGNESIUM NITRATE DECOMPOSITION

Magnesium nitrate may be used as an oxidizing agent to decompose biological material for selenium analysis. This method will give consistently low readings when applied to sediments, and should not be used with sediments. We have modified the technique so that all reactions take place in a single test tube, and samples of small and variable size can be conveniently decomposed for analysis in batches of 6 or 10. We have used this procedure for selenium only, but essentially the same procedure should work for arsenic as well. This procedure has been successfully used in our laboratory for approximately three years.

The same procedure may also be performed in a beaker using a larger sample aliquot, a common practice in other laboratories.

Equipment. A glassware drying oven and ball mill or mortar and pestle are used to prepare the samples for analysis.

The decomposition reaction is run in Pyrex screw-capped culture tubes 20 x 150 mm or 25 x 150 mm. The reaction runs faster using the smaller tubes and less reagent. There is less trouble with boiling over or particles being carried up in the tube using the larger tubes. The tubes are numbered or otherwise labeled with a diamond scribe before use.

At first the tubes are heated in an aluminum heating block set upon a hotplate. A different block is used for each tube size, with holes drilled to provide a moderately snug fit for the tubes (13/16 inch and 1 inch diameter, respectively). The blocks are 2" thick. The block for the 20 x 150 tubes holds twelve of them, and the block for the 25 x 150 tubes holds sixteen. Block temperature is monitored using a mercury thermometer, and may be precisely controlled using a thermocouple, each set in a hole of appropriate size drilled in the block. The block has a detachable metal handle, used to put it in and out of the furnace. When used, thermocouple is connected to a proportionating 10 amp electronic temperature controller. The hot plate used should allow the

block to reach at least 300°C at full power. A thermostatted 750W hot plate with a 6.25" square cast aluminum top is normally used in our laboratory. Precise temperature control is not necessary, and the built-in thermostat in the hotplate allows adequate control without the electronic controller. 10-20 degrees of temperature overshoot can be tolerated.

The second stage of the reaction takes place in a box furnace at 510°C. Select a furnace large enough to put the whole block with tubes into it. (CAUTION: Remember that pure aluminum melts at 660°C, and aluminum alloys, lower.)

During the procedure magnesium nitrate decomposes to magnesium oxide, releasing copious amounts of highly toxic and irritating nitrogen oxides. THE HOTPLATE WITH THE HEATING BLOCK AND THE BOX FURNACE MUST BE SET UP INSIDE A FUME HOOD.

The last part of the reaction requires a boiling water bath. A large beaker on a hotplate is used.

An analytical balance, 1 ml and 5 ml pipettors, a wash bottle, test tube racks, and a 25 ml graduated cyclinder are also required.

An ultrasonic bath is useful but not essential.

Reagents. Magnesium nitrate reagent solution is prepared by dissolving 65g of $Mg(NO_3)_2 \cdot 6H_2O$ in 100 ml of 70% ethanol (USP grade).

Pure ethanol, 7N HCl, 12N HCl, and either clean quartz sand or boiling chips are also required.

Procedure. The samples are prepared by drying them under air at 100°C using a glass-drying oven. Samples above 200 mg are pulverized in a ball mill (a mortar and pestle may also be used), and a 30-100 mg split is analyzed. Pulverizing the sample homogenizes it and makes it easier to take a representative split; otherwise pulverization is unnecessary, and actually makes the samples harder to process. Smaller samples are coarsely crushed in an agate mortar to expedite processing; e.g. whole mosquito fish or large insects. Samples smaller than about 100 mg are normally analyzed undivided. Samples 100 to 200 mg are usually crushed and mixed,

and a 30-100 mg split is analyzed.

The amount of reagent and tube size depend on the size of the sample, as summarized in Table C1. The analytical recipes are scaled to ensure roughly constant ratios of sample : magnesium nitrate : HCl. The proportions in this table are adequate even to decompose fatty animal tissues. With samples above 200 mg, take a 30-40 mg split and analyze it as a 20-40 mg sample, or take a 40-100 mg split and analyze it as that size sample.

Table C1. Recipes for magnesium nitrate decomposition.

Sample size (mg)	Tube (mm)	MgNitrate (ml)	7N HCl (ml)
0-20	20 × 150	1	5
21-40	20 × 150	2	10
41-100	25 × 150	5	25
100-200	25 × 150	10	30

Usually, samples are run in sets of 16, which include 13 production samples, two standard reference materials, and one reagent blank. Test chemicals for blank value before using.

Set the controller to 150°C, allow the temperature of the heating block to stabilize near that value. (Or set hotplate to 450°F.) Weigh samples into tared culture tubes, record sample weight. Pipette magnesium nitrate reagent into the tube. Add small amount of clean quartz sand or an amorphous carbon boiling chip. Briefly hold tubes in ultrasonic bath to help reagent penetrate the solid sample. (Pulverized fish samples disperse with difficulty. In this case mix sample with 1-2 mls pure ethanol and disperse before adding reagent.) Place tubes in block. Wait until rapid boiling subsides (about 20 minutes). Foaming of the liquid and adhesion of particles to the sides of the tube is a particular nuisance with pulverized samples. Reset temperature controller to 250°C (or the hotplate to 600°F). Wait until block temperature reaches 250°C, and boiling subsides to gentle foaming action at the bottom of the tube. By this time solid sample should have largely dissolved in the viscous, yellow molten salt liquid that remains. Turn controller up to

300°C (or the hotplate to "High"). The liquid will start to foam, sometimes rising in the tube. Bubbles of dark red nitrogen dioxide will escape from the foam. Gradually the foam will dry out and collapse. This part of the reaction has been completed when the foam and the liquid remaining at the bottom of the tube have turned into a beige or yellowish solid. At this time there should be no solid remnants of the sample. If solid particles remain stuck to the sides of the tube, wash them down with a small amount of concentrated nitric acid and continue heating until the salt cake again dries out.

Using the metal handle, place block with tubes inside the preheated furnace (510°) for 20 minutes. This part of the reaction is complete when the generation of red fumes ceases, and the dark red color dissipates from the tubes. Remove the tray from the furnace and allow it to cool so the tubes may be handled. At this time the solid material in the tubes should be pure white, consisting predominantly of magnesium oxide. All selenium is now in the form of magnesium selenate. Excessive foaming or boiling over in the furnace indicates insufficient heating time on the hot plate before going into the furnace.

Add appropriate amount of 7N HCl to each tube. Cap the tubes and shake if necessary to dissolve all of the white magnesium oxide. After all of the magnesium oxide has been dissolved, loosen the caps and transfer tubes to boiling water bath for 20 minutes. (Twenty minutes are required instead of ten because the magnesium oxide neutralizes part of the HCl, reducing its concentration.) After 20 minutes remove tubes from bath, allow then to cool, and seal the caps. This last reaction reduces selenic acid to selenious acid. Place tape labels on tubes, as inscribed labels will be hard to read.

Analyze the liquid using an atomic absorption spectrometer equipped with a hydride generator. Convert analytical results to concentration of selenium in the sample using the formula:

$$C_s(\text{ppm}) = C_l(\text{ppb})\frac{V_{HCl}(\text{ml})}{W_s(\text{mg})}$$

where

C_s = ppm selenium in solid sample

C_l = ppb selenium in liquid analyzed

V_{HCl} = volume of the liquid in mls

W_s = weight of the solid sample in mg

After discarding the liquid, clean the tubes with glass cleaning liquid and water and brush. The tubes will become frosted inside with repeated use; this is unimportant.

Sources of error. The magnesium nitrate method should not be used with sediment samples because it will give consistently low readings. Probably, the magnesium oxide reacts with clay minerals to produce magnesium silicate phases that sorb selenium.

Several sources of error have been identified and eliminated:

- The detailed procedure varies with sample size and confusion is possible. Never mix recipes for different size ranges in one batch. If necessary to combine samples of different size, lump smaller samples into the next larger size range and use the recipe appropriate to the latter for all. Before beginning to enter sample I.D.'s and weights in the notebook, write down range of sample size, tube size, volume of reagent, and volume of HCl.
- Part of sample may lost to excessive foaming, boiling over or burping. Be sure to use boiling chips. Avoid excessive hot plate temperature in the early part of the procedure. Wash particles down with nitric acid as needed. Heat liquid to dryness before transferring tubes to the oven.
- Part of magnesium oxide cake may remain undissolved if stuck to the upper part of the tube. Cap and shake tube after adding HCl until MgO has dissolved completely, then loosen cap and place tube in boiling water bath.
- Solid residues may carry over between determinations to cross-contaminate samples. Clean tubes thoroughly between uses using cleaning liquid and brush.

- An experienced operator can process four batches in one day. To avoid confusing the different batches, we use a dual labeling system; for example, "6-291" means that tube no. 6 in this batch corresponds to sample 291. The single digit number corresponds to the number permanently inscribed on the tube. This dual label is written on the tape label placed on the tube at the end of the procedure, in the notebook, and in the first stage log sheets.

Reagent blanks usually read about 0.6 ppm, and the blank reading determines the useful limit of detection, which is approximately 1 ppm. The LOD determined by the sensitivity of the AAS is approximately 0.2 ppm. While the LOD is moderately large, this method is reliable, and samples as small as 3mg dry weight to be analyzed, a tremendous convenience when dealing with difficult to collect insect specimens.

APPENDIX E. SODIUM PEROXIDE DECOMPOSITION METHOD

Sodium peroxide is a strong oxidizing agent that can be used both for decomposition of minerals and oxidation of organic materials. The method described here is normally used for analysis of selenium in sediments containing less than 3 ppm selenium, but can also be used to determine higher selenium concentrations.

Equipment and supplies. Laboratory balance. Permanently labeled zirconium tubes, 1x4 in. Metal tray to hold tubes in furnace. No. 4 rubber stoppers to fit the tubes. A laboratory centrifuge with rotor to accommodate the zirconium tubes. A laboratory furnace capable of reaching 500° C. A hot plate. Universal pH paper. Adjustable 5 ml hand held pipettor and tips. Adjustable 5 ml bottle top pipettor. Screw top glass culture tubes 20x125 mm or similar. Facilities to analyze selenium in water by hydride generator AAS.

Each zirconium tube is made from a 4" long piece of 1" O.D., 0.0625" wall zirconium tube stock. The bottom of the tube is disk of 0.0625" zirconium sheet welded to that end of the tube. The tubes are stamped for identification and matched by weight before use. If necessary, the open end of a tube may be filed to match the weight.

Chemicals needed. Reagent grade sodium peroxide. 5N HCl. 12N HCl. 5N NaOH. 2% solution of ammonium persulfate prepared weekly. Amorphous silica powder prepared by drying out DuPont Ludox TM colloidal silica sol, then crushing and sieving to 50+ mesh.

Procedure. Preheat the furnace to 510° C. Weigh 0.1 gm sample aliquots into zirconium tubes and weigh 1.0 gm sodium peroxide directly into tubes along with samples. Matrix blanks are prepared by loading tubes with 1.0 gm of silica powder. Place zirconium tubes in the metal tray and set in furnace for fifteen minutes at 500° C. After removing the zirconium tubes from the furnace, allow them to cool, then add 5 ml of distilled or dionized water to each tube to dissolve the fused cake at the bottom. Allow the bubbling to subside before adding 5 ml of 5N HCl. Test

the pH of each solution with the universal pH paper and adjust the pH to 8-10 by adding a few drops of 5N NaOH as needed. The mildly alkaline condition at pH 10 favors the polymerization and flocculation of dissolved silica. This is done at this stage to prevent the formation of silica floc at later steps in the procedure when it may adsorb silica or plug the tubes of the hydride generator AAS. Place the rubber stoppers in the zirconium tubes and place them in a boiling water bath for ~ 20 minutes to destroy the remaining peroxide and accelerate the polymerization of silica.

Remove the zirconium tubes and allow them to cool before centrifuging them to separate the silica floc. After the floc has been precipitated, pipette 5 ml of the supernatant liquid into one of the glass culture tubes, add 5 ml of 12N HCl and 0.2 ml of the 2% ammonium peroxide solution, to oxidize any remaining reducing agents and organic selenium compounds. A noticeable fine silica gel forms at this stage but this does not interfer with the hydride generator AAS. Place the culture tubes in a boiling water bath for about 10 minutes and, when cool, analyze the contents for selenium using the hydride generator AAS. For this process 1 ppb of selenium in the final solution analyzed on the AAS corresponds to 210 ppb selenium in the sediment.

Blanks and cleaning. Zirconium has a tendency to absorb selenium, resulting in high blank values for tubes that have previously been used to process samples with high selenium concentrations. When approximate levels of selenium in samples are known *a priori*, the simplest and most reliable technique is to dedicate sets of tubes to samples of certain expected selenium concentration ranges. After long use, the furnace chamber may accumulate enough selenium oxides to contaminate subsequent samples. This source of contamination may be eliminated by occasionally heating the empty furnace to 1100°C for one hour to drive-off the contaminants.

Since it is not always possible to know in accurately in advance the selenium concentration of a sample, occasionally a tube may become contaminated. It is then necessary to clean it. The following methods have been developed:

Sodium peroxide cleaning. This method cleans most thoroughly. Load the tubes to be cleaned with 1 to 2 grams of sodium peroxide. Place the tube in a preheated furnace at 510° C.

for 15 minutes. Remove the tube and allow it to cool before adding distilled water to dissolve the cake. Place tubes in a sonic bath for 10 minutes and rinse thoroughly with distilled water when complete.

Sodium nitrate cleaning. Load the tubes to be cleaned one quarter full with a mixture of three parts potassium hydroxide and one part sodium nitrate. Place the tubes in a furnace preheated to 350° C. for 10 minutes. After removing the tubes and allowing them to cool, fill the tubes with distilled water and place them in a sonic bath for 10 minutes. Remove and rinse thoroughly with distilled water.

APPENDIX F. CARBONATE-NITRATE DECOMPOSITION METHOD

In this method the sample is decomposed by reacting it with a partially molten mixture of sodium and potassium carbonates and nitrates. The procedure appropriate for analyzing sediments is described here. The modifications needed to analyze biological samples are described at the end of the Section.

Equipment needed. Muffle furnace capable of safely operating at 1000°C. Reaction tubes of Inconel 600, 1 inch O.D., 4 inches tall, 0.0625" wall. Bottom of tube made from 0.0625" Inconel sheet welded to the tube. Stainless steel tray suitable for putting tubes in and out of the furnace. Rubber stoppers to fit reaction tubes. Shaker table. Centrifuge configured for 50 ml tubes. Plastic 50 ml centrifuge tubes. Analytical balance. Hot plate set up inside a fume hood. A 1 ml pipettor and tips, a 5 ml pipettor and tips, a 5 ml glass pipette and rubber pipette bulb, a 5 ml bottle-top pipettor, a large asbestos tile (to set hot tray and tubes on), pliers (to take tray in and out of furnace), screw-capped culture tubes 20x150 or 25x150 mm, rubber gloves.

Weigh tubes, and adjust weight by filing edges to closely match pairs of tubes. Stamp an identification number on each reaction tube. The tubes must be properly annealed before use. Anneal tubes overnight in muffle furnace at 700°C to eliminate local stresses from metal. Without removing tubes from furnace, increase temperature setting to 950°C, and anneal for one hour at this temperature. The second annealing produces an inert oxide coating which confers corrosion resistance. Properly treated, these tubes will survive quite a few runs before they fail. Avoid exposing them to strong acids, particularly HCl or HNO_3.

Chemicals needed. The composition of the flux is:

Weight %	
$NaNO_3$	10
KNO_3	10
Na_2CO_3	40
K_2CO_3	40

First weigh and grind the nitrates. Then add the carbonates, mix thoroughly, and grind the mixture. Dry the mixture overnight at 200°C. Briefly grind and mix the dried mixture and store it in a tightly sealed container.

Hydrogen peroxide, 30%, reagent grade.

Concentrated HCl.

Procedure. Set muffle furnace and allow to stabilize at 700°C.

Process the samples in sets of twelve, including a standard reference material, a blank, and a duplicate sample in each set. Weigh 0.200g of the dry, pulverized sample into tube. Add 2.0g of the flux mixture, and mix flux and sample well using a clean metal spatula. Load tubes into trays and place into muffle furnace. Allow to react 20 minutes. The nitrate salts will fuse, and part of the carbonates will dissolve in the nitrate melt. This alkaline nitrate melt will completely decompose and oxidize organic matter in the sediments and dissolve most of the clay. The fusion reaction converts most (or all) of the selenium in the sample into sodium selenate.

After 20 minutes remove trays with tubes from the furnace. Set them on the asbestos tile and let them cool for about 15 minutes. Add 20 ml of deionized water to each tube. Plug with rubber stoppers, and mount on shaker table. Shake 30 minutes or however long it takes salt cake to dissolve. Briefly shake stoppered tube by hand to resuspend sediment, and pour contents over into a 50 ml centrifuge tube. Using glass pipette, slowly add 5 ml c. HCl to each centrifuge tube to decompose carbonates and dissolve calcium carbonate precipitate. (Overly rapid addition of the acid using pipettor would cause the liquid to foam and spill.) Allow foaming to subside, then centrifuge briefly to settle the sediment. Pipette 5 ml of liquid from each tube into a labeled culture tube. Add 2 ml 30% H_2O_2 and 5 ml c.HCl. The hydrogen peroxide oxidizes residual

organic matter and eliminates interference by nitrite which may be formed from residual nitrate in the solution. Loosely cap tubes, and simmer in boiling water bath. Watch the tubes for disappearance of fine bubbles characteristic of H_2O_2 decomposition. Continue heating tubes for 10 minutes after fine bubbles have disappeared. This final reaction reduces selenate to selenite, which is the form that is directly determined by hydride generator - AA. Remove tubes from bath and allow to cool. Analyze liquid for selenium using hydride generator AA on the same day.

We have in effect taken 0.200g of sample to 61.2 ml of the solution that is actually analyzed. Volume of 20.0 ml water + 2.0 g flux + 5.0 ml c. HCl = 25.5 ml. Volume of 5.0 ml of this solution + 5.0 ml c. HCl + 2.0 ml 30% H_2O_2 = 12.0 ml. Dilution factor = 25.5 (12.0/5.0) / 0.2 = 61.2/0.2 = 306. Therefore, 1ppb Se in the solution analyzed corresponds to 0.306 ppm Se in the dried sediment.

The acid washed solid residue from the fusion reaction consists mostly of quartz with subordinate felspar and possibly clay, containing very little selenium.

Analysis of biological samples. Pulverized biological samples may also be analyzed in this manner. In this case, the method is modified as follows:

- 50 mg of sample is used (instead of 200 mg) giving a sample:flux ratio of 1:40.
- The flux composition is changed to 20% $NaNO_3$, 30% Na_2CO_3, 20% KNO_3, and 30% K_2CO_3.
- To reduce the problem of high blank readings, two separate sets of Inconel tubes are used for samples containing Se < 10ppm and Se > 10ppm.
- After the cake is dissolved in water and acidified no precipitate forms and centrifugation is not necessary.

The doubled concentration of nitrate in the flux increases the risk of rapid reaction and possible deflagration. While we have never observed deflagration of the sample-flux mixture in our

laboratory, be aware of the possibility, and exercise necessary precautions.

Blanks and clean-up. The blank reading practically limits the LOD with this method. Commonly some solid residue remains in the Inconel tube, and should be cleaned out before the using the tube again. The following technique gives consistent and relatively low blank values. Add approximately 20 ml deionized water and 2 ml liquid laboratory detergent to each tube and boil on the hot plate for approximately ten minutes. Decant liquid and place in ultrasonic cleaning bath for about ten minutes, then rinse with D.I. water. The screw-cap of the culture tube may also carry-over cross contamination with selenium. Boil the caps in water with detergent between uses.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720