

1988-89 TECHNICAL PROGRESS REPORT

UC SALINITY/DRAINAGE TASK FORCE

DIVISION OF AGRICULTURE AND NATURAL RESOURCES
UNIVERSITY OF CALIFORNIA

This report was prepared by Kenneth K. Tanji, Special Programs Coordinator, UC Salinity/Drainage Task Force. Principal Investigators contributed the annual technical progress reports.

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Mission

The mission of the UC Salinity/Drainage Task Force is to develop, interpret and disseminate research knowledge addressing critical agricultural and environmental problems on salinity, drainage and toxic trace elements in the West Side of the San Joaquin Valley, California.

Background

The UC Salinity/Drainage Task Force was formed in January 1985 by Lowell Lewis, then Assistant Vice President of the Division of Agriculture and Natural Resources and Director of the Agricultural Experiment Station. Lewis appointed André Läuchli, Chairperson of the Department of Land, Air and Water Resources, Davis Campus, and Jewell Meyer, Program Director for Soils, Water and Agricultural Engineering, Cooperative Extension, Riverside Campus, as Co-Chairs of the Task Force. Allen Knight, Vice Chairperson of Department of Land, Air and Water Resources, replaced Läuchli in December 1986 when the latter went on a sabbatical leave. Kenneth Tanji, Assistant Director, Soil and Water Area, Agricultural Experiment Station served as administrative coordinator to the Task Force.

In July 1985, six months after the formation of the Task Force, a \$1.05 million research program was implemented. Thirty-four projects were funded through a competitive grant process in high priority research topics jointly identified by the Task Force and state and federal action agencies. Funds for the first-year research program consisted of a one-time redirection of \$398,000 from the UC Kearney Foundation of Soil Science which was about to embark on a new five-year research mission and \$651,000 budget augmentation from the State of California. Projects funded by Kearney Foundation were for 1, 1½ and 2-year periods while those funded by State Funds were for one year.

The 1985-86 technical progress reports of research projects and principal accomplishments of the UC Salinity/Drainage Task Force were distributed in September 1986 (1985-86 Technical Progress Report, UC Salinity/Drainage Task Force, 233 pages). Based on the first year accomplishments, this Task Force demonstrated that University of California has the potential to respond quickly to high priority research and provide timely contributions. A second year report (1986-87 Technical Progress Report, UC Salinity/Drainage Task Force, 160 pages) was distributed in October 1987. The second year research program consisted of 19 projects receiving \$558,614 of research funds and involving 42 principal and co-principal investigators from agricultural experiment station and cooperative extension supported by 72 research collaborators and staff. The 1987-88 and 1988-89 Technical Progress Reports document a sustained effort in research and public service activities of this Task Force.

1987-89 Administration

Under the leadership of Vice President Kenneth Farrell, the Division of Agriculture and Natural Resources (DANR) was reorganized in 1987-88. The details of this reorganization are spelled out in "Research and Extension Program Structure for the Division of Agriculture and Natural Resources", dated September 1988. The primary aim of this reorganization was decentralization of ANR to the Berkeley, Davis and Riverside campuses with College Deans serving as both campus director of agricultural experiment station and cooperative extension. Reorganization pertinent to this Task Force are Kenneth Farrell, Vice President, DANR, and statewide Director of both Agricultural

Experiment Station and Cooperative Extension; Lowell Lewis, DANR Associate Vice President, Programs; Kenneth Tanji, DANR Special Projects Coordinator of the UC Salinity/Drainage Task Force; and elimination of Co-Chairs of this Task Force.

Table 1 includes the present administrative organization of the UC Salinity/Drainage Task Force. Administrative coordination is provided by the Division of Agriculture and Natural Resources, including the Agricultural Experiment Station and Cooperative Extension. An Administrative Advisory Committee chaired by Robert Webster, Acting Dean of the College of Agricultural and Environmental Sciences, Davis Campus, provides advice on policy matters as needed and approves the budget and allocation of funds through the competitive grant process. A Technical Review Committee recommends priority areas for research, evaluates project proposals, ranks them in priority, and recommends project proposals for funding.

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Table 1. Task Force Administration Organization

Division of Agriculture and Natural Resources & UC Salinity/Drainage Task Force:

Kenneth E. Farrell, Vice President - Agriculture and Natural Resources.

Lowell M. Lewis, Associate Vice President, Programs.

Kenneth K. Tanji, Professor and Task Force Coordinator.

Task Force Administrative Advisory Committee (1988-89):

Robert K. Webster, Committee Chairperson, Acting Dean - College of Agricultural and Environmental Sciences, Davis Campus and Acting Campus Director - Agricultural Experiment Station and Cooperative Extension.

William W. Allen, Associate Dean - College of Natural Resources, Berkeley Campus.

William R. Hambleton, Regional Director - South Central Region Counties, Agriculture and Natural Resources Program, Kearney Agricultural Center, Parlier.

André E. Lüscherli, Professor and Chairperson, Department of Land, Air and Water Resources, Davis Campus.

Lanny J. Lund, Professor and Chairperson, Department of Soil and Environmental Sciences, Riverside Campus.

Seymour Van Gundy, Acting Dean - College of Natural and Agricultural Sciences, Riverside Campus and Acting Campus Director - Agricultural Experiment Station and Cooperative Extension.

Lawrence J. Waldron, Associate Professor and Chairperson, Department of Plant and Soil Biology, Berkeley Campus.

(Table 1 continued next page)

Task Force Technical Review Committee (1988-89):

Kenneth K. Tanji, Committee Chairperson, Professor and Task Force Coordinator, Davis Campus.
James E. Ayars, Drainage Engineer, USDA-ARS Water Management Research Laboratory, Fresno.
James W. Biggar, Professor, Department of Land, Air and Water Resources, Davis Campus.
Harvey E. Doner, Professor, Department of Plant & Soil Biology, Berkeley Campus.
Robert J. Gilliom, Hydrologist, U.S. Geological Survey, Water Resources Division, Sacramento.
John Letey, Professor, Department of Soil and Environmental Sciences, Riverside Campus.
James D. Rhoades, Supervisory Soil Scientist, USDA-ARS, U.S. Salinity Laboratory, Riverside.
Larry J. Schwankl, Extension Specialist, Cooperative Extension, Davis Campus.
Henry J. Vaux, Professor, Department of Soil and Environmental Sciences, Riverside Campus.
Lin Wu, Associate Professor, Department of Environmental Horticulture, Davis Campus.

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1988-89 Budget

The Task Force budget for 1988-89 was \$691,700 of which \$539,475 (78%) was allocated to the 19 research projects. The remaining funds were used to support administrative and support services including the UC Committee of Consultants, conferences and publications.

1988-89 Principal Accomplishments

- o A call for research proposals in February, 1988, resulted in the approval of 19 new and continuing projects supported by \$539,475 for one to three years in duration.
- o The 1988-89 research program involved 33 faculty and extension principal investigators and 12 external collaborators supported by a research staff of 65.
- o The fourth annual research conference was held at the Hotel El Rancho on March 3-4, 1989, with an attendance of 160 participants. In addition to annual reports from the UC Salinity/Drainage Task Force, this conference featured a "Panel Discussion on Research Needs" led by John Letey as Moderator; an after-dinner presentation by Jan van Schilfgaarde, Chair of the NRC Committee on Irrigation Induced Water Quality Problems, on "Sustained Irrigation - Is There a Solution?", and a half-day session on the "USBR Kesterson Program," chaired by Susan Hoffman, Kesterson Program Manager.
- o The panelists for the discussion on Research Needs consisted of Don Swain (USBR), Robert Gilliom (USGS), Stephen Moore (FWS), Dennis Westcott (RWQCB), Jerry Johns (SWRCB), and Stephen Hall (LPA). They addressed subsurface drainage water reduction, management and use of shallow ground waters, agricultural evaporation ponds, and discharges into the San Joaquin River system. The following are some of the major points made:
 - o In the short term, subsurface drainage needs to be reduced. Interim drainwater disposal options include limited discharges into the San Joaquin River system, evaporation ponds and drain water reuse in croplands.

- o Longer term solutions to the drainage problem must be sought. The San Joaquin Valley Drainage Program's activities must be continued by action agencies and UC and other research institutions.
- o Subsurface drainage water reduction may reduce costs up to 80% for final disposal.
- o Subsurface drainage reduction results in a concurrent reduction in the load of TDS and B, but what about Se?
- o Is it possible to measure directly deep percolation from the crop root zone? If not, how can we get estimates? How do we measure achievement and compliance to regulations?
- o What are the costs for drainage reduction, and who should pay?
- o If what is already known is applied, the problem of drainage will be partially solved. Site-specific nature of the drainage problems will be required for effective management.
- o In addition to improved irrigation practices, management of shallow ground water will help solve the problem. The potential of shallow ground water contribution to crop ET should be investigated, along with long term effects on salt balance in the crop root zone.
- o Use of agroforestry systems to reduce drainage is another option.
- o How viable are evaporation ponds? Are they safe? If not, can they be designed and managed to avoid Kesterson-like toxic effects on waterfowl and shore birds?
- o In addition to Se, drainage waters contain significant concentrations of B, Mo, As, U, V, and others. What are the synergistic and the antagonistic interactions amongst these elements as far as plant and animal uptake are concerned?
- o A new geographic area, i.e. Tulare Lake Basin, where hazards have emerged, urgently needs water-quality management.
- o Reclamation and restoration of native wetland habitat is a novel solution, and exposure pathways and changes over time need to be researched.
- o KPA requires by February, 1990, water-quality objectives for 126 priority pollutants. What are the safe levels for discharge into the San Joaquin River and, eventually, into the Bay-Delta complex?
- o A considerable body of new knowledge has been generated on hydrogeology and toxic element reactivity, mobility, and accumulation in ground waters. There is a need to integrate and assess newly acquired knowledge and follow up with intensive studies that may not necessarily be in line with decision- and policy-making.
- o Agencies should identify gaps in research knowledge to focus future research activities.
- o The following are some remarks by Jan van Schilfegaarde from his paper on "Sustained Irrigation - Is There a Solution?":

- o Irrigated agriculture has made substantial contributions to world food production for thousands of years.
- o The practice of irrigation, however, results in varying degrees of water quality degradation.
- o Without proper management, the land becomes water logged and saline, and drainage and salt disposal are essential.
- o In many instances, the natural drainage rate is sufficient to prevent soil salinization. In other instances, man-made drainage collector systems must be installed.
- o In most natural systems, drainage from uplands finds its way into rivers and to the ocean. Irrigation tends to accelerate this displacement phenomenon.
- o In other systems, drainage water collects at some terminus and evaporates, leaving its constituents behind. Terminal lakes typically have significant value for fish and wildlife and recreation early in its life. But over time, they become more saline, lose biological value and become less attractive for recreation.
- o It follows that a permanent irrigation agriculture requires the sacrifice of some value elsewhere.
- o There are ways of minimizing or delaying the effects of irrigation on downstream salinity such as improved irrigation, drainage water reuse, and desalting.
- o The presence of toxic trace elements has added an entirely new dimension and complexity. Research and development are underway to treat drainage waters and remove toxic elements.
- o Competing demands are stressing the limits of water resources. Society no longer considers irrigation as necessarily the preferred beneficial use of water.
- o Irrigated agriculture must adapt to changing physical and social conditions in order to survive.

The DANR Special Publication in "Selenium Contents in Animal and Food Crops Grown in California", published in October 1988, continues to be in heavy demand, with about 600 copies distributed thus far.

- o Several members of this Task Force have heavily contributed to the Agricultural Water Management Subcommittee, chaired by Suzanne Butterfield and succeeded by Jonas Minton, both of Department of Water Resources. This subcommittee is a technical subcommittee to the Interagency Technical Advisory Committee of the San Joaquin Valley Drainage Program. In the past year, Office of Water Conservation (DWR) and the State Water Resources Control Board pooled their resources of over \$1 million to support a number of contracts involving field demonstration projects, grower surveys and water conservation information and education activities. The drainage reduction demonstration projects required development of requests for proposals and a peer-review process for the selection of contractors. Task Force

members assisted in both activities. Drainage reduction field demonstration projects consist of improved furrow irrigation, emerging irrigation technologies, shallow ground water management, and load/flow relationships. A field tour on June 26, 1989, of the Westside Drainage Reduction projects sponsored by Westlands Water District and DWR was well attended.

- o Members of the Task Force are participating for the second year in the USBR Kesterson Program, which focuses on field trial plots on soil water and vegetation management options to contain and dissipate selenium in upland and filled areas. In addition, several more campus-based projects are providing research support on selenium uptake and volatilization from crop and native vegetations.
- o Three members of the Task Force were invited to participate in a Nonpoint Source Pollution Control Workshop - Technical Issues, sponsored by the Western States Water Council on July 25-28, 1989, at Irvine, California.
- o A UC Committee of Consultants on "Potential Usage of Evaporation Pond Materials as Soil Amendments" was appointed in April, 1989. This Committee, chaired by Al Page and Robert Sheasley, is charged with exploring the possible beneficial use of residual pond materials in regions where deficiencies in trace elements occur, e.g., the east side of the San Joaquin Valley, where levels of selenium in feeds and forage grown on certain soils are inadequate to meet the dietary requirements of livestock, poultry, and probably wildlife.
- o Members of the Task Force have presented numerous papers arising from their projects at annual meetings of professional societies, symposia, and workshops. A growing body of publications and reports are contained herein.

1988-89 Research Projects

Table 2 shows that 19 projects were allocated a total of \$539,475 of funds. During 1985-89, the area of bioaccumulation of selenium and other toxic ions by food and forage crops as well as trace element chemistry and microbiology received slightly more than half of the research funds. For 1988-89 these two areas received 67% of the funds allocated with a decrease in the other three research areas.

Table 3 contains a summary of the number of personnel involved and their FTE (full-time equivalent) contribution to this research program. External Research Collaborators represent USDA-ARS Water Management Laboratory from Fresno, California State University-Fresno Center for Irrigation Technology, USDA-ARS U.S. Salinity Laboratory from Riverside, Dellavalle Laboratory in Fresno, Department of Food and Agriculture, Lawrence Berkeley Laboratory, U.S. Geological Survey and Regional Water Quality Control Board.

Several growers and organizations have provided research facilities and support, including Tulare Lake Drainage District, J. G. Boswell and Sons, Stone Land Company, U.S. Bureau of Reclamation and Neves Brothers.

Table 2. 1988-89 Budget Allocation for Research

<u>Subject Matter Areas</u>	<u>No. of Projects</u>	<u>Amount</u>	<u>Percentage</u>
Bioaccumulation	6.5	\$199,666	37
Chemistry/Microbiology	6	156,000	29
Irrigation/Drainage	3.5	114,780	21
Hydrology/Transport	2	50,229	9
Economics	<u>1</u>	<u>18,800</u>	<u>4</u>
TOTAL	19	\$539,475	100

Table 3. Commitment to Research Activities of the
UC Salinity/Drainage Task Force, 1988-89

	<u>Number of Personnel</u>	<u>Total Full-Time Equivalents</u>
UC Faculty	26	3.90
UC Cooperative Extension	7	1.85
External Collaborators	12	.90+
Postgraduate Researchers	19	7.72
Graduate Research Assistants	16	6.69
Staff Research Associates	13	3.89
Undergraduate Student Assistants	13	3.25
Other Assistants	<u>4</u>	<u>1.60</u>
TOTAL	110	29.80+

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Table 4 contains a listing of the 19 research projects supported by the UC Salinity/Drainage Task Force. Technical progress reports for each of these projects are included in this report.

Table 4.

UC SALINITY/DRAINAGE TASK FORCE RESEARCH PROJECTS (1988-89)

Project Number	Funding Sources	Project Period	Principal Investigators/Affiliations	*see last page	Project Title
HYDROLOGY AND TRANSPORT OF SALTS AND TRACE ELEMENTS:					
88-7	State Budget	7/88 - 6/90	Goldhamer (CE/Kearney Ag Ctr); Nielsen, Grismer, Biggar, Alemi (LAWR)		Influence of Aeration and Water-Logging due to Fluctuating Water Tables on the Fate of Selenium in Contaminated Soils
88-12	State Budget	7/88 - 6/89	Biggar, Morkoc, Nielsen (LAWR)		Movement and Modeling of Selenium and Sulfate in Soil Profiles at the West Side Field Station in Relation to Movement and Quality of Shallow Groundwater
TRACE ELEMENT CHEMISTRY AND MICROBIOLOGY:					
87-1	State Budget	7/87 - 6/89	Frankenberger, Bradford, Karlson (S&ES)		Biochemistry of Microbial Selenium Volatilization in Soil and Water
88-3	State Budget	7/88 - 6/90	Sposito (P&SB)		The Effect of Oxidation-Reduction Conditions on Transformations of Selenium in Soils of the Western San Joaquin Valley
88-15	State Budget	7/88 - 6/90	Firestone (P&SB)		Microbial Mediation of Selenium Oxidation and Reduction
88-16	State Budget	7/88 - 6/90	Doner, Lipton (P&SB)		Soil Organic Interactions with Selenium
88-17&18	State Budget	7/88 - 6/90	Bradford, Bakhtar, Lund (S&ES)		Distribution and Sources of Uranium and Associated Trace Elements in Selected Waters of the San Joaquin Valley of California
BIOAVAILABILITY AND BIOACCUMULATION OF TRACE ELEMENTS IN THE FOOD CHAIN:					
86-27	State Budget	7/86 - 6/89	Burau, Grattan (LAWR); Shennan (VC)		Prediction of Selenium Uptake into Crop Plants from Seleniferous Soils of the Central Valley of California
86-9	State Budget	7/86 - 6/89	Knight (LAWR)		Determination of the Toxicity & Biomagnification Potential of Agricultural Drain Water Contaminants in Aquatic Food Chains
87-6	State Budget	7/87 - 6/89	Page, Khattak (S&ES)		Effect of Competitive Interactions of As, Mo and Se under Cl and SO ₄ Salinity on Crop Yield and Bioavailability
86-29	State Budget	7/86 - 6/89	Amundson, Doner, Waldron (P&SB)		Selenium & Other Trace Element Transformations & Disbursements in Soil/Plant Systems & in the Field

Project Number	Funding Sources	Project Period	Principal Investigators/Affiliations	*see last page	Project Title
88-1	State Budget	7/88 - 6/90	Wu, Sachs (EH); Bureau, Epstein (LAWR)		A Study of the Effects of Chloride and Sulfate Salinity on Selenium Accumulation by Se and Salt Tolerant Genotypes of Native Halophyte Grass Species
SALINITY, SELENIUM, DRAINAGE AND IRRIGATION MANAGEMENT OPTIONS:					
86-20	State Budget	7/86 - 6/89	Rains, Qualset (ARS); Läuchli, Biggar, Nielsen, Rolston (LAWR)		Saline Drainage Water Reuse in San Joaquin Valley
86-28	State Budget	7/86 - 6/89	Sherman (VC); Grattan, Hanson (CE/UCD); May (CE/Fresno)		Potential for the Long-Term Cyclic Use of Saline Drainage Water for Irrigation of Vegetable Crops
86-2	State Budget	7/86 - 6/89	Ayars, Hoffman, Phene (ARS/WMRL); Letey (S&ES); Solomon (CSUF/CIT); Oster (CE/UCR); Shouse (ARS/USSL); Hanson (CE/UCD); Wallender (LAWR)		Effect of Irrigation Quantity & Application Uniformity on Crop Yield & Se Uptake When Irrigated with Drainage and Surface Water Supplies
86-30	State Budget	7/86 - 6/89	Oster (CE/UCR); Hanson, Goldhamer (CE/UCD); Phene (ARS/WMRL); Fulton (CE/Kings Co); Dellavalle (Dellavalle Lab/Fresno)		On-Farm Demonstration of Surface and Subsurface Irrigation Systems
87-5	State Budget	7/87 - 6/88	Nielsen, Rolston (LAWR); Hanson, Goldhamer (CE/UCD); Phene, Hoffman (ARS/WMRL); Oster (CE/UCR); Kerby (CE/Shafter); Fulton (CE/Kings Co)		Crop Response to Nonuniformities of Soil Water & Salinity for Subsurface Drip, Surge, and Furrow Irrigation Systems
88-9	State Budget	7/88 - 6/89	Vaux, Stevens (S&ES)		Irrigation Water Surcharges and Selenium Control: an Intraseasonal Approach
88-13	State Budget	7/88 - 6/90	Wallender, Hopmans (LAWR)		Soil Spatial Variability Considerations in Salt Emission and Drainage Reduction

AE = Agricultural Economics, UCD
 A&PE = Agriculture and Resource Economics, UCB
 A&ES = Agronomy and Range Science, UCD
 APS/WFRL = ARS/Water Management Research Laboratory, Fresno
 ARS/USSL = ARS/US Salinity Laboratory, Riverside
 B&PS = Botany and Plant Sciences, UCR
 CE/___ = Cooperative Extension (campus or county)
 CSUF/CIT = CSUF/Center for Irrigation Technology, Fresno
 E&P = Entomology and Parasitology, UCB
 EH = Environmental Horticulture, UCD
 LAWR = Land, Air & Water Resources, UCD

P&A = Physiology and Anatomy, UCB
 P&SB = Plant and Soil Biology, UCB
 POM = Pomology, UCD
 S&ES = Soil and Environmental Sciences, UCR
 USDA/CRS = USDA-Cotton Research Station, Shafter
 VC = Vegetable Crops, UCD
 WSFS = West Side Field Station, Five Points

TECHNICAL PROGRESS REPORTS

HYDROLOGY AND TRANSPORT OF SALTS AND TRACE ELEMENTS

PROJECT TITLE: Influence of aeration and water-logging due to fluctuating water tables on the fate of selenium in contaminated soils.

PROJECT NUMBER: 88-7

DURATION OF FUNDING: July 1988 - June 1990

PROJECT INVESTIGATORS:

Name: D. A. Goldhamer, Specialist
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ABSTRACT:

Columns packed with contaminated pond sediments and planted to saltgrass are being irrigated biweekly and monitored for selenium concentration in the soil solution, gaseous selenium from the soil and plant surface, gaseous selenium in the soil, and selenium concentration in the effluent. Soil temperature, redox potential, and suction head are also measured. Results obtained indicate that volatilization of Se from the soil surface was greater for the sediments that were not covered with the fill material. However, Se volatilization was observed in the sediments covered with the fill material as well. Se volatilization was observed within the soil profile. The rate of Se volatilization from the soil surface and within the soil profile decreased with time. The maximum rate of volatilization within the profile coincided with the location of maximum soluble SE concentration in the profile. Soluble Se at all depths decreased with time due to leaching, volatilization and perhaps immobilization and plant uptake.

PROJECT OBJECTIVES ADDRESSED:

- 1) The fate and distribution of selenium in contaminated soil under transient water flow as influenced by aeration induced by and in the presence of saltgrass,
- 2) the fate of selenium in tainted drain water reintroduced by irrigation in a closed cropped system as described in part 1,
- 3) the fate of selenium in the soil as influenced by water table fluctuations.

RESEARCH PLAN AND PROCEDURES:

We are investigating the transport of Se in contaminated soil under variable oxidation states in lysimeters planted to saltgrass under various irrigation and drainage regimes. These include irrigating

with aqueduct water in the presence of fluctuating water tables, continuously rising water tables, and in the absence of a water table. These studies will simulate conditions found in Se contaminated soils in the presence of unstable perched groundwater that reaches minimum and maximum depths in late winter and summer, respectively, as well as agricultural soils with drainage systems.

Sediments from pond 7 of Kesterson Reservoir were collected from 0-15, 16-30, 31-60, and 61-100 cm depth intervals and brought to the greenhouse. Subsequently sediments were air-dried in the greenhouse over a three week period. Sediments from each depth increment were sieved and thoroughly mixed to get a homogeneous material. Sediment columns approximately one m in length and 15 cm (i.d.) were packed and placed in a controlled temperature chamber inside greenhouse. The top of the columns are exposed to the greenhouse conditions at temperatures similar to summer conditions at the Kesterson Reservoir. A total of six columns were prepared (columns I-VI). In one case sediments were packed in the same order as collected from the reservoir (columns I, III and V). This set of columns are referred to as non-filled sediments. In another case (columns II, IV, and VI) 30 cm of fill material used to fill the low areas of Kesterson ponds was placed on the top of the upper 65 cm pond sediments (0-15, 16-30, 31-60, and 5 cm material from the 61-100 cm layer). This was done to simulate the filled areas of the ponds and are referred to as filled sediments. A 3 cm sand layer was placed at the bottom of all columns to facilitate the drainage from the bottom of the profile.

Initially aqueduct water was applied from the bottom of the columns at zero pressure to wet the columns by upward infiltration. After wetting was complete the monitoring instruments were installed and soil samples were taken for water (1:5) and acid-extractable (perchloric acid) Se analysis. Native plants (saltgrass) were transplanted to these columns. The irrigation started by applying aqueduct water. The irrigation interval was 14 days (biweekly). Columns I and II will have a fluctuating water table, columns III and IV will have continuously rising water table and columns V and VI will have a constant water table at the depth of 95 cm. The drainage water in columns V and VI will be recycled by mixing the effluent with aqueduct water.

An automatic drip irrigation system is used to apply irrigation water. The actual evapotranspiration (ETc) is measured in a separate column by weighing the column weekly.

Total water extractable, and total acid extractable Se initially present in the sediments were determined. Thermocouples, redox potential electrodes, and tensiometers were installed for monitoring soil temperature, redox potential, and soil water pressure head, respectively. Porous cups were installed at various depths (Figure 1) for soil water sampling. To determine the soil zone from which Se volatilization might occur, soil gaseous Se was sampled at various depths periodically for volatile Se analysis. Perforated stainless steel tubes (gas probes) were installed at various depths (Figure 2) for this purpose. After purging the probes with nitrogen gas, charcoal cartridges containing 0.4 g of charcoal filter were placed in the probes for a period of about 24 hr. A hydrogen peroxide-sodium hydroxide solution was used to extract Se from the charcoal. The solutions were heated at 90° C before analysis. Se gas sampling was performed prior to and after irrigation.

Volatilization of Se from the soil surface and plant canopy were measured before and after irrigation by covering the plants and circulating the air inside the chamber through a Se gas washing assembly (Figure 2). Alkaline solution of hydrogen peroxide was used for gas washing. The solution was heated for about one hour at 90° C before analysis. Soil solution samples were collected one day after irrigation from various depths. Approximately 2 ml of soil solution was collected using the suction cups and the vacuum manifold. Effluent samples were collected for the duration of irrigation interval and was analyzed for acid-extractable Se. Saltgrass was clipped on August 17, 1989 and Se analysis will be performed on the plant samples. The water table in columns I, II, III, and IV is being gradually raised by applying water from the bottom of the profile to simulate the groundwater rise.

RESULTS AND DISCUSSION:

The distribution of selenium in the soil profile before irrigation for the filled and non-filled sediments is shown in Figure 3. The distributions of selenium concentration in the soil solution (microgram/liter) after application of 3.8, 26.5, and 54 cm of irrigation water for both non-filled (columns I, III, and V) and filled (II, IV, and VI) sediments are shown in Figures 4 and 5, respectively. The concentration of soluble Se in the non-filled sediments decreased with both time and depth due presumably to downward movement, volatilization, plant uptake and immobilization mechanisms. In the case of filled sediments the concentration of soluble Se in the fill layer increased substantially after wetting due to upward movement of Se during upward wetting (see also Figure 3). However, the concentration of soluble Se decreased in the first measurement depth (7.5 cm) following application of 26.5 cm of irrigation water. After application of 54 cm of water soluble Se decreased even further at all depths.

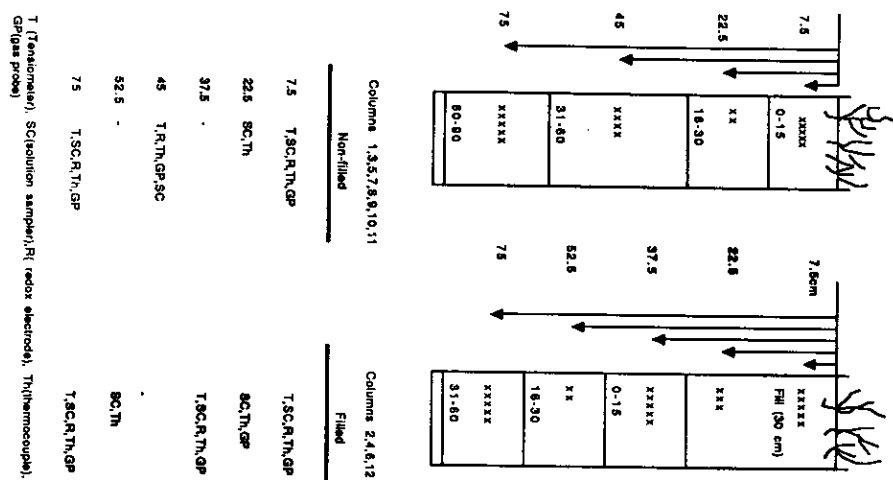
The average selenium volatilization before and after irrigation events from the soil surface measured after application of 3.8, 26.5, and 54 cm of irrigation water for both filled and non-filled soil is shown in Figure 6. Addition of fill material to the top of the columns reduced the volatilization rate drastically. More volatilization was observed in non-filled sediments than with filled sediments perhaps due to more organic matter and higher Se concentration in the non-filled soils.

Selenium volatilization from within the soil profile indicates that selenium is volatilized from all layers. The selenium volatilization rate measured within the columns after the columns had received 3.8, 26.5, and 54 cm of irrigation water for non-filled and filled soils is shown in Figure 7 and 8, respectively. Maximum volatilization rates occurred near the soil surface for the non-filled sediments and decreased with soil depth and time. Except for the volatilization after 3.8 cm of irrigation (one week after the onset of irrigation), Se volatilization in the filled sediments increased with depth of fill material and the maximum occurred at the interface between the fill material and sediments which coincides with the location of maximum selenium concentration measured in soil solution (see also Fig. 5). In general, Se volatilization rate decreased with time which is perhaps due to less soluble Se and microbial activity.

REFERENCES CITED:

- Alemi, M. H., D. A. Goldhamer, and D. R. Nielsen. 1989. Modeling selenium transport in steady-state unsaturated soil column. Submitted for publication to Journal of Environmental Quality.
- Alemi, M. H., D. A. Goldhamer, and D. R. Nielsen. 1988a. Selenate transport in steady-state water-saturated soil columns. Journal of Environmental Quality. 17:608-613.
- Alemi, M. H., D. A. Goldhamer, M. E. Grismer, and D. R. Nielsen. 1988b. Elution of selenium from contaminated evaporation pond sediments. Journal of Environmental Quality. 17:613-618.

Figure 1. Schematic diagram of filled and non-filled sediment columns and instruments.



T, (Tensiometer), SC (solution sampler), R, (redox electrode), Th (thermocouple), GP (gas probe)

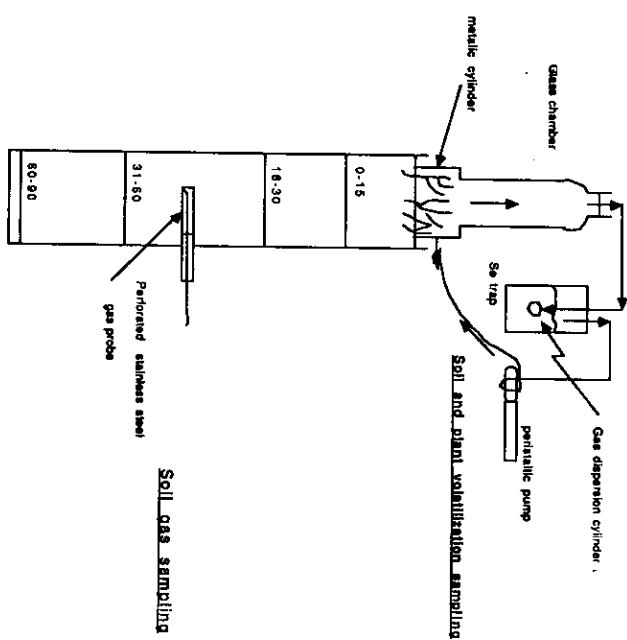


Figure 2. Schematic diagram of monitoring equipment for selenium volatilization from the soil surface and within the soil profile.

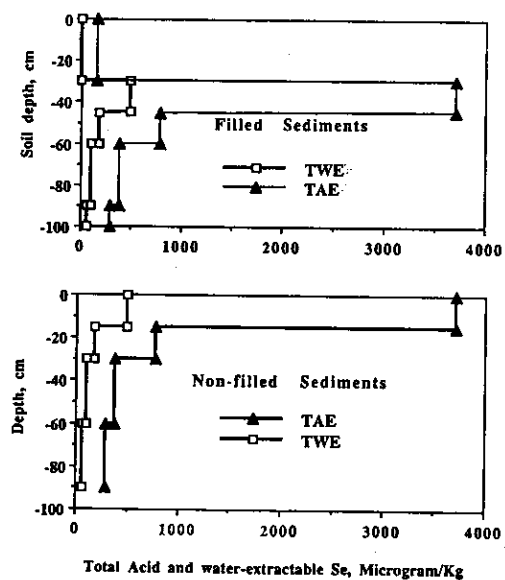


Figure 3. Total water extractable (TWE) and acid-extractable (TAE) Se in the sediments after air-drying.

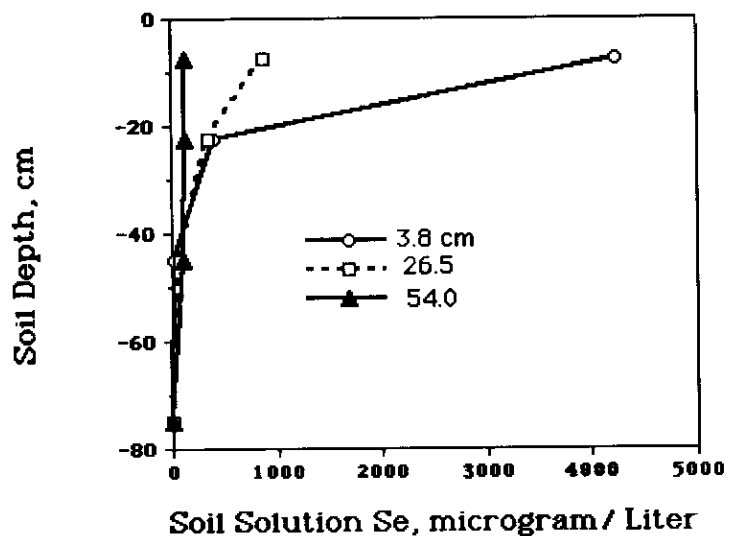


Figure 4. Total Se in soil solution after application of 3.8, 26.5, and 54 cm of irrigation water in non-filled sediments.

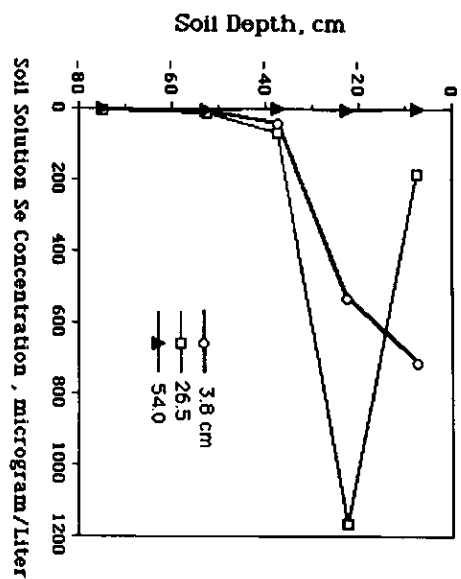


Figure 5. Concentration of total Se in soil solution after application of 3.8, 26.5, and 54 cm of irrigation water for the filled sediments.

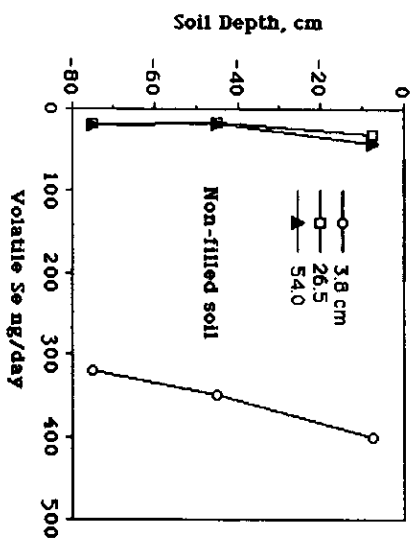


Figure 7. Se volatilization within the soil profile after application of 3.8, 26.5, and 54 cm of irrigation water.

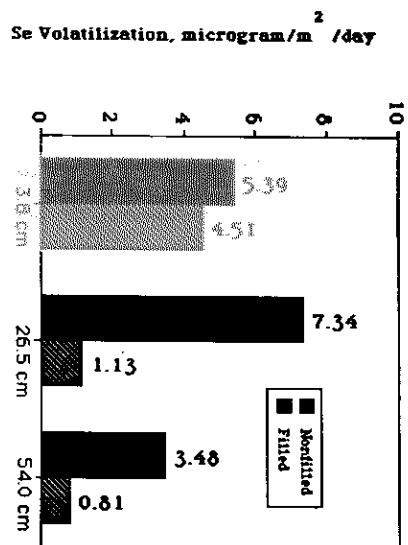


Figure 6. Se volatilization from soil surface after application of 3.8, 26.5 and 54 cm of irrigation water.

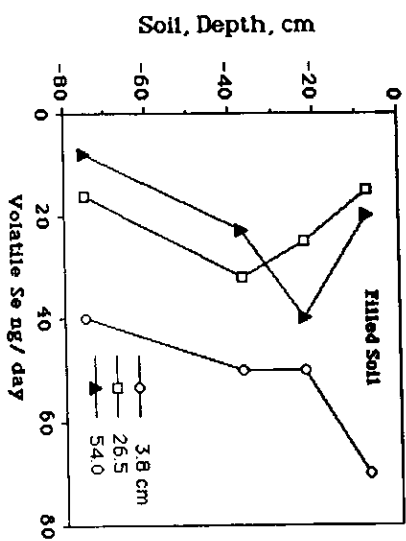


Figure 8. Se volatilization within the profile after application of 3.8, 26.5, and 54 cm of irrigation water.

PROJECT TITLE: MOVEMENT AND MODELING OF SELENIUM AND SULFATE IN SOIL PROFILES AT THE WEST SIDE FIELD STATION IN RELATION TO MOVEMENT AND QUALITY OF SHALLOW GROUNDWATER

PROJECT NUMBER: 88-12

DURATION OF FUNDING: July 1988 - June 1989

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ABSTRACT:

Monitor of water level and quality of shallow groundwater continues at the WSFS. Important temporal interactions between various water quality parameters can be identified with methods described here. Weekly concentrations of Se and SO_4 were successfully predicted from biweekly measurement and a significant input-output relation for Se- SO_4 established. Other parameters can be examined in similar manner. The Se distribution under an irrigated rotation experiment has been ascertained to provide background for model development.

PROJECT OBJECTIVES ADDRESSED:

All objectives.

RESEARCH PLAN AND PROCEDURES:

Monitoring of the water table depth at the West Side Field Station by Piezometer #1 indicates the rise may have stabilized after 296 months of monitoring. The rise began about the time canal water was introduced in the area as shown in Figure 1. Monitoring of the water table depth and quality continues.

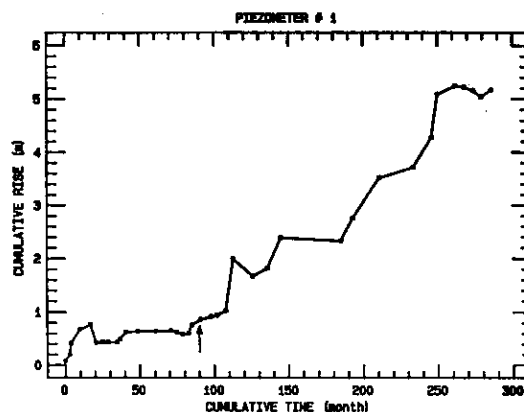


Figure 1. Cumulative rise in the water table at the WSFS with time. Arrow indicates introduction of canal water to the area.

Short term fluctuations in the water table and the variability of these changes with time are best demonstrated by measurement being made on the various wells an example of which is included later in this report and illustrated last year.

Cropping and Se Movement

Movement of selenium through soil profile and the vadose zone as a result of crop irrigation is being examined by sampling plots receiving different water qualities.

The plots are located at the WSFS with samples removed after the 1988 season at 30 cm intervals to the water table. Two sites reported on here were cropped and irrigated as shown in Table 1.

Table 1. Water quality and crop grown on two plots sampled for Se in 1988.

Year	Site 38	Site 24	Site 36
1986	CF	CS	TS
1987	CF	CF	CF
1988	TS	TS	CF

C = cotton; T = tomatoes; F = low salt; S = high salt

The low salt water is canal water with no Se and the HS water is shallow saline water with measurable Se content.

Both Site 24 and 38 reflect the addition of Se during the 1988 season as shown by the concentrations at 21 ppb in Figures 2 and 3. The peak at 50 ppb in Plot 24 could be attributed to the addition of high salt water in 1986 followed by displacement in 1987 with low salt water. On the other hand Plot 38 shows a similar peak of 40 ppb with Se being added only in 1988 after 2 years of low salt water. In addition another major peak is observed at 200+ cm and lesser peaks at 550 cm. These latter concentrations reflect the addition of Se water to the area prior to 1986 when the experiment was initiated. Displacement of the Se by low salt water ensued.

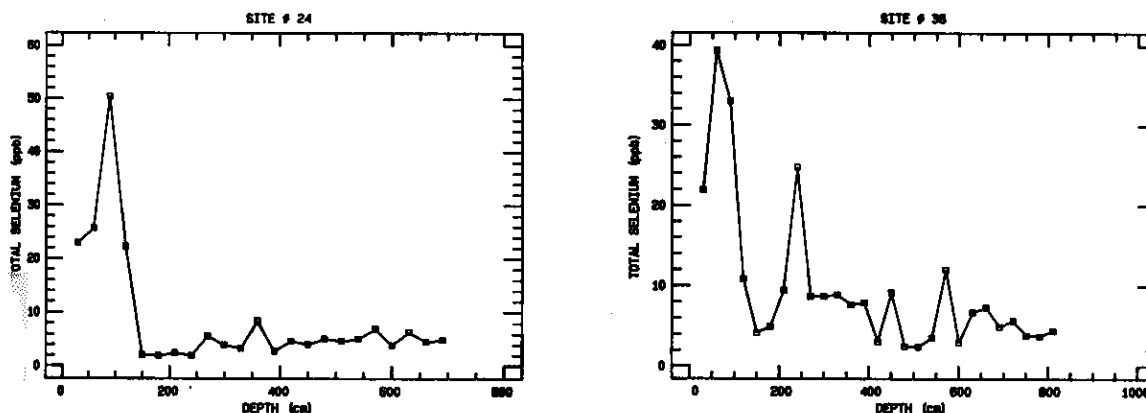


Figure 2. Selenium distribution with depth in Plots 24 and 38 after treatments give in Table 1.

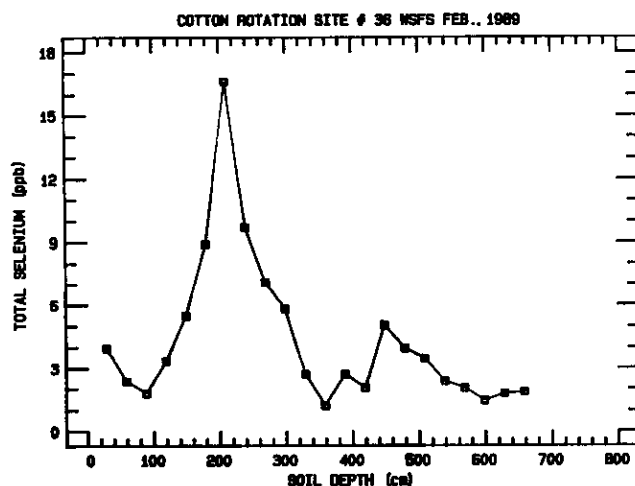


Figure 3. Selenium distribution with depth in Plot 36.

In Plot 36 salt water was added in 1986 as was plot 24 and the order of the crops grown was reversed. However, not only the concentration but also the depth of displacement of the major peak is quite different in the two plots. Differences in water application as well as crop uptake will influence the resultant distribution and these factors will be included in the model currently being examined.

Selenium and Sulfate

The interrelation between sulfate, selenium and nitrate in the groundwater has been examined more thoroughly and methods of testing the interactions on other parameters explored. Se and SO_4 concentrations of the groundwater were determined biweekly and state space methods applied. A third order covariate and second order univariate state space models for estimating Se and SO_4 , respectively, on a weekly basis were found satisfactory.

A correlation coefficient of 0.99 was obtained for both Se and SO_4 when the model was used to estimate the measured values. The order of the model used is based on a discriminant criteria of Akaike's Information Criteria (AIC). Figure 4 presents the estimated and measured values of Se and SO_4 . Even for weekly "observations" of these two variables there appears to be significant temporal variability.

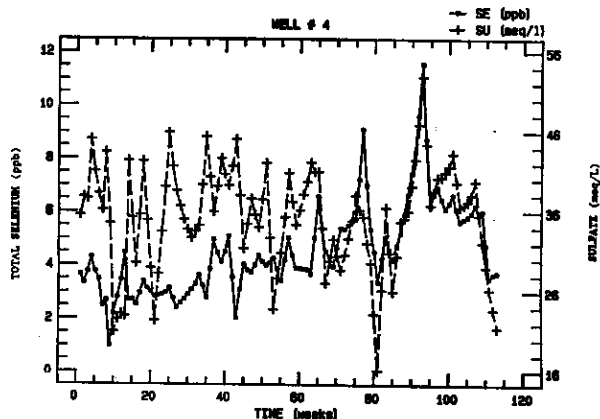


Figure 4. Combined measured and estimated Se and SO_4 in groundwater from well #4.

The input-output relationship between Se and SO_4 is illustrated in Figure 5 for well 4. The solid lines are ± 2 standard error and the following model illustrates the output.

$$\text{Se}(t) = 0.044 \text{SO}_4(t) - 0.036 \text{SO}_4(t+1) + 0.042 \text{SO}_4(t-2) - 0.036 \text{SO}_4(t-12)$$

This equation reflecting what is shown in Figure 5 indicates a strong lagging interaction at (t-2) and (t-12), immediate interaction at (t) and leading interaction at t+1 between Se and SO_4 . Other relationships that are barely significant were not included in the model equation for that reason.

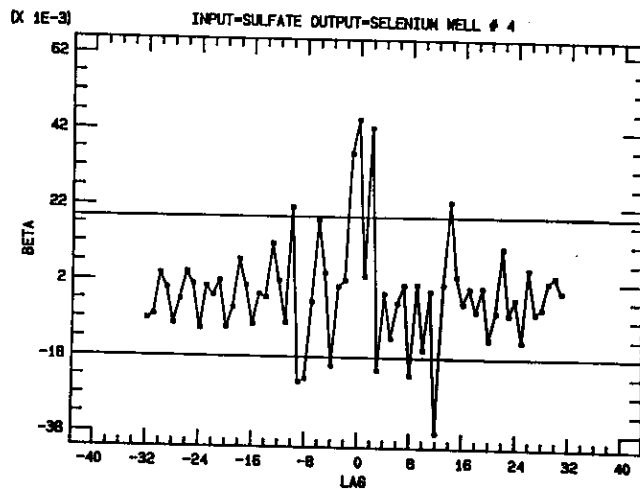


Figure 5. Input-output relationships for Se- SO_4 from water analyses of well #4.

Water table depth and parameters concentrations are being compared for congruent or random behavior in order to examine the influence of transient local conditions or water quality. This is illustrated in Figure 6 for Se in well #1. Similar trends appear in the changes of both parameters with time although the changes are more erratic for concentrations as might be expected. Nevertheless the changes in water level are 2.2 m in the time period of 96 weeks!

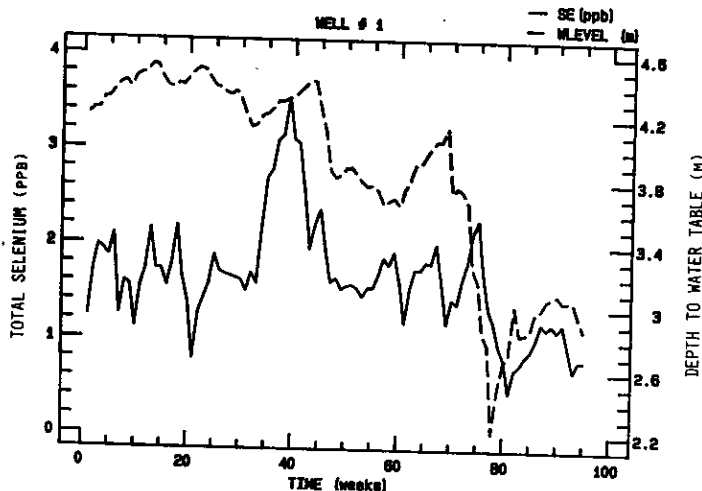


Figure 6. Changes in water depth and Se concentrations in well #1 over a 90-week period.

To analyze the temporal behavior of any one of a large number of water quality parameters, it is important to determine and identify the proper order and type of time series model to be used. This can be initiated by calculating sample autocorrelation and partial autocorrelations as shown for Se from well #1 in Figure 7 and 8. The dashed lines indicate the 95% confidence interval. The sample auto correlation shows four significant values with a lag corresponding to 4 weeks.

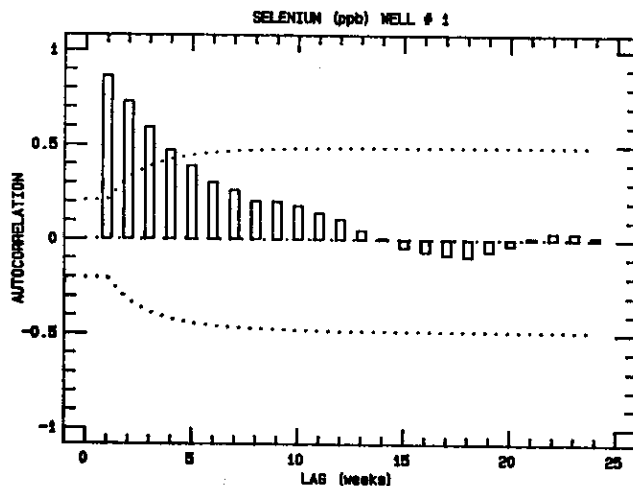


Figure 7. Autocorrelation of Se from well #1. Correlation up to 4 lags is indicated.

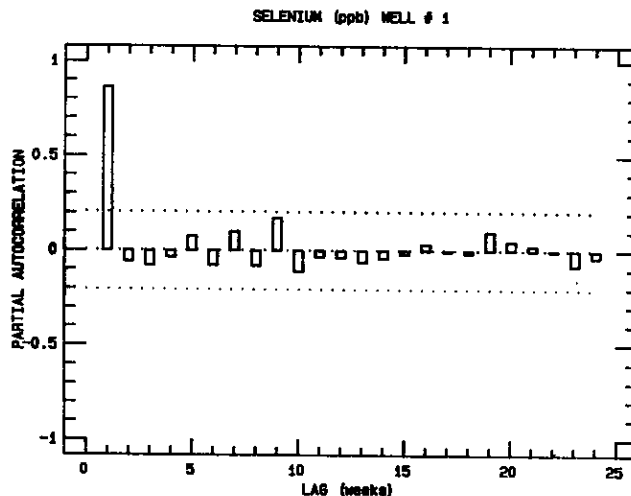


Figure 8. Partial autocorrelation of Se from well #1.

Partial autocorrelation shows only one significant value in Figure 8. These indicators suggest that Se in well #1 can be described by a first order auto regressive model. Fitting such a model to the data lead to computation of the indicated coefficients

$$Se(t) = \mu + \phi_1 Se(t-1) + \epsilon_t$$

$$Se(t) = 0.14 + 0.896 Se(t-1) + \epsilon_t$$

$$\text{Standard error of } \phi_1 = 0.049$$

The probability density function of the model residuals should be normally distributed as shown in Figure 9.

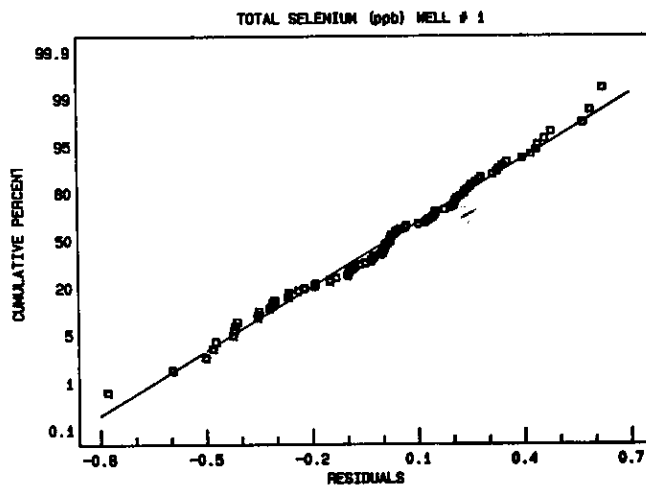


Figure 9. Probability density functions of model residuals of Se concentration in well #1.

For a valid model the autocorrelation and the partial autocorrelation functions should not yield any significant values and that is demonstrated in Figure 10.

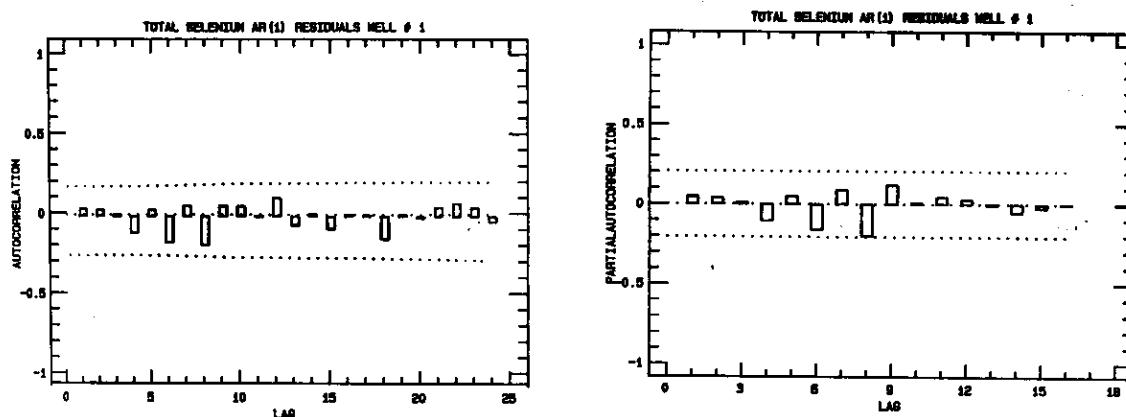


Figure 10. Autocorrelation of residuals of model describing temporal concentration of Se in well #1.

As a further criteria concerning the validity of the model, a one-to-one relationship should exist between the integrated periodogram and the frequency. That is illustrated in Figure 11. The solid lines on either side of the periodogram represent the 90% and 95% confidence intervals.

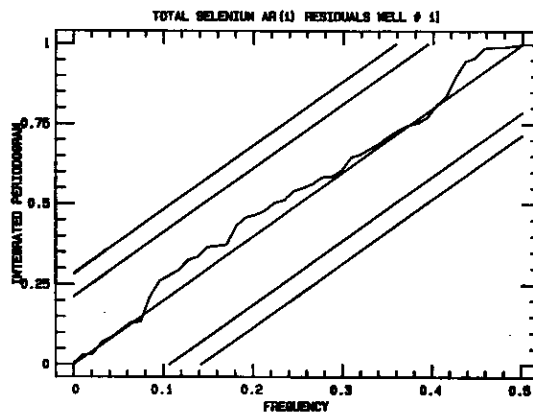


Figure 11. Periodogram of total Se autoregressive (1) residuals for well #1.

The methods outlined here appear to provide useful means for evaluating the temporal and perhaps spatial behavior and interaction of various water quality parameters in the shallow water table-unsaturated zone of the earth materials at the WSFS and the corresponding alluvial fans.

Se-SO₄-NO₃

Recent investigations suggest interactions between Se-SO₄-NO₃. In the presence of SO₄, Se is excluded and in the presence of NO₃, the transformation and immobilization of selenate in shallow groundwater is inhibited. Assuming that Se is the output and SO₄ the input to the system the impact of NO₃ on the system can be examined by inclusion and exclusion in the model. When this was done for the current water samples from wells at WSFS, the inclusion of NO₃ in the model was not justified.

This is illustrated in Table 2. For NO₃ to be significant the F-test would have to exceed 9.15 whereas it is only 0.047. It is therefore not justified to include NO₃ and we conclude NO₃ is not influencing the Se-SO₄ interaction.

Table 2. Analysis of power for NO₃ given SO₄.

Source	Power Frequency 0.047	df	F-Test 0.047
NO ₃	0.01317	4	0.053
Error	0.384	6	
Total	0.3977	14	

PUBLICATIONS AND REPORTS:

Morkoc, F. and J. W. Biggar. 1989. Time series modeling of Selenium and Sulfate in groundwater. Trans. ASAE (in press).

TRACE ELEMENT CHEMISTRY AND MICROBIOLOGY

PROJECT TITLE: BIOCHEMISTRY OF MICROBIAL SELENIUM VOLATILIZATION IN SOILS AND WATER

DURATION OF FUNDING: July 1987 - June 1989

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RESEARCH STAFF:

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PROJECT COLLABORATORS:

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ABSTRACT:

Selenium (Se) poisoning from agricultural wastewater has been blamed for wildlife deaths and deformities at Kesterson Reservoir (Merced County, CA). One approach in reducing the Se content in seleniferous sediments is based on microbial methylation of Se. This study was conducted to determine the optimum environmental conditions for volatilization of Se. A saline ($>20 \text{ dS m}^{-1}$) seleniferous soil collected from Pond 4, Kesterson Reservoir was assayed for dimethylselenide (DMSe) production by incubating it for up to 120 hours at 22°C under various treatments. DMSe was monitored by gas chromatography and identified by gas chromatography-mass spectrometry. The conditions or additions optimum for DMSe production were: pH 8.0; moisture content, field capacity ($\sim 33 \text{ kPa}$); temperature, 35°C ; L-methionine, 100 mg kg^{-1} soil; galacturonic acid, 3.6 g C kg^{-1} soil; and protein sources including casein (2.0 g C kg^{-1} soil) and albumin (0.05 to 2.0 g C kg^{-1} soil). Albumin applied to soil enhanced gaseous Se production 19.3-fold over the unamended control. It should be possible to apply these findings in a management practice to detoxify seleniferous sediments.

KEYWORDS: Volatilization, biomethylation, dissipation of selenium, bioremediation

PROJECT OBJECTIVES:

The objective of this study was to determine the environmental factors which stimulate biomethylation of Se from an actual problem site, i.e., a soil with high salinity ($>20 \text{ dS m}^{-1}$) and with the native Se species being comprised of both inorganic and organic fractions. Attempts were made to maximize Se volatilization. The parameters which were evaluated included:

pH, moisture content, temperature, organo-Se substrates, and amendments such as L-methionine, carbohydrates and proteins.

RESEARCH PLAN AND PROCEDURES:

The seleniferous soil used in this study had been collected from Pond 4, Kesterson Reservoir (Fig. 1) and had the following properties: pH, 7.7 (1:2 soil:water); organic C (wet oxidation), 37.0 g kg⁻¹; total nitrogen, 2.53 g kg⁻¹; total Se, 60.7 mg kg⁻¹; boron, 19 mg kg⁻¹; electrical conductivity of a saturated extract (EC_e), 22.0 dS m⁻¹; sodium absorption ratio (SAR), 25; exchangeable sodium percentage (ESP), 26; and texture, 15% clay and 58% sand. The soil was air-dried and sieved (2 mm) prior to use.

Method of Assay

Routinely, DMSe production was monitored as follows: 25 g of soil were placed in a 125-mL screw-cap Erlenmeyer flask and treated with 12 mL of deionized water. The soil was maintained at approximately -33 kPa unless otherwise noted. The flasks were sealed with Mininert valve-septa (Dynatech, Baton Rouge, LA) and incubated at room temperature (22 ± 2°C). DMSe was determined by sampling the headspace above the soil with a gas-tight 1-mL glass syringe and injecting the sample into a gas chromatograph (GC). The GC (Shimadzu, Kyoto, Japan) was equipped with a flame-ionization detector (FID) and a 3-m 10% Carbowax 1000, Chrom W-AW 60/80 mesh column (Alltech, Deerfield, IL). The column temperature was 50°C. The operating conditions consisted of the following: carrier gas, N₂, 13 mL min⁻¹; H₂ flow, 50 mL min⁻¹; air flow, 500 mL min⁻¹; injector temperature, 105°C; detector temperature, 105°C. Signal peak area and retention times for DMSe were recorded using a Hewlett-Packard (Avondale, PA) Model 3390A integrator. They were compared with reference standards which had been made by evaporating weighed amounts of 99.5% DMSe in large containers closed with a Mininert valve-septum. After analyzing the sample headspace, the cap was removed and the flask was flushed with air for 30 min. Analysis for DMSe was carried out at 24-h intervals up to 120 hours.

Gas Chromatography-Mass Spectrometry

The methylated gas was identified by gas chromatography-mass spectrometry (GC-MS). The gas chromatograph (Hewlett-Packard Model 5890) was equipped with a 30 m by 0.25 mm db-5 capillary column (J&W Scientific, Folsom, CA) and connected to a Hewlett-Packard Model 5970 MSD mass spectrometer. The operating conditions were as follows: injector temperature, 220°C; column temperature, 50°C rising to 180°C after 2 min at 10°C min⁻¹; mass range, 40 to 270; scan rate, 1 sec⁻¹; threshold, 600; electron impact, 70 eV; and ionizing source temperature, 250°C. A 5-mL sample was taken from the headspace using a gas-tight syringe and injected directly. Mass spectra were interpreted on the basis of molecular weight and fragmentation pattern of reference standards.

Factors Affecting Biomethylation of Selenium

pH

For this experiment, 25 g of soil were saturated with 50 mL MUB having the following pH values: pH 5, 6, 7, 8, and 9. Tests showed that with a soil:MUB ratio of 1:2, the pH of the soil-buffer mixture did not deviate more than ± 0.1 pH unit. All other experiments were conducted at the native pH of 7.7.

Moisture

The soil (25 g) was treated with the following moisture regimes: air-dry, and 12 mL (-33 kPa), 25 mL (1:1 paste) and 75 mL (1:3, soil:water) of deionized water. In the experiments to follow, a moisture content of -33 kPa (field capacity) was maintained.

Temperature

The soil (25 g) was moistened with 12 mL of deionized water and incubated at the following temperatures: 5, 15, 20, 25, 30 and 35°C. To one set of flasks, D-galacturonic acid (2 g C kg⁻¹ soil) was added and incubated at 25°C. The effect of temperature on the biomethylation reaction was expressed in terms of a temperature coefficient (Q_{10}) which is the factor by which the rate constant is increased by raising the temperature 10°C.

$$Q_{10} = \left(\frac{\text{Biomethylation at } T_2}{\text{Biomethylation at } T_1} \right)^{\frac{10}{T_2 - T_1}}$$

Organo-Selenium Substrates

The soil (25 g) was treated with the following organic Se compounds on an equivalent carbon basis (200 mg C kg⁻¹ soil): seleno-DL-cystine, seleno-DL-ethionine, 6-selenoguanosine, 6-seleninosine, seleno-DL-methionine, 6-selenopurine and selenourea. The organo-selenium compounds served as substrates for microbial methylation in addition to the native Se. Their respective controls consisted of DL-cystine, DL-ethionine, guanosine, inosine, DL-methionine, purine and urea.

L-Methionine

The influence of L-methionine on volatilization of Se was tested by applying 0, 0.1, 1, 10, 100 and 1000 mg L-methionine kg⁻¹ soil.

Carbohydrates

Among the C sources assessed for stimulation of Se methylation, the following compounds were added at an equivalent of 2 g C kg⁻¹ soil: glucose, fructose, fucose, sucrose, lactose, maltose, and rhamnose. Other compounds tested (equivalent of 2 g C kg⁻¹ soil) included: cellobiose, cellulose, chitin and starch. Further studies were conducted to determine the optimum con-

centration of D-galacturonic acid to promote Se methylation. The concentrations applied were 0, 0.09, 0.4, 0.9, 1.8, 3.6 and 9.0 g C kg⁻¹ soil.

Proteins

Casein, egg albumin, and gluten were evaluated for their effect on DMSe production. The optimum concentration was determined by applying an equivalent of 0, 0.05, 0.1, 0.5, 1.0 and 2.0 g C kg⁻¹ soil. In addition, a protein hydrolysate, peptone (equivalent of 2 g C kg⁻¹ soil) was evaluated as an amendment for stimulating Se volatilization.

Method of Data Analysis

All experiments were conducted in replicates of five. The gaseous Se released in the headspace was expressed in cumulative amounts of DMSe evolved (mg Se kg⁻¹ soil). Error bars in each figure depict the standard error of the data.

RESULTS:

The evolved gas was unequivocally identified as DMSe. Dimethylselenone and dimethyldiselenide were not detected. DMSe appeared to be the only gaseous form of Se released from this sediment.

Factors Affecting Biomethylation of Selenium

pH

The optimum pH for methylation of Se in the presence of MJB was pH 8.0 (Fig. 2). MJB was selected because of its buffering capacity over a wide pH range. For comparison, DMSe production by *Alternaria alternata* isolated from evaporation pond water was reported to have an optimum pH of 6.5 (Thompson-Eagle et al., 1989). In this study, the Se methylation activity at pH 8.0 was approximately 1.34X and 1.16X higher than at the extreme pH values of 5.0 and 9.0, respectively.

Moisture

Figure 3 illustrates the biomethylation rates for DMSe at various moisture regimes. Very little DMSe was evolved under air-dried conditions. The optimum moisture content appears to be field capacity (-33 kPa, approximately 70% of the water holding capacity). DMSe production at field capacity was increased 53-fold over air-dry, 1.8-fold over a 1:1 paste, and 3.3-fold over the 1:3 soil:water regime.

Temperature

The rate of Se methylation increased with increasing temperature (5-35°C) (Fig. 4). The methylation activity was approximately 17.8-fold higher at 35°C than at 5°C. The average Q_{10} was calculated to be 2.60. That is, for every 10°C rise in temperature, the rate of biomethylation of Se increased 2.6-fold. In another set of flasks, soil was treated with D-galacturonic acid (2 g C kg⁻¹ soil) and incubated at 25°C. With the addition of C, the rate of the biomethylation

reaction was increased 2.63-fold over the unamended soil when incubated at the same temperature. Adding C was as effective in promoting biomethylation of Se as raising the temperature by 10°C.

Organo-Selenium Substrates

Among the organo-Se compounds added to the seleniferous soil, the one most readily utilized for production of DMSe was selenomethionine (Fig. 5). Selenomethionine enhanced the methylation reaction 6.18-fold over the pooled average of the other organo-Se substrates tested. Doran and Alexander (1977a) reported similar findings with substantial amounts of DMSe being produced from selenomethionine added to soil. The addition of selenoethionine, selenoguanosine, selenopurine and selenourea slightly inhibited biomethylation of Se in comparison to the unamended control. Figure 5 also reveals that methionine and ethionine stimulated DMSe production 3.6-fold over the unamended control, while cystine, guanosine, purine, inosine and urea had little effect.

L-Methionine

Since L-methionine (L-MET) applied to the seleniferous soil enhanced microbial methylation of Se, it was of interest to determine the optimum concentration for DMSe production. Figure 6 shows that there was little effect at 0.1 and 1.0 mg L-MET kg⁻¹ soil. The optimum L-MET concentration appears to be 100 mg kg⁻¹ soil. Production of DMSe was even evident at 1000 mg L-MET kg⁻¹ soil.

Carbohydrates

Among the carbon sources tested, glucose was most effective in enhancing DMSe production (2.69-fold) (Fig. 7). Other carbohydrates which stimulated DMSe production included: sucrose (2.27-fold), maltose (2.15-fold), fructose (1.69-fold), lactose (1.15-fold), fucose (1.10-fold), and rhamnose (1.05-fold). Polysaccharides were less effective in stimulating Se methylation, with only cellobiose (1.76-fold) and chitin (1.21-fold) promoting DMSe production (Fig. 8). Starch and cellulose caused no enhancement under short term incubation (120-h).

D-Galacturonic Acid

Karlson and Frankenberger (1988b) reported that volatilization rates of ⁷⁵Se (IV and VI) were increased 3-fold upon incorporation of pectin into soil at an equivalent of 2 g C kg⁻¹. Pectin is a polysaccharide present in cell walls of plant tissues functioning as intercellular material. It is a methylated polymer of D-galacturonic acid with small amounts of galactose and arabinose. Since pectin was so effective in stimulating DMSe production, this experiment was conducted to determine if D-galacturonic acid would also be active in promoting this microbial reaction. Figure 9 indicates that there was little difference in biomethylation of Se between D-galacturonic acid applied at an equivalent of 0.09, 0.4 and 0.9 g C g⁻¹ soil and the unamended control. However, when galacturonic acid was added at 1.8 and 3.6 g C kg⁻¹ soil, biomethylation of Se was enhanced 1.97- and 3.70-fold, respectively. The highest amount of D-galacturonic acid applied (9 g C kg⁻¹ soil) was less effective.

Proteins

Among the proteins tested as soil amendments, casein and egg albumin dramatically enhanced DMSe production (Fig. 10). No other treatment tested in this study was as effective. The optimum protein treatment was 0.1 g C as albumin kg^{-1} soil. This treatment enhanced gaseous Se emission 19.3-fold over the unamended control. Other application rates of albumin (0.05 to 2.0 g C kg^{-1} soil) were also effective in stimulating DMSe production. Casein had a strong stimulatory effect (16.7-fold increase) when applied at an equivalent of 2.0 g C kg^{-1} soil, while other loading rates of casein were considerably less effective. Gluten applied to the seleniferous soil enhanced DMSe production from 1.32-fold (1.0 g C kg^{-1} soil) to 2.60-fold (0.5 g C kg^{-1} soil). The highest application rate of gluten (2.0 g C kg^{-1} soil) slightly inhibited biomethylation of Se. Peptone (2 g C kg^{-1} soil) also enhanced DMSe production (1.42-fold) in comparison with the unamended control.

DISCUSSION AND SUMMARY:

Effects of pH, moisture and temperature

Chemically, the formation of DMSe, i.e., the reduction of Se(VI) and Se(IV) to the selenide state, should be favored at a low pH (Geering et al., 1968). However, in this study the pH optimum observed for DMSe production coincides with the native pH of this sediment. The indigenous microflora apparently had the highest activity when exposed to the pH it presumably had adapted to.

A decrease in Se evolution under waterlogged conditions was expected since obligate aerobic fungi are thought to be the predominant Se methylating organisms among the soil microflora (Karlson and Frankenberger, 1989). However, it should be noted that considerable DMSe was evolved from the submerged soil. Chau et al. (1976) also found substantial amounts of DMSe being produced by sediment samples saturated with water (3:1) in the laboratory. Cooke and Bruland (1987) reported the presence of methylated Se compounds (DMSe, DMDSe and DMSe^+-R) in diverse natural aquatic systems and suggested that biomethylation of Se is a widespread process.

Volatilization of Se is highly temperature-dependent. Increasing the temperature to 35°C promoted volatilization of Se. The average Q_{10} calculated for DMSe production was 2.60. Zieve and Peterson (1981) reported similar findings with ^{75}Se added to soil samples as Se(IV). The total amount of Se being evolved after 4 days at 20°C was more than 3X that at 10°C and more than 15X that at 4°C. Soil samples collected in the spring were found to evolve more Se than those collected in the summer, autumn or winter months.

Effects of organic substrates

The stimulation of DMSe production by selenomethionine was most likely caused specifically by the methionine constituent. It has been speculated that methionine or its metabolites (e.g., S-adenosylmethionine [SAM]) could serve as a methyl donor in transferring a methyl group

directly to the Se atom during the microbial methylation reaction (Doran, 1982). Doran and Alexander (1977b) reported that SAM enhanced production of DMSe from Se(IV) and elemental Se when catalyzed by cell-free extracts of Corynebacterium sp. To obtain a better understanding of the mechanism involved in the formation of DMSe, further work is needed to determine if SAM added to soil also stimulates DMSe production.

Increased Se volatilization in response to the addition of various carbohydrates was expected, since previous studies have shown that plant residues which are comprised of many of these constituents also stimulate the evolution of DMSe from soils through enhanced microbial activity (Abu-Erreish et al., 1968; Doran and Alexander, 1977a; Karlson and Frankenberger, 1988b). Substrate-specific effects apparently play a role, since some carbohydrates stimulated DMSe production strongly, while others had no effect. Stimulation of methylating vs. non-methylating microflora by specific carbonaceous soil amendments was postulated earlier (Karlson and Frankenberger, 1988b). The findings of this study confirm those speculations. This is particularly true for specific protein amendments. The results observed with the application of albumin constitute the largest enhancement of Se volatilization. Actually, of the three proteins tested, two had a strong stimulatory effect on DMSe production. Further studies are underway to identify the active ingredients of these proteins, so that lower organic loads may be applied. In addition, other economical protein sources are being screened.

Se volatilization as a bioremediation treatment

The results show that microbial methylation of Se can be stimulated in Se-contaminated sediments by specific organic amendments and basic principles which favor aerobic microbial processes. Field application of these findings may be possible, provided that similar conditions can be maintained on a large scale over a sufficient period of time. A rehabilitation program would consist of adding a specific C source, frequent tilling and irrigation with intense management being practiced in the warm summer months.

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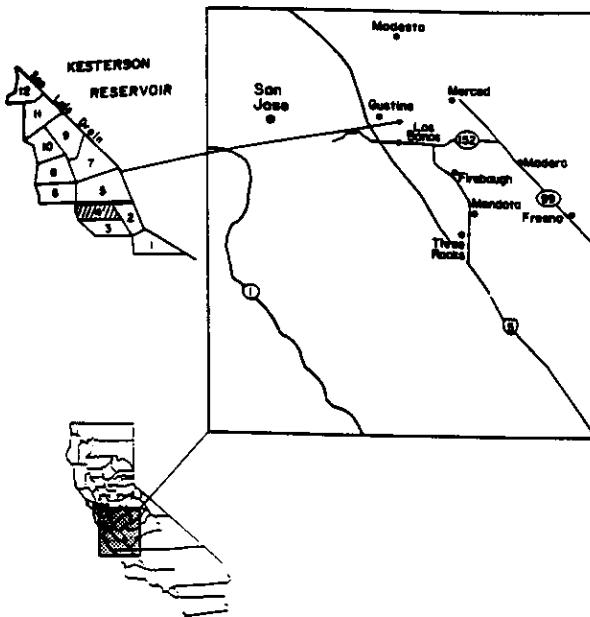


Fig. 1. Location of Kesterson Reservoir (Merced County, CA).

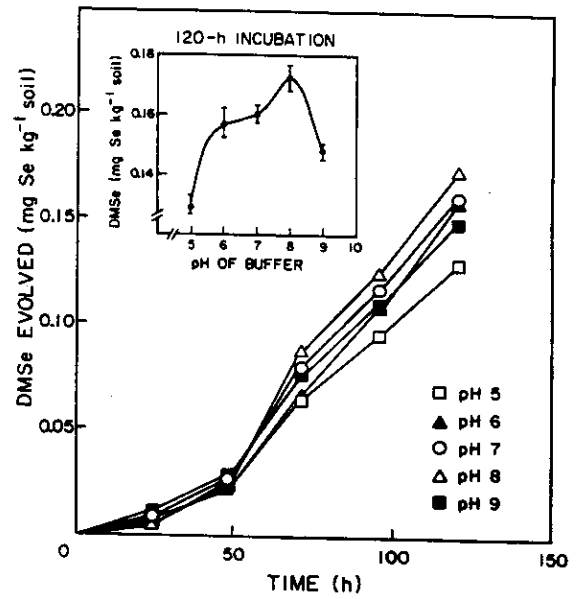


Fig. 2. Influence of soil pH on DMSe production.

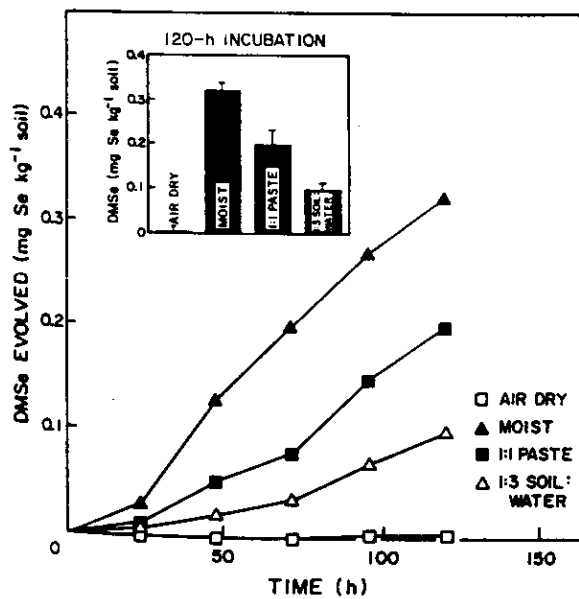


Fig. 3. Influence of moisture content on DMSe production from soil.

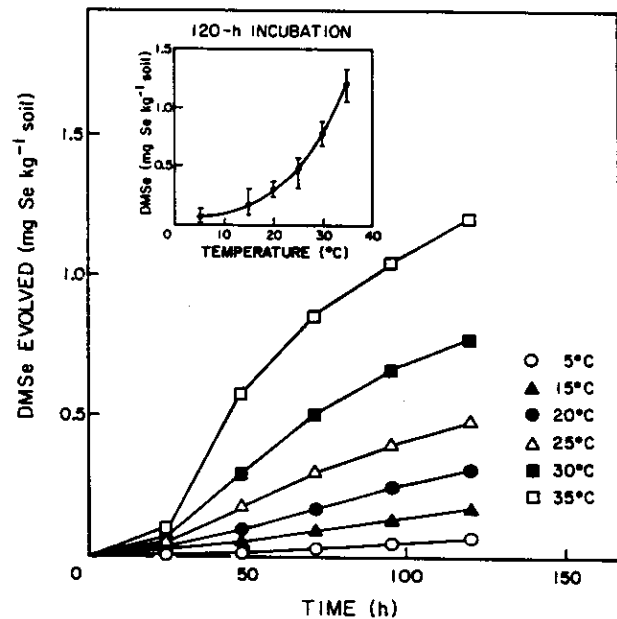


Fig. 4. Influence of temperature on DMSe production from soil.

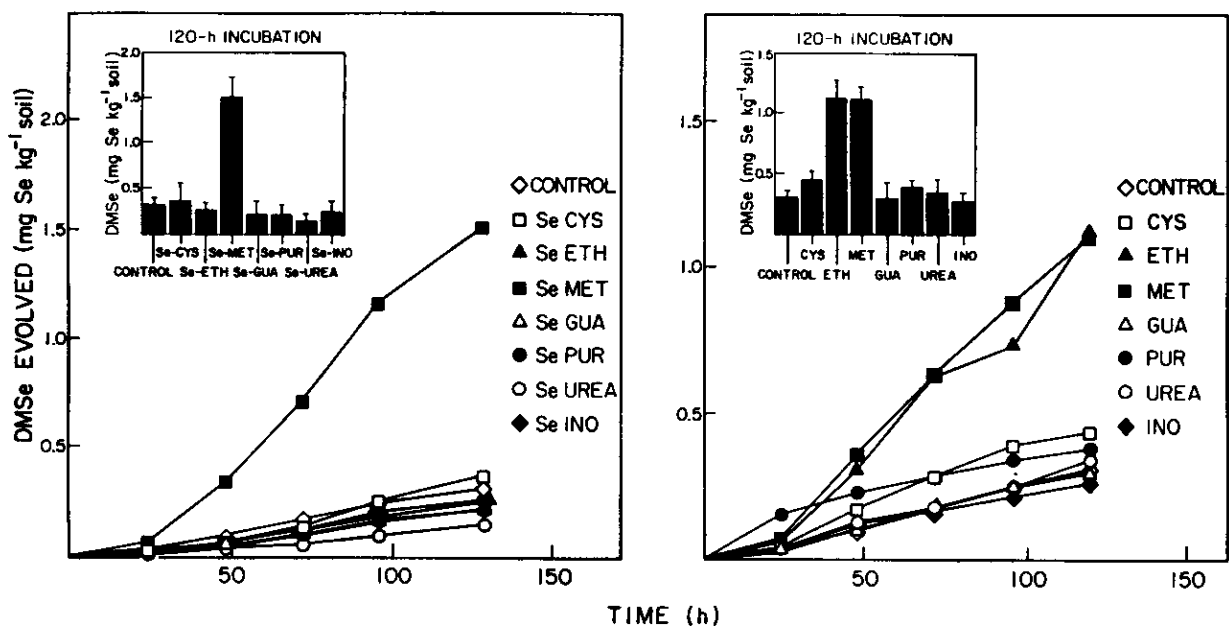


Fig. 5. Influence of organo-Se compounds on DMSe production from soil.

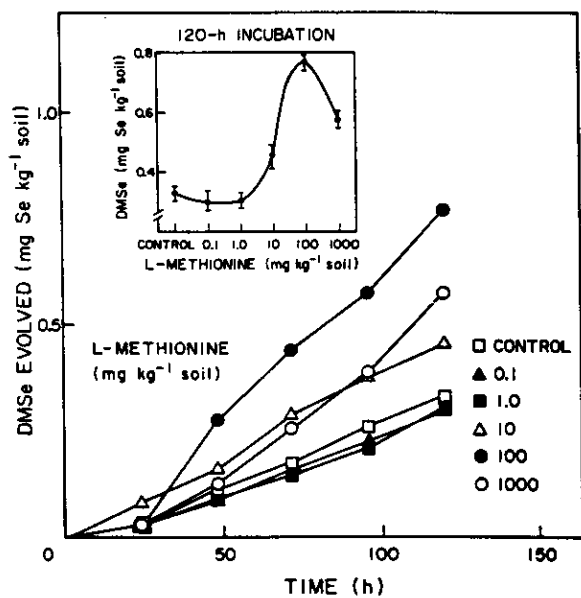


Fig. 6. Influence of L-methionine on DMSe production from soil.

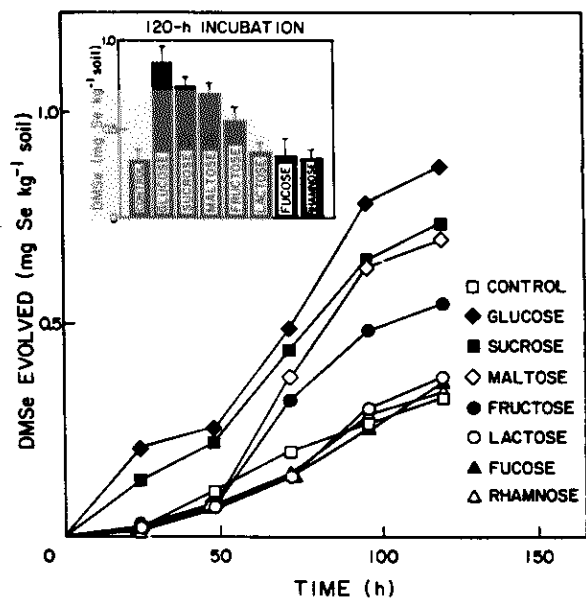


Fig. 7. Influence of carbohydrates on DMSe production from soil.

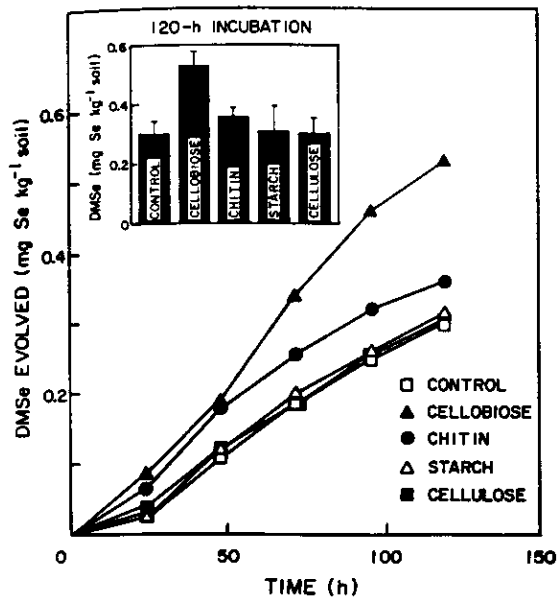


Fig. 8. Influence of polysaccharides on DMSe production from soil.

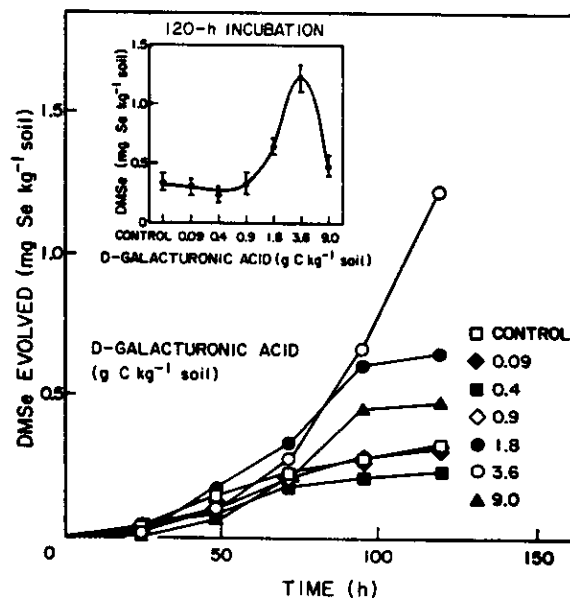


Fig. 9. Influence of D-galacturonic acid on DMSe production from soil.

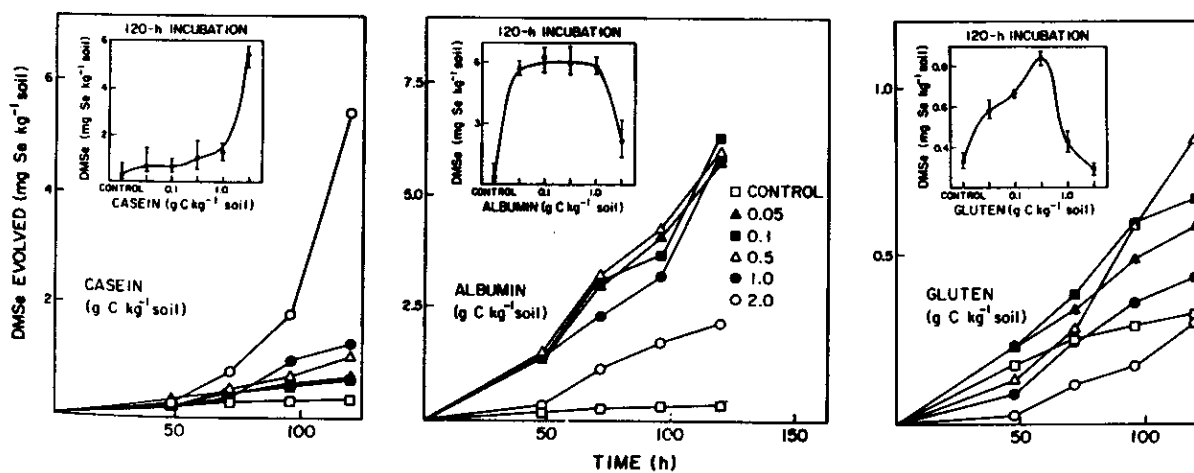


Fig. 10. Influence of proteins (casein, albumin and gluten) on DMSe production from soil.

PROJECT TITLE: THE EFFECT OF OXIDATION-REDUCTION CONDITIONS ON TRANSFORMATIONS OF SELENIUM IN SOILS OF THE WESTERN SAN JOAQUIN VALLEY

PROJECT NUMBER: 88-3

DURATION OF FUNDING: July 1988 - June 1990

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FTE Commitment: 0.10

RESEARCH STAFF:

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Staff Research Associate: Andy Yang 0.1 FTE

PROJECT COLLABORATOR:

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ABSTRACT:

An incubation apparatus was designed, constructed, and tested for the study of reduction reactions in soil suspensions. The resulting experimental assembly consisted of a reaction vessel, with provisions for continuous stirring and monitoring of electrode potential, and a sampling system for removing suspension aliquots under vacuum and replacing them with argon gas. Preliminary experiments showed that reduction processes in the Panhill soil studied in the apparatus followed the expected sequence with decreasing electrode potential over a time period of 100 hr.

KEYWORDS: Reduction Kinetics, Panhill Series, Selenate, Selenium

PROJECT OBJECTIVES ADDRESSED:

To investigate experimentally the oxidation-reduction transformations of selenium species in representative San Joaquin Valley soils under varying pH, O₂ concentration, and adsorption conditions.

RESEARCH PLAN AND PROCEDURES:

The soil to be used is the Panhill series (fine-loamy, mixed, thermic, Typic Haplargids). Experiments will be carried out in a specially-designed incubation system adapted from that of Turner and Patrick (1968). Soil in a 1:8 (w/w) suspension with its saturation extract and added starch will be placed in an incubation vessel and stirred magnetically. Electrode potential and pH will be monitored, and aliquots of the suspension will be withdrawn for analysis of soluble nitrate, manganese, iron, and selenate. Nitrate will be determined using a Lachat autoanalyzer. Manganese, iron, and selenate will be determined by inductively-coupled plasma spectrometry (Perkin-Elmer Plasma 40 emission spectrometer). Changes in the concentrations of all four constituents with time will be measured over periods of up to several weeks.

RESULTS:

Much of the first year of the project was spent in designing the incubation apparatus and performing preliminary experiments to optimize sampling and chemical analysis techniques. A diagram of the final apparatus design is shown in Fig. 1. The principal components are: (1) a 400 mL reaction vessel which contains the soil suspension, sampling tube, and Orion combination redox electrode and (2) a sampling system comprising a three-way valve to allow the introduction of argon gas equal in volume to that of the sample withdrawn under vacuum. The entire assembly is placed in a thermostatted room where temperature is controlled at $21 \pm 1^\circ\text{C}$. Approximately

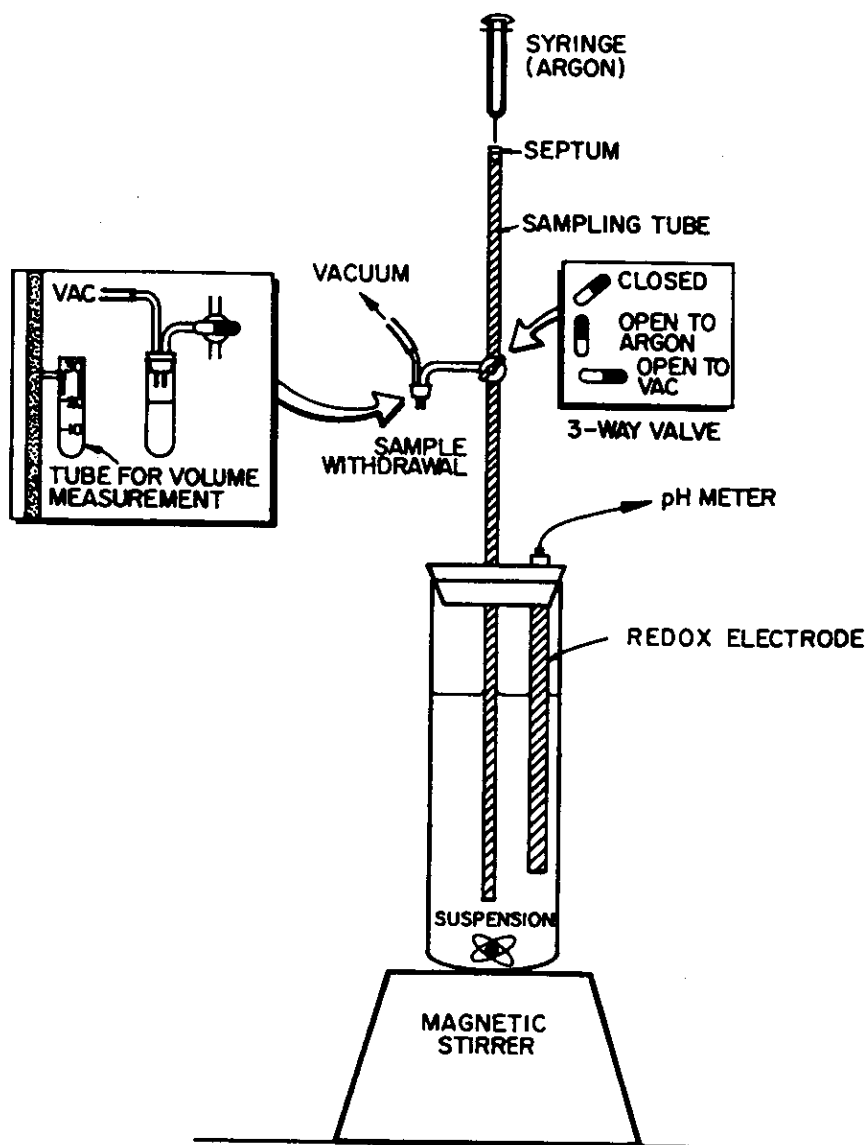


Fig. 1. Schematic diagram of the incubation vessel and sampling apparatus used in the redox experiments.

400 mL of the saturation extract of the Panhill soil is placed in the reaction vessel along with about 2 g starch and 50 g of the extracted soil. The apparatus is sealed against oxygen entry as the incubation period is initiated. The electrode potential in the suspension is monitored continuously via the redox electrode and a strip chart recorder. The pH value of the suspension is measured immediately in each withdrawn sample using a micro-combination electrode. A portion of each sample then is centrifuged and analyzed for nitrate, manganese, and iron. In experiments where the soil extract has been amended to contain 2 mmol m⁻³ selenate, both selenate and selenite are determined also. (The Panhill saturation extract contains negligible selenium.)

Table 1 shows some preliminary results obtained with the apparatus diagrammed in Fig. 1. The evident trends with incubation time are the downward trend in electrode potential (E_H), pH, and nitrate concentration and the upward trend in manganese concentration. The erratic time-variation of the iron concentration is believed to be caused in part by the presence of colloidal iron in the suspension aliquot, even after centrifugation.

Table 1. Time-variation of the concentrations of nitrate, manganese, and iron in an incubated Panhill soil suspension.

Elapsed time, hr	E _H mV	pH	NO ₃ T	Mn _T mmol m ⁻³	Fe _T
0.0	+212	8.02	474	0.13	0.39
5.0	+215	7.83	478	0.42	25.7
21.3	+199	7.68	480	0.33	10.3
23.8	+230	7.63	398	0.25	15.6
25.8	+227	7.52	393	0.66	41.7
28.8	+222	7.56	390
45.4	+155	7.42	338	0.20	4.0
47.8	+147	7.35	242	10.1	6.8
49.8	+180	7.61	228	11.3	1.4
52.8	+230	7.32	211	10.0	27.7
69.8	-42	7.20	141	6.5	2.9
72.3	-103	7.29	68	20.9	1.6
75.0	-35	7.45	50	24.8	4.1
77.0	-2	7.03	28	24.9	29.4
93.0	-175	6.76	4	36.2	3.2

DISCUSSION AND SUMMARY:

Electrode potential measurements made in soil suspensions usually have only qualitative significance (see, e.g., Sposito, 1989, Chap. 6). For reference, the reduction of nitrate usually commences when E_H is in the range 200-500 mV; that of manganese in the range 200-400 mV; and that of iron in the range 100-300 mV in "pure" systems (Sposito, 1989, Table 6.1). These ranges are only in approximate agreement with the data in Table 1, since negative E_H values were observed before nitrate was depleted. This discrepancy notwithstanding, the data do indicate that reduction processes were occurring in the soil suspension in the proper sequence: E_H drops were followed by decreases in nitrate and increases in manganese concentrations. According to

the thermodynamics of reduction, the pH value should also increase (proton consumption); but instead a decrease of about 1.25 units was measured. This fact serves to emphasize that all of the variables measured are net effects of several processes, including reduction, adsorption, desorption, and dissolution.

The range of E_H over which selenate reduction takes place at pH 6 to 8 is 400 to 550 mV (Neal and Sposito, 1989). Therefore, it is expected that selenate added to the Panhill soil suspension should begin to transform approximately when manganese does. This hypothesis will be investigated during the second year of the project along with a refinement of the measurements of E_H and the chemical constituents listed in Table 1.

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PROJECT TITLE: MICROBIAL MEDIATION OF SELENIUM OXIDATION AND REDUCTION

PROJECT NUMBER: 88-15

DURATION OF FUNDING: July 1988 - June 1990

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FTE Commitment: 0.05

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Staff Research Associate: 1 @ 0.50 FTE: Tom Jones
Student Assistant: None
Other Assistance: None

PROJECT COLLABORATORS:

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Affiliation:	Plant and Soil Biology	Affiliation:	Lawrence Berkeley Laboratory
Location:	Berkeley Campus	Location:	Berkeley, CA

ABSTRACT:

Simply establishing the relative importance of abiotic versus biotic reactions during the oxidation of reduced Se species is complicated by the effects of sterilization procedures on the speciation and solubility of Se present in soil. Autoclaving was found to increase the exchangeable SeO_3^{2-} pool as well as an "available" mineral pool. Propylene oxide fumigation increased the soluble (KCl-extractable) Se pool in soil when compared to nonsterilized soil.

Analysis of the solution phase of autotrophic enrichment cultures indicates that microbiological oxidation of colloidal Se^0 occurs in excess of that result from abiotic reaction.

KEYWORDS: Selenium, Microbial, Oxidation

PROJECT OBJECTIVES ADDRESSED:

I. To identify the microbial processes occurring in Se-enriched soils and sediments which are responsible for the reduction of $\text{Se}(+6)$ and $\text{Se}(+4)$ under anaerobic conditions and contribute to the oxidation of $\text{Se}(0)$ and $\text{Se}(-2)$ under aerobic conditions.

II. To identify the products of microbial oxidation and reduction of Se using microbial cultures isolated from soils and sediments.

RESEARCH PLAN AND PROCEDURES:

As requested by the technical committee, we have focused our work on microbiological Se oxidation. Our general plan was to assess the potential for biological Se oxidation in soils from the Kesterson ponds by testing sterile versus nonsterile aerobic soil samples for rates of selenate and selenite production from reduced forms of Se. If biological Se oxidation was

significant, we would attempt to isolate chemoautotrophic bacteria from the soil and test their ability to oxidize Se in pure culture.

I. Sample collection.

Soil samples were collected from Pond 1 at Kesterson on 9/22/88. The sampling site which was under study by T. Tokunaga, had not yet been covered. Samples were taken at two depths: 0-1 cm and 1-9 cm from the soil surface. Soils were ground, sieved (2 mm mesh) and stored at room temperature.

II. Sterilization experiments.

All of the following work was done on the 1-9 cm soil samples from Kesterson Pond 1.

A. Sterilization treatments:

1. Autoclaved - twice at 1-day interval.
2. Propylene oxide - fumigated 24 h.
3. Gamma irradiation - in progress, no results reported here.

Sterility was assessed by plating onto dilute ($1/10$) tryptic soy agar.

B. Se extraction procedures:

The following fractionation sequence is based on the method of Chao and Sanzalone (1989) and Fujii et al. (1988). The sequential extraction of sterilized soil samples was as follows:

<u>Extractant</u>	<u>Se form</u>
0.25M KCl	Water soluble, nonspecifically adsorbed SeO_4^{2-}
0.1M KH_2PO_4	Exchangeable, specifically adsorbed SeO_3^{2-}
4M HCl	"Available" minerals: carbonates, some sulfides, Fe, Mn, Al oxides, amorphous minerals, some SOM

C. Quantification of Se in various fractions:

1. Total Se: determined via an LBL procedure (D. Lipton, personal commun.) quantifying Se via hydride generation/atomic absorption spectrometry (HGAAS). Samples analyzed: KCl, PO_4 extracts. Soil digests and HCl extracts were made to 6N HCl, boiled 20 min and analyzed.
2. SeO_3^{2-} : direct HGAAS analyses. Samples analyzed: KCl, PO_4 extracts.

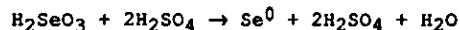
D. Total soil selenium:

Determination procedure: perchloric:nitric acid digestion [R. Glauser, from Analyst (1977) v. 102:193-200]. "Unavailable" Se = Total Se minus Extractable Se ($\text{KCl} + \text{PO}_4 + 4\text{M HCl}$). "Unavailable" Se - may include sulfides, complex humified OM, silaceous materials.

III. Culture experiments.

Autotrophic and heterotrophic enrichment cultures for Se oxidizers were established. Colloidal Se^0 was used as the reduced Se substrate. Changes in solution SeO_3^{2-} were determined with time.

A. Synthesis of colloidal Se^0 was based on Weiser (1933) and Sarathchandra and Watkinson (1981). The reaction used was:



B. Media used for enrichment cultures were as follows:

Autotrophic enrichment media was a complex mineral salts media from Collins (1969). Heterotrophic enrichment media was from Sarathchandra and Watkinson (1981). Both types of media were supplemented with a solution of elemental colloidal Se^0 to give a final concentration of 2500 ppb.

C. Enrichment media was inoculated with either field soil, propylene oxide-sterilized soil (both 0.3 g soil/20 ml media), or no soil. Cultures were sampled at 0, 5, and 12 days for analysis. There were 4 replicates per treatment.

RESULTS:

I. Effects of sterilization on Se oxidation in soil. Before assessing the significance of chemical versus biological oxidation in soil, it has been necessary to determine how the sterilization procedures themselves altered the amounts of Se found in the various fractions.

Autoclaving significantly increased the exchangeable Se pool which is predominantly SeO_3^{2-} (Figs. 1, 2, and 3). Autoclaving also caused a major increase in the size of the available mineral pool (Figs. 2 and 3).

Propylene oxide fumigation significantly increased the size of the soluble Se pool (KCl extractable (Figs. 1, 2, and 4).

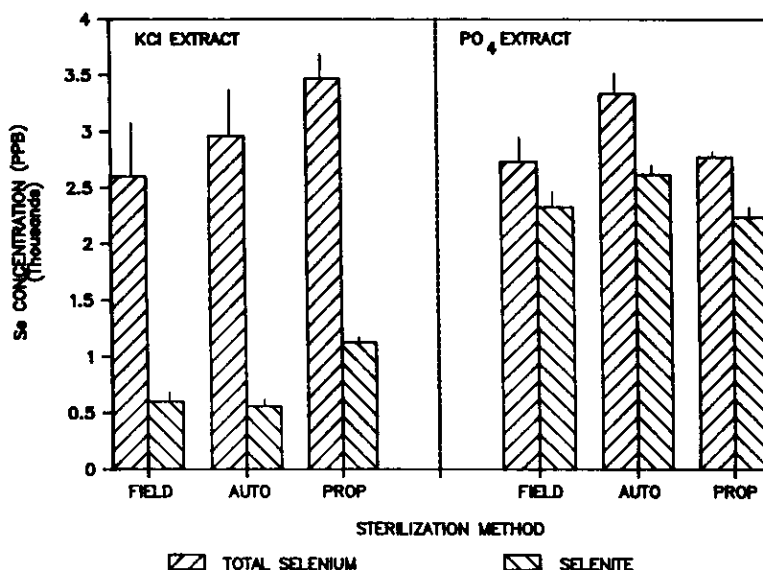


Figure 1. Effects of sterilization on soluble and exchangeable selenium pools in soil. Field: nonsterile soil; Auto: autoclaved soil; Prop: propylene oxide treated soil.

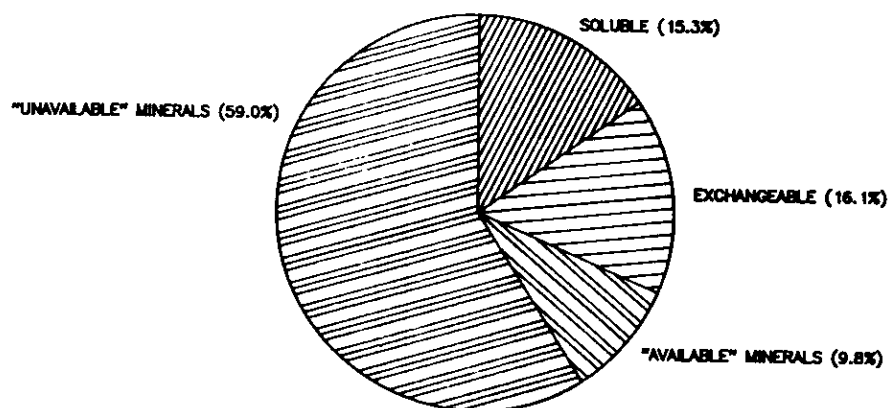


Figure 2. Distribution of Se in field (nonsterile) soil.

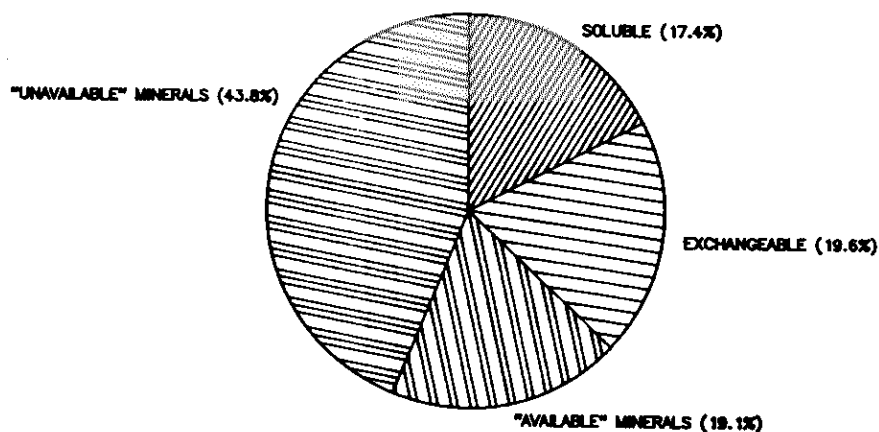


Figure 3. Distribution of Se in autoclaved soil.

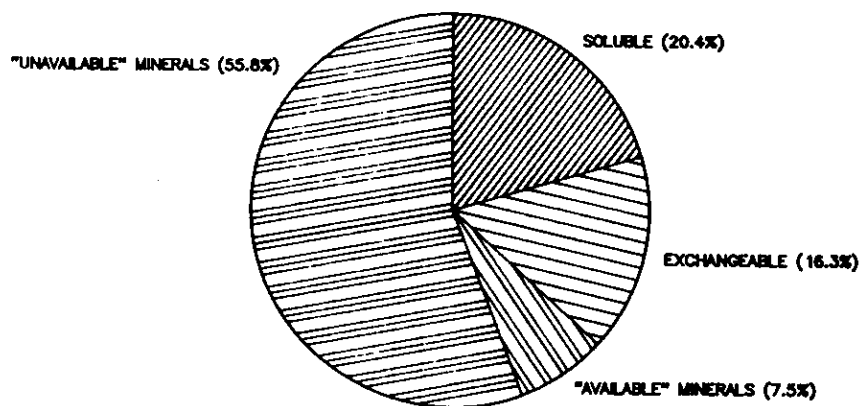


Figure 4. Distribution of Se in propylene oxide treated soil.

II. In the autotrophic enrichment, production of SeO_3^{2-} in solution was greater in media receiving biologically active soil than in media receiving propylene oxide-sterilized soil or no soil (Fig. 5).

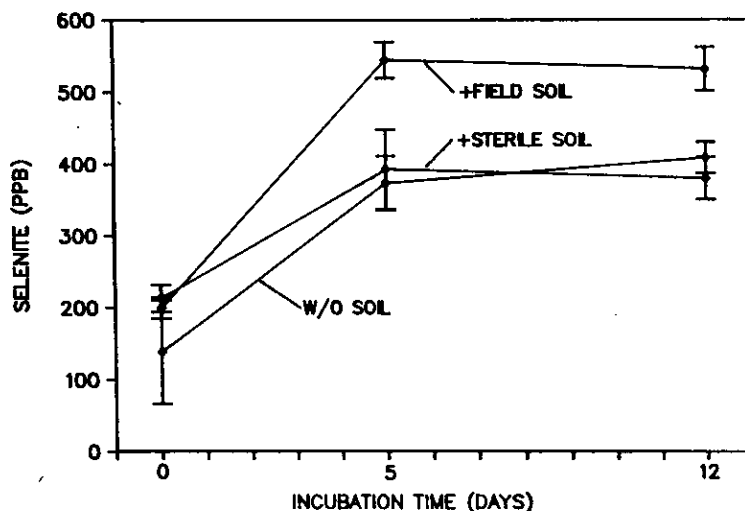


Figure 5. Changes in selenite concentration, autotrophic medium.

However, changes in the total Se in solution were more complex. The organic compounds present in the heterotrophic media appeared to interfere with the assay procedures. Secondly, colloidal Se^0 cannot be used with the total Se assay.

DISCUSSION AND SUMMARY:

It has not been as simple as we had hoped to establish the relative importance of abiotic and biotic reactions during the oxidations of reduced Se species which occur when flooded soils or sediments are drained. The procedures commonly used to sterilize soils can have significant and complex effects on speciation, oxidation state, and solubility of soil Se.

The traditional method of autoclaving increases exchangeable SeO_3^{2-} as well as increasing the size of an "available" mineral pool. Autoclaving is well known to catalyze precipitation of salts generally; it is likely that this sterilization method catalyzed formation of insoluble Se salts. Autoclaving is also commonly used to extract solubilizable organic constituents from soil. Hence one must also be concerned with effects of this sterilization method on organic forms of Se.

Propylene oxide fumigation appears to be less disruptive overall than autoclaving. However, its effects on the highly available soluble Se pool are problematic. We hope that our ongoing work on gamma irradiation indicates a sterilization method more compatible with our experimental needs.

Some evidence exists in the literature for both autotrophic Se oxidation (Torma and Habashi, 1972) and heterotrophic Se oxidation (Sarathchandra and Watkinson, 1981). Heterotrophic sulfur oxidation is known to be common in soil (Lawrence and Germida, 1988). Evidence also

exists that colloidal Se^0 is a more "useable" substrate by microbial oxidizers than grey Se^0 (Sarathchandra and Watkinson, 1981).

Analysis of the solution phase of our autotrophic enrichment cultures does indicate microbiological oxidation of colloidal Se^0 in excess of abiotic oxidation processes. While this preliminary work supports the occurrence of autotrophic oxidation reactions under laboratory conditions, it cannot be extrapolated to field soils.

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PUBLICATIONS AND REPORTS:

None

PROJECT TITLE: SOIL ORGANIC MATTER INTERACTIONS WITH SELENIUM

PROJECT NUMBER: 88-16

PROJECT DURATION: July 1988 - June 1990

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FTE Commitment: 0.10

Name: Douglas S. Lipton
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FTE Commitment: 0.50

RESEARCH STAFF:

Student Assistants: 1 @ 0.5 FTE

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ABSTRACT:

A Panoche sandy-loam (Typic Torriorthent) and Ciervo clay-loam (Typic Torriorthent) were sequentially extracted in order to remove soluble-, adsorbed-, and carbonate-Se before characterizing SOM-associated Se. Total SOM-associated Se, as determined by a NaOCl (pH 9.5) boil, was 166 $\mu\text{g kg}^{-1}$ for the Panoche soil and 248 $\mu\text{g kg}^{-1}$ for the Ciervo soil. For both soils, SOM-associated Se comprised about 1/4 of the total soil Se and about 1/2 of a potentially labile pool of Se consisting of soluble, adsorbed, carbonate, and SOM fractions. Another procedure was used to determine Se in isolated SOM fractions: 1) pyrophosphate-soluble SOM was removed with 0.1 mol L⁻¹ Na₄P₂O₇ (pH 13) and acid-soluble fulvic acids (FA-1) separated from flocculated humic acids (HA-1) at pH 1.5, and 2) clay-bound SOM was solubilized by sonification in water and fulvic acids (FA-2) separated from humic acids (HA-2) as above. This method removed approximately 50% of the SOM and showed that SOM-associated Se was partitioned evenly between FA-1 and HA-1 in the pyrophosphate-soluble SOM while HA-2 dominated Se retention in the clay-bound SOM. The unextractable SOM in the soil residue (RES) contained 66% and 41% of the SOM-associated Se for the Panoche and Ciervo soil, respectively. Organic C and N were highly correlated with the distribution of SOM-associated Se in the various SOM fractions.

KEYWORDS: Selenium, Organic Selenium, Soil Organic Matter, Fulvic Acids, Humic Acids, Clay-bound SOM

PROJECT OBJECTIVES ADDRESSED:

1. To quantify Se in SOM of semi-arid soils.
2. To determine the partitioning of Se into fulvic acids, humic acids, and clay-bound SOM and to evaluate in terms of organic C and N.
3. To explore the interaction of Se(IV) and Se(VI) with soil-extracted humic acids.

RESEARCH PLAN AND PROCEDURES:

Two alluvial soils (0 to 0.15 m) from the Panoche Fan on the western side of the San Joaquin Valley, California were used in this study. Chemical properties of the Panoche sandy-loam (Typic Torriorthent) and the Ciervo clay-loam (Typic Torriorthent) are summarized in Table 1. Air-dried soils (2 mm sieve) were ground to pass a 0.5 mm sieve for all experiments.

Table 1. Summary of some important soil characteristics.

	Total Se $\mu\text{g kg}^{-1}$	pH	Clay	Organic C %	CaCO_3
Panoche	790	8.2	17	0.48	1.3
Ciervo	990	8.6	57	1.18	0.6

Two different SOM removal approaches were taken in this study: 1) the destructive isolation of SOM by oxidizing organic C with NaOCl (Anderson, 1963), and 2) the non-destructive removal of SOM by alkali-pyrophosphate followed by sonification (Anderson et al., 1974). In order to assure that Se solubilized by the various procedures was directly associated with the SOM, labile pools of Se were sequentially extracted with 0.25 mol L⁻¹ KCl (2 h), 0.1 mol L⁻¹ KH₂PO₄ (pH 8, 20 h), and 1 mol L⁻¹ sodium acetate (pH 5, 1 h + 4 h) followed by 0.1 mol L⁻¹ KH₂PO₄ (pH 8, 20 h) to isolate Se associated with soluble, adsorbed, and carbonate fractions, respectively. A soil:solution ratio of 1:10 (w/v) was used for all extractions. Supernatant solutions were collected by centrifugation and the soil residue was rinsed with 0.25 mol L⁻¹ KCl after each extraction. Rinses were combined with the preceding extraction, vacuum-filtered (Whatman #40), and stored in polyethylene bottles at 4°C for up to 2 weeks. Extracts with pH > 5 were acidified with 2-4 drops of concentrated HCl prior to storage. A schematic diagram of the sequential extraction used to prepare the soil for SOM removal is shown in Figure 1. For the destructive

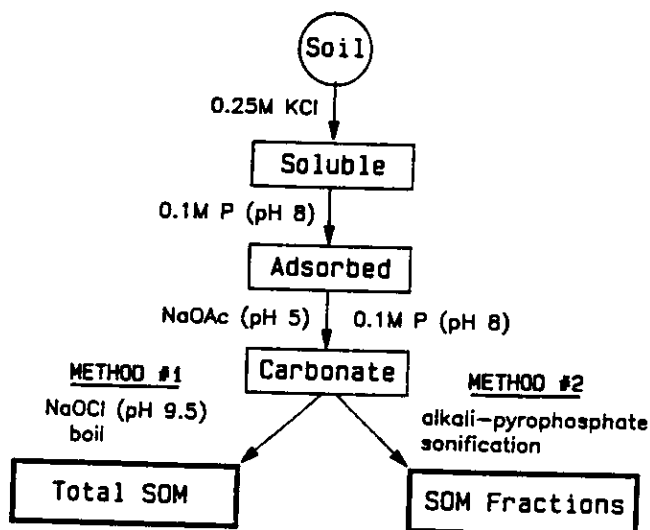


Figure 1. Sequential extraction method used to isolate "potentially labile" Se.

removal of SOM by NaOCl (Method #1), 2.5×10^{-3} kg samples of soil were reacted with 0.025 L of the respective extracting solution in 0.040 L Teflon centrifuge tubes. A 20.0×10^{-3} kg sample of soil was used for the non-destructive procedure (Method #2) in order to increase the production of humic substances, and was reacted with 0.200 L of extracting solution in 0.250 L polyethylene containers. To determine organic Se in the first fractions of fulvic acid (FA-1) and humic acid (HA-1), the soils were pre-extracted with only 0.25 mol L⁻¹ KCl because of the small, but significant, release of organic Se by phosphate (pH 8).

After extracting soluble-, adsorbed-, and carbonate-Se, Se associated with the total SOM fraction was solubilized by oxidizing organic carbon with NaOCl adjusted to pH 9.5 (Anderson, 1963). Sodium hypochlorite (4-6% NaOCl; purified, Fisher Co.) was adjusted to pH 9.5 with concentrated HCl and 0.010 L was pipetted into the Teflon tubes containing the pre-extracted soil residue (4:1 solution to soil ratio). Sample tubes were capped tightly, vortexed for 10-15 s, and then placed in a beaker of boiling water for 20 min. Samples were centrifuged ($20,000 \times g$) for 10 min at 15°C in a refrigerated Sorvall RC-2 centrifuge and the supernatant solution was decanted into pre-weighed polyethylene containers. This procedure was repeated once more to maximize organic carbon oxidation without significant dissolution of hydrous oxides or silicates (Lavkulich and Wiens, 1970). The soil residue was rinsed with 0.010 L of 0.25 mol L⁻¹ KCl by vortexing, and the supernatant solution was added to the NaOCl-extracted solution after centrifugation. The 0.030 L of extracted solution was vacuum filtered (Whatman #40), acidified with 4 drops of conc HCl, and stored at 4°C until further analysis. Analysis of total organic carbon (TOC) of the air-dried soils by dry combustion at 800°C with a Dorman Carbon Analyzer showed that about 90% of the TOC had been removed after two NaOCl boils.

The non-destructive removal of SOM was conducted using a procedure developed by Anderson et al. (1974) that extracts two separate SOM fractions: 1) an alkali-pyrophosphate extractable component, and 2) a clay-bound SOM fraction removed by sonification (see Figure 2). The

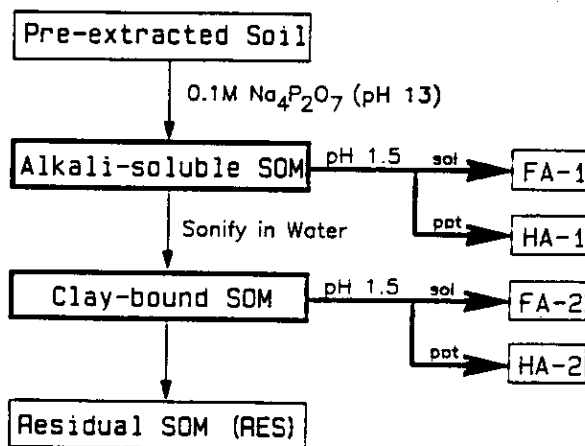


Figure 2. Alkali-pyrophosphate/sonification method used to fractionate SOM.

pre-extracted soil was sequentially extracted with 0.200 L of 0.1 mol L⁻¹ Na₂P₄O₇ in 0.1 mol L⁻¹ NaOH for 20 h after purging the soil-solution slurry with N₂ gas for 6 min. Samples were centrifuged and the supernatant solution was decanted into 0.25 L polyethylene bottles containing 0.005 L of 6 mol L⁻¹ HCl to inhibit oxidation of the organic C. The soil residue was rinsed with 0.050 L of the N₂-purged alkali-pyrophosphate solution and centrifuged, and the supernatant solution was decanted into the 0.25 L container. The pyrophosphate-extracted SOM was acidified to pH 1.5 with 6 mol L⁻¹ HCl in order to separate acid-soluble fulvic acids (FA-1) from flocculated humic acids (HA-1). After allowing the acidified solution to sit for 24 h at room temperature and then centrifuging, FA-1 was decanted into pre-weighed 0.5 L polyethylene containers. The pellet, HA-1, was rinsed with 0.1 mol L⁻¹ HCl and centrifuged, and the supernatant solution was decanted into the 0.5 L container. Because of the extremely small amount of HA-1 produced after freeze-drying ($< 5.0 \times 10^{-5}$ kg), HA-1 was resuspended in 0.040 mL of 0.1 mol L⁻¹ NaOH, acidified to pH 7-8, and brought to volume in a 0.050 L volumetric flask. All samples were stored in polyethylene containers at 4°C for further analysis.

The pyrophosphate-extracted soil residue was transferred to a 0.100 L glass beaker with 0.070 L of distilled de-mineralized water for sonification (cell disrupter 350; Branson Sonic Power Co.). The beaker was placed in an ice bath and the soil slurry was sonified for 6 min at setting '4' such that the power output read '48' (78.6 ± 7.1 J s⁻¹). The sonified soil was transferred to a 0.250 L polyethylene bottle with 0.130 L of water and allowed to stand for 48 h at room temperature. The slurry (pH > 11) was centrifuged ($16,300 \times g$) for 15 min and the supernatant solution (containing clay-bound SOM) was decanted into a 0.250 L polyethylene container. The clay-bound SOM was acidified to pH 1.5 with 6 mol L⁻¹ HCl in order to separate acid-soluble fulvic acids (FA-2) from flocculated humic acids (HA-2). After allowing the acidified solution to sit for 24 h at room temperature and then centrifuging, FA-2 was decanted into a pre-weighed 0.5 L polyethylene container. The pellet, HA-2, was rinsed with 0.050 L of 0.1 mol L⁻¹ HCl and centrifuged, and the supernatant solution was combined with FA-2. The FA-2 solution was filtered (Whatman #40) and stored at 4°C for further analysis. HA-2 was vacuum-dried in a desiccator at room temperature for at least 2 weeks before oven drying at 50°C for 24 h. HA-2 dries into a rock-like pellet with a dark black color because of the coating of SOM. The HA-2 pellet was finely-ground with an agate mortar and pestle, oven-dried at 50°C for 24 h, and stored in a desiccator. The soil residue (RES) was dried as described for HA-2.

In preparation for Se analysis by hydride generated atomic absorption spectroscopy (HGAAS) samples were treated with a variety of predigestion and speciation techniques. Total Se in FA-1 and FA-2 was determined after predigesting 0.005 L of sample with 0.005 L conc HCl and 0.0005 L of 20 g L⁻¹ K₂S₂O₈ in a boiling water bath for 20 min. Se(IV) in FA-1 and FA-2 was measured directly by HGAAS without predigestion. Organic Se in FA-1 and FA-2 was determined by isolating organic compounds with the hydrophobic resin, XAD-8 (Abrams and Burau, 1989) except that hydrophobic acids were also isolated at pH 1 in addition to pH 2. A detailed description of this

method has been given elsewhere (Leenheer, 1981; Abrams and Burau, 1989). The types of organic Se compounds isolated by this procedure are hydrophobic bases (compounds uncharged at neutral pH), hydrophobic acids (compounds uncharged at acid pH), and hydrophilics (compounds charged at pH 1 to 7). Organic Se was only detectable in the hydrophobic acid fraction. Predigestion of the organic fractions was accomplished using the method for total Se determination described above.

HA-1 was digested for Se analysis by HGAAS by reacting a 0.0025 L sample with 0.0025 L 30% H_2O_2 at 60-70°C for 30 min before adding 0.0005 L of conc HCl and placing in a boiling water bath for 30 min. The determination of organic Se in HA-2 was entirely different. Because HA-2 was comprised primarily of mineral constituents, including Fe oxides that contain substantial amounts of Se (data not reported), the NaOCl (pH 9.5) boil described above was selected in order to minimize the dissolution of Fe and Al hydroxides. A well-ground 0.0005 kg subsample was placed in a 0.040 L Teflon centrifuge tube for organic removal by boiling NaOCl (pH 9.5). The amount of NaOCl used for each boil was reduced from 0.010 L to 0.005 L and the 0.25 mol L^{-1} KCl rinse was similarly reduced to 0.005 L. In order to assess the amount of Se remaining in the SOM fraction of the soil residue (RES), a 0.001 kg subsample of RES was treated with NaOCl in an identical fashion. Preparation of the NaOCl-extracted Se for analysis by HGAAS required a special predigestion in order to mitigate the intense oxidizing effect of NaOCl on the generation of the Se hydride, SeH_2 . Se in the extract was reduced to Se(IV) by reacting 0.002 L of the sample with 0.010 L conc HCl in a tightly capped 0.040 L Kimax tube in a boiling beaker of water for 40 min. Precipitated salts were filtered (Whatman #40) and the digested sample diluted 1:1 with distilled, de-mineralized water for Se analysis by HGAAS. Standards of 25 $\mu g L^{-1}$ Se(IV) in NaOCl (pH 9.5) carried through the boiling procedure and predigestion steps demonstrated a recovery of $104.0 \pm 3.5\%$.

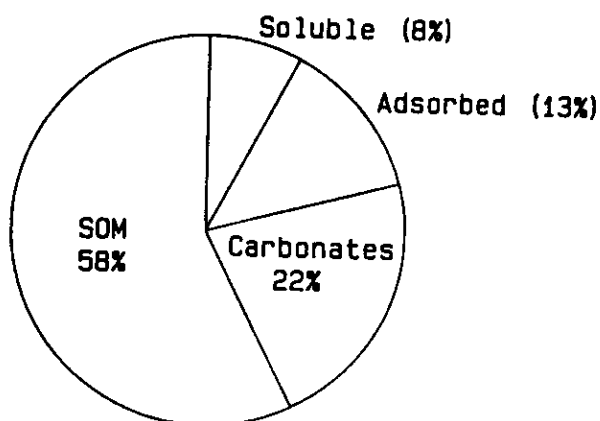
Total organic carbon (TOC) in liquid and solid samples was analyzed using a Dohrman Carbon Analyzer DC-80. To assure that only organic C was measured, inorganic C was purged from acidified liquid samples with oxygen, and organic C in solid samples was oxidized at 800°C after removal of carbonates. Nitrogen (N) was solubilized by Kjeldahl digestion with conc H_2SO_4 and a Se catalyst and N analyzed as NH_4 on a Lachat FIA. Total N measured by this method was assumed to be organic because of the removal of inorganic N by the pre-extractions.

Another study was undertaken to explore the possible inorganic Se interactions with SOM by reacting Se(IV) and Se(VI) with humic acids extracted from a grassland Ultisol following procedures outlined by Schnitzer (1982). A 1.00×10^{-4} kg sample of purified humic acid (< 2% ash) was equilibrated with a 0.025 L solution containing 40 $\mu g L^{-1}$ of Se(IV) or Se(VI) and 0.01 to 0.02 mol L^{-1} $CaCl_2$. The pH was adjusted with HCl and NaOH to between 5 and 9. The concentration of Ca was effective at precipitating more than 90% of the TOC so that the amount of Se adsorbing to the humic acid-Ca complex could be determined by HGAAS after centrifugation and filtering (0.45 μm).

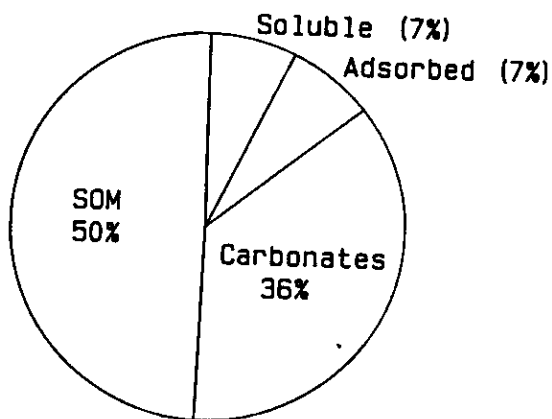
RESULTS:

The amount of Se released from the Panoche and Ciervo soils upon oxidation by a NaOCl boil was $166 \pm 9 \mu\text{g Se kg}^{-1}$ soil and $248 \pm 12 \mu\text{g Se kg}^{-1}$ soil, respectively. These levels of SOM-associated Se accounted for 21% and 25% of the total Se pool in the Panoche and Ciervo soils. The relative importance of SOM-associated Se compared to soluble-, adsorbed-, and carbonate-Se is illustrated in Figure 3. The potentially labile pool of soluble-, adsorbed-, carbonate-, and SOM-Se accounted for 36% and 50% of the total Se in the Panoche and Ciervo soils, respectively, and was dominated by the SOM fraction that comprised about 50% of the potentially labile pool of Se for both soils.

% Se in "Labile" Soil Fractions



Panoche Soil



Ciervo Soil

Figure 3. Percentage Se in isolated fractions relative to the total potentially labile pool.

The results for the partitioning of Se into isolated SOM fractions by alkali-Pyrophosphate/sonification are given in Table 2. The total Se determined to be associated with

Table 2. Isolated fractions of SOM and their content of SOM-associated Se, organic C and organic N.

	Se	C	N	C/N ratio
	$\mu\text{g kg}^{-1}$ soil	g kg^{-1} soil		
<u>PANOCHÉ:</u>				
FA-1	18 ± 1 (10)*	0.47 ± 0.01 (11)	0.05 ± 0.01 (14)	9.4
HA-1	20 ± 2 (11)	0.28 ± 0.02 (7)	0.04 ± 0.00 (12)	7.0
HA-2	23 ± 2 (13)	0.91 ± 0.15 (22)	0.08 ± 0.00 (24)	11.4
RES	121 ± 11 (66)	2.57 ± 0.10 (61)	0.17 ± 0.02 (49)	15.1
Totals:	182 ± 11	4.23 ± 0.18	0.34 ± 0.02	12.4
<u>CIERVQ:</u>				
FA-1	34 ± 4 (15)	0.92 ± 0.04 (8)	0.09 ± 0.01 (10)	10.2
HA-1	36 ± 2 (16)	1.47 ± 0.38 (12)	0.08 ± 0.00 (9)	18.4
HA-2	66 ± 5 (29)	3.98 ± 0.52 (34)	0.38 ± 0.00 (42)	10.5
RES	94 ± 11 (41)	5.38 ± 0.52 (46)	0.35 ± 0.02 (39)	14.9
Totals:	230 ± 13	11.74 ± 0.74	0.89 ± 0.05	13.2

*Numbers in parenthesis are percentages of totals by column.

SOM by this procedure (Method #2) was not significantly different from total SOM-associated Se quantified by the destructive NaOCl boil (Method #1) for both soils studied. Organic Se was measured directly in FA-1 and FA-2 using an XAD-8 resin while Se in HA-1, HA-2, and RES was determined to be associated with SOM in accordance with the digestion techniques described earlier. Organic Se in FA-1 was entirely composed of hydrophobic acids while no organic Se was detected in the FA-2 fraction. The relative importance of the SOM fractions in the retention of Se is illustrated in Figure 4. The figure shows that FA-1 and HA-1 were both important for retaining Se in the pyrophosphate-soluble SOM, HA-2 clearly dominated the clay-bound SOM fraction, and that RES contained the largest amount of SOM-associated Se.

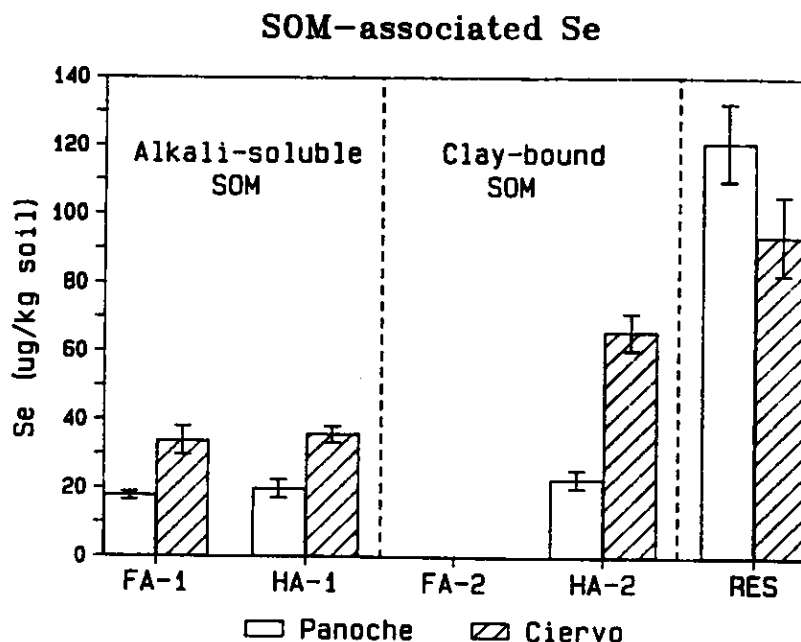


Figure 4. SOM-associated Se present in isolated SOM fractions.

virtually all of the SOM extracted by sonification (clay-bound SOM) was precipitated out into HA-2, leaving FA-2 devoid of organic Se and containing only a trace of inorganic Se. The HA-2 fraction consisted of a substantial amount of inorganic materials as the percentage of TOC in the flocculated clay-bound SOM was about 2% for each soil. The greatest amount of SOM-associated Se was found in RES that, prior to the removal of HA-2, has often been referred to as humin (Stevenson, 1982). Although the percentage of TOC in RES was < 0.1% in both soils, RES held approximately 50% of the total reservoir of SOM. Because of the use of NaOCl to determine SOM-associated Se in HA-2 and RES, much of the Se measured may be inorganic Se(IV) released upon oxidation. The use of the term "SOM-associated Se" is valid, however, when one considers that HA-2 and RES were collected after the soil had been extracted with 0.1 mol L⁻¹ KH₂PO₄ (pH 8) and 0.1 mol L⁻¹ Na₂P₂O₇ (pH 13) that should effectively remove Se adsorbed to hydrous oxide surfaces (Lipton et al., 1989). Although Se(IV) may be released from HA-2 and RES during the oxidation of organic C with NaOCl, the authors contend that the Se(IV) had been previously protected by SOM and is, therefore, reasonable to describe as SOM-associated Se.

Organic C and N in the various SOM fractions are reported in Table 2 and presented as g C or N kg⁻¹ soil for comparison purposes. Ratios of C:N were calculated so that the extent of humification can be evaluated for SOM in each fraction. Although C:N ratios for organic materials added to soils narrows during microbial degradation, for HA-1, HA-2, and RES isolated by the alkali-pyrophosphate/sonification procedure, narrower C:N ratios may indicate less humification because of the protection of nutritive SOM side chains, containing more N than the carbon-rich humus backbone, by clays (Anderson et al., 1963; Bettany et al., 1979). These authors reported that for Canadian soils, SOM in HA-2 was stabilized by the clay and, protected from further degradation by microorganisms, had lower C:N ratios than HA-1 which was more highly humified according to several other criteria. In this study, the trend was not so clear since HA-2 for the Panoche soil (TOC = 0.48%) had a higher C:N ratio than HA-1, suggesting more humification and less protection of SOM in HA-2 according to the Canadian authors' hypothesis. The C:N ratio of HA-2 for the Ciervo soil (TOC = 1.18%), in compliance with the Canadian studies, was significantly lower than HA-1, suggesting a greater level of microbial protection by the clay-bound SOM. Similar levels of humification were observed between soils for FA-1, HA-2, and RES.

SOM-associated Se in the various SOM fractions was highly correlated with organic C and N when considering each soil independently. For the Panoche soil, there were strong correlations between SOM-associated Se and organic C ($r^2 = 0.95$), organic N ($r^2 = 0.93$), and C:N ($r^2 = 0.75$). For the Ciervo soil, correlations of SOM-associated Se were high for organic C ($r^2 = 0.98$) and organic N ($r^2 = 0.80$), but C:N ($r^2 = 0.00$) showed no ability to predict SOM-associated Se. For both soils evaluated together, the distribution of Se in the SOM fractions showed poorer correlation to organic C ($r^2 = 0.58$), organic N ($r^2 = 0.44$), and C:N ($r^2 = 0.27$). When RES was excluded from the regression analysis for both soils combined, organic carbon ($r^2 = 0.95$) and

organic N ($r^2 = 0.90$) demonstrated a strong relationship to SOM-associated Se. Considering only FA-1 and HA-1 for both soils combined, organic C ($r^2 = 0.83$), organic N ($r^2 = 0.87$), and C:N ($r^2 = 0.56$) to a limited extent, were significantly correlated to SOM-associated Se.

The possibility that humic acids may retain the inorganic oxyanions of Se(IV) and Se(VI) by some sorption or complexation process was examined using soil-extracted humic acids. Humic acids that were purified to remove clays (ash content < 2%), demonstrated only minimal sorption of Se(IV) (< 10%) and no ability to sorb Se(VI) in the presence of 0.01 to 0.02 mol L⁻¹ calcium over a pH range of 5 to 9. Unpurified humic acids with an ash content of almost 50% also showed no ability to sorb Se(VI), but the sorptivity of Se(IV) increased slightly to 10 to 15% with no effect of pH over a range of pH 5 to 9.

DISCUSSION AND SUMMARY:

The importance of Se in SOM has been recognized for 50 years since Olson and Moxon (1939) reported that the SOM in seleniferous soils of South Dakota contained 10 to 44% of the total Se pool. Only recently (Abrams and Burau, 1989) has an attempt been made to determine Se in the SOM. Although Abrams and Burau (1989) reported that only 7% of the total Se for a Panoche Fan soil was organic, less than 25% of the SOM was removed by their extraction technique.

In this study, two new methods for determining Se in the SOM, a destructive oxidation and an alkali-pyrophosphate/sonification extraction, demonstrated that SOM-associated Se comprised a higher proportion of the total soil Se than has previously been recognized for the semi-arid soils from the western side of the San Joaquin Valley, California. Although the Panoche and Ciervo soils that were studied contained only 0.5% and 1.2% TOC, respectively, the percentage of total soil Se associated with the SOM was determined to be 21% and 25%, respectively. Considering that a potentially labile pool of Se is one that can be released by common abiotic and biotic processes, soluble, adsorbed, carbonate, and SOM fractions all play an important role in effecting Se release into drainage waters. The impact of SOM on Se mobility was highlighted by the observation that about 50% of the Se in the potentially labile pool was associated with SOM.

The association of Se with SOM was explored by isolating operationally-defined SOM fractions and determining SOM-associated Se, organic C and organic N within each isolate. In the pyrophosphate-extractable SOM, FA-1 and HA-1 contained approximately equal amounts of SOM-associated Se while HA-2, rather than FA-2, dominated the retention of Se in the clay-bound SOM fraction. Because only about 50% of the SOM was solubilized by the alkali-pyrophosphate/sonification procedure, large amounts of SOM-associated Se were also quantified in RES. Some of the SOM-associated Se in RES and HA-2 may be Se(IV), adsorbed to hydrous oxide surfaces, that was protected from release into the pre-extractions of phosphate and alkali by a coating of SOM, hence the term "SOM-associated Se." In a study of the partitioning of organic sulfur into the same SOM fractions (FA-1, HA-1, FA-2, HA-2, and RES) isolated from Canadian soils, Bettany et al.

(1979) have reported similar results, except that FA-1 contained about twice as much organic sulfur as HA-1.

According to linear regression analysis, organic C and organic N correlated poorly with the SOM-associated Se contents of the various fractions when considering both soils together. The relationship between SOM-associated Se and organic C and organic N, however, became significant when each soil was considered separately. Furthermore, if RES was excluded from the regression analysis, organic C and organic N were useful indicators of SOM-associated Se for both soils combined. The C:N ratio only correlated strongly with SOM-associated Se in the Panoche soils.

The possibility that inorganic Se, Se(IV) and Se(VI), might be complexed by SOM has been suggested by several investigators (Levesque, 1974; An and Langqiu, 1987) although data for this phenomenon is lacking. In this study very small, but measurable, amounts of Se(IV) were observed to sorb to humic acids purified from a grassland soil. Experimentation is now under way to explore the potential interaction of Se(IV) and Se(VI) with fulvic acids.

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PROJECT TITLE: DISTRIBUTION AND SOURCES OF URANIUM AND ASSOCIATED TRACE ELEMENTS IN SELECTED WATERS OF THE SAN JOAQUIN VALLEY OF CALIFORNIA

PROJECT NUMBER: 88-17 & 18 (A)

DURATION OF FUNDING: July 1988 - June 1990

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ABSTRACT:

One hundred sixteen agricultural drainage and evaporation pond water samples were collected from the San Joaquin Valley in June 1988. A chelation solvent extraction method was developed for removal and concentration of 20 trace elements from saline waters. Samples were analyzed for 40 elements and salinity indices. Elevated concentrations of uranium, boron, vanadium, selenium, arsenic and molybdenum were associated with different geological zones and salinity indices.

KEYWORDS: Water, Salinity, Trace elements, Solvent extraction, ICAP.

PROJECT OBJECTIVES ADDRESSED:

1. The application of suitable analytical techniques for measurement of trace elements in saline waters to determine chemical speciation and distribution in drainage and evaporation pond water samples from the San Joaquin Valley, California.
2. The use of principal component and other statistical analyses to characterize factors affecting trace element speciation and solubility in evaporation pond waters.

RESEARCH PLAN AND PROCEDURES:

One hundred sixteen agricultural drainage and evaporation pond waters were collected by personnel of the Central Valley Region Water Quality Control Board in June 1988. Fourteen well water samples were collected by personnel of the State Department of Water Resources from areas adjacent to agricultural evaporation ponds during the summer of 1988.

A chelation solvent extraction method has been developed to simultaneously separate and concentrate 20 trace elements from saline waters. Samples were pH buffered by the addition of ammonium acetate and trace elements chelated by the addition of a 3% (m/v) aqueous solution of ammonium pyrrolidine dithiocarbamate. Three extractions with chloroform were combined, evaporated to dryness and dissolved in a small volume of dilute nitric acid for analyses by simultaneous multielement inductively coupled argon plasma optical emission spectroscopy (ICAP-OES). Experiments are in progress to determine the extractability of additional elements.

Separate aliquots of water samples were also analyzed directly at different dilutions by pneumatic cross flow nebulization and by continuous flow hydride generation using ICAP-OES. Anions were analyzed by Technicon AutoAnalyzer methods.

Tables 1 and 2 compare salinity indices and trace element concentrations in 116 agricultural drainage and evaporation pond water samples within three different geological zones of the San Joaquin Valley. Table 3 summarizes the trace element content of 14 well water samples from near agricultural evaporation ponds in the San Joaquin Valley.

DISCUSSION AND SUMMARY:

Selenium levels are elevated (mean 0.45 mg L^{-1}) in drainage and evaporation pond waters from the alluvial fan zone compared to other zones (Table 2). Schroeder et al. (1988) found elevated Se concentrations ($0.1\text{--}0.2 \text{ mg L}^{-1}$) in Westfarmers ponds and implicated Se as a cause of deleterious effects on wildlife as observed at Kesterson National Wildlife Refuge (NWR). Twenty-four water samples from the alluvial fan have Se levels in excess of 0.1 mg L^{-1} and may therefore be expected to cause deleterious effects on wildlife.

Concentrations of As are elevated (mean 0.36 mg L^{-1}) in the lakebed samples. Arsenic levels ranging between 0.012 and 0.040 mg L^{-1} in the Kern NWR were not accompanied by high arsenic in fish (Schroeder et al., 1988). Arsenic levels ranging from 10 to 100 times higher in lakebed samples justify concern for health of aquatic life. The State of California (1989) has set a limit of 0.05 mg L^{-1} As in drinking water.

Uranium concentrations are highest (mean 0.896 mg L^{-1}) in lakebed samples; however, all samples contain high uranium levels compared to saline waters from other areas (Bradford et al., 1989). Twenty-eight percent of all samples have uranium levels in excess of 0.5 mg L^{-1} ; the limit suggested by (McNeely et al., 1987) for protection of saltwater fish and wildlife.

Boron and molybdenum are also elevated in all samples. Vanadium is highest in lakebed water samples.

It is significant that although all samples were analyzed for Co, Tl, Ga, Sn, Sb, Bi, Te, and Hg, no positive values were measured above a low $\mu\text{g L}^{-1}$ detection limit.

Table 4 shows the most significant correlations between trace elements and salinity indices in samples from the alluvial fan zone.

Principle component and other statistical analyses will be used to characterize factors affecting trace element speciations and solubility in evaporation pond waters.

Limited data from well water analyses (Table 3) show levels of uranium well above background in three wells and relatively high arsenic (0.1 mg L^{-1}) in one well. Well water sampling and analyses will be expanded to other areas.

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Table 1. Salinity indices in 116 agricultural drainage and evaporation ponds of the San Joaquin Valley of California.

	Alluvial fan		Basin rim		Lakebed	
	Range	Mean	Range	Mean	Range	Mean
pH	7.2-8.9	8.3	0-8.7	7.6	7.3-9.6	8.1
EC(dS/m)	9.6-98.	43	8.7-92	34	5.7-140	38
SAR	23-198	92	22-138	70	29-500	101
-----meq/L-----						
SO ₄	97-1899	440	75-2170	623	16-1282	299
Cl ⁻	25-1768	391	15-971	161	22-2564	389
Alkalinity	6.5-32	14	.20-40	13	.30-47	15
Ca	25-41	31	4.7-37	20	.00-46	10
Mg	12-366	72	15-743	137	1.8-374	71
Na	100-2417	701	103-2235	667	69-3309	614
K	.16-5.1	.84	.13-1.5	.43	.08-5.9	1.2

Table 2. Trace element concentration in 116 agricultural drainage and evaporation ponds of the Joaquin Valley of California.

	Alluvial fan		Basin rim		Lakebed	
	Range	Mean	Range	Mean	Range	Mean
-----mg/L-----						
Al	.00-1.7	.48	.00-1.6	.32	.00-1.8	.40
As	.002-.020	.007	.001-.132	.031	.013-4.490	.364
B	6.0-333	80	3.6-203	45	3.3-392	32.
Ba	.00-.10	.016	.00-0.05	.01	.00-.04	.01
Cd	.00-.001	.00	.00-.00	.00	.00-.00	.00
Cr	.00-.01	.002	.00-.01	.001	.00-.00	.00
Cu	.003-.014	.008	.001-.012	.005	.001-.012	.005
Fe	.003-.041	.014	.004-.144	.034	.005-.056	.019
Li	.00-1.7	.540	.00-1.15	.073	.00-4.1	.349
Mn	.00-.025	.007	.004-.685	.120	.00-.793	.041
Mo	.061-12.7	2.07	.117-2.21	.628	.138-22.7	2.86
Ni	.001-.012	.005	.001-.016	.005	.00-.027	.005
P	.00-.434	.090	.00-2.35	.402	.00-1.70	.432
Pb	.00-.035	.003	.00-.007	.002	.00-.10	.005
Se	.003-2.06	.451	.0001-.0124	.002	.000-.061	.0084
Si	.265-26.7	5.09	.374-23.5	11.5	.075-30.0	9.62
Sr	4.5-32.8	13.7	1.34-21.5	6.22	.063-20.1	3.84
U	.075-2.16	.421	.011-.499	.183	.04-9.9	.896
V	.003-.071	.029	.004-.096	.030	.004-.544	.087
Zn	.00-.036	.007	.002-.027	.008	.00-.08	.006

00. = < detection limit, which varies with sample concentration factor.

Table 3. Trace elements in 14 San Joaquin Valley well water samples from areas near agricultural evaporation ponds.

Element	Range	Mean	Median
-----mg L ⁻¹ -----			
B	.24-3.6	.87	.9
Mo	.007-.135	.037	.017
Fe	.024-.482	.081	.029
Mn	.001-.087	.008	<.001
Cu	.001-.017	.003	.002
Zn	.006-.065	.013	.008
As	<.001-.102	.022	.021
U	<.005-.044	.012	<.005
Se,Cd,Pb,V,Ni,Co,Cr <.001 mg L ⁻¹			

Table 4. Correlation coefficients between trace elements occurring at relatively high concentrations and salinity indices in the alluvial fan zone.

	B	Mo	U	V	As	Se
Ca	.339	.203	.052	.409	.331	-.310
Mg	.864	.974	.949	.618	.618	.275
Na	.974	.829	.713	.885	.896	.149
K	.729	.902	.972	.436	.405	.481
SO ₄	.864	.932	.950	.610	.589	.357
Cl	.662	.343	.120	.849	.893	-.148
Alkalinity	.328	.383	.427	.024	.134	.381
E.C. (dS m ⁻¹)	.902	.681	.544	.924	.928	.045

PROJECT TITLE: PHYSICAL CHEMISTRY OF U AND V IN SOILS AND WATERS OF THE WEST SIDE OF THE
SAN JOAQUIN VALLEY

PROJECT NUMBER: 88-17 & 18 (B)

DURATION OF PROJECT: July 1988 - June 1990

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ABSTRACT:

Uranium (U) and vanadium (V) have been identified in relatively high soluble concentrations in evaporation pond sediments. These concentrations may be of concern in wildlife habitat and in the event of burial or removal of pond sediments. These elements may have leached from soil or geologic materials from either the west or east side of the San Joaquin Valley. The U was probably mobilized by either CO_3^{2-} or organic complexes of UO_2^{2+} and deposited in response to evaporative processes in the drainage ponds. Coprecipitation of UO_2^{2+} with gypsum or calcite or formation of the U-V minerals carnotite or tyuymanite may account for the behavior of UO_2^{2+} as a sparingly soluble mineral when soil samples are extracted with water. Further work is underway to identify the mechanisms of U and V mobilization and accumulation in drainage pond soils and waters.

KEYWORDS: Uranyl, vanadate, ion chromatography, evaporation ponds, U-complexation

PROJECT OBJECTIVES ADDRESSED:

1. Describe the chemical reactions controlling concentrations of U and V in soil and waters from the San Joaquin Valley.
2. Identify mineral and soluble forms of U and V in soils and solutions.
3. Compile relevant thermodynamic data for the solubility of U and V minerals likely to be found in soils and sediments of this region.

RESEARCH PLAN AND PROCEDURES:

1. We are assembling thermodynamic data on the solubility of various U and V minerals and in the CO_3^{2-} , PO_4^{3-} , SO_4^{2-} , and F^- complexes believed to be present in natural waters. These data will

be compared with the measured composition of soil extracts and water samples collected from irrigation canals, drains, and evaporation ponds in the western San Joaquin Valley. The GEOCHEM program (Sposito and Mattigod, 1980) was used to calculate chemical activities of measured component concentrations of some soil extracts.

2. Three soil profiles were sampled at Kesterson Reservoir Cells 1, 4, and 9 for characterization of the soil-water interactions controlling U and V composition. Saturation extracts (18-hour incubation) of these soils were prepared for field-moist and air-dried soils. These extracts were analyzed for major cations and anions, pH, and alkalinity by standard techniques and trace elements using ICAP. Uranium was analyzed as UO_2^{2+} by cation exchange ion chromatography in an acidic $(\text{NH}_4)_2\text{SO}_4$ eluant. The level of detection was approximately $5 \mu\text{g}\cdot\text{U}\cdot\text{L}^{-1}$ and the precision was controlled by including one replicate or spiked sample for every two samples analyzed. Since standard reference materials for U in water are not available, accuracy was checked by using a commercially available 1000 $\mu\text{g U/mL U}$ solution for QC preparation. Vanadium was measured using atomic absorption and a graphite furnace. The level of detection was approximately $1 \mu\text{g V}\cdot\text{L}^{-1}$ for our analyses. Precision was controlled by including replicate analyses of each sample and an NIST standard reference material (Trace Elements in Water SRM 1643b) for every four samples analyzed. Accuracy was checked by the use of a commercially available 1000 $\mu\text{g V}\cdot\text{L}^{-1}$ solution for standard preparation and rejecting analytical runs in which the true concentration of the NIST-SRM was not reproduced within 10%. If the relative percent deviation (RPD) of replicate analyses exceeded 20%, then the data were rejected and solutions reanalyzed. Values reported which are one order of magnitude or greater above the detection level are generally within 10% of the RPD for replicates and spikes.

The CaCO_3 composition of the soil profiles was measured by reaction of 1 to 5 g soil with dilute HCl in a closed vessel and manometric measurement of CO_2 evolution.

A series of water extracts of the soils were prepared at water:soil ratios of 2:1, 4:1, 10:1, 16:1, 25:1, 40:1, 60:1, 80:1, 100:1, depending on the amount of soluble salts found in the saturation extracts. The soil-water suspensions were allowed to equilibrate over 18 hour periods to allow gypsum dissolution to approach equilibrium. Extracts were analyzed for the same components as the saturation extracts.

RESULTS:

1. The most recent extensive compilation of thermodynamic data for U and V mineral-solution equilibria is that of Langmuir (1978). More recent, partial compilations of data are available (e.g., Sadiq, 1988), but need to be critically compared before a new, complete data base is presented (Nordstrom and Munroe, 1985). The data base of the chemical speciation program GEOCHEM (Sposito and Mattigod, 1980) contains data on complexes of UO_2^{2+} and VO_4^{3-} and these data were used for preliminary calculations of UO_2^{2+} speciation.

2. The composition of major cations and anions in saturation extracts of samples from three soil profiles is presented in Table 1. Calculations of Ca^{2+} activities showed that all extracts were saturated with respect to calcite and that extracts of the surface horizons, at least, were saturated with respect to gypsum. The presence of calcite is confirmed by the data in Table 2. The concentrations of UO_2^{2+} and VO_4^{3-} tended to be greatest in subsurface horizons (Table 3). Preliminary calculations of UO_2^{2+} and VO_4^{3-} activities indicated that in all samples, UO_2^{2+} was entirely complexed with CO_3^{2-} and VO_4^{3-} existed entirely as HVO_4^{2-} or H_2VO_4^- .

The amounts of Ca^{2+} , SO_4^{2-} , and UO_2^{2+} extracted per kg of soil increased to a limit as the water:soil ratio was increased. This is illustrated in Figure 1a for UO_2^{2+} extracted from the profile sampled in Cell 1. These results indicate that UO_2^{2+} is sparingly soluble. A similar plot for Ca^{2+} (Figure 1b) shows that in the surface horizon Ca^{2+} is released in a pattern similar to UO_2^{2+} ; however, the relationship is not the same in subsurface horizons. Preliminary calculations indicate that UO_2^{2+} concentrations may be correlated with alkalinity (CO_3^{2-} and HCO_3^-) and with dissolved organic carbon. Further analyses are underway.

DISCUSSION AND SUMMARY:

The trace elements U and V have been found in relatively high concentrations in water extracts of soils from irrigation drainage water evaporation ponds at one location. Concentrations of UO_2^{2+} -U approach toxic levels for humans of $250 \mu\text{g U}\cdot\text{L}^{-1}$ (Berlin and Rudell, 1986). While evaporation pond water and sediments should pose no immediate threat to humans, there should be some concern regarding wildlife use and the effects of eventual removal or burial of the evaporation pond sediments. By understanding the geochemistry of U and V in the San Joaquin, we may be able to anticipate potential problems before they occur.

The concentration of U and V found in the soil profiles analyzed are influenced by evaporation of water at the soil surface. The parent materials from which these soils were formed are believed to be from the Sierra foothills, transported to the basin by the San Joaquin River (Cole et al., 1952). These granitic materials contain an average of about 4 mg U/kg and 100 mg V/kg (Dodge, 1972). Concentrations of U in Panoche soil and Ciervo soil have been reported as 2.96 and 2.04 $\text{mg}\cdot\text{kg}^{-1}$, respectively (Amundson et al., 1987). Leaching of U from these soils by irrigation water may have contributed to an increase in U accumulation in the evaporation pond areas. The soils in this area have always been affected by salt accumulations to some degree and the soil analyzed exhibit typical high Na^+ , Cl^- and SO_4^{2-} concentrations. Gypsum and CaCO_3 are also present. The environment described for soil formation in the evaporation ponds is not unlike that described for formation of uranium ore (carnotite) deposits of the Yeerl district, Australia (Dall'aglio et al., 1974). In that area, evaporative concentration of waters in an arid climate has produced a caliche locally high in U.

Two mechanisms for the mobilization of U in water have been identified. One is the formation of solution complexes with CO_3^{2-} , a mechanism which is supported by calculation of thermodynamic

equilibria (Langmuir, 1978). Second, complexation of UO_2^{2+} by organic matter has been shown to operate as a mechanism of maintaining UO_2^{2+} concentrations in sea water (Anderson, 1982).

The accumulation of UO_2^{2+} in these soils occurs in response to evaporation. The form of the UO_2^{2+} in the solid phase is not quite clear. Extracts of soils at increasing water:soil ratios indicate the presence of slightly soluble minerals. Gypsum is present in the surface horizon of the Cell 1 profile, for example. The UO_2^{2+} appears to have a similar behavior, but at all 4 depths shown, not just at the surface. The UO_2^{2+} may be associated with gypsum or calcite as a coprecipitate, substituting for Ca^{2+} . An investigation of this process has been initiated. Precipitation of the minerals carnotite ($\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2$) or tyuymanite ($\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2$) is also a possibility.

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Figure 1a.

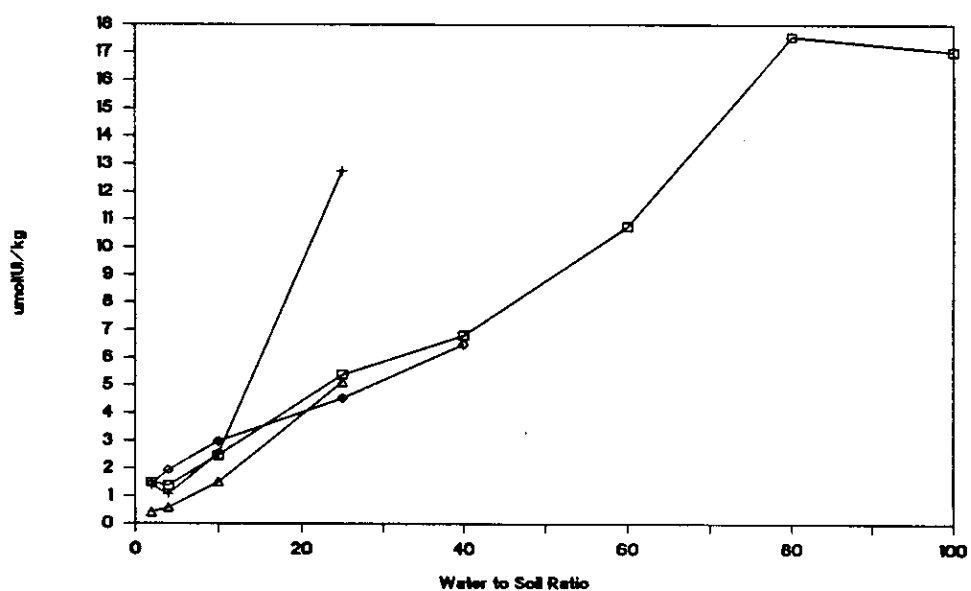


Figure 1b.

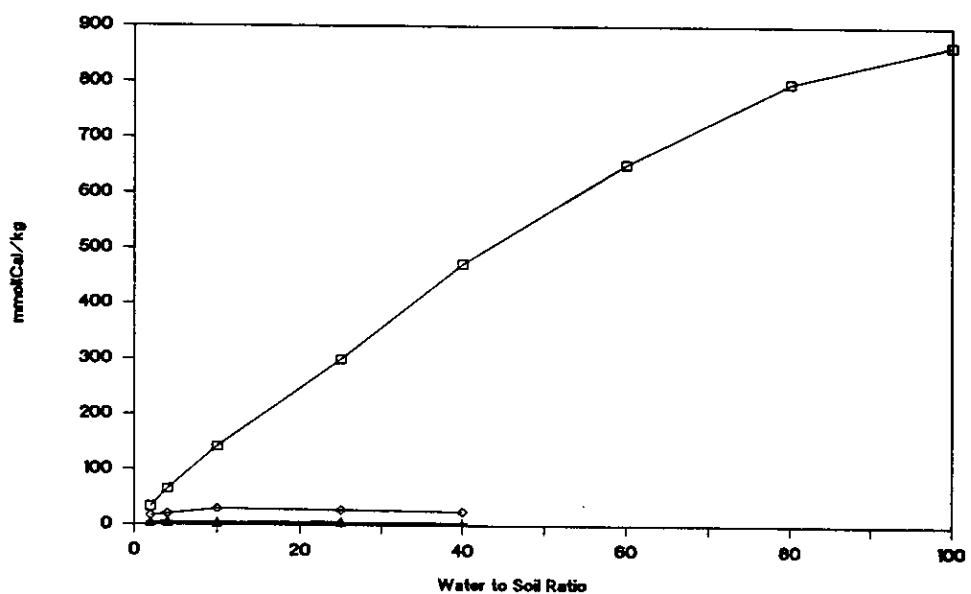


Figure 1. (a) UO_2^{2+} and (b) Ca^{2+} extracted from soil samples from a profile in Kesterson Reservoir Cell 1. Water:soil ratios increase from left to right. Squares indicate 0-2.5 cm; diamonds, 2.5-46 cm; crosses, 46-76 cm; and triangles 76-102 cm.

Table 1. Concentration of major cations and anions in saturation extracts of soils from three profiles in Kesterson Reservoir.

Sample	Soil:water ratio	pH	Alk	Ca	Mg	Na	K
			mEq/L	-----mmol/L-----			
1-1	0.300	7.90	5.794	16.11	4.73	17.5	1.53
1-2	2.644	7.62	1.179	9.84	8.84	97.0	1.11
1-3	2.836	7.98	1.504	10.07	18.57	190.7	0.40
1-4	4.004	6.87	1.219	11.09	20.69	208.2	0.26
4-1	0.059	7.99	8.633	14.12	8.29	39.8	1.09
4-2	3.229	7.26	0.914	12.26	18.63	153.4	1.17
4-3	2.654	7.87	0.964	9.64	1359	104.9	0.52
4-4	3.277	7.96	1.386	5.00	7.44	85.8	0.32
9-1	0.865	7.91	6.637	15.46	6.23	21.5	1.17
9-2	3.342	7.95	1.979	10.68	6.73	38.2	0.56
9-3	2.379	7.85	1.056	9.93	8.66	89.0	0.28
9-4	2.552	8.03	1.255	7.24	13.06	162.9	0.12
9-5	2.718	7.42	1.243	1.73	4.89	109.7	0.04

Sample	NH ₄ ⁺	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻	Cl ⁻	DOC	Si
	-----mmol/L-----					mg/L	mmol/L
1-1	0.502	8.80	0.022	15.17	2.76	148.6	1.17
1-2	0.043	2.02	0.002	36.17	27.09	56.4	0.48
1-3	0.020	0.09	0.004	52.66	112.12	26.0	0.39
1-4	0.024	0.12	0.004	67.67	114.19	32.4	0.43
4-1	1.251	4.38	0.062	20.83	20.57	210.7	0.61
4-2	0.387	2.79	0.002	58.80	78.24	84.1	0.29
4-3	0.018	0.35	0.001	40.82	50.40	22.0	0.13
4-4	0.021	0.11	0.003	26.51	29.42	12.9	0.19
9-1	0.540	9.39	0.021	18.48	3.95	125.3	1.05
9-2	0.022	2.67	0.010	28.27	5.35	37.6	0.47
9-3	0.016	2.50	0.013	27.85	30.93	21.7	0.47
9-4	0.026	0.84	0.006	55.31	37.00	22.8	0.24
9-5	0.032	0.04	0.004	27.66	35.88	22.7	0.19

Table 2. Carbonate content of study soils as CaCO₃.

Sample	Depth	CaCO ₃
	m	%
<u>Cell 1</u>		
1-1	0.00-0.025	21.2
1-2	0.025-0.46	0.5
1-3	0.46-0.76	0.7
1-4	0.76-1.02	0.8
<u>Cell 4</u>		
4-1	0.00-0.05	19.2
4-2	0.05-0.20	0.2
4-3	0.20-0.61	0.8
4-4	0.61-0.91	0.5
<u>Cell 9</u>		
9-1	0.00-0.05	27.6
9-2	0.05-0.075	0.5
9-3	0.025-0.30	2.1
9-4	0.30-0.70	3.2
9-5	0.70-0.91	5.8

Table 3. Concentrations of soluble U and V measured in saturation extracts of field-moist soils from Kesterson Reservoir.

Sample name	UO_2^{2+} †	V ‡
	----- $\mu\text{mol/L}$ -----	
1-1	0.14	0.85
1-2	0.09	1.04
1-3	0.11	3.47
1-4	0.17	2.65
4-1	0.22	0.61
4-2	0.14	0.49
4-3	0.13	1.74
4-4	0.05	2.40
9-1	0.13	1.68
9-2	0.15	2.39
9-3	0.59	11.07
9-4	-99.00	12.64
9-5	0.06	2.44

† determined by ion chromatography, detection limit 0.02 $\mu\text{mol/L}$, -99 indicates level below detection limit.

‡ determined by AA-graphite furnace, detection limit 0.025 $\mu\text{mol/L}$.

BIOAVAILABILITY AND BIOACCUMULATION OF TRACE ELEMENTS IN THE FOOD CHAIN

PROJECT TITLE: PREDICTION OF SELENIUM UPTAKE INTO CROP PLANTS FROM SELENIFEROUS SOILS OF THE CENTRAL VALLEY OF CALIFORNIA

PROJECT NUMBER: 86-27

DURATION OF FUNDING: July 1986 - June 1989

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ABSTRACT:

Experiments were completed to speciate selenium in water extracts of soils in order to determine which forms of selenium are important in regulating uptake by crops. Other experiments are reported on the effect of pH on the adsorption and desorption of selenite from four soils. Not all soils studied conformed to conventional concepts of soil adsorption of oxyanions with weak acid properties. All soils showed desorption hysteresis. Another study was conducted to determine the effect of temperature on adsorption of selenite by soils.

PROJECT OBJECTIVES ADDRESSED:

1. To measure features of soil water chemistry of selenium that regulate solubility and availability of selenium.
2. To study the mechanisms in the rhizosphere that controls selenium uptake by plants.

RESEARCH PLAN AND PROCEDURES:

All of the research reported was conducted in the laboratory. One study on speciation was conducted to develop a systematic process that would detect the presence of interferences so that those special samples could be given a more exhaustive analytical treatment to overcome the interferences. The other objective was to better understand the behavior of selenite, one of two major source compartments of selenium. This included a thermodynamic study as well as adsorption-desorption measurements at different pH values. The soils used included those from the west side of the San Joaquin Valley as well as comparison soils from other parts of California.

RESULTS:

Selenium Speciation

Analytical procedures were developed to reliably measure selenate, selenite and total selenium in water extracts of soil. The procedure is to add water to soil in a 1:2, soil:solution ratio. This is equilibrated with shaking for four hours and then the aqueous phase is separated by centrifugation and filtering through cellulose membrane filters. The water extract is then acidified to 4M with concentrated HCl. An aliquot of this solution is analyzed immediately by continuous flow hydride generation (borohydride reduction) for selenite selenium. Another aliquot is spiked with a known amount of selenite. If the recovery of added selenium is greater than 90% of added, the value is accepted. If the recovery does not reach this level, some of the original extract is acidified to pH 1.8 and then is passed through Amberlite XAD-8 resin. Again, one aliquot is acidified to 4M HCl and another aliquot is not only acidified to 4M HCl but is also spiked with selenite to determine recovery. If the recovery is not satisfactory, there is no generally accepted remedy. Additional experiments in this area suggest that a different matrix may reliably remove the interference in the determination of selenite.

Total selenium is determined in soil extracts by persulfate oxidation in a sulfuric acid system followed by reduction using HCl. This procedure is much more rapid than the conventional nitric-perchloric digest and gives very accurate and reproducible results. Total inorganic selenium is determined by acidifying the extract pH 1.8 and passing it through the XAD-8 resin. Selenite plus selenate is determined by persulfate oxidation. The above procedure is somewhat laborious. Additional experiments are being performed with other solid phase adsorbents to remove organic selenium.

Effect of pH on Selenite Adsorption

Subsamples of four soils (Lillis, Panoche from the west side of the San Joaquin Valley and Sites from the foothills of the Sierra, and Yolo) were acidified with sulfuric acid and alkalized with calcium hydroxide to produce soil samples with pH values ranging from 4 - 9. Subsamples of these prepared soils were then studied for selenite adsorption using standard techniques. The initial concentration of selenite in solution for Lillis, Panoche and Yolo soils were 20, 50 and 120 ppb Se. The initial concentration for Sites soil were 3, 6 and 10 ppm Se because the energy and capacity of adsorption for Sites soil is so much greater than Valley soils. Adsorption was carried on for four hours in saturated gypsum solution and then desorption was carried out on the same samples in four steps each of four hours duration. The adsorption and desorption performance of the Lillis soil is shown in Figure 4-19. Adsorption isotherms for Lillis as well as all other soils were essentially linear as shown. However the slopes of the adsorption lines were a function of pH and of soil. It is important to note that the hysteresis shown by Lillis soil at all pH values was also true of all soil studied; hysteresis was universal.

The effect of pH on adsorption is shown in Figure 4-18. In all soils studied there was relatively little effect of pH on adsorption at the lowest loading levels. Both Sites and Yolo soils showed, at the medium and highest loading levels, an expected decrease of adsorption with increase of pH. On the other hand, the west side San Joaquin Valley soils, Lillis and Panoche, showed a minimum of adsorption

conditions.

Thermodynamics of Selenite Adsorption

Subsamples of Lillis and Ciervo soils were taken for studies of adsorption over time and at three different temperatures: 4°, 25°, and 60°C. Samples of the system were taken at times ranging from 0-96 hours. The results are depicted in Figures 4-20.

One of the reasons for performing this experiment was because one explanation for the hysteresis shown by desorption of selenite is that it is due to solid state diffusion of selenite into soil crystalline or amorphous materials. Since diffusion is a temperature dependent process, greater adsorption would be expected at higher temperature. The relative independence of the adsorption process of temperature suggests that the diffusion hypothesis should be abandoned as an explanation of the behavior. One explanation of the relative temperature insensitivity of the adsorption reaction is that there are two different processes of adsorption; e.g. solid state diffusion and bond transformation. It is possible, although unlikely that one of these processes is exothermal and the other endothermal so that the net effect is temperature independence.

Fig. 4-18 Adsorption envelopes of four soils

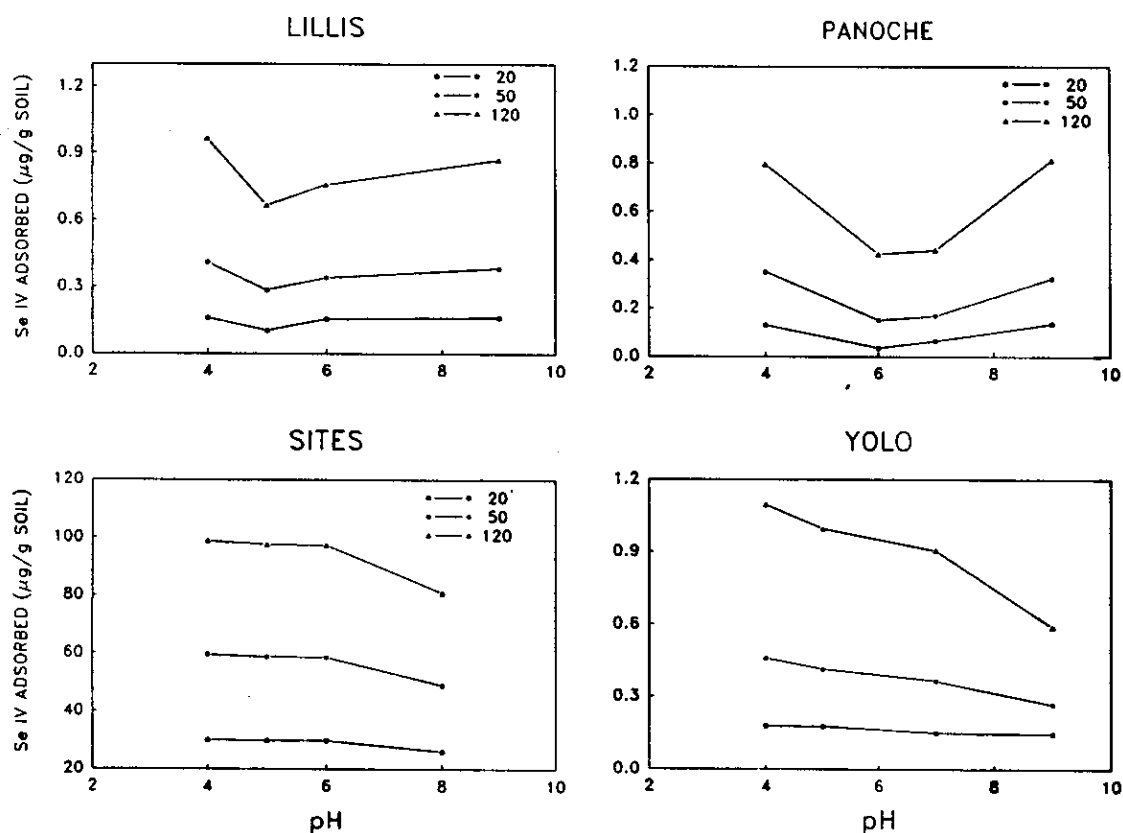


Fig. 4-19 Desorption isotherms at different pH

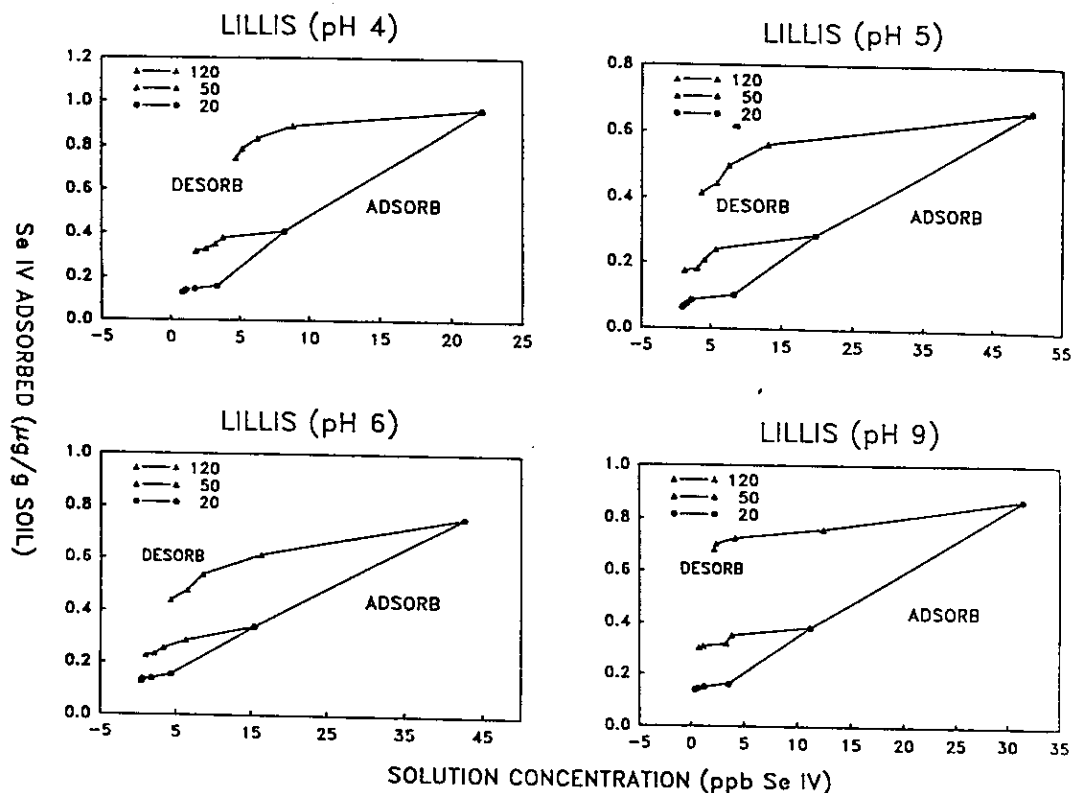
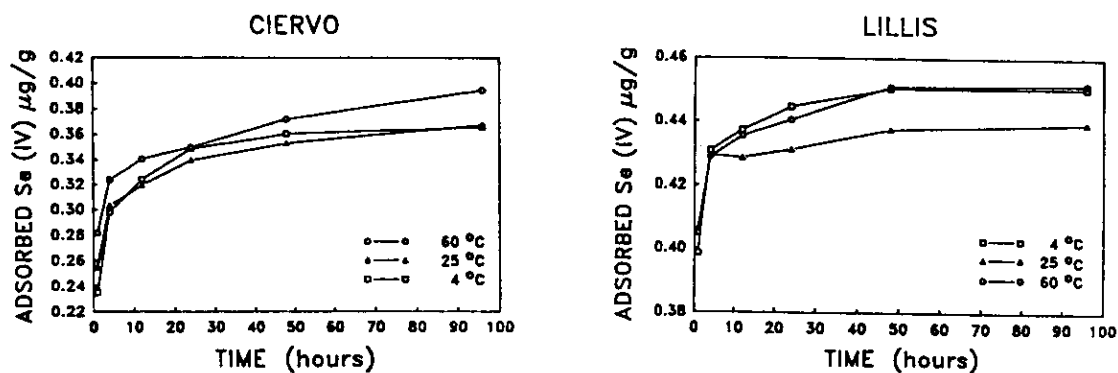


Fig. 4-20. Temperature dependence of selenite adsorption.



DISCUSSION AND SUMMARY:

A very important problem in selenium chemistry in arid-zones soils is the determination of the relative quantities of selenium in the selenate, selenite and organic selenium forms. The development of a reliable and relatively efficient process to determine the absolute quantities of these different species will be important. A serious problem in this area is that there are interferences "which have not been identified" and which appear sporadically and unpredictably. Of the inorganic forms of

selenium, the selenite form is more insoluble because of adsorption and therefore it may not be directly important in transport or in availability for plant uptake. However, some of the soils in the west San Joaquin Valley contain considerable amounts of adsorbed selenite. This selenium is potentially available for oxidation to the selenate form where it will be available to plants and also to leaching to shallow aquifers.

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No new citations from previous reports and original proposal.

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PROJECT TITLE: DETERMINATION OF THE TOXICITY, BIOACCUMULATION, BIOTRANSFORMATION, AND TRANSFER OF SELENIUM IN AQUATIC FOOD CHAINS.

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ABSTRACT:

Problems associated with elevated concentrations of trace elements in aquatic ecosystems are being reported with increasing frequency throughout the United States. High selenium (Se) levels in aquatic systems impacted by coal fly ash and irrigation drainage water have been associated with death, teratogenesis and reproductive failure in important fish and waterfowl populations. The bioaccumulation and resultant toxicity of Se in aquatic organisms results from two processes: bioconcentration, which is the uptake of Se from the water column; and biomagnification, which is the uptake of Se through the food chain and which can include organic Se compounds biosynthesized by primary producers. We are continuing our investigations into the toxicity, bioaccumulation, biotransformation and transfer of Se in algae (primary producers), invertebrates (primary consumers) and fish (secondary consumers), which constitute the three major trophic levels present in aquatic food chains.

KEYWORDS: selenium, toxicity, bioaccumulation, biotransformation, food chain, algae, invertebrates, fish.

PROJECT OBJECTIVES ADDRESSED:

The ultimate objective of this project is to develop a series of assay methodologies to evaluate the toxicological dynamics of agricultural return water contaminants in aquatic organisms and food chains. Utilizing Se as a representative agricultural drain water constituent, we are examining the toxicity, bioaccumulation, biotransformation and transfer of these elements in the principle components of an aquatic food chain: primary producers (algae), primary consumers (herbivorous and detritivorous invertebrates) and secondary consumers (fish). Each trophic level contains specific objectives which we are addressing.

Primary producers: The research objectives outlined are to study the bioaccumulation, biotransformation, and toxicity of Se in representative species from three algal classes (greens, blue-greens, and diatoms) common to the Central Valley of California.

Primary consumers: Extending our evaluations of the acute and chronic sublethal toxicity of waterborne and dietary Se (seleniferous algae) to aquatic invertebrates (herbivores and detritivores) is the primary objective of this research. Secondary objectives include evaluation of the interactions of Se with other drainwater contaminants including salinity and boron.

Secondary consumers: Determine the roles of bioconcentration and biomagnification in the bioaccumulation of Se by fathead minnows (Pimephales promelas) and bluegill (Lepomis macrochirus).

RESEARCH PLAN, PROCEDURES, RESULTS AND DISCUSSION:

Primary Producers: Se has been implicated in the degradation of several aquatic ecosystems across the United States. As early as 1957, mortality of stocked gamefish in Sweitzer Lake (CO) was linked to Se contamination (Barnhart, 1957). More recently, Se contamination from coal-fired power plant operations resulted in disappearance of 16 fish species in Belews Lake (NC), apparently a result of reproductive failure (Cumbie and VanHorn, 1978; Lemly, 1985). And use of Se-contaminated agricultural drainwater in the Kesterson National Wildlife Refuge (CA) led to the much publicized reproductive toxicity in aquatic birds using the reservoirs in the refuge (Ohlendorf et al., 1986).

In all of these cases, the investigating scientists concluded that bioaccumulation of Se through the food chain was responsible for the observed toxicity problems. Subsequent feeding studies with both fish and waterfowl indicate that it is selenomethionine (a methionine molecule in which Se has been used instead of sulfur) that is responsible for reproductive impairment (Woock et al., 1987; Heinz et al. 1988, 1989). As an analog to methionine, selenomethionine cannot be synthesized by invertebrates and vertebrates, which rely on lower trophic level organisms, such as algae, to supply these amino acids. Clearly then, the uptake of Se by algae is a critical process in the ultimate bioaccumulation of toxic Se species by higher trophic level organisms such as fish and waterfowl.

With this in mind, we are conducting studies to compare the toxicity and accumulation of inorganic and organic Se compounds by common freshwater algae. Studies on the toxicity and bioaccumulation of selenite and selenate by the green alga Selenastrum capricornutum have been completed (Foe and Knight, 1986; Williams et al., 1989) and described in previous reports.

Similar experiments with the blue-green algae Anabaena flos-aquae have been completed during this past year. The specific methods used in this study were described in detail in last year's annual report. Briefly, A. flos-aquae was exposed to either selenate, selenite, or selenomethionine and growth (as chlorophyll a) and algal Se levels were determined after 0, 48, 96, 144, and 240 hours of exposure. These experiments indicate that algal Se reaches a maximum for selenate, selenite and selenomethionine by day two, and that selenomethionine is accumulated to greater levels than is selenite, which in turn is greater than for selenate (Figure 1).

In the selenomethionine experiment, growth was unimpaired at 0.5 ppm, significantly decreased at 0.1 ppm and ceased at 0.3 ppm selenomethionine. For both selenate and selenite, growth was unaffected at 1.0 ppm, significantly decreased at 3.0 ppm and essentially ceased at 5.0 ppm. In comparing the toxicity of selenite to the green alga S. capricornutum and the blue-green alga A. flos-aquae, it appears that the blue green alga is more tolerant to selenite. At 0.075 ppm selenite the growth of S. capricornutum was significantly decreased (Foe and Knight, 1986) while the growth of A. flos-aquae was not inhibited at levels less than 3.0 ppm selenite.

An M.S. Thesis based on these experiments has been accepted and a manuscript (Kiffney and Knight, 1989) has been accepted for publication in Archives of Environmental Contamination and Toxicology.

The effects of sulfate on the accumulation and toxicity of selenate by the green alga S. capricornutum has been reported previously and demonstrates that there is a significant interaction between the two similar anions, supporting the hypothesis that both are accumulated by a single uptake mechanism (Williams et al., 1989). As a component of the Daphnia magna feeding study (described later), a separate experiment determining the effects of very low levels of sulfate on selenite uptake and toxicity by S. capricornutum was conducted. The culture methods and conditions are the same as those in the previous study except that the cultures were inoculated to algal densities of 50×10^6 cells/ml, initial media selenite concentrations were 150 ppb, and culture media sulfate concentrations of 0, 1.2, 2.4, 3.6, 4.8, and 9.6 mg S/l were used. S. capricornutum was grown for 96 hours with algal weights and Se concentrations being determined after 96 hours of exposure. The experiment was conducted using a completely randomized design of six treatments each with three replicates, and the data statistically analyzed using ANOVA.

The results (Table 1) indicate that there is a significant increase in Se accumulation and decreased algal growth at very low sulfate concentrations. These results are not easily explained as a review of the available literature (Ogle et al., 1988) indicates the existence of separate cellular uptake mechanisms for sulfate and selenite. In the absence of sulfate, the algae is being compromised in some fashion which results in the accumulation and toxicity of the selenite. We hypothesize that this may involve a shift in metabolic routes to utilize the available selenite as an analog to sulfur.

As stated in the beginning of this section, feeding studies with both fish and waterfowl indicate that it is selenomethionine that is responsible for reproductive impairment. Thus, knowledge of the biochemical nature of Se will be necessary for a complete understanding of the mechanisms of bioaccumulation, biotransformation, toxicity and cycling of Se in aquatic ecosystems. The objective of this study is to develop analytical procedures which will allow us to determine the biochemical speciation of Se in the green alga S. capricornutum.

S. capricornutum was cultured (as described in the previous annual report) in media containing 33.67 mg S/l and either 0 or 10 µg Se/l as selenate. After incubating for four days, the algae

samples were centrifuged, rinsed and recentrifuged using a Sharples supercentrifuge. The algae was then freeze-dried and stored at -4°C until used.

The extraction method was very similar to that of Zingaro et al. (1977). Deviations from the published procedure included a CHCl₃/methanol extraction (2:1 v/v) of the dried ethanol extract (Polch et al., 1951), and the use of gas chromatography-mass spectroscopy (GC-MS) for the identification of seleno-amino acids (Anderegg, 1985). At various stages throughout the extraction, a total Se analysis was performed on small portions of the resulting samples. The results of these analyses, in terms of Se mass recovered, are shown in Figure 2.

Although the study is not complete, some interesting information has been gathered. Algae grown in the Se-containing medium accumulated a majority of the Se in the residue fraction. Subsequent proteolysis of this residue fraction showed that 70% of the Se recovered was in a soluble form and probably was the result of protein breakdown into Se-containing amino acids. Since less than 50% of the Se was recovered after proteolysis, the actual values may be somewhat different; it is not clear why the recovery was so low.

Upon completion of this project we expect to know which free amino acids and which protein amino acids contain Se. They may not be the same types, indicating that proteins may incorporate Se into their amino acid structure directly, rather than by the addition of seleno-amino acids from the free amino acid pool. We anticipate submitting samples of both free and protein-derived amino acids to the Facility for Advanced Instrumentation for analysis by GC-MS.

Despite not having the entire picture before us, results from the distribution experiments imply that some chemical transformation from an inorganic to an organic form of Se has occurred in algae grown in Se-containing media. Algae growing in Se-impacted ecosystems may also have a very high protein-Se content. It is possible that aquatic organisms from higher trophic levels feeding on seleniferous algae may encounter higher Se concentrations and a more toxic chemical form of Se in algal tissue than in the water column. Depending on how the feeding organism utilizes algal protein, food chain biomagnification is likely a more significant problem than bioconcentration directly from the water in Se-impacted aquatic systems.

Primary Consumers:

(1) Waterborne Toxicity:

In the previous annual report, we described our experiments determining the toxicity of waterborne selenate and selenite to the amphipod Hyalella azteca in acute LC₅₀ bioassays of 48, 96, and 240 hours. During this past year, we have completed the 24 day chronic sub-lethal bioassays to determine the effect of long-term Se exposure on H. azteca reproduction. Two experiments were conducted, one with selenite-Se levels of 0, 50, 100, 200, 300, and 400 µg/l, and the other with selenate-Se levels of 0, 10, 100, 250, 300, 500, and 700 µg/l. There were four replicates at each treatment level. Ten animals (approximately two months old and 2 mm in length) were placed in each

replicate. Neonate H. azteca were counted and removed every 24 hours. A one-way ANOVA was used to determine the effect of Se level on number of young per female.

Selenate had no effect on H. azteca reproduction at the Se levels used. Selenite effect was significant and a comparison of means using Duncan's multiple range test and indicate a significant decrease in H. azteca reproduction at 200 µg/l (Table 2). An M.S. Thesis based on these experiments has been accepted and a manuscript is in preparation and will be submitted to an appropriate journal.

In previous annual reports we have described experiments examining the comparative acute toxicity of waterborne selenate, selenite and seleno-DL-methionine to Chironomus decorus, resulting in 48 hr. LC₅₀ values of 23.7, 48.2 and 194 mg Se/l, respectively. The comparative chronic sublethal toxicities of selenate, selenite and seleno-DL-methionine were determined as significant growth reductions at 6.0, 0.75 and 0.10 mg Se/l, respectively. The relative ranking of the Se forms in the sub-lethal growth studies are different from those determined in acute toxicity studies. Bioaccumulation studies conducted at Se concentrations where growth reduction was observed indicated that Se from the water column became associated with the cerophyll utilized by the midge larvae for food and substrate. Midge Se concentrations increased in response to cerophyll Se increases. The kinetics of Se accumulation in this experimental system indicate that the different route of exposure and biotransformation of Se by microbes associated with the food and substrate may explain the different relative toxicities observed in the acute and chronic studies.

(2) Dietary Se Toxicity:

The bioaccumulation and toxicity of a Se-laden diet has been evaluated by culturing green algae as a diet for the aquatic insect, Chironomus decorus. The research approach for this study was described in detail in the previous annual report. Briefly, S. capricornutum was cultured for 96 hours in three concentrations of sodium selenite and sodium selenate (0, 10, and 40 ppb). The algae was then centrifuged, and freeze-dried. The freeze-dried algae was then utilized as the diet for C. decorus (midge) larvae in 96-hour assays after which midge growth and Se levels were determined. As treatment Se levels increased, there were significant increases in algal Se levels, which in turn resulted in significant increases in midge Se levels and significant decreases in midge growth (Table 3). These results demonstrate that significant bioaccumulation and toxicity of Se can occur in a benthic/detrital food chain at environmentally relevant Se levels. An M.S. Thesis and a manuscript based on these experiments are in preparation.

In addition to the benthic/detrital midge food chain just described, we are currently conducting experiments examining the transfer and toxic effects of Se through a planktonic food chain by feeding seleniferous algae (S. capricornutum) to a filter-feeding crustacean (D. magna). We have previously fed D. magna seleniferous (295 ppm dry weight) and normal algal diets and observed no alteration in survival, growth and reproduction (Foe and Knight, 1986). Similar results were reported by Boyum and Brooks (1988).

The lack of dietary Se toxicity may be due to a lack of assimilation and bioaccumulation of Se from the algae to the daphnids. We are testing this hypothesis by determining the bioaccumulation of

Se in daphnids fed the seleniferous algal diet. Preliminary studies have again demonstrated no significant effects on survivorship, growth or reproduction (Table 4). After the chemical analyses were accomplished it appeared that Se was not accumulated by the daphnids. We are presently conducting the final series of experiments in this area.

Secondary Consumers:

In the previous annual report, we described our investigation into the effects of elevated dietary Se on the growth and reproduction of the fathead minnow. That study demonstrated an apparent lack of reproductive toxicity resulting from Se biomagnification in fathead minnows (Ogle and Knight, 1989). However, other laboratory studies have shown that reproductive toxicity does occur in bluegills (Woock et al., 1987; U.S. FWS 1988). The results of this and other studies confirm the results of field studies showing that cyprinid reproduction is apparently relatively unaffected, while sunfish reproduction can be impaired to the point of population extinction. We have hypothesized that the reasons for the disparity in reproductive toxicity in these two fish groups involve significant differences in the way these two fish groups bioaccumulate Se and are currently conducting a series of experiments investigating the roles of bioconcentration and biomagnification in the comparative bioaccumulation of Se by fathead minnows and bluegill.

Based on our previous studies which demonstrated an antagonistic effect of sulfate on Se bioconcentration and/or toxicity in algae and invertebrates, the first set of experiments in this investigation studied the effect of sulfate on the bioconcentration of selenate and selenite by the fathead minnow. Two experiments were conducted in which fathead minnows were exposed to each Se species in the water but not in the diet. Se treatment levels of 0, 5, 10, and 50 ppb were selected. These levels were chosen for the following reasons: the EPA and agencies in several states have established 5 ppb as their new criteria for waterborne Se, the reproductive toxicity observed in Belews Lake and other systems occurred at waterborne Se levels of 10 ppb, and lastly, 50 ppb is a compromise representative value for a highly contaminated system. Sulfate-S levels of 3.4 and 108.6 mg/l, equivalent to U.S. EPA "very soft" and "very hard" reconstituted waters, were selected. There were four replicates at each of the eight treatment combinations for a total of 32 experimental units in each of the two experiments. Eight 60-day-old fathead minnows were placed in each container and were maintained for 28 days. Fish were sampled at 2, 4, 7, 14, 21, and 28 days, immediately frozen, and later analyzed for wet weight tissue Se levels.

These experiments have been completed; analysis of fish samples through day 14 for both experiments are complete and the data is presented in Table 5. As can be seen, there was no effect of increasing Se treatment or of increasing sulfate treatment on fish selenium levels. There is a dramatic difference in fish Se levels between the selenate and selenite treatments; however, this difference extends to the control fish as well, and as the fish for these two experiments were obtained from different commercial suppliers, we believe that this is an artifact due to two different strains of fathead minnows. Nevertheless, the lack of effect of increasing Se and sulfate

levels on fish tissue Se levels is significant and surprising as previous studies by others have suggested that bioconcentration of Se by fish does occur, as well as studies (including our own) that demonstrate a significant interaction between sulfate and Se uptake in other taxa. This indicates that fathead minnows are extremely efficient at regulating uptake of waterborne Se, and may be one reason why fathead minnows, and cyprinids in general, accumulate less Se than do other fish such as the bluegill.

We are currently completing the analysis of the fish samples for days 21 and 28 after which we will statistically analyze the results and prepare a manuscript for publication. We are also currently conducting similar experiments for both fathead minnows and bluegill with an additional Se treatment of 100 µg/l; this will allow us to compare minnow and sunfish bioconcentration, and to examine whether this apparent regulation of tissue Se levels persists at concentrations two-fold higher than previously used. The new 28-day fathead minnow (selenate and selenite) and the bluegill (selenate) experiments have been completed and the bluegill (selenite) experiment is underway. Subsequent experiments will investigate the role of "food chain" and of "food chain+waterborne" uptake of selenate and selenite by these fish.

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In Preparation:

Brasher, A. M. and A. W. Knight. Acute and sub-lethal toxicity of selenate and selenite to the amphipod Hyaella azteca.

Maier, K. J., C. G. Foe and A. W. Knight. Comparative toxicity of selenate, selenite and selenomethionine to Daphnia magna and the effects of water hardness and sulfate on their toxicities.

Maier, K. J. and A. W. Knight. The toxicity of waterborne borate to Daphnia magna and Chironomus decorus.

Malchow, D. and A. W. Knight. Toxicity and bioaccumulation of dietary selenium to the aquatic larvae of the midge, Chironomus decorus.

Table 1. The effects of sulfur on the bioaccumulation of Se and growth of Selenastrum capricornutum exposed to Selenite (150 µg/l Se).

Media [S]	Algal [Se]	Algal Biomass
ppm	ppm	mg/50 ml culture
9.6	12.6 (A)	6.6 (A)
4.8	32.6 (A)	8.2 (A)
3.6	18.4 (A)	6.9 (A)
2.4	20.9 (A)	6.3 (A)
1.2	23.0 (A)	6.0 (A,B)
0.0	363.0 (B)	3.4 (B)

All values with the same letter in any column are not significantly different ($P \leq 0.05$).

Table 2. Effects of waterborne selenite on reproduction of Hyalella azteca.

Se treatment	0 µg/l	50 µg/l	100 µg/l	200 µg/l	300 µg/l	400 µg/l
Mean young per female	2.00 (a)	1.58 (a,b)	1.45 (a,b)	0.80 (b,c)	0.53 (b,c)	0.11 (c)

Means with the same letter are not significantly different at $p < 0.01$.

Table 3. The bioaccumulation and toxicity of selenium in Chironomus decorus fed seleniferous Selenastrum capricornutum.

Se Species	Media [Se]	Algal [Se]	Midge [Se]	Midge Growth
Selenate	0 (a)	0 (a)	0 (a)	0.49 (a)
	4 (b)	1.1 (b)	0 (a)	0.45 (a)
	10 (c)	2.1 (c)	2.6 (b)	0.42 (b)
	40 (d)	7.2 (d)	6.6 (c)	0.40 (b)
Selenite	0 (a)	0 (a)	0 (a)	0.46 (a)
	10 (b)	2.8 (b)	4.0 (b)	0.25 (b)
	40 (c)	10.0 (c)	8.6 (c)	0.28 (b)

For each selenium species, column values with different letters are significantly different at the 0.05 level.

Media [Se] concentrations are in µg/l.

Algal and midge Se concentrations are in ppm, dry weight.

Midge growth is in mg/organism/96 hrs.

Table 4. The toxicity and bioaccumulation of Se in Daphnia magna fed a diet of seleniferous Selenastrum capricornutum.

H ₂ O/Algal Exp.	H ₂ O [Se]	Algal [Se]	Daphnid [Se]	Growth	Reprod.
0/0	0.3±0.4	1.5±2.6	4.49±1.3	8.5±2.4	16.6±18.3
10/0	10.7±1.4	1.3±1.4	9.7 ±4.6	5.0±1.6	16.0± 8.0
10/10	10.4±0.6	1.7±1.6	6.9 ±1.9	6.7±1.5	12.6± 6.0
10/100	10.6±1.1	8.5±6.2	12.2 ±2.2	7.6±2.3	24.0±17.4
10/150	10.2±1.3	9.4±6.8	12.8 ±2.7	7.4±2.2	19.6±14.9

H₂O Se concentrations are in µg/l, mean ± s.d.

Organismal Se concentrations are in ppm dry weight, mean ± s.d.

Daphnia growth was in µg/org/day over a 10 day period, mean ± s.d.

Daphnia reproduction is in number of neonates/rep/10 days, mean ± s.d.

Table 5. Effects of sulfate on the bioconcentration of selenate and selenite by the fathead minnow (*Pimephales promelas*).

Se Species & Level			[SO4-S]	Fish Tissue [Se], ppm			
				48 hr	96 hr	7 d	14 d
Selenate	0 µg/l	3.4 mg/l	0.65±0.07	0.76±0.06	0.66±0.01	0.65±0.01	
	5 µg/l		0.64±0.06	0.69±0.01	0.63±0.02	0.63±0.02	
	10 µg/l		0.71±0.04	0.72±0.02	0.66±0.08	0.63±0.04	
	50 µg/l		0.68±0.02	0.75±0.05	0.72±0.03	0.68±0.06	
	0 µg/l	108.6 mg/l	0.71±0.09	0.66±0.08	0.63±0.05	0.63±0.04	
	5 µg/l		0.66±0.06	0.77±0.06	0.65±0.05	0.64±0.06	
	10 µg/l		0.70±0.06	0.71±0.08	0.64±0.03	0.62±0.05	
	50 µg/l		0.66±0.06	0.75±0.10	0.63±0.04	0.69±0.02	
Selenite	0 µg/l	3.4 mg/l	0.52±0.04	0.50±0.03	0.48±0.04	0.53±0.07	
	5 µg/l		0.54±0.06	0.50±0.03	0.50±0.04	0.52±0.03	
	10 µg/l		0.48±0.03	0.53±0.03	0.53±0.03	0.51±0.04	
	50 µg/l		0.54±0.02	0.53±0.04	0.53±0.04	0.58±0.08	
	0 µg/l	108.6 mg/l	0.50±0.05	0.47±0.01	0.45±0.04	0.52±0.03	
	5 µg/l		0.50±0.03	0.48±0.02	0.55±0.03	0.54±0.03	
	10 µg/l		0.51±0.03	0.50±0.04	0.53±0.03	0.53±0.02	
	50 µg/l		0.55±0.05	0.50±0.01	0.56±0.04	0.62±0.02	

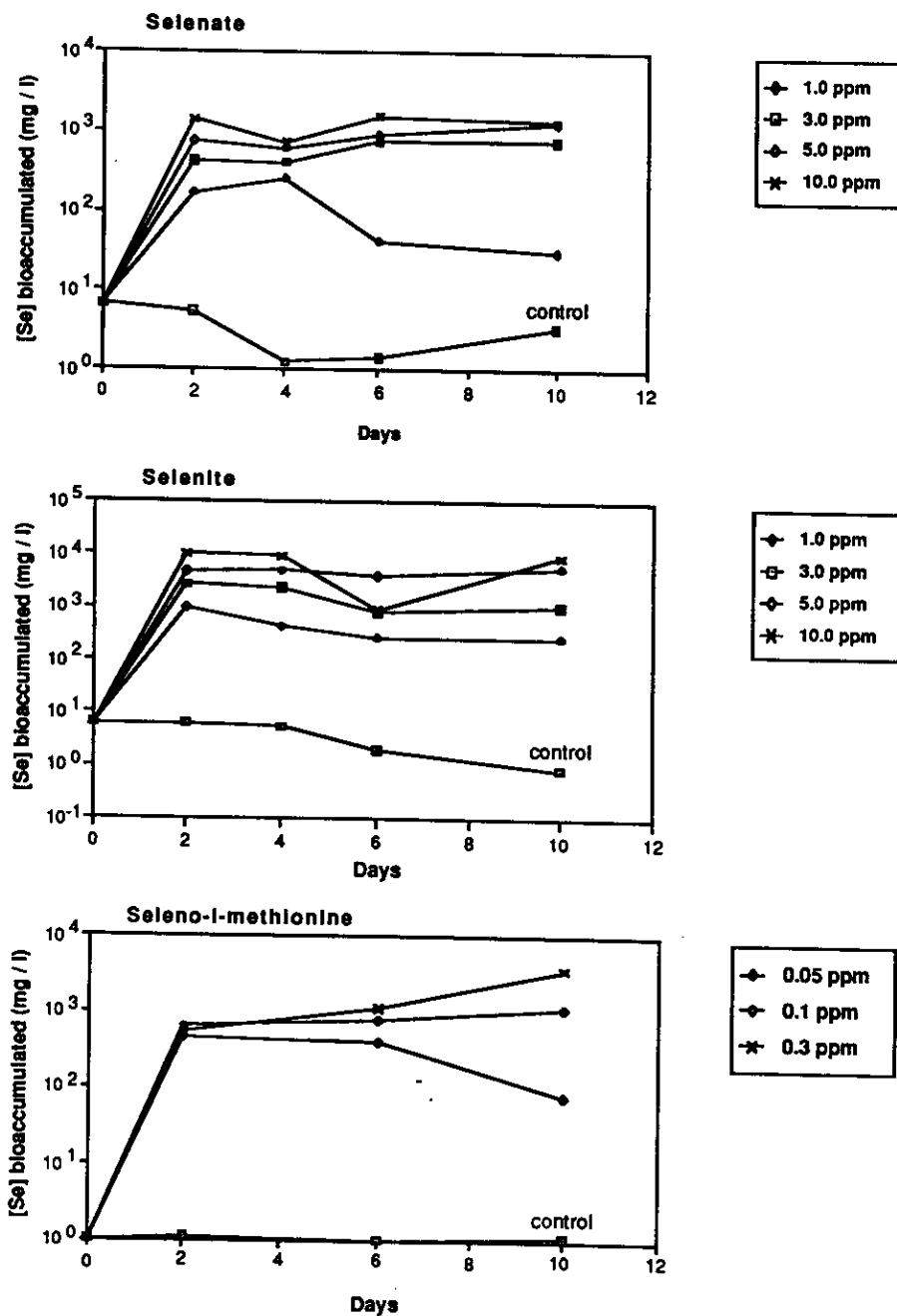


Figure 1. The bioconcentration of Selenate, Selenite and Seleno-l-methionine in *Anabaena flos-aquae*.

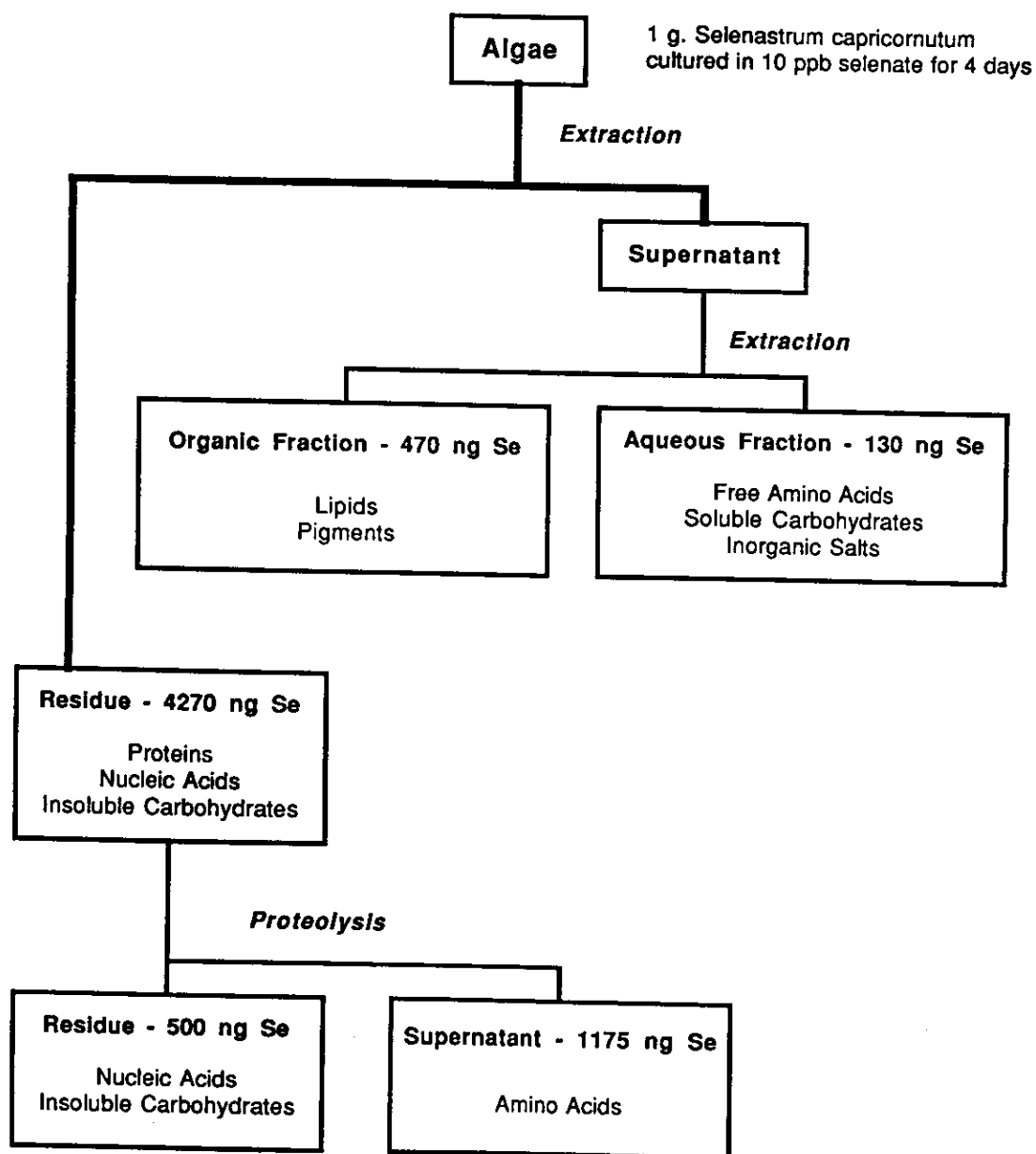


Figure 2. Biochemical speciation of Selenium in *Selenastrum capricornutum* exposed to Selenate.

PROJECT TITLE: COMPETITIVE INTERACTION BETWEEN As, Se, Mo AND P

PROJECT NUMBER: 87-6

DURATION OF PROJECT: July 1987 - June 1989

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Student Assistants: 2

ABSTRACT:

Arsenic (As), selenium (Se), and molybdenum (Mo) have become increasingly important in the terrestrial and agrobiological environment in some parts of the western United States. Four factorial [3 As x 3 Se x 2 Mo x 2 P] glasshouse studies were conducted to evaluate the competitive interactions between As(V), Se(VI), Mo(VI) and P using nutrient solution concentrations representative of soil solutions and agricultural drainage waters. Alfalfa [*Medicago sativa* L., Germain WL 512] was grown in sand culture and irrigated 5 times in 24 h with half-strength Hoagland's solution containing 2 (background), 50 and 100 $\mu\text{g As(V) L}^{-1}$ as NaHAsO_4 ; 0, 50, and 100 $\mu\text{g Se(VI) L}^{-1}$ as Na_2SeO_4 ; 0.0 (background) and 1.0 mg Mo(VI) L^{-1} as Na_2MoO_4 ; and 1.0 and 4.0 mg P L^{-1} as KH_2PO_4 in completely randomized factorial design. To reduce the possible interference of SO_4 with Se, 8.0 mg $\text{SO}_4\text{-S L}^{-1}$ were used as a background in the nutrient solution, instead of 16.0 mg $\text{SO}_4\text{-S L}^{-1}$ (commonly used in half-strength Hoagland's solution). The results indicated no adverse effect of Se on shoot yield at the 20 mg Se kg^{-1} . The 100 $\mu\text{g Se L}^{-1}$ and 4.0 mg P L^{-1} strongly depressed shoot As concentration. The 100 $\mu\text{g As L}^{-1}$ promoted shoot Se, Mo and P concentrations. The 4.0 mg P L^{-1} showed no significant effect on shoot Se and Mo, while 1.0 mg Mo L^{-1} showed consistent increase in shoot P concentration as compared with 0.01 mg Mo L^{-1} (control). These results should improve our understanding of the complex soil-plant system where the anions of AsO_4 , SeO_4 , MoO_4 , H_2PO_4 , coexist in the soil solutions, and when fertilizers are applied to soils containing elevated concentrations of As, Se and Mo.

KEYWORDS: Arsenic, Selenium, Molybdenum, Phosphorus, Competitive interaction

PROJECT OBJECTIVES ADDRESSED:

1. To evaluate the competitive interactions between As, Se, and Mo at levels representing those observed in the soil solution and agricultural drainage waters in the western San Joaquin Valley.
2. To investigate the influence of P concentrations on the competitive interaction between As, Se and Mo.

RESEARCH PLAN AND PROCEDURES:

A completely randomized four factorial [3 As x 3 Se x 2 Mo x 2 P] experiment was conducted in the glasshouse using sand culture system. Alfalfa (*Medicago sativa* L., Germain WL 512) was planted into 11-L plastic pots filled with coarse-grained silica sand. Two pots were placed above 100-L plastic-lined reservoir which contained half strength nutrient solution. The basal nutrient solution contained the same nutrients as reported earlier (Khattak et al., 1989) except for $\text{PO}_4\text{-P}$ and $\text{SO}_4\text{-S}$ concentrations. Two levels of P, 1.0 and 4.0 mg L^{-1} were added and closely maintained, and $\text{SO}_4\text{-S}$ was lowered to 8.0 mg L^{-1} instead of the commonly used 16.0 mg $\text{SO}_4\text{-S L}^{-1}$.

The plants were irrigated automatically five times/24 h by pumping the nutrient solution from reservoir onto the surface of the sand and allowed to slowly drain back into the reservoir. After emergence, each pot was thinned to 10 plants/pot, having 2 pots/tank and 3 tank/treatment. Ten days after emergence of seeds, 3 levels of As (0, 0.05 and 0.1 mg L^{-1} arsenate), 3 levels of Se (0, 0.05 and 0.10 mg L^{-1} sodium selenate) and 2 levels of Mo (.01 and 1.0 mg L^{-1} sodium molybdate) were imposed in six replications per treatment. The nutrient solution pH was closely monitored and maintained between 6.5 and 7.0 with addition of HCl or KOH as needed. Based upon the periodic (15 d) analysis of nutrient solution, the basal nutrient solution was replenished to initial concentration of the macro- and micronutrients. The added concentrations of As, Se, Mo and P were checked regularly (no later than 15 d) and were maintained.

Plants were harvested after 30 d and a total of 3 harvests were obtained. Shoot yield (oven dry weight) was recorded after drying at 65°C. The oven-dried plant material was ground in a Wiley mill and 250 mg ground tissues were digested first using a 1 mL HNO_3 for predigestion and then 2:1 nitric:perchloric acid mixture (Ganje and Page, 1974). Plant digests were analyzed for total Se following the procedure of Perkin-Elmer Corporation (1979) and total As (Ganje and Rains, 1982) by hydride generation-flame atomic absorption with a heated quartz cell and utilizing argon as the carrier gas. An atomic absorption spectrophotometer (Perkin-Elmer Model 5000, Norwalk, CT) equipped with a 10-cm Standard burner head (using air-acetylene flame) and hydride generator (MH-10) was used. This method quantified up to 0.20 ng As g^{-1} and 0.10 ng Se g^{-1} of plant material quite accurately. Molybdenum and P was analyzed with inductively coupled argon plasma spectroscopy with ICAP spectrometer (Jarrell Ash Atom Corp. Series 8000).

RESULTS:

Statistical analysis presented in Table 1 summarizes the main effect and the effect of binary and tertiary interactions between As, Se, Mo and P on the alfalfa shoot yield (oven dry weight) and composition. To avoid redundancy, yield and shoot concentrations data for As, Se, Mo and P of a single harvest are discussed under a given element. The nutrient solution concentrations of As, Se and Mo refer to arsenate, [As(VI)], selenate (Se(VI)), and molybdate [Mo(VI)], while shoot concentrations represent total As, Se and Mo.

Shoot Yield

The shoot yield generally showed nonsignificant variations within the mean values (Tables 2 and 3). However, the analysis of variance (Table 1) showed that As, P, Se x Mo and As x Se x Mo had a significant effect on the shoot yield. This effect appeared to be associated with the tissue P concentrations, which showed small but consistent increases with addition of As, Se and Mo (Tables 2 and 3). Some of the variations in yield wherever applicable are discussed under the individual element.

Arsenic

As the solution As increased from 2 to 100 $\mu\text{g L}^{-1}$, tissue As progressively increased at any level of Se, Mo, and P (Tables 2 and 3). At a given level of As particularly 50 and 100 $\mu\text{g As L}^{-1}$, the treatment of 100 $\mu\text{g Se L}^{-1}$ and 4.0 mg P L^{-1} caused a significant ($P = 0.05$) decrease in the shoot As (Tables 2 and 3). Although a nonsignificant but consistent decrease in tissue As can be noted with addition of 1.0 mg Mo L^{-1} , in any given interactive system, the other anions (selenate, orthophosphate and molybdate) tended to depress As uptake in a consistent fashion. This was more obvious when 4.0 mg P L^{-1} was added with 100 $\mu\text{g Se L}^{-1}$ (Table 2). This observations confirmed the antagonistic effect of Se on As uptake (Khattak et al., 1989) where 250 to 1000 mg Se L^{-1} caused a drastic decrease in As uptake in the presence of 16 mg P L^{-1} in the half-strength Hoagland's solution. The present data also suggested that at low levels of P (1.0 and 4.0 mg L^{-1}) the antagonistic effect of solution Se was not as strong as in the presence of 16 mg P L^{-1} .

The antagonistic effect of P on As uptake has been reported (Woolson et al., 1973; NRC, 1977; Wallace et al., 1980), but it is important to realize the implication of the effect of P interference on As and Se uptake. Elevated levels of As in areas where As-based chemicals have been applied to soils (Johnson and Hiltbold, 1969) could be phytotoxic (Kabata-Pendias and Pendias, 1984), but it is equally important to understand the role of As in relation to P and Se in soil-plant system.

Addition of high rates of P fertilizer reducing the As uptake may also decrease the uptake and accumulation of Se to nontoxic levels.

RESULTS:

Statistical analysis presented in Table 1 summarizes the main effect and the effect of binary and tertiary interactions between As, Se, Mo and P on the alfalfa shoot yield (oven dry weight) and composition. To avoid redundancy, yield and shoot concentrations data for As, Se, Mo and P of a single harvest are discussed under a given element. The nutrient solution concentrations of As, Se and Mo refer to arsenate, [As(VI)], selenate (Se(VI)), and molybdate [Mo(VI)], while shoot concentrations represent total As, Se and Mo.

Shoot Yield

The shoot yield generally showed nonsignificant variations within the mean values (Tables 2 and 3). However, the analysis of variance (Table 1) showed that As, P, Se x Mo and As x Se x Mo had a significant effect on the shoot yield. This effect appeared to be associated with the tissue P concentrations, which showed small but consistent increases with addition of As, Se and Mo (Tables 2 and 3). Some of the variations in yield wherever applicable are discussed under the individual element.

Arsenic

As the solution As increased from 2 to 100 $\mu\text{g L}^{-1}$, tissue As progressively increased at any level of Se, Mo, and P (Tables 2 and 3). At a given level of As particularly 50 and 100 $\mu\text{g As L}^{-1}$, the treatment of 100 $\mu\text{g Se L}^{-1}$ and 4.0 mg P L^{-1} caused a significant ($P = 0.05$) decrease in the shoot As (Tables 2 and 3). Although a nonsignificant but consistent decrease in tissue As can be noted with addition of 1.0 mg Mo L^{-1} , in any given interactive system, the other anions (selenate, orthophosphate and molybdate) tended to depress As uptake in a consistent fashion. This was more obvious when 4.0 mg P L^{-1} was added with 100 $\mu\text{g Se L}^{-1}$ (Table 2). This observations confirmed the antagonistic effect of Se on As uptake (Khattak et al., 1989) where 250 to 1000 mg Se L^{-1} caused a drastic decrease in As uptake in the presence of 16 mg P L^{-1} in the half-strength Hoagland's solution. The present data also suggested that at low levels of P (1.0 and 4.0 mg L^{-1}) the antagonistic effect of solution Se was not as strong as in the presence of 16 mg P L^{-1} .

The antagonistic effect of P on As uptake has been reported (Woolson et al., 1973; NRC, 1977; Wallace et al., 1980), but it is important to realize the implication of the effect of P interference on As and Se uptake. Elevated levels of As in areas where As-based chemicals have been applied to soils (Johnson and Hiltbold, 1969) could be phytotoxic (Kabata-Pendias and Pendias, 1984), but it is equally important to understand the role of As in relation to P and Se in soil-plant system.

Addition of high rates of P fertilizer reducing the As uptake may also decrease the uptake and accumulation of Se to nontoxic levels.

Selenium

For any given treatment of As, Mo and P, the tissue Se increased with increasing solution Se from 0 to 100 $\mu\text{g L}^{-1}$. Although elevated tissue Se concentrations cause reduction in yield (Soltanpour and Workman, 1980; Mikkelsen et al., 1980a, 1988b; Khattak et al., 1989) under the given experimental condition where 50 and 100 $\mu\text{g Se L}^{-1}$ were added, the tissue Se ranging from 5.34 to 20.4 mg kg^{-1} shoot (Tables 2 and 3) caused no yield reduction. At any given level of Mo and P, 50 and 100 $\mu\text{g As L}^{-1}$ significantly ($P = 0.05$) increased the shoot Se (Table 2). The 4.0 mg P L^{-1} tended to promote tissue Se with significant increase at 100 $\mu\text{g Se L}^{-1}$ and 50 and 100 $\mu\text{g As L}^{-1}$ (Table 2). This suggests the combined effect of P and As on tissue Se uptake. The addition of Mo had no significant effect on tissue Se (Tables 1-3).

Molybdenum

The shoot Mo concentrations increase proportionately with increasing solution Mo (Tables 2 and 3). For a given level of As and P, the Se treatment had no significant effect on shoot Mo (Tables 1-3). However, a significant increase was observed in the shoot Mo concentration with addition of 100 $\mu\text{g Se L}^{-1}$ in combination with 100 $\mu\text{g As L}^{-1}$ and 1.0 mg Mo L^{-1} (Table 2, As x Se x Mo). Since the yield for Se treatments was similar, this increase in Mo concentrations may be related to the interactive effect of As x Se on Mo uptake (Table 1). At 0.01 mg Mo L^{-1} , As treatment showed no effect on shoot Mo, but the 50 $\mu\text{g As L}^{-1}$ showed higher shoot Mo concentrations as compared to 0 and 100 $\mu\text{g As L}^{-1}$ (Table 2). The shoot yield for these treatments happened to be significantly ($P = 0.05$) higher (36.7 g) which explains the relatively higher shoot Mo concentrations.

At given levels of As (As x Mo x P) and Se (Se x Mo x P), 4.0 mg P L^{-1} had no significant effect on shoot Mo at 0.01 mg Mo L^{-1} , but showed a consistent increase in shoot Mo concentration at 1.0 mg Mo L^{-1} (Table 3). This observation is in agreement with the synergistic effect of P on plant Mo uptake as commonly reported (Gupta and Munro, 1969; Singh and Kumar, 1979).

Phosphorus

Phosphorus being a major essential plant nutrient was concentrated in higher amounts as compared with As, Mo and Se (Tables 2 and 3). Because of the high plant demand, up to 2307 and 4641 mg P kg^{-1} shoot was observed at 1.0 and 4.0 mg P L^{-1} , respectively, whereas concentrations of As, Se and Mo reached 2.97, 20.4 and 115.6 mg kg^{-1} shoot, respectively, for 100 $\mu\text{g As L}^{-1}$, 100 $\mu\text{g Se L}^{-1}$ and 1.0 mg Mo L^{-1} treatments. Statistically, As, Mo, As x Se, Mo x P, and Se x Mo x P interactions did show significant effects on shoot P (Table 1).

It can be seen that the 100 $\mu\text{g L}^{-1}$ As and Se caused a significant increase in shoot P at 1.0 mg P L^{-1} (Table 2, As x Se x P) while Se alone showed no effect on shoot P. At any given level of As and Se, 1.0 mg Mo L^{-1} treatment caused significant increase in the shoot P (Table 3) which was also evident from the highly significant F value (49.5***, Table 1).

Since the differences in the yield were nonsignificant the Mo-induced increases in P concentration suggest a synergistic effect of Mo and P uptake.

DISCUSSION AND SUMMARY:

These results showed existence of competitive anionic interactions between As, Se, Mo and P at concentrations closely representing those found in soil solution and in agricultural drainage waters such as found in the western San Joaquin Valley. The data suggested a strong depressing influence of Se and P on the alfalfa shoot As and on the As x Se interactions. The coexistence of these anions in soil solutions may exert strong influence on the uptake and accumulation of one another. As a consequence of such influence it is imperative to understand the overall competition for absorption by the plant and subsequent consumption by foraging animals in terrestrial ecosystems where phosphatic fertilizers are used on soils high in As, Se and Mo.

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Table 1. Summary of the Analysis of Variance.

Source of variation	Element Analyzed (mg kg ⁻¹ shoot)				Shoot yield (g)
	As	Se	Mo	P	
	----- F Ratio -----				
As	597.1***	56.8***	6.28**	4.97**	12.83***
Se	5.58**	185.3***	NS	NS	NS
Mo	16.83**	NS	2031	49.5**	3.65 (NS)
P	246.8***	NS	NS	833***	10.75***
As x Se	4.36*	34.61**	4.84**	2.64*	NS
As x Mo	3.84*	5.22**	10.97***	NS	2.68 (NS)
As x P	52.66***	5.35**	NS	NS	NS
Se x Mo	2.51 (NS)	NS	3.56*	NS	4.07*
Se x P	NS	14.72***	7.03**	3.8*	NS
Mo x P	2.38 (NS)	5.17**	NS	39.7**	NS
As x Se x Mo	2.09 (NS)	NS	4.63**	NS	3.02*
As x Se x P	NS	NS	NS	NS	NS
As x Mo x P	NS	4.69**	NS	2.33 NS	NS
Se x Mo x P	4.08*	3.41*	5.56**	6.32**	NS

*, **, and ***, significant at P = 0.05, 1.01, and 0.001, respectively;
NS = not significant.

Table 2. Alfalfa shoot yield (oven dry weight) and composition as influenced by competitive interactions of [As x Se x Mo] and [As x Se x P] in nutrient solution system.

Nutrient added		$\mu\text{g Se L}^{-1}$					
		0	50	100	0	50	100
As x Se x Mo							
mg As L ⁻¹	mg Mo L ⁻¹	mg As kg ⁻¹			mg Se kg ⁻¹		
2	0.01	0.18 E	0.15 E	0.15 E	-	6.14 F	11.8 D
	1.0	0.15 E	0.09 F	0.08 F	-	6.68 F	12.2 D
50	0.01	1.71 BC	1.44 CD	1.33 D	-	7.20 E	15.3 C
	1.0	1.48 CD	1.26 D	1.21 D	-	7.85 E	17.6 B
100	0.01	2.47 A	2.44 A	2.13 AB	-	8.58 E	18.8 AB
	1.0	2.14 AB	1.98 BC	1.71 BC	-	8.70 E	19.0 AB
mg Mo kg ⁻¹ shoot yield (g)							
2	0.01	10.5 E	9.70 E	8.63 E	33.1	32.4	29.3
	1.0	72.4 D	92.2 BC	82.4 CD	30.9	29.7	32.0
50	0.01	8.8 E	7.75 E	7.05 E	27.7	34.6	34.8
	1.0	103.5 B	102.6 B	92.2 BC	36.7	35.5	33.4
100	0.01	7.3 E	6.56 E	5.98 E	30.0	29.7*	29.8
	1.0	85.3 C	93.01 BC	115.9 A	30.0	30.8*	29.6
As x Se x P							
mg P L ⁻¹	mg As kg ⁻¹			mg Se kg ⁻¹			
2	1.0	0.21 E	0.15 E	0.15 E	-	5.34 G	11.6 D
	4.0	0.12 E	0.09 E	0.07 E	-	7.48 EF	12.4 D
50	1.0	1.93 C	1.86 C	1.84 C	-	6.75 F	15.6 C
	4.0	1.06 D	0.99 DE	0.76 DE	-	8.30 E	17.3 B
100	1.0	2.88 AB	2.70 AB	2.58 B	-	7.22 EF	17.4 B
	4.0	1.64 C	1.64 C	1.26 D	-	8.05 E	20.4 A
mg P kg ⁻¹ Shoot yield (g)							
2	1.0	2129 DEF	1814 EF	1731 F	29.6	30.9	28.5
	4.0	3692 BC	3976 ABC	3741 BC	34.4	31.2	32.8
50	1.0	1869 EF	2307 D	2137 DEF	32.5	33.3	32.0
	4.0	4356 A	3735 BC	3563 C	31.9	36.8	36.2
100	1.0	2194 DE	1990 DEF	2298 DE	29.9	29.5	29.4
	4.0	4038 AB	4027 AB	3985 ABC	30.1	30.9	30.0

† Means followed by different letters within a given interaction are significantly (P = 0.05) different by Duncan's multiple range test.

*Values below the detection limit.

*Mean yield significantly different at P = 0.05.

Table 3. Alfalfa shoot As, Se, Mo and P concentration as affected by competitive interactions of [As x Mo x P] and [Se x Mo x P] in the nutrient solution system.

Nutrient added (mg L ⁻¹)		As x Mo x P			Se x Mo x P		
		2	50	100	0	50	100
P	Mo	mg As kg ⁻¹			mg Se kg ⁻¹		
1.0	0.01	0.19 G	2.03 C	2.97 A	-	6.47 D	15.4 B
4.0		0.12 GH	0.95 F	1.65 D	-	8.15 C	15.4 B
1.0	1.0	0.15 GH	1.72 D	2.52 B	-	6.40 D	14.9 B
4.0		0.07 H	0.92 F	1.37 E	-	7.74 C	17.4 A
----- mg Mo kg ⁻¹ -----							
1.0	.01	9.6 E	7.5 E	5.9 E	7.8 E	7.9 E	7.3 E
4.0		9.6 E	8.3 E	7.3 E	9.9 E	8.1 E	7.2 E
1.0	1.0	81.0 D	92.2 BC	95.0 A	78.2 D	92.0 BC	89.7 C
4.0		83.7 CD	106.7 A	101.0 AB	95.9 ABC	99.9 AB	104.0 A
----- mg P kg ⁻¹ -----							
1.0	.01	1785 D	2057 CD	2243 C	2021 DE	2108 DE	1957 DE
4.0		3374 B	3542 B	3501 B	3403 C	3540 C	3474 C
1.0	1.0	1497 CD	2152 C	2077 CD	1841 E	2175 DE	2209 D
4.0		4218 A	4228 A	4531 A	4641 A	4285 B	4052 B
----- shoot yield (g) -----							
1.0	.01	29.7	34.4	29.8	32.3	32.1	29.6
4.0		33.5	36.3*	29.8	34.3	32.4	33.0
1.0	1.0	29.7	30.8	29.4	29.1	30.4	30.4
4.0		32.1	33.6	30.8	30.0	33.6	32.9

† Means followed by different letters within a given interaction are significantly (P = 0.05) different by Duncan's multiple range test.

*Values below the detection limit.

PROJECT TITLE: SELENIUM AND OTHER TRACE ELEMENT TRANSFORMATIONS AND DISBURSEMENTS IN SOIL/PLANT SYSTEMS AND IN THE FIELD

PROJECT NUMBER: 86-29

DURATION OF FUNDING: July 1986 - June 1989

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ABSTRACT:

Gaseous dimethyl selenide (DMS) was collected from five plant species growing in Panoche fine sandy loam (initial total Se of 576 $\mu\text{g/kg}$) to which selenium was added as sodium selenate in the amount of 500 $\mu\text{g Se/kg}$ soil. In periods ranging from 5 to 7 days the total Se removed from the soil, measured by the Se concentration in plant tissue and DMS collected on charcoal filters, was from 33 to 51% of the Se added. Volatilization accounted for only a small fraction of the Se removed, ranging from 0.5% for alfalfa to 6.1% for *Astragalus bisulcatus*. DMS collected included that coming from the soil, so it is not possible to assess microbial DMS production independently.

KEYWORDS: Selenium, Dimethyl Selenide (DMS), Selenium Volatilization, Selenium Uptake, Selenium Mass Balance, *Astragalus bisulcatus*

PROJECT OBJECTIVES ADDRESSED:

1. To measure the rates of disbursement of soil selenium into plant uptake and gaseous dimethyl selenide (DMS).
2. To explore the feasibility of using different plant species to remove selenium from the soil by plant uptake and volatile DMS production.

RESEARCH PLAN AND PROCEDURES:

A Plexiglas chamber was built to capture volatile selenium from plants growing in 150 mm plastic pots containing 1.55 kg of Panoche fine sandy loam to which 775 μg of selenium was added as sodium selenate (500 $\mu\text{g Se/kg}$ soil). The transparent chamber was 0.6 x 0.6 m in horizontal

cross section and 1 m high, with a sloped roof to funnel rising air warmed inside toward 85 x 85 mm activated carbon filters in a chimney at the top of the chamber. Thermal convection drew air in at the floor of the chamber through four 10-mm diameter filtered inlets.

The chamber was partially shaded during tests to prevent temperatures inside exceeding 35°C. Irradiance and temperature were monitored in and around the chamber with mercury thermometers and a LI-COR LI-190S quantum sensor. During DMS collection periods (3.3 to 6 days), the condensed water which collected on the chamber walls was removed with a plastic blade and analyzed for Se.

The five plants used were: tomato (Better Girl Hybrid), broccoli (Waltham 29 Midseason variety), tall fescue (Olympic), alfalfa (Vernal), *Astragalus bisulcatus* (PI 241039, Utah). The plants were cultured for 10 to 15 weeks during which time they were watered daily with deionized water and fertilized several times with NH_4NO_3 and/or $\text{Ca}(\text{H}_2\text{PO}_4)_2$. Forty hours before beginning DMS collection, dissolved sodium selenate was added to the soil in the amount of 500 μg Se/kg soil. (The Panoche fine sandy loam contained initially a total of 576 μg Se/kg soil.) At 25% gravimetric soil water content, this added Se would result in an initial soil solution concentration of 2 mg/kg Se(VI). Zieve and Peterson (1984) found that barley and *Agrostis tenuis* seedlings began volatilizing measurable amounts of selenium within 10 hours after ^{75}Se application. Lewis et al. (1966) found that although *Astragalus* volatilized selenium within 24 hours after it was applied to the roots, young alfalfa plants took about 1 week to begin volatilizing selenium. Therefore, this experiment would be biased against plants, such as alfalfa, which do not begin volatilizing Se within 40 hours.

At the end of the 3-to-6 day DMS collection period, the test plant was removed, the above-ground tissue harvested, and the leaf area measured with a Delta-T device leaf area meter. The tops were then dried at 67°C, ground in a Wiley mill, and stored for analysis. Leaf tissue from control plants grown in soil without added selenate was treated in the same way.

Volatile Se captured on the activated carbon air filters (Booda Products, 439 S. Detroit St., Los Angeles, CA 90036) was removed by cutting the filters into small pieces and washing with water in a 50 ml syringe. The concentration of Se in the wash water was measured by atomic absorption with hydride generation.

Leaf tissue was analyzed for Se by ICP spectrograph after wet digestion by the method of Carlson (1987).

RESULTS:

The amounts of selenium volatilized from the five plant types growing in the Panoche fine sandy loam to which sodium selenate was added are shown in Table 1. It was not possible to distinguish between volatile selenium produced by soil microbes and that produced by plants; however, differences in net volatilization between plant types were very large. The daily rate of volatilization from *Astragalus* was the highest, both in total amount and on the basis of leaf area per kg of soil. Broccoli had the second highest volatilization rate. On a leaf area basis the broccoli volatilization rate was 17% that of *Astragalus*, and tomato, fescue, and alfalfa

rates were 5.8%, 3.3%, and 2.6%, respectively, of the *Astragalus* rate. When volatilization rates per kilogram of soil are compared, the ranking of plant types is the same, but the differences are not as large (Table 1).

Table 1. Selenium volatilization from plants growing in Panoche fine sandy loam with added sodium selenate.

Plant type	Age	Selenium volatilized	Leaf area	Dry weight	Time	Rate	
	weeks	ng Se	cm ²	g	days	μg Se/m ² /d	μg Se/kg soil/d
Tomato	10	2772	2050	20.7	3.3	4.0	0.54
Broccoli	11	8610	1460	16.8	5	11.8	1.11
Tall fescue	12	2263	1994	21.0	5	2.3	0.29
Alfalfa	13	1656	1747	14.3	5	1.8	0.214
<i>Astragalus</i>	15	15687	372	3.0	6	69	1.69

Selenium was not detected in the water condensed on the interior walls of the plant chamber.

The plants differed in their ability to extract "native" and added selenium from the soil (Table 2). *Astragalus* and broccoli had the highest tissue Se concentrations and had the highest volatilization rates. Although selenium tissue concentration of alfalfa was almost equal to that of broccoli, the rate of volatilization from alfalfa was only 15% of that from broccoli. During the single week following the application of sodium selenate, plant tissue concentrations of Se reached levels more than 100 times those of plants growing 10 to 15 weeks in the unamended soil, even though the latter contained a total amount of selenium slightly exceeding the amount of Se(IV) added (576 vs. 500 μg/kg).

Table 2. Leaf tissue selenium concentration and volatilization rate.

Plant type	Leaf tissue selenium concentration		Leaf area selenium volatilization rate
	"native" Se	Se(VI) added	
	ng Se/g leaf tissue		ng Se/m ² /d
Tomato	105 ± 145*	16,600	4,000
Broccoli	207 ± 166	22,300	11,800
Tall fescue	50 ± 9	11,700	2,300
Alfalfa	108 ± 8	22,100	1,800
<i>Astragalus</i>	720 ± 44	80,600	69,000

*Standard deviation is included because it is large for some of these low values.

The amounts of selenium removed from the Se(VI) amended soil by volatilization and by plant uptake are shown in Table 3. The removal of selenium from unamended soil was negligible compared to these values. From 33 to 51% of the added Se(VI) was removed by the two pathways over the few days from Se(VI) addition to plant harvest. The ranking in order of highest selenium removal was broccoli, tomato, alfalfa, *Astragalus*, and tall fescue. Plant uptake was the dominant pathway accounting for from 99.5% (alfalfa) to 93.9% (*Astragalus*) of the selenium removed.

Table 3. Removal of added Se(VI) from soil by uptake and volatilization during the tests.*

Plant type	Selenium uptake [†]	Selenium volatilized	Selenium removed from soil	Percentage of added Se(VI) removed	Percentage removed by volatilization
	µg Se	µg Se	µg Se		
Tomato	343	2.8	346	46	0.8
Broccoli	374	8.6	383	51	2.2
Tall fescue	245	2.8	248	33	0.9
Alfalfa	315	1.6	317	42	0.5
<i>Astragalus</i>	241	15.7	257	34	6.1
Totals/ means	1,521	31.0	1,552	41	2

*Uptake, 5-7 days; volatilization, 3-6 days.

[†]Leaf tissue concentration x dry weight of plant top.

DISCUSSION AND SUMMARY:

Selenium volatilization rates from plant and soil confined in a closed transparent chamber varied greatly among 5 plant species over 3-to-6 day collection periods. *Astragalus bisulcatus* and broccoli showed the highest rates of volatilization. Although it was not possible to separate plant and soil microbial volatilization, the large differences between plant species suggest the dominance of plant volatilization.

Se(VI) added as sodium selenate was rapidly taken up by all 5 plant types to the extent that plant uptake dominated Se removal from the soil. Volatilization accounted for only 0.5% (alfalfa) to 6.1% (*Astragalus bisulcatus*) of the selenium lost from the soil. Although *Astragalus* had the highest leaf selenium concentration and selenium volatilization rates, it ranked fourth behind broccoli, tomato, and alfalfa in order of selenium removal because of its small biomass at 15 weeks.

Alfalfa accumulated 22.1 µg Se/g plant tissue from the Se(VI) amended soil, a concentration exceeded only by *Astragalus* (80.6) and broccoli (22.3). However, alfalfa had the lowest net volatilization rate of the 5 plant types. Lewis et al. (1966) reported that young alfalfa plants required about 1 week to begin volatilizing selenium applied to the roots, whereas *Astragalus* began to volatilize selenium within 24 hours of application. It is possible that in these tests

alfalfa had not had time to develop its full capacity for volatilization and selenium was accumulating in the leaves. It is also possible that alfalfa plants had a greater tendency than the other plants to absorb DMS released by soil microorganisms.

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PROJECT TITLE: A STUDY OF THE EFFECTS OF CHLORIDE AND SULFATE SALINITY ON SELENIUM ACCUMULATION BY Se AND SALT TOLERANT GENOTYPES OF FORAGE AS WELL AS NATIVE HALOPHYTE GRASS SPECIES.

PROJECT NUMBER: 88-1

DURATION OF FUNDING: July 1988 - June 1990

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ABSTRACT:

Greenhouse and field experiments were conducted to examine the effects of chloride and sulfate salt on Se accumulation in 'Olympic', 'Falcon', and 'Alta' tall fescue cultivars. Both the greenhouse and field studies showed that sulfate salt significantly reduced the phytotoxicity and inhibited Se uptake by the plants. Chloride salt concentrations slightly enhanced the Se uptake. Field study showed that tall fescue cultivation considerably reduced soil Se concentration in the top 15 cm of soil. No apparent difference in tissue Se concentration among the three cultivars was detected when the plants were grown under field conditions. However, the field experiment showed that the cultivar which produced greater amount of biomass had greater amount of total Se accumulation.

KEYWORDS: Chloride, Salinity, Selenium accumulation, Sulfate, Tall fescue

PROJECT OBJECTIVES ADDRESSED:

The objective of this study is to examine how different chloride and sulfate salinity affect the Se uptake and Se accumulation by forage and turfgrass. Information obtained through this research may be useful for water and land management in soils contaminated by Se and salinity.

RESEARCH PLAN, PROCEDURES, RESULTS AND DISCUSSION:

Greenhouse studies

For the study of the effects of chloride or sulfate salt on Se uptake from nutrient solution culture, 'Olympic' tall fescue cultivar was used. Twenty tall fescue seeds were sown on an 8 cm

diameter fiberglass sheet and a stretched nylon mesh supported by a styrofoam frame. The whole apparatus floated in a 2 liter plastic container of 1/4 Hoagland nutrient solution. Each salt treatment combination was replicated three times. The containers were kept in a temperature controlled greenhouse at 21°C day and 18°C night with an average sunlight of 315 $\mu\text{mol photon m}^{-1}\text{s}^{-1}$.

For sulfate and chloride salt treatment, 0, 20, 40 and 60 meq $\cdot \text{Na}_2\text{SO}_4$ and NaCl were used. The combinations of the salt concentrations are presented in Table 1. Except for the control treatment, 3 ppm Se was added into the culture solution of all the salt combinations. The culture solutions were replaced every four days and aerated with compressed air.

After two weeks, the plants in each container were thinned to five plants. At the end of the fifth week, the plants were harvested, and the root and shoot dry weights were measured.

For Se accumulation measurement, plants were separated into root and shoot tissues and were dried at 60°C for 72 hours. Five ml of concentrated HNO_3 , and 2.5 ml of HClO_4 were added to 25 g of dry plant material in a 75 ml volumetric digestion tube and allowed to digest overnight at room temperature. Further tissue digestion and Se oxidation to Se (IV) were conducted at 150 to 120°C on a heating block. After cooling, the pH of the samples was adjusted to 1.0 to 1.1 with 1.2 M HCl. Selenium was determined using hydride generation-flame atomic absorption (Perkin-Elmer) with heated quartz cell, utilizing argon as the carrier gas.

Table 1 shows that the NaCl concentrations slightly enhanced Se accumulation in both shoot and root tissues. However, the Se uptake was markedly inhibited by sodium sulfate. For example, the shoot tissue Se concentration was reduced from about 1,000 ppm under conditions without the presence of sodium sulfate to only about 30 ppm in the presence of 20 meq sulfate. The tissue Se concentration was further reduced with the increase of sulfate up to 60 meq. Se uptake was severely inhibited by the presence of sodium sulfate, regardless of the NaCl concentration in the culture solution. Root tissue had less Se accumulation than shoot tissue and selenium uptake by the roots was also inhibited by the presence of sulfate.

Plant dry weight production exhibited a negative correlation with the tissue Se concentration of both the shoot and root tissues. In the presence of 20 meq sodium sulfate, 2 ppm Se did not show significant growth inhibition. The dry weight of both shoot and root tissue was slightly reduced by the presence of 60 meq sodium sulfate. The dry weight reduction was probably due to the increase of salinity in the culture solution rather than the increase of sulfate concentration.

Field experiment

For field studies, three tall fescue cultivars ('Olympic', 'Falcon', and 'Alta') were seeded in October, 1987 with a seeding rate of 10 g/m² at the West Side Field Station. A randomized block design was used. Each block contained four 1.3 x 1.3 m² plots. The three cultivars as well as a bare plot were randomly assigned to each of the four plots of each block. Two duplicate blocks were either irrigated with high salinity (EC = 6.3 mmhos, 80 ppb Se and 2816 ppm sulfate), or irrigated with low salinity water (EC = 1.6 mmhos, 9 ppb Se and 681 ppm sulfate). The Se and sulfate concentrations of the background field soil are negligible (Table 2). The field plots were irrigated once a week through

the growing season. Additional 0.2 ppm Se was added into both the high and low salinity irrigation water, twice in March, April, May and June and once in July 1988. Approximately 390 l of water was used for each block per irrigation. The plants were harvested during the third week of July. Plant biomass and tissue Se concentration were measured. Soil samples were collected from the plots of Olympic tall fescue cultivar as well as the bare soil plots at five soil depths (Table 3). The soil pH, EC, sulfate and Se concentration were measured. For sulfate analysis, the Barium Sulfate Turbidimetric Method was used.

Table 3 shows that tall fescue produced slightly greater amount of dry weight under high salinity water irrigation than the plants that were irrigated with low salinity water. Plants irrigated with low salinity water had tissue Se concentration of about 5 $\mu\text{g/g}$, but those plants irrigated with high salinity water had only about 3 $\mu\text{g/g}$ Se, even though the high salinity water had higher Se concentration than did the low salinity irrigation water. No apparent difference was found in tissue Se concentration among the three tall fescue cultivars. The 'Alta' cultivar produced a greater amount of biomass than did the 'Olympic' and 'Falcon' cultivars. The 'Alta' cultivar had a greater amount of total Se uptake, 13 mgM^{-2} and 33 mgM^{-2} , than the 'Olympic' and 'Falcon' cultivars of 10 mgM^{-2} and 25 mgM^{-2} respectively.

Table 4 presents the results of soil analysis for the field soils. For the top 15 cm of soil, high salinity irrigated plots had 10 times more Se concentration than the low salinity irrigated plots. Bare plots had about three times more soil Se concentration than the soils of the tall fescue grown plots.

Along the soil profile, the Se concentration decreases with the increase of the soil depth. The highest Se concentration was in the top 15 cm of soil. Bare plots had higher Se concentration than the tall fescue grown plots. Overall, the high salinity irrigated field plots had higher soil Se than the field plots irrigated with low salinity water.

Several conclusions may be drawn from the present studies:

1. Chloride salt slightly enhanced Se accumulation by tall fescue, but sulfate salt inhibited Se uptake.
2. The biomass production of the plants was found to be negatively correlated with the tissue Se concentration.
3. No apparent difference in tissue Se concentration of field grown plants was detected among the three cultivars.
4. The amount of total Se uptake was associated with the ability of biomass production of the cultivar under Se stress.
5. The highest soil Se concentration was found in the top 15 cm of soil, and two thirds of the soil Se was removed by tall fescue cultivation. Soil Se concentrations below 15 cm depth were similar between the bare plots and the tall fescue field plots.

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Table 1. Dry weight production and selenium accumulation of tall fescue grown in nutrient solution culture supplemented with 3 ppm Se and different concentrations of NaCl and Na₂SO₄.

Combination of salt concentrations (meq) in culture solution	Dry weight (mg/5 plants)		Se concentration (µg/g)	
	Shoot (% Control)	Root (% Control)	Shoot	Root
NaCl - Na ₂ SO ₄				
control	2067 (100)	462 (100)	1.0	0.5
0 - 0	513 (25)	80 (17)	1064.9	499.0
20 - 0	404 (19)	78 (16)	1133.1	610.7
40 - 0	375 (18)	62 (13)	1182.2	691.4
60 - 0	354 (17)	60 (12)	1212.0	670.4
0 - 20	1776 (90)	380 (90)	26.2	20.3
0 - 40	1528 (84)	365 (80)	19.6	13.0
0 - 60	1434 (68)	345 (74)	13.8	10.7
20 - 60	1233 (59)	306 (66)	13.7	9.8
60 - 20	965 (47)	279 (60)	25.3	17.6

Table 2. Chemical analysis of background field soil and irrigation water used for the Se uptake experiment at the West Side Field Station.

	EC (mmhos)	pH	Sulfate (ppm)	Selenate (ppb)	Selenite (ppb)
Soil Depth (cm)					
0 - 15	1.6	8.0	0.4	-	-
15 - 30	0.9	8.2	0.3	-	-
30 - 60	1.0	8.5	0.4	-	-
60 - 90	1.3	8.3	0.4	-	-
90 - 120	1.5	8.3	0.4	-	-
High salinity irrigation water	6.3	7.9	2816	50.0	0.18
Low salinity irrigation water	1.6	7.9	681	8.8	-

Table 3. Biomass production, tissue selenium concentration and total selenium uptake of tall fescue grown under field conditions irrigated with high or low saline waters.

	Low salinity water irrigation			High salinity water irrigation		
	Biomass kg/m ²	Tissue Se µg/g	Total Se uptake mg/m ²	Biomass kg/m ²	Tissue Se µg/g	Total Se uptake mg/m ²
Olympic	4.8 ± 0.7	5.05 ± 1.0	24.2 ± 3.4	5.32 ± 0.11	1.83 ± 1.0	9.7 ± 3.1
Falcon	5.0 ± 1.0	4.98 ± 0.9	24.9 ± 5.2	5.66 ± 0.15	1.70 ± 0.9	9.6 ± 2.0
Alta	6.6 ± 1.7	5.00 ± 1.0	33.0 ± 4.0	8.06 ± 1.53	1.65 ± 0.3	13.2 ± 2.0

Table 4. Soil analysis for the field plot soils irrigated with high or low salinity water.

Soil Depth (cm)	Parameters	Low salinity irrigation		High salinity irrigation	
		Bare plot	Tall fescue plot	Bare plot	Tall fescue plot
0-15	Selenite (ppm)	5.5	1.9	52.3	20.4
	Selenate (ppm)	4.5	2.9	41.3	15.5
	Sulfate (mg/g)	0.14	0.12	19.6	9.5
	EC (mmhom/cm)	1.10	1.25	11.8	15.1
	pH	8.0	7.9	8.2	8.0
15-30	Selenite	0.8	1.3	12.9	16.8
	Selenate	0.3	0.03	21.7	19.0
	Sulfate	0.2	0.2	6.4	7.2
	EC	1.2	1.3	10.3	12.8
	pH	8.1	8.1	8.2	8.2
30-60	Selenite	0.2	1.0	8.4	14.3
	Selenate	0.2	0.1	13.9	18.6
	Sulfate	0.2	0.3	3.1	3.4
	EC	1.1	1.5	6.3	5.9
	pH	8.3	8.2	8.3	8.0
60-90	Selenite	0.2	-	10.8	0.2
	Selenate	0.4	0.4	9.8	12.5
	Sulfate	0.2	1.8	2.1	12.1
	EC	1.4	0.4	4.2	4.6
	pH	8.3	8.3	8.4	8.3
90-120	Selenite	-	-	0.2	0.2
	Selenate	0.4	0.4	0.9	14.5
	Sulfate	0.5	2.3	2.4	1.0
	EC	2.1	0.3	1.9	3.3
	pH	8.3	8.3	8.4	8.4

SALINITY, SELENIUM, DRAINAGE AND IRRIGATION MANAGEMENT OPTIONS

PROJECT TITLE: SALINE DRAINAGE WATER REUSE IN THE SAN JOAQUIN VALLEY

PROJECT NUMBER: 86-20

DURATION OF FUNDING: July 1986 - June 1989

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ABSTRACT:

The purpose of this paper is to evaluate the potential for reuse of saline water for irrigation as a partial solution to the disposal of saline drainage water. Strong evidence exists that saline drainage water at levels up to 3000 mg/L TDS (4.7 dS/m) can be used for irrigation of salt tolerant crops as long as some leaching occurs through preplant irrigations with good quality water. Our research indicates that drainage water as high as 4500 mg/L TDS (7 dS/m) can be used for irrigation of cotton for at least 3 years as long as preplant irrigations with good quality water are used. We now have completed four years of application of saline drain waters and have observed a significant reduction in yield of seed cotton and lint at all levels of salinity above 400 mg/l TDS. There was no harvestable seed cotton at 6000 and 9000 mg/l TDS treatment levels. A similar reduction in yield is apparent in the safflower crop planted this last winter '88, however, it appears a crop has been established and some yield will be attained, even at the highest levels of salinity in the applied drain water. The primary effect on the cotton crop has been on stand establishment. The presence of Na in the irrigation water has caused a dispersal of soil particles when good quality water is

applied which results in a very dense soil structure that inhibits seed germination and emergence. Continued use of saline drain water will require intensive management of the soil with focus on seed bed preparation.

KEYWORDS: Soil salinity, drainage, crop salt tolerance, irrigation, cotton, safflower.

PROJECT OBJECTIVES ADDRESSED:

Growers in the San Joaquin Valley are considering reuse of subsurface drainage water irrigation of crops as a means of decreasing the volume of drainage water which must be discharged in regional drainage networks or pumped to evaporative sinks. Reuse of drainage water would also decrease the need for imported irrigation water. The purpose of this research is to evaluate the effect of drainage waters of varying salinity levels applied as irrigation on the growth response and yield of crop grown in a typical cropping rotation and on soil physical and chemical properties. The information generated by this research will eventually benefit growers, irrigation and drainage district managers, and water resource planners.

Specific objectives are:

1. To evaluate the effect of drainage waters of varying salinity levels applied as irrigation water on the growth response and yield of crops grown in a typical cropping rotation.
 - a. To determine the effects of differential salinity on biomass and mineral nutrient partitioning in cotton and safflower in relation to crop growth and development, and to evaluate the effects of spatial and temporal variability in soil salinity on growth and yield of crops.
2. To evaluate the effect of drainage water of varying salinity levels applied as irrigation water on the spatial and temporal distribution of physical and chemical soil characteristics.

RESEARCH PLAN AND PROCEDURES:

Methodology

1. Description of Field Site

The field site consists of 10.5 ha of land on the El Rico Ranch of J. G. Boswell Co. near Corcoran, California in the Tulare Lake Basin. The soil type is Tulare clay. The main site consisting of 8-ha of land was divided into 24 separate plots. The experimental treatments consisted of irrigating with water of six different salinity levels each replicated four times. The six salinity levels used for irrigation were approximately 1, 2, 5, 7, 9, and 12 dS/M (400, 1500, 3000, 4500, 6000, and 9000 ppm, respectively). All plots received a pre-irrigation with the water of the lowest salinity. The test crop for 1984, 1985, 1987 and 1988 was cotton and for 1986 and 1989 safflower. A smaller area of the field was divided into 16 plots for studies on wheat, barley, and tomatoes in order to identify cultivars with greater tolerance to salinity. The safflower crops were grown only with a pre-irrigation of 400 ppm water. The crop was planted into the plots that had been previously irrigated with varying levels of saline drain water.

2. Soil Salinity Measurements

Prior to initiation of the salinity treatments, the soil was sampled at 60 locations at five depths in order to characterize the initial physical and chemical soil characteristics of the site.

The samples have been analyzed for pH, EC, Ca, Mg, Na, K, Cl, CO₃, HCO₃, and moisture content of a saturated paste. Of these 360 locations, 72 are compared with samples taken from similar transects of 72 locations after harvest of the cotton in 1985 and after planting of the cotton in 1987. The results of soil analyses from previous cropping years were published in earlier reports.

Soil samples were collected in November 1988 on a transect from north to south located centrally between the two tile drains. The borings were spaced 17 feet apart with 3 borings falling in each replication of each irrigation water treatment for a total of 12 locations per water treatment and 72 borings overall.

Table 1. Mean values of the constituents in the saturation extract of soil samples from plots irrigated with different water salinities. Samples were taken in November 1988 at 0-15 cm depth.

Treat (ppm)	SW %	EC mmhos/cm	pH	Ca meq/l	Mg meq/l	Na meq/l	K meq/l	Cl meq/l	SO ₄ meq/l	NO ₃ ppm	B	SAR
Mean												
400	59.7	1.46	8.70	2.12	2.02	8.45	1.08	4.09	3.65	0.25	0.41	5.87
1500	61.8	3.82	8.63	4.97	4.12	31.11	1.30	14.18	26.25	0.85	0.68	14.59
3000	65.5	6.49	8.69	8.82	6.29	64.98	1.37	22.88	48.69	4.71	1.12	23.64
4500	66.2	9.10	8.82	10.00	7.53	110.35	1.44	35.54	68.98	2.23	1.88	37.27
6000	68.9	10.63	8.78	9.50	6.40	119.65	1.30	52.20	72.12	3.89	2.07	42.44
9000	69.5	15.24	8.75	13.16	8.50	186.09	1.51	75.12	113.62	4.99	3.19	56.55
S.D.												
400	1.4	0.40	0.22	0.60	0.76	3.05	0.21	2.39	2.31	0.16	0.14	
1500	1.7	0.59	0.23	1.83	1.11	6.50	0.15	5.25	8.95	0.42	0.31	
3000	1.8	1.09	0.11	3.84	2.14	14.29	0.27	6.58	11.31	10.75	0.46	
4500	2.3	1.20	0.15	2.42	1.61	18.99	0.14	7.53	14.01	0.47	0.45	
6000	1.0	2.09	0.15	3.63	1.68	23.60	0.21	13.62	16.71	1.41	0.78	
9000	2.7	2.15	0.10	2.14	1.36	33.77	0.14	15.01	14.48	0.97	0.62	
C.V.												
400	0.02	0.27	0.03	0.28	0.38	0.36	0.19	0.58	0.63	0.64	0.34	
1500	0.03	0.15	0.03	0.37	0.27	0.21	0.12	0.37	0.34	0.49	0.46	
3000	0.03	0.17	0.01	0.44	0.34	0.22	0.20	0.29	0.23	2.28	0.41	
4500	0.03	0.13	0.02	0.24	0.21	0.15	0.10	0.21	0.20	0.21	0.24	
6000	0.01	0.20	0.02	0.38	0.26	0.20	0.16	0.26	0.23	0.36	0.38	
9000	0.04	0.14	0.01	0.16	0.16	0.18	0.09	0.20	0.13	0.19	0.19	

Analyses of the saturation extract of the 0-15- cm depth are reported in Table 1 as mean values with standard deviation and CV. The electrical conductivity (EC) and sodium adsorption ration (SAR) for the 6 water treatments are presented in Figures 1 and 2, respectively.

The high salinity and SAR achieved with the waters of 4500-9000 ppm are clearly in a range where response of some crops to salinity will be affected and the effects may become evident at lower water salinities with time. The SAR levels would appear to be adversely high in all but the two lowest water salinities particularly for germination and emergence of plants.

The adverse physical condition was most evident after heavy rainfall occurred last year in the spring leading to soil dispersion in the presence of high exchangeable sodium and reducing salinity. It is evident the range of water salinities selected has produced a range of soil salinities and sodium which demonstrate some of the problems involved in the reuse of drainage water.

Growth and Development of Cotton

The results presented in the following section do not include cotton irrigated with 6000 and

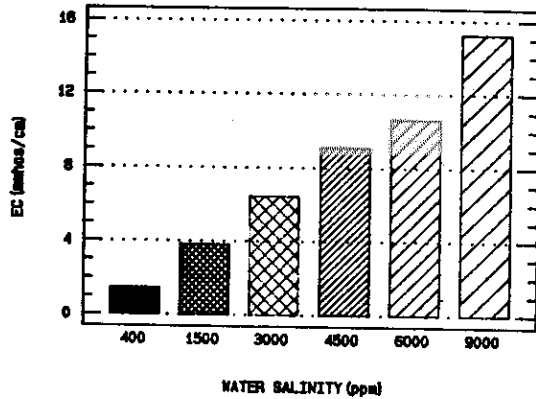


Figure 1. Mean electrical conductivity (EC) of saturation extracts from the 0-15 cm depth according to water salinity.

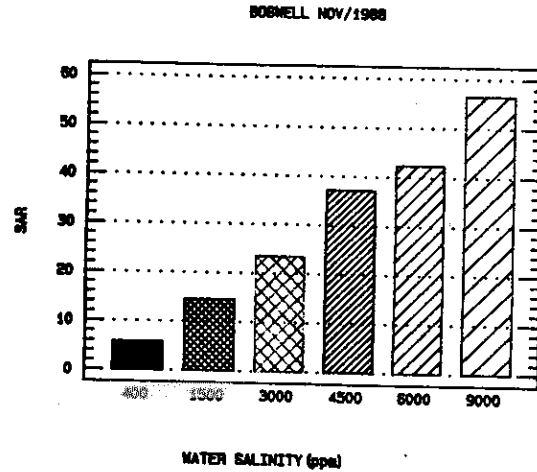


Figure 2. Mean Sodium Adsorption Ratio (SAR) of saturation extracts of soil samples from the 0-15 cm depth.

9000 mg/l saline drain water since we were unable to establish a crop on those plots.

Development of the 1988 cotton crop was delayed 20 days or more when plants were irrigated with saline drain water. A similar observation was made in 1987. Approximately 100 days after seeding the 1988 crop plants irrigated with 400 ppm water had accumulated 7 times more shoot biomass than the plants irrigated with 4500 ppm drainage water (see Figure 3). After 100 days of growth the shoots irrigated with 4500 ppm water were 1/3 the length of shoots irrigated with good quality water (Figure 4). A similar effect was observed with root biomass and root length.

Fig. 3. Effect of salinity on cotton biomass accumulation as a function of time after planting.

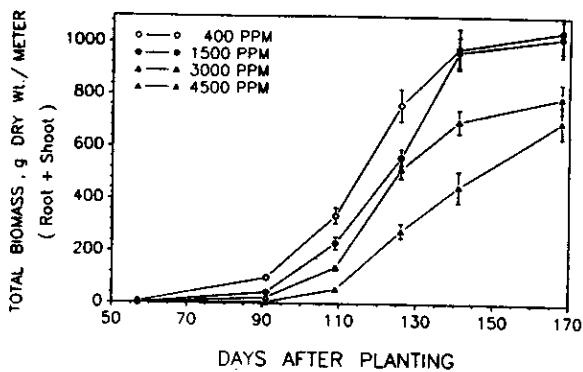
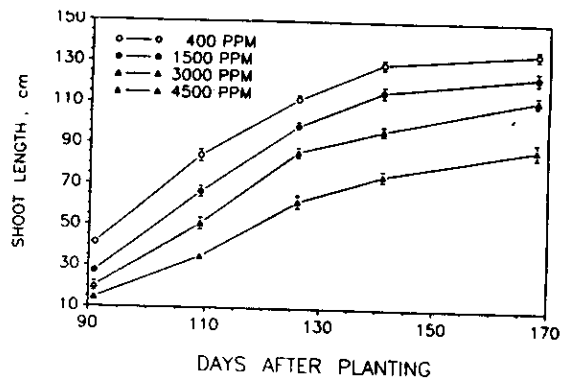
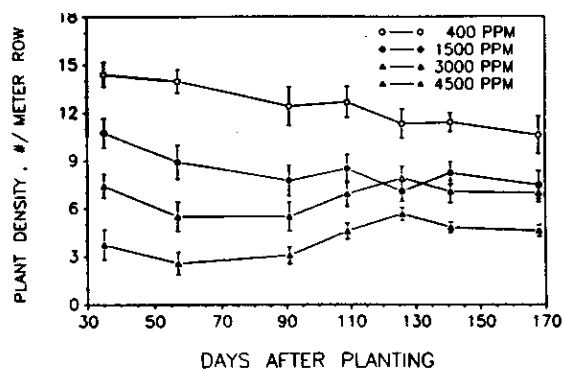


Fig. 4. Effect of salinity on shoot length of cotton plotted as a function of time after planting.



The reduction in plant biomass and subsequently cotton seed and lint yield are directly correlated with plant density. As detailed in figure 5 the number of plants per meter row is substantially reduced with increasing levels of salinity in the irrigation water. With time there is a slight increase in plant density at the higher levels of salinity. This could result from late germination, a common observation in the saline treatments.

Fig. 5. Plant density of cotton exposed to salinity.



The development of flowers and squares show a differential response to salinity. The effect of salinity on delaying biomass is reflected in flower and square formation. It appears that these two processes level off and then decrease approximately 15 days earlier for the plants irrigated with 400 mg/l water as compared to plants irrigated with 1500, 3000 and 4500 mg/l water (Figures 6 and 7).

Fig. 6. Square formation of cotton exposed to various levels of salinity.

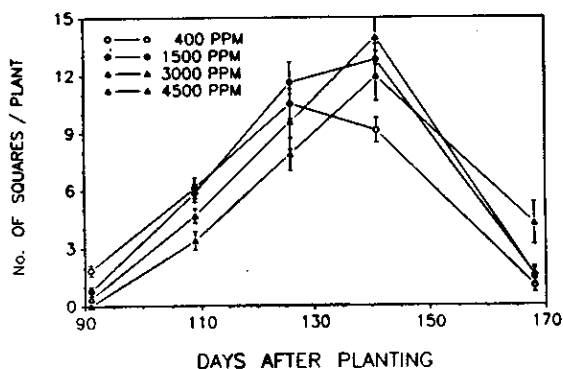
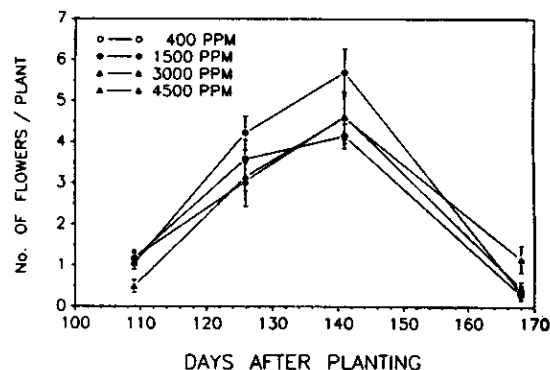


Fig. 7. Effect of salinity on flower formation.



At the onset of boll development the numbers of bolls per plant appears to be delayed in response to salinity (Figure 8). As the boll set proceeds there is very little treatment effect between 110-150 days after planting. Towards the end of the boll development period the number of bolls per plant show a divergence in response to treatment.

The yield data presented in Table 2 are from 1987 and 1988. The comparison of these two years illustrates the dramatic effect one additional year of irrigating with saline drain water has on crop yields. Not only did we fail to establish a stand on the plots irrigated with 6000 and 9000 ppm water but a significant reduction in yield was observed with the use of all irrigation waters

Fig. 8. Number of bolls produced by cotton plants exposed to salinity.

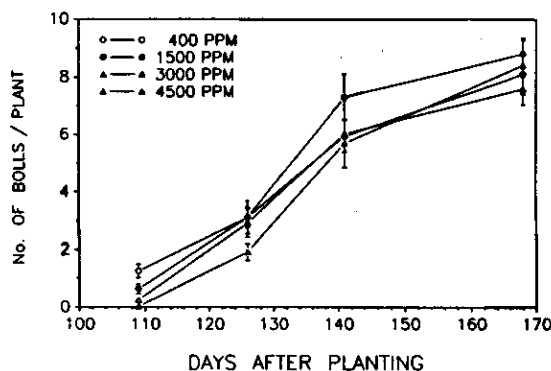


Table 2. Cotton lint yield as affected by salinity levels of irrigation water.

Salinity, ppm	1987 yield, lbs/ac	% Control	1988 yield, lbs/ac	% Control
400	900 ± 30	100	948 ± 36	100
1500	900 ± 29	100	800 ± 36	84
3000	859 ± 11	95	652 ± 31	69
4500	1101 ± 9	122	352 ± 31	37
6000	869 ± 45	97	--	
9000	639 ± 20	71		

with salinity greater than the control. In 1987 the only significant effect on lint yield was observed at the highest level of salinity (9000 ppm). The magnitude of the yield response in 1988 is complicated by a significant rain that occurred within a few days after planting. The effect was to disperse the soil and create a hard crust on the soil surface. The severity of this crusting was directly related to the level of salinity in the irrigation waters previously applied to these plots which resulted in a decreasing emergence of the cotton seedlings.

Lint Quality

The quality of cotton lint is affected by environment. One of the potential effects of salinity is to disrupt potassium nutrition, and since potassium appears to affect lint quality this parameter was evaluated (Bennett et al., 1965).

Lint harvested from the last two years (1987, 1988) was evaluated for quality factors. Fiber strength was found to show a small decrease with increasing salinity. The main difference, however, was between years and not within treatments (Figure 9). In contrast micronaire, a measure of

fineness of the fiber increased with salinity (Figure 10). The difference in micronaire was also maintained between the two sampling years. The overall effect of increasing salinity on fiber quality is inconsistent and there appears to be no specific change in response to increasing salinity of irrigation water.

Fig. 9. Effect of irrigation water salinity on cotton fiber strength.

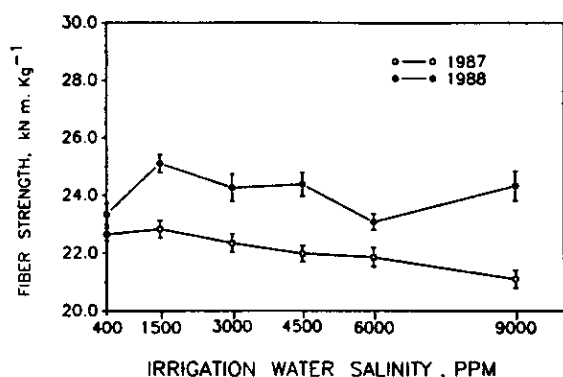
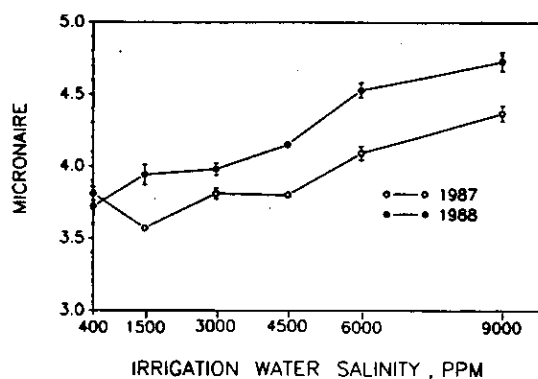


Fig. 10. Effect of irrigation water salinity on micronaire of cotton fiber.



The cation content of lint was determined for both the 1987 and 1988 crop. There were no significant effects of salinity on the cation content of fiber grown in the treated plots. This would support the observation that salinity, which could upset mineral nutrition of cotton fiber had only minor effects on lint quality (Table 3).

Table 3. Cation content of lint, mg/g dry wt.

Treatment, ppm	1987			1988		
	Na	K	Ca	Na	K	Ca
400	0.21	4.05	0.87	0.29	4.21	0.65
1500	0.48	3.64	0.89	0.42	4.08	0.88
3000	0.56	3.71	1.01	0.56	3.92	0.55
4500	0.30	3.67	0.92	0.25	3.97	0.67
6000	0.32	3.53	0.96	0.35	4.33	0.67
9000	0.37	3.61	1.05	0.37	3.89	0.75

Increasing salinity did have minor effects on cation content of cotton seed (Table 4). There appeared to be a decrease in seed potassium at the highest level of salinity, however, there was substantial variability in the results and no firm conclusions can be drawn. Measurement of oil quality of seed harvested from the plots was not affected by the level of salinity in the irrigation water.

Table 4. Cation content of seed, mg/g dry wt.

Treatment, ppm	1987			1988		
	Na	K	Ca	Na	K	Ca
400	0.32	5.78	1.50	0.20	6.37	0.90
1500	0.62	6.79	1.33	0.30	7.66	0.95
3000	0.20	8.79	1.30	0.47	6.70	0.89
4500	0.25	7.61	1.12	0.19	4.67	1.15
6000	0.86	5.88	1.38	0.56	5.87	1.23
9000	0.40	4.22	1.14	0.22	3.11	1.10

Ion Content of Cotton Tissue

Anions--The anion content of cotton blades and petioles was determined over the growing season on tissue from plants irrigated with 4 levels of saline drain water. Plants treated with the two highest levels of salinity were not sampled.

Chloride content of leaf petioles showed a response to treatment over the season. The Cl content of the irrigation water increases 35 times from the lowest to the highest salinity treatment. In the blades the Cl content of tissue sampled 60 days after planting was proportional to the level of Cl in the irrigation water (Figure 11). As the season progressed and with subsequent irrigations the Cl content decreased and treatment differences were reduced to a minimum. The reduction in Cl concentration in the blade tissue was possibly due to growth dilution as the plants increased in biomass. In contrast the Cl content in the petioles increased with time and the increase was proportional to the level of Cl in the irrigation water (Figure 12). The differences in Cl content between the petioles and the blades could be the result of an exclusion process. The

Fig. 11. Chloride content of leaf blades of cotton as a function of time and salinity level of irrigation water.

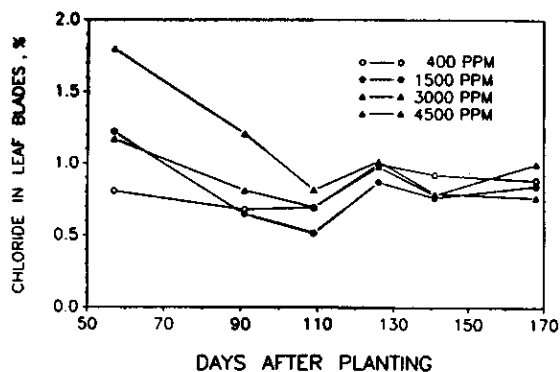
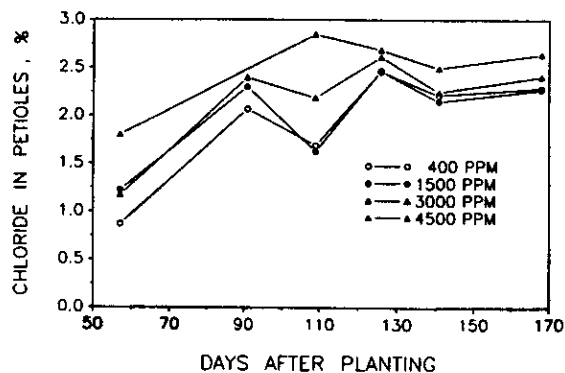


Fig. 12. Chloride content of cotton petioles as a function of time and salinity level of irrigation water.



petioles were shown to increase in Cl concentration and this could effectively reduce the amount of Cl translocated to the blade.

Nitrate concentrations were determined in cotton blades and petioles of plants irrigated with varying levels of saline drain water (Figure 13 and 14). Nitrate levels in petioles later in the season generally increased with salinity levels. The increase in NO_3 in the tissues is in response to an increase in NO_3 in the drain water and to reduced growth. Petioles also store NO_3 to be exported to the blades later. In cotton blades NO_3 declines over the growing season. This could be the result of growth dilution and depletion of NO_3 in the root environment.

Fig. 13. Nitrate content of cotton leaf blades as a function of time and salinity level of irrigation water.

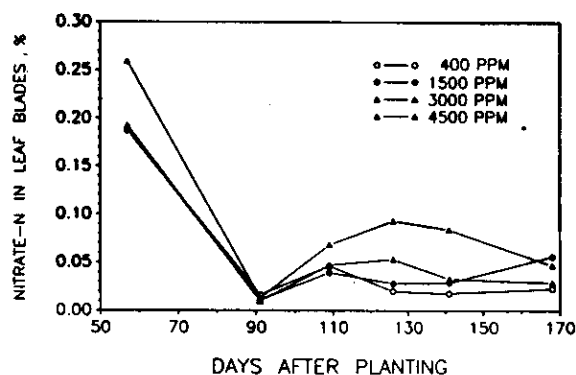
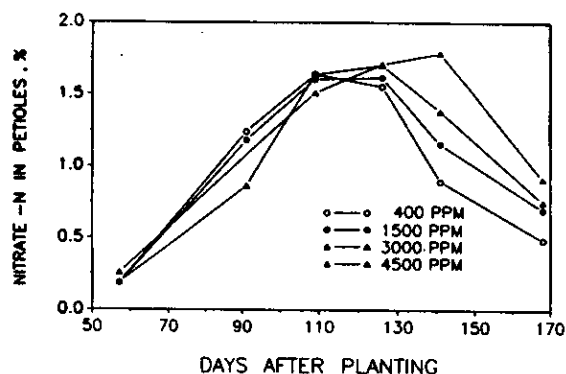


Fig. 14. Nitrate content of cotton petioles as a function of time and salinity level of irrigation waters.



Cations--The cations of primary interest were Na and K. Sodium was a dominant cation in the saline drain water increasing 25 times from the lowest to the highest saline treatment. Potassium concentrations in contrast did not change in the irrigation water over the entire range of saline additions.

Potassium in the cotton blades did not show a treatment effect, however, the concentration declined over the season, possibly as a result of growth dilution (Figure 15). The K concentrations in the petioles were significantly higher than in the blades and showed a small but progressive decline in concentrations over the season (Figure 16). In contrast to last year's data the petioles appear not to accumulate and do not appear to be involved in regulating the content of K for the blade.

Fig. 15. Potassium content of cotton leaf blades as a function of time and salinity level of irrigation water.

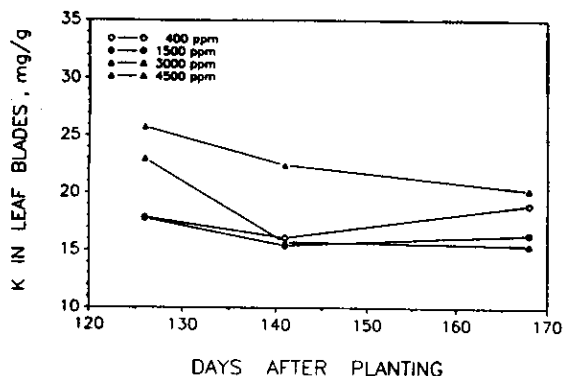
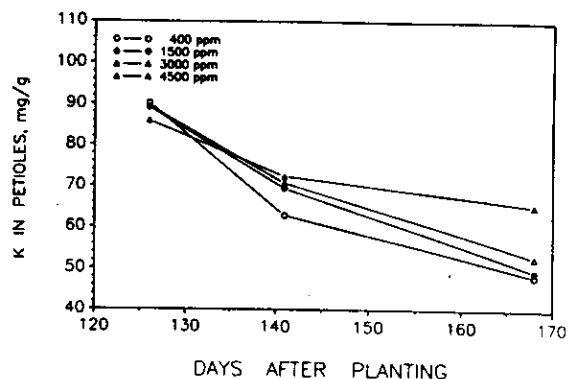


Fig. 16. Potassium content of cotton petioles as a function of time and salinity level of irrigation water.



Sodium concentrations in petioles and blades show similar responses to the salinity treatments. As salinity levels in the irrigation water increase so do the Na levels in these two tissues. The highest Na concentration in the tissue is found at the highest salinity treatment (Figure 17 and 18).

Fig. 17. Sodium content of cotton leaf blades as a function of time and salinity level of irrigation water.

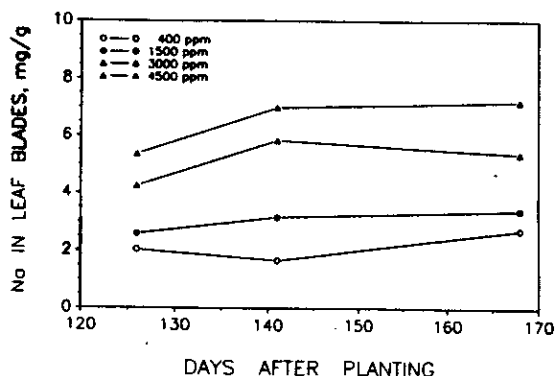
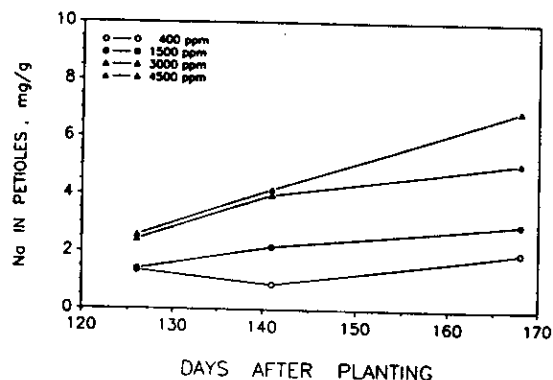


Fig. 18. Sodium content of cotton petioles as a function of time and salinity levels of irrigation water.



Safflower

The 1989 safflower crop shows the effects of previous irrigation with saline drain water (Table 5). The data are preliminary and the means are presented with no statistical treatment. It appears that the primary response is reduced plant height and delayed development. There is little if any effect on stand establishment. This is in sharp contrast with the response of the 1988 cotton crop in which the major effect was on stand establishment.

Table 5. Growth and development of safflower crop grown on plots irrigated with saline drain water. Sampling date May 30, 1989. Data are means of six samples.

Treatment, ppm	# of plants	Plant height	# of open bloom
9000	127	17.25	0
4500	153	23.25	0.125
400	158	33.88	16.0

Searching for Salinity Tolerance in Wheat

At the Boswell Co. El Rico Ranch salinity research site approximately 5 acres were developed for small-plot research. This site includes 15 basins, approximately 60' x 350' in size which can be independently irrigated. Three irrigation regimes have been used, each following a river water (low salt, about 450 TDS) preplanting irrigation: S1, control 450 TDS; S2, intermediate 4500 TDS; and S3, high 9000 TDS salinity levels. Basins were designated for S1, S2, or S3 and have received the same salinity irrigation treatment since the first crop cycle of 1984-85.

Several experiments have been conducted each year to assess the grain and above-ground biomass yields and milling and baking quality of wheat. Year-to-year variation has been more of a problem than anticipated in this research. In the first year (1985), the yields were very high, 8,000 to 10,000 lbs/acre of grain, with only a 10% yield reduction in the S3 treatment. In the second year (1986), excessive rainfall delayed planting and resulted in a very poor seedbed, especially for S3. In 1987 all experiments were successful, while in 1988 volunteer wheat and excessive bird damage made most experiments useless. In 1989 these problems were rectified by summer irrigation to induce germination and reduce volunteers and by installing bird-prevention netting over all of the critical yield plots.

Kelman (1988) completed his Ph.D. dissertation in which he studied Anza and Cajeme 71 bread wheat varieties and 43 recombinant inbred lines (RIL) derived from the hybrid Anza x Cajeme 71. To assess salinity tolerance or resistance of individual wheat varieties or RILs we have used the Fischer and Maurer (1978) stress index (S):

$$S = (1 - S_{di}/S_{pi}) / (1 - \bar{S}_d/\bar{S}_p)$$

where S_{di} is the grain yield of the i th genotype in a saline treatment, S_{pi} is the grain yield of the i th genotype in a control treatment, and \bar{S}_d and \bar{S}_p are the mean yields of all genotypes in the saline and control treatments. Low values of S indicate salinity resistance. Figure 19 shows the results for 1985 and 1986 for the parents and the RIL. Anza was more stress tolerant than Cajeme 71 in both years and the progenies showed a wide range of S values in the first year, but less variation in the second year. Both parents are well-adapted to San Joaquin Valley so these results demonstrated that this method may be useful as a selection criterion in breeding for salinity tolerance.

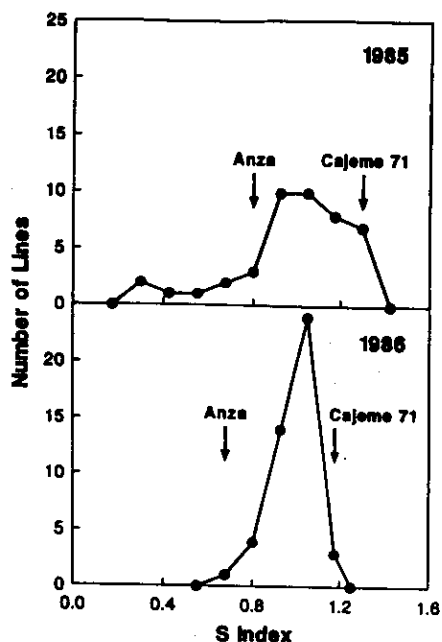


Figure 19. Distribution of stress (S) index values for Anza, Cajeme 71, and A3 derived inbred lines, based on grain yields in saline and nonsaline irrigation treatments in 1985 and 1986.

In another study (Table 6) 52 bread wheat, durum wheat, and triticale varieties were compared in three years. Soil salinity increased over the three years and the three PI entries showed good salinity tolerance, which was expressed to a greater degree in 1987 than in 1985, suggesting these lines may be good sources of genes for breeding purposes. These lines, and Kharchia, are poorly adapted to the San Joaquin Valley environment. Anza was one of the better bread wheats, and measurably more tolerant than Yecora Rojo (a sib line of Cajeme 71).

Table 6. Fischer stress index for yield (stress index) and ranks of stress index of 52 genotypes, shown for selected genotypes. Genotypes in each year were grown under control and high (9000 TDS) levels of salinity.

	Stress Index			Stress Index Rank		
	1985	1986	1987	1985	1986	1987
Anza	1.0	0.8	0.7	24	9	12
Yecora Rojo	1.9	1.1	2.4	42	39	49
Ramona 50	0.3	1.1	1.5	15	37	37
Mexicali (durum)	1.4	1.2	2.0	35	46	43
Kharchia	2.2	1.0	2.5	47	36	50
Nainari 60	-2.0	0.8	-0.1	3	12	20
D7316	2.1	1.2	2.0	46	50	44
UC 442	2.7	1.1	1.9	51	42	42
Modoc (durum)	2.0	1.2	2.3	43	51	48
PI 137733	-0.3	0.6	-1.8	11	3	5
PI 137743	-0.6	0.5	-1.5	10	2	6
PI 178160	-1.0	0.6	-3.7	8	5	3
Mean (n=52)	0.68	0.93	0.37	-	-	-

Table 7 illustrates data from a genetic analysis of the salinity tolerance in the cross Anza x Kharchia. Kharchia is widely known in India to have salinity tolerance and was identified in the early tank culture studies of Kingsbury and Epstein (1984). Under field conditions in California, however, Kharchia does not express its tolerance very well, at least as measured by the Fischer Stress Index (Tables 5 and 6). Sixty-one RIL and the parents have been studied for several years at the El Rico site. Since Kharchia is poorly adapted (tall and lodging susceptible) it has been difficult to get reliable data; however, there is an apparent difference between the parents for the stress index and also among the RIL. This provides further evidence for heritability of salinity tolerance that warrants further study. Greenhouse response studies on the RILs are in progress and C_{13}/C_{12} ratio studies are planned in the field in 1989-90 to provide additional information for salinity tolerance and to hopefully develop a reliable selection criterion for use in plant breeding.

Table 7. Grain yield in kg/ha (yield), harvest index (HI), and Fischer stress index for yield (stress index) at each of two salinity levels, S1 (control, about 450 ppm), and S2 (about 4500 ppm) for the Anza x Kharchia cross experiment. Genotypes were Anza, Kharchia, and 61 random recombinant inbreds derived from their cross. Note: lower stress index values are relatively stress resistant. Data from 1987 harvest.

	Grain Yield		Yield Stress index	HI*	
	S1 Control	S2 inter		S1	S2
Anza	3450	2600	0.6	48.5	66.7
Kharchia	3860	1540	1.9	52.7	48.1
Mean (all lines)	2640	1790	0.8	43.3	46.3
Range (all lines)	1410 to 4410	730 to 3250	-1.5 to 2.2	21.4 to 55.3	33.3 to 58.6

*HI = grain yield/(grain + straw yield).

SUMMARY AND CONCLUSIONS:

Previous studies indicate that relatively high salinity drain water can be used successfully for irrigation of certain crops. Several studies indicate that water up to a salinity level of about 3000 mg/L TDS (4.7 dS/m) have been used successfully to irrigate fairly tolerant crops for reasonably long time periods. Cotton has been grown commercially with respectable yields in Israel for nearly 15 years using water of this salinity level. Rhoades et al. (1988 a&b) have been successful in using water of 3000 mg/L for irrigation under actual commercial conditions in the Imperial Valley of California over a four year period by substituting up to 25-50% of the irrigation requirements with saline drainage water on tolerant crops at mature growth stages. Leaching occurred between applications of saline water by irrigating more sensitive crops of the rotation with good quality water.

Waters of up to 6000 mg/L (9.4 dS/m) are often classified as acceptable for irrigation and are being used. Rhoades (1983) was able to grow cotton on the west side of the San Joaquin Valley using water of 6000 mg/L for four years with only a 15% decrease in yield during the fourth year even in

the presence of a highly saline water table. Ayars et al. (1986 a&b) have also been able to get reasonable yields of cotton, wheat, and sugar beets in the San Joaquin Valley for three years using water of about 6000 mg/L level by giving preplant irrigations using good quality water. It is likely that any approach for using saline drainage waters will require that lower soil salinity values be established in the seedbed for good germination and stand establishment even for the generally tolerant crops.

A long-term research program underway in the Tulare Lake Basin of the San Joaquin Valley by the authors is using saline drainage water at several salinity levels up to 9000 mg/L (14 dS/m) with good quality water of 400 mg/L used for preplant irrigations on a typical cropping rotation of two years of cotton followed by one years of safflower (Rains et al., 1987). At this stage, four crops of cotton (1984, 1985, 1987 and 1988) and one of safflower (1986) have been grown. A second crop of safflower is currently being grown (1989). No yield reductions occurred for the first two years of cotton. Safflower, more salt-sensitive than cotton, had significant reductions in yield at the highest salinity level of 9000 mg/L due to poor stand establishment and subsequent retarded growth. The 1987 cotton crop had poor stand establishment at both the 6000 and 9000 mg/L salinity levels and decreased yield at the 9000 mg/L level. Major effects on the structure of the soil have been observed in plots irrigated with the two highest salinity drainage waters which greatly contributed to the poor stand (Rolston et al. 1988).

Strong evidence exists that saline drainage water at levels up to 3000 mg/L TDS (4.7 ds/m) can be used for irrigation of salt tolerant crops as long as some leaching occurs through preplant irrigations with good quality water or irrigation of salt sensitive crops in the rotation with good quality water. For levels of saline drain water greater than 3000 mg/L, the potential for long-term use of these waters for irrigation is less clear since most experiments have not proceeded long enough to fully test the impacts on crop productivity and soil degradation. Our research on a heavy clay in the San Joaquin Valley indicates that a level as high as 4500 mg/L of TDS (7 dS/m) in drainage water can be used for irrigation of cotton for at least 3 years as long as preplant irrigations with good quality water are used for cotton and for safflower in the rotation. After four years of cotton the yields are depressed even at the lowest level of salinity (1500 ppm). The primary effect appears to be stand establishment. This year a 1 1/4" rain storm occurred within 3 days after planting. This dispersed the surface of the seedbed and effectively sealed the surface on the 6000 and 9000 ppm treatment plots. Those plots were not harvested for biomass or lint yield as a result of the poor stand, however, we were able to harvest adequate samples of lint for quality measurements. Preliminary results indicate that there is no major effect of salinity on the quality characteristics of lint harvested from these plots. The 1989 safflower crop growth and development is markedly reduced with increasing salinity, however, stand establishment is only slightly decreased. This crop has not been harvested and therefore we are unable to quantify the effect reduced growth and development will have on grain yield. These data will be collected during harvest in August, 1989.

We have now completed two full rotations of the cotton-safflowers cropping systems. The primary effect on cotton after five years of irrigating with various levels of salinity in drain waters is the establishment of an adequate stand. For that reason the 1990 cotton crop will be used to establish methodology for improving seed bed conditions. We anticipate using physical, chemical and biological techniques to address this problem.

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PROJECT TITLE: POTENTIAL FOR THE LONG-TERM CYCLIC USE OF SALINE DRAINAGE WATER FOR IRRIGATION OF VEGETABLE CROPS

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ABSTRACT:

The volume of saline irrigation water produced by irrigation on the westside of the San Joaquin Valley must be reduced in order to sustain crop production in this area. Use of drainage water for irrigation is one method of conserving California aqueduct water and reducing drainage volume, while also improving processing tomato fruit quality without reducing yield. A three-year rotation of tomato-cotton-cotton, typical of this area, was initiated in 1986 with three irrigation regimes: (1) three years of California aqueduct water ("fresh"), (2) one year of drainage water ("saline") applied to tomato crop and two years of fresh, (3) two years of saline applied to the tomato crop and subsequent cotton crop, followed by one year of fresh water. Crop yields, fruit quality, selected physiological parameters and soil physical and chemical properties were measured. Selenium and boron accumulation in soil and plant tissues were also monitored. Results from the first two years have been covered in previous reports, this report focuses on the results from the 1988 field season.

In 1988, as in previous years, there was no detrimental effect of any drainage treatment on either tomato fruit yield or cotton lint production. Cotton stand establishment was reduced in all plots that received drainage water in 1987, but this was not reflected in final lint yields. Tomato green fruit yield and vegetative biomass were higher in plots receiving saline water than in those receiving fresh water for all three years. This effect was probably caused by the high nitrate levels in the drainage water (approximately 330 Kg N per hectare-meter) and is reflected in higher tissue N levels in the saline-treated plants. Selenium concentrations in tomato tissues were increased between two- and

three-fold by drainage water application, with the highest levels found in leaves, intermediate levels in stems and lowest in fruit.

The application of saline drainage water for one or two years significantly increased soil EC_e , Ca, Mg, Na, B and Se in the upper 125 cm of the profile. The tomato plots that received drainage water in 1986 and 1988 had similar profiles of EC_e and all elements, except boron, as plots that received drainage water only in 1988, indicating that the fresh water applied in 1987 was effective at moving the majority of salts from the upper part of the profile. Similarly, the profiles for EC_e and elements other than boron were the same in cotton plots that had received saline water in 1986 and 1987 followed by fresh in 1988, as plots that received saline water only in 1987. In all cases, soil Se showed a similar pattern to EC_e and the other major ions. Boron, however, was less effectively leached than all other elements. The data suggest that soil boron levels are likely to increase steadily over time, particularly if only one year of fresh water is used to leach the profile and may limit crop productivity over the long term. Two years of fresh water application, however, can further reduce the salinity profile and boron to levels only slightly higher than the fresh water control plots.

PROJECT OBJECTIVES ADDRESSED:

1. To determine whether the use of drainage water for irrigation is a feasible management practice for vegetable production on the westside of the San Joaquin Valley.
2. To determine the long-term effects of saline drainage water application on crop yield, crop quality and soil quality.
3. To assess the potential long-term hazard from toxic element accumulation in soils and tomato fruit.

RESEARCH PLAN AND PROCEDURES:

A six-year study was initiated in 1986 at University of California, Westside Field Station (WSFS) to address the objectives above. Many researchers have explored the possibility of using saline and/or agricultural drainage water for irrigation (Meiri et al., 1986; Pasternak et al., 1986; Rains et al., 1987; and Rhoades, 1987). We designed a "cyclic" irrigation strategy similar to that described by Rhoades (1987). That is, rather than blend water of different qualities before irrigation, we designed treatments that would cycle on a year-to-year basis between fresh California aqueduct water and saline drainage water. A cyclic strategy has advantages over the blending strategy in that (1) more salt-sensitive crops can be included in the rotation, (2) a blending facility is not needed, (3) drainage water of higher salinity can be used, and (4) the crop is more likely to actually utilize the drainage water (Grattan and Rhoades, 1989).

We chose to study the dynamics of a rotation typical of this region, consisting of one year of processing tomatoes followed by two years of cotton. We superimposed three irrigation water treatments on this typical three-year crop rotation. The three water treatments were: (1) irrigation with fresh California aqueduct water each year of the study, regardless of the crop, (2) irrigation with saline drainage water on tomatoes the first year followed by irrigation with fresh water on the cotton crops in the next two years, and (3) irrigation with saline water on tomatoes the first year and on the subsequent cotton crop the next year, followed by fresh water on the cotton crop in the third year. The

three-year rotation/irrigation regime was begun at the three possible rotation entry points. Therefore, the study consists of nine treatments replicated four times in a randomized complete block design (table 1).

Table 1. Irrigation/Rotation Treatments. F = fresh California aqueduct water, S = saline drainage water, t = tomatoes, c = cotton.

Irrigation Regime	Irrigation/Rotation Treatment		
	Trt. Year 1	Year 2	Year 3
1. Fresh water all 3 years	1. F _t	F _c	F _c
	2. F _c	F _t	F _c
	3. F _c	F _c	F _t
2. One year saline water (on tomato crop)	4. S _t	F _c	F _c
	5. F _c	S _t	F _c
	6. F _c	F _c	S _t
3. Two years saline water (on tomato and the following cotton crop)	7. S _t	S _t	F _c
	8. F _c	S _t	S _c
	9. S _c	F _c	S _t

The tomato plots contain five 1.7 m (66-inch) beds with a single row tomatoes on each bed. The cotton plots contain eight 1.0 m (40-inch) beds with one row per bed. The two outer beds in both the tomato and the cotton plots were not used for data collection. In 1988, one variety of tomato (FM785) and two varieties of cotton (SJ-2 and GC-510) were used. Tomatoes were planted on March 11, and the cotton was planted on April 11. Both crops were sprinkle irrigated with fresh water for germination. Due to very poor emergence, all cotton plots were replanted on May 11.

Fresh water was applied to all tomato plots, regardless of treatment, prior to first bloom. The drainage water was applied at first bloom to tomatoes in the saline water treatments and continued at weekly intervals thereafter.

In cotton plots assigned the saline irrigation treatment, the drainage water was applied for all irrigations after the first irrigation. The timing of irrigations in the cotton plots were dependent upon weekly cotton leaf water potential measurements. The cotton plots were irrigated when mid-day leaf water potentials fell below -16 bars for the first irrigation and -18 bars thereafter.

The quantity of water applied at each irrigation was calculated based on soil water depletion information from neutron probe measurements and on CIMIS weather station ETo estimates modified by a site-specific crop coefficient. Neutron probe measurements were made before each weekly irrigation in the tomato plots and every two weeks in cotton plots. Flow meters were used to measure the quantity of applied water. Samples were taken from both types of irrigation water and analyzed to determine content of anions and cations.

Tomato fruit yield, fruit soluble solids, citric acid content, total solids, fruit color and pH data were collected at time of harvest. A total biomass study of the mature tomato plant was conducted in which biomass was partitioned into red fruit, green fruit, senescent vegetative material, and green vegetative material. The amounts of boron, selenium and inorganic salts accumulated, in the fruit and vegetative parts were determined. Cotton lint was harvested and yield data collected.

Soil salinity was determined by measuring the electrical conductivity of saturation extracts (EC_e) of soil samples at the beginning and end of the season and by a modified Martek salinity probe used in the field during the season. The salinity probe provides estimates of EC_b , the EC of the bulk soil (which includes an integrated average of the solid, liquid and gas phase in the soil). The soil content of B, Se, SO_4 , Cl, Na, Ca, and Mg in each plot was measured at the end of the season. Soil water-infiltration rates were evaluated in the spring of 1989 using a rain simulator.

RESULTS:

Crop establishment and yield.

Cotton emergence in 1988 after the first planting was extremely poor. Emergence in plots which had saline water irrigation applied in 1987 were significantly lower than emergence in plots that received fresh water irrigations in that year (table 2). Stand establishment after the second planting was improved but still poor. Lint yields reflected no significant yield response to the irrigation/rotation treatments using the least significant difference mean separation test at the $\alpha = 0.05$ level. However, yield values for both varieties suggest the trend that the $S_c S_c F_c$ treatments produce the lowest yields (table 3).

Table 2. Emergence of cotton seedlings. Each number is the mean of 48 one-meter subplots. Letters indicate significant differences at $\alpha = .05$ using LSD mean separation tests.

Treatment	Seedling emergence (individuals/m of row)	
$F_t F_c F_c$	9.94	a
$F_c F_t F_c$	7.52	b
$S_c F_t F_c$	9.438	a
$F_c S_t F_c$	5.50	c
$S_c S_t F_c$	5.52	c
$F_c S_t S_c$	4.625	c

Table 3. Cotton lint yield data. There were no significant differences at $\alpha = .05$ using LSD mean separation tests.

Cotton Yield Data (kg/ha)		
Treatment	SJ - 2	GC - 510
$F_t F_c F_c$	1178	1188
$F_c F_t F_c$	1381	1387
$S_c F_t F_c$	1240	1272
$F_c S_t F_c$	1330	1305
$S_c S_t F_c$	1089	998
$F_c S_t S_c$	1249	1168

Tomato red fruit yield was not reduced by saline drainage water application. On the contrary, yields of tomato fruit from control plots (FFF) were less than those from drainage water treatments presumably due to an inadvertent water stress imposed on the plants in fresh water plots. There were significant differences in yield of green fruit, total fruit, green vegetative biomass and total biomass among treatments (table 4). Over the season the water from the saline source contained an average of 330 Kg of N per hectare-meter (90 lbs N per acre-foot) of water (data from Kent Tyler). The higher biomass

production in the $F_cF_cS_t$ and $S_cF_cS_t$ treatment plots were probably due in part to these high levels of nitrogen in the saline irrigation water.

Table 4. 1988 fruit yield. Letters indicate significant differences at $\alpha = .05$ using LSD mean separation tests.

Tomato fruit yield data from 9.15 m harvest (metric tons/ha)

Treatment	Red fruit	Green fruit	Rotten fruit	Total fruit
$F_cF_cF_t$	58.1 a	3.7 b	5.4 a	67.3 b
$F_cF_cS_t$	78.5 a	14.3 a	5.0 a	67.9 a
$S_cF_cS_t$	62.5 a	12.8 ab	6.9 a	81.8 ab

Tomato biomass data from 1.83 m harvest (metric tons/ha)

	Red fruit	Green fruit	Green vegetative	Senescent vegetative	Total biomass
$F_cF_cF_t$	64.0 b	2.9 b	85.7 b	13.8 a	166.0 b
$F_cF_cS_t$	87.6 a	23.0 a	114.5 a	10.5 a	234.1 a
$S_cF_cS_t$	81.5 ab	22.7 a	119.1 a	6.0 a	229.3 a

Tomato quality and tissue analysis

There were no significant treatment effects on the fruit quality parameters: pH, citric acid content, and color, but some differences in fruit soluble solids ($^{\circ}$ Brix) were observed (table 5). The response in 1988 differed from that in previous years in that soluble solids in fresh water treated tomatoes were high and extremely variable. Previously, the trend was for higher solids in the salt treated plots, which is in agreement with other studies. The abnormally high solids observed in the fresh water plots was due to water stress caused in part by malfunctioning of the flow meter used in the fresh water irrigation systems and an inadequate preirrigation.

Table 5. Influence of irrigation and saline and canal water on soluble solids in ripe tomato fruit. Letters indicate significant differences at $\alpha = .05$ using LSD mean separation tests.

Irrigation Treatment	1986 $^{\circ}$ Brix	1987 $^{\circ}$ Brix	1988 $^{\circ}$ Brix
Fresh	5.1	5.4 a	6.7
Saline	5.2	5.6 b	6.5

Data indicating element concentrations in tomato tissues are shown in table 6. In general, few significant trends are observed in the major ions. Leaf chloride was increased by saline water application, whereas, sodium increased significantly in the stem tissue. Both minor element concentrations, Se and B, were increased in most of the tissue types with the highest concentrations found in leaf tissue, intermediate in stems and the lowest in fruit. No significant differences were found in element accumulation between plants receiving drainage water in 1986 and 1988 (SFS) than those receiving it in 1988 only (FFS).

Table 6. Mean concentrations of selected elements in tomato tissue at final harvest on a dry weight basis. Letters indicate significant differences at $\alpha = .05$ using LSD mean separation tests.

Treatment	Cl(%)	SO ₄ (%)	NO ₃ (%)	Ca(%)	Na(%)	K(%)	B(mg/kg)	Se(mg/kg)
Green stem								
F _c F _c F _t	.74	1.60	.29	2.06	.33 b	4.00	32.0	.12 b
F _c F _c S _t	.77	1.56	.86	1.80	.50 a	3.79	37.0	.26 a
S _c F _c S _t	.78	1.55	.73	1.79	.53 a	3.69	36.3	.31 a
Green leaves								
F _c F _c F _t	.45 b	9.42 a	.22	6.49	.18	1.27	149.3 b	.53
F _c F _c S _t	.60 a	7.11 ab	.31	6.70	.36	1.64	183.3 ab	1.05
S _c F _c S _t	.57 a	5.92 b	.35	6.25	.37	1.45	211.5 a	1.14
Green fruit								
F _c F _c F _t	.16	.89	.16	.04	.07 b	6.26	17.3	.07 b
F _c F _c S _t	.19	.93	.19	.04	.15 ab	6.65	21.0	.15 a
S _c F _c S _t	.19	.96	.15	.03	.17 a	6.34	19.3	.20 a
Red fruit								
F _c F _c F _t	.15	.66	.18	.03 b	.05	6.98	14.8 b	.07 b
F _c F _c S _t	.17	.68	.13	.04 b	.10	7.10	17.8 a	.15 a
S _c F _c S _t	.13	.53	.18	.06 a	.10	7.16	18.5 a	.16 a

Tissue N was generally increased in plants given drainage water (table 7), reflecting the additional N supplied by the drainage water.

Table 7. Mean nitrogen concentration on percent dry weight basis in tomato plant tissue. Letters indicate significant differences at the .05 significance level using LSD mean separation tests.

Treatment	Green stem	Green leaves	Green fruit	Red fruit	Senescent Stem	Senescent leaves
	% N (dry wt.)					
F _c F _c F _t	1.17 a	2.23 b	2.10 b	2.33 b	1.12 a	1.80 b
F _c F _c S _t	1.24 a	2.93 a	2.40 ab	2.84 a	1.25 a	1.78 b
S _c F _c S _t	1.33 a	2.99 a	2.56 a	2.75 a	1.51 a	2.16 a

Soil quality data

Selected element concentrations and EC_e from saturated past extracts are given in figures 1 through 5. Calcium, magnesium and sodium data were collected but are not presented since their relative distribution follows closely that of EC_e. In general, element concentrations decreased with depth in plots that have received drainage water at some time. Plots given drainage water in 1986 and 1988 (SFS) had a similar profile of EC_e, Se and major cations (not shown) to plots having only one year of drainage application (FFS). Boron levels were higher, however, in the former than the latter (figures 1-3). This indicates that one year of leaching is effective at removing a majority of salts from the upper part of the profile such that no residual effect is seen after salt has been reapplied in the third year. This was not the case for boron which was less effectively leached and shows a cumulative increase. Profiles for EC_e and all other elements (not shown), with the exception of boron, were identical in plots irrigated with drainage water in both 1986 and 1987 (SSF) to those given drainage water in 1987 only

(FSF) (figures 4-5). This indicates that one year of leaching with fresh water irrigation lowers the profile salinity to a similar level following one or two years of salt application. In the case of boron, however, higher levels remain after two years of salt application than after one. Comparison of data from cotton plots SFF, FSF and FFF (figures 4-5) clearly demonstrates that two years of fresh water application can further reduce both the salinity profile and boron relative to one year to levels only slightly higher than the fresh water control plots.

GENERAL DISCUSSION AND SUMMARY

Use of saline drainage water for irrigation is one strategy growers on the westside of the San Joaquin Valley are considering to reduce the volume of drainage produced in this area. Although most of the growers considering drainage water reuse views salt-tolerant crops (e.g. eucalyptus and cotton) as the preferred crop to irrigate, others are considering more salt-sensitive crops such as tomato and melon because they are economically more attractive. Earlier studies (Grattan et al., 1987) have shown that tomato fruit quality can be improved by saline drainage water application without reducing crop yield. Therefore, this experiment was designed primarily to study drainage water irrigation of the tomato crop.

After completion of one three-year cycle, we have shown that drainage water irrigations did not reduce the yield of either tomatoes or cotton even when applied two out of three years. Cotton stand establishment was reduced the third year in plots that had been salinized the previous year(s). This effect, however, did not reduce final lint yield. Furthermore, this effect was not observed in the fourth year (1989) probably due to the preplant irrigation volume applied as compared to 1988. This irrigation was sufficient to prevent serious crusting and displaced much of the accumulated Na from the upper 10 cm of the soil profile.

The effect of drainage water of tomato fruit quality varied depending upon the year. Typically, saline water improves fruit quality by increasing soluble solids (Grattan et al., 1987; Pasternak et al., 1986). The data followed this trend in 1986 and 1987. In 1988, the water stress inadvertently imposed on fresh water treatments increased soluble solids in controls, thus masking any effect of the drainage water treatments.

Selenium concentrations were increased by drainage water application, but the absolute levels accumulated in the tomato tissue were not high enough to cause health concerns and were similar to those observed in previous studies (Grattan et al., 1987). The drainage water at the Westside Field station contains 30 to 40 µg/l Se, which is lower than levels observed in drainage water from some other areas (e.g. Mendota). Clearly, absolute tissue Se concentrations resulting from drainage reuse will depend in part upon the Se concentration in the drainage water and the existing soil Se content.

The data indicate that overall soil salinity can be managed in a reuse scheme such that moderately sensitive crops can be incorporated into the rotations and benefit from the supplemental nitrogen and quality improvements induced by some degree of salt stress. Potential limitations suggested by this study are the long-term buildup of boron in the soil, particularly if only one year of fresh water is used to leach the profile, and secondly, stand establishment problems in previously salinized plots. The latter have only been observed in one out of three years and may have been related to inadequate

preirrigation. Poor stand establishment in previously salinized plots has also been observed by others (Rains et al., 1987). Further information is needed to adequately address these concerns. Reduction in water infiltration rates have not been encountered to date, but may be a potential problem in the longer term. Future work should consider the potential for accumulation of other minor elements such as Cr, U, Mo, and As, which could also limit the feasibility of cyclic reuse systems.

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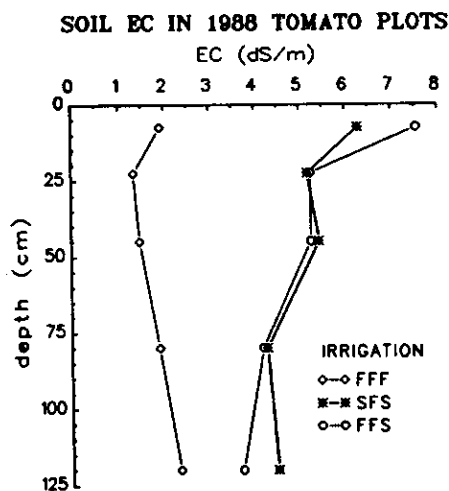


Figure 1. Electrical conductivity (EC) of the saturated soil extract at various depths in tomato plots subjected to different cyclic reuse treatments.

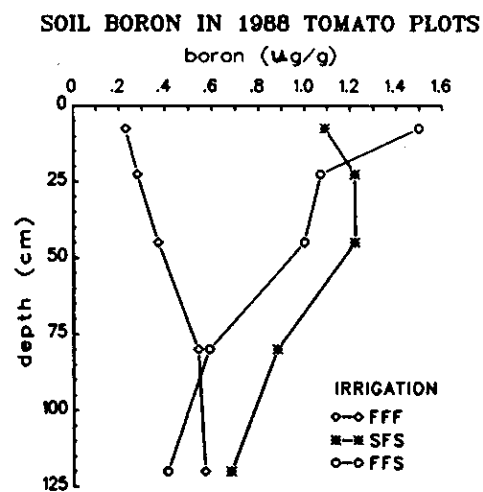


Figure 2. Boron concentration of the saturated soil extract at various depths in tomato plots subjected to different cyclic reuse treatments

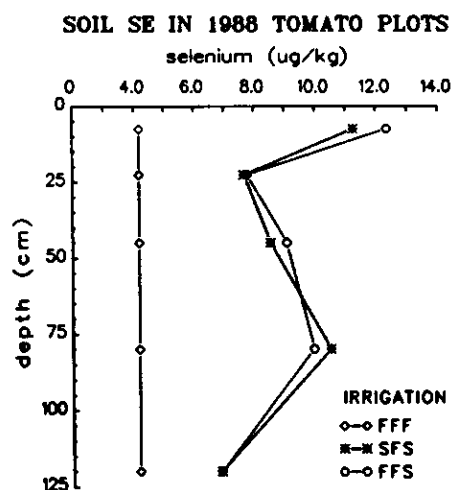


Figure 3. Selenium concentration of the saturated soil extract at various depths in tomato plots subjected to different cyclic reuse treatments.

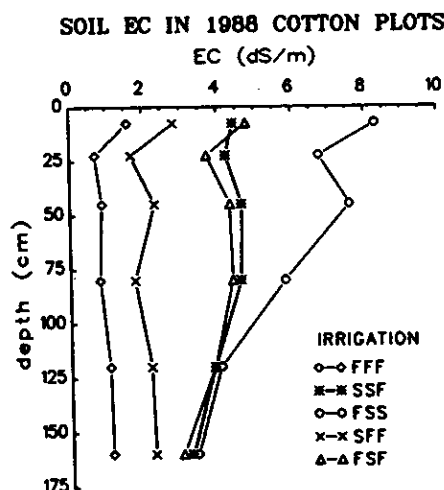


Figure 4. Electrical conductivity (EC) of the saturated soil extract at various depths in cotton plots subjected to different cyclic reuse treatments.

SOIL BORON IN 1988 COTTON PLOTS

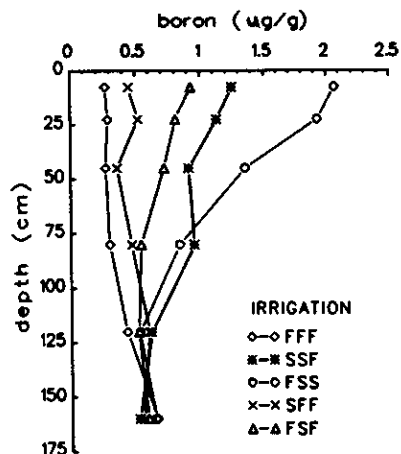


Figure 5. Boron concentration of the saturated soil extract at various depths in cotton plots subjected to different cyclic reuse treatments.

PROJECT TITLE: EFFECT OF IRRIGATION QUANTITY AND APPLICATION UNIFORMITY ON CROP YIELD AND SE UPTAKE WHEN IRRIGATED WITH DRAINAGE AND SURFACE WATER SUPPLIES

SOURCE OF FUNDING: State General Fund

DURATION OF FUNDING: July 1986 - June 1989

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ABSTRACT:

A field project was conducted to evaluate the effect of irrigation uniformity and water quality on cotton and sugar beet growth, yield, and elemental uptake in the presence of shallow (1.2 to 1.5 m), saline (EC >10 dS/m) groundwater. Application uniformities of 60%, 80%, and >90% CUC (Christiansen Uniformity Coefficient) were tested under conditions of long (L) and short (S) scale lengths using a modified linear travel sprinkler irrigation machine. Scale length corresponded to the wave length of the sinusoidal pattern of applied water for each treatment. Uniformity treatments were evaluated using both saline (3.5 - 5.0 dS/m) and non-saline (0.4 - 0.7 dS/m) water. All sugar beet plots received irrigation equivalent to 0.9 times estimated crop evapotranspiration (ET_c), while cotton plots were irrigated at 0.7, 0.9, 1.1 and 1.3 ET_c rates. Crop fresh weight yields were highly correlated with the depths of applied water across rows in the uniformity treatments, as shown in previous reports. Most Se contained in the saline irrigation water was retained within the upper 1 m of the soil profile, with less than 4 percent of applied Se accounted for in

above-ground crop biomass. Nitrate, chloride and boron concentrations were significantly higher in plants irrigated with saline water. The relationship between levels of these constituents and applied water on a row-by-row basis was strongly dependent on irrigation level and water quality.

KEYWORDS: irrigation uniformity, crop yield responses, selenium, drainage, cotton, saline water, sugar beets, boron.

PROJECT OBJECTIVES ADDRESSED:

This project is a large field project in which a number of objectives are being evaluated concurrently. The specific objectives are: (1) Determine the effect of water application uniformity of various quantities of irrigation water on crop growth, yield and element uptake (in particular Selenium) when the crop is irrigated either with saline drainage water containing selenium ($>150 \mu\text{g kg}^{-1}$) or with non-saline surface water with low selenium ($<5 \mu\text{g kg}^{-1}$); (2) evaluate the temporal and spatial variability of soil salinity and soil elemental composition as influenced by water quality, quantity and application uniformity; (3) assess the influence of application uniformity of the two water qualities on calculated leaching rate and quantities; and (4) monitor the movement and/or accumulation of selenium and other potentially toxic constituents in the crop and within the root zone.

RESEARCH PLAN AND PROCEDURES:

A seven span linear-move sprinkler irrigation machine was utilized in a field experiment conducted to evaluate the influence of irrigation nonuniformity and irrigation water quality on crop growth, yield, and the disposition of salts and specific elements within the plant-soil system. The experiment was conducted on the west side of the San Joaquin Valley in a saline soil (Oxalis clay loam) underlain by shallow (1.3 - 2.0 m), saline (EC $>10 \text{ dS/m}$) ground water. These conditions are fairly typical of large areas on the west side of the San Joaquin Valley and of many other irrigated areas.

The field experiment, located 6 km south of Mendota, CA, was an 11 ha cooperative research site established by Murrieta Farms in conjunction with the Water Management Research Laboratory (USDA-ARS). The site is instrumented with a weather station which is part of the California Irrigation Management Information System (CIMIS) network. Subsurface drains under the research plots were instrumented with flow meters and data on quantity and quality of drain effluent have been collected for the past 4 years. The site had access to both surface irrigation water from the Westlands Irrigation District and a reservoir suitable for blending subsurface drain water with surface water sources to obtain specific salinity levels in the irrigation water. Facilities were in place to pump water from one of the Westlands Water District's main drains to the reservoir.

The linear move system was modified to create five irrigation uniformity treatments, which included combinations of three levels of uniformity of applied water (60, 80, >90 percent) as

calculated using Christiansen's Uniformity Coefficient (CUC) and two scale lengths (2.4 and 4.9 m), which were designated as short (S) or long (L) scale lengths, respectively. Scale length was equal to the wave length of the sinusoidal pattern of applied water achieved with each sprinkler configuration. The five treatments utilized in this study were designated as 60-L (60% CUC, long (L) wave length), 60-S (60% CUC, short (S) wave length), 80-L (80% CUC, long wave length), 80-S (80% CUC, short scale length), and UNIFORM (<90% CUC). Only one treatment was applied across each 54 m wide span of the linear irrigation system. The combinations of uniformity and scale length were achieved through design of a spray application system using 180 degree flooding-type nozzles with the number of nozzles, nozzle size, and spray direction altered to achieve the desired uniformity and scale length.

Cotton and sugarbeet were the crops grown during the two years of the experiment. The yield response to the irrigation treatments were reported in previous annual reports. Plant samples were taken from both crops to determine the presence and distribution of Se and B in the plant tissue.

Soil samples were taken in .3 m increments to a depth of 1.8 meters in the UNIFORM and 60-L treatments following each cropping season and in the Spring of each year. A complete analysis of the soil solution extract was done for each sample.

RESULTS:

The results for the soil salinity distributions and Se accumulations for the .7 and 1.1 ET_c treatments in the UNIFORM water application will be used to demonstrate the effect of depth of application on soil salinity and Se accumulations. The soil salinity and Se data for the Fall 1986 and Fall 1987 sampling dates are given in Table 1. The water quality of the applied water for 1986 and 1987 is given in Table 2.

Table 1. Soils salinity and Se distribution in uniform applications with .7 ET_c and 1.1 ET_c treatments.

EC			Se Concentration						
SPAN	Plot # (Irrig. Level)	Irrigation Water Quality	Depth (cm)	Spr 86 (dS/m)	Fall 86 (dS/m)	Fall 87 (dS/m)	Spr 86 (µg/L)	Fall 86 (µg/L)	Fall 87 (µg/L)
4	1 (1.1)	Saline	30	1.3	5.4	6.0	ND*	75	187
			90	6.8	8.6	10.2	ND	37	118
			150	10.5	11.0	12.0	ND	125	120
	4 (.7)	Saline	30	1.3	4.1	6.4	ND	47	134
			90	6.8	10.1	8.3	ND	48	105
			150	10.5	10.7	15.8	ND	61	26
	6 (.7)	Non-saline	30	1.2	3.3	3.6	ND	3	4
			90	7.0	13.8	15.6	ND	31	62
	8 (1.1)	Non-saline	30	1.2	2.3	1.5	ND	10	2
			90	7.0	11.2	13.7	ND	25	56

*ND = no data

Table 2. Average irrigation water quality used in uniformity experiment 1986 and 1987 seasons.

Year	Water Quality	EC dS/m	CL meg/L	B ms/L	SE mg/L
1986	Non-saline	.4	2.1	.2	<1
	Saline	4.1	13.8	3.5	140
1987	Non-saline	.7	3.0	.4	7.5
	Saline	5.0	16.7	4.2	184

Plots 1 and 4 were in the area receiving saline water applications while plots 6 and 8 received only non-saline irrigations. The plots receiving saline irrigation had larger increases in the EC of the surface layers than did the side being irrigated with non-saline water. There was a trend for the salinity to have larger increases at the .9 and 1.5 m depths on the side irrigated with non-saline water than on the side irrigated with saline water. The EC data in plot 6 indicate that substantial quantities of water were extracted from the groundwater.

The soil Se data show consistent increases over time. The increase in plots 1 and 4 are proportional to the depth of applied water and concentration of Se in the water. In plots 1 and 4 the largest increases are occurring in the upper layers of the soil profile indicating the increase is due to the application of Se in the irrigation water. In plots 6 and 8 the increases are in the lower parts of the profile indicating that the source of the selenium was the shallow groundwater.

The amount of Se applied to both the saline and non-saline sides was established using the irrigation depth and water quality data. This was compared to the increases in the soil profile estimated from the soil solution data.

The total measured increase during the Spring to Fall, 1987 period in Se in the soil profile to a depth of 1.5 m was .5 and .3 kg/ha for the 1.1 Etc and .7 Etc treatments, respectively, on the saline side of the field. On the non-saline side the increases were .14 and .2 kg/ha for the 1.1 and .7 Etc treatments respectively. The total Se applied during irrigation was .9 and .7 kg/ha for the 1.1 and .7 Etc treatments on the saline side and .04 and .03 kg/ha for the 1.1 and .7 Etc non-saline treatments respectively. There is less than .03 kg/ha taken from the soil by either the cotton or the sugarbeet crops during a season.

These data indicate that the potential exists for Se to be transported to the groundwater in the soil receiving irrigation by saline water. On the other hand the soil irrigated with non-saline water extracted Se from the groundwater, particularly when the crop was underirrigated and extracted a portion of its water requirement from the groundwater.

Plant Nitrate, Chloride, Boron, and Selenium Uptake

While the irrigation water for plots designated as "Non-saline" received water averaging less than 3 mg NO₃- per liter, water used in the plots receiving saline irrigation water averaged in excess of 35 mg NO₃- per liter during the irrigation season. This saline irrigation water added the

equivalent of approximately 0.8 to 0.9 kg N per ha for each cm of depth of applied water. Since the water was applied during the growing season using sprinklers, the N present in the water could become plant available through both foliar uptake and uptake from applied water reaching the soil. The influence of saline water application on nitrate concentrations of petioles of new fully-expanded leaves is shown for sugar beets and cotton in Figures 1a and 1b, respectively for the "Uniform" water application uniformity treatment. In the sugar beets receiving saline irrigation water with a high nitrate load, significantly higher petiole NO_3^- levels were maintained during the

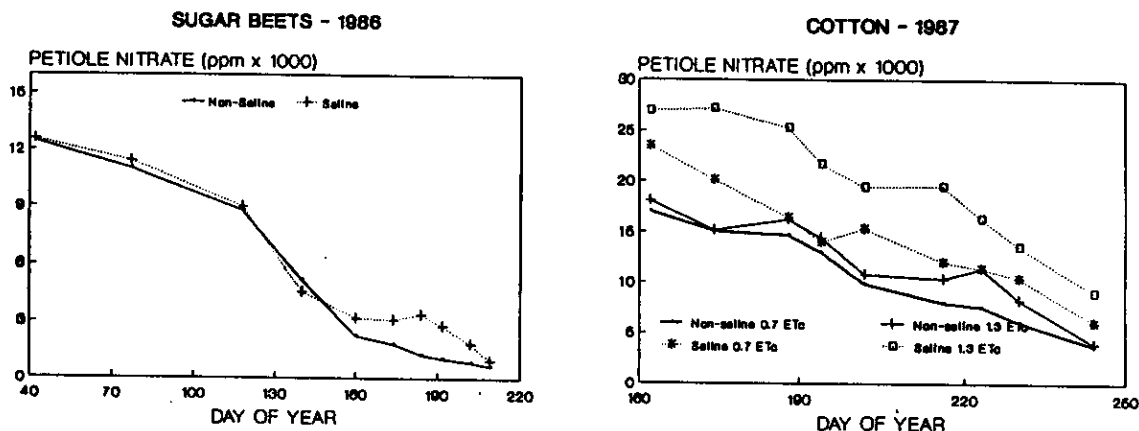


Figure 1. Petiole nitrate levels of the most fully-expanded leaves of (a) sugar beets in the "Uniform" water application treatment under non-saline and saline irrigation, and (b) cotton under non-saline and saline irrigation at the 0.7 and 1.3 ET_c level.

period from about day 140 through 210 when compared to those receiving non-saline water. This corresponded to the period of irrigation with high nitrate water. This higher nitrate concentration produced greater late-season vegetative growth and also higher root nitrate levels (data not shown).

Similarly, in cotton, significantly higher petiole NO_3^- levels were maintained throughout the season in plants receiving saline irrigation when compared to those receiving non-saline irrigation water (Figure 1b). In the saline plots, all pre-plant and germination irrigations prior to approximately day 190 were with non-saline, low NO_3^- content water. Despite this fact, petiole NO_3^- levels in saline plots prior to the initiation of saline water applications in 1987 (day 192) were substantially higher than in plants from non-saline plots. This data indicates the likelihood of significant residual N carried over in the soil from prior applications of high- NO_3^- water during the 1986 (sugar beet) season.

Petiole nitrate levels were also determined across rows of plants receiving different water application amounts in the water application uniformity treatments. In a treatment such as the 60-L plots, applied water amounts on a row-by-row basis corresponded to a sinusoidal pattern repeating with a frequency of 7 to 8 rows. When high-nitrate saline irrigation water was applied either at the 0.7, 0.9, 1.1, or 1.3 ET_c level in cotton, petiole nitrate levels were highly correlated with water application on a row-by-row basis, with both water application amounts (data not shown) and

petiole nitrate levels (Figure 2) exhibiting a repeating 7 to 8 row pattern in the 60-L treatment. Similar patterns were consistently found in all mid- to late-season measurements in saline-irrigated cotton and also in sugar beets in 1986 (data not shown). Deficit irrigation (0.7 ET_c) with non-saline, low-nitrate water consistently produced a negative correlation between applied water and petiole nitrate levels on a row-by-row basis (Figure 2), with the highest petiole nitrate levels occurring in plant rows receiving the least irrigation water. The likely explanations for this phenomena are that deficit irrigation (1) reduced plant growth and had a concentrating effect on

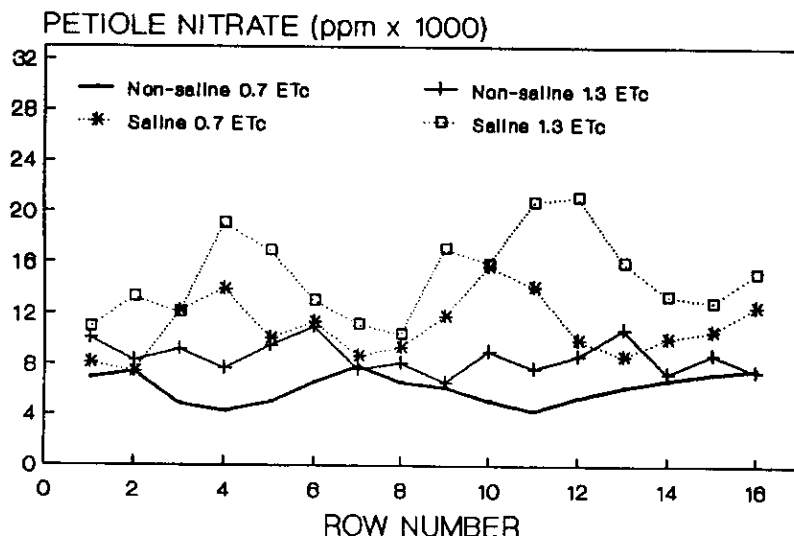


Figure 2. Petiole nitrate levels of the most recent fully-expanded leaves of saline and non-saline irrigated cotton on a row-by-row basis in the low water application uniformity treatment 60-L at 0.7 and 1.3 ET_c levels on day 230.

accumulated chemical constituents; and (2) encouraged both plant uptake from the shallow (1.2 m deep), nitrate-containing groundwater and maintenance of a soil hydraulic gradient for upward water flow.

Leaf blade chloride levels similarly exhibited different row-by-row patterns of accumulation according to the irrigation level and water quality used (Figure 3). At high water application levels (1.3 ET_c) with saline, high chloride irrigation water, leaf blade chloride levels in non-uniform water application treatments such as 60-L (Figure 3) were highly correlated with applied water on a row-by-row basis. When the plants received low water application levels (0.7 ET_c) under either low chloride (non-saline) or high chloride (saline) irrigation, leaf blade chloride levels on a row-by-row basis were negatively correlated with water application levels. As with the petiole nitrate data for these plots, these findings suggest that plants in rows receiving low water application amounts had to rely on soil water depletion and groundwater uptake to a greater extent than those receiving relatively higher water application amounts, resulting in greater accumulated chloride.

Boron levels in the most recent fully expanded leaves of sugar beets and cotton increased significantly in plots receiving saline high-boron irrigation water when compared to plots receiving

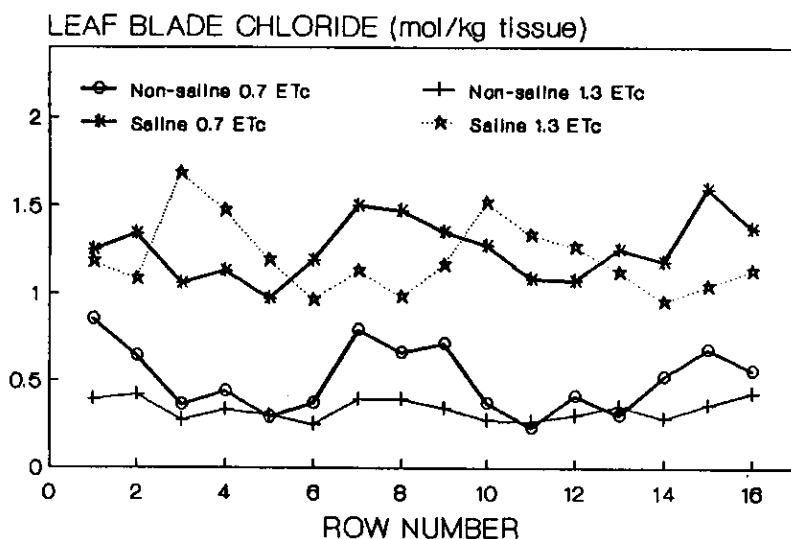


Figure 3. Chloride levels of the most recent fully-expanded leaf blades of saline and non-saline irrigated cotton on a row-by-row basis in the low water application uniformity 60-L treatment at 0.7 and 1.3 Etc levels on day 234.

non-saline, low-boron content water (Figures 4a and 4b). Even in plots irrigated with non-saline water, boron levels in the soil and groundwater were quite high, resulting in considerable tissue boron accumulation. In comparing leaf B levels in plant rows in the 60-L, 0.7 Etc treatment which were in the high (H) water application portion of the water application pattern with those in the low (L) water application portion, boron concentration was negatively correlated with water application amount.

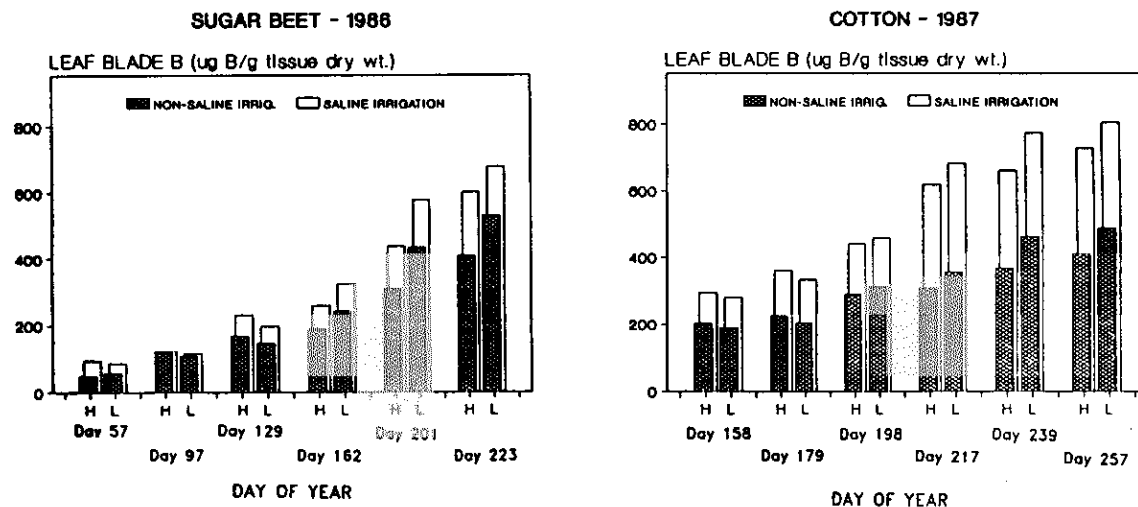


Figure 4. Leaf blade boron (B) levels of recent fully-expanded leaf blades of cotton as a function of day of year and irrigation-water quality for (a) sugar beet and (b) cotton in uniformity treatment 60-L at the 0.7 Etc level. "H" and "L" designations refer to values determined for plants in rows receiving high (H) and low (L) water application amounts, respectively.

Plant selenium analyses completed to date indicate that peak tissue Se levels are generally found in the leaves in both sugar beets and cotton (Table 3). Selenium levels in all measured plant parts were significantly higher in plants irrigated with saline, high-Se (>120 μg inorganic Se/L) water

when compared with those receiving non-saline, low-Se water. In sugar beets, root Se content was generally less than 0.3 mg total Se per kg of dry tissue at harvest in plots receiving saline water as compared to approximately 0.1 mg in plots irrigated with non-saline water. In cotton plants irrigated with saline water, leaf and seed Se content was roughly proportional to differences in water application between 0.7 and 1.1 ET_c plots, with significantly higher Se levels prevailing in plants from the 1.1 ET_c plots. Plants deficit irrigated with non-saline water at the 0.7 ET_c level had higher leaf Se levels than those irrigated at the 1.1 ET_c level, again suggesting greater potential uptake from the high-Se groundwater in the deficit irrigated 0.7 ET_c plants. Continuing analyses on plant samples collected from these plots should yield a clearer picture of these elemental uptake responses.

Table 3. Tissue Se content on a dry weight basis as a function of crop, water quality, and irrigation in 1986 and 1987.

Year	Crop	Water Quality	Irrigation Uniformity Treatment	Water Application Treatment	End of Season Tissue Total Se Content *			
					leaf	root	stem	seed
% Etc					mg total Se/kg tissue			
1986	Sugar Beet	Non-Saline	Uniform	100	0.5	0.1	-	-
			60-L	100	0.6	0.1	-	-
		Saline	Uniform	100	1.7	0.2	-	-
			60-L	100	1.9	0.3	-	-
1987	Cotton	Non-Saline	Uniform	70	1.0	-	0.3	0.6
			60-L	70	1.1	-	0.4	0.6
			Uniform	110	0.4	-	0.3	0.5
			60-L	110	0.4	-	0.3	0.5
		Saline	Uniform	70	1.8	-	0.6	0.9
			60-L	70	2.1	-	0.5	1.0
			Uniform	110	3.2	-	0.4	1.1
			60-L	110	3.2	-	0.6	1.3

* Analyses conducted on samples collected on the following dates:

Sugar Beets: leaves (August 8-10)
 roots (August 28-30)
 Cotton: leaves, stem (September 6-10)
 seed (October 17-23)

Discussion and Summary:

Results of this study described in previous reports indicated that, for sugar beet and cotton, growth and total plant dry matter yields were highly correlated with depths of applied water on a row-by-row basis under both nonsaline and saline irrigation water treatments. Under saline irrigation, accumulation of salts on any individual row were below the average soil salinity levels expected to affect either sugar beet or cotton yields, therefore, observed plant responses were a result of differential water applications, not different soil salinity profiles produced under nonuniform irrigation.

A much more complex relationship was found in analyzing the relationship between depths of applied water and crop harvestable yields on a row-by-row basis. In sugar beets, the reduced beet root size associated with low water application tended to be offset by the concentrating effects of water deficits on increasing sugar percentage. In cotton, particularly in plots receiving saline, high-nitrate water, plant rows receiving large depths of water tended to have excessive vegetative growth and lower seed cotton yields than rows receiving less water. In general, across the uniformity treatments evaluated, the lowest water use efficiencies were obtained under low uniformity and long scale length, such as in treatment 60-L.

Soil salinity, boron, chloride, and selenium levels increased in the surface 1 m of the profile as a result of the use of saline irrigation water. Similarly, plant tissue chloride, boron, nitrate, and selenium levels increased significantly as a result of use of saline water. Of the amount of Se applied in the saline irrigation water, approximately 4% could be accounted for in above-ground plant biomass. In 1987, when irrigation applications ranging from 0.7 to 1.3 ET_c were used, the row-by-row pattern of soil and plant accumulation of these constituents was greatly affected by the water application amount. Data suggested that under nonsaline and saline irrigation, moderate to severe deficit irrigation rates promoted utilization of groundwater and uptake of chloride, boron, selenium, and nitrate from the groundwater, while under nonsaline irrigation higher application amounts reduced groundwater uptake. Plant tissue concentrations of these constituents were roughly proportional to water application amounts under saline irrigation with high application amounts.

PUBLICATIONS AND REPORTS:

Ayars, J.E., R.B. Hutmacher, S.S. Vail, and R.A. Schoneman. Response of cotton to nonuniform irrigation. (Manuscript in preparation)

Ayars, J.E., R.B. Hutmacher, R.A. Schoneman, and D.D. Dettinger. Effect of cotton canopy on irrigation uniformity. (Manuscript in preparation)

Ben-Asher, J. and J.E. Ayars. Deep-seepage under nonuniform irrigation: Theory. Submitted to ASCE.

Ben-Asher, J. and J.E. Ayars. Deep-seepage under nonuniform irrigation: Field data. Submitted to ASCE.

Ayars, J.E., R.B. Hutmacher, G.J. Hoffman, J. Letey, J. Ben-Asher, and K.H. Solomon. Response of sugar beet to non-uniform irrigation. Submitted to Irrigation Science.

Hutmacher, R.B., J.E. Ayars, G.J. Hoffman, R.A. Schoneman, and S.S. Vail. Use of saline water for irrigation: Impact on cotton seedling establishment and surface soil leaching requirements. Submitted to Irrigation Science.

Hutmacher, R.B., J.E. Ayars. Effects of irrigation nonuniformity on canopy temperature and evapotranspiration estimates in cotton. (In preparation).

Hutmacher, R.B., J.E. Ayars, R.A. Schoneman, S.S. Vail. Effects of irrigation method, frequency, and water quality on plant elemental uptake and composition in the presence of shallow groundwater. (In preparation).

PROJECT TITLE: ON-FARM DEMONSTRATION OF SURFACE AND SUBSURFACE IRRIGATION SYSTEMS

PROJECT NUMBER: 86-30

DURATION OF FUNDING: July 1986 - June 1989

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ABSTRACT

Subsurface drip, continuous furrow, and surge irrigation were used to irrigate cotton on a 30 A field site located near Stratford on property owned by Stone Land Company. During 1988 the subsurface drip laterals were installed 18 in. deep at a spacing of 40 in. Run lengths for preirrigation were reduced from 2520 to 1260 ft. to improve irrigation uniformity. In 1988, the total infiltrated water for the subsurface, surge, and continuous furrow treatments were 25.3, 27.9, and 27.5 in., respectively; the corresponding lint yields were 2.9, 2.6, and 2.6 bales/A. Preliminary estimates indicate cotton production costs of a subsurface drip system with 80 in. lateral spacing are about \$300/A greater than for surface irrigation systems. Further data analysis is required to estimate

differences in crop ET and drainage volumes among treatments and to finalize differences in potential profitability among the irrigation treatments.

PROJECT OBJECTIVES ADDRESSED:

1. To demonstrate the following field-scale irrigation systems on property owned by Stone Land Co. near Stratford, California:
 - a. surface irrigation with tailwater return system designed and managed using computer simulation techniques.
 - b. subsurface drip irrigation using CIMIS reference evapotranspiration and appropriate crop coefficients to control daily irrigation.
2. To compare operating costs and associate on-farm management requirements of demonstrated irrigation methods to current irrigation practices of the farmer cooperator.
3. To transfer the information to growers and the general public through field days, newspaper articles, research reports, and oral presentations at appropriate conferences.

RESEARCH PLAN AND PROCEDURES:

Cotton was irrigated with two furrow irrigation methods, continuous flow and surge, and subsurface drip on a 30 A field site located near Stratford on property owned by Stone Land Company. The irrigated area for each method was about 10 A, the furrow spacing was 40 in. and the field length was 2520 ft.

Furrow Systems. The run length in 1987 was 2520 ft., the growers normal practice. Based on 1987 evaluation data, a 1260 ft. run length was used for preirrigation in 1988 for both furrow systems. Thereafter, the furrow length was 2550 ft. Runoff from each system was measured separately. Set times for continuous flow were determined by computer estimates of soil intake rates and by soil probing at the end of the furrow; the furrow inflow rate for preirrigation was 37 gpm, and for the crop irrigations it was 45 gpm. The initial furrow inflow rate for surge was 40 gpm; during the cutback phase it was 20 gpm. Irrigation scheduling for both furrow systems was based on leaf water potentials measured by a pressure chamber. Nitrogen, phosphorus, and zinc fertilizer was applied in 1988 by the grower at a rate of 240, 40, and 5 lb/A, respectively.

Drip System. The subsurface drip system (Netafim Irrigation Inc., Ram Drip) was installed at a depth of 18 in. with laterals spaced 80 in. apart beneath alternate furrows in 1987, and 40 in. apart beneath each bed in 1988. The drip system was divided into two plots of equal area in 1988, and irrigation was scheduled independently on each plot to maximize water use from the shallow water table at the east end of the field. Irrigation was applied daily based on CIMIS reference evapotranspiration and the ARS coefficient for drip irrigated cotton. Nitrogen, phosphorus, and potassium fertilizers (8-8-8) were injected daily from 5/24 to 8/6/88; total N, P_2O_5 , and K_2O applications for the west and east sections were 162 and 154; 220 and 199; and 161 and 154 lb/A, respectively. Vapam (ICI chemical) was also injected to fumigate the system pre-season at a rate of

32 gal/A before the irrigation season and 9 gal/A after the irrigation season.

Plant nutrition. Cotton leaf petioles were collected from the first or second mature leaf below the top of the plant in all treatments. After drying and grinding these samples were analyzed in an aluminum sulfate extract for $\text{NO}_3\text{-N}$, PO_4 and K.

Crop yield. Stone Land Co. machine harvested 5.7 A in each treatment and ginned the cotton the same day. Each treatment was ginned separately; the gin was cleaned before and after each treatment.

RESULTS:

Water. Year-to-year variations in total infiltrated water (Table 1) resulted primarily from changes in water management for all treatments. In 1987 infiltrated water for the subsurface drip was greater than for surface irrigation; the crop irrigation for drip was approximately 7 in. greater than for the surface irrigation treatments. In 1988, water infiltration from the crop irrigations was approximately the same for all treatments, but the preplant surface irrigations resulted in somewhat more than 3 in. of infiltrated water than for drip. The lateral spacing of 40 in. in 1988 made it possible to complete preplant irrigation for the drip treatment using only the drip irrigation system. Because of the 80 in. spacing in 1987, this was not possible and it was necessary to apply some of the preplant irrigation using surface irrigation. Reducing the length of run in 1988 for the preplant surface irrigation 1988 resulted in less infiltrated water than in 1987. One additional irrigation for the continuous furrow in 1988 as compared to 1987 increased infiltrated water by about 4 in.

Plant nutrient. Petiole N data was collected for all treatments from June 17 to August 12. The concentrations were similar ranging from 22000 mg/kg at the beginning to 2000 mg/kg at the end. Substantial differences in P concentrations occurred between the surface and drip (SSD-W, west; SSD-E, east) treatments. The P levels for surface irrigation were continuously deficient (600 - 1200 mg/kg), whereas those for drip started at about 1200 mg/kg and increased to near adequate levels (1700 mg/kg) by August 12. The K levels for all treatments were similar, ranging from about 70000 mg/kg early in the season to 53000 mg/kg at end. The SSD-E departed slightly from this general trend ending with about 63000 mg/kg at the end of the season. This may reflect increased use of water from the water table at the end of the irrigation season. Note the lower amount of crop irrigation for this treatment in Table 1.

Yield. Lint yields for the drip treatment exceeded those for the other treatments by 0.3 to 0.6 bales/A (Table 2.); the average increase was .32 bales/A. Several factors could account for this difference: improved infiltration uniformity, larger fertilizer applications, daily irrigation, and use of Vapam fumigant in the drip treatment.

Irrigation system costs. The system costs based on the irrigation practices in 1988 are detailed in Table 3. The 40 in. lateral spacing in the subsurface drip resulted in high system costs. Subsurface drip irrigation with a lateral spacing of 80 in. can be done provided sprinkler or furrow

irrigation is used for preirrigation. The high fertilizer costs in 1988 for the drip treatment reflect concerns for safety and convenience. A low analysis, premixed fertilizer was used because no mixing facilities were available at the site. Although little is known about optimum fumigation rates, the rates used are likely high by a factor of two.

Estimated costs for two different subsurface systems using drip tubes which can be buried at a depth of 18 in. are given in Table 4. Although the estimated costs are about \$560 per acre less than for the demonstration drip costs in 1988, they are about \$330 per acre higher than for the surface irrigation systems. Higher system and fertilizer plus fumigation costs each account for about half of the increased costs. A yield increase of 0.3 bales/A would offset about \$100/A of these costs.

DISCUSSION AND SUMMARY:

Further data analysis is required to evaluate the question, was the drainage volume reduced? Hydraulic gradient and chloride distributions with depth, crop mass data, and aerial distribution of crop uniformity remain to be analyzed. The question is, what was the ET? The increased crop yield for subsurface drip with about the same amount of infiltrated water as for the surface irrigation treatments suggests drainage water was reduced as a result of higher ET in the subsurface drip treatment. But the yield and cost data indicate the overall result was reduced profitability.

PUBLICATIONS AND REPORTS:

Technical papers.

1. Hanson, B. 1989. Drainage reduction potential of furrow irrigation. California Agriculture 43(1): 6.
2. Hanson, B., and A. Fulton. 1989. Water advance and infiltration in a cracking soil. Presentation at a joint meeting of American Society of Agricultural Engineering and the Canadian Society of Agricultural Engineering, June 25-28, Quebec, Canada. Paper Number 90-2182.
3. Phene, C. J., J. D. Oster, D. A. Clark, J. Misake, D. A. Goldhamer, B. R. Hanson, A. E. Fulton, C. McNiesh and R. Strohman. On-farm demonstration of subsurface drip irrigation: I. yields, II. soil water, and III. effect of fertigation on leaf petiole content of NPK.

Technical presentations.

1. Hanson, B., 1989. Comparative evaluation of furrow and subsurface drip irrigation of cotton. California Irrigation Institute, Jan. 25-26, Sacramento.
2. Hanson, B., 1989. Subsurface and surface irrigation demonstration report. Salinity and Drainage Task Force, Mar. 4-5, Sacramento.
3. Fulton, A., 1989. Subsurface drip irrigation: commercial demonstration. California Irrigation Institute, Jan. 25-26, Sacramento.

Press releases.

1. Hanford Sentinel, July 1, 1988. Drip irrigation system tested for row crops.
2. Fresno Bee, July 24, 1988. Underground drip irrigation could benefit valley farmers.

3. California-Arizona Farm Press, Sept. 24, 1988. Soil governs irrigation strategy.
4. California-Arizona Farm Press, Oct. 15, 1988. Subsurface drip cotton defended by researcher.

Field Days

1. Kings Co. Cotton Tour, Sept. 15, 1987.
2. Western Regional Research Project (W-160) and Western Regional Coordination Group 54 Tour, Aug. 17, 1988.
3. Kings Co. Cotton Tour, Sept. 27, 1988.

Table 1. Infiltrated Water

a. 1987

	Cont. Fur	Surge	Drip
	-----	in. -----	
Preplant	7.7	6.7	7.6 (3.6 surface)
Crop Irrigation (N)	14.9(3)	15.7(4)	22.5
Rainfall	2.9	2.9	2.9
Total	25.5	25.3	33.0

b. 1988

			E	W
Preplant	5.4	5.6	2.3	2.2
Crop Irrigation	18.7(4)	18.9(4)	18.8	20.5
Rainfall	3.4	3.4	3.4	3.4
Total	27.5	27.9	24.5	26.1

Table 2. Machine Harvested Cotton Yields.

Treatment	Harvested Area A	Lint Yield		Gin Turnout Z	
		Bales/A 1987	1988	1987	1988
Drip	5.7	3.6	2.9	28	31
Surge	5.7	3.4	2.6	32	32
Continuous	5.7	3.0	2.6	32	32
Grower	5.7(130)*	3.4	2.6	--	31

*1987 harvest area

Table 3. 1988 Irrigation Costs

	Drip	Surge	Continuous
	----- dollars per acre -----		
System ¹	335(40in.)	31 ³	30 ³
Water ²	50	35	35
Irrigation Labor	13 ³	18 ²	18 ²
Cultural ²	325	394	394
Fertilizer	331	36	36
Fumegant	255	--	--
WWD Assessment	34	34	34
Taxes, Ins., Maintenance repair ⁴	108	8	8
Depreciation of Non- Irrigation equipment ³	47	47	47
Management	40	40	40
Land	<u>102</u>	<u>102</u>	<u>102</u>
Total	1,640	745	745

1. System cost using capital recovery factor over an eight year life at five percent real interest.
2. Information provided by Stone Land Company.
3. From UC Committee of Consultant Report, associated costs of drainage water reduction.
4. Calculated as five percent per year of initial capital cost of system.

Table 4. Estimated subsurface drip irrigation costs for 80 in. lateral spacing using "in line" and "RAM" drip tubing.

	RAM	IN LINE
	-----\$ per acre-----	
System	200	170
Water	50	50
Irrigation labor	13	13
Sprinkler preirrigation	10	10
Cultural	325	325
Fertilizer		
170 lb/A -N	42	42
132 lb/A-P ₂ O ₅	37	37
Fumigant	130	130
WWD Assessment	34	34
Taxes, Ins., Maint., Repair	65	55
Dep. Nonirr. Eqmt.	47	47
Management	40	40
Land	102	102
	<hr/> 1095	<hr/> 1055

PROJECT TITLE: CROP RESPONSE TO NONUNIFORMITIES OF SOIL WATER AND SALINITY FOR SUBSURFACE DRIP, SURGE, AND FURROW IRRIGATION SYSTEMS

PROJECT NUMBER: 87-5

DURATION OF FUNDING: July 1987 to June 1989

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RESEARCH STAFF:

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Staff Research Associate	No.: 2	FTE: 0.20	
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PROJECT COLLABORATORS:

Name: Stone Land Company
Location: Kings County, Stratford

ABSTRACT:

Nonuniformities of soil properties and infiltration rates were considered to be a major reason for the inefficiencies of some surface irrigation systems. The objectives of this study were to determine the spatial and temporal variability of soil water content, soil salinity, and crop response for three different irrigation systems: subsurface drip (SD), continuous furrow (CF), and surge furrow (SF); and determine if inherent non-uniformities in soil properties can be overcome by well-managed irrigation systems. The results for the 1988 season on fields in Kings County indicate that the variability of cotton plant height was related more to the variability in soil salinity than to water content. Cotton heights early in the season were more variable in the SD treatment. At the end of the season, the mean height was significantly greater and the variability lower than the furrow treatments. The number of squares, yellow and red flowers, bolls, and fruiting positions on plants were also measured along the

transect. They had no correlations with the total storage or water content of the 0-90 cm depth in the SD treatment. Correlations did exist, however, with the total storage and the water content of the 0-30 cm depth in the furrow systems. The soil layer above the emitter line in the SD treatment was maintained at the lowest mean water content when compared with the post-irrigation mean water contents in the furrow systems. There was also more variability around the mean in the SD treatment which could be due to differences in the location of access tubes from the buried emitters. In the depth below the emitter line, the mean water contents became more similar between the three treatments, and the variability was more affected by the water table than by the non-uniformity of water application.

Non-stationarities were generally present in all water content data mostly due to trends across the fields. The detrended data showed the storage to not generally be spatially correlated. However, in all treatments, the water contents of the 0-30 cm depth were generally auto-correlated up to 30.5 m away. The water contents of the 30-60 cm depth in the SF & CF treatments were generally auto-correlated up to 30.5 m away. No auto-correlations were observed in the SD treatment in the 30-60 cm depth.

Soil salinity was correlated up to 45.7, 15.2, and 26.7 m for SD, SF, and CF treatments, respectively. Weak periodicities in salt content were observed in all treatments and were believed to have been present in the soil prior to this experiment. Plant response to these periodicities were also weak but definite and were strongest for the SF treatment for which the mean soil salinity was also the highest.

PROJECT OBJECTIVES ADDRESSED:

1. Measure the spatial and temporal variability of soil-water content, soil salinity, plant characteristics, and crop yield for subsurface drip, surge, furrow irrigation systems.
2. Determine if the inherent nonuniformity of soil properties and infiltration can be partially overcome by well-managed irrigation systems.

RESEARCH PLAN AND PROCEDURES:

The field site is located in Kings County at the Stone Land Company near Stratford, CA. The soil is classified as a Westhaven clay loam. Based on field samples, the soil profile depth suitable for rooting exceeds 1.5 m and is stratified. The top soil layer (Ap horizon) is loamy textured, followed by about 80 cm of clay loam. A sandy clay loam layer lies below a depth of 90 cm. The depth to the water table exceeds 2.1 m. The field site is about 0.8 km west to east with a slope of 0.2-0.3 %. A north to south slope of about 0.2% also exists. The Westhaven series may have isolated saline-sodic soils.

The cotton crop is irrigated by three different irrigation systems: subsurface drip, surge, furrow, and continuous furrow. Each system irrigates a field consisting of 50 rows of cotton, 0.8 km in length. The drip irrigation system was installed at a depth of 45 cm with laterals spaced 2 m apart in alternate furrows and emitters spaced 1 m apart with a discharge rate of 4 L/h. Irrigation water with an EC of 0.4 dS/m is used for all three systems. Irrigations are scheduled using the CIMIS reference evapotranspiration from the West Side Field Station weather station and an established crop coefficient for cotton.

A transect of 50 neutron access tubes was installed in each of the fields for the three different irrigation systems along the 0.8 km length of field. Access tubes to a depth of 3 m were installed at a spacing of 15.2 meters. Soil-water content measurements were made several times during the growing season. In addition, plant height and soil salinity measurements using the electromagnetic device were made at 200 locations (spaced every 3.8 m) along the transects at several times during the season. Other measurements such as boll count etc were made at selected times.

RESULTS:

The data obtained after last year's report reinforces the conclusion that the variability around the mean of both total storage and the water content of the 0-30 cm depth was highest in the SD treatment. The major reason for this was thought to be the inconsistent location of access tubes in relation to the emitters. The SD treatment not only had the highest degree of variability in the water content above the emitters but had the least amount of temporal persistence in the spatial pattern of variability in this depth. Figure 1 shows the rank correlations between the first measurement of water content and each subsequent measurement for the 0-30, 30-60, and 60-90 cm depths for the 3 treatments. It shows that below the emitter depth, a higher degree of persistence of spatial pattern existed in the SD treatment. Table 1 shows that the surface 0-30 cm of the SD treatment remained driest of the 3 treatments. There was also a much higher variability in the mean soil water content in the SD treatment than the other two. Below this depth the gap in variabilities between the SD and the other two was eliminated, and in the 60-90 cm depth, the SD system had lower variability than the other two.

Table 2 shows the statistics for plant height, salinity and the 0-30 cm depth water content for the three irrigation systems. It shows that in the SD treatment plant height initially responded to the variability in water content. However, as the roots passed the top 30 cm of the soil and started drawing water from deeper depths, the variability in plant height decreased and became less than for the other two treatments. The plant population densities were not significantly different between the treatments. Therefore, it seems plausible that the early high variability in the plant height in the SD treatment was mostly due to the variability in the water content of the top 0-30 cm depth. This was also supported by the observations of temporal change in the rank correlations between plant height and storage in Table 3.

In Table 3, the percentage of concordant pairs refer to the percentage of pairs of data points with the same ranking in the two data sets. Table 3 shows that the plant height became less and less correlated with water storage as time increased during the season. As deeper soil layers were explored, more stable water supplies offset the effect of the early variability in the availability of water. For the SD treatment, plant height was correlated significantly with storage only on 7-5-88 and not later. The difference with CF and SF treatments was presumably due to the higher frequency irrigation in the SD treatment which kept water storage at a more stable level below the 0-30 cm layer.

Plant heights were significantly negatively correlated (-0.55, -0.37, -0.16 for SF, SD, & CF treatments, respectively) with the salinity. The ranking of the correlations follows the ranking in mean salt content among the three treatments (Table 2). An analysis of statistics regarding plant parameters

indicates that the plant's reproductive organs responded initially in similar ways to the irrigation treatments. However, about two weeks later, the SD treatment was clearly different than the other two. By the middle of August, the number of fruiting positions in SD was decidedly higher than the other two and had less variability. This was probably the major component which caused the higher yields in the drip treatment compared with the other two.

Much of the water content and storage data for all three irrigation treatments was quite nonstationary along the transects due primarily to changing water table depth from one end of the field to the other (Fig. 2). Detrended data and those cases which were fairly stationary, indicated autocorrelations on the order of 1 or 2 lags (1 lag=15.2 m) with much of the spatial dependence occurring at the surface 0-30 and 30-60 cm depths.

Even though generally no spatial correlations existed beyond 45.7 m distance for any of the parameters measured in this study, some periodicities present themselves in the periodograms of the variables. Figures 3 and 4 show the salinity and plant height periodicities for the CF treatment. Significance tests for periodograms usually give very large confidence intervals indicating non-significance for many peaks. However, periodograms are better indicators of deterministic processes in data than power spectrums for which better significance tests are available. Figures 3 and 4 indicate 262 and 78 m in the salinity, and 191 and 61 m in the plant height data to be the dominant periodicities. Analysis of other periodograms shows other peaks corresponding to other periodicities some of which were common between all 3 treatments. However, the periodicities which were most common among treatments and among parameters seem to fall in the 183-244 and 55-79 m range. Since low-salt irrigation water was used in all treatments, the periodicities in salinity were not due to water applications even though soil surface water content data show generally the same periodicities. Data on the physical characteristics of the soil along the transects are not available to decide whether the periodicities are the result of some cyclical behavior in the soil physical parameters or caused by salinity introduced into the soil as a result of agricultural practices previous to this experiment.

Plants responded to the cyclical behavior in salinity at all dominant frequencies. Figure 5 shows coherencies between the power spectrums of the salt content of the top meter of the soil and plant height for all three treatments. The horizontal line of each figure corresponds to the 95% confidence level. These indicate the salinity in surge to have the highest impact on the plant height as it has the highest coherencies at lower frequencies.

Other plant parameters measured were mostly correlated with salinity with all correlations being significantly negative. They were not generally correlated with storage in the SD treatment. In the furrow systems, positive significant correlations developed with the 0-30 cm water content by the end of July.

DISCUSSION AND SUMMARY:

Variability in soil-water content, soil salinity, and several plant parameters were evaluated in fields irrigated by three different irrigation systems; subsurface drip, continuous furrow, and surge furrow. It has been observed visually that the growth of cotton varied between these irrigation systems.

The expected differences have been attributed to variability in infiltration and salinity leaching. This study was undertaken to evaluate the extent of spatial and temporal variability of important soil physical characteristics and how that variability may be related to crop response.

Mean cotton plant height at the end of season was significantly higher in the SD than in the furrow systems where the heights were not significantly different from each other. Variability was much lower in the SD than in the other two treatments. On the other hand, the variability of the water content in the surface 0-30 cm of the SD system was greater than the other two. This seems to have affected plant height early in the season. Later when the plants' roots were beyond the top 30 cm of soil, they encountered a more uniform availability of water in the SD than the other two treatments, and many of the plants recovered. Therefore, over the length of the season and for a deep rooting plant like cotton, the SD treatment seems to provide a more favorable growth environment. However, no large increase in yield was observed in SD over the furrow systems. The yields in the SD, SF, and CF treatments were 1.59, 1.43, and 1.44 MT/Ha, respectively. No statistical comparisons can be performed to ascertain whether the yields are statistically different.

The water content of the 0-30 cm depth in all treatments was more correlated with the plant development parameters than any other depth. As such, the effects of variability in water content on plant response were observed to be greatest in the SF and CF treatments where periods of dry and wet conditions alternate at the soil surface layers.

Plant response was more correlated with salinity than water content. The amount of salts (EC) in soil of the treatments was much less than the established threshold value for cotton. However, plants seemed to respond to these low levels of salt. Chemical or physical processes other than EC associated with salinity may be influencing plant growth. Whenever correlations between any of the plant parameters and salinity were significant, they were negative.

Some periodicities seem to dominate the variabilities in the salt content. These periodicities were similar in all three treatments. Even though no clear conclusions could be reached about the cause of this, plant response followed a similar cyclical pattern.

Table 1. Temporal mean of the spatial mean of the water contents of the 0-30, 30-60, and 60-90 cm depths of the 3 treatments.

Depth, cm	SD*			CF†			SF†		
	Mean (cm ³ /cm ³)	Std dev	C.V.%	Mean (cm ³ /cm ³)	Std dev	C.V.%	Mean (cm ³ /cm ³)	Std dev	C.V.%
0-30	18.8	4.3	22.9	32.8	2.1	6.4	34.5	2.1	6.1
30-60	34.4	2.1	6.1	37.1	1.4	3.8	37.5	1.5	4.0
60-90	36.8	1.4	3.8	33.3	3.0	9.0	34.7	2.7	7.8

* Excludes the last 4 measurements when irrigation had been stopped.

† Includes only measurements taken immediately after each irrigation.

Table 2. Statistics for plant height, salinity as measured by the electromagnetic probe in vertical direction, and the water content of the 0-30 cm depth for the three irrigation systems.

Irrigation System	Plant Height (m)	θ_{0-30} (cm ³ /cm ³)	Plant Height (m)	θ_{0-30} (cm ³ /cm ³)	Soil Salinity (dS/m)	Plant Height (m)	θ_{0-30} (cm ³ /cm ³)
Date	7-5	7-1	7-19	7-20	7-20	9-7	9-1
SD							
Mean	0.57	13.4	1.05	17.5	4.1	1.47	17.3
Variance	0.009	27.9	0.008	70.5	0.758	0.018	39.8
C.V. %	16.6	39.4	8.3	48.0	21	9.1	36.5
Date	7-5	6-27	7-20	7-15	7-15	9-7	9-15
CF							
Mean	0.63	30.0	0.94	35.2	3.8	1.13	12.1
Variance	0.003	4.0	0.008	15.9	0.633	0.026	5.9
C.V. %	9.1	6.7	9.7	11.3	21	14.2	20.1
Date	7-5	6-27	7-20	7-15	7-15	9-7	9-15
SF							
Mean	0.57	15.3	0.94	16.5	4.4	1.08	14.7
Variance	0.006	5.9	0.007	11.7	0.742	0.03	10.3
C.V. %	13.1	15.9	9.1	20.7	19.5	16.2	21.8

Table. 3 Rank correlations between plant height and storage for the three treatments.

Tmt	Plant ht Date	& Storage Date	Rank Corr.	P-value	% of Concordant Pairs
CF	7-5-88	& 7-11-88	0.32	0.00	66
	7-20-88	& 7-15-88	0.46	0.00	73
	9-7-88	& 9-15-88	0.12	0.20	50
SF	7-5-88	& 7-7-88	0.44	0.00	72
	7-20-88	& 7-14-88	0.24	0.01	62
	9-7-88	& 9-8-88	0.06	0.53	50
SD	7-5-88	& 7-1-88	0.33	0.00	66
	7-19-88	& 7-20-88	-0.05	0.63	50
	9-7-88	& 9-1-88	0.04	0.72	50

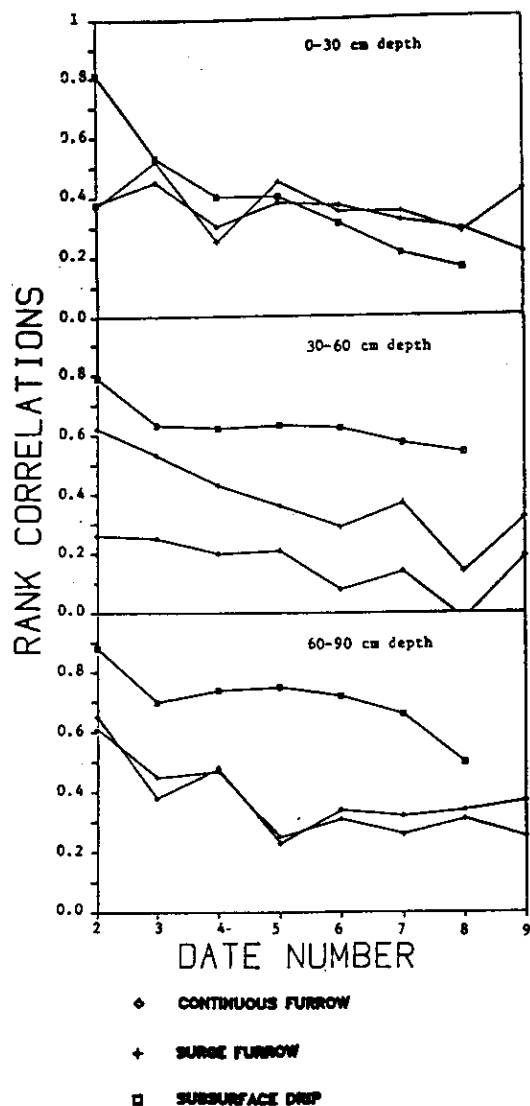


Fig. 1. Rank correlations between the water contents on the first measurement day and each subsequent measurement.

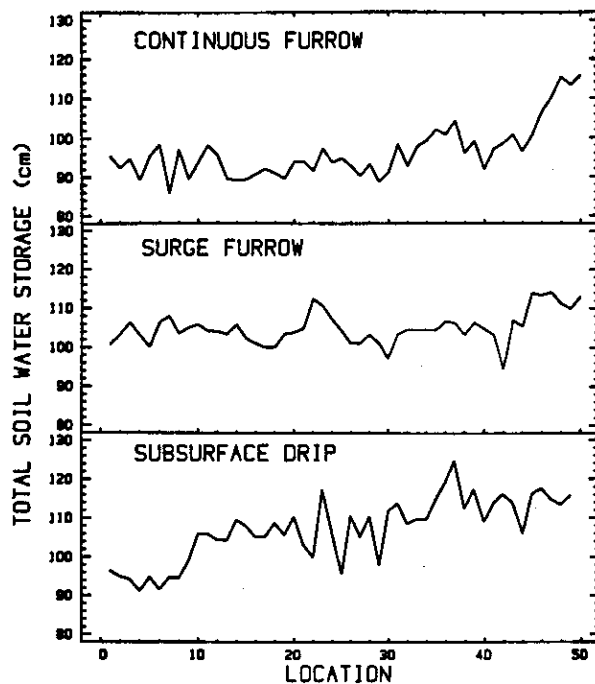


Fig. 2. Total soil water storage as a function of location along transects in mid July 1988.

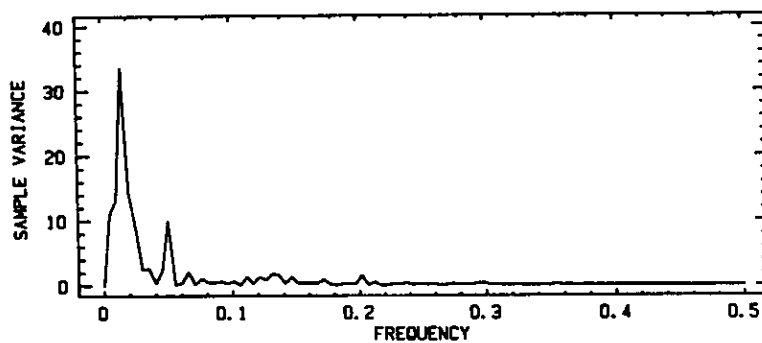


Fig. 3. Periodogram for salinity measured in vertical direction in the continuous furrow treatment on 7-20-88.

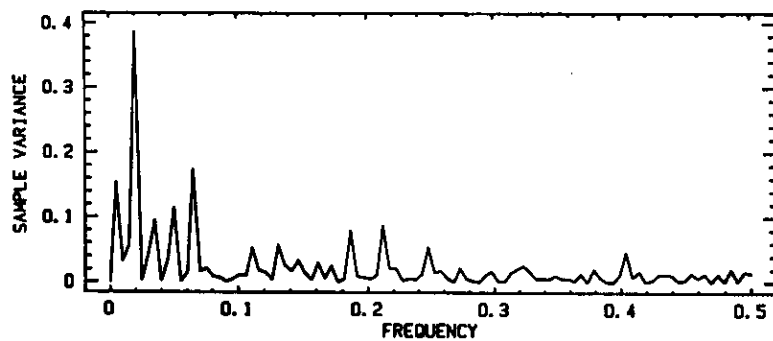


Fig. 4. Periodogram for plant height in the continuous furrow treatment on 7-20-88.

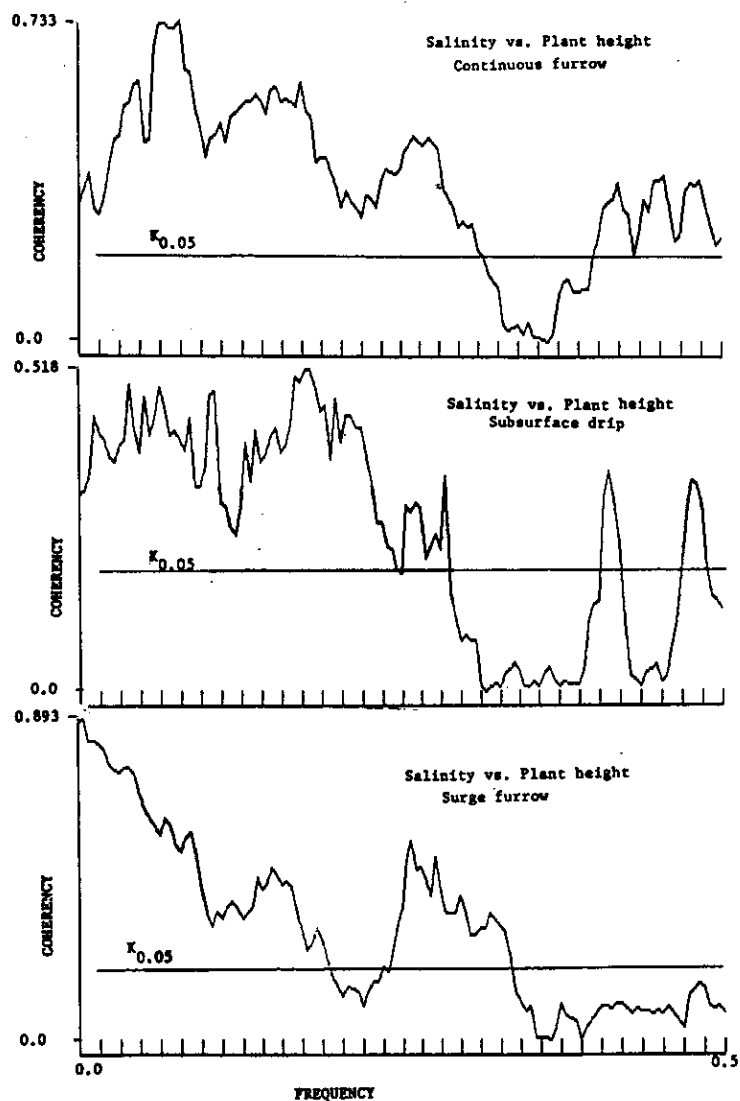


Fig. 5. Coherency spectrum between the salinity and plant height for the three treatments. X-axis tick spacing = 0.015625 cycles/point.

PROJECT TITLE: IRRIGATION WATER SURCHARGES: AN INTRASEASONAL APPROACH

PROJECT NUMBER: 88-9

DURATION OF PROJECT: July 1988 - June 1989

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ABSTRACT:

This study focuses on an intraseasonal analysis of irrigation water surcharges. Although economic theory shows that two-tiered pricing systems are economically efficient and can substantially reduce surcharge payments, the dynamic nature of agricultural production presents a unique problem for tiered pricing systems.

The theoretical model indicates that grower response differs depending upon whether a seasonal tier or an intraseasonal tier is employed. In general, an intraseasonal two-tiered pricing system can meet specified environmental goals while lowering the social costs of environmental protection.

The project will also generate empirical estimates of growers' responses to different types of two-tiered pricing strategies. A simulation model of agricultural production is near completion; estimates of the price elasticity of irrigation water demand by stage of the growing season are now being developed.

PROJECT OBJECTIVES ADDRESSED:

According to economic theory, irrigation water surcharges can mitigate environmental damages, such as selenium contamination, from drainage water. Empirical studies indicate that the social costs of drainage water reductions are not large, but growers would bear substantial costs to defray them when they are manifested as irrigation water surcharges. Given the already precarious financial condition of agriculture, the merits of surcharges are questionable. However, a two-tiered pricing system can retain the economic efficiency properties of seasonal surcharges while reducing surcharge payments. A tiered pricing system would allow growers to purchase a given amount of irrigation water at a base price and additional amounts at the base price plus the surcharge. Since only a portion of irrigation water purchased is surcharged (rather than all irrigation water), surcharge payments would (other things equal) be significantly lower.

The available literature on tiered pricing systems deals with static rather than dynamic production processes. For many environmental problems (for example, air pollution), the static view of production is a reasonable assumption. Agricultural production is typically dynamic in nature - growers adjust input use at different stages of the growing season based on the state of the crop. For example, irrigation water applications late in the season are dependent (in part) on how well the crop has done thus far, which is itself a function of previous irrigation water use and random disturbances such as unusually cool or hot weather.

This project examines tiered pricing systems for the purpose of drainage water management. The

project objectives include:

1. analysis of a theoretical model of tiered pricing with dynamic production
2. construction of a simulation model of grower behavior with tiered pricing.

The theoretical analysis is complete. Substantial progress on the simulation model has been made. Statistical analysis of recently available data is continuing prior to further work on the simulation model.

RESEARCH PLAN AND PROCEDURES:

The theoretical work analyzes growers' behavior under alternative tiered pricing systems (see Stevens and Vaux, 1989). The optimal use of irrigation water is examined for a surcharge with three tiers:

1. a surcharge with no tier
2. a surcharge with a seasonal tier
3. a surcharge with an intraseasonal tier

Suppose, for example, that the irrigation season consists of two time periods. With a \$1 per acre-foot surcharge, a grower uses 100 acre-feet in the first time period and 200 acre-feet in the second time period. Under the first policy, the surcharge is paid on all irrigation water purchased. Under the second policy, the seasonal tier allows growers to purchase water at the base price, in each time period, so long as total water use up to that point of the growing season (including the present time period) does not exceed a seasonal allowance. For example, if the seasonal allowance is 250 acre-feet, the grower pays the base price in the first time period and the surcharge of \$1 on the last 50 acre-feet purchased in the second time period. Under the third policy, the intraseasonal tier specifies an allowance for each time period, instead of the entire growing season. Growers pay a base price in each time period and a surcharge on excess water in each time period. Thus, if the allowance in the first time period is 75 acre-feet and 175 acre-feet in the second time period, the grower pays a surcharge of \$1 on the last 25 acre-feet used in each time period.

RESULTS:

A two period model similar to Antle (1983) is analyzed. This model assumes sequential decision-making for irrigation water applications and random disturbances that affect production. Growers choose an irrigation water quantity in period 1 and then choose an irrigation water quantity in period 2 based on the crop state at the end of period 1. The crop state at the end of period 1 is a function of irrigation water applied in period 1 and the random disturbance. The decision-maker is assumed to be risk-neutral and therefore chooses input(s) in each time period to maximize expected profit.

A comparison of the decision-rules for choosing inputs in each time period shows that the surcharge and the intraseasonal tiered surcharge have identical decision-rules. Thus, the tiered pricing system, in this case, reduces surcharge payments but the grower's irrigation water use (in each time period) is the same with or without the water allotment. Policy-makers can therefore treat the issue of how much pollution to control - via the size of the surcharge - independently from the issue of the magnitude of total surcharge payments. However, the seasonal tiered surcharge differs from the other

two policies with respect to the decision-rule in the first time period but not the second time period. With the seasonal tiered surcharge, the grower faces a higher expected marginal factor cost in period 1 compared to the other two policies. Other things equal, this would reduce period 1's output and would affect input use in time period 2 (regardless of the similarity of the decision-rules). Intuitively, the decision-rule for the seasonal tiered surcharge differs because of the dynamic nature of production - in period 1, the decision-maker is aware that an increase in irrigation water use in the present uses up more of the seasonal allotment. Thus, additional irrigation water use now has an additional implicit present cost equal to the second period surcharge. The grower will have to pay a surcharge on a larger amount of "excess" water in the second time period since more of the seasonal allowance has already been used up. For this type of surcharge, the attempt to reduce surcharge payments affects the grower's irrigation water use (and thus, the amount of pollution controlled).

DISCUSSION AND SUMMARY:

Our results suggest two important conclusions. First, ignoring the dynamic nature of irrigated crop production when implementing a tiered pricing strategy may lead to unanticipated responses to the policy. In particular, a larger reduction in irrigation water use will occur early in the growing season for a seasonal tiered pricing strategy relative to a surcharge or an intraseasonal tiered surcharge. Moreover, this effect is magnified if there are more than 2 time periods since the implicit cost from future surcharges is higher in earlier time periods. For example, growers typically apply water to cotton three to five times per season. Second, if the timing of drainage water flows is important from an environmental perspective, the reduction in drainage water flows could occur at an inopportune time of the calendar year. For example, regulation of drainage into the San Joaquin River for the purpose of controlling selenium concentrations could be quite sensitive to the timing of drainage flow reductions. This is clearly an important issue since the water quality standard for selenium concentrations is not an annual (average) standard.

The theoretical work suggests that any tiered pricing policy must recognize the dynamic aspect of agricultural production. Indeed, it is possible that the social costs of a poorly designed tiered pricing system may be larger than a non-tiered surcharge policy. The purpose of a tiered pricing system is to relieve growers of some of the financial burden of surcharges. In achieving this goal, policy-makers do not want to increase the costs of drainage water management to the rest of society.

Empirical analysis of tiered surcharges is continuing. One issue not addressed by the theoretical work is the magnitude of social losses imposed by poorly designed tiered pricing systems. In addition, the surcharge need not be the same in all time periods. We hope to be able to develop some theoretical and empirical analysis addressing the optimal pattern of surcharges over the growing season when environmental constraints are present. This issue seems particularly important given empirical evidence (see Antle and Hatchett [1986]; Dinar, Knapp and Rhoades [1986]) that the price elasticity of demand for irrigation water varies considerably over the growing season.

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PROJECT TITLE: SOIL SPATIAL VARIABILITY CONSIDERATIONS IN SALT EMISSION AND DRAINAGE REDUCTION

PROJECT NUMBER: 88-13

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ABSTRACT:

A better understanding of soil physical properties and their variability, especially as they relate to infiltration and the transport of salt and water within the soil profile, is necessary to develop optimal management strategies to reduce drainage and emission of salts. After measurement of soil hydraulic properties at 50 locations within a farmers field, these will be introduced in numerical models to assess the spatial distribution of drainage losses and the salt profiles following each irrigation event. Field measurements of water content and salinity will be used to verify the model results. From independent infiltration measurements during the irrigation events, we will be able to connect a surface hydraulic model with a subsurface water and salt transport model. Stochastic modeling will be used to evaluate best management practices targeted to reduce drainage and salt emissions. For example, field size may be adjusted to meet salt emission criteria within engineering and economic constraints.

KEYWORDS: salt, drainage, soil spatial variability, infiltration

PROJECT OBJECTIVES ADDRESSED:

1. To investigate whether soil spatial variability consideration in drainage and irrigation management may reduce mass emission of salts by decreasing drainage.
2. If mass emissions can indeed be significantly reduced in the experimental field, it remains further to be investigated whether a large number of soil physical measurements can be carried out routinely and quickly.
3. To determine if the costs of the proposed irrigation management practices, including intensive soil sampling, are acceptable from an engineering and economic perspective.

RESEARCH PLAN AND PROCEDURES:

At the suggestion of Bill Weir, a farm advisor in Merced County, we selected the Neves Brothers ranch in Los Banos as the location for the field study. This field was of special interest since soil textures varies widely from silty clay soils in the western corner to loamy sand and sandy soils in the northeastern corner and northern side of the field. Textural analysis is given in Table 1 for locations marked in Figure 1. The 53-acre cotton field (Figure 1) is furrow irrigated south to north with furrows spaced at 40 inches. Thus far the preirrigation (3/5 - 3/9/89) and the first and second irrigations (6/22 - 6/24 and 7/17 - 7/19, respectively) have been monitored.

Seven monitoring furrows were established to characterize the hydrology of the field. These furrows were evenly spaced with 128 rows between each. In each monitored furrow, aluminum neutron probe access pipes were installed with a fixed spacing of 36 m. Table 2 shows the number of pipes in each of the 7 furrows for a total of 51. Despite the large variability in soils, one calibration curve was representative of the field. At selected time intervals before, during and after each irrigation event neutron probe readings were taken at depths of 15, 30, 45, 60, 75, 90, 105, 120, 135 and 150 cm. Changes in total water stored over time gave infiltration amount along the furrow.

Soil samples were collected in 6 cm height and 8.5 cm diameter cores near each of the 51 aluminum access pipes. The samples were collected to allow measurement of the water retention and unsaturated hydraulic conductivity curves and their variation within the field.

At the head and tail end of each of the monitoring furrows, 3m long PVC-pipes were driven into the ground. From these, groundwater level was measured during and between irrigations.

In addition to measuring water content and groundwater levels in each access tube row, infiltration was measured in a furrow near each of the access tube rows and at locations along the row corresponding to every other aluminum access pipe. Infiltration measurements were started when the advance front had reached the location to be measured and lasted until the irrigation in the monitoring furrow was stopped or steady infiltration was reached. Thus, during each of the three irrigation events, between 20 and 30 infiltration tests were taken which each lasted between a few hours to half a day, depending on the position along the monitoring furrow.

Infiltration was measured with a bypass furrow infiltrometer during the pre-irrigation and a flow-through bypass infiltrometer during the two subsequent irrigations. Metal infiltrometers were 100 cm long and 50 cm wide. The long side was at the centerline of the furrow and the short sides returned to the seed bed allowing the flow to pass around the outside of the infiltrometer. Within the confined area, the remaining long side was open along the bed to allow lateral flow. For the preirrigation, infiltration rates were determined from measurements of cumulative water added through time to raise the inside water depth up to the outside depth.

In preparation for the second and third irrigations, holes were installed in the infiltrometers to allow water to flow through and therefore more closely simulate field conditions. These 9.0 cm diameter holes were stoppered for an infiltration measurement, but open otherwise. Infiltration rate during short times was calculated directly rather than by differentiating the cumulative function as

for the preirrigation. Advantages of the flow-through infiltrometer are that the geometry, sedimentation, and roughness of the furrow inside is similar to the outside since the flow inside is not zero and that each infiltrometer station can be left unattended between measurements.

In addition to the infiltration tests, time for the water to advance to and recede from locations along the furrow gave intake opportunity time. This time was substituted into the infiltration functions to calculate infiltration amount.

RESULTS:

Moisture content decreased with depth to 75 cm and became relatively constant at the south end of monitored furrow 5 (head end, location designation 5-1) before the preirrigation (Figure 2). During the first 3.3 hours of preirrigation, water content increased more slowly at 15 cm than at the 30 to 60 cm depths because water transport was by matric potential gradients without gravitational force and was only in the smaller pores since flow was unsaturated. The increase in stored water was large between 30 and 60 cm but the increase was less deeper in the profile because the soil was already moist before irrigation. Infiltration decreased as shown by the small increase in water content between 3.3 and 7 hours. By waiting until two hours after the 22-hour irrigation, before taking another set of moisture readings, an increase in water content was measurable to 155 cm. The decrease in water content of the upper profile during the week following irrigation is primarily caused by drainage since evaporation rate low during late winter.

Soil moisture before the preirrigation was less at the tail end of furrow 5 (location 5-9, Figure 3) than at the head end (Figure 2). Irrigation raised water content at the tail end to approximately the same as the head end, therefore more water was infiltrated at the tail end. Again, probe readings taken one and two weeks after irrigation show drainage from the upper profile.

Total soil water before and after irrigation is shown in Figure 4 for all monitored locations along furrow 5 to illustrate both the dramatic decrease in storage downstream of location 4 and the similarity in storage after the irrigation. The storage increase along the furrow (Figure 5) may be related to an increase in sand content which caused greater infiltration. Average change in water storage along the furrow was 33 cm which agreed with an estimate of total water intake to the field. Runoff, which was difficult to measure, was not included in these calculations, however.

Groundwater level at the upstream (Figure 6) and downstream end (Figure 7) began to rise before furrow 5 was irrigated on 6 March. Recharge from the delivery and runoff collection ditches, and seepage from other already irrigated sets most likely contributed to the rise. The watertable was consistently higher at the downstream end and rose sharply to within 25 cm of the soil surface during irrigation. The dramatic rise of the groundwater to near the surface is congruent with the relatively uniform high water contents with depth and distance along the furrow measured with the neutron probe (Figures 2 and 3, and Figure 4). Furthermore, the high water contents would not be possible in the sandy soils near the downstream end without the existence of a high watertable.

During the 22-hour preirrigation, cumulative infiltration was measured for 2 to 8 hours at half minute intervals at the beginning of the test and later at 10 minute intervals. A branched function

was fitted to the measured data with the first three hours fitted to a modified Kostiaikov equation and thereafter using the steady infiltration rate value (Figure 8). Integrating this function gave infiltration depths 2 to 3 times greater than water diverted into the field. This overprediction of infiltration could be attributed to measurement error caused by excess lateral flow out of the bypass infiltrometer through the bed. The field was ripped before the pre-irrigation, thereby allowing infiltrated water to seep away to adjacent furrows. In addition, because the infiltration tests were not run for the full 22 hours of irrigation, the steady infiltration rates shown may have been too high.

Infiltrimeters were modified to allow water to flow through the test area during the first and second irrigation. For each infiltration measurement the holes were stoppered, volume of water added was measured one to three consecutive times and an average infiltration rate was calculated. A modified infiltration function was fitted to the data (Figure 9) and integrated over intake opportunity time to find cumulative infiltration shown in Figure 10. Intake opportunity time was found by subtracting recession time from advance time (Figure 11). Infiltration rate and intake opportunity time were less for the first irrigation compared to the preirrigation and predicted infiltration depth was 22.8 cm compared to a field diversion of 22.5 cm.

DISCUSSION AND SUMMARY:

The hydrology of an irrigated field planted to cotton is being investigated with special interest in reducing drainage and salinity. Soil moisture, groundwater table and infiltration measurements are used to characterize the transport and storage of water and solutes in the vadose and saturated zone. Salinity, prior to irrigation is shown in Table 1. Soil samples will be taken at the end of the season to study changes in the profile in conjunction with water transport.

During the preirrigation, much of the applied water contributed to a dramatic rise in the watertable. This rise in groundwater level gave a nearly constant water distribution with depth and distance despite large changes in soil texture.

Attempts to measure infiltration during the preirrigation were less successful than for the first and second irrigations. Infiltration measured with infiltrometers for the preirrigation was 2 to 3 times greater than was diverted into the field. For the second irrigation, water diverted matched measured infiltration.

In conclusion, excess water was applied during the preirrigation and the magnitude of excess application will be the focus of further data analysis on this and later irrigations.

TABLE 1. Soil textural analysis and saturation extracts of 5 locations within Neves Bros field (3/24/89).

Site Location	Depth cm	sand %	silt %	clay %	EC _{ex} (dS/m)
1 Southwest	20	13.5	34.3	52.2	1.01
	50	17.9	44.5	37.6	1.46
	90	6.6	49.0	44.0	1.90
	120	9.7	35.9	54.4	2.56
	160	5.3	38.8	55.8	2.34
2 Center South	30	57.5	16.4	26.1	0.71
	60	52.5	21.1	26.4	0.94
	90	44.7	31.0	24.3	1.65
	120	40.0	36.3	23.7	1.75
	160	48.1	34.8	17.1	2.28
3 South East	30	37.8	26.8	35.4	1.02
	60	28.0	31.2	40.8	1.10
	90	36.2	43.3	20.4	1.71
	110	38.8	42.6	18.6	1.48
	150	41.5	40.7	17.7	1.20
4 North East	30	66.4	16.9	16.7	0.59
	60	64.2	18.2	17.6	0.48
	90	49.9	39.2	10.9	0.59
	120	82.1	11.3	6.6	0.66
	150	81.3	13.6	5.1	1.11
5 North Center	30	46.6	29.1	24.4	2.94
	60	86.6	8.5	4.9	0.61
	100	91.6	4.4	4.1	0.40
	130	93.8	3.1	3.1	0.93
	170	91.2	5.7	3.1	1.70

TABLE 2. Distribution of aluminum access pipes in monitoring furrows.

Monitored furrow	Length (feet)	Access pipes no.
1 (west)	270	3
2	490	5
3	840	7
4	930	9
5	1020	9
6	1125	9
7	1016	9

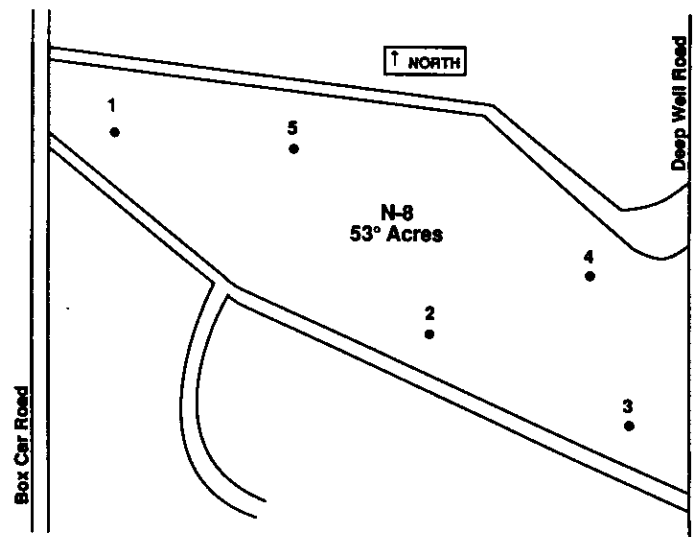


Figure 1. Schematic of field showing soil sample location.

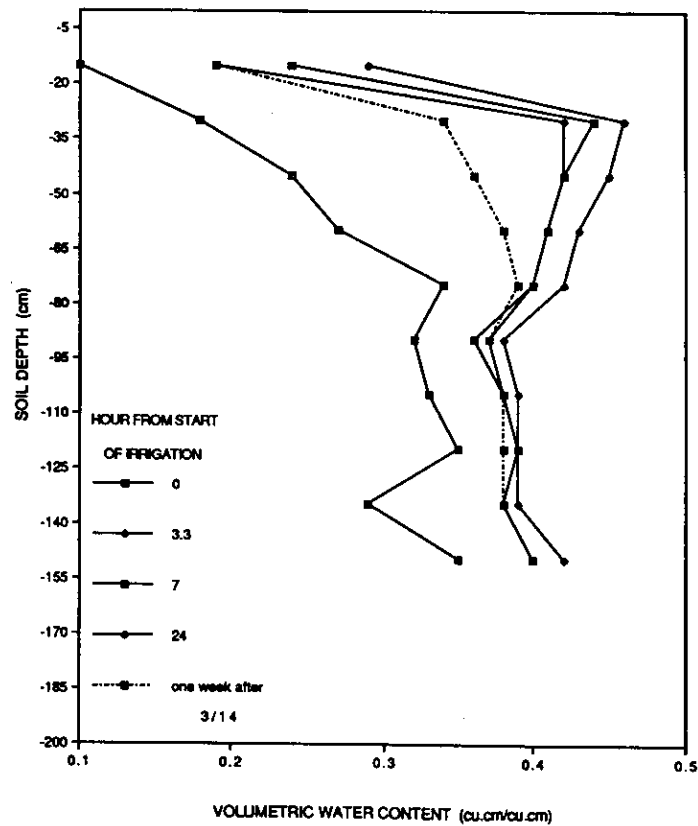


Figure 2. Soil moisture profile before during and after preirrigation at the head end of monitored furrow 5 (location 5-1).

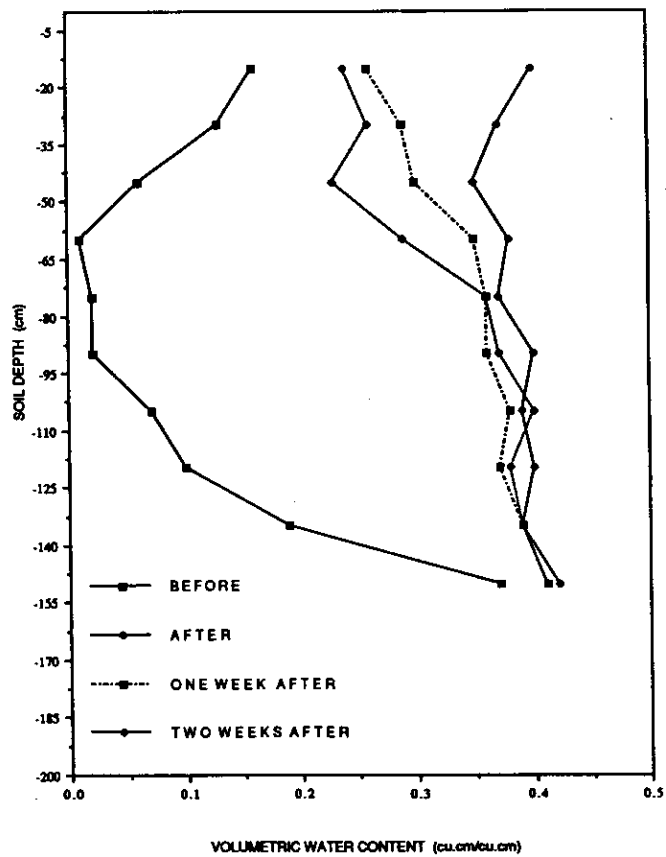


Figure 3. Soil moisture profiles before and after preirrigation at the tail end of monitored furrow 5 (location 5-9).

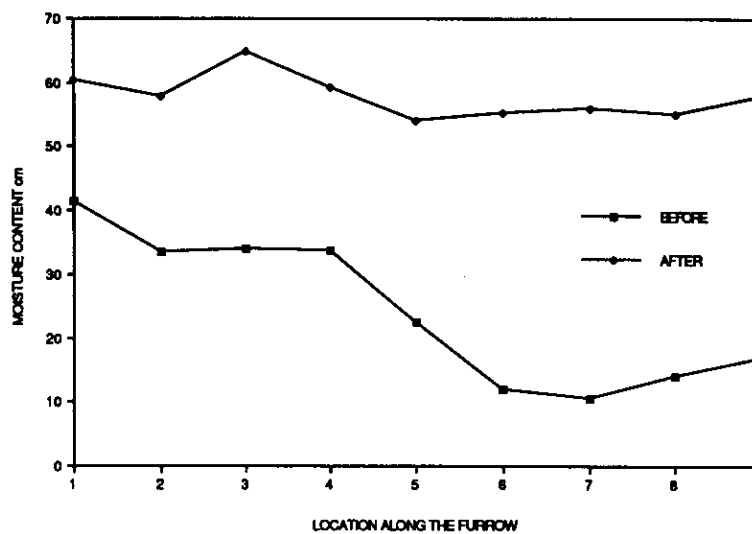


Figure 4. Total soil water before and after preirrigation along monitored furrow 5.

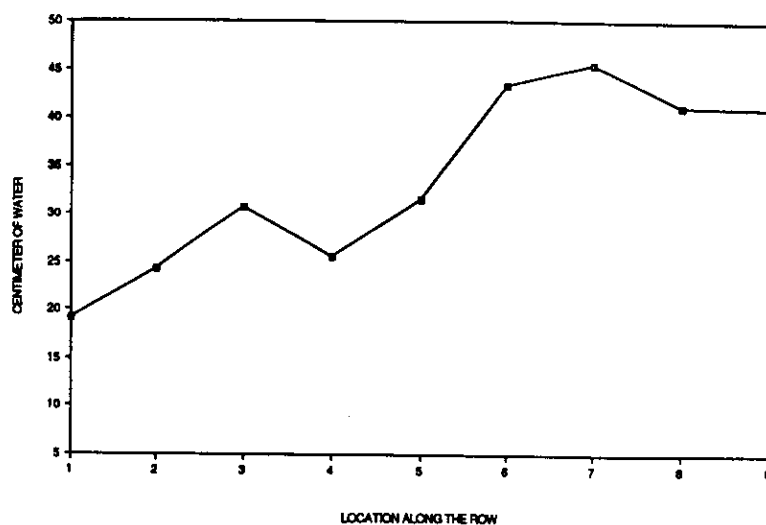


Figure 5. Change in total moisture storage from preirrigation along monitored furrow 5.

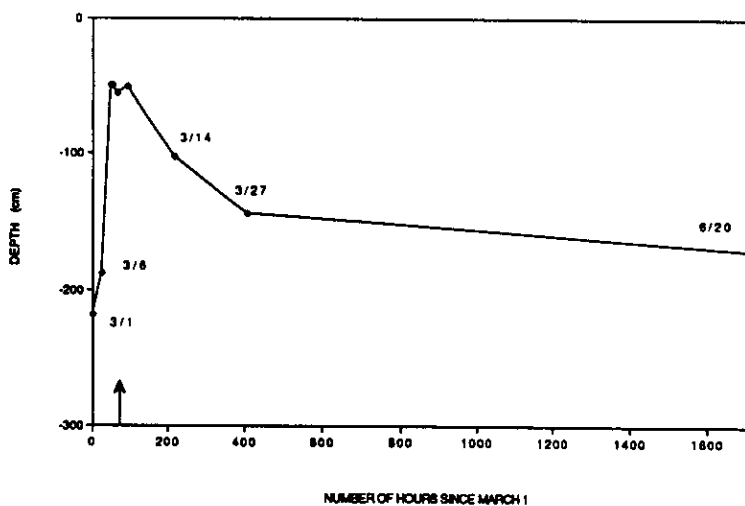


Figure 6. Groundwater depth at monitored furrow 5 location 1.

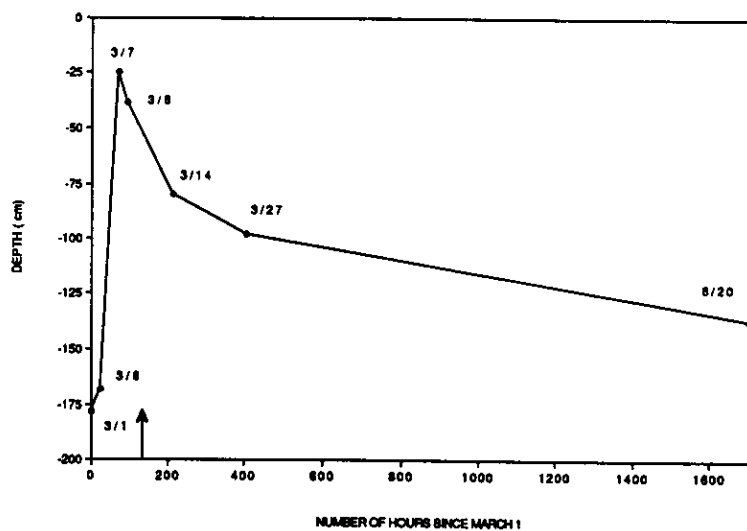


Figure 7. Groundwater depth monitored at furrow 5 location 9.

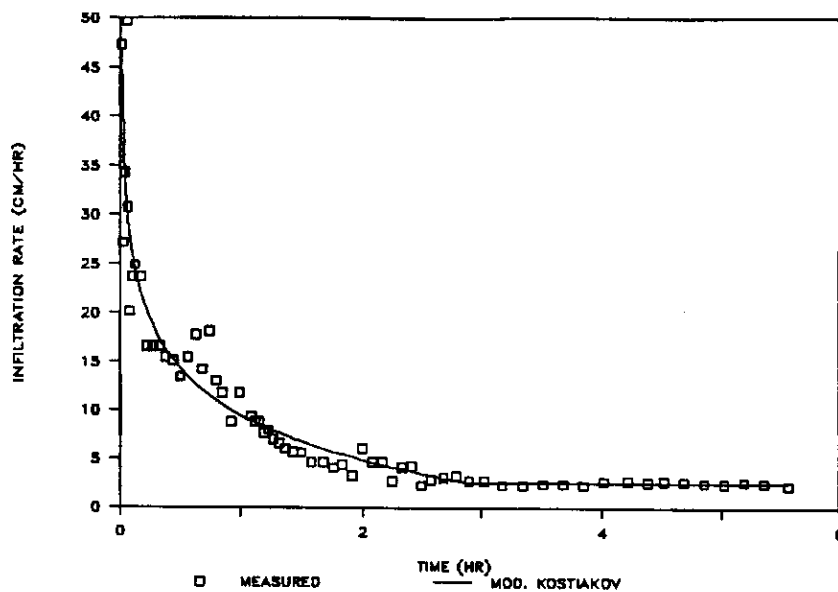


Figure 8. Infiltration rate curve for monitored furrow 5 location 1, preirrigation.

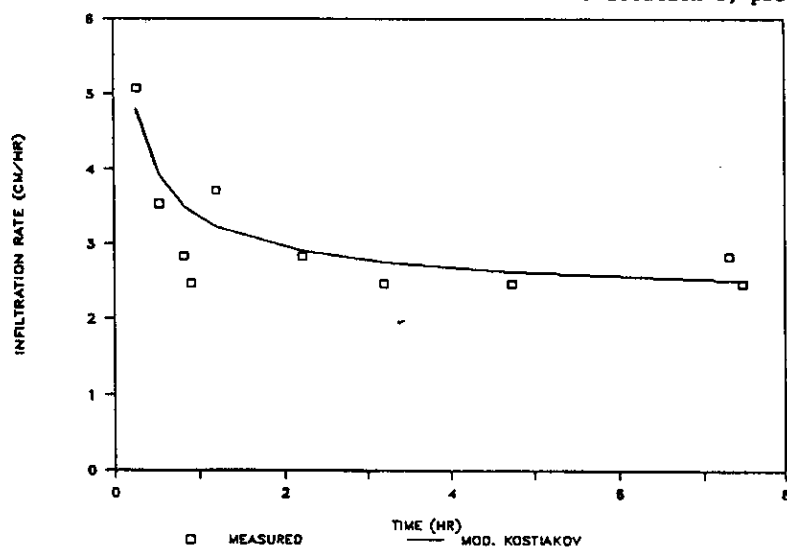


Figure 9. Infiltration rate curve for monitored furrow 3 location 1, irrigation 1.

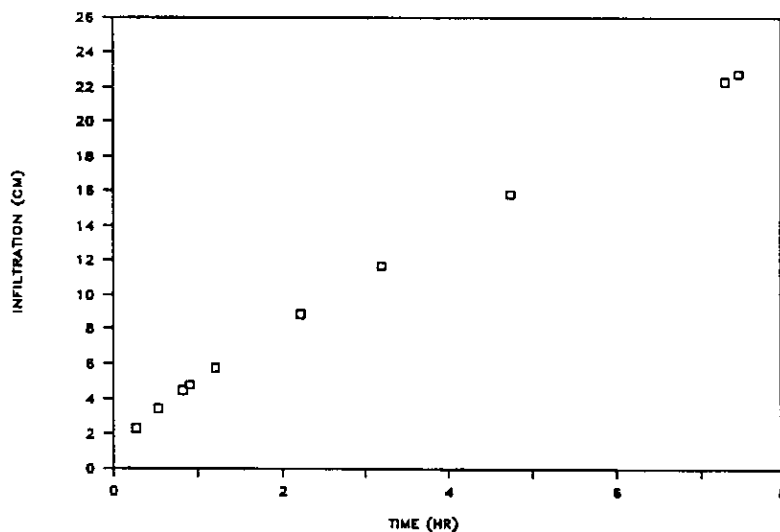


Figure 10. Cumulative infiltration for monitored furrow 3 location 1, irrigation 1.

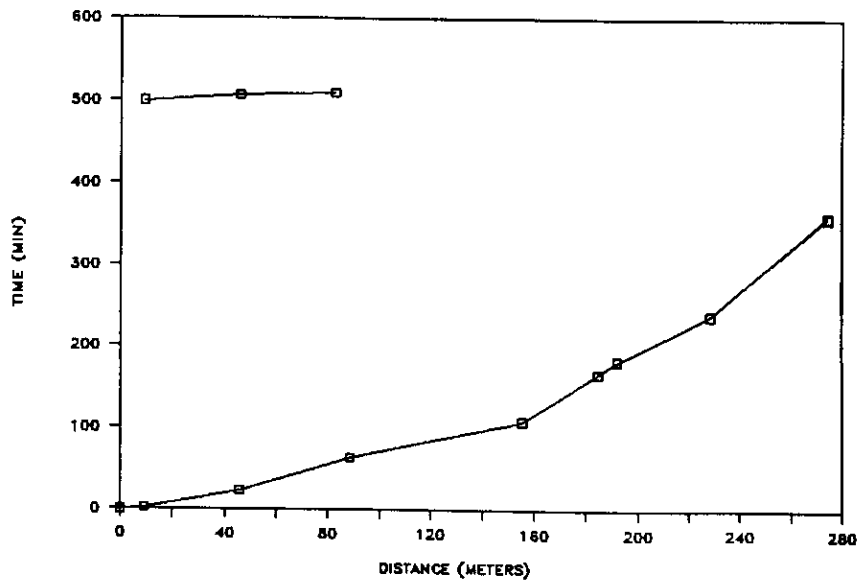


Figure 11. Advance and recession time along monitor furrow 3, first irrigation.