2002-2003
Technical Progress
Reports

University of California

Salinity/Drainage Research Program
and Prosser Trust

Division of Agriculture and Natural Resources
University of California

October 2003

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FOREWORD

The UC Salinity/Drainage Program was initiated in 1985 to develop, interpret and disseminate research knowledge addressing critical agricultural and environmental problems of salinity, drainage and toxic trace elements in the West Side of the San Joaquin Valley in California.

The Water Resources Center and the Salinity/Drainage Program were administratively combined with the UC Center for Water Resources in 1993. John Letey serves as Director of the Center for Water Resources and is the coordinator of the Salinity/Drainage Program. He also has administrative responsibility for the Prosser Trust Fund. This report documents the 2002-2003 accomplishments of the Salinity/Drainage Program and Prosser Trust Fund.

A major function of the UC Salinity/Drainage Program is to support research and extension activities that will contribute to developing optimal management strategies to cope with salinity/drainage/toxics problems in the western San Joaquin Valley. Funded research projects must be both relevant and scientifically sound. An external advisory committee consisting of individuals listed on page iv evaluates the relevancy of proposals. Appreciation is expressed to all the individuals that devoted time and made valuable contributions to the selection of the research to be supported.

The Prosser Trust Fund, which is administered through the Salinity/Drainage Program, funded several of this year's projects. Joseph G. Prosser and his son developed the tensiometer as a soil water-sensing device. Subsequent relationships he developed with scientists at the Citrus Experiment Station in Riverside, led to his providing the University of California an endowment to support the development of efficient irrigation activities. The annual income from this trust fund is distributed for research and extension activities pursuant to the terms of the trust.

The annual Salinity/Drainage Program meeting was held March 26, 2003, in Sacramento. The United States Bureau of Reclamation (USBR) San Luis Drainage Feature Evaluation was the main focus of the meeting. Jason Phillips of USBR presented an overview. Components of the Plan included drain water reuse for irrigation, water treatment, and evaporation ponds. Technical reports were presented on each of these topics. Posters of the U. C. Salinity Drainage and Prosser Trust funded research projects were available at the meeting with principle investigators available for discussion. The full research reports on each project are contained in this report.

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Salinity/Drainage Annual Meeting

March 26, 2003

8:15 am	**Welcome, John Letey**, Director, UC Center for Water Resources
8:30	**Wes Wallender, Jan Hopmans, Richard Howitt**, UC Davis Water and Land Management in Irrigated Ecosystems
9:30	**Jason Phillips**, USBR Overview of the San Luis Drainage Features Re-Evaluation
9:50	***BREAK – Posters***
10:20	**<u>Drain Water Reuse for Irrigation</u>**
	Roger Burnett, USBR Soils Investigation at Potential Reuse Sites
	Joe McGahan, Summers Engineering Regional Reuse in the Grassland Drainage Area
	Steve Kaffka, UC Davis
	Steve Grattan, UC Davis Crop Selections for Drainage Water Use
11:30	**Scott Irvine**, USBR RO Treatment of Reused Drainage Water
12:00 pm	***LUNCH – Posters***
1:15	**<u>Selenuim Treatment Technology</u>**
	Brad Walquist, Applied Biosciences Corp. ABMet Biological Water Treatment Process
	Tryg Lundquist, Lawrence Berkeley Laboratory Panoche Algael – Bacterial Selenuim Removal
	Carla Scheidlinger, Agrarian Co. Open Channel Biobarrier for Selenuim Removal
2:15	**Susan Hootkins**, URS Corp. Environmental Impact of Drain Water Management
2:45	***BREAK – Posters***
3:15	**<u>Evaporation Pond Issues</u>**
	Charles H. Hanson, Hanson Environmental Inc. Evaporation Pond Compensation Evaluation
	Joe Skorupa, USFWS Drainage Solution for the San Joaquin Valley: The View From a Wildlife Biology Perspective
4:15	**Open Discussion**

Interaction of Se Biogeochemistry with Foodchain Disruption in Full-Scale Evaporation Basins and Pilot-Scale Drain Water Systems

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Staff:

2 PGR
1 volunteer SRA
1 professional series researcher

ABSTRACT

The goal of this project is to evaluate the Se bioremediation potential (via reduction of ecotoxic risk) of combined foodchain disruption and Se volatilization in full-scale TLDD evaporation basins and pilot-scale drain water systems at the Red Rock Ranch, CA.

The data acquired in 2002-2003 indicate that waterborne Se concentration ([Se] did not increase as a result of increasing salinity, as repeatedly observed for previous years. Cell 9 of the South Evaporation Basin (SEB 9) continues to be the most saline, most Se volatilizing, of lowest water [Se], and of best brine shrimp yield. It is also interesting to note that microalgae such as *Synechococcus* that are poorly grazed by brine shrimp possess relatively high Se volatilization activity. All of these may have contributed to a lower water [Se] and Se burden in microalgae biomass and protein fraction, as well as somewhat reduced protein Se load in brine shrimp. SEB 9 has the longest history of brine shrimp harvest (since 1998).

In contrast, Cell C4 of Hacienda Evaporation Basin (HEB C4), which has never been harvested for brine shrimp, shows higher water [Se]. This difference again supports the notion that brine shrimp harvest and associated Se volatilization may have contributed to maintaining lower water [Se] and Se status in the biota of TLDD basins.

PURPOSE

The purpose of this project is to evaluate the Se bioremediation potential (via reduction of ecotoxic risk) of combined foodchain disruption and Se volatilization in full-scale TLDD evaporation basins and pilot-scale drain water systems at the Red Rock Ranch, CA.

Preliminary investigation in hypersaline ponds of TLDD indicates that Se volatilization may be combined with brine shrimp harvest to reduce Se load in waters and biota. In addition, it appears that both processes could be enhanced by manipulating the water chemistry via fertilizer input, which would increase microphyte population that functions to dissipate Se by volatilization and/or as food for brine shrimp. If mechanistically understood, this coupled process should prove to be a highly economical and flexible option for remediating Se ecotoxic risk in agricultural drainage systems. These advantages are in part due to a market demand for brine shrimp and the practicality of implementing the option together with other drainage mitigation plans such as IFDM and reverse osmosis.

OBJECTIVES AND APPROACH

OBJECTIVES

Our objectives are to investigate and understand the effect of fertilization and brine shrimp harvest on Se biogeochemistry and to uncover conditions that simultaneously favor Se volatilization and brine shrimp production while minimizing the accumulation of Se ecotoxic indicators. We will approach these objectives by both full-scale monitoring and pilot-scale studies as follows:

1. Change in Se status in TLDD hypersaline ponds (Hacienda A4 in particular since we have data on its Se status before harvest began) elicited by brine shrimp harvest;
2. Changes in water chemistry at TLDD associated with fertilizer input;
3. Effects of fertilizer input on nutrient status of microalgae and brine shirmp, microalgal community, as well as Se status in TLDD hypersaline ponds so that these effects may be related to changes in water chemistry, thereby guiding additional nutrient supplementation.
4. Establish pilot-scale drain water system at the Red Rock Ranch to better control the water chemistry (which in turn regulates microalgal populations and community) to optimize Se volatilization and brine shrimp harvest.

APPROACH

On a monthly basis, water, microalgae, and brine shrimp samples have been collected from TLDD evaporation basins, processed, and analyzed for total Se and/or Se speciation into proteins. The microalgal community is also being profiled using 16S cDNA in combination with Denaturing Gradient Gel Electrophoresis (DGGE). In July, 2002, extensive field sampling was conducted at TLDD basins to collect water column and benthic macroinverte-brates, with the assistance of Julie Vance from Dept. of Water Resources, Fresno. These samples have been processed and their Se status analyzed. In situ Se volatilization measurements were also made at selected TLDD basin cells during this field trip (see also Richard Higashi's report). Moreover, additional strains of microalgae were isolated from hypersaline waters of TLDD basins and their volatilization potential measured in the laboratory.

We have also begun to establish pilot-scale pond system at the Red-Rock Ranch in the summer of 2002, with the assistance of Jim Cooper and Des Hayes of Dept. of Water Resources, Fresno. The main funding for this project came from the State

Water Resouces Control Board, managed by Wayne Verrill. Unfortunately, this funding was taken back by the State due to budget shortfall in January 2003, which made it difficult for us to conduct intensive monitoring and experiments. In the attempt to replace this loss, we have submitted a Prop 204 proposal and are waiting for the outcome. In the meantime, DWR personnel are maintaining the Red Rock Ranch system.

RESULTS

SE VOLATILIZATION BY MICROALGAE

Figure 1 shows the volatile Se content of TLDD basin waters in comparison with bioconcentration factor (BCF, on a dry wt basis) of Se by microalgae for the 2002 field campaign. The basin cells with the longest history and/or highest amount of Artemia harvest (i.e. SEB 9 and SEB A4) exhibited the highest content of volatile Se and lowest algal BCF while those that have not been harvested (i.e. SEB 1 and HEB A2) or fertilized but only harvested recently (i.e. SEB 10) showed the opposite trend. The intermittently harvested SEB 8 cell had Se volatilization and algal BCF properties in between the two opposite ends. A similar trend was also observed for the 2001 field measurement. These results suggest that sustained brine shrimp harvest may help enhance Se volatilization while reducing Se bioaccumulation into microalgae.

In addition to in situ field measurement, we continued to isolate microalgae from the hypersaline TLDD basin cells and investigate their Se volatilization and bioaccumulation properties under controlled conditions. Figure 2 illustrates the time course of Se volatilization, Se bioaccumulation in algal biomass, and extent of Se depletion in the culture medium. It is evident that the two microalgae (*Synechococcus* sp. and a filamentous sp.) exhibited a different property of Se volatilization and bioaccumulation. Although the two strains depleted Se from the medium to a similar extent (Fig. 2, left panel), Synechococcus sp. dissipated Se more by volatilization while the filamentous algae accomplished this more by bioaccumulation into biomass (cf. Fig. 2 left and right panels). Thus, from the standpoint of reducing Se ecotoxic risk, it would be more beneficial to encourage the growth of *Synechococcus* than the filamentous strain.

It is also interesting to note that *Synechococcus* sp. did not appear to be grazed extensively by brine shrimp, possibly due to their inappropriately small size (Fig. 3 and also Figure 10 of Fan 2001 report). Thus, it is possible that this species may contribute to the higher extent of Se volatilization observed consistently in TLDD hypersaline cells (Fig. 1, SEB 9, HEB A4), where brine shrimp harvest has been sustained.

SE STATUS IN TLDD MICROALGAE AND MACROINVERTEBRATES

Water, algae, and invertebrate samples were collected monthly from TLDD basin cells and analyzed for chlorophyll A (chl A) fluorescence, total Se of water, algae, and brine shrimp, as well as protein Se content of algae and brine shrimp. Figure 4 shows the monthly trend of in vivo chl A fluorescence of the 5 most saline basin cells, where SEB 8-10 and HEB A4 have been harvested while HEB C4 has not. The chl A fluorescence, which reflected total algal populaton, fluctuated wildly from month to month with two peaks occurring in March and June, 2002. HEB C4, HEB A4, and SEB 10 were overall among the highest while SEB 9 had the lowest fluorescence or algal population. This result can be compared with the corresponding amount of brine shrimp harvest, as shown in Figure 5. The peak fluorescence in March, 2002 may have caused an increase in brine shrimp population that allowed its harvest to begin in April, 2002. On the other hand, the lag in shrimp harvest in June, 2002 may be related to the boost in fluorescence or algal population occurring in the same month. This account is consistent with the notion that brine shrimp grazing regulates microalgal population in these hypersaline basin cells.

In addition to chl A fluorescence, salinity, pH, and water Se concentration ([Se]) also exhibited seasonal changes and differences among the basin cells, as shown in Figures 6-8. As expected, the salinity (in parts per thousand or ppth) of SEB 8 & 10 were largely lower than that of SEB 9, HEB A4, and HEB C4, since the latter cells are terminal evaporation cells (Fig. 6). This salinity difference may underlie the greater harvest yield of brine shrimp from SEB 9 and HEB A4 than from SEB 10 (Fig. 5). This is presumeably that brine shrimp is better adapted at higher salinities than its competitors such as coriixids. The pH of the harvested cells (i.e. HEB A4, SEB 8-10) was less variable than the unharvested cell (i.e. HEB C4) (Fig. 7). In addition, the pH of SEB 9 and HEB A4 was largely lower than that of SEB 10, which may also contribute to the difference in harvest yield of brine shrimp (Fig. 5). The water [Se] of all harvested cells was comparable all year round and lower than that of the unharvested HEB C4 (Fig. 8). This difference may be due to excess Se removal via the combination of algal volatilization and brine shrimp harvest. It would be interesting to see if microalgae not grazed by brine shrimp (e.g. *Synechococcus*) but possess a higher Se volatilization activity than those grazed may be related to this excess Se removal.

The effect of brine shrimp harvest on algal Se status is shown in Figures 9 (total Se), 10 (Se bioconcentration factor or BCF), and 11 (protein Se). The algal Se body burden fluctuated monthly but no buildup trend was observed year-round for all saline cells (Fig. 9). Also noted is that the algal Se burden of the most harvested cells (SEB 9 and HEB A4) had overall lower values than that of the less harvested cells (SEB 8 & 10). The Se BCF in algae showed a similar trend as the total body burden (Fig. 10), i.e. the BCF for SEB 9 and HEB A4 was largely lower than that for SEB 8 & 10). Moreover, the protein Se burden in algae varied monthly and was overall lowest in SEB 9 (Fig. 11), which has the longest history of brine shrimp harvest. Thus, as observed in previous years, brine shrimp harvest activity continues to have a positive effect on reducing Se status of algae in TLDD basins.

As for the Se status in brine shrimp, there was no discernible difference among the harvested cells on total Se body burden or Se BCF of the shrimp (data not shown). However, the protein Se burden of the shrimp was slightly lower for SEB 9 than for the other harvested cells (Fig. 12). No data for the unharvested HEB C4 was available due to lack of adequate samples.

In addition to monthly sampling of algae and brine shrimp in hypersaline cells, a composite each of water column and benthic organisms was collected from TLDD basin cells of low to high salinity on July 2, 2002. The Se status of these samples along with the water [Se] is shown in Figure 13A (total Se) and 13B (protein Se). As with the case of the monthly samples, the Se burden of the algal composite was much lower in the most saline or harvested cells (S9 and A4) than the rest. A similar but less pronounced trend was observed for the Se burden of water column and benthic macroinvertebrates composites (Fig. 13A). In addition, no clear correlation was observed from the water [Se] to the Se burden of algae, water column or benthic invertebrates, which indicates that water [Se] is not a good predictor of Se accumulation in aquatic biota. This is presumably due to the influence of complex Se biogeochemistry on Se bioaccumulation.

The protein Se content of the water column composite (Fig. 13B) did not exhibit a discernible relationship to salinity or harvest activity, which differs from the case of total Se burden (Fig. 13A). However, for the benthic composite, the distribution pattern of protein Se tracked closely that for the total Se burden (Fig. 13B). Thus, it may be possible to use total Se burden as a surrogate for protein Se content; the latter is likely to be a better Se ecotoxic indicator for the benthic community. Moreover, water [Se] also showed little relationship to the protein Se content of both types of invertebrates.

MICROALGAL COMMUNITY ANALYSIS

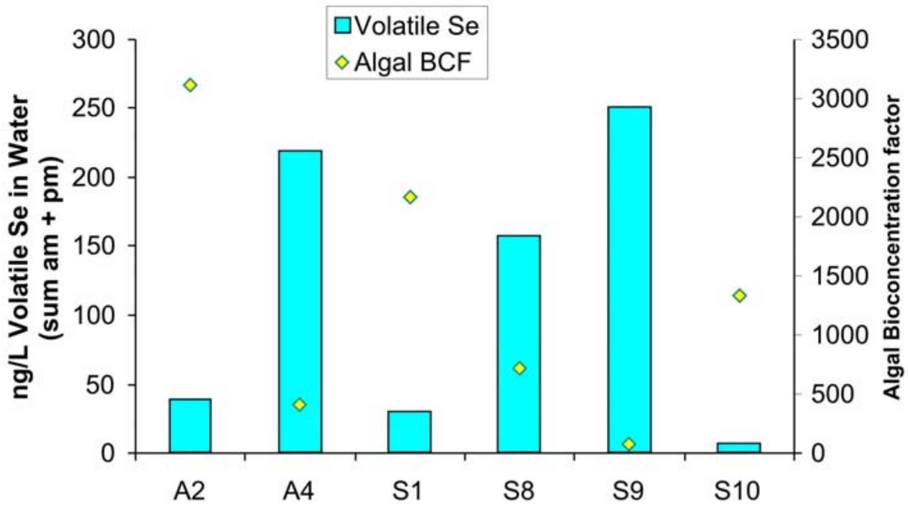
The monthly collected microalgal composite was extracted for total DNA, amplified with cyanobacterial 16S DNA probe, and the resulting products analyzed by DGGE. Figure 14A and 14B show the DGGE gel patterns for algae collected during 2002-2003 from the four harvested saline cells, along with an electrophoretic mobility marker (PM1) for comparing band position from gel to gel. There are several notable features of the gel patterns. First, a number of the samples had the same two gel bands, as indicated by arrows. The appearance of these two bands for the HEB A4 samples seemed to relate to the strength of the harvest activity. Namely, the two bands was present starting 4/4/02 (lane 1, Fig. 14B) and persisted until 7/19/02 (lane 10, Fig. 14A), after which they were not detected. Correspondingly, the amount of brine shrimp harvest increased rapidly during April to July 2002 (Fig. 5) when the two bands were present at relatively high intensity, and reduced substantially thereafter when the two bands disappeared. Thus, it is likely that the microalgae strains associated with these two bands promote brine shrimp growth.

This conclusion is consistent with the frequent presence of these two bands for all four harvested cells. However, this property did not appear to be the only determining factor for brine shrimp population since there was no clear correlation between the change pattern of the two bands and harvest yield for HEB 8-10 (Fig. 14A & B). We are currently attempting to identify the microalgal strains associated with these two bands.

CONCLUSION

The data acquired in 2002-2003 indicate that waterborne Se did not increase as a result of increasing salinity, as repeatedly observed for previous years. Cell 9 of the South Evaporation Basin (SEB 9) continues to be the most saline, most Se volatilizing, of lowest water [Se], and of best brine shrimp yield. It is also interesting to note that microalgae such as *Synechococcus* that are poorly grazed by brine shrimp possess relatively high Se volatilization activity. All of these may have contributed to a lower water [Se] and Se burden in microalgae biomass and protein fraction, as well as somewhat reduced protein Se load in brine shrimp. SEB 9 has the longest history of brine shrimp harvest (since 1998). In contrast, Cell C4 of Hacienda Evaporation Basin (HEB C4), which has never been harvested for brine shrimp, shows higher water [Se]. This difference again supports the notion that brine shrimp harvest and associated Se volatilization may have contributed to lower water [Se] and Se status in the biota of TLDD basins.

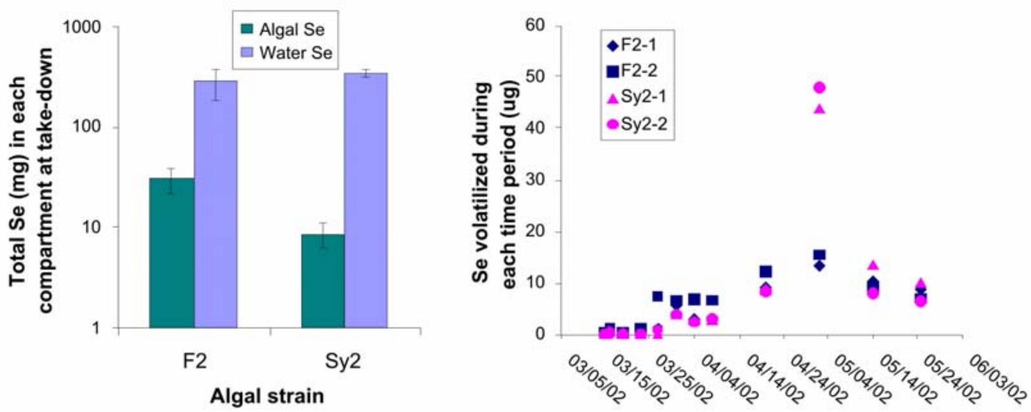
FIGURE 1 Volatile Se vs. Algal BCF



Algal communities in basins with the highest production of volatile Se tend to accumulate less selenium. Three types of communities can be discerned in the basins using Se volatilization/accumulation descriptors: High/low which are prevalent in ponds with the longest history of Artemia harvest (S9 & A4); Low/high in fertilized but either only recently harvested or unharvested (S10, S1, & A2); and the occassionally-harvested S8 fell in between. These patterns for 2002 are similar to the data presented last year for 2001.

FIGURE 2

Selenium Bioaccumulation & Volatilization in Isolated Algae



As shown in the left panel, although both filamentous (F2) and Synechococcus (Sy2) cultures depleted the media of Se to the same extent, the F2 culture accumulated more total Se over the experimental period than did the Sy2 culture *(as measured at completion)*.

The "missing" Se appears to have been removed by the Sy2 cultures through volatilization (right panel), which reached a much higher peak in the time course of Sy2 cultures than that of the F2 cultures *(24 h collections every 3 days)*.

FIGURE 3
Microscopic Assay of Selective Grazing

As shown last year, the top two photomicrographs show the same view of a beaker sample that lacked brine shrimp. The left uses a fluorescence stain (DAPI) and the right autofluorescence (Chla). The latter shows only algae.

The bottom two photos show one of the brine shrimp grazed samples. Compared with the top two photos, note the lack of the large algae, and that some algae (e.g. *Synechococcus* sp.) are left behind by the brine shrimp.

Using these techniques, it was feasible to enumerate the various species of algae in the laboratory microcosm experiments.

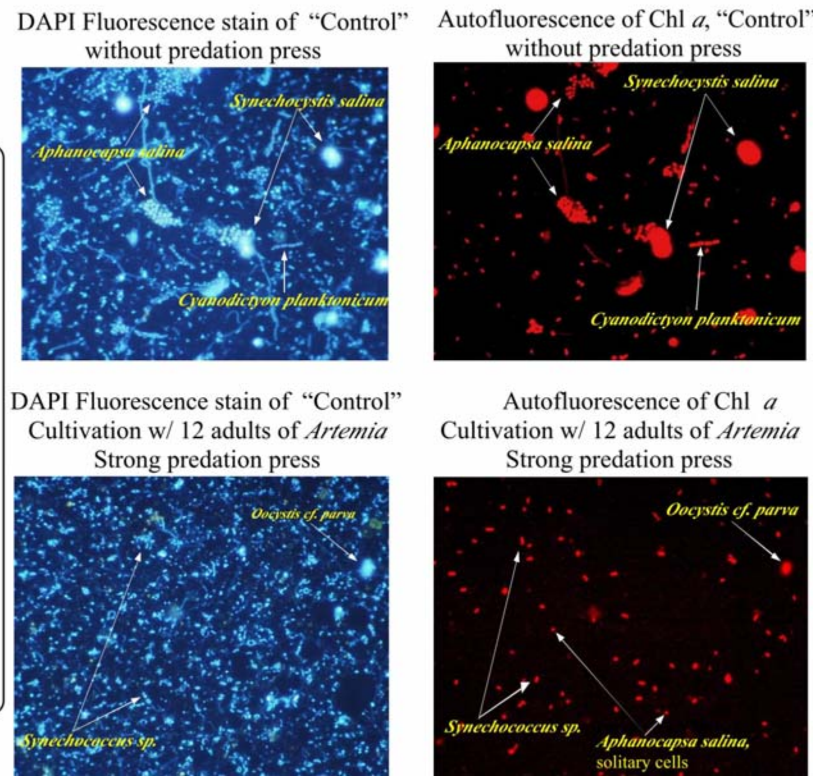


FIGURE 4

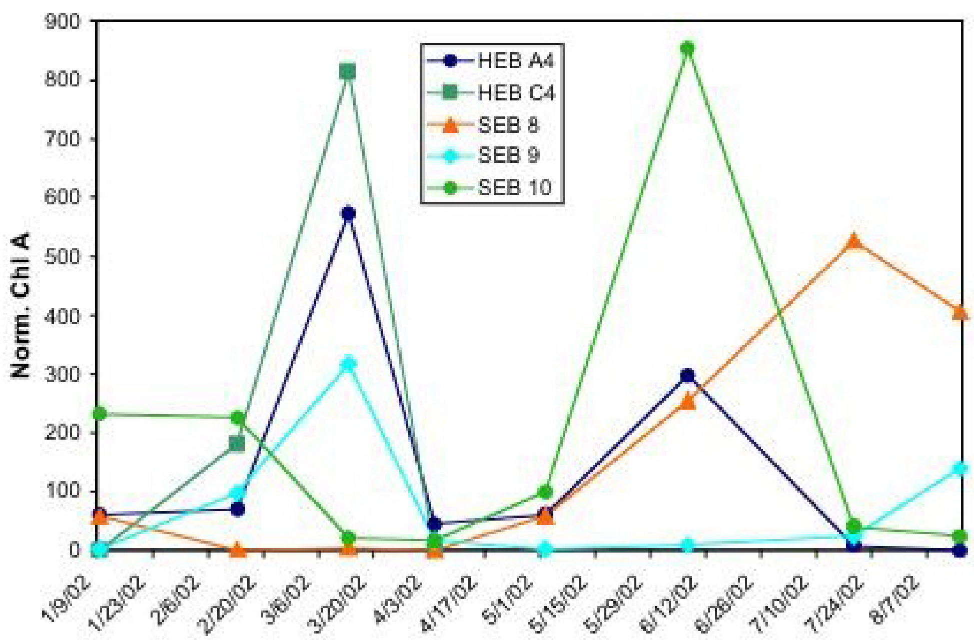


FIGURE 5

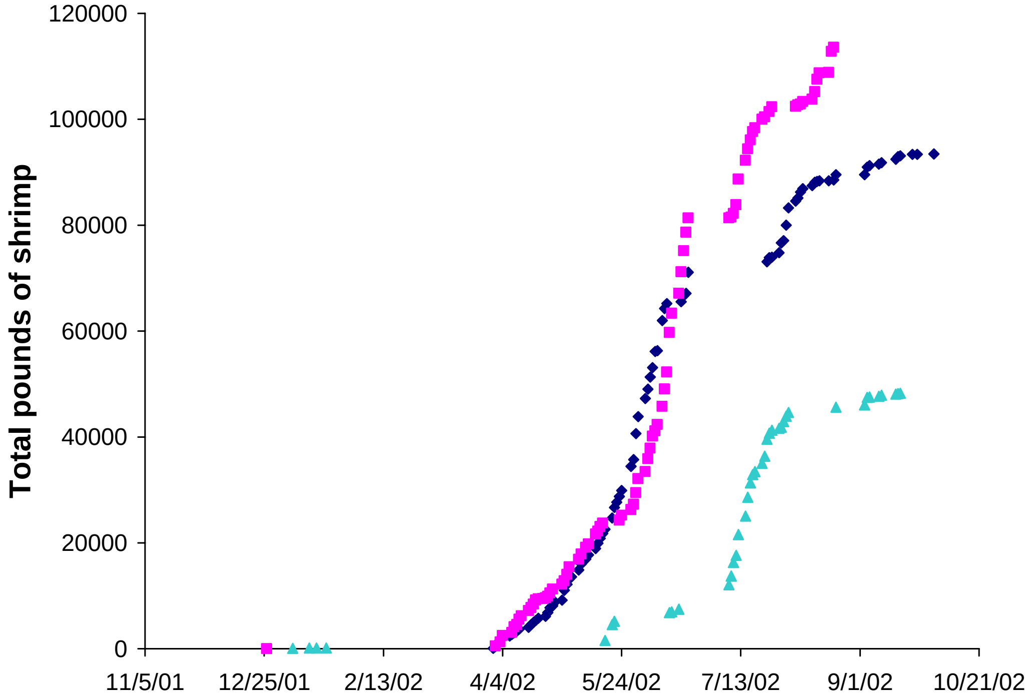


FIGURE 6

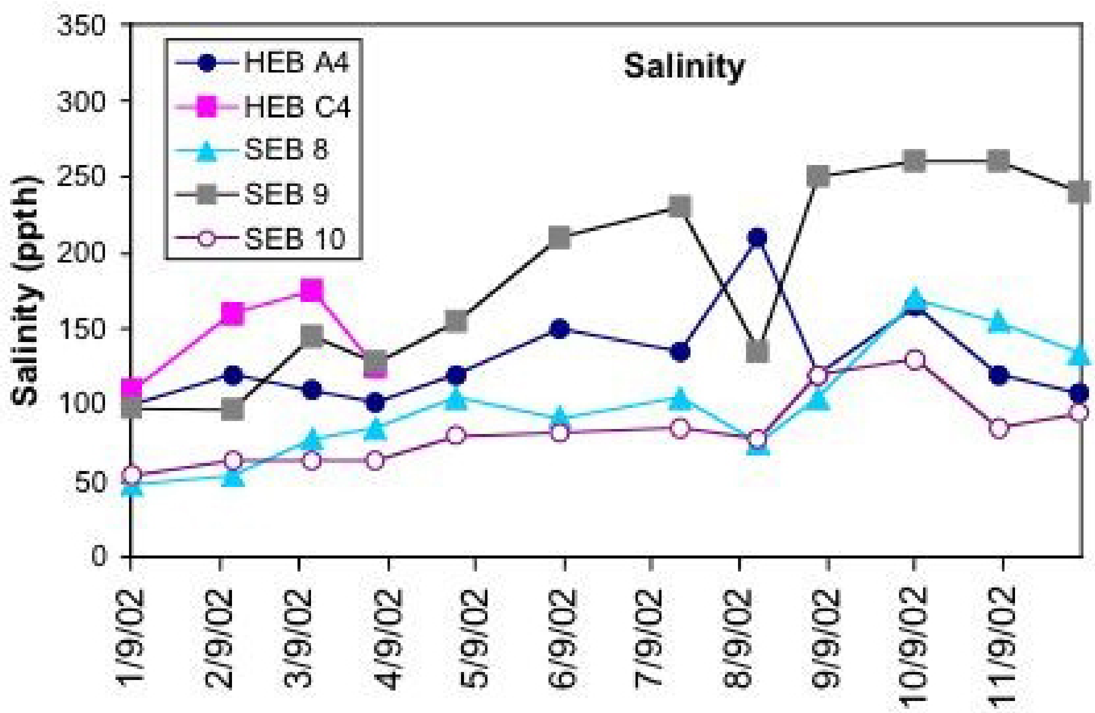


FIGURE 7

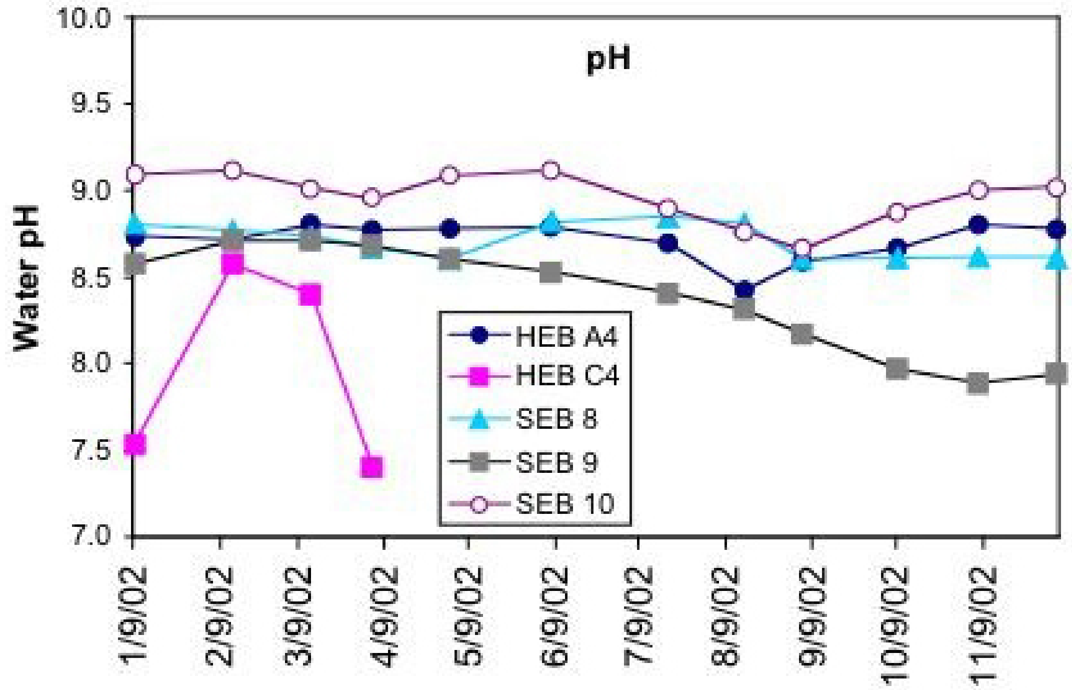


FIGURE 8

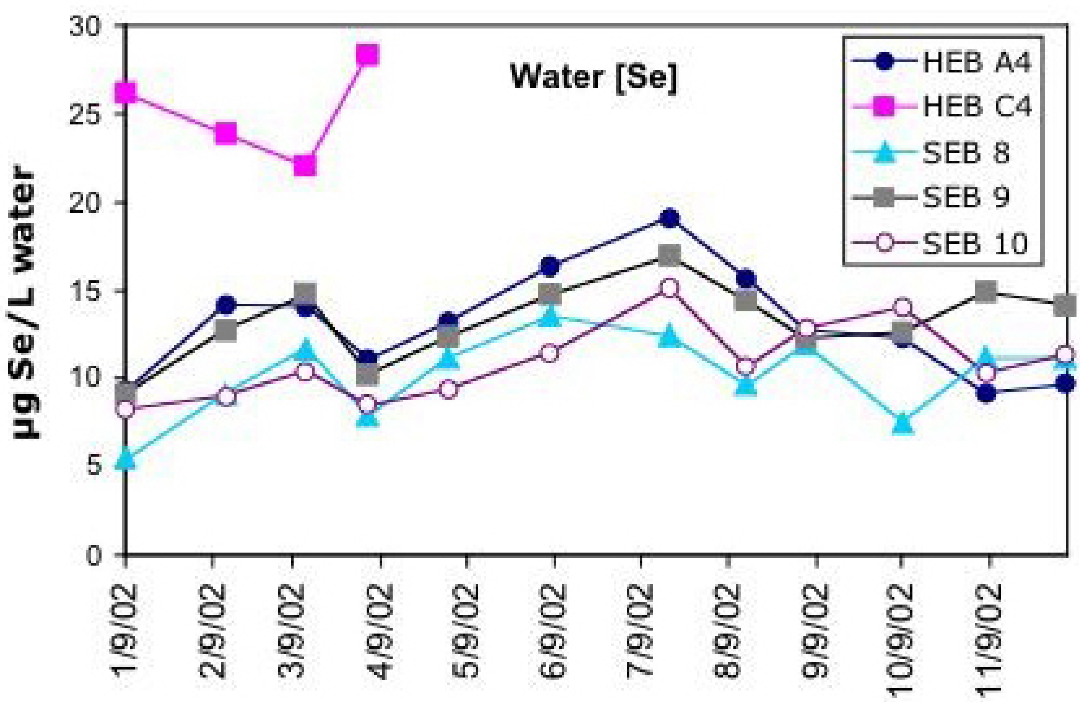


FIGURE 9

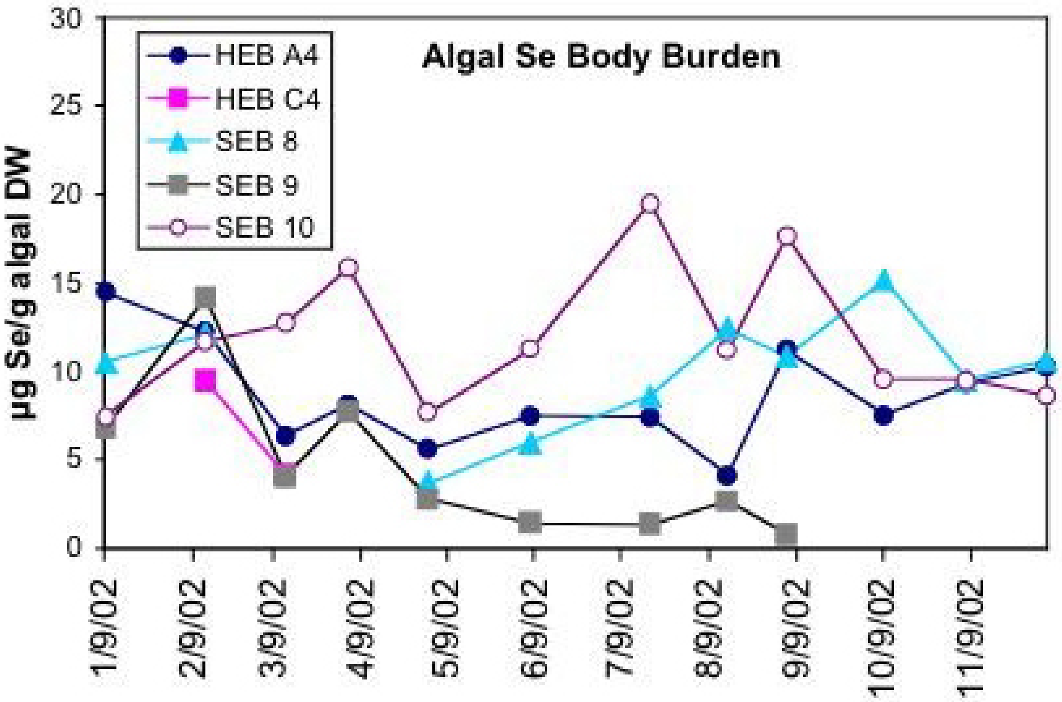


FIGURE 10

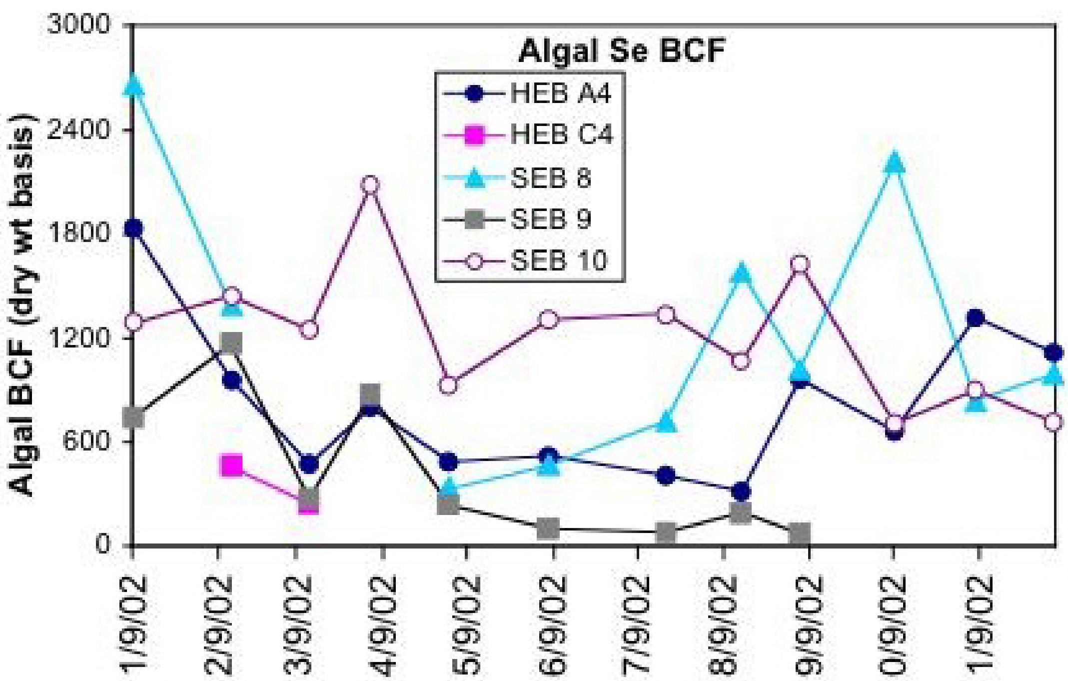


FIGURE 11

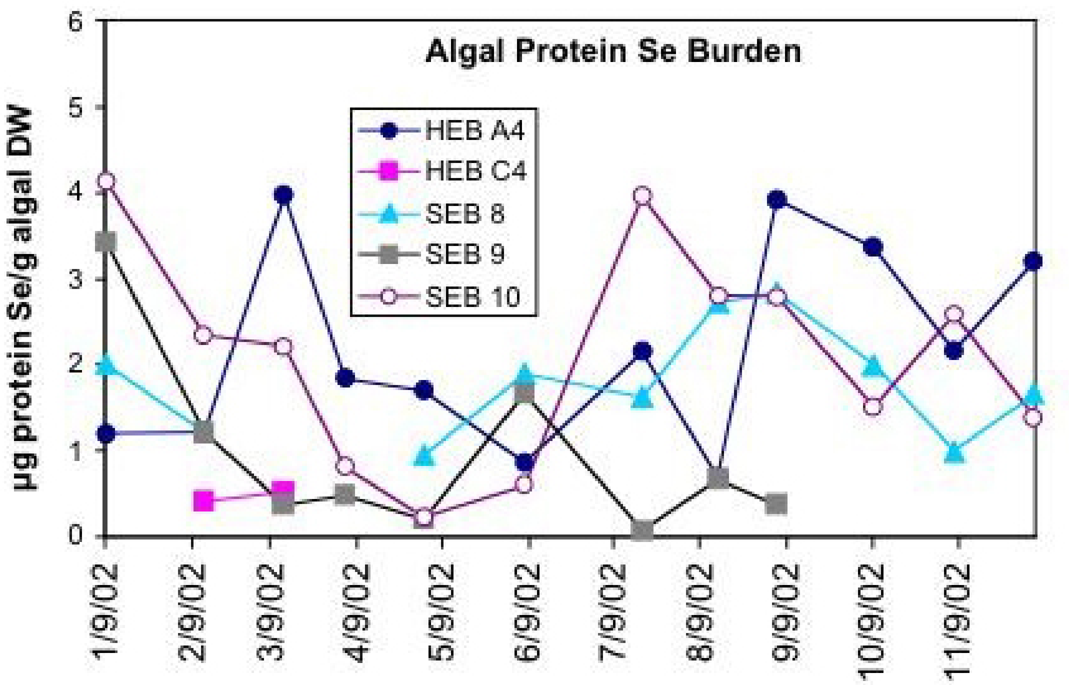


FIGURE 12

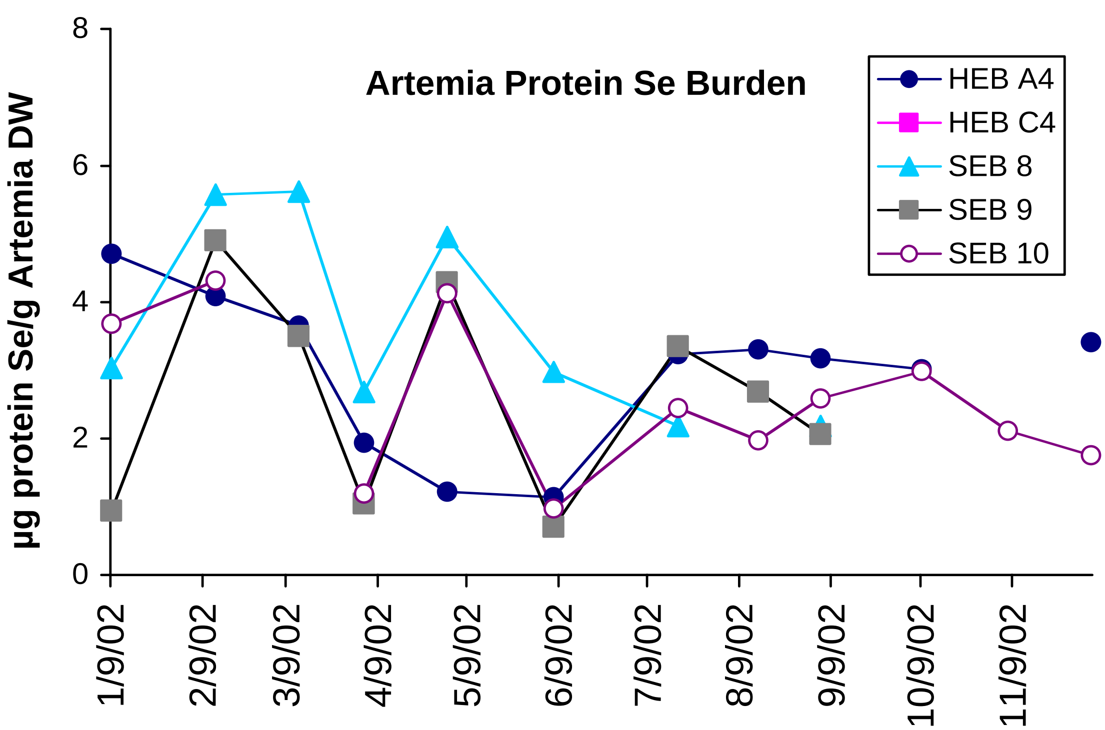


FIGURE 13A

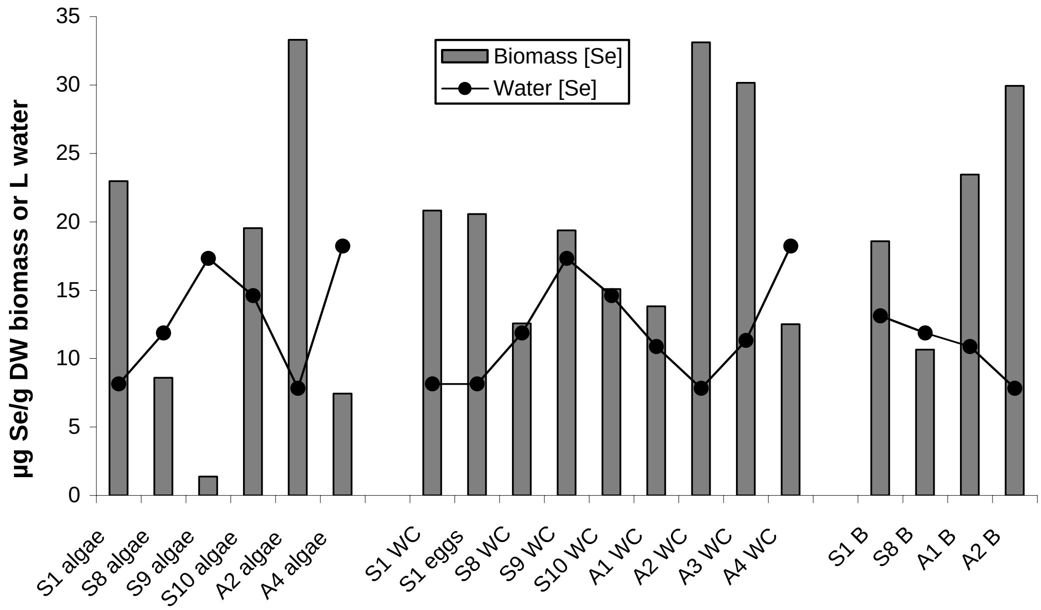
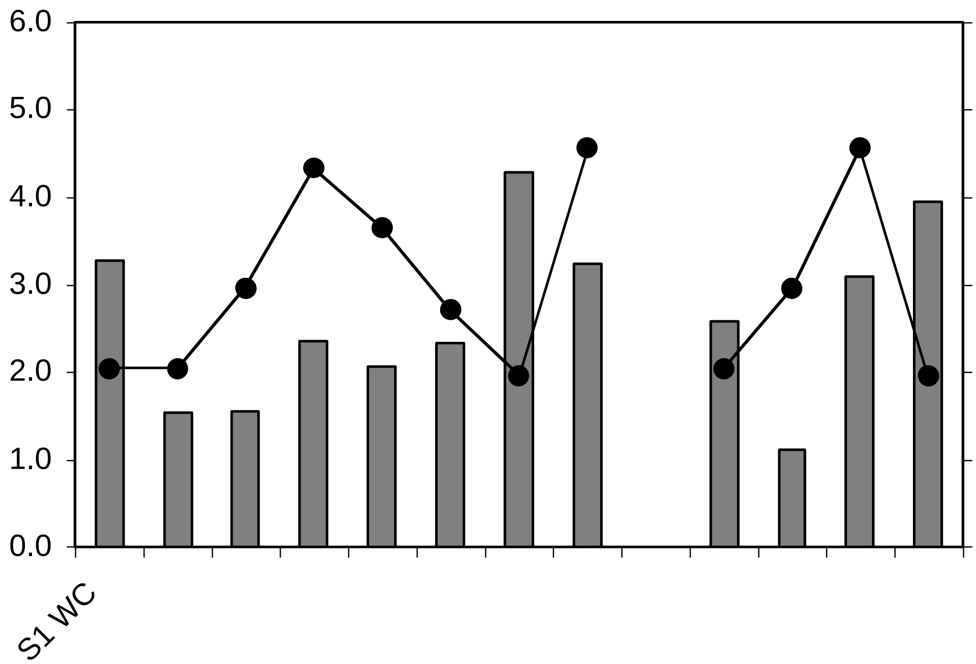
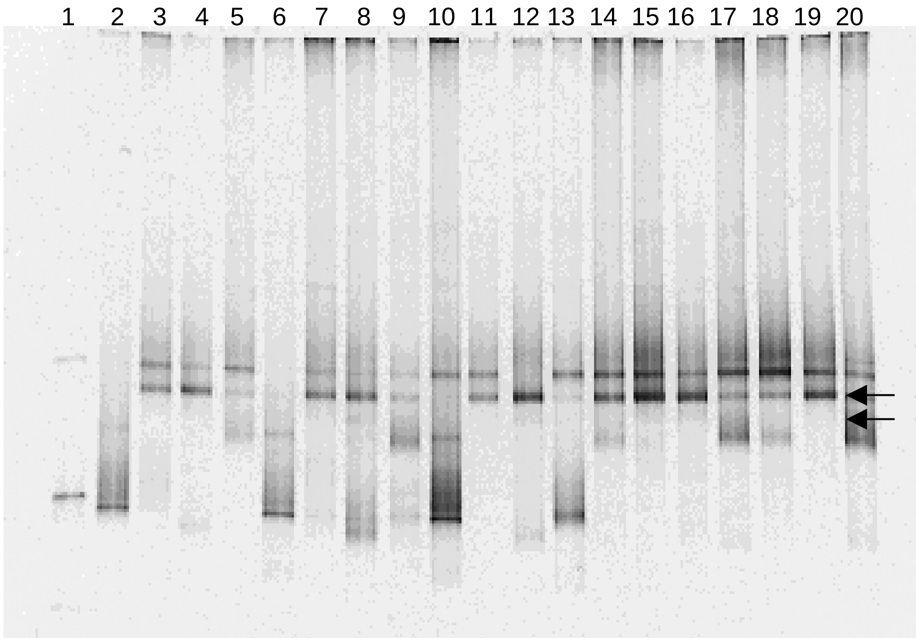


FIGURE 13B



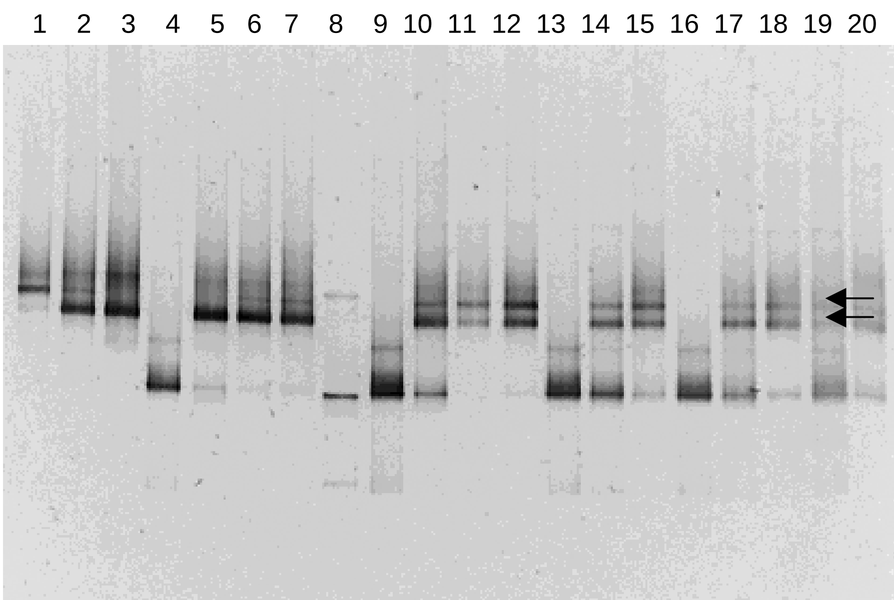
Water column (WC) and benthic (B) macroinvertebrates were collected from South Evaporation basin S1, S8, S9, S10 and Hacienda Evaporation basin A1, A2, A3, A4 on July 2, 2002. Both water column and benthic samples were composites of randomly collected macroinvertebrates. In hypersaline cells (S9 and A4), brine shrimp dominated while in less saline cells (S8, S10, A3), coriixids were also abundant in water column. In the least saline cells, nononactids were seen frequently. The benthic samples were largely brine fly larvae in the saline cells of S8-10, A3-4, while the rest were abundant in midge and mosquito larvae. More detailed species analysis will be performed by Julie Vance of DWR.

FIGURE 14A



1- PM1
2- A4 9-5-02
3- SEB 8 9-5-02
4- SEB 9 9-5-02
5- SEB 10 9-15-02
6- A4 8-15-02
7- SEB 8 8-15-02
8- SEB 9 8-15-02
9- SEB 10 8-15-02
10- A4 7-19-02
11- SEB 8 7-19-02
12- SEB 9 7-19-02
13- SEB 10 7-19-02
14- A4 6-7-02
15- SEB 8 6-7-02
16- SEB 9 6-7-02
17- SEB 10 6-7-02
18- A4 5-2-02
19- SEB 8 5-2-02
20- SEB 10 5-2-02

FIGURE 14B



1- A4 4-4-02
2- SEB 9 4-4-02
3- SEB 10 4-4-02
4- A4 12-5-03 (FIL)
5- SEB 8 1-16-03 (FIL)
6- SEB 9 1-16--03 (FIL)
7- SEB 10 1-16-03 (FIL)
8- PM1
9- A4 1-16-03
10- SEB 8 1-16-03
11- SEB 9 1-16-03
12- SEB 10 1-16-03
13- A4 12-5-02
14- SEB 8 12-5-02
15- SEB 10 12-5-02
16- A4 11-7-02
17- SEB 8 11-7-02
18- SEB 10 11-7-02
19- SEB 8 2-5-03

Salinity Tolerance of Pistachio Rootstocks

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ABSTRACT

A 1999 greenhouse rootstock salinity tolerance trial by our research group (Ferguson et al., 2002) established the salinity tolerances of, and the relative rankings among, the four commercial California pistachio rootstocks. This greenhouse study used budded seedlings, and measured growth in response to soil salinity. The long-term field trial presented here measured individual tree marketable yield, the final product of growth, as the indicator of salinity tolerance. This field trial is an attempt to corroborate in a field production orchard the tolerance limits and relative rootstock rankings we observed in the controlled greenhouse trial.

This trial was planted in 1989 and trees achieved full bearing in 1997. The four rootstocks being evaluated in this trial are *Pistacia integerrima*, Pioneer Gold I (PGI), *P. atlantica,* Atlantica, and two hybrids of these two species, *P. atlantica* X *P. integerrima,* known as Pioneer Gold II (PGII), and University of California Berkeley 1 (UCB1). The saline irrigation treatments began in 1994 and by 1997 produced salinity levels in the soil approaching or surpassing that of the respective irrigation water treatments. The yield data discussed in this report will focus on 1997 through 2002. The tree and soil water status data will focus on 1999 – 2002.

Yield results from 1997 through 2002 demonstrated nine sequential seasons, 1994 through 2002, of irrigation with 8 dS/m (6,720 TDS) water produced no significant effect on the marketable yield of trees grown on all four rootstocks. Above 8 dS/m, at 12 dS/m (11,040 TDS) trees on all four rootstocks displayed consistent, but not always significant, decreases in yield, particularly in 2000 through 2002. Trees on UCB1 rootstocks had the most marked decreases annually averaging 35% less marketable crop than control trees when irrigated with 12 dS/m water. Trees on PGII and Atlantica rootstocks had 15% and 18% annual average decreases in yield. Trees on PGI rootstocks had a 10% decrease in yield. These rankings differ with our earlier greenhouse study in that trees on PGI rootstocks demonstrated decreased growth when irrigation water salinity was above 8 dS/m and had significantly less growth than trees on UCB1 or Atlantica rootstocks when irrigation water was 16 dS/m.

As would be expected with the lack of effect on yield reported above, none of the trees, on any or rootstock at any treatment level, were measurably stressed. Leaf water potentials, photosynthetic rate and stomatal conductance measurements were all within normal ranges for trees on all rootstocks at all treatment levels. Leaf nutrient levels are all within normal ranges with few exceptions.

Since 1999, despite the lack of statistically significant yield decreases or differences in plant stress indictors, all irrigation salinity treatments have shown significantly less water use than the control (0.75 dS/m). This is consistent with our earlier greenhouse trial that demonstrated vegetative growth decreases in trees on all rootstocks when soil salinity levels were greater than 8 dS/m. Further, when annual circumference measurements are graphed it appears the highest salinity treatment is beginning to impact tree growth. All the above evidence indicates the salinity tolerance threshold of all the pistachio rootstocks in this trial is about 8 dS/m.

INTRODUCTION

Pistachios can be grown in microclimates with combinations of heat, and poor soil and water quality, not favorable to other tree crops. The lower West Side of the San Joaquin Valley, where surface irrigation water is expensive, or poor quality if it is ground or reclaimed drainage water, is an example. If irrigation in this microclimate could be supplemented by using poor quality ground or drainage water, profitable production would be more possible. Or more importantly, as water supplies become less available to agriculture, reclaimed drainage water or poor quality ground water could be a regular source of irrigation water. Currently, unused ground water supplies in the Shafter area are reporting salinities of 5-6 dS/m. The decreased water allocations of the early 1990s are sure to be repeated as competition for California's better quality water supplies become more acute in future droughts. Some West Side districts received 47% of their allocation in 2001. If the salinity tolerance of our current commercial pistachio rootstocks are known poor quality water can be used with confidence that growth and productivity will not be harmed.

Our 1999 greenhouse trial demonstrated pistachios are potentially among the most salt tolerant of the tree nut crops (Ferguson et al, 2002). However, measuring scion growth of two year old nonbearing, budded, seedling rootstocks for ten months and monitoring yield of mature bearing trees in a production orchard for nine years are completely different situations. This long-term field trial, with mature bearing trees, is an attempt to corroborate the salinity tolerance limits demonstrated in our earlier greenhouse trial. A long term field trial with bearing trees is particularly important as the effects of sustained salinity are slow to develop and subtle. Field trials like this one should be conducted until soil salinities cause statistically significant declines in growth and yield.

There are two ways saline irrigation can harm a plant. The first is by osmotic influences. The second is by specific – ion toxicities. Osmotic pressures manifest in slowed plant growth and productivity over a number of years. Specific ion toxicities manifest within a season. The former is more difficult to detect than the latter.

Osmotic effects are the more common way salts in irrigation water reduce plant growth and yield. Normally the concentration of solutes in root cells is higher than that in soil water. This allows water to move freely into the plant root. But, as the salinity of soil water increases, this difference in concentration between constituents in the soil water and those in the root lessens, initially making the soil water less available to the plant. To prevent salts in the soil from reducing the soil water available to the plant the plant cells must adjust osmotically. They must either accumulate salts, or synthesize organic compounds, generally sugars or organic acids, that raise the osmotic level of the plant root cells. This osmotic adjustment through the acquisition or synthesis of new cellular constituents allows the plant roots to compete more effectively for the available soil water. However, this synthesis process uses energy that would otherwise be used for plant growth and yield. The net result is a smaller plant that appears otherwise healthy. Some plants are more efficient at osmotic adjustment and are therefore more salinity tolerant. However, there are limits to a plant's ability to osmotically adjust.

The second way salts harm plants is specific ion toxicity. Specific-ion toxicities occur when chloride, boron or sodium ions in the soil water are absorbed by, and accumulate within, the plant, generally in stems or leaves. The most common manifestation of specific ion toxicity is marginal and tip leaf burn. Boron toxicity is an example of this. However, visible leaf symptoms do not necessarily result in compromised tree performance. Our 1999 greenhouse rootstock salinity trial demonstrated boron did not harm pistachio growth until it was above 1500 ppm in dried leaf tissue. However, boron commonly produces marginal leaf burn at much lower levels. This study also demonstrated sodium and chloride do not produce specific ion toxicity in 'Kerman' on any the rootstocks used in this field trial.

Our 1999 greenhouse trial demonstrated trees on PGI, Atlantica, and UCB-1 rootstocks tolerated irrigation with water up to 8dS/m. This greenhouse trial also demonstrated Atlantica and UCB-1 rootstocks were equally tolerant, and significantly more tolerant of salinity, than the PGI rootstocks (Ferguson et al, 2002).

The objectives of this trial were:

1. Demonstrate at what soil salinity levels pistachio production declines.
2. Rank the relative salinity tolerance levels of the four pistachio rootstocks in this trial.
3. Determine if salts harm pistachio productivity through osmotic effects, by preventing water extraction from the soil or through specific ion damage.
4. To determine if greenhouse trials are an accurate predictor of field performance.

PROCEDURES

EXPERIMENTAL PLOT

This trial is located within a larger rootstock trial established by our research group in 1989 and maintained by Paramount Farms in Kern County, CA. Female trees were established with buds from one female tree, thus differences among trees should be the result of rootstock influence as all the scions are genetically identical. All female trees were the same distance from a male pollinator tree.

The soil type at this field site, located approximately 15 miles southwest of Kettleman City, CA, has been classified as a silty loam, mixed, thermic Typic Haplargid. Since planting, ranch personnel have performed good commercial fertilization, pest and disease control, pruning and harvest practices.

SALINE IRRIGATION

The unit, decisiemen per meter, dS/m, is a measure of the electrical conductivity, EC, of a solution. The units dS/m and milliho per centimeter, mmho/cm, are equal. EC in dS/m X (740-920) = TDS ppm. The range of irrigation water salinities used in this experiment ranged from 0.75 to 12 dS/m, or 555 to 11,040 ppm TDS.

Four saline irrigation treatments with ECw values of 0.75, 4.0, 8.0 and 12.0 dS/m were randomly replicated four times across 20 rows within a 400 tree pistachio rootstock trial established at Paramount Farms, in Kern County, in 1989. The experiment was conducted on 64 female 'Kerman' trees. There were four replications of four salinity treatment levels applied to sets of four trees budded onto four different rootstocks: *P. atlantica* (Atl), *P. integerrima* (PGI), and *P. atlantica* X *P. integerrima* (PGII and UCB1); 4 X 4 X. 4 = 64 trees. Two high salt concentration nurse tanks, one at 0.27 lbs / gal sodium sulfate and the other at 0.13 lbs/gal calcium chloride, 0.33 lb/gal NaCl and 0.006 lb/gal Solubor (20.5% B) were used as salt water sources for creating saline treatments with a Na:Ca ratio of 5:1 and increasing B concentration of 1 ppm for each 1 dS/m increase in salinity These ratios are representative of Westside drain waters. Salt treatments were injected from each high salt concentration nurse tank using an impeller pump into a manifold equipped with flowmeters and then at differential rates into four sets of irrigation lines pressurized at 22 psi with canal water to produce the desired salinity treatment levels as measured with a portable EC meter. One irrigation line, the control treatment which was California Aqueduct canal water, received no salt injection. Each of the four irrigation lines were equipped with water meters to measure seasonal irrigation delivery. Each of the four irrigation lines appeared as headers at each of the twenty rows of trees to provide source outlets for drip irrigation lines to achieve the appropriate salinity treatment replication. Existing irrigation lines were plugged and new 360º microsprinklers, (14.4 gph) were installed four feet from trunks of treatment trees with the water outlet pattern being directed back towards the trunk. Irrigations were scheduled using normal year evapotranspiration data. Excessive saturation has been a problem on the 8 and 12 dS/m treatments so reduced flow microsprinklers (12.0 gph) were installed on these trees in 2001. This still provides a 20 – 40% leaching fraction.

WATER AND SOIL SALINITY MEASUREMENTS

Field samples of irrigation water were collected in 400 ml containers over the course of each irrigation in order to determine water quality. Individual tree soil samples were collected before the irrigation season in April and after the irrigation season in November of each growing season. Water and soil analysis were conducted using established laboratory procedures at the Division of Agriculture and Natural Resources Laboratory in Davis, CA.

HORTICULTURAL MEASUREMENTS

Individual annual trunk growth and yield were determined on all trees. Individual tree yield samples were commercially graded at the Paramount Farming Processing Facility. Annual individual tree leaf samples were collected for nutritional analysis at the same lab as above.

TREE WATER STATUS MEASUREMENT

Tree water status by midday, bagged leaf water potential was measured immediately prior to each irrigation, when trees should be most stressed, and within 24 hours after irrigation. Tree water status was measured by bagging one leaf from the lower internal part of the canopy, from each tree of four replications of each rootstock-saline irrigation treatment combination. Bags were constructed from black polyethylene and aluminum foil with the intent of excluding measured leaves from light and micrometeorological environments. Leaves were bagged at 0900 Pacific Standard Time, then removed three hours later for water potential determination using a Scholander type pressure vessel. All leaves were selected based upon similar age and canopy position.

PHOTOSYNTHETIC GAS EXCHANGE MEASUREMENTS

A Licor LI-6400 portable photosynthesis system was used to measure gas exchange of individual tree leaves annually in August. The reference CO2 was set at 400 ppm. The PAR (photosynthetically active radiation) level was 1500 microeinsteins. Sample relative humidity was maintained at 55% =/- 5%. The flow rate was maintained at 500 micromoles and adjusted as required. Sample leaves were mature, fully expanded, and selected for maximum sun exposure and height. The same sample leaves were used each time and measured at the end of the irrigation cycle, immediately prior to the next irrigation. Measurements were made between 0900 and 1500 hours. Photosynthesis measurements were done in 2000 through 2002 as a more discriminating indicator of tree water stress in addition to bagged leaf water potentials.

SITING OF NEUTRON PROBE ACCESS TUBES, REPLICATION AND MEASUREMENT OF SOIL WATER CONTENT

Using a measurement of the backscatter of thermalized (slowed) neutrons, the neutron probe determines soil water content of a volume of soil the size of a basketball. For this study, 2 inch PVC Class 125 pipe access tubes have been installed to allow for repeated measurements of soil water content from 0.5 to 5 feet in one-foot increments. As demonstrated in figure 1, from 1994 through the 2000 season, one neutron probe access tube per tree was installed to a depth of 5.5 feet on every tree in the trial in approximately the same location relative to the trunk and the opposing fanjet; about 4 feet east of the trunk, 4.5 feet west of the fanjet and 1.5 feet south of the hose. This placed the access tube in an area that represented average to slightly better than average application of irrigation water. This wetted area, and the subsurface redistribution of water, gave the tree an active root volume of about 50% of the entire orchard floor. This meant that a 1-inch irrigation over the whole orchard equaled about 2 inch around the site of the neutron probe tube. Likewise, neutron probe readings that show a 2 inch extraction of water between irrigations represented about 1 inch of tree water use as transpiration over the whole orchard.

However, the variability in spatial distribution of tree roots and the precipitation pattern of the fanjets can result in different rates of water application and subsequent tree uptake throughout the root zone of a given tree. For this study, to get the most comparative information possible across all treatments, we measured soil water content to maximize replication across the most trees instead of opting for complete ET estimates using many tubes on only a few trees. The assumption was that the location of the neutron probe tube represented an equal water application and extraction opportunity for each tree and provided a relative comparison suitable for statistical analysis. Therefore results reported through 2000 were generated from neutron probe data taken from 4 replications times 4 rootstocks times 4 levels of salinity; a total of 64 tubes as demonstrated in figure 1.

However, water extraction figures from 1999 through 2000 suggested we were not obtaining an accurate picture of water extraction from the soil. Consequently, for the 2001 season the number of neutron probe tubes was increased to four per tree and sited as demonstrated in figure 2. As previous years showed very little difference in water extraction among trees on the different rootstocks we dropped neutron probe monitoring on trees on the Atlantica and PGII rootstocks. The result was a doubled number of access tubes to 128 concentrated our ET estimates on trees on PGI and UCB-1 rootstocks. Tubes were also installed to a depth of 6.33 feet to allow for water content measurements to 6 feet. This new tube placement was designed to monitor the locations that receive the most water, tube 1, T1. The areas that receive somewhat less, T2. The areas adjacent to the fanjet, a little bit of surface wetting and at the edge and the substantial subbing of water to the 1-3 foot depths, T3. And areas that receive no surface wetting and minimal subbing in the middle of the drive row, T4. This tube arrangement effectively monitored a much larger area of the root system laterally and vertically. This siting of neutron probe tubes compensated for both the irregular fanjet irrigation pattern and the highly variable subsurface water redistribution during and after irrigation. It also compensated for the irregular root distribution. The net result was a better estimate of soil water content.

A further field site modification was done in 2001. Direct soil water status measurements by neutron probe and tree transpiration calculations from 1997 through 2000 suggested trees at the 8 and 12 dS/m irrigation salinity levels were extracting and transpiring only a fraction of the applied water. Roots were proliferating outside the wetted zone, obtaining fresh water outside the saline irrigation zone. To prevent this 0.006 inch thick plastic barriers were installed around all treatments to a depth of 1.5 m, fig.3. Trenching to sink the barriers cut many small roots in the top three feet of the profile, but this did not appear to adversely affect tree vigor during the 2001 and 2002 seasons.

RESULTS AND DISCUSSION

The larger rootstock trial that contains this salinity trial was planted in 1989 and reached full bearing in 1998. The salinity treatments commenced in 1994. By 1998, when the trees were full bearing, the soil salinity levels, as measured by soil saturation extract, were reflective of the irrigation water salinity. As the tables 1,2, and 3 below demonstrate, nine sequential seasons of irrigation with 0.75 through 8.0 dS/m water had no consistent significant effect on mature tree marketable yield. As Table 4 shows irrigation water at 12 dS/m produced decreases, generally insignificant, in marketable yield of trees on all four rootstocks. However, trees on UCB-1 rootstocks appeared to be most adversely affected. This contradicts our greenhouse trial in which Atlantica was the most saline tolerant rootstock followed by an almost equally tolerant UCB-1. PGI was the most saline sensitive rootstock in the greenhouse trial.

Table 5 synthesizes the data given in the four tables above. This table demonstrates the effect of salinity on average annual yield, 1997-2002, of individual trees, on all four rootstocks. This graph corroborates our greenhouse study demonstrating irrigation water up to 8 dS/m, which produces an average root zone salinity of 13.4 dS/m, has no effect on marketable yield of trees on any of the rootstock. However, and again consistent with our 1999 greenhouse trial, all four rootstocks produced decreased yields when irrigation water salinity was 12 dS/m and soil salinity averaged 14.3 dS/m. At this level, relative to controls trees on PGI rootstocks had a 10% decrease in yield, followed by trees on PGII with a 15% decrease and trees on Atlantica with an 18% decrease in yield. Unlike the greenhouse study, trees on UCB1 rootstocks, were the most saline sensitive and had a 35% decrease in yield at this salinity level.

EFFECT OF SALINE IRRIGATION ON GROWTH

Table 6 gives the annual increase in rootstock growth of ‘Kerman‘ trees on the four different rootstocks. Trees all rootstocks are displaying slightly lower, though not significant, decreases in annual growth. As stated earlier, the effects of salinity are slow to develop. However, these small decreases in the rate of trunk growth suggest the sustained salinity in the root zone may be beginning to affect growth. If so, yield will eventually be impacted.

EFFECT OF SALINE IRRIGATION ON TREE NUTRIENT STATUS AND SPECIFIC ION TOXICITY

No differences in tree macronutrient or micronutrient status, including sodium, boron or chloride, have been observed. All leaf nutrient levels have remained within normal ranges throughout this trial. This is consistent with the results of our earlier greenhouse trial. The single exception is trees on PGI rootstocks that had consistently and significantly higher leaf levels of sodium and chloride relative to trees on the other rootstocks.

No consistent, visible, specific ion tonicities have been observed. Our 1999 greenhouse trial demonstrated that if they did manifest they were a result of boron accumulation, not sodium or chloride.

EFFECT OF SALINE IRRIGATION TREATMENTS ON SOIL WATER CONTENT, PLANT STRESS AND TREE WATER USE

The following discussions address the impact of salinity averaged over all rootstocks for 1999 through 2002. This provides 12 replicates of data for each salinity level for the factors being discussed: irrigation water applied, leaf water status, available amount of soil moisture, transpiration and rates of photosynthesis and stomatal conductance.

IRRIGATION APPLICATION; CIMIS ET AND APPLIED IRRIGATION

Irrigations during the season were scheduled using normal year CIMIS potential evapotranspiration (ET_0) multiplied by pistachio crop coefficients determined in a previous study by Goldhamer (1985). When the orchard was young and coverage of the orchard floor was about 50%, crop ET was further discounted to 95% of a mature orchard depending on age (Snyder, 1989). As the orchard matured this was adjusted upward. Irrigation was timed to match this demand with the same depth applied to all salinity treatments. Separate flowmeters record the application depth for each treatment. Figure 4 shows pistachio ET for the 2002 season calculated using the real time CIMIS ET_0 at the Shafter Field Station multiplied by the appropriate crop coefficient for that time of year along with individual treatment irrigation depths. CIMIS ET_0 from the Shafter Field Station was used instead of Lost Hills or Dudley Ridge due to the quality of data and weather station siting. Initially general, application depths matched calculated ET fairly well. Total water application in the higher salinity treatments was less than the 0.75 dS/m control treatment; probably due to some precipitation of calcite around fanjet nozzles and declines in meter accuracy due to some marginal calcite precipitation in the meters. However, as the experiment has progressed and salinity in the soil has increased the ability of the trees, on all rootstocks, to extract water for the soil has decreased significantly. For this reason water application rates in the two highest treatments, 8 and 12 dS/m, were decreased to avoid soil saturation in 2001 and 2002.

LEAF WATER STATUS MEASUREMENTS

A mid day leaf water potential is an indicator of overall trunk water potential, and therefore tree water status. Midday bagged leaf water potentials for 1999 through 2002, indicated the trees were not under water stress. Midday bagged leaf water potentials for 2002 are shown in figure 5.

EFFECT OF SALINE IRRIGATION TREATMENT ON PHOTOSYNTHETIC EFFICIENCY AND STOMATAL CONDUCTANCE

Because midday bagged leaf water potentials did not demonstrate any significant difference in tree water status, photosynthetic rate and gas exchange measurements, generally more accurate indicators of tree stress, were attempted. As with bagged midday leaf water potentials there were no significant differences within each rootstock or among the four salinity treatments (data not shown). By these measurements in 2000 through 2002 the trees were not stressed. This is consistent with the appearance of leaves of trees on all four rootstocks at all four salinity levels, and with the results of bagged midday leaf water potential measurements. It is also consistent with our greenhouse study; as salinity rose from 3.5 to 16.7 dS/m stomatal conductance decreased only 10%.

SOIL WATER STATUS MEASUREMENTS

Figures 6 demonstrates major differences in root zone soil water content. This pattern of soil water content has been consistent through the 2000 – 2002 seasons. Generally, 12 and 8 dS/m treatments beginning the season with strikingly higher soil water contents and maintaining this pattern throughout the season. This indicates that the depth of irrigation in the control treatment was insufficient to meet all the ET demand for these trees; causing excessive extraction of available soil water. The maintenance of near 100% field capacity in the higher salinity treatments indicates the trees are extracting less water, and that leaching is occurring in these treatments. This water extraction picture suggest that the salinity content of the soil water is preventing water extraction from the soil, or is exerting osmotic pressure. These results support the argument that the mechanism by which salinity harms the trees is osmotic and not specific ion damage.

TREE WATER USE

Figure 7 shows evapotranspiration (ET), water transpired by the tree plus evaporation from the soil surface. The pattern of decreasing evapotranspiration with increased soil water salinity has become increasingly marked through the past four seasons; 1999 – 2002. The data collected in 2002 demonstrated trees receiving the 0.75 control and 4 dS/m treatments transpired almost equal amounts of water. Trees receiving the 8 and 12 dS/m irrigation water transpired less water. This is partially a function of 20% less water being applied when 12 gph emitters were substituted for the 15 gph emitters to avoid marked soil saturation. However, the two higher salinity treatments are clearly producing an osmotic effect that is decreasing the water extraction ability of the trees on all rootstocks.

DISCUSSION AND CONCLUSIONS

In summary, field trial results from 1994 through 2002 indicate soil water extract salinities up to 8 dS/m did not significantly decrease the yield of pistachios grown on all four rootstocks tested. Using marketable yield as an indicator of salinity tolerance, the rootstocks ranked as follows, from least to most saline tolerant; UCB-1, Atlantica, PGII and PGI. These results are not consistent with our 1999 greenhouse trial in which the effects of salinity on tree growth were tested in a controlled environment in which the trials were free of the effects of soil saturation. Thus all the damage can be attributed to either osmotic effects or specific ion damage. In the greenhouse trial trees on Atlantica and UCB-1 rootstocks were significantly more tolerant of salinity, as judged by growth, than trees on PGI rootstocks.

Not surprisingly, considering the lack of significant effects on tree growth, nutritional status or yield, the trees on all rootstocks also have normal leaf water status, photosynthetic rate and stomatal conductance. However, measurements of tree water application, extraction and use indicate salinities above 8 dS/m are deleteriously affecting the trees' ability to extract water from the soil. These results are consistent with our 1999 greenhouse trial in which soil water salinities above 8 dS/m significantly deceased growth of trees on all four rootstocks.

Leaf macronutrient and micronutrient levels, including boron, sodium and chloride have generally remained at normal levels for trees on all rootstocks throughout the duration of this experiment. The single consistent exception is trees on PGI rootstocks. Trees on this rootstock have significantly higher levels of sodium and chloride in the leaves relative to trees on the other three rootstocks. This is consistent with results of our greenhouse trial which demonstrated trees on PGI rootstocks have significantly higher levels of sodium and chloride in their scion wood than trees on the other three rootstocks. This suggests trees on PGI rootstocks would eventually suffer specific ion damage from sodium and chloride accumulation in the scion.

The results from these two trials strongly suggest osmotic pressure, not specific ion toxicity, is the mechanism by which salinity harms pistachios.

This trial was conducted on trees planted in 1989. Saline irrigation began in 1994. Soil water extract levels did not achieve irrigation water salinity levels until 1998. Therefore these results cannot be applied to orchard establishment. The results here demonstrate what will happen if an established orchard five years and older is irrigated with saline water. It does not demonstrate what will happen if a young orchard is established with water of this quality. This is the next experiment that should be done.

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Table 1. Individual tree yields, Kg of dry, inshell splits per tree, for trees receiving 0.75 dS/m irrigation water.

	Mean Rootzone Salinity as ECe (dS/m) for 0.75 dS/m irrigation					
	2.1	**1.8**	**1.2**	**2.3**	**2.4**	**
Rootstock			**Yield (Kg/tree)***			
	1997	**1998**	**1999**	**2000**	**2001**	**2002**
Atlantica	6.0 a	8.4 a	0.2 a	13.6 a	7.0 a	11.1 a
PGI	7.6 a	11.9 a	1.7 a	14.8 a	9.9 a	11.4 a
PGII	6.5 b	10.8 a	0.3 a	14.0 a	8.7 a	10.0 a
UCB1	6.3 b	11.9 a	0.5 a	14.8 a	8.8 a	12.0 a

*Values for a specific rootstock for a given year followed by the same letter are not significantly different from the same rootstock at a different salinity level within that same year.
**Soil samples not yet analyzed.

Table 2. Effect of irrigation water salinity (dS/m)* and average root zone soil water extract. Water averaged over 1-6 ft depth (dS/m) on yield of trees on four pistachio rootstocks. The top line of the table is the irrigation water salinity. The line below is the salinity of the soil water extract that year.

	Salinity of Irrigation Water (ECw) 4.0 dS/m					
			Salinity of Soil (ECe) in dS/m			
	2.1	**5.3**	**5.4**	**6.2**	**8.7**	**
Rootstock			**Yield (kg/tree)**			
	1997	**1998**	**1999**	**2000**	**2001**	**2002**
Atlantica	6.1 a	7.6 ab	0.5 a	13.3 a	7.6 a	12.2 a
PGI	8.6 a	9.0 b	3.4 a	12.4 a	10.1 a	8.6 a
PGII	7.8 a	10.9 a	0.4 a	13.1 a	9.5 a	10.1 a
UCB1	8.2 a	12.3 a	0.8 a	16.1 a	10.7 a	13.9 a

*Values for a specific rootstock for a given year followed by the same letter are not significantly different from the same rootstock at a different salinity level within that same year.
**Soil samples not yet analyzed.

Table 3. Effect of irrigation water salinity (dS/m)* and average root zone soil water extract. Water averaged over 1-6 ft depth (dS/m) on yield of trees on four pistachio rootstocks. The top line of the table is the salinity of the irrigation water. The next line is the salinity of the soil water extract that year.

	Salinity of Irrigation Water (ECw) 8.0 dS/m					
	Salinity of Soil (ECe) in dS/m					
	6.0	**6.9**	**8.5**	**9.5**	**13.4**	**
Rootstock	**Yield (kg/tree)**					
	1997	**1998**	**1999**	**2000**	**2001**	**2002**
Atlantica	6.5 a	8.3 a	0.7 a	11.3 a	8.5 a	7.1 a
PGI	8.1 a	10.8 b	2.3 a	10.6 a	8.5 a	11.3 a
PGII	8.1 a	10.8 a	1.2 a	15.3 a	10.1 a	9.1 a
UCB1	8.8 a	10.9 a	0.4 a	13.3 a	10.2 a	10.0 a

*Values for a specific rootstock for a given year followed by the same letter are not significantly different from the same rootstock at a different salinity level within that same year.
**Soil samples not yet analyzed.

Table 4. Effect of irrigation water salinity (dS/m)* and average root zone soil water extract. Water averaged over 1-6 ft depth (dS/m) on yield of trees on four pistachio rootstocks. The top line of the table is the salinity of the irrigation water. The next line is the salinity of the soil water extract that year.

	Salinity of Irrigation Water (ECw) 12.0+ dS/m					
	Salinity of Soil (ECe) dS/m					
	7.5	**10.3**	**11.5**	**10.0**	**14.3**	**
Rootstock	**Yield (kg/tree)***					
	1997	**1998**	**1999**	**2000**	**2001**	**2002**
Atlantica	5.2 b	6.9 b	0.7 a	10.5 a	7.51 a	7.2 a
PGI	7.7 a	10.3 b	0.7 a	13.0 a	10.1 a	10.1 a
PGII	6.7 b	9.0 b	1.2 a	11.4 a	7.2 a	7.4 a
UCB1	5.1 c	6.1 b	0.3 a	9.3 a	6.5 a	8.9 a

*Values for a specific rootstock for a given year followed by the same letter are not significantly different from the same rootstock at a different salinity level within that same year
+12 dS/m irrigation was only applied for 1997 through 2000 seasons.
**Soil samples not yet analyzed.

Table 5. Effect of irrigation water salinity (dS/m) and resulting final root zone salinity in 2001** averaged over a 1-4 ft. depth on cumulative and average annual per tree yield from 1997 – 2002.

Yield (kg/tree) Rootstock	**Cumulative and Average Annual Yield per tree; 1997 - 2002** Irrigation Water / Root Zone Salinity*				
	0.75 / 2.4*	**4.0 / 8.7***	**8.0 / 13.4***	**12.0+ / 14.3***	**12 dS/m yield as a % of control yield**
Atlantica	46.3 (7.7)	47.3 (7.8)	42.4 (7.1)	38.0 (6.3)	82%
PGI	57.3 (9.6)	52.1 (8.7)	51.6 (8.6)	51.8 (8.6)	90%
PGII	50.3 (8.4)	51.8 (8.6)	54.6 (9.1)	42.9 (7.2)	85%
UCB1	56.0 (9.3)	62.0 (10.3)	53.6 (9.4)	36.2 (6.0)	65%

*Soil salinities are end of season 2001 values.
+12 dS/m irrigation was only applied for 1997 through 2002 seasons.
**2002 soil samples not yet analyzed.

Table 6. Effect of irrigation water salinity (dS/m) and resulting final root zone salinity in 2001** averaged over a 1-4 ft. depth on average trunk growth diameter percentage increase from 1998 – 2002.+

	Average Percent Increase in Trunk Diameter; 1998 - 2002 Irrigation Water / Root Zone Salinity*			
Rootstock	**0.75 / 2.4***	**4.0 / 8.7***	**8.0 / 13.4***	**12.0+ / 14.3***
Atlantica	33 a	32 a	31 a	26 b
PGI	29 b	37 a	31 b	24 c
PGII	42 a	32 b	31 b	32 b
UCB1	38 a	37 a	32 b	31 b

*Soil salinities are end of season 2001 values.
**2002 soil samples not yet analyzed.
+ Values within a row followed by a different letter are significantly different from one another.

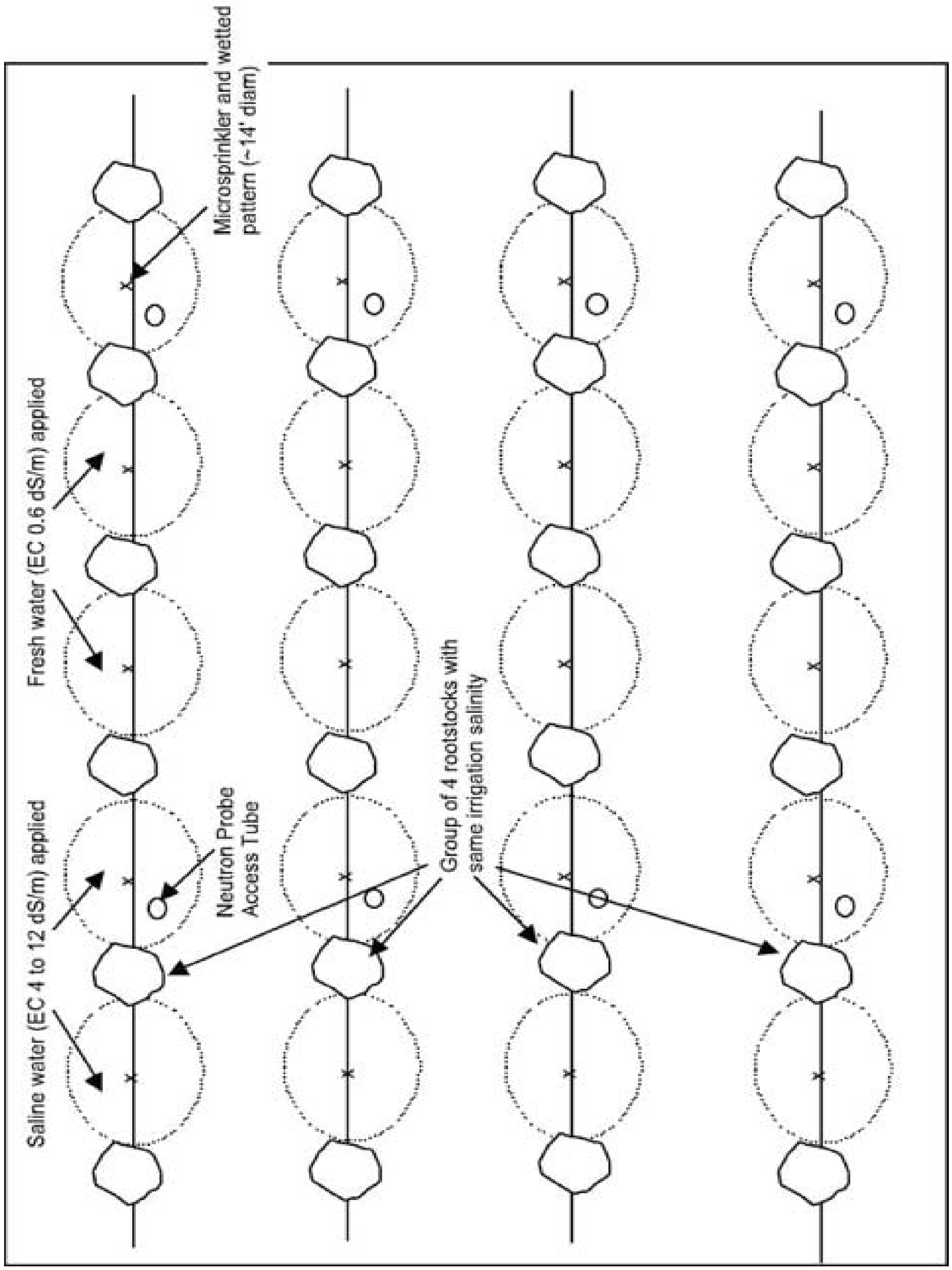

Figure 1. Neutron probe tube placement 1994 through 2000.

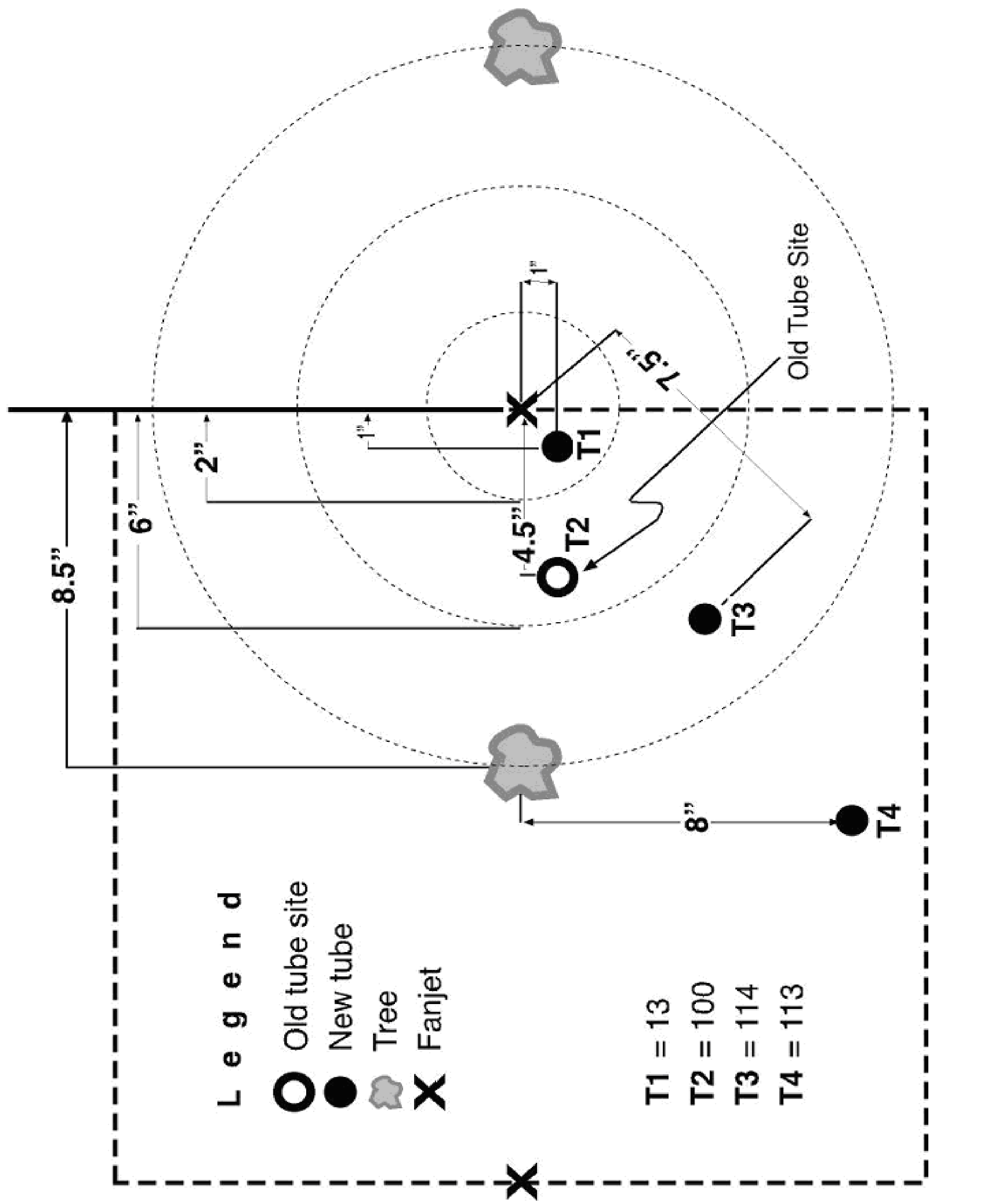

Figure 2. Neutron tube placement in 2001 and 2002. Note that the number of tubes was increased to four per tree.

Figure 3. Barriers of 0.006 inch plastic were sunk to 1.5m depth around each irrigation treatment replication in March, 2001.

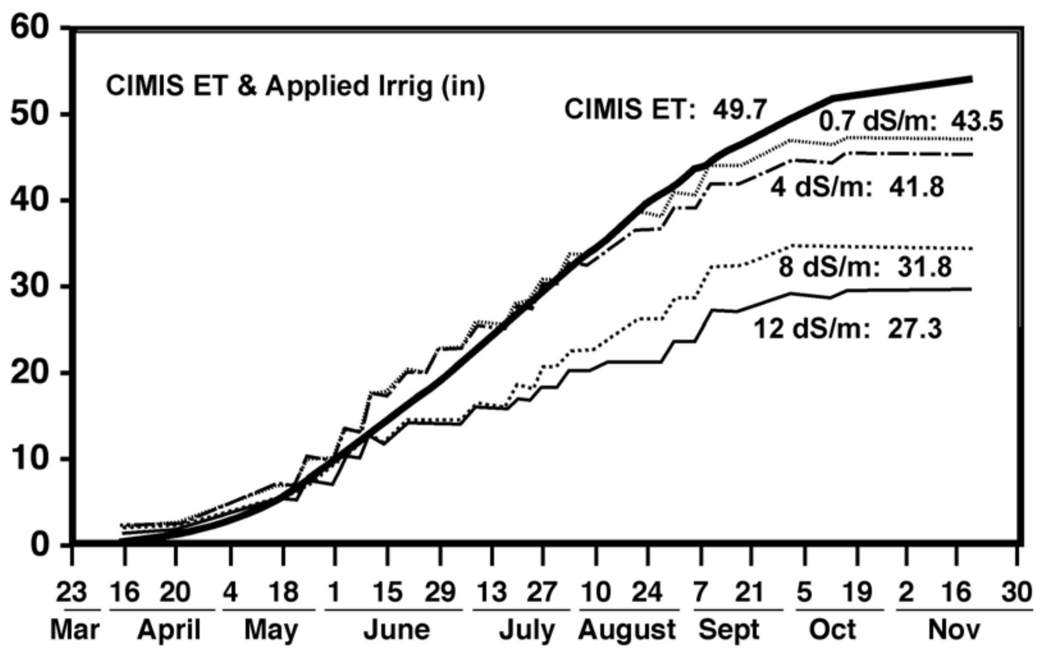

Figure 4. Cumulative seasonal applied irrigation water to all treatments and calculated pistachio ET using 2002 CIMIS ET_0 as measured at the Shafter Field Station multiplied by crop coefficients described by Goldhamer (1987).

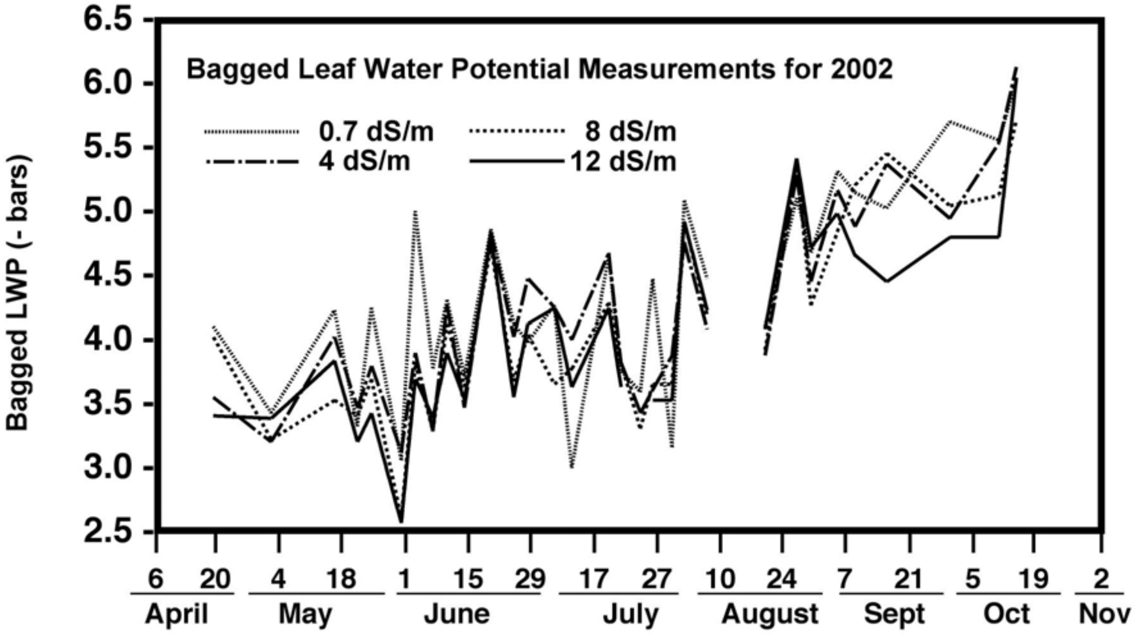

Figure 5. Bagged midday leaf water potentials showing cumulative differential from 0.75 control treatment.

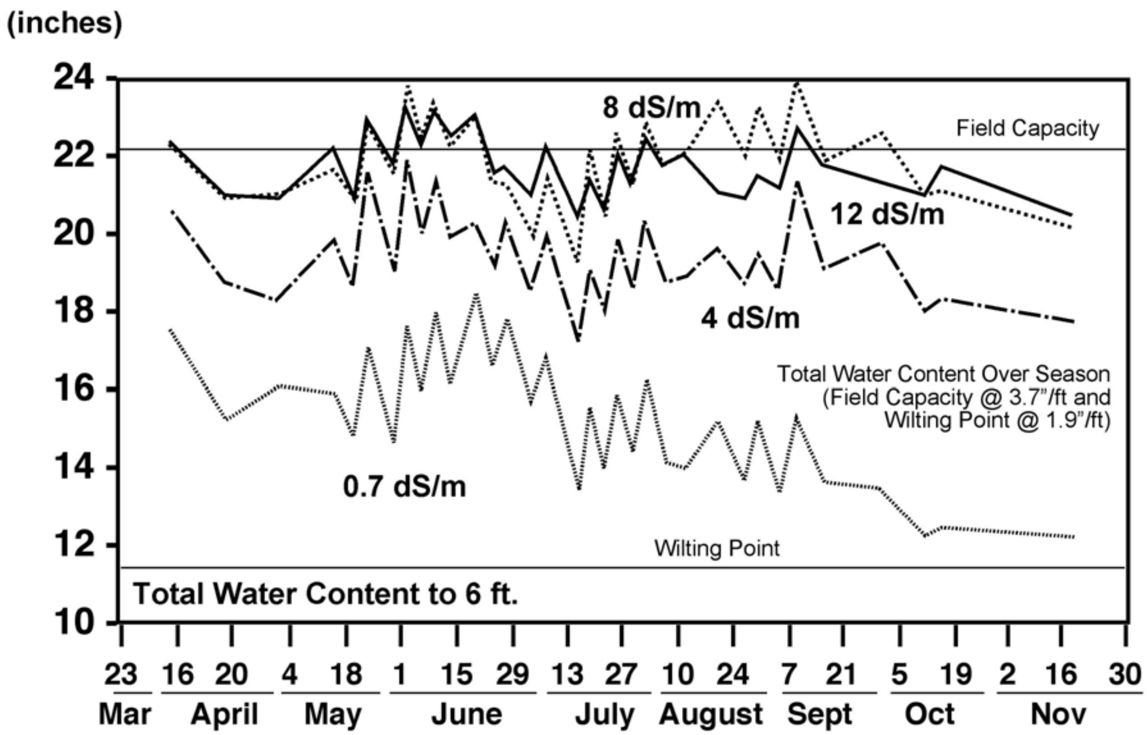

Figure 6. Available water and total water content in inches for all treatments from 0.2 to 5.2 foot depth. Calculated using field capacity at 3.7in/ft, 18.5 inches total over 5 feet, and wilting point of 1.9 in/ft, 9.5 inches total over 5 feet. Total water available at 100% = 9.0 inches.

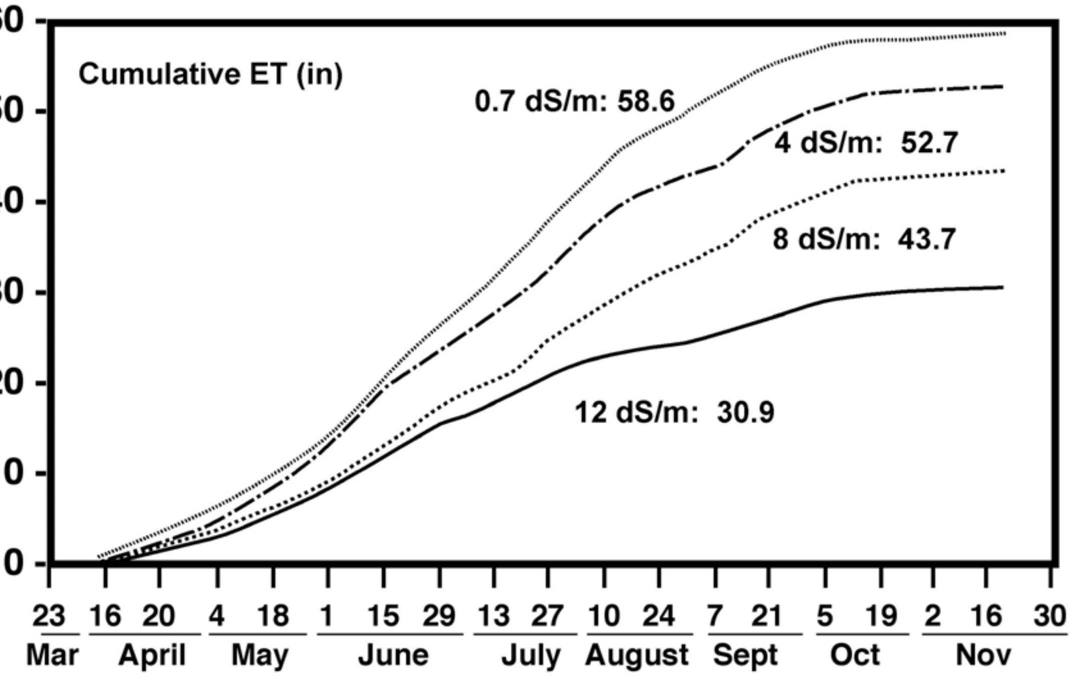

Figure 7. Comparative seasonal evapotranspiration for all treatments as determined by soil water content depletion between irrigations.

Selenium Removal from Agricultural Drainage Water by Selenate-Reducing Bacteria

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ABSTRACT

Microbial reduction of selenate [Se(VI)] to elemental selenium [Se(0)] is a useful technique for removing Se from agricultural drainage water. A series of batch experiments were conducted in the laboratory to determine the effects of yeast extract (0.005 to 0.1%), salinity (EC, 5 to 75 dS/m), and NO_3^- (5 to 100 mg/L) on the removal of Se(VI) (2000 µg/L) from drainage water by *Enterobacter taylorae*. Results showed that relatively high amounts of yeast extract (0.05%) were needed for *E. taylorae* to effectively reduce Se(VI) to Se(0). During a 7-day experiment, about 95% of added Se(VI) was reduced to Se(0) in the low-salinity drainage water (5 dS/m) with NO_3^- values of 5-50 mg/L. In the high-salinity drainage water (50-75 dS/m), reduction of Se(VI) to Se(0) was limited. *E. taylorae* was also capable of reducing Se(VI) to Se(0) in the San Joaquin Valley drainage water, with a reduction of the added Se(VI) to Se(0) (73.8%) and Se(-II) (20%). This study suggests that *E. taylorae* may be used to treat Se(VI)-contaminated drainage water in the field.

INTRODUCTION

Selenium (Se) contamination in the San Joaquin Valley wetlands, California is mainly associated with agricultural drainage water containing Se (mostly as selenate [Se(VI)]) (*1-3*). Bioaccumulation of Se in Kesterson Reservoir, CA has created hazard to the waterfowl (*1*, *2*). In order to protect wetland wildlife, Se in agricultural drainage water needs to be removed before its disposal to wetlands.

Bacterial reduction of Se(VI) to elemental Se [Se(0)] is a feasible technology in the removal of Se from agricultural drainage waters because of the insolubility of Se(0) (*3-8*). In the reduction process, Se(VI) can be used in microbial respiration as an alternative terminal electron acceptor for growth and metabolism. Many selenate-reducing bacteria isolated from different aquatic environments are capable of reducing Se(VI) to Se(0) (*3-9*), such as strain SES-3 isolated from estuarine sediment (*10*), *Thauera selenatis* from Se(VI)-contaminated waste water (*11*), *γ-proteobacteria* from a solar evaporation pond salinity (*12*), and *Enterobacter taylorae* from rice straw (*13*). In this study, we used *E. taylorae* to reduce Se(VI) to Se(0) in synthetic and natural drainage water and to determine the effects of yeast extract, salinity and nitrate (NO_3^-) on the reduction of Se(VI) to Se(0) in a series of batch experiments.

MATERIALS AND METHODS

MATERIALS

Natural drainage water was collected from the San Joaquin Valley, California. The water, with a pH of 7.9 and a salinity (electrical conductivity [EC]) of 7.4 dS/m contained 38.6 µg/L Se(VI), 4.29 µg/L of selenite [Se(IV)], 0.567 µg/L of organic Se, 3725 mg/L of SO_4^{2-}, 509 mg/L of Cl^-, 51.1 mg/L of NO_3^-, 0.31 mg/L of NH_4^+ and 0.125 mg/L of PO_4^{3-}. Synthetic agricultural drainage water with an EC of 5.1 dS/m and a pH of 8 was prepared with the following constituents (in g/L): Na_2SO_4, 1.48; NaCl, 0.659; $NaHCO_3$, 0.275; $CaCl_2 \cdot 2H_2O$, 0.733; $MgSO_4$, 0.745; $(NH_4)_2SO_4$, 0.073; $Na_2B_4O_7 \cdot 4H_2O$, 0.176; KCl, 0.019; NaH_2PO_4, 0.044; $FeCl_2$, 0.0002; yeast extract, 0.5 (from 0.05 to 1 in the yeast extract-effect experiment described below); glucose 0.5; and a trace element solution (*14*), 1 mL/L. $CaCl_2 \cdot 2H_2O$, $MgSO_4$ and other chemicals were separately dissolved in deionized water and autoclaved (18 psi at 121 °C) for 20 minutes before mixing on cooling. After mixing, a Se(VI) standard solution was added to the drainage water to a Se(VI) concentration of 2000 µg/L. In the salinity-effect experiment described below, synthetic drainage water was autoclaved after salts (NaS_2O_4 and NaCl) were added to the drainage water. The Se(VI) and NO_3^- standard stock solution (10,000 mg/L) was passed through a sterile 0.2 µm membrane filter prior to its addition to the drainage water.

Enterobacter taylorae was pregrown in a 1 % tryptic soy broth (TSB) solution and incubated (30 °C) for one day. The solution was then centrifuged at 5000 rpm for 20 min. To remove the TSB residues, cells were washed three times by centrifugation (5000 rpm, 20 min) with 35 ml of the sterile synthetic drainage water described above. Washed cells were resuspended in the same solution to give an OD_{600} of 1.3.

REDUCTION OF SE(VI) IN SYNTHETIC DRAINAGE

A series of batch experiments were conducted in the laboratory to determine the effects of yeast extract, salinity and NO_3^- on Se(VI) reduction to Se(0) in synthetic drainage water. The terms "yeast extract–effect", "salinity–effect" and " NO_3^-–effect" represent three batches of experiments. In the yeast extract–effect experiments, 200 ml of synthetic drainage water with yeast extract levels of 0.005, 0.01, 0.05 and 0.1 % were placed in each 250–ml flask, followed by 0.5 ml of washed cell suspension. In the salinity–effect experiments, 200 ml of synthetic drainage water prior to autoclaving were placed in each 250–ml flask, followed by adding Na_2SO_4 and NaCl with a weight ratio of 3:1 to EC levels of 5, 25, 50 and 75 dS/m. The drainage water was autoclaved (18 psi at 121 °C) and cooled to room temperature, followed by the addition of 2000 µg/L Se(VI) and 0.5 ml of washed cell suspension. In the NO_3^-–effect experiments, 200 ml of sterile synthetic drainage water were placed in each 250–ml flask, followed by spiking NO_3^- to concentration levels of 5, 25, 50 and 100 mg/L and 0.5 ml of the washed cell suspension. All of the flasks were capped with sterile stoppers and incubated at room temperature (21 °C). All three batches of the experiments were run in triplicate for 7 days. The samples were collected daily for analysis of Se species.

REDUCTION OF SE(VI) IN NATURAL AGRICULTURAL DRAINAGE WATER

In order to examine whether *E. taylorae* can survive in natural drainage water and reduce Se(VI) to Se(0), 200 ml of natural drainage water spiked with a Se(VI) concentration of 2000 µg/L and 0.5% of yeast extract were added to each 250–ml flask, followed by adding 0.5 ml of the washed cell suspension. The drainage water without adding the washed cell suspension served as a control. All flasks were capped with sterile stoppers and incubated at room temperature (21 °C). The experiment was run in triplicate for 7 days. The water samples were collected daily for analysis of Se species.

ANALYSIS

Selenium species in the drainage water were determined using a method developed by Zhang and Frankenberger (*15*, *16*) after Se(0) was removed from solution by centrifugation at 12,000 for 10 min. In brief, Se speciation was carried out as follows: Se(IV) in the water samples was determined in a pH 7 buffer solution. The sum of Se(IV) and selenide [Se(-II)] [organic Se and inorganic Se(-II)] was determined when the Se(-II) in the water samples was oxidized to Se(IV) by $Na_2S_2O_8$, which was indicated by precipitation of Mn oxides formed from the oxidation of added Mn^{2+}. The Se(-II) concentration was calculated as the difference between Se in this water sample and Se(IV) concentration determined in another subsample. Total soluble Se in the water samples was determined by oxidizing all Se to Se(VI) by $Na_2S_2O_8$, followed by reduction to Se(IV) in 6 N HCl. Se(VI) concentration was calculated as the difference between total soluble Se concentration, and the sum of Se(IV) and Se(-II) concentration determined in another subsample. Se(0) was determined as the difference between added Se(VI) and total soluble Se. Se concentrations in all prepared solutions were analyzed by hydride generation atomic absorption spectrometry (HGAAS) (*15*, *17*). The detection limit in the prepared solution was 0.5 µg/L.

RESULTS

EFFECT OF YEAST EXTRACT ON SE(VI) REDUCTION

The efficiency of the Se(VI) reduction is related to the amount of yeast extract added to the drainage water (Fig. 1). In the high-yeast extract (0.05-0.1%) drainage water, Se(VI) dropped rapidly during a 7-day experiment, from 1950 to 38.6-93.2 µg/L. Se(IV) formed from Se(VI) reduction increased to 802-841 µg/L on day 3. Then, Se(IV) decreased with time to about 5 µg/L. Se(0) and Se(-II) also increased with time. On the final day of the experiment, Se(0) was 1742-1800 µg/L, and Se(-II) was 97.2 to 110 µg/L in the high-yeast extract drainage water.

In the low-yeast extract (0.005-0.01%) drainage water, Se(VI) also dropped rapidly during the 7-day experiment, from 2000 to149-152 µg/L. Se(IV) formed from Se(VI) reduction increased to1006 µg/L at day 3 in the 0.005% yeast extract drainage water, and 1310 µg/L at day 4 in the 0.01% yeast extract drainage water. Se(IV) was maintained at these levels during the rest of the experiment. Se(0) formed from Se(IV) reduction increased slowly with time. On the final day of the experiment, Se(0) and Se(-II) was 408 and 37.5µg/L, respectively in the 0.005% yeast extract drainage water. In the 0.01% yeast extract drainage water, Se(0) and Se(-II) was 820 and 64.4 µg/L, respectively.

EFFECT OF SALINITY ON SE(VI) REDUCTION

The relationship between the Se(VI) reduction and salinity (EC=5, 25, 50 75 dS/m) in the synthetic drainage water is shown in Fig. 2. In the high-salinity (EC=50, 75 dS/m) drainage water, Se(VI) decreased slowly during the 7-day experiment, from the 2039 to 1237-1588 µg/L. With the decrease of Se(VI) in the drainage water, Se(IV) formed from Se(VI) reduction increased slowly to a range of 60-61.6 µg/L in the 75 dS/m drainage water and 170-178 µg/L in the 50 dS/m drainage water at days 4-5, and then slightly decreased with time. During the experiment, Se(0) increased to 339 µg/L in the 75 dS/m drainage water and to 624 µg/L in the 50 dS/m drainage water. Se(-II) was relatively stable in the drainage water, with a concentration range of 31 to 67.6 µg/L.

In the relatively low-salinity (EC=5-25 dS/m) drainage water, Se(VI) dropped rapidly during the 7-day experiment, from 2043 to 31.5-318 µg/L. Se(IV) formed from Se(VI) reduction increased to 900 µg/L at day 2 in the 5 dS/m drainage water, and 528 µg/L at day 3 in the 25 dS/m drainage water. Then, Se(IV) decreased to 14.1 and 145 µg /L on the final day of the experiment in the 5 and 25 dS/m drainage water, respectively. Se(0) formed from Se(IV) reduction increased rapidly to 1964 and 1536 µg /L in the 5 and 25 dS/m drainage water, respectively. Se(-II) was low during the experiment, with a concentration range of 7.82 to 60.6 µg/L.

EFFECT OF NITRATE ON SE(VI) REDUCTION

The effect of NO3- on Se(VI) reduction in synthetic drainage water with NO3- levels of 5, 25, 50 and 100 mg/L is presented in Fig. 3. In the relatively low NO3- (5-50 mg/L) drainage water, Se(VI) dropped rapidly from 1960 to 26.8-58.6 µg/L during the 7-day experiment. With the decrease of Se(VI) in the drainage water, Se(IV) formed from Se(VI) reduction increased with the highest detection on day 2 (540-703 µg/L). Then, Se(IV) decreased with time to about 5 µg/L. Se(0) formed from Se(IV) reduction increased rapidly to 1839-1878 µg/L on the last day of the experiment. Se(-II) was relatively stable during the experiment, with a concentration range of 9.11 to 68.1 µg/L.

In the relatively high NO3- (100 mg/L) drainage water, Se(VI) decreased slowly during the 7-day experiment, from 1979 to 506 µg/L. However, Se(IV) formed from Se(VI) reduction was maintained at a very low level of 10-20 µg/L during this experiment, with an increase of Se(0) and Se(-II). On the final day of the experiment, Se(0) and Se(-II) were 1352 and 111 µg/L, respectively.

SE(VI) REDUCTION IN NATURAL DRAINAGE WATER

Reduction of Se(VI) in natural drainage water with and without inoculation of E. taylorae is presented in Fig. 4. In the drainage water with inoculation of E. taylorae, Se(VI) decreased rapidly during the 7-day experiment, from 2030 µg/L at the beginning of the experiment to 95.3 µg/L at day 7. Se(IV) formed from Se(VI) reduction increased up to 469 µg/L on day 2. On the final day of the experiment, Se(IV) was 32.7 µg /L. Se(0) and Se(-II) increased with time to 1490 and 402 µg /L, respectively. In contrast, Se(VI) decreased slowly with time in the control to 1187 µg/L, with a low Se(IV) range of 0-32.5 µg /L during the 7-day experiment in the non-inoculated drainage water. With the decrease of Se(VI) in the natural drainage water, Se(0) and Se(-II) increased to 500 and 316 µg/L, respectively.

DISCUSSION

Bacterial reduction of soluble Se(VI) to insoluble Se(0) has been proposed as a remedial technology in treating Se-contaminated drainage water in San Joaquin Valley, California (*3*, *18*). Recently, Zahir et. al (*13*) isolated a Se(VI)-reducing bacterium, *E. taylorae* from rice straw and used it to successfully reduce Se(VI) to Se(0) in an artificial high-salinity (15.5 dS/m) drainage water. We characterized the pathway of Se(VI) reduction in the drainage water as Se(VI) → Se(IV) →Se(0) →Se(-II). This study showed that the efficiency of Se(VI) reduction by *E. taylorae* was related to the amount of yeast extract added, salinity and NO_3^- levels in the drainage water.

Yeast extract is commonly used in culture media for microbial reduction of Se(VI) to Se(0) (*7*, *10*, *12*, *19-21*). Fujita et al. (*19)* reported that yeast extract, as a growth factor, was required for *Bacillus sp*. SF-1 to reduce Se(VI) to Se(0) and casamino acids, a DNA/RNA mixture, or a vitamin mixture cannot replace the yeast extract. In this study, yeast extract was also shown to promote Se(VI) reduction to Se(0) by *E. taylorae.* In the drainage water with a relatively high level of yeast extract (0.05-0.1%), about 89-93% of the added Se(VI) was reduced to Se(0) and 5 % to Se(-II). In the drainage water with low levels of yeast extract (0.005-0.01%), only 20-40% of the added Se(VI) was reduced to Se(0) although the amount of glucose added in the drainage water, was the same in all of the experiments. The amount of yeast extract in the drainage water also affected the reduction process. In the high yeast extract drainage water, Se(IV) was rapidly reduced to Se(0) when it was formed from rapid reduction of Se(VI). In contrast, in the low yeast extract drainage water, reduction of Se(IV) to Se(0) was limited although Se(VI) reduction to Se(IV) preceded rapidly. During the last 3-4 days of the experiment, a decrease in Se(VI) concentration, a slight change in the concentration of Se(IV), and an increase in Se(0) concentration in the low-yeast extract drainage water suggested that low amounts of yeast extract in the drainage water does not provide enough essential growth factors to support rapid bacterial reduction of Se(IV) to Se(0), which occurred in the high-yeast extract drainage water.

High-salinity drainage water often is the by-product of agricultural irrigation in farmlands. The salinity in drainage water affected the efficiency of Se(VI) reduction to Se(0). In a study on the effect of sulfate, a major anion in agricultural drainage water, on the rate of Se(VI) reduction with washed cell suspension of *Desulfovibrio desulfuricans*, Zehr and Oremland (*22*) reported that the rate of Se(VI) reduction was negatively related to the amounts of SO_4^{2-} with a range of 0.2 to 50 mM. In this study, the reduction efficiency of Se(VI) to Se(0) by *E. taylorae* was also negatively associated with the salinity in the drainage water, with the major anions being SO_4^{2-} and Cl^-. During this 7-day experiment, the percentage of Se(VI) reduction to Se(0) followed a reverse trend with salinity levels in the drainage water: 95% (EC=5 dS/m) > 81% (EC=25 dS/m) > 30.5% (EC=50 dS/m) > 16.7% (EC=75 dS/m).

Nitrate is one of the most common anions found in agricultural drainage water, due to the application of fertilizers in the San Joaquin Valley. NO_3^- is a competitive electron acceptor to Se(VI) in Se[VI] reduction to Se(0) in aquatic system (*23*, *24*). In a study on the microbial reduction of NO_3^- and Se(VI), Steinberg et al. (*21*) reported that NO_3^- reduction by an anaerobic, freshwater enrichment preceeded than that of Se(VI) reduction in an anaerobic medium with an equal amounts of Se(VI) and NO_3^- of 20 mM. Fujita et al. (*19*) reported that Se(VI) reduction by *Bacillus sp*. SF-1 in a basal medium with 1 mM of Se(VI) was completely inhibited when 20 mM of NO_3^- was added to the medium. NO_3^- and Se(VI) can also be simultaneously reduced in the medium with washed-cell suspensions of *Sulfurospirillum barnesii* and lactate as the electron donor (*8*). In this study, reduction of Se(VI) to Se(0) was related to the amounts of NO_3^- in the drainage water. A NO_3^- range of 5 to 50 mg/L did not affect Se(VI) reduction to Se(0). About 95% of added Se(VI) was reduced to Se(0) in the drainage water during our 7-day experiment. Se(VI) reduction was slightly slowed when NO_3^- was increased to 100 mg/L in the drainage water. Similar results can be also found in a recent study on bacterial Se(VI) reduction using rice straw, when Zhang and Frankenberger (*25*) reported that the presence of NO_3^- in a rice straw solution retarded Se(VI) reduction to Se(0). During a 14-day study, about 93% of the added Se(VI) (1000 µg/L) was reduced to Se(0) during a period of 7 days in the rice straw solution with the 100 mg/L NO_3^-. It took 12 days that 93% of the added Se(VI) was reduced to Se(0) in the rice straw solution with 250 mg/L NO_3^-. In the rice straw solution with 500 mg/L NO_3^-, Se(VI) was not reduced until day 14 was approached, when almost all the NO_3^- was removed from solution via denitrification.

This study showed that *E. taylorae can* survive in natural drainage water and also effectively reduce Se(VI) to Se(0). In the absence of *E.*

taylorae, only 24.6 and 15.6% of the added Se(VI) was reduced to Se(0) and Se(-II) in the drainage, respectively. Upon the addition of *E. taylorae* to the drainage water, 73.8 and 20% of the added Se(VI) was reduced to Se(0) and Se(-II), respectively.

CONCLUSIONS

The results from this study reveal that *E. taylorae* was capable of reducing Se(VI) to Se(0) in synthetic and natural drainage water. The optimum Se(VI) reduction occurred in the drainage water containing EC values < 25 dS/m and NO_3^- values < 50 mg/L. In the San Joaquin Valley, California, the values of EC in drainage water, with the major anions of SO_4^{2-} and Cl^-, ranges from 2.25 to 21.5 dS/m (*26*). NO_3^- typically ranges from 3 to 234 mg/L (*26*). Therefore, *E. taylorae* may be a potential Se(VI)-reducer to remediate Se-contaminated drainage water with relatively low NO_3^- levels in the San Joaquin Valley, California

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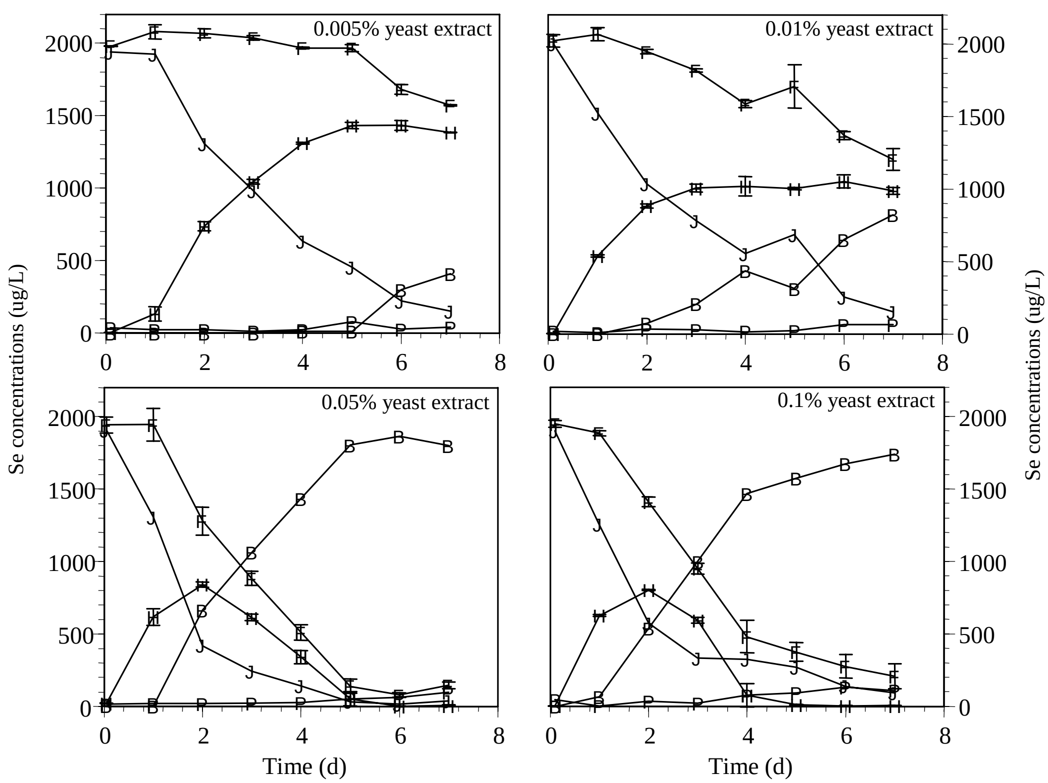

Figure 1. Effects of yeast extract (0.005-0.1%) on the changes in Se species in a synthetic drainage water upon inoculation with *E. taylorae*. Symbols: ◆:Total soluble Se, ●:Se(VI), ▲:Se(IV), ■:Se(0), ▼:Se(-II).

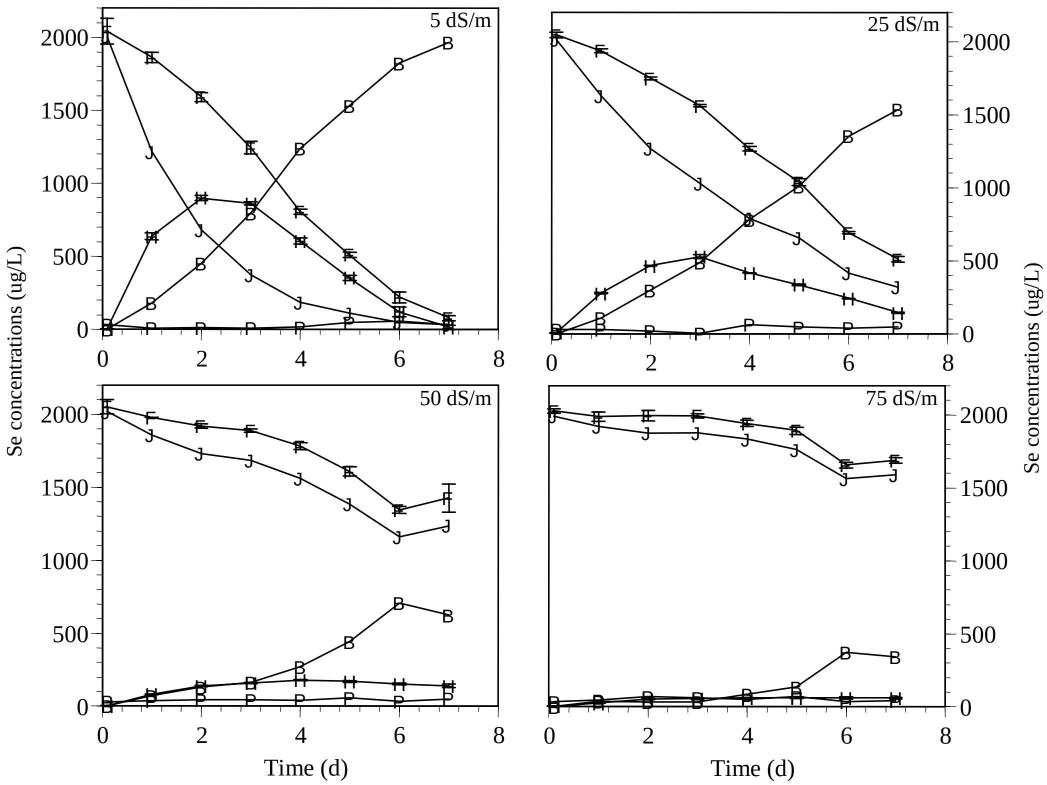

Figure 2. Effects of salinity (5-75 dS/m) on the changes in Se species in a synthetic drainage water upon inoculation with *E. taylorae*. Symbols: ◆:Total soluble Se, ●:Se(VI),▲:Se(IV),■:Se(0),▼:Se(-II).

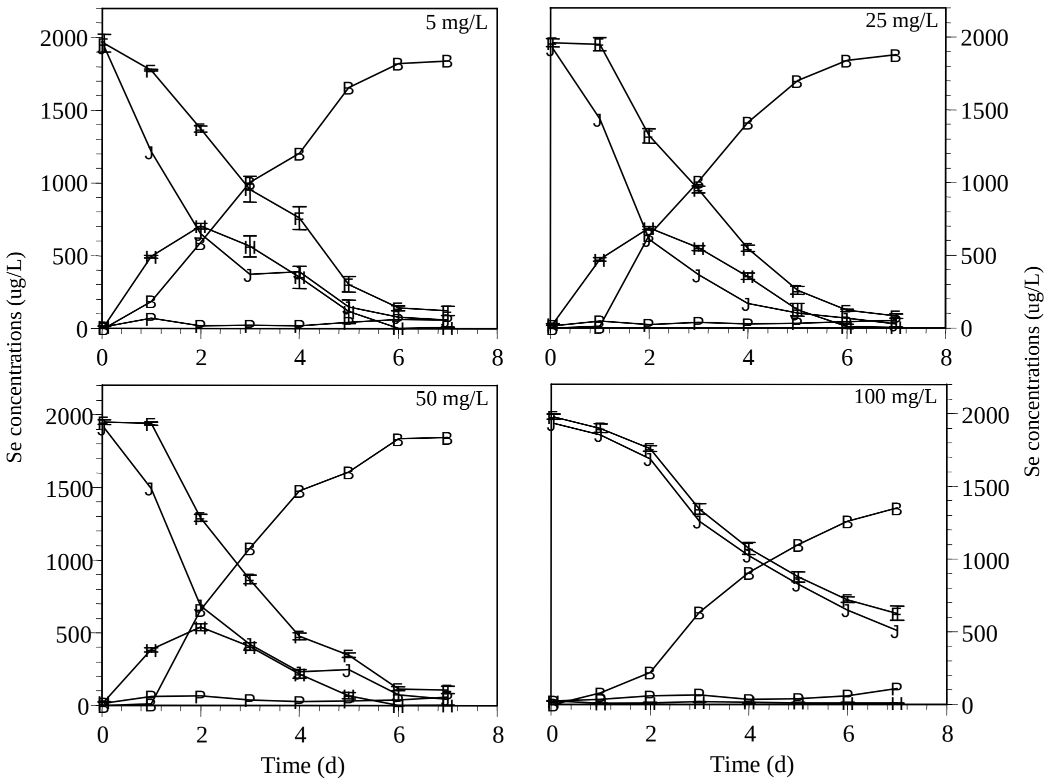

Figure 3. Effects of nitrate (5-100 mg/L) on the changes in Se species in a synthetic drainage water upon inoculation with *E. taylorae*. Symbols: ◆:Total soluble Se, ●:Se(VI),▲:Se(IV),■:Se(0),▼:Se(-II).

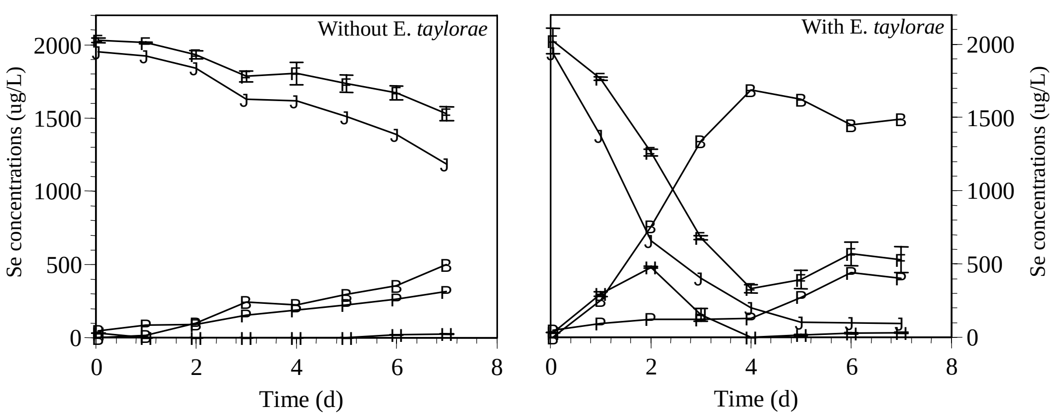

Figure 4. Reduction of Se(VI) in a natural agricultural drainage water spiked with 2000 ug/L of Se(VI), with and without inoculation of E. *taylorae*. Symbols: ◆:Total soluble Se, ●:Se(VI),▲:Se(IV),■:Se(0), ▼:Se(-II).

Management Effects on Selenium Fractionation, Speciation and Bioavailability in Sediments from Evaporation Basins

(Part of a Team Project Entitled "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation")

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ABSTRACT

This research is a component of the joint research project "Mitigating Selenium (Se) Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation." The joint research project involves a team of multidisciplinary investigators and cooperators joining forces to conduct a comprehensive investigation of Se biogeochemistry and ecotoxicity associated with disposal of agricultural drainage waters in evaporation basins within the San Joaquin Valley, California. The primary objective of the joint project is to minimize environmental hazards associated with using evaporation basins for removal of Se from agricultural drainage waters. The method investigated includes breaking the foodchain by harvesting invertebrates and volatilization of selenium by aquatic microorganisms.

This research component seeks information about the relationship between management activities and Se chemical forms in water and sediments, as well as bioavailable Se. The objectives of this study were to determine patterns of Se speciation in the water column and fractionation of solid-phase Se in sediments from evaporation ponds under contrasting management practices, and to evaluate the bioavailable Se in sediments using Se speciation and bioavailability indicators. This investigation was conducted at evaporation basins in Tulare Lake Drainage District (TLDD) in the southern San Joaquin Valley, California. Pond water, sediment core and detrital layer samples were taken from ponds with and without brine shrimp harvesting. Aqueous Se speciation and sediment Se fractionation in detrital layer and surface sediments were carried out. Proteinaceous Se (peptidic constituents), a potential site-specific Se risk indicator, was determined for both detrital layer material and sediment extracts. Results showed that Se undergoes significant biochemical transformations in both the water column and sediments. The interface between pond water and sediment is an important linkage regulating the bioavailable Se pool. Surface detrital layer enriched in organic matter contain most of the proteinaceous Se. Invertebrate harvesting appeared to reduce total Se accumulation in the detrital layer but had no effect on Se speciation. Overall results indicate that evaporation basins reduce Se concentrations from agricultural drainage water by incorporating Se into the sediment, mostly by adsorption of Se(IV), association with organic matter, and formation of elemental Se. Management options that reduce accumulation of Se in surface water and in the surface detrital layer can be beneficial in reducing Se ecotoxicity potential to water birds.

INTRODUCTION

Evaporation basins are a proven economic means for disposing of agricultural drainage water in the San Joaquin Valley, California, however, there remains great concern about potential Se toxicity to migratory waterfowl. The top predators in the food chain receive Se primarily through their diet of aquatic invertebrates and fish. Thus, Se ecotoxicity risk largely depends on the transfer of Se into the food chain. Recent research by Fan and Higashi has demonstrated the potential for managing evaporation basins to break the foodchain, such as harvesting invertebrates and Se volatilization by aquatic microorganisms. Brine shrimp production and harvesting in evaporation basins have been practiced in the last few years and this activity is assumed to break the transfer of Se into the foodchain by reducing the food source for invertebrates as well as for higher trophic levels.

This research is part of a joint research project "*Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation*", proposed by a team of multidisciplinary investigators and cooperators for selenium (Se) ecotoxicity remediation in evaporation basins in the San Joaquin Valley. The *overarching* objectives of the joint project are focused on Se in the foodchain of evaporation ponds and include:

- evaluating the efficacy of reducing Se risk by intensive commercial harvest of brine shrimp (*Artemia franciscana*) and other macroinvertebrates,
- assessing effects of fertilizer inputs on algal dynamics for optimizing the harvest of brine shrimp and other macroinvertebrates, as well as Se volatilization so that total and bioavailable Se are reduced, and
- evaluating the ecotoxicological status in different evaporation basins of widely varying salinity and physio-chemical conditions so that general factors leading to reduced ecotoxic risk can be discerned.

Studies using flow-through wetlands to remove Se from agricultural drainage water show that selenate (Se VI), the dominant form of Se in the drainage water, undergoes reduction to selenite (Se IV) and organic Se (org-Se) as water flows through the wetland (Gao et al., 2000; 2003). The major mechanism removing Se in flow-through wetlands is reduction to elemental Se [Se(0)] and immobilization in the organic phase of the sediments. Vegetation plays an important role in Se reduction and immobilization in wetlands by providing a carbon source for aquatic microorganisms. Similar processes are expected to occur in agricultural evaporation basins mainly due to microphyte and microbial activity, although vascular plants are not present in the evaporation basins.

A scientific consensus is that sediments harbor important pools of Se that may have potential ecotoxic effects (EPA Office of Water, 1998). The surface sediment is a zone of high microbial activity and accumulates Se in the fine organic detrital layer and surface mineral sediments (Gao et al., 2003). Thus, the surface sediment serves as an important source of potentially bioavailable Se. Selenium partitioning in the sediments can be evaluated by sequential selective-extractions methods for soluble, ligand-exchangeable or adsorbed, carbonate associated, organic matter (OM) associated, and Se (0) and other resistant forms of Se (Chao and Sanzolone, 1989; Lipton, 1991; Huang and Fujii 1996). The soluble and ligand-exchangeable Se may be considered readily bioavailable. The bioavailability of OM-associated Se is not known; however, it is assumed that there is a wide range of potential bioavailabilities associated with different forms of organic-associated Se. Insoluble Se(0) immobilized in sediments is generally considered stable and non-bioavailable in reduced (anoxic) sediments and can be mobilized when exposed to oxidized conditions (Zhang and Moore, 1996; Zawislanski and Zavarin, 1996; Tokunaga et al., 1996).

Selenium speciation is a key factor determining Se bioavailability. The major aqueous species of Se are Se(VI), Se(IV) and org-Se. Org-Se is generally considered more toxic and bioavailable than inorganic Se to fish and wildlife, both in waterborne and dietary exposure (Fan and Higashi, 2000). An example of relative toxicity of various Se species follows: selenomethionine (Se-Met) 100-1,000X > selenite 10X > selenate 1 (Lemly et al., 1993). Org-Se as Se-Met is much more available to algae and invertebrates than the typical inorganic forms (selenate and selenite) (Rosetta and Knight, 1995; Maier and Knight, 1994). Aquatic hazard assessment of Se is characterized in terms of the potential for food-chain bioaccumulation and reproductive impairment in fish and aquatic birds (Lemly, 1995). Recent discussions, however, indicate that *waterborne exposure* to Se in all its various forms is much less important than *dietary exposure* in determining the potential for chronic effects in aquatic organisms in general and for fish in particular.

Proteinaceous (peptide- and protein-bound) Se in the diet of aquatic organisms is emerging as a critical factor for assessing the potential for chronic effects in aquatic organisms (US-EPA, 1998). Fan (2001) pointed out that because Se is expected to be transformed into proteins by primary producers and considering that proteins are highly available to consumers and predators, proteinaceous Se should be biomagnified through the food chain. Their research did indicate that proteinaceous Se appears to be biomagnified up the food chain and is better correlated with symptoms observed in fish reproductive systems compared to total biomass or waterborne Se concentrations (Fan et al., 2002). It is possible that similar Se forms in detritus and sediment are also highly available to benthic organisms. Thus, proteinaceous Se may serve as a site-specific indicator of Se risk. Use of this indicator and examination of Se speciation may offer better tools in evaluating Se bioavailability in the evaporation basins.

The specific objectives of this research were to determine patterns of Se speciation in the water column and fractionation of solid-phase Se in sediments from evaporation ponds under contrasting management practices, and to evaluate the bioavailable Se in sediments using Se speciation and bioavailability indicators.

STUDY METHODS

FIELD SAMPLING AND ANALYSIS

Field sampling for pond waters and sediments was carried out three times from Fall 2001 through Spring 2003 in Hacienda Evaporation Basin (HEB) and South Evaporation Basin (SEB) in Tulare Lake Drainage District (TLDD) (Fig 1). Two cells in HEB (C4 and A4) were sampled in Fall 2001 and three cells in SEB (S1, S8 and S9) were sampled in Fall 2002. Two sampling locations were selected in each cell following prevailing wind directions in this area from northwest (NW) to southeast (SE) or southwest (SW). Harvesting activity for brine shrimp in these cells is shown in Table 1. For each location, triplicate samples of pond water, detrital materials (DM) or detrital materials mixed with mineral sediments (refer as detrital layer), and the underlying mineral sediment cores (~ 25 cm depth) were collected. In addition, a visible layer of detrital materials buried a few cm below the surface of the sediment in C4-NW was also collected. To verify some findings, water samples were taken a second time in May 2003 from S1, S8 and S9 along with inlet water and S10 water. Water flow direction basically followed the order of cell numbers in both basins; however, when drainage water was limited in SEB, flow of drainage water was diverted directly from Cell 1 to Cell 7 through Cell 6. In addition, drainage water was more continuously added to SEB compared to HEB.

Water samples were stored in ice coolers for transfer to the laboratory. Samples were stored at 3 °C through completion of analyses. Solutions were analyzed for pH, electrical conductivity (EC), total Se concentration and Se speciation [Se(VI), Se (IV) and org-Se].

Sediment cores were taken using 5-cm diameter acrylic tubes. The cores were sealed immediately with a plastic cap and duct-tape and stored on ice. After transferring to the laboratory, the core samples were frozen until ready for processing and analyses. Organic detrital layer materials were separated from the mineral sediment cores by scraping off the materials with visible detrital matter color. The samples from three cores were composited for locations in HEB but treated individually for locations in SEB. The mineral cores were then sectioned into the 0-5, 5-10, 10-15 and 15-20 cm segments. Subsamples were used for selective sequential extractions, determination of moisture content, and total Se by chemical digestion.

Sequential selective dissolution procedures for fractionation of sediment Se were based on research by Chao and Sanzolone (1989), Lipton (1991), and Velinsky and Cutter (1990). The detailed procedures are described in Gao et al. (2000). In this study, Se in the detrital layer and surface mineral sediments (0-5 cm) was fractionated into soluble, adsorbed or ligand-exchangeable, and OM-associated using (1:10, solid:water ratio) water, 0.1 *M* K_2HPO_4 (PO_4, pH 8.0), and 0.1 *M* NaOH, respectively. The non-extractable fraction, i.e., the difference between the total and the extracted, was comprised primarily of Se(0) and a very small amount of residual (most-resistant) Se based on previous findings by Gao et al. (2000).

As a potential bioavailability indicator, proteinaceous Se was determined in collaboration with project collaborators. Peptidic Se constituents in the detrital layer and sediment sequential dissolution extracts were determined using pyrolysis-GCMS by Higashi. This methodology can detect and structurally identify most of the bound selenoamino acids in a single analysis, including Se-Met, Se-Cys, and methyl-Se-Cys (Fan et al., 1998).

SELENIUM ANALYSIS

Selenium speciation [Se(VI), Se(IV) and org-Se] for water and 0.1 M NaOH extracts was determined using the methods of Zhang et al. (1999). Three determinations were made: (i) direct measurement of Se(IV) using phosphate pH 7 buffer (for NaOH extracts, solution pH was adjusted to pH 7 with HCl prior to the analysis), (ii) Se(IV) + org-Se using persulfate to selectively oxidize org-Se(-II) to Se(IV) using manganese oxide as an indicator for completion of oxidation, and (iii) total Se using persulfate digestion followed by reduction to Se (IV) (Cutter, 1982, Yoshimoto, 1992). Se(IV) in solution was analyzed using HGAAS (hydride generation atomic absorption spectroscopy). Org-Se(-II) is obtained as the difference between Se(IV)+org-Se and Se(IV), and Se(VI) is calculated as the difference between total Se and Se(IV)+org-Se analysis. Total Se in detrital samples and sediments was determined using a modified $HClO_4$-HNO_3 digestion (Zasoski and Burau, 1977), followed by a reduction of Se(VI) to Se(IV) for HGAAS analysis.

RESULTS AND DISCUSSION

SELENIUM CONCENTRATION AND SPECIATION IN WATERS

Due to evapoconcentration, pond waters in HEB and SEB are hypersaline (EC of 83 to 119 dS m^{-1}), except for S1 (EC of 19 dS m^{-1}), the initial cell receiving inlet drainage water in SEB from TLDD (Table 2). The dominant ionic constituents are sodium, chloride and sulfate. The pH values range from 7.5 to 8.9 and were similar among the two evaporation ponds.

Total Se concentrations ranged from 6 to 29 µg L^{-1} and demonstrated some spatial variability in each cell, especially in HEB (Fig 2). Most sampling locations show Se concentration below 10 µg L^{-1} except C4-SE that shows a rise to 29 µg L^{-1}. In HEB, Se speciation in pond waters was dominated by inorganic Se (about 60% Se(VI) and 40% Se(IV)) with very low concentrations of org-Se (<2%). In SEB, however, data for Fall 2002 showed a significantly higher percentage of Se(IV) and org-Se than that in HEB. The averages for Se(VI), Se(IV), and organic-Se species were 31%, 47%, and 22%, respectively. A second sampling taken in SEB in Spring 2003 was consistent with these findings showing Se(VI), Se(IV) and org-Se average values of 32%, 42%, and 22%, respectively (Fig 3). Inlet water to S1 had a total Se concentration of 15 µg L^{-1}, with a species distribution of Se(VI) = 84%, Se(IV) = 16% and org-Se was not detectable. This is consistent with previous analysis that showed agricultural drainage water in TLDD to be dominated by Se(VI) (>90%) (Gao et al., 2003). The relatively higher proportion of Se(IV) in the inlet water to S1 indicates that Se reduction has occurred to some degree in the drainage ditch delivering the water.

Results indicate that significant microbial reduction occurs in both evaporation basins with higher activity in SEB than in HEB as indicated by the higher proportion of reduced Se species (*i.e.,* Se(IV) and org-Se in water). The reason for these differences between the two basins is not readily apparent. Except for C4-SE, most pond waters have a much lower Se concentration than the inlet water. This demonstrates that evaporation basins reduce Se concentration in the water columns relative to input waters from agricultural drainage. Thus, evaporation basins serve a valuable role in removing Se from agricultural drainage waters and potentially reducing ecotoxic risk of Se in the environment.

SELENIUM IN SEDIMENTS

Total Se concentrations in the sediment profiles varied greatly with depth, as well as spatially within the evaporation basins (Fig 4). Sediments in HEB (C4 and A4) had much lower Se concentrations (<1.5 mg kg^{-1}) that those in SEB (S1, S8, and S9) where Se concentration reached about 6 mg kg^{-1} at the surface and about 9 mg kg^{-1} in the underlying sediment in S1-SW. The unevenly distribution of Se with depth and the accumulation of Se in the underlying sediment in SEB may be linked to historic pond management activities, such as changing quantities of drainage water disposed to each basin and deposition of materials. Sediments of SEB S1, especially the SW location, accumulated very high Se concentrations. This finding contradicts our expectations that Se should be more highly accumulated in the end cells (*i.e.,* those cells with the greatest evapoconcentration) as water travels moves through the evaporation basin. S1 is the cell that receives the initial drainage water as reflected in its low EC values (Table 2). Apparently, water residence time and microbial reactivity favor Se deposition in this environment. It is unknown, however, whether the high Se concentration in the underlying sediment is due to historical deposition of Se-containing materials or Se transport through the sediment. A very thin layer of detrital materials that was buried several cm below the sediment surface at C4-SE also showed high Se concentrations of 4.1 and 3.8 mg kg^{-1} (data not shown) indicating that biological activity has an important role in Se transformation and accumulation in the sediments.

It is expected that harvesting brine shrimp during the past several years should primarily affect Se concentration at the sediment surface, especially the detrital layer. In terms of concentration, ditrital layer showed lower Se concentration in the cells with harvesting activity (S8 and S9) than without (S1) in SEB, but no appreciable difference was observed in HEB. However, in terms of total Se mass collected from the detrital layer, the effect of brine shrimp harvesting on reducing Se is clearly shown (Table 3), i.e., a much smaller mass of Se in the cells with harvesting activity than those without. Although the number of locations sampled in this study was limited, the benefit of harvesting invertebrates to reduce Se accumulation in detrital layer is demonstrated in both evaporation basins.

SELENIUM FRACTIONATION, SPECIATION AND BIOAVAILABILITY INDICATOR

Fractionation

In addition to surface water, the detrital d surface sediments are considered the most important zone for Se transfer into the foodchain because the majority of the benthic invertebrates reside in this zone. Selenium fractionation results for the detrital layer and the immediate underlying mineral sediments (0-5 cm) from both HEB and SEB are shown in Fig 5. It also includes the buried detrital materials collected a few cm below the surface in C4-NW.

Generally speaking, water soluble and PO_4 extractable (adsorbed) Se are a much smaller percentage of the total Se than the 0.1 M NaOH extractable (OM-associated Se) and the non-extractable fraction (mainly Se(0) (Fig 5). The distribution of water soluble, PO_4 extractable, NaOH extractable and non-extractable fractions were 10, 10, 37 and 43%, respectively for the detrital layer, and 4, 5, 49, and 43%, respectively for 0-5 cm mineral sediments in HEB. These values were 19, 8, 33 and 41%, respectively for the detrital layer, and 8, 4, 37 and 53%, respectively for the 0-5 cm mineral sediments in SEB. The detrital layer contained a significantly higher fraction of soluble and adsorbed Se compared to the 0-5 cm mineral sediments, except for the buried detrital materials in C4. These results indicate that more available Se is residing in the immediately exposed surface detrital layer. The buried detrital materials in C4 showed a much lower percentage of soluble and adsorbed Se compared to the detrital layer materials collected at the surface. This may indicate transformation of Se to more immobile forms after the materials were buried.

Differences in the various fractions between cells with brine shrimp harvesting and those without harvesting were evident for detrital layer materials in HEB (C4 vs. A4) and 0-5 cm mineral sediments for both HEB and SEB. A large variation is observed in DM layer materials in SEB although S9 showed a higher proportion of soluble and adsorbed Se compared to S1, the cell without harvesting activity.

Speciation in NaOH Extract

The Se-associated organic phase is of particular interest in evaluating Se bioavailability. Thus, Se speciation in 0.1 M NaOH extracts was carried out for both the detrital layer and 0-5 cm mineral sediments (Fig 6). Differences between the basins, detrital layer and 0-5 cm mineral sediments, as well as cells with and without invertebrate harvesting activities were investigated.

There were no apparent differences of Se speciation in NaOH extracts between cells with and without harvesting activity in HEB (C4 vs. A4). However, differences of Se species between detrital layer and 0-5 cm mineral sediments are clear. The detrital layer extracts contained a relatively higher percentage of Se (VI) (average 28% - range 22-37%) compared to the 0-5 cm mineral sediments (average 15% - range 10-22%), and a relatively lower percentage of Se (IV) (average 33% - range 25-38%) compared to sediment extracts (average 52% - range 45-58%). The detrital layer extracts also showed relatively higher org-Se (average 40% - range 30-49%) than the 0-5 cm mineral sediment extracts (average 34% - range 20-40%).

In SEB, there are no apparent differences of Se speciation in NaOH extracts from the detrital layer and 0-5 cm mineral sediments. However, differences between cells with and without brine shrimp harvesting (S1 vs. S8 and S9) were evident. The detrital layer extracts from S1 showed a much lower Se(VI) average of 1% than S8 (13%), a much higher average of Se(IV) (82%) than S8 (46%) and S9 (47%), and a lower average of org-Se (19%) than S8 (41%) and S9 (52%). A similar trend is followed for the 0-5 cm mineral sediment extracts. The results further indicate that significant transformation processes in S1 have resulted in differences of Se speciation and partitioning in the solid phase.

Se fractionation and speciation data in water and extracts were combined to estimate Se speciation in the detrital layers and 0-5 cm mineral sediments (Table 4). This estimate attempts to provide a more accurate portrayal of Se speciation in evaporation basin sediments. Se speciation in the water-soluble fraction is based on its similarity to surface water speciation (Gao et al., 2000). An assumption is made that PO_4 extractable Se is dominated by Se(IV) based on findings in the literature. The fraction that was not extractable by water, PO_4 and NaOH contained mostly Se(0) (Gao et al., 2000). These data indicate the following distribution of Se species in the solid-phase materials: Se(0) and resistant forms (41-52%) > Se(IV) (25-35%) > org-Se (15-17%) > Se(VI) (5-16%). This quantitative estimate of Se(IV) in the basin sediments indicates the important role of Se(VI) reduction to Se(IV) following by subsequent adsorption onto the sediment.

Bioavialibility Indicator

Peptidic Se constituents in the detrital layer and surface sediments were determined for the sequential extracts (Fig 7). First of all, the detrital layers contained significantly higher peptidic Se than the 0-5 cm mineral sediments. In addition, the majority of the peptidic constituents were found in the adsorbed and OM-associated Se fractions. In conjunction with the data in Fig 5, it is concluded that the OM-associated fraction may harbor the most proteinaceous Se. Because Se is expected to be transformed into proteins by primary producers and proteins may be highly available to consumers and predators, Fan and others that proteinaceous Se can be biomagnified through the food chain (Fan 2001). Their research findings did support this hypothesis that proteinaceous Se appeared to be biomagnified up the food chain and was better correlated with symptoms observed in fish reproductive systems than total biomass or waterborne Se concentrations. Our results have shown that the adsorbed and OM-associated Se phases are the most important phases to consider in Se transfer into the food chain and the interface between surface waters and detrital layer is the most important zone for Se transfer into the foodchain.

In collaboration with other researchers in the joint project, detrital layer materials and surface mineral sediments from a microcosm study for testing nutrient treatments on productivity and Se concentration were also taken for Se fractionation and peptidic constituent measurement. Selenium fractionation data were analogous to those reported above. A small difference was that the adsorbed fraction had more peptidic materials than the 0.1 M NaOH extracts. The presence of brine shrimp always reduced the peptidic materials and the addition of N+P generally increased it. These treatment effects were demonstrated for a short period of the experiment (7 days). For details, refer to the reports by Rejmankova and Higashi/Flocchini.

CONCLUSIONS

Selenium transformation processes reflected by speciation and fractionation in water and sediments appear largely affected by many evaporation basin management factors that may include water delivery and residence time as well as invertebrate harvesting activity. Evaporation basins have shown able to reduce Se concentration in surface waters relative to agricultural drainage water inputs and this may have benefits in reducing potential ecotoxic risk of Se in the environment. However, Se undergoes significant biochemical transformations in both the water column and sediments as indicated by the increase of reduced selenite and org-Se forms compared to the dominant oxidized form (selenate) in drainage water. Microbial transformations involved in these processes varies significantly from basin to basin.

Harvesting brine shrimp during the past several years appears to reduce the build up of detrital materials and thus accumulation of Se in the surface sediments, but had no effect on Se transformation as reflected in Se speciation. The benefit of harvesting invertebrates in reducing Se accumulation in the detrital layer sediments is demonstrated in both evaporation basins in this study.

Estimates of Se speciation in the detrital layer and 0-5 cm mineral sediments showed following distribution: Se(0) and other resistant forms (41-52%) > Se(IV) (25-35%) > org-Se (15-17%) > Se(VI) (5-16%). This quantitative estimate of Se(IV) in the basin sediments quantitatively validated the important role of Se(VI) reduction to Se(IV) following by subsequent adsorption onto the sediment in regulating the concentration and speciation of Se in the evaporation pond environment.

Peptidic Se constituents are significantly higher in the detrital layers than the underlying sediments. The majority of the peptidic constituents were found in the adsorbed and OM-associated Se fractions. These results indicate that the most important phase to consider in Se transfer into the food chain are the adsorbed and OM-associated Se fractions and that the interface between surface waters and the DM materials is the most important zone for Se transfer into the foodchain.

Overall, evaporation basins reduce Se concentration in surface waters to certain degree from agricultural drainage water. Use of evaporation basins with management activities such as brine shrimp production and harvesting that reduce Se accumulation appears beneficial in reducing the potential Se ecotoxic risk to water birds.

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Table 1. Evaporation ponds sampled for water column and sediment Se analysis

Basin and Pond	Management activity for brine shrimp
Hacienda Basin:	
C4	No harvesting
A4	Continuous harvesting
South Basin:	
S1	No Harvesting
S8	Occasional harvesting
S9	Continuous harvesting

Table 2. Pond water pH and EC values

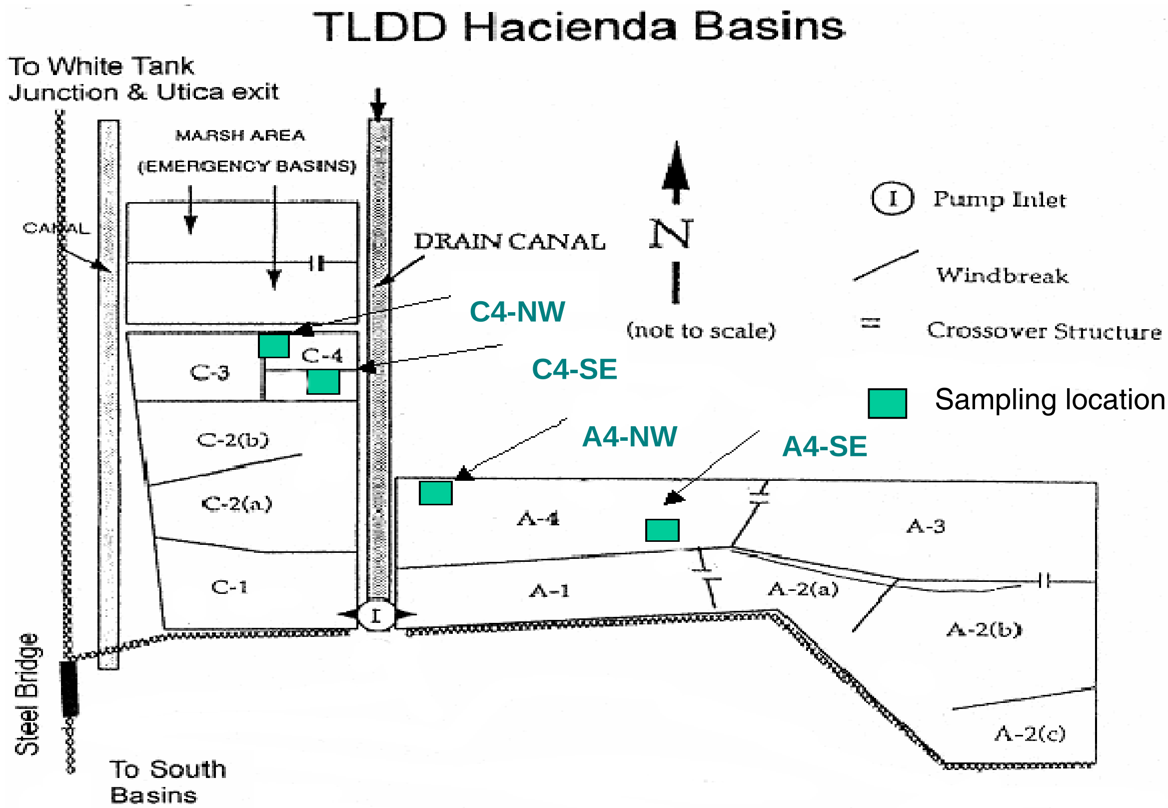
Pond	pH	EC (dS/m)	Standard deviation of pH	Standard deviation of EC
C4-NW	8.5	118.7	0.0	0.8
C4SE	7.5	95.5	0.0	3.1
A4-NW	8.7	95.0	0.0	1.8
A4-SE	8.7	89.5	0.0	0.8
S1-NW	8.9	18.8	0.1	0.1
S1-SW	8.9	19.1	0.0	0.2
S8-NW	8.8	113.3	0.0	0.3
S8-SE	8.7	115.8	0.0	1.8
S9-NW	8.2	113.6	0.0	2.2
S9-SE	8.3	83.2	0.0	4.6

Table 3. Total Se in detrital layer sediment samples

Pond	Total Se (µg)	Standard deviation
C4 NW	11.5	--
C4-SE	14.1	--
A4-NW	6.0	--
A4-SE	7.8	--
S1-NW	31.5	10.5
S1-SW	55.8	27.4
S8-NW	10.2	1.7
S8-SE	4.6	1.6
S9-NW	7.9	4.5
S9-SE	6.2	0.6

Table 4. Estimate of Se speciation in detrital layer and surface sediments

	Se(VI)	Se(IV)	Org-Se	Se(0) and others
			(% of total Se)	
C4-NW-DM	13.5	26.7	17.1	42.7
C4-SE-DM	16.9	29.7	10.8	42.6
A4-NW-DM	20.6	21.5	11.6	46.3
A4-SE-DM	16.3	25.0	19.4	39.3
C4-DM-Buried	13.1	22.7	20.5	43.8
Ave.	16.1	25.1	15.9	42.9
C4-NW, 0-5 cm	6.0	28.3	22.3	43.4
C4-SE, 0-5 cm	13.8	38.0	12.7	35.5
A4-NW, 0-5 cm	5.9	32.7	13.7	47.7
A4-SE, 0-5 cm	8.1	27.8	19.7	44.4
Ave.	8.4	31.7	17.1	42.8
S1-NW-DM	3.4	38.8	7.9	49.8
S1-SW-DM	3.8	28.8	8.4	59.0
S8-NW-DM	13.9	33.2	16.4	36.5
S8-SE-DM	9.2	30.4	22.4	38.0
S9-NW-DM	5.8	44.3	23.2	26.6
S9-SE-DM	14.2	32.4	24.3	29.1
Ave.	8.4	34.7	17.1	37.9
S1-NW 0-5 cm	2.2	35.0	5.9	56.8
S1-SW 0-5 cm	2.6	32.5	5.5	59.4
S8-NW 0-5 cm	8.1	23.1	16.5	52.3
S8-SE 0-5 cm	9.2	30.1	22.0	38.7
S9-NW 0-5 cm	2.5	19.2	19.6	58.8
S9-SE 0-5 cm	7.8	21.0	18.1	53.1
Ave.	5.4	26.8	14.6	52.5



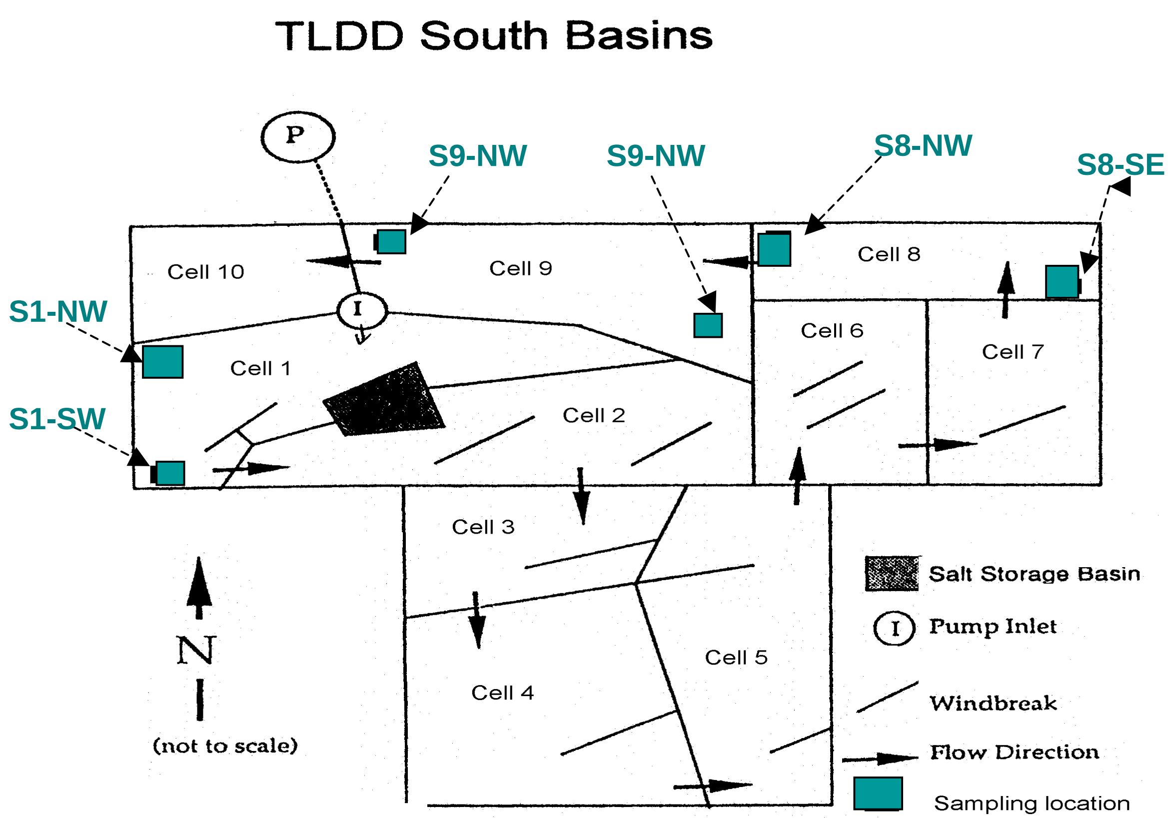


Figure 1. Sampling locations in Hacienda Evaporation Basin (top) and South Evaporation Basin (bottom) in Tulare Lake Drainage District (TLDD)

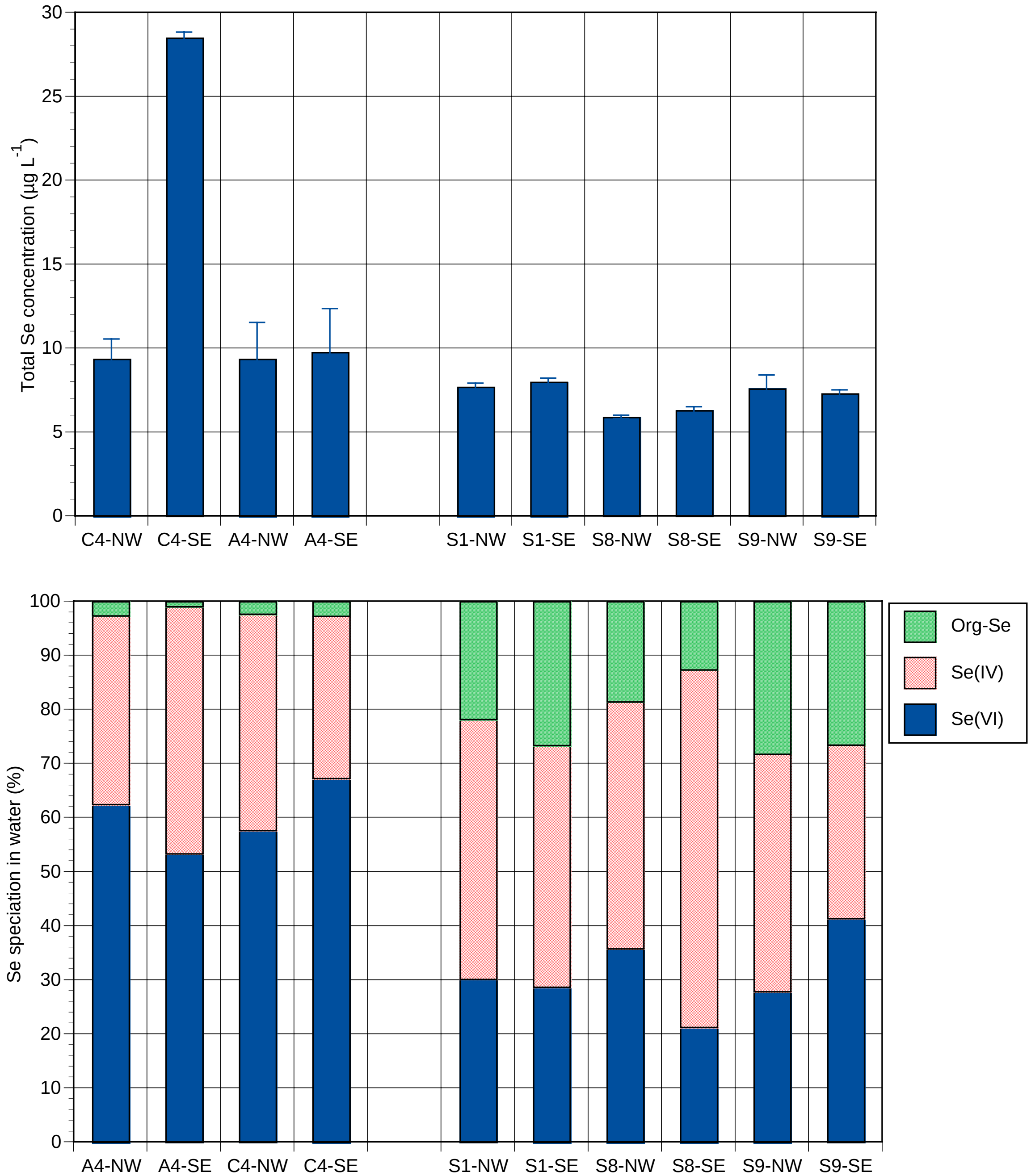


Figure 2. Se concentration (top) and speciation (bottom) in evaporation pond waters in Fall 2001 (HEB) and 2002 (SEB).

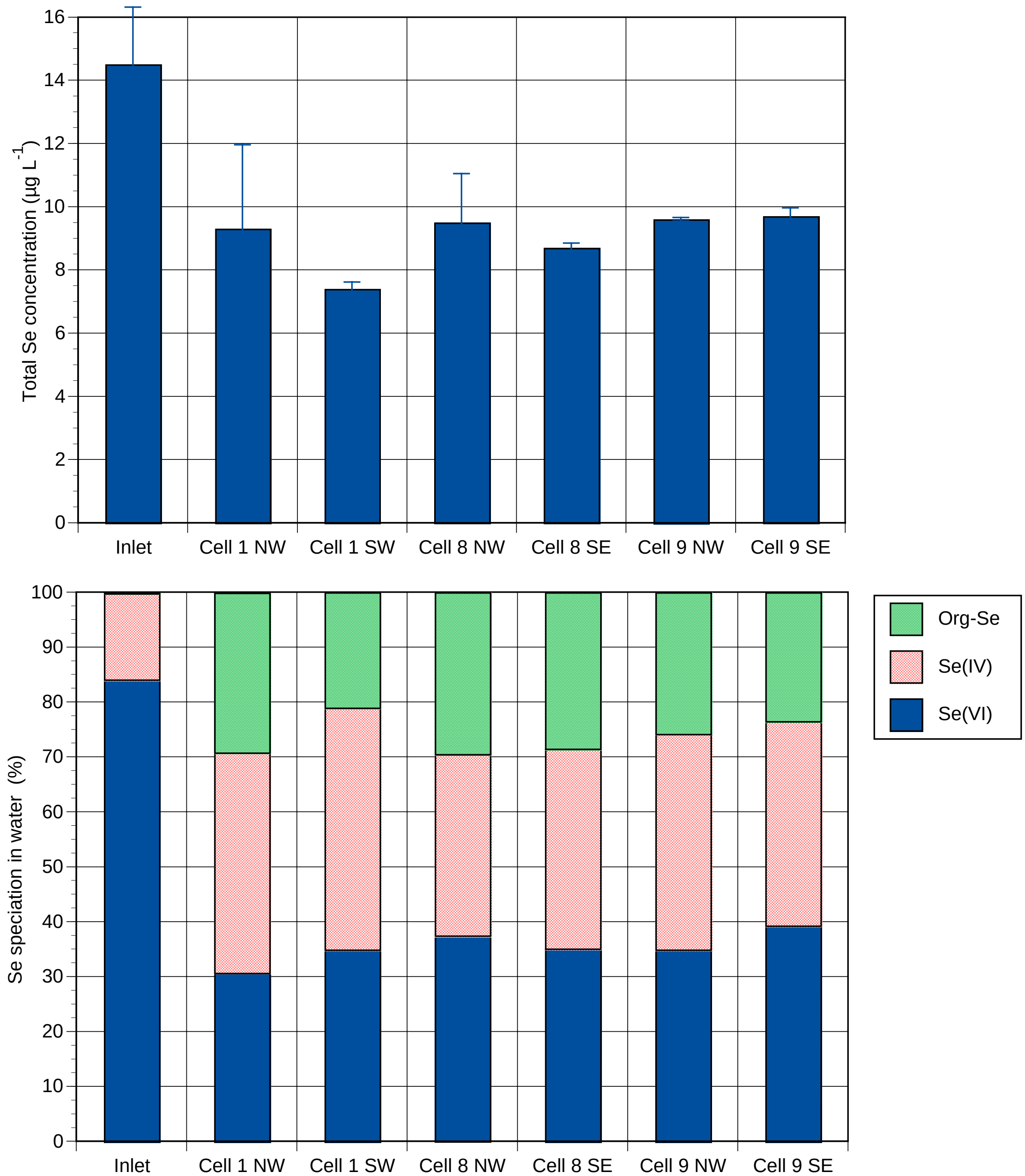


Figure 3. Se concentration and speciation in South Evaporation Basin pond waters collected in May, 2003

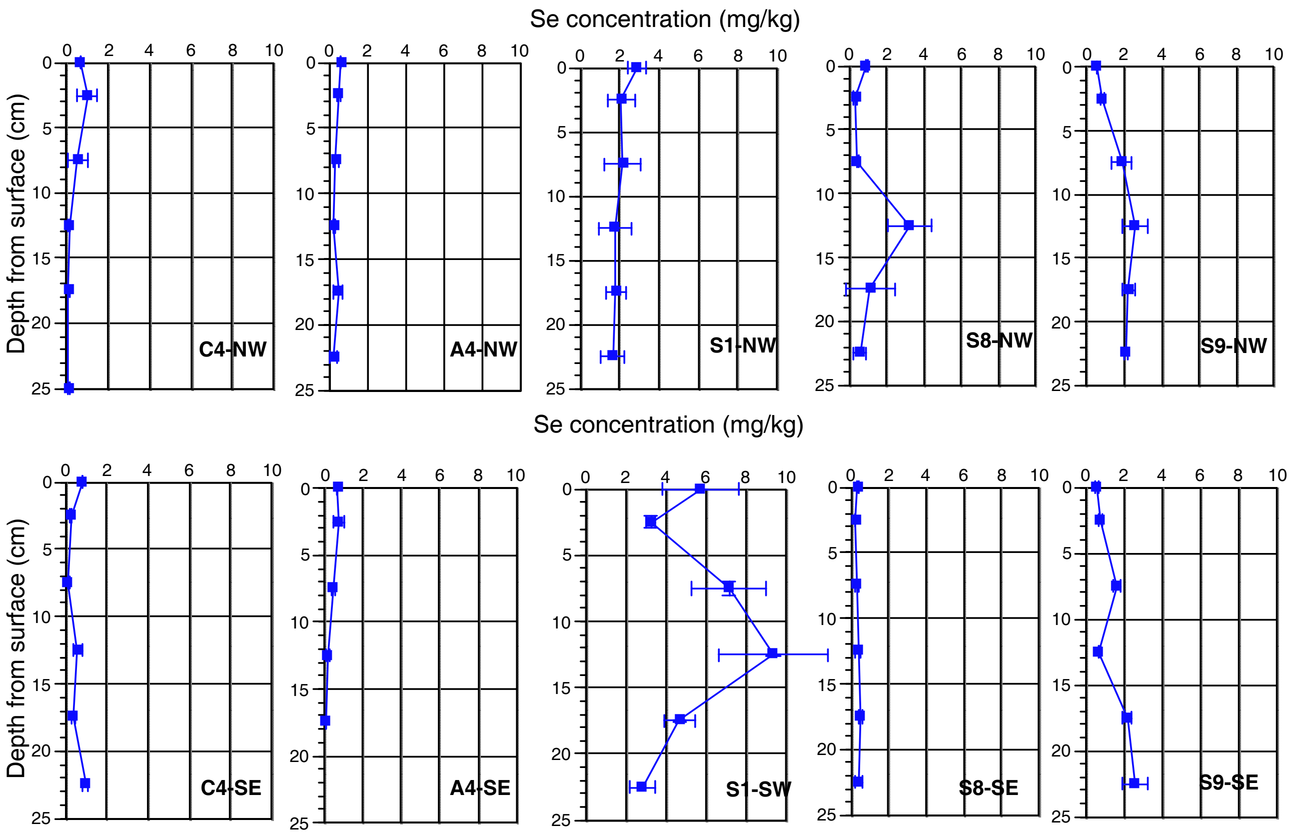


Figure 4. Se concentration profile in pond sediments

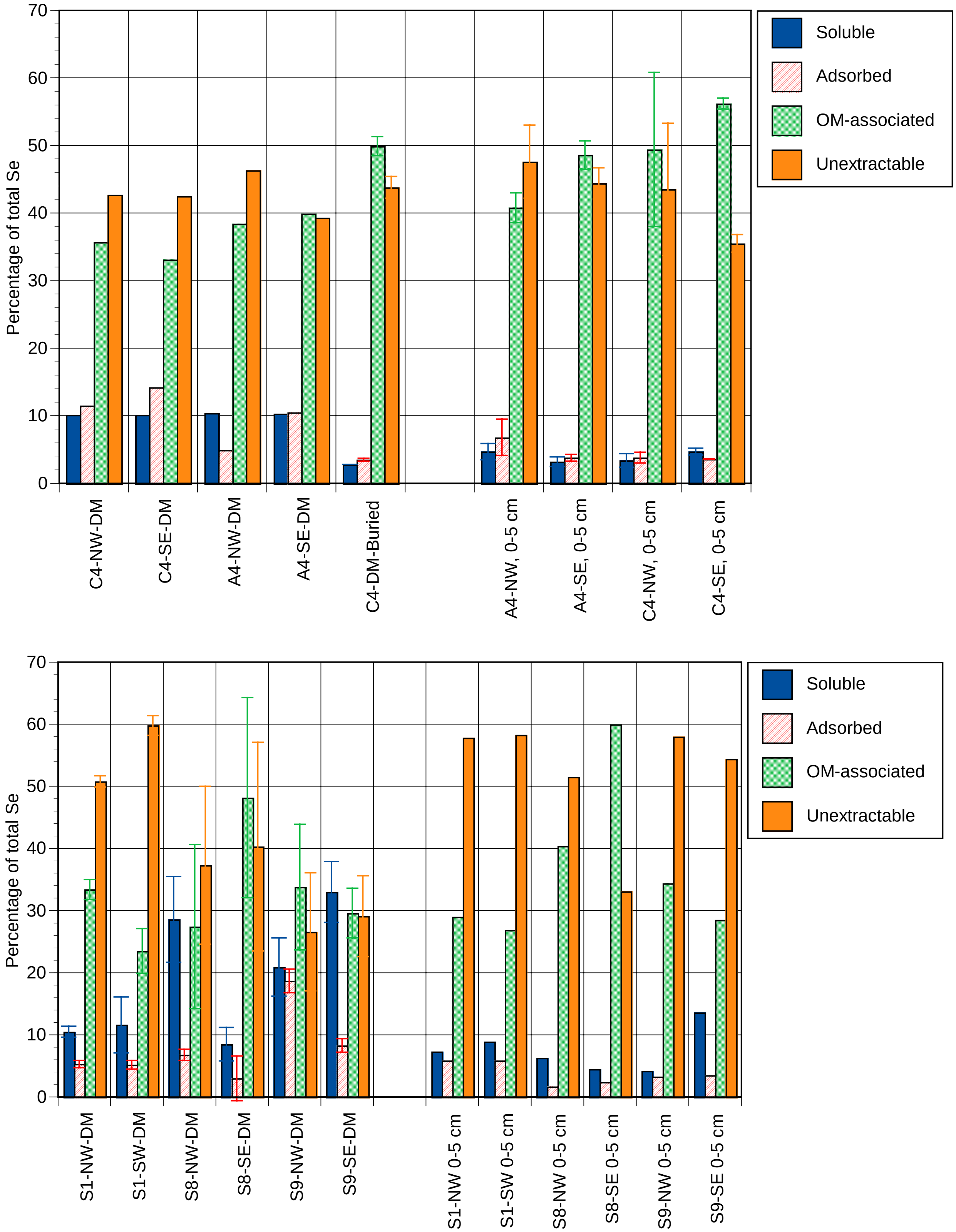


Figure 5. Se fractionation data in detrital layer (left columns) and surface sediment (right columns) in HEB (top) and SEB (bottom)

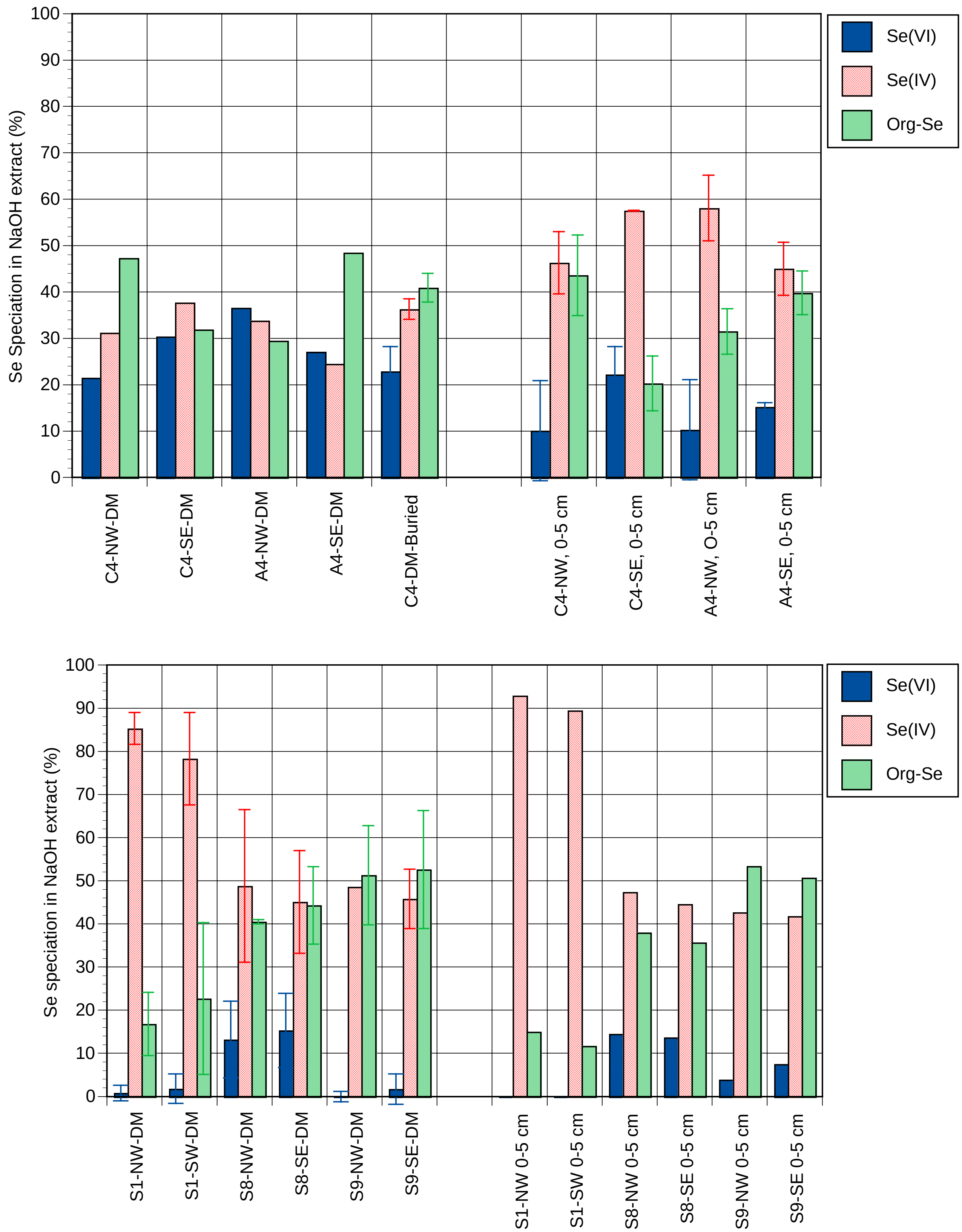


Figure 6. Se speciation in 0.1 N NaOH extracts from detrital layer (left columns) and surface sediment (right columns) in HEB (top) and SEB (bottom)

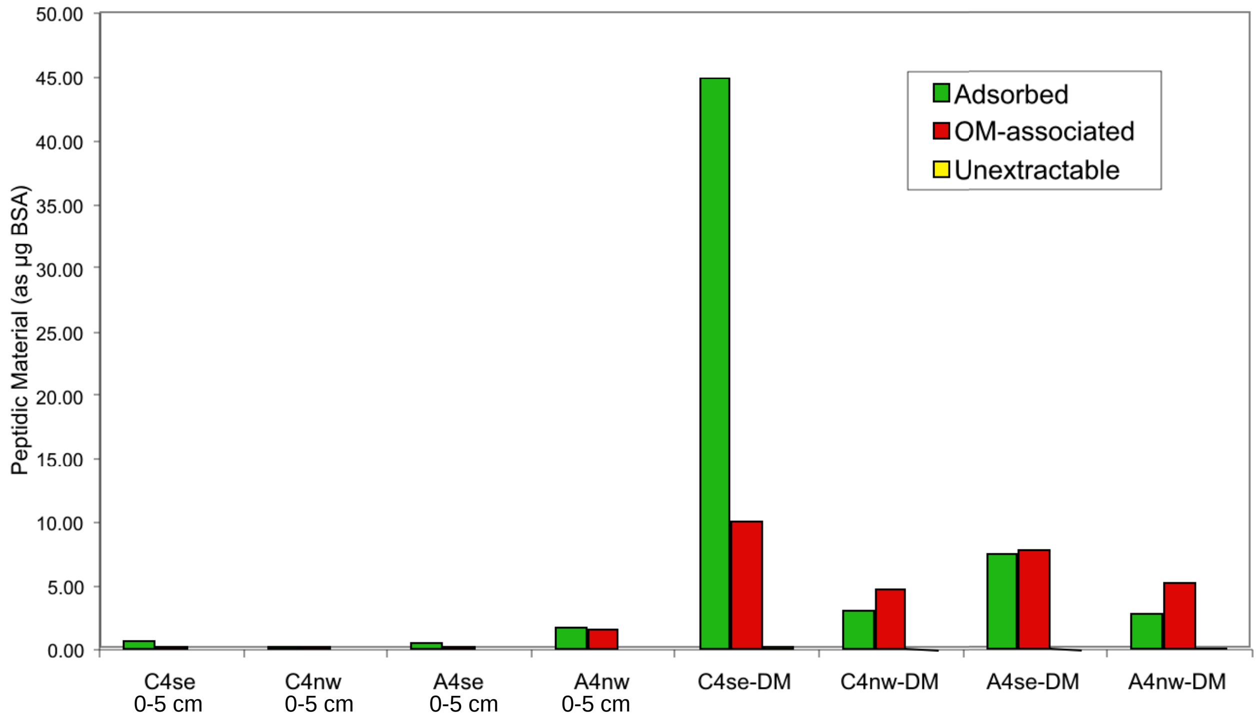


Figure 7. Peptidic constituents in 0-5 cm mineral sediment and detrital material fractions (analysis performed by Higashi)

Does Saline Drainage Water Affect Crop Tolerance to Boron?

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ABSTRACT

Reuse of saline drainage water is a management option on the west side of the San Joaquin Valley (SJV) that is necessary for reducing the volume of drainage water (San Joaquin Valley Drainage Implementation Program, 2000). A potential limitation is determining the extent by which boron, a naturally occurring element in the drainage water, affects the selection, growth and yield of crops in the reuse system.

Boron is a concern for several reasons. First, boron is a microelement that is essential for crops but has a small concentration window between deficiency and toxicity. Second, it has a higher affinity to the soil than most common salts requiring much more water to reduce soil B than it does to reduce the salinity. Furthermore, the B concentration in San Joaquin Valley drainage water varies widely but in nearly all cases, far exceeds levels that would result in toxic conditions based on B-tolerance guidelines.

Unlike guidelines for salt tolerance, the guidelines for boron tolerance are limited. With the exception of a few sand tank studies that actually provide B coefficients (i.e. threshold and slope) for a few crops (see Maas and Grattan, 1999), most of the B classification has come from work conducted over a half a century ago by Eaton et al.(1944). More importantly, these older studies defined the B-tolerance limit based on the development of incipient injury on the crop (i.e. foliar burn), not yield response under a range of B concentrations.

The question is often raised, are the effects of salinity and boron on crops additive, synergistic or antagonistic? Despite the common occurrence of high boron and high salinity in many parts of the world, very little research has been done to study the interaction of the two. For those that have been done, contradictory results have been obtained. A combination of both field and controlled greenhouse studies are underway to evaluate B tolerance particularly in relation to salinity. Our goal is answer this question. Should the answer be that the effects of the two are antagonistic, B may not be as much a limiting factor in reuse systems as previously thought.

To date, one greenhouse experiment at the US Salinity Laboratory in Riverside and one field experiment at Red Rock Ranch near Five Points have been conducted to evaluate the interactions between B and saline drainage water and to determine how limiting B really is to plants grown in drainage reuse systems. Broccoli was the crop selected in the greenhouse and processing tomato was selected for the field.

In the greenhouse study particular interest was directed towards the composition of the salinizing solution to determine what role various salts have on the salinity-boron interaction. Results from this first study indicate that both Cl based salts and those characteristic of shallow saline drainage water (i.e. a mixture of salts dominated by sodium sulfate) showed a significant salinity-boron interaction. That is at high salinity, increased B concentration was less detrimental, both visually and quantitatively (i.e. biomass), than it was at low salinity. However there was no significant difference between salt types. Spectral analyses showed striking differences among treatments in NDVI with a strong decline in non-saline-treated plants at high B.

In the field, there were obvious trends that both salinity and B reduced tomato yields yet there was no significant interaction between salinity and B. This lack of significance is related to field variability and insufficient treatment responses.

INTRODUCTION

Reuse of saline drainage water is a management option on the west side of the San Joaquin Valley (SJV) that is necessary for reducing the volume of drainage water (San Joaquin Valley Drainage Implementation Program, 2000). Several methods of utilizing saline water (i.e. sequential, cyclic and blending) have been tested experimentally or demonstrated under field conditions. In addition to these methods of reuse, saline water table control has also been tested as a means of allowing certain agronomic crops (such as cotton and safflower) to extract water directly from this saturated zone. Regardless of how crops utilize this saline drainage water, crop roots are exposed to water containing both high concentrations of sulfate and chloride salts as well as high concentrations of boron.

There is considerable controversy over the extent by which boron limits the reuse of SJV drainage water. On the one hand, there is concern that boron is one of the most limiting factors in the long-term success of drainage water reuse systems. The concern stems from several relationships. First, there is a small concentration window between the boron level in the soil that is required for optimal crop growth and that which is toxic (Gupta et al., 1985). Second, the boron concentrations in drainage water exceed the published boron tolerance coefficients for most crops grown in the San Joaquin Valley, despite the fact that many are classified as moderately B-tolerant to B-tolerant

(Maas and Grattan, 1999). Third, boron is adsorbed tightly to the soil and therefore is not as readily leached from the crop rootzone as are other salts. This phenomenon provides the opportunity for boron to accumulate in the root zone more rapidly than salinity, eventually affecting crop selection and ultimately have a negative effect on crop growth and yield. Because of these concerns, it has long been thought that B is a much more limiting factor in drainage water reuse than is the salinity of the drainage water.

On the other hand, some argue that the boron coefficients might be too conservative (Letey et al., 2001). Most of the coefficients are based on the concentration of B in the soil water that produces incipient injury and are not based on yield reduction criteria (ie yield reduction as a function of increased B in the soil solution). Moreover, these coefficients were developed in non-saline environments suggesting that they may not be appropriate for crops grown under saline conditions.

Toxicity occurs in crops when boron concentrations increase in either stem and leaf tissues to lethal levels, but soil and plant-tissue analyses can only be used as general guidelines for assessing the risk of B-toxicity (Nable et al., 1997). Although experimental evidence indicates that plants absorb B passively as H_3BO_3, contradictions between experimental results and observations in the field suggest that other factors, yet unknown, may affect B uptake (Hu and Brown, 1997). Once B has accumulated in a particular organ within the shoot, it has restricted mobility in most plant species but not all (Brown and Shelp, 1997). In some plant species, particularly those that produce substantial amounts of polyols, B is readily translocated as B-polyol complexes.

The question has recently been raised, are the effects of salinity and boron on crops additive, synergistic, or antagonistic? Despite the common occurrence of high boron and high salinity in many parts of the world, very little research has been done to study the interaction of the two (Grattan and Grieve, 1999). From a review of the limited number of studies that addressed the combined effects of salinity and boron on the plant, it appears that the results are contradictory.

In sand-culture experiments conducted in a greenhouse, researchers found that wheat responded to boron in the soil solution independently of salinity, made up of sodium chloride (NaCl) and calcium chloride ($CaCl_2$) salts (Bingham et al., 1987). That is, there was no salinity - B interaction with respect to leaf B concentration. Similarly, others have found that boron and salinity effects were independent of each other for corn, barley and alfalfa (Shani and Hanks, 1993 and Mikkelsen et al., 1988).

However in more recent studies, investigators found that Cl-based salinity enhanced B sensitivity in wheat (Grieve and Poss, 2000; Lauchli et al. 2001). Wheat is one of those crops that are tolerant to salinity but sensitive to B. Grieve and Poss (2000) found that Cl-salinity increased B accumulation in leaves and was associated with more injury. Lauchli et al. (2001) attribute its effect on B compartmentalization within the plant. They found that under saline conditions, total B concentration was reduced in the root, was unaffected in the basal portion of the leaf, and increased in the leaf tip. Therefore salinity enhanced B mobility within the plant.

In two separate greenhouse studies, investigators came to different conclusions regarding tomato's behavior to combined salinity and B stresses. In one study using soil in pots, investigators found that NaCl salinity increased B sensitivity in tomato and cucumber (Alpaslan and Gunes, 2001). However they found that salinity reduced B concentration in tomato but increased it in cucumber. These investigators found that NaCl increased membrane permeability but increasing B in the soil to toxic levels did not, except in the presence of salinity. In a more recent study using soil-filed lysimeters in a greenhouse, Ben-Gal and Shani (2002) found that NaCl-$CaCl_2$ salinity reduced boron's detrimental effect. Plants were most adversely affected under high B and low salinity. At high B, as salinity of the irrigation water increased to 6 dS/m, plant growth and yields increased. These studies suggest that the composition of the salinizing solution may influence the salinity-B interaction.

Investigators who used a mixture of salts (i.e. Na^+, Ca^{2+}, Cl^- and SO_4^{2-}) also found that salinity may reduce B boron's toxic effect. In one field study conducted in Northern Chile, a number of vegetable crop species and prickly pear cactus were irrigated with saline water (8.2 dS/m) containing a mixture of ions including 17 mg/L of boron (Ferreyra et al., 1997). Plant growth and crop yields of artichoke, asparagus, broad bean, red and sugar beets, swiss chard, carrot, celery, a local variety of sweet corn, potato, prickly pear cactus, onion, shallot, spinach, were all greater than expected based on published salt and boron tolerance coefficients. These investigators found that salinity reduced leaf boron levels. If separate effects of salinity and boron were additive, little or no growth would be expected for any of these crops. Interactions likely occur which increase the crop's tolerance for boron in the presence of saline conditions. The investigators suggested that a reduction in plant water uptake, due to higher salinity levels, would reduce the rate boron accumulation in the plant tissue thereby extending the time during which boron levels are not affecting plant growth.

Others also found that salinity, using a mixture of salts, reduced leaf B concentration of chickpea (Yadav et al., 1989), wheat (Holloway and Alston, 1992) as well as reduced B uptake and accumulation in the stem of several *Prunus* rootstocks (El-Motaium et al., 1994), thereby decreasing B-toxicity symptoms. In the latter study, the investigators found a negative relationship between B and SO_4^{2-} concentrations in tissue suggesting that SO_4^{2-} could be responsible for the salinity-induced reduction in tissue B. Others have also found that a mixture of chloride and sulfate salinity reduces leaf B accumulation in *Eucalyptus camaldulensis* (Grattan et al., 1996). Studies that include a mixture of salts (i.e Na^+, Mg^{2+}, Ca^{2+}, Cl^- and SO_4^{2-}) are much more appropriate for conditions of the San Joaquin Valley as well as a number of coastal valleys than those using chloride salts alone.

In no study, however, were investigators able to suggest the actual mechanism that supports this phenomenon such as direct ion interactions, reduced transpiration in salt-stressed conditions or both. Consequently, many questions regarding the interactions between salinity and boron remain unresolved. Questions related to (1) the relationship between visual leaf symptoms and yield; (2) the dynamic relationships between boron concentration in irrigation water, adsorption of boron, boron uptake and distribution within the plant; (3) the influence of salinity, both concentration and composition, on boron tolerance of the crop; and (4) whether boron damage will ever exceed salinity damage when using saline drainage water.

The most important information that is needed is to have boron tolerance coefficients related to yield rather than visual symptoms, and that the boron tolerance coefficients be evaluated as a function of salinity (i.e. saline drainage water).

We are currently conducting experiments in the field and in sand cultures in the greenhouse to address these questions. Sand-culture facilities are useful because salt concentrations and compositions can readily be controlled creating uniform profiles such that true comparisons can be made among the treatments. A field experiment was also conducted at Red Rock Ranch near Five Points where drainage water reuse is being practiced to provide an indication of how the plants are actually responding to varied combinations of salinity and B in a pre-salinized profile. An interdisciplinary research project involving scientists from the University of California and the USDA-ARS with expertise in soils and irrigation management, plant physiology, salinity and plant nutrition are currently conducting experiments to evaluate salinity – B interactions and to develop crop response functions to B in both the presence and absence of salinity.

MATERIALS AND METHODS

Experiments are being conducted over a two-year period in both greenhouse sand tank facilities and the field. To date, one field experiment and one greenhouse experiment have been completed.

GREENHOUSE – SAND CULTURE STUDY

The greenhouse experiment was conducted at the USDA-ARS, George E. Brown, Jr. Salinity Laboratory located at the UC Riverside campus. The experiment was designed to determine the interactive effects of salinity and boron on broccoli performance including growth, yield, injury, and ion relations. Broccoli (*Brassica oleracea* L., botrytis group**,** cv Seminis PX511018) was selected because it is a crop common to the Westside of the SJV and it is known to be moderately sensitive to salinity and moderately sensitive to B in non-saline systems (Maas and Grattan, 1999).

The greenhouse experiment was conducted using an elaborate sand tank system. This system creates a uniform and controlled environment and consists of 60 large tanks (1.2 m x 0.6 m x 0.5 m deep) filled with washed sand having an average bulk density of 1.2 Mg m^{-3}. At saturation, the sand has an average volumetric water content of 0.34 m^3 m^{-3}. Each tank is irrigated with a solution prepared in individual reservoirs having a volume of approximately 745 L. Salinity-B treatments were complemented with modified half-strength Hoagland's nutrient solution. Solutions were pumped from the reservoirs, located below the sand-tank facility, to the tanks and then returned to the reservoirs through a subsurface drainage system at the bottom of each sand tank. Irrigation frequencies (i.e. several times per day) were sufficient to allow the sand-water concentration to approach that in the irrigation water, thereby creating a uniform distribution of salt in the crop rootzone. Calculations indicate that the salinity of the irrigation water was more or less equivalent to that of the sand water and previous studies (Wang, 2002) have indicated that the EC of the sand water is approximately 2.2 times the EC of the saturated soil extract (ECe), the salinity parameter used to characterize salt-tolerance in most studies. Total evapotranspiration from each tank was measured by solution-volume changes in the storage reservoirs and water lost was replenished to maintain constant osmotic potentials in the treatment irrigation waters.

Several sand tanks were not planted but irrigated to provide maximum evaporation estimates. These tanks were also used as a reference for stable isotope analyses in order to separate evaporation from transpiration in the planted tanks using an approach described in a previous report (Grattan et al. 1998). These measurements were done so that crop growth can be expressed relative to consumptive water use (T) and that comparisons can be made to the total water consumed by the crop, the total boron absorbed by the crop, and B concentration relative to visual injury. This is an important component of the study since B uptake is thought to occur passively by plants and its distribution follows the transpiration stream (Marschner, 1995).

The irrigation treatments consisted of three salinity levels representing non-saline (2.0 dS/m), moderately saline (11dS/m) and saline (18 dS/m) conditions. Each salinity level was comprised of either 1) chloride dominated salts or 2) synthetic saline drainage water with an ion composition typical for that found in the western SJV. The SJV salt solutions were prepared from predictions based on appropriate simulations (Suarez and Simunek, 1997). Each of these treatments had three boron concentrations ranging from very low, such as that found in solution cultures (i.e. 0.23 mg), high (12 mg/L) and very high B concentrations (30 mg/L). The pH of the solutions were maintained between (5.7 and 6.7) using additions of sulfuric acid.

Broccoli was planted on 4 February, 2003 and salinization began 16 days later when plants had approximately two leaves. Several plants were periodically harvested from each tank for biomass and ion accumulation. Broccoli was first harvested on March 28th and again on April 24th. The remainder of the plants were harvested at maturity on May 21st (90 days after saliniization). Broccoli shoots were divided into heads, stems, young leaves (most fully expanded leaf and younger, and old leaves (all remaining leaves). Immature heads, from salt-stressed treatments, where given the opportunity to mature and these heads were harvested on May 29th. Fresh and dry weight measurements were made on all harvested biomass. Tissue ion concentrations (e.g. B, Na, Ca, Mg, Cl, K and S) will be determined in various organs of the crop. ANOVA and surface regression model analysis were preformed on the data.

Remote sensing was used to characterize treatment effects on broccoli visual injury and to quantify specific reflectance data. The leaf normalized difference vegetative index (NDVI) has been used in many studies to quantify remotely sensed reflectance data. Primarily NDVI has been related to chlorophyll concentration and photosynthetically active leaf area (Broge and Leblanc, 2000, Gamon and Surfus, 1999). For example, elephant grass that was exposed to salinity had reduced total chlorophyll content on a per plant basis and was proportional to a remotely determined single ratio vegetation index (SRVI). The salinity stress reduced the SRVI primarily by reducing reflectance in the near-infrared spectrum region (Wang, et al., 2002).

Leaf reflectance of the lower leaves in the canopy was measured on March 15th, 2003, a time close to initial development of the broccoli heads. Percent reflectance was obtained with an Analytical Spectral Devices™, FieldSpec Pro JR fitted with a High Intensity Contact Probe Model A122300 using a 4.25 VDC 4W reflectorized bulb. To standardize the probe spectra, an optimization and calibration procedure was performed every other measurement. The portable instrument is a fast scanning spectroradiometer covering the 350nm to 2500nm region. The spectral resolution is 3nm at 700nm and 10nm at 1400 nm and 2100 nm. The 1.5-meter fiber optic input was adapted with the contact probe and light source.

Leaf reflectance NDVI was calculated as:

$$NDVI = (R_{745:755} - R_{700:710}) / (R_{745:755} + R_{700:710})$$

where R is the reflectance at the specified spectral region (nm) of interest.

FIELD STUDY

Previous studies have shown that processing tomato can be irrigated with saline drainage water (ECi = 7-8 dS/m and 8 mg/L boron) from first flower onwards without suffering losses in yield or quality (Shennan et al., 1995). However their success was attributed to the fact that the soil profile was initially non-saline and low in boron. In many cyclic reuse practices, it is valuable to include a moderately salt-sensitive crop within the rotation. In these cases, the crop would likely be planted in a previously salinized soil condition (i.e. after irrigation with saline drainage water on a salt-tolerant crop such as cotton) and then applying non-saline water. It is uncertain how the crop would respond to these transient conditions.

The experiment was conducted at the Red Rock Ranch in Five Points (NW Section 9, T.18S, R.16E, MDB&M) in a field planted to processing tomato (cv 9665). The soil texture at the site is a clay loam to a depth of 1.5 m (5 feet) with past history of salinity and boron problems. A drainage system was installed 4-5 years ago improving field conditions to the point where moderate salt sensitive crops can be now grown successfully where they failed before. Soil samples collected before pre-salinization on 10 February, 2002 indicated that the EC_e and B_e in the top two feet are 3.2 dS/m and 2.0 mg/L, respectively. Plots were established in the field by pre-salinization with variable concentrations of saline drainage water (0.5, 10, 20, 30, 40 and 50 dS/m) and boron (0, 10, 20, and 30 mg/L) to achieve targeted levels (see below). The concentrated San Joaquin Valley salt- mixtures were prepared in a 500 gallon tank. Soil salinity and boron levels were measured after the pretreatments were applied and post harvest at various depths and positions across the bed. The crop was grown under the grower's irrigation and cultural management practices. A buried drip-tape irrigation system was installed at a depth of 30 cm in December 2001 and supplied each plot with aqueduct water. The quantity of applied water equaled ET estimated by a CIMIS weather station (ETo) and a crop coefficient developed locally. The goal here was to evaluate the performance of a moderately salt-sensitive crop, one that is important in cyclic reuse systems, that is drip-irrigated with non-saline water in a field previously salinized by drainage water.

RESULTS AND DISCUSSION

GREENHOUSE-SAND TANK STUDY

Shoot biomass data indicate that both increased salinity and boron reduced shoot growth. There were no significant effects regarding the salt composition of the irrigation waters. Therefore Cl based salts behaved similarly to SJV-type salts. As such, data from both salt types were pooled together and the predicted three-dimensional surface plot is shown in Figure 1. There was, however, a significant salinity-B interaction. At low B concentration, increased salinity reduced biomass relatively more than it did at high B. Similarly, at low salinity, increased B was far more damaging than it was at high salinity. Ridge analysis of the biomass surface indicates that the minimum biomass would be at ECe equivalent to 8 dS/m and Be of 8 mg/L whereas the maximum biomass would occur at 2.7dS/m and 1.3 mg/L, respectively, assuming that the extract concentration is half that in the soil water (i.e. treatment water).

These data indicate that broccoli is more tolerant to boron in the presence of salinity. For example, the relative dry weight reduction of broccoli due to salinity that increased from 1.5 to 16 dSm^{-1} was 50% when B was controlled at 1 mg L^{-1}, but when the B was controlled at 28 mg L^{-1}, the reduction due salinity was only 10%. Boron alone with no salinity present also reduced biomass by approximately 50% at the 28 mg L^{-1} treatment. For the intermediate treatments, biomass reductions associated with mid-range B (eg., 14 mg B L^{-1} / 1.5 dSm^{-1} treatment is 87 % of control) appear to be similar to biomass reductions associated mid-range salinity (eg., 1 mg B L^{-1}/ 10 EC treatment is 90% of control). The answer to the question of regarding the combined effects of salinity and boron on broccoli biomass appears to be antagonistic. That is, salinity mitigates, to some extent, the yield losses

Pre-Treatments of salinity and boron at the Red Rock Ranch (2002).

Treatment	Targeted Soil Salinity (EC_e)	Targeted Soil Boron (B_e, mg/L)
1. Low salinity, low B	1-3	1-3
2. Low salinity, mod B	1-3	5-6
3. Low salinity, high B	1-3	10-12
4. Mod salinity, mod B	4-6	5-6
5. Mod salinity, high B	4-6	10-12
6. High salinity, mod B	7-10	5-6
7. High salinity, high B	7-10	10-12
8. High salinity, v. high B	7-10	15-20

Plots were 3 beds wide (5.0 m or 16.5 feet) and 3 m long. The two outside rows served as border rows and the center row was used for all data collection. One meter at the end of each row also served as a buffer region allowing the middle 1.2 m section for plant measurements and sampling.

Plant growth was monitored at various times throughout the season. At the end of the season, plants were harvested and weighed. Plants were separated into various organs and the plant tissue will be dried, ground and analyzed for various inorganic elements such as B, Na, Ca, Mg, Cl, K and S.

that would be associated with B in the absence of significant salinity.

Similar results were found with fresh broccoli heads (Figure 2). The only difference is that the relative effects are more exaggerated. These data indicate that head yields are more sensitive to both salinity and B than are broccoli shoots. These results indicate that predicting yield under simultaneous salinity and boron stress is best approximated by relative reduction functions similar to those proposed here but based on some ratio of maximum yield.

A surface regression model analysis was used with the following form:

$$\text{Yield, Biomass} = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_1^2 + \beta_4 x_1^2 + \beta_5 x_1 x_2 + \varepsilon$$

where x_1 and x_2 represent salinity and boron, respectively, and ε is experimental error. The coefficients for the model for total biomass and broccoli head yield are reported so that reduction functions for broccoli can be approximated (table 1). A lack-of-fit test was insignificant indicating this model acceptably accounts for variation in boron and salinity.

Analyses regarding tissue ion concentrations, consumptive water use, and detailed inferences related to B absorption, accumulation and distribution in the shoot are still pending.

REMOTE SENSING

The composition of salinity (chloride vs mixed salt) and the magnitude (EC) at each composition indicated trends, but were not significant. The complete experimental model was significant but the NDVI index only accounts for about 40% of the variation in the target variables for this preliminary analysis ($r^2 = 0.40$). Other relationships will be performed once the tissue ion concentrations are available. Boron and the interaction of boron and salinity treatments were highly significant as the reflectance was significantly reduced by the high B concentration - low EC combination. These same plants also showed visual symptoms atypical of the rest of the experimental population with extensive leaf curl and mottled chlorosis.

When the two salt compositions were pooled, significant effects of both salinity and boron were observed with the effects primarily explained by linear and crossproducts for broccoli heads. For total biomass, the quadratic term was also significant in addition to the linear and crossproduct term. The predicted surface (Figure 3) indicates little change in the NDVI index except for the case of low salinity and high B concentrations where the effect was profound. The NDVI index is comprised of wavelengths sensitive to leaf chlorophyll. Therefore B toxicity may be indirectly detected due to the effect on chlorophyll distribution, concentration, or development.

FIELD STUDY

Pre-treatment of plots with variable concentrations of B and salinity levels affected processing tomato yields. When individual regressions were preformed with increased salinity or boron in relation to fresh red tomato yield, significant correlations were found (r2 values of 0.63 and 0.69, respectively). When the data were analyzed using both B and ECe variables, the r^2 value was 0.70. However there was no indication that a salinity-B interaction occurred. The data are expressed as a surface plot (figure 4) and there was a strong tendency that both salinity and boron decreased yields but ANOVA indicated that there were no significant effects from salinity, boron or their interactions.

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Table 1. Regression parameters of reduction functions for broccoli dry weight and total fresh weight head production

Parameter	Dry Weight Parameter Estimate	Total Head Parameter Estimate
Intercept	419[t]	2043[t]
EC	3.57	-71.4
B	-9.58[t]	-61.8[t]
EC*EC	-1.07[t]	-3.09
EC*B	0.448[t]	3.61[t]
B*B	0.031	0.17

[t]parameter estimate significant based on t-test.

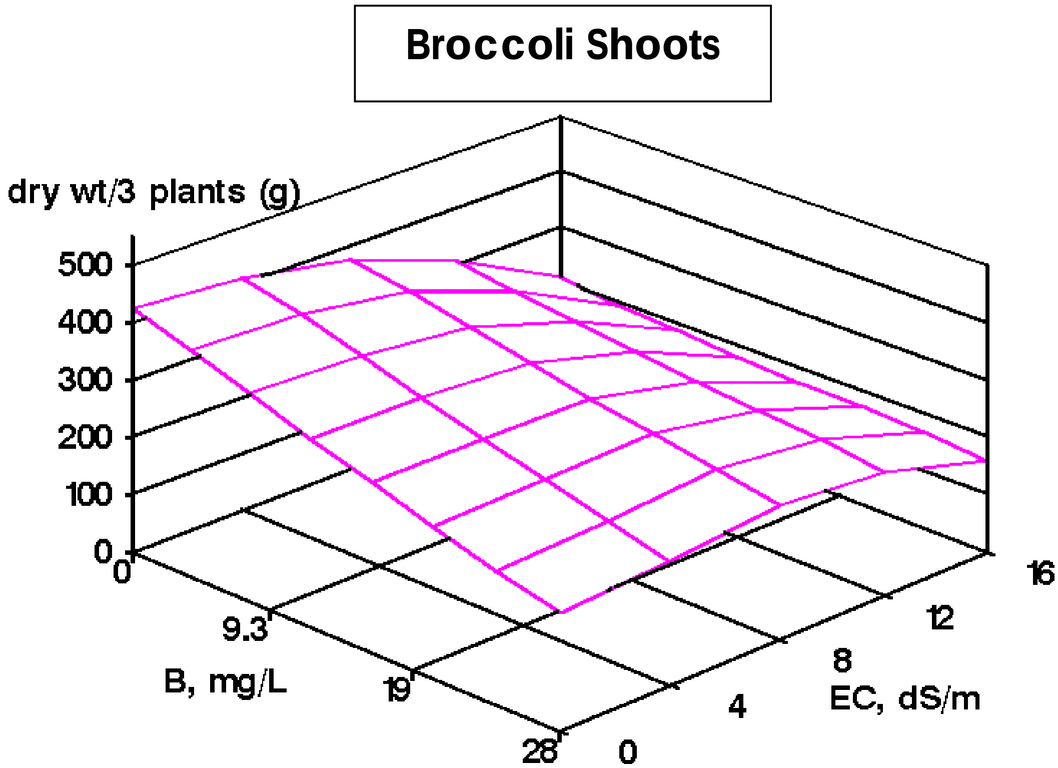

Figure 1. Predicted surface plot based on dry-weights of three harvested broccoli shoots/tank in relation to both the salinity and boron in the irrigation water.

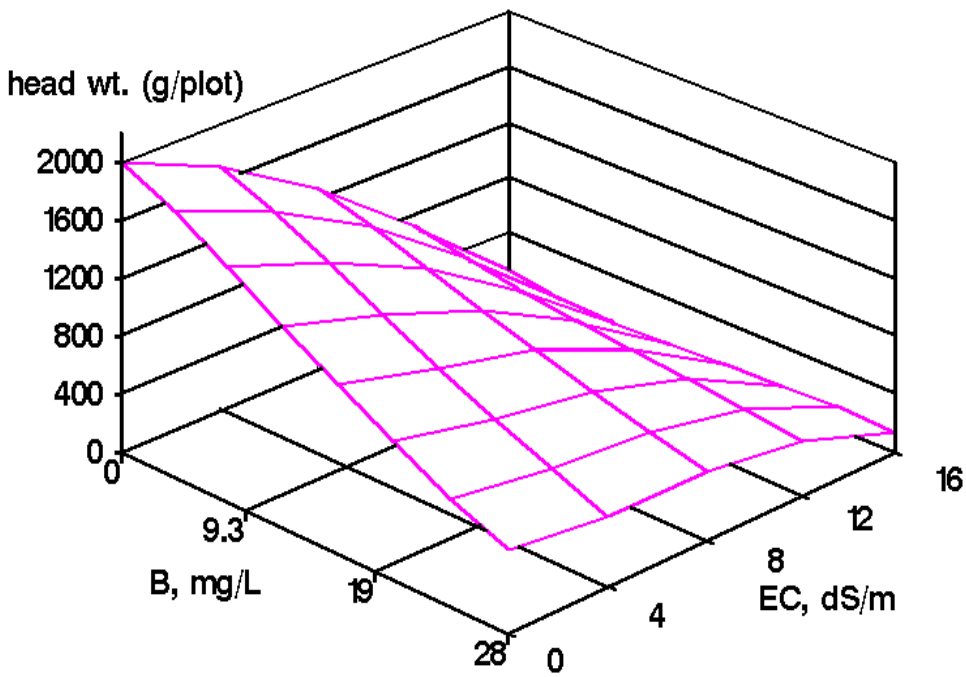

Figure 2. Predicted surface relationship of broccoli head fresh weights as a function of salinity and boron in the irrigation water.

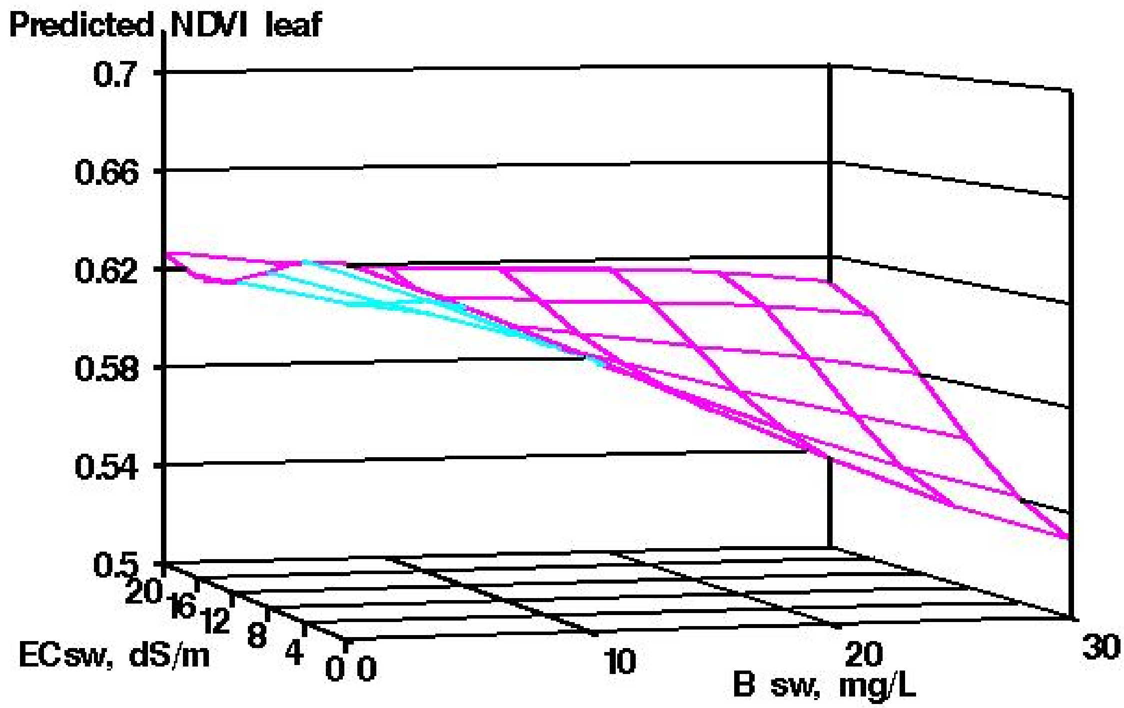

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Figure 3. NDVI index on broccoli leaves as influenced by salinity and boron in irrigation water.

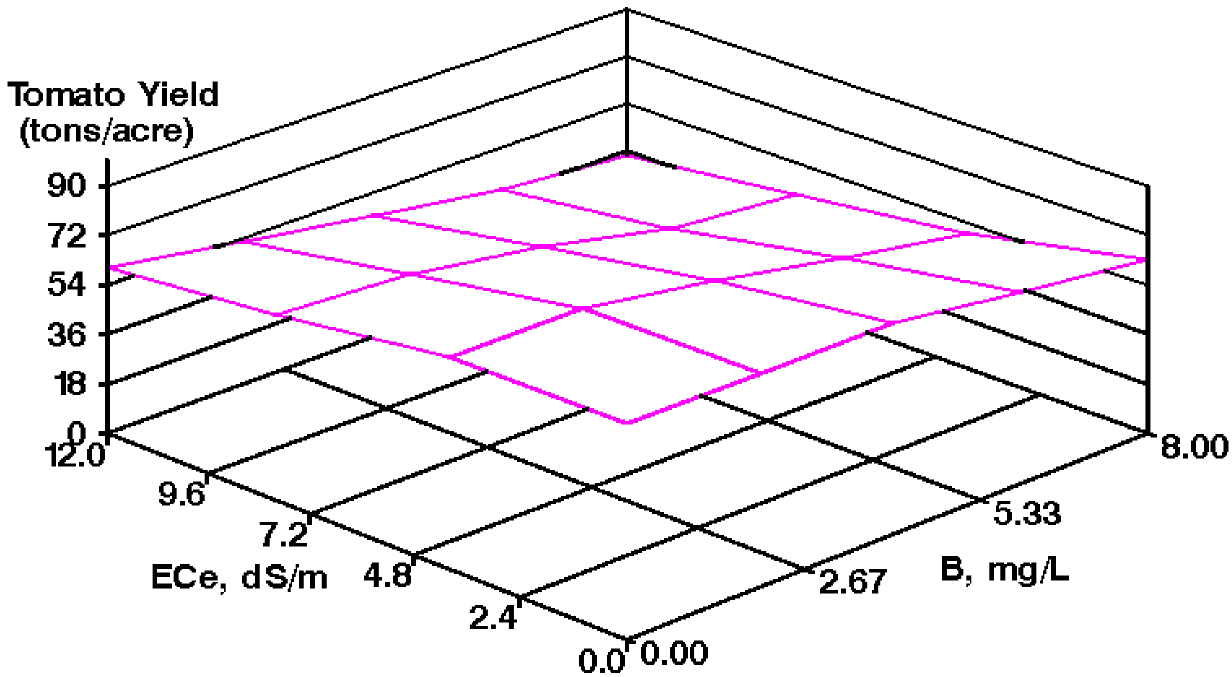

Figure 4. Predicted surface plot of red tomato yields (tons/ac) in relation to the EC and B in the saturated soil paste (averaged to a 60cm depth) at the beginning of the season.

Salinization of Deep Production Wells in the Western San Joaquin Valley: Risk Analysis, Uncertainty, and Data Needs

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ABSTRACT

The alluvial aquifer system of the central part of western San Joaquin Valley, California consists of a highly heterogeneous semi- confined aquifer overlying a similarly complex confined aquifer. Groundwater in the shallow part of the semi-confined aquifer is highly saline. Based on regional groundwater models, the projected time of encroachment of the saline groundwater to the lower depths of the semi-confined aquifer and the confined aquifer is 200-600 years. The objective of our work is to quantify the risk of locally accelerated encroachment due to the presence of highly permeable pathways within the alluvial fan. Specifically, we are interested in the statistical properties of the arrival time of the salt front at deep production wells and its sensitivity to the hydrostratigraphic structure of the alluvial fan and interfan deposits in the region, which itself is subject to considerable uncertainty. Well drilling logs and soil survey map information are used in conjunction with a transition probability/Markov chain geostatistical methodology to quantify the spatial variability of the aquifer system hydrostratigraphy. In the current reporting year, a sensitivity analysis has been completed to determine the effect of uncertainty in the geostatistical parameters. We find that a meaningful risk analysis will depend to a large degree on the accurate characterization of: the number of hydrostratigraphic facies that make up the aquifer, the proportion of coarse grained sediments that may carry large amounts of salt to depth over relatively short periods of time, the mean lengths of important stratigraphic units, particularly the ratio of length and thickness of coarse materials, and the degree of entropy (sorting, juxtapositional preference) found among the hydrostratigraphic facies. Significantly different results are obtained between the facies approach that we use and the more commonly used Gaussian heterogeneity model to characterize geologic variability. Based on these findings we carried out a site-specific geostatistical analysis and are generating a non-stationary, facies-based aquifer model with distributed pumping. Within this stochastic framework, risk is defined as the probability that individual wells become contaminated within a specified time horizon. Risk of water quality degradation in the lower semi-confined and confined aquifers will be quantified as a function of well placement and sub-regional area.

OBJECTIVES

Current project work continues the research started during a previous 2-year project funded by the University of California Salinity/Drainage Program. The updated project objectives are 1) to continue to develop geostatistical models of the hydrostratigraphy and water quality for the semi-confined aquifer and the Corcoran clay layer; 2) to continue to develop the groundwater flow and salt transport model by incorporating the geostastical models of the aquifer-system hydrostratigraphy and defining pumping and recharge inputs using data from previous modeling studies; 3) to assess the reliability of the risk predictions by performing a sensitivity analysis; 4) to determine the risk of well-water degradation in the deep semi-confined and confined aquifers for 25, 50, and 100 year forecast horizons for two different management scenarios evaluated by Belitz and Phillips (1995); and 5) to develop recommendations for future data needs that can improve the risk predictions. The project area is shown in Figure 1.

METHODS

Background to our research work and an extensive overview of our methods can be found in our 2002 annual report (Harter, 2002). We are currently in the final project year (scheduled for completion in the fourth quarter of 2003) and a complete final report will be submitted for the next annual report. Here, we briefly summarize project progress during the current reporting period.

GEOSTATISTICAL MODELING

Database Development - Products: A database of collected drilling well logs, a classification scheme used to assign texture descriptions to hydrostratigraphic categories, and the interpretation of each well log using the classification scheme has been completed. The well log analysis includes a map showing the spatial locations of each log and relevant well log statistics. A classification scheme used to interpret the soil survey map was also developed.

Geostatistical analysis - Products: A geostatistical model characterizing the hydrostratigraphy of the semi-confined aquifer for several sub-areas on the Westside has been developed. Generic models have also been developed for two-, three-, and four-texture category classifications.

GROUNDWATER FLOW AND SALT TRANSPORT MODELING

Model Development - Products*:* We are using a three-dimensional transient flow and salt transport model for the implementation of the risk analysis via Monte Carlo simulation. We developed a Fortran Code to automate the modeling setup including the generation of input files, and to couple the three software programs TSIM (geostatistical aquifer property generation; Carle 1999), MODFLOW (flow model; McDonald and Harbaugh, 1988), and

RWHET (transport model; LaBolle, 2002) into single super-program called SASHA-RB (Sensitivity Analysis of Stochastic Hydrostratigraphy in a Aquifer – Rectangular Box). We also completed a version with distributed pumping (DP) and nonstationary, composite geostatistical facies model specifically for the Westside stratigraphy (Westside Implementation – WI). We call this the SASHA-DP/WI model (Sensitivity Analysis of Stochastic Hydrostratigraphy in an Aquifer with Distributed Pumping - Westside Implementation). This model is more specific to Westside hydrologic conditions than the more general model SASHA-RB used for the sensitivity study. It will be used to implement the final risk analysis.

DETERMINE RELIABILITY OF RISK PREDICTIONS

Sensitivity analysis: The reliability of our risk analysis depends on the reliability of the underlying parameters as discussed in Harter (2002). We completed the sensitivity analysis and also developed our own algorithm and Fortran Code ("FLOWPATH") to check for connectivity (percolation clusters in random media, see discussion below). We have also written Fortran programs to analyze the percolation properties of random hydrostratigraphic media (Stauffer and Aharony, 1991) generated with TSIM. This, together with SASHA applied to the above issues provides the confidence intervals to be added to the probability plots/risk analysis.

NONLINEAR DETERMINISTIC DYNAMICS

Based on the results of the sensitivity analysis, the potential use of a nonlinear deterministic framework for understanding the dynamic nature of solute transport processes in subsurface formations was investigated. Time series of solute particle transport in the heterogeneous aquifer medium, simulated using an integrated probability/Markov chain (TP/MC) model, groundwater flow model, and particle transport model, were studied. The correlation dimension method, a popular nonlinear time series analysis technique, was used to identify nonlinear determinism. Sensitivity of the solute transport dynamics to the four hydrostratigraphic parameters involved in the TP/MC model: (1) number of facies; (2) volume proportions of facies; (3) mean lengths (and thereby anisotropy ratio of mean length) of facies; and (4) juxtapositional tendencies (i.e., degree of entropy) among the facies is also studied.

RESULTS

NUMBER OF HYDROSTRATIGRAPHIC FACIES

The number (and type) of hydrostratigraphic facies used to represent the aquifer heterogeneity in the transition probability/Markov chain approach is arguably the most dominant factor influencing the outcomes of the approach. Categorization of number and type of hydrostratigraphic facies typically relies on a significant quantity of reliable well drilling and soils data, as demonstrated the case in the Kings River alluvial fan [e.g., Weissmann et al., 1999; Weissmann and Fogg, 1999] and at the Lawrence Livermore National Laboratory site [e.g., Carle, 1996; Fogg et al., 2000]. Such a categorization, however, is difficult when one deals with sparse data of poor quality, as is the case in the Western San Joaquin Valley aquifer system, studied herein.

Based on the borehole logs made available for the San Joaquin Valley system, two, three, or four facies may be used to represent the system heterogeneity. If two and three facies are used, then the entire system is generally represented by coarse and fine grained sediments. The two categories case may include sand (coarse) and clay (fine), whereas the three categories may include sand (coarse), muddy sand or loam (intermediate to fine) and clay (fine). In the four categories case, in addition to the coarse (sand and gravel) and fine (clay) grained sediments, fine coarse grained sediments (clayey sand and clayey gravel) and coarse fine grained sediments (sandy clay and gravelly clay) may also be included.

For the sensitivity analysis we focused on classifications with two (sand and clay) and three (sand, loam and clay) facies, i.e. dual and triple media aquifers. In each of these two cases, different combinations of proportions, anisotropy conditions (i.e. mean lengths), and juxtapositional tendencies (i.e. entropy) are considered.

Figure 2 compares the travel time probability of salt transport for dual [Figure 2(a), (b), and (c)] and triple [Figure 2(d), (e), and (f)] media systems. The horizontal axis represents the travel time in years and the vertical axis represents the probability at which salt arrives at the bottom of the aquifer. The dual media consists of 21.26% sand and 78.74% clay, whereas the triple media consists of 21.26% sand, 25.46% loam, and 53.28% clay. As coarse-grained sediments play a major role in flow and transport processes, the sand proportion in the triple media is identical to the one in the dual media, and the clay proportion is reduced (from 78.74% to 53.28%) to accommodate the loam proportion (25.46%). The hydraulic conductivity of sand is 31 ft/d, that of clay is 0.004 ft/d, and that of loam is 0.04 ft/d. Figure 2 compares the effect of the facies categorization for each of the three different facies anisotropy conditions (to be discussed later).

The travel time probability curves, shown in Figure 2, reveal significant differences (irrespective of the anisotropy conditions) in the salt transport behavior between the two and three facies representation, in spite of the fact that the proportion of sand is the same in both the cases. In general, the travel time probability curves are negatively skewed in case of the two facies system, whereas they are found to exhibit positively skewed structures when the system is represented by three facies. The negatively skewed curves indicate a mostly late arrival time probability with few earlier arrivals. Hence, in this two-facies system, transport is dominated by the presence of clay. The mode of the arrival time probability in the two-facies case is close to the travel time in a homogeneous clay system (t = 1972 years) and close to the travel time in a perfectly layered system (t = 1679 years), equivalent to a homogeneous harmonic mean K system) given the facies fractions. The consideration of the loam, although it has a K value that is much closer to clay than to sand, allows for significantly earlier arrival probability causing the positive skewness in the breakthrough curve. This suggests that the decision to include a higher number of facies , e.g. loam as a third facies, plays an important role in representing the aquifer heterogeneity and, hence, the salt transport process. Moreover, the travel time probability curves obtained for the triple media are, in general, much broader than that obtained for the dual media, indicating large effective field dispersion generated by the internal heterogeneity of the aquifer in the former.

PROPORTIONS OF FACIES

Different combinations of facies proportions are considered in the two facies medium, where sensitivity of the travel time distribution is higher than in the three facies medium. Note that the two-facies Markov chain model is equivalent to an indicator random field model [Deutsch and Journel, 1992]. On the Westside, facies proportions may change ostensibly between sub-areas (actual variability). They may also differ due to differences in well log implementation among drilling contractors (data uncertainty). Thirty simulations are implemented with sand facies varying from 15% to 60%, which covers the range of sand facies proportions observed. Increments of 0.5% are used at low sand proportions and larger increments of 5% at high sand proportions.

Figures 3 and 4 compare the salt transport travel time probability results for the lower and upper bounds of facies fractions, at different anisotropy ratios. The two cases exemplify significant differences in the travel time probability curves as the proportion of the high permeability facies changes. First, as anticipated, there is a considerable shift in the salt arrival time (first moment of the travel time distribution), with the longest travel times at the lowest sand content. Second, the shape of the travel time probability curve is negatively skewed for the 15% sand medium and positively skewed for the 60% sand medium (as observed in the three facies case, with 21.26% sand and 25.46% loam, shown in Figure 2).

The dependency of the arrival time distribution with facies proportion is mapped in Figure 5. The results shown are for the 2:1 & 300:1 anisotropy condition [shown in Figure 3(a) and 4(a)]. Contour lines represent various levels of cumulative mass arrival at the lower boundary (i.e. 1%, 5%, 10%, 20%, 30%, 50%, 80%, 90%, 95%, 99%), mapped in the facies proportion × travel time space. The results identify the decreasing trend of arrival time with increasing sand proportion. The extreme parts of the cumulative travel time distribution at 1% and 99% total mass are subject to notable sampling bias due to the single realization basis for sampling. The change in the third moment (skewness) of the travel time distribution is indicated, e.g., by the shift of the 50% mass contour relative to the 1% and 99% mass contour: at low sand facies proportions, the 50% mass contour is closer to the 99% contour; as sand facies proportions increase, the bulk of the mass arrives earlier, whereas the tail of the mass remains late. Hence, the 50% contour moves closer to the 1% contour and away from the 99% contour.

With increasing proportions of sand facies, the participation of the sand facies in the solute transport increases disproportionately (Figure 6). In this strongly layered system, the total flow rate at low sand proportions is almost identical to the flow rate computed for the equivalent harmonic mean medium, which represents the perfectly stratified case with the same proportion of sand facies. Nonetheless, the heterogeneity of this highly anisotropic system is sufficient to induce significant acceleration of solute transport relative to the perfectly stratified case. As sand proportion increases, the actual outflow rate, even at anisotropy conditions of 300:1 increases significantly above the harmonic mean, consistent with stochastic models based on Gaussian random fields. The proportion of outflow directly from sand asymptotically approaches total outflow. At sand proportion above 40%, outflow from sand is practically identical to total outflow (Figure 6).

The influence of the facies proportions on the solute transport process may be explained from a “connectivity” or “connected-network” perspective. Connectivity is defined as the degree at which the individual facies are inter-connected to similar facies (e.g. sand to sand) throughout the aquifer medium. Connectivity plays a crucial role in the salt transport process, as the presence of adjacent high K facies may accelerate the migration of salt transport. Connectivity depends upon the volume proportions of facies, which is reflected in the salt transport process. Complete connectivity throughout the flow domain exists within the sand medium, even at sand proportions as low as 15%. However, due to the strong anisotropy, flow paths intersect significant proportions of clay. The regional flow gradient is across layers. Hence, at low sand proportions it is energetically more efficient to “cut through” short vertical distances of low permeable facies than to take a highly tortuous path completely contained within the sand facies. At higher proportions, vertical connections between sand facies are more likely, even if the effective mean lengths (and mean length ratios) do not change, providing energetically more efficient flow paths contained entirely within the high permeability facies.

MEAN LENGTHS OF HYDROSTRATIGRAPHIC UNITS

Besides proportions, mean length ratios (facies anisotropy) are the most critical control on the tortuosity of potential flow paths that are completely contained within the high permeability facies. The mean length parameters in the transition probability/Markov chain approach define the structure or arrangement of the facies. It is important to note that this mean length is not the same as the “mean connectivity length” used in aquifer connectivity studies [e.g., Western et al., 2001], even though connectivity is the basis in both. For instance, the mean length of sediment deposits in the analysis of soil maps or aerial photos may be a few hundred feet, while the connected length may be much longer, since the channel traverses the entire study area [Fogg et al., 2000]

The relationship between mean length and tortuosity are illustrated in Figure 7. Tortuosity of the downward path (given by the ratio of solid line to the dashed line) in the facies of high conductivity (in white) increases with an increase in the facies anisotropy (ratio of mean width along the bedding plane to mean depth across the bedding plane), as the net flow direction is orthogonal to the bedding plane. Despite identical proportions of facies, the tortuosity of the shortest possible flowpath in the high permeability facies (white) decreases significantly as the facies anisotropy decreases. Lower flowpath tortuosity increases the hydraulic gradient along the flowpath and hence shortens the travel time. Note, that a similar dependency on facies anisotropy would not be observed or be of much less influence, if the regional groundwater gradient were oriented parallel to the main bedding plane: In the example shown in Figure 7, the tortuosity along the main bedding plane would in fact be identical between the two examples.

The effects of mean length on the salt transport process are shown in Figures 2, 3, and 4. A change in mean length ratio results in a change in the travel time probability curves (in terms of both salt arrival time and the shape of the curve), irrespective of the number of facies. The effect of mean length is observed when the change is made in either dip to strike ratio (from 2:1 to 5:1, with dip to vertical ratio at 300:1) or in dip to vertical ratio (from 300:1 to 50:1, with dip to strike ratio at 2:1). This stems from the fact that an increase in the dip to strike ratio of mean length at constant dip to vertical ratio implies a reduction in the strike to vertical mean length ratio that is inversely proportional to the increase in the dip to strike ratio. The 2.5× increase in dip to strike ratio is less than the 6× decrease in dip to vertical ratio, hence the latter has a greater impact on the salt transport process, e.g. much earlier arrival time. In all cases a reduction of one or both of the horizontal mean lengths relative to vertical mean length decreases arrival time, irrespective of the number of facies considered or the proportion of high permeability material. Smaller facies anisotropy also increases the effective dispersion and skewness of the travel time distribution function.

The sensitivity of salt transport process to facies anisotropy is particularly obvious in the early arrival time distribution. Figure 8 shows the arrival time of 1% of mass of particles for each of the three anisotropy conditions. The arrival time at the highest facies anisotropy is always later than in the 5:1 & 300:1, which in turn is later than in the 2:1 & 50:1 anisotropy condition.

JUXTAPOSITIONAL TENDENCIES

As previously explained, connectivity (between hydrostratigraphic facies) plays a vital role in flow and transport processes in a heterogeneous aquifer medium. The influence of proportions of facies on the extent of connectivity and, hence, the salt transport process has already been discussed. However, the degree of order in the structure of the hydrostratigraphic facies in the aquifer medium may also play an important role in flowpath tortuosity, connectivity, and hence solute transport. This degree of (dis)order of structure is commonly referred to as “entropy” (Hattori, 1976). Low entropy refers to a high amount of order or internal organization of the hydrostratigraphic facies in the aquifer medium. For example, fluvial deposits with a high degree of fining upward such that gravel transitions upward are almost exclusively to sand, but rarely to muddy sand or mud [e.g., Weissmann et al., 1999] represent a high degree of internal organization (low entropy). On the other hand, when little juxtapositional preference is found between specific facies, the aquifer medium is considered to exhibit high entropy.

In classical stochastic theory [e.g., Gelhar, 1993], an aquifer medium is generally considered to be a Gaussian random field and the log hydraulic conductivity is distributed normally. In transition probability theory, the field is composed of several facies. Here maximum entropy means the distribution of facies is random, no preference. In the transition probability/Markov chain approach, however, different levels of entropy may be considered to represent the aquifer medium. The embedded transition probabilities obtained, e.g., from borehole logs define the juxtapositional tendencies of the bedding sequences. In this way, the transition probability approach allows for parameterization of the entropy in the facies arrangement from deterministic (e.g., sand is always above gravel) to completely random. Therefore, the approach has (at least theoretically) a higher degree of freedom to represent actual aquifer stratigraphy than Gaussian approaches (which assume only complete randomness).

In the present study, the influence of degree of order of facies on the salt transport process is studied by using three different entropy conditions in the transition probability/Markov chain model: low entropy, high entropy, and (intermediate) field entropy. The arrival time plots for the three entropy conditions in a three facies medium (sand 21.26%, loam 25.46%, and clay 53.28%) with high facies anisotropy (2:1 & 300:1) are shown in Figure 9. Although the differences observed between the three entropy conditions are small, a noticeable difference exists between the low entropy condition vs. the field and high entropy conditions. This may be due to the fact that the field entropy is similar to the high entropy condition. It appears that a higher degree of order in the arrangement of facies is equivalent to a stronger (more perfect degree of) layering, which significantly slows solute transport. In particular, higher order of facies arrangement in this case cuts down on early solute arrival.

The latter has an important implication, as there exist aquifers with high degree of order of facies. In such cases, the Gaussian approaches, assuming normally distributed hydraulic conductivities, may indicate early arrival of particles, while in reality the arrival of particles may be much slower depending upon also other characteristics of the medium, e.g. anisotropy condition. The effect of degree of order of facies in the aquifer medium on the salt transport process is also studied using an inverse approach, by estimating the (correlation) dimension of the (time series) of the particle travel [Sivakumar et al., 2003], whose results also support the present ones.

DISCUSSION

The results reflect the importance of the four hydrostratigraphic parameters involved in the transition probability/Markov chain model for aquifer heterogeneity representation and the associated flow and contaminant transport phenomena. We observe distinct differences in the character of the travel time distribution, not only indicated by changes in the first and second moments of the distribution (as known from Gaussian stochastic analysis), but also in the third moment. In general, the travel time probability curves for the triple facies media are broader than those for the dual facies media, which is an indication that the salt particles travel in a more tortuous way from top to bottom in the former compared to that in the latter. In other words, a larger macrodispersion of salt particles is observed in the triple media. In addition to the number of facies, the volume proportions of facies seem to play a significant role in the macrodispersion of particles, with a larger macrodispersion when the sand content is higher. This may be seen from Figures 3 and 4, as the travel time probability curves shift from a negatively skewed structure to a positively skewed structure when the sand proportion increases from 15% to 60% in the dual facies medium. To study more intensively the effect of volume proportion on macrodispersion, we investigate the changes in macrodispersion against the proportions of sand/clay.

Representing the (logarithm of) hydraulic conductivity K of any particular facies as f = ln(K), the mean (m_f) and the variance (σ_f^2) of the logarithm of hydraulic conductivity in the dual facies medium are, respectively, given by:

$$m_f = f_s * V_s + f_C * V_C \qquad (1)$$

$$\sigma_f^2 = (f_s - m)^2 V_s + (f_C - m)^2 V_C \qquad (2)$$

where V_s and V_C are the volume proportions of sand and clay, respectively. Figure 10 presents the variance of ln(K) against the volume proportion (of clay). As may be seen, the variance of ln(K) increases when the clay content increases from 40% to 50%, but then decreases with further increase in the clay content (up to 84%). In other words, the effect of volume proportions on macrodispersion changes direction at 50% clay (or 50% sand), i.e. when the volume proportions of facies in the two facies medium are equal.

Moments of the travel time (mean, variance and skewness) vary with the proportion of facies respectively. The mean of arrival time increases with the proportion of clay in the two facies Markov chain model [Fig.11].

The macrodispersive spreading, measured in terms of the longitudinal dispersitivity aL, can be derived from the (variance of the) dimensionless residence time (DRT) as [e.g., Desbarats, 1990]:

$$\alpha_L = \frac{D}{\bar{u}} = S^2 \frac{L}{2} \quad (3)$$

where D is macrodispersion, S^2 is the variance of dimensionless residence time($t_D = t / \bar{t}$); $\bar{u}$ is the mean pore fluid velocity, and $\bar{q}$ is the average specific discharge in the longitudinal (y) direction.

The logarithmic variance of dimensionless travel time (σ_f^2) may also be used as an alternative measure of tracer spreading, using the distribution of the logarithm of dimensionless residence time [i.e. $\ln(t_D)=\ln(t\bar{u}/L)$]. Such a distribution for the dual medium with the above three anisotropy conditions is shown in Figure 12. In general, a decrease in variance is observed with an increase in clay content above 50%. This indicates that the flow paths formed by sand become less tortuous with increase in clay proportion and most of the particles come out of clay at very high clay proportion. In a complementary finding, Desbarats [1990] observed that the log variance of dimensionless travel time increases with an increase in low conductivity facies proportion from 10% to 50%.

We note that significant differences in travel time variance occur even for small changes in clay proportion at very high sand proportions (above 80%). This seems to indicate that estimation of dimensionless travel time becomes much more complex when the clay content is significantly higher. The effect of anisotropy conditions on the log variance of dimensionless travel time is also observed. The variances are relatively smaller for stratified medium (i.e. anisotropy 2:1 & 300:1 and 5:1 & 300:1), when compared to less stratified medium (i.e. anisotropy 2:1 & 50:1).

Figure 13 presents the variation of macrodispersivity in the longitudinal (vertical) direction against the variance of ln(K) for the dual medium with the three anisotropy conditions. The results indicate a consistent linear increase in macrodispersitivity with an increase in variance of ln(K), except at very high ln(K) values, where it seems to oscillate even for slight changes in ln(K). These results are somewhat consistent with past studies [e.g., Warren and Skiba, 1964; Heller, 1972; Smith and Schwartz, 1980], as such studies also reported a linear increase of longitudinal macrodispersivity with an increase in variance of logarithm hydraulic conductivity. However, in those studies, the linear relationship was observed only for $\sigma_f^2<1$, whereas in the present case $\sigma_f^2>10$ (because of the highly contrasting hydraulic conductivities of sand and clay). The sensitivity of macrodispersivity to anisotropy conditions is also evident from Figure 13, as macrodispersivity increases with decrease in stratification.

The effect of volume proportions of facies on the structure of the travel time probability curves is also investigated using the coefficient of skewness as an indicator, and the results are presented in Figure 14. The skewness coefficient increases with an increase in sand proportion. In general, a negative coefficient is observed at very low sand proportion (typically less than 20%), and the skewness coefficient is significantly higher at very high sand proportions. The effect of anisotropy on the structure of the travel time probability curve is also evident, as a less stratified medium (i.e. anistropy 2:1 & 50:1) yields significantly higher skewness coefficients compared to a highly stratified medium (i.e. 2:1 & 300:1 and 5:1 & 300:1). This is the case particularly when the sand proportions are very high, indicating the combined influence of facies volume proportions and mean lengths.

NONLINEAR DETERMINISTIC DYNAMICS

The results of the nonlinear deterministic dynamics analysis describe, in general, the nonlinear deterministic nature of solute transport dynamics (dominantly governed by only a very few variables, on the order of 3), even though more complex behavior is possible under certain (extreme) hydrostratigraphic conditions. The sensitivity analysis with respect to nonlinear dynamics reveals: (1) the importance of the hydrostratigraphic parameters (in particular, volume proportions of facies and mean lengths) in representing aquifer heterogeneity; and (2) the ability of the correlation dimension method in capturing the complexity of the underlying dynamics. Verification and confirmation of the present results through use of other nonlinear deterministic techniques and assessment of their reliability for a wide range of solute transport scenarios are still needed. However, we hypothesize that the analysis may lead to a potential decision-tool to select the proper geostatistical model characterizing the aquifer heterogeneity (e.g., Gaussian or Markov chain model).

COMPARISON TO GAUSSIAN RANDOM FIELD TRANSPORT

In the process of generation of field, Gaussian method and Markov chain method are fundamentally different. In a Gaussian model, hydraulic conductivities are normally distributed, while in a Markov model, the whole field is characterized by several facies (2, 3 or 4, etc.). We compared solute transport in Gaussian field with that in Markov chain field, where both have identical hydraulic conductivity variograms and variances, and identical fluxes.

In the test example, the proportion of clay is 80%, and the proportion of sand is 20%. The anisotropy of this field is 2:1 & 300:1. Hydraulic conductivities of sand (k_s) and of clay (k_c) are 31ft/day and 0.004ft/day respectively. Then $\ln(k_s)$=3.43ft/d and $\ln(k_c)$=-5.52ft/d. Mean, variance and standard deviation of two conductivity are:

$$m=0.2*3.43+0.8*(-5.52) = -3.73$$

$$\sigma^2= (3.43+3.73)2 * 0.2+(-5.52+3.73)2*0.8 =12.8; \sigma=3.58 \quad (4)$$

With the result from two facies (clay and sand) Markov chain model (disretization: 101*101*101 cells), we perform a variogram analysis [Fig.15] and obtaine the appropriate Gaussian variogram range, sill, and nugget.

Fig.16 shows the breakthrough curve in the Gaussian random field obtained from the Gaussian variogram. The breakthrough curve is positively skewed as known from analytical results. The mass remaining at the end of the simulation period is 18.1%. For comparison, the breakthrough curve from the Markov chain model is negatively skewed, and the remaining mass at the end of the simulation period is less than 0.1% [Fig.17]. The large difference between two curves is due to the different hydraulic conductivity fields. In the Gaussian field, log hydraulic conductivities vary greatly around its mean -2.21, which includes some very large and very small hydraulic conductivities. Hence, some particles come out of the domain very early, while more particles come out late and many of them still remain in the domain after 2000 years. In contrast, in Markov chain model, only two facies exist, and nearly all of the particles flow out of the Markov chain model domain within the simulated time period.

In addition to these, the juxtapositional tendencies among the facies in the aquifer medium also play an important role in the connectivity of the facies and, hence, the flow and salt transport phenomena, as presented above. The present results indicate that salt travels more slowly in a relatively ordered medium compared to a disordered medium, indicating that the salt arrival time estimated if a Gaussian representation is used could be much earlier than that in reality, since not all real aquifer systems are completely random. Whether or not this is indeed true needs to be studied through a sensitivity analysis of a real system.

CONCLUSIONS

The transition probability / Markov chain approach for geostatistical characterization of the Westside alluvial aquifer system is well suited for simulating alluvial fan stratigraphy when hydraulic conductivity data are sparse. It provides extensive opportunities to test the degree of uncertainty that exists about the hydrostratigraphy in the Westside aquifers given the limited reliability and/or interpretability of existing data, primarily driller's logs. A sensitivity study was implemented to determine the critical factors in the alluvial sediment structure affecting salt transport to deeper aquifer zones. We found that a meaningful risk analysis will depend to a large degree on the accurate characterization of: the number of hydrostratigraphic facies that make up the aquifer, the proportion of coarse grained sediments that may carry large amounts of salt to depth over relatively short periods of time, the mean lengths of important stratigraphic units, particularly the ratio of length and thickness of coarse materials, and the degree of entropy (sorting, juxtapositional preference) found among the hydrostratigraphic facies. The results indicate that a significant risk for early salinization of deep wells potentially exists, given the range of input data that we determined to be reasonable. With the completion of the sensitivity analysis, which was based on a simplified representation of aquifer hydraulic conditions, we now focus on the development of a more detailed, site-specific aquifer representation that limits uncertainty particularly in those geostatistical descriptors of the Westside aquifer system to which the risk analysis is most sensitive. A selection of high-quality well logs provide the basis for defining as many as four specific hydrostratigraphic groups within each of five aquifer sub-regions identified (semi-confined proximal fan are, semi-confined distal fan and interfan area, semi-confined Sierran sands, Corcoran Clay, confined aquifer).

We also investigated the possible existence of fractal behavior in the solute transport phenomenon in a heterogeneous aquifer medium, characterized by a transition probability/Markov chain model. Time series of solute particle transport were analyzed for this purpose. Application of a variety of methods, ranging from common statistical tools to specific fractal techniques, indicate the presence of fractal behavior (of multi-fractal type) in the solute transport process.

CONTRIBUTIONS TO THE SALINITY/ DRAINAGE PROGRAM

In this study, we evaluate the long-term risk of groundwater degradation in the deep semi-confined and confined aquifers due to increased pumping in these zones. We have developed a tool box that includes an "aquifer generator" to study various random arrangements of alluvial fan deposits, a groundwater flow model, and a transport model. We developed an integrated program to bundle the third-party software elements and process results. The program, called SASHA, is a tool specifically designed for this project to estimate the probability of early arrival of highly saline water in these zones due to the presence of vertically extensive interconnected coarse-textured bodies in the semi-confined aquifer and in the Corcoran Clay or to leakage inside wells and boreholes hydraulically connecting these zones. The risk analysis accounts for the sub-regional spatial variability of aquifer-system hydrostratigraphy, vertical and horizontal flow rates, and salinity concentrations.

By employing a stochastic approach, we can estimate the percentage of wells likely to become unusable as a function of time. The sensitivity analysis allows us to focus on key elements in the stochastic analysis, and to provide a measure of prediction reliability. The results of the risk analysis could then be used in cost-benefit analyses of various groundwater management alternatives. It is also worth noting that historical pumping rates during the 1970s and 1980s were approximately 60% of those recommended by Belitz and Phillips (1995). However, potential reductions in surface water deliveries in this region due to the implementation of the Central Valley Project Improvement Act (CVPIA) may result in an increase in groundwater pumping to levels recommended by Belitz and Phillips (1995). Consequently, our risk analysis may also be used to assess the impacts of reduced surface water allocations on groundwater quality on a sub-regional basis.

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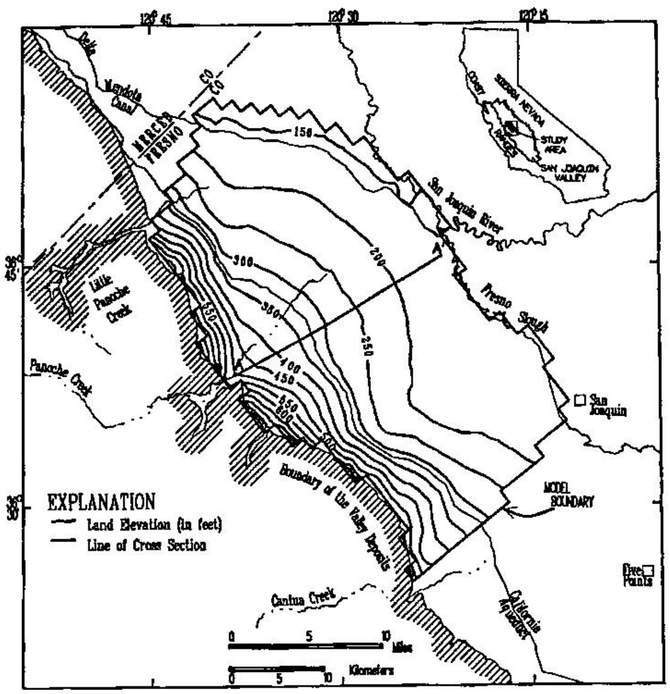

Figure 1: Topography and location of the project area (Belitz and Phillips, 1995).

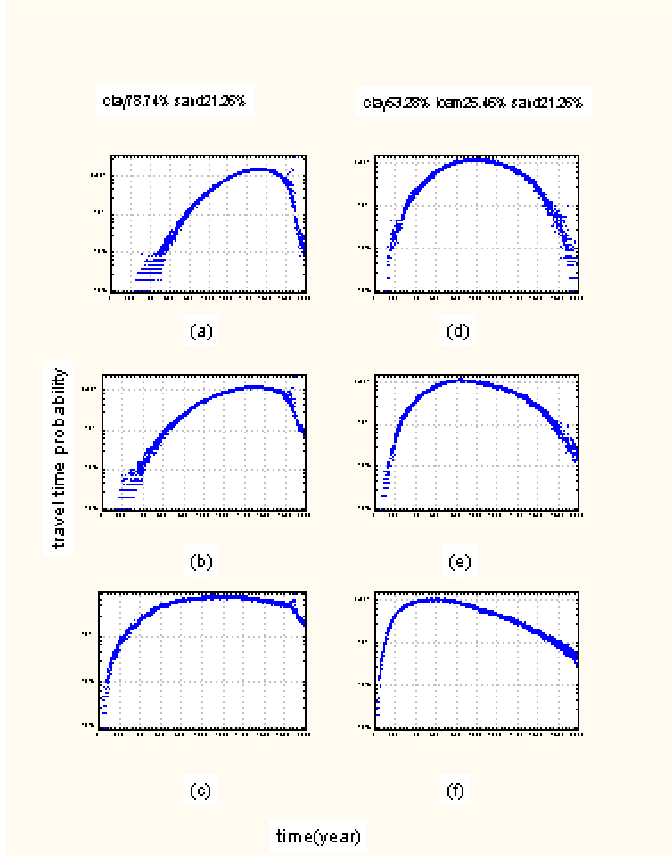

Figure 2. Effect of Number of Hydrofacies on Travel Time Probability
(a),(d)--anisotrophy 1:2,300:1; (b),(e)--anisotropy 5:1,300:1; (c),(f)--anisotropy 2:1,50:1

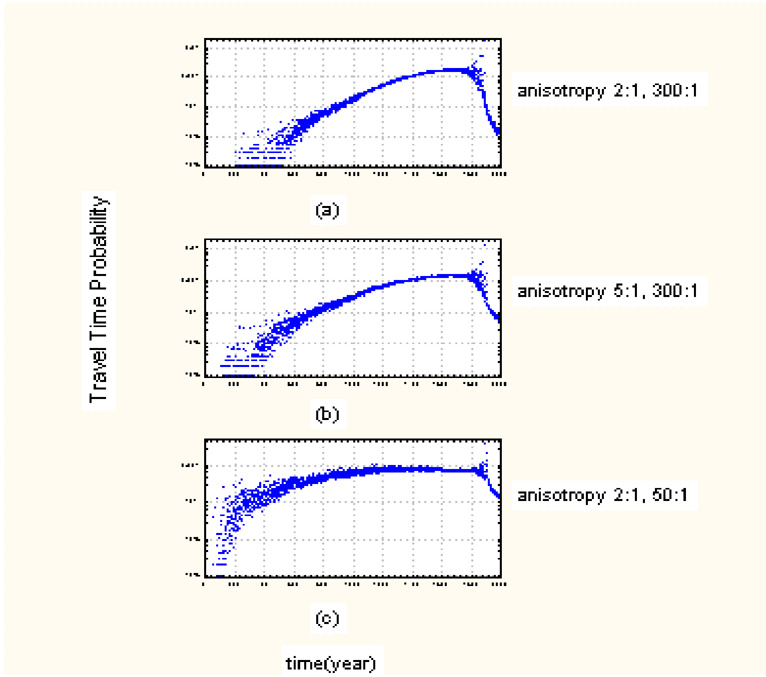

Figure 3. Effect of Anisotropy on Travel Time Probability in dual hydrofacies material clay 85% sand 15%

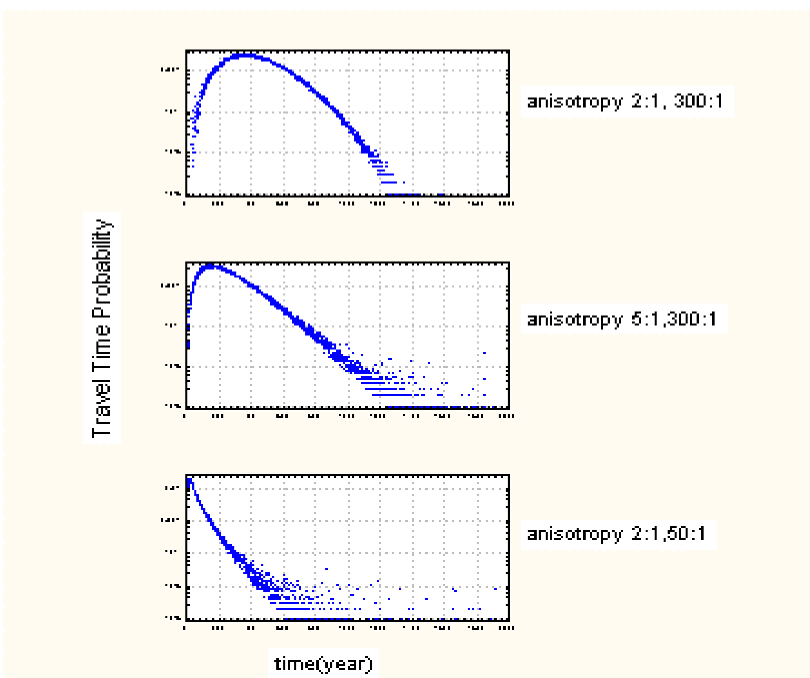

Figure 4. Effect of Anisotropy on Travel Time Probability in Dual Hydrofacies Material clay 40% sand 60%

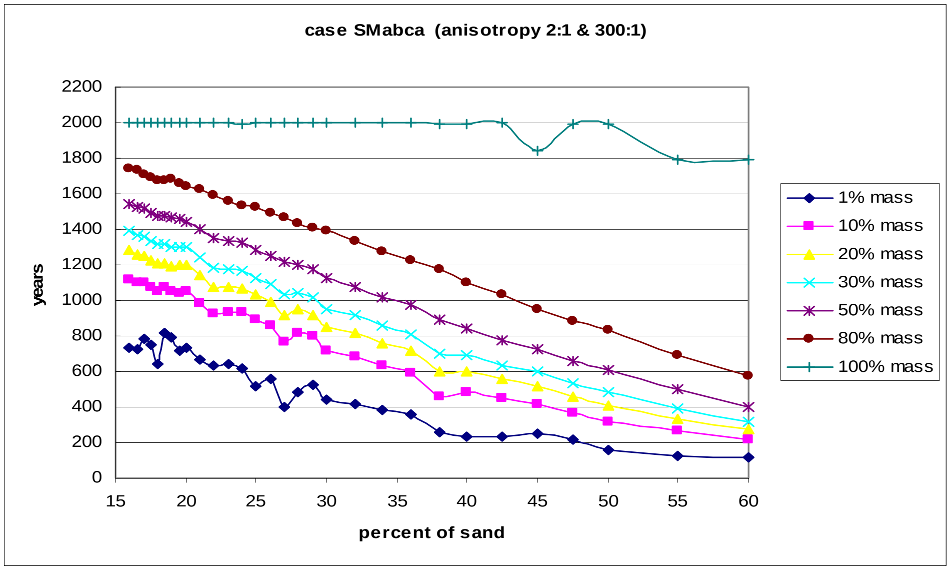

Figure 5. Arrival time of mass with change in sand proportion

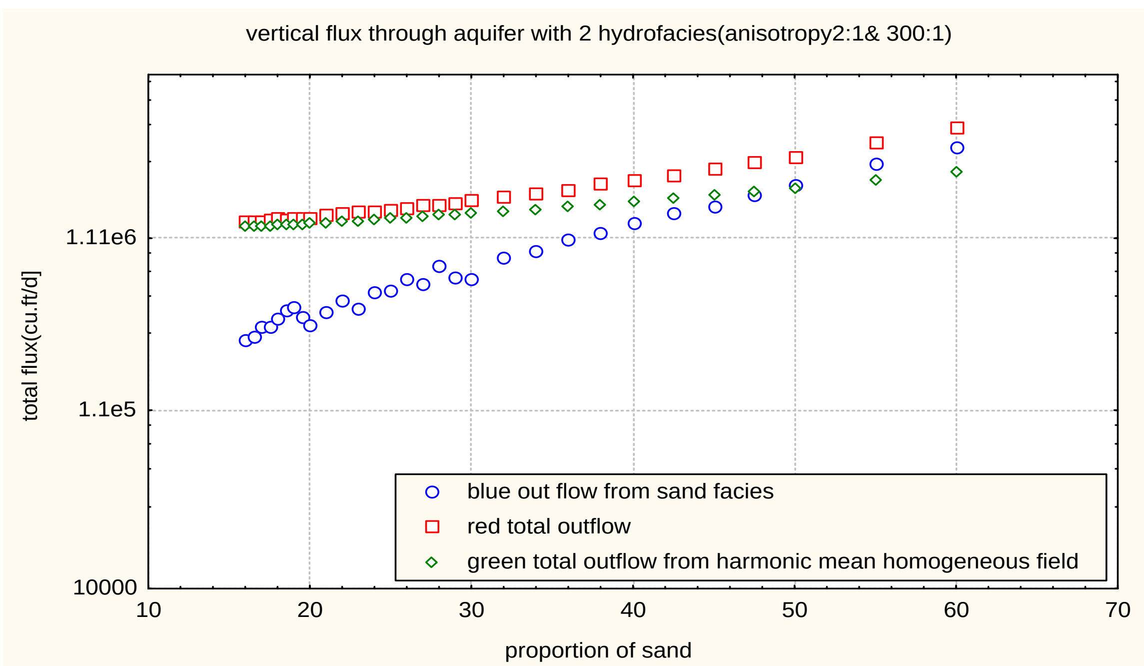

Figure 6. Vertical flux through aquifer with 2 hydrofacies (anisotropy 2:1& 300:1)

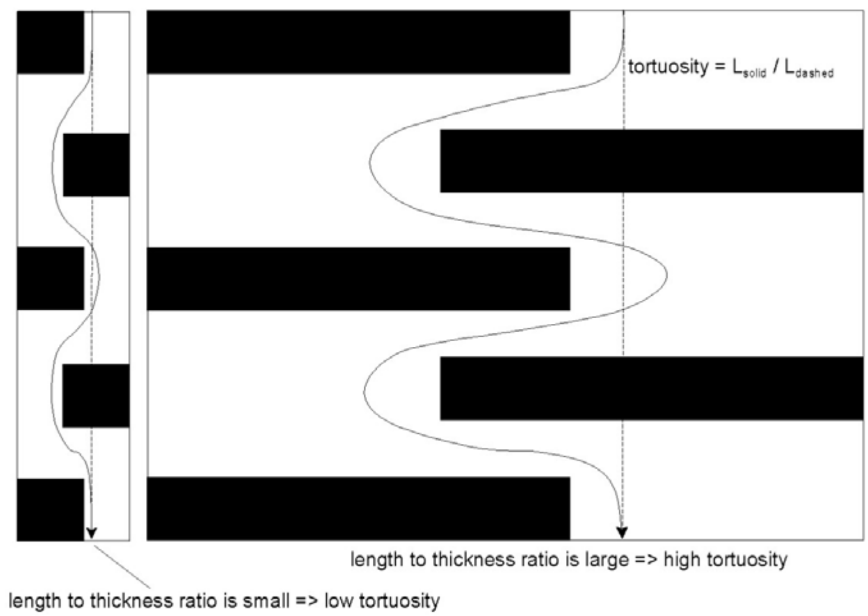

Figure 7. Illustration of the link between tortuosity and mean length ratios

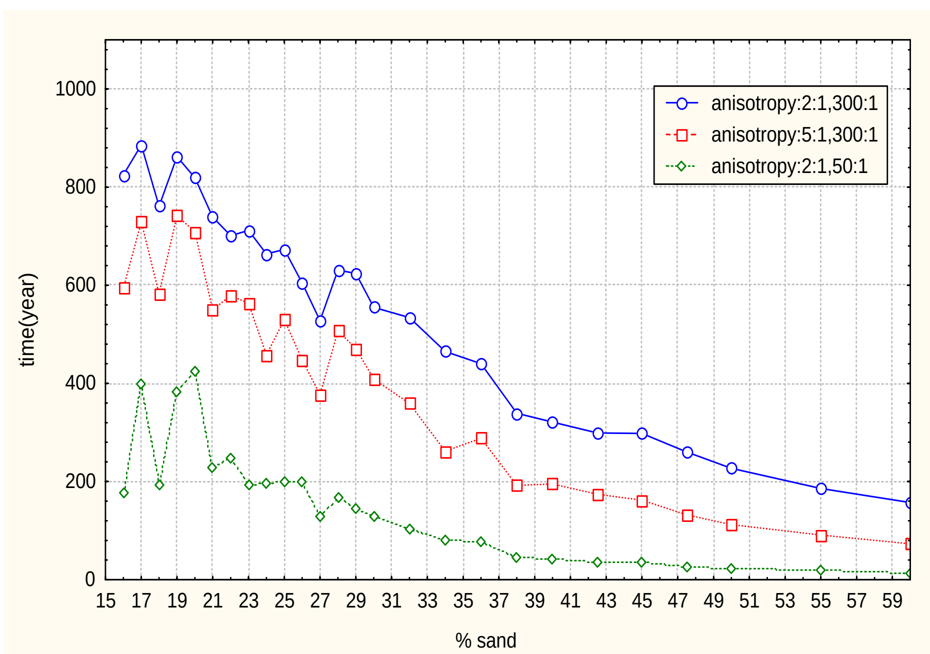

Figure 8. Effect of anisotropy on salt arrival time in dual media: Arrival time of first 1% of mass

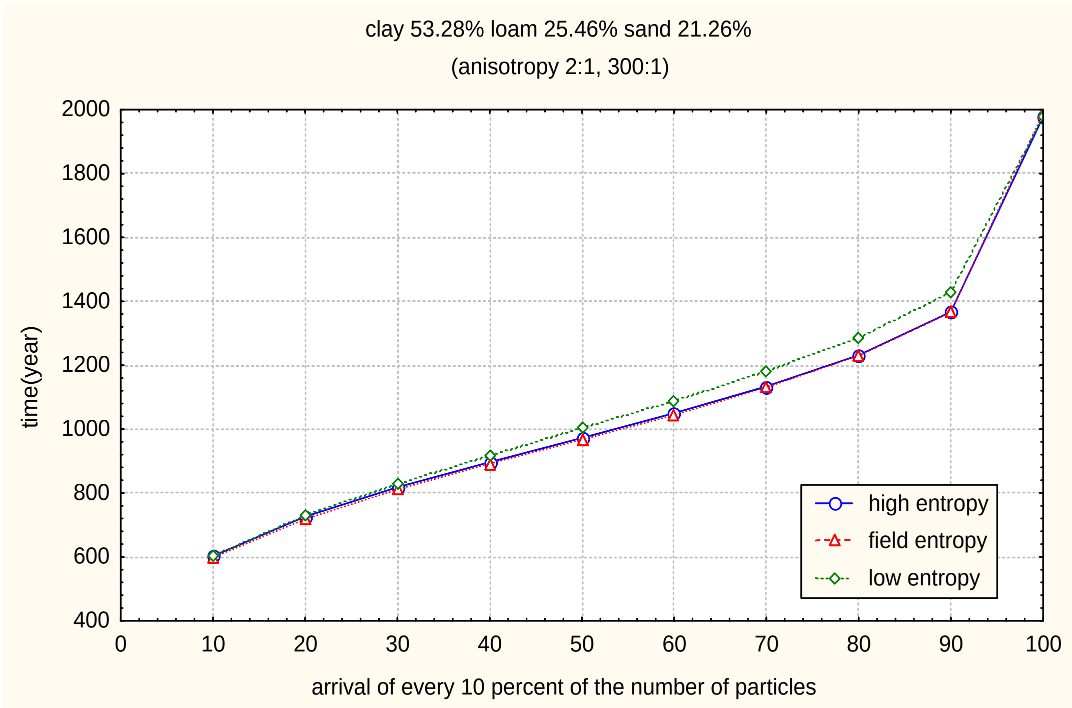

Figure 9. Effect of entropy on salt arrival time in triple media (sand 21.26%, loam 25.46%, and clay 53.28%)

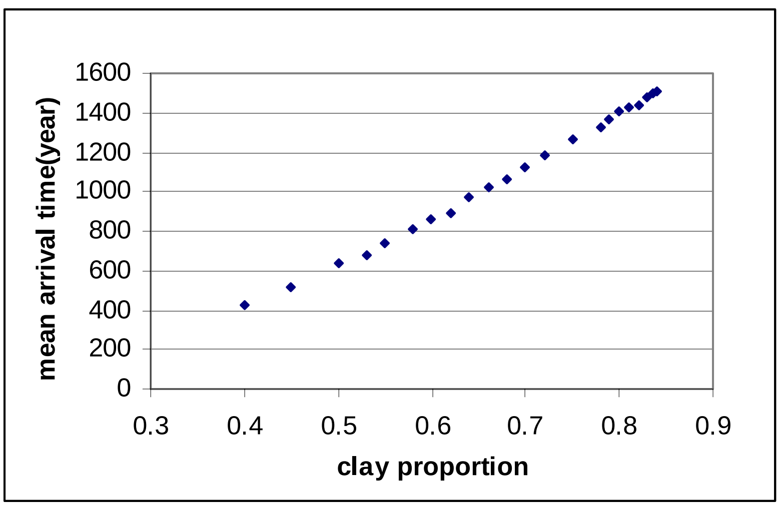

Figure10. Increase of mean arrival time of salt particles with the increase of clay proportion (anisotropy ratio 2:1&300:1)

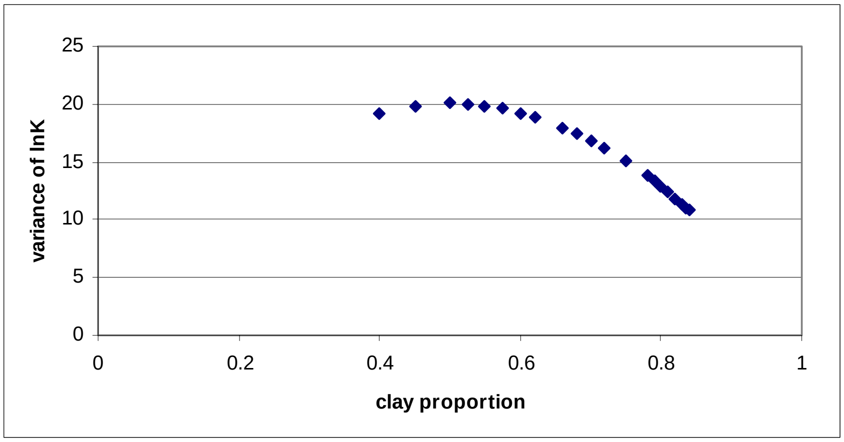

Figure 11. Variance of LnK in a dual facies media

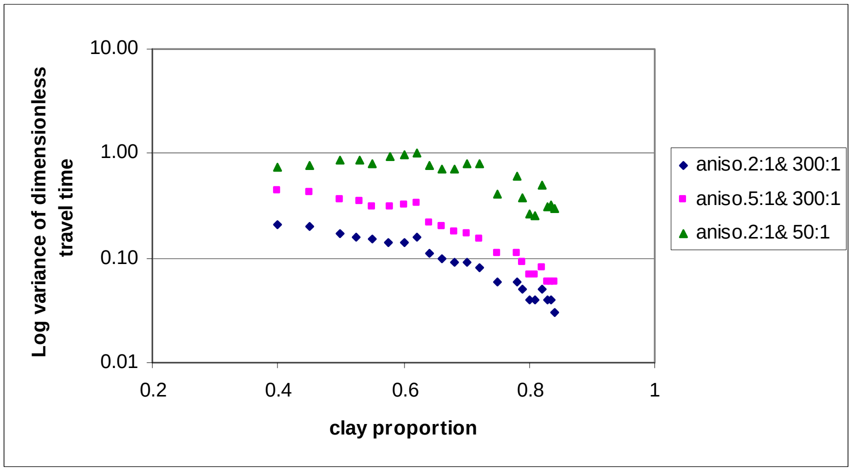

Figure 12. Log variance of dimensionless travel time

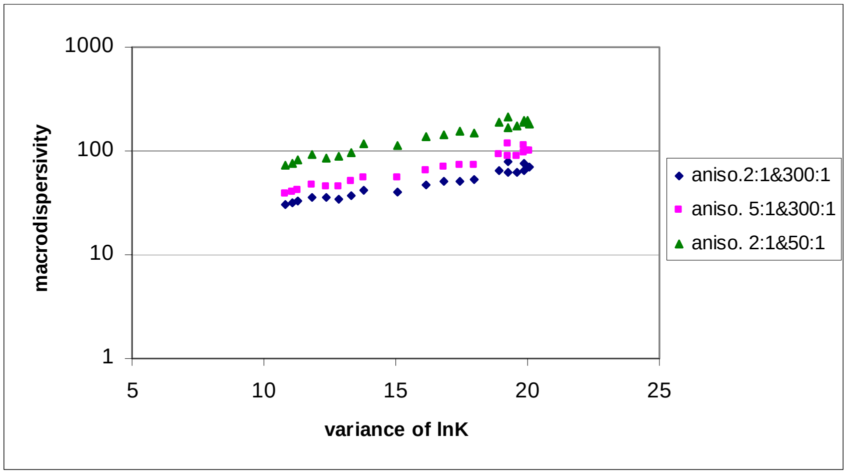

Figure 13. Variation of macrodispersivity with variance of LnK

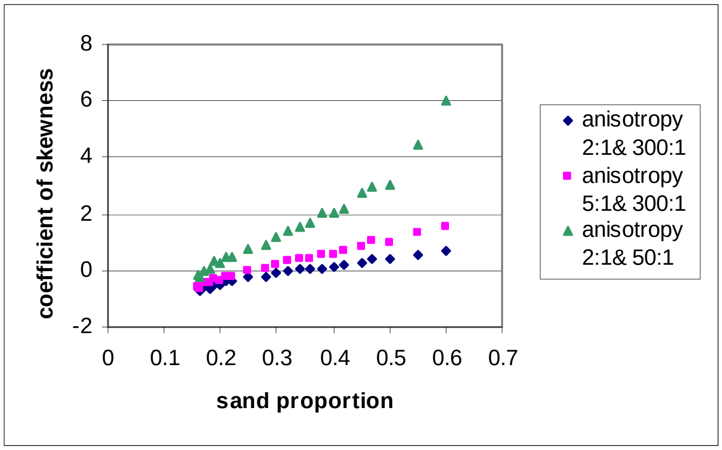

Figure 14. Coefficient of skewness at different anisotropy ratios and sand proportions

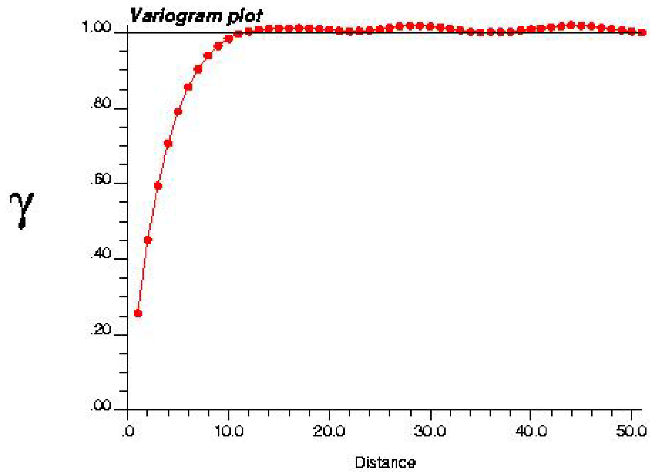

Figure 15. Variogram of logarithm hydraulic conductivities in Markov chain model

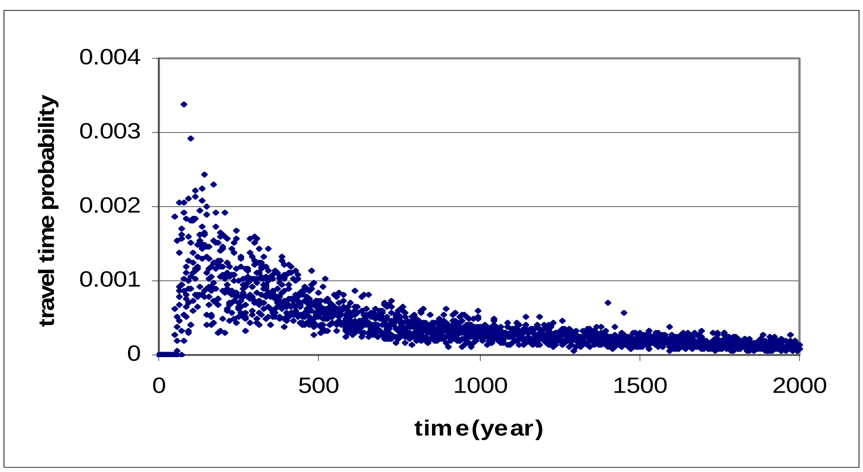

Figure 16. Travel time probability using the Gaussian model

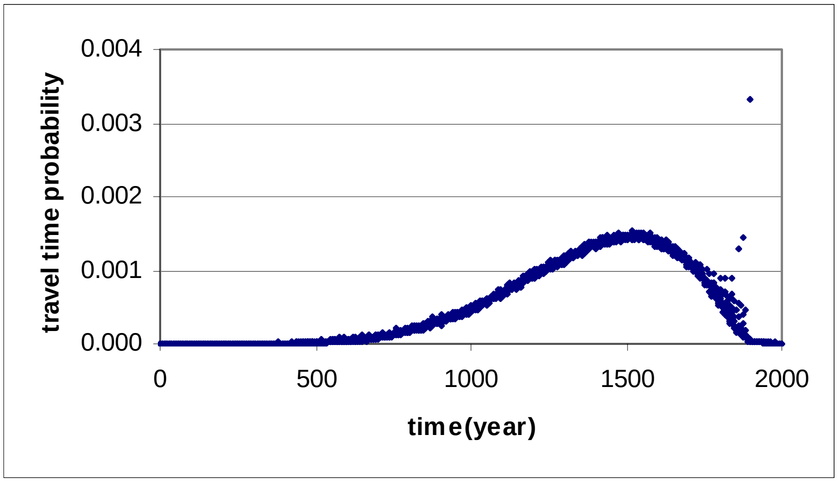

Figure 17. Travel time probability using the Markov chain model

Physical-Chemical Nature of Sediment Selenium with Implications for Bioavailability

(Part of a Team Project Entitled "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation")

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ABSTRACT

OVERVIEW OF THE JOINT PROJECT

The project proposed here is one part of a larger, Joint Research effort proposed for selenium (Se) ecotoxicity remediation in evaporation basins. Our focus on evaporation basins has several major endorsements: (a) it is a proven, economical means by which to dispose of waste agricultural water and contain the salt; (b) it is a "no discharge" technology for the disposal of water since it is terminal, thus capable of avoiding almost all aspects of the Total Maxiumum Daily Load (TMDL) regulations; (c) historically, its principal detracting feature has been Se toxicity to migratory waterfowl, yet in recent years, basin management schemes have significantly reduced this risk; (d) most recently, we have obtained field-scale evidence that remediation thru a combination of foodchain breakage with natural volatilization may be possible. This last is the topic of the Joint Research project.

In the San Joaquin Valley agricultural drainage waters, the only known issue with Se is toxicity to top predators such as aquatic birds, which receive Se primarily through their diet, such as aquatic invertebrates and fish. The research shows that waterborne Se concentration is not always a reliable predictor of Se content in aquatic organisms (Skorupa and Ohlendorf, 1991; Bowie et al., 1996) or observed toxicity (e.g. Reash et al., 1997). It is now clear that Se "biogeochemistry" - that is, how Se chemically transforms both inside and out of organisms - plays a pivotal role in determining the ecotoxic risk at particular sites (EPA Office of Water, 1998). Consequently, there has been scientific consensus that tissue or protein-bound Se concentrations are possibly better markers of ecotoxic risk (EPA Office of Water, 1998) than waterborne Se. There is additional scientific consensus that sediments harbor key pools of Se for ecotoxic effects (EPA Office of Water, 1998).

Thus, Se biogeochemistry is where the solution must be sought for the best chance at Se remediation. These processes must be evaluated for any remediation effort and may even be exploited to mitigate Se ecotoxic problems. These concepts form the foundation of the proposed projects at the Tulare Lake Drainage District (TLDD) evaporation basin site. This is in contrast to most projects in the San Joaquin Valley, which keyed on simple, but unfortunately unreliable, indicators such as Se water concentration.

The overarching objectives of the joint project, "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation", which involves the PIs listed above in separate but linked projects, plus cooperators at Novalek, DWR, and TLDD, are keyed around the foodchain system in TLDD evaporation basins, which include:

- Evaluating the efficacy of reducing Se risk resulting from intensive commercial harvest of brine shrimp (Artemia franciscana) and other macroinvertebrates in TLDD basins.
- Assessing effects of fertilizer inputs on algal dynamics for optimizing the harvest of brine shrimp and other macroinvertebrates as well as Se volatilization so that total and bioavailable Se are reduced in TLDD basins.
- Evaluating ecotoxic status in different basins of widely varying salinity and other conditions, so that general factors leading to reduced ecotoxic risk can be discerned.

OBJECTIVES AND APPROACH FOR THIS PROJECT BY HIGASHI AND FLOCCHINI

The biogeochemistry of Se must be at the core of design and implementation of remediation on Se ecotoxic impact. Part of the biogeochemistry is trophic transfer of Se which is being examined by Salinity/Drainage investigators (Fan & Higashi, and Fry). However, the chemical basis of bioavailability - that is, the molecular mechanisms of lower trophic level entry of Se into the foodchain - remains largely unknown and unstudied. There is only a general consensus that organic forms are much more bioavailable than inorganic forms of Se (e.g. Rosetta and Knight, 1995), yet such impressions have already worked their way into the regulatory arena for water (EPA, 1996; EPA, 1997). Moreover, the sediment is the major Se sink, yet it is essentially uninvestigated (EPA Office of Water, 1998).

The specific objectives of this proposal key on newly-deposited sediment (0-3 months old, using a sediment trap), from both in situ test enclosures (proposed by the Rejmankova and Fan & Meeks projects) and existing evaporation basins at TLDD. These represent basins that are both commercially harvested and non-harvested. The objectives are to probe the:

i. Microphysical basis for bioavailability of Se in sediments, by determining gaseous, “mobile” (waterborne), and “immobile” (solid) states of Se;

ii. Chemical basis for bioavailability, by analyzing mobile and immobile states for several known and hypothesized organo-Se structures, such as proteineceous Se;

iii. Physico-chemical basis of bioavailability, by extraction of the organic matter (“humic”) from the immobile Se state, and coarse size fractionation of the mobile Se into particulate-

detrital and colloidal-soluble fractions, followed by (ii).

We found that basins with the highest levels of volatile Se also experienced the largest variation in volatile Se production. Qualitatively, basins of higher salinity tended to have higher volatile Se and diurnal fluctuations, and these are the basins with higher brine shrimp harvests (see project report of Fan and Meeks). Such volatile Se would be considered non-bioavailable and lost from the system. Jointly with the project of Drs. Gao and Dahlgren, we have found relationships of the organic forms of Se to protenaceous material, largely present in detrital material. These forms could be considered as major forms of Se that enter the foodchain.

BACKGROUND & OBJECTIVES

BACKGROUND AND OBJECTIVES FOR THE JOINT PROJECT

The project proposed here is one part of a larger, Joint Research effort proposed for selenium (Se) ecotoxicity remediation in evaporation basins. Our focus on evaporation basins has several major endorsements: (a) it is a proven, economical means by which to dispose of waste agricultural water and contain the salt; (b) it is a "no discharge" technology for the disposal of water since it is terminal, thus capable of avoiding almost all aspects of the Total Maxiumum Daily Load (TMDL) regulations; (c) historically, its principal detracting feature has been Se toxicity to migratory waterfowl, yet in recent years, basin management schemes have significantly reduced this risk; (d) most recently, we have obtained field-scale evidence that remediation thru a combination of foodchain breakage with natural volatilization may be possible. This last is the topic of the Joint Research project.

In the San Joaquin Valley agricultural drainage waters, the utmost issue with selenium (Se) is toxicity to top predators such as aquatic birds, which receive their Se primarily through their diet, including aquatic invertebrates and fish. Past research has shown that waterborne Se concentration is not always a reliable predictor of Se content in aquatic organisms (Skorupa and Ohlendorf, 1991; Bowie et al., 1996). In turn, Se content is not always related to observed toxicity (e.g. Reash et al., 1997; Fan et al., 2002).

The worldwide research efforts on Se contamination in wastewaters, including research on the diet items, now indicates that Se "biogeochemistry" (biotransformations and foodchain transfer, in particular) plays a pivotal role in determining the ecotoxic risk of particular sites (EPA Office of Water, 1998; SJVDIP report, 2000). Consequently, protein-bound Se concentrations in food items and top predators may be more reliable markers of Se ecotoxic risk (EPA Office of Water, 1998; Fan et al., 2002).

Thus, the hard-learned lesson is that the complex "Se biogeochemistry" process lies at the heart of Se problems. Therefore, it is where the solution must be sought for the best chance at Se remediation. These concepts form the foundation of the proposed project at the Tulare Lake Drainage District (TLDD) evaporation basins. This is in contrast to most previous projects in the San Joaquin Valley, which depended on simple but unreliable indicators such as waterborne Se concentration.

The overarching objectives of the joint project, "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation", which involves the PIs listed above in separate but linked projects, plus cooperators at Novalek, DWR, and TLDD, are keyed around the foodchain system in TLDD evaporation basins, which include:

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- Evaluating ecotoxic status in different basins of widely varying salinity and other conditions, so that general factors leading to reduced ecotoxic risk can be discerned.

The first two objectives will be fulfilled in cooperation with Dr. R. Rofen who has been conducting brine shrimp harvest at the TLDD South Evaporation Basin (S) and Hacienda Evaporation Basin (HEB) systems. These harvests have been sold as valued feedstock to aquarium and aquaculture industries. The HEB site, consisting of two sequential series "A" and "C", have been studied by Fan and Higashi for several years. These two series, despite receiving on average the same drainage water, have very different Se volatilization and algal communities (Fan and Higashi, 1997, 1998, 1999). Thus, the HEB site is a very interesting, and potentially a very important site to expand our work. The third objective will be a continuation of our previous effort (funded by this program and in collaboration with Julie Vance and John Shelton at DWR) to track foodweb Se for Se bioremediation.

Macronvertebrates are major food items (Cooper et al., 1997) - and constitute the major route (Skorupa, 1998, and references cited therein) - by which birds are exposed to Se. It therefore follows that reducing the abundance of food invertebrates (objective #1) as well as their Se concentration (objective #2) will lead to reduced risk. Figure 1 and its legend illustrate these concepts.

Our preliminary investigation at these basins had indicated that both waterborne Se concentration and Se bioavailability from algae and brine shrimp appeared to be reduced by commercial harvest of macroinvertebrates. Encouraging an appropriate algal community that dissipates Se by volatilization, while sustaining brine shrimp production, may further enhance this reduction. Dr. Rofen has obtained permission for such manipulation at TLDD. To guide such effort, relationships among water chemistry, algal dynamics, and brine shrimp production must be understood. Understanding of these relationships will also avoid the situation whereby undesirable algal blooms may lead to an increase in bioavailable Se both in the water column and sediment.

RATIONALE FOR THIS PROJECT, "PHYSICAL-CHEMICAL NATURE OF SEDIMENT SELENIUM WITH IMPLICATIONS FOR BIOAVAILABILITY", HIGASHI & FLOCCHINI, PIS.

As stated above, it has been known that the major risk of Se toxicosis to aquatic top predators such as shorebirds occurs thru their diet, and therefore thru the foodchain (e.g. Skorupa, 1998 and references cited therein). Other routes of exposure, e.g. direct exposure to Se-contaminated water, are not considered to be significant. The chemical form(s) of Se that moves through the foodchain is not known, but a recent consensus (e.g. EPA Office of Water, 1998) proposes that protein-bound Se in food organisms may be the most available form to the next trophic level. Currently, UC Salinity/Drainage Program projects (those of Fan & Higashi, and Fry), as well as other agencies, are investigating these aspects.

On the other hand, little attention has been paid to the non-living forms of Se that enter the foodchain in the first place: that is, the bioavailability of Se to lower trophic levels. Organic forms appear to be important, as laboratory studies have shown that, directly from water, organic Se as selenomethionine (Se-Met) is much more available to algae and invertebrates than the typical inorganic forms, selenite (SeO_3) and selenate (SeO_4) (Rosetta and Knight, 1995; Maier and Knight, 1994 and references cited therein). However, commercially available organic forms such as Se-Met occur only at very low concentrations in the water (Fan and Higashi, unpublished data), so they may not be relevant model compounds. Luoma et al. (1992) have shown that more complex, but unknown organic form(s) such as Se-enriched diatoms and sediments have high bioavailability to clams. The sediment is often the largest pool of Se and considered to be an important source of foodchain Se (e.g., EPA Office of Water, 1998). In the sediment, Se is likely to be resident in all particle sizes, ranging from algal mats and detrital floc to colloidal and small-molecule sizes; but only the latter has been investigated. Thus, what is needed are studies of bioavailability of the various organic forms and sizes of Se – in water, food items, and particularly the sediment – to gain an understanding of how Se enters the foodchain.

Unfortunately, such studies are not feasible at the present stage of knowledge, because the relevant forms of Se in the sediment are simply not known. This is not a trivial list to compile, if we consider briefly the biogeochemical cycles of Se. Figure 1 illustrates a sort of biogeochemical "refluxing" of Se depicting the relatively simple system of an evaporation basin, which is devoid of vascular plants and infaunal vertebrates. Waterborne and sediment Se as SeO_3 and SeO_4 are initially "fixed" into organic forms mostly by algae and microbes, some of which can head up the foodchain, or turn into organic material that is relatively unaltered - termed detritus - upon death. The detrital material can re-enter the foodchain immediately via microbes or invertebrates that are exposed (physically or thru ingestion) to the detritus. Other paths are for Se to re-enter the foodchain thru microbes or invertebrates after considerable chemical transformation has occurred to the detrital material - for the purposes of brevity, this aged material is lumped into the term humic material.

In any of the steps in Fig. 1, multiple chemical forms of Se are involved, and for the most part these forms are unknown. In most cases, even the physical state (gaseous, soluble, insoluble) is unknown, which is also important to bioavailability. Furthermore, the size distribution of organic Se as it converts from detritus to humic material is likewise unknown. Size is of gross importance as it determines the target organism, exposure route, and chemistry of Se uptake, ranging from direct sorption or membrane transport for molecular-sizes, to ingestion and digestion for macroscopic particles and debris.

These considerations form the impetus for the proposed project. Evaporation basin systems (alkali ponds) in the southern San Joaquin Valley are a good place to conduct these studies, since the biogeochemistry and ecology are simpler relative to most other systems, and are already under study by the other PIs of the Joint Project.

The specific objectives of this proposal key on newly-deposited sediment (0-3 months old, using a sediment trap), from both *in situ* test enclosures (proposed by the Rejmankova and Fan projects) and existing evaporation basins at TLDD. These represent basins that are both commercially harvested and non-harvested. The objectives are to probe the:

i. Microphysical basis for bioavailability of Se in sediments, by determining gaseous, “mobile” (waterborne), and “immobile” (solid) states of Se;

ii. Chemical basis for bioavailability, by analyzing mobile and immobile states for several known and hypothesized organo-Se structures, such as proteineceous Se;

iii. Physico-chemical basis of bioavailability, by extraction of the organic matter (“humic”) from the immobile Se state, and coarse size fractionation of the mobile Se into particulate-detrital and colloidal-soluble fractions, followed by (ii).

APPROACH

RATIONALE FOR APPROACH AND METHODS: PRIOR RESEARCH

In past UC Salinity/Drainage program research of Fan and Higashi, we have compared the Se concentrations in several evaporation basins at TLDD HEB basins, as well as several locations within these basins. Differences in Se concentration in sediment were found to be a function of the prevailing wind patterns, and irrespective of the inlet/outlet locations of each basin (Figure 2). This, in turn, was apparently due to the prevalence of floating cyanobacterial mats in these basins, a major reminder that biogeochemistry drives the Se, even the physical distribution, in these systems.

Once we established the wind-driven distribution phenomenon, we were able to design sediment-sampling schemes with upwind and downwind locations at each basin, and we also installed sediment traps. Figure 3 shows the entire data set of the sediment and trap contents for 1997-2000. Note that the traps (dots) are generally higher in both OC and Se concentrations than the cores (squares). This is consistent and expected from trap contents, which contain primarily "new" (<3 months old) detrital material. In contrast, cores would be "diluted" with non-detrital as well as older Se-laden material. Thus, comparison of Se forms in cores vs. traps would be important to interpretations of bioavailability.

Thus, Figure 2 (wind-driven deposition) and Figure 3 (positive OC-Se relation) comprise evidence for the probable strong coupling between the organic carbon (OC) and Se biogeochemical cycles, as alluded to back in Fig. 1. At first, this appears to support contentions by some (most notably, Canton and Van Derveer, 1997) that sediment OC can be utilized for ecotoxic risk assessment.

However, Figure 4 shows that caution should be exercised, and that a more mechanistic approach is needed. These data from the TLDD south basins, which have a truncated biogeochemistry due to brine shrimp harvest (see Fig. 1), show very little sediment relationship between OC and Se concentrations. Thus, when the biogeochemistry is disturbed - as will be the case for ecotoxic remediation schemes such as shrimp harvesting - potential indicators such as that in Fig. 3 are no longer reliable. It follows that simple indicators such as OC is not valid for assessing the progress of biogeochemical-based remediation technologies. And, since ecotoxic risk is a function of the biogeochemistry, the latter cannot be readily dismissed in remediation efforts.

To improve the mechanistic understanding of bioavailability, our previously funded research (1999-2001) by the UC Salinity/Drainage program performed more detailed examination of the sediments. We have applied a physical-chemical fractionation approach to survey sediment trap contents. Figure 5 reveals clearly that "sediments" are not just a single compartment; the legend here explains the importance of distinguishing between the "mobile" and "immobile" fractions of the sediment. Recently, we have eschewed the traditional pore water approach in favor of the more bioavailability-oriented fractionation of Fig. 6, that additionally account for the effect of fresher water flux events that occur in these basins. The legend for Figure 6 explains the concept of the bioavailability-based fractionation.

In summary, this project keys on both extant and newly deposited sediment (0-3 months old, using sediment traps), expanding on the scheme in Fig. 6. The trap deployment and analyses will be coordinated with the project of Gao & Dahlgren, which will provide a comparison with Se speciation on flocculant and sediment core depth profiles. One type of sampling activity was at existing evaporation basins at TLDD at appropriate downwind locations. In addition, we examined the sediments within *in situ* test enclosures at TLDD, that were conducted by the Rejmankova and Fan/Meeks projects. The Rejmankova project is conducting *in situ* enclosure experiments that tests three hypotheses regarding algal-nutrient-grazer (e.g. Brine shrimp) relationships, and provide morphological community structure analyses. The Fan/Meeks project will calibrate 16s RNA community typing (e.g. Ferris et al., 1996) and comprehensive pigment analyses (Fan and Higashi, 1998b) with the morphology-based community analyses, to be used as future high-throughput tools for assessment of lower foodchain Se biogeochemistry. Our contribution of conducting sediment traps within these multi-trophic level *in situ* enclosure experiments will enable the joint research project to cover all the major components outlined in Fig. 1.

SITES AND SAMPLING

As stated above, we have continued to focus on TLDD HEB and South evaporation basins because of the extensive algal environmental Se biochemistry work (e.g. Fan and Higashi, 1997; Fan et al., 1997; Fan and Higashi, 1998; Fan et al., 1998a; Fan et al., 1998b, Fan et al., 2002) as well as the existence of brine shrimp harvested and non-harvested basins.

Samples for water-column volatile Se survey were taken from HEB A4 (brine, harvested) and C4 (brine, not harvested), the non-harvested basins of medium salinity HEB A2 and C2, and from S1 (low salinity, not harvested) and the high salinity harvested basins S8, S9, S10. The methods were as described previously (Higashi and Flocchini, 2001)

Water and sediment core samples were taken from the same HEB basins, at upwind and downwind locations identified as NW (northwest) and SE (southeast), respectively. These covered a wide range of salinities and Se water concentrations, as well as both harvested and non-harvested basins. For volatilization, water samples were analyzed on site as reported previously, while those for other analyses were transported on ice and stored in a refrigerator (3°C) until use. Solutions were analyzed for pH, electrical conductivity (EC), total Se concentration and Se speciation (selenate (Se VI), selenite (Se IV), and organic Se (org-Se) as described below.

Sediment cores were taken using 5-cm diameter acrylic tubes. The cores were sealed immediately with a plastic cap and duct-tape and stored on ice. After transferring to the lab, the core samples were frozen until ready for analysis. Organic detrital materials were sectioned from the mineral sediment cores. The mineral cores were then sectioned into the 0-5, 5-10, 10-15 and 15-20 cm segments. Both detrital and mineral sediments were determined for total Se and fractionation. Sub samples of each sample were used for selective sequential extractions, determination of moisture content, total Se by chemical digestion.

In addition, we have sampled within the *in situ* enclosure experiments of the Rejmankova project. Lastly, sediment samplers were deployed at the HEB and South basins. All sediment sampling and analyses were coordinated with the project of Gao/Dahlgren.

RESULTS AND DISCUSSION

SE CONCENTRATION AND SPECIATION IN WATERS

As reported by the project of Gao and Dahlgren, total Se concentrations ranged from 9.4 to 28.5 ppb in the Hacienda basins (Gao and Dahlgren, 2002), while the range was very narrow, from 6-8 ppb in the South basins (see Gao and Dahlgren, this issue). For both basins for both 2001 and 2002, basin waters were dominated by inorganic Se species (about 60% selenate and 40% selenite), but only about 20-40% was SeVI, with the remainder more reduced forms (see Gao and Dahlgren, this issue). Since agricultural drainage water input to TLDD are dominated by selenate (>90%) (Gao et al., 2000; Tanji and Gao, 2001), the results of this study indicate that there is considerable Se reduction occurring in these sequential evaporation basins.

VOLATILE SE ANALYSIS

Analysis of total Se volatiles present in TLDD evaporation basin waters were conducted on cells varying in salinity and brine shrimp harvest/non-harvest. Methods used were described previously (Higashi and Fan, 1999; Higashi and Flocchini, 2001). The Se volatilization measurements were performed twice in each location, in the morning and afternoon. Figure 7 shows the ng of Se purgeable from 800 ml of waters from the 2002 campaign. Also shown is the salinity or conductivity of the water (triangles). Except for S10, the amount of Se volatiles was much higher than the less saline cells of the same series. This general trend has been consistently observed for the last five years at TLDD basins (Higashi and Flocchini, 2001 & 2002).

As with the previous year (Higashi and Flocchini, 2002), we found that the Se volatile content varied with time of day, with no clear or consistent trend, reflecting the complex, multiple mechanisms at work. For example, the volatile Se in water is not simply a physical-chemical phenomenon (e.g. Henry's law relationship) due to temperature differences, since it is of very recent (e.g. seconds to minutes) biogenic origin that is likely dependent on - at the least - photon flux, nutrient status, and algal community composition.

The relationships of volatile Se to harvest practice, as well as brine shrimp and algal Se loads, is discussed here and in the present Fan & Meeks project report. Very briefly stated, Figure 8 shows the volatile Se content of TLDD basin waters in comparison with bioconcentration factor (BCF, on a dry wt basis) of Se by microalgae for the 2002 field campaign. The basin cells with the longest history and/or highest amount of Artemia harvest (i.e. S9 and A4) exhibited the highest content of volatile Se and lowest algal BCF while those that have not been harvested (i.e. S1 and HEB A2) or fertilized but only harvested recently (i.e. S10) showed the opposite trend. The intermittently harvested S8 cell had Se volatilization and algal BCF properties in between the two opposite ends. A similar trend was also observed for the 2001 field measurement. These results suggest that sustained brine shrimp harvest may help enhance Se volatilization while reducing Se bioaccumulation into microalgae.

In addition to in situ field measurement, the project of Fan and Meeks continued to isolate microalgae from the hypersaline TLDD basin cells and we investigated their Se volatilization properties under controlled conditions. Figure 9 illustrates the time course of Se volatilization, Se bioaccumulation in algal biomass, and extent of Se depletion in the culture medium. It is evident that the two microalgae (Synechococcus sp. and a filamentous sp.) exhibited a different property of Se volatilization and bioaccumulation. Although the two strains depleted Se from the medium to a similar extent (Fig. 9, left panel), Synechococcus sp. dissipated Se more by volatilization while the filamentous algae accomplished this more by bioaccumulation into biomass (cf. Fig. 9 left and right panels). Thus, from the standpoint of reducing Se ecotoxic risk, it appears to be more beneficial to encourage the growth of Synechococcus than the filamentous strain.

It is also interesting to note that Synechococcus sp. did not appear to be grazed extensively by brine shrimp, possibly due to their inappropriately small size (see Fan and Meeks, this issue). Thus, it is possible that this species may contribute to the higher extent of Se volatilization observed consistently in TLDD hypersaline cells (Fig. 8, S9, HEB A4), where brine shrimp harvest has been sustained.

SEDIMENT DEPTH PROFILES OF TOTAL SE

Total Se in the detrital materials and sediments was determined, adding the South basins to the Hacienda basins from the previous year. As reported by the project of Gao and Dahlgren, the depth profile of total Se concentration in the sediment showed variations with depth in the South basins, similar to that obtained for the Hacienda basins (Gao and Dahlgren, 2002). Further results and discussion of these profiles are found in the present Gao and Dahlgren project report.

DETERMINATION OF SE CHEMICAL FORMS IN SEDIMENT

As stated above, there are three gross physical states of importance to bioavailability: gaseous, mobile (e.g. waterborne), and immobile (e.g. solid), which are represented in Fig. 6.

Our recent study (Higashi and Fan, 1999) shows that the gaseous compartment in field sediments appears to consist entirely of alkyl selenides, produced by microphytes (e.g., Fan, Higashi, and Lane, 1998; Fan, Lane, and Higashi, 1997) and microbes (e.g., Frankenberger and Karlson, 1994). Since they are very volatile with rapid diffusion from the sediment, they are likely to be only a minor source of bioavailable Se. However, all of the structures observed are very hydrophobic and reactive, which implies high intrinsic bioavailability; if concentrations are sufficiently high, there could be significant direct sorption of Se by organisms. The very same characteristics - extreme volatility and high reactivity - make them unreliable to quantify by conventional approaches such as difference total Se analysis, e.g., of whole vs. dried sediment.

Thus, we removed the gaseous chemical forms directly from sediment under inert conditions. This was accomplished by freeze-drying the frozen whole sediment (see Fig. 6) and trapping the high-vacuum extracted vapor at liquid N_2 temperature. This separates the gaseous Se compounds (Fig. 6) from the continuously frozen sediment matrix in a high vacuum, minimizing decomposition while maximizing extraction of the volatiles. We have successfully used this technique to isolate reactive gaseous components such as dimethylsulfide from organic-rich matrices of wastewater and sediment (Higashi et al., 1992a; Higashi et al., 1992b). The freeze-drying process chemically stabilized the non-volatile portion of the sediment (see Fig. 6) for further processing. Of this portion, the mobile, or extractable, state is the Se that is potentially present in the sediment pore water, which can be in contact or ingested by organisms. This includes particulate matter (e.g. algae, detritus) that has neutral or positive buoyancy. The immobile, or solid state is operationally defined as negative buoyancy, particulate-bound Se that is transported only with substantial water current (generally not present at evaporation basins), and conceivably must be ingested to become bioavailable.

To obtain these states, sequential selective dissolution procedures were adopted from those previously used(Chao and Sanzolone 1989, Lipton, 1991, and Velinsky and Cutter 1990, Higashi and Flocchini, 2001, Gao et al. 2000). Non-volatile Se (Fig. 6) in the sediments was fractionated into water-soluble, ligand-exchangeable, and organic matter-associated fractions using (1:10 soilid:water ratio) of water, 0.1 M K_2HPO_4 (PO_4, pH 8.0), and 0.1 M NaOH, respectively. The unextractable fraction, i.e., the difference between the total and the extracted, was comprised primarily of elemental Se and a very small amount of residual (most -resistant) Se based on previous findings by Gao et al. (2000).

Selenium speciation (Se VI, Se IV, and org-Se) for water and 0.1 M NaOH extracts was determined based on the methods developed by Zhang et al. (1999). Three determinations were performed: direct measurement of Se(IV) using phosphate pH 7 buffer (for NaOH extracts, solution pH was adjusted to pH 7 with HCl prior to the analysis), Se(IV) + org-Se using persulfate to selectively oxidize organic-Se(-II) to Se(IV) using manganese oxide as an indicator for completion of oxidation, and total Se. Total Se concentration in water samples was determined using persulfate digestion followed by reduction to Se (IV) (Cutter, 1982, Yoshimoto, 1992). The Se(IV) in solution was analyzed using HGAAS (hydride generation atomic absorption spectroscopy). Organic-Se(-II)) is defined as the difference between Se(IV)+org-Se and Se(IV) and Se(VI) is obtained by the difference between total Se and Se(IV)+org-Se analysis.

Selenium fractionation results below for detrital materials are also discussed in the present report for the Gao and Dahlgren project. Detrital materials are expected to harbor high levels of organic matter (OM), and hence potentially higher levels of organic Se. Briefly, as shown in Figure 10, there is a substantial amount of OM-associated Se at all locations, as is elemental Se. Also note that 10-30% of the Se is very water-soluble, and probably should not be considered part of the "sediment", a lesson similar to that portrayed in Figure 5. Se in OM-associated fractions could be bioavailable through sediment ingesting. There is no clear trend from comparing the upwind (NW) with downwind (SE) locations.

The OM-associated Se fraction is of particular interest because we assume this phase is related to Se accumulation in the food chain. Thus 0.1 M NaOH extracts (see Fig. 6) containing the organic-Se fraction were speciated to determine the form of Se contained in this fraction. As is seen in Figure 11, the percentage of organic-Se was highest in basins S8 (occasionally harvested) and S9 (heavily harvested). It must be kept in mind that these are percentages; the total deposition of sediment in S9 is far lower than in S8 or S1 (data not shown), so that the total organic-Se production in S9 is the lowest among the South basins.

In previous years we showed a relationship between total organic carbon (TOC) and total Se in sediment (Fig.3). The top panel of Figure 12 shows such data from Sept. 2001 sampling, showing that the trend still holds. The bottom panel of Figure 12 plots the relationship of TOC vs. Se in the OM-associated fraction. It is clear that OM-associated fraction does not contribute to the strength of the correlation in the top panel. Therefore, one of the other fractions, e.g. the adsorbed fraction, probably accounts for the strong relationship with TOC. This is currently under investigation.

We are also probing whether selected organic structures co-occurred with Se. For example, since detrital material is only slightly degraded, considerable proteinaceous material should be present. Even in many humics, which are highly degraded biogenic substances, there is thought to be substantial proteinaceous material still intact (Hayes, 1991 and references cited therein), as we have recently shown (Fan et al., 2000). Recall that protein-bound Se is hypothesized to be very bioavailable, as discussed above. Therefore, it is reasonable to place a priority on detecting proteinaceous Se forms in detritus and humic materials, and in fact the latter possibility has been demonstrated by Rael and Frankenberger (1995). Last year (Higashi and Flocchini, 2002), we showed that the majority peptidic Se constituents in the detrital materials and surface sediments were were found in the adsorbed and OM-associated fractions. This analysis for the most recent sampling campaign is currently underway.

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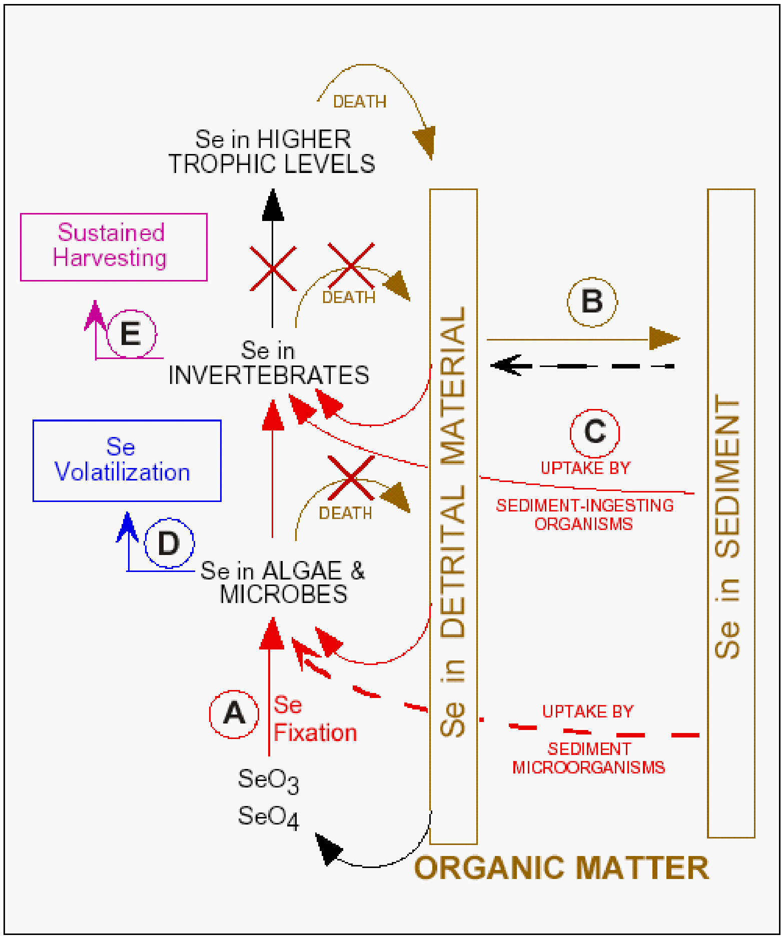


Figure 1. Reducing Se ecotoxic risk in drainage basins by invertebrate harvest and Se volatilization

In this "biogeochemical reflux" scheme, the drainage inorganic Se forms are initially biologically fixed by aquatic algae & microbes **(A)**. The fixed Se does not directly head up the foodchain in the water column, as is often portrayed. Instead, a major fraction enters into organic matter, taking a detour through detritus (recently dead organic matter) and sediment, then re-entering the foodchain at several trophic levels. Over longer periods, part of the detrital material is converted to recalcitrant humic material **(B)**, locking up the Se until sediment-ingesting organisms reintroduce them to the foodchain **(C)**.

Through sustained harvesting **(D)** of water-column invertebrates that consume algae and microbes, the bioavailable Se is removed from water, plus detrital formation resulting from the death of water-column organisms is also blocked. Both types of blockages are shown by the three "X"s. In turn, this would help minimize the sediment-detritus foodchain pathway for Se. In the meanwhile, additional Se can be removed by manipulating the algae/microbe community for optimal Se volatilization **(E)**. This scheme would greatly improve the ecological “safety” margin of operating drainage basins. The economic efficacy of the approach is clear: (a) much of the scheme is water management; (b) costs of encouraging and managing rine shrimp growth is offset by marketing harvested materials.

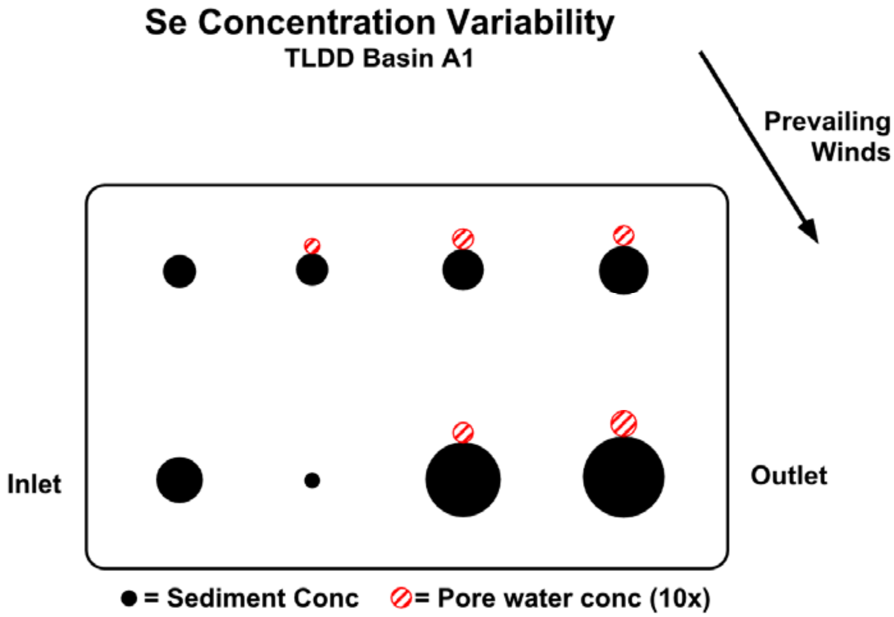


Figure 2. Heterogeniety of Se Distribution in a Basin.

Selenium concentrations in sediments - expressed here by dot size - are known to be highly variable. This diagram illustrates that, at TLDD, the distribution of Se was wind-driven, probably deposition via the floating cyanobacterial mats. This also affects the chemical form and compartment (see Fig. 1). The uncovering of this phenomenon was the basis of our prior surveys of upwind & downwind locations for sediment sampling. (Fan & Higashi, 1997)

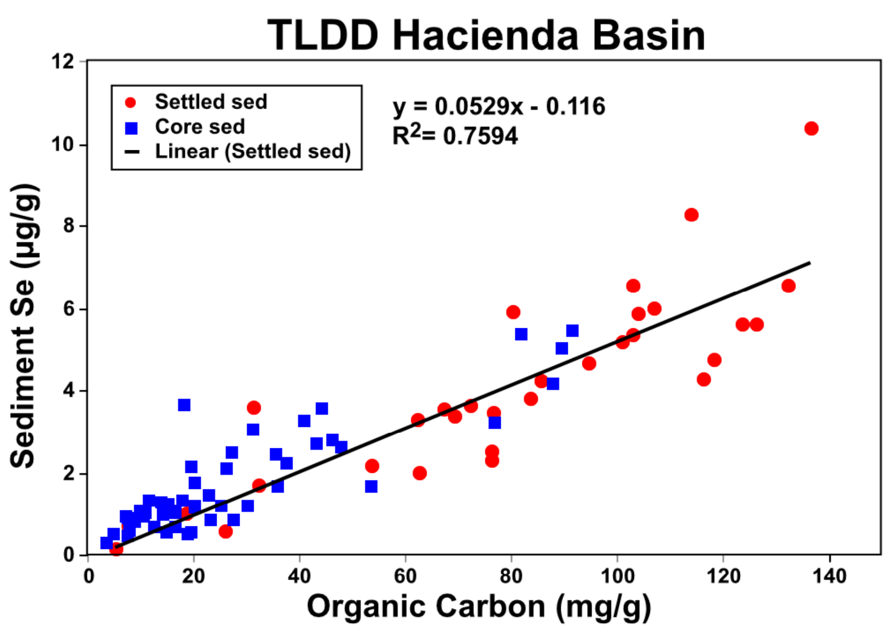


Figure 3. Global Data Set of Sediment Se vs. Organic Carbon (OC) for TLDD Hacienda Basins, 1997-2000 (Fan and Higashi, unpublished data).

Note the wide range of Se concentration and organic carbon among these basins, and sites within each basin. The sediment traps (round) generally contained both more Se and more OC than the cores, clearly indicating that the sources of both Se and OC are in the water column, e.g. algal detritus.

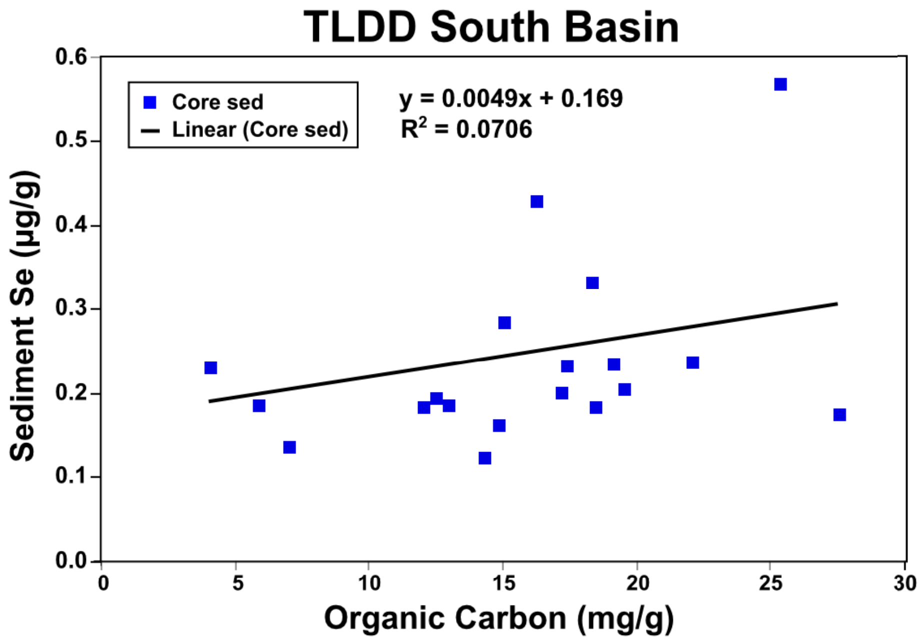


Figure 4. Global Data Set of Sediment Se vs. Organic Carbon (OC) for TLDD South Basins, 1999-2000 (Fan and Higashi, unpublished data).

Some of these basins are being harvested for brine shrimp, thereby truncating the food chain. There is no clear relationship present, in contrast with the non-harvested Hacienda basins.

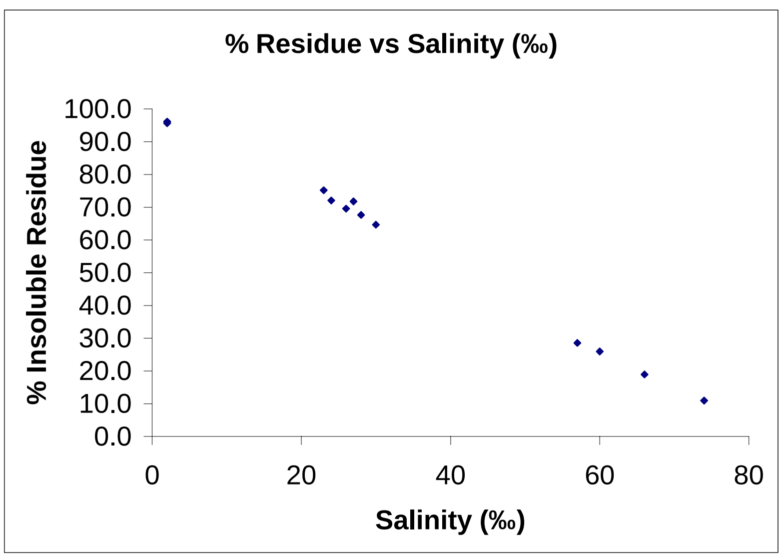
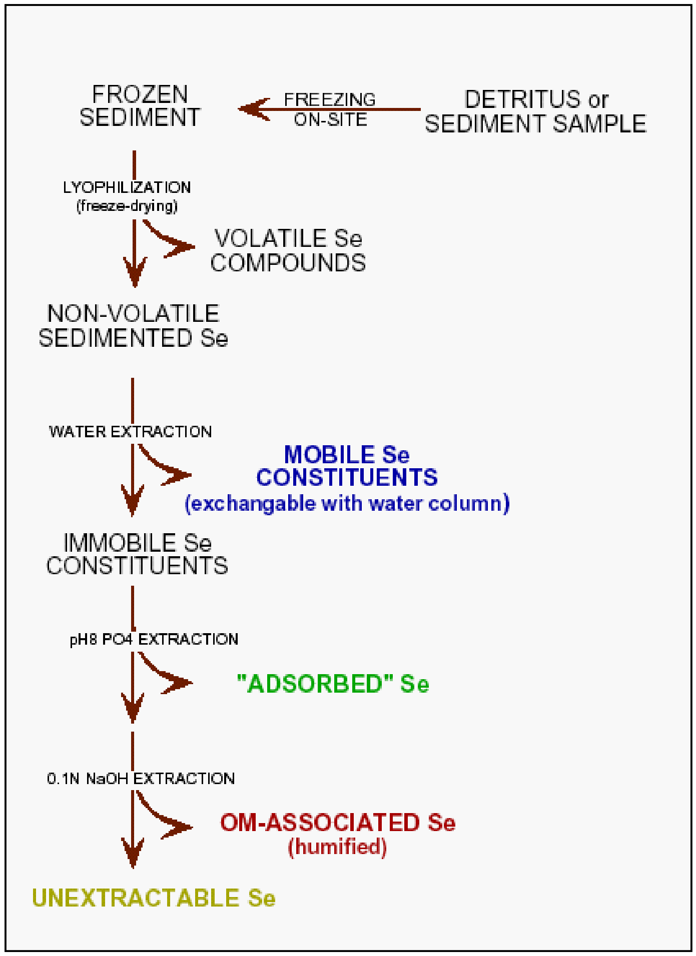


Figure 5. Non-soluble residue of sediment samples as a function of basin salinity.

These data from sediment traps deployed in TLDD basins (Apr –July, 2000) illustrates that "sediment" samples may consist of salts that can dissolve. These are very transient and are <u>not</u> a feature of the fixed sedimented material. Since evaporation basins routinely experience fluxes of fresher water, it is important to distinguish between such soluble ("mobile") and insoluble ("immobile") materials. Specifically, sediment and water-column algae and other organisms will be exposed differently to the mobile and immobile fractions of sediment and any associated Se.

Figure 6. Fractionation Scheme for this study.

In order to understand the chemical basis of bioavailability, the sediment and detritus must be chemically fractionated. All steps are designed to minimize breakdown of potentially labile organic Se constituents.



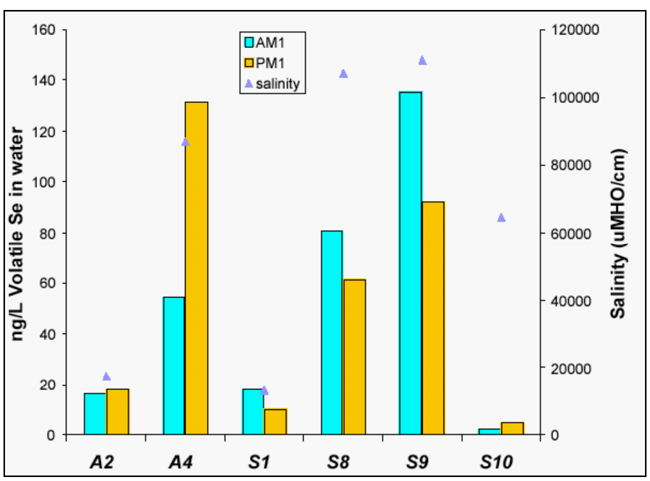


Figure 7. Volatile Se in Hacienda and South Basins - 2002 Campaign.

Basins with the highest levels of volatile Se (S9 and A4) also experienced the largest variation in volatile Se production. Qualitatively, basins of higher salinity had higher volatile Se and diurnal fluctuations, though S10 is an exception. Volatile Se would be considered nonbioavailable and lost from the system. These results are similar to those reported last year on our 2001 measurement campaign.

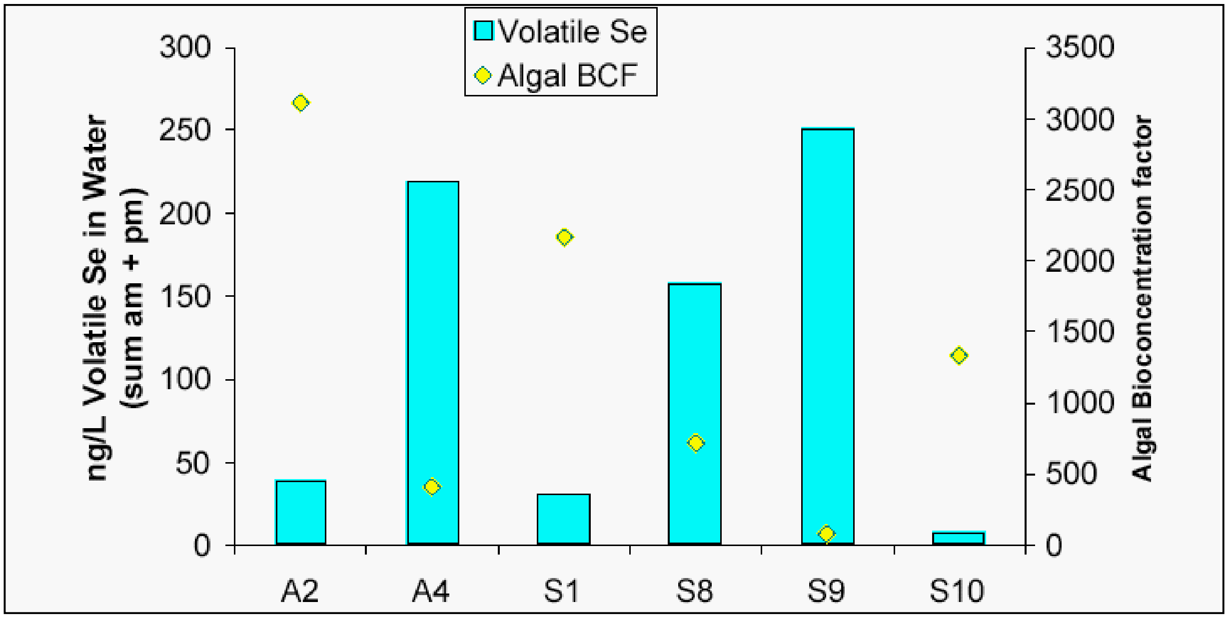


Figure 8. Volatile Se vs. Algal BCF, 2002 Campaign.

Algal communities in basins with the highest production of volatile Se tend to accumulate less selenium. Three types of communities can be discerned in the basins using Se volatilization/accumulation descriptors: High/low which are prevalent in ponds with the longest history of artemia harvest (S9 & A4); Low/high in fertilized but either only recently harvested or unharvested (S10, S1, & A2); and the occassionally-harvested S8 fell inbetween. These patterns for 2002 are similar to the data presented last year for 2001.

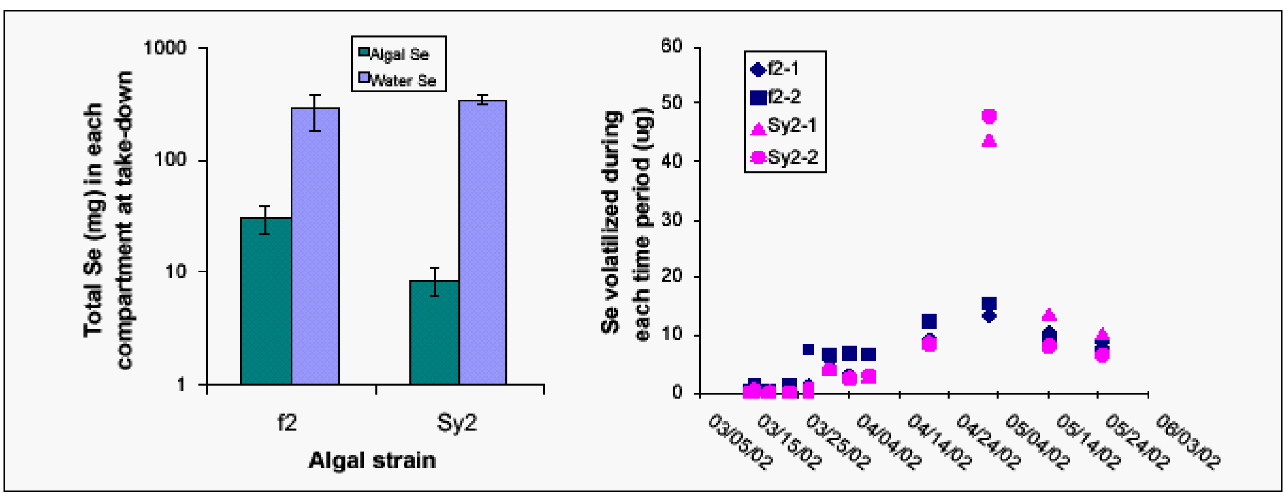


Figure 9. Selenium Bioaccumulation & Volatilization in Isolated Algae.

As shown in the left panel, although both filamentous (f2) and Synechococcus (Sy2) cultures depleted the media of Se to the same extent, the f2 culture accumulated more total Se over the experimental period than did the Sy2 culture (as measured at completion). The “missing” Se appears to have been removed by the Sy2 cultures through volatilization (right panel), which reached a much higher peak in the time course of Sy2 cultures than that of the f2 cultures (24 h collections every 3 days).

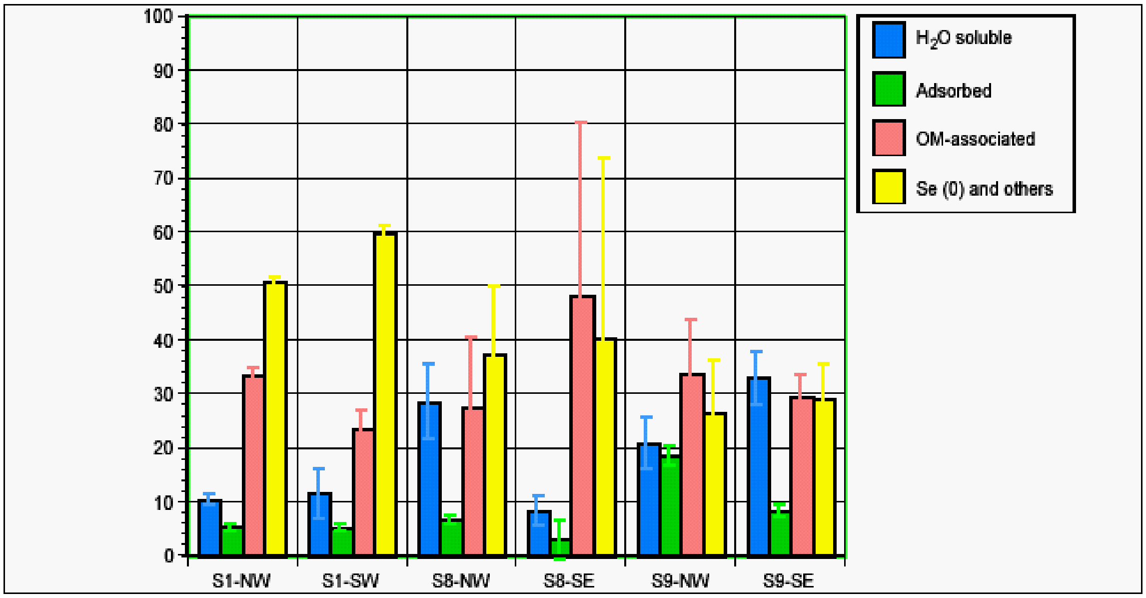


Figure 10. Se Distribution in Detrital Materials of South Basins

Detrital materials are expected to harbor high levels of organic matter (OM), and hence potentially higher levels of organic Se. The OM-associated fractions are more humified material that is strongly associated with sediments. Se in OM-associated fractions could be bioavailable to sedimentingesting organisms (see Fig. 1).

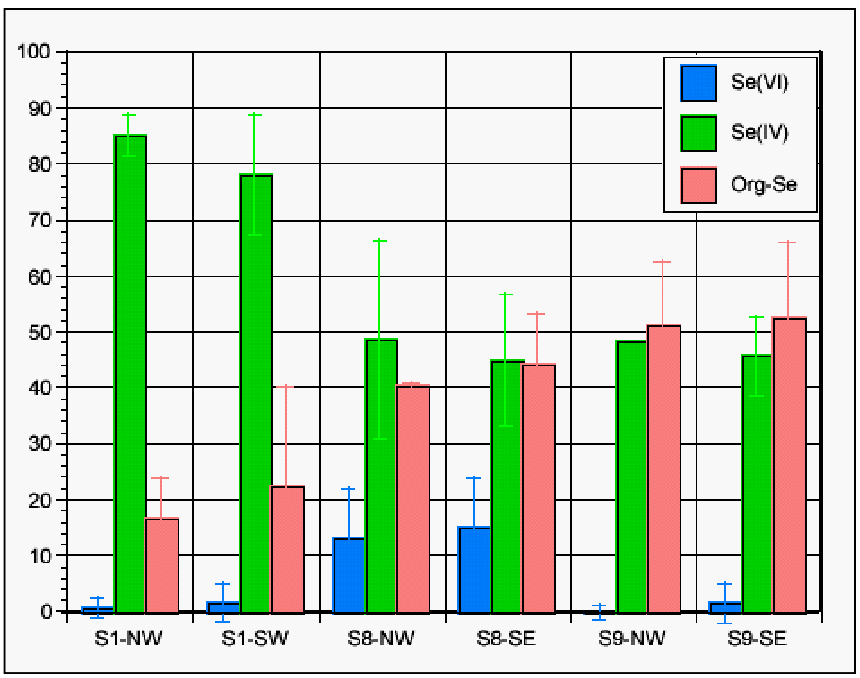


Figure 11. Se Speciation in OM-associated Fractions from Surface Sediments

The OM-associated fraction from the detrital layer (see previous figure) was speciated with regards to Se. As is seen here, the percentage of organic-Se was highest in basins S8 (occasionally harvested) and S9 (heavily harvested). It must be kept in mind that these are percentages; the total deposition of sediment in S9 is far lower than in S8 or S1 (data not shown), so that the total organic-Se production in S9 is the lowest among the South basins.

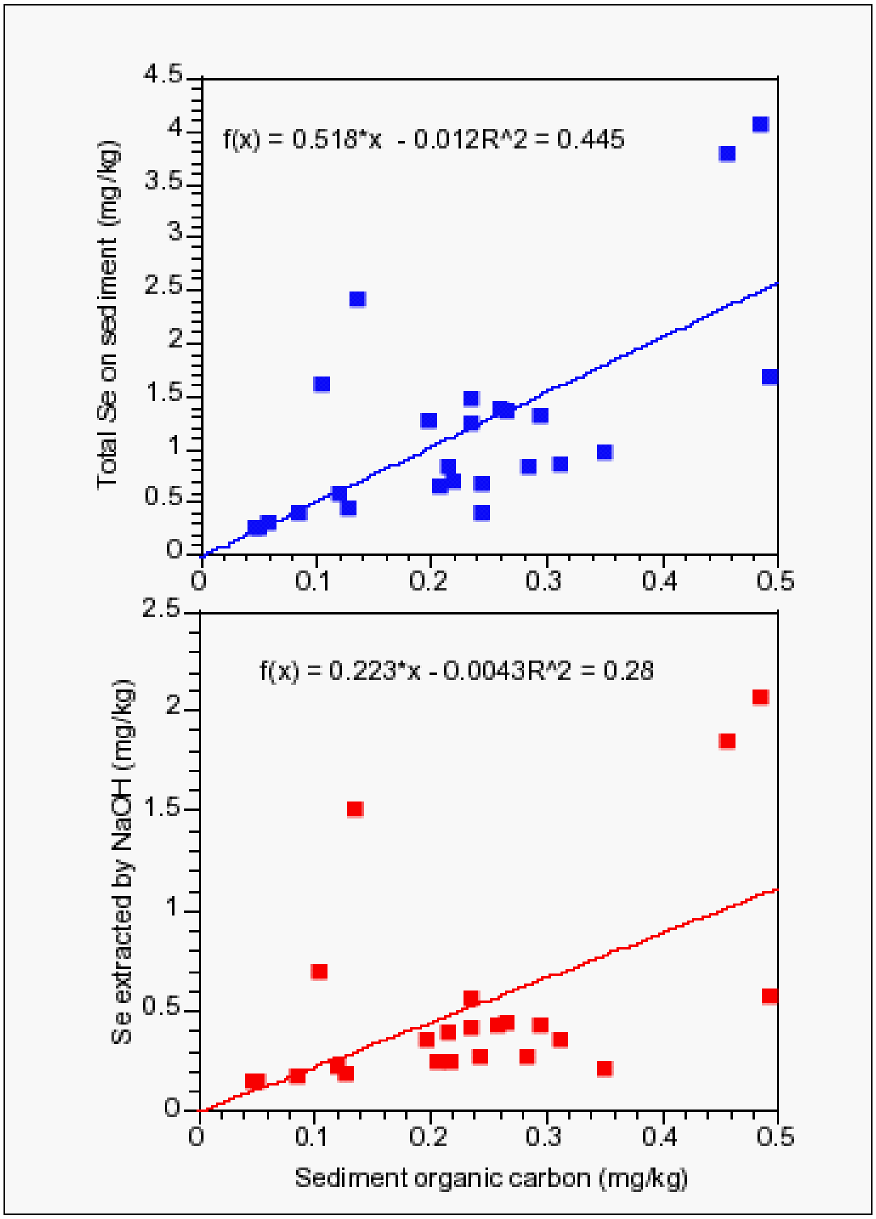


Figure 12. Relationship Between Organic Carbon Content vs. Total Se and Se in the OM-associated Fraction

In previous years we showed a relationship between total organic carbon (TOC) and total Se in sediment. The top panel shows such data from Sept. 2001 sampling, showing that the trend still holds. The bottom panel plots the relationship of TOC vs. Se in the OM-associated fraction. It is clear that this fraction does not contribute to the strength of the correlat i ion in the top panel. Therefore, one of the other fractions, e.g. the adsorbed fraction, must account for the strong relationship with TOC. This analysis is currently underway.

Conceptual Modeling of Salt Management Problems in the Western San Joaquin Valley of California

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ABSTRACT

Sequential reuse of agricultural drainage water recovered in tile lines has been proposed as a strategy for reducing drainage volume in the western San Joaquin Valley of California. The dominant effect of travel time on performance of the sequential reuse operation was demonstrated using a conceptual mathematical model of water and chemical movement through the soil and to the tile drain. Results indicated that system design strategies based on steady-state behavior of the operation would not be appropriate for salt management problems due to the requirements for dilution of concentrated drainage water to levels suitable for irrigation of all but the most salt-tolerant of crops. Moreover, performed two dimensional numerical modeling efforts supported the results of conceptual modeling approach. In both barrier cases, the numerical modeling showed that soil layering should be considered with combination of other factors for evaluating the performance of the system. Especially, higher horizontal/vertical conductivity ratio caused enormous impact on drain concentration in the deep barrier case than the shallow barrier case.

In addition to local scale management options, several numerical studies of the regional hydrogeologic system were conducted for the evaluation of management alternatives to agricultural drains in order to avoid long-term salinization and shallow groundwater. These management alternatives were retiring land, reducing recharge through improvements in irrigation efficiency, and increasing groundwater pumping. Although these alternatives had some potential for reducing drain flow and land preservation, the feasibility of implementing the proposed management alternatives in the regional water budget was potentially limited by water quality and therefore sustaining agricultural productivity. Moreover, to assess the long-term sustainability of the proposed management alternatives, the consequences of applying alternative strategies needs to be investigated at a smaller scale where the water budget components and drainage parameters are represented in more detail.

The conceptual and numerical hydrologic modeling efforts were limited to assessment of the effects on surface or groundwater quality. However, development of a spatially and temporally distributed agroeconomic model using economic and hydrologic submodels might be a promising approach for better evaluation of management strategies. After accomplishing integration of hydrologic processes with economic submodels, the economic, environmental and social impact of management alternatives proposed by San Joaquin Valley Drainage Program (1990) will be quantified to serve as a case study of the ubiquitous salt and pollution issues of irrigated agriculture with potential application to similar regions.

FARM-SCALE APPROACH TO SALT MANAGEMENT PROBLEMS

California's Western San Joaquin Valley is experiencing a variety of irrigation-induced problems such as water scarcity, deteriorating water quality, and salinization of agricultural soils (Letey et al., 1986; San Joaquin Valley Drainage Program, 1990; Letey, 2000). A largely impermeable subsurface layer has caused drainage water to accumulate over many years, resulting in rising water tables and saline seepage into low-lying flood plains (San Joaquin Valley Drainage Program, 1990). As a consequence, agricultural fields in this region are commonly tile drained to keep the root zone aerated and free of salts. Earlier plans for surface detention and export of excess drainage water to the ocean through the San Francisco bay area were canceled because of high selenium levels in evaporation ponds, and concerns that export through the bay would have adverse environmental consequences for the local habitat (Letey, 2000). Since that plan was disrupted, efforts to control salinization have focused more on water reuse or various forms of land management (Letey and Oster, 1993; Belitz and Philips, 1995).

An idea for drainage and salt control that is attracting considerable attention is a water-management program involving reuse of drainage water on successively more salt-tolerant crops, sometimes referred to as sequential reuse (Drainage Reuse Technical Committee, 1999). In this system, high-quality water is used to grow a salt-sensitive crop, and the drainage from this operation is collected by tile lines and subsequently used on a more salt-tolerant crop. This process is continued on progressively more salt-tolerant species until the final residual is collected and sent to evaporation ponds. Since substantial water is evaporated at each stage, the drainage water volume available for irrigation is progressively reduced, while the salt concentration is correspondingly magnified.

Although a demonstration project for sequential reuse operation in the Western San Joaquin Valley was conducted and designed based on the steady-state assumption that the concentration of water collected in the drainage system of each stage was the same as the concentration of water leaving the root zone, the drain water concentrations during the years of operation of this project have differed significantly from their anticipated steady-state values (Cervinka et al., 1999). The results suggested that the transition times to adjust to the new management may be considerable, and that correct design of a sequential reuse system will require knowledge of the response time of the soil to a change in surface management (Letey et al., 2001).

Based on the work of Jury (1975), Jury et al. (2003) developed a conceptual-mathematical model of water and chemical movement through the soil and to the tile drain that is used to represent the sequential reuse system and calculate the buildup of salinity in the soil and drainage water over time.

CONCEPTUAL MODELING EFFORTS

The purpose of the analysis made by Jury et al. (2003) was to construct a simple model of the tile-drain concentrations in a system where agricultural drainage water is sequentially pumped to fields containing increasingly more salt-tolerant crops. Tile drain concentrations are easily modeled as transfer functions, where the input concentration to the field is converted to an output concentration at the drain using the drainage probability density function (pdf) (Jury and Roth, 1990). The solute flux or concentration of water collected at the tile contains contributions from all parts of the field being drained, in proportions which depend on tile line spacing, variations in soil hydraulic properties, and travel time to the drain. Assuming constant travel time through the unsaturated zone, the travel time of salt concentration from point of entry at the water table to the drain was calculated based on the solution of the stream function equation proposed by Kirkham and Powers (1972) through the saturated zone of a tile-drained system restricted by a subsurface layer (Figure 1). Since any water entering between two adjacent streamlines must remain between the lines all the way to the drain, the travel time of any mobile solute in the water is approximately equal to the amount of time required to replace the amount of water in storage between lines. The travel time probability distribution was calculated from the streamline geometry of the system and was subsequently used to model solute concentration arriving at the drain (Jury and Roth, 1990). Applying the model to the sequence of drains, the tile drain concentration from each stage of sequential reuse system was calculated as a function of cumulative drainage and converted to time.

Results of the calculations showed that response times of fields managed in this way are extremely long, so that the drain lines primarily capture resident ground water for decades or more after the operation is started, especially if the barrier is assumed to be at a substantial depth below the surface (Figure 2).

During the sequential reuse of drainage water, each successive field required longer time to reach steady state than previous one and steady state concentrations can be exceeded during transient stage because the high concentration of the resident groundwater can magnify as it passes through the system (Figure 3A). The behavior of the field with deep barrier was qualitatively same as the field with shallow barrier except the time scale for transition to the steady state was expanded considerably because of the significantly greater volume of resident water that must be leached (Figure 3B).

If a requirement that irrigation water must be less than 5 dS m^{-1} is imposed on the system, the concentration of the drainage water coming from stage 1 did not need any dilution according to a steady-state model, but using the transient model substantial dilution was required to reduce the drainage water to levels suitable for irrigation for 20 yr in the shallow barrier case, and indefinitely in the deep barrier case (Figure 4).

Groundwater flow effect

The extremely long travel times calculated in the model that assumes zero groundwater movement greatly exceed the residence time of the groundwater below the field. To see this, we assume a typical groundwater flow rate of 0.3 m/day and a drain spacing of 120 m. Thus the groundwater residence time under the field is 400 days. In contrast, the leaching times of the shallow and deep systems at Red Rock Ranch are about 10 and 250 years for the shallow and deep systems, respectively. The implication of these different time scales is unclear, since the tile lines will continue to intercept the water as it flows by. Obviously, one potential effect is that drain water under a particular field would be able to escape the tile line more easily, and move laterally, while at the same water from the upgradient field would move into the drainage zone. A second factor that might influence the drain behavior is the possibility that lateral groundwater flow is less pronounced in the zone near the water table.

Regardless of the effect, however, it seems very likely that groundwater flow will not speed up the approach to steady state. In the extreme case, the entire groundwater zone would act as a well-mixed reservoir, so that successive stages of a sequential reuse operation would simply be adding groundwater to their fields.

NUMERICAL MODELING EFFORTS

In addition to demonstration of conceptual modeling efforts on the effect of travel time on the management of sequential reuse drainage water, more sophisticated numerical modeling exercises were performed to simulate the water and solute flow through soil and to the tile drains. For this analysis, the HYDRUS-2D model (Simunek et al., 1999) was used to simulate drain concentration as a function of time for the first stage of a reuse operation system overlying a shallow (3-m) and deep (60-m) barrier. To investigate the overall system behavior, the tile drain concentration in a simple homogeneous system was simulated. In this system, continuous irrigation water of constant input concentration of 0.276 kg m^{-3} was added to the first stage from the top of an initially salt free unsaturated zone. There was a constant water table level at the tile drains and the initial concentration of 4.864 kg m^{-3} was uniform throughout groundwater. The tile drain system was established at 2.4 m depth from the soil surface with a drain spacing of 120 m. In addition to simulations with the homogeneous system, we repeated the simulations changing the horizontal/vertical conductivity ratio, doubling and quadrupling the horizontal conductivity component to evaluate the response of the system.

Figure 5 shows the numerical analysis of the response time and equilibration time of the first stage of the reuse operation for the shallow and deep barrier cases. It is obvious that the system showed a similar trend as in the conceptual analysis (Jury et al., 2003) in which the system was inherently transient for both barrier cases, and did not reach steady state in any practical time as well.

Jury et al. (2003) cautioned that soil layering might distort the streamlines before reaching deep into the saturated zone. To illustrate this effect, we changed the horizontal/vertical conductivity ratio in the simulated system (Figure 6). Figure 6 shows the effect of increasing conductivity ratio on response time and equilibration time of the system. This effect was insignificant in the shallow barrier case, but significantly decreased the travel time in the deep barrier simulation. However, travel times still were very long in the latter case.

REGIONAL-SCALE APRROACH TO SALT MANAGEMENT PROBLEMS

The unique geological setting and long term irrigation practices have caused a variety of problems, such as salinization and drainage of agricultural soils in the western San Joaquin Valley. Several management options have been proposed to deal with these problems (San Joaquin Valley Drainage Implementation Program, 1999; Letey, 2000). Especially, high salinity in drainage water requires appropriate management and disposal not only to sustain agricultural productivity but also to protect environment and wildlife habitat (Letey et al., 2003).

In recent years, water table height control has been receiving substantial discussion as a drainage management option. The western San Joaquin Valley is underlain by a low permeability clay barrier that separates the unconfined upper aquifer from the confined lower aquifer. Use of imported drainage water since the 1950's has resulted in steadily rising water tables in the unconfined zone, which are causing water logging in the lower regions of the Valley and salt buildup from evaporation in a number of locations with shallow water tables. Among the management schemes proposed for water table height control are land retirement in regions with poor drainage and reducing tile drainage interception in conjunction with crop extraction from the water table to promote leakage through the lower clay layer and reduce tile drainage volume. In addition to determination of hydrologic characteristics of the San Joaquin Valley, several approaches have been studied to evaluate management alternatives for reducing subsurface drainage and consequently retaining the salts and toxic elements below the soil surface. In the following, we will discuss these management studies conducted in regional scale rather than farm scale.

NUMERICAL MODELING EFFORTS FOR THE MANAGEMENT ALTERNATIVES

Recharge and groundwater pumping

The most cited studies on regional problem of salt management in the San Joaquin Valley are those of Belitz and Phillips (1992; 1995) who conducted a regional hydrogeologic numerical study of management alternatives to agricultural drains in the central part of the San Joaquin Valley in order to avoid long-term salinization of soil and shallow groundwater. The transient, three-dimensional model was used to evaluate the response of the water table to three management alternatives that alter recharge to or discharge from the groundwater flow system. These management alternatives were retiring land, reducing recharge through improvements in irrigation efficiency, and increasing groundwater pumping. The study focused on two major measures of system state which are the number of model cells subject to bare-soil evaporation and the volume of drain flow in the area of on-farm drains. The bare-soil evaporation was of concern due to its potential for salinization of soils and the problem of disposal of poor-quality water was related to drain flow.

The model results showed that land retirement management practices resulted in major elimination of bare-soil evaporation and drain flow only in retired areas and had a minor to no effect on neighboring areas. Although land retirement has some potential for reducing drain flow and for land preservation, it cannot be used as a major strategy for sustaining agricultural productivity at the regional scale. In contrast, modeling efforts indicate that reducing recharge through irrigation efficiency and/or increasing groundwater pumping were much more effective at reducing bare-soil evaporation and drain flow. Since all modeling efforts were made using data averaged or applied over relatively large areas and time periods, the feasibility of implementing the proposed management alternatives in the regional water budget was potentially limited by water quality and land subsidence constraints. Moreover, to assess the long-term sustainability of the proposed alternatives in the hydrologic budget, they suggested investigating consequences of these alternatives at the subarea scale where the water budget components and drainage parameters were more refined.

Similarly, Wu (1997) conducted a comprehensive study on modeling a two-dimensional groundwater flow system in the central part of western San Joaquin Valley using management practices proposed by Belitz and Phillips (1995). The study investigated the effect of aquifer hydraulic properties and management practices on water table height and piezometric head. The results of two-dimensional groundwater modeling agreed with the findings from Belitz and Phillips (1995). Since the hydrologic impacts of agricultural management practices were evaluated based on regional scale groundwater flow systems at the western San Joaquin Valley, Wu (1998) used a two-dimensional transient model in a vertical transect along the direction of the regional flow which includes two on-farm drain lines. Moreover, Wu (1998) chose to use finer model grids for adequate representation of source and sink terms in the governing groundwater flow equations. With these numerical simulations, it was shown that groundwater flow had pronounced horizontal and vertical components and flow was transient at the early stage of drainage operation. In fact, the drains captured a significant portion of lateral flow as suggested in previous one-dimensional, steady state flow studies (Letey and Oster, 1993).

Although source control such as amount of recharge and groundwater management were effective alternatives with respect to management practices, land retirement when implemented to the whole transect was the most effective means for reducing drainage and maintaining the water table. Unfortunately, the U.S. Bureau of Reclamation was not granted sufficient resources to purchase every parcel of land that was offered for practicing land retirement management.

Land retirement strategy

Land retirement is one of the management strategies proposed to reduce the volume of drainage water requiring surface disposal (San Joaquin Valley Drainage Implementation program, 2000). In addition to regional modeling efforts of land retirement strategy, the need for more refined work at the subarea scale was essential for better assessment the long-term consequences of the proposed strategy. Purkey and Wallander (2001a) focused on land retirement strategy for determining the drainage reduction potential in a region where discharge to the San Joaquin River is possible. A portion of the little Panoche Creek Alluvial Fan in the Western San Joaquin Valley with 11.38 km-long transects was selected as a study area which runs across seven fields counting from south to north. Their numerical analysis for different land retirement scenarios over 50 years suggested that the retirement of large contiguous tracts of land produced the greatest drainage reduction benefit. The practical application of contiguous scenario seems unrealistic to preclude the acquisition of any such vast holding. A much realistic approach would be to proceed with land retirement through multiple, disjointed acquisitions of smaller parcels. In this case, simulations revealed that maximum benefit in drainage reduction would be gained with the retirement of downgradient parcels that are already plagued by shallow groundwater and equipped with subsurface tile drains (Purkey and Wallender, 2001a).

Since habitat for terrestrial and wildlife species might be created on retired lands in the region, the suitability of retired lands with respect to surrounding and neighboring field conditions is an issue that needs to be studied. To assist the US Bureau of Reclamation in defining appropriate selection criteria for land retirement, Purkey and Wallender (2001b) conducted a groundwater modeling study examining the effect of neighboring parcels receiving irrigation water on retirement parcels. Moreover, in this study, the potential for sustainability of agricultural production and habitat restoration under land retirement scenario were investigated over short, medium, and long time periods. Using a threshold depth value of unsaturated zone above a shallow water table level as a selection criterion for habitat suitability, the model results revealed that land currently free from a shallow water table and well aerated would provide useful habitat for a long period after it was retired. While the long-term habitat value gained through upgrade retirement was more favorable, the contiguous retirement scenario would have an important benefit with respect to habitat value along the centerline of retired land. In this case, the simulated water table eventually declined after certain initial drainage time period (Purkey and Wallender, 2001b). Because it maintained long term sustainability of the integrated production and habitat system, up gradient land retirement strategy could emerge as the most logical step in long run.

Water balance concept

To understand the dynamics of the basin and the effects of changes in water use, conceptual models can be developed for the flow system of San Joaquin Valley. Specific efforts to gain information about the dynamics of the basin has been made for calculating water balance with their specific components at various spatial scales for groundwater modeling and irrigation efficiency studies (Gronberg and Belitz, 1992). Particularly, accurate determination of water balance components and calculation of water balances are essential to specify the recharge boundary in groundwater modeling efforts. However, the spatial resolution of the data collected determines the accuracy of information on water use to manage the region's drainage problems. Recently, Young and Wallender (2002) calculated an annual water balance for 98 regions with Panoche Water District of the west side of the San Joaquin Valley, California. Using geographic information system and collected data made available by the district, a high spatial resolution annual water balance was calculated for capturing spatial variability of water fluxes throughout entire water district. Since the characterization of spatial variability in deep percolation has often been failed by assumptions made by researchers (Leighton and Fio, 1995), creating maps of spatially varied fluxes can improve groundwater model boundary conditions, model calibration and verification. Moreover, Young and Wallender (2002) showed that results for groundwater recharge which occurs in upslope, undrained areas and groundwater discharge which occurs in down slope, drained areas are in agreement with studies made at a lower spatial resolution (Fio, 1994).

CONCEPTUAL MODELING EFFORTS FOR THE MANAGEMENT ALTERNATIVES

While numerical simulations of regional flow in the subsurface have shed some light on possible ways of managing this problem, some fundamental conceptual problems remain. The high water table is a consequence of the agricultural drainage water, but the water table is also a driving force for seepage through the clay layer into the confined aquifer, and the slope of the water table is a driving force for moving water laterally through the unconfined aquifer out of Western Valley Basin. Drainage extraction by tile lines decreases the amount of seepage moving to the water table, but creates a disposal problem at the surface for the drainage water. Partial land retirement in the salt-affected areas at lower elevation will reduce water requirements and subsurface flow to the water table, but may alter hydraulic gradients and attract flow from higher points in the system. Increasing or decreasing drainage below the farms will change the water table position, but it is not clear by how much, since lateral flow and leakage through the clay layer will also change. To explore the possibility of reducing the need for drainage and salt accumulation, Letey and Oster (1993) used a conceptual steady state approach to estimate quantities of controlling practices in Westland water district and developed several strategies to reduce subsurface drainage outflow entailing adjustments in irrigation, water pumping, and drainage practices. Their results suggested that several approaches can be applied to reduce subsurface drainage outflow: (1) To manage the water table level within the root zone to increase its use to meet crop evapotranspiration (ET); (2) To shut drainage lines for increasing leakage though Corcoran Clay barrier; (3) To apply irrigation water in quantities less than crop ET; (4) To increase groundwater pumping.

CONCLUSIONS

In the studies summarized above, the conceptual or numerical hydrologic modeling efforts were limited to either surface water or groundwater related processes. To a certain extent, conclusions drawn were a function of the constraints of the modeling exercise. However, there was general agreement about the merits of systematic land retirement for salt management. More recent studies have shown that some of the consequences (high cost, habitat effects) of the different schemes may be significant factors in decision-making. For this reason, studies combining hydrologic modeling with cost-benefit analysis and environmental analysis should be the most valuable to policy makers.

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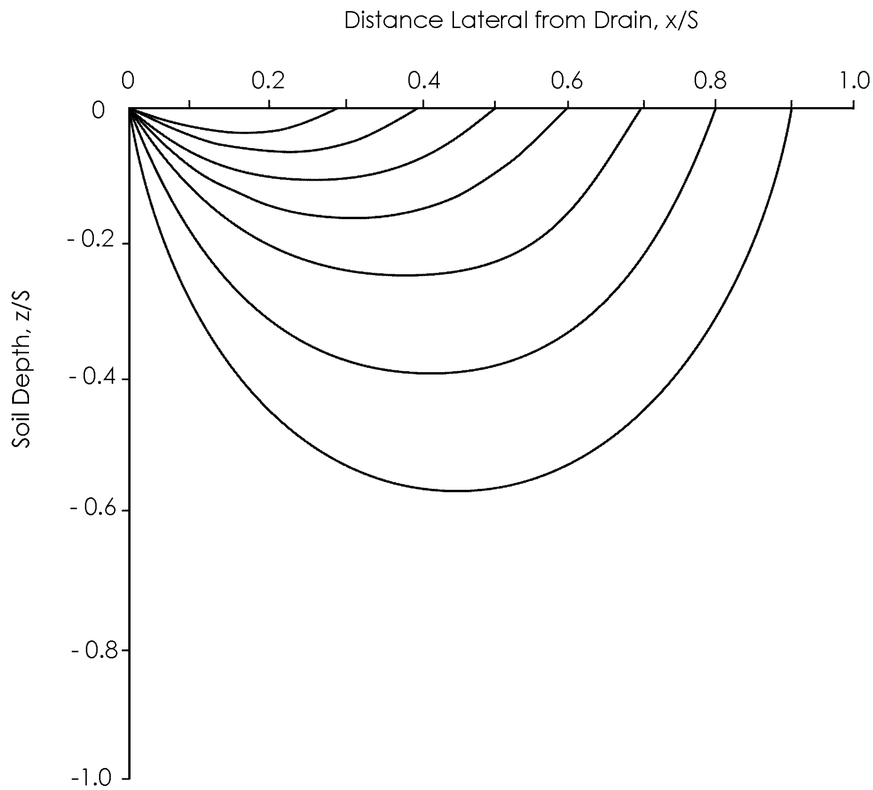

Figure 1. Water flow streamlines through the saturated zone of a tile drain where tile half-spacing equals to depth from tile to barrier.

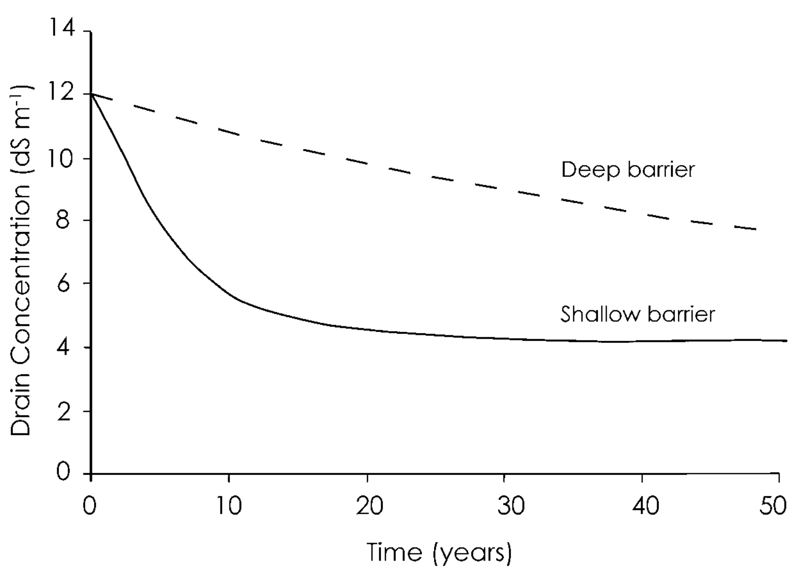

Figure 2. Response time and equilibration time of first stage of a reuse operation system overlying a shallow (3-m) and deep (60-m) barrier, using parameters from the Red Rock Ranch of Cervinka et al., (1999).

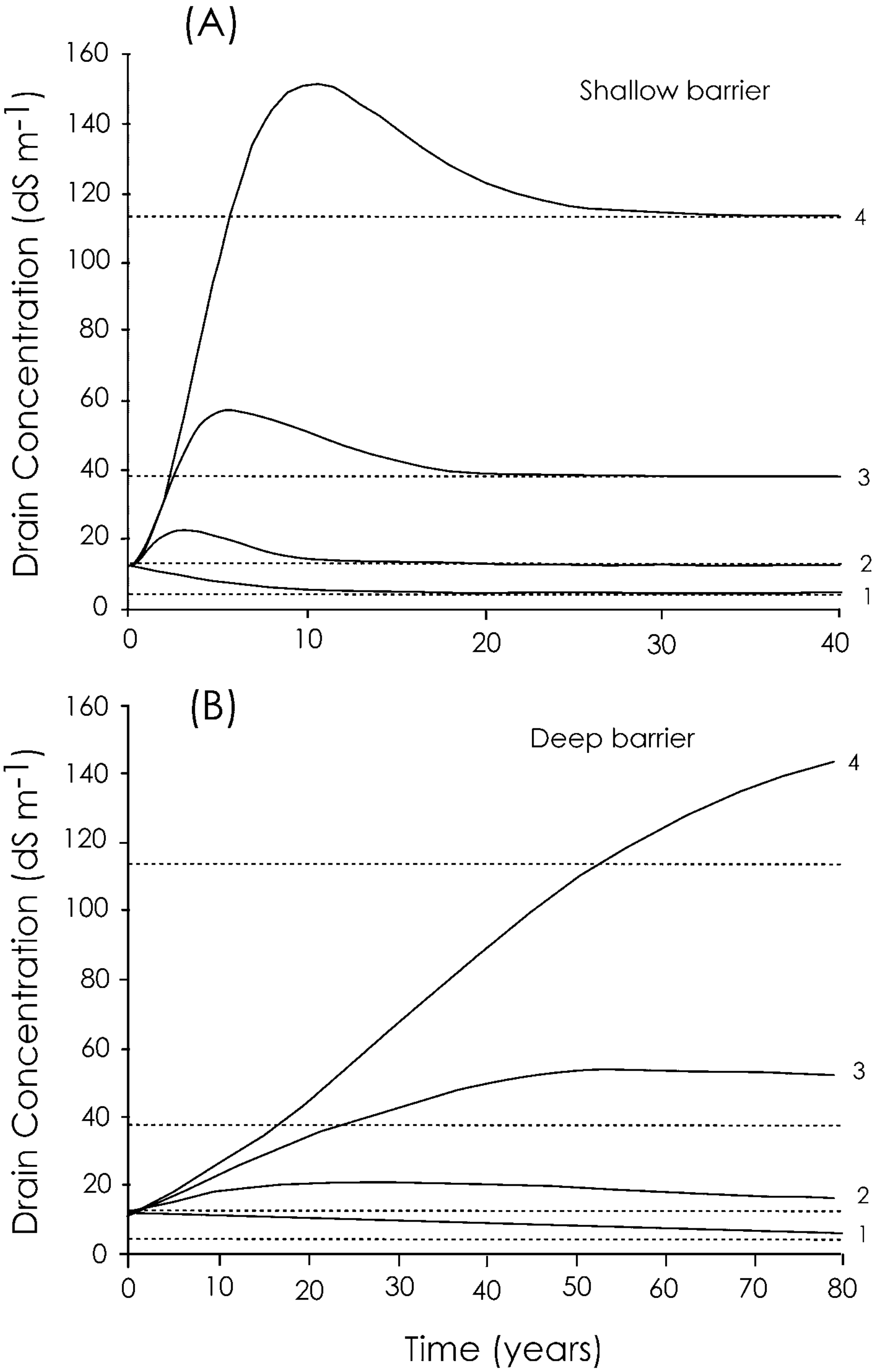

Figure 3. Drain concentration from all four stages of reuse operation overlying (A) a shallow (3-m) barrier, (B) a deep (60-m) barrier, using parameters from the Red Rock Ranch of Cervinka et al., (1999). Dashed lines represent steady state concentrations.

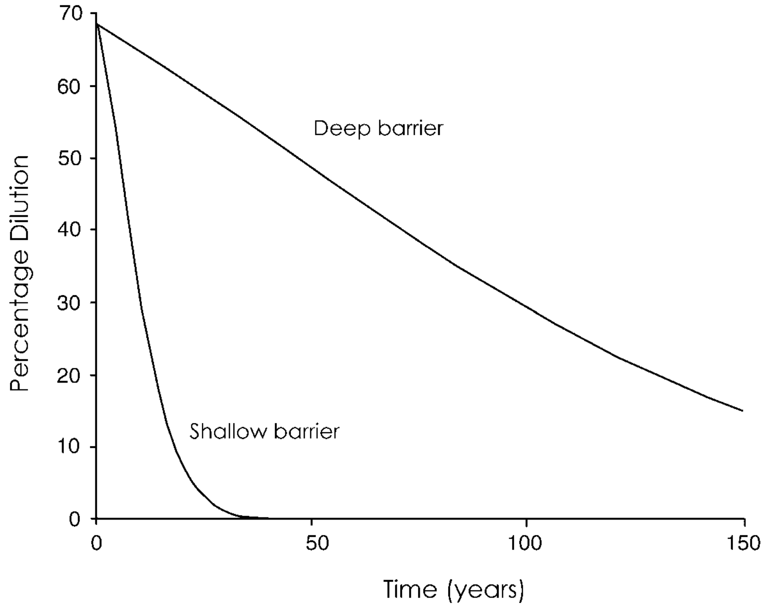

Figure 4. Percentage dilution required to maintain the irrigation water of stage 2 of a reuse operation overlying a shallow (3-m) and deep (60-m) barrier at 5 dS m^{-1} or less, using parameters from the Red Rock Ranch of Cervinka et al., (1999). The predicted dilution using the steady state model is zero.

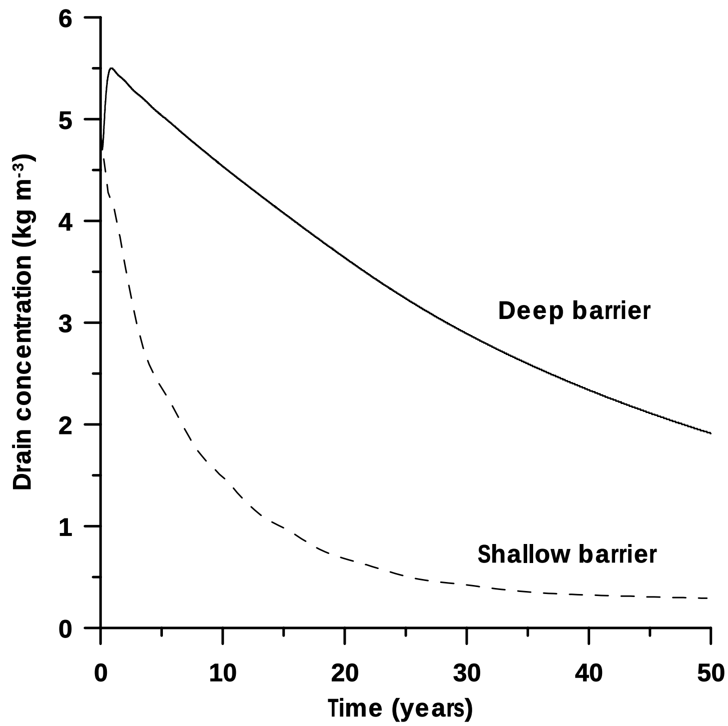

Figure 5. Numerical analyses of response time and equilibration time of first stage of a reuse operation system overlying a shallow (3-m) and deep (60-m) barrier, using parameters from the Red Rock Ranch of Cervinka et al., (1999).

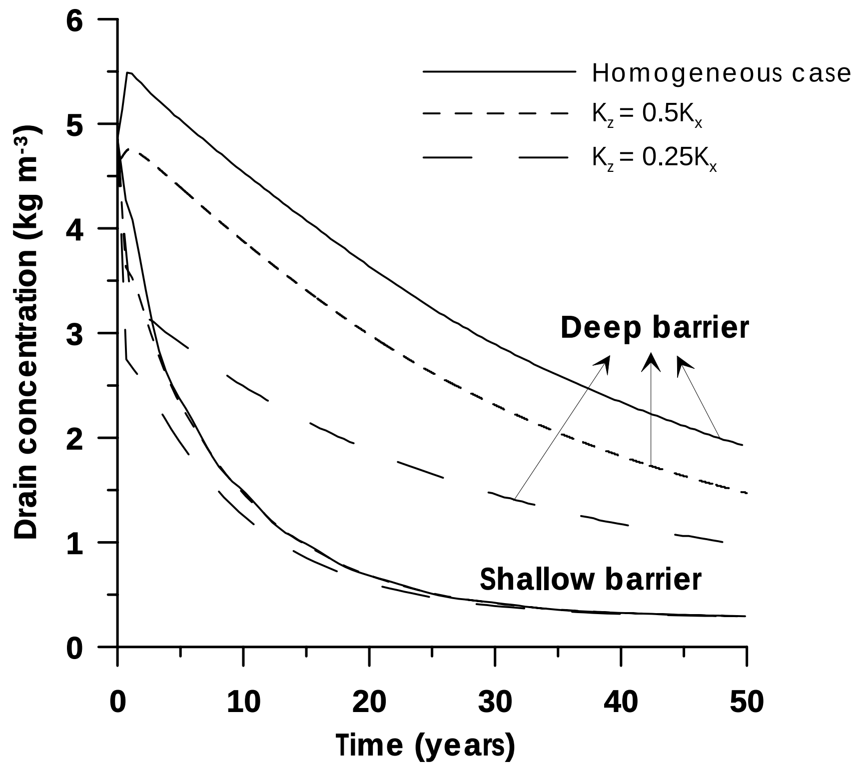

Figure 6. Numerical analyses of response and equilibration time of first stage of a reuse operation system overlying a shallow (3-m) and deep (60-m) barrier with different horizontal/vertical conductivity ratio.

Contrasting Irrigation Application Methods for Drainage Reduction and Soil Salinity Management

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ABSTRACT

Irrigation studies were conducted that compared hand-move sprinkler lines with conventional furrow irrigation methods on ground having historically high surface salinity levels and shallow groundwater levels. The objective in the first study year (2001) was to evaluate the potential of alternative sprinkler irrigation practices that could give rise to improved soil salinity levels and elevate the likelihood that improved plant stands and plant growth would lead to improved crop performance and yield in cotton. We evaluated a single large block of irrigated cotton in western Fresno County using high quality canal water run through hand-move sprinklers and contrasted this with conventional furrow irrigation. First year results found clear improvements in plant stands and crop yield improvements following a single season use of sprinklers with high quality water compared to the conventional surface irrigation system program.

During the second year of evaluation, our project goal shifted to develop more specific and comprehensive information on the causes of poor plant performance and yield inhibition resulting from high soil salinity levels. Year two of the study was conducted on an adjacent field having an in-season shallow water table depth that ranged from 0.5 to 1.5 m below the surface and contained salt affected surface soils that impeded cotton performance in many areas. Cotton crop vigor was more closely tied to surface salt concentrations in the top 30 cm although vigorous growth sites had higher soil salts in the 30 to 60 cm depth. Elevated crop performance from unique cotton varieties tested in a replicated manner found highly significant differences in yield at this study site. The differences observed primarily resulted from improved performance of plants that produced a stand and was not a function of improved germination and plant stand.

Brief estimates of yield reduction associated with stand reduction in the field could underestimate the magnitude of the problem at this site. We found that approximately 45 percent of the field stand did not establish as a result of high surface salinity and this was the most important factor in limiting yield. The Pima variety S7 was the most sensitive variety with a stand reduction of 64 percent. In order to improve yields at this site, any reclamation method must address the problem of high salt levels in the top 30 to 45 cm thereby ensuring a high seedling survival rate. This could be accomplished with sprinkler irrigation practices, but must also consider methods to keep in-season water tables levels below 1.0 m year-round. Large reductions in salinity for the soil surface can not only translate into improved plant stands during a very crucial period, but can also result in much higher yields as salt tolerance increases following the seedling stages. Once established, varieties such as HA195 can be very economical due to their ability to better tolerate higher levels of soil salts.

INTRODUCTION

Drainage problems continue to afflict large areas of the most productive agricultural region worldwide resulting in billions of dollars worth of lost income annually. The lack of adequate drainage in this irrigated agricultural region has resulted in the accumulation of soil salts in or near the soil surface with few opportunities for soil amelioration. This situation produces management challenges to the producer that is trying to maintain profitability in a few select crops that demonstrate characteristics of salt tolerance or salt avoidance. Crops such as cotton and sugar beets are grown in large acreage in the area and are good examples of crops exhibiting salt tolerance, while crops such as lettuce and onions can fit in these systems and avoid the salinity buildup using salt avoidance mechanisms. The shallow root systems of lettuce and onions for instance, can be exploited and if surface salinity levels are maintained at low levels, high subsurface salinity may exist without detracting from yield.

Salt tolerant crops can also experience many of the same problems that salt sensitive crop do when salinity levels rise to relatively high levels. One of the first indicators that surface salinity problems are manifesting is in the erratic emergence of seedlings planted. The germinating seed and the seedling stage are the most sensitive time of a plant's development, and it is often this stage that struggles most as surface soil salt levels rise. Many times it can occur that when surface salinity levels can be managed, the yield reductions associated with soil salts can be minimized. It has been suggested, but seldom practiced, to improve the management of fields having poor drainage by modifying the timing, volume and approach of applied water during the season to improve the distribution of the large salt load present in or near the surface soil. Though the total salt load might change little, it is often considered helpful to reduce the incidence of poor early germination performance.

To accomplish this task we created a project that would help develop information related to the impact of in-season sprinkler irrigation on the distribution of soil surface salts and compare these patterns with those of the conventional practice of furrow irrigation in large-scale agricultural fields having poor drainage. The approach considered in this project was to make soil and plant observations in the field prior to and following the changes in irrigation practices that would ultimately lead to improved short and long term practices when compared with the existing irrigation systems management approach.

METHODS

The field site selected in western Fresno County historically contained significant drainage problems similar to many locations in the region. The 34-acre production field we evaluated had a shallow water table level that varies from 0.8 to 2.0 meters depending on the time of season and location in the field. The shallowest depth to groundwater typically occurs during the early Summer period from areas near the north end of the field which corresponded with the fields lowest elevation point and where highest opportunity time occurs as standing water is present for 48 or more hours following the application period. Irrigation water in this field runs south to north and is located ½ mile SE of the Halophyte block portion of the study on integrated farm drainage management at the Red Rock Ranch, Five Points, CA. Traditional field management practices were used to prepare the field following the previous years crop with Winter pre-irrigation activities preceding cotton planting applied 6 inches of water using furrow irrigation coming from gated pipe.

Following Spring bed preparation practices in the week prior to planting, Extra-long staple cotton of the Pima Type, *Gossypium barbadense*, was planted on April 4th, 2002 under favorable weather conditions. The field was planted using Individual plant lines spaced 28 inches apart on a raised bed having 60-inch center spacing. Cotton varieties were planted in 12-row plots running the length of the field in a randomized complete block design having four replicates. The varieties S7, PSC-57, PHY-76, DP-HTO, DP-340, DP-744, and HA-195 were planted at approximately 60,000 seeds per acre. Once the plants emerged and growth had reached early square development (25 to 35 cm tall) 6 monitoring sites were established in the field representing low, medium and high vigor growth areas of the field at two locations for each growth category.

Soil, water and Plant samples were collected at each of the six sites to assess soil salinity, water table depth, and the effect of these factors on seedling survivability, stand establishment and crop performance. The GPS coordinates of the six sample sites are reported in table 1. Slotted 2-inch PVC piezometers were installed in early July at each of the six locations to a depth of 2 m and monitored every 7 to 10 days through mid-October to establish shallow water table depth. Irrigation water quality was sampled at 2 irrigation events during the season and was found to range from 360 ppm to 450 ppm TDS, quality typically delivered by the CVP project. In-season Irrigation was initiated in late May and concluded in the first week of September. A composite sample of 5 to 7 soil cores was collected at each of the six sites from the surface, to a depth of 61 cm. Individual samples were collected from the bed center, 38 cm, and 76 cm from the bed center at the 0 to 15 cm, 15 to 30 cm, 30 to 45 cm, and 45 to 61 cm depth. Soil samples were processed at the ANR Analytical Lab with standard salinity assessment tests conducted including salinity (EC), boron, SAR and saturation percentage.

Using handheld GPS technology to create field reference points, we conducted a mapping activity that established the location and severity of the plant stand reductions in the field allowing us to estimate stand reduction impacts on yield. The field was walked on July 1 through July 3 and visual estimates were made at 7-m intervals on each cotton row. Because of plant compensation effects that result from the increased light nutrient and water environment, plant skips were recorded only for skips of 1-m or greater. Plant growth and development data were collected on July 15, August 1 and a final plant map on September 27, 2002 to establish fruiting patterns at the six sample areas allowing us to evaluate the key boll set period for each of the sample locations.

The entire field was harvested with a spindle picker equipped with a yield monitor that continuously measured yield on two of the four rows harvested. A time-averaged value of yield accompanied a GPS location value. The yield monitor was calibrated with weigh wagons equipped with pressure transducers to verify the accuracy of strips harvested at 25 locations throughout the field. Using the seedcotton weights of individually harvested strips to set yield coefficients used by the monitor that uses GPS technology to distinguish location and process the yield map image. Cotton was sub-sampled to establishes the quality of the cotton fiber as well and determine if irrigation practices had any influence on the quality of cotton produced. A 3 kg sub-sample was collected and ginned for each variety on all plots to determine the seedcotton turnout and percent lint allowing an accurate determination of crop yield throughout the field.

RESULTS

SHALLOW WATER TABLE FLUCTUATION

Our approach to identify general spatial and temporal water table relationships in the study field was successful and allowed us to make inferences on key soil quality and crop growth issues. We observed water table fluctuations characteristic of the region's general pattern, noting a gradual rise in level during the post-plant irrigation season. Irrigation events earlier in the season tend to be less efficient as a result of low crop evapotranspiration (ET) and higher soil infiltration rates that result in excessive local drainage below the root zone. The study field water table levels, Figure 1, show a general level rise in mid-July through mid-August following in-field irrigation events. A significant drop in the shallow water table level was first seen in late August coinciding with the period of high ET, general reductions in soil infiltration rates and reduced percolation below the root zone. Upon termination of water in early September, water table levels receded to their lowest levels in the monitoring period near the end of the cropping season.

Water table levels were highest along the western edge of the study field, sites 1 and 4, but also receded late in the season to levels similar to those at the 4 other sample sites. Water table levels were measured as high as 40 to 50 cm of the soil surface on two of the six sites. Both sites 1 and 4 were not only the highest during most of the monitoring period, it was the site slowest to draw down late in the season. This indicates either an adjacent source of water from the up-gradient area was allowing high lateral movements that forestalled drainage, or a low hydraulic transmission rate down gradient of the area was resulting in the maintenance of the higher water table level.

Whatever the cause, it appears clear that minimizing the source of drainage from mid-July through late August is critical in reducing salinization of the surface soils should future surface reclamation efforts be employed.

SOIL SALINITY EVALUATION

Observations of soil salinity were conducted in three primary areas of the field including low, medium and high crop vigor zones. The evaluation of salt concentration with depth and location on the bed can be used to aid in identifying root causes of any yield declines that might be observed in a field having high surface salinity and also help in the diagnosis and ameliorative capabilities of any potential reclamation activities. Soil samples processed showed a trend for high salinity levels close to the soil surface with a general decrease in salinity with depth, figure 2. This type of salinity profile is characteristic of soils having a general net movement of water and salts from the subsurface to the surface. This often occurs where water table levels come within 1 to 1.5 m of the soil surface and where deep leaching of salts is not feasible during pre-irrigation events. Soils samples taken from the high vigor areas of the field tended to have lower total salinity in the top 30 to 45 cm, however that this was not particularly true for the subsurface. The highest subsurface salinity levels were found in the high vigor areas but at sub-threshold levels.

Soil boron levels in the study generally paralleled the salinity concentration in the collected samples. Soil boron levels in the 0 to 45 cm depths ranged from 1 to 3 ppm with the 45 to 61 cm samples all less than 1 ppm. The surface samples collected in the 0 to 15cm depth averaged 3.2 ppm, indicating soil boron in some field locations could be considerably higher. These moderately high boron levels could play some role in discouraging young seedling emergence at this site though B levels in excess of 6 ppm have been observed in cotton fields with satisfactory plant stands resulting.

Interpretation of soil salinity levels using two-dimensional contour diagrams can also help in understanding the differences in soil properties at each of the three contrasting plant vigor locations, figure 3. Soil EC measured among the three composite samples collected showed a soil surface with higher salt concentrations near the soil surface. Intuitively, it could be expected that plants having the poorest growth would have the highest soil salinity values. While this was true for the soil surface, soil salinity in the 45 to 61 cm depth was higher in the high vigor when compared to low- or medium vigor growth areas. This indicates a surface leaching regime that is effective at reducing the impacts of high soil salt levels that suppress crop growth. Although soil EC values of 8.0 to 10.0 dS/m were present in the high vigor samples, soil EC in the 0 to 45 cm zone appeared to be the more important factor controlling crop vigor. Low and medium vigor areas of the field had significant zones of surface soil with salt concentrations ranging from 8 to 14 dS/m. Similar to 2001 season data (Munk, 2002), we found that in all three plant vigor conditions, salt concentrations increased toward the center of the bed and the planting strategy which used bed shoulders for the seed lines is an effective strategy for plant avoidance of critical salt levels.

Relationships between the various soil parameters were analyzed and some definite trends identified, figures 4-5. The strongest relationship was observed between soil EC and Boron. Soil boron levels were highest in high EC zones while SAR of the soil extract was also found to have a strong positive correlation with the soil EC. These relationships indicate that with a doubling of soil EC, there is a six-fold increase in the concentration of boron present. However due to the issue of ion pairing and the non-linear nature of soil EC and high constituent ion concentrations, a more in-depth analysis would be required before a more exact statement can be made of the relative leaching of ion species at this site. However, we can generally say that salts other than boron have been transported (leached) out of these surface soils, while boron has accumulated. Though the data trends are evident, the least correlated variables analyzed were the soil EC and SAR with soil depth, figures 6 and 7. This indicates that from the collected samples, concentrations of boron and soil sodicity can vary considerably with depth, though some positive correlation remains.

PLANT STAND REDUCTIONS

Monitoring the plant stand present was basic to understanding the distribution and intensity of soluble salts in the soil surface. Furthermore it can be a tool in distinguishing the reasons for field performance limitations and therefore the proper management steps to take in improving yield and farm profitability. Because seed quality is thought to be generally high within each cotton variety, carefully examining seedling survival in stressed soil environments allows us to evaluate cotton genetic sensitivity and better establish undesirable soil profile distribution patterns. As with the 2001 season observations there were numerous areas in which the plants germinated but did not emerge through the soil crust or areas of unsuccessful stands that emerged but due to their weakened state, experienced high losses to seedling diseases such as pythium and Rhizoctonia.

Whether directly or indirectly, plant stands in most areas of the field experienced significant yield reductions as a result of reduced plant stands. The most highly impacted areas of the field were in the north or tail end of the field, however the western edge of the field also experiences significant stand problems. Pima cotton variety did appear to have a significant influence on plant emergence and subsequent plant stand and can help explain some of the linear patterns observed in the plant stand map, figure 8.

PLANT GROWTH AND CANOPY DEVELOPMENT

In-season plant monitoring described plant vigor, fruiting potential and maturity both in relative and absolute terms, table 2. The vigor index or height-to-node ratio index (HNRI) developed, allows us to compare long term SJ2 data with the plants at each of the sample sites. The HNRI of each of the sample sites was considerably below expectations of Pima cotton for this period and typically ranges from 0.75 to 0.9 indicating early season factors limiting vigorous growth were present in many parts of the field. As might be expected, the most vigorous sites were those sites identified in early June as being most vigorous, though by the July 15th sample date, there was some site variation. The most vigorous sites also expressed increases in fruiting node number, indicating the plant's ability to produce more fruit earlier in the season. This trend for higher fruiting branch numbers at sites 3 and 6 continued later in the season, table 3**,** with 2 to 5 additional fruiting branches produced compared to the low and medium vigor sites. Plants at both in-season monitoring dates had high bottom and top retention indicating that the plant was not significantly influenced by insect pests.

End-of-season plant monitoring information detailed the final vigor and fruiting relationships at each of the six sites. Late-season average plant heights ranged from 56 to 85 cm at the sites with the sites having the highest and lowest height-to-node ratio expressing the lowest yield. These two sites were also found to have the lowest first position (FP1) fruit retention levels in the plant zone responsible for yield.

Plant canopy development was not only evaluated using plant monitoring as described above, but also using a technique that would rapidly estimate percent canopy cover. The Dycam camera that samples in the near infra-red spectral region captured site images of 4.8 square meters. As generally seen with the plant monitoring data, the sites most consistently showing increased plant vigor, demonstrated consistently higher canopy cover throughout the season, figure 9. There was a relatively good linear relationship between canopy cover and plant height with plants greater that 45 cm, figure 10.

YIELD RELATIONSHIPS

The patterns of yield harvested in salt affected fields having a shallow saline water table can be related to toxic ion concentration buildup or to total salt buildup in soils affecting key processes such as water uptake and cell expansion. With the recent introduction of yield monitors in cotton, location specific yield estimates can be used to obtain a large and varied yield sample that can be used to identify specific causes for poor crop performance in the field, figure 11. Cotton planted in soils with elevated salinity can produce either yield reductions as a consequence of plant stand reductions or caused later in the season by inadequate access to carbohydrates as the plant expends energy to maintain itself. Identifying which factor is most important to yield and profitability, can lead us to more specific mitigation approaches that are effective and economical. The yield map produced at the site shows patterns very similar to the patterns expressed in the plant skip data, though some patterns do not appear to relate well to plant stand.

Pima cotton variety was a significant variable in the determination of factors influencing yield at this site, table 4. Other 2002 variety trials conducted in a similar manner and scale, found yield differences at non-saline soil sites were typically less than 12 percent from highest to lowest yielding variety. It is highly significant to find cotton variety choice plays an even more important role than in non-saline sites. HA195, a vigorously growing inter-specific hybrid cotton had a 735 lb. yield advantage when compared to the industry standard S7. While large plant stand differences were observed between S7 and all other varieties, HA195 was equally suscept-ible to stand emergence problems, figure 12.

CONCLUDING REMARKS

Growers in areas impacted by shallow water tables and high surface salts are faced with extremely difficult decisions on land that is marginally profitable. Crop management methods and agronomic tools are needed to keep the grower profitable and to address the sustainability of limited production soil systems. Our work during the last two years allowed us to demonstrate that in the local setting, sprinkler irrigation systems can modify surface soil quality in short term by moving surface soil salts to the subsurface thereby increasing cotton plant stands, vegetative growth and overall productivity.

Overcoming crop production obstacles at these locations can be partially overcome by reducing drainage volumes in resident and adjacent fields. Areas having water table levels that come within 1m of the soil surface were most negatively affected by salts in the top 30 cm. We demonstrated the importance of having a high quality surface soil allowing the plant stand to develop as the most important way to improve crop yield. The second year activity found that stand reductions of 45 percent resulted in similar reductions in crop yield, while high yielding areas were well above 1200 kg per ha and considered profitable.

Combining production practices that also incorporated agronomic improvements can also serve the grower. While all cotton varieties were severely impacted by high soil salts concentrations, some varieties were less negatively affected. Both differences in seedling survivability and tolerance by some commercially available varieties were responsible for large differences in yields between Pima varieties. Other methods successfully used at the site included the growers unique approach to bed establishment. When working with furrow irrigated sites, the 150 cm bed appears to be effective at concentrating salts in the bed center and away from the developing roots near the surface. This appears to allow better plant stands to develop.

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Table 1. Sample locations with relative plant vigor rating and GPS Latitude & Longitude coordinates.

Sample Locations	Plant Vigor	GPS Coordinates
1	Medium	N 36^0 22.728' W 120^0 13.740'
2	Low	N 36^0 22.727' W 120^0 13.682'
3	High	N 36^0 22.715' W 120^0 13.646'
4	Low	N 36^0 22.927' W 120^0 13.716'
5	Medium	N 36^0 22.938' W 120^0 13.650'
6	High	N 36^0 22.934' W 120^0 13.601'

Table 2. In-Season plant characteristics measured on July 15^{th} at six locations including Height-to-Node Ratio(HNRI) and Node Number Above White Flower(NAWF).

	Med. Vigor 1	Low Vigor 2	High Vigor 3	Low Vigor 4	Med. Vigor 5	High Vigor 6
Height (cm)	50.8	48.3	66.0	35.6	50.8	66.0
HNRI	53%	56%	64%	51%	51%	76%
Fruiting Nodes	10.9	10.3	13.7	8.4	11.6	11.5
Total Nodes	18.2	17.0	19.2	15.1	18.4	17.1
Top 5 Retention	98%	98%	100%	98%	98%	100%
Bot. 5 Retention	98%	98%	94%	96%	98%	96%
NAWF	7.6	8.8	5.8	8.0	5.8	4.8

Table 3. In-Season plant characteristics measured on August 1st at six locations including Height-to-Node Ratio and Nodes Above White Flower (NAWF).

	Med. Vigor 1	Low Vigor 2	High Vigor 3	Low Vigor 4	Med. Vigor 5	High Vigor 6
Height (cm)	55.9	73.7	76.2	61.0	58.4	71.1
HNRI	36%	60%	65%	57%	52%	60%
Fruiting Nodes	11.4	14.6	16.5	12.2	13.3	16.9
Total Nodes	26.9	21.9	20.9	19.7	20.4	21.4
Top 5 Retention	96%	96%	94%	92%	86%	94%
Bot. 5 Retention	96%	96%	98%	94%	94%	94%
NAWF	4.6	5.7	5.0	2.8	2.6	2.0

Table 4. End of season plant characteristics and plant population on Sept. 27th.

Field Locations	Plant Vigor	Plant Pop./ ac. x 1000	Bolls per Plant	Bolls per Meter	#Fruiting Branch	Average Height (cm)	H/N Ratio	% FP1 Ret. in bot. 5 FB	95% Zone (all FB bolls	% FP1 Ret. in 95% Zone
1	Med.	28.3	22.3	118.8	14.3	56.1	1.04	70.0	16.9	68.2
2	Low	20.5	52.4	202.3	18.8	85.1	1.31	88.0	20.5	87.3
3	High	33.7	24.3	154.2	16.7	78.0	1.35	74.0	18.2	74.6
4	Low	33.2	20.1	125.7	11.7	62.5	1.24	80.0	17.1	74.0
5	Med.	29.0	27.4	149.6	15.5	65.8	1.17	78.0	18.1	77.7
6	High	23.2	23.4	102.2	15.9	78.2	1.41	86.0	17.9	68.6

Table 5. Yield averages from four replications. Harvested on Oct. 30th.

	Variety	Seed Cotton	Lint/ Acre	
1	S-7	1126	340	*C*
2	PSC-57	1998	619	*BC*
3	PHY-76	2445	773	*B*
4	DP-HTO	1707	576	*BC*
5	DP-340	2187	706	*B*
6	DP-744	1962	629	*B*
7	HA195	3274	1075	*A*

LSD 0.05 = 284.7

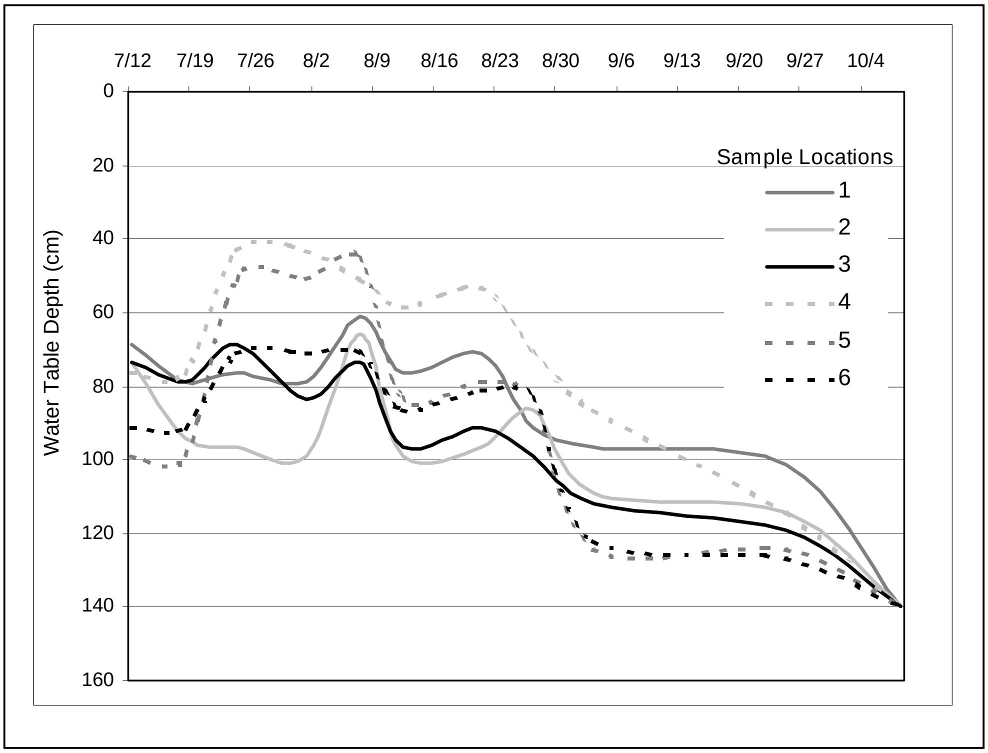

Figure 1. Water table depths taken at the 6 sample locations during the growing season.

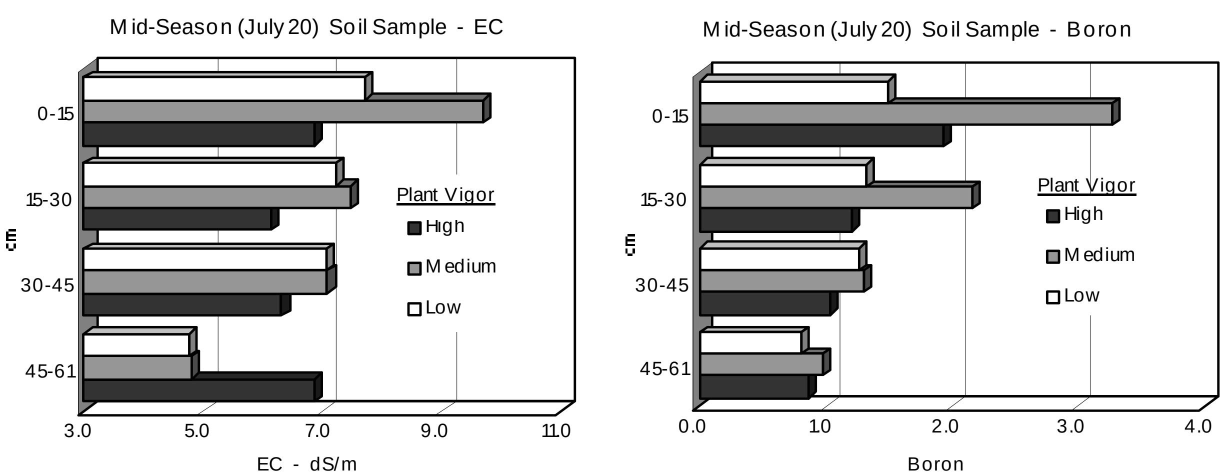

Figure 2. Soil EC (dS/m) and Boron sampled down to 61cm at the low, medium, and high vigor sample locations.

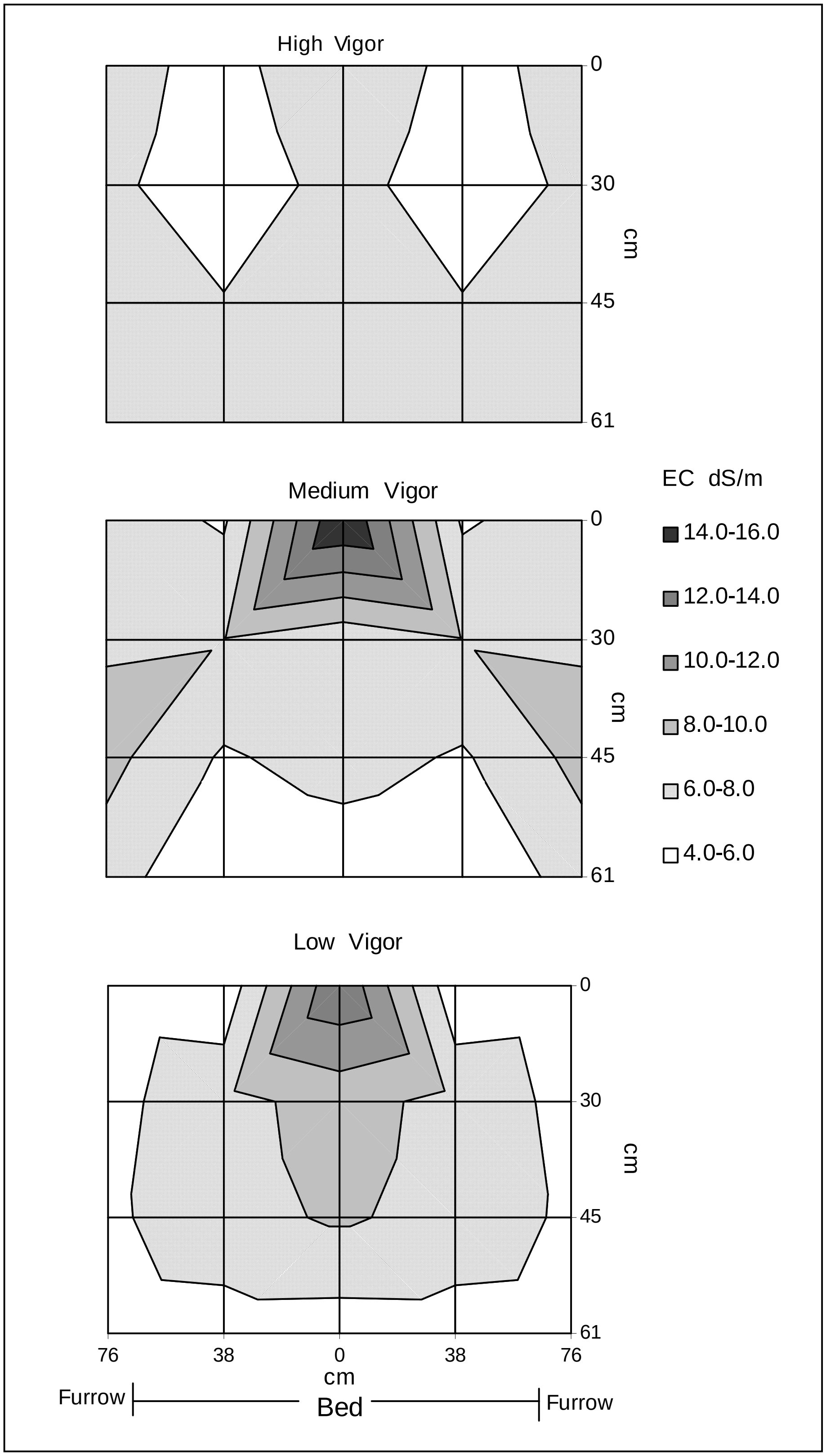

Figure 3. Cross sectional view of plant beds and furrows - Soil EC (dS/m) from the surface down to 61cm from low, medium, and high vigor areas of the field. Soil samples taken on July 20th.

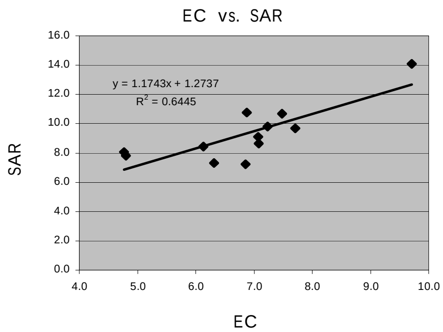

Fig 4. Linear relationship between soil EC (dS/m) and SAR. Samples taken from the six sample locations on July 20.

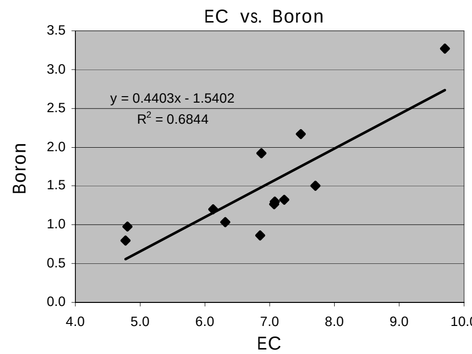

Fig 5. Linear relationship between soil EC (dS/m) and Boron. Samples taken from the six sample locations on July 20.

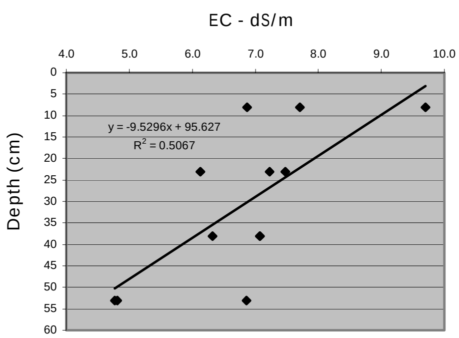

Fig 6. Linear relationship between soil EC (dS/m) and soil depth. Samples taken from the six sample locations on July 20.

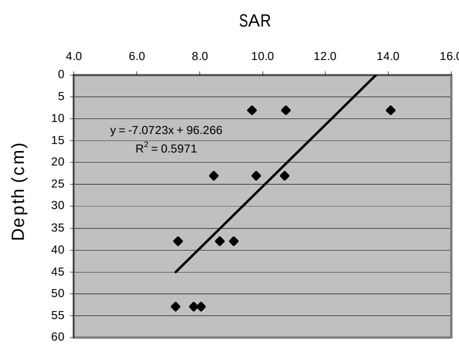

Fig 7. Linear relationship between SAR and soil depth. Samples taken from the six sample locations on July 20.

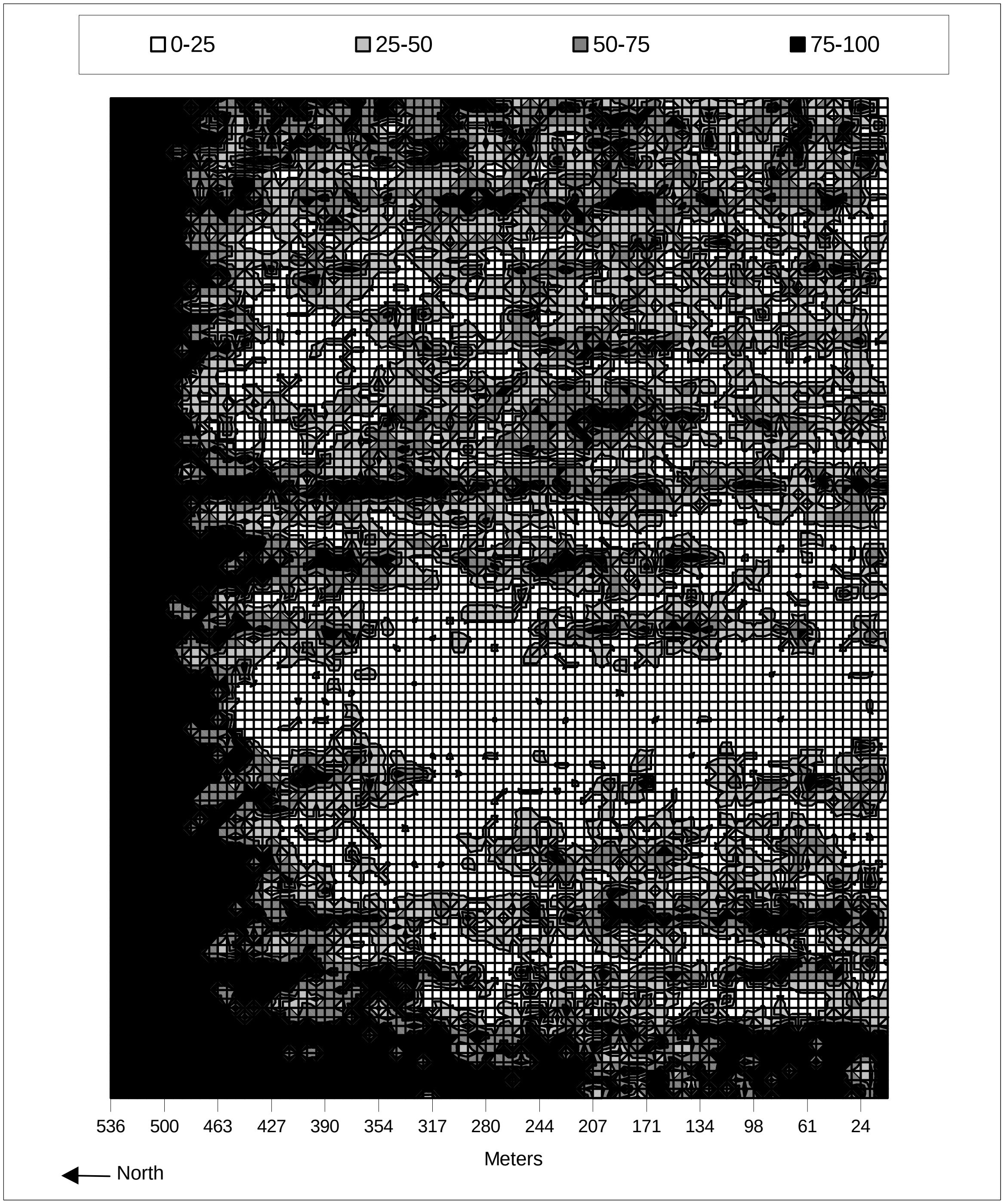

Figure 8. Percentage of plant skips in the west half f the field – measured in 6-meter sections.

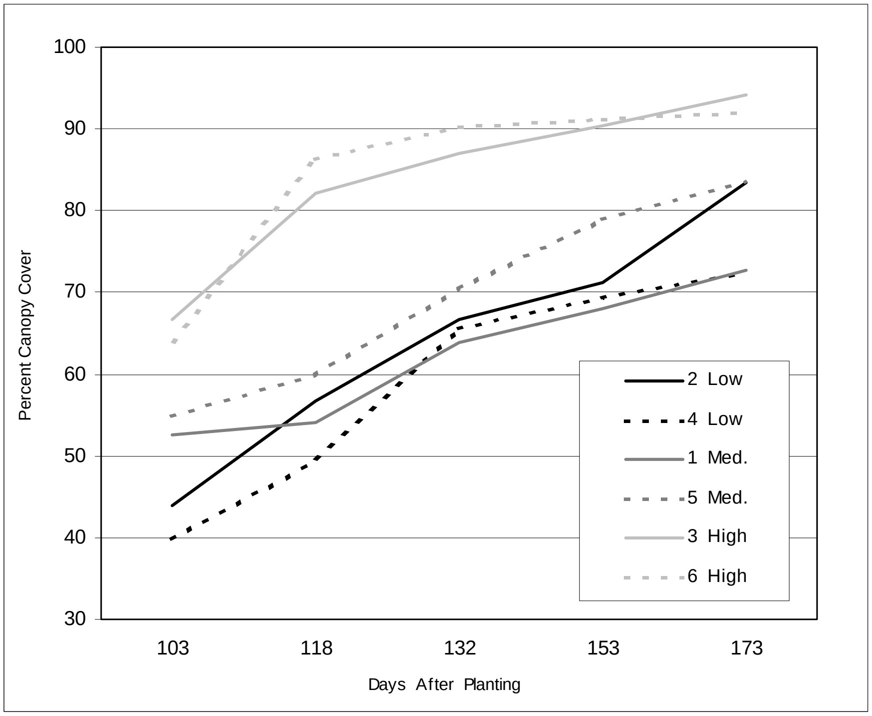

Figure 9. Percent canopy cover during the growing season. Data from near infrared images using the Dycam camera. Area sampled was 4.8 square meters.

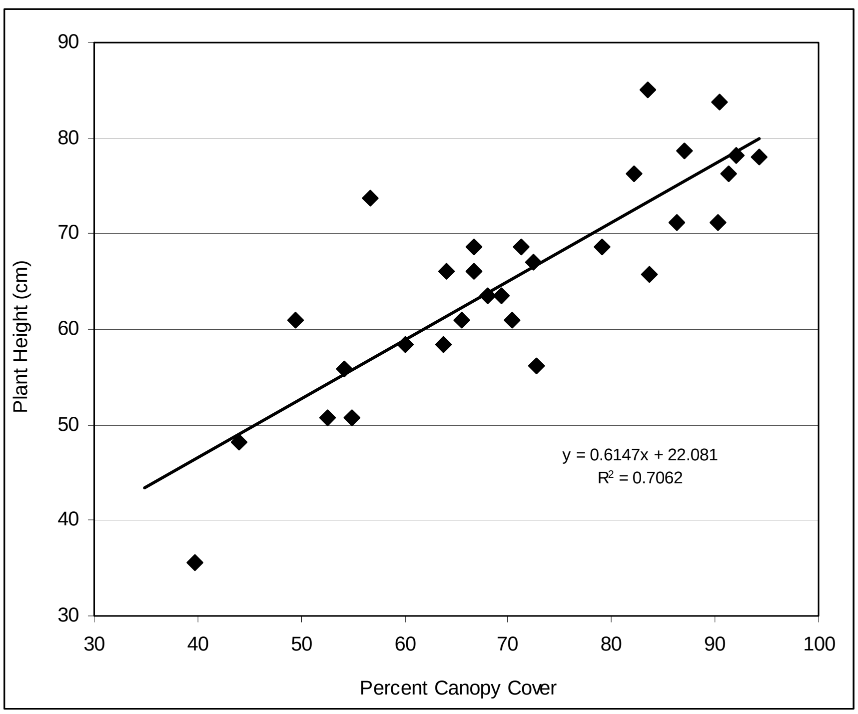

Figure 10. Linear relationship between percent canopy cover and plant height from July 16th to Sept. 25th.

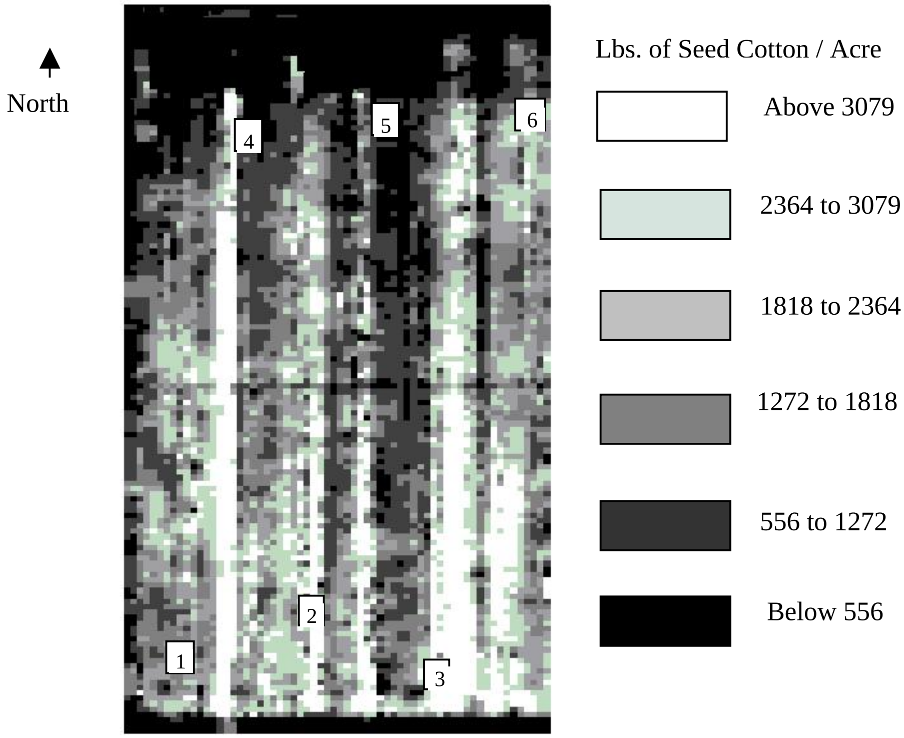

Figure 11. Yields measured throughout the field using a yield monitor. Sample locations are indicated by the small white boxes labeled 1 through 6. Rows run north to south and are 540 meters in length on 152 cm beds.

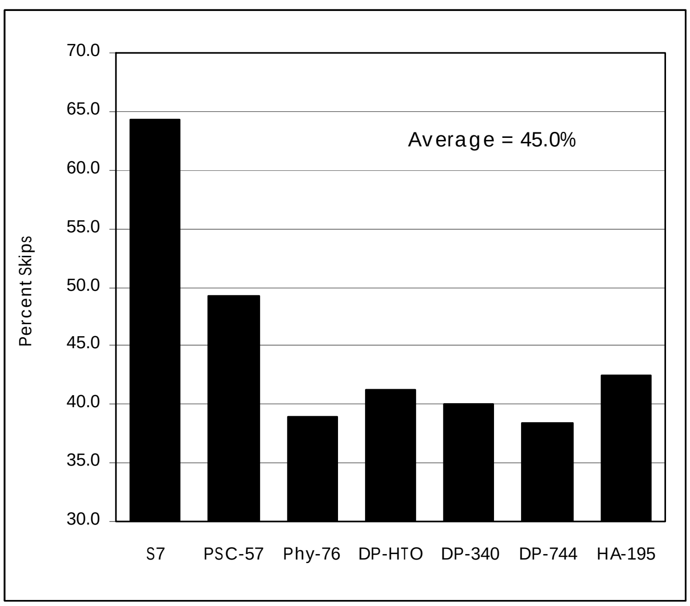

Figure 12. Percentage of skips within the field by variety. Skips of 1 meter and greater were recorded and averaged. Percentage of field not established was 45.0%.

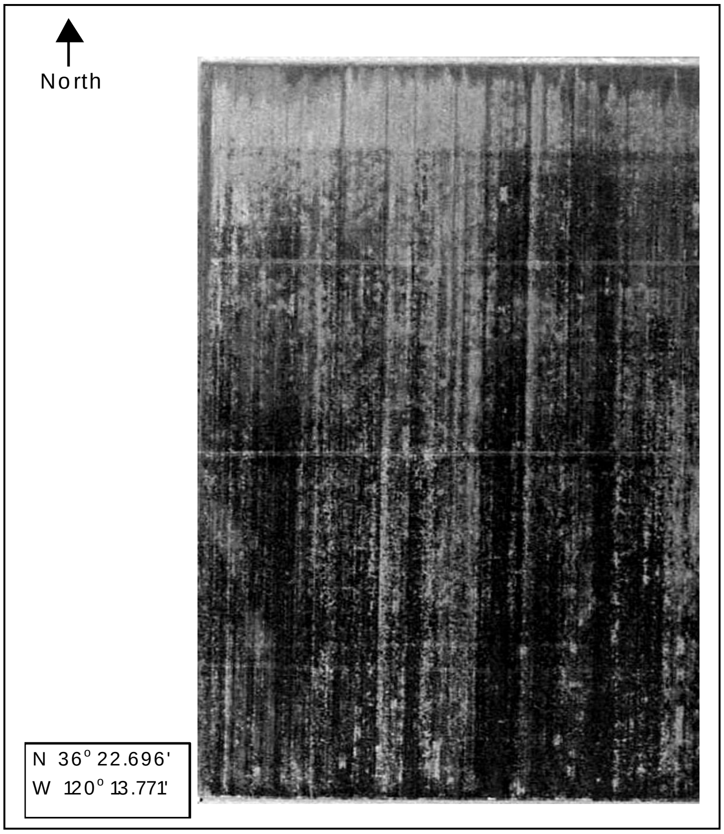

Figure 13. Aerial photograph of the study site taken July 24th 2002.

Algal Community Assessment Under Different Nutrient and Grazing Intensity Regimes: Selenium Volatilization and Ecotoxic Risk

(Part of a Team Project Entitled "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation")

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ABSTRACT

Previous research has noted that isolated cultures of microorganisms exhibit varying rates of selenium (Se) volatilization, which implies that Se volatilization depends on the taxonomic composition of microphyte communities (i.e., communities of green algae and cyanobacteria). Microphyte community composition is very important, as microphytes simultaneously act as the base of the food chain and as the primary "fixers" of Se into organic forms. Our project was designed to assess effects of grazing by brine shrimp (*Artemia franciscana*) and other macroinvertebrates in combination with nutrient additions on microphyte community structure in TLDD and LHWD basins. We hypothesize that differences in grazing pressure by primary consumers affect microphyte community composition in individual basins. The main objective of this part of the multi-project Joint Research effort is to characterize the microphyte communities and evaluate the effects of grazing as well as nutrient input on the population dynamics of individual components of these microphyte communities.

During the first year of the project (2001) we conducted two microcosm experiments to study changes in microphyte composition in response to various grazer (brine shrimp) densities. We have also conducted two field experiments in LTDD ponds. During 2002 we conducted another two microcosm experiments (3 and 4) dealing with the effect of selenium forms on the assemblages and food web. So far, microphyte composition from the microcosm experiments 1 and 2 has been evaluated and the results of the field experiments are almost complete. This second annual report presents all the results of the microcosm experiment 1 and 2, field experiment 2 and a brief description of the microcosm experiments 3 and 4. Microcosm experiments 3 and 4 are in a process of species determination and will be presented in the final report and in a special publication.

Our data should confirm the first hypothesis: H1: “Brine shrimp production increases with overall microphyte production”. The results of the field experiment are in support of the second hypothesis: H2: “Overall microphyte production increases with addition of nutrients”. For the third hypothesis: H3: “The microphyte species composition is affected more by grazing (“top down” effect), than by nutrients (“bottom up” effect)”, we have positive data from laboratory experiments. Our results show that grazing by brine shrimp IS strongly selective. Cyanobacteria are grazed most heavily, followed by other groups, e.g., flagellates. Green algae are grazed least. The selective grazing leads to special species composition and depletion of grazed species. The resulting species composition is highly variable and depends on algae species offer as well as on other conditions of cultivation (nutrients addition, Se addition, temperature, light and/or the conditions of grazers).

The results of the Microcosm experiment 1 on assemblages of picocyanobacteria were recently published (Komárková & Šimek 2003).

INTRODUCTION

Volatilization of Se from aerobic saline waters by microphytes is probably a widespread and global phenomenon (Amouroux and Donnard, 1996). In evaporation basins, the volatilization of Se by microphytes must be considered together with Se accumulation and potential ecotoxic risk, since the processes are linked. Fan and Higashi have previously demonstrated in evaporation basins of the San Joaquin Valley that a substantial amount of Se (up to 70% of added Se) was removed from aerated culture media via volatilization by filamentous cyanobacteria isolated from TLDD waters (Fan et al., 1998). They have also shown that several other microphytes isolated from these basins behave similarly (Fan et al., 1997; Fan and Higashi, 1998; Fan and Higashi, 1999a). There are differences in rates of Se volatilization by isolated cultures, which implies that Se volatilization depends on the composition of microphyte communities (i.e., communities of green algae and cyanobacteria). The process of biovolatilization first requires "fixation" of Se by microphytes into their biomass. Fan et al. (Fan and Higashi, 1999a; Fan, 2000) have shown that the extent of bioaccumulation varies by microphyte species. These interspecific differences could cause the ecotoxic risk to vary by basin, a phenomenon that could be strategically exploited to reduce overall Se risk in evaporation basins. Fan (2000) documented the effect of this variation in evaporation pond biogeochemistry and provided data on some of the Se bio-concentration factors (BCF) of microphytes and invertebrates observed in TLDD and LHWD evaporation basins. Across a wide range of salinities and waterborne Se concentrations, the microphytes range approximately 10-fold in BCF, while the next trophic level, the invertebrates, range even wider. However, the microphytes and invertebrates BCFs are not related to either salinity or waterborne Se concentration; current evidence from these basins and elsewhere indicates that it is a function of the basin biogeochemistry (Fan et al., 1998; EPA Office of Water, 1998). The biogeochemistry, in turn, is likely a function defined (in part) by the microphyte community composition, as they act simultaneously as the base of the foodchain and as primary "fixers" of Se into organic forms (see Fig. 1 Report of Higashi, this volume).

In summer 2000 and 2001 we surveyed the microphyte composition of TLDD and LHWD basins. This effort resulted in the identification and cataloging of species collected from these basins. Based on these preliminary results we hypothesized that grazing pressure by brine shrimp cause changes in microphyte composition. A paper on the species composition related to all the salinity concentrations in the sampled pools is in preparation.

OBJECTIVES AND HYPOTHESES

Our current project is designed to assess effects of grazing by brine shrimp (*Artemia franciscana*) and other macroinvertebrates in combination with nutrient additions on microphyte community structure in TLDD and LHWD basins. The main objective of this part of the multi-project Joint Research effort is to characterize the microphyte communities and evaluate the effect of grazing as well as effect of nutrient input on the changes in population dynamics of individual components of these microphyte communities. Ultimately, we tried to modulate microphyte communities in our experiments in two aspects: (1) create conditions that are most favorable for microphytes that contribute most to the volatilization process, and, at the same time (2) create conditions that would provide enough microphyte food for brine shrimp production.

This study uses both observations and experiments in the field to confirm or reject the following hypotheses:

H1: Brine shrimp production increases with overall microphyte productivity.

H2: Overall microphyte primary production increases with addition of nutrients.

H3: The microphyte species composition is affected more by grazing (“top down” effect), than by nutrients (“bottom up” effect).

The specific objectives are:

1. Monitor the microphyte composition and primary production (PP) indicators in basins;
2. Correlate the changes in microphyte composition and PP with water/nutrient chemistry data (projects of Gao/Dahlgren and Higashi/Flocchini) and with data on brine shrimp harvest;
3. Correlate the changes in the microphyte composition with 16S DNA and pigment analyses of the microphytes (project of Fan/Meeks). Correlate the changes in microphyte composition with Se volatilization and BCFs in the algae (project of Fan/Meeks). In the field experiment, assess responses of microphyte communities to factorial combinations of brine shrimp presence/absence, nitrogen, phosphorus, combined N and P, and chicken manure additions in terms of species composition and growth response (e.g. PP, chlorophyll a);
4. Relate these responses to Se volatilization (project of Fan/Meeks) and detritus chemistry (projects of Gao/Dahlgren and Higashi/Flocchini).
5. Correlate the microphyte composition with Se BCFs in the algae (project of Fan/Meeks).

METHODS

MICROCOSM EXPERIMENT 1

The algae assemblages were collected from several LTDD ponds and mixed to create a suspension representative of algae species as potential food source for *Artemia franciscana*. The water samples were filtered through a 50 µm net to screen out all invertebrates. Suspensions were cultivated in 200 ml of water in 400 ml beakers under ambient light and temperature conditions for 6 days. The first experiment included only a control and two treatments, each in two replicates. In treatment 1 we added 6 shrimp/beaker and in treatment 2 we added 12 shrimp/beaker. The biomass of algae was estimated by counting in Utermöhl chambers as number of cells per ml and expressed in mg/l. Samples for assessment of the microphyte composition were collected daily.

MICROCOSM EXPERIMENT 2

The second experiment was conducted in order to evaluate the feeding preferences of adult and larval brine shrimp. It was also designed to evaluate the timing of brine shrimp development under the experimental conditions.

The second experiment lasted five days and included three treatments and a control:

The treatments were:

O- Control (with no shrimp)

EGS - Eggs (added from the field collection)

AD - Adults (filtered each day to remove eggs and larvae)

ADE - Adults (newly laid eggs and hatched larvae kept in beakers)

Water salinity and volume were kept constant. pH was measured three times during the experiment. Light intensity was 100 W m^{-2}. Temperature ranged from 25 to 35^{0}C. Three ml water samples were taken daily from each beaker and fixed in Lugol solution and 4% formaldehyde for quantification and identification algal species. At final shrimp harvest, larval and egg abundance was assessed in all treatments. Numbers of cells/ml of phytoplankton was counted in Bürker chambers.

FIELD ENCLOSURE EXPERIMENTS

Nutrient addition experiment was set up within the C4 basin. Experimental treatments included brine shrimp presence/absence, additions of N, P, N&P, turkey manure, straw, and straw & manure, and a control with no additions. Three replicates were set up for each treatment. Enclosures were made of clear plastic. Each enclosure was filled with filtered basin water and inoculated with the same microphyte inoculum present in the basin pond. Treatments with brine shrimp received a shrimp density corresponding to typical densities experienced in that pond prior to harvest (data provided by Dr. Rofen). The enclosure experiments were run for two weeks with nutrients added twice. Phosphorus was added in form of K_2HPO_4 and N was added as KNO_3. The chicken manure addition corresponded to the amount that has been used by Novalek, Inc. for successful shrimp cultivation in the TLDD basins (data provided by Dr. Rofen).

Species composition of the microphyte assemblages was evaluated using a microscope at the beginning and at the end of the experiment. The microphyte biomass was estimated using chlorophyll *a* concentrations (Rejmánková & Komárková 2000). At the time of harvest, microphyte and brine shrimp samples were collected for the concentration of N and P in the biomass and Se analysis. Growth of brine shrimp under different treatments was assessed at the end of the experiment as total change in their biomass.

Unexpected problems due to stormy weather on day 3 resulted in the loss of several replicates. Thus the results of this experiment should be considered only preliminary.

MICROCOSM EXPERIMENT 3

The third microcosm experiment was focussed on the interaction of the feeding preferences of adult and larval brine shrimp with different growth intensities of algae/cyanobacteria assemblages due to selenate and selenite treatments. It was also designed to evaluate the timing of brine shrimp development under the experimental conditions.

The third experiment lasted seven days and included crossed conditions of three animals treatments and two Se addition treatments and a control:

The animal treatments were:

O - Control (with no shrimp)

L - Larvae (added from the field collection)

A - Adults

AL - Adults and Larvae

The Selenium treatments were

Selenate - Sodium selenate (2.3924 mg/l)

Selenite - Sodium selenite (2.1897 mg/l)

Control - no Selenium added

Water salinity (100 ‰) and volume (250ml) were kept constant. pH was measured three times during the experiment. Light intensity was 100 W m^{-2}. Temperature ranged from 25 to 30^{0}C. Three ml water samples were taken daily from each beaker and fixed in 4% formaldehyde for quantification and identification algal species. At final shrimp harvest, larval and egg abundance was assessed in all treatments. We recorded the changes in the development of *Artemia franciscana* life stages and counted them in the final state of the experiment. The mortality of animals was one of the studied features. Dead animals were removed and replaced from the subculture kept in similar conditions. The response variables were amount of brine shrimp biomass, abundance in the final harvest, algae species abundance and their biovolume (biomass).

MICROCOSM EXPERIMENT 4

The fourth microcosm experiment was focussed to interaction of the feeding preferences of adult brine shrimp with different growth intensities of algae/cyanobacteria assemblages due to selenium addition in form the of selenite and nutrient treatments.

The experiment lasted six days and included crossed conditions of animal treatment, Se addition treatment, three nutrient treatments and a control in three replicates:

The treatments were:

C - Control (with no shrimp)

AD - Adults (filtered each day to remove eggs and larvae)

C - Control with no selenite

Sni - Selenite (2.1897 mg/l)

N- KNO3 (521.025 mg/l)

P- KH2PO4 (16.65 mg,l)

NP- both

Control - No nutrients

Water salinity and volume were kept constant as in the experiment 3. pH was measured three times during the experiment. Light intensity was 100 W m^{-2}. Temperature ranged from 25 to 30^{0}C. Three ml water samples were taken daily from each beaker and fixed in Lugol solution and 4% formaldehyde for quantification and identification algal species. At final shrimp abundance was assessed in all treatments.

RESULTS AND DISCUSSION

MICROCOSM EXPERIMENT 1

In our Microcosm experiment #1, brine shrimp grazing had a statistically significant effect on the algae population (Fig.1). The presence of brine shrimp was responsible for a significant reduction in algal biomass starting day 3 of the experiment. Figure 2 shows the changes in proportions of individual algal species biomass in the control in the course of the experiment. The algal assemblage in the control was influenced only by inter-specific competition and experimental conditions. The phytoplankton species in this experiment can be classified into four groups: 1) species whose biomass increased and achieved higher level than at the day zero, 2) species whose biomass decreased due to the predation by Artemia, 3) species whose biomass did not change and, finally, 3) minority species that were not an important food source, but were also influenced by the life activity of the brine shrimps.

The structure and biomass of the algal population shifted with additions of shrimp. Grazing at both high and low intensity as shown in Fig. 3, decreases the biomass of all species except for genus Oocystis. This is in strong contrast to the control, which was dominated by Synechocystis salina. Apparently S. salina is a food source favored by Artemia franciscana. The next taxonomic groups to be grazed substantially were cyanobacterial picoplanktic species forming colonies of short filaments (CPP – col), Cyanobacteria filaments (Cyano-fil), and to some degree Anabaenopsis mulleri (ABPSISsal). The only species that were not grazed were both species of Oocystis genus; Oocystis cf marssonii and Oocystis parva + composita. We can conclude that predation pressure is advantageous for the Oocystis cf. marssonii under conditions of the first experiment.

Figures 5a-f show the proportion of the most important species in control and the two treatments. The individual species development in this experiment was as follows:

The increase in the biomass of Oocystis species (Fig. 5a & b) in the two treatments as compared to control may be caused by the suppression of other algal species by brine shrimp. The relative increase of Oocystis parva + composita in the 2 treatments follows a pattern similar to the control. While Oocystis is known as not digestible alga, the green alga Chlorella sp. together with Picocystis salinarum (Fig. 5c.) which showed a similar response, i.e., increase in biomass as a response to grazing pressure, passed through the filtration apparatus of the brine shrimp because of its small size. Cyanobacterial filaments group (Fig. 5d) were a good feeding source for Artemia franciscana as were CPP colonies (Fig. 5e.) and partly also flagellates (Fig. 5f). These were all significantly grazed by brine shrimp as evidenced by a sharp decrease in their relative biomass.

The distribution of the samples with different Brine shrimp abundance related to the algae/cyanobacteria community can be seen at the Fig. 6. The interesting feature here is an obvious stagnation of the treatment without Artemia franciscana. Treatment with Artemia addition completely changed the species composition and abundance of algae. The final assemblage appeared in the left bottom quadrant dominated by Chlorella and Picocystis together with Oocystis.

Species composition changes immediately at the first day of experiment and differences are not directly dependent on the amount of shrimp see the Fig. 7. The earlier differences are more pronounced than later differences, because the system is not in equilibrium and tends to form two areas in the diagram. One without shrimp seems to be fluctuating between the equilibrium positions of algal species competition. The second is relatively steady state around the final position of the algal source, which was depleted by grazing.

The diagram (Fig. 8) clearly shows the time development of the communities under and without grazing pressure. The ungrazed community develops relatively slowly and the species abundance goes from the right bottom quadrant to the left side of the upper right quadrant. The grazed communities both finish their development at the left bottom quadrant coming there with different speed through the left upper quadrant. The grazing effect becomes obvious starting on the third day of experiment. Large species (Chaetoceros, Arthrospira, bottom diatoms) were consumed the first day and were not very frequent even in the Control treatment.

Picocyanobacteria assemblage from this experiment was sampled every day. The samples were preserved by formaldehyde and counted using the autofluorescence of cyanobacterial pigments on the Nuclepore filters. The assemblage dominated by filamentous and colonial cyanobacteria and bacteria changed due to the filtration bioturbation activity of adult and larval stages of Artemia (Komárková & Šimek 2003).

MICROCOSM EXPERIMENT 2

The goal of this second experiment was to determine the differences in selective grazing between larval and adult life stages of brine shrimp. The final brine-shrimp counts at harvest time have not yet been completed and will be presented in the final report of this project.

The algal assembly was grazed most heavily in Adults and Adults & Larvae treatments (Fig. 9). The biomass fluctuations seen in this figure were most probably caused by a behavior of the alga *Oocystis* cf. *marssonii* during the course of this experiment (See Fig. 10). The substantial decrease in *Oocystis* cf. *marssonii* biomass followed by its recovery after four days was apparently due to the stress caused by cultivation conditions.

The Eggs treatment (Fig. 11) was not different from the control. On the contrary to the Eggs treatment, the Adult treatment showed a distinct decrease in the population of *Synechocystis salina* (Fig. 12). The *Oocystis* biomass did not recover to the same level as in control, which indicates some level of grazing. No significant changes were seen in the *Picocystis salinarum* (PICSAL2) and *Prymnesium* sp. (PRYMsal5) species. *Synechocystis salina*, the most abundant alga, was more extensively depleted than less abundant algal species at the end of experiment when the number of feeding animals increased in Adults/Eggs treatment (Fig. 13). The individual species response to treatment conditions is summarized in Fig. 14 a-f.

The second experiment was not carried out under ambient light conditions and was conducted at higher temperatures than the first one (see Fig. 15). The grazer effects can be seen (similar to the first experiment) as increasing the variability of species composition over the second axis after second day of the experiment. Considering the hatching and fast growth of young larvae the effect of eggs can be seen from the fifth day of the experiment. This means that the development of young larvae and their remarkable influence on phytoplankton lasts about three to four days.

The time classification of the experiment two (Fig. 16.) shows the increase of the variability in algal community between treatments. In high temperatures the community fluctuated between cyanobacteria *Myxobactron* and *Synechocystis salina* dominants. On the other hand, the grazed community cycled between much higher spectrums of algae and probably increased the diversity during the time due to the fluctuation between several dominants. The disturbance was definitely caused by predation, which is not so obvious or common for the biotop. It means that the biotope character comes to temporal equilibrium and the development will follow the approximate cycles. This phenomenon can be studied only by long term cultivation under laboratory conditions.

FIELD ENCLOSURE EXPERIMENT 1 + 2

As stated above, we are still in the process of evaluating the species composition of microphytes from this experiment, due to a very large number of samples. Data on chlorophyll concentration indicate changes in biomass of the whole algal community as a response to different treatments. The addition of nutrients, especially combined N&P, and manure caused significant increases in both chlorophyll a and pheophytin concentrations (Fig. 17 and 18). The N&P treatment also shows a difference between presence and absence of brine shrimp. For information on Se content see report of Higashi (this Volume) (Fig 19).

The main gradient of environmental factors in Enclosure experiment No1 followed phosphorus concentration (Fig. 20). It can be seen that the amount of phosphorus in P and NP treatment represents about one third of the phosphorus concentration in Manure treatment. So the highest effect on the algal population should be seen in the Manure treatment. Samples are still being analyzed and the results will be presented in the final report.

The main gradient at the enclosure experiment 2 follows more NH_4 than PO_4 concentration. Interesting point is that several species are following the increase of NH4, which is sign of the nutrient increase as well as shrimp abundance increase (Fig. 21). This is the situation when the algae assemblage losses their diversity and probably increase the biomass. The other two factors are the effect of water management of the evaporation pond and weather.

The presence of grazer increases the variability of the response to the nutrient increase in the same way as it was found in the microcosms experiments. The system increases also the variability between the samples in time (see Fig. 22).

MICROCOSM EXPERIMENT 3

The goal of third experiment was to determine the interaction between differences in selective grazing between larval and adult life stages of brine shrimp and with the sufficient concentration of Selenium. The data analysis has not been completed yet and will be included in the final report.

MICROCOSM EXPERIMENT 4

The goal of the fourth experiment was to determine the interaction between the grazing and nutrients application and possible effect of Se addition on algae/ cyanobacteria community.

The preliminary results show again the increase of variability between samples of the phytoplankton assemblage (Fig. 23). Differences inside of the *Artemia* group can be seen as the decreasing of feeding in the selenium presence (see Fig. 23). The data are now only preliminary and the determination and evaluation of all the samples will be finished for the final report. Figure 24 shows the higher difference of samples between the presence and absence of in *A. franciscana*. The samples spread over three quadrants as a result of the grazing effect.

CONCLUSIONS

The microcosm experiments show the remarkable influence of *Artemia franciscana* grazing on different species of microphytes. Cyanobacteria were grazed most, followed by other groups, e.g., flagellates. Green algae with a cellulose cell membrane consisting of several layers like *Oocystis* or *Nephrochlamys* are resistant to ingestion while very small cells of *Chlorella* and *Picocystis salinarum* are not filtrated. In high salinity and high predation pressure green algae become dominant in our experiments. An important factor influencing shrimp grazing was the abundance of individual algal species. More abundant species were grazed more intensively than less abundant ones with the exception of green algae, which are not a very suitable food source for brine shrimp. The enclosure experiments showed the effect of fertilization on selenium volatilization (see Higashi, last year volume). In the second year of the project we conducted experiments to obtain more conclusive data on the strength of the effects of grazing by shrimp *vs.* nutrient addition.

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ABPSISsal6	Anabaenopsis mulleri
CPP-col	Cyanobacterial picoplankton, colonies
Cyano-fil	Cyanobacterial fillaments
Flagel	Flagellates
CHLORsal1	Chlorella sp. + Picocystis salinarum
MYXBAK	Myxobactron salinum
NEPsal	Nephrochlamys subsolitaria
OOCMAsal10	Oocystis cf.marsonii
OOCPAR	Oocystis parva+composita
PRYMsal8	Prymnesium sp.
SYNCOsal2	Synechococcus salinarum
SYNCYsal4	Synechocystis salina

Table 1. The list of abbreviation and whole names of algae species.

MICROCOSM EXPERIMENT #1

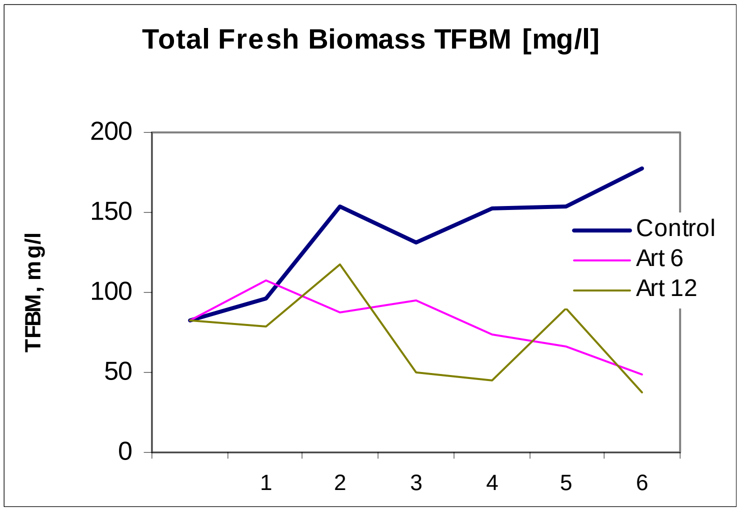

Figure 1. The total biomass of algal species in control and two treatments. (Art 6 = 6 brine shrimps added, Art 12 = 12 brine shrimps added)

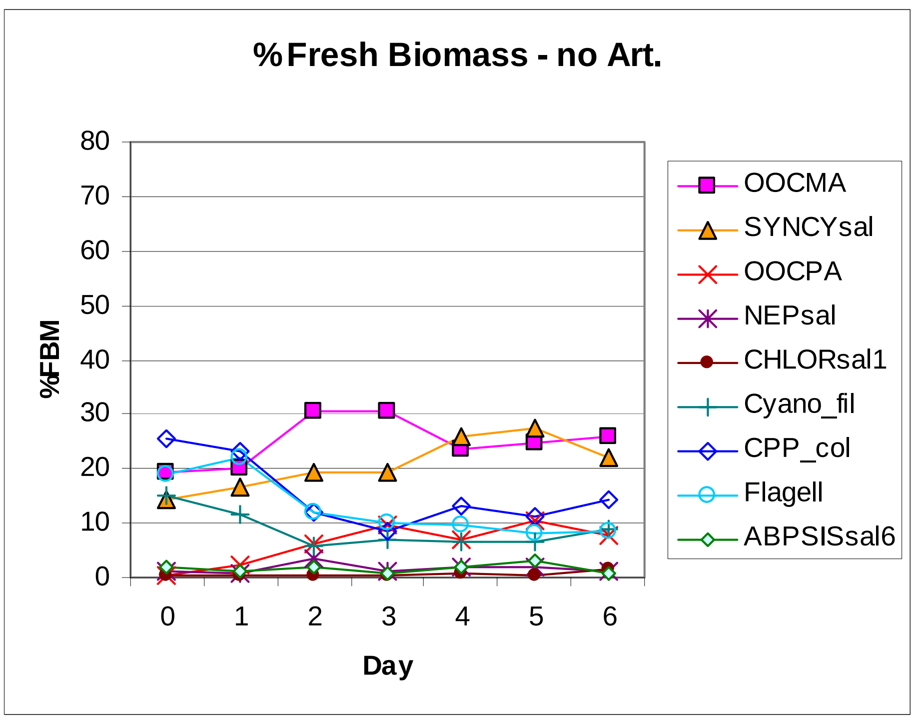

Figure 2. The control of the experiment with no predator pressure. Symbols in Table 1.

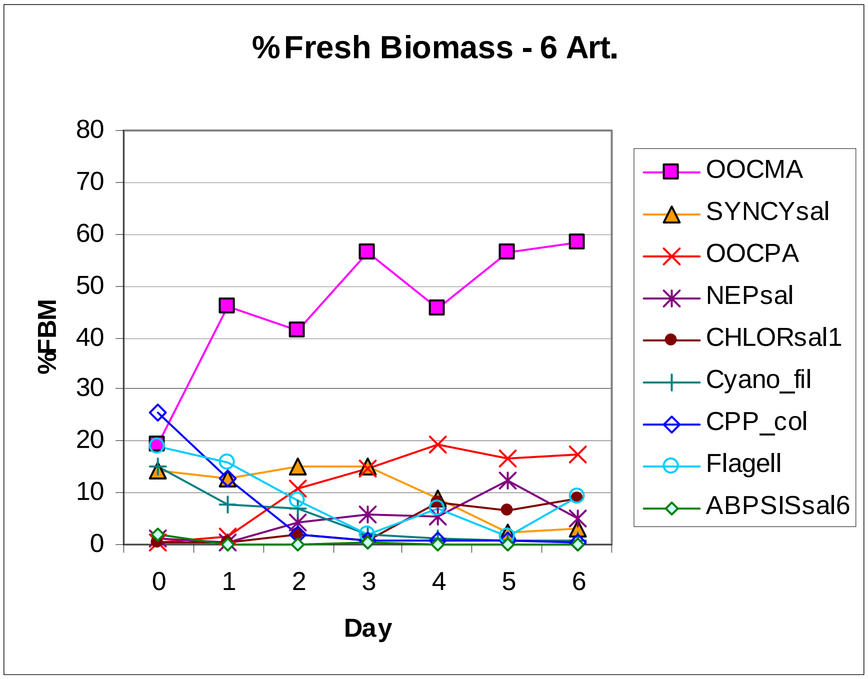

Figure 3. The biomass of the algae species under low grazing pressure (6 Artemia individuals in each beaker). Symbols in Table 1.

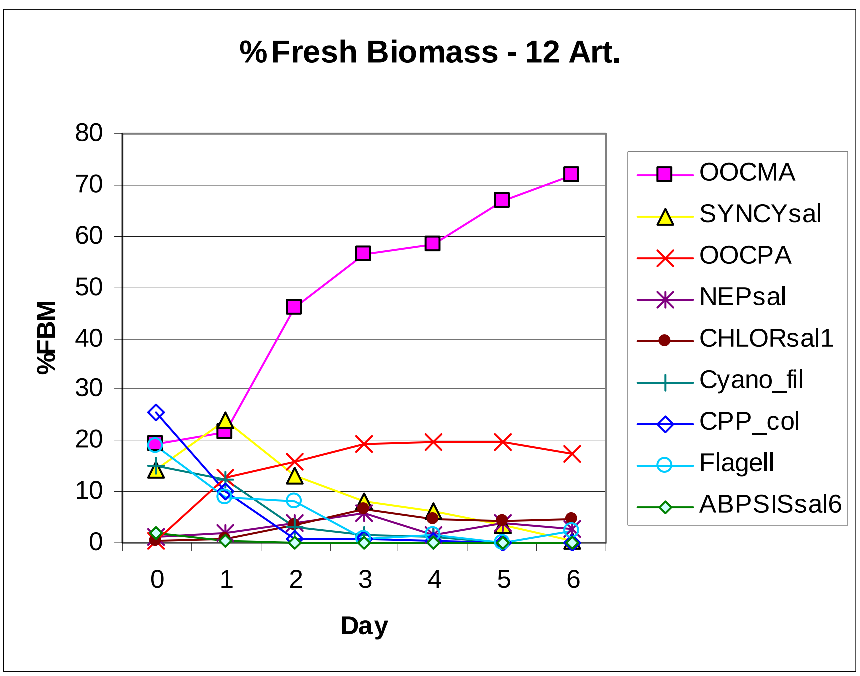

Figure 4. The experiment under high grazing pressure (12 individuals of *Artemia* in each beaker) Symbols in Table 1.

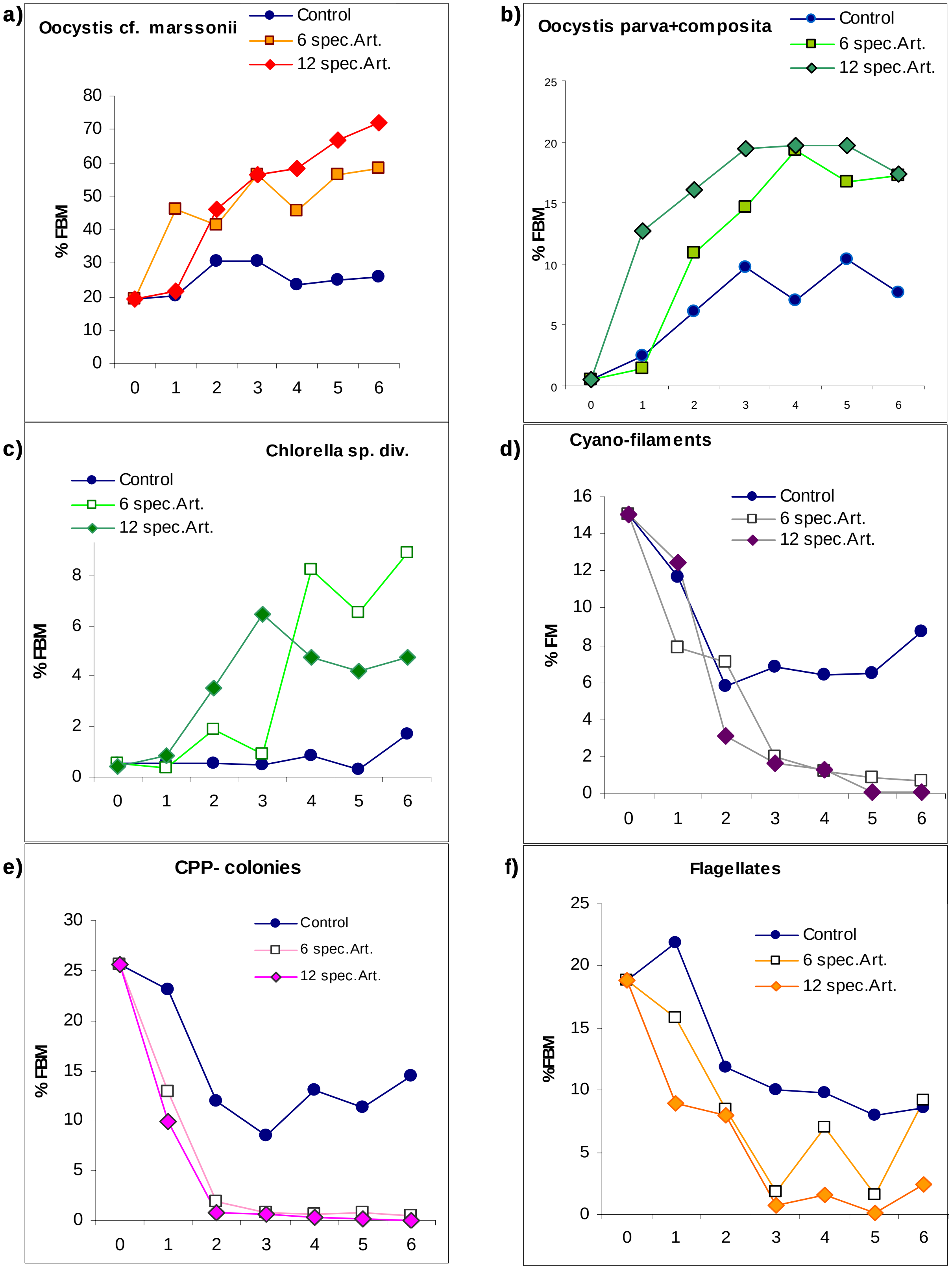

Figure 5: The relative percentage of fresh biomass of the *Oocystis* cf. *marsonii* , *Oocystis parva* + *composita*, *Chlorella* sp. div. + *Picocystis salinarum*, Cyano – filaments, Cyanobacterial picoplanktic colonies (CCP) and Flagellates in the control and two treatments.

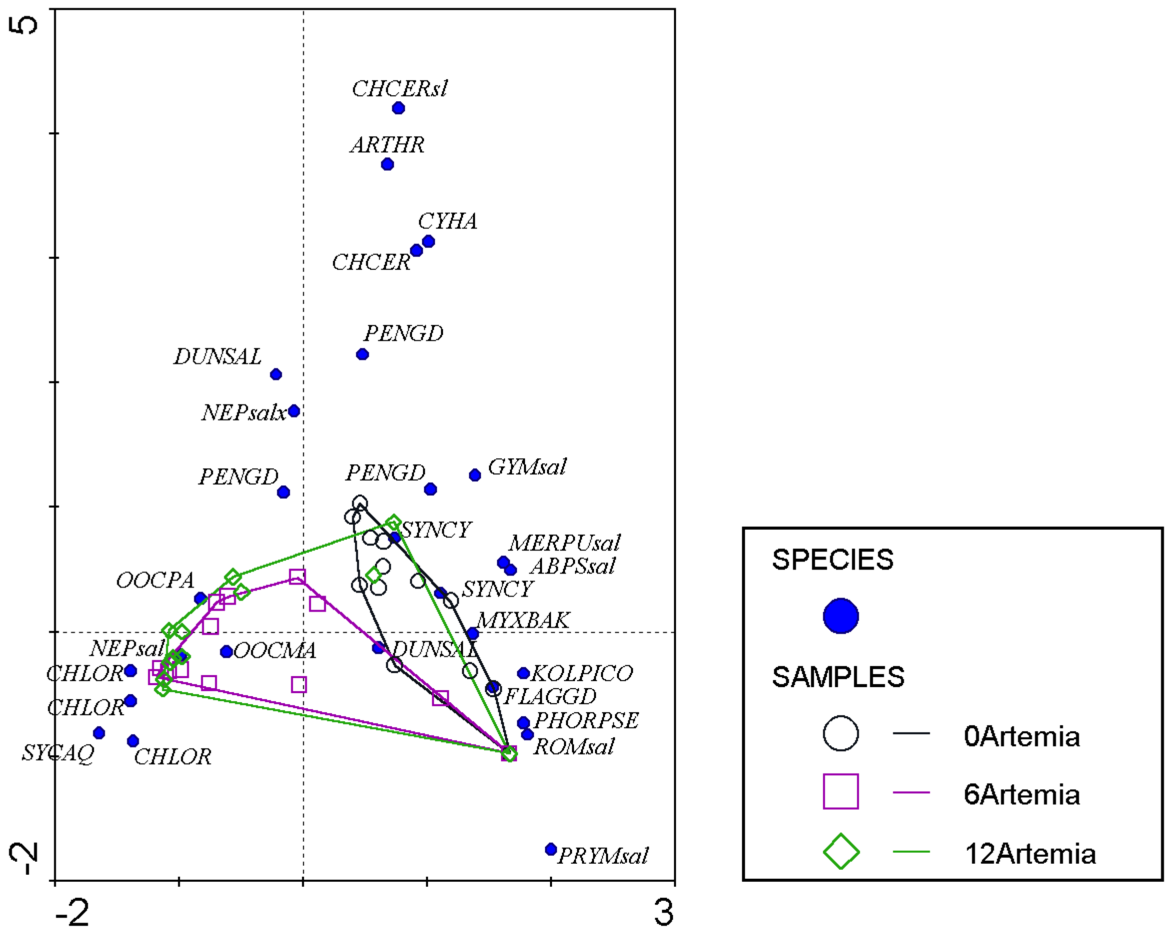

Figure 6. The distribution of species and samples in space of first and second ordination axis at the DCA with the samples classification due to the *Artemia franciscana* number treatment.

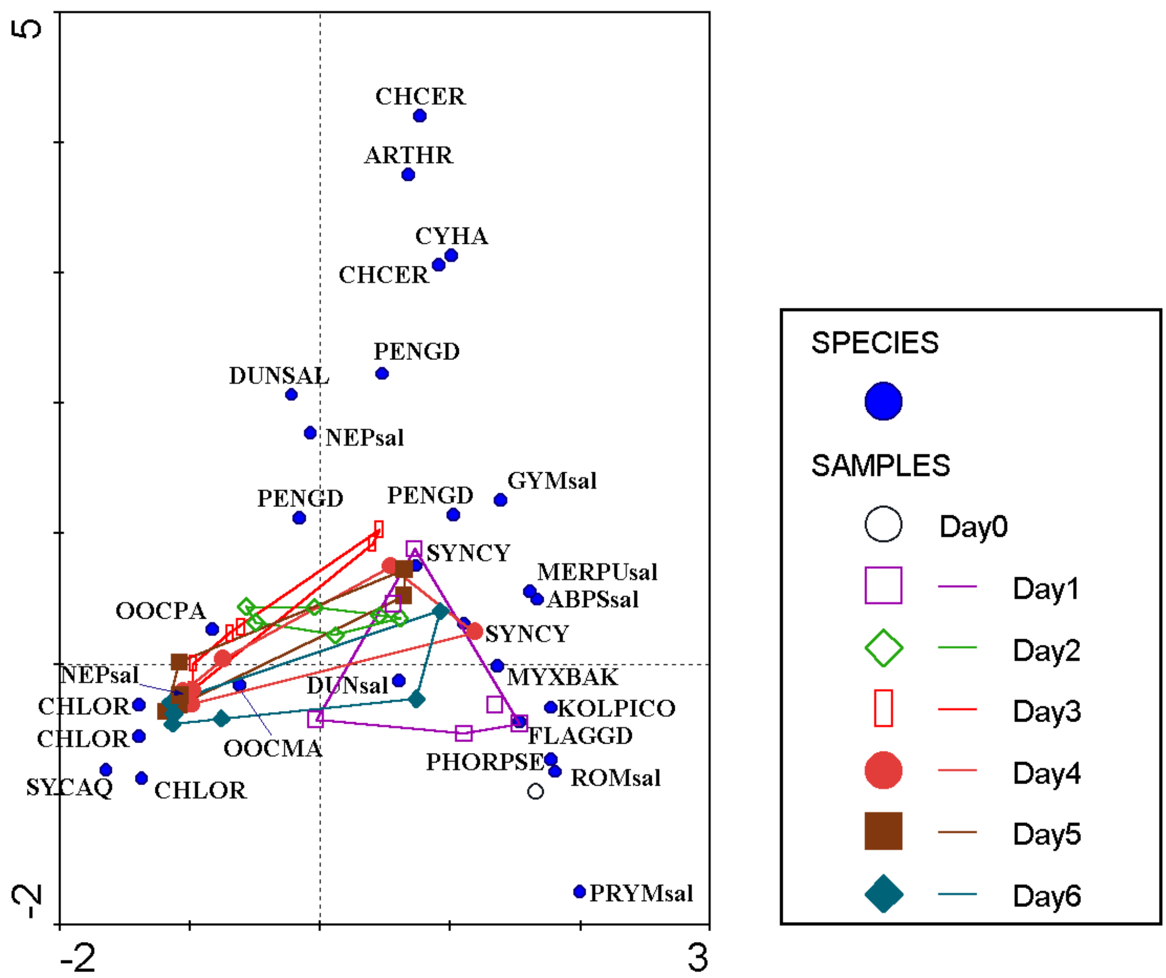

Figure 7. The distribution of the species and samples in ordination space of DCA with samples classified by time of experiment.

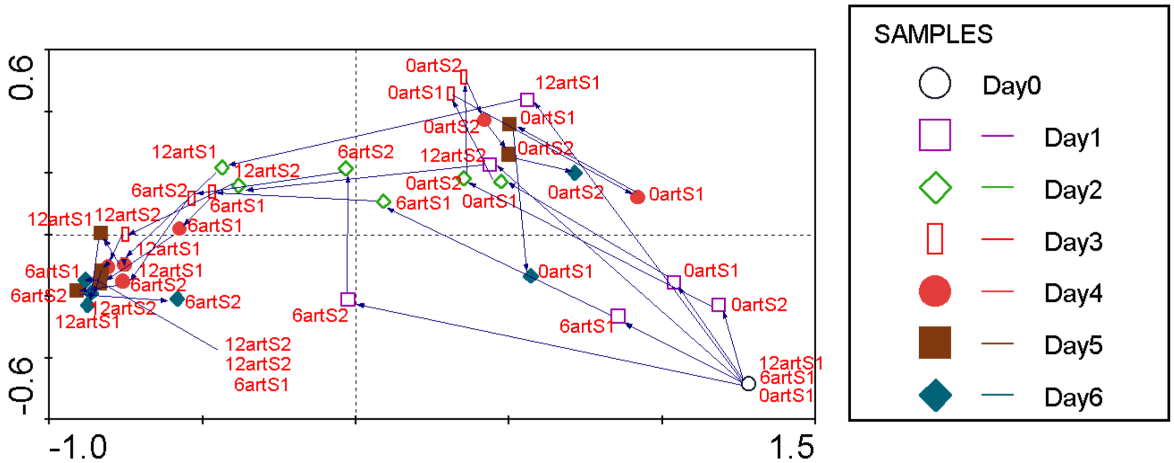

Figure 8. The distribution of samples in space of first and second ordination axis of DCA with the classification by time. Samples are manually connected by arrows to show development of each treatment in time.

Microcosm experiment # 2

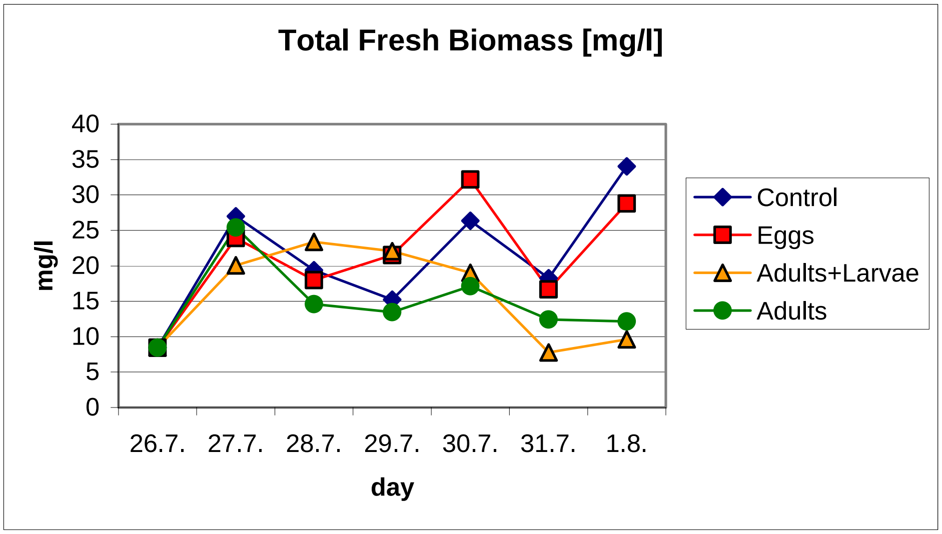

Figure 9. The time course of the Total Fresh Biomass of algae in control and the three treatments. Each point is the average of 5 replications.

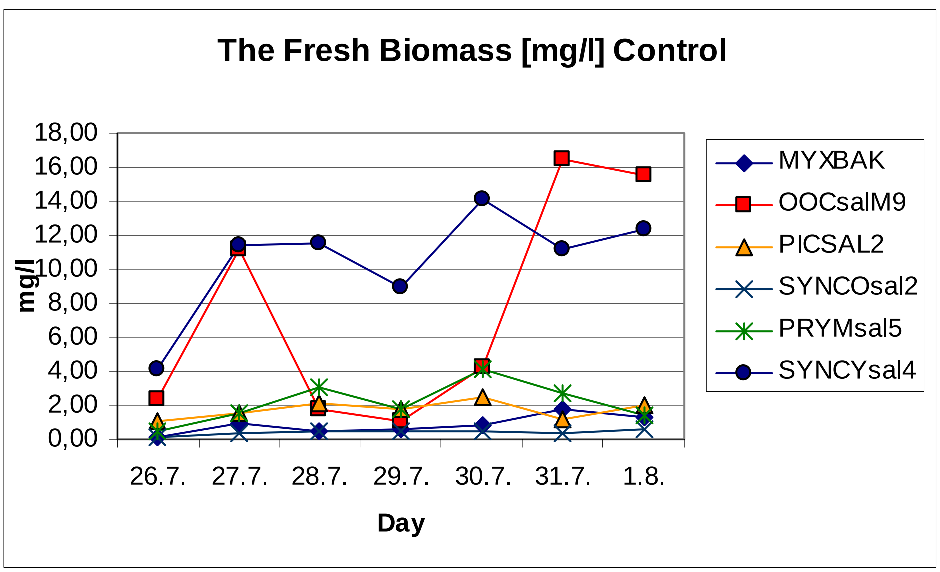

Figure. 10: The fresh biomass of the algal species in control set of the experiment. Symbols in Table 1.

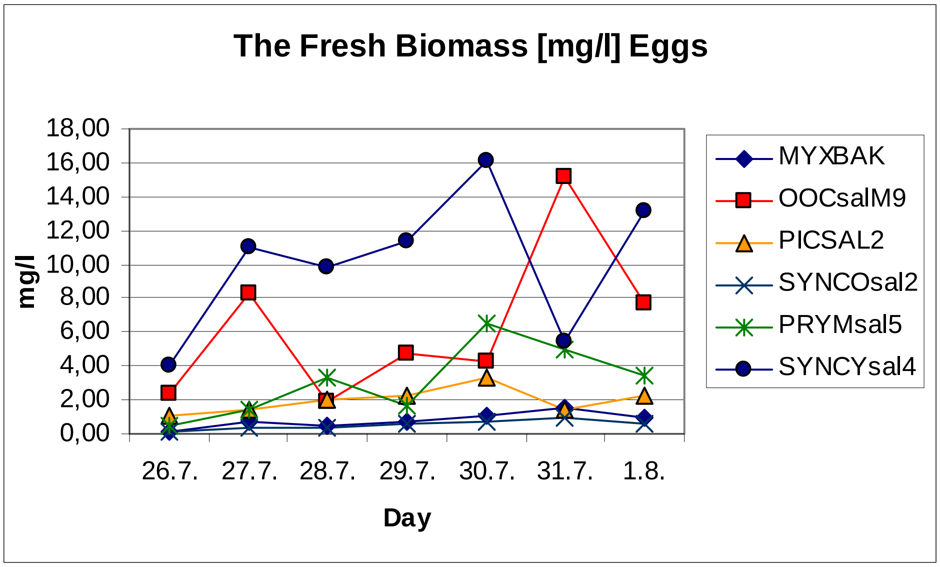

Figure 11. Biomass of individual species of algae in the treatment with eggs of *Artemia franciscana*. Symbols in Table 1.

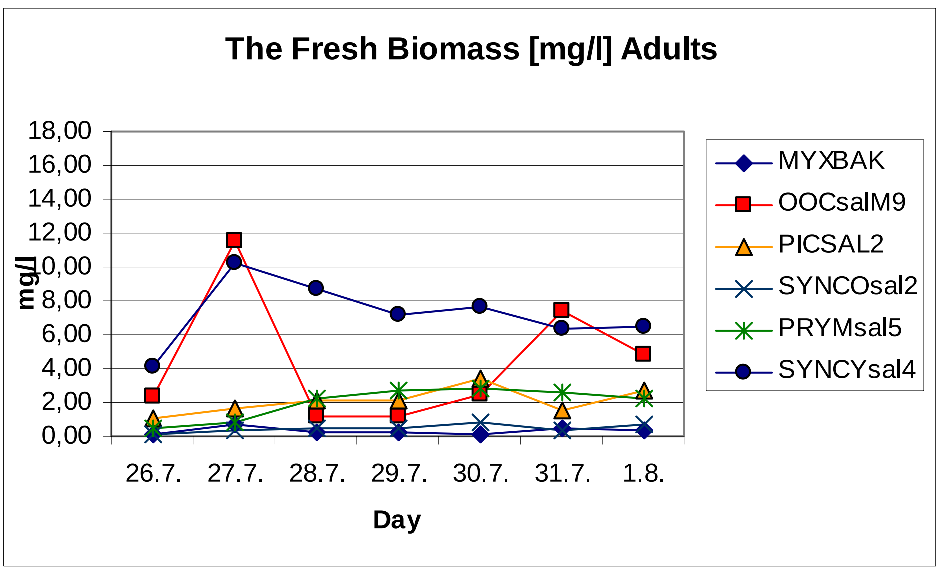

Figure 12. Fresh biomass of the individual algae species in the Adult *Artemia franciscana* treatment.

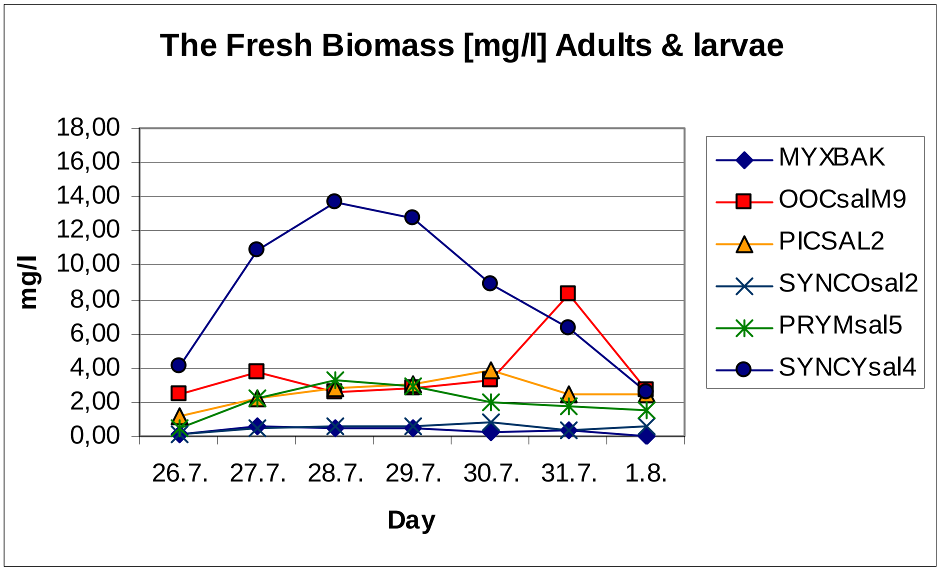

Figure 13. The fresh biomass of the individual algae species in set of treatment with Adults and larvae (rested eggs for hatching) of *Artemia franciscana*.

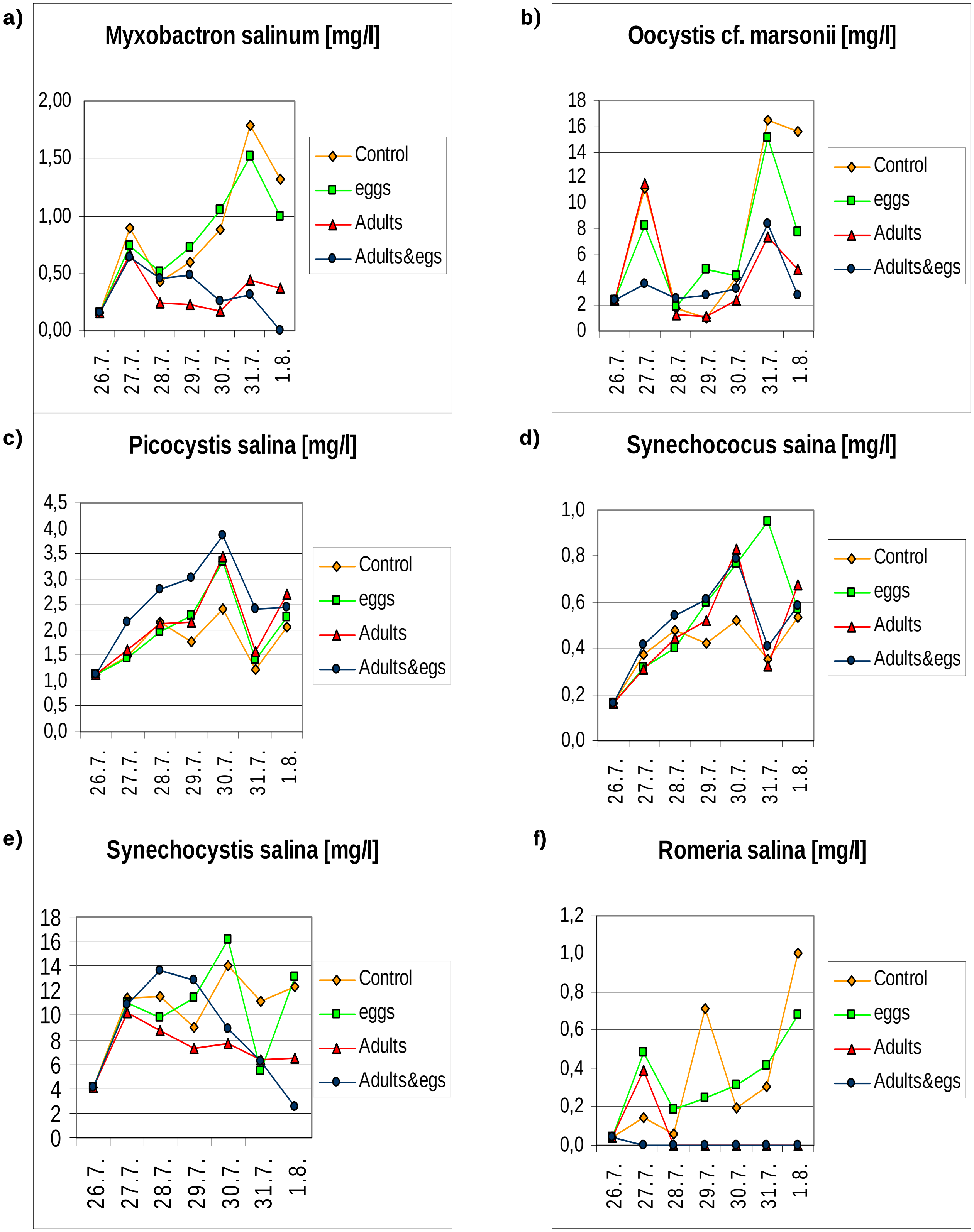

Figure 14. The fresh biomass of the Myxobactron salinum, Oocystis cf. marssonii, Picocystis salinarum, Synechococcus salinarum, Synechocystis salina and Romeria sp. at control and treatments.

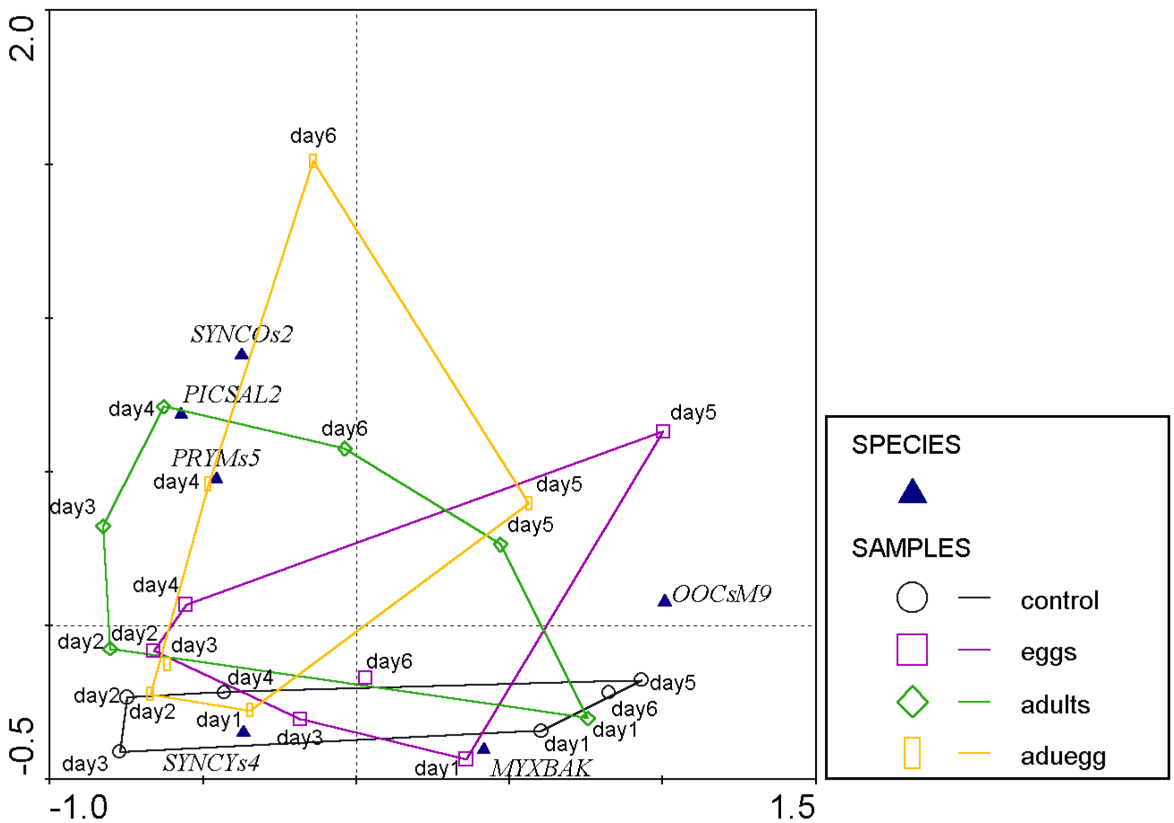

Figure 15. Microcosmos experiment 2 - The distribution of samples and species in the DCA ordination space of the first and second axis. The classification with envelopes is due to grazer treatment.

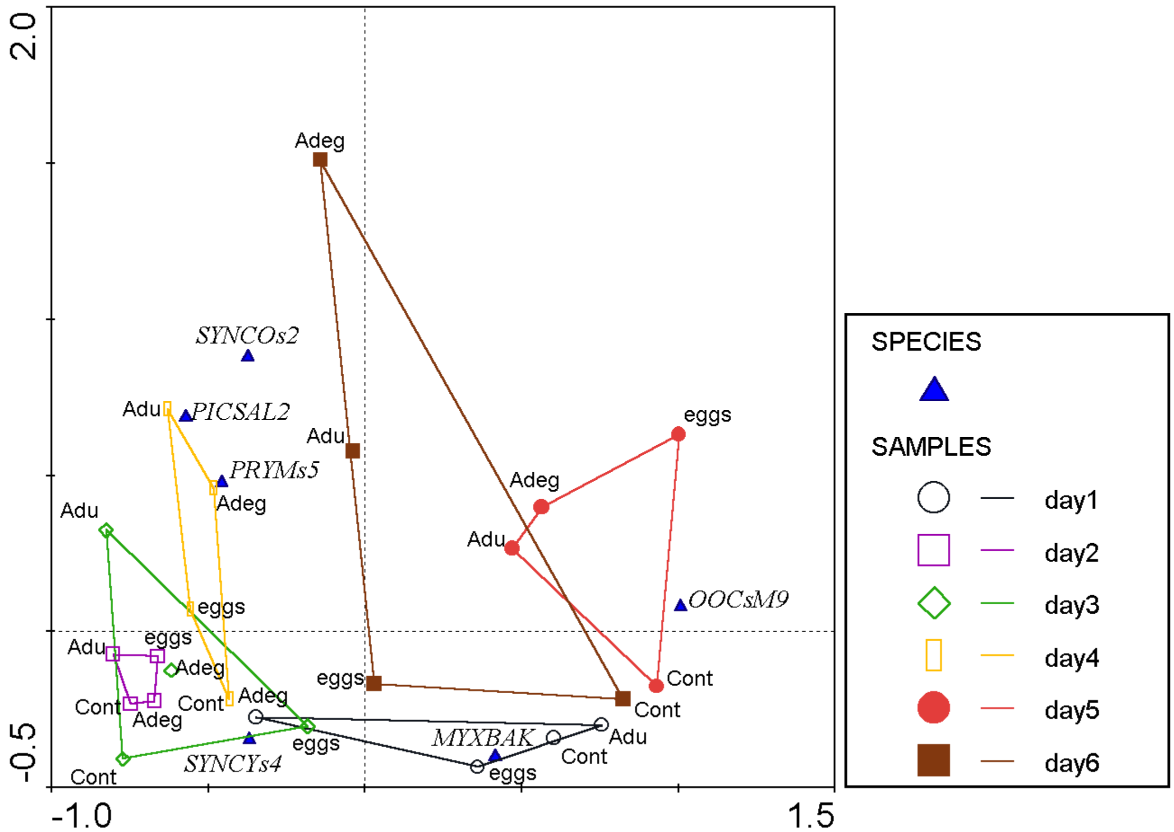

Figure 16. The distribution of species and samples in ordination space of the first and second axis of DCA. Classification envelops samples with the same time during the experiment.

Field experiment #1

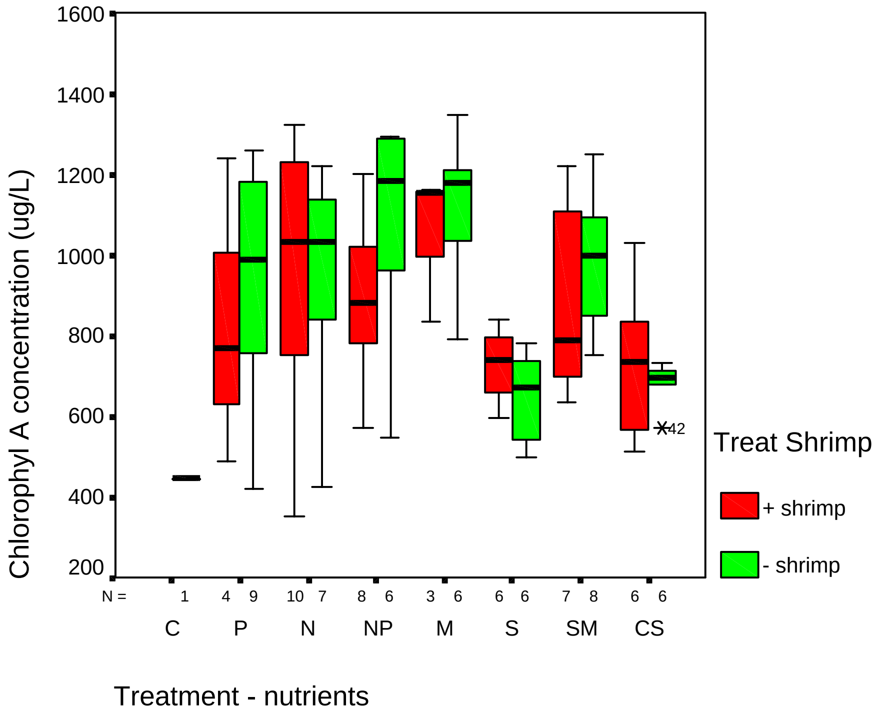

Figure 17. Chlorophyll a concentration under different treatments of enclosure experiment.

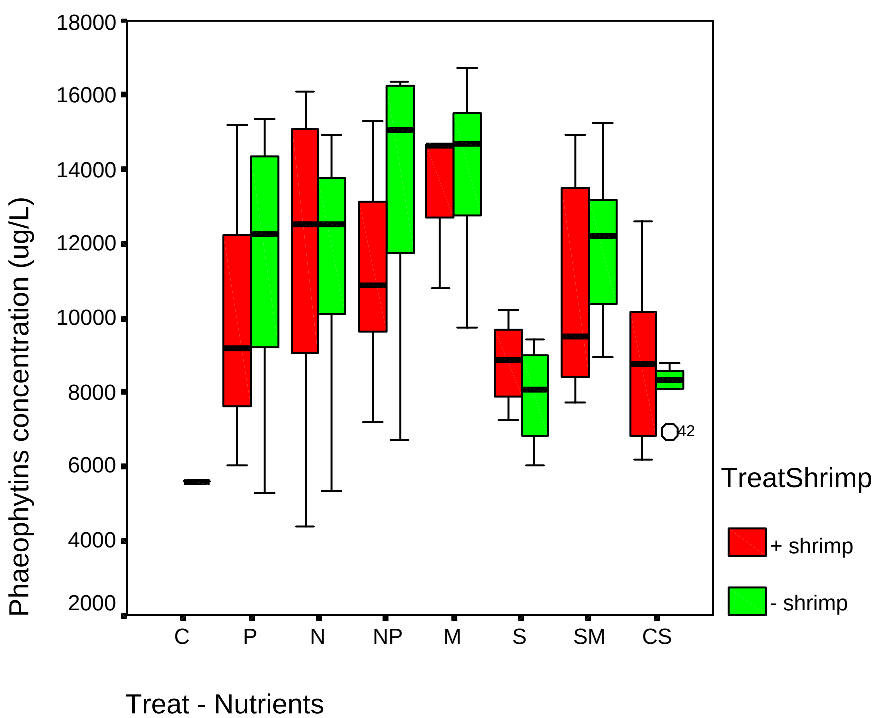

Figure 18. Phaeophytins concentration under different treatments of enclosure experiment.

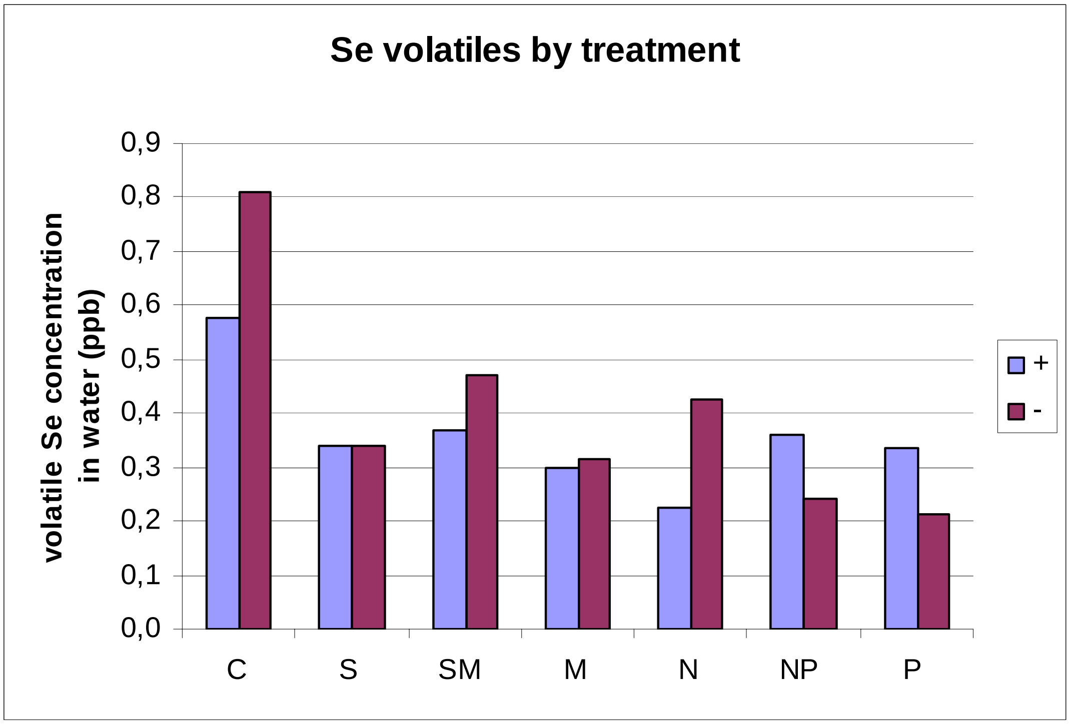

Figure 19. The volatile Selenium concentrations in water in different treatments (T.Fan and R.Higashi).

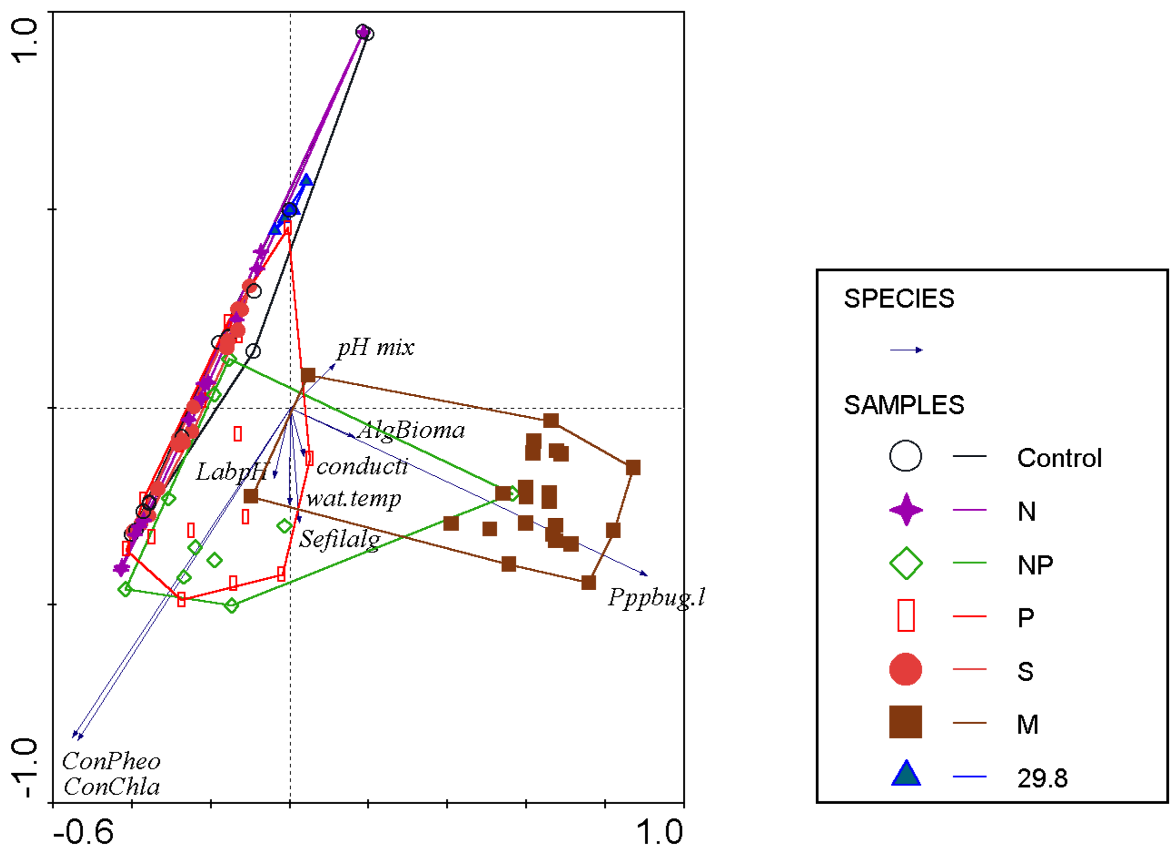

Figure 20. The PCA of the measured physical/chemical conditions at Field experiment 1 with enclosures on the pool C4 (Tulare drainage district).

FIELD EXPERIMENT #2

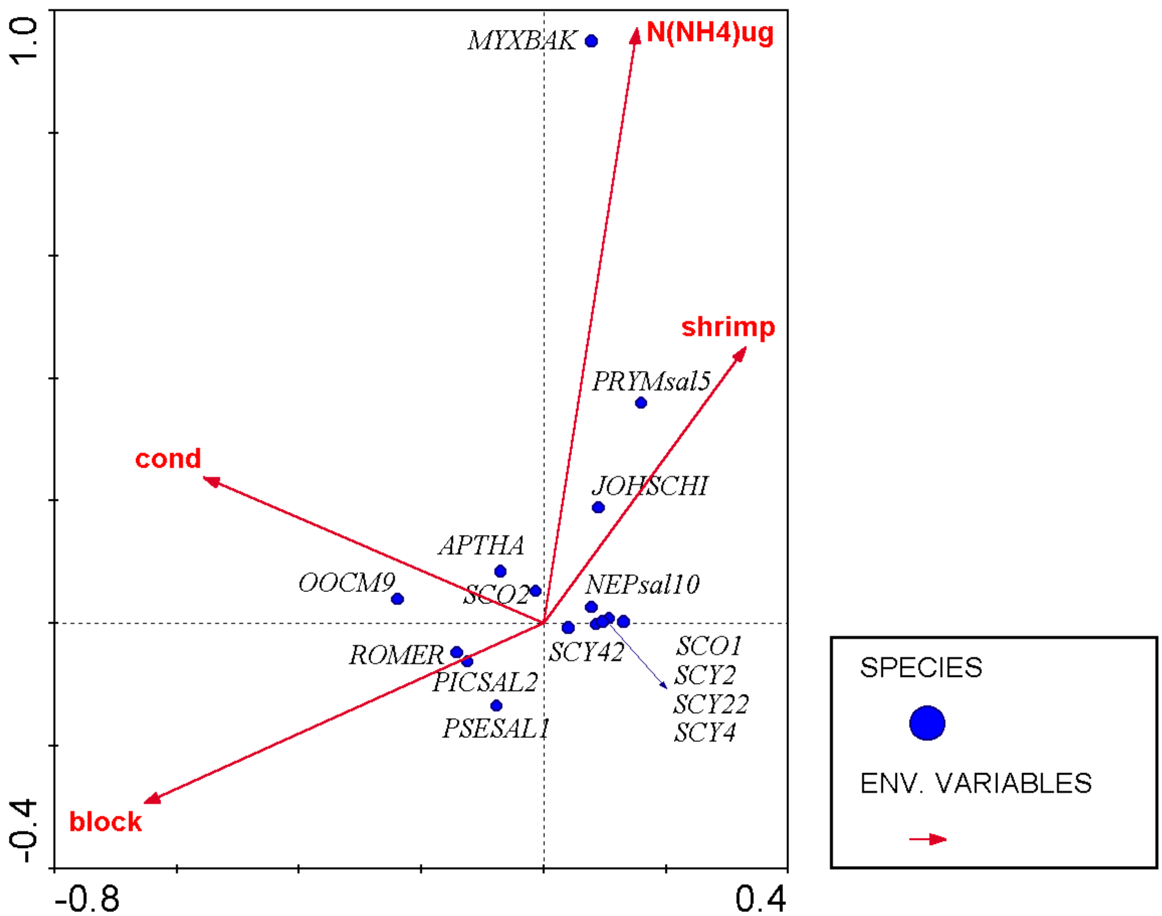

Figure 21. The distribution of species and factors in the space of the first and second ordination axes of CCA.

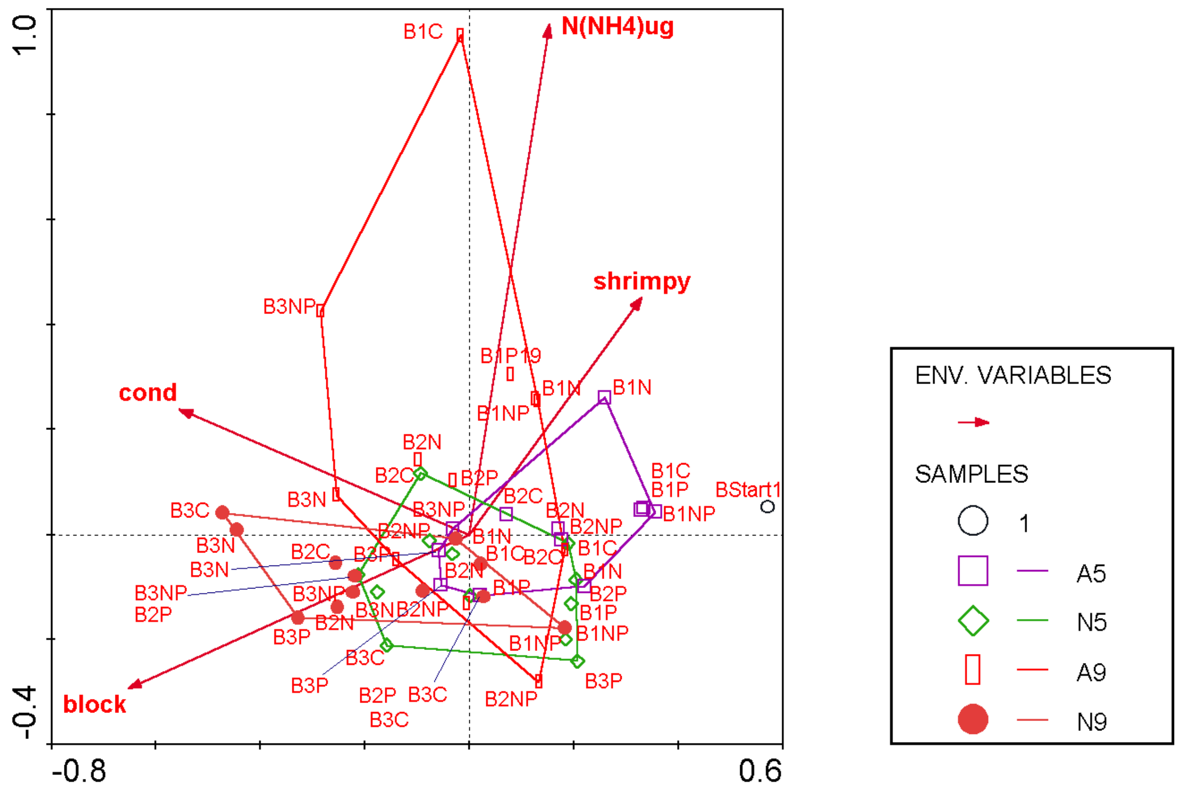

Figure 22. Distribution of Samples and factors in ordination space of first and second axis of CCA. Classification: A = Artemia present, N = No Artemia, 5 and 9 are days of experiment.

MICROCOSMOS EXPERIMENT 4.

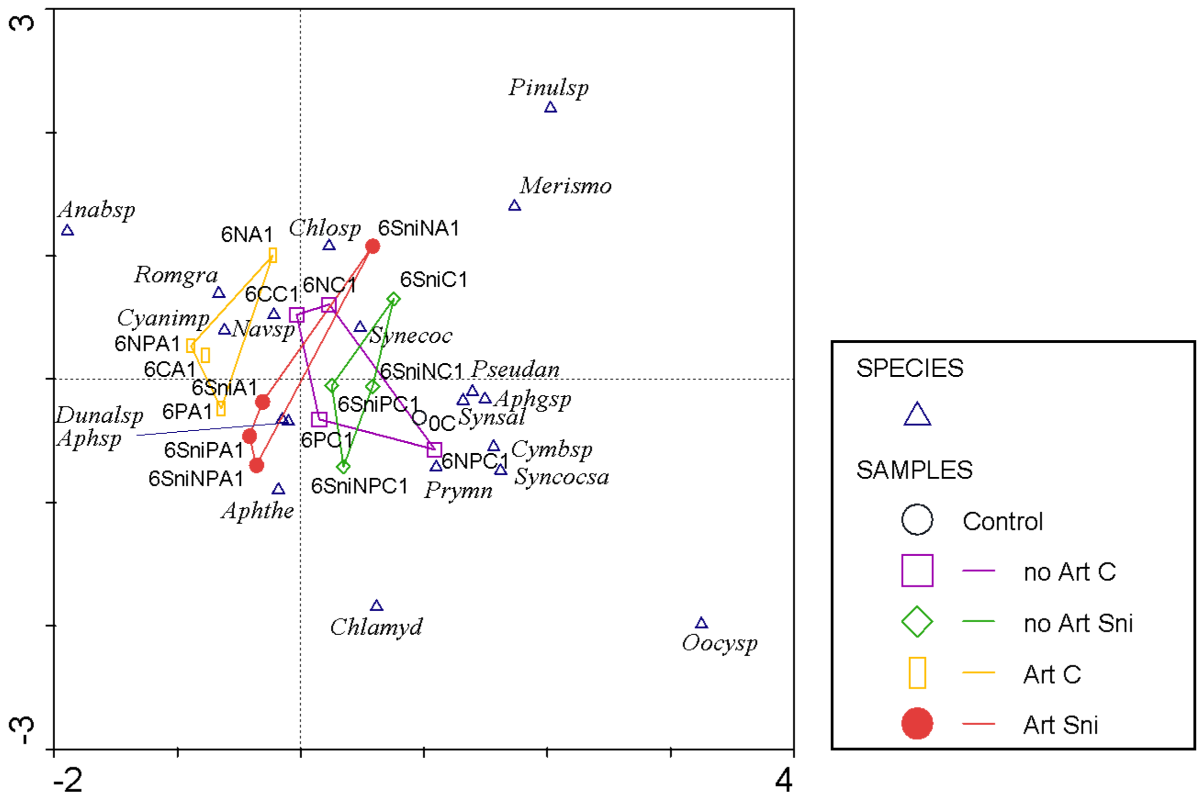

Figure 23. The distribution of species and samples over first and second ordination axes of DCA.The classification is done due to the Se and Artemia treatments.

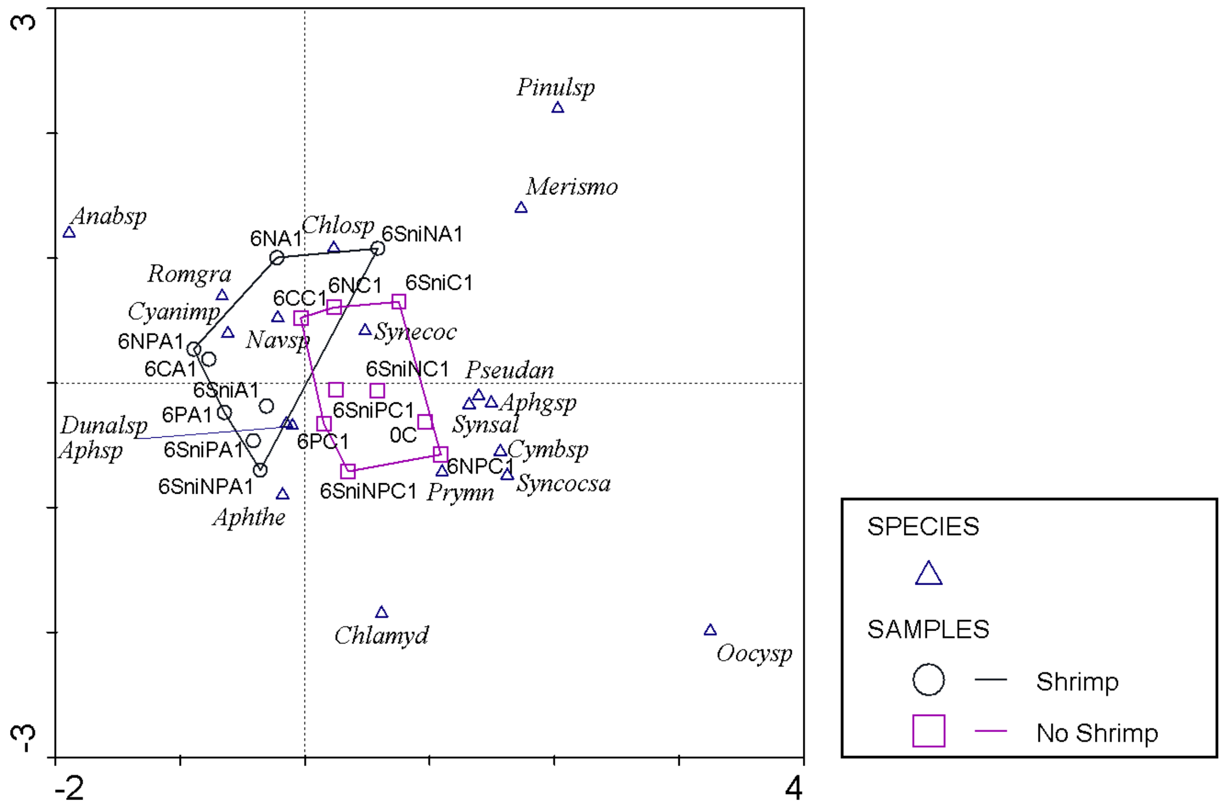

Figure 24. The distribution of species and samples in space of the first and second ordination axis of DCA The classification of samples is done due to the *A. franciscana* treatments.

Integrated Drainwater Management In the Central Valley

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ABSTRACT

Traditionally, the installation of drainage systems that discharge effluent to streams solved many of the problems associated with high water tables arising from deep percolation flows. Environmental damages linked to this effluent have led to restrictions on out of region discharges. Solutions to the drainage problem, consequently, have shifted to alternate management strategies, including source control, drainage water reuse on salt-tolerant crops, drainage reclamation, and in-region disposal options. Given the array of on-farm management decisions confronting growers and recognition of the physical links between these decisions and their potential environmental impacts, developing a management strategy that is both economically attractive and environmentally sustainable poses a significant task to any grower or policymaker.

Previous research (Schwabe, Knapp and Kan 2002) illustrated that a high level of agricultural production may be possible for some period of time in the Central Valley while still maintaining environmental quality. This current research illustrates the sensitivity of these conclusions to changes in various physical and economic factors that currently characterize the situation growers confront in the Central Valley. Under short term conditions that maintain hydrologic balance, yet not salt balance, grower profits are shown to be sensitive to changes in both cotton and surface water prices, two factors that have shown some volatility in recent years. In particular, given the importance of cotton in meeting the environmental drainage restrictions through its role as a potentially profitable reuse crop, the recent downward trend in upland cotton prices may threaten the ability of growers to meet the in-region drainage restrictions while maintaining reasonable profits. With respect to changes in the physical system, increases in groundwater salinity are shown to decrease grower profits, the magnitude of which is impacted by the degree to which growers shift into more efficient irrigation schemes and move more of their reuse acreage into wheat. Finally, it is shown that efforts to maintain salt balance in addition to hydrologic balance can reduce profits by approximately 11%.

INTRODUCTION

Currently, irrigated agriculture in the western part of the San Joaquin Valley (SJV) is operating as a semi-closed basin; surface water is imported for irrigation but external drainage is either not allowed or is greatly restricted. Finding a solution to this drainage problem, a solution that maintains both agricultural productivity and environmental quality, requires consideration of a broad array of biophysical management options. These options will likely include some combination of source control, drain water reuse, and in-region disposal methods. Examples of source control options include more uniform irrigation systems and crop-switching. Reusing the drainage water for crop production is another option, similar to source control, which can reduce waste emissions and conserve scarce freshwater supplies. Finally, in-region disposal methods include options such as evaporation ponds and solar evaporators. Identifying an efficient solution among these many different management combinations is a complex exercise that requires an understanding of both the relationships that exist between the options themselves and their impact on production and the environment. Furthermore, once a viable solution is identified, an understanding of the responsiveness of this solution to ever changing physical and economic factors can be useful to in the overall objective to informing management on how best to achieve agricultural productivity while meeting environmental objectives.

The objective of this research is to evaluate alternative management strategies confronting growers in the Central Valley with recognition of the current regional environmental restrictions associated with drainage water. Such strategies consist of a combination of land, crop, water type (surface and ground), irrigation system, and drainage disposal choices. Additionally, the responsiveness of these strategies to changes in both physical and economic factors is highlighted. Physical factors include the salinity concentration of the groundwater used for reuse irrigation, the amount of compensating habitat required for each acre of evaporation pond, and the imposition of a salinity balance constraint; economic factors include cotton and water prices. The empirical analysis consists of using a regional mathematical programming model of irrigated agriculture in the Central Valley.

THE STUDY AREA AND DATA

Our primarily focus will be on the Westland Water District (WWD) within the Central Valley. WWD consists of approximately 600,000 acres and is located in the agriculturally rich San Joaquin Valley. A high water table due to irrigation that takes place over the impermeable Corcoran clay layer affects the WWD. Initially, a system of drainage tiles were installed as a response to the high water table easing both the potential for waterlogging of the crops and the leaching of toxic contaminants from the soil surface. For a period of time, the drainage waters from these tile systems were exported out of the region along the federal San Luis Drain with an interim terminus at Kesterson Reservior. Following a series of environmental incidences in the early 1980s associated with these discharges, such out-of-region disposal relief was eliminated.

Our model includes six crops and five irrigation systems. The crops include cotton, processing tomatoes, wheat, lettuce, alfalfa, and bermuda grass. Non-water production costs and market prices for each cropping system are derived from both the UC Cooperative Extension Service (crop budgets) and Fresno County Crop Report (2000). The irrigation systems (and their respective Christensen Uniformity Coefficient) include Furrow 0.5 mile (CUC=70), Furrow 0.25 mile (CUC=75), Linear move sprinklers (CUC=85), Low-energy precise application system (CUC=90), and Subsurface drip (CUC=90). The costs of irrigating include amortized capital costs along with maintenance and operating costs. One option for disposal of drainage water is through the use of evaporation ponds. Our evaporation pond infrastructure construction and pumping costs come from Posnikoff and Knapp (1997). To calculate surface and groundwater cots, we assume a weighted-average of surface water prices in WWD for cost of surface water to growers. Groundwater pumping costs from the confined aquifer are calculated based on energy requirements (http://www.westlandswater.org/). Finally, to account for heterogeneous land quality characteristics, we will calibrate the model with attention to historic crop acreage allocations in WWD.

EFFICIENT MANAGEMENT

The first column in Table 1 reports results with no constraints on net flows to the water table. This serves as a baseline for the hydrologic balance analysis and also to help verify the model. In effect, it represents the situation in WWD prior to 1985 when growers were allowed to discharge their drainage into nearby waterways. As the results indicate, traditional irrigation systems are selected, there is no reuse, and deep percolation flows average slightly over 1 ft/yr, which is consistent with the historical average for deep percolation flows in this region.

The second column in Table 1 enforces the hydrologic balance constraint while not allowing reuse. This scenario mimics the WWD after the in-region disposal requirement but before the compensating habitat mandate imposed in 1995. The results suggest that efficient management entails both a substantial level of source control as well as in-region disposal of deep percolation flows to evaporation ponds. Total crop area declines to accommodate the evaporation ponds. Irrigation systems switch from traditional systems (furrow with ½ mile runs) to more uniform systems. Average deep percolation flows decline by over 50% due to both improvements in irrigation efficiency as well as reductions in applied water. The pond area amounts to 8% of the regional area. While the results show that significant returns to land and management can be sustained while maintaining hydrologic balance, social net benefits decline by 9% compared to the unconstrained case. In column three, the compensating habitat (CH) requirement is introduced with the intention to mimic regulations in the WWD post-1995. As shown, there is a dramatic shift to more uniform irrigation systems that contribute to a pronounced reduction in deep percolation flows as compared to the unconstrained case. There is also a reduction in surface water use and pond acreage, some of which was used for the compensating habitat. While still positive, social net benefits decrease by 34% as compared to column one.

Column four in Table 1 allows growers the choice of evaporation ponds (including compensating habitat) and/or reuse as a drainage disposal option. The results suggest that drainwater reuse offers great promise in maintaining agricultural production and hydrologic balance in the region. As shown, the area devoted to crop production with freshwater is reduced quite substantially to allow for reuse production. Compared to the baseline solution, reuse opportunities require little source control from growers. There is a 5% reduction in the use of the less uniform irrigation systems and, surprisingly, deep percolation flows increase slightly. While the details of the crop mix for freshwater crops is not shown, column three does illustrate that most of the drainwater reuse is applied to cotton. The constraint on total cotton acreage was binding at the upper bound of its observed historical levels, implying that additional acreage would lead to even larger gains. Cotton as a reuse crop is practical since it is both profitable and moderately salt tolerant (Mass and Hoffman 1977). In the presence of the reuse option, no evaporation ponds were chosen. Most noteworthy, though, is that with reuse the net returns to land and management are not only positive – implying that agriculture can be sustained in the region for some time - but also are only 5% below the unconstrained case.

Finally, column five in Table 1 illustrates the impacts of maintaining salt balance within the system. As shown, profits decrease by approximately 16% as compared to the baseline scenario. Also, you see a combination drainwater strategy consisting of both reuse and evaporation ponds (with their requisite compensating habitat).

CHANGES IN COTTON PRICES

An important outcome gleaned from Table 1 is that over the intermediate future (maintaining hydrologic balance yet not salt balance), growers seem to be able to meet the in-region drainage restrictions and still maintain agricultural productivity by engaging in reuse as means of drainage disposal. An important characteristic of this management response is the use of cotton as a reuse crop. The downward trend in the price for upland cotton by nearly 50% over the past 8 years does suggest there is a need for concern about the relative attractiveness of cotton as a reuse crop in the future. And while overall cotton acreage is slowly being allocated towards prima cotton, whose price is substantially higher and hasn't experienced as great a downward trend, upland cotton still comprises over 70% of cropped cotton acreage. Hence, it may be useful to understand the responsiveness of growers to changes in cotton prices under the in-region drainage restriction.

Table 2 presents results that illustrate the potential impacts on grower profits and management strategies in response to a change in cotton prices. The base year is 1999, the outcome of which is presented in first column. The hydrologic balance constraint is binding, but not the salt balance constraint. Three scenarios are evaluated by using the highest, average, and lowest yearly price for cotton over the 1997 to 2001 harvest seasons (California Agricultural Statistics 2002). The second column presents the results associated with using the highest price; column three with the average price; and column four with the lowest price, respectively. The prices are calculated by using a weighted average of prima and upland cotton prices based on their respective acreage as a percentage of the total harvested. The highest price is associated with the 1997 harvest year, while the lowest price is associated with the 2001 harvest year. The change in cotton prices would result in a near 37% decrease in grower profits. This is likely an upper bound on losses given we have put minimum bounds on crop acreage. It is evident, though, that change in cotton prices can have substantial impacts on the ability of growers to maintain agricultural productivity under an in-region disposal restriction.

CHANGES IN SALINITY CONCENTRATIONS

A concern with using groundwater as a long run source of irrigation is the possible increase in its salinity concentration. To illustrate the potential implications of such an outcome, Table 3 highlights the impacts on grower profit and management strategies from changes in groundwater salinity concentrations. As a point of reference, the results from the efficient solution from Table 1 (column 4) are presented in column 1. This "baseline" solution uses the current estimate of groundwater salinity concentration in WWD (10 ds/m) while maintaining hydrologic balance (but not salt balance). As shown, as the salinity concentration of groundwater increases from 10 to 20 ds/m, profits decrease by approximately 20%. The efficient response by growers to the increased salinity levels consists of both switching out of reuse acreage as a whole, and allocating more of the remaining reuse acreage to wheat production and less to cotton production. Such a response is efficient given that cotton becomes less of a profitable "reuse" alternative as the salinity concentrations increase and essentially begins to serve as simply a means for disposal (with very little if no positive profit potential). Without the potential for profit using reuse water, cotton loses its relative advantage and thus wheat becomes a less costly option for reuse.

CHANGES IN SURFACE WATER PRICES

An analysis of grower response to changes in surface water prices is presented in Table 4. Prices are calculated using weighted average water costs (www.westlands.org). Similar to Tables 2 and 3, the hydrologic balance constraint is binding but not the salt balance constraint. The baseline scenario using 1999 water prices under the in-region disposal restriction is presented in column one for means of comparison (from column four, Table 1). Columns three and four present the water costs in 2000 and 2001, respectively. Notice the increase in water costs relative to 1999 prices. These price increases translate into profit losses of 11% and 13%, respectively. Growers respond to the increased surface water price by switching to more reuse crop production and using less surface water in total, although the application rate per acre increases slightly. Notice the growers also switch to drip irrigation for surface water crops and reallocate the cotton acreage entirely to reuse production.

For comparison sake, the second column of Table 4 presents the results from a water price reflective of the 2001 "1963 Contract Water" rate. Given the expected fallowing of more land in the WWD which may reduce the overall demand for "Contract" water, and water markets that might be implemented in the future, it is arguable that some growers may be able to purchase water for reduced rates depending on the type of contract they hold. Our results indicate that lower water prices have marginal impacts on grower profits.

CHANGES IN COMPENSATING HABITAT REQUIREMENT

Finally, Table 5 presents the impacts on grower profits and management strategies from changes in the compensating habitat requirement when reuse is not an alternative. As a point of reference, Table 5 includes the solution consisting of the no compensating habitat requirement as well. Currently, the recommended ratio of compensating habitat (CH) to evaporation pond (EP) acreage is one to one (UC SD Program 1999), the results of which are presented in column 3. Currently, there has been some discussion of whether the 1:1 ratio is appropriate, and that perhaps a less stringent requirement would still meet the environmental objectives of provided necessary avian habitat. Columns 2 and 4 illustrate the implications on growers from a less stringent CH:EP ratio (0.5:1) and a more stringent CH:EP ratio (1.5:1), respectively. As shown, as the CH:EP ratio increases, grower profits decrease, as do water use and deep percolation flows. This is expected given that increases in the ratio essentially serve to increase the cost of drainage disposal to growers. Notice that while there is no change in the mix of crops produced, there is a substantial shift towards more uniform irrigation strategies as the ratio is increased. This result is also expected since the more uniform irrigation strategies become relatively less expensive to operate as the costs of disposal increase.

CONCLUSIONS

A regional economic model is developed to evaluate and compare alternative management strategies confronting growers in the WWD with recognition of the current regional environmental restrictions associated with drainage water. Given the outcomes that mimic conditions representative of 1999, sensitivity analysis is performed to illustrate the responsiveness of grower profits and management strategies to changes in critical physical and economic factors. For the baseline solutions calibrated to 1999 data, our results suggest some level of source control is efficient since deep percolation flows generate disposal costs and/or environmental damages. Absent reuse, a very high level of source control is efficient due to the relatively high cost associated with evaporation ponds. This is accomplished largely through adoption of highly uniform/high-cost irrigation systems and allocating some cotton acreage to reuse production.

While our empirical results imply that reuse appears to be an extremely promising solution to the drainage problem, much of the attractiveness of this solution relies on cotton as a somewhat profitable reuse crop. The results from this current analysis indicate that changes in cotton prices or the salinity concentration of the groundwater may threaten the attractiveness of this management strategy. From a temporal perspective, cotton prices have shown a downward trend in recent years and thus present a real concern in the short run for the apparent viability of achieving profitable agricultural production while meeting the in-region drainage disposal restriction. From a more long term perspective, increases in the salinity levels of the groundwater may cause a shift away from cotton as the reuse alternative and into some other less costly crop, such as wheat. Another concern over the long run is the build up and disposal of salts entering the system. Our results suggest that efforts to control salt buildup will also impact grower profits.

The impacts of changes in surface water prices and compensating habitat requirements are analyzed as well. Efficient responses to surface water price increases primarily consist of allocating more acreage towards reuse production using groundwater, and in particular tomato acreage. Alternatively, efficient responses to the changes in the compensating habitat requirement consist primarily of source control though employing more uniform irrigation strategies that result in substantially less water being applied and, consequently, a 77% reduction in deep percolation flows.

While our empirical analysis implies that a high level of agricultural production may be possible in the intermediate future while still maintaining environmental quality, this process is probably best answered with a dynamic analysis that is well beyond the scope of this study. Such a dynamic analysis will involve groundwater hydrology, as well as possible buildup of human and physical capital, which might substitute in full or part for hydrologic degradation.

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Table 1. Evolution of Baseline

		No Reuse Allowed		Reuse Allowed	
	Baseline	Without Compensating Habitat	With Compensating Habitat	Without Salt Balance	With Salt Balance
Profit	$311	$282	$206	$295	$262
Crop Production					
Total Acres	0.83	0.75	0.75	0.51	0.5
Cotton(%)	58	53	53	37	36
Tomatoes(%)	24	27	27	39	40
Wheat(%)	4	4	4	0	0
Lettuce(%)	6	7	7	10	10
Alfalfa(%)	8	9	9	14	14
Water (ac-ft)					
Water Use	3.28	2.52	2.05	3.18	3.17
Deep Percolation	1.23	0.57	0.19	1.21	1.21
Irrigation(%)					
FUR2	94			90	90
FUR4		76	13		
SPR					
LEPA					
LIN	0	17	80		
DRIP	6	7	7	10	10
Reuse Production					
Total Acres				0.32	0.25
Cotton(%)				91	88
Tomatoes(%)					
Wheat(%)				9	12
Lettuce(%)					
Alfalfa(%)					
Bermuda(%)					
Water(ac-ft)					
Water Use				3.85	3.8
total dp reuse:				1.89	1.86
Irrigation(%)					
FUR2					
FUR4				100	100
SPR					
LEPA					
LIN					
DRIP					
Land Disposal(acres)					
Evaporation Pond Acres		0.08	0.03		0.02
Compensating Habitat			0.03		0.02

F4 = furrow with 1/4 mile runs. Land areas and social net benefits are per regional acre. Irrigation system and crop specific results are percent of the respective crop or reuse areas. Water variables are average depths over the cropped areas in the crop production and reuse sectors. CH = Compensating Habitat

Table 2. Changes in Price of Cotton

	Price of Cotton			
	p_c= $1490 Baseline	p_c= $1560 High	p_c= $1280 Average	p_c= $1140 Low
Profit	$ 295	$ 303	$ 227	$ 191
Crop Production				
Total Acres	0.51	0.51	0.46	0.45
Cotton(%)	37	37	30	29
Tomatoes(%)	39	39	43	44
Wheat(%)				
Lettuce(%)	10	10	11	11
Alfalfa(%)	14	14	15	16
Water (ac-ft)				
Water Use	3.18	3.17	3.2	3.21
Deep Percolation	1.21	1.2	1.27	1.27
Irrigation(%)				
FUR2	90	90	89	89
FUR4				
SPR				
LEPA				
LIN				
DRIP	10	10	11	11
Reuse Production				
Total Acres	0.32	0.32	0.29	0.3
Cotton(%)	91	91	90	90
Tomatoes(%)				
Wheat(%)	9	9	10	10
Lettuce(%)				
Alfalfa(%)				
Bermuda(%)				
Water(ac-ft)				
Water Use	3.85	3.86	3.85	3.85
total dp reuse:	1.89	1.9	1.9	1.93
Irrigation(%)				
FUR2		9	10	100
FUR4	100	91	90	
SPR				
LEPA				
LIN				
DRIP				
Land Disposal(acres)				
Evaporation Pond Acres				
Compensating Habitat				

Table 3. Alternative Salinity Concentrations with Reuse

	Salinity Concentration of Groundwater			
	ec=10	ec=12	ec=15	ec=20
Profit	$ 295	$ 280	$ 259	$ 229
Crop Production				
Total Acres	0.51	0.55	0.56	0.63
Cotton(%)	37	42	43	49
Tomatoes(%)	39	36	36	32
Wheat(%)				
Lettuce(%)	10	9	9	8
Alfalfa(%)	14	13	13	11
Water (ac-ft)				
Water Use	3.18	2.9	2.51	2.17
Deep Percolation	1.21	0.93	0.57	0.27
Irrigation(%)				
FUR2	90	42		
FUR4		49	55	11
SPR				
LEPA				
LIN			36	81
DRIP	10	9	9	8
Reuse Production				
Total Acres	0.32	0.28	0.19	0.12
Cotton(%)	91	89	84	75
Tomatoes(%)				
Wheat(%)	9	11	16	25
Lettuce(%)				
Alfalfa(%)				
Bermuda(%)				
Water(ac-ft)				
Water Use	3.85	3.85	3.79	3.73
total dp reuse:	1.89	1.99	2.1	2.31
Irrigation(%)				
FUR2		11	16	25
FUR4	100	89	84	75
SPR				
LEPA				
LIN				
DRIP				
Land Disposal(acres)				
Evaporation Pond Acres				
Compensating Habitat				

Table 4. Changes in Price of Surface Water

	Price of Surface Water			
	p_w= 49.90	p_w= \$38.69	p_w= \$63.48	p_w= \$69.80
Profit	\$295	\$299	\$263	\$257
Crop Production				
Total Acres	0.51	0.51	0.32	0.32
Cotton(%)	37	37		
Tomatoes(%)	39	39	63	63
Wheat(%)				
Lettuce(%)	10	10	16	16
Alfalfa(%)	14	14	22	22
Water (ac-ft)				
Water Use	3.18	3.18	3.28	3.2
Deep Percolation	1.21	1.21	1.45	1.37
Irrigation(%)				
FUR2	90	90	84	84
FUR4				
SPR				
LEPA				
LIN				
DRIP	10	10	16	16
Reuse Production				
Total Acres	0.32	0.32	0.43	0.43
Cotton(%)	91	91	93	93
Tomatoes(%)				
Wheat(%)	9	9	7	7
Lettuce(%)				
Alfalfa(%)				
Bermuda(%)				
Water(ac-ft)				
Water Use	3.85	3.85	3.9	3.9
total dp reuse:	1.89	1.89	1.92	1.92
Irrigation(%)				
FUR2			7	7
FUR4	100	100	93	93
SPR				
LEPA				
LIN				
DRIP				
Land Disposal(acres)				
Evaporation Pond Acres				
Compensating Habitat				

Table 5. Changes in Compensating Habitat with No Reuse

	Compensating Habitat to Evaporation Pond Ratio			
	0:1	0.5:1	1:1	1.5:1
Profit	$ 282	$ 230	$ 206	$ 189
Crop Production				
Total Acres	0.75	0.75	0.75	0.75
Cotton(%)	53	53	53	53
Tomatoes(%)	27	27	27	27
Wheat(%)	4	4	4	4
Lettuce(%)	7	7	7	7
Alfalfa(%)	9	9	9	9
Water (ac-ft)				
Water Use	2.52	2.19	2.05	1.98
Deep Percolation	0.57	0.27	0.19	0.13
Irrigation(%)				
FUR2				
FUR4	76	13	13	9
SPR				
LEPA				0
LIN	17	80	80	84
DRIP	7	7	7	7
Land Disposal(acres)				
Evaporation Pond Acres	0.08	0.04	0.03	0.02
Compensating Habitat	0	0.02	0.03	0.03

Improving Water and Nutrient Management Practices on Dairies in the Southern San Joaquin Valley

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ABSTRACT

Many of the dairies in the San Joaquin Valley use a water flush system to clean the manure from free-stall barns. This flush water is collected and held in large ponds until it can be mixed with freshwater and applied to cropland as part of furrow or border irrigation practices. Due to the nutrients in the manure water, high irrigation and nutrient application efficiency and uniformity are important to minimize deep percolation of nitrates.

This two-year project investigated: (1) various management techniques (surge irrigation, furrow torpedoes, and reduction of field length) to improve furrow irrigation performance, and (2) controlling the timing of manure water additions during an irrigation set to improve the nutrient application efficiency and uniformity.

Surge irrigation use reduced the applied water during an irrigation event by 30 – 35%. Furrow torpedo use reduced the applied water by 15 – 25%. Reducing the field length (1250 ft. to 600 ft. in trial) was the most effective, reducing applied water by 40 – 50%. Delaying the addition of manure water to irrigation water until the advancing fresh water has nearly reached the end of the field allowed a lesser amount of nutrients to be applied more uniformly. In this study, delaying manure water additions until fresh water had reached the 1000' mark of a 1200' field allowed less than 50 lbs/acre of nitrogen to be applied (vs. 242 lbs/acre for a continual manure water addition strategy) at a distribution uniformity of 90% (vs. 64% uniformity for continual manure water additions).

INTRODUCTION

There are over 600 dairies in the southern San Joaquin Valley with a total animal population of well over a half-million cows. The fate of the dairy manure nutrients and concerns over groundwater contamination are major water quality and environmental issues in the San Joaquin Valley. Many of these dairies handle their manure with a combination of scraping and hauling of solid manure from corrals, and a water flush system of liquid manure of the free-stall barns and other dairy facilities. For a 1000 cow dairy, it is estimated that 50,000 gallons of liquid manure water is generated daily. This manure water is stored in ponds until it is mixed with freshwater and applied to fields using furrow or border strip irrigation. The most common crop irrigated with manure water is corn silage but other crops such as cotton and winter forage are also grown using manure water.

Operating furrow and border irrigation systems at a high irrigation efficiency and a high irrigation uniformity is a challenge. Irrigation efficiency is a measure of how much of the applied irrigation water is beneficially used. The primary beneficial use of irrigation is satisfying crop water needs. Inefficient irrigation uses are deep percolation – water draining below the crop's root zone – and tailwater runoff that is not reused. High irrigation efficiency indicates that most of the applied irrigation water goes to satisfy crop water needs. Irrigation uniformity is a measure of how evenly water is applied to a field. High irrigation uniformity means that all portions of a field receive nearly the same amount of water.

Irrigation efficiency of furrow and border irrigation systems is often low due to over-irrigation and poor irrigation system uniformity. No waters containing manure can leave the grower's property, and the standard practice is to generate minimal tailwater during irrigation. The major contributor to irrigation inefficiencies is deep percolation. Over-irrigation and poor irrigation efficiency is often the result of fields that are too long. A set amount of irrigation water is required to simply advance water to the end of the field. This is the minimum amount of applied water per irrigation event and this applied amount is often in excess of the water required to refill the crop's root zone; resulting in inefficient irrigation.

Poor irrigation uniformity of furrow irrigation systems – the predominant irrigation method on dairy field crops in the southern San Joaquin Valley – results in over-irrigation at the head of the field and potentially under-irrigation near the tail of the field. Over-irrigation, combined with irrigation non-uniformity, often results in significant deep percolation. Manure water additions to the irrigation water can therefore result in deep percolation of both water and nutrients.

PROJECT OBJECTIVES

1. Investigate and demonstrate the use of furrow torpedoes and surge irrigation to improve the irrigation water management of dairy manure water irrigation systems.
2. Investigate the effect of controlling the timing of manure water additions during irrigation events to improve manure water nutrient application uniformity and efficiency on dairies.
3. Extend the information developed in the project through field days and newsletters targeted at the dairies in the Southern San Joaquin Valley.

RESULTS

FURROW TORPEDOES

Furrow torpedoes are steel cylinders, often filled with concrete, which are dragged in the furrow to break up soil clods and smooth the soil surface.

They can be effective in allowing water to advance across a field more quickly; resulting in improved irrigation uniformity and improved irrigation efficiency. Torpedo use is beneficial after field preparation or cultivation. They are not effective if there is no cultivation to disturb the furrow between irrigations.

The impact of torpedo use for manure water irrigations was evaluated by comparing 3 blocks of 25 torpedoed furrows each with a similar number of furrows (75) that were not torpedoed. All furrows were 1250 ft. long. For continuous flow irrigation, the amount of water required for irrigation was reduced from 12.9" to 9.4" – a 27% reduction (Table 1). For surge irrigated fields (4 surge cycles), there also seemed to be an advantage to using torpedoes (Table 1) although Check 5 (surge irrigation / torpedoes) required more water for irrigation than did the non-torpedoed checks. There were field slope problems in Check 5, verified by surveying, and it was difficult to get water to the end of the field.

Torpedo use is not widespread in the San Joaquin Valley, primarily due to the difficulty and cost of their use. The torpedoes are dragged behind a tractor on a sled arrangement and it is often difficult to turn at the end of the field with the torpedoes attached. Some growers have solved this problem by having the sled and torpedoes connected so that they can be hydraulically lifted at the field ends. Because of these complications, furrows are usually torpedoed as a separate pass through the field – an added cost.

Alternatives to torpedoes are "packer wheels". Packer wheels are tires which are run in the furrows to break up soil clods, similar to the effect of torpedoes. The packer wheels can often be used in conjunction with other field preparation equipment and thus save making a separate pass through the field.

SURGE IRRIGATION

Surge irrigation is the on-off cycling of water during irrigation. This practice can improve irrigation uniformity by advancing water across the field while using less water. Research has shown an infiltration reduction on soil wetted by a previous surge cycle. This infiltration rate reduction is likely due to a sealing of the soil surface. Surge irrigation has not been previously investigated on manure water irrigated fields. Manure water contains a substantial amount of fine solids which may have a significant positive impact on surge irrigation performance.

Surge irrigation was evaluated by comparing 2 blocks of 25 furrows each, irrigated with continuous flow, with 4 blocks of 25 furrows each which were surge irrigated. Four surge cycles were used. Water was allowed to advance 1/4 of the way down the field (300') and then the water was transferred to another section of furrows. By the time the water was transferred back to the original section, water had infiltrated into the furrow. During the second surge, water was allowed to advance another 1/4 of the field (to 600'). Water was again transferred to another set of furrows. This continued for surge 3 (advance to 900') and surge 4 (advance to the end of the field – 1250'.

Surge irrigation use was effective in reducing the amount of water required to irrigate the field. For furrows not torpedoed, applied water was reduced from 12.9" to 9.1" – a 30% decrease, and from 12.9" to 8.4" – a 35% decrease (Table 1). For torpedoed furrows, results were mixed with applied water on one section of furrows being reduced from 9.4" to 7.8" – a 17% decrease (Table 1). On another check of 25 furrows, the torpedoed furrows required more water (9.4" vs. 10.5" – a 12% increase, see Table 1). Again, note that this check (Check 5) had field slope problems.

A reduction in applied water of 17 – 35%, using surge irrigation is respectable. It is likely that the excess applied water would go to deep percolation which could leach nitrates. It would seem that surge irrigation would therefore be a common practice for growers to adopt, but the furrow irrigation systems on most dairies do not lend themselves to surge irrigation.

Surge irrigation using freshwater is done using gated pipe and an automatic surge valve. Dairies seldom use gated pipe because the manure solids and trash (weeds, baling twine, etc.) in the water clog the discharge openings. Instead, dairies often use alfalfa valve(s) which discharge water into a block of furrows. An added complication is that the automatic surge valve has an internal, motorized, butterfly valve and this valve could easily become entangled with any trash in the water. To use surge irrigation on dairies now would require irrigators to manually open and close alfalfa valves – an increase in labor and management costs for irrigation.

REDUCTION IN FIELD LENGTH

The most effective change which can be made to improve irrigation and nutrient applications is to shorten the field length. San Joaquin Valley field lengths vary widely but a 1/4-mile field length is common. This is often too long a field to allow water applications to match crop water needs. As mentioned previously, the minimum irrigation application amount is determined by the amount of water needed to advance water to the end of the field. For example, if 6 inches of water is required to advance water to the end of the field but the crop water use since the last irrigation has been 4 inches, 2 inches of water would be lost to deep percolation. If nutrients are available to be leached, the excess water could be the vehicle for carrying them below the crop's root zone.

Shortening the field length allows a lesser irrigation amount to be applied during an irrigation set, more closely matching the water depleted from the crop's root zone and thereby increasing irrigation efficiency. Irrigation uniformity is also improved when shorter fields are used. The 1250 foot furrows were evaluated to see how much water would be required if field length was reduced to 600 feet (Table 2). Applied irrigation amounts could be reduced by 35 – 55% when field lengths were reduced from 1250 ft. to 600 ft.

Field length reduction has the greatest impact on irrigation performance, but it is also the most costly and inconvenient. To reduce a 1/4-mile length field to two 1/8-mile fields would require a new pipeline ($15,000 - $20,000 for a 40-acre field), a new road (a capital cost and land lost from production), and possibly new tailwater collection facilities. Shorter field lengths are also a significant inconvenience for equipment movement through the field. This would impact field preparation, cultivation, pest and weed control, and harvest activities.

TIMING OF MANURE WATER APPLICATIONS

Field tests were done to manipulate the timing of manure water additions to irrigation water during an irrigation event. The objectives of this are: (1) to improve the uniformity of nutrient additions, and (2) provide a method of applying smaller amounts of nutrients per irrigation event as compared to manure water additions during the entire irrigation event. This strategy hinges on infiltration characteristics varying during irrigation. The infiltration rate is high when water first comes in contact with a soil location and then decreases, often significantly, until a final, relatively constant, intake rate is reached. Due to the time required for water to advance across the field, water is in contact with the soil (intake opportunity time) at the head of the field for a significantly greater time than it is at the tail of the field. The result is greater infiltrated water at the head of the field than at the tail. The same is true of nutrient applications if manure water is added continuously to the irrigation water.

Irrigation events at a commercial dairy in Tulare County were evaluated. A tracer (sulfur fertilizer) was added to the irrigation water at various delayed times during the irrigation event. The sulfur fertilizer tracer turns the irrigation water milky in appearance and can be tracked as it moves down the furrow. From these tests, it was determined that addition of manure would start when clean irrigation water had advanced approximately 900 feet along a 1200-foot long field. This resulted in the manure water / freshwater mix advancing front catching the advancing front of the freshwater at the 1050 foot furrow distance. It took the clean irrigation water 4 to 5 hours to advance to 1050', but it took the delayed manure water advancing front less than an hour to reach the 1050' mark.

Water samples were also collected at frequent time intervals and at numerous spatial locations along the furrow. This sampling served two purposes. First, it traced the advance of manure water along the furrow and provided the spatial and temporal distribution of water quality during the irrigation event. Secondly, the sampling provided information on whether the quality of manure mixed water changed along the furrow length. In other words, does the nutrient content of the water moving along the furrow change due to solids settling out, etc.?

As part of the irrigation evaluation of the delayed manure water addition event, RBC flumes were placed in furrows to monitor furrow flow rate, the slope of the fields was surveyed and determined, and advance / recession measurements were gathered.

The results from the irrigation evaluation were used to provide inputs to a Two-Point Volume Balance furrow irrigation model which was used to determine infiltrated water amounts along the furrow and to determine the irrigation uniformity.

WATER QUALITY

The fresh irrigation water / manure water mix used for irrigation had 100 mg/l ammonium and 150 mg/l total nitrogen. As is standard with dairy manure waters, there was no nitrate in the manure water since the dairy manure ponds are anaerobic. The manure water used for irrigation was relatively low in solids since the dairy had a solids separator and a multi-pond manure handling system. There was no change in nitrogen content of the water sampled along the furrow. Once water containing manure reached a furrow location, the water's nitrogen concentration remained constant during the irrigation event.

INFILTRATION AND IRRIGAITON UNIFORMITY

The monitored irrigation event advanced water across the field quite rapidly – full advance occurred in approximately 5.6 hours. The average irrigation depth applied was 7.1 inches with irrigation uniformity of 64% (Table 3). As with many dairies in Tulare County, the irrigation systems are operated to minimize generation of tailwater. Therefore, once water advances to the end of the field, it is allowed to run only a short period of time before the irrigation set is switched. This results in the top end of the field receiving substantially more infiltrated water than the tail end of the field. For this irrigation event, the head of the field received approximately 9.4 inches of infiltrated water while the tail of the field received approximately 3.1 inches.

If manure water was added to the irrigation flows during the entire irrigation event, the uniformity of nitrogen application would be the same as the water application uniformity – 64%. The top end of the field would receive significantly more nitrogen than the tail of the field. Adding manure water during the entire irrigation event would result in the field receiving an average of 242 lbs. of nitrogen per acre (Table 3).

When manure water was added to the irrigation water after freshwater had advanced 900' along the furrow, the manure water application uniformity was increased from 64% to 69%. At least as importantly though, the average nitrogen application to the field was reduced from 242 lbs/acre to 86 lbs/acre (Table 3).

With the field data available for model verification, simulations of other irrigation and manure timing strategies were investigated. They included:

Simulation 1

Manure water additions began when freshwater reached 900 ft. along the furrow. Irrigation water was shut off one hour after it reached the end of the field. This strategy results in a nutrient application uniformity nearly the same as the irrigation uniformity (Table 3), but the average nitrogen application amount is reduced from 242 lbs/acre for the continuous manure water addition strategy to 102 lbs/acre for this delayed manure water addition practice.

Simulation 2

Freshwater is allowed to advance 1000 ft. along the furrow before manure water is added to the irrigation water. The irrigation supply is shut off shortly after water reaches the end of the field. The result of this practice is that a small amount of nitrogen (31 lbs/acre) is applied to the field and it is applied very uniformly (DU = 91%). This would be a good strategy if frequent, small applications of nitrogen were desired.

Simulation 3

In this delayed manure water addition strategy, manure water is added to the irrigation water after freshwater has advanced to 1000 ft. Irrigation is allowed to continue for 1 hour after water advances to the end of the field. This stategy allows the application of a limited amount of nitrogen to the field (49 lbs/acre) while applying it with a high uniformity (88%).

Table 1. Effects of surge irrigation and furrow torpedoes on furrow irrigation performance.

Check No.	Torpedoed	Continuous Flow	Surge Flow	Applied Water – in.
1	No	Yes		12.9
2	No		Yes	9.1
3	No		Yes	8.4
4	Yes		Yes	7.8
5	Yes		Yes	10.5
6	Yes	Yes		9.4

Table 2. Effect on irrigation performance of shortening field lengths.

Check No.	Irrigation Treatment	Field Length – ft.	Applied Water – in.
1	Not torpedoed / Continuous flow	1250	12.9
1	Not torpedoed / Continuous flow	600	7.1
2	Not torpedoed / Surge flow	1250	9.1
2	Not torpedoed / Surge flow	600	5.4
3	Not torpedoed / Surge flow	1250	8.4
3	Not torpedoed / Surge flow	600	5.2
4	Torpedoed / Surge flow	1250	7.8
4	Torpedoed / Surge flow	600	5.0
5	Torpedoed / Surge flow	1250	10.5
5	Torpedoed / Surge flow	600	4.8
6	Torpedoed / Continuous flow	1250	9.4
6	Torpedoed / Continuous flow	600	4.3

Table 3. Irrigation evaluation results of various manure water irrigation strategies. Field is furrow irrigated and 1200 ft. long.

Nutrient Application Strategy	Avg. Irrigation Amount (in.)	Irrigation Uniformity (DU - %)	Avg. Manure Water Infiltrated (in)	Manure Water Uniformity (DU - %)	Nitrogen Applied (lbs/ac)
Manure water added during entire irrigation	7.1	64	7.1	64	242
Manure water started when freshwater advance = 900’. Shut-off when advanced to end of field.	7.1	64	2.5	69	86
Manure water started when freshwater advance = 900’. Shut-off = end of field advance + 1 hr.	7.63	70	3.0	69	102
Manure water started when freshwater advance = 1000’. Shut-off when advanced to end of field.	7.1	64	0.9	91	31
Manure water started when freshwater advance = 1000’. Shut-off = end of field advance + 1 hr.	7.63	70	1.4	88	49

Phytoremediation of Selenium-Contaminated Drainage Sediments and Chemical Characterization of Potentially Ecotoxic Selenium Forms

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ABSTRACT

Extensive accumulation of selenium in drainage sediments represents a potential ecotoxic threat to wildlife. The goal of this work is to evaluate the efficiency and ecotoxic risk associated with different types of phytoremediation for attenuating Se contamination of drainage sediments. To achieve this goal, we tested different genotypes of Indian mustard (*Brassica juncea*) plants and a halophyte, *Salicornia bigelovii*, to determine (1) their efficiencies in removing Se from agricultural drainage sediment taken from the San Luis Drain and (2) the chemical speciation of Se present in plant material and sediment before and after phytoremediation. By determining total Se in sediment and in plant tissue, Se speciation, and total Se volatilized in a microcosm experiment, we will be able to assess the effectiveness of these different plant genotypes for Se phytoextraction and phytovolatilization and for alleviating Se ecotoxic risk.

Analysis of the sediment showed that it had an alkaline pH (8.42), a high EC value (100 dS m^{-1}), and high extractable concentrations of Na, S, Mg, Se, B, and Mo. In order to determine the highest ratio of sediment upon which these plants could survive, a preliminary pot experiment was carried out in the greenhouse. Indian mustard plants grown in pots in a greenhouse could only survive and grow on soil containing not more than 15% (v/v) of the sediment; at 10% sediment, Indian mustard shoot growth was 50% of that of the plants growing on no-sediment soil. This mixture was used for all additional experiments. *Salicornia* on the other hand, could tolerate up to 40% sediment in soil, with shoot growth at that level being as high as 64% of the no-sediment control. The concentration of Se in the shoots of Indian mustard plants increased upon increasing the ratio of sediment from 0 to 15%. Transgenic Indian mustard plants overexpressing γ-glutamylcysteine synthetase (γ-ECS) accumulated more Se in the shoots than any other genotype. Se concentration in *Salicornia* shoots grown on 10, 20, 30, to 40% sediment/soil were not significantly different. Greatest total Se was extracted by *Salicornia* grown on 10% sediment/soil because of its larger biomass. Shoot Se concentrations strongly correlated with the shoot S concentrations in Indian mustard transgenic lines overexpressing ATP sulfurylase (APS) and glutathione synthetase (GS), while the correlations in the transgenic ECS line and wildtype were insignificant.

Changes in the concentrations and ratios of inorganic/organic Se in the sediment/soil mixture after the treatment of plants were monitored by extraction of soluble Se from sediment/soil. After a 22-day period of Indian mustard treatment, water-extractable and total Se concentrations decreased 69% and 41% in the 10% sediment/soil mixture. Chemical speciation of the water-extractable Se showed that the proportion of selenate decreased, while that of selenite and organic Se increased. Future work will include experiments using microcosm to evaluate the Se volatilization in the presence/absence of plants, in order to build up a mass balance sheet of Se to determine the extent to which different plant genotypes can enhance phytoremediation of Se-contaminated drainage sediment through phytoextraction and phytoremediation.

INTRODUCTION

Large amounts of Se-contaminated sediments have been deposited in drainage canals in the Central Valley of California. For example, the drainage sediments in the Broadview Water District of the San Luis Drain contain ~50 to 60 mg Se kg^{-1}. Such high levels of Se pose a substantial ecotoxic risk to local wildlife. In this regard, the EPA has expressed serious concerns about future treatment of the drainage sediment in the San Luis Drain (Federal Register: March 23, 2001, V. 66, No. 57).

Another potential source of Se-contaminated sediments could arise from the use of constructed wetlands as a treatment system for removing Se from agricultural drainage water. Constructed wetlands have been shown to be highly efficient at removing Se from oil refinery wastewater (Hansen et al., 1998), and there is considerable promise in using them as a treatment system for agricultural drainage water, i.e., to decrease the ecotoxicity of solar evaporation ponds (Terry, 1998; Tanji, 1999). Our research at the Tulare Lake Drainage District (TLDD) flow-through constructed wetland at Corcoran showed that vegetated constructed wetland cells removed on average of 69% of the monthly mass Se input to each wetland cell (Lin and Terry, 2000). In the wetland study carried out at the Chevron oil refinery, almost 90% of the Se was removed from the inflow (Hansen et al., 1998). However, constructed wetlands suffer from the disadvantage that substantial quantities of Se are immobilized in the sediments. Most of the Se removed from drainage water at the TLDD wetlands was retained in the top 10-cm layer of sediment; for example, this Se sink accounted for up to ~56% of the total Se mass input in the wetland cell planted with cordgrass (Lin and Terry, 2000). Over three years, the Se concentration in the top 5-cm layer of sediment in the TLDD wetlands increased from their original background level of ~0.25 to ~10 mg Se kg^{-1}. This buildup of Se in wetland cells over time poses a potential ecotoxic risk to wildlife, which must be considered and dealt with if constructed wetlands are to be used as a cost-effective water treatment system for agricultural drainage water.

There is an urgent need to remediate the large amount of drainage sediments that already exist from drainage canals and will exist if constructed wetlands are to be used to treat agricultural drainage water. One way of achieving this cleanup is by phytoremediation. This is a relatively inexpensive and environment-friendly approach for Se removal (Terry and Banuelos, 2000). There are two ways in which plant- (or plant-microbe-) based systems can be used to remove Se from soils or sediments: phytoextraction and phytovolatilization. The effectiveness of phytoextraction has already been demonstrated in experiments carried out by Banuelos et al. (1997a). These researchers tested the ability of several different crop plants to remediate Se-contaminated soils, showing that Indian mustard vegetation reduced ~47% of the Se from the contaminated soil under field conditions (Banuelos et al., 1997b). Phytovolatilization is the use of plant-microbe systems to absorb selenate or selenite from soil and metabolize it to volatile Se forms. Measurements of volatilization at the TLDD wetland suggest that volatilization (by plants and microbes) can represent a significant pathway of Se removal: for example, up to 49% of the Se mass input was removed via volatilization in June of 1998 in the rabbitfoot grass cell. This observation is in line with our other Se volatilization studies in an upland ecosystem in which significant amounts of Se were volatilized from contaminated soil in a Salicornia field (Lin et al. 2000; Lin et al. 2002). The removal of Se from sediments by volatilization has distinct advantanges as a remediation technology. This is because volatilization removes Se from the local sediment-plant ecosystem into the atmosphere, thereby minimizing its entry into the food chain. The predominant form of volatile Se produced by plants and microbes, dimethyl selenide (DMSe), is ~600 times less toxic than selenate (Wilber, 1980). Even if volatile Se is deposited at sites distant from the point of origin, this is a relatively small problem in California because most of the state is deficient in Se, and farmers currently provide Se supplements to their sheep and cattle to overcome the deficiency. Thus, the development of Se volatilization as a strategy for the remediation of Se-contaminated sediments is an innovative and environment-friendly way for Se cleanup.

Research in our laboratory over the past seven or eight years has centered on developing plant-based systems for enhancing phytoextraction and phytovolatilization of Se. To this end, we have genetically engineered Indian mustard plants that have different potentials for Se phytoremediation. One such transgenic line (referred to as APS) overexpresses the gene encoding ATP-sulfurylase, the rate-limiting enzyme responsible for the reduction of selenate to selenite (Pilon-Smits et al. 1999). Transgenic Indian mustard lines overexpressing γ-glutamylcysteine synthetase (γ-ECS) and glutathione sythetase (GS) have increased production of γ-glutamylcysteine (γ-EC) and glutathione (GSH), compounds that are important in protecting against oxidative and metal/metalloid stresses (Zhu et al. 1999a and 1999b). GSH is a major component of the active oxygen scavenging system of the cell and protects plant cells from metal-related oxidative stress damage (Noctor and Foyer, 1998). The APS lines have superior abilities to 1) tolerate high concentrations of Se, and 2) take up 3-fold more Se per plant than the wild type. As the mechanism of the toxicity of selenite is reportedly similar to oxidative stress in yeast (Pinson et al., 2000), overexpressing γ-ECS and GS could increase the tolerance of transgenic plants to high Se. With regard to phytovolatilization, we identified *Salicornia bigelovii* as a plant species with an exceptional ability to volatilize Se; it has a rate of volatilization 15 times greater than other plant species tested in the field (Lin et al., 2000; Lin et al., 2002). This unique ability correlates with the fact that *Salicornia* accumulates a large proportion of Se in its tissues in organic forms (as does the APS line of transgenic Indian mustard referred to above).

A major goal of this work is to test the efficacy of using different phytoremediating plant systems for the remediation of drainage sediments. We are especially interested in comparing genetically engineered Indian mustard, and *Salicornia*, for their efficiencies in Se phytoextraction and phytovolatilization. Thus, we are currently investigating three different phytoremediation treatments, i.e., wildtype Indian mustard, genetically engineered Indian mustard, and *Salicornia bigelovii*, as well as the unplanted control. The experiments are being carried out by growing plants in drainage sediments contained in microcosms situated in a greenhouse. The microcosms are used because they avoid the need for special regulatory permission to do field tests with genetically modified organisms, they are far less expensive than field studies, and because they allow for more accurate control over experimental conditions. Indian mustard was chosen because of its known ability for Se phytoextraction (Banuelos et al., 1997b); it is tolerant to many toxic conditions, accumulates high concentrations of Se, and rapidly produces a large biomass. The use of the genetically engineered Indian mustard enables us to determine whether these transgenic plants, which have performed well under hydroponic conditions, are also capable of superior Se phytoremediation when planted in soil.

Salicornia was chosen because of its superior ability for Se phytovolatilization (Lin et al., 2002). Below we report the results of preliminary pot experiments designed to determine the proportion of Se-contaminated sediments to clean soil as well as other conditions necessary to carry out the microcosm and eventually field experiments.

MATERIALS AND METHODS

PLANT AND SEDIMENT MATERIALS

Wildtype Indian mustard (*Brassica juncea*) seeds were acquired from the North Central Regional Plant Introduction Station, Ames , IA (accession no. 173847). Different transgenic lines of Indian mustard were chosen to compare their efficiency for drainage sediment phytoremediation. The transgenic plants were developed by earlier researchers in our laboratory (Pilon-Smits et al., 1999; Zhu et al., 1999a and 1999b). APS lines (APS8 and APS9, overexpressing ATP sulfurylase) were chosen because of their higher tolerance and accumulation of selenate. ECS lines (ECS3 and ECS8, overexpressing γ-glutamyl-cysteine synthetase) and GS lines (GS2 and GS7, overexpressing glutathione synthetase) were selected for their increased contents of glutathione, beneficial in scavenging any oxidative stress caused by selenite (Pinson et al., 2000). The halophyte, *Salicornia bigelovii*, was chosen for its superior capacity for Se phytoremediation, especially phytovolatilization (Lin et al., 2000). The seeds were collected from Red Rock Ranch at Five Points, California in early November of 2002. Seeds were removed from the dried branch of the plants manually and stored at room temperature before use. Drainage sediment was collected from the San Luis Drain, east of Mendota, at depths ranging from 0-25 cm. After being air-dried at room temperature, the sediment was ground to fine powder to pass a 2-mm sieve before being mixed with clean potting soil.

GROWTH CONDITION OF THE PLANT MATERIALS

Indian mustard seeds were sown on a synthetic potting medium moistened with half-Hoagland's solution and kept at 4°C for 2 days to achieve uniform germination. After two weeks the plants were transferred to 6-inch pots containing compost (Genetic Mix) in the Oxford Greenhouse Facility at UC Berkeley and watered with half-Hoagland's solution every other day. Three weeks after germination, the plants were transferred to soils containing drainage sediment while being careful to maintain the root systems in the original potting soil. *Salicornia bigelovii* seeds were sown on a synthetic potting medium moistened with half-Hoagland's solution, covered with a transparent plastic lid and left in the greenhouse to germinate. Young plants were watered with half-Hoagland's solution until 1 month old. Older plants were then watered with artificial sea water every other day. The growth conditions of the greenhouse were 22±2 °C and 16 h light.

POT EXPERIMENT

Three week-old Indian mustard plants were transferred into 12-inch pots containing clean potting soil, and potting soil containing different ratios of sediment in clean soil. Plants grown in clean soil were irrigated with half-Hoagland's solution regularly, while those grown in soils containing sediments were watered with deionized water to avoid further buildup of salinity. A plastic tray was placed under each pot to collect the leachate, which was returned to the same pot in each case to avoid the leaching of Se and other salts. On the 10th and 22nd days, the plants were harvested and their shoots washed with clean deionized water; they were then dried in an oven at 60°C for two days. The days of harvest were chosen according to the development stage of the plants: the start of bolting and the end of production for more biomass. After drying, the samples were weighed and ground into a fine powder for the measurement of Se and S contents. Eight-week-old *Salicornia* plants were transferred to 6-inch pots containing clean potting soil or different ratios of sediment vs. clean soil. The plants in clean soil were watered with half-Hoagland's solution or artificial seawater; those in sediments were watered with deionized water. A plastic tray was placed under each pot for the collection of leachate, which was returned to the pot to avoid the loss of any salts from the sediment. After 45 days the plants were harvested, washed in de-ionized water and dried for the determination of Se. The sediment-soil was left to dry in the greenhouse, removed of any plant debris and gravel, well mixed, and passed through a 2-mm sieve. Soil samples were then collected for the determination of total and extractable Se as described below.

ANALYSES OF PLANT AND SEDIMENT SAMPLES

Total Se concentrations in plant and sediment/soil samples were determined following the procedures described in USEPA Methods 3050B (USEPA 1996). The electrical conductivity (EC) values of the sediment were determined by 1:1 soil-to-water method, using an Orion Model 150 conductivity meter. The water-extractable concentrations of different kinds of metals were determined in the extract of 1:1 soil-to-water solution using inductively coupled plasma atomic emission spectrometry (ICP-AES). The speciation of Se in the sediment was carried out according to Zhang et al. (1999). The statistical analyses (one-way

ANOVA, Pearsons product's moment correlation) were performed using SAS Enterprise Guide software (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

PROPERTIES OF DRAINAGE SEDIMENT

Several chemical properties of the drainage sediment were analyzed. The sediment had an alkaline pH (pH 8.42) and a high EC value (100.5 dS m^{-1}). Total Se concentration in the sediment was high (~60-70 mg kg^{-1}) compared to the average Se concentration in most soils, which ranges from 0.1 to 4 mg kg^{-1} (Kabata-Pendias and Pendias, 1992); up to 23% of the total Se is extractable (Figure 1). The sediment was also analyzed for the concentrations of 17 elements (Figure 1): sodium (Na), sulfur (S), calcium (Ca), iron (Fe), potassium (K), and magnesium (Mg) were present at high levels compared with soils from the same area (e.g., compared to a San Joaquin standard reference soil from NIST, no. 2709). The water extractable concentrations of these elements showed that the predominant solutes were Na (19.04±0.11 mg g^{-1} sediment), S as sulfate anion (7.98±0.12 mg g^{-1} sediment), Mg (1.88±0.02 mg g^{-1} sediment), and Ca (0.28±0.04 mg g^{-1} sediment). The soluble concentrations of boron (B) and molybdenum (Mo) are considered to be high and are probably toxic for plant growth (Figure 1B): B toxicity has been reported in soils containing 20-50 mg kg^{-1} extractable B, and Mo toxicity at extractable Mo levels in soil of 0.2 mg kg^{-1} (Peverill et al. 1999). Cobalt (Co), copper (Cu), manganese (Mn), nickel (Ni), phosphorus (P), lead (Pb), and zinc (Zn) were present at lower concentrations (Figure 1B).

GOWTH OF INDIAN MUSTARD AND SALICORNIA PLANTS ON SEDIMENT/SOIL

Since the Se-contaminated sediment contained high levels of salts, Se, and other trace elements such as boron, plant growth was likely to be severely inhibited. A pot experiment was carried out in the greenhouse in order to determine the optimum ratio of sediment to clean soil for the establishment of Indian mustard. Young Indian mustard plants were transplanted into soils containing a range of sediment to clean soil proportions varying from 0 to 40%. Indian mustard plants could not survive in soils with more than 20% sediment (data not shown). The growth of two genotypes of Indian mustard, wildtype and APS8, grown on 0 to 15% sediment/soil mixtures for 14 and 28 days is shown in Figure 2; shoot dry weights decreased with increasing proportion of sediment. After 28 days the APS line had 2-fold higher shoot biomass than the wildtype grown on 15% sediment/soil mixture (Figure 2B). However, half of the plants growing on 15% sediment exhibited severe growth retardation, and the leaf margins and shoot tips exhibited necrosis most likely due to B toxicity (Marschner, 1995). Therefore, 10% sediment/clean soil is considered to be optimal for for the establishment of Indian mustard plants.

When all the Indian mustard genotypes were compared at one time, the results showed that

plants growing on 10% sediment in clean soil exhibited a 50% decrease in shoot growth on average compared to growth on clean soil (Figure 3A and B). The transgenic line APS9 performed slightly better than other genotypes at 10 days and continued to be better until 22 days; however, the differences are not statistically significant.

Salicornia exhibited a higher tolerance than Indian mustard to sediment. Because *Salicornia* is a halophyte, the plants grew better on the highly saline sediment-soil mixture than on the low-salt no-sediment soil (Figure 4). Plants were able to survive and grow on 10 to 40% sediment/soil for the 45-day growth period. Shoot dry weights of plants growing on 10%, 20% and 30% sediment were 2-, 1.8-, and 1.2-fold greater than the control, respectively (Figure 4). At 40% sediment, only half of the plants survived, and there was a 36% decrease in shoot dry weight compared with control. No plants survived when the sediment proportion reached 50%.

ACCUMULATION OF SELENIUM IN INDIAN MUSTARD AND *SALICORNIA* PLANTS

Determination of Se concentrations in the shoots of Indian mustard plants growing on sediment/soil proportions ranging from 0 to 15% sediment showed that shoot Se concentrations increased with increase in sediment percentage (Figure 5A and B). No significant differences were observed for shoot Se concentrations between the wildtype and APS line. Selenium concentrations in the shoots of both wildtype and APS8 grown on the sediment for 28 days were half those at 14 days, probably due to the dilution effect as plants increased in size.

Among the transgenic lines, the ECS lines had the highest Se concentrations and accumulated the most Se, both at 10 days and 22 days (Figure 6A and B). ECS3 and ECS8 lines had 2.4- to 3.3-fold higher Se concentrations, and 2.1- to 2.8-fold higher Se accumulation, in their shoots than the wildtype, respectively. The APS8 line, after 10 days, accumulated 47%, and after 22 days 96% higher Se concentrations than the wildtype growing on 10% sediment. The APS9 line did not have higher shoot Se concentration than wildtype during the whole period of treatment, but due to its higher shoot biomass, accumulated 30 to 40% more amount of Se than the wildtype. One of the GS lines, GS2, had

89% and 65% higher Se concentrations in the shoot than wildtype after 10 and 22 days of growth on the sediment. However, the final accumulation of Se in both GS2 and GS7 lines were not significantly higher than the wildtype, taking into account of the size of the plants.

Because the shoot biomass of *Salicornia* decreased with the increase in sediment/soil proportions from 10 to 40% (Figure 4), the amounts of Se accumulated in shoots decreased accordingly (Figure 7A). Selenium concentrations on the other hand, did not show very much variation from each other at the different sediment/soil proportions (Figure 7B). The optimal percentage of sediment in soil for establishing *Salicornia* was 10%.

As selenate is taken up and assimilated via the sulfur (S) assimilation pathway, there is usually a strong correlation between Se and S concentrations in plant tissues (Terry et al., 2000). Furthermore, APS, ECS, and GS lines are known to accumulate higher Se and S concentrations in their shoots than wildtype (Pilon-Smits, 1999; Zhu et al., 1999a and 1999b). In the present work, ECS plants accumulated significantly higher concentrations of Se and S (37.16±2.10 mg Se kg^{-1} dw, 23.40±0.79 g S kg^{-1} dw) than APS (19.34±4.45 mg Se kg^{-1} dw, 10.82±2.11 g S kg^{-1} dw) or GS (24.29±4.51 mg Se kg^{-1} dw, 13.19±2.39 g S kg^{-1} dw) plants, which in turn had higher Se and S concentrations than wildtype (12.30±1.15 mg Se kg^{-1} dw, 8.01±0.70 g S kg^{-1} dw). However, positive correlations of Se with S were obtained only for the shoot tissues of APS (Figure 8B, $r = 0.98$, $P < 0.01$) and GS (Figure 8D, $r = 0.99$, $P < 0.01$) lines; there were no significant correlations of Se with S in the ECS or wildtype plants (Figure 8A and C). There was some indication that APS and GS plants were able to take up selenate selectively over sulfate. This is based on the fact that these lines had higher [Se]/[S] ratios in their shoot tissues than ECS or wildtype, i.e., 1.842×10^{-3} for APS and 1.841×10^{-3} for GS compared to 1.588×10^{-3} for ECS and 1.535×10^{-3} for wild type.

SPECIATION OF WATER-EXTRACTABLE SOIL SELENIUM

A major concern of phytoremediation is its impact on the transformation of Se chemical form in the sediment. Se, like S, can exist in –II (selenide Se^{2-}), 0, -IV (selenite SeO_3^{2-}) and –VI (selenate SeO_4^{2-}) oxidation states. In order to determine changes in the proportions of these chemical species after the treatment of different genotypes of Indian mustard, chemical speciation of the soluble Se was performed.

The result in Table 1 showed that after 10 and 22 days of treatment with different genotypes of Indian mustard, both total and water-extractable Se concentrations in the sediment have decreased significantly to about 60% and 30% of their original concentrations in the 10% sediment. Moreover, the percentages of organic Se and selenite in the water-extractable fraction of Se in the sediment/soil increased from 8% and 6% in the original sediment/soil mixture to 19% and 23% after 22 days of the treatment with Indian mustard. On the other hand, the percentage of selenate decreased from 86% to 58%. These data clearly demonstrated that in the process of phytoremediation changes of ratios between different chemical species of Se occurred, the ratio of inorganic Se (selenate and selenite) decreases and the ratio of organic Se increases.

FUTURE WORK AND PERSPECTIVE

To this point, we have shown that the Indian mustard plant and *Salicornia bigelovii* are capable of extracting Se from the sediment/soil, if given on an appropriate ratio of sediment to soil. These plants not only extract and accumulate Se in their shoots, but are also recognized as being able to volatilize Se. A mass balance sheet of Se in the sediment before and after the treatment of plants needs to be built in order to access their capacity in Se volatilization. To achieve this end, microcosm experiments will be carried out in the greenhouse.

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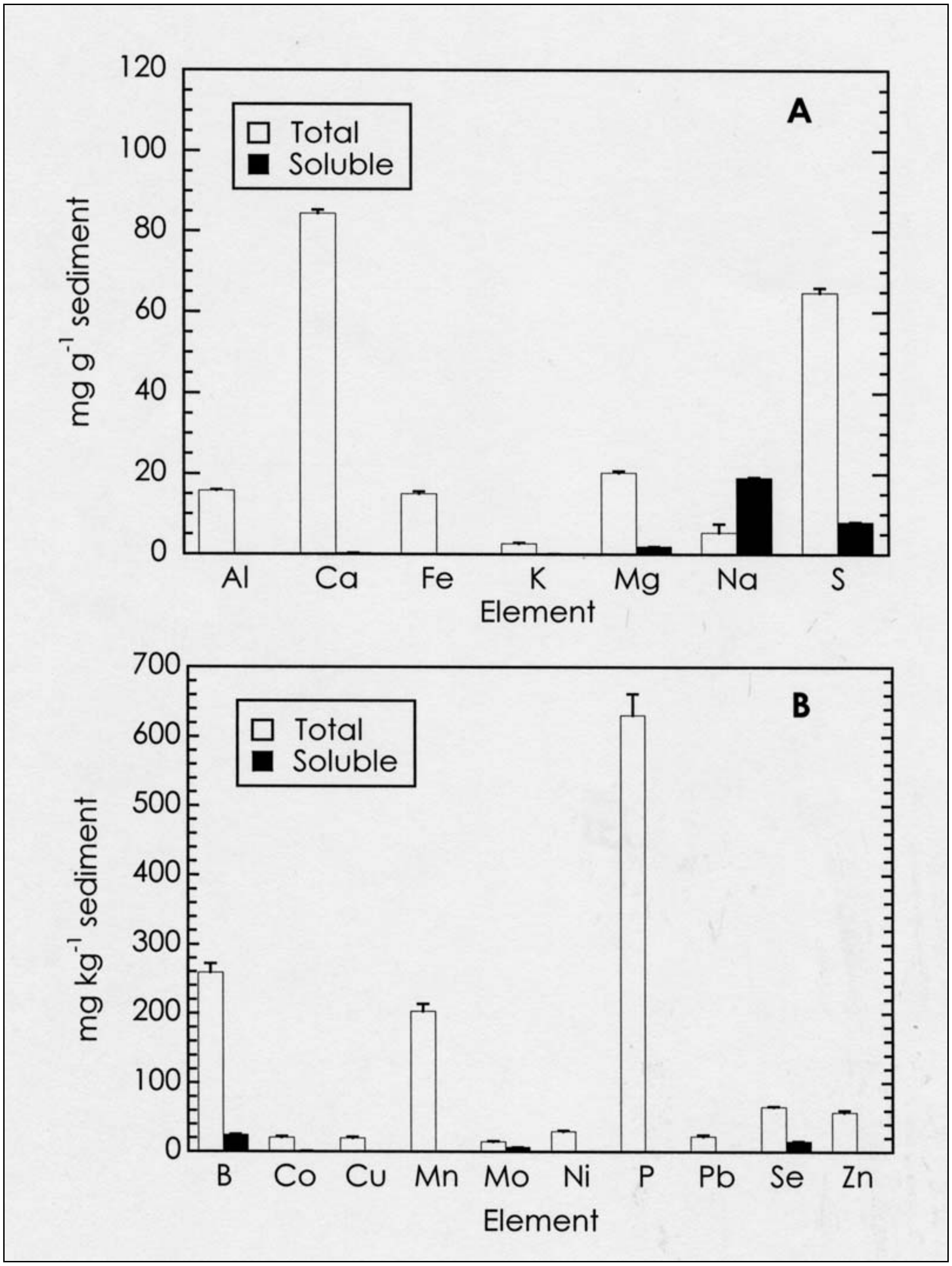

Figure 1. Concentrations of 17 elements in the sediment from San Luis Drain. Total and water-soluble concentrations of A) aluminum (Al), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na) and sulfur (S) are expressed in mg g^{-1} sediment, and B) boron (B), cobalt (Co), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), phosphorus (P), lead (Pb), selenium (Se), zinc (Zn) are shown in mg g^{-1} sediment. Bars represent the mean and s.e. of 3 samples.

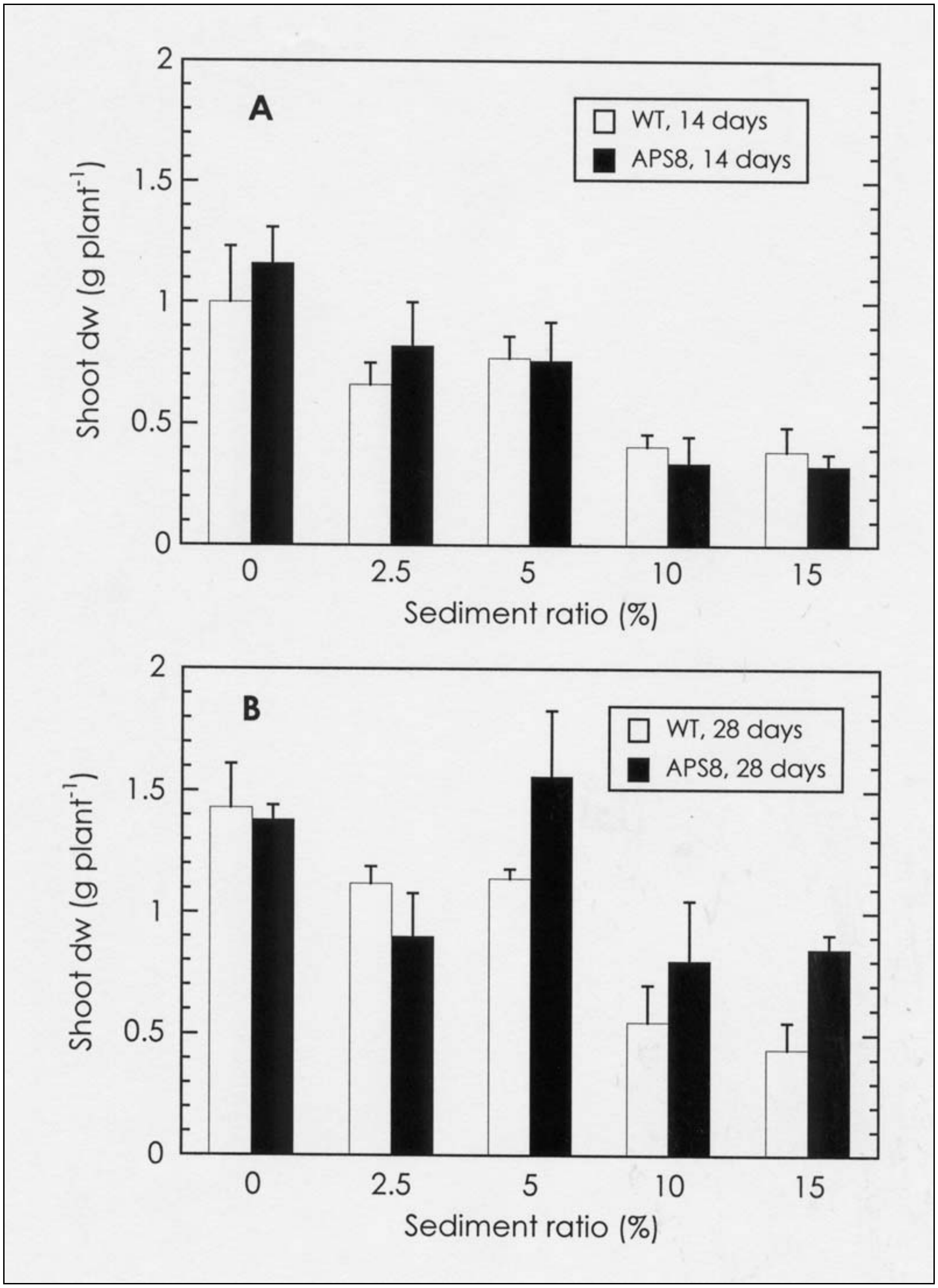

Figure 2. Growth of wildtype and transgenic (line APS8) Indian mustard plants on different ratios of sediment/soil mixture for (A) 14 and (B) 28 days. Bars represent the means and s.e. of three samples.

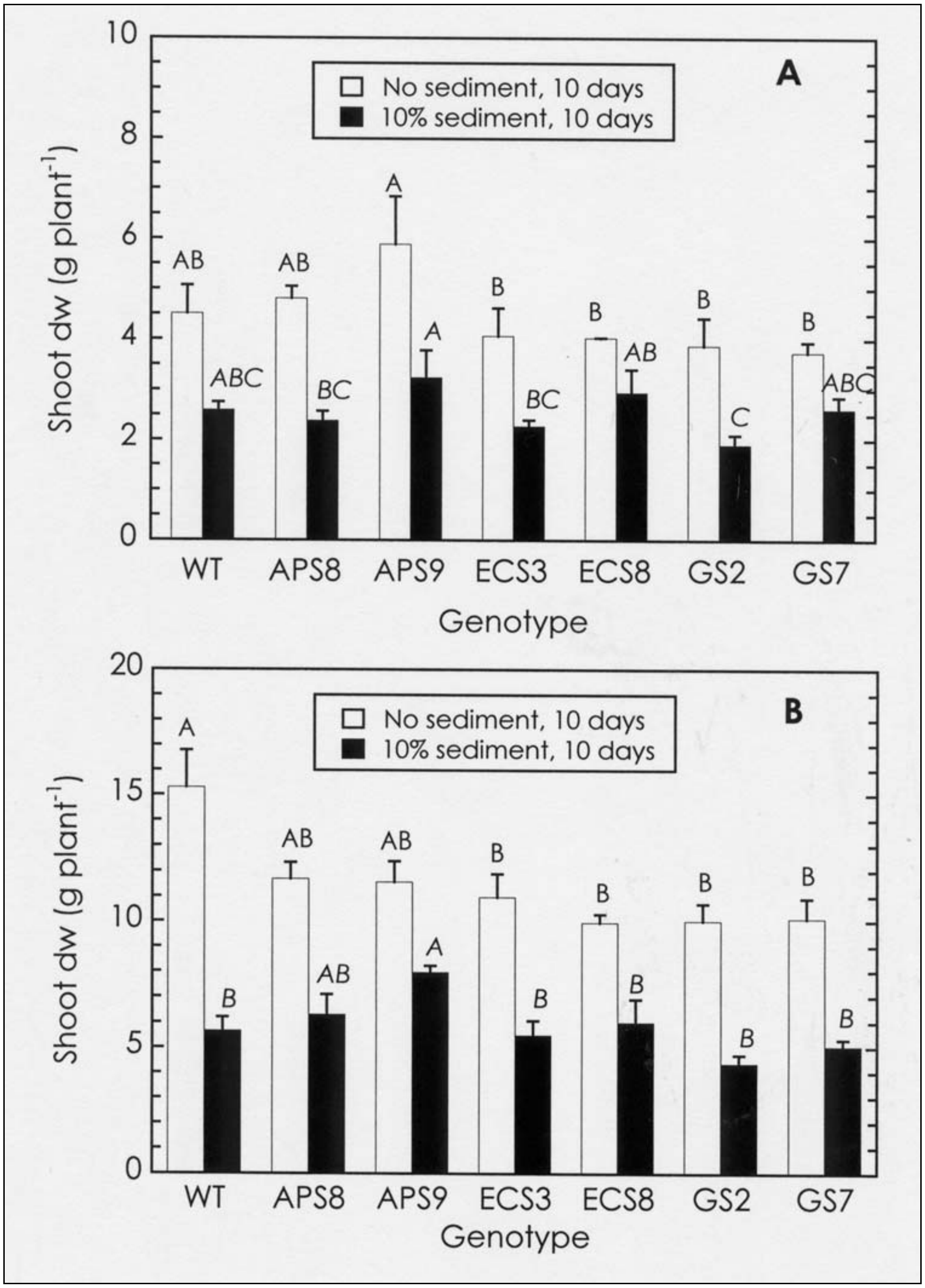

Figure 3. Growth of different genotypes of Indian mustard on no-sediment soil and 10% sediment/soil mixture for (A) 10 and (B) 22 days. Bars represent means and s.e. of 3 to 6 samples.

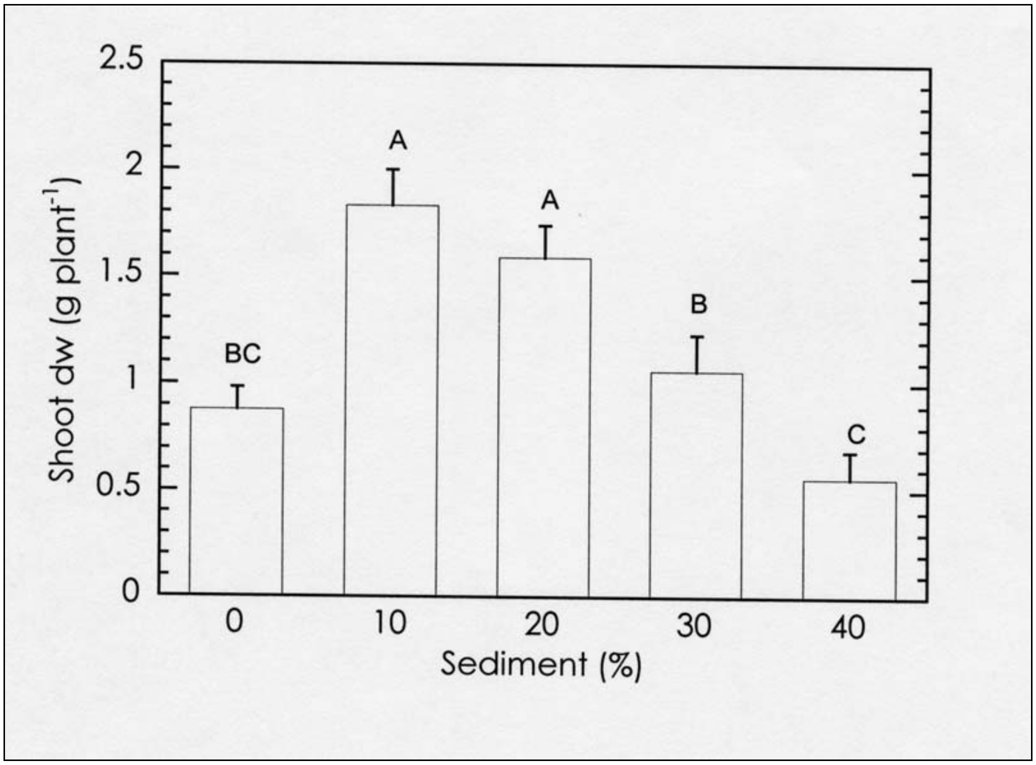

Figure 4. Growth of *Salicornia bigelovii* on sediment/soil mixtures with different ratios of sediment. Two-month-old Salicornia plants were transferred to the sediment/soil mixture, watered with deionized water, and harvested after 45 days for the determination of shoot dry weight. Bars represent means and s.e. of 10 (0, 10, 20% sediment), 7 (30% sediment) and 5 (40% sediment) samples.

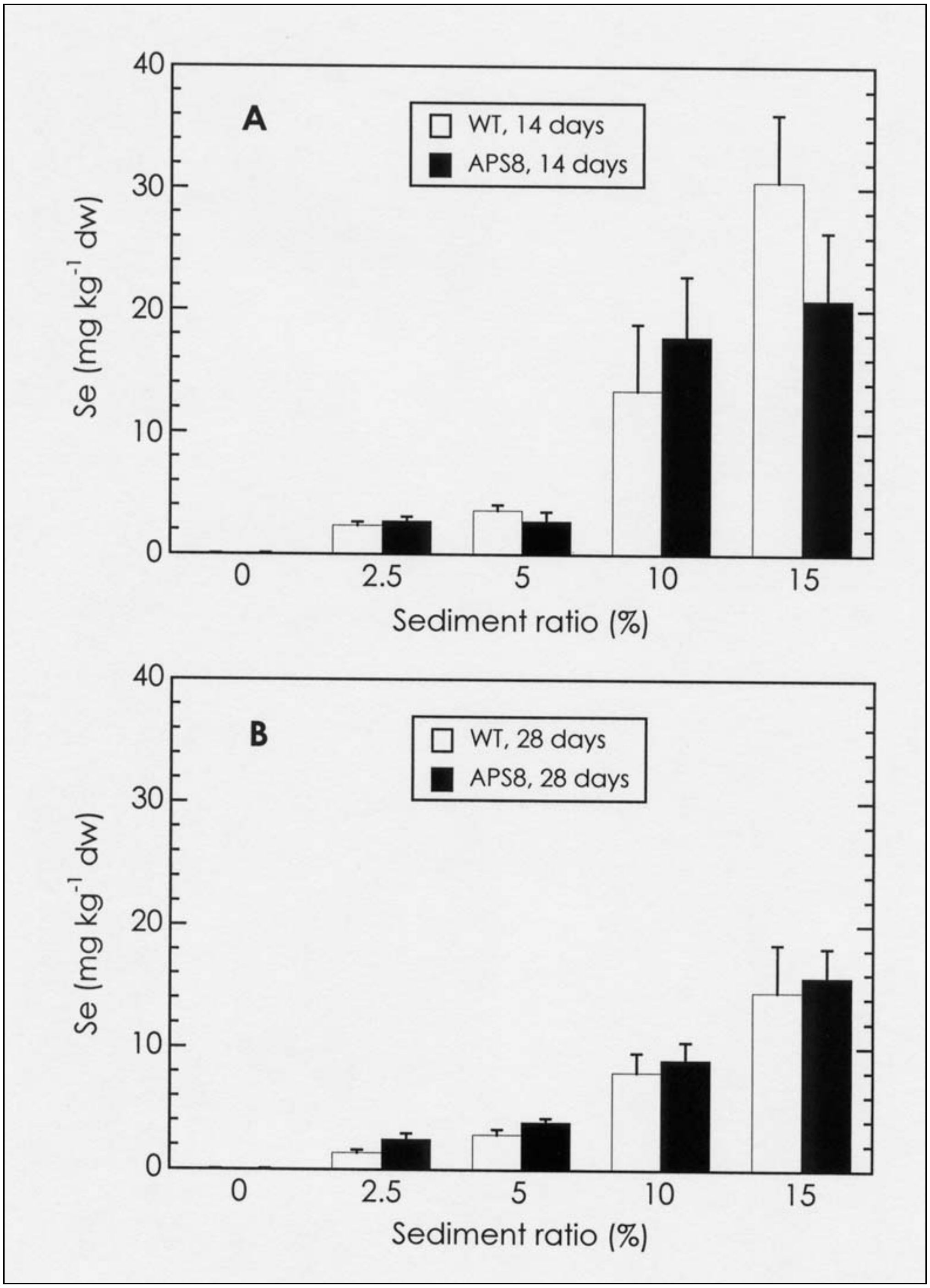

Figure 5. Se concentrations in the shoots of Indian mustard plants growing on 0 to 15% sediment/soil mixtures for (A) 14 and (B) 28 days. Bars represent means and s.e. of 3 samples.

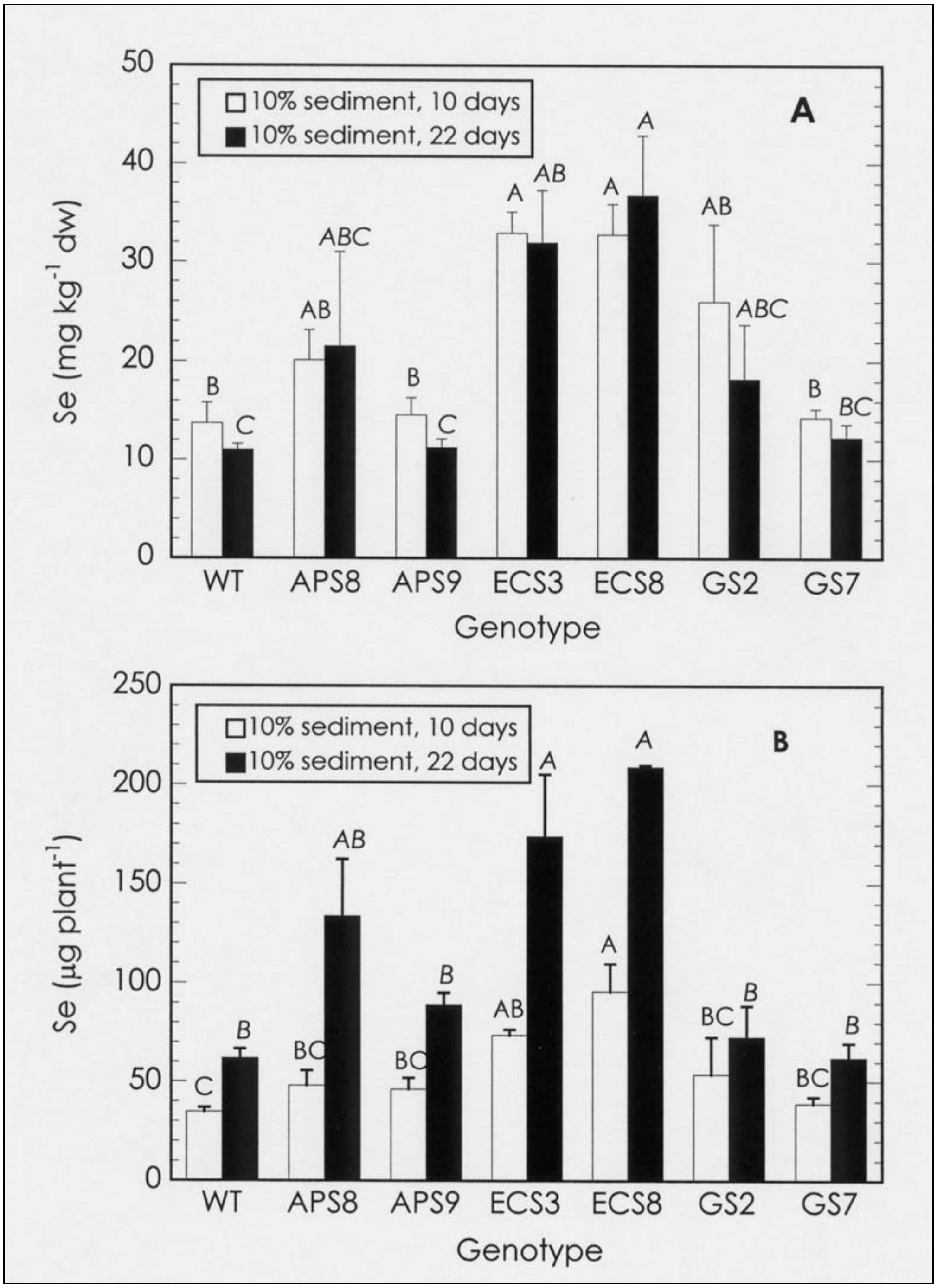

Figure 6. Concentrations (A) and total amout (B) of shoot Se of different genotypes of Indian mustard plants after growing on soil with 10% sediment for 10 and 22 days. Bars represent mean and s.e. of 3 to 6 samples.

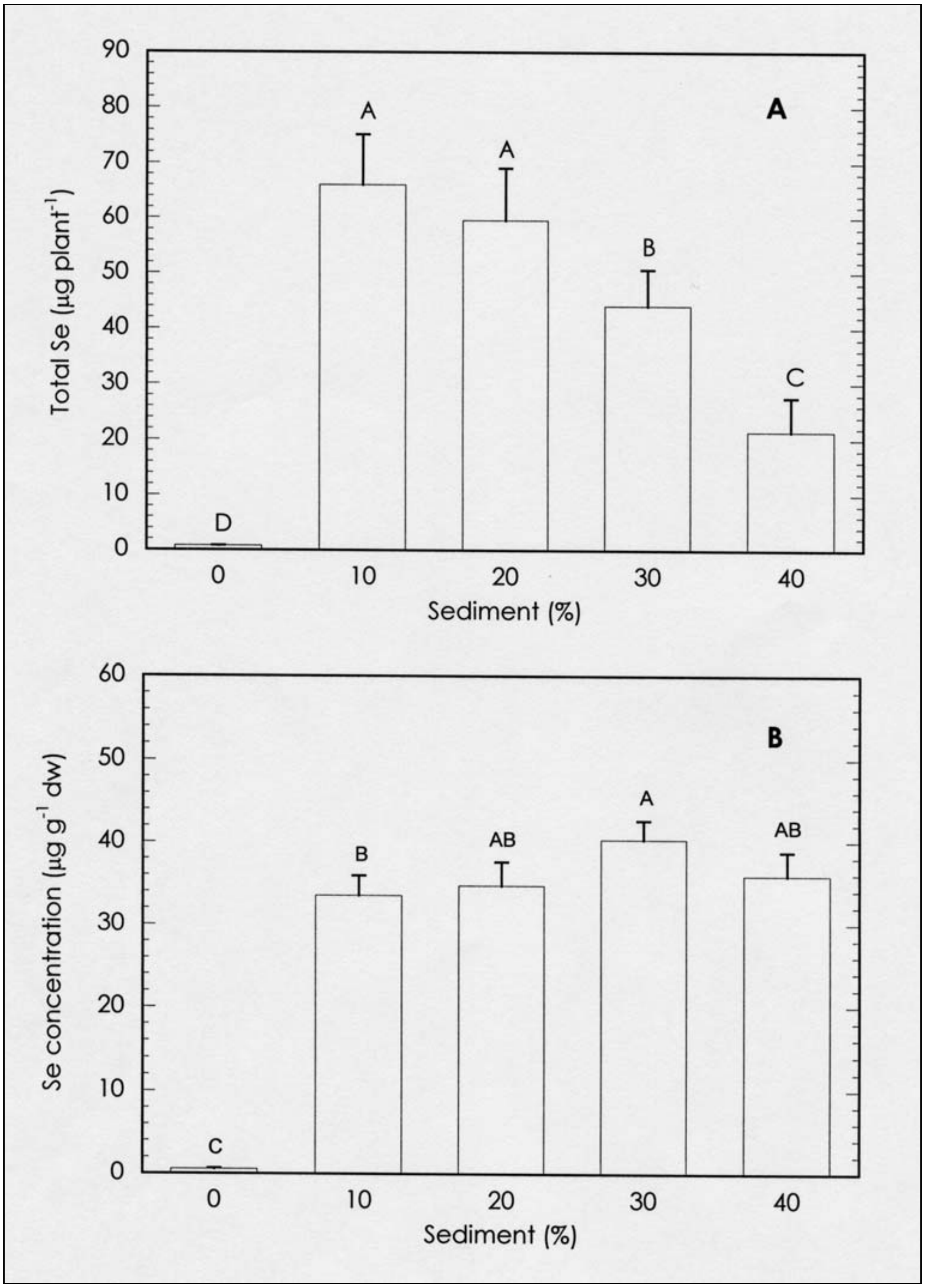

Figure 7. Se content (A) and concentration (B) in the shoots of *Salicornia bigelovii* growing on different ratios of sediment/soil. Bars represent mean and s.e. from 10 (0, 10, 20% sediment), 7 (30% sediment) and 5 (40% sediment) samples.

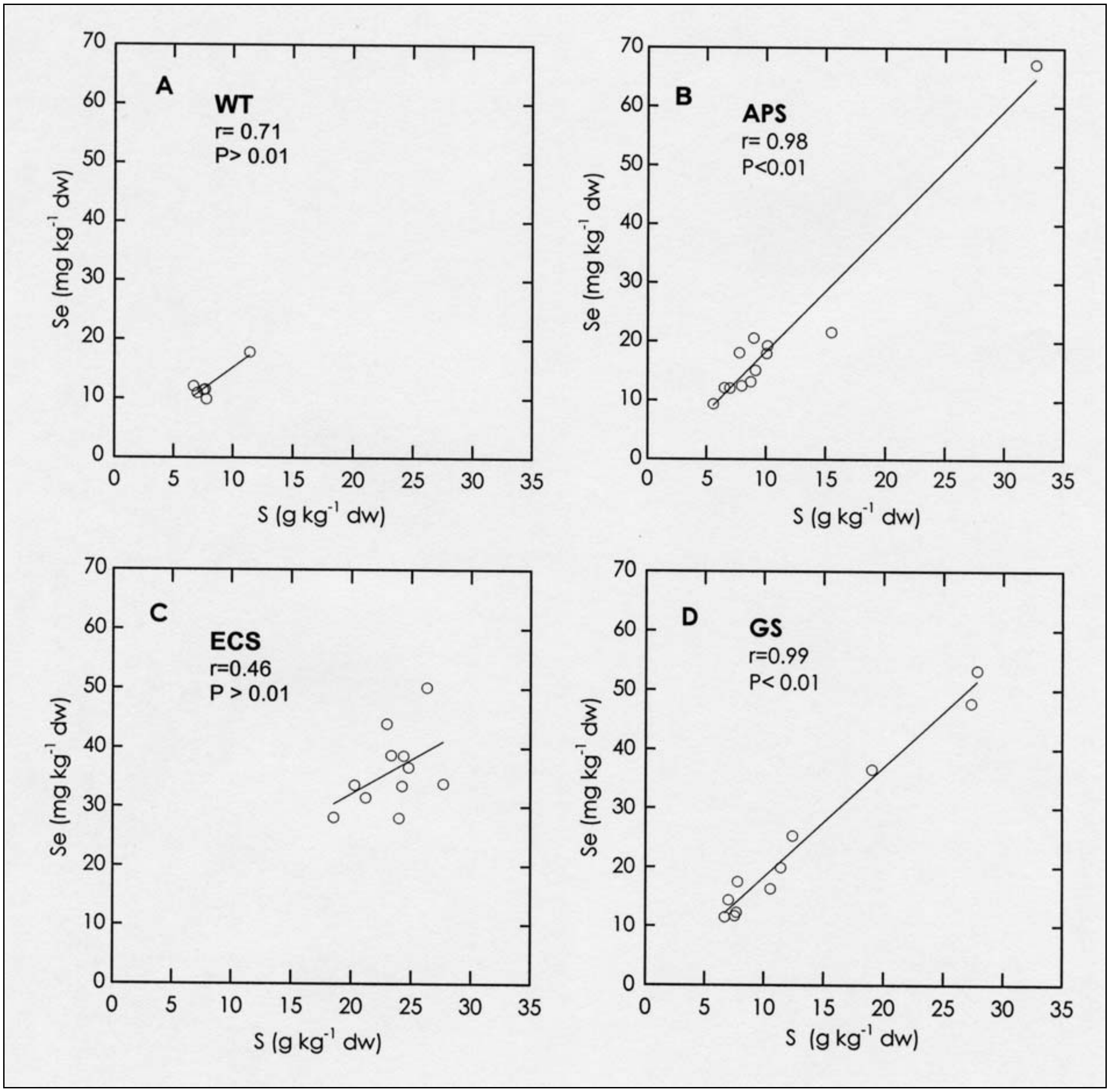

Figure 8. Correlations between S and Se concentrations in the shoots of WT (A), APS (B), ECS (C) and GS (D) lines of Indain mustard plants. The data points are from 10-day and 22-day plants growing on 10% sediment.

Table 1. Changes in the concentrations of total and water-extractable Se and the percentage of different Se chemical species in the water-soluble Se in 10% sediment before (0 day) and after 10 and 22 days of the treatment of different Indian mustard genotypes. Means and s.e. are from 3 to 6 samples.

Time	0 day				
	Se (mg kg^{-1} sediment/soil)		%		
Sample	Total	Soluble	Se(II)	Se(IV)	Se(VI)
10% sediment	11.24±0.12	4.85±0.28	8.2	6.0	85.8

Time	10 days				
	Se (mg kg^{-1} sediment/soil)		%		
Genotype	Total	Soluble	Se(II)	Se(IV)	Se(VI)
WT	6.23±0.31	0.71±0.11	15.7	32.9	51.4
APS8	7.25±0.51	1.62±0.30	10.4	23.3	66.3
APS9	7.76±0.48	2.07±0.15	9.7	22.7	67.6
ECS3	6.84±0.32	1.96±0.24	8.1	13.7	78.2
ECS8	6.63±0.12	2.32±0.57	9.5	17.7	72.8
GS2	6.15±0.38	1.32±0.33	8.9	25.0	66.1
GS7	6.50±0.31	1.62±0.44	9.8	18.4	71.8
Average	6.76±0.16	1.67±0.14	10.3	22.0	67.7

Time	22 days				
	Se (mg kg^{-1} sediment/soil)		%		
Genotype	Total	Soluble	Se(II)	Se(IV)	Se(VI)
WT	6.18±0.52	1.09±0.18	37.3	26.9	35.8
APS8	5.92±0.59	1.43±0.18	21.7	16.8	61.5
APS9	7.01±0.12	1.53±0.11	13.1	31.4	55.6
ECS3	6.39±0.41	1.65±0.35	20.0	12.1	67.9
ECS8	7.11±0.55	1.15±0.14	13.0	45.2	41.7
GS2	7.42±0.62	1.67±0.30	8.7	16.8	74.5
GS7	6.56±0.29	1.73±0.20	17.9	13.3	68.8
Average	6.62±0.19	1.52±0.10	18.8	23.2	58.0

Fate of Colloidal-Particulate Elemental Selenium in Aquatic Systems

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ABSTRACT

Bacterial reduction of selenate [Se(VI)] to elemental Se [Se(0)] is considered as an effective bioremediation technique to remove selenium (Se) from agricultural drainage water. However, the fate of the newly-formed Se(0) in aquatic systems is not known when it flows out of the treatment system. A set of laboratory experiments were conducted to determine the fate of the colloidal-particulate Se(0) in a water column and in a water-sediment system. Results showed that the newly-formed colloidal-particulate Se(0) followed two removal pathways in aquatic systems: i) flocculation-precipitation to the bottom of the water and ii) oxidation to selenite [Se(IV)] and Se(VI). During 58 days of the experiments, 51% of the added Se(0) was precipitated to the bottom of the water and 47% was oxidized to Se(IV) in the water column. In the water-sediment system, Se(IV) in the water accounted for 21-25% of the added Se(0). Adsorption of Se(IV) to the bottom sediment resulted in a relatively low amount of Se(IV) in the water. This study indicates that the newly-formed Se(0) may be an available form of Se for uptake by organisms if it flows to aquatic systems from a treatment site. Therefore, an effective bioremediation system for removing Se from drainage water must reduce Se(VI) to Se(0) and remove Se(0) directly from the drainage water.

INTRODUCTION

An aquatic system is a complex aggregate of water, sediment and various types of organic materials. Selenium (Se) in this system exists in four different oxidation states (-II, 0, IV and VI) and a variety of organic compounds. The bioavailability of Se is largely dependent on the speciation of Se (Besser et al., 1993; Lemly et al., 1993; Wang and Lovell, 1997). Selenate [Se(VI)], selenite [Se(IV)] and organic forms of Se are available Se forms to aquatic organisms (Besser et al., 1993; Lemly et al., 1993; Wang and Lovell, 1997). Elemental Se (Se[0]) has been commonly considered as an unavailable form of Se because of its insolubility. However, Se(0) is one of the largest pools of Se in aquatic systems (George et al., 1996; Weres et al., 1989), accounting for about 30 to 60% of total Se in sediment (Gao et al., 2000; Velinsky and Cutter, 1991; Weres et al., 1989; Zhang and Moore, 1996). Therefore, changes in its stability could affect its availability to aquatic organisms.

Recent studies have shown that Se(0) can contribute toxic levels of Se to aquatic organisms through two pathways (Dowdle and Oremland, 1998; Luoma et al., 1992; Schlekat et al., 2000). Particulate Se(0) in sediment may be available directly to aquatic organisms. Luoma et al. (1992) and Schlekat et al. (2000) found that a significant amount of added Se(0) in sediment was assimilated by bivalve, *Potamocorbula amurensis* and *Macoma balthica*. Se[0] can also be available indirectly to aquatic organisms through its oxidation to Se(IV) and Se(VI) (Dowdle and Oremland, 1998; Schlekat et al., 2000). These studies have provided valuable information regarding the bioavailability of particulate Se(0) in aquatic systems.

Formation of Se(0) in aquatic systems generally involves a two-step reduction process from Se(VI) to Se(IV), and then to colloidal Se(0). If this process occurs in the sediment, Se(0) can directly attach on the surface of the sediment when it is formed. If this reduction process occurs in the water, newly-formed colloidal Se[0] may remain in the water column for a long period of time due to its small size. The subsequent colloidal aggregation/ flocculation or attachment to inorganic and organic particles in water can lead to settling and removal of Se(0) from the water column to the bottom sediment. In a pilot scale Se bioremediation system, conducted by Cantafion et al. (1996) in the San Joaquin Valley, California, it was found that bacterial Se(VI) reduction to Se(0) proceeded rapidly in a series of four columns. About 98% of the Se(VI) and Se(IV) in agricultural drainage water were reduced. However, flocculation and precipitation of the newly-formed Se(0) in the columns proceeded very slowly. Some of the Se(0) flowed out of the columns. At days 184 and 186, Se(0) accounted for 91 to 96% of the total Se in the outflow water. This physicochemical character of the slow flocculation and precipitation of newly-formed colloidal Se(0) in aquatic systems can make Se(0) directly available to organisms living in the water, and indirectly available to organisms by its oxidation to Se(IV) and Se(VI). Therefore, a detailed study on the fate of colloidal-particulate Se(0) is needed to understand the bioavalability of Se(0) in aquatic systems.

The purpose of this study was to determine the fate of newly-formed colloidal-particulate Se(0) in a water column and a water-sediment system.

MATERIALS AND METHODS

Sediment samples used in this study were collected from Stewart Lake, UT and Tulare Lake, CA. Air-dried rice straw was obtained from the Broadview Water District, CA. Artificial drainage water was prepared in the laboratory with a salinity [electrical conductivity (EC)] of 10.4 dS/m and a pH of 8.1. This artificial drainage water contained the major elements present in agricultural drainage water including: SO_4^{2-} (5,000 mg/L), Cl^- (1,500 mg/L), HCO_3^- (300 mg/L), Ca^{2+} (550 mg/L), Mg^{2+} (300 mg/L) and Na^+ (2,285 mg/L). Before mixing the chemical solutions, each chemical (NaCl, Na_2SO_4, $NaHCO_3$, $CaCl_2 \cdot 2H_2O$ and $MgSO_4$) was separately dissolved in deionized water and autoclaved (18 psi at 121 °C) for 20 minutes. Se(VI) was added to the drainage water at a concentration of 10 mg/L after passing through a sterile 0.2 µm membrane.

PREPARATION OF RED COLLOIDAL-PARTICULATE ELEMENTAL SELENIUM

Colloidal-particulate Se(0) was produced from bacterial reduction of Se(VI) in artificial drainage water in the presence of rice straw (Zhang and Frankenberger, 2003a). In this experiment, 4 L of drainage water containing 10 mg/L of Se(VI) was added to a 4 L flask and 20 g of rice straw was added to the water. The flask was incubated in the laboratory at a room temperature (21 °C) until almost all of the Se(VI) was reduced to Se(0) [Se(VI) plus Se(IV) was less than 50 µg/L]. After an analysis of the red particles in the flask with transmission electron microscopy (TEM) coupled with X-ray energy dispersive spectroscopy (EDS) (Losi and Frankenberger, 1997), the red particles were found to be Se(0) with a size of about 0.1 µm. The separation of particulate Se(0) and colloidal Se(0) in the water samples were based on the size of newly-formed Se(0). In this study, Se(0) with its size > 0.4 µm was defined as particulate Se(0) and Se(0) with its size ≤ 0.4 µm was defined as colloidal Se(0). The drainage water (3.6 L) containing colloidal-particulate Se(0) was then passed through a 5 µm filter to an 8 L flask. The drainage water was diluted by half with 3.6 L deionized water. After mixing, the water contained 1,860 µg /L of colloidal Se(0), 557 µg/L of particulate Se(0), 11.2 µg/L of Se(VI), 11.3 µg/L of Se(IV) and 73.5 µg /L of organic Se, and was used immediately for the experiments on the fate of colloidal-particulate Se(0) in aquatic systems.

BATCH EXPERIMENTS

Batch experiments were conducted to determine the fate of newly-formed colloidal-particulate Se(0) in a water column and in a water-sediment system. In this experiment, the sediment sample (Stewart Lake and Tulare Lake) was added to the bottom of a 1 L glass cylinder (44 cm in length and 10 cm in internal diameter) to a thickness of 5 cm, followed by the addition of water containing the high amount of colloidal-particulate Se(0). The experiment without the sediment (water column) was set up as a control for the effect of sediment on the fate of the newly-formed Se(0) in aquatic systems. Depth of the water column was 42 cm in the water column and 37 cm in the water-sediment system. The experiment was run in duplicates with a plastic cover on the top of the cylinder at room temperature (21 °C). The cover had 20 holes, so that air can easily diffuse into the water. Water samples at a depth of 5 cm below the surface of the water were collected at 2 to 3 day intervals for 37 days, and then for a 1 to 2 week interval for Se species analysis. At day 37, water samples at a depth of 30 cm below the surface of the water were also collected for Se species analysis. Upon completion of the experiments, water was removed from the cylinders, and the top 2 to 3 cm of sediment was collected for Se speciation analysis.

SELENIUM SPECIES ANALYSIS

Figure 1 shows our procedure for determination of Se species in the water samples as described by the method developed by Zhang et al. (1999) and Zhang and Frankenberger (2003a). The Se species included total Se, total soluble Se, particulate Se(0), colloidal Se(0), Se(VI), Se(IV) and organic Se.

Selenium speciation in the experimental sediment samples was determined using a parallel extraction procedure (Zhang and Frankenberger, 2003b). After collecting the sediment, samples were immediately extracted with deionized water, 0.1 M NaOH, and 30% of H_2O_2 and 6 N HCl. Deionized water was used to extract water soluble Se(VI), Se(IV) and organic Se in the sediment samples; 0.1 M NaOH was used to extract Se(VI), Se(IV) and 0.1 M NaOH soluble organic Se in the sediment samples; and 30% of H_2O_2 and 6 N HCl were used to digest total Se. Before extraction, the wet sediment was placed into a plastic bag and mixed by hand. Then, the mixed sample was put into a 60-ml beaker, and mixed again with a spatula. For the deionized water and 0.1 M NaOH extraction, 1.7 to 2 g of the wet samples were placed in 40 ml Teflon centrifuge tubes, followed by 30 ml of the extractant. The centrifuge tubes were tightly capped and placed horizontally in a gyrotory shaker and shaken for 20 hours. Then, the tubes were centrifuged at 17300 x g (R.C.F) for 20 minutes. The supernatant from each tube was passed through a 0.2 µm membrane filter (Fisher Scientific) into a 40-ml glass vial. For the H_2O_2-HCl sediment digestion, 1 to1.2 g sediment was used. The moisture content of wetland sediment was determined on air-dry basis (21 °C). A detailed extraction procedure used in this study can be found in the work of Zhang and Frankenberger (2003b). Determination of Se species in the deionized water and 0.1 M NaOH extracts in the sediment was the same as the determination of Se species in water samples after Se(0) was removed from the samples (Fig. 2). Adsorbed Se(IV) in the 0.1 M NaOH extract was estimated by the difference between Se(IV) in the experimental sediment samples and in the original sediment after soluble Se(IV) was removed from 0.1 M NaOH extractable Se(IV).

Selenium concentrations in prepared solutions (water samples, and different sediment extracts) were analyzed by hydride generation atomic absorption spectrometry (HGAAS) (Zhang and Frankenberger, 2003a; Zhang et al., 1999). pH and redox potential in the water was measured using a 720A pH/ISE meter (Thermo Orion, Beverly, MA) (Jayaweera and Biggar, 1996; Zhang and Frankenberger, 2003a).

RESULTS AND DISCUSSION

Elemental Se is a stable form of Se in aquatic systems under a reducing condition (Elrashidi et al., 1987). However, it can become unstable when a reducing environment is transited to an oxidizing environment. In a study on Se(VI) reduction to Se(0) in a water-sediment system, Tokunaga et al. (1996) found that 60% of the newly-formed Se(0) in sediment during an experiment was reoxidized to Se(IV) and Se(VI) at day two after collection. In a flooded sediment system at pH 7, Masscheleyn and Patrick (1993) reported that the boundary between Se(VI) and Se(IV) is at an Eh of about 250 to 285 mV, and between Se(IV) and Se(0), at an Eh of about -10 to -40 mV. In this study, the redox potential in the water column and water-sediment system increased during the experiments (Fig. 2) from 260 to 410 mV with a pH range from 7.3 to 8.3. In such an environment, the newly-formed Se(0) was unstable in the water column and its fate was controlled by flocculation/precipitation and oxidation to Se(IV) and Se(VI).

Removal of Se(0) from water is partially caused by its flocculation, followed by its precipitation to the bottom of the system (Fig. 2). In the first 9 days of the experiments, particulate Se(0) (560 to 992 μg /L) was relatively higher than that (557 μg /L) at the beginning of the experiments upon a decrease in the concentration of colloidal Se(0) in the water column and water-sediment system. During this period of the time, total soluble Se, Se(IV) and Se(VI) were stable, ranging from 68.5 to 95.9, 7.3 to 46.8 and 0 to 14.5 μg /L, respectively. Red precipitates were observed at the bottom of the cylinder in the water column and on the surface of the bottom sediment in the water-sediment system. As the size of the particulate Se(0) was larger than colloidal Se(0), its relatively rapid precipitation resulted in the settling of Se(0) to the bottom of the systems.

Removal of Se(0) from water is also caused by its oxidation to Se(IV) in the water column and water-sediment system (Fig. 2). In the first 5 days, the concentration of Se(IV) was very low, ranging from 7.3 to 11.3 μg /L, revealing that oxidation of Se(0) to Se(IV) did not occur. During the rest of the experiment, Se(IV) increased rapidly in the water column with an average rate of 22.3 μg /L/d, from 12.2 at day 7 to 1151 μg /L at day 58. In the water-sediment system, Se(IV) in the first 5 days ranged from 7.65 to 12.7 μg /L in the water. Then Se(IV) increased from 12.7 μg /L at day 5 to 401 μg /L in the water-UT sediment system at day 23 with an average rate of 19.5 μg /L/d, and from 10.7 μg /L at day 5 to 397 μg /L in the water-CA sediment system at day 23 with an average rate of 19.3 μg /L/d. During the rest of the experiment, Se(IV) in the water column increased slightly with an average rate of 3.06 and 6 μg /L/d, respectively in the water-UT sediment system and water-CA sediment system. On the final day of the experiment, Se(IV) was the dominant form of Se in the water with a small amount of Se(VI) and organic Se. Upon 58 days of the experiment, 47% of the added Se(0) in the water column was oxidized to Se(IV) and about 3% of the added Se(0) was further oxidized to Se(VI). In the water-sediment system, Se(IV) and Se(VI) in the water accounted for 21 to 25% and 2% of the added Se(0). These results reveal that the newly-formed Se(0) formed in a reducing environment is not a stable form of Se(0) in an open aquatic system. Se(0) in the water can be easily oxidized to Se(IV) which can be further oxidized to Se(VI).

Elemental Se can also be oxidized to Se(IV) at the bottom of aquatic systems (Fig. 2). At day 37 when almost all of the colloidal Se(0) and particulate Se(0) were removed from the water (Table 1), which was indicated with very low concentrations of the colloidal Se(0) and particulate Se(0) in the water at 5 and 30 cm below the surface of the water, Se(IV) still increased rapidly with time in the water column from 790 μg /L to 1151 μg /L at day 58. Se(IV) also increased slightly in the water-sediment system. These results suggest that oxidation of Se(0) to Se(IV) also occurred at the bottom of the water column and on the surface of the sediment in the water-sediment system.

Lower amounts of Se(IV) in the water-sediment system than in the water column was partially caused by the adsorption of Se(IV) to the bottom sediment in the water-sediment system (Tables 1 and 2). In aquatic systems, Se(IV) has a stronger affinity to sorption sites of sediment than Se(VI) (Balistrieri and Chao, 1987; 1990; Glasauer et al., 1995; Kuan et al., 1998). Therefore, Se(IV) can be adsorbed to the bottom sediment when it is formed from the oxidation of Se(0). During the first 19 days of the experiment, Se(IV) concentrations (349 μg /L) in the water column were similar to 351 μg /L in the water-UT sediment system and 364 μg /L in the water-CA sediment system, and then increased much greater in the water column than the water-sediment system during the rest of the experiment. Analysis of Se species in the bottom sediment showed that Se(IV) was 7.75-8.71 µg/g in the UT sediment and 2.95-3.68 µg/g in the CA sediment after the experiment, which was much higher than in the original sediment before the experiment (Table 2). After removing soluble Se(IV) from the sediment, Se(IV) was 3.2 to 4.2 µg /g higher in the UT sediment and 2.6 to 2.8 µg/g higher in the CA sediment than the original sediments. In a recent study, Dowdle and Oremland (1998) reported that soluble Se(VI) and Se(IV) formed from the oxidation of spiked Se(0) occurred in soil slurries under an end-over-end rotation condition and a large amount of Se(IV) was bound to soil particles. These results indicate that a significant amount of Se(IV) formed from the oxidation of Se(0) can be adsorbed to the soil under a rotation condition and the UT and CA sediments under a standing condition.

CONCLUSIONS

The results from this work show that the fate of the newly-formed Se(0) can follow two removal pathways within a water column when it enters aquatic systems. The first is flocculation-precipitation to the bottom of the water column and the second is oxidation to Se(IV) and Se(VI). During 58 days of the experiments, 51% of the added Se(0) was precipitated to the bottom of the water and 47% was oxidized to Se(IV) in the water column. In the water-sediment system, Se(IV) in the water accounted for 21 to 25% of the added Se(0). Because of the difficulty to preparing colloidal-particulate Se(0) for studying pure abiotic processes to determine the fate of newly-formed colloidal-particulate Se(0) in aquatic systems without changing the characteristics of the newly-formed colloidal-particulate Se(0), pure abiotic oxidation of Se(0) to Se(IV) was not studied in this work. Therefore, oxidation of the newly-formed Se(0) to Se(IV) in the water column and in the water-sediment system may include both abiotic and microbial processes. This study suggests that a bioreactor effective only in reducing Se(VI) to Se(0) is not enough to remove Se available to aquatic organisms if the outflow water contains Se(0) from the treatment system and is allowed to enter aquatic systems. The complete removal of Se(VI) and Se(IV) from Se-contaminated agricultural drainage water needs a two-step remediation system (Barton et al., 1994): i) a bioreactor to reduce Se(VI) and Se(IV) to colloidal Se(0) by using Se-reducing bacteria and ii) a flocculation separator to remove colloidal Se(0) from the water by using a flocculant.

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Table 1. Concentrations (μg/L) of Se species in water samples collected from the sites at 5 (shallow site) and 30 (deep site) cm below the surface of the water at day 37.

Se species	Water column		Water-UT sediment		Water-CA sediment	
	Shallow site	Deep site	Shallow site	Deep site	Shallow site	Deep site
Total Se	899±74.3	885±63.3	559±3.6	551±6.55	542±25.9	540±28.5
Particulate Se(0)	57.9±37.2	49.3±15.1	14.4±9.9	10.4±9.4	12.8±0.2	0.75±0.25
Colloidal Se(0)	2.90±5.6	7.2±8.1	12.8±2.85	8.1±9	1.55±7.05	6.3±0.00
Total soluble Se	835±42.7	828±40.0	531±3.4	534±13.7	528±19.0	536±29.3
Se(VI)	7.85±1.05	4.3±8.3	4.85±11.95	17.25±1.95	4.95±1.15	12.7±5.9
Se(IV)	790±45.8	786±40.8	470±1.95	469±2.9	477±16.9	476. ±18.0
Organic Se	36.8±2.05	38.0±8.95	56.0±10.5	48.2±14.7	45.5±3.25	47.1±5.45

Table 2. Speciation of Se (μg/g) in sediment samples before and after the experiments.

	Soluble Se			0.1 M NaOH extractable Se			Total Se
Samples†	Se(IV)	Se(VI)	Organic Se	Se(IV)	Se(VI)	Organic Se	
Stewart Lake							
UT	0.318±0.002	0.334	0.047	4.31±0.084	0.64	0.929	9.96±0.03
UT1	0.569±0.052	0.195	0.104	7.75±0.16	0.793	0.502	29.2±0.83
UT2	0.423±0.043	0.288	0.069	8.71±0.22	0.772	0.272	33.1±0.75
Tulare Lake							
CA	0.039+0.002	0.023	0.025	0.101+0.004	0.024	0.054	0.44±0.01
CA1	0.656±0.038	0.389	0.187	2.95±0.04	0.416	0.662	18.0±0.29
CA2	0.826±0.018	0.56	0.195	3.68±0.1	0.566	0.627	20.9±0.65

†: Sample UT and CA: Speciation of Se in original sediment before the experiments.
Sample UT1, UT2, CA1 and CA2: Speciation of Se in sediment after the experiments.

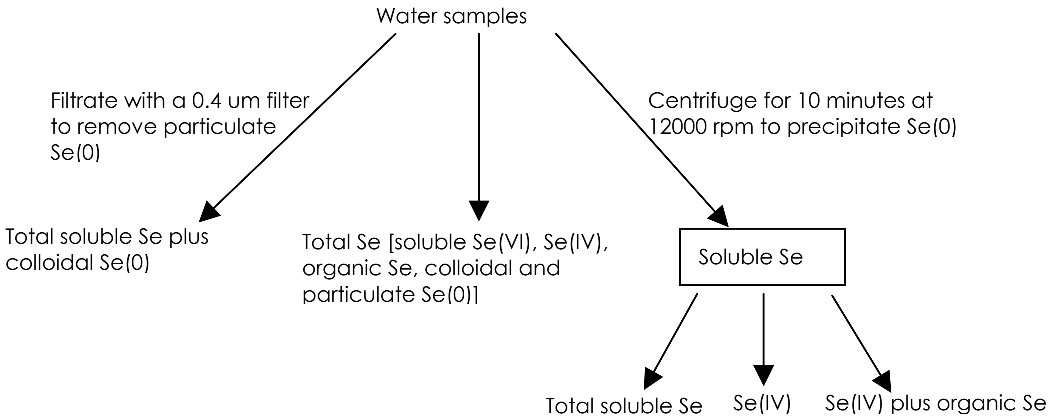

Figure 1. A procedure to determine Se species in water samples. Particulate Se(0) = total Se – total soluble Se plus colloidal Se(0); Colloidal Se(0) = total soluble Se plus colloidal Se(0) – total soluble Se; Se(VI) = total soluble Se – Se(IV) plus organic Se; and organic Se = Se(IV) plus organic Se – Se(IV).

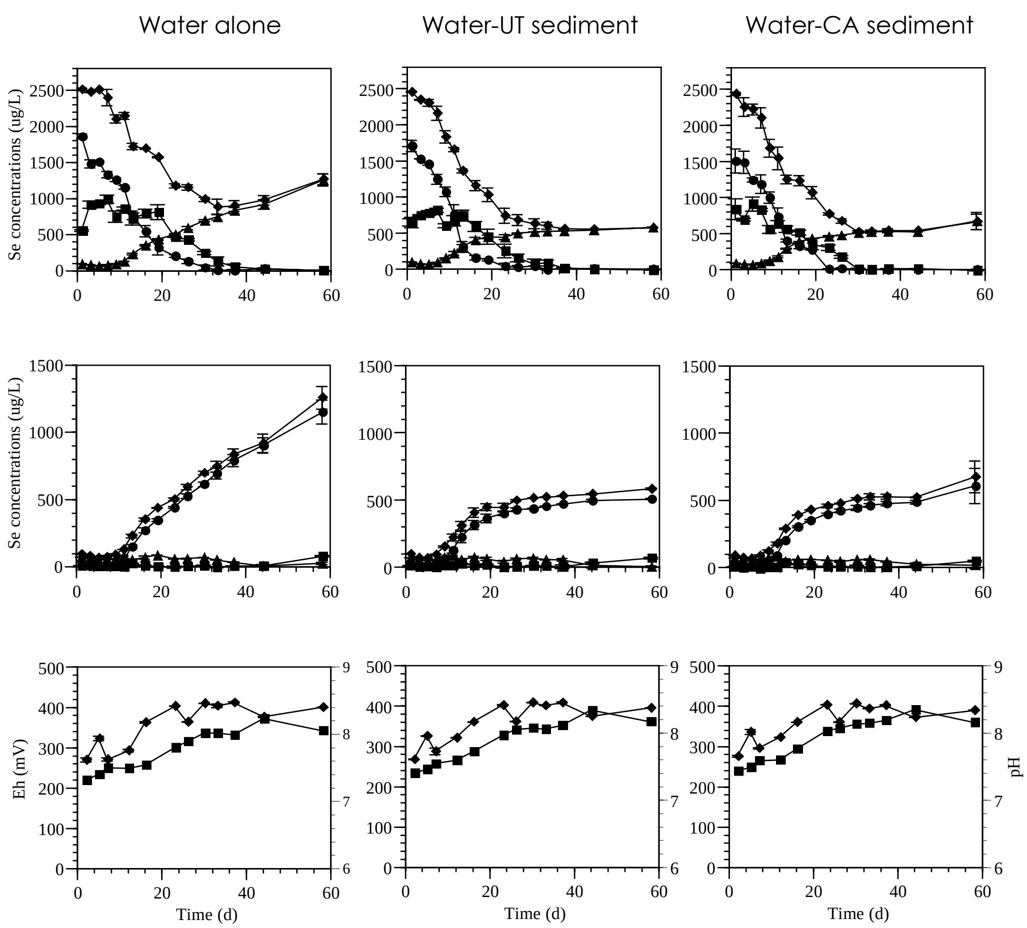

Figure 2. Changes in redox potential (Eh), pH, and concentrations of Se species in a water column and a water-sediment system during 58 days of the experiments. Upper figures: ◆:Total Se, ●:Colloidal Se(0), ■:Particulate Se(0), ▲:Total soluble Se; Middle figures: ◆:Total soluble Se, ●:Se(IV), ■:Se(VI), ▲:Se(-II); Bottom figures: ◆:Eh ■:pH.