# Salinity/Drainage Annual Project Progress Report

# 2004/2005


UC Center for Water Resources

This publication is a continuation of the Salinity/Drainage Program Annual Report series. It is published by the DIRECTOR'S OFFICE of the UC CENTER FOR WATER RESOURCES. The Center sponsors projects in salinity and drainage and related research within the state of California with funds provided by various state and federal agencies and private industry. Copies of this and other reports published by the Center may be downloaded from:

www.waterresources.ucr.edu

Correspondence to the UC Center for Water Resources regarding this publication should be directed to:

UC CENTER FOR WATER RESOURCES
RUBIDOUX HALL – 094
UNIVERSITY OF CALIFORNIA
RIVERSIDE, CA 92521-0436
ATTENTION: PUBLICATIONS
(951) 827-4327
cwres@ucr.edu

Copies of Center publications may be examined at:

Water Resources Archives
410 O'Brien Hall
University of California
Berkeley, CA 94720
(510) 642-2666

# TABLE OF CONTENTS

# 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.

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 evaluates the merits of all proposals. Appreciation is expressed to all the individuals that devoted time and made valuable contributions to the selection of the research to be supported.

This publication reports the research findings of projects funded by the Salinity/Drainage Program in 2004-2005.

# Membrane Desalination of Agricultural Drainage Water: Water Recovery Enhancement and Brine Minimization

**Principal Investigator**

Yoram Cohen
Department of Chemical Engineering
University of California, Los Angeles
Los Angeles, CA 90095
Phone: (310) 825-8766; Fax: (310) 206-4107
Email: Yoram@ucla.edu;
http://www.watercenter.ucla.edu
http://www.polysep.ucla.edu

## ABSTRACT

The salinity of brackish groundwater in the San Joaquin (SJ) Valley is typically in the range of about 2000-4000 mg/L total dissolved solids (TDS) However, salinity levels as high as 15,000 mg/L have been documented in some areas. In recent years there has been a growing interest in the potential use of membrane desalination technology to reduce the salinity of brackish groundwater in the SJ Valley. Membrane desalination for SJ Valley brackish water would have to be carried out at relatively high water recovery in order to reduce the volume of generated RO concentrate. However, at high water recoveries the concentration of mineral salt ions on the feed-side of the membrane may increase to levels that exceed the solubility limits of sparingly water soluble mineral salts such as calcium sulfate, calcium carbonate and barium sulfate. The ensuing crystallization of these mineral salts, onto on the membrane surface and surface deposition of bulk crystals, results in scale build-up that leads to permeate flux decline, shortening of membrane life, and as a consequence reduction in process efficiency and increased operational cost. Therefore, it is imperative that process strategies are designed so as to enhance product water recovery while reducing the potential for mineral salt scaling. Accordingly, the principal objective of the present study is to evaluate the feasibility of high recovery RO desalting of brackish water.

The present project focuses on evaluating the integration of accelerated mineral salt precipitation (AMSP) for scale mitigation with membrane RO desalting to enable high RO recovery. AMSP treatment would serve to de-supersaturate the RO primary or secondary feed with respect to mineral salt scalants. In the first phase of the project, a systematic theoretical analysis was carried out to evaluate the limits on product water recovery due to mineral salt precipitation. The approach was based on multi-electrolyte thermodynamic solubility calculations to: (a) determine the operational pH range required to mitigate calcite scaling and the achievable level of recovery with feed pH adjustment, and (b) determine the required level of calcium removal by AMSP to enable enhanced water product water recovery. The analysis, based on a typical field water feed composition, revealed that primary RO recovery of up to about 54% is feasible with feed pH adjustment to a level of about 6. Recovery can be increased up to about 80% with the use of antiscalants to suppress gypsum and barite scaling. Recovery in excess of 90% is feasible via secondary RO desalting of the primary RO concentrate, provided that about 92% of the dissolved calcium is removed by AMSP in order to de-supersaturate the RO concentrate with respect to gypsum. Given the high TDS level of the concentrate, the required transmembrane pressure could exceed 500 psi in order to reach a recovery levels in excess of 90%. An alternative process configuration that utilizes nanofiltration in conjunction with primary and/or secondary RO desalting could enable operation at lower pressure. Such an alternative will be considered in the second phase of the study.

Preliminary cost analysis of the integrated Primary RO-AMSP-Secondary RO process was carried out using as a basis an RO plant that desalts a feed of $5x10^6$ gal/day (i.e., 5 MGD). The overall desalination cost, at overall recoveries of 80%, 90% and 95%, for permeate quality of 750 mg/L total dissolved solids (TDS) or better, was estimated to be $0.56/kgal ($185/acre-ft), $0.87/kgal ($284/acre-ft) and $0.98/kgal ($319/acre-ft), respectively. If the required capital would be secured by an amortized loan, the desalination cost would increase by ~ 5%. The above preliminary economic analysis suggest that the cost of high recovery brackish water desalination is reasonable and lower by about a factor of 2-5 relative to the cost of seawater desalination. In the second phase of the study, the process analysis will be refined and alternate process configurations will be considered for additional water source compositions that represent the lower and upper limits of mineral salt scaling potential. IN addition, alternate process configurations will be explored to assess the potential for cost reduction. Experimental evaluation of a water source at the high scaling potential limit will then be carried out to assess the kinetics of AP treatment and verify that scale mitigation is indeed achievable at recovery levels of 95% or potentially higher.

## WATER RECOVERY ENHANCEMENT AND BRINE MINIMIZATION

### OVERVIEW OF APPROACH

San Joaquin Valley brackish water is high in concentrations of divalent cations such as calcium, magnesium, barium as well as carbonate and sulfate anions [1]. Membrane desalination of this water is accompanied by the concentration of the above ions in the retentate stream and near the membrane surface [2]. With increased product water recovery, the concentration of sparingly soluble mineral salts of the above ions (e.g., calcium sulfate, calcium carbonate and barium sulfate) can rise above their saturation level, thereby increasing the potential for mineral salt precipitation and thus membrane scaling [3]. Mineral salt precipitation limits the RO process to operation at water recovery levels at which the concentrations of potential mineral salt scalants will be maintained below saturation. The limit on recovery is specific to the water feed chemistry and thus must determined for the source water under consideration. One possible approach to high recovery is to de-supersaturate the concentrate from primary RO desalting to its scaling potential, followed by secondary RO desalting to attain product water recovery in excess of 95%. An evaluation of the feasibility of high recovery RO for every possible water source composition in the SJ Valley is outside the scope of the present project. Therefore, the present study focuses on illustrating the feasibility of high RO desalination for typical SJ Valley water source chemistry and for a water source with the highest scaling potential.

In the first phase of the study, analysis of the recovery limits was carried out based on the water source composition given in Table 1. This water composition is typical of SJ Valley brackish water. The first step in analyzing RO feasibility involved thermodynamic solubility calculations for the major scalants (gypsum, calcite and barite) using the OLI software [4] for multi-ion systems subsequent to reconciliation of the data to ensure appropriate charge balance. The limit on recovery was calculated by evaluating the expected saturation levels, expressed in terms of the mineral salts saturation indices, at various recovery levels. The theoretical product water recovery limit was specified when the mineral salt saturation index reached unity. Based on the above analyses, the required feed pH adjustment and degree of calcium removal were determined so as to reach reasonably high recovery limits (above 90%). Subsequently, a series of process simulations were carried out along with costing analysis to estimate the cost of water desalination. The above analysis was carried out for a typical water source composition from the San Joaquin Valley (Table 1). Analysis for the highest scaling potential SJ Valley water source will be carried out in the second phase of the study. Initial experiments of accelerated mineral salt precipitation were also carried out with a water source of the highest scaling potential in the SJ Valley (determined based on analysis of DWR groundwater water quality data [1]) to provide preliminary assessment of the feasibility of AMSP and the expected precipitation kinetics. The assessment of RO recovery limits and economic feasibility will be refined in the second phase of the project using selected field samples for which experimental AMSP and RO desalting data will be obtained.

### PH DEPENDENCE OF MINERAL SALT SOLUBILITY

The limit imposed by mineral salt scaling on product water recovery was first determined, by calculating the saturation indices, for the mineral salts of concern as a function of pH. This analysis provided information on the feasibility of feed pH adjustment to reduce scaling potential with respect to calcium carbonate scaling since its solubility is pH sensitive. The saturation indices for calcite, gypsum and barite are defined as follows:

$$SI_{calcite} = \frac{(Ca^{2+})(CO_3^{2-})}{K_{sp_{calcite}}}, \quad SI_{gypsum} = \frac{(Ca^{2+})(SO_4^{2-})}{K_{sp_{barite}}}, \quad SI_{barite} = \frac{(Ba^{2+})(SO_4^{2-})}{K_{sp_{barite}}} \tag{1}$$

Where $(Ca^{2+})$, $(Ba^{2+})$, $(SO_4^{2-})$ and $(CO_3^{2-})$ are the activities of the calcium, barium, sulfate and carbonate ions, respectively, and $K_{sp_{calcite}}$, $K_{sp_{gypsum}}$ and $K_{sp_{barite}}$ are the solubility constants (products) for calcite, gypsum and barite, respectively. Variation of the above saturation indices with pH is depicted in Fig. 1 for source water OAS-2548 (Table 1). It is clear that calcite is most sensitive to pH while the saturation indices of calcium sulfate and barium sulfate are pH insensitive. Barite has the highest saturation index; however, barite is a metastable mineral salt (up to $SI_{barite}$~60) present at very low concentrations ( $\lesssim$ 0.5 mg/L ) with slow nucleation kinetics [5]. Given the above, it is likely that the amount of barite scale (per unit surface area), if it could form, would be lower by about two orders of magnitude relative to gypsum. Therefore, given its low concentration and slow precipitation kinetics, barite is not expected to precipitate over the course of typical residence times in commercial RO modules.

**Table 1.** Composition of Agricultural Drainage Water from Monitoring Station OAS-2548 in the San Joaquin Valley.

| Concentration (mg/L) | |
|---|---|
| $Na^+$ | 1,080 |
| $SO_4^{2-}$ | 2,340 |
| TDS | 3,828 |
| $Cl^-$ | 468 |
| Total Alkalinity | 239 |
| $HCO_3^-$ | 290 |
| EC | 5,610 |
| Hardness | 988 |
| $Ca^{2+}$ | 224 |
| $Mg^{2+}$ | 104 |
| $K^+$ | 2.7 |
| B | 9.3 |
| $Ba^{2+}$ | 0.25 |
| Se | 0.061 |
| | |
| pH | 7.1 |
| Temp, $^oC$ | 21 |
| Gypsum SI | 0.41 |
| Calcite SI | 6.3 |
| Barite SI | 41 |

[a] DWR San Joaquin Valley Drainage Monitoring Program Database [1]. Sample Location: OAS-2548, Sampling Date: 9/9/2003. SI – saturation index, TDS – total dissolved solids (mg/L).

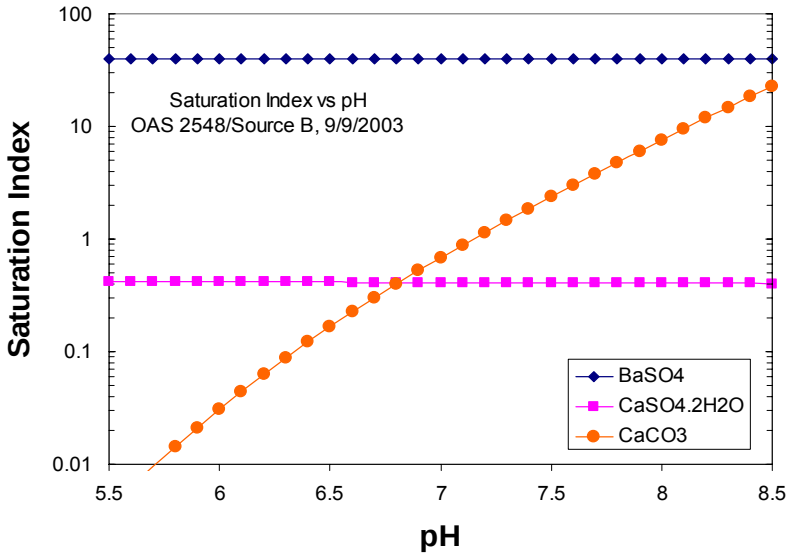


**Figure 1.** Saturation indices for calcite, gypsum and barite for the OAS-2548 source water (Table 1).

## RECOVERY LIMITATIONS DUE TO SCALING and RECOVERY ENHANCEMENT via FEED pH ADJUSTMENT and ANTISCALANT DOSING

The saturation index for gypsum, for the typical feed water composition given in Table 1, is below unity over the pH range of practical interest (Fig. 1), while $SI_{calcite}$=0.88 at the native pH (~7.1) of this water source. The saturation index for calcite reaches unity at pH~7.15 and therefore this mineral salt is the primary limiting scalant for RO desalting of the above water source. As water recovery increases, the concentrations of the various ions increase, leading to an increase in of the saturation indices of the various mineral salts. In order to ensure that, for a given product water recovery operation, that calcite concentration does not exceed saturation, it is necessary to

reduce the feed pH. A series of calculations was carried out to determine the pH level required to keep the saturation index of calcite at unity for different levels of desired product water recoveries (Fig. 2). Clearly, RO desalting at the feed's native pH (~7.1) would not be feasible due to calcite scaling. With increased recovery the feed would have to be adjusted to increasingly lower pH (Fig. 2). For example, adjustment of the feed to pH~6 would mitigate calcite scaling and enable RO recovery of up to ~92% (Fig. 2 and Table 2). However, as demonstrated in the analysis of Fig.3, gypsum saturation is reached at recovery of about 53%. At this recovery the saturation index of barite is above the recommended level for RO desalting [6]. The above analysis is conservative since feed antiscalants dosing can provide some degree of scale suppression and thereby attain a higher recovery relative to the above thermodynamic-based estimate (i.e., 53%). Effective antiscalants are available for suppression of gypsum precipitation and such antiscalants are also known to also assist in mitigating barium sulfate scaling. Effective use of antiscalants for gypsum scale control is generally recommended for RO desalting in which the saturation index of gypsum does not exceed about 2.3 [6]. Accordingly, antiscalants treatment would enable RO desalting up to recovery of about 81% (Fig. 3). It must be recognized that strategic pH adjustment and antiscalant use must be determined based on process optimization with respect to the target recovery, permeate quality and overall water production cost.

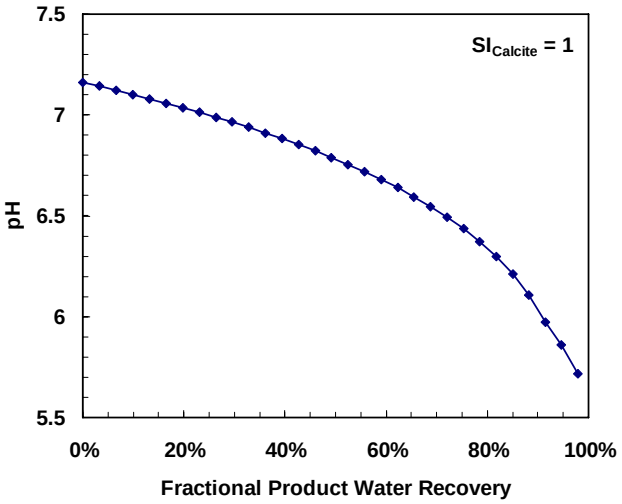


**Figure 2.** Feed pH adjustment at various product water recovery levels needed to keep the saturation index of calcite at unity for source water OAS-2548 (Table 1).

**Table 2.** Summary of RO Product Water Recovery Limits for Primary RO Desalting of San Joaquin Valley Source Water from Location OAS-2548.

| | **Percent Recovery Limit[(a)] due to Scaling** | |
|---|---|---|
| | Mineral Salt Scalant | |
| **pH** | Gypsum | Calcite |
| 7.1 | 54% | ~ 0% |
| 6 | 53% | 90% |
| | | |
| **Osmotic Pressure (psi)** | **Limiting Recovery Due to Osmotic Pressure (pH=6)** | |
| 200 | 84.6% | |
| 250 | 87.9% | |
| 300 | 90% | |
| 600 | 95.1% | |

(a) The limiting recoveries are set at SI = 1. All calculations were performed at 20 ºC and 200 psia. (b) The limiting recoveries for osmotic pressure were calculated at pH=6 as adjusted with the addition of HCl.

**RECOVERY LIMIT IMPOSED BY OSMOTIC PRESSURE**

Commercial vessels for nano-filtration (NF) and ultra-low pressure RO membranes are typically rated for ~350 psi maximum pressure limit. Low pressure RO and extra high rejection modules are generally rated for a 600 psi pressure limit, while seawater desalination RO module are usually made to withstand pressure of up to about 1200 psi. In order to determine the pressure limit imposed by the feed, the osmotic pressure of the retentate stream for the OAS-2548 source water was determined for different levels of water recovery. Accordingly, the osmotic pressure as a function of product water recovery is shown in Fig. 4. Also, recoveries that correspond to osmotic pressure over the range of 200 psi to 600 psi are listed in Table 2. Clearly, if ultra-low pressure RO is the process of choice, then water recovery would be limited to less than about 75% in order to ensure that the maximum operating

transmembrane pressure of 350 psi is not surpassed (Fig. 4). Higher recoveries would necessitate membranes and modules that can withstand higher pressures. For example, at 600 psi transmembrane pressure, the osmotic limit on achievable recovery would be about 93%. The above analysis suggests that high recovery membrane desalination could be achieved using a combination of low-pressure high rejection membranes for the primary RO and extra high rejection RO membranes (rated up to 600 psi) for the secondary RO desalting stage.

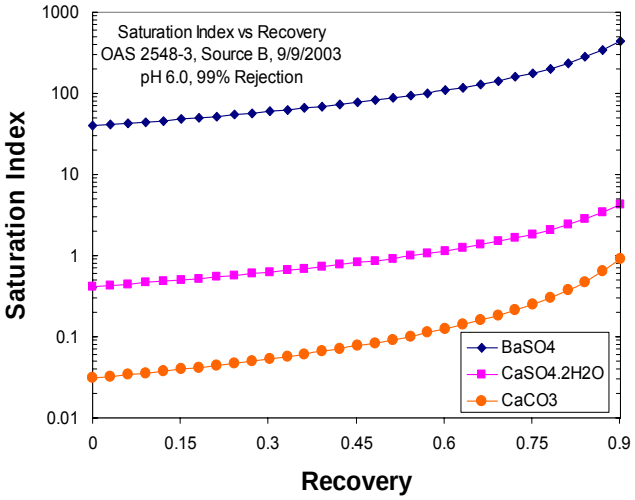


**Figure 3.** Dependence of mineral salt saturation indices on the level of product water recovery for membrane desalting (at 99% salt rejection and feed pH=6) of brackish ground-water from location OAS 25485 (Table 1).

## CALCIUM REMOVAL REQUIREMENTS for SCALE SUPPRESSION and ENHANCED PRODUCT WATER RECOVERY

Accelerated mineral salt precipitation (AMSP) under alkaline conditions is a potential approach to reducing the scaling potential of the primary RO concentrate. This can be achieved by a combination of sodium hydroxide and/or sodium bicarbonate ($Na_2CO_3$) to increase the pH [5] and increase the carbonate ion concentration, respectively, along with calcium carbonate seeding to accelerate the crystallization kinetics. The purpose of AMSP is to reduce the supersaturation level of mineral salts scalants in the primary RO feed or the primary RO concentrate as a pre-treatment prior to a secondary RO desalting stage. The AMSP treated stream is then filtered and further desalted in a secondary RO stage with the feed pH adjusted to acidic condition. Antiscalant makeup can also be added to reduce the potential for calcite scaling. The required percent of calcium removal by AMSP to achieve specified overall water, recovery via the addition of a secondary RO desalting, is shown in Fig. 5. The analysis was carried out by requiring calcium removal such that the gypsum saturation index would be unity at the desired level of secondary RO recovery. The secondary RO recovery was set at the level needed to attain the desired overall recovery above the 54% recovery limit (due to gypsum scaling) attained in the primary RO desalting step. For example, to reach an overall recovery of 95% would require 90% calcium removal from the primary RO concentrate and secondary RO desalting at 75% recovery. It is noted that, the above analysis of the thermodynamic recovery limit is conservative since primary RO desalting can be carried out up to a product water recovery of about 80% via antiscalants dosing of the RO feed.

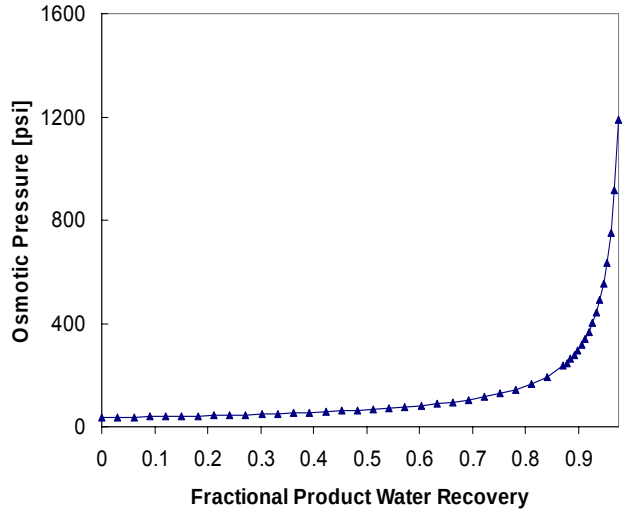


**Figure 4.** Variation of osmotic pressure of the RO retentate for Water source B (Table 1) produced from desalting at 99% rejection.

A preliminary evaluation of calcium removal by AMSP was carried out for model water solutions based on the composition of a high TDS water source from location OAS-2548 which was monitored on 3/22/2004 [1]. This particular source water was determined to have the highest saturation index with respect to gypsum (~0.99) when compared to other monitored groundwater locations in the SJ Valley [1]. A theoretical analysis of the percent of calcium removal from the above model solution via precipitation induced by NaOH and $Na_2CO_3$ was carried with the results depicted in Fig. 6. The source water listed in Table 3 is limited in terms of its carbonate concentration. Therefore, if one would only add NaOH to this RO feed, this will result in calcium carbonate precipitation up to the point where the carbonate ion has been exhausted. Therefore, the addition of NaOH alone is insufficient and $Na_2CO_3$ addition is needed to increase the carbonate concentration. It is feasible to remove calcium as precipitate by a combination of NaOH and $Na_2CO_3$ dosing as shown in Fig. 6.

An initial experimental verification of the above analysis was carried out via batch equilibrium tests. Five AMSP runs were conducted for each AMSP condition in 50-mL capped vials immersed in a temperature-controlled water bath (20°C). Precipitation was induced with 1.4 g/L calcite seed loading and varying amounts of sodium carbonate. The precipitation reaction was allowed to proceed for a period of ~30 hours (to ensure that equilibrium was reached). At the termination of the AMPS treatment the solution was filtered through a 0.1-micron filter and the pH and calcium ion potential were measured with a calcium specific electrode (Orion 97-20 BN, Orion, Beverly, MA). The experimental precipitation results (expressed as calcium potential depletion) followed the theoretical calculations (Fig. 6), thus suggesting that the process is indeed feasible. The use of NaOH was previously demonstrated [5] for

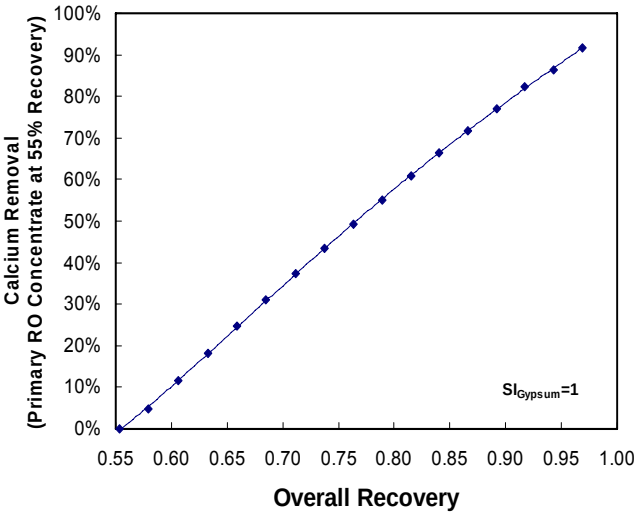


**Figure 5.** Required percent of calcium removal from primary RO concentrate of source water OAS-2548 (produced from desalting at 99% salt rejection and 51% recovery) required to keep the saturation index of gypsum at saturation (i.e., saturation index of unity).

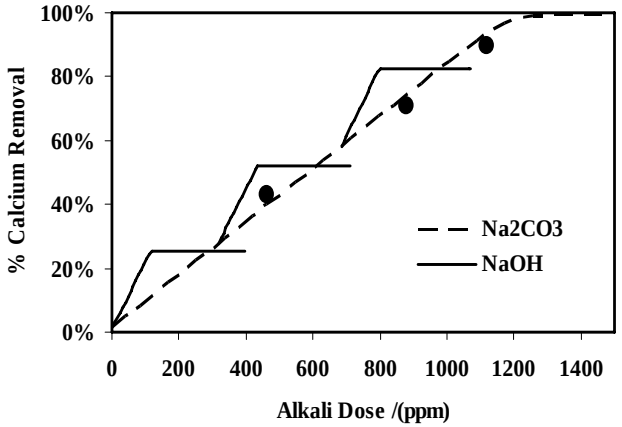


**Figure 6**. Theoretical equilibrium analysis of calcium removal by accelerated mineral salt precipitation for a model solution (Table 3) with a high scaling potential.

**Table 3.** Composition of OAS-2548 source water based on 3/22/04 monitoring [1] and corresponding model solutions (a)

| **3/22/04 OAS-2548 Water Source** | | **Model Solution[(b)]** | |
|---|---|---|---|
| *Ions* | *Concentration (mg/L)* | | **Concentration** (mM) |
| Sodium | 2,379 | $Na_2SO_4$ | 49.28 |
| Barium | 0.5 | $MgSO4.7H_2O$ | 9.15 |
| Calcium | 454 | $CaCl_2.2H_2O$ | 11.29 |
| Potassium | 10 | $NaNO_3$ | 0.73 |
| Magnesium | 223 | $NaHCO_3$ | 2.91 |
| Sulfate | 5,630 | pH | 7.8 |
| Chloride | 847 | $SI_{Gypsum}$ | 0.99 |
| Nitrate | 45 | $SI_{Calcite}$ | 3.98 |
| Bicarbonate | 178 | | |
| TDS | 9,703 | | |

(a) Reconciled at 20°C (b) pH adjusted with HCl

a water source of a similar TDS but lower saturation indices with respect to calcite and gypsum. Clearly, the combined use of NaOH and $Na_2CO_3$ would have to be optimized based on cost and this would be assessed in the second phase of the study. Although the above precipitation experiments were carried out over a 30 hr period, steady-state was reached over a much shorter period as verified based on a simple kinetic precipitation test. The precipitation test was carried out using 500-mL of the model solution in a 600 mL a magnetically-stirred beaker. Precipitation was induced by dispersing a charge of calcite seeds, followed by the addition of a predetermined amount of 1-M sodium carbonate stock solution. Precipitation kinetics was followed by continuous monitoring of both pH and calcium ion potential until steady was reached. The results (Fig. 7) illustrate that the removal of calcium (in the form of precipitate of calcium carbonate and calcium sulfate) in this open system was accompanied by a decrease in pH (also due to absorption of atmospheric carbon dioxide). It is noted that the steady-state removal, which was approached within a reasonable period of ~ 15 minutes, was closely predicted by the equilibrium prediction.

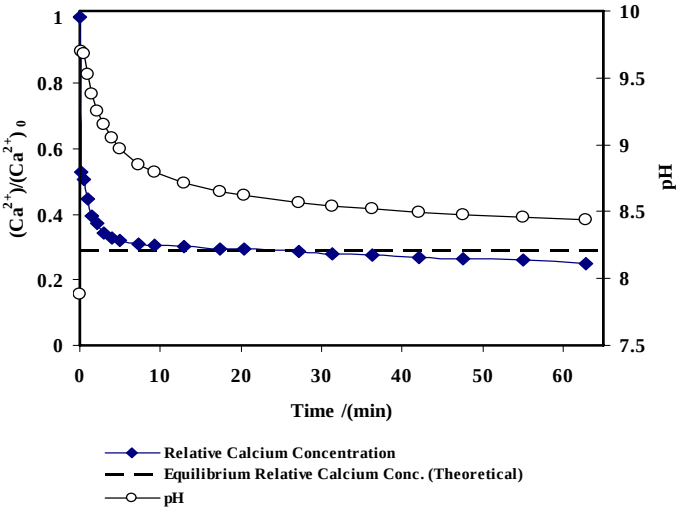


**Figure 7**. Kinetics of accelerated precipitation of a high scaling potential model solution (Table 3). Precipitation was initiated with 841 mg/L $Na_2CO_3$ and 1.4 g/L calcite seed load.

## INCREASING PRODUCT WATER RECOVERY via ACCELERATED MINERAL SALT PRECIPITATION TREATMENT OF RO FEED

### *Two-Step Membrane Desalting with an Interstage Accelerated Mineral Salt Precipitation*

High product water recovery is feasible via a two-step membrane desalting process. The conceptual system configuration is shown in Fig. 8. The feed is pre-treated by microfiltration and the pH is adjusted to suppress calcite scaling. A primary RO desalting step is then applied (with about 3 ppm antiscalants feed dosage) to achieve a recovery level of about 80%. Subsequently, calcium removal is achieved by accelerated mineral salt precipitation in a crystallizer reactor. After a subsequent filtration step to remove the mineral salt precipitate, the treated primary RO concentrate is desalted in a second RO step (with feed pH adjustment and antiscalant addition) to achieve the desired overall recovery with permeate quality of 750 mg/L total dissolved solids (TDS) or better.

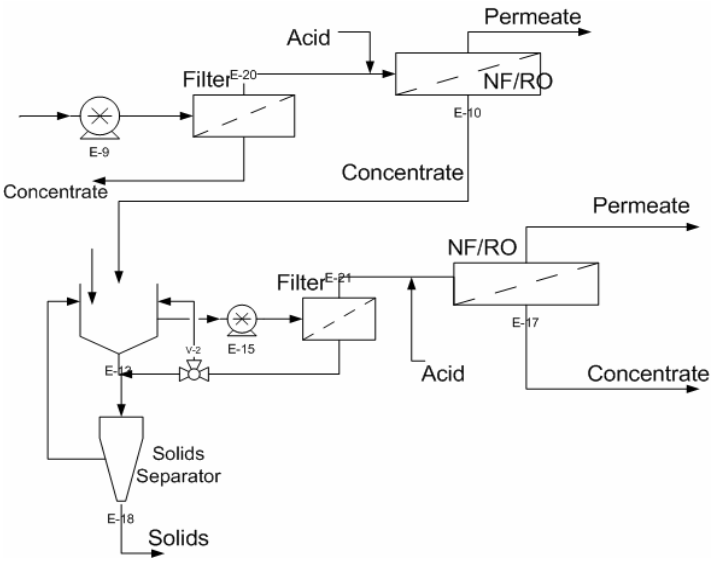


**Figure 8.** Two-step high recovery RO desalination – Integration of accelerated mineral salt precipitation.

Economic evaluation of water desalting was carried out for the two-step process (Fig. 4) considering overall recovery levels ranging from 80% to 95%. The analysis was carried out for the water source composition of Table 1 which is typical of the composition of SJ Valley brackish groundwater. The cost analysis was based on a desalination plant that would process $5x10^6$ gallons/day feed water (5 MGD). Process simulations and costing analysis were carried out using the two interfaced membrane process simulators RO-PRO and Cost-PRO [7] with the membranes TF C-ULP, TFC-HR and TFC-XR considered in various stages of the primary and secondary RO desalting process. Equipment costs for membrane modules, pumps, piping, filters, crystallizer and control equipment were assessed based on information provided from various equipment manufacturers. Operational cost included membrane replacement based on a four year cycle, membrane cleaning, chemical additives, energy and maintenance. Energy cost was determined based on pumping costs and bulk rate cost of chemical additives (e.g., NaOH, $Na_2CO_3$, HCl, $H_2SO_4$, and antiscalants) was obtained from their respective manufacturers.

For all cases considered the primary RO recovery was set at 80% (Tables 4-7). The capital cost was dominated by the primary RO step since it involved processing of 80% of the feed (Table 4). The capital cost for the accelerated mineral salt precipitation step was about 30% of the total operating cost. The secondary RO step, which increased with overall product water recovery, was about 14%-23% of the total operating cost (Table 5). The capital cost associated with the AMSP was independent of the overall recovery since the volume of treated primary RO concentrate was identical for all three process configurations. The contribution of capital cost to the overall water production cost was 9%-11% (Tables 4 and 5). In the absence of interest charges the overall water production cost ranged from $185/acre-ft to $319/acre-ft with increased product water recovery from 80% to 95%, respectively (Table 5). The operating cost for AMSP increased by 12% as the overall recovery was increased from 90% to 95%, owing to the increase in chemical cost needed for greater removal of calcium from the primary RO concentrate (Table 6). The primary RO step represented the dominant cost of about 56%-60% of the total operating cost. Finance charges were estimated based on a 15 year amortization of the capital cost of the plant at an annual interest rate of 5.75 % (Table 7). The overall product water cost increased by about 6% when interest charges were included resulting in an overall water production cost of $0.59-$1.04 per kgal (equivalent to $195-$340 per acre-ft). It is interesting to note that the cost seawater (~$2-$3) is about a factor of 2-5 higher than the estimated cost of desalination of SJ Valley brackish water.

The present analysis suggests that the integration of membrane RO desalination and accelerated mineral salt precipitation for high recovery desalting is technically and economically feasible. The integrated desalination process consists of a primary RO step, followed by accelerated mineral salt precipitation treatment of the primary RO concentrate and subsequently a secondary RO desalting step. The second phase of the project will extend the present analysis by considering a range of SJ Valley brackish groundwater with the highest scaling potential. Alternate process configurations will be considered to explore means of lowering the overall water desalination cost. In conjunction with the above analysis, diagnostic membrane RO scaling tests and AMSP tests will be conducted to verify the conclusions reached based on the present theoretical analysis of recovery limits.

**Table 4. Capital Cost for Brackish Water Desalination[(a)]**

| Percent Product Water Recovery | | Capital Cost ($) | | | |
|---|---|---|---|---|---|
| Secondary RO | Percent Overall Recovery | Primary RO | AMSP | Secondary RO | Total Capital Cost |
| 0% | 80% | $1,390,000 | $0 | $0 | $1,390,000 |
| 50% | 90% | $1,390,000 | $170,000 | $165,000 | $1,725,000 |
| 75% | 95% | $1,390,000 | $170,000 | $685,000 | $2,245,000 |

[(a)] Based on 5 MGD water feed. Primary RO is carried out at 80% recovery.

**Table 5.** Estimated Cost of Brackish Water Desalination by integrated RO and accelerated mineral salt precipitation at various levels of overall product water recovery[(a)]

| Water Recovery | | | Total Capital Cost ($) | Cost of Water Production ($/kgal) | | | $/ Acre-ft |
|---|---|---|---|---|---|---|---|
| Primary RO | Secondary RO | Overall Recovery | | Capital Cost | Operating Cost | Total Cost | |
| 0.8 | 0 | 80 | $1,390,000 | $0.063 | $0.50 | $0.56 | $185 |
| 0.8 | 0.5 | 90 | $1,725,000 | $0.070 | $0.80 | $0.87 | $284 |
| 0.8 | 0.75 | 95 | $2,245,000 | $0.086 | $0.89 | $0.98 | $319 |

(a) Based on 5 MGD feed. Cost per 100 gallons or acre-ft s on the basis of total permeate produced. Note: Cost values expressed per kgal were rounded to two significant digits.

**Table 6**. Operating Cost for RO Desalting

| Percent Product Water Recovery | | Operating Cost ($/kgal) | | | |
|---|---|---|---|---|---|
| Secondary RO | Overall | Primary RO[(a)] | AMSP[(b)] | Secondary RO [(c)] | Total [(d)] |
| 0% | 80% | $0.50 | $0 | $0 | $0.50 |
| 50% | 90% | $0.50 ($0.45) | $1.09 ($0.24) | $1.01 ($0.11) | $0.80 |
| 75% | 95% | $0.50 ($0.42) | $1.22 ($0.26) | $1.33 ($0.21) | $0.89 |

(b) Cost per water permeate produced in the primary RO step. [(b)] Cost per kgal of primary RO concentrate treated. The cost in parenthesis is per kgal of total product water produced. [(c)] Cost per kgal of secondary permeate water product. (d) Cost per total kgal of product water permeate produced. Note: Cost values expressed per kgal were rounded to two significant digits.

**Table 7.** Cost of water desalination including financial charges[(a)]

| Water Recovery | | | Total Capital Cost ($) | Cost of Water Production ($/kgal) | | | $/ Acre-ft |
|---|---|---|---|---|---|---|---|
| Primary RO | Secondary RO | Overall Recovery | | Capital Cost | Operating Cost | Total Cost | |
| 0.8 | 0 | 80 | $2,073,427 | $0.09 | $0.50 | $0.59 | $195 |
| 0.8 | 0.5 | 90 | $2,588,054 | $0.12 | $0.80 | $0.92 | $300 |
| 0.8 | 0.75 | 95 | $3,348,807 | $0.15 | $0.89 | $1.04 | $340 |

(c) Based on 5 MGD feed. Cost per 100 gallons or acre-ft s on the basis of total permeate produced. Operating cost is as given in Table 4. Capital cost is amortized over 15 years at 5.75% interest rate. Note: Cost values expressed per kgal were rounded to two significant digits.

## REFERENCES


[1] DWR, San Joaquin ValleyY, Drainage Monitoring Program Database, State of California, The Resources Agency, Department of Water Resources, San Joaquin District, 2003.

[2] R.-W. Lee, J. Glater, Y. Cohen, C. Martin, K. Kovac, M.N. Milobar, and D.W. Bartel, Low-pressure RO membrane desalination of agricultural drainage water, Desalination, 155 (2003) 109.

[3] W.Y. Shih, A. Rahardianto, R.W. Lee, and Y. Cohen, Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes, Journal of Membrane Science, 252 (2005) 253.

[4] OLI, OLI Analyzer 2.0. 2005, OLI Systems, Morris Plains, NJ.

[5] A. Rahardianto, Y. Cohen, and D.M. Williams, Enhanced water recovery from primary membrane desalination concentrate by precipitative softening and secondary RO desalting, in AIChE 2004 Annual Meeting. 2004, AIChE: Austin, TX.

[6] Hydranautics, Chemical Pretreatment of RO/NF, 2002.

[7] Koch Membrane Systems, ROPRO Reverse Osmosis system design software.

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


**Project Investigators**

Teresa Fan
Dept. of Land, Air & Water Resources
University of California, Davis
(530) 752-1450, twfan@ucdavis.edu

Richard Higashi
Center for Health and the Environment
University of California, Davis
(530) 752-1830, rmhigashi@ucdavis.edu

**Research Staff**

Chris Coelho, PGR
William Schilling, PGR
Teresa Cassel, SRA
Krassimira Hristova, Assistant Professional Researcher

## ABSTRACT

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. Our approach has been to assess the influence of ongoing brine shrimp harvest and drainage water manipulation on water chemistry, water and biota Se status, Se volatilization activities, and algal community. Analyses have been conducted for monthly water and brine shrimp samples from selected saline basin cells, both harvested and non-harvested, as well as for the annual collections of water and macroinvertebrate samples from both saline and less saline cells. Brine shrimp harvesting was shown to reduce the efficiency of Se transfer from algae to invertebrates, enhance algal growth, and reduce Se incorporation into benthic organisms. Salinity was shown to be an important determinant to Se volatilization rates.

The compilation of data collected over several years of this type of monitoring revealed that the microalgal communities in the basins are serving a variety of functions relative to Se biochemistry. Whether these communities tend to accumulate or volatilize Se and whether they provide food for brine shrimp has a measurable influence on the amount and compartmentalization of Se in the system. As these communities were better functionally described in this work, they are also being quantitatively described using a newly developed procedure for tracking populations of *Synechococcus* sp.

## 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.

Preliminary investigation in hypersaline ponds of TLDD indicates that Se volatilization may be combined with brine shrimp harvest to reduce ecotoxic Se load in waters and biota. In addition, it appears that both processes could be enhanced by manipulating the water chemistry to increase a 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 that produce brine such as IFDM and reverse osmosis.

## INTRODUCTION

### OBJECTIVES

Our objectives are to investigate and understand the effect of 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 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. Effects of brine shrimp harvest on selenium status of microalgae and brine shirmp, microalgal community, as well as waterborne Se status in TLDD hypersaline ponds.
3. 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

Rates of brine shrimp harvest in each of the TLDD evaporation basins have been compiled from daily records provided by Novlek. 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 has also been profiled using 16S cDNA in combination with Denaturing Gradient Gel Electrophoresis (DGGE). In July, 2004, extensive field sampling was conducted at TLDD basins to collect water column and benthic macroinvertebrates, with the assistance of Julie Vance from Dept. of Water Resources, Fresno. Selenium status of these samples should indicate the distribution of Se in the ecological niches of the basins. In situ Se volatilization measurements were also made at selected TLDD basin cells.

## RESULTS

### CHANGES IN TLDD WATER MANAGEMENT

Water management in 2005 was similar to that in 2004. As it was last year, harvest from Cell A4 of the Hacienda basins (HAC A4) was minimal and the un-harvested C4 comparison basin was not monitored due to low water supplied to those basins. The rise in salinity seen in HAC A4 coincided with the water low volume time period beginning in early June. At the South basins, water continued to be drawn from SEB 8 to both SEB 9 and SEB 10. This had the desired effect of stabilizing the water level and salinity in the three ponds and made salinity comparable in all of them. Shrimp harvest was greatest in SEB 9 and also substantial in SEB 10, with production in SEB 9 about twice that in SEB 10. Of the regularly monitored basins, the most saline basin (HAC A4) continues to be the most Se volatilizing (cf. Fig. 16), though it was harvested only lightly for brine shrimp. The basin with the highest brine shrimp yields actually had the second highest rate of Se volatilization, of the four monitored basins

### WATER CHEMISTRY AND 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 1 shows the monthly trend of in vivo *chl a* fluorescence of the 4 monitored basin cells. Variations in fluorescence or algal population in the harvested ponds can be compared with the corresponding cumulative brine shrimp harvest, as shown in Figure 2. In general, the declining algae population at the end of the year (September and October) was met with tailing off of shrimp harvest in both active ponds (SEB 9 and 10). In SEB9, where shrimp harvest was most active (Fig. 2), the *chl a* fluorescence was consistently low year-round (Fig. 1). This may be attributed to the grazing of the consistently high population of brine shrimp in SEB 9. In SEB10, *chl a* fluorescence readings are seen to peak

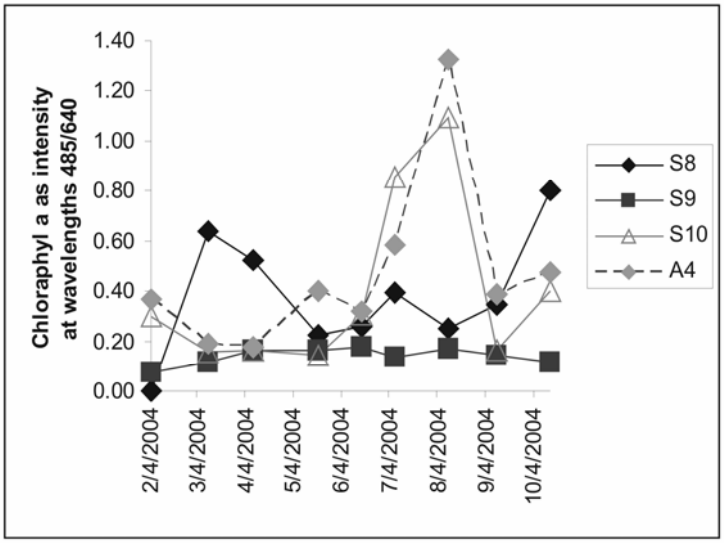


**Figure 1:** Monthly trend of Chl a fluorescence in water samples.

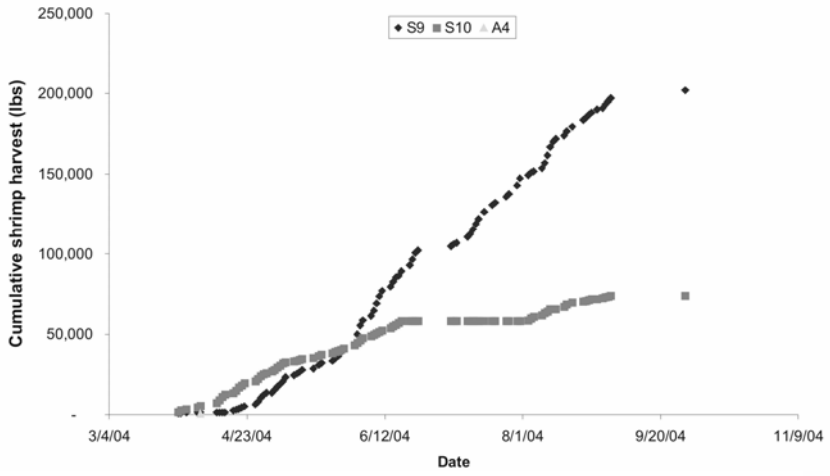


**Figure 2:** Cumulative brine shrimp harvest.

when harvest slowed in June and fall again when harvest activity resumes in August. These observations are consistent with the notion that brine shrimp grazing regulates microalgal population in these hypersaline basin cells. Interestingly, in 2004, the chl a fluorescence readings were similar in the moderately harvested pond SEB 10 and the significantly less harvested basin HAC A4. Although it was only harvested once in 2004, the long history of brine shrimp harvest in HAC A4 may still be influencing the algal population there.

In addition to *chl a* fluorescence, salinity and water Se concentration ([Se]) also exhibited seasonal changes and differences among the basin cells (as observed in previous years), which is shown in Figures 3-6. As mentioned above, the salinity (in parts per thousand or ppth) of South Basins 8, 9, and 10 (Fig. 3) was relatively low, compared with previous years, and stable over time. However, the salinity of HAC A4 was more variable and peaked higher than that observed previously. As stated above, this was due to the differences in TLDD water management between the two systems. As observed previously, salinity and water Se concentration did not correlate, as would be expected from simple evaporite chemistry (Figs. 3 and 5). The pH was similar and stable over time in all cells (Fig. 4). The water Se concentration of all cells was comparable all year round, with the exception of the uniformly higher Se concentrations measured in SEB 10 (Fig. 5). Though the source water (SEB 8) and the shrimp harvest patterns, though not in magnitude, are comparable to those of SEB 9, the waterborne Se concentrations of the latter are similar to the two unharvested basins (HAC A4 and SEB 8).

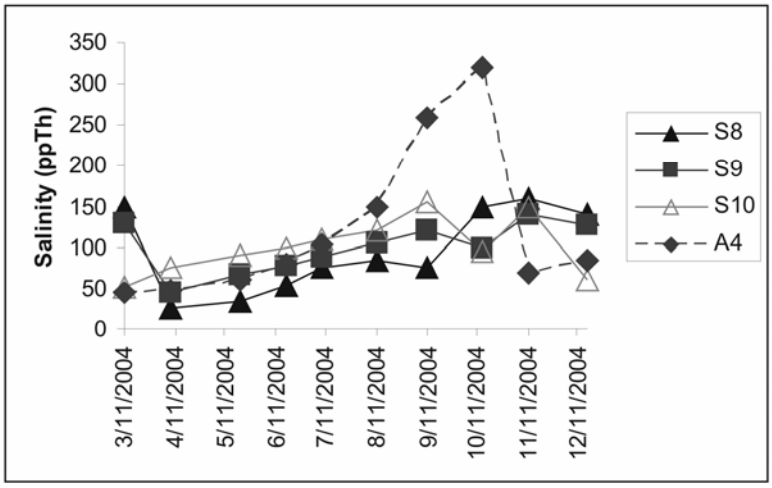


**Figure 3:** Salinity in monthly water samples.

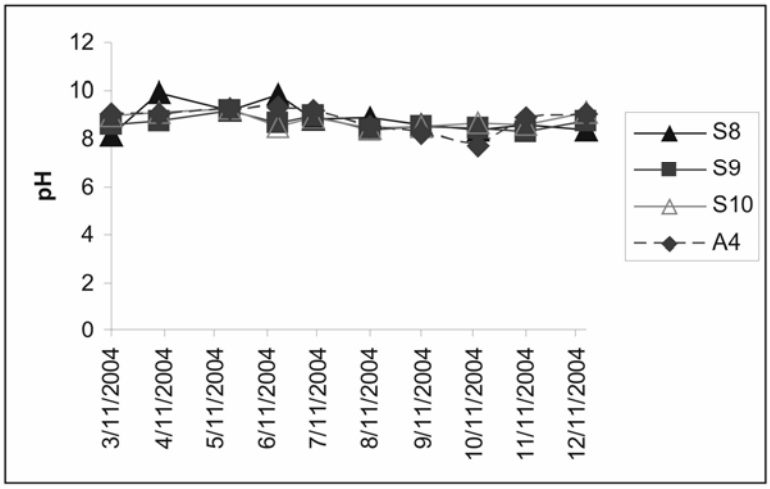


**Figure 4:** pH in monthly water samples.

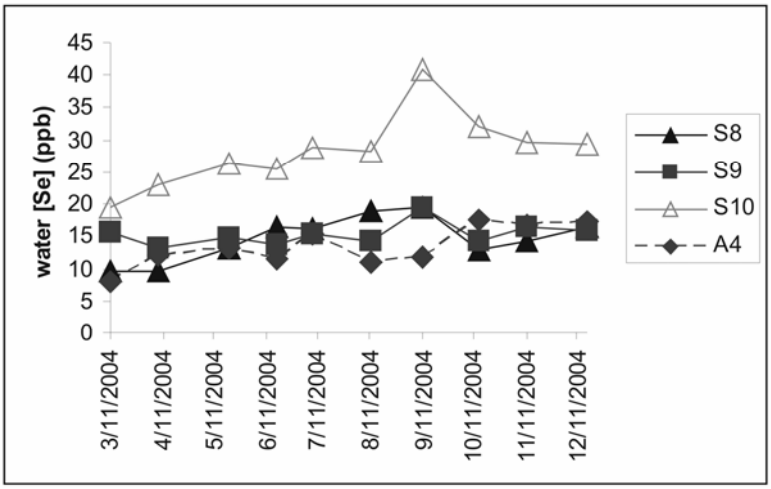


**Figure 5:** Se concentrations in filtered

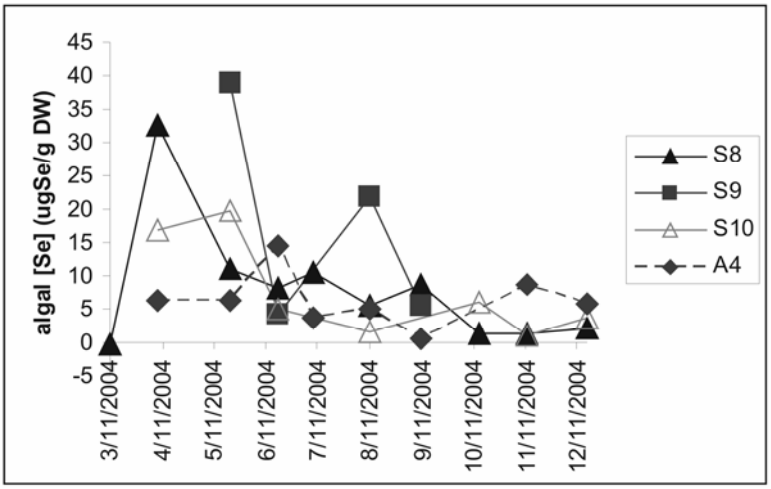


**Figure 6:** Algae Se concentrations.

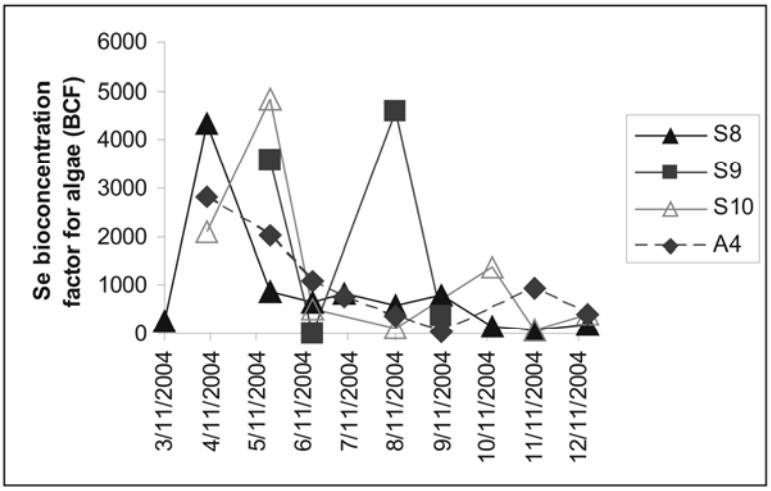


**Figure 7:** Se bioconcentration factor or BCF of algae,

The effect of brine shrimp harvest on algal Se status is shown in Figure 6 (algae Se concentrations), Figure 7, (Se bioconcentration factor or BCF based on dry mass), and Figure 8 (protein Se concentrations) in the TLDD basins. The algal Se body burden data of the three ponds for which data are most complete (HAC A4 and SEB 8 and 10) follow the same patterns over time, peaking at the beginning of the year when conditions favor algal growth and declining towards the end of the year, though algal Se returned to early season levels in HAC A4 in November, 2004 (Fig. 6). The heavily harvested basin SEB 9 had so little algal biomass that samples were usually not available for analysis of algal Se body burden and the few data points presented are difficult to interpret (Fig. 6). Also noted is that the algal Se burden of the historically harvested cells (SEB10 and HEB A4) was lower at the start of the harvest season (April, Fig. 2) than that of the unharvested cell (SEB 8), similar to trends reported previously. The concentrations of Se in the protein of algae were similar in all ponds and generally followed the trend of the total Se body burden but unrelated to harvest activity. The Se BCF in algae varied similarly over time among the South Basins (SEB 8 and 10) while it declined steadily throughout the year in the Hacienda basin, HAC A4 (Fig. 7). Again, data are scarce for SEB 9 due to low recovery of algal biomass. Measurements of concentrations of Se associated with protein in algae represent Se that is readily bioavailable to the next tropic level (invertebrates). Protein Se in algae was similar in the historically harvested HAC A4 and SEB 10 basins, declining over the harvest season and increasing slightly at the end of the year (Fig. 8). Again, data are difficult to interpret for SEB 9 because there were only four samples collected for the year. Wide variation was seen in the protein Se content of algae in the unharvested basin, SEB 8, showing a cyclic trend similar to that noted in the algal density (Fig. 1).

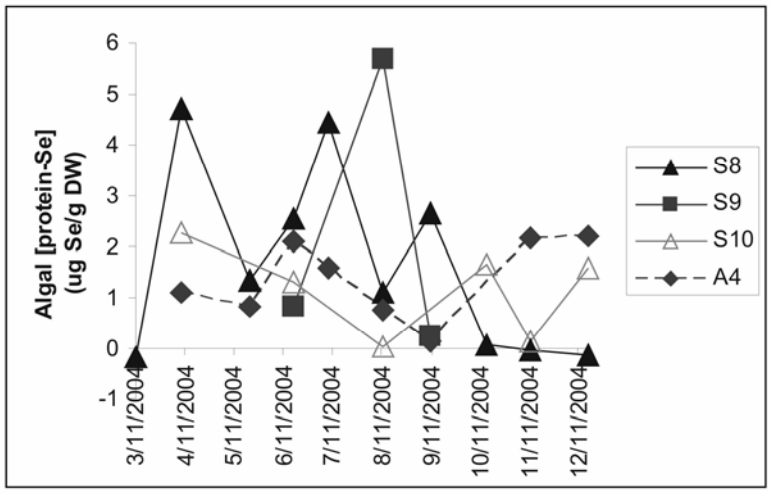


**Figure 8:** Algal protein Se concentrations.

Considering the Se status in brine shrimp, the one effect of harvesting appears to be a disruption of Se transfer from microalgae to the macro-invertebrates, as noted in previous years. For example, the negative correlation between water Se concentration and brine shrimp BCF is more scattered in the harvested basins than in those that were not harvested (Fig. 9). Also, while the lowest water-borne Se concentrations were seen in un-harvested basins, the highest shrimp BCF were also seen there. This observation indicates a greater efficiency in the un-harvested basins at

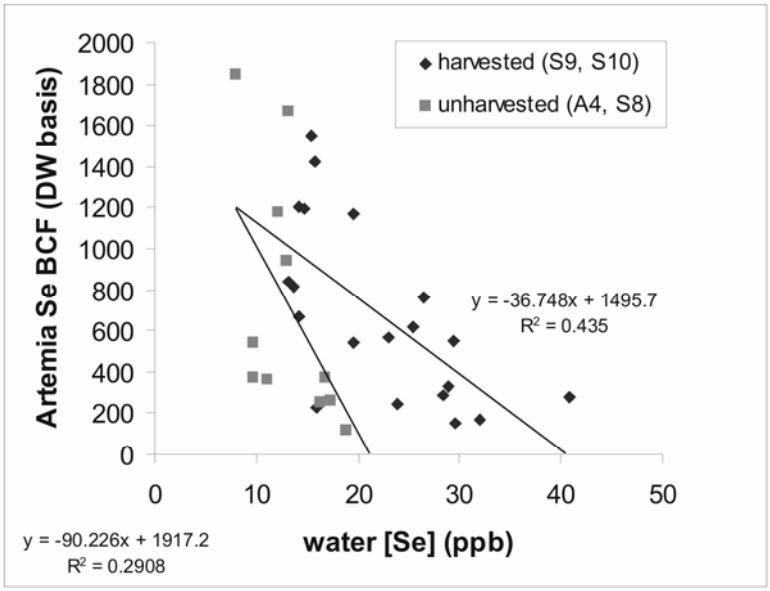


**Figure 9:** Water Se concentration and brine shrimp BCF.

transferring Se from the water column into the invertebrates, relative to harvested basins.

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 19 and 20, 2004. The Se status of these samples along with the water [Se] is shown in Figure 10 (total Se) and 11 (protein Se). As in the monthly monitoring, the highest waterborne Se concentration measured was in the most heavily harvested basin, SEB 9. The algae of this basin also had the lowest Se body burden of any measured, with low Se concentrations in invertebrates as well (Fig. 10). In SEB 10 the Se body burden of the water column macroinvertebrates was also consistently higher than that in the algae or in the benthic organisms. The total Se concentration measured in biota from the unharvested basins (SEB 1, SEB 8, and HAC A3, HAC C1, HAC C3) exhibited no trend related to taxa. Exhaustive harvest of the brine shrimp in SEB 9 have helped to funnel Se to the water column organisms via enhancing algal growth, while reducing Se incorporation into benthic organisms by limiting detrital deposition and, thus, growth and consumption of Se by benthic organisms. A similar trend was observed for the proteinaceous Se burden of algae, water column and benthic macroinvertebrates composites (Fig. 11). In fact, total and proteinaceous Se concentrations were well correlated in the annual survey samples (data not shown). As observed in previous years, no clear correlation was discerned from the water [Se] to the Se burden of algae, water column or benthic invertebrates and from salinity (cf. Fig. 10) to water [Se]; the former 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 bioconcentration. The lack of water Se buildup with increasing salinity is consistent with Se removal via volatilization and/or brine shrimp harvest (see Se volatilization by Microalgae).

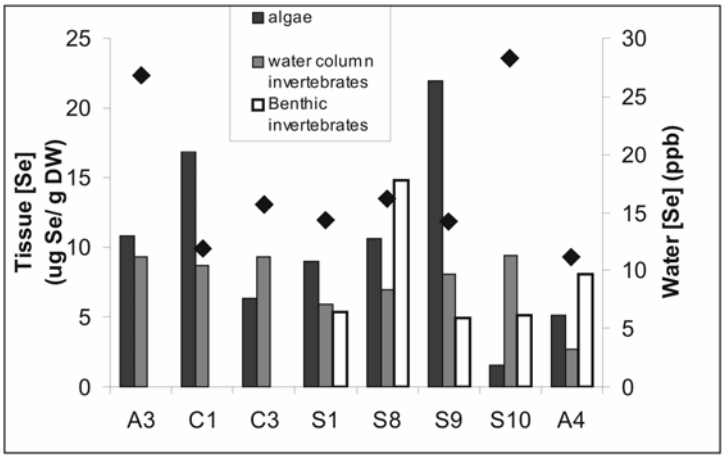


**Figure 10:** Total Se concentrations in algae, water column invertebrates, benthic invertebrates, and water samples collected on July 19, 2004.

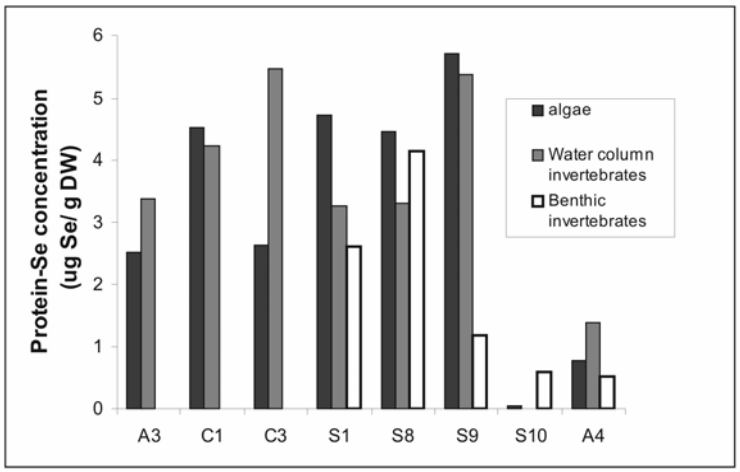


**Figure 11:** Proteinaceous Se concentrations in algae, water column invertebrates, benthic invertebrates, and water samples collected on July 19, 2004.

**SE VOLATILIZATION BY MICROALGAE**

As in previous years, measurements of volatile Se of water collected at the upwind and downwind corners of the basins in both morning and afternoon were made on site during the annual field sampling trip (July 19, 2004). Figure 12 shows the volatile Se content of TLDD basin waters in downwind locations (collected from the south shores) in the morning and in the afternoon in comparison with basin salinity. Diurnal differences were not

consistent, as they have been previously, with the terminal ponds for the two Hacienda series basins (C3 and A4) showing a different pattern (higher in the afternoon) than the other ponds. As seen previously, there appears to be a rough relationship between salinity and volatile Se production. The least saline ponds (SEB 1 and HAC C1) had non-detectible Se volatilization and, of the regularly monitored ponds, the most saline (HAC A4) had the highest rate of Se volatilization. The other terminal pond in the Hacienda system (HAC C3) had the highest total Se volatilization, though at the time of testing salinity was not as high there as in HAC A4.

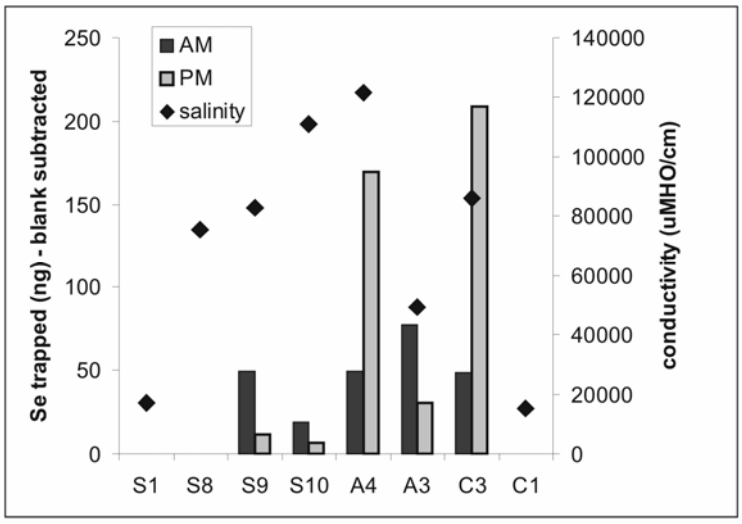


**Figure 12:** Volatile Se content of TLDD basin waters at a down-wind location in the morning and in the afternoon in comparison with basin salinity.

Figure 13 shows the average downwind volatile Se content of TLDD basin waters in comparison with the bioconcentration factor (BCF, on a dry wt basis) of Se by microalgae for the 2004 field measurement. As noted above, of the basins which are regularly monitored, the basin with the highest Se volatilization was HAC A4. This basin also tended to accumulate the very little Se (Fig. 13). This basin was only occasionally harvested in 2004, but has been extensively harvested in past years. It also had the highest average salinity for 2004. The other terminal basin in the Hacienda series (HAC C3) also had high Se volatilization, but the algal BCF was not among the lower measured values. Basins SEB 9 and SEB 10, which were most heavily harvested, show mid-level Se volatilization, but one had very low algal BCF (SEB 10) while the other had high algal BCF (SEB 9). The un-harvested basins, SEB 1 and SEB 8 show negligible Se volatilization and low algal BCF. Un-harvested basin HAC C1 shows negligible volatile Se and highest measured algal BCF, which has been repeatedly observed in less saline un-harvested basins in previous years. These results indicate that high salinity is an important factor in modulating Se volatilization.

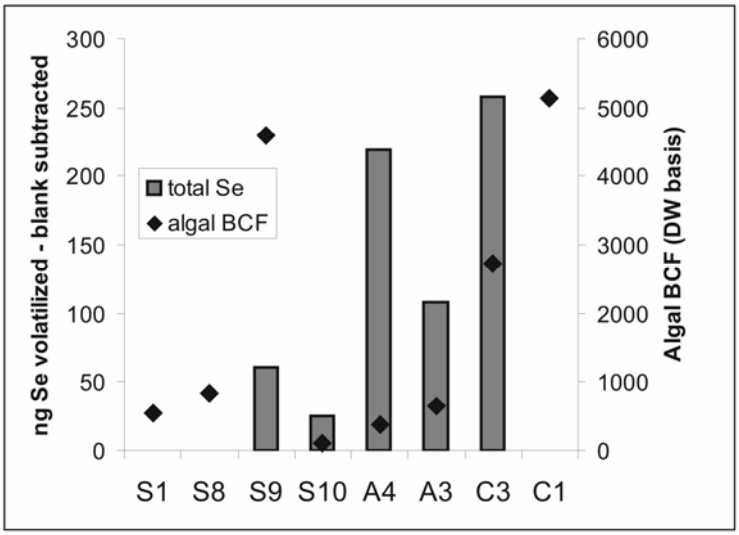


**Figure 13:** Total (am and pm) downwind volatile Se content of TLDD basin waters in comparison with the algal Se bio-concentration factor (BCF, on a dry wt basis).

**MULTI-YEAR TRENDS**

The chl a fluorescence and harvest activity observations described above and compiled for the multiple years of this study suggest relationships between harvest activity and algae yields. However, algae yields obtained in this study are calculated from monthly sampling and brine shrimp harvest data is monitored on a daily basis.

Furthermore, the timing of the monthly sampling is not explicitly linked to harvest activity such that the day of sampling may not be representative of the harvest that month. Also the effects of harvest activity will not be translated onto the algal community within a 24 hour period. Therefore, the algae yield was related to a period of harvest activity longer than one day to develop a connection to shrimp harvest. A period of 7 days was chosen such that the net effects of brine shrimp harvest on the algal population at the beginning and end of the time frame are representative of the entire time frame. High salinity and the presence of corixids may also interfere with algae yield calculation. Data obviously impacted by these conditions were excluded from analysis of harvest activity versus algae yield.

Consistently, when compiled over multiple years, reliable algae yield data and significant shrimp harvest were attained in South Basins S9 and S10. Figure 14 shows a plot of a cumulative 7 day brine shrimp harvest versus algae yield for basin S9 in years 2001, 2002 and 2004. Figure 15 shows a plot of cumulative 7 day brine shrimp harvest versus algae yield for basin S10 in years 2001, 2002 and 2004. The data from basins S9 & S10 in 2001 and 2004 show the algae yield decreasing as brine shrimp harvest increases in both basins, supporting the hypothesis of algal consumption by brine shrimp production drawn from the chl a fluorescence and harvest activity data. However, in 2002 the algae yield in basin S9 and S10 increased with increasing brine shrimp. This suggests that there was a large portion of the algal population that was not consumed by brine shrimp and continued to grow despite the grazing of brine shrimp.

The algal communities in each basin can be categorized as Se accumulating or Se

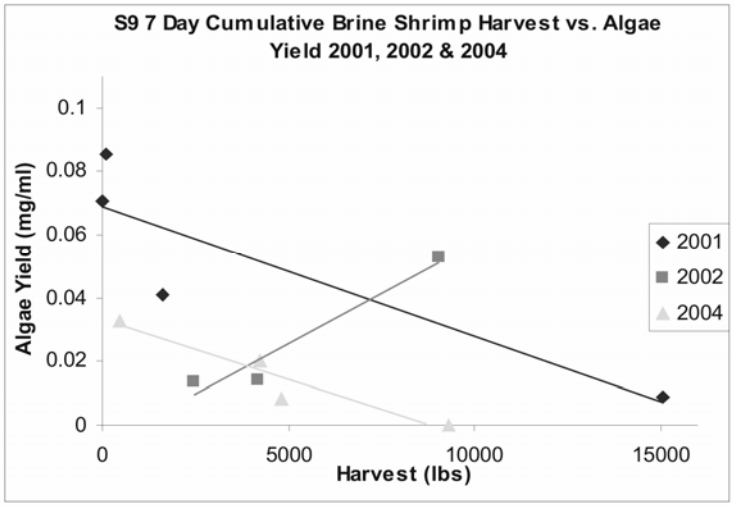


**Figure 14:** Cumulative 7 day brine shrimp harvest versus algae yield for basin S9 in years 2001, 2002 and 2004

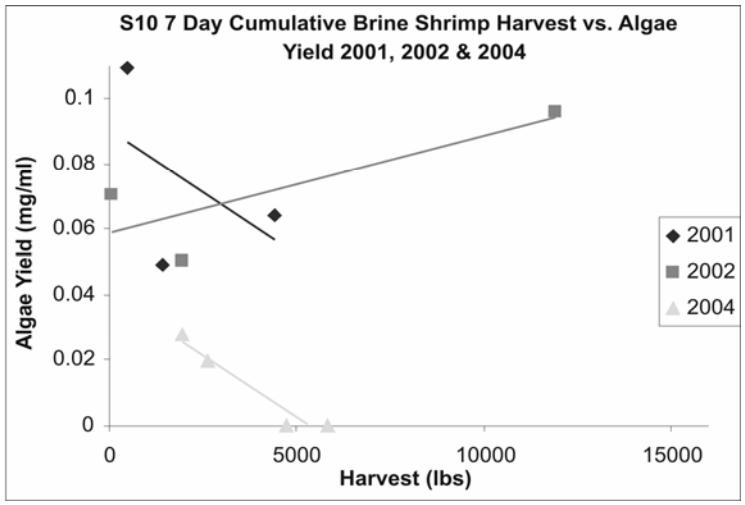


**Figure 15:** Cumulative 7 day brine shrimp harvest versus algae yield for basin S10 in years 2001, 2002 and 2004

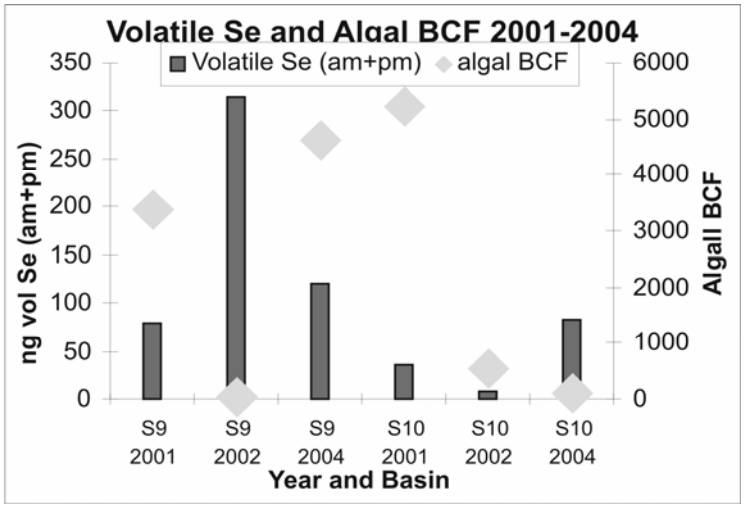


**Figure 16:** Se bioconcentration factors (BCF) for algae and pond water Se volatilization potential derived from annual sampling data for SEB9 and SEB10 in 2001, 2002, and 2004.

volatilizing communities based on data collected from yearly sampling (Figure 16). When the algal bioconcentration factor (BCF) is large relative to the Se volatilization potential, the community can be considered accumulating, while the opposite relationship characterizes a volatilizing community. These assignments along with the fact of shrimp harvest as a net consumption of algae or not (figures 14 and 15) can be used to understand the movement of Se in each basin.

The algal community in basin S9 year 2001 can be designated as an accumulating community (figure 16) being consumed by brine shrimp (figure 14). The same can be said of the algal community in basin S10 in 2001 and S9 in 2004. In these basins and years the whole water [Se] remains very close to the filtered water [Se] as algae yield increases (figure 17 a and c). These observations support the notion that the portion of the algal community accumulating Se is being eaten by and accumulating in the brine shrimp.

The algal community in S9 year 2002 can be designated as a volatilizing community (figure 16) with a larger portion of the community not being consumed by brine shrimp (figure 14). As in 2001 and 2004 the whole water [Se] remains very close to the filtered water [Se] as algae yield increases in basin S9 (figure 17 b). Although less algae is being removed from the system, Se is not accumulating in the algae. This suggests that Se is being removed from the algal compartment through volatilization with less accumulation.

The algal community in S10 year 2002, although the BCF is low relative to other years, can be designated as a primarily accumulating community (figure 16) with a large portion of the community not consumed by brine

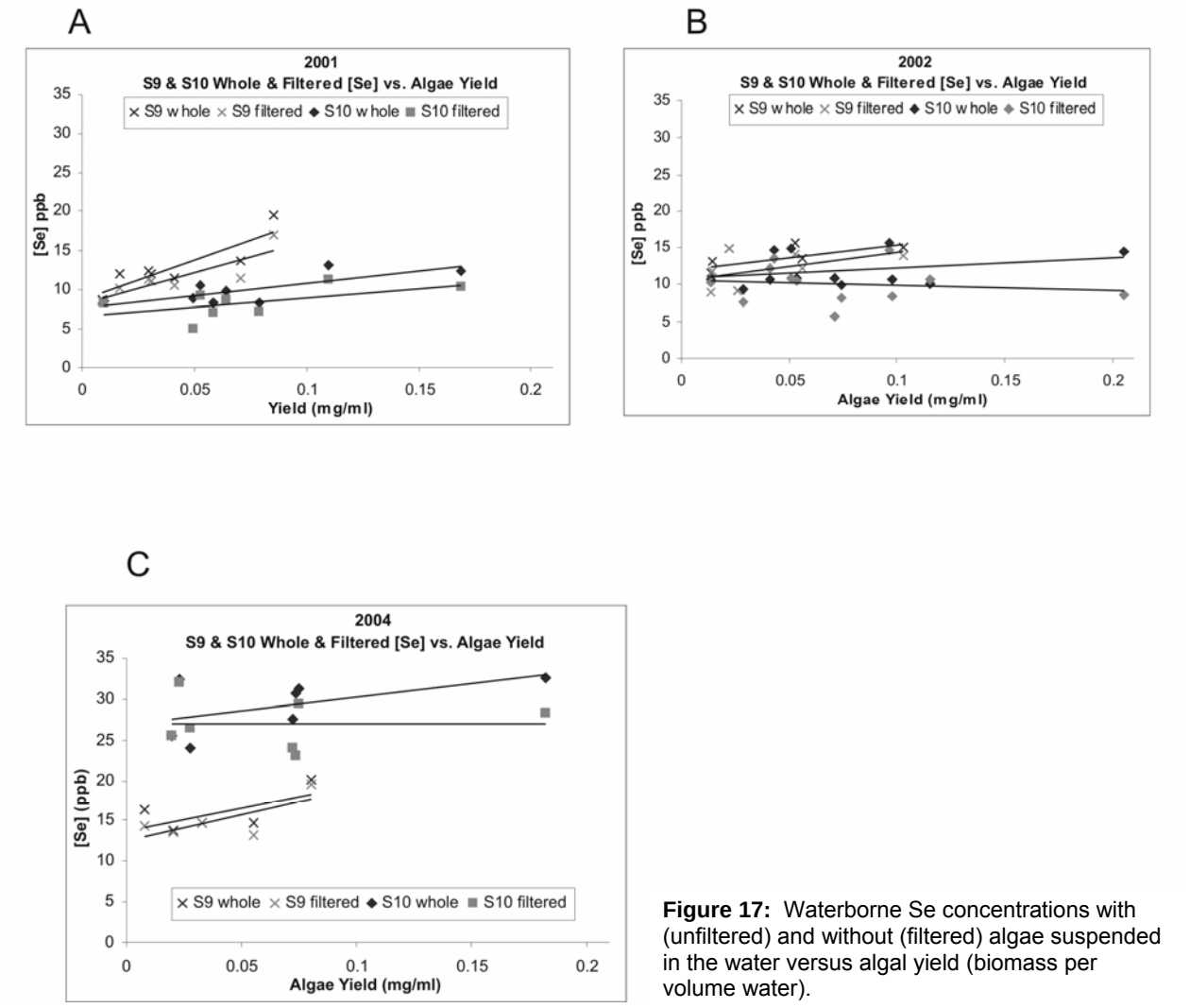


**Figure 17:** Waterborne Se concentrations with (unfiltered) and without (filtered) algae suspended in the water versus algal yield (biomass per volume water).

shrimp (figure 15). The difference between whole water [Se] and filtered water [Se] increases with increasing algae yield in this basin (figure 17 b). Low removal of algae through consumption, low removal of Se from the basin through volatilization, and an accumulation of Se in the algae compartment as the algae yield increases supports these observations. In 2004 the algal community in basin S10 is primarily, although low, a volatilizing community (figure 16) that is being consumed by brine shrimp (figure 15). The difference between the whole water [Se] and filtered water [Se] increases with increasing algae yield (figure 17 c). This supports the idea that the volatilizing algae are being removed from the system through consumption by brine shrimp and Se is accumulating in the portion of the algal community left behind.

Although, these relationships illustrate the movement of Se in the evaporation basins at TLDD, they also demonstrate the importance of continued study of algal typing and Se loads, together with shrimp harvest, invertebrate loads, and Se volatilization in these basins.

**MICROALGAL COMMUNITY ANALYSES**

Monthly microalgal composite samples were extracted for total DNA, amplified with cyanobacterial 16S rDNA primers, and the resulting Polymerase Chain Reaction (PCR) products analyzed by Denaturing Gradient Gel Electrophoresis (DGGE). Figure 18 shows the DGGE gel patterns for environmental algae samples collected during 2003 from TLDD basins

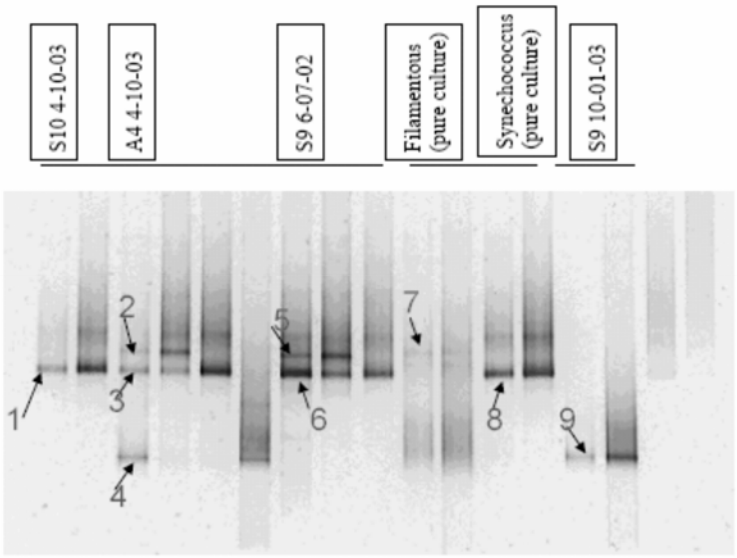


**Figure 18:** DGGE gel used for identification of algal strains through DNA sequencing. Various field and laboratory isolate samples are identified in lanes 1, 3, 7, 10, 12, and 14. Lanes immediately following each of these are further amplified samples of the numbered bands (e.g. band #1 in lane one was further amplified to produce bands in lane 2).

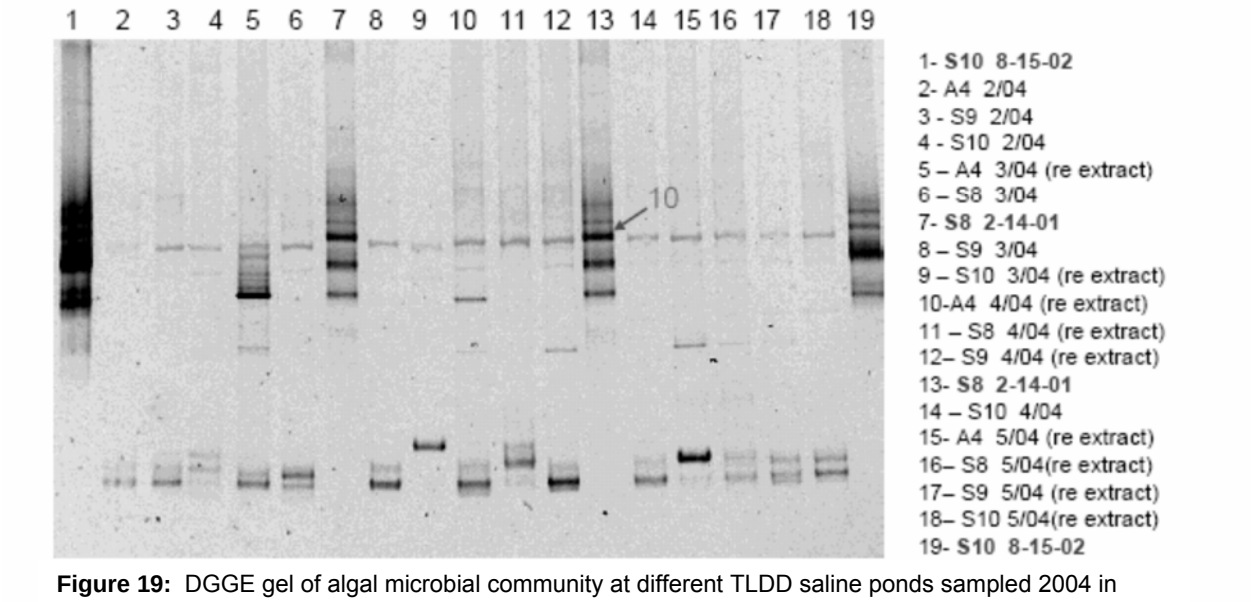


**Figure 19:** DGGE gel of algal microbial community at different TLDD saline ponds sampled 2004 in comparison with samples from previous years.

SEB 10, SEB 9, SEB 8, and HAC A4, along with two isolated monocultures. Our effort was to identify the dominant DGGE bands by DNA sequencing and thus reveal the microalgal community composition. Bands indicated with arrows ( #1-9, Fig. 18) were cut, re-amplified, run on agarose gel, and purified with Quiagen kit before sending for sequencing. Based on sequencing comparison with the available 16S rRNA data base (Gene Bank and RDP) we identified the following algal species: *Chlorella mirabilis* (band # 1, 3, 6, and #8 –pure culture), *Koliella spiculiformis* (band # 2, #5), *Synechococcus* sp. (band # 4, band #9), and *Oscillatoria neglecta* (# 7, pure culture filamentous alga). Band #10 (Fig. 19) is most similar to uncultured phototophic eukaryotic clone from hypersaline Mono Lake, CA, and is dominant band in all samples from year 2004.

Our previous observations of the gel patterns of algae collected during 2002-2003 were that a number of the samples had the same 2 gel bands (#2 and 3), now identified as the green algae *Chlorella* and *Koliella* sp. For example, the appearance of these 2 species for the HEB A4 samples seemed to relate to the strength of the harvest activity. The 2 green algae were present starting 4/4/02 and persisted until 7/19/02, after which they were not detected (cf. Fan's report, 2003). The opposite is true for the *Synechococcus* sp. (band # 4), which was not present during this intensive harvest period (4/4/02 to 7/19/02), but was very persistent after 7/19/02 and during the 2003 sampling. It is likely that the green algae *Chlorella* and *Koliella* sp. promote brine shrimp growth, while *Synechococcus* sp. was left behind by the brine shrimp. It should also be noted that *Synechococcus* sp. is very active in Se volatilization (cf. Fan's report, 2003).

Significant change in microalgal community composition was observed in 2004 samples in comparison with the previous three years, probably due to changes in management operation (e.g. due to differences in water availability) of the TLDD saline basin cells (Figure 19).

To follow up on studying the ecological role and significance in Se volatilization of *Synechococcus* sp., we utilized quantitative PCR approach to estimate the cell densities of *Synechococcus sp.* in relationship with total micro-eukaryotic cell densities present in the ponds. During the past year we optimized PCR conditions and generated standards by cloning rDNA from *Synechococcus sp.* and rDNA from *Sacchromyces cerevizae* pure cultures. Figure 20 shows the standard curves used for quantification of rDNA copy numbers of *Synechococcus* and total micro-eukaryotes in environmental samples. For year 2002 monthly samples we determined the relative abundance of *Synechococcus* sp. at four different ponds. In general, PCR quantified total micro-eukaryote's copy numbers, are in the range of $10^7$ to $10^8$ copies per µg extracted DNA per mg dry algal biomass in all four ponds, indicating that the same size of population is present at this hypersaline environment (Figure 21). Additionally we observed that *Synechococcus* sp. are representing significant portion (more than 90 %) of algal community during the summer months (July to September) in S10 and S8 ponds. Also the population size of

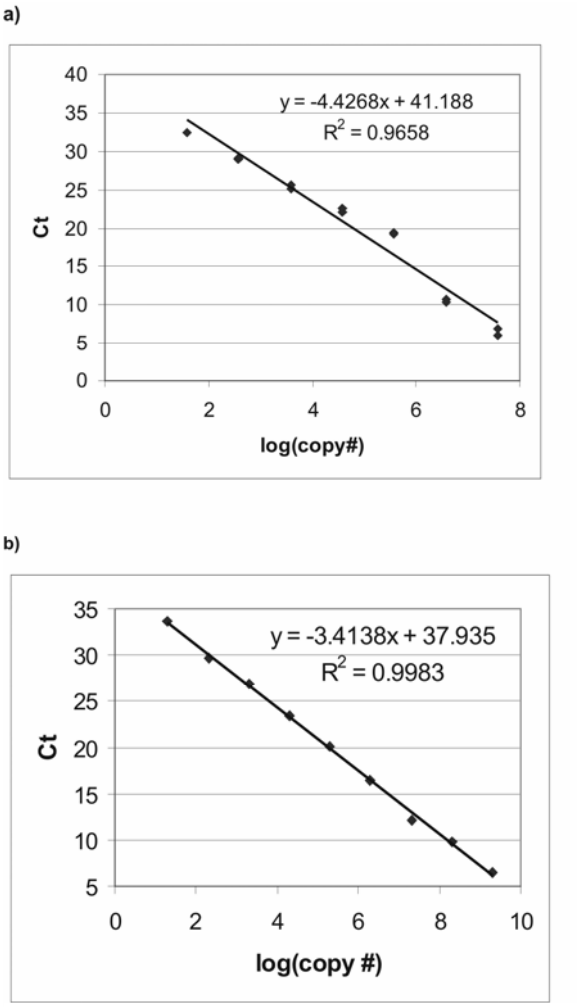


**Figure 20:** Quantitative PCR standard curves for quantification of total micro-eukaryotes (a) and *Synechococcus* algal species (b).

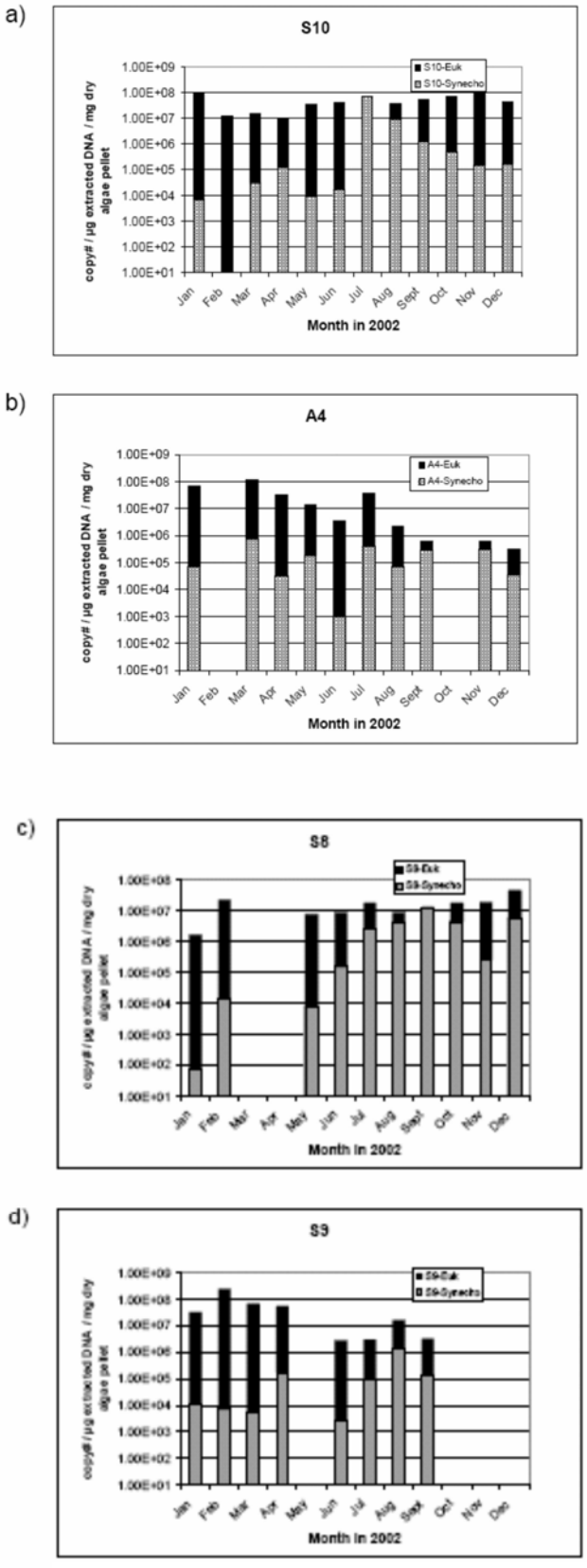


**Figure 21:** PCR quantification of total eukaryotic microbial community and *Synechococcus* algal species at four different hypersaline ponds during year 2002.

*Synechococcus* was larger in S8 pond (July to December) ranging from $10^5$ to $10^7$ copies/µg DNA/ mg dry biomass in comparison with the other three ponds (Fig. 21). Note that, for these samples, S8 and S10 are the less saline and harvested cells than the rest (cf. Fan et al., 2001), although that may not be generally true.

We are currently in the process of quantifying by qPCR the eukaryotes and *Synechococcus* populations for years 2001 and 2003 samples.

## CONCLUSION

The data acquired in 2004 indicate that waterborne Se, algal Se, and invertebrate Se did not increase as a result of increasing salinity, as repeatedly reported for previous years. Biotic and abiotic dynamics of Se that were observed in the TLDD evaporation basin system during the 2004 monitoring effort included:

- Brine shrimp grazing had a measurable effect on microalgal population density
- Brine shrimp harvesting reduced the efficiency of Se transfer from algae to invertebrates as determined by comparison of shrimp BCF in harvested and un-harvested basins.
- Brine shrimp harvest, while enhancing algal growth, reduced Se incorporation by benthic organisms in some basins.
- Salinity was an important determinant in Se volatilization rates by microalgal communities.

Data collected during many years of monitoring have demonstrated the stability with regards to Se water and biota concentrations of the TLDD evaporation basin system in both un-manipulated and brine shrimp producing scenarios. Specific conditions present at certain times in certain basins produced algal communities observed to serve a variety of functions relative to Se biochemistry. They were shown to:

- accumulate Se and provide food for brine shrimp, passing Se up the food chain,
- remove Se from the system via volatilization,

- accumulate Se without supporting brine shrimp growth, and
- volatilize Se and provide food for brine shrimp.

Our recently developed ability to quantify the percent of the algal population represented by a proven Se volatilizer (*Synechococcus* sp.) will further investigations into the exact make-up of microalgal communities exhibiting each of the functionalities observed. Further documentation of changes in microalgal community accompanying the harvest operations and mechanisms for directing community development to support shrimp harvest and/or Se volatilization are the future focus of this project.

## PUBLICATION

Higashi, R.M., Cassel, T.A., Skorupa, J.P., and Fan, T.W-M. 2005. Remediation and Bioremediation of Selenium-Contaminated Waters. In: Water Encyclopedia, John Wiley & Sons, Int'l Digital Object Identifier (DOI): 10.1002/047147844X.wq496. Available at: http://www.mrw.interscience.wiley.com/eow/articles/wq496/frame.html

# Removal of Selenium from River Water in Organic Carbon Coated Sand Columns by *Enterobacter taylorae* Isolated from a Rice Straw Bioreactor


**Project Investigators**

William T. Frankenberger, Jr.
Department of Environmental Sciences
University of California, Riverside
Riverside, CA 92521
Phone: (951) 827-3405, E-mail: william.frankenberger@ucr.edu

Yiqiang Zhang
Department of Environmental Sciences
University of California, Riverside
Riverside, CA 92521
Phone: (951) 827-5218, E-mail: yqzhang@ucr.edu

## ABSTRACT

Discovering an effective means to remove selenium (Se) from Se-contaminated water is fundamental in minimizing environmental contamination and ensuring wildlife protection. In this study, *Enterobacter taylorae* attached to tryptic soy agar (TSA) coatings was used in sand columns to remove Se from a natural river water. During 80 days of the experiment, *E. taylorae* and indigenous Se(VI) reducers in the water used organic carbon coatings to effectively reduce Se(VI) to Se(0). About 95 and 70% of the influent Se (469 µg/L) was reduced to Se(0), respectively in the columns with and without *E. taylorae* and 94-98% of the newly-formed Se(0) was trapped in the columns. Analysis of Se species in effluent at the end of the experiment revealed that organic Se from the columns with *E. taylorae* was similar to that in influent (0.567 µg/L). This study indicates that using organic coatings attached with Se(VI) reducers in a biotreatment system may be a potentially feasible method to remove Se from Se-contaminated water in field.

## INTRODUCTION

Elevated selenium (Se) of agricultural drainage water had created serious hazards to fish and waterfowl in the San Joaquin Valley, California (Ohlendorf, 1989; Presser and Ohlendorf, 1987). Concerns for the safety of these waterfowl production areas make it very important for scientists and wetland managers to find ways for removing Se from agricultural drainage water before it is disposed into aquatic systems.

Reduction of Se(VI) to Se(0) is one of the major biogeochemical processes in aquatic systems (Gao et al., 2000; Velinsky and Cutter, 1991; Weres et al., 1989; Zhang and Moore, 1996). Many bacteria isolated from aquatic systems have been found to be capable of reducing Se(VI) to Se(0), i.e. *Wolinella succinogenes*, *Pseudomonas stutzeri*, *Sulfurodpirillum barnesiii*, *Enterobacter cloacae*, *Thauera selenatis*, *Enterobacter taylorae*, and *Citrobacter freundii* (Francisco et al., 1992; Lortie et al., 1992; Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2004a). The reduction rates of Se(VI) are affected by microbial activity, competitive electron acceptors, effective organic carbon sources as energy/electron donors, and various environmental conditions (Francisco et al., 1992; Lortie et al., 1992; Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003; 2004a). Because of the insolubility of Se(0) in aquatic systems, reduction of Se(VI) to Se(0) is considered to be a useful technique for removing Se from Se-contaminated water.

A general bacterial treatment system for removal of Se from Se-contaminated water often uses a liquid phase of organic carbon sources such as acetate, lactate, and glucose (Cantafio et al., 1996; Losi and Frankenberger, 1997; Oremland et al., 1999; Zahir et al., 2003; Zhang et al., 2003; 2004a). Only small amounts of the liquid phase of organic carbon are commonly used by Se(VI) reducers to reduce Se(VI) before it flows out of the system with the treated water (Tucker et al., 1998). A large amount of organic carbon often goes waste due to inefficient usage, which results in a high cost of these expensive chemicals for biotreatment in the field. Therefore, if the organic carbon is fixed in a biotreatment system as a solid particle on which Se(VI) reducers can attach and use it as a source of energy and electron donors to reduce Se(VI) to Se(0) when soluble Se(VI) passes through, the loss of organic carbon by flowing water would be limited, which would potentially reduce the cost for treating Se-contaminated water.

In this study, we tested the use of an organic carbon-coated sand column for removal of Se from Se-contaminated water by a Se(VI)-reducing bacterium, *Enterobacter taylorae*.

## MATERIALS AND METHODS

### RIVER WATER

River water used in this study was collected from New River, California. The water, with a pH of 8.2 and salinity [electrical conductivity (EC)] of 2.3 dS/m, contained 5 µg/L Se(VI), 1 µg/L of selenite [Se(IV)], 0.567 µg/L of organic Se, 9.23 mg/L of $NO_3^-$-N, 0.04 mg/L of $NH_4^+$-N and 0.88 mg/L of $PO_4^{3-}$-P. The river water was passed through a 5 µm filter to remove detritus prior to use. Se standard solution [Se(VI), 10,000 mg/L] was passed through a sterile 0.2 µm membrane filter prior to its addition to the water. The final Se concentration in the water (influent) was 469 µg/L.

### TRYPTIC SOY AGAR-COATED SAND COLUMN

In one of our previous studies, we had isolated a Se(VI)-reducing bacterium, *E. taylorae* from a rice straw bioreactor and used this bacterium to reduce Se(VI) in artificial and natural drainage water in the laboratory batch studies (Zahir et al., 2003; Zhang et al., 2003). During the isolation, we found that the bacterium colonies can tightly attach to the surface of tryptic soy agar (TSA) (DIFCO, Becton Dickinson, MD) and rapidly reduce Se(VI) to red Se(0). Slow-moving deionized water did not wash away these colonies. Inspired by these observations, we fixed tryptic soy agar (an organic carbon source) on the surface of sand in this study and then used the organic coatings as sites for *E. taylorae* to attach and use this fixed carbon source to reduce Se(VI) to Se(0). Sand and 5% of the TSA solution with 0.05% of each glucose and yeast extract (DIFCO, Becton Dickinson, MD) were separately autoclaved (18 psi at 121 °C) for 20 minutes. Hot sand was moistened with the hot TSA solution, and then spread onto a sterile plate until cooling to room temperature (21 ºC). Aggregates of the TSA-coated sand were separated by hand.

### FLOW-THROUGH BIOREACTOR

The flow-through bioreactor consisted of three units: a flask containing the river water spiked with Se(VI) to a final Se concentration of 469 µg/L, a peristaltic pump, and 60-ml syringes used as TSA-coated sand columns. The columns were filled with sterile glass wool at the bottom, TSA-coated sand, and sterile glass beads on top. After the addition of a washed *E. taylorae* cell suspension, the columns were incubated for 3 days, and then the river water (without adding any additional organic carbon sources) was pumped through the columns with a hydraulic residence time of ~0.7 day. The experiment was run in duplicate at a room temperature (21 ºC). The columns without the addition of *E. taylorae* served as a control. Effluent water samples were collected twice a week for the first 54 days and then weekly for the rest of the experiment. The water samples for total Se and total soluble Se were stored in a freezer until analysis. Se species in water samples were analyzed at the end of the experiment.

### ANALYSIS

Total Se, total soluble Se, and Se species [Se(VI), Se(IV) and organic Se] in the water samples were determined by a method developed by Zhang and Frankenberger (2003a). Se concentrations in prepared solutions were analyzed by hydride generation atomic absorption spectrometry (HGAAS) (Zhang et al., 1999). The methods for calculation of Se(0) and Se mass in the biotreatment system are presented in Table 1.

Table 1. Equations for calculating Se mass in the columns.

| Se | Equations |
|---|---|
| Total input Se to the columns | $\sum_t$ (water flow rate * Se in influent) |
| Total soluble Se output from the columns | $\sum_t$ (water flow rate * soluble Se in effluent) |
| Total Se(0) output from the columns | $\sum_t$ (water flow rate * Se(0) in effluent) |
| Total trapped Se(0) in the columns | $\sum_t$ (total Se in influent - total Se in effluent in each column) |

The term t is time.

## RESULTS AND DISCUSSION

Changes in concentrations of Se in the influent and effluent from the TSA-coated columns are illustrated in Fig. 1. During 80 days of the experiment, total Se in the influent had little change, ranging from 464-473 µg/L. However, total Se and total soluble Se were dramatically altered in the effluent when Se passed through the TSA-coated columns. In the columns with *E. taylorae*, total Se and total soluble Se dropped rapidly to a level of 15.3-20 µg/L in the first 20 days of the experiment, and remained at this level to day 52. Total Se and total soluble decreased to a low level of 3.45-6.54 µg/L during the rest of the experiment. Rapid removal of the added Se(VI) in the TSA-coated sand columns was attributed to bacterial reduction of Se(VI) to Se(0), which was visible by the observation of red Se(0) precipitates on the surface of the coatings at the lower part of the columns after the experiment. The Se(VI) reducing bacterium, *E. taylorae* was isolated from a rice straw bioreactor for removal of Se(VI) from drainage water (Zhang and Frankenberger, 2003b). It has been used to effectively reduce 95% of the added Se(VI) (1000 µg/L) to Se(0) in a medium consisting of 500 mg/L of yeast extract during a 7-day batch experiment and directly reduce Se(VI) in natural drainage water collected from the western San Joaquin Valley, California (Zhang et al., 2003). This study reveals that *E. taylorae* can also effectively reduce a large amount of Se(VI) to Se(0) in a flow-through experiment. When a Se(VI)-reducing environment was optimized in the columns, reduction of Se(VI) to Se(0) occurred more effectively. In the final several days of the experiment, about 99% of added Se(VI) was reduced to Se(0) in the columns with *E. taylorae* added.

Not all of the reduction of Se(VI) to Se(0) was caused by *E. taylorae*. In the control columns without the addition of *E. taylorae*, total Se and total soluble Se also dropped to a range of 40.1-78.8 µg/L during the first 34 days and slowly decreased to 10.4-36 µg/L at the end of the experiment (Fig.1). In a batch study on the reduction of Se(VI) to Se(0) in the same New River water by *Citerobacter freundii*, Zhang et al. (Zhang et al., 2004a) reported that Se(VI) concentration slightly changed in the non-sterile river water without the addition of *C. freundii* during the first 5 days of the experiment, and then decreased rapidly from 968 to 168 µg/L, revealing that the existence of indigenous Se(VI) reducers in this river water that can contribute to Se(VI) reduction after acclimation. In this study, the existence of unknown indigenous Se(VI) reducers in the water resulted in reduction of Se(VI) to Se(0) in the control columns. However, the addition of *E. taylorae* into the columns significantly enhanced the reduction of Se(VI) to Se(0), with a 94.6-95% reduction of the added Se(VI) to Se(0) in the columns with *E. taylorae* added and a 70-70.2% reduction in the columns without the addition of *E. taylorae*.

Effective trapping of the newly-formed Se(0) in a biotreatment system is important to determine the effectiveness in bioremediation of Se-contaminated water (Barton et al., 1994; Zhang and Frankenberger, 2003b; Zhang et al., 2004b). In a recent study on the fate of newly-formed Se(0) in aquatic systems, Zhang et al. (2004b) reported that newly-formed Se(0) can be easily oxidized to Se(IV), and further to Se(VI) if newly-formed Se(0) flows out of a treatment system to a nearby aquatic system. Therefore, newly-formed Se(0) must be trapped before it flows

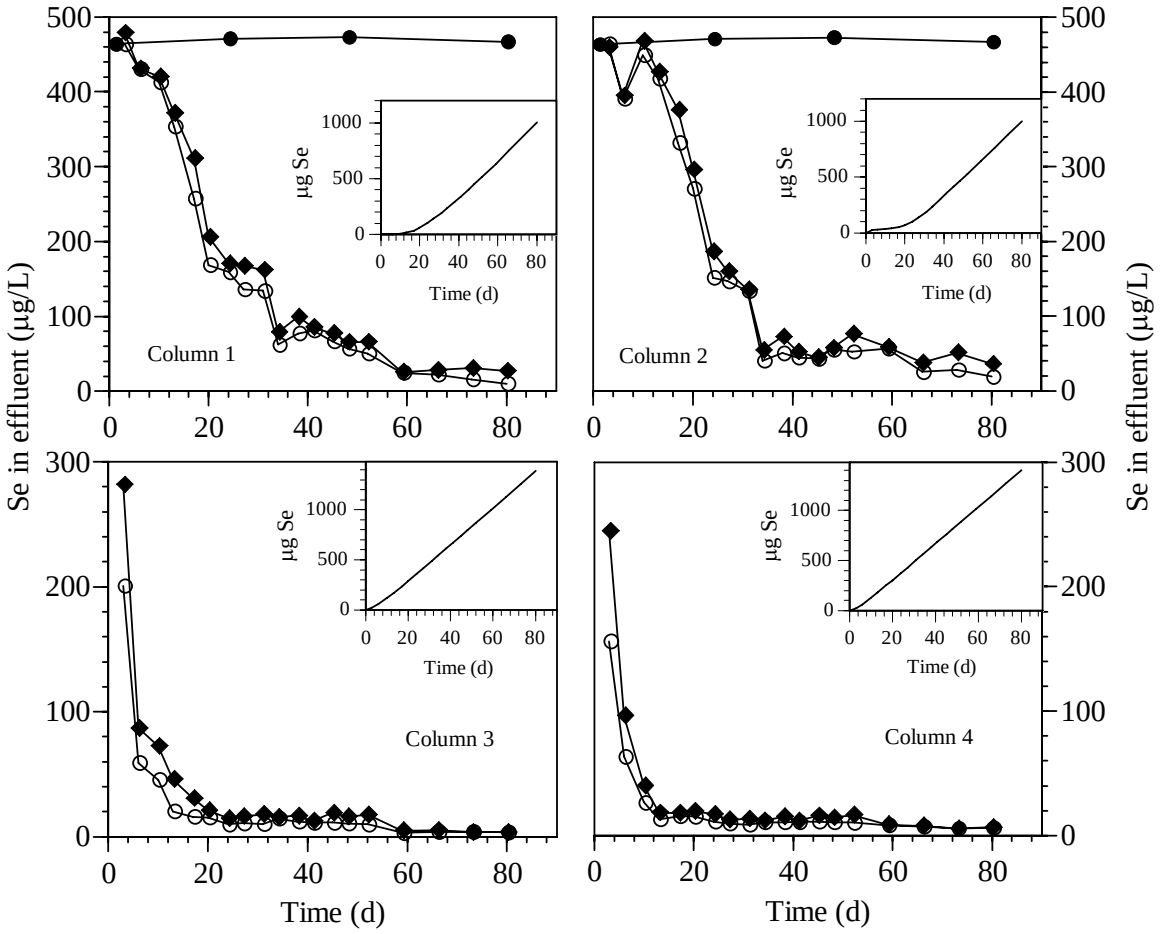


Fig. 1. Removal of Se from New River water with (duplicated columns 3 and 4) and without (duplicated columns 1 and 2) *Enterobacter taylorae* in the tryptic soy agar-coated sand columns. ◆: Total Se; ○: Total soluble Se; and ●: Total Se in influent. Inserted small figures show cumulative elemental Se in each column.

out of a biotreatment system with treated water. This study reveals that the newly-formed Se(0) was effectively trapped in the columns. Calculation of Se mass in the influent and effluent indicated that 95 and 70% of the added Se(VI) in the water was reduced to Se(0) when it passed through the columns with and without *E. taylorae*, respectively, and 94-98% of the newly-formed Se(0) was trapped in the columns (Table 2).

Fixation of organic carbon on the surface of sand particles as solid organic coatings can significantly reduce the cost for the removal of Se from Se-contaminated water because large amounts of the fixed organic carbon would

Table 2. Mass of Se (µg) in the TSA-coated sand treatment system.

| Columns | Total input Se | Trapped Se(0) | Soluble Se output | Se(0) output | Trapped Se(0) /Total input Se |
|---|---|---|---|---|---|
| 1 | 1501 | 1002 | 440.7 | 58.3 | 66.8 |
| 2 | 1501 | 998 | 447.1 | 55.9 | 66.5 |
| 3 | 1501 | 1388 | 81.8 | 31.2 | 92.5 |
| 4 | 1501 | 1402 | 75.1 | 23.9 | 93.4 |

be efficiently used by Se(VI)-reducing bacteria to reduce Se(VI) instead of flowing out of the system with treated water. In this study, only very small volumes of the TSA solution were used to moisten sand. During 80 days of the experiment, we did not add any additional organic carbon sources to the columns and influent. *E. taylorae* and other unknown indigenous Se(VI) reducers in the New River water used TSA coatings to effectively reduce Se(VI) to Se(0), with a 93% removal of the added Se(VI) in the columns inoculated with *E. taylorae*.

Concerns on bioavailability of Se in treated water have increased recently since the discovery of much higher bioavailability of Se in treated water than the influent in an algal-bacterial treatment system (Amweg et al., 2003). The bioavailability of Se in aquatic systems is largely dependent on the speciation of Se present (Besser et al., 1993; Lemly et al., 1993; Wang and Lovell, 1997). Studies by Besser et al. (1993) and Wang and Lovell (1997) showed that organic forms of Se have higher bioavailability than Se(IV)] or/and Se(VI), and bioaccumulate more rapidly. Increases in concentration of the most bioavailable organic Se in treated water creates greater problems to biota than that in influent (drainage water) (Amweg et al., 2003). Production of soluble organic Se may be related to the amounts of soluble organic materials used by bacteria to reduce Se(VI) to Se(0) in biotreatment systems. Although we do not know the total amounts of organic Se produced during this experiment because we did not monitor the changes of organic Se in the effluent throughout the study, analysis of Se species on the final day of the experiment shown that organic Se was 0.44-0.61 µg/L in the columns inoculated with *E. taylorae*, which was very close to the concentration of organic Se in the influent river water. Organic Se was relatively higher (2.25-2.95 µg/L) in the effluent from the columns without *E. taylorae* (Table 3).

Table 3. Soluble Se species in the effluent on the final day of the experiment.

| Columns | Se(VI) | Se(IV) | Organic-bound Se | Total Se |
|---|---|---|---|---|
| 1 | 4.05 | 3.38 | 2.92 | 10.35 |
| 2 | 4.05 | 25.7 | 2.25 | 32 |
| 3 | 1.58 | 1.43 | 0.44 | 3.45 |
| 4 | 1.65 | 4.04 | 0.61 | 6.3 |

Agricultural activity in California generates high-Se drainage water (Sylvester, 1990; Setmire and Schroeder, 1998). Se needs to be removed before its disposal to the nearby wetlands. This study shows that Se(VI) reducers attached to organic coatings can effectively reduce soluble Se(VI) to Se(0) when it passed through sand columns and it may be a potentially feasible method to remove Se from agricultural drainage water.

## REFERENCES


Amweg EL, Stuart DL, Weston DP. Comparative bioavailability of selenium to aquatic organisms after biological treatment of agricultural drainage water. Aquatic Toxicol. 2003; 63: 13─25.

Barton LL, Nuttall HE, Lindemann WC, Blake II RC. Biocolloid formation: an approach to bioremediation of toxic metal wastes. In Wise DL, Trantolo DJ, Eds. Remediation of hazardous waste and contaminated soils. New York, NY: Marcell Dekker Inc., 1994; pp 481─496.

Besser, J. M.; Canfield, T. J.; La Point, T. W. Bioaccumulation of organic and inorganic selenium in a laboratory food chain. Environ. Toxicol. Chem. 1993, 12, 57─72.

Cantafio AW, Hagen KD, Lewis GE, Bledsoe TL, Nunan KM, Macy JM. Pilot-scale selenium bioremediation of San Joaquin drainage water with Thauera selenatis. Appl. Environ. Microbiol. 1996; 62: 3298-3303.

Francisco AT, Barton LL, Lemanski CL, Zocco, TG. Reduction of selenate and selenite to elemental selenium by *Wolinella succinogenes*. Can. J. Microbiol. 1992; 38:1328-1333.

Gao S, Tanji, KK, Peters DW, Herbel M J. Water selenium speciation and sediment fractionation in a California flow-through wetland system. J. Environ. Qual. 2000; 29: 1275─1283.

Lemly AD, Finger SE, Nelson MK. Sources and impacts of irrigation drainage contaminants in arid wetlands. Environ. Toxicol. Chem. 1993; 12: 2265─2279.

Lortie L, Gould WD, Rajan S, Mccready RGL, Cheng KJ. Reduction of selenate and selenite to elemental selenium by a *Pseudomonas stutzeri* Isolate. Appl. Environ. Microbiol. 1992; 58:4042-4044.

Losi ME, Frankenberger Jr. WT. Reduction of selenium oxyanions by Enterobacter cloacae strain SLDaa-1: Isolation and growth of the bacterium and its expulsion of selenium particles. Appl. Environ. Microbiol. 1997; 63: 3079-3084.

Ohlendorf HM . Bioaccumulation and effects of selenium in wildlife. In: Jacobs LW, editor. Selenium in agriculture and the environment. Madison, WI: ASA and SSSA, 1989:133-177.

Oremland RS, Blum JS, Bindi AB, Dowdle PR, Herbel M, Stolz JF. Simultaneous reduction of nitrate and selenate by cell suspensions of selenium-respiring bacteria. Appl. Environ. Microbiol. 1999; 65: 4385-4392.

Presser TS, Ohlendorf HM. Biogeochemical cycling of selenium in the San Joaquin Valley, California, USA. Environ. Manage. 1987; 11: 805─821.

Setmire JG, Schroeder RA. Selenium and salinity concerns in the Salton Sea area of California. In Frankenberger Jr. WT, Engberg RA, Eds. Environmental Chemistry of Selenium. New Tork, NY: Marcel Dekker Inc., 1998; pp205─221.

Sylvester MA. Overview of the salt and agricultural drainage problem in the western San Joaquin Valley, California. US Geological Survey Circular, No. 1033c 1990; pp119-124.

Tucker MD, Barton LL, Thomson BM. Reduction of Cr, Mo, Se and U by Desulfovibrio desulfuricans in polyacrylamide gels. J. Indu. Microbiol. Biotechnol. 1998; 12: 13─19.

Velinsky DJ, Cutter GA. Geochemistry of selenium in a coastal salt marsh. Geochim. Cosmochim. Acta. 1991; 55: 179─191.

Wang C, Lovell RT. Organic selenium sources, selenomethionine and selenoyeast, have higher bioavailability than an inorganic selenium source, sodium selenite, in diets for channel catfish (Ictalurus punctatus). Aquaculture 1997; 152: 223─234.

Weres O, Jaouni AR, Tsao L. The distribution, speciation and geochemical cycling of selenium in a sedimentary environment, Kesterson Reservoir, California, U.S.A. Appl. Geochem. 1989; 4: 543─563.

Zahir AZ, Zhang YQ, Frankenberger Jr. WT. Fate of selenate metabolized by Enterobacter taylorae. J. Agric. Food Chem. 2003; 51: 3609─3613.

Zhang YQ, Frankenberger Jr. WT. Characterization of selenate removal from drainage water utilizing rice straw. J. Environ. Qual. 2003a; 32: 441─446.

Zhang YQ, Frankenberger Jr. WT. Removal of selenate in simulated agricultural drainage water by a rice straw bioreactor channel system. J. Environ. Qual. 2003b; 32: 1650─1657.

Zhang YQ, Moore JN. Selenium speciation and fractionation in a wetland system. Environ. Sci. Technol. 1996; 30: 2613─2619.

Zhang YQ, Moore JN, Frankenberger Jr. WT. Speciation of soluble selenium in agricultural drainage waters and aqueous soil-sediment extracts using hydride generation atomic absorption spectrometry. Environ. Sci. Technol. 1999; 33: 1652─1656.

Zhang YQ, Siddique T, Wang J, Frankenberger Jr. WT. Selenate reduction in river water by Citerobacter freudii isolated from a selenium-contaminated sediment. J. Agric. Food Chem. 2004a; 52: 1594─1600.

Zhang YQ, Zahir AZ, Frankenberger Jr. WT. Factors affecting reduction of selenate to elemental selenium in agricultural drainage water by Enterobacter taylorae. J. Agric. Food Chem. 2003; 51: 7073─7078.

Zhang YQ, Zahir AZ, Frankenberger Jr. WT. Fate of colloidal-particulate elemental selenium in aquatic systems. J. Environ. Qual. 2004b; 33: 559─564.

## PUBLICATIONS

Siddiue, T., Y.Q. Zhang, B.C. Okeke, and W.T. Frankenberger Jr. 2005. Characterization of sediment bacterial assemblages involved in selenium reduction. Biores. Tech. (in press).

Zhang, Y.Q. and W.T. Frankenberger, Jr. 2005. Removal of Selenium from River Water by a Microbial Community Enhanced with *Enterobacter taylorae* in Organic Carbon Coated Sand Columns. Sci. Total Environ. 346: 280-285.

# Continued Investigation into the Interactions of Saline Drainage Water on Crop Tolerance to Boron


**Project Investigators**

Steve Grattan
Department of Land, Air and Water Resources
University of California, Davis
srgrattan@ucdavis.edu

Catherine Grieve
USDA-ARS George E. Brown, Jr. Salinity Laboratory
450 West Big Springs Road
Riverside, CA 92507-4617
cgrieve@ussl.ars.usda.gov

Jim Poss
USDA-ARS George E. Brown, Jr. Salinity Laboratory
jposs@ussl.ars.usda.gov

Don Suarez
USDA-ARS George E. Brown, Jr. Salinity Laboratory
dsuarez@ussl.ars.usda.gov

Andre Läuchli
Department of Land, Air and Water Resources
University of California, Davis
aelauchli@ucdavis.edu

**Research Staff**

Tim Smith, Ph.D. Student, Soil Science, UC Davis
Several casual part-time UC Riverside students

## ABSTRACT

A potential limitation in implementing a drainage water reuse system in the drainage impacted areas on the westside of the San Joaquin valley (SJV) 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. 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. We are currently conducting greenhouse studies to evaluate B tolerance particularly in relation to salinity.

A comprehensive greenhouse experiment was conducted in 2003 at the US Salinity Laboratory in Riverside to evaluate the interactions between B and salinity (Cl-based salinity and SJV salinity composition) on the performance of broccoli and to get a better indication how limiting B actually is to plants grown in drainage reuse systems. Particular interest in this study was directed towards the composition of the salinizing solution to determine what role various salts have on the salinity-boron interaction. Results from this study indicated 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. At high salinity, increased B concentration was less detrimental, both visually and quantitatively (i.e. biomass), than it was at low salinity. That is, plants could tolerate a higher solution B-concentration at higher salinity. However there was no significant difference between salt types. The effects on head weights were more exaggerated than those on shoot biomass. Therefore these data indicate that salinity reduces boron's detrimental influence.

We conducted another study in 2004 on cucumber, a crop that has been documented as more sensitive to boron in the presence of salinity than broccoli. In this outdoor lysimeter study, pH was added as an additional variable because of the alkaline nature of Westside SJV soils and its known influence on B uptake by plants.

Analysis of variance indicated that increased salinity and pH significantly reduced total biomass, vine fresh weight, fruit yield, fruit number per plant and cumulative water use of cucumber. Increased boron, on the other hand, significantly reduced total biomass, fruit number and cumulative water use. It did not significantly affect fruit yield.

Significant interactions were found between boron and pH, but not between salinity and pH or between salinity and boron. These data indicate that under slightly acidic conditions, increased B caused a much more dramatic reduction in plant biomass and yield than did the same increase under slightly alkaline conditions. The alkaline conditions are characteristic of soils on the Westside of the SJV.

Cumulative water use of cucumber was evaluated in relation to the various treatments. Cumulative ET was, for the most part, directly related to cumulative biomass; the higher the cumulative biomass the higher the cumulative ET.

Remote sensing with hyperspectral leaf reflectance can characterize salinity, pH, and boron effects on cucumber. The differences in remote vegetative index values due to salinity, boron, and pH are primarily related to changes in leaf pigment concentrations influenced first by salinity and later by boron as the leaf ages before senescence.

Ion concentrations were determined on fruit, stem and leaf tissues from samples collected at the end of the season. Salinity, boron and pH treatments had profound and often interactive effects on ion relations within the plant.

It was not surprising to find that increased salinity increased tissue Na and Cl concentration. However it was interesting that B and pH treatments also influenced the accumulation of these monovalent ions. For example as solution boron increased fruit sodium increased. In the leaf, as pH increased, leaf Na increased at low salinity but decreased at high salinity. Increased pH reduced Cl concentration in all tissues. In the stem, increased B increased Cl concentration but there were some inconsistencies even though this relationship was significant.

Tissue B concentration increased with boron in the solution but as salinity increased, stem and fruit B concentrations were reduced in most cases. In addition, an increase in pH reduced B concentration in the fruit although this relationship was rather weak, yet significant. Boron isotope analyses in the soil water and the plant tissue indicate that cucumbers did not discriminate between boron isotopes($^{10}B$ or $^{11}B$) in the soil solution.

In broccoli, like many other crops where experiments were conducted using SJV type drainage water, we found that salinity reduced boron's detrimental effect. This was not the case, however, with cucumber. In this study, we did not find any significant interactions between salinity and boron on plant biomass or yield but significant interactions were found between B and pH. An increase in pH had a profound influence on reducing yield and plant biomass. The increase in pH may have altered nutrient relations as significant reductions were found in Ca, P and key micronutrients. It is not clear as to the extent by which these reductions may have adversely affected plant growth or whether or not other more complex nutritional interactions were playing are role. Therefore another broccoli study is underway to investigate the role of pH on the salinity-boron interactions in more detail and allow comparisons with our findings in cucumber.

## 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 (Grattan and Oster, 2003). 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.

Considerable controversy exists over the extent by which boron limits the reuse potential of SJV drainage water. This concern stems from several relationships. First, there is a small concentration window between the level of boron in the soil that is required for optimal crop growth and that considered 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 the other salts are. This phenomenon provides the opportunity for boron to accumulate in the root zone more rapidly than salinity, eventually affecting crop selection and ultimately having 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 (e.g. 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 (i.e. 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.

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; Läuchli et al., 2001; Wimmer et al., 2003). 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. Wimmer et al., (2003) 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 a greenhouse 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 results question the hypothesis that B is taken up passively by plants via the transpiration stream. Furthermore, 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.

On the other hand, investigators who used a mixture of salts (i.e. $Na^+$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$) found the opposite 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 are 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, composed of 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 injury in *Eucalyptus camaldulensis* (Grattan et al., 1996) and pistachio (Ferguson et al., 2002) by reducing tissue B concentrations and in pistachio (Ferguson et al. 2002) by some unknown mechanism. Studies that include a mixture of salts (i.e $Na^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$) are much more typical of the drainage waters of the San Joaquin Valley as well as a number of coastal California 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.

A comprehensive greenhouse experiment was conducted in 2003 at the US Salinity Laboratory in Riverside to evaluate the interactions between B and saline drainage water on the performance of broccoli and to get a better indication how limiting B really is to plants grown in drainage reuse systems. Particular interest in this study was directed towards the composition of the salinizing solution to determine what role various salts have on the salinity-boron interaction. Results from this 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. Plants could tolerate a higher solution B-concentration at higher salinity. However there was no significant difference between salt types. The effects on head weights were more exaggerated than those on shoot biomass. Therefore these data indicate that salinity and B are antagonistic.

Shoot B concentration was influenced by salinity, but interestingly the direction of influence was dependent upon the B concentration in the solution. Regardless of the composition of the salinizing solution, increased salinity increased shoot B concentration when B concentrations in the solution were relatively low (i.e. 0.5 mg/L). At the highest solution B concentration (28 mg/L), increased salinity reduced shoot B concentration. Solution B in itself had very little influence on shoot ion accumulation but both salinity (i.e. EC) and salinity composition had very strong influences on shoot tissue ion composition.

Cumulative water use of broccoli was evaluated in relation to the various treatments. Cumulative ET was, for the most part, directly related to cumulative biomass; the higher the cumulative biomass the higher the cumulative ET. Stable isotopic ratios of oxygen in the solution were used to separate evaporation and transpiration. With these estimates, we were able to provide insight into whether B uptake is truly passive with the transpiration stream as many have suggested in the literature or whether the plant is able to regulate the amount of B absorbs and transports to the shoot. In no treatment did shoot B accumulate to a level predicted based on transpiration volume times solution B-concentration. Plants treated with low B contained the largest percent of B uptake (10-60%), expressed relative to predicted passive uptake. Salinity treatments, regardless of composition, represented the higher percentage range. On the other hand, plants treated with high B (14 or 28 mg/L) only accumulated 1-2% of that predicted if uptake and accumulation were truly passive. Therefore based on our data, it appears that a mechanism is present in broccoli that can reduce that amount of B absorbed and/or transported to the shoot at high solution B concentrations.

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 continuing our investigation into salinity-boron interactions using sand cultures at the US Salinity laboratory to better understand the relationship between SJV salinity and boron interactions in crops. This report describes research conducted in 2004 where the interactive effects of SJV salinity on B tolerance were investigated under both slightly acid and slightly basic conditions. The later is more representative of the soil conditions in the SJV and it is known that pH affects B speciation in the soil solution and uptake by the plant.

## MATERIALS AND METHODS

An experiment in large, outdoor sand tanks 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 SJV salinity, boron and pH on cucumber performance including growth, yield, injury, and ion relations. Cucumber (Cucumis sativus L.), cv 'Turbo' (hydrid) was selected because it is a crop grown the Westside of the SJV and is known to be moderately sensitive to salinity and moderately sensitive to B in both saline and non-saline systems.

### OUTDOOR SAND TANK SYSTEM

The experiment was conducted using an elaborate sand-tank system arranged in a completely randomized complete block design. The system consists of 24 large tanks (82 cm x 203 cm x 85 cm deep) filled with washed sand with a high, saturated soil hydraulic conductivity (400 cm $day^{-1}$). Each tank was plumbed with 5.1 cm PVC pipes, one for irrigation to the sand tank, and the other for return flow to separate 1740-L reservoirs in the basement below. The sand tank system was equipped with automated data acquisition system that characterized the fluid dynamics, temperature, and electrical conductivity within the system (Poss et al., 2004).

Salinity-B-pH treatments were complemented with modified half-strength Hoagland's nutrient solution. Solutions were pumped from the reservoirs below the sand tank facility to the tanks and then returned to the reservoirs several times per day. This irrigation frequency and volumes used each irrigation 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. Total evapotranspiration from each tank was measured by solution-volume changes in the storage reservoirs as well as by pressure transducers wired to a computer that plotted real-time water level dynamics in the reservoirs. Water lost was replenished to maintain constant osmotic potentials in the treatment irrigation waters.

The irrigation treatments consisted of two salinity levels, 3 and 8 dS/m; three boron concentrations, 0.7, 5 and 8 mg/L and two pH levels where solutions were frequently adjusted to 6.5 and 8. The salt solutions were prepared from predictions based on appropriate simulations using compositions typical to those found in the SJV (Suarez and Simunek, 1997).

### CUCUMBER SAMPLING AND HARVEST

Cucumber was planted on 21 July, 2004 and salinization began 11days later when plants had approximately two leaves. Plants were routinely observed for foliar injury and fruit development. Several plants were periodically harvested from each tank for biomass (fresh and dry weights of fruit, leaves, stems and roots) and fruit number. Ion concentrations (i.e. N, P, K, B, Na, Ca, Mg, Cl, S, Zn, Mn, Cu and Fe) were determined on dry ground tissue to assess their distribution within the plant and possible ion interactions within the plant. Shoot tissue samples were also analyzed for isotopic compositions of boron (i.e. $^{10}B/^{11}B$) to determine if there was preferential uptake of one isotope over the other.

### REMOTE SENSING

Remote sensing using hyperspectral leaf reflectance is a useful tool for characterizing and possibly distinguishing crop response to salinity and boron stresses. In our study we used a hyperspectral characterization of leaf reflectance where the foreoptic was close to the leaf surface. Reflectance of the second leaf developed from the

cotyledon was measured at 350 to 2500 nm with a peak-to-peak bandwidth of about 1.5 nm with an ASD FieldSpec Pro spectroradiometer (Analytical Spectral Devices, Inc., Boulder, CO)[1]. During each measurement day, three scans were obtained for three plants from each plot. The spectroradiometer was equipped with a fiberoptic cable configured with an 8° foreoptic accessory and was positioned about 5 cm from and perpendicular to the leaf surface for a spot size of less than 1 cm diameter. Measurements were made as quickly as possible under full sun on DOY 223, 229 and 236. Special attention was made to avoid shadows and minimize the effect of glare by positioning the foreoptic between the sun and the plot. Immediately following leaf reflectance measurements, leaf discs were taken to the laboratory for pigment extractions and determinations including chlorophylls a and b, total carotenoids and anthocyanins.

## RESULTS AND DISCUSSION

### BIOMASS, FRUIT YIELD, FRUIT NUMBER AND WATER USE

Analysis of variance indicated that increased salinity and pH significantly reduced total biomass, vine fresh weight, fruit yield, fruit number per plant and cumulative water use of cucumber (Table 1). Increased boron, on the other hand, significantly reduced total biomass, fruit number and cumulative water use. The concentration of B in the irrigation water did not significantly affect fruit yield.

Table 1. Influence of salinity, boron and pH on cucumber biomass, fruit yield, fruit number and cumulative water use.

| Dependent Variable | Significant ANOVA ($p<0.05$) | Significant Interaction ($p<0.05$) | Mean Separation ECw (alpha = 0.05) | Mean Separation Boron (alpha = 0.05) | Mean Separation pH (alpha = 0.05) |
|---|---|---|---|---|---|
| Vine Fresh Wt (kg/ 3 plants) | ECw | B-pH | ECw= 3 A 2.7 kg | | pH = 6 A 2.7 kg |
| | pH | | ECw =8 B 1.3 kg | | pH = 8 B 1.4 kg |
| | | | | | |
| | | | | | |
| Fresh Cucumber (kg/ 3 plants) | ECw | B-pH | ECw= 3 A 4.9 kg | | pH = 6 A 4.9 kg |
| | pH | | ECw =8 B 3.0 kg | | pH = 8 B 3.1 kg |
| | | | | | |
| Fruit number per 3 plants | ECw | None | ECw= 3 A 24.1 | B = 5 A 21.8 | pH = 6 A 24.1 |
| | B | | ECw =8 B 15.9 | B = 0.9 A 21.7 | pH = 8 B 15.9 |
| | pH | | | B = 8 A 16.6 | |
| | | | | | |
| Total Biomass (kg/ 3 plants) | ECw | B-pH | ECw= 3 A 7.7 kg | B = 0.9 A 6.6 kg | pH = 6 A 7.7 kg |
| | B | | ECw =8 B 4.4 kg | B = 5 A 6.5 kg | pH = 8 B 4.4 kg |
| | pH | | | B = 8 A 4.9 kg | |
| | | | | | |
| Water Use (L/tank) | ECw | B-pH | ECw= 3 A 770 l | B = 0.9 A 701 l | pH = 6 A 742 l |
| | B | | ECw =8 B 568 l | B = 5 AB 686 l | pH = 8 B 596 l |
| | pH | | | B = 8 B 621 l | |
| | | | | | |

[1] Use of a company or product name is for the convenience of the reader and does not imply endorsement of the product by the USDA to the exclusion of others that may also be suitable.

Significant interactions were found between boron and pH, but not between salinity and pH or between salinity and boron. These data indicate that under slightly acidic conditions, increased B had a much more dramatic reduction in plant biomass and yield than did the same increase under slightly alkaline conditions. This significant interaction between boron and pH is not surprising since pH has a profound influence on boron speciation and availability to the plant (Marschner, 1995).

Cumulative water use of cucumber was evaluated in relation to the various treatments. Cumulative ET was, for the most part, directly related to cumulative biomass; the higher the cumulative biomass the higher the cumulative ET.

**REMOTE SENSING**

Remote sensing indices were strongly correlated with pigment concentrations. Pigment concentrations were significantly influenced by boron, salinity, and pH treatments (Table 2) and depended upon the time of sampling. Salinity influenced all pigment concentrations when the second leaf was young but as the plant developed and the leaf aged, the influence of boron became more significant. At the time of the final sampling, when leaves were beginning to senesce, salinity effects were no longer apparent but boron continued to influence the chlorophyll b and anthocyanin concentrations. The effect of pH was significant only for chlorophyll a, chlorophyll a+b, and anthocyanin with an indication of a pH x boron interaction for chlorophyll b and anthocyanin on DOY 229 only.

Table 2. Factorial analysis of variance for pigments in cucumber as influenced by boron, salinity, and pH and the boron*pH interaction.

| Sample | Type of leaf pigment | Full model | Boron | EC | pH | b*pH |
|---|---|---|---|---|---|---|
| DOY | mg $dm^2$ | r2 | | P > F | | |
| 223 | Chl a | 0.84 | NS | <0.0001 | NS | NS |
| | Chl b | 0.94 | NS | <0.0001 | 0.005 | 0.0296 |
| | Chl a&b | 0.9 | NS | <0.0001 | NS | NS |
| | Carotenoids | 0.55 | NS | 0.0051 | NS | NS |
| | Anthocyanins | 0.91 | NS | <0.0001 | 0.0036 | 0.0165 |
| 229 | Chl a | 0.83 | 0.03 | <0.0001 | NS | NS |
| | Chl b | 0.8 | NS | <0.0001 | 0.0042 | NS |
| | Chl a&b | 0.85 | 0.04 | <0.0001 | 0.0275 | NS |
| | Carotenoids | 0.6 | NS | 0.0083 | NS | NS |
| | Anthocyanins | 0.72 | NS | <0.0016 | NS | NS |
| 236 | Chl a | 0.53 | 0.04 | NS | NS | NS |
| | Chl b | 0.65 | NS | NS | 0.031 | NS |
| | Chl a&b | 0.54 | 0.04 | NS | NS | NS |
| | Carotenoids | 0.41 | NS | NS | NS | NS |
| | Anthocyanins | 0.51 | 0.05 | NS | NS | NS |

Data from the early leaf-measurement indicate a strong relationship between the concentration of pigments (expressed on an area basis) with increasing salinity stress (Table 3). This may be partially due to a thickening of leaves with salinity stress resulting in more leaf volume. Although similar results were found upon a fresh weight and dry weight basis, they were most significant on a leaf area basis.

Several remote sensing indices were sensitive to salinity primarily by an association between salinity and pigment concentration (Figure 1). Salinity increased the concentration of chlorophyll a+b and its linear correlation with the Leaf Chlorophyll Index as defined by Datt et al. (2003) was quite good ($r^2$ = 0.82).

Boron concentration in leaves was significantly correlated with nine indices with the best index only accounting for about 35% of the variation in leaf boron ($r^2$= 0.21, Bmm = 9.438 * T1445vapos + 12619). A linear

model of indices including T1445vapos and NDVIshi, a normalized difference vegetation index, increased this relationship $r^2$ to 0.35.

Table 3. Leaf pigment concentration means ± standard error in cucumber sampled on DOY 222.

| Treatment | | | Pigment Mean ± Standard Error | | | | |
|---|---|---|---|---|---|---|---|
| EC | Boron | pH | Chlorophyll a | Chlorophyll b | Chlorophyll a + b mg dm$^2$ | Total Carotenoids | Total Anthocyanins |
| 3 | 0.9 | 6 | 2.99± 0.34 | 0.931± 0.084 | 3.92± 0.43 | 0.755± 0.087 | 0.307± 0.025 |
| 3 | 5 | 6 | 2.77± 0.41 | 0.745± 0.051 | 3.51± 0.46 | 0.738± 0.107 | 0.288± 0.029 |
| 3 | 8 | 6 | 2.41± 0.20 | 0.789± 0.043 | 3.20± 0.16 | 0.556± 0.130 | 0.261± 0.002 |
| 3 | 0.9 | 8 | 2.48± 0.00 | 0.706± 0.023 | 3.19± 0.02 | 0.700± 0.011 | 0.252± 0.006 |
| 3 | 5 | 8 | 2.78± 0.21 | 0.876± 0.010 | 3.64± 0.20 | 0.742± 0.143 | 0.303± 0.032 |
| 3 | 8 | 8 | 2.00± 0.46 | 0.651± 0.045 | 2.65± 0.50 | 0.531± 0.171 | 0.236± 0.030 |
| 8 | 0.9 | 6 | 3.63± 0.15 | 1.19± 0.221 | 4.83± 0.37 | 0.840± 0.059 | 0.364± 0.039 |
| 8 | 5 | 6 | 3.67± 0.18 | 1.00± 0.087 | 4.67± 0.20 | 0.954± 0.030 | 0.341± 0.031 |
| 8 | 8 | 6 | 3.71± 0.03 | 1.23± 0.110 | 4.94± 0.14 | 0.887± 0.094 | 0.347± 0.018 |
| 8 | 0.9 | 8 | 3.34± 0.06 | 0.970± 0.050 | 4.31± 0.11 | 0.820± 0.052 | 0.318± 0.006 |
| 8 | 5 | 8 | 3.26± 0.19 | 1.02± 0.010 | 4.27± 0.20 | 0.821± 0.010 | 0.308± 0.008 |
| 8 | 8 | 8 | 3.09± 0.07 | 0.915± 0.072 | 4.01± 0.08 | 0.752± 0.024 | 0.293± 0.000 |

Remote sensing with hyperspectral leaf reflectance can characterize salinity, pH, and boron effects on cucumber. The differences in remote vegetative index values due to salinity, boron, and pH are primarily related to changes in leaf pigment concentrations influenced by the salinity at first and then by boron later as the leaf ages before senescence. All three factors were significantly related to various leaf reflectance indices and the explanations for these differences are under study.

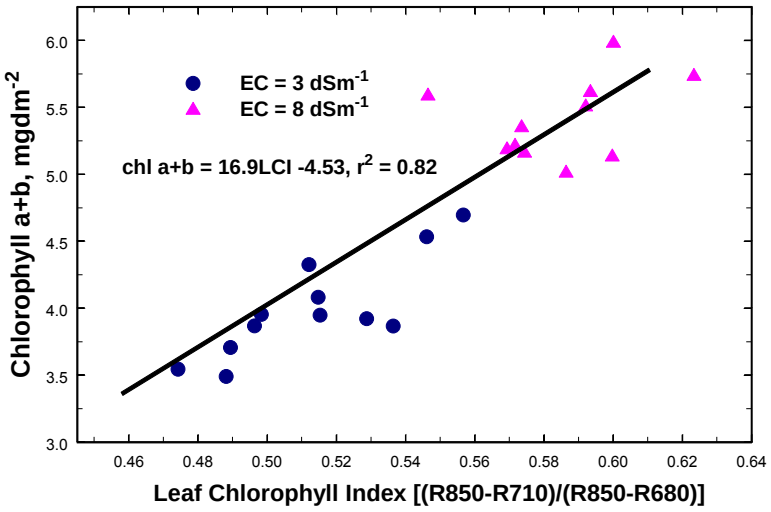


Figure 1. Leaf chlorophyll index in cucumber is linearly related to leaf chlorophyll a+b concentrations. Leaf tissue from salinized plots had higher chlorophyll concentrations.

**ION RELATIONS**

Ion concentrations were determined on fruit, stem and leaf tissue from samples collected at the end of the season. Salinity, boron and pH treatments had a profound and often interactive effect on ion relations within the plant (Tables 4-6). These results and relationships among ions will require a more thorough evaluation than are presented here but some of the highlights are discussed below.

Many studies have found that increased salinity reduces plant N concentration (Grattan and Grieve, 1999). This was the case in this study as well. As salinity increased, N concentrations (both nitrate and total N) in the leaf, stem and fruit were significantly decreased (data not presented).

The influence of treatments on tissue P concentration was different from that of N. In the leaf, as salinity increased, P decreased. Effects from solution changes in boron concentration or pH did not significantly affect leaf P.

The opposite was found in the stem and fruit tissue. Increased salinity did not affect P concentrations in stems or fruits but increased pH reduced tissue P concentrations.

Table 4. Concentrations ± standard error of macronutrient elements in fruit, stems, and leaves of cucumber when grown under varying salinity, boron, and pH in the irrigation water.

| Organ | EC | Boron | Ph | P± SE | K± SE | S± SE | Ca± SE | Mg± SE | Na± SE | Cl ± SE |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | mmoles $kg^{-1}$ | mmoles $kg^{-1}$ | mmoles $kg^{-1}$ | mmoles $kg^{-1}$ | mmoles $kg^{-1}$ | mmoles | mmoles |
| Fruit | 3.0 | 0.9 | 6.0 | 397.2 ± 32.3 | 2146.2±205.1 | 139.7±15.3 | 174.7±17.5 | 189.3±4.1 | 101.8±15.7 | 430.2 ± 49.4 |
| Fruit | 3.0 | 5.0 | 6.0 | 337.5 ± 9.4 | 2175.6±88.5 | 143.5±1.3 | 160.9±11.2 | 185.2±4.1 | 112.4±3.7 | 468.2 ± 2.8 |
| Fruit | 3.0 | 8.0 | 6.0 | 335.8 ± 32.3 | 1988.5±60.3 | 131.9±1.3 | 132.2±7.5 | 172.8±0.0 | 122.7±11.3 | 427.3±12.7 |
| Fruit | 3.0 | 0.9 | 8.0 | 243.8±1.6 | 1446.2±153.9 | 138.7±9.5 | 107.3±5.0 | 174.9±2.1 | 120.3±3.7 | 231.3±0.0 |
| Fruit | 3.0 | 5.0 | 8.0 | 243.8±4.8 | 1588.5±44.9 | 128.4±7.6 | 112.3±5.0 | 168.7±0.0 | 91.1±5.9 | 227.1±4.2 |
| Fruit | 3.0 | 8.0 | 8.0 | 237.3±1.6 | 1826.9±152.6 | 147.7±14.2 | 106.0±16.2 | 162.5±2.1 | 136.2±4.4 | 265.1±42.3 |
| Fruit | 8.0 | 0.9 | 6.0 | 332.6±0.0 | 1661.5±105.1 | 165.8±14.8 | 146.0±1.3 | 176.9±16.5 | 295.6±55.0 | 538.7±50.8 |
| Fruit | 8.0 | 5.0 | 6.0 | 301.9±59.7 | 1515.4±169.2 | 145.7±7.5 | 132.2±7.5 | 166.6±10.3 | 298.0±3.9 | 534.5±29.6 |
| Fruit | 8.0 | 8.0 | 6.0 | 303.5±12.9 | 1538.5±92.3 | 152.7±9.8 | 124.8±7.5 | 164.6±8.2 | 401.9±52.6 | 600.8±2.8 |
| Fruit | 8.0 | 0.9 | 8.0 | 192.1±40.4 | 1371.8±82.1 | 148.5±1.3 | 131.0±1.3 | 183.1±6.2 | 247.9±4.4 | 380.8±0.0 |
| Fruit | 8.0 | 5.0 | 8.0 | 213.1±25.8 | 1415.4±107.7 | 136.2±1.1 | 114.8±17.5 | 166.6±6.2 | 244.0±67.0 | 393.5±21.2 |
| Fruit | 8.0 | 8.0 | 8.0 | 214.7±21.0 | 1442.3±9.0 | 138.0±2.7 | 97.3±10.0 | 172.8±8.2 | 382.6±2.4 | 427.3±4.2 |
| Stem | 3.0 | 0.9 | 6.0 | 272.8±4.8 | 2347.4±29.5 | 108.9±1.6 | 467.8±6.2 | 226.3±8.3 | 187.0±23.1 | 853.2±15.5 |
| Stem | 3.0 | 5.0 | 6.0 | 221.2±56.5 | 2355.1±109.0 | 95.8±1.3 | 386.7±7.5 | 218.1±4.1 | 249.9±18.5 | 894.1±0.0 |
| Stem | 3.0 | 8.0 | 6.0 | 250.2±53.3 | 2234.6±55.1 | 92.3±0.6 | 336.8±37.4 | 230.4±8.2 | 281.7±17.2 | 936.5±50.8 |
| Stem | 3.0 | 0.9 | 8.0 | 127.5±1.6 | 2116.7±6.4 | 106.1±10.0 | 290.7±3.7 | 265.4±6.2 | 251.9±21.8 | 368.1±4.2 |
| Stem | 3.0 | 5.0 | 8.0 | 151.8±6.5 | 2180.8±119.2 | 88.0±5.6 | 273.2±21.2 | 261.3±10.3 | 270.3±29.4 | 307.5±16.9 |
| Stem | 3.0 | 8.0 | 8.0 | 125.9±32.3 | 2135.9±64.1 | 117.0±10.9 | 338.1±81.1 | 290.1±10.3 | 293.8±73.3 | 359.6±4.2 |
| Stem | 8.0 | 0.9 | 6.0 | 256.7±17.8 | 1587.2±64.1 | 158.9±2.3 | 415.4±83.6 | 351.8±10.3 | 707.1±138.5 | 1188.9±29.6 |
| Stem | 8.0 | 5.0 | 6.0 | 240.6±53.3 | 1561.5±23.1 | 131.0±8.4 | 410.4±48.7 | 364.1±18.5 | 584.6±1.3 | 1167.7±0.0 |
| Stem | 8.0 | 8.0 | 6.0 | 218.0±50.1 | 1464.1±133.3 | 143.2±1.9 | 502.7±53.6 | 390.9±20.6 | 746.4±53.9 | 1276.3±15.5 |
| Stem | 8.0 | 0.9 | 8.0 | 127.5±33.9 | 1450.0±126.9 | 127.6±1.9 | 331.8±27.5 | 417.6±26.7 | 563.7±57.0 | 904.0±57.8 |
| Stem | 8.0 | 5.0 | 8.0 | 138.8±16.1 | 1646.2±25.6 | 130.1±0.6 | 344.3±15.0 | 395.0±28.8 | 483.3±40.9 | 898.4±12.7 |
| Stem | 8.0 | 8.0 | 8.0 | 135.6±16.1 | 1656.4±25.6 | 123.2±5.9 | 364.3±17.5 | 411.4±20.6 | 580.3±18.3 | 940.7±4.2 |
| Leaf | 3.0 | 0.9 | 6.0 | 240.6±1.6 | 1207.7±71.8 | 234.9±5.3 | 1242.5±54.9 | 364.1±22.6 | 90.7±12.4 | 310.3±62.1 |
| Leaf | 3.0 | 5.0 | 6.0 | 229.3±32.3 | 1238.5±84.6 | 231.3±7.6 | 1202.6±89.8 | 411.4±4.1 | 106.1±13.9 | 335.7±36.7 |
| Leaf | 3.0 | 8.0 | 6.0 | 258.3±3.2 | 1301.3±96.2 | 217.4±17.5 | 1175.2±122.3 | 479.3±63.8 | 105.1±8.5 | 397.7±16.9 |
| Leaf | 3.0 | 0.9 | 8.0 | 182.4±30.7 | 1134.6±50.0 | 244.5±6.9 | 1180.1±20.0 | 652.1±14.4 | 108.3±11.3 | 124.1±16.9 |
| Leaf | 3.0 | 5.0 | 8.0 | 326.1±42.0 | 1191.0±19.2 | 210.4±4.2 | 1109.0±43.7 | 711.8±28.8 | 113.5±8.7 | 107.2±8.5 |
| Leaf | 3.0 | 8.0 | 8.0 | 192.1±53.3 | 1197.4±123.1 | 265.6±6.7 | 1167.7±77.4 | 722.1±121.4 | 111.4±27.4 | 124.1±0.0 |
| Leaf | 8.0 | 0.9 | 6.0 | 185.7±11.3 | 701.3±29.5 | 427.3±5.6 | 1508.2±143.5 | 722.1±51.4 | 340.8±69.4 | 588.1±24.0 |
| Leaf | 8.0 | 5.0 | 6.0 | 201.8±43.6 | 880.8±91.0 | 374.5±1.1 | 1492.0±104.8 | 736.5±24.7 | 262.7±12.2 | 662.9±59.2 |
| Leaf | 8.0 | 8.0 | 6.0 | 198.6±40.4 | 782.1±48.7 | 345.0±9.7 | 1341.1±131.0 | 685.0±14.4 | 312.1±66.3 | 658.6±12.7 |
| Leaf | 8.0 | 0.9 | 8.0 | 156.6±50.1 | 800.0±28.2 | 399.7±25.7 | 1294.9±25.0 | 892.8±28.8 | 197.3±6.3 | 356.8±40.9 |
| Leaf | 8.0 | 5.0 | 8.0 | 166.3±50.1 | 823.1±41.0 | 380.2±24.0 | 1407.2±187.1 | 884.6±8.2 | 184.4±11.3 | 372.3±25.4 |
| Leaf | 8.0 | 8.0 | 8.0 | 179.2±1.6 | 847.4±11.5 | 347.2±5.3 | 1235.0±39.9 | 845.5±10.3 | 213.8±15.0 | 372.3±33.9 |

Table 5. Concentrations ± standard error of micronutrient elements in fruit, stems, and leaves of cucumber when grown under varying salinity, boron, and pH of irrigation water.

| Organ | EC | Boron | Ph | B ± SE | Zn ± SE | Mn ± SE | Fe ± SE | Cu ± SE |
|---|---|---|---|---|---|---|---|---|
| | | | | ppm | ppm | Ppm | ppm | ppm |
| Fruit | 3.0 | 0.9 | 6.0 | 33.5 ± 2.5 | 68.0 ± 7.0 | 30.5 ± 0.5 | 133.0 ± 13.0 | 7.1 ± 0.7 |
| Fruit | 3.0 | 5.0 | 6.0 | 132.0 ± 6.0 | 58.5 ± 1.5 | 29.5 ± 0.5 | 244.5 ± 26.5 | 12.5 ± 2.4 |
| Fruit | 3.0 | 8.0 | 6.0 | 180.0 ± 4.0 | 53.5 ± 0.5 | 24.5 ± 0.5 | 171.0 ± 8.0 | 7.4 ± 0.0 |
| Fruit | 3.0 | 0.9 | 8.0 | 31.0 ± 1.0 | 40.5 ± 1.5 | 23.5 ± 3.5 | 161.0 ± 42.0 | 3.9 ± 1.1 |
| Fruit | 3.0 | 5.0 | 8.0 | 88.0 ± 17.0 | 24.0 ± 3.0 | 18.0 ± 0.0 | 172.0 ± 59.0 | 4.0 ± 1.3 |
| Fruit | 3.0 | 8.0 | 8.0 | 180.0 ± 16.0 | 38.5 ± 13.5 | 16.0 ± 0.0 | 149.0 ± 26.0 | 5.3 ± 2.3 |
| Fruit | 8.0 | 0.9 | 6.0 | 32.0 ± 3.0 | 57.0 ± 1.0 | 23.0 ± 3.0 | 169.0 ± 18.0 | 9.2 ± 2.4 |
| Fruit | 8.0 | 5.0 | 6.0 | 98.0 ± 9.0 | 51.0 ± 6.0 | 19.5 ± 0.5 | 125.5 ± 19.5 | 6.1 ± 1.3 |
| Fruit | 8.0 | 8.0 | 6.0 | 172.0 ± 6.0 | 49.5 ± 5.5 | 19.5 ± 1.5 | 98.0 ± 12.0 | 6.9 ± 1.0 |
| Fruit | 8.0 | 0.9 | 8.0 | 34.5 ± 1.5 | 30.5 ± 1.5 | 18.0 ± 2.0 | 150.5 ± 49.5 | 3.7 ± 1.3 |
| Fruit | 8.0 | 5.0 | 8.0 | 90.5 ± 1.5 | 30.0 ± 0.0 | 16.0 ± 1.0 | 116.5 ± 23.5 | 3.0 ± 0.4 |
| Fruit | 8.0 | 8.0 | 8.0 | 153.0 ± 11.0 | 31.5 ± 1.5 | 14.5 ± 2.5 | 103.0 ± 17.0 | 3.3 ± 1.2 |
| Stem | 3.0 | 0.9 | 6.0 | 36.5 ± 0.5 | 50.5 ± 2.5 | 31.0 ± 1.0 | 371.0 ± 165.0 | 11.2 ± 3.1 |
| Stem | 3.0 | 5.0 | 6.0 | 104.0 ± 2.0 | 35.5 ± 1.5 | 28.5 ± 0.5 | 258.0 ± 5.0 | 8.9 ± 1.2 |
| Stem | 3.0 | 8.0 | 6.0 | 136.5 ± 5.5 | 38.5 ± 0.5 | 26.0 ± 3.0 | 683.0 ± 487.0 | 15.4 ± 7.6 |
| Stem | 3.0 | 0.9 | 8.0 | 31.5 ± 3.5 | 44.5 ± 22.5 | 41.0 ± 14 | 5262.5 ± 5017 | 65.2 ± 58.7 |
| Stem | 3.0 | 5.0 | 8.0 | 90.5 ± 1.5 | 16.5 ± 0.5 | 17.0 ± 0.0 | 435.0 ± 51.0 | 11.1 ± 1.7 |
| Stem | 3.0 | 8.0 | 8.0 | 166.0 ± 16.0 | 22.5 ± 4.5 | 17.5 ± 0.5 | 215.0 ± 14.0 | 6.9 ± 1.1 |
| Stem | 8.0 | 0.9 | 6.0 | 32.0 ± 1.0 | 38.0 ± 2.0 | 21.5 ± 0.5 | 580.0 ± 354.0 | 14.2 ± 5.4 |
| Stem | 8.0 | 5.0 | 6.0 | 84.0 ± 5.0 | 36.5 ± 7.5 | 21.0 ± 2.0 | 465.0 ± 262.0 | 11.4 ± 5.2 |
| Stem | 8.0 | 8.0 | 6.0 | 166.5 ± 27.5 | 32.0 ± 0.0 | 23.0 ± 2.0 | 373.5 ± 88.5 | 11.1 ± 1.7 |
| Stem | 8.0 | 0.9 | 8.0 | 29.5 ± 0.5 | 26.0 ± 7.0 | 18.0 ± 3.0 | 1486.0 ± 1124 | 24.2 ± 16.0 |
| Stem | 8.0 | 5.0 | 8.0 | 69.5 ± 0.5 | 17.5 ± 1.5 | 13.5 ± 1.5 | 350.5 ± 20.5 | 10.9 ± 3.0 |
| Stem | 8.0 | 8.0 | 8.0 | 97.5 ± 11.5 | 17.0 ± 1.0 | 11.5 ± 1.5 | 447.0 ± 114.0 | 9.8 ± 0.6 |
| Leaf | 3.0 | 0.9 | 6.0 | 108.0 ± 6.0 | 62.0 ± 3.0 | 84.0 ± 3.0 | 268.5 ± 7.5 | 8.3 ± 0.7 |
| Leaf | 3.0 | 5.0 | 6.0 | 639.0 ± 30.0 | 53.5 ± 0.5 | 85.5 ± 1.5 | 282.5 ± 13.5 | 8.5 ± 0.9 |
| Leaf | 3.0 | 8.0 | 6.0 | 1069.0 ± 125.0 | 58.0 ± 3.0 | 72.5 ± 9.5 | 285.0 ± 66.0 | 6.8 ± 0.8 |
| Leaf | 3.0 | 0.9 | 8.0 | 121.0 ± 2.0 | 34.0 ± 2.0 | 76.0 ± 16 | 260.0 ± 22.0 | 5.7 ± 0.7 |
| Leaf | 3.0 | 5.0 | 8.0 | 604.0 ± 0.0 | 26.0 ± 1.0 | 57.5 ± 0.5 | 227.0 ± 15.0 | 6.6 ± 0.5 |
| Leaf | 3.0 | 8.0 | 8.0 | 1140.0 ± 5.0 | 36.0 ± 10.0 | 49.5 ± 2.5 | 196.5 ± 14.5 | 4.8 ± 0.2 |
| Leaf | 8.0 | 0.9 | 6.0 | 127.5 ± 0.5 | 50.5 ± 3.5 | 59.0 ± 7.0 | 272.0 ± 28.0 | 9.7 ± 3.0 |
| Leaf | 8.0 | 5.0 | 6.0 | 696.0 ± 25.0 | 49.5 ± 7.5 | 52.5 ± 0.5 | 279.5 ± 50.5 | 7.1 ± 1.5 |
| Leaf | 8.0 | 8.0 | 6.0 | 1072.5 ± 34.5 | 48.5 ± 1.5 | 54.0 ± 4.0 | 249.0 ± 7.0 | 7.4 ± 0.9 |
| Leaf | 8.0 | 0.9 | 8.0 | 118.5 ± 2.5 | 30.0 ± 2.0 | 34.0 ± 4.0 | 232.0 ± 13.0 | 6.3 ± 0.3 |
| Leaf | 8.0 | 5.0 | 8.0 | 612.5 ± 67.5 | 26.5 ± 3.5 | 35.0 ± 2.0 | 195.5 ± 1 .5 | 5.9 ± 0.2 |
| Leaf | 8.0 | 8.0 | 8.0 | 928.0 ± 13.0 | 31.0 ± 0.0 | 32.0 ± 6.0 | 694.0 ± 483.0 | 10.5 ± 3.5 |

Table 6. Factorial analysis of variance for mineral elements in fruit, stems and leaves of cucumber as influenced by main effects of boron, salinity, and pH and interactions.

| Ion | Organ | full model r2 | Boron | EC P > F | EC*Boron | pH | b*pH | EC*pH | EC*B*pH |
|---|---|---|---|---|---|---|---|---|---|
| N | Fruit | 0.64 | NS | <0.0025 | NS | NS | NS | NS | NS |
| P | Fruit | 0.77 | NS | NS | NS | <0.0001 | NS | NS | NS |
| K | Fruit | 0.84 | NS | 0.0002 | NS | 0.0005 | NS | 0.0373 | NS |
| S | Fruit | 0.53 | NS | NS | NS | NS | NS | NS | NS |
| B | Fruit | 0.98 | <0.0001 | 0.0477 | NS | 0.0329 | NS | NS | NS |
| Ca | Fruit | 0.82 | 0.0191 | NS | NS | 0.0001 | NS | 0.0427 | NS |
| Mg | Fruit | 0.56 | NS | NS | NS | NS | NS | 0.0471 | NS |
| Na | Fruit | 0.93 | 0.007 | <0.0001 | NS | NS | NS | NS | NS |
| Cl | Fruit | 0.95 | NS | <0.0001 | NS | <0.0001 | NS | NS | NS |
| Zn | Fruit | 0.87 | NS | NS | NS | <0.0001 | NS | NS | NS |
| Mn | Fruit | 0.89 | 0.0043 | 0.0002 | NS | <0.0001 | NS | 0.0434 | NS |
| Fe | Fruit | 0.61 | NS | 0.0252 | NS | NS | NS | NS | NS |
| Cu | Fruit | 0.77 | NS | NS | NS | 0.0002 | NS | NS | NS |
| NO3 | Fruit | 0.65 | NS | 0.0035 | NS | NS | NS | NS | NS |
| | | | | | | | | | |
| N | Stem | 0.85 | 0.0017 | 0.0306 | NS | 0.0002 | NS | 0.0265 | NS |
| P | Stem | 0.72 | NS | NS | NS | 0.0002 | NS | NS | NS |
| K | Stem | 0.95 | NS | <0.0001 | NS | NS | NS | 0.0357 | NS |
| S | Stem | 0.93 | 0.0125 | <0.0001 | NS | NS | NS | 0.005 | 0.0195 |
| B | Stem | 0.96 | <0.0001 | 0.0299 | NS | 0.0529 | NS | 0.0167 | 0.006 |
| Ca | Stem | 0.7 | 0.0191 | NS | NS | 0.0021 | NS | NS | NS |
| Mg | Stem | 0.95 | NS | <0.0001 | NS | 0.0007 | NS | NS | NS |
| Na | Stem | 0.93 | NS | <0.0001 | NS | NS | NS | 0.019 | NS |
| Cl | Stem | 0.99 | 0.0119 | <0.0001 | NS | <0.0001 | NS | <0.0001 | NS |
| Zn | Stem | 0.68 | 0.0458 | NS | NS | <0.0051 | NS | NS | NS |
| Mn | Stem | 0.76 | 0.0321 | 0.0046 | NS | <0.0525 | NS | 0.0434 | NS |
| Fe | Stem | 0.45 | NS | 0.0252 | NS | NS | NS | NS | NS |
| Cu | Stem | 0.42 | NS | NS | NS | NS | NS | NS | NS |
| NO3 | Stem | 0.9 | NS | <0.0001 | 0.0436 | 0.0222 | NS | NS | NS |
| | | | | | | | | | |
| N | Leaf | 0.52 | NS | 0.0336 | NS | NS | NS | NS | NS |
| P | Leaf | 0.61 | NS | 0.0174 | NS | NS | NS | NS | NS |
| K | Leaf | 0.91 | <0.0001 | NS | NS | NS | NS | NS | NS |
| S | Leaf | 0.97 | 0.0066 | <0.0001 | 0.0056 | NS | NS | NS | NS |
| B | Leaf | 0.98 | <0.0001 | NS | NS | NS | NS | NS | NS |
| Ca | Leaf | 0.61 | NS | 0.0047 | NS | NS | NS | NS | NS |
| Mg | Leaf | 0.93 | NS | <0.0001 | NS | <0.0001 | NS | 0.0454 | NS |
| Na | Leaf | 0.88 | NS | <0.0001 | NS | 0.018 | NS | 0.006 | NS |
| Cl | Leaf | 0.976 | NS | <0.0001 | NS | <0.0001 | NS | NS | NS |
| Zn | Leaf | 0.9 | NS | 0.0395 | NS | <0.0001 | NS | NS | NS |
| Mn | Leaf | 0.89 | NS | <0.0001 | NS | <0.0001 | NS | NS | NS |
| Fe | Leaf | 0.44 | NS | NS | NS | NS | NS | NS | NS |
| Cu | Leaf | 0.54 | NS | NS | NS | NS | NS | NS | NS |
| NO3 | Leaf | 0.66 | NS | 0.0008 | NS | NS | NS | NS | NS |

The effect of salinity on tissue K concentration was characteristic of those treatments where Na concentrations increase in the soil water environment. As salinity increased, tissue K decreased presumably due to competitive effects between these two monovalent cations. Surprisingly this effect was only significant in the stem and fruit tissue, not the leaves despite a similar trend of reduction of K with increasing salinity. In the leaves, on the other hand, increased boron increased leaf K.

Increases in sodium-sulfate salinity increased the sulfur concentration in stems and leaves, but not significantly in the fruit. In addition, increased boron in solution reduced the S concentration in the stems and fruits in most cases.

In most cases, increased salinity increased the Ca concentration in the leaves but not stems or fruit. Increased pH generally resulted in lower tissue Ca concentrations. In the fruit, increased boron in the solution decreased tissue Ca concentration. However in the stem, increased boron increased Ca, but not at low pH or low salinity.

Increased salinity and pH increased Mg concentrations in stems and leaves. This influence was not significant in the fruit.

It was not surprising to find that increased salinity increased tissue Na concentration. However it was interesting that B and pH treatments had influence as well. For example as boron increased fruit sodium increased. In the leaf, as pH increased, leaf Na increased at low salinity but decreased at high salinity.

Tissue Cl also increased with increased salinity but it too has some interesting relations with B and pH. Increased pH reduced Cl concentration in all tissues. In the stem, increased B increased Cl concentration but there were some inconsistencies even though this relationship was significant.

Tissue B concentration increased with boron in the solution but as salinity increased, stem and fruit B concentrations were reduced in most cases. In addition, an increase in pH reduced B concentration in the fruit although this relationship was rather weak, yet significant. Boron isotope analyses in the soil water and the plant tissue indicate that cucumbers did not discriminate in boron uptake regarding in the isotopic composition of boron ($^{10}B$ or $^{11}B$) in the soil solution (data not presented).

There were also significant relationships among treatments and micronutrient concentrations. The relationships that were most notable were Mn and Zn concentrations being reduced under alkaline and to some extent saline conditions.

## CONCLUDING REMARKS

Many plant experiments that have been conducted over the years using water compositions typical of the Westside SJV drainage water have found that the plants appear more tolerant of boron in the presence of salinity than in its absence. From our salinity-boron experiments over the past few years, data indicate that interactions can occur between salinity, boron and pH. In broccoli, we found that salinity, regardless of its composition, reduced boron's detrimental effect. This was not the case, however, with cucumber. In this study, we did not find any significant interactions between salinity and boron on plant biomass or yield but significant interactions were found between B and pH. An increase in pH had a profound influence on reducing yield and plant biomass. The increase in pH may have altered nutrient relations as significant reductions were found in Ca, P and key micronutrients. It is not clear as to the extent by which these reductions may have adversely affected plant growth or whether or not other more complex nutritional interactions were playing are role. We therefore found it important to conduct an additional experiment with broccoli get a better understanding of its increased tolerance to boron in the presence of salinity and to what extent the pH of the media plays in the salinity-boron interactions.

## REFERENCES


Alpaslan, M. and A. Gunes. 2001. Interactive effects of boron and salinity stress on the growth, membrane permeability and mineral composition of tomato and cucumber plants. Plant Soil 236: 123-128

Bingham, F.T., Strong, J. E., Rhoades, J. D. and Keren, R., 1987. Effects of salinity and varying boron concentrations on boron uptake and growth of wheat. Plant Soil 97: 345-351.

Datt, B., T.R. McVicar, T.G. van Niel, D.L.B Jupp and J.S. Pearlman. 2003. Preprocessing EO-1 hyperion hyperspectral data to support the application of agricultural indexes. IEEE transactions on geoscience and remote sensing. 41: 1246-1259.

El-Motaium, R., Hu, H. and Brown, P. H., 1994. The relative tolerance of six Prunus rootstocks to boron and salinity. J. Amer. Soc. Hort. Sci 119: 1169-1175.

Ferguson, L., J.A. Poss, S.R. Grattan, C.M. Grieve, D. Wang, C. Wilson, T.J. Donovan and C.-T. Chaao. 2002. Pistachio rootstocks influence scion growth and ion relations under salinity and boron stress. J. Am. Soc. Hort. Sci. 127:194-199.

Ferreyra, R.E., A.U. Alijaro, R.S. Ruiz, L.P. Rojas and J.D. Oster. 1997. Behavior of 42 crop species grown in saline soils with high boron concentrations. Agric. Water Manag 32:111-124.

Grattan, S.R. and C.M. Grieve. 1999. Salinity – mineral nutrient relations in horticultural crops. Sci. Hort. 78: 127-157.

Grattan, S. R. and J. D. Oster 2003. Use and Reuse of Saline-sodic Waters for Irrigation of Crops. In : S. S. Goyal, S. K. Sharma, and D. W. Rains (eds). Crop Production in Saline Environments: Global and Integrative Perspectives. Haworth Press, New York. Pp 131-162.

Grattan, S.R., Shannon, M. C., Grieve, C. M., Poss, J. A., Suarez, D. L. and Francois, L. E. 1996. Interactive effects of salinity and boron on the performance and water use of eucalyptus. Acta Hort. 449:607-613

Grieve, C.M. and J.P. Poss. 2000. Wheat response to interactive effects of boron and salinity. J. Plant Nutr. 23: 1217-1226.

Gupta, U.C., Jame, Y. W., Campbell, C. A., Leyshon, A. J. and Nicholaichuk, W., 1985. Boron toxicity and deficiency: A review. Can. J. Soil Sci. 65: 381-409.

Holloway, R.E., and A.M. Alston. 1992. The effects of salt and boron on growth of wheat. Aust. J. Agric. Res., 43:987-1001.

Läuchli, A., M.A. Wimmer, K.H. Muehling, P.H. Brown, and H.E. Goldbach. 2001. Interaction of salinity and boron toxicity: The significance of boron partitioning. Am. Soc. Plant Biologists (ASPB). Annual conference. July 21-25 Rhode Island.

Letey, J., S. Grattan and J. Oster. 2001. Findings and recommendations to develop the six-year activity plan for the Department's drainage reduction and reuse program. Task Order 5. Final Report Submitted to the California State Department of Water Resources Contract # 98-7200-B80933 156 pp.

Maas, E. V. and S. R. Grattan. 1999. Crop yields as affected by salinity. In: Agricultural Drainage, Agronomy Monograph 38. (R. W. Skaggs and J. vanSchilfgaard, eds.) Am. Soc. Agron., Madison, WI.

Marschner, H. 1995. Mineral nutrition of higher plants. Second Edition. Academic Press. London pp 395-396.

Mikkelsen, R.L., B.H. Haghnia, A.L. Page, and F.T. Bingham. 1988. The influence of selenium, salinity and boron on alfalfa tissue composition and yield. J. Environ. Qual. 17:85-88.

Nable ,R.O., G.S. Bañuelos and J.G. Paull. 1997. Boron toxicity. Plant Soil, 193:181-198.

Poss, J. A., W. B. Russell, P. J. Shouse, R. S. Austin, S. R. Grattan, C. M. Grieve, J. H. Leith, and L. Zeng. 2004. A volumetric lysimeter system (VLS): and alternative to weighing lysimeters for plant-water relations studies. Comput. Electronics Agric. 43:55-68.

San Joaquin Valley Drainage Implementation Program. 2000. Evaluation of the 1990 Drainage Management Plan for the Westside San Joaquin Valley, California. Final Report submitted to the Management Group of the San Joaquin Valley Drainage Implementation Program (SJVDIP).
January, 2000. SJVDIP and University of California Ad Hoc Coordination Committee 87pp

Shani, U., and R.J. Hanks. 1993. Model of integrated effects of boron, inert salt, and water flow on crop yield. Agron. J. 85:713-717.

Suarez, D.L. and J. Simunek, 1997. UNSATCHEM: Unsaturated water and solute transport model with equilibrium and kinetic chemistry. Soil Sci. Soc. Am. J. 61:1633-1646.

Wang, D. 2002. Dynamics of soil water and temperatures in above ground sand cultures used for screening plant salt tolerance. Soil Sci. Soc. Am. J. 66:1484-1491.

Wimmer, M. A., K.H. Muhling, A. Lauchli, P.H. Brown, and H.E. Goldbach. 2003. The interaction between salinity and boron toxicity affects the subcellular distribution of ions and proteins in wheat leaves. Plant, Cell Environ. 26: 1267-1274

Yadav, H. D., O. P.Yadav, O. P. Dhankar, and M. C. Oswal. 1989. Effect of chloride salinity and boron on germination, growth, and mineral composition of chickpea (Cicer arietinum L.) Ann. Arid Zone 28:63-67.

# Regulated Deficit Irrigation of Alfalfa


**Project Investigators**

Blaine Hanson
Department of Land, Air, and Water Resources
University of California, Davis
One Shields Ave., Davis, CA 95616.
Phone: 530-752-1130;  FAX: 530-752-5262
Email: brhanson@ucdavis.edu

Dan Putnam
Department of Plant Science
University of California, Davis
One Shields Ave., Davis, CA 95616
Phone: 530-752-8982; FAX: 530-752-4361
Email: dhputnam@ucdavis.edu.
Website:  http://alfalfa.ucdavis.edu

## ABSTRACT

Alfalfa is California's single largest agricultural water user due to its large acreage (445,000 ha) and long growing season. A total of 494,000 to 679,000 ha-m (4 to 5.5 million-acre feet) of water are applied to California's alfalfa crop each year, depending on alfalfa acreage of a given year, weather patterns, and method of estimation. Growers normally fully irrigate alfalfa throughout the growing season to maximize yield. However, yields tend to be highest during spring harvests, and lower during summer months. In addition, forage quality of alfalfa tends to be lower during summer months due to the hot weather, resulting price reductions of up to 40%.

The Department of Water Resources has shown interest in deficit irrigation of alfalfa as a source of water available for transfer elsewhere. One strategy is to cutoff irrigation water during July and August when yields are the lowest. The amount of water available for transfer is the difference in the evapotranspiration of an adequately irrigated field and the evapotranspiration of a deficit-irrigated field.

Evapotranspiration (ET) was determined in a commercial field where part of the field was fully irrigated and part was deficit irrigated during the later summer months. The eddy covariance energy balance method and the surface renewal energy balance method were used in the fully irrigated area, and the surface renewal method was used in the deficit irrigated part of the field. Both methods use climatic and soil temperature data to calculate ET.

Results thus far have shown the daily ETc of the fully irrigated area in August to range between 3.5 mm/day to 4 mm/day just after cutting and between 6 mm/day and 7 mm/day after the first irrigation between cuttings. For the deficit-irrigated part of the field, ET ranged between 2 mm/day and 3 mm/day just after cutting, increased to between 5 mm/day and 5.5 mm/day for about 10 days after the first irrigation and then decreased to between 1.5 mm/day and 3 mm/day. ET of the deficit irrigated areas ranged between 1 mm/day and 2 mm/day after the September cutting, whereas, ET of the fully irrigated area was about 3.5 mm/day prior to the next irrigation and then was about 5 mm/day after the irrigation.

## INTRODUCTION

Alfalfa is California's single largest agricultural water user due to its large acreage (445,000 ha) and long growing season. A total of 494,000 to 679,000 ha-m (4 to 5.5 million-acre feet**)** are applied to California's alfalfa crop each year, depending on alfalfa acreage of a given year, weather patterns, and method of estimation.

Growers normally fully irrigate alfalfa throughout the growing season to maximize yield. Evapotranspiration (ET) or water use for alfalfa is highest during summer months and lowest during spring and fall months. Yields tend to be highest during spring harvests, and lower during summer months. In addition, forage quality of alfalfa tends to be lower during summer months due to the hot weather, resulting price reductions of up to 40%.

The Department of Water Resources has shown interest in deficit irrigation during the late summer of alfalfa as a source of water available for transfer elsewhere. The amount of transferable water is the difference in the evapotranspiration of a fully-irrigated crop and the evapotranspiration of a deficit-irrigated field. However, little information is available on the evapotranspiration of deficit-irrigated alfalfa during July and August and the effect of deficit irrigation on crop yield and on the yield of subsequent alfalfa crops. This project examines different methods of deficit irrigation and estimates the potential water savings and economic effects of deficit irrigation.

## OBJECTIVES

The objectives of this research/demonstration project on controlled deficit irrigation of alfalfa are:

1. Determine the response of alfalfa yield and quality to regulated deficit irrigation to help identify the strategies most appropriate for alfalfa growers to implement for reducing water use of alfalfa.

2. Estimate the potential water savings and the economics associated with different approaches,

3. Estimate the crop evapotranspiration of fully-irrigated alfalfa and deficit-irrigated alfalfa to be used to estimate the water savings that might be used for transfer elsewhere.

4. Identify deficit irrigation strategies and management practices that will minimize yield loss and plant mortality.

## PLAN OF ACTION

### COMMERCIAL FIELD EXPERIMENT

Two sites have been selected in Yolo County for a farm level demonstration. Defict irrigation is being imposed on selected checks in each field. The experimental design is a randomized complete block design, with 3 irrigation treatments and 4 replications. The three irrigation treatments are: 1) Full irrigation treatment 2) Deficit irrigation for short period, (1 month) 3) Deficit irrigation for long period (2 months). Data collected are yield, yield quality parameters, soil water potential, and applied irrigation water. Flood irrigation is used by both growers, the normal irrigation method of alfalfa in the Sacramento/San Joaquin Valley.

At one site, evapotranspiration of the full treatment is being determined. The Bowen Ratio energy balance method (Todd et al. (2000) was used in 2004, but because of problems with this method, the eddy covariance or correlation energy balance method (Kizer and Elliott, 1991; Tanner et al., 1985) and the surface renewal energy balance method (Spano, 1997) are being used in 2005. The surface renewal system is installed in the deficit-irrigated field. Canopy coverage was also measured with a digital, infrared camera in both the full-and deficit-irrigated treatments. Crop coefficients are calculated as the ratio of crop ET to reference crop ET, provided by the California Irrigation Management Information System.

### UC DAVIS EXPERIMENT

In addition to the farm sites, an experiment has been established at UC Davis which includes varieties and irrigation treatments using a randomized block split plot design with four replicates. Plots were established in the fall of 2002. The irrigation treatments are the main treatments and varieties are the secondary treatments. The irrigation treatments are:

1. Full irrigation according to normal grower practice on check-flood fields,
2. Ceasing irrigation during 4 weeks in August,
3. Ceasing irrigation for 8 weeks during July and August, and
4. Reducing irrigations from 2-3 per month to 1 per month during the months of June, July and August.

Different varieties are used in the subplots. Data collected include applied water and yield for all plots, and yield quality and soil water potential on selected plots. A cutting schedule is being used that reflects farm-level conditions. Yield quality parameters include acid detergent fiber (ADF), neutral detergent fiber (NDF) and crude protein (CP).

## RESULTS

### COMMERCIAL FIELD EXPERIMENT

The 2004 alfalfa evapotranspiration (ETc) data showed small ETc values on about day of year (DOY) 100 and DOY130, the result of the harvest or cutting (Fig. 1). After a cutting, ETc increased with time to maximum values, which occurred just before the next cutting. At the same time, both canopy coverage and plant height also were the smallest just after a cutting and increased with time after cutting (Fig. 2).

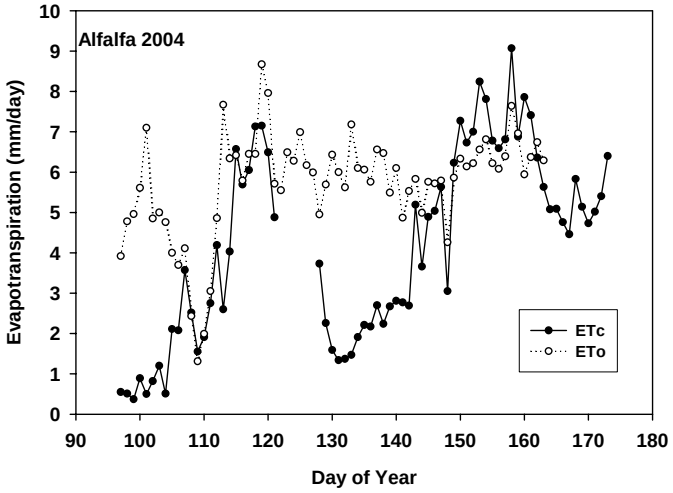


Fig. 1. Daily alfalfa evapotranspiration and reference crop evapotranspiration of a commercial field in 2004.

The ETc data in Fig. 1 were determined with the Campbell Scientific Bowen Ratio energy balance method. The method resulted in reasonable values until after about DOY180. Thereafter, the BR latent heat flux density data, used to calculate daily ETc, became very erratic. The main reason for this behavior was felt to be caused by the dew point temperature measurements. The BR method requires water vapor pressure data at two elevations above the canopy. The difference between the two measurements is used to calculate the latent heat flux density. The Campbell Scientific BR system measures the dew point temperature at the two elevations and converts those data into water vapor pressure. The dew point temperatures are measured by drawing in samples of air through tubing at each elevation and flowing the air through a chilled mirror hygrometer. This method worked quite well for calculating ETc of tomatoes in the Westlands Water District (Fresno County), but apparently, the climatic conditions at this alfalfa field resulted in condensation in the tubing. Thus, no differences in dew point temperatures could be detected until about mid-day, resulting in unreliable data. Because of this problem, the 2005 ETc data were determined with the Campbell Scientific eddy covariance (EC) energy balance system and with the surface renewal (SR) energy balance method, developed at UC Davis.

The 2005 data showed increasing ETc and reference crop ET (ETo) with day of year up to about DOY130 (Fig. 3).

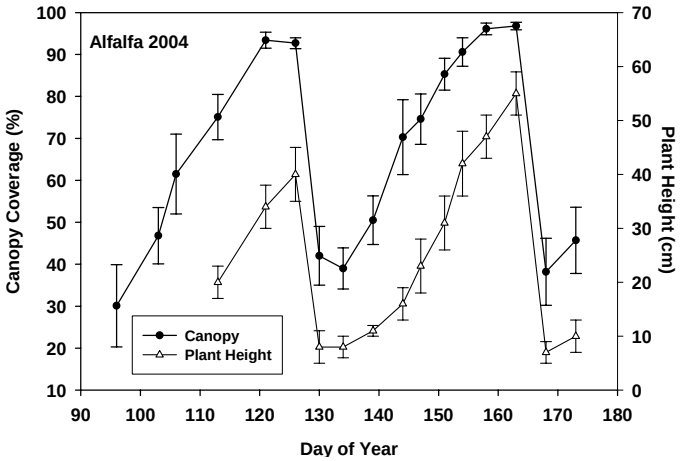


Fig. 2. Canopy coverage and plant height (cm)

Considerable variability occurred in the data due to the highly variable climate behavior during the first part of the year. However, just after a cutting, small values of ETc occurred, as did in 2004, and then ETc increased with time after cutting until the next cutting. This pattern is very obvious after DOY180, but is less so earlier in the year because of the day-to-day climate variability. However, it can be seen that while ETc was small on about DOY110 and DOY 146, high ETo values occurred for both time periods, indicating that the small ETc values were due to cutting. Cumulative

ETc as of September 9, 2005 was 946 mm (37 inches).

Canopy coverage and plant height data have been collected during 2005. Those data will be evaluated this fall.

Figure 4 shows the effect of deficit irrigation on alfalfa ETc. Deficit irrigation started on July 25. It was desired to start the deficit irrigation at the end of June, but we failed to communicate this to the irrigator, which resulted in July irrigations. After the July 25 cutting, ETc of the deficit irrigated part of the field was less than that of the fully irrigated field and eventually decreased to values between 1 and 2 mm/day. Cumulative ETc between July 25 and September 9 was 254 mm for the fully irrigated treatment and 128 mm for the deficit irrigated treatment.

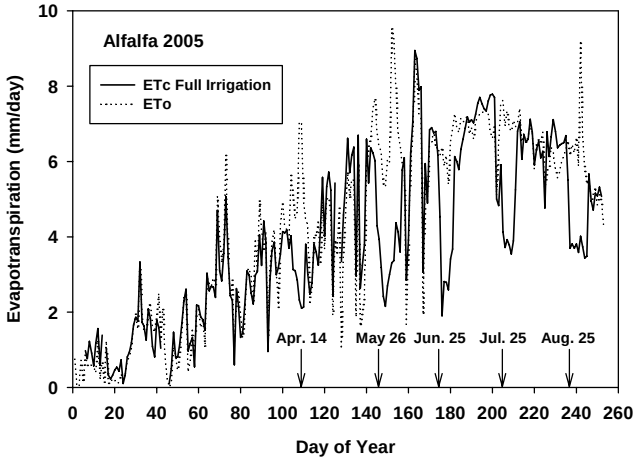


Fig. 3. Daily alfalfa and reference crop evapo-transpiration with time of a commercial field in 2005. The arrows with the dates are the cutting or harvest times.

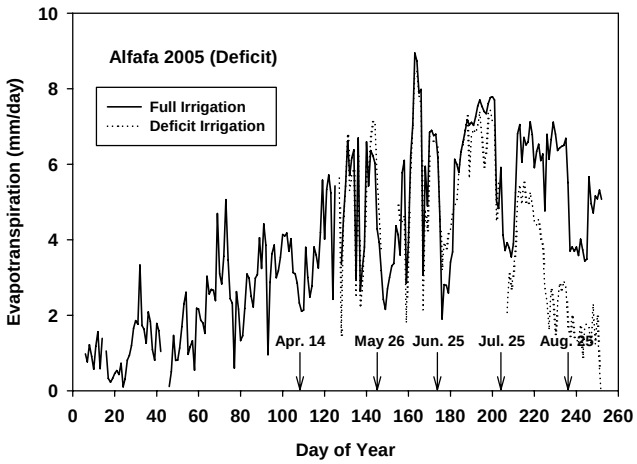


Fig. 4. Daily alfalfa evapotranspiration of fully irrigated and deficit irrigated alfalfa in a commercial field in 2005. Deficit irrigation started on July 25.
The arrows with the dates are the cutting times.

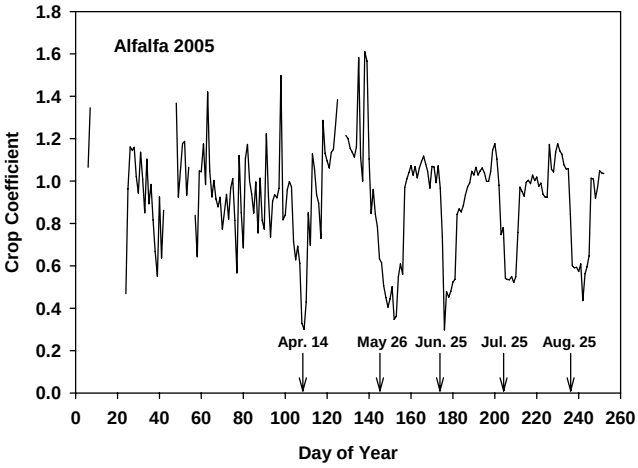


Fig. 5. Daily crop coefficients of alfalfa in a commercial field in 2005. The arrows with the dates are the cutting times.

No trend with time was found for the crop coefficients of the fully-irrigated treatment prior to DOY100, although considerable variation in the coefficients occurred due to climate variability (Fig. 5). After DOY100, a strong pattern occurred with crop coefficients just after cutting ranging between 0.4 and 0.5 and then increasing to values between 1.0 and 1.2.

Yields in the two commercial fields are shown in Tables 1 and 2. Yields were substantially reduced by the deficit irrigation. There was some recovery in yield due to the fall irrigation, but yields of that treatment were still smaller than those of the fully-irrigated treatments. The difference in applied water between the fully irrigated treatment and the deficit –irrigated treatments was 853 mm for the mid-summer cutoff and 599 mm for the mid-summer cutoff followed by a fall irrigation for Site C (location of the ETc experiment). Data on applied water at the other site was only recently received.

Table 1. Yield (Mg/ha) for cuttings 5 and 6 for the Site G commercial field in 2004.

| Treatment | Yield (Mg/ha) | | |
|---|---|---|---|
| | Cutting 5 | Cutting 6 | Total |
| Full irrigation | 2.46 | 1.90 | 4.39 |
| Cutoff in mid-summer | 0.85 | 0.52 | 1.39 |
| Mid-summer cutoff with fall irrigation | 0.83 | 1.03 | 1.84 |
| LSD (0.05) | 0.43 | 1.37 | 1.75 |

Table 2. Yield (Mg/ha) for cuttings 4, 5 and 6 for the Site C commercial field in 2004.

| Treatment | Yield (Mg/ha) | | | |
|---|---|---|---|---|
| | Cutting 4 | Cutting 5 | Cutting 6 | Total |
| Full irrigation | 3.49 | 3.02 | 1.90 | 8.42 |
| Cutoff in mid-summer | 0.78 | 0.56 | 0.94 | 2.26 |
| Mid-summer cutoff with fall irrigation | 0.60 | 0.36 | 2.15 | 3.14 |
| LSD (0.05) | 0.63 | 0.38 | 1.39 | 1.25 |

**UC DAVIS EXPERIMENT**

Seven cuttings were conducted and fifteen irrigations were applied from beginning of April to beginning of October in 2004.

Seasonal amounts of irrigation water applied to each treatment over the season are in Table 3. The July cutoff resulted in a reduction of 838 mm of water, and the August Cutoff resulted in a reduction of 432 mm of water compared to the fully irrigated treatment. The July cutoff treatment, with irrigation in the fall (September), resulted in a reduction of 406 mm.

Table 4 shows no significant differences in yield before the deficit treatments were applied prior to the July 6 harvest. After July 6, the irrigation water was cutoff for treatments 2 and 4. After the treatments were imposed in July, significant yield differences were seen between the control plots and deficit-irrigated plots (treatments 2 and 4) at the 95% level of confidence. These differences due to irrigation were seen in the last 3 harvests of the year, resulting in an over-all significant reduction in yield for the year (Table 4). The yield in the control (fully irrigated) plots reflects the yield levels commonly observed in field plot studies on the UC Davis campus. It should be noted that yield measurements from small-plot studies such as these are typically 20-40% higher than the yield commonly found in commercial fields. The average yield level in Yolo County for alfalfa is approximately 16.8 Mg/ha. This is largely due to the fact that the UC Davis soil is a class 1 soil; near zero harvest losses (5-20% harvests losses are common); no deteriorated sections of fields (as can occur in commercial fields); and more flexibility to obtain timely harvests than growers have.

Table 3. Seasonal amount of applied irrigation water (mm) for each treatment of the UC Davis experiment in 2004.

| Treatment | Applied Water (mm) |
|---|---|
| Full Irrigation | 1,371 |
| July Cutoff | 533 |
| August Cutoff | 940 |
| July Cutoff; Sep. irrigation | 965 |

Table 4. Average yield (Mg/ha) vs. irrigation strategy for each cutting date of the UC Davis experiment in 2004.

| Treatment | Apr 5 | May 9 | Jun 4 | Jul 6 | Aug 4 | Aug 31 | Sep 30 | Total |
|---|---|---|---|---|---|---|---|---|
| Full | 3.1584 | 4.3456 | 4.2336 | 4.9504 | 4.5472 | 4.592 | 3.9648 | 29.792 |
| Jul. cutoff | 3.2704 | 4.256 | 4.0544 | 4.5248 | 1.904 | 1.0304 | 0.2688 | 19.2864 |
| Aug. cutoff | 3.1584 | 4.5472 | 4.5024 | 5.1744 | 4.5248 | 4.0768 | 1.7472 | 27.7088 |
| Jul. cutoff; Sep. irrig. | 3.1584 | 4.48 | 4.4576 | 5.3088 | 2.4864 | 1.5232 | 4.032 | 25.424 |
| | ns | ns | ns | ns | *** | *** | *** | ** |
| LSD (0.05) | | | | | 0.18144 | 0.18368 | 0.17472 | 0.80192 |

## FUTURE RESEARCH

The ETc measurements of 2005 will continue until the end of October or November. Thereafter, the eddy covariance and surface renewal instruments will be removed and installed in another field. Measurements will be made in the new field into the fall of 2006. The UC Davis experiment will also be continued in 2006. Data from 2005 will continue to be evaluated.

## REFERENCES


Kizer, M.A. and Elliott, R.L. 1991. Eddy correlation systems for measuring evapotranspiration. *American Society of Agricultural Engineers Transactions* 34(2): 387-392.

Spano, D., Snyder, R.L., Duce, P., and Paw U, K.T. 1997. Surface renewal analysis for sensible heat flux density using structure functions. *Agricultural and Forest Meteorology* 86: 259-271.

Tanner, B.D., Tanner, M.S., Dugas, W.A., Campbell, E.C., and Bland, B.L. 1985. Evaluation of an operational eddy correlation system for evapotranspiration measurements. In: Advances in Evapotranspiration: Proceedings of the National Conference on Advances in Evapotranspiration, American Society of Agricultural Engineers. Chicago, IL. December 16-17, 1985.

Todd, R.W., Evett, S.R., and Howell, T.A. 2000. The Bowen ratio-energy balance method for estimating latent heat flux of irrigated alfalfa evaluated in a semi-arid, advective environment. *Agricultural and Forest Meteorology* 103: 335-348.

# Large-Scale Utilization of Saline Groundwater for Development and Irrigation of Pistachios Interplanted with Cotton


**Project Investigators**

Blake Sanden
Irrigation and Agronomy Advisor, UCCE Kern County
1031 S. Mt. Vernon Ave.
Bakersfield, CA 93307
Phone: (661) 868-6218; Fax: (661) 868-6208; E-mail: blsanden@ucdavis.edu
http://cekern.ucdavis.edu

Louise Ferguson
UCCE Pomology Specialist, Kearney Ag. Center
9240 S. Riverbend Ave.
Parlier CA, 93648
Phone: (559) 646-6541; Fax: (559) 646-6593; E-mail: louise@uckac.edu
http://pom.ucdavis.edu/

Craig Kallsen
Subtropical Crops and Pistachio Advisor, UCCE Kern County
Phone: (661) 868-6218; Fax: (661) 868-6208; E-mail: cekallsen@ucdavis.edu

Brian Marsh
Agronomy Farm Advisor, UCCE Kern County
Phone: (661) 868-6218; Fax: (661) 868-6208; E-mail: brmarsh@ucdavis.edu
http://danrrec.ucdavis.edu/shafter/home_page.html

Bob Hutmacher
UCCE/AES Cotton Specialist, Shafter Research & Extension Center
17053 Shafter Ave.
Shafter CA, 93263
Phone: (661) 746-8020; Fax: (661) 746-1619; E-mail: rbhutmacher@ucdavis.edu
http://danrrec.ucdavis.edu/shafter/home_page.html

**Special Collaboration, ECa Survey**

Dennis Corwin
Soil & Environmental Scientist USDA George E. Brown, Jr. Salinity Laboratory
450 West Big Springs Road
Riverside, CA 92507-4617
Phone: 909-369-4819; Fax: 909-342-4962; E-mail: dcorwin@ussl.ars.usda.gov
http://www.ussl.ars.usda.gov/

**Research Staff**

Michael Mauro, Lab Assistant II

## ABSTRACT

Cotton has long been known as a salt tolerant crop, but despite many small-scale field trials over 30 years almost no marginally saline water in the San Joaquin Valley is used for long-term production Over this same period water costs have increased four to tenfold while acala cotton prices have actually declined to those seen in the early 1960's. Farmers are looking for less expensive, more secure water supplies and more profitable crops. Work in Iran, salt tank studies at the USDA Salinity Lab, Riverside, and a small plot study in NW Kern County indicate pistachios may tolerate an ECe up to 8 dS/m, but this has not been proven on a commercial scale in CA.

This project utilizes twelve, 19.5 acre test plots arranged in a randomized complete block design set within two 155 acre fields to provide a realistic production environment to demonstrate the economic viability of using marginally saline water for cotton production and development of a new pistachio orchard. These blocks of well-drained Panoche clay loam were formerly irrigated with California Aqueduct water and sprinklers for the last 30 years. Overall field EC's ranged from 0.5 to 4.5, averaging 1.57 dS/m to a three foot depth. Saturation extract boron was 0.6 ppm. The area is underlain by a semi-saline aquifer that has been made worse over the decades by contamination from oilfield leachate water. Several production wells were drilled in fall 2003 to begin using this water. A drip tape irrigation system was set up to allow the planting of 6 rows of cotton every 22 feet the first year of the project (2004) followed with the planting of 1 year old pistachio seedling rootstocks March 2005 in 22 foot rows interplanted with 4, 38 inch rows of pima cotton.

Salinity of the shallow groundwater for test fields varies from 4 to 5 dS/m with 8 to 10 ppm B. Three treatments were imposed: AQUEDUCT/CONTROL: EC ~ 0.4 dS/m (Aqueduct water only), BLEND: EC ~ 2.5 dS/m (50/50 mix) and WELL: EC ~ 5 dS/m. Cl content in late season cotton petioles and average seasonal soil water content were significantly higher in the WELL treatment compared to the Control. Saturation extract EC and B in the top three feet of rootzone were significantly increased in the BLEND and WELL treatments over the Control at the end of the season, with most salts increasing significantly to 3 feet with a significant increase in Cl to 5 feet. Total measured salt increase (as EC) to a depth of 5 feet was 176, 69.1 and 77.8% of the mass applied in the irrigation water for the Control, BLEND and WELL treatments, respectively. Cl increased by 287, 92.9 and 84.4% of the mass applied for the same respective treatments. Saturation extract B showed a similar trend; increasing 367% of the mass applied for the Control treatment but only a 21.7 and 25.2% increase for the BLEND and WELL treatments respectively – indicating that B, was being sequestered in the soil at higher levels of EC and B concentration, and potentially desorbed from the soil matrix back into solution using the low salinity Aqueduct water. No toxicity effects were seen on the cotton. Average yield was 1,718 lb/ac of lint for the total acreage, showing no treatment effects except for slightly reduced water use as salinity increased.

## INTRODUCTION

A recently completed nine year field study on the salt tolerance of pistachios on the Westside of the San Joaquin Valley (Ferguson et. al., 2004 and Sanden, 2003), and previous pistachio studies in Iran (Fardooel, 2001) have shown the viability of using saline water up to 8 dS/m for irrigating these trees. A rootstock trial in sand tanks at the USDA Salinity Lab in Riverside (Ferguson et al., 2002) showed a significant increase in leaf burn when 10 ppm boron was added to irrigation water but no reduction in the biomass of year old trees. The salinity and B tolerance of cotton has been reported at similar levels in tank trials (Ayars and Westcott, 1985) and investigated in long-term field trials (Ayars et al., 1993).

In the early 1990's a number of studies investigated the use of thick-walled drip tubing for permanent subsurface drip irrigation (SDI). This system usually increased irrigation uniformity and efficiency, reduced deep

percolation and helped to control perched water tables, and boosted yield to some degree. However, at a system cost of $1,000+/acre and water costs in the range of $30 to $50/ac-ft there was often an economic disadvantage using SDI compared to furrow irrigation (Fulton et al., 1991).

In 1990, State Water Project allocations to Westside irrigation districts went to zero; unleashing California's infant water market with the establishment of "Emergency Pool" water that could be bought for $100/ac-ft. Given the salt tolerance of cotton and other rotation crops on the Westside (such as processing tomatoes), some studies investigated utilizing fresh water blended with drainage from tile systems as a means of boosting available water supplies for furrow irrigation (Ayars et al., 1993, Sheenan et al., 1995). This approach generated some interest, since yields were maintained at similar levels to fresh water irrigations, but required a high degree of management with the possibility of long-term residual salinity problems that growers did not want to deal with. Even though in the middle of a six-year drought, most growers viewed the situation as a temporary aberration. In addition, cotton prices were low and interest rates high, making new capital investment into irrigation systems an unwise move.

This situation changed dramatically as California entered the 21$^{st}$ century. Restrictions on pumping from the Delta, rising urban demand and new legislation requiring builders to secure water before starting the construction of new subdivisions, along with opportunities for marketing and banking potable quality water have driven the "opportunity cost" of irrigation water to levels that can make the production of traditional field crops unprofitable. Water costs on the Westside over the last 15 years have increased four- to ten-fold depending on the irrigation district and total allocation for a given year. The current cost ranges from $60 to $160/ac-ft in an average water year depending on the irrigation district. Due to these costs, decreasing supply due to legislative mandates, pumping restrictions from the Delta and stagnant cotton prices until the last two years, a significant amount of cotton rotation acreage has been fallowed or converted to other crops.

The Cal Fed process, ushered into California's confusing water world at the start of the new millennium, is attempting to accommodate the state's growing water needs. Part of that process has identified "Agricultural Water Use Efficiency (AGWUE) Draft Quantifiable Objectives" for many regions of the state. Two of these objectives for Sub-region 19, western Kern County are reduction of irrigation deep percolation losses to saline sinks, and reducing "non-productive ET" as priority areas for efficiency improvements (Cal Fed, 2000). The total savings for both these numbers is estimated at < 5,500 ac-ft/year. This relatively low number is mostly due to the efficiencies of microirrigation systems applying the aqueduct water used to irrigate the permanent crops dominating Westside saline sink areas.

With the exception of some small inclusions in other districts, Westside Kern County irrigation districts are the ones overlaying saline sinks (TDS > 2000 ppm). Much of the marginal acreage has been fallowed and the accompanying water allocation shifted to the almonds and pistachios with micro irrigation systems that dominate the landscape. Several thousand acres of cotton, wheat, alfalfa, carrots and onions are still rotated in the better areas.

The Belridge Water District in western Kern County is one such district. The slightly rolling topography in this area has a bit too much relief for economic land leveling and thus requires either sprinkler or micro irrigation. Covering about 95,000 acres total, there are 41,000 acres of trees, 10,000 acres (maximum) rotated into cotton and alfalfa, and about 3,000 acres of vegetable crop rotation. Most of these crops have an ET requirement of 3 to 4 feet, where the district 100% allocation is only 1.99 ac-ft/ac. Thus, 40% of the District must remain fallow to supply additional water for the planted acreage. In water short years growers must often buy water from the Kern County Water Bank or other sources.

The groundwater in the southeast part of the District (underlaying about 15,000 acres in the project area) varied from 1,000 to 3,000 ppm TDS and 1 to 10 ppm boron, with a depth of about 50 to 80 feet below the surface. From 400,000 to 800,000 ac-ft of water at this quality may have been available in this area – enough water to irrigate

more than 3,000 acres of cotton for 50 years! Unfortunately, highly saline production water separated from oil pumping in this area has been leached into the western zone of this aquifer for more than 30 years, continuing to degrade water quality. One new production well was shut down after only one season when salinity climbed to 18 dS/m.

At the same time water supplies have decreased and costs have soared, SDI systems using improved, thin-walled drip tape have become cheaper than ever before, with capital costs as low as $750/acre for grower installed systems. With a much lower energy requirement than sprinklers, greater uniformity and reduced loss to evaporation (a total savings of 6 to 8 inches) this type of system becomes the most cost effective in this setting. All these factors have combined to make the time right for developing irrigation system management approaches that can use hybrid fresh and saline water supplies to irrigate salt tolerant crops.

With a 100% water allocation the grower/cooperator farming this area will normally plant 3,000+ acres of cotton with alfalfa, almonds and pistachios on other fields. He has not had a 100% allocation for the last three years, and even when he does water costs are around $100/ac-ft. The marginally saline groundwater in this area can be pumped for < $30/ac-ft using diesel boosters. After a successful test using drip tape on a 140 acre field planted to cotton in 2003, with a better yield than the ranch average for sprinkler irrigated fields, the grower has begun a phased development of nearly 1,800 acres of this type of system. Even though total salinity levels are well within the tolerance ranges of cotton and pistachio, minimizing potential boron accumulation and boron/salinity interactions are the big unknowns (Grattan, et al., 2003). This is the long-term “make or break” issue for the project.

The physical setting, the current economic constraints and water supply picture in this project area present a unique opportunity to accomplish the overarching objective of decades of salinity research in California: namely, proving the sustainability of profitable long-term irrigation using significant quantities of marginally saline water in a large-scale production setting. That is the primary objective of this project.

## OBJECTIVES

1. Assess the viability of large-scale cotton production over four years using saline shallow groundwater (EC 4 to 5 dS/m and B @ 8 to 10 ppm) and optimal irrigation scheduling with SDI.
2. Using the same water, establish a new pistachio orchard interplanted with cotton starting the second year. Determine crop ET for this system and impact of salinity.
3. Maintain acceptable soil salinity levels for cotton stand establishment/production and maximum growth of young pistachios.
4. Compare total project profitability under SDI using 3 different levels of salinity: saline water, non-saline CA Aqueduct water and a 50/50 blend. Compare the economics of drip tape SDI with typical Belridge Water District cotton production using sprinklers.

## MATERIALS AND METHODS

### SITE

Located in the Belridge Water District in southwestern Kern County, soils are primarily Panoche clay loam and have been planted to a cotton/alfalfa/fallow rotation for more than 20 years and irrigated with California Aqueduct water and hand-move sprinklers. Drainage is excellent with a marginally saline aquifer of 4 to 5 dS/m starting at a depth of 50 feet below the ground surface and going down to 500 to 600 feet. Seven ag wells, each producing 1,200 to 2,000 gpm, were drilled between fall 2002 and fall 2003. The grower has installed shallow subsurface drip tape on six quarter sections, with plans for another 6 to follow. Drip tape has been installed at spacings that allow for the interplanting of cotton and pistachios. The project site for this study consists of two adjacent quarter sections (9-1

**Site:** 2, 160 acre blocks will be used to set up a cotton/pistachio interplant for a large-scale production trial testing the viability of using saline shallow groundwater for irrigation.

**Treatments (RCB Design):**

Control: Aqueduct water only
EC ~ 0.5 dS/m
Well: Shallow groundwater only
EC ~ 4.5 dS/m
Blend: 50/50 mix of above
EC ~ 2.5 dS/m

**2004 Season**: Cotton only. Solid plant
**2005-2007:** Pistachios planted in April on 22 ft row spacing with 4-38" rows of cotton in the middle.

**Irrigation System:**
System flowrate requires 4 subunits open per set, 2 per submain running opposite of each other. A small road divides the 160 acres into 2, 80 ac blocks but are treated as one field. Drip tape adjacent to pistachios has separate manifold to allow for separate scheduling of young trees starting 2005. Schedules to be provided to grower.

**Data Collection:**
**Soil water content:** replicated neutron probe sites for weekly measured depletion/ET, data logger/Watermark blocks recording estimated matric potential using electrical resistance.

**Soil salinity patterns:** sampling, at planting and post harvest. GIS survey with EM38 and aerial imagery.

**Plant data:** leaf water potential monthly just prior to the start of irrigation. Trunk diameter annually. Leaf tissue Ca, Mg, Na, Cl, B and petiole NO3, P and K. Lint yield and quality.

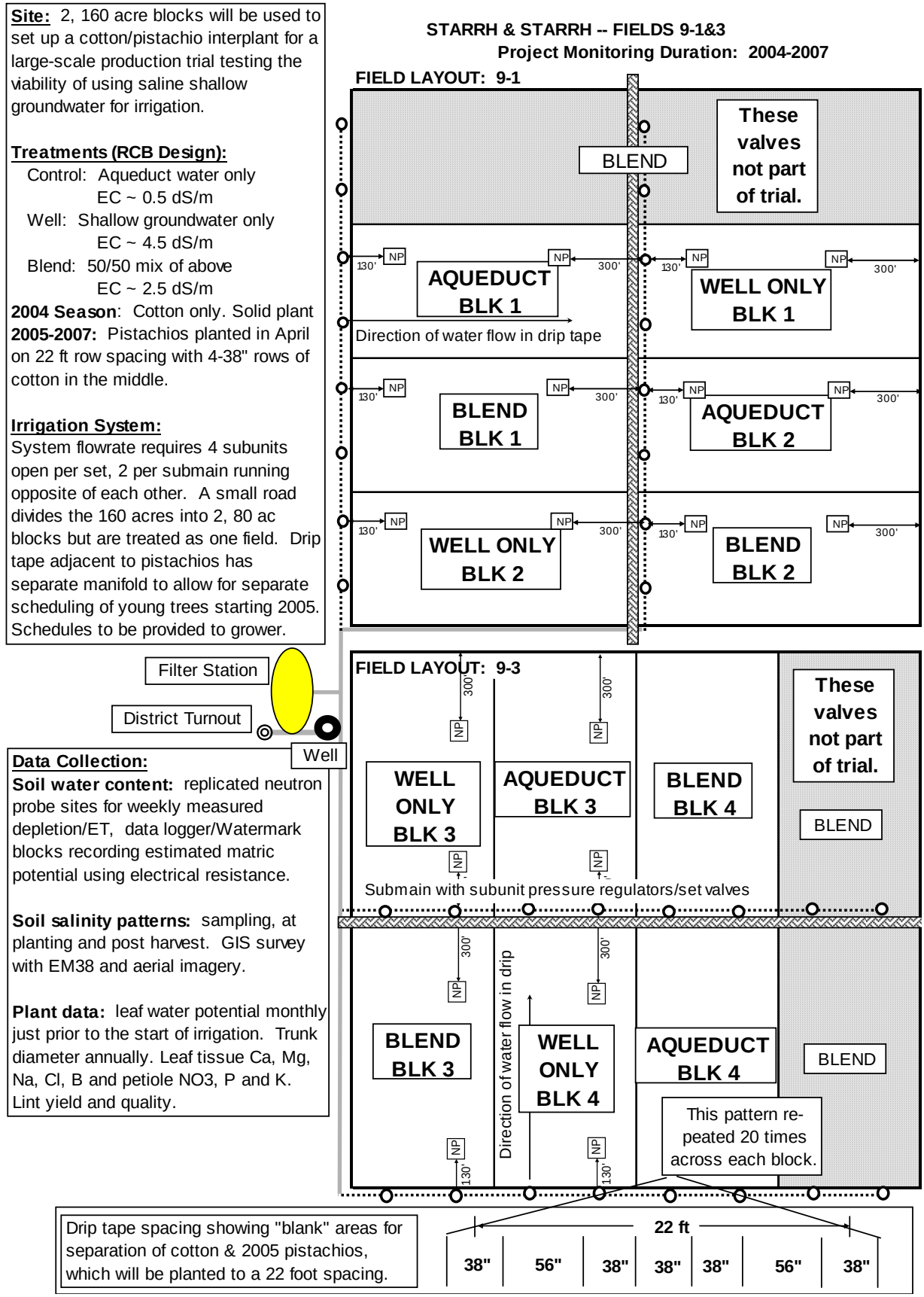


Fig. 1. Project site design.

and 9-3) containing three treatments replicated four times, divided into a Randomized Complete Block Design as illustrated by Figure 1.

**IRRIGATION SYSTEM and CROPPING PATTERN**

T-Tape TSX 708-12-220, 0.875 inch diameter drip tape with emitters every 12 inches was injected at 9 to 10 inches below field grade in January 2004. Designed for a final tree spacing of 22 feet, the tape was installed under 4 contiguous 38 inch rows followed by a 56 inch skip, 2 more 38 inch rows and a second 56 inch skip (see Figure 1). A separate underground manifold connected to the two hoses with the 56 inch spacing to either side was installed for irrigating pistachios and to allow for separate scheduling from the cotton. Hose runs are 1280 feet long with the manifold connected at the high side of the field with the outlets connected to a common flush line. Each block has 16 separate pressure regulating subunit valves. Sixty hoses are served by a single cotton manifold tied to each subunit valve that also delivers water to 30 hoses connected to the manifold serving the interplanted pistachios. The grower's booster and filter station are designed to irrigate 8 subunits at a time (78 net acres); making for 4, 24 hour set changes during irrigation. Flow from the well, however, is not sufficient to meet this demand when no additional canal water is blended for irrigation. Therefore, the "WELL" only treatment is irrigated in two sets to maintain pressure uniformity. The system is operated @ 15 psi at the subunit regulators, yielding 0.27 gpm/100 feet of drip tape. All irrigations are scheduled for a 24 hour duration due to restrictions on canal water delivery. Randomized, replicated treatments are applied to 19.5-acre plots (2 adjacent subunit valves each, 440 feet wide by 1280 feet long). Valves have been color coded to indicate the appropriate treatment water and are operated by farm staff.

In 2004 the entire field was planted to pima cotton and irrigated up from 3/11-25 (variety, Delta Pine 340). The average application rate of the six hoses over the 22 foot spacing was 1.76 inches/day. In 2005, Pioneer Gold rootstocks were planted March 5-11 at an18 x 22 foot spacing. Blocks of 20 UCB rootstocks were planted adjacent to the replicated PG trees at all monitoring sites to allow for evaluation of differential vigor/salt impacts from a rootstock interaction. Four, 38 inch rows of DP340 pima cotton were interplanted and irrigated up between March 25 and April 15. At this spacing the cotton receives 1.99 inches/day and the pistachios receive 0.57 inches/day from the two adjacent hoses. All pistachio trees were budded with Kerman buds from August 12-19.

**TREATMENT**

Aqueduct water (a 6 to 9 inch depth) was used for the cotton germination irrigation and for "heeling in" pistachio rootstocks for optimal stand establishment in all subunits. Subsequent irrigation was applied in 24 hour sets as required over the season using the following treatments with four replications (Figure 1):

**AQUEDUCT/CONTROL:** Aqueduct water only EC ~ 0.4 dS/m
**BLEND:** 50/50 mix of Aque and WELL EC ~ 2.5-3 dS/m
**WELL:** Shallow groundwater only EC ~ 4 - 5 dS/m
(Note: Well water salinity and flow fluctuate slightly.)

**MONITORING and ANALYSIS**

***Soil water content and applied water***

For the 2004 cotton season, neutron probe access tubes for weekly measured soil water content were installed in Blocks 1, 2 and 3 to a depth of 6 feet @150 feet from the head and 300 feet from the tail ends of the drip tape. In Block 1, 6 electrical resistance blocks (Watermarks®) are used to estimate matric potential at the 12, 24 and 48 inch depths adjacent to neutron probe access. A Hanson AM400 data logger records these readings every 8

hours. These loggers allow the grower a quick graphic check on moisture status trends over five weeks and help with optimal irrigation scheduling. Small flow meters were installed at the entrance to each replicated run of drip tape adjacent to neutron probe access tubes. For the 2005 season, a similar network of access tubes and resistance blocks was set up for the newly planted pistachios and reinstalled in the cotton after planting. "Tail" end monitoring of soil water was deemed unnecessary for the 2005 season due to the high uniformity of the system and lack of real differences between the head and tail ends. Eliminating these sites allowed for the installation of access tubes in the head end of Block 4 to increase replication.

***Soil and water salinity***

Replicated soil samples are taken at germination and post harvest each year from the area adjacent to access tube locations from the 0-6, 6-18, 18-36 and 48-60 inch depths and analyzed by the ANR Lab at UCDavis for EC, Ca, Mg, Na, Cl, HCO3, and B. Treatment water samples are collected in June and the end of August (near irrigation cutoff) and analyzed for the same constituents. In addition, weekly to biweekly (June – Aug) the EC of treatment water samples are checked with a portable EC meter in our Kern County office.

***Seedbed salinity***

For each treatment, a transect of closely spaced samples taken at the time of cotton emergence (about one week after the end of irrigation) and perpendicular to the drip tape will be used to characterize EC and B patterns at the time of stand establishment for each treatment. A similar transect will be done for pistachios but with wider spacing. To improve the characterization of an "average" transect, individual samples representing a given distance from the drip hose(s) will be obtained by compositing separate samples of the same distance from 5 separate transects along 50 to 100 feet of the same drip hose near, but not adjacent to, a "head" access tube.

***Plant data***

Leaf water potential (LWP) was measured biweekly once cotton plants were about 12 inches high. Petiole NO3, P, K, Na, Cl and B was determined for the end of June and again just before defoliation in September. Foliage was rated visually for leaf burn. Plant mapping was done in July and just before defoliation. Cotton lint was determined using a 2-row and 4- row commercial picker harvesting over the 1280 foot length of the row and weighed in a separate "boll buggy". Lint quality was be determined by subsampling each plot and using HVI automated classing. Starting in 2006, LWP and N, P, K, Na, Cl and B will be determined for the Kerman scion that was budded into all trees 8/12-19/05. Trunk circumference in pistachios will be measured annually in late fall, starting 2005. Three extra trees per plot were planted in 2005 and will be sacrificed at the end of the experiment to determine shoot, scaffold and trunk weights and B accumulation in the woody tissue.

***GIS / ECa / Aerial survey***

Both fields were surveyed for $EC_a$ using a tractor mounted dual dipole EM38 from the USDA Salinity Lab in Riverside, CA with GPS (Section 9-1, on May 14,26-27 and field 9-3, May 5-6). GPS way points for anchoring aerial imagery and field mapping were done with HGIS and a hand-held NavMan GPS unit mounted to an IPAQ pocket PC. This data was compared to field aerial imaging analysis (Ag Recon of Davis, CA) shot on 7/29/04. Reflectance is digitally recorded for three different band widths: visible red light (VIS 0.4 to 0.7 µm), near infrared (NIR, 0.7 to 1.1 µm) and far (thermal IR, 6 to 15 µm) infrared. The relative intensity of thermal IR and the Normalized Difference Vegetation Index (NDVI = (NIR — VIS)/(NIR + VIS)) was calculated for each plot where 1 pixel equals a 2 meter diameter. As plots are 440 feet wide by 1280 feet long (6.71 x 390.1m) this equals 1308 pixels per plot – providing a

much greater number of pixels for analysis than is often available for replicated studies. These two surveys will be repeated at the end of the trial.

***Data analysis***

All data was tested for significance using a 2-way ANOVA for a completely randomized block design. Some tables are presented with a Fisher's least significant difference ($LSD_{0.05}$) means separation. Adobe Photoshop was used to analyze average plot gray-scale pixel intensity of a modified NDVI calculation of spectral data for significant differences between treatments and field variability. In a similar manner, average plot values of the vertical electromagnetic conductance (EMv in milliSeimens/meter) were calculated from filled contours generated from the EM38 survey and regressed against mean values of plot NDVI.

## RESULTS AND DISCUSSION

### IRRIGATION WATER QUALITY AND SYSTEM PERFORMANCE

Average EC (dS/m), SAR and B (ppm) for the 2004 season were, respectively, 4.5, 5 and 10.2 for the WELL treatment, 3.0, 4 and 5.7 for the BLEND and 0.41, 2 and 0.2 for the AQUEDUCT treatment. The EC of grab samples of well water varied from a low of 4.04 to a high 5.69 dS/m. Irrigation system application distribution uniformity (DU) was 95.6 % for an evaluation on 9/7/04. Two more evaluations were conducted on 7/16/05 and 8/29/05. Out of 36 emitters unearthed for the test (different locations from 2004) one was found to be plugged – either by silt in the hose or a manufacturing defect. Root intrusion was not a problem. Final DU was 94.2% without the plugged emitter, 85.1% when included. It is doubtful that 3% of the emitters in the field are plugged. The average application from the catch test was 2.32 inches/day for a 38" row spacing. This is 15% higher than the manufacturer's specifications, but may be an artifact of errors in the evaluation. The average tape flowrate measured by the small flowmeters serving one of the hoses in the manifolds that were evaluated was 1.91 inches/day. These same meters recorded most irrigation applications of 1.9 to 2.1 inches/day throughout the season.

### WATER USE and SALT LOAD (TABLE 1)

Due to early variability in subunit regulator pressures, 6.1 to 8.4 inches of Aqueduct water were used to establish the cotton at the start of the 2004 season. The young cotton plants were well established by April 1, after which time only the appropriate treatment water was applied; for a total of 32 (+/-0.5) inches for the season. Using the Belridge CIMIS station estimate of ETo and published crop coefficients (Pruitt, et al., 1987) the calculated ET for the 2004 season was 38.2 inches. Neutron backscatter estimates of soil moisture for the AQUEDUCT treatment

Table 1. Applied water, mean soil water content/matric potential, rootzone EC and salt balances for the 2004 season.

| Treat-ment | Aqueduct Water to Establish (inch) | Season Total (inch) | [1]Mean Available Water Content (%) | [2]Mean Matric Potential 0-4 foot (cb) | [3]Mean Soil EC to 5 Feet 3/22/04 (dS/m) | Mean Soil EC to 5 Feet 10/6/04 (dS/m) | [4]Total Increase in Soluble Salts (lb/ac) | Total Salts Applied in Irrigation (lb/ac) | Measured Salt Increase / Applied (%) | Measured Chloride Increase / Applied (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| Aque | 7.6 | 31.5 | 68% | -37 | 2.07 | 2.71 | 3334 | 1898 | 175.7% | 287.0% |
| Blend | 8.4 | 32.2 | 70% | -33 | 2.53 | *4.08 | 8075 | 11680 | 69.1% | 92.9% |
| Well | 6.1 | 32.3 | *95% | *-22 | 2.10 | *4.68 | 13441 | 17285 | 77.8% | 84.4% |

*Significantly different at the 0.05 level.

[1]To 6 feet as determined by neutron backscatter. Based on a refill water content of 1.1 in/ft and a field capacity of 3.1 in/ft.

[2]As determined by Watermark electrical resistance blocks @ 12, 24 and 48" depths.

[3]Weighted average of the saturation extract EC of four soil samples taken from the following depths 0-6, 6-18, 18-36 and 36-60 inches.

[4]Increased mass of salt = increase in EC*(640ppm/dS/m) * 5 feet * 4 million lbs soil/ft * 0.407, the average SP%.

measured an additional 3 inches of depletion beyond the total applied irrigation for the season; exhausting all available soil moisture to 6 feet by the end of the season. For the BLEND there was 10% (1.2 inch) available water remaining and 44% (5.3 inch) remaining in the WELL treatment at the end of the season. The whole season average available soil water content to 6 feet (from weekly measurements) in the AQUEDUCT and BLEND treatments was significantly less than the WELL at 68, 70 and 95%, respectively; indicating the increased osmotic potential of the WELL water restricted ET. Figure 2 confirms this finding as the changes in soil matric potential are less dynamic and less negative as salinity increases.

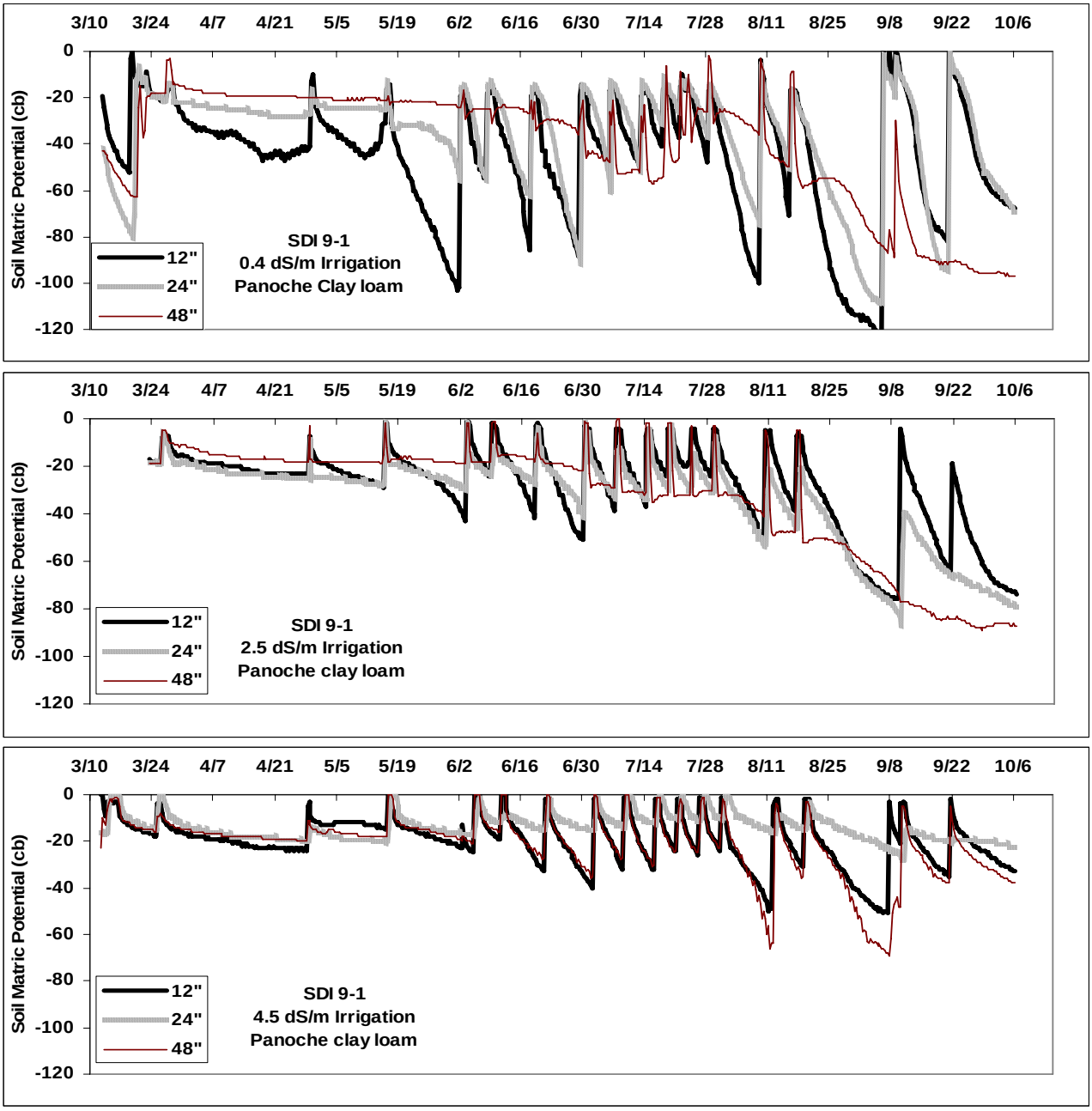


Fig. 2. Changes in soil matric potential over the season for the AQUEDUCT (0.4 dS/m), BLEND (2.5 dS/m) and WELL (4.5 dS/m) irrigation treatments as measured by Watermark® electrical resistance blocks, recorded every 8 hours with a Hanson AM400 logger.

The increase in average soil saturation extract EC to 5 feet was used to calculate the increase in the mass of soluble salts remaining in the profile at the end of the season (using 640 ppm = 1 dS/m EC and an average soil extract saturation percentage, SP = 40.7%). This number divided by the mass of salts applied in the respective irrigation water treatments provides an indication of irrigation efficiency. This increase, expressed as a percentage, was 175, 69 and 78% for the AQUEDUCT, BLEND and WELL treatments, respectively. A more accurate estimate of the leaching can be obtained from the chloride mass balance. Again expressed as a percentage of the increase over applied this number was 287, 92.9 and 84.4% for the AQUEDUCT, BLEND and WELL treatments, respectively (Table 1); meaning that the leaching fraction (LF) was 0% for the AQUEDUCT treatment, 7.1% for the BLEND and 15.6% for the WELL. While there is no logical way to explain where the large excess of Cl came from for the AQUEDUCT treatment (other than sampling error) these ratios support the general trends shown in the water content and matric potential data. Indeed, an analysis of projected steady state salinity of the cotton rootzone using a Windows-based WATSUIT model (Wu, 2004 and Oster and Rhodes, 1990) calculated a steady-state average soil water EC of 1.91 dS/m @ a 5% LF for the AQUEDUCT treatment. Using the average SP of 40.7% reduces this number to 0.78 dS/m saturation extract salinity ($EC_e$); far less than the 2.71 dS/m $EC_e$ found at the end of the season. The same calculation for the BLEND with a 10% LF yields a final average $EC_e$ of 3.15 dS/m and for the WELL treatment, a 20% LF resulted in a final calculated average $EC_e$ of 4.63 dS/m. These model numbers corroborate the field findings and the above estimates of LF determined for the end of the 2004 season.

**SEEDBED SALINITY**

Table 2 shows average saturation extract EC and boron concentrations at the beginning and end of the 2004 season, and then for the beginning of the 2005 season. The critical issue at stake is to insure a seedbed salinity suitable for establishing the young cotton seedlings. Spring 2005 was much colder than 2004. Because of this the decision was made to apply 4.5 to 5 inches of Aqueduct water from 2/25 – 3/10 to wet the soil to both mellow the seed bed, store more heat in the beds and to add to about 1.5 inches of effective rainfall in January and February

Table 2. Seedbed and rootzone saturation extract EC and B levels by depth for the beginning and end of the 2004 season and the beginning of the 2005 season.

**2004 Saturation Extract EC (dS/m)**

| 3/22/04 | 0-6" | 6-18" | 18-36" | 36-60" |
|---|---|---|---|---|
| Aque | 1.95 ab | 1.15 a | 2.38 b | 2.33 a |
| Blend | 2.33 b | 1.60 a | 1.01 a | 4.18 a |
| Well | 1.81 a | 1.00 a | 0.94 a | 3.58 a |
| *$LSD_{0.05}$* | *0.14* | *0.65* | *1.09* | *2.14* |
| **10/6/04** | **0-6"** | **6-18"** | **18-36"** | **36-60"** |
| Aque | 4.02 a | 1.61 a | 1.96 a | 3.49 a |
| Blend | 5.73 b | 3.12 b | 4.13 b | 4.1 a |
| Well | 7.61 c | 3.64 b | 4.18 b | 4.83 a |
| *$LSD_{0.05}$* | *0.34* | *0.79* | *0.99* | *1.62* |
| **Change** | **0-6"** | **6-18"** | **18-36"** | **36-60"** |
| Aque | 2.07 a | 0.46 a | -0.42 a | 1.16 a |
| Blend | 3.40 b | 1.52 ab | 3.12 b | -0.08 a |
| Well | 5.80 c | 2.64 b | 3.24 b | 1.25 a |
| *$LSD_{0.05}$* | *1.33* | *1.19* | *1.3* | *1.98* |

**2004 Saturation Extract B (ppm)**

| 3/22/04 | 0-6" | 6-18" | 18-36" | 36-60" |
|---|---|---|---|---|
| Aque | 0.8 a | 0.5 a | 1.0 b | 1.5 a |
| Blend | 0.8 a | 0.5 a | 0.4 ab | 2.0 a |
| Well | 0.7 a | 0.4 a | 0.3 a | 1.3 a |
| *$LSD_{0.05}$* | *0.2* | *0.2* | *0.6* | *1.6* |
| **10/6/04** | **0-6"** | **6-18"** | **18-36"** | **36-60"** |
| Aque | 1.1 a | 0.6 a | 1.0 a | 2.9 a |
| Blend | 1.6 a | 2.0 b | 1.9 a | 2.2 a |
| Well | 3.2 b | 3.2 c | 3.1 b | 2.1 a |
| *$LSD_{0.05}$* | *1.0* | *0.6* | *1.0* | *2.7* |
| **Change** | **0-6"** | **6-18"** | **18-36"** | **36-60"** |
| Aque | 0.3 a | 0.1 a | 0.1 a | 1.4 a |
| Blend | 0.8 a | 1.5 b | 1.5 b | 0.2 a |
| Well | 2.5 b | 2.8 c | 2.7 c | 0.8 a |
| *$LSD_{0.05}$* | *1.1* | *0.9* | *1.1* | *2.3* |

**2005 Saturation Extract EC (dS/m)**

| 4/26/05 | 0-6" | 6-18" | 18-36" | 36-60" |
|---|---|---|---|---|
| Aque | 2.78 a | 2.70 a | 1.47 a | 1.21 a |
| Blend | 3.21 a | 2.88 a | 1.96 a | 3.07 b |
| Well | 2.39 a | 3.23 a | 1.65 a | 3.49 b |
| *$LSD_{0.05}$* | *0.89* | *2.34* | *1.72* | *1.47* |

**2005 Saturation Extract B (ppm)**

| 4/26/05 | 0-6" | 6-18" | 18-36" | 36-60" |
|---|---|---|---|---|
| Aque | 0.6 a | 0.9 a | 0.5 a | 1.7 |
| Blend | 1.3 ab | 1.0 a | 1.1 ab | 1.6 |
| Well | 2.3 b | 2.0 a | 2.3 b | 1.7 |
| *$LSD_{0.05}$* | *1.1* | *1.84* | *1.69* | *2.82* |

to maximize leaching of salts out of the beds. This caused a two week delay in planting cotton with final true "establishment" of seedlings delayed about one month until April 25, and a total application of Aqueduct water of 9.3, 7.7 and 9.0 inches for the AQUEDUCT, BLEND and WELL, respectively. The final result was a two- to three-fold decrease in seedbed $EC_e$, depending on the treatment, compared to the end of the 2004 season to an average of 2.79 dS/m in the 0-6 inch depth for all treatments – a very acceptable salinity level for the germination of cotton. Figure 3 on the other hand, indicates that salinity levels were much higher in some specific locations. (Contours generated from data from one bed per treatment only.) According to these data, the $EC_e$ in the 0-2 inch (0-0.5m) depth runs about 6 dS/m in the seed row and about 4 dS/m for the 0-6 inch depth. The replicated data in Table 2 is more representative as stand establishment did not appear to suffer from salinity treatments, but was overall less dense than 2004 due to the incidence of seedling diseases brought on by the cold weather. It should be noted, however, that salts appear concentrated to the right side of the graphs for all three treatments. This was the south side of the bed with the greatest sun exposure and, hence, evaporation and movement of salts toward the surface. Saturation extract B concentration ranged from 0.9 to 3.7 ppm in the top 2 inches.

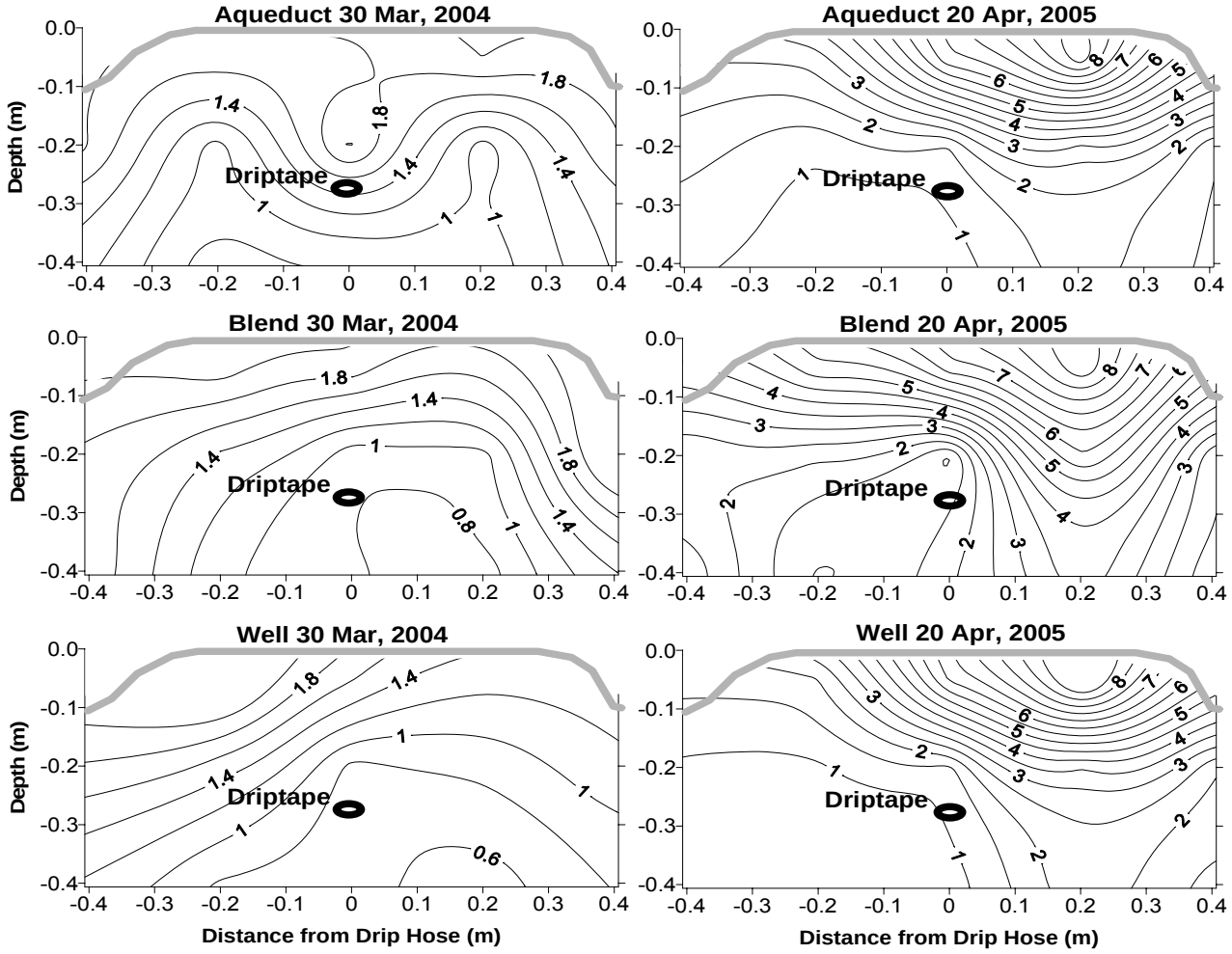


Fig. 3. Contours of seedbed salinity comparing the start of the 2004 and 2005 seasons. Contours generated from composite samples from three different transects across one bed for each treatment.

**PLANT CHARACTERISTICS and YIELD**

Table 3 shows that plant height trended taller for the AQUEDUCT treatment but was not statistically different. Only Cl levels in the petioles sampled 8/27 were significantly elevated in the BLEND and WELL treatments over the AQUEDUCT. There was no difference in Na or B. Nor was there any difference in fiber quality or lint yield among treatments. Average lint yield was 1,718 lb/ac for the total acreage. Calculated on planted acreage only, the average yield was 1,959 lb/ac with the WELL treatment yielding highest @ 4.03 bales/ac.

Table 3. Plant mapping characteristics just prior to defoliation 9/14/04, petiole Cl 8/27/04 and lint quality and yield at harvest 10/6/04.

| | | | | | | Retained Positions | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Treat-ment | Plant Ht. (inch) | Nodes | Veg Nodes | Fruiting Branches | Total Bolls | Top 5 FP1 | Bottom 5 FP1 | FP1 Bolls | Petiole Cl (ppm) | Fiber Width ($10^{-6}$m) | Staple Length (inch) | [1]Lint (lb/ac) |
| Aque | 42.2 | 26.9 | 2.1 | 18.0 | 23.4 | 5.0 | 4.9 | 16.7 | 2.58a | 3.90 | 1.38 | 1670 |
| Blend | 35.9 | 24.3 | 2.8 | 17.3 | 27.1 | 5.0 | 4.9 | 15.8 | 3.23c | 3.88 | 1.37 | 1665 |
| Well | 38.8 | 25.3 | 2.8 | 17.6 | 28.2 | 5.0 | 4.9 | 16.2 | 2.99b | 3.93 | 1.37 | 1740 |

Numbers with different letters are significantly different at the 0.05 level.
[1]Total yield based on 6-38" rows/22 feet. Planted width @ 6-38" rows = 19 feet. Average planted yield = 1959 lb/ac.

Except for the last 3 weeks of the season for the BLEND, biweekly treatment leaf water potentials were greater (less negative) than -18 bars and averaged around -15 bars for most of the season (Figure 4), indicating that the cotton was able to grow without any significant stress. There was no significant difference between treatments.

For the 2005 season to date, there have been no observed toxicity symptoms or differential stress to either cotton or pistachios related to any treatment.

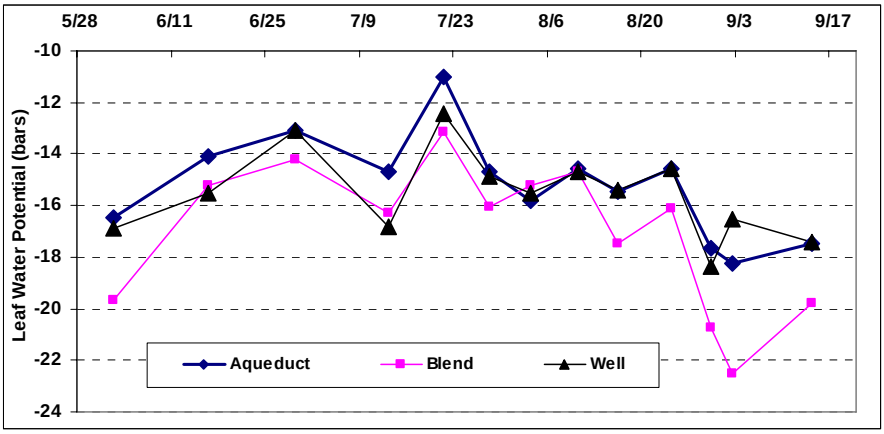


Fig. 4. Biweekly mean leaf water potential for all treatments for the 2004 season.

**ELECTROMAGNETIC CONDUCTANCE ($EC_a$)**

Transects of EM38 readings were taken in an effort to calibrate $EC_a$ estimates to actual soil $EC_e$. For field 9-1 a total of 11,521 horizontal and vertical EM readings were acquired across 89 transects. The field average vertical and horizontal readings were 61.0 and 40.3 mS/m, with standard deviations of 11.6 and 6.2 mS/m, respectively. The minimum to maximum observed readings were 28.9 to 102.9 for the vertical and 20.5 to 61.0 for the horizontal. Both signal data distributions appeared to be approximately symmetric. The horizontal / vertical signal correlation was

0.695. For field 9-3, a total of 13,409 horizontal and vertical EM readings were acquired across 86 transects. The field average vertical and horizontal readings in field 9-3 were 56.8 and 41.8 mS/m, with standard deviations of 8.8 and 5.6 mS/m, respectively. The minimum to maximum observed readings were 36.5 to 89.3 for the vertical and 24.4 to 64.6 for the horizontal. Both signal data distributions appeared to be slightly right-skewed. The horizontal / vertical signal correlation was 0.749. The relatively low EM average levels and lower than normal signal correlation show that both fields are well reclaimed and basically non-saline, and that the spatial EM signal pattern may have been significantly influenced by within-field textural and/or water content variation.

Thirty-six soil samples (identified by GPS coordinates to represent the random variability of salinity in the field as determined by the EM38) were collected in 30 cm increments to a depth of 1.2 meters for both fields in between the two drip hoses. Saturation extract salinity (ECe, dS/m) and Boron (ppm) measurements were performed on each soil sample, with reported accuracies of 0.01 (ECe) and 0.1 (Boron), respectively. Duplicate samples were also acquired at six locations so that the local scale variation in these two soil properties could be quantified. A few sample sites were excluded from the final analysis due to missing data and two outliers with extremely high EC. Values for other missing data observations were estimated using a regression-based expectation algorithm (i.e., missing data for a specific depth were estimated using the measured data in adjacent depths). The depth-specific average ECe ranged from 1.44 to 2.67 dS/m for field 9-1 and from 2.00 to 2.64 dS/m for 9-3. The maximum ECe readings over the four sampling depths for both fields ranged from 3.5 to 7.2 dS/m.

The optimal regression model structures for each field were found by performing a standard jack-knifing analysis (Lesch et al., 2005). The best model was deemed to be the model exhibiting the smallest jack-knifed prediction error. In field 9-1 this regression model included both EM signal readings and a second order trend surface equation. Table 4 shows that the correlation of EM readings with ECe was marginal for the 0 to 2 foot depths (likely due to greater differences in water content and soil structure), but highly significant for the 2 to 4 foot depths and the overall 0 to 4 foot average ECe. Thus, the predicted values of ECe for a given site agreed well with the actual sample means. Figure 5 compares the ECa readings with the regression model bulk ECe for field 9-1. Regression modeling of 9-3 produced statistically significant correlations for the same depths as field 9-1, however, $R^2$ values were 0.32 or less and deemed unsuitable for accurate bulk mapping, but still suitable for describing general field salinity. The corresponding range interval estimates suggest that both fields exhibit both non-saline (ECe < 2 dS/m) and mildly-saline (2 < ECe < 4 dS/m) areas. With respect to the bulk average (0-120 cm) estimates, about 47.8% of the soil in field 9-1 can be classified as non-saline and 50.5% mildly-saline. In field 9-3, 35.7% would be classified as non-saline and 63.4% as mildly-saline.

Table 4. Regression model and summary statistics for estimating ECe with EM38 readings for field 9-1

$$ECe = b_0 + b_1(EMv) + b_2(EMh) + b_3(x) + b_4(y) + b_5(xy) + b_6(x^2) + b_7(y^2)$$

| Depth | R-square | Root MSE | F-value | Prb > F |
|---|---|---|---|---|
| 0-30 | 0.268 | 0.625 | 1.36 | 0.265 |
| 30-60 | 0.339 | 0.530 | 1.9 | 0.109 |
| 60-90 | 0.643 | 0.808 | 6.69 | 0.001 |
| 90-120 | 0.582 | 1.331 | 5.16 | 0.001 |
| **0-120** | **0.630** | **0.553** | **6.31** | **0.001** |

The lack of a strong salinity / conductivity correlation in either field is disappointing, but perhaps not that surprising given the sample duplication variability estimates. In general, the root MSE of the optimal regression model can not be any smaller than the micro-scale salinity (site duplication) variation, which was 0.76 and 0.96 dS/m for fields 9-1 and 9-3, respectively. This level of variability is statistically equivalent to the 0-30, 30-60, and 60-90 cm root MSE estimates in the regression models. From this perspective, one would not expect to find a strong

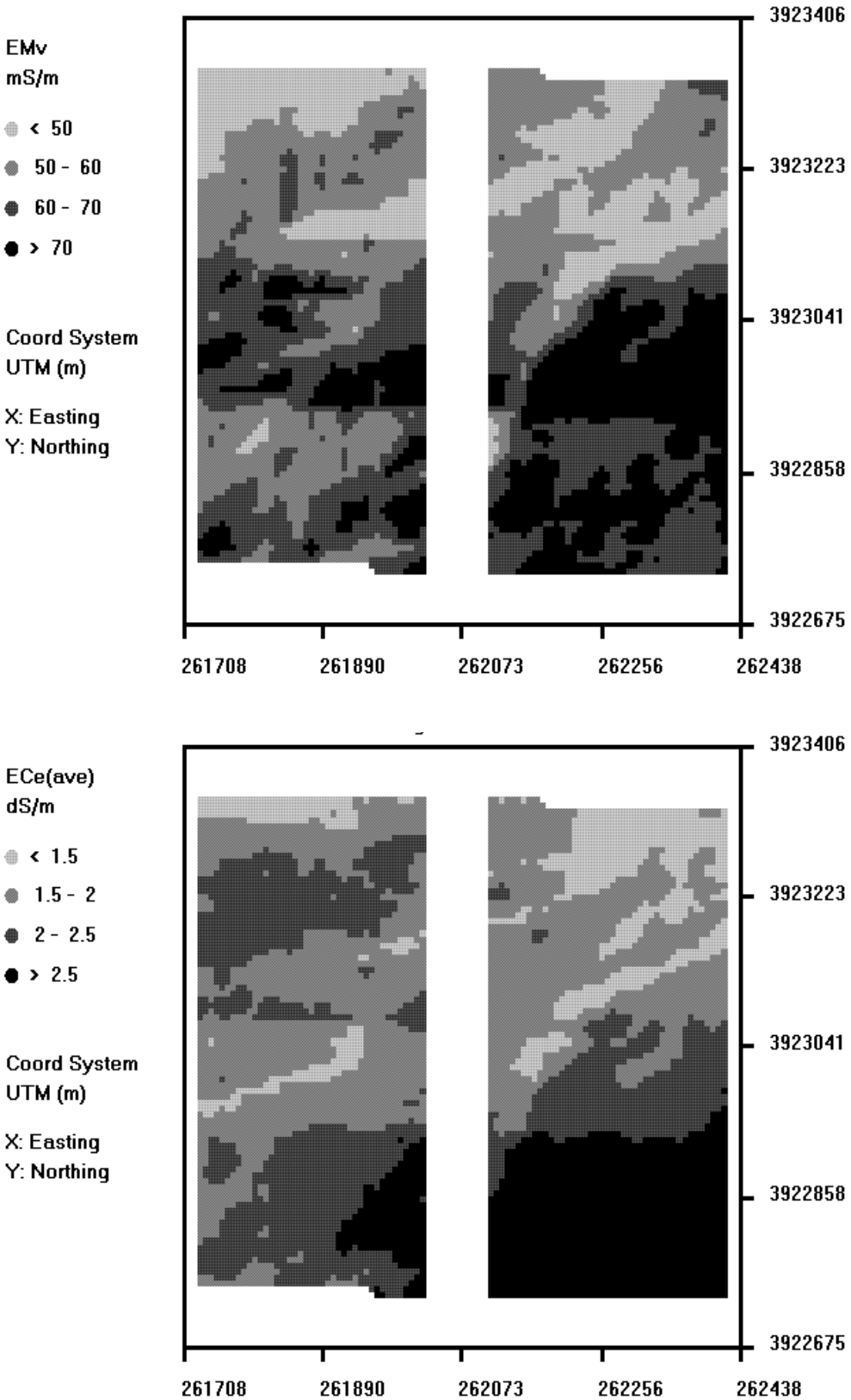


Fig. 5. EM38 readings as ECa (mS/m, above) and calibrated bulk average ECe as estimated by regression model for field 9-1.

correlation. Finally, in both fields the EM survey data may have been strongly influenced by spatial texture and/or water content variations. Incorporation of laboratory SP (saturation percentage) and/or gravimetric water content readings into the regression model could greatly improve the correlation with bulk ECe (Lesch & Corwin, 2003). Some water content data is available but has not yet been incorporated into the model.

### AERIAL IMAGRY/SPECTRAL ANALYSIS

Two-way analysis of variance of the relative intensity of long-wave (thermal) infrared radiation (IR) and the Normalized Difference Vegetation Index (NDVI) on 7/29/04 showed no significant difference between treatments. The relative mean canopy temperature (Figure 6) was 96.6% of the field average for the AQUEDUCT treatment, 97.9% for the BLEND and 105.5% for the WELL. The NDVI (Figure 7), which has a maximum range of -1 to +1, was 0.751 for the AQUEDUCT, 0.734 for the BLEND and 0.716 for the WELL treatment. Correlation analysis of plot values of NDVI with the EMv values generated with the EM38 probe for the same plots yielded a weak $R^2$ of only 0.414 and only 0.352 for correlation of NDVI and lint yield.

## CONCLUSION

Season-long irrigation with saline water @ 4.5 dS/m significantly increased average rootzone salinity by nearly two-fold above that of fresh water to 4.7 dS/m ECe. This level is still well below the threshold tolerance of cotton and, as expected, produced no measurable adverse impacts on the crop. ET in the WELL treatment was reduced by 15.6% by Cl mass balance. Eight to nine inches of fresh water in the spring of 2005, delivered through drip tape buried at a depth of 9 inches, was sufficient to leach salts below the seedbed, recharge depleted soil moisture to 5 feet and establish the second year cotton crop as well as newly planted pistachio rootstocks. No adverse treatment impacts to either the second year cotton crop or pistachios has been seen as of the end of August 2005.

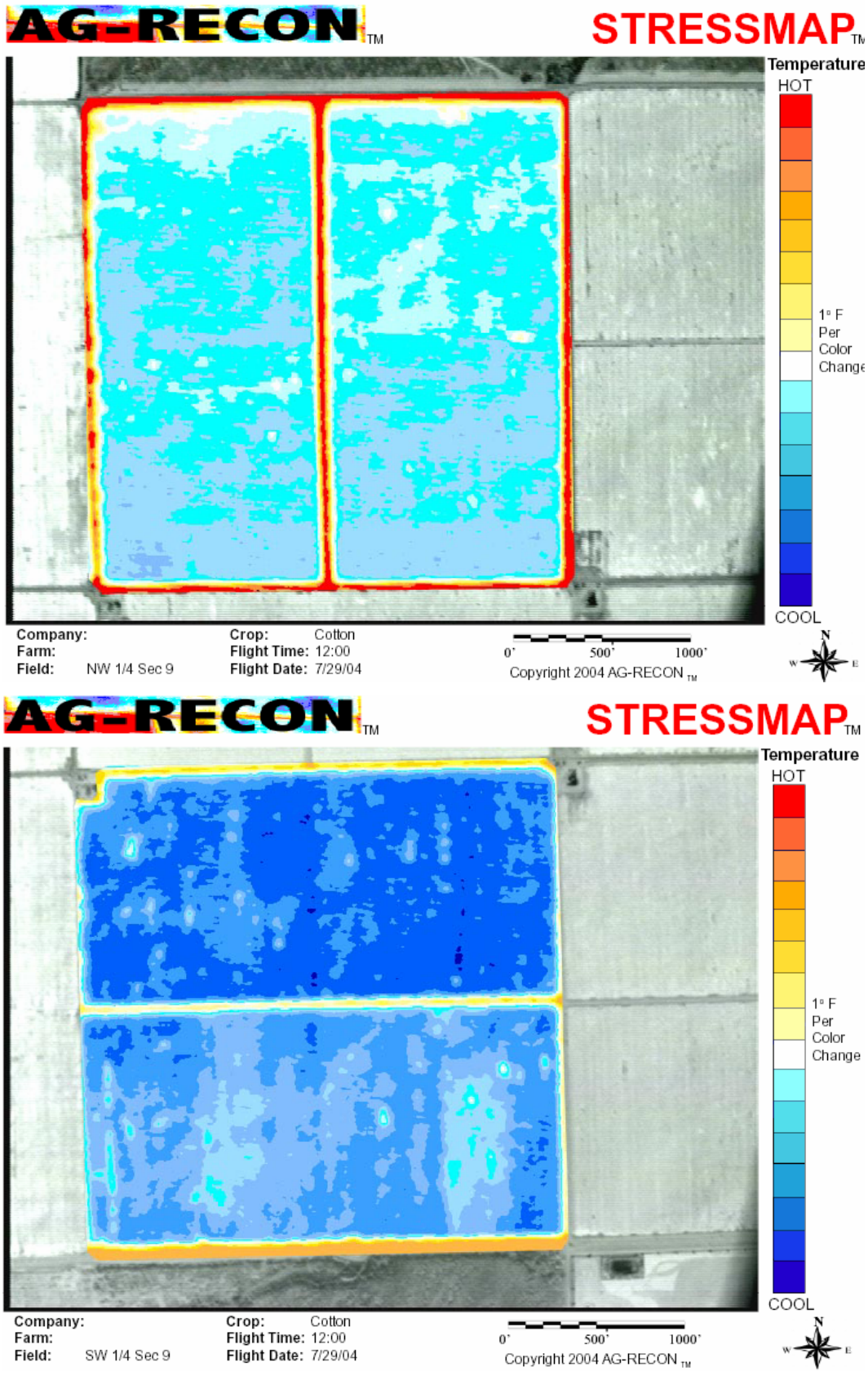


Fig. 6. Color enhanced thermal infrared variation for fields 9-1 and 9-2 on 7/29/04.

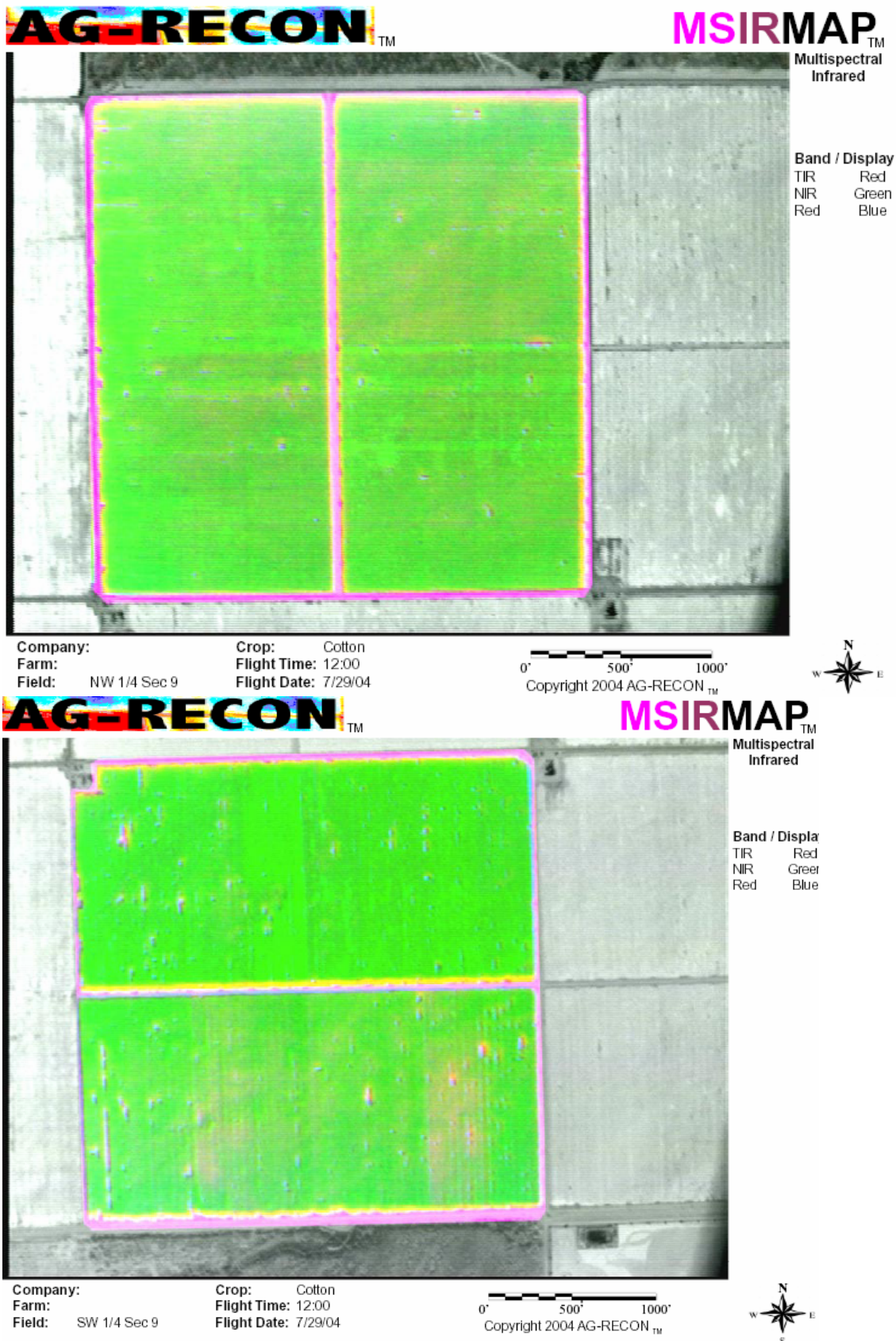


Fig. 7. Color enhanced multispectral NDVI analysis for fields 9-1 and 9-3 on 7/29/04.

## REFERENCES


Ayars, J.E., R.B. Hutmacher, R.A. Schoneman, S.S. Vail, T. Pflaum. 1993. Long term use of saline water for irrigation. Irrigation Science 14(1):27-34.

Ayers, R.S. and D.W. Westcott. 1985. Water quality for agriculture. United Nations FAO Irrig & Drainage Paper No. 29, Rev.1.

CalFed. 2000. *CALFED Water Use Efficiency, DRAFT Details of Quantifiable Objectives.* Calif. Dept. of Water Resources, http://calwater.ca.gov/Archives/WaterUseEfficiency/adobe_pdf/qo_appendixA_19.pdf.

Fardooel, A.R. 2001. Evaluation of salt and drought resistance of two pistachio species (Pistacia chin-up and P. musica) in terms of growth and ecophysiological characteristics. Ph.D. dissertation. University of Ghent, Belgium.

Ferguson, L., B. Sanden, S. Grattan, 2003. Salinity tolerance of pistachio rootstocks. Annual Report, UC Salinity/Drainage Program Water Resources Center and Prosser Trust, 2002-2003, pp. 13-27.

Ferguson, L., P.A. Poss, S.R. Grattan, C.M. Grieve, D. Want, C. Wilson, T.J. Donovan and C. T. Chao. 2002. Pistachio rootstocks influence scion growth and ion relations under salinity and boron stress. J. Amer. Soc. Hort. Sci. 127(2):Pp.194-1999.

Fulton, A.E., J.D. Oster, B.R. Hanson, C.J. Phene, and D.A. Goldhamer. 1991. Reducing drainwater: Furrow vs. subsurface drip irrigation. California Agriculture 45(2):4-7, March/April 1991.

Grattan, S., C. Grieve, J. Poss, D. Suarez. 2003. Does saline drainwater affect crop tolerance to boron. Annual Report, UC Salinity/Drainage Program Water Resources Center and Prosser Trust, 2002-2003, pp. 58-69.

Lesch, S.M. and Corwin, D.L. 2003. Predicting EM / soil property correlation estimates via the Dual Pathway Parallel Conductance model. Agron J. 95:365-379.

Lesch, S.M., Corwin, D.L., and Robinson, D.A. 2005. Apparent soil electrical conductivity mapping as an agricultural management tool in arid zone soils. Com. & Electron. in Ag. 46, 351-378.

Oster, J.D., and J.D. Rhoades. 1990. Steady-state rootzone salt balance . K.K. Tanji (ed), Agricultural Salinity Assessment and Management. ASCE Manuals and Reports on Engineering Practice No. 71. ASCE, New York. pp 469-481.

Pruitt, W.O., Fereres, E., Kaita, K. and Snyder, R.L. 1987. Reference Evapotranspiration (ETo) for California. UC Bulletin 1922.

Sanden, B.L., L. Ferguson, H.C. Reyes, and S.C. Grattan. 2004. Effect of salinity on evapotranspiration and yield of San Joaquin Valley pistachios. Proceedings of the IVth International Symposium on Irrigation of Horticultural Crops, Acta Horticulturae 664:583-589.

Shennan, C., S.R. Grattan, D. M. May, C. J. Hillhouse, D. P. Schactman, M. Wander, B. Roberts, S. Tafoya, R. G. Burau, and L. Zelinski. 1995. Feasibility of cyclic reuse of saline drainage in a tomato-cotton rotation. J. Environ. Qual. 24 (3):476-486.

Wu, L. 2004. Windows-based water suitability determination model (WATSUIT). Univ. CA, Riverside. http://envisci.ucr.edu/index.php?file=faculty/wu/wu.html

# Mechanisms of Arsenic Accumulation and Biogeochemistry in Evaporation Ponds


**Principal Investigators**

Kenneth K. Tanji
Department of Land, Air and Water Resources
University of California, Davis
Phone: (530) 752-6540; Fax: (530) 752-5262,
E-mail: kktanji@ucdavis.edu

Suduan Gao
USDA-ARS, Water Management Research Unit
Parlier, CA 93648
Phone: (559) 596-2870; Fax: (559) 596-2851
E-mail: sgao@fresno.ars.usda.gov

**Collaborator**

Douglas Davis, Manager
Tulare Lake Drainage District
Corcoran, CA 93212

**Research Staff**

Ji-hun Ryu, Postdoctoral Research Associate
Department of Land, Air and Water Resources
University of California, Davis

## ABSTRACT

Selenium (Se) is known to be affected by several sink mechanisms in evaporation basins and does not accumulate in concentration in the water column with evapoconcentration but may accumulate in the underlying thin organic detrital matter and mineral sediments. The selenium ecotoxicity hazards to waterbirds in evaporation basins are minimized by these sink mechanisms and by establishment of compensation and alternative habitats when Se risk is high. In contrast, our preliminary data indicates that arsenic (As) in impounded water column in evaporation basins is subject to accumulation during evapoconcentration and may become a future possible environmental concern but not currently fully understood. The goal of this study is to acquire essential data to more fully understand the biogeochemical processes and conditions affecting arsenic accumulation in evaporation ponds. This research project has three specific objectives: 1. Determine primary productivity and biological factors affecting arsenic transformations in evaporation ponds. 2. Determine the potential for arsenic accumulation in pond waters and sediments as controlled by redox chemistry and precipitation/dissolution processes. 3. Predict the fate of arsenic by examining its speciation and partitioning, and compare with selenium from an ongoing study in the same evaporation basin. The study site is the 726 ha South Evaporation Basin facility in Tulare Lake Drainage District (TLDD) that contains 10 cells and is operated in series when subsurface drainage water production is high. In this first year, we examined water and sediment arsenic concentration and speciation within the cells and water samples following the flow path between cells. Pond water chemistry was also characterized. Results indicate that water arsenic concentration increased linearly with increases in EC and almost linearly with increases in concentrations of Cl. Reduced arsenic species as arsenite [As(III)] and organic arsenic also increased with increases in salinity. Water samples with elevated ECs (e.g., towards the end of flow path in the terminal cells) had high dissolved organic matter, depletion of dissolved oxygen, $NO_3$ and Fe(III), leading to a more reducing environment with elevated sulfide concentrations. These reducing conditions may have lead to reduction of arsenate to arsenite and organic species as the major mechanisms controlling the fate of drainage water arsenic disposed into in the evaporation basin.

## INTRODUCTION

Although the hazards of selenium (Se) ecotoxicity to waterbirds in evaporation basins are a major concern, they are minimized by several sink mechanisms reducing selenium (Se) concentration in the evapoconcentrating water columns and by installation of compensation and alternative habitats when risk is high (Tanji et al., 2003). In contrast, our data indicate that the behavior and fate of arsenic (As) in impounded drainage water is different from Se but are not currently fully understood. Arsenic may be subject to accumulation when EC of waters increases from evaporation as in Owens dry lake (Ryu et al., 2002). We are investigating whether arsenic will accumulate to very high levels in evaporation pond facilities that are heavily relied for disposal of irrigation drainage in the Tulare Basin area of the San Joaquin Valley.

According to the National Recommended Freshwater Water Quality Criteria, the Criteria Maximum Concentration (CMC) for arsenic is 340 µg/L and the Criterion Continuous Concentration (CCC) for arsenic is 150 µg/L (USEPA, 1999). These recommended criteria were derived from data on As(III), but is applied to total arsenic assuming that As(III) and As(V) are equally toxic to aquatic life. Currently, there is no evidence of arsenic toxicity to waterbirds in the San Joaquin Valley. There is a need to investigate the mechanisms or processes governing arsenic biogeochemistry in evaporation ponds because arsenic tends to accumulate to elevated concentrations. Such basic knowledge would be essential to help establish whether or not arsenic is likely to be a future constituent of concern in evaporation basins.

The goal of this proposed study is to acquire essential data to more fully understand the processes and mechanisms of arsenic accumulation and biogeochemistry in evaporation basins. We hypothesize that arsenic accumulation in evaporation pond waters are affected by microbial transformations that affect arsenic speciation and evapoconcentration that affects precipitation and dissolution of arsenic minerals. Three specific objectives to be pursued are:

1. Determine primary productivity and biological factors affecting arsenic transformations in evaporation ponds.
2. Determine the potential for arsenic accumulation in pond waters and sediments as controlled by redox chemistry and precipitation/dissolution processes.
3. Predict the fate of arsenic by examining its speciation and partitioning, and compare with selenium from an ongoing study.

## STUDY METHODS

### STUDY SITE AND SAMPLING

The field study site is TLDD's South Evaporation Basin (Fig. 1), which consists of ten cells operated in series and covers a total surface area of 726 ha. The drainage water flows basically following the order of cell numbers. But when drainage water is limiting (e.g., late summer and winter), flow of drainage water is directed from Cell 1 to Cell 7 through Cell 6, and Cells 3 to 5 are kept dry. To avoid terminal Cell 10 from drying up, fresh drainage water has been

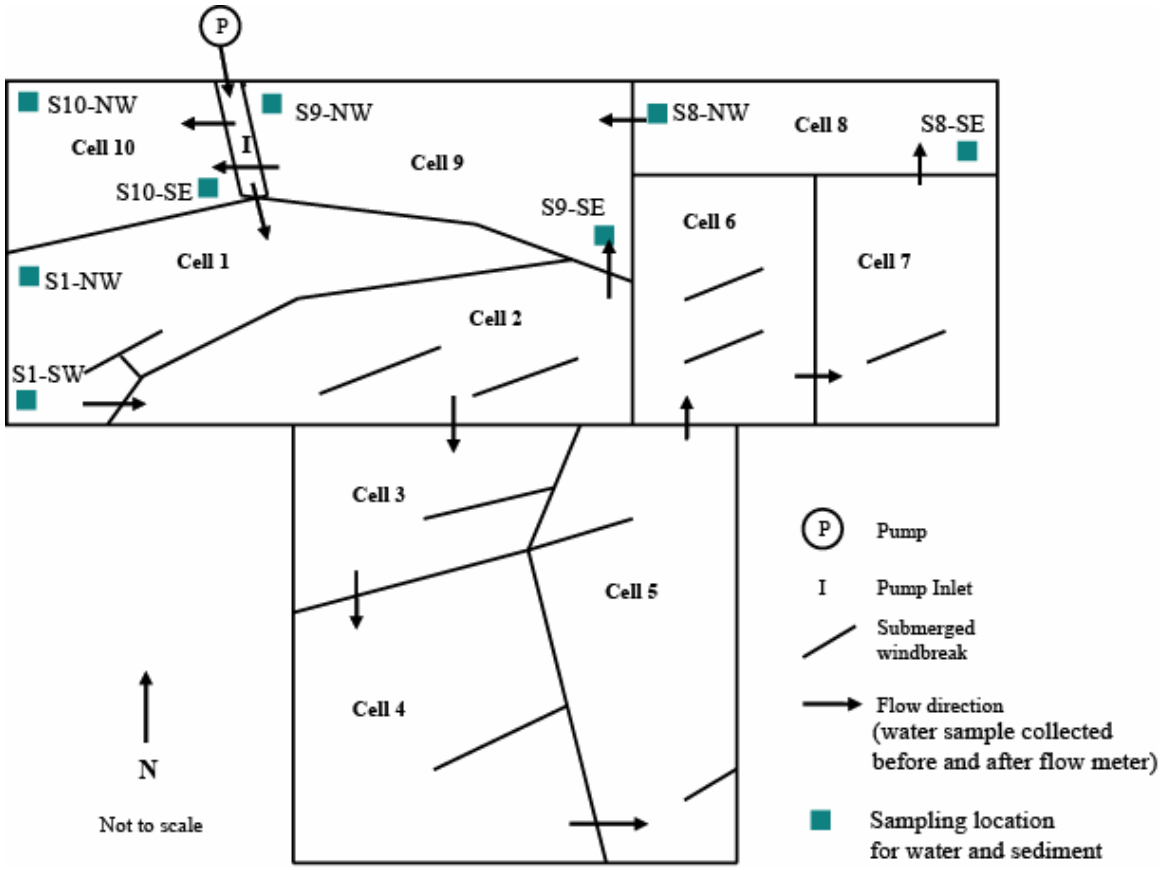


Figure 1. Sampling locations in the 726 ha South Evaporation Basin in Tulare Lake Drainage District (TLDD)

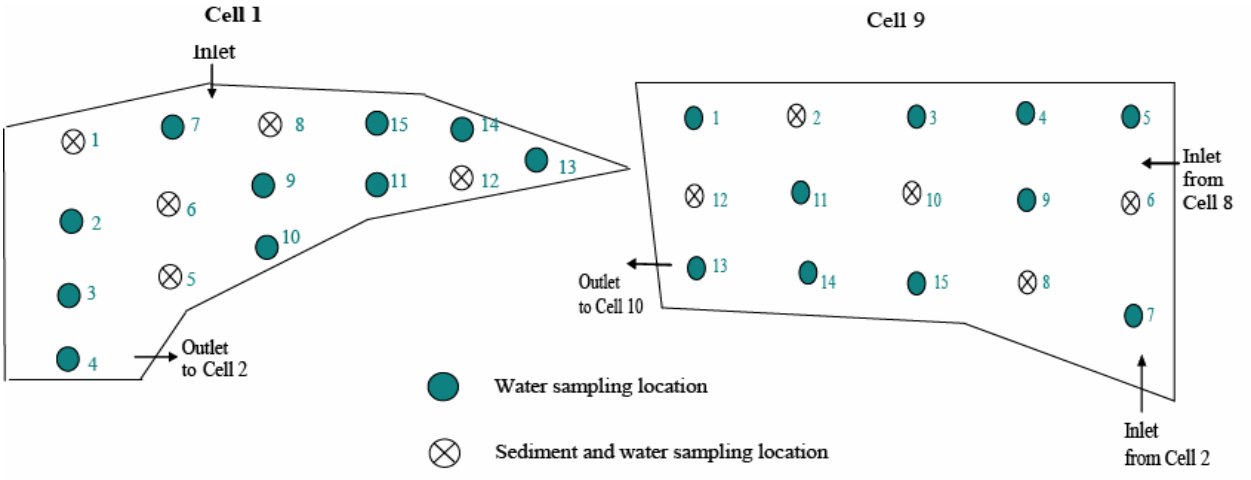


Figure 2. Sampling locations within Cells 1 and 9 for water and sediment samples.

occasionally introduced into Cell 10 to sustain Artemia (brine shrimp) production. Harvesting activity for brine shrimp were more active in Cells 9 and 10, and occasionally in Cell 8 but none in Cell 1 and others.

Before this project was funded, we sampled water along the flow path between cells and within Cells 1, 8, 9 and 10 in 2003, and also obtained intact core sediment samples. Two sampling locations were selected in each cell following prevailing wind directions in this area from northwest (NW) to southeast (SE) or southwest (SW). For each location, sediment cores (~25 cm depth) were also taken. The sampling locations are indicated in Figure 1. This report covers analytical data completed up to date. Since the initiation of this funded project in 2004, comprehensive sampling within Cells 1 and 9 have been carried out three times as well as water sampling along the flow path monthly. Sampling locations for the comprehensive sampling are shown in Figure 2. Water samples were taken from the top (near water surface) and the bottom (near sediment) in the water column. Sediments samples were taken at selective locations as indicated.

Water samples were stored in ice coolers in the field and during transfer to the lab at UC Davis. Field measurements were done on site for water temperature, EC, dissolved oxygen and treatments for chlorophyll-a and sulfide measurements. In the laboratory, water samples were filtered through 0.45 µm and analyzed for pH, major cations, major anions, and total As concentration and As speciation. Arsenic speciation was determined for arsenate [As(V)], arsenite [As(III)], and organic-As as monomethylarsonic acid [MMAA, $CH_3AsO(OH)_2$] and dimethylarsinic acid [DMAA, $(CH3)_2AsOOH$]. MMAA and DMAA are the dominant organic species of arsenic in aquatic systems and others are minor (Andreae, 1977; Cullen and Reimer, 1989). The samples were stored in a refrigerator (3 $^oC$) until completion of analyses. For arsenic speciation that was done at later times, a portion of the samples was frozen until ready for analysis.

Sediment cores were taken using 5-cm diameter acrylic tubes. The cores were sealed immediately in the field with a plastic cap, duct-taped, and stored on ice. After transferring to the lab, the core samples were frozen until ready for processing and analysis. Organic detrital materials (DM) were separated from the mineral sediment cores by scrapping off the top materials containing visible brownish DM. The mineral cores were then sectioned into 0-5, 5-10, 10-15, 15-20, and below 20 cm segments. The samples were freeze-dried, ground, sieved and mixed thoroughly before digestion for total As analysis.

## CHEMICAL ANALYSIS

### *Water characterization and redox chemistry*

After measuring pH and EC, water samples were passed through a 0.45 μm pore-size membrane filter. The filtrate were analyzed for major cations (Na, Mg, K, Ca) and anions (Cl, $SO_4$, Br, $NO_3$, $PO_4$) by atomic absorption spectrophotometry (AAS) and ion chromatography (IC), respectively. Alkalinity was determined by titration to an end-point of pH 4.5 using an autotitrator and corrected for ions that consume protons. Boron was analyzed using azomethine-H method (John et al., 1975; Bingham, 1982). Dissolved organic carbon was determined on the filtrate (0.45 μm) using a Shimadzu carbon/nitrogen analyzer. Chlorophyll-a samples were collected by filtering an aliquot of sample through a pre-ashed Gelman A/E glass fiber filter (0.45 μm). The filters were placed in a vial, immediately frozen, and stored in darkness until analyzed. Chlorophyll-a was extracted in 90% reagent-grade ethanol and determined by a fluorometric method (APHA, Standard Methods, 1992). As an indication of redox conditions in pond waters, dissolved oxygen (DO) was measured when sampling in field using a YSI model 54A oxygen meter with DO probe. Fe(II) and total Fe were determined by the ferrozine method. Sulfide concentration was determined by ion selective electrode (model 9416; Orion Research Inc., Beverly, MA).

### *Total As and As speciation for As(V), As(III), MMAA, and DMAA*

Total As concentration in water samples was determined using Cutter's procedure (Cutter, 1982) modified by Yoshimoto (1992). This method uses a combination of heat, acid (HCl and $HNO_3$), and oxidizer (persulfate) to oxidize all As species to As(V), which was then reduced to As(III) by KI following the procedures in Glaubig and Goldberg (1988). Arsenic was quantified by hydride generation atomic absorption spectrophotometry (HGAAS) technique. Total As for sediment samples were determined using acid digestion (Zasoski and Burau, 1977) and quantified by HGAAS.

Prior to setting up the apparatus for organic As speciation, As(III) species and total As in water samples were determined previously using the method by Glaubig and Goldberg (1988). In this case, the difference between the total and As(III) was the sum of As(V) plus org-As. Arsenic speciation in selected water samples was further performed using a modified hydride generation with cold trapping and atomic absorption spectrophotometry (HGCT-AAS) technique from Andreae (1977), Crecelius et al. (1986) and Masscheleyn et al. (1991). This method is time-consuming but can accurately identify all arsenic species. The detailed procedure is described in Gao and Burau (1997). The followings are a brief description of the method. When As(V), As(III), MMAA and DMAA in solution react with nascent hydrogen from the decomposition of $NaBH_4$, volatile arsine ($AsH_3$), monomethyl arsine (MMA, $AsH_2CH_3$), and dimethyl arsine (DMA, $AsH(CH_3)_2$) are produced respectively from corresponding arsenic compounds [As(V and III), MMAA, and DMAA]. These volatile compounds are trapped in a column immersed in liquid nitrogen. When the liquid nitrogen is removed and as the column is warmed up by heating, these arsines are released serially as their boiling points (-55, 2, and 35$^{o}$c for arsine, MMA, and DMA, respectively) are reached. The released arsines are then introduced into a heated quartz cell by an inert carrier gas. The absorbance by arsenic atoms measured by AAS is used for quantification of arsenic species. Because As(V) and As(III) form the same volatile compound ($AsH_3$), As(III) was analyzed by forming arsine at pH 6 when other forms of arsenic could not react in formation of arsines. As(V) was obtained from the difference between total inorganic As (V + III) and As(III).

Table 1. Important parameters and constituents in pond waters of South Evaporation basin, TLDD.

| | EC | pH | $HCO_3^-$ | Cl | $SO_4$ | $NO_3$-N | $NH_4$-N | $PO_4$ | Na | Ca | Mg | K | B | Br- |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | dS/m | | meq/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L | mM/L |
| | | | | | | | Average | | | | | | | |
| S1-NW | 18.8 | 8.9 | 7.9 | 94.8 | 71.5 | 0.04 | 0.02 | 0.00 | 210.7 | 1.5 | 14.6 | 0.7 | 1.1 | 3.3 |
| S1-SW | 19.1 | 8.9 | 8.1 | 92.0 | 72.1 | 0.01 | 0.06 | 0.00 | 217.5 | 1.4 | 14.5 | 0.6 | 1.2 | 2.2 |
| S8-NW | 113.3 | 8.8 | 56.3 | 1060.2 | 552.2 | 0.02 | 0.01 | 0.02 | 1951.1 | 2.1 | 130.9 | 7.9 | 11.6 | 9.0 |
| S8-SE | 115.8 | 8.7 | 57.4 | 1054.9 | 349.0 | 0.00 | 0.02 | 0.02 | 1514.0 | 2.0 | 127.5 | 6.7 | 11.4 | 9.1 |
| S9-NW | 113.7 | 8.2 | 84.0 | 2343.2 | 621.5 | 0.02 | 0.02 | 0.02 | 3141.5 | 4.5 | 330.0 | 24.4 | 26.7 | 0.1 |
| S9-SE | 116.4 | 8.6 | 83.0 | 2371.3 | 535.3 | 0.03 | 0.02 | 0.02 | 2950.2 | 4.6 | 314.5 | 23.9 | 27.5 | 0.0 |
| Cell10 NW | 81.5 | 8.8 | N/A | 474.6 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| Cell10 SE | 81.4 | 8.8 | N/A | 483.8 | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A | N/A |
| | | | | | | | Standard | deviation | | | | | | |
| S1-NW | 0.1 | 0.1 | 0.6 | 2.5 | 0.8 | 0.03 | 0.03 | 0.00 | 14.2 | 0.0 | 1.0 | 0.1 | 0.3 | 0.6 |
| S1-SW | 0.2 | 0.0 | 0.3 | 4.4 | 3.3 | 0.01 | 0.01 | 0.00 | 1.9 | 0.1 | 2.1 | 0.1 | 0.2 | 0.0 |
| S8-NW | 0.3 | 0.0 | 2.2 | 41.2 | 86.4 | 0.02 | 0.01 | 0.00 | 64.0 | 0.1 | 6.6 | 0.5 | 0.7 | 3.7 |
| S8-SE | 1.8 | 0.0 | 2.7 | 28.1 | 47.1 | 0.00 | 0.02 | 0.00 | 82.9 | 0.2 | 11.2 | 1.4 | 0.3 | 4.1 |
| S9-NW | 1.5 | 0.0 | 4.0 | 74.3 | 78.8 | 0.00 | 0.00 | 0.00 | 190.9 | 0.2 | 5.3 | 1.8 | 0.3 | 0.1 |
| S9-SE | 4.6 | 0.0 | 4.4 | 130.2 | 57.1 | 0.00 | 0.00 | 0.00 | 291.9 | 0.1 | 23.0 | 1.2 | 2.1 | 0.0 |

## RESULTS AND DISCUSSION

### GENERAL WATER CHEMISTRY

General pond water chemical characteristics and constituents in pond waters are shown in Table 1. EC of water samples ranged from 19 to 116 dS/m. pH was in the range of 8.2 to 8.9, reflecting carbonate dominated buffer system. Major anions were Cl and $SO_4$. Nutrients level (N and P) were very low. The dominant cations were Na followed by Mg. Ca concentrations were much lower than Mg, especially when EC was high. The increase of EC in pond water was mainly due to evapoconcentration. Chloride is considered the most conservative element in water. A relationship between EC and Cl was obtained for pond waters in this basin was: Cl (mmol/L) = 9.06 * EC (dS/m) - 95.8. When EC exceeds 120 dS/m, this linear relationship does not hold anymore due to precipitation of minerals and relatively high proportional increase of Cl in solution. The ratio of $[Cl]_{pond\ water}$ / $[Cl]_{inlet}$ is defined as Evapoconcentration Factor or ECF (Tanji, 1990). The values of ECF obtained for Cells 1, 8, and 9 were 2, 22, and 48, with standard deviations of 0.1, 0.6 and 2.0, respectively. This indicates that as water flows from Cell 1 to the terminal cells, such as Cells 9 and 10, water can be significantly concentrated. As the waters evapoconcentrate, the solubility product constants (Ksp) of minerals can be exceeded and certain minerals (calcite, gypsum, etc.) precipitate out from the water column and along the shoreline. Chloride minerals such as halite (NaCl) have very high Ksp and will precipitate only in hypersaline waters. Thus, evapoconcentration based solely on increases in EC may not be an appropriate evapoconcentration index.

The correlations between Cl and other constituents are plotted in Figure 3. As Cl concentration increased, Na and B as well as Mg increased linearly indicating no significant precipitates associated with these ions. Sulfate increased linearly only up to a certain level (~500 mM/L). There were no apparent correlations of alkalinity and Ca concentration increase as Cl concentration increased. This is most likely due to the formation of calcite ($CaCO_3$), which has the lowest solubility and thus readily precipitates out from evapoconcentrating waters. Using a brine chemistry model for hypersaline waters, Smith (1989) predicted that Mg and $SO_4$ as well as Na can accumulate to relatively high levels in brines before their precipitates form. The typical sequence of minerals to precipitate out in San Joaquin Valley evaporation basins as evapoconcentration continues (Smith et al., 1995) is $CaCO_3$, $CaSO_4.2H_2O$, $Na_2Ca(SO_4)_2$,

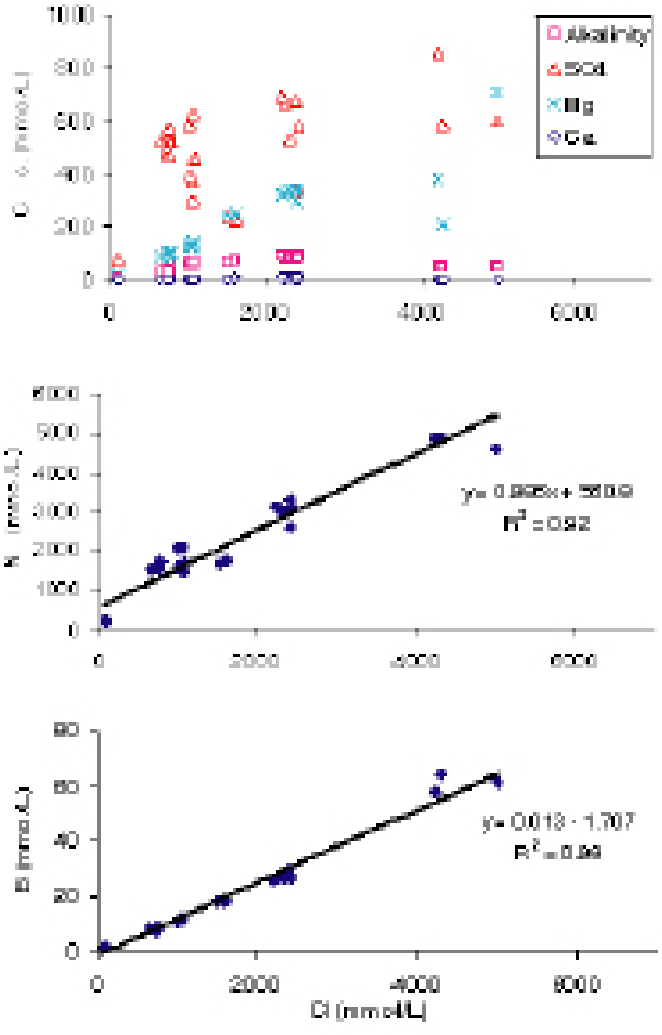


Figure 3. Correlation between chemical constituents with conservative Cl concentration.

$Na_2SO_4$, $Na_2Mg(SO_4)_2.4H_2O$ and NaCl. Generally speaking, hypersaline waters would have solute abundances in a typical order of Na > Mg > Ca and Cl > $SO_4$ > $HCO_3$, which we have observed for the pond waters.

To examine increases in arsenic concentration from evapoconcentration, changes in arsenic concentration in pond waters as a function of EC and Cl are plotted in Figure 4. Arsenic increased dramatically in a linear relationship with increases in EC and up to a certain level of Cl concentration (~500 mmol/L). When Cl concentration continues to rise, the increase in As concentration reduced indicating some removal of As from the water column. This indicates that arsenic behaves initially as a conservative element in pond waters but not at elevated salinities. Precipitation from evapoconcentration or other mechanisms in removal of As during evapoconcentration from pond waters appears to be occurring in this pond facility. This phenomenon begs further in-depth examination because it is important in understanding how high As concentration may accumulate in the pond water columns. A similar phenomenon was observed in brine shallow groundwaters in Owens dry lake (Ryu et al., 2002) where dissolved arsenic concentrations ranged from 0.1 to 96 mg/L and showed a general increase from the shoreline to the center of the lakebed as evapoconcentration factor increased. Arsenic concentrations were found to be strongly correlated to EC and δD suggesting that evapoconcentration was an important process regulating total As concentrations to very high levels. The pond water conditions in TLDD Southern Evaporation Basin may be different from Owens dry lake groundwater but a similar trend was observed.

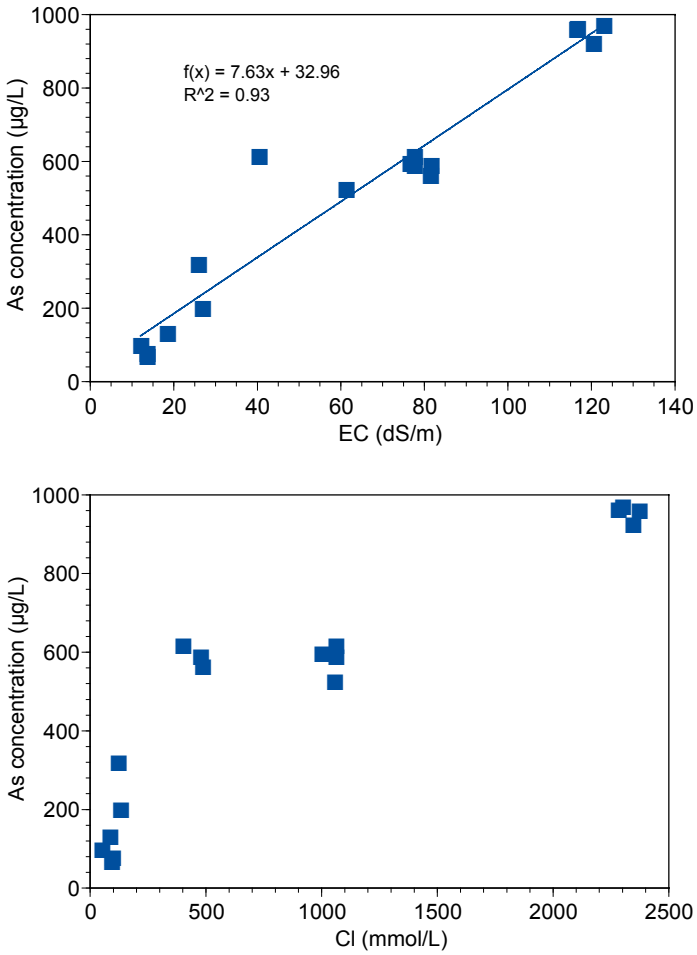


Figure 4. Relationship between EC or Cl and total concentrations of arsenic in the evaporation pond waters.

**ARSENIC SPECIATION**

Reduced As (III) species and total As were initially determined for samples taken in Year 2003 using the method by Glaubig and Goldberg (1988) (Figure 5). Total As concentrations dramatically increased along the flow path (ascending cell number). As(V) was dominant in drainage water and As(III) was less than 1% of the total As in the inlet drainage water. Along the flow path between cells, As(III) was a minor species until the water reached Cell 8.

Within the cells, Cells 8 and 9 contained similar As(III) concentrations. Cell 10 contained a much lower As(III) concentration or percentage as compared to Cells 8 and 9 and this is probably due to the dilution factor from introduction of fresh drainage water. The difference between As(III) and the total is the sum of oxidized As(V) and org-As. As the concentration of reduced As(III) increases, it is expected that oxidized As(V) would decrease.

Additional arsenic speciation, including both inorganic [As(V), As(III)] and organic [MMAA, DMAA], were performed for pond water samples taken in the Year 2004. The speciation results are shown in Table 2. Reported are water samples collected from top (near surface) and bottom (near sediment) of the water column as well as along the flow path: from main inlet channel to terminal ends of Cells 1, 8, 9 and 10. The main inlet channel (fresh drainage water from agricultural fields) was dominated by the oxidized form of As(V) (95%) with 5% As(III) and non-detectable organic As. Cell 1 showed almost similar percentage of As speciation with non-detectable org-As. Cell 8 showed lower (87%) As(V) and higher As(III) (11%) and org-As (MMAA+DMAA, 2%) compared to the inlet channel and Cell 1. The percentage of As(V) continuously decreased in Cell 9 to 75-84% corresponding to increases in As(III), 8-16%. Organic –As increased to 3-11% in Cell 9 for all the samples monitored. Cell 10 showed much lower total As concentration due to the dilution factor from addition of fresh drainage from the inlet channel but the highest reduced As (III) (34%) and org-As (14%) was observed.

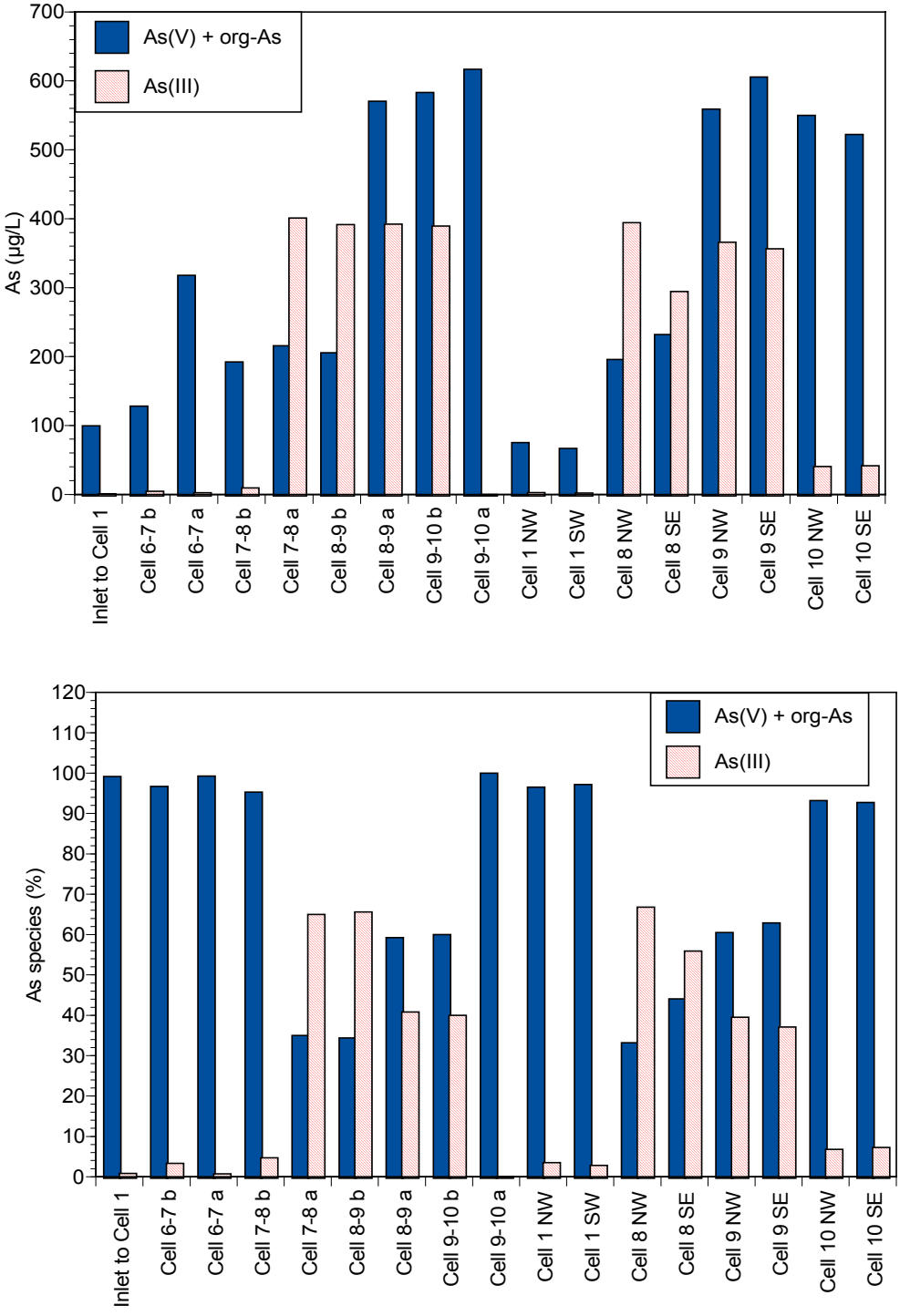


Figure 5. Total arsenic and As(III) speciation data. The symbols “b” and “a” indicate water samples taken before and after flowing to next cell, respectively. The left columns are samples taken along water flow path. The right columns are samples taken within cells.

Table 2. Arsenic speciation for inlet and pond water samples collected from March through November, 2004 (n=4).

| Time | Description | Total As (µg/L) | % As(III) | %MMAA | %CA | %As(V) |
|---|---|---|---|---|---|---|
| | | | | Averages (Stdev) | | |
| Mar., 2004 | Cell 1-top | 116.0 (7.6) | 5.5 (0.6) | 0.0 (0.0) | 0.0 (0.0) | 94.5(0.6) |
| | Cell 1-bottom | 125.5 (6.9) | 5.1 (0.3) | 0.0 (0.0) | 0.0 (0.0) | 94.9 (0.3) |
| | Cell 9-top | 526.0 (48.2) | 16.5 (1.9) | 0.7 (0.2) | 2.3 (0.6) | 80.5 (2.5) |
| | Cell 9-bottom | 1444.7 (489.9) | 15.7 (1.8) | 1.9 (1.1) | 7.3 (5.8) | 75.1 (8.6) |
| Nov., 2004 | Cell 1-top | 142.3 (7.2) | 4.6 (0.4) | 0.0 (0.0) | 0.0 (0.0) | 95.4 (0.4) |
| | Cell 1-bottom | 141.5 (9.2) | 5.1 (0.8) | 0.0 (0.0) | 0.0 (0.0) | 94.9 (0.8) |
| | Cell 9-top | 737.9 (78.7) | 8.3 (1.0) | 3.8 (3.0) | 7.9 (2.0) | 80.0 (4.2) |
| | Cell 9-bottom | 768.4 (101.2) | 8.3 (1.9) | 2.1 (0.3) | 4.9 (0.7) | 84.7 (1.8) |
| Mar. & Nov., 2004 | Central Inlet | 119.0 (10.3) | 4.9 (2.7) | 0.0 (0.0) | 0.0 (0.0) | 95.1 (2.7) |
| | End of Cell 1 | 124.1 (13.3) | 7.0 (2.8) | 0.0 (0.0) | 0.0 (0.0) | 93.0 (2.8) |
| | End of Cell 8 | 1219.6 (747.8) | 11.4 (7.1) | 0.6 (0.4) | 1.2 (0.6) | 86.8 (7.8) |
| | End of Cell 9 | 681.9 (252.0) | 16.3 (7.3) | 2.0 (0.8) | 4.1 (1.0) | 77.6 (6.9) |
| | End of Cell 10 | 535.2 (400.7) | 33.9 (25.3) | 6.1 (4.3) | 8.3 (3.5) | 51.6 (31.6) |

Distribution of As(V) and As(III) was primarily regulated by reducing condition, because the pH is relatively constant for all sample sites. The proportion of As(III) increased through water paths as reducing processes occurred. Increases in organic arsenic indicate microbially-mediated activity that results in methylation. Organic arsenic is often in trace amount unless microbial activity is very high such as in a wetland environment (Andreae, 1977; Cullen and Reimer, 1989). An earlier report indicated even higher organic As species (31-50% DMAA and 11-17% MMAA of total soluble arsenic) in an agricultural evaporation pond (Tanji and Dahlgren, 1993). Methylation process also can lead to volatilization by forming volatile organic As compounds as monomethyl arsine (MMAA), dimethyl arsine (DMAA) and trimethyl arsine (TMAA). We have not been able to measure this transformation that causes loss of As from the water. Apparently, arsenic volatilization is not significant enough to suppress As concentration in water columns. Further, it should be noted that although arsenic reduction occurred in pond waters, oxidized As(V) was still predominant in all pond waters (>50%). It is believed that this partial reduction controlled by pond conditions is critical in understanding the fate of As entering the pond facility.

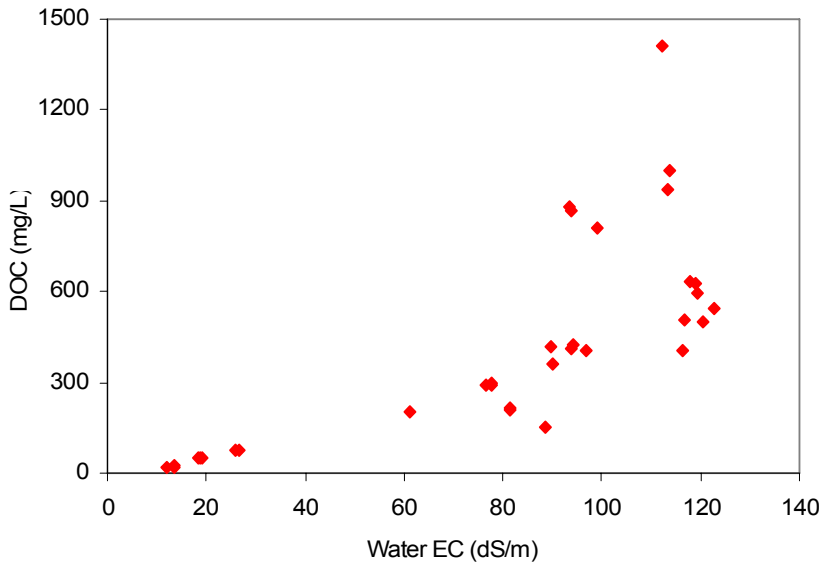


Figure 6. Relationship between total dissolved organic carbon (DOC) and water EC.

Some of parameters that represent microbial activity and redox conditions of the water were measured (Figure 6 and Table 3). Organic

matter is the primary energy source driving microbial activity and occurs as both solid and dissolved organic matter. Figure 6 shows total dissolved organic carbon (DOC) in the pond waters. The concentrations of DOC were surprisingly high with increase in EC values. There may be two reasons that cause increases in DOC with increases in EC: First, transport of DOC with soluble salts and concentration as the evapoconcentration process takes place, i.e., recalcitrant organic carbon fraction leads to accumulation of organic carbon in waters with lower consumption of DOC by microbes. Second, addition of chicken manure to enhance production of brine-shrimp in Cells 9 and 10 can be a source of organic carbon in the water. Both factors may be involved since neither one singly could fully explain the increases in DOC.

While EC and solute concentrations showed a strong evapoconcentration pattern from the inlet to the terminal end of the pond facility, reducing conditions also developed due to growth, death and decay of phytoplankton and increased hydrologic residence time (Table 3). In the decomposition of phytoplankton and other organic debris bacteria successively consume $O_2$, $NO_3^-$, Fe(III) and $SO_4^{2-}$ as electron acceptors. The depletion of dissolved oxygen (DO) concentrations occurred as drainage water reached the terminal end of the pond facility. The lowest average dissolved DO (2.1 mg/L) was found at the bottom layer of Cell 9. These values indicate that anaerobic respiration occurred at the bottom layer of Cell 9. The depletion of nitrate concentrations was also observed in water flows from Cells 1 to 9. In addition, dissolved Fe(III) decreased in water flows from Cells 1 to 9. The depletion of electron acceptors such as $O_2$, $NO_3$, and Fe(III) allow for the development of sulfate reduction resulting in elevated sulfide concentrations in the bottom layer of Cell 9 (up to 69 mg/L). The sulfide concentrations were much higher than other previous cells within the water flow paths where the sulfide concentrations were often under detection limit. Although reducing condition showed a general trend in the drainage flow path, we found significant spatial variance in reducing condition at different locations within the cells. The results indicated that reducing processes may have occurred in rather isolated spots in a cell.

Table 3. Redox species measurements in pond waters (n=15).

| Time | Description | DO (mg/L) | $NO_3$-N (mg/L) | Fe (total) (mg/L) | Fe(II) (mg/L) | $SO_4$ (mg/L) | Sulfide (mg/L) |
|---|---|---|---|---|---|---|---|
| Mar-04 | Cell 1-top | 14.6 (0.9) | 7.0 (1.2) | 0.46 (0.55) | 0.06 (0.08) | 4545 (224) | <0.01 |
| | Cell 1-bottom | 11.8 (0.8) | 7.5 (1.2) | 0.45 (0.46) | 0.13 (0.13) | 4619 (132) | <0.01 |
| | Cell 9-top | 4.4 (1.0) | 2.4 (0.3) | 0.46 (0.60) | 0.22 (0.30) | 28003 (5001) | 0.10 (0.17) |
| | Cell 9-bottom | 2.1 (1.4) | 3.2 (0.7) | 0.40 (0.56) | 0.29 (0.51) | 32699 (7927) | 18.37 (37.57) |

**ARSENIC IN SEDIMENTS**

Total As concentrations in the sediment profiles varied greatly with depth, as well as spatially among locations in a cell (Figure 7). Arsenic concentration was the lowest in Cell 1 near the inlet location and reached a high value of about 80 mg/kg in the surface sediment of Cell 9. The distribution of arsenic with depth is somewhat uneven. The SW location of Cell 1 (S1-SW), a stagnant area, accumulated very high arsenic concentrations. This indicates that As tends to accumulate in the sediments. However, this trend is not reflected in all cells and may due to bank erosion from wind-driven wave action that causes deposition of soils (bank materials) on near shore areas where sediment core samples were taken. Arsenic concentration profiles in the sediments at S8-NW, S10-NW and S10-SE appear to show buried surface sediments. It is certain, however, that the sediment serves as a sink for arsenic in the pond facility.

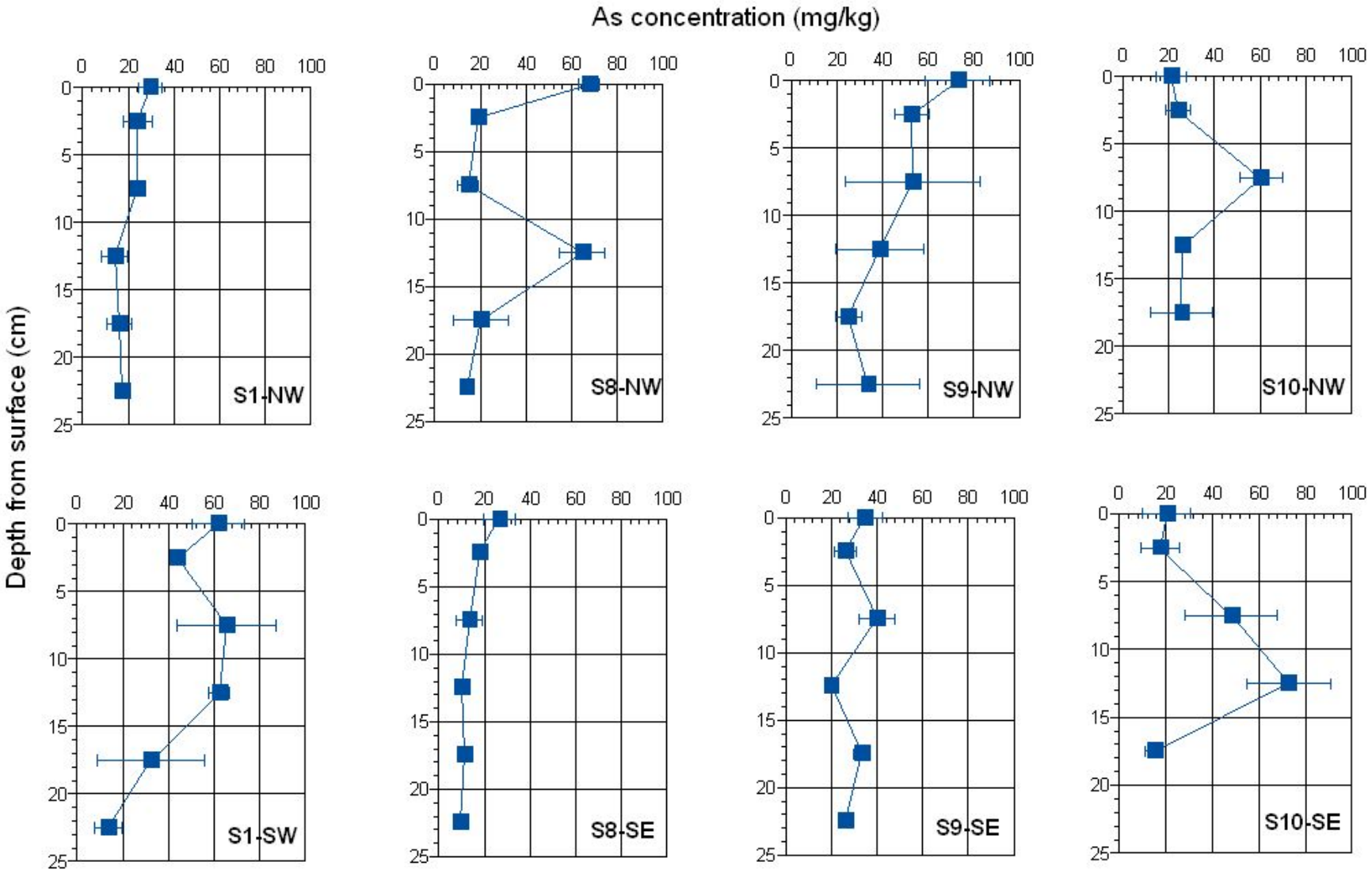


Figure 7. Arsenic concentration profile in pond sediments sampled in 2003.

## SUMMARY AND CONCLUSIONS

This study demonstrates that arsenic distribution and speciation in the evaporation ponds were strongly affected by evaporation and redox chemistry. Arsenic concentration increases linearly with increasing evapoconcentration factor or EC due to evapoconcentration in the studied pond facility operated in-series. The reducing condition due to the decay of organic debris affected arsenic speciation. Although arsenic toxicity to wildlife has not been reported, high accumulation of arsenic in some ponds may become a potential environmental concern of the future.

## REFERENCES


American Public Health Association. 1992. Standard Methods for Examination of Water and Wastewater. 18th edition. APHA. Washington, DC.

Andreae, M.O. 1977. Determination of arsenic species in sea water. Anal. Chem. 49:820-823.

Bingham, F.T. 1982. Boron. Azomethaine–H method. p. 535-436 *In* Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties. Agronomy Monograph no. 9 (2nd editions). American Society of Agronomy, Madison, WI.

Crecelius E. A., N.S. Bloom, C.E. Cowan. and E.A. Jenne. 1986. Speciation of selenium and arsenic in natural waters and sediments. Vol. 2. Arsenic speciation. EPRI EA-4641. Final Report. Research Project 2020-2. Electric Power Res. Inst., Palo Alto, CA.

Cullen W. R. and Reimer K. J. 1989. Arsenic speciation in the environment. Chem. Rev. 89, 713-764.

Cutter, G.A., 1982. Selenium in reducing waters Science 217: 829-831.

Gao, S. and R.G. Burau. 1997. Environmental factors affecting rates of arsine evolution from and mineralization of arsenicals in soil. J. Environ. Qual. 26:753-763.

Glaubig, R.A., and S. Goldberg. 1988. Determination of inorganic arsenic (III) and arsenic (III plus V) using automated hydride-generation atomic absorption spectrometry. Soil Sci. Soc. Am. J. 52:536-537.

John, M.K., H.H, Chuah, and J.H. Neufeld. 1975. Application of improved azomethine-H method to the determination of boron in soils and plants. Anal. Lett. 8:559-568.

Masscheleyn P. H., Delaune R. D. and Patrick Jr. W. H. 1991. A hydride generation atomic absorption technique for arsenic speciation. J. Environ. Qual. 20, 96-100.

Ryu, J., S. Gao, R. A. Dahlgren and R. Z. Zierenberg. 2002. Arsenic distribution, speciation and solubility in the shallow ground water of Owens Dry Lake, California. Geochim. Cosmochim. Acta. 66:2981-2994.

Smith, G.R. 1989. Brine Chemistry Model for Agricultural Evaporation Ponds and Other Hypersaline Waters. Ph.D. Dissertation. Shields Library, University of California, Davis, CA.

Smith, G.R., K.K. Tanji, R.G. Burau, and J.J. Jurinak. 1995. C Salt-A chemical equilibrium model for multicomponent solutions. Chapter 15, p. 289-324, *In* R.H. Loeppert, A.P. Schwab and S. Goldberg (Editorial Committee) Chemical Equlibrium and Reaction Models. SSSA Special Publication No. 42, Soil Science Society of America, Madison, WI.

Tanji, K.K. 1990. Accumulation of salts and trace elements in agricultural evaporation ponds. Transaction, 14th International Congress of Soil Science Vol, VII: 180-185.

Tanji, K.K. and R.A. Dahlgren. 1993. Acidification of Evaporation Ponds to Reduce Contamination Hazards to Wildlife – Phase I (Chemical Aspects). Project Report to Division of Wildlife Resources Agreement # B58194. 170 pp.

Tanji, K.K., D. Davis, C. Hanson, A. Toto, R. Higashi, and C. Amrhein. 2003. Evaporation ponds as a drainwater disposal management plan. Irrig. Drain. Syst. 16(6):279-296.

U.S. Environmental Protection Agency. 1999. National Recommendation Water Quality Criteria – Correction. EPA 822-Z-99-001. National Center for Environmental Publications and Information, Ohio. http://epa.gov/waterscience/pc/1999table.pdf

Yoshimoto, J.T. 1992. Potential mechanisms controlling soluble selenite in Sierran Sands. Master of Science Thesis, University of California, Davis.

Zasoski, R.J. and R.G. Burau. 1977. A rapid nitric-perchloric acid digestion procedure for multi-element tissue analysis. Commun. Soil Sci. Plant Anal. 8:425-436.

## ACKNOWLEDGEMENTS

Mike Almeda (Novalek, Inc.) assisted in sampling water and sediment within the cells of the evaporation basin, piloting the boats. Larry Davis (TLDD) also assisted us with field sampling as well as measurements on monthly water flows.