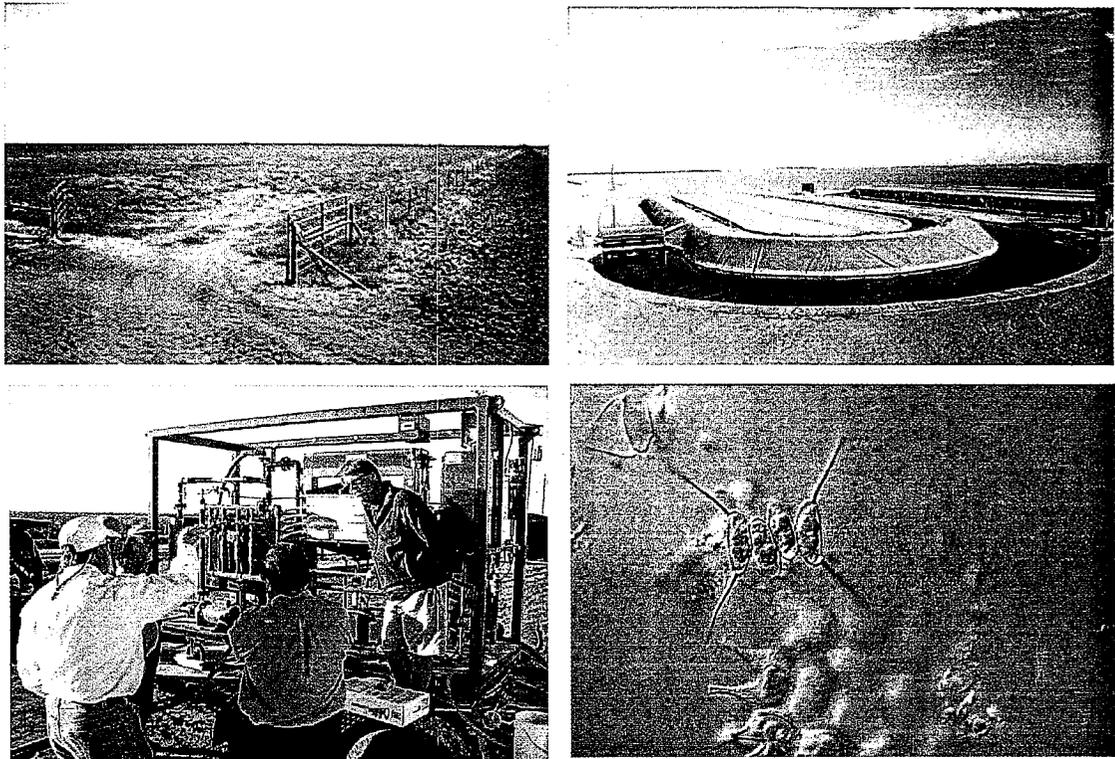


**DEVELOPMENT OF DRAINAGE TREATMENT
FOR THE
SAN JOAQUIN RIVER WATER QUALITY IMPROVEMENT PROJECT
AND THE PANOCHÉ DRAINAGE DISTRICT**

FINAL REPORT



Prepared for

**CALIFORNIA DEPARTMENT OF WATER RESOURCES
FRESNO, CALIFORNIA**

under

Agreement No. 46000002271

Prepared by the

University of California, Berkeley
School of Public Health
and
Lawrence Berkeley National Laboratory
Berkeley, California

January 2004



February 24, 2004

José I. Faria
Proposition 204 Coordinator
California Department of Water Resources
3374 East Shields Avenue, Room A-2
Fresno, CA 93726

Dear Mr. Faria,

Please find enclosed five copies of our final report entitled Development of Drainage Treatment for the San Joaquin River Water Quality Improvement Project. This research was conducted at the Panoche Drainage District with support from the California Department of Water Resources and Proposition 204 under Agreement No. 46000002271.

The support provided by the California Department of Water Resources, you and your staff of our ongoing drainage treatment research has resulted in the improved efficiency and demonstration of the Algal Bacterial Selenium Removal process and our exploration of the influence and potential inhibition of higher salt concentrations typical of recycled drainage or secondary drainage on the biological reduction and ultimate removal of nitrate and selenate from irrigation drainage in the San Joaquin Valley. As reported, we observed very little inhibition of biological nitrate and selenate reduction from twice higher salt concentrations found in primary irrigation drainage in the Panoche Drainage District, and this is indeed a very promising result for the San Joaquin River Water Quality Improvement Project and other irrigation drainage management strategies being considered by the Panoche Drainage District, other drainage districts, the California Department of Water Resources and other California State resource agencies. We have identified several areas worthy of further investigation including the use of salt-tolerant cyanobacteria and green microalgae as an alternative carbon-rich substrate in the ABSR Process to stimulate and sustain nitrate-reducing and selenate-reducing bacteria and as a pre-treatment for Reverse Osmosis to remove membrane clogging bicarbonate and carbonate. Finally, we have gained important operational performance data that have guided our design of the intermediate-scale ABSR Facility that will soon be constructed at the site of the pilot-scale ABSR Facility.

We look forward to your review of this report and to receiving your comments and further guidance in our development of irrigation drainage treatment.

Sincerely yours,

William J. Oswald, Ph.D., P.E.
Co-Principal Investigator

F. Bailey Green, Ph.D.
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FORWARD AND ACKNOWLEDGMENTS

The pilot-scale Algal-Bacterial Selenium Removal (ABSR) Facility was designed and constructed in 1995 and 1996 at Enrico Farms in the Panoche Drainage District, and since June of 1996 has operated continuously through 2002 with support from most recently the California Department of Water Resources, and also from the U.S. Bureau of Reclamation, the CALFED Bay-Delta Program, and the Panoche Drainage District. Important data have been collected on the removal of selenium salts and nitrate from subsurface irrigation drainage. Initial difficulties due to the requirement that shallow drain tiles could not be disturbed during construction of the pilot-scale ABSR Facility were mitigated to some extent by building the Reduction Ponds berms 4 feet above grade to create a 10-foot depth and by covering the surface of the Reduction Ponds. However, the minimal depth in the Reduction Ponds remains a constraint on selenate reduction, and nitrate reduction, in the 1996 pilot-scale ABSR Facility at the Panoche Drainage District. Since the pilot-scale Reduction Ponds cannot completely prevent the intrusion of dissolved oxygen into the anoxic bottom zone where selenate and nitrate reduction take place, selenate reduction to insoluble selenide has been incomplete.

To help simulate the performance of deeper reduction ponds that would have been possible to construct had the irrigation tile drains been removed and the Reduction Ponds made deeper, we covered each pilot-scale Reduction Ponds with black plastic floating covers. The covered Reduction Ponds better simulate, but do not completely achieve, the optimal and more stable anoxic conditions expected in deeper and better protected anoxic Reduction

Ponds with internal reduction zones. Although the results reported herein are quite favorable, they do not fully represent what might be attained in future ABSR Facilities with sufficiently deep and properly protected Reduction Ponds with internal reduction cells. An intermediate-scale ABSR Facility that will better overcome the problems associated with minute oxygen intrusion and more completely reduce selenate, and selenite, to insoluble selenide is now being designed and will be constructed during the spring and summer of 2004. This intermediate-scale (one acre-foot per day capacity) ABSR Facility will be located adjacent to the existing pilot-scale ABSR Facility at the Panoche Drainage District.

This report covers work during 2001 and 2002 generously supported by the California Department of Water Resources through a Proposition 204 grant. We are most grateful to the California Department of Water Resources, and to José Faria, Kurt Kovac, David Lara, and Kathleen Buchnoff-Kirn in particular, for supporting our continued research on biological treatment of irrigation drainage in the San Joaquin Valley of California and our further development of the ABSR Process.. We also wish to express our great appreciation to the Panoche Drainage District, especially Dennis Falaschi, General Manager, the Directors and Staff for their support of the project and their many and substantial in-kind and financial contributions. Marcos Hedrick, Chase Hurley, Carl Westbrook, Joe Westbrook, Betty Hurley, and Michael Gardner at the Panoche Drainage District all greatly contributed to our studies and collective efforts to improve drainage treatment and drainage management. We also gratefully acknowledge the support and participation of the following members of the Earth Sciences Division at the Lawrence Berkeley National Laboratory: Dr. Nigel Quinn, Dr.

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GLOSSARY

assimilation	Incorporation of nutrients or trace elements into living organisms.
atomic absorption	Spectrometric analytical method for element determination.
denitrification	Reduction of nitrate (NO_3^-) ultimately to nitrogen gas (N_2).
dissimilation	Release of elements from organisms through metabolic action.
dissolved air flotation	Method to remove suspended particles from water.
elemental selenium	Selenium in the 0 oxidation state; a solid under most environmental conditions.
High Rate Pond	A shallow, paddle wheel-mixed, raceway pond designed to grow microalgae at a high rate.
oxidation	Change in the chemical oxidation state of an atom by the loss of one or more electrons; the reverse of reduction.
reduction	Change in the chemical oxidation state of an atom by the gaining of one or more electrons; the reverse of oxidation.
Reduction Pond	A pond specially designed to reduce oxygen, nitrate, selenate, and selenite.

GLOSSARY, CONTINUED

selenate (SeO_4^{2-})	Selenium in this compound has a +6 oxidation state.
selenide (Se^{2-})	Selenium with a -2 oxidation state; selenide can be found in water in the forms of metal selenides, selenopolysulfides, and organic selenium compounds.
selenite (SeO_3^{2-})	Selenium in this compound has a + 4 oxidation state.
selenium (Se)	A metalloid and sulfur analog that, in trace amounts, is essential for human (0.001 to 1 mg/kg/day) and animal health, but which, at higher concentrations may be toxic and/or teratogenic.
substrate	An energy and/or carbon source necessary for the growth or metabolism of microorganisms; a substance upon which an enzyme acts.
supernatant	Clarified water overlying water with a high solids concentration.

ABBREVIATIONS

ABSR	Algal-Bacterial Selenium Removal
AF	acre-foot
ASP	Algae Settling Pond
atm	atmospheric pressure
BOD	biochemical oxygen demand
c	circa
d	day
DAF	Dissolved Air Flotation
DDI	distilled deionized water
DI	deionized water
DO	dissolved oxygen
ft	feet
gal	gallon
K	degrees Kelvin
kJ	kilojoule
kWh	kilowatt hours
HGAAS	hydride generation atomic absorption spectrometry
HP	horsepower
HRP	High Rate Pond
in	inches
IODMF	Integrated On-Farm Drainage Management Facility at Red Rock Ranch
L	liter
LBNL	Lawrence Berkeley National Laboratory
lbs	pounds
M	molar; moles per liter
mil	one thousandth of an inch thickness

ABBREVIATIONS, CONTINUED

mV	millivolt
N	nitrogen or as nitrogen
NTU	nephelometric turbidity units
O&M	operations and maintenance
P	phosphorus; as phosphorus
PI	Panoche influent from Panoche Drainage District Drainage Point #25
PDD	Panoche Drainage District
psi	pounds per square inch
QA/QC	quality assurance/quality control
RO	reverse osmosis
RP	Reduction Pond
SJRWQIP	San Joaquin River Water Quality Improvement Project
TDS	total dissolved solids
TSS	total suspended solids
s	second(s)
Se(0)	selenium in the 0 oxidation state; elemental selenium
Se(-II)	selenium in the -2 oxidation state
Se(IV)	selenium in the +4 oxidation state
Se(VI)	selenium in the +6 oxidation state
SSF	slow sand filter
VSS	volatile suspended solids
yr	year

ABSTRACT

This report describes continuing studies to improve the efficiency of irrigation drainage treatment using a primarily biological process: the Algal-Bacterial Selenium Removal (ABSR) Process, that has been demonstrated to be effective in removing soluble forms of selenium from irrigation drainage in the western San Joaquin Valley of California. The studies described herein have proved that selenate reduction and removal within the ABSR Process can be effective at the higher salt concentrations typical of secondary drainage, some 2.5 times as concentrated as primary drainage found in the western San Joaquin Valley. These studies have led further to the conclusion that reduction of selenate, Se(VI), to permanently removable selenide, Se(-II), cannot be fully achieved in our current reduction system because the Reduction Ponds and internal reduction cells are too shallow to permanently exclude dissolved oxygen. The current reduction system in the pilot-scale ABSR Facility allows minute amounts of dissolved oxygen that partially inhibit the reduction of selenate beyond selenite, Se(IV). We have observed that selenite becomes temporarily and weakly fixed in colloidal particles that are either organic, inorganic or mixtures of each. The weakness of the selenite binding is seen as selenite slowly separates from the absorbing colloidal particle under aerobic conditions such as in extended aeration and various filtration processes. Since time is required to free selenite from its associated colloidal particle, it follows that the selenite-particle adsorption may also be a slow process that may be avoided by maintaining anoxic redox conditions between -0.3 and -0.5 volts in order to more quickly reduce selenate to its most reduced form, selenide, that may be precipitated and rendered insoluble in the presence of polyvalent cations thus avoiding the weaker binding of selenite into colloidal solids. The work herein indicates that deeper reduction cells, now funded and under design for the intermediate-scale ABSR Facility at the Panoche Drainage District, will be able to more completely exclude oxygen and, with adequate carbon substrate, reach and sustain the essential anoxic, reducing conditions for quick selenide formation and co-precipitation.

ABSTRACT, CONTINUED*IMPROVING ABSR FACILITY PERFORMANCE*

During this project, the pilot-scale ABSR Facility achieved the highest selenate removal rates measured at the ABSR Facility—34 milligrams of selenium removed per cubic meter of pond volume per day. This removal rate was made possible by increasing both the treated drainage flow rate and the dosing rate of the organic carbon substrate (molasses) beyond those of earlier studies. Despite the higher substrate dose, the substrate utilization efficiency remained high—0.85 grams of selenium removed per kilogram of molasses added. This efficiency was approximately the 80th percentile of efficiencies measured during 1997 through 2002.

Particulate selenium, which includes some bioavailable organic selenium and adsorbed selenite, is created from soluble inorganic selenate (SeO_4^{2-}) during biological reduction within the ABSR Process. This particulate selenium must be removed by physical-chemical means in order to minimize discharge of bioavailable forms of selenium and to more nearly complete the reduction and removal of total selenium. Pilot-scale studies evaluated sedimentation, dissolved air flotation, slow sand filtration, rapid sand filtration, and diatomaceous earth filtration. We found that particulate selenium concentration and turbidity are highly correlated in rapid sand filter effluent (**Figure A1**). The correlation indicates that $<10 \mu\text{g/L}$ of particulate selenium will be present when turbidity is $<1 \text{ NTU}$. This level of clarity is regularly achieved in tertiary treatment of municipal wastewater using multi-media filtration. Membrane filtration usually achieves an additional one log removal to $<0.1 \text{ NTU}$. However, the best performance of our pilot-scale filters was 2 NTU and $16 \mu\text{g/L}$ of particulate selenium. We expect better performance in planned future tests due to improvements in scale, filter media and operating conditions. Additional filtration processes including membrane filtration will be tested for their effectiveness in the physical removal of particulate selenium.

We also observed that under aerobic conditions, the selenite concentration in the

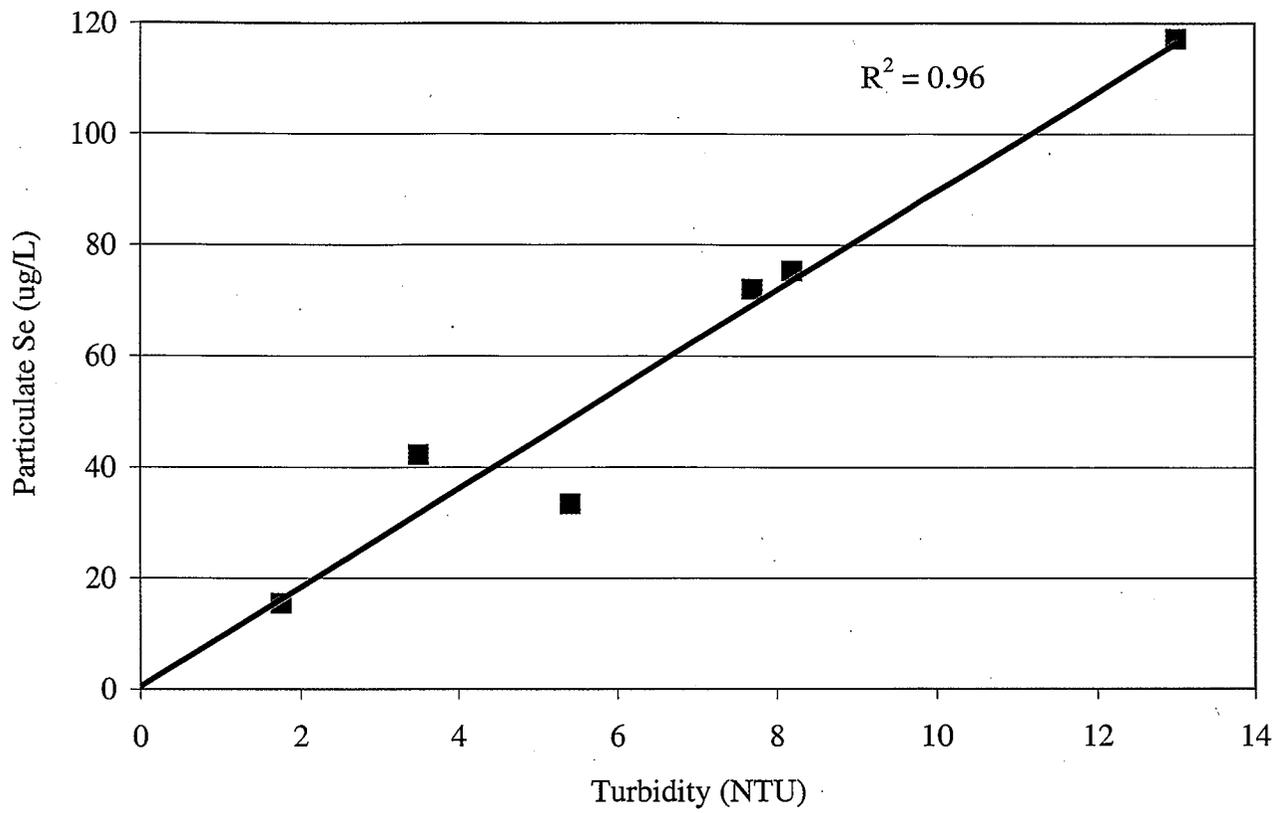


Figure A1. Correlation of particulate selenium and turbidity in the final sand filter effluent of the Panoche Algal-Bacterial Selenium Removal Facility. Full-scale wastewater recycling facilities typically achieve turbidity <2 NTU with sand filtration and <0.1 NTU with microfiltration.

ABSTRACT, CONTINUED

effluent from the Reduction Ponds of the ABSR Process rapidly increases, apparently due to selenite being released from colloidal particles by which it is absorbed. Therefore, Reduction Pond effluent should remain anoxic while any particulate selenium residuals are physically removed. This finding requires that, if oxygen-producing High Rate Ponds are to be used to cultivate organic reductant as part of the ABSR Process, the High Rate Ponds should be secondary to filtration of particulate selenium.

INTEGRATION WITH OTHER DRAINAGE MANAGEMENT METHODS

Reverse osmosis (RO) treatment of irrigation drainage, while costly and energy-intensive, would produce freshwater and would remove salt and selenium that is detrimental to San Joaquin River water quality. However, the brine produced during RO would be hazardous due to its selenium content unless the selenium is removed prior to drainage RO treatment or unless the resulting RO brine is treated for selenium removal. Similarly, recycling primary drainage for irrigation of salt-tolerant crops produces secondary drainage that may contain elevated selenium and salt concentrations. Treatment of such secondary drainage may have the advantage of increased selenium removal rates due to first-order kinetics and decrease the total volume of drainage to treat. However, higher salt concentrations were expected to inhibit biological selenium removal. In laboratory studies, however, we found that sodium chloride concentrations of 22 g/L did not inhibit biological denitrification or selenium reduction. RO brines with 22 g/L salinity would be produced by RO systems operating with 73% recovery when treating irrigation drainage having with 6 g/L TDS. While higher sodium and sulfate concentrations need to be tested for inhibitory effects, our results suggest that secondary drainage and RO brines may be treated by the ABSR Process.

Secondary drainage may be much less costly to treat for selenium removal than primary drainage. Like RO, drainage reuse decreases the volume treated, but unlike RO,

ABSTRACT, CONTINUED

crop uptake of nitrate decreases the concentration of this major inhibitor of selenium reduction. In fact, at the Panoche Drainage District's drainage reuse project, the San Joaquin River Water Quality Improvement Project (SJRWQIP), we found that secondary drainage contained almost no residual nitrate (<1 mg/L N, indicating a loss of 59 mg/L N). Denitrification in the soil of the irrigated fields is a possible cause of the nitrate loss. Evidence of such reductive processes were found in the form of elevated selenite concentrations in the secondary drainage and the apparent loss of nearly 400 $\mu\text{g/L}$ of selenate. The elimination of nitrate and some selenium during irrigation should decrease cost of treating the secondary drainage by the ABSR Process.

The apparent treatment during the drainage irrigation was not seen at the Red Rock Ranch drainage reuse project. The more positive results at the SJRWQIP are probably the result of biological denitrification and selenium reduction occurring in the flooded soil of the fields. The mass of organic carbon in algae growing in the primary drainage and in manure from grazing cattle was sufficient for complete denitrification of the primary drainage. Lysimeter studies should be conducted at SJRWQIP to confirm the existence of treatment in the soil, to determine the fate of the selenium removed in the soil, to determine salt accumulation rates, to develop methods to improve and control the treatment, and to determine the operating parameters and costs of ABSR Process treatment of the resulting low-nitrogen secondary drainage.

Overall, this project indicates that selenium removal using the ABSR Process can be effective at high salt concentrations and, therefore, can be combined with reverse osmosis or drainage reuse projects thereby lessening the hazard of brine disposal. Treatment of brines by the ABSR Process will likely cost less than the \$200 to \$300 per acre-foot estimated for treatment of primary drainage by the Process.

INTRODUCTION

This project concerned the improvement of the primary drainage treatment process known as the Algal-Bacterial Selenium Removal (ABSR) Process and investigation of the ABSR Process' ability to treat more concentrated drainage. Such concentrated drainage, referred to here as secondary drainage or brine or, is produced from sequential drainage reuse sites, reverse osmosis plants and evaporation processes. We summarize herein the research activities and results from September 1, 2001 through December 31, 2002. The effort was supported by the California Department of Water Resources with Proposition 204 funds under Contract Agreement No. 4600002271.

DRAINAGE RECYCLING FOR CONTAMINANT CONTROL

The amount of irrigation water used in the Central Valley of California includes that water provided for plant growth and transpiration and that water used to leach hard-pan-forming and plant-toxic salts from the plant root zone. Consequently, the production of subsurface drainage often exceeds 1.5 acre-feet per acre per year. Such drainage typically contains nitrate (c. 60 mg/L as N) and selenate (c. 0.5 mg/L as Se) along with plant toxicants such as sodium and boron, hard-pan-forming magnesium and calcium sulfates and carbonates, and reverse osmosis membrane-fouling silica.

At present, the Panoche Drainage District (PDD) discharges primary subsurface agricultural drainage to the San Joaquin River via the Grasslands Bypass and Mud Slough (Summers Engineering, 2003). During the 2001-2002 water year, monthly average discharge was approximately 2,400 acre-feet per month bearing some 700 kg of total selenium (SFEL, 2003). Drainage from the PDD (and from other drainage districts) to the San Joaquin River through the Grasslands Bypass is subject to legally imposed selenium mass discharge limits. These mass limits on selenium have been decreased by 5% each year over the past six years and will continue to be decreased in the future (Summers Engineering, 2003). In addition to selenium, the drainage contaminants nitrate, boron, and salt may become subject to discharge limits in the near future (RWQCB/CVR, 2004; 2003).

During the past twenty years, the PDD has decreased its drainage discharge by increased irrigation efficiency and, more recently, by drainage reuse. In the San Joaquin River Water Quality Improvement Project (SJRWQIP), the PDD recycles primary drainage for irrigation of salt-tolerant crops. As drainage recycling increases with the SJRWQIP and other similar future programs, final discharge or evaporation of a fraction of the reused drainage will become necessary. Prior to discharge or pond evaporation, treatment of secondary drainage will be essential to meet limits on selenium. Proposed limits on total dissolved solids (primarily sodium), boron, and other drainage contaminants may require final drainage treatment with reverse osmosis prior to discharge. In order to prepare for such final treatment, low-cost treatment processes and technologies must be readied.

ALGAL BACTERIAL SELENIUM REMOVAL PROCESS

During 1997 to 2002, the pilot-scale research and demonstration Algal-Bacterial Selenium Removal Facility treated up to 35,000 gallons per day of primary agricultural drainage from the Panoche Drainage District on the west-side of the San Joaquin Valley. In the ABSR Process, we use a series of ponds specially designed to promote the growth of indigenous microorganisms that in turn create the environmental conditions that foster the economic removal of nitrate and selenium from primary agricultural drainage (Green *et al.*, 2003).

ABSR Modes of Operation

Two modes of operation have been evaluated at the PDD ABSR Facility. Each mode has potential advantages due to its nitrate removal mechanisms and its internal recycle of nutrients. In Mode 1, primary drainage water is brought into an algal High Rate Pond (HRP) where 15 to 30 mg/L of nitrate-N are removed by algal assimilation. The HRP effluent is transferred into the Reduction Pond where the algae and eventually are decomposed by anaerobic and/or facultative heterotrophic bacteria which then reduce the remaining nitrate to nitrogen gas. Some advantages of this mode of operation are that an

Algal Settling Pond is not needed, less supplementary carbon substrate is required for nitrate reduction since algae have already taken up a portion of the nitrate, and the algae themselves become bacterial substrate. A disadvantage is that carbon dioxide, phosphate, and trace nutrients, at least initially, must be added to the High Rate Pond in order to achieve maximum algal growth rates and concentration requirements. Some nutrients can later be provided by recirculation from the anaerobic Reduction Pond to the High Rate Pond. A problem with a High Rate Pond in direct series with a Reduction Pond is that dissolved oxygen in the High Rate Pond effluent increases the redox potential in the Reduction Pond, possibly compromising denitrification.

In Mode 2, drainage water and carbon-rich substrates, such as inexpensive molasses, are added to the Reduction Pond. In the Reduction Pond, nitrate and selenate are reduced by anaerobic and/or facultative heterotrophic bacteria. The Reduction Pond effluent contains bacterial metabolites, such as ammonium, phosphate, and dissolved carbon dioxide, that are conveyed into the High Rate Pond. These metabolites are utilized as plant nutrients during algal growth thereby decreasing the need to supplement carbon dioxide and other plant nutrients. Microalgae grown in the flocculating environment of the paddlewheel-mixed High Rate Pond are removed from the water column by gravity sedimentation in an Algal Settling Pond and, in this study, by dissolved air flotation (DAF) and filtration. This algal biomass is then added to the Reduction Pond as a carbon-rich bacterial substrate. More carbon substrate likely will be required in Mode 2 than in Mode 1 since the Mode 2 Reduction Pond is not preceded by a nitrate-removing High Rate Pond. Dissolved oxygen in the drainage may compromise the attainment of the low redox potential needed to reduce nitrate. However, a dense culture of algae (c. 100 mg/L) held in total darkness will generally respire and deplete any free molecular oxygen, O_2 within 24 hours.

In both Modes, the specially-designed Reduction Pond has deep anoxic zones that both promote reduction reactions and prevent colonization by invertebrates which require dissolved oxygen.

Past ABSR Facility Performance

Based on influent and effluent analyses during the period 1997 through 1999, the Mode 2 system at the ABSR Facility in the PDD has removed on average 95% of the mass of influent nitrate and 80% of the mass of influent selenate (Oswald *et al.*, 2001). However, these analyses included laboratory removal of a selenium-bearing floc. The bacterial biomass containing reduced selenium that settles and accumulates on the bottom of the Reduction Pond is continuously undergoing anaerobic decomposition resulting in a reduction in the volume of settleable solids. According to our field experience with this and similar facilities, physical removal and disposal of selenium-bearing solids (settled and anaerobically digested solids) from the Reduction Ponds would not be required for many years, if not for decades (Oswald *et al.*, 1999; Zárate, 2001). Solids requiring removal quickly dry on underdrained sand beds and could be disposed either in a regulated landfill, or alternatively, those dry solids that are rich in organic nitrogen, potassium, and phosphorus, as well as selenium, might be beneficial if scientifically applied as a soil amendment and fertilizer in the selenium-deficient soils of the eastern San Joaquin Valley.

Not all particulate selenium settles in the Reduction Ponds. As a result, the effluent of the Reduction Ponds contains selenium-bearing suspended solids which, for protection of wildlife in receiving waters, must either not be produced or be removed. The current studies have focused on increasing the efficiency of removal of the non-settleable or resuspended selenium species. A study of particulate selenium and selenite removal was made using dissolved air flotation followed by slow sand filtration (Stuart, 2001; Oswald *et al.*, 2002). Selenium-bearing particulates appeared to penetrate the surface of the slow sand filter and to decompose within the filter releasing selenite into the filtrate. The aerobic conditions of the slow sand filters was believed to contribute to the selenite release. To avoid such in-filter decomposition, in the current study, we evaluated (1) anoxic slow sand filters, (2) intermittently-backwashed rapid sand filtration, and (3) diatomaceous earth filtration.

THE ABSR FACILITY AT THE PANOCHE DRAINAGE DISTRICT

LOCATION OF THE ABSR FACILITY

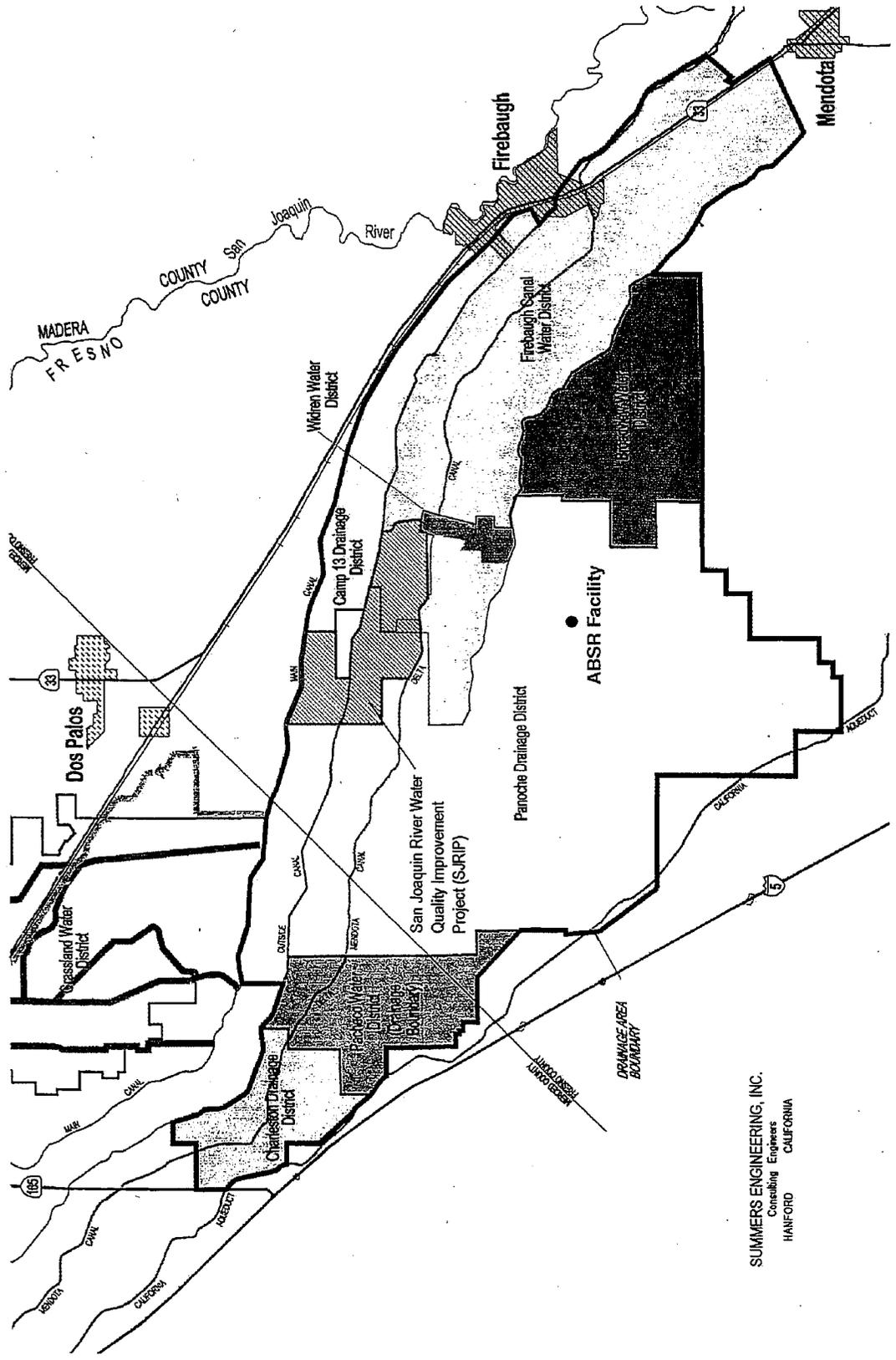
The demonstration-scale ABSR Facility is located within the Panoche Drainage District next to a drainage sump that collects subsurface agricultural drainage. This site was chosen to obtain drainage containing among the highest concentrations of selenium in the PDD. The PDD lies in the Panoche Creek Alluvial Fan west of the San Joaquin River, a region of the San Joaquin Valley with elevated soil selenium levels (Fio and Fujii, 1990). The levels of soluble selenium contained in the agricultural drainage water of the site typically range from 150 to 480 $\mu\text{g/L}$. The geographic location of the ABSR Facility is shown in **Figure 1**.

DESCRIPTION OF THE ABSR FACILITY

The Panoche ABSR Facility (**Table 1, Figure 2, Photograph 1**) consists of two parallel systems each having a covered Reduction Pond (RP); a paddle wheel-mixed High Rate Pond (HRP) designed to maximize algae production; and an Algae Settling Pond (ASP). A parallel control system can be used to normalize the inevitable changes in drainage composition and climatic conditions. Using two systems also allows side-by-side evaluation of various bacterial substrates, substrate treatments, and flow regimes.

REDUCTION PONDS

The two 0.1-acre (0.04-ha) RPs were designed to provide an absence of dissolved oxygen (DO) in order to promote the growth of nitrate and selenate reducing bacteria. Many of these organisms require an absence of DO in order to reduce nitrate and selenate. Consequently, the RPs were constructed as deep as the underdrained, agricultural site allowed in order to help prevent significant oxygen concentrations in the reaction zone near the floor of the pond. Floating covers on the RPs were also used to reduce wind-induced mixing of oxygenated surface water to the pond floors. The covers were constructed of 36-mil (0.9-mm), scrim-reinforced polypropylene supported by floats. A 1-ft (30-cm) long skirt



SUMMERS ENGINEERING, INC.
 Consulting Engineers
 HANFORD CALIFORNIA

Figure 1. Location map for the ABSR Facility in the Panoche Drainage District in the western San Joaquin Valley of California near the town of Firebaugh.

Table 1. Volume and surface area of each pond of the ABSR Facility at the PDD.

	Volume (m ³) (gallons)	Surface Area (m ²) (sq. ft.)
Reduction Ponds (10 ft deep)	758 200,000	435 4680
High Rate Ponds @ 8 in depth	90 23,700	471 5,070
High Rate Ponds @ 12 in depth	140 36,850	501 5,390
High Rate Ponds @ 16 in depth	193 50,830	532 5,720
Algae Settling Ponds (4.9 ft deep)	100 26,510	112 1210

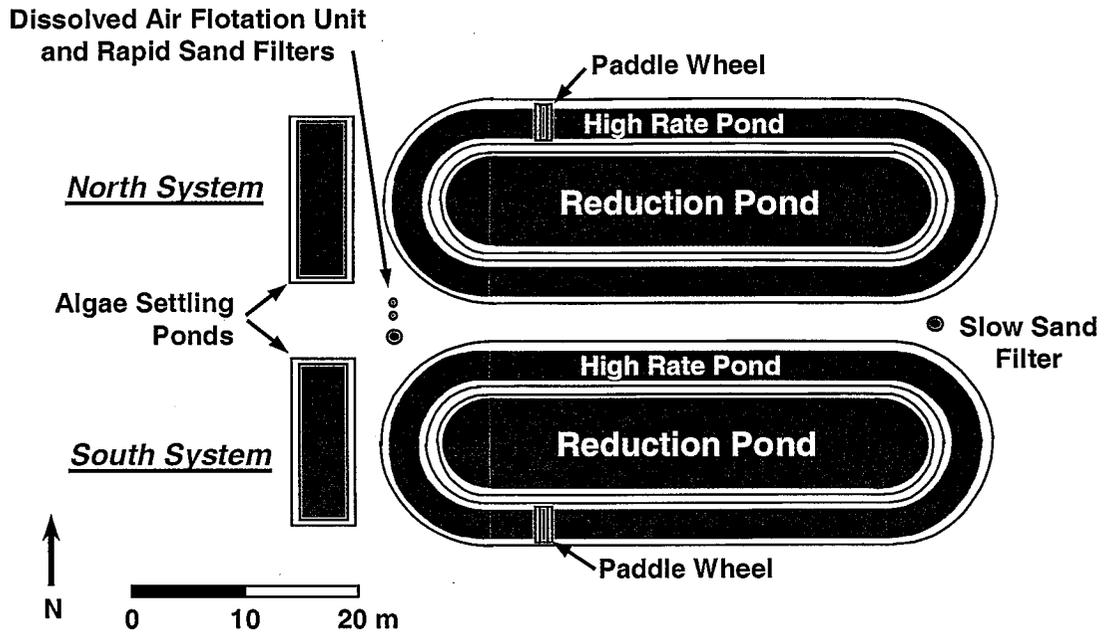
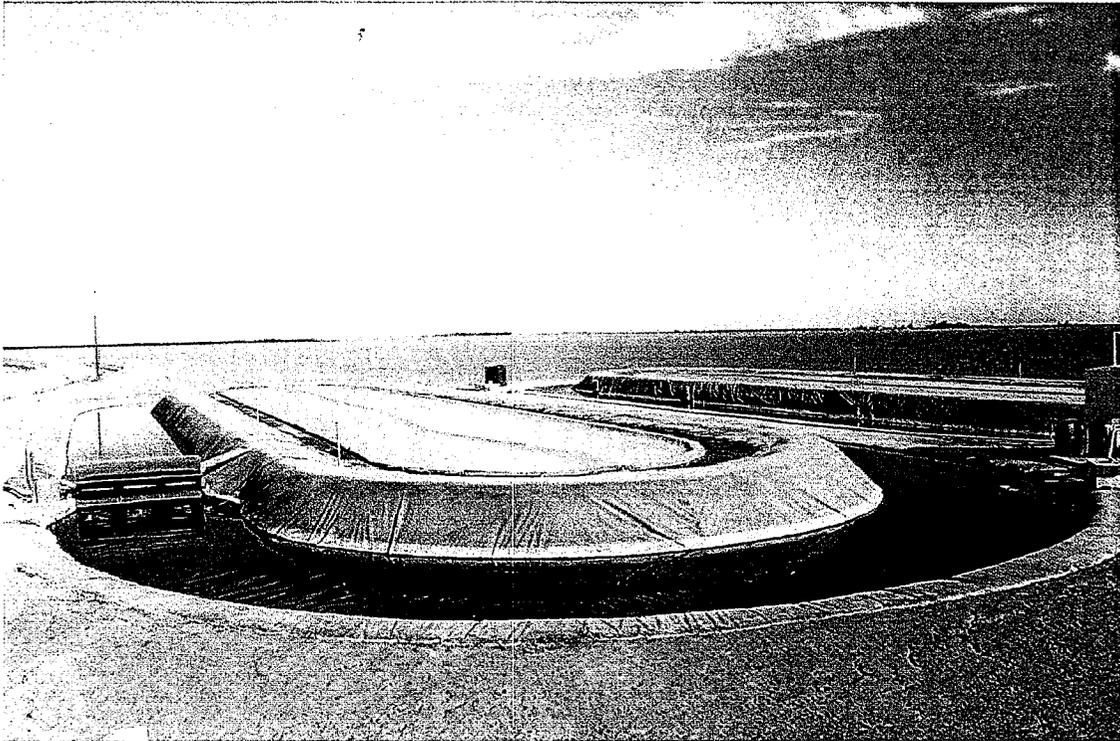
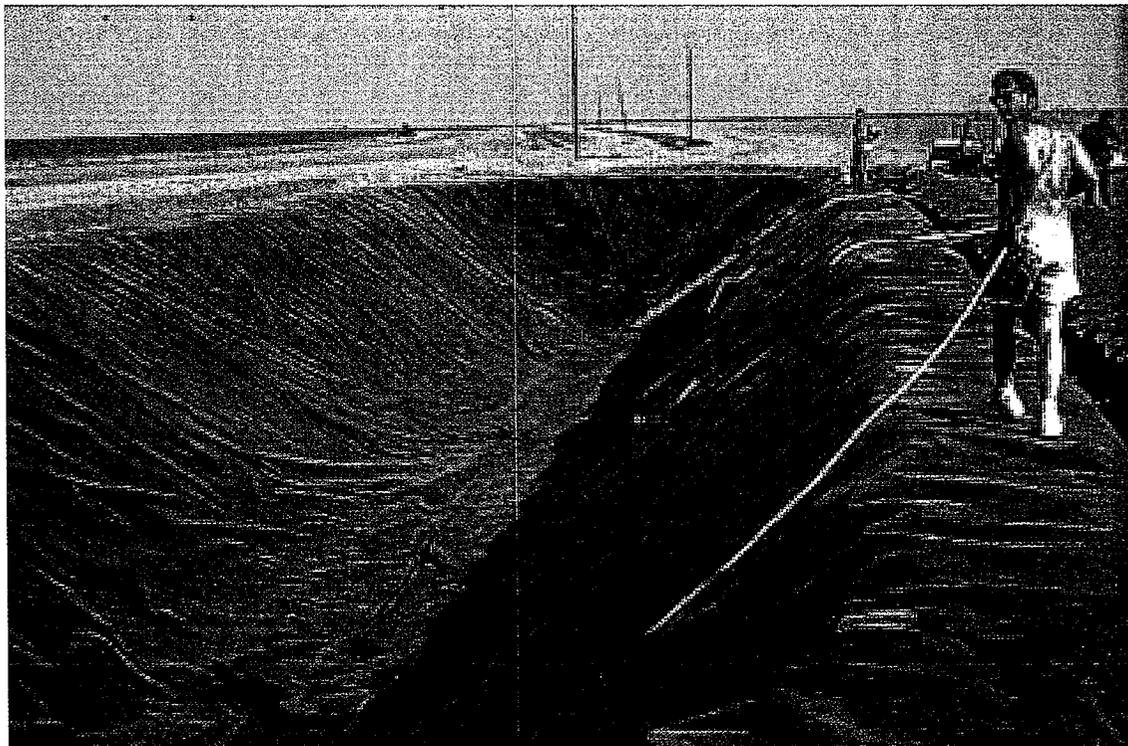


Figure 2. Plan view of the pilot-scale Algal-Bacterial Selenium Removal Facility, Panoche Drainage District, western San Joaquin Valley, California.



Photograph 1. The North System of the ABSR Facility in the Panoche Drainage District. The paddle wheel-mixed High Rate Pond is in the foreground. The covered Reduction Pond is surrounded by the elevated berm in the center.



Photograph 2. The North Reduction Pond basin during installation of the black, high-density polyethylene liner.

of cover material descended into the pond to prevent wind from blowing under and displacing the cover. The cover skirt was weighted at the edge with a chain.

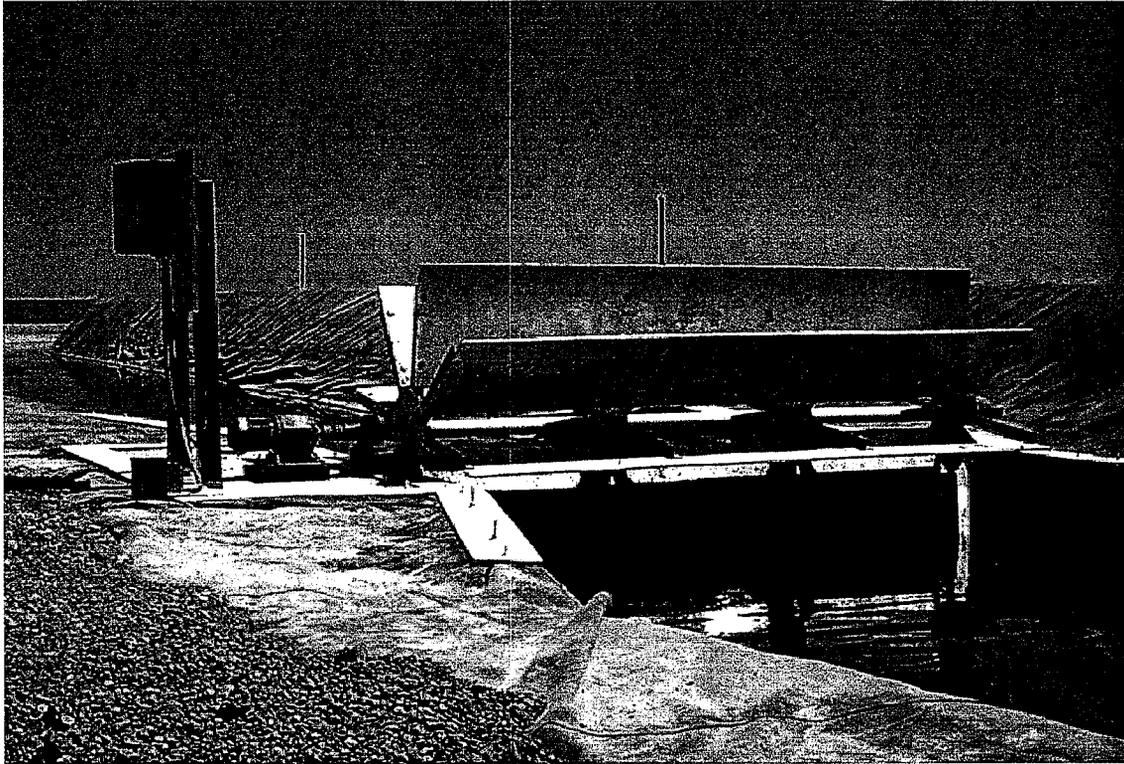
The RPs have a nearly V-shaped cross section and a 4:1 length to width ratio. For their construction, the RPs were excavated to depth of 6 ft (1.8 m) (**Photograph 2**). This shallow cut was chosen to avoid groundwater and to prevent damage to the existing subsurface drain lines. The RP berms were built up with an excavator and compacted with a vibrating roller compactor to achieve a final basin depth of 11 ft (3.6 m), corresponding to a 10-ft (3.0-m) maximum water depth. The RPs were lined with 40-mil (1-mm) thick, high density polyethylene (HDPE). HDPE was selected for its long-term resistance to UV degradation and its low cost. The influent pipelines delivered drainage water to 8 in (20 cm) above the RP floor at the west ends of the RPs. Effluent was taken at mid-depth from the east end of the RPs.

Two vertical baffle walls constructed of scrim-reinforced plastic were installed across each of the RPs. The baffles divided the RPs into three cells with approximately equal volumes. The baffles were supported at the top with floats and weighted along the bottom and sides with galvanized chain inserted in a hem in the baffle. Three 2-in (5-cm) diameter holes in each baffle allowed water to pass between cells.

HIGH RATE PONDS

The two 0.1-acre, paddle wheel-mixed HRP were designed to cultivate microalgae in high concentrations and at high productivity. The HRP floors were laser leveled to ± 0.5 inch (13 mm) and compacted to 95% of optimum. Level HRP floors were required to improve the efficiency of the paddle wheel mixing. The HRPs were lined with a 36-mil, scrim-reinforced, vinyl-based liner, known as XR5, which was manufactured by Seaman Corporation.

The HRPs were operated at depths of 8 in to 24 in (20 cm to 61 cm) and were continuously mixed by eight-bladed, 10 ft-long (3 m) paddle wheels (**Photograph 3**) which maintained a mean surface velocity around the pond circuit of 0.5 ft per second (15 cm/s).



Photograph 3. The paddle wheel of the North High Rate Pond of the pilot-scale ABSR Facility at the Panoche Drainage District. The 0.3 HP gear reducing motor was operated with a rotational speed of 3 rpm providing a 15-cm/sec water velocity in the channel.

This velocity is sufficient to keep most microalgae and bacteria in suspension. The paddle wheels were driven at 3.0-3.5 rpm by 0.33 HP (0.25 kW) motors with variable frequency speed controllers.

In the Mode 2 North ABSR System, Reduction Pond effluent was split among the North HRP, a slow sand filter, and a dissolved air flotation unit depending on the experiments being conducted at the time.

ALGAE SETTLING PONDS

ASPs provided a quiescent zone for the algae grown in the HRPs to settle. ASPs clarified the HRP effluent and provided a simple means to harvest algae for use as bacterial substrate. Earlier research showed that the ASPs could be eliminated from the process if algae did not need to be harvested for heat treatment before use as bacterial substrate. During the present study, the ASPs were not required.

FINAL CLARIFICATION

Following the last pond in the ABSR series, additional clarification and algae harvesting was performed using chemical flocculation followed by dissolved air flotation (DAF) and several forms of filtration. These processes will be described in detail under the Methods section.

ANALYTICAL METHODS FOR WATER QUALITY EVALUATION

The primary analytes during this project were the pollutants to be removed (nitrate, nitrite, and several forms of selenium), indicators of microbial growth (total and volatile suspended solids and turbidity), and salt concentration (total dissolved solids). This section describes the analytical methods used.

Suspended solids and total dissolved solids were determined using Whatman GF/C glass fiber filters with a nominal pore size of 1.2 μm (APHA, 1995).

NITROGEN ANALYTICAL METHODS

Nitrite was determined colorimetrically via Method 4500-NO₂⁻-B (APHA, 1995) with the calibration concentrations of 0, 100, 200, 500, and 800 µg/L. Nitrate+nitrite were determined using the Szechrome NAS method with calibration concentrations of 0, 2.5, 5, 10, and 15 mg/L-N (Polysciences, Inc., Warrington, PA).

The quality of the nitrogen analyses were determined by blanks, standards, splits, and matrix spikes in each analytical session. If split concentrations differed by >10% or if spike recoveries were greater than +/-15%, all samples in the session were reanalyzed until split and spike recoveries were within the percentage tolerances. For both the nitrate+nitrite test and nitrite test, the optical density for blanks ranged from -0.007 to +0.050, and the r² values for the calibrations curves were always >0.98.

SELENIUM ANALYTICAL METHODS

Selenium analyses of drainage samples were performed by hydride generation atomic absorption spectrometry (HGAAS) following guidelines of the Standard Methods for Analysis of Water and Wastewater, 19th edition (APHA, 1995). Method APHA 3500-Se C was modified slightly to analyze water samples to monitor performance of the ABSR Facility (Zarate, 2001).

It is well-known that the predominant soluble form of selenium (Se) in water samples is selenate [SeO₄²⁻; Se(VI)]. Selenite [SeO₃²⁻; Se(IV)] is also found in smaller amounts and mostly in reducing environments. Selenium is also known to exist in other soluble forms. Selenopolysulfide ions [SSe²⁻; Se(-II)] may occur in the presence of hydrogen sulfide in or nearby waterlogged, anoxic soils or sediments (APHA, 1995). In addition, organic selenium [Se(-II)] may also occur in some waters (Benson *et al.*, 1990).

In the case of the ABSR Facility at the PDD, we determined that the natural matrix contained various forms of soluble selenium. The selenium form in the influent is predominantly selenate while each of the ABSR Facility ponds contain forms of soluble selenium more reduced than selenate. Alkaline digestion using hydrogen peroxide and sodium

hydroxide is recommended by the APHA 3500-Se A method as one of the ways to determine total selenium in natural waters. This method recommends the digestion of unfiltered samples to determine the natural matrix including soluble and particulate selenium by using preparatory steps to convert other chemical selenium species to selenite. We adapted the alkaline digestion method to validate results for total soluble selenium determination digested with concentrated hydrochloric acid and different additions of 2% ammonium persulfate, as described below.

Subsurface agricultural drainage water treated by the ABSR Facility had very low turbidity and color. Samples from both the Mode 1 and Mode 2 ABSR systems were often colored. (The modes of operation are explained in the section *ABSR Modes of Operation* above). Occasionally, samples from the Mode 1 System were whitish and presented hydrogen sulfide odor. Samples from the Mode 2 System presented yellowish/brownish coloration due to the presence of molasses and suspended bacteria. Color and odor characteristics may indicate the presence of soluble selenium compounds other than selenite and selenate (APHA, 1995). In addition, those color characteristics of the samples may indicate that some soluble matter, mainly organic matter, would interfere during analytical determinations (Fio and Fujii, 1990).

HCl-Persulfate Digestion for Total Soluble Selenium Determination

The 0.2 μm filtrate from each sample was digested in a heating block. In preparation for digestion, the heating block was warmed to 95°C (~45-60 min). Test tubes were prepared by adding 2.5 mL of sample to each tube. Five tubes were prepared for QA/QC analysis: two separate split-sample tubes were prepared using 2.5 mL PI and three spiked-sample tubes were prepared with 2.25 mL of sample (randomly selected among the sample points) + 0.25 mL of 1000 $\mu\text{g/L}$ standard selenium stock solution. 2.5 mL of HCl was added to each test tube and 2% ammonium persulfate was added to the samples in varying concentrations to assist in the digestion process as follows: two PI tubes received 0 and 0.1 mL; 1.5x, 2.0x, 2.5x brine experiment samples received 0.1 mL, 0.2 mL, 0.3 mL; the splits received 0 and 0.1

mL; and, the spikes received 0.1 mL, 0.2 mL, and 0.3 mL.

Excessive ammonium persulfate level can oxidize selenite causing total selenium to be under-estimated by HGAAS. Too little ammonium persulfate can also have a negative influence on selenium measurement by not allowing full oxidation of organic Se and organic carbon. Thus, these varying concentrations persulfate for each sample were used to establish a curve in light absorbance. The highest absorbance value of the various persulfate additions was reported.

Following persulfate addition, the tubes were lightly capped and digested in a fume hood for 35-40 minutes. After digestion the test tubes were removed from the heating block and allowed to cool.

Alkaline Digestion for Total Selenium Determination

Total selenium analyses also were performed via a variation on APHA 3500-Se A. Samples were prepared using the alkaline digestion procedure using 2.5 mL of sample with addition of 1.5 mL 30% hydrogen peroxide in one 50-mL test tube and 2.0 mL in a second 50-mL tube. Each tube received 1 mL 1N sodium hydroxide. The mixture was placed in a digestion block and heated at 95-100°C until foam formation subsided (usually 30 minutes). If a white precipitate formed, 0.1 mL 1.5 N HCl was added dropwise until the precipitate dissolved. The higher Se concentration result of the 1.5 mL and 2.0 mL hydrogen peroxide additions was deemed more accurate.

Atomic Absorption Spectrometry

In preparation for atomic absorption analysis, the Varian AA-100 was warmed up for 60 minutes and the lamp optimized using the Spectra AA controlling software. Next, the acetylene gas regulator was opened to 11 psi and the argon gas regulator was opened to 54 psi. The air flow was started, and the flame was lit. After ignition, the AA was allowed to operate for another 30 minutes to stabilize the temperature of the burner and quartz T-cell.

For hydride generation, 6M HCl was used and a solution of 1.25 g NaOH and 1.5 g

NaBH₄ in 500 mL DI water. Three calibration standards (1, 5, 10 ppb) were also prepared daily from a 1000 µg/L stock solution. Each 100 mL of standard included 2.5 mL of HCl.

The digested samples were diluted with DDI water as needed to achieve selenite concentrations of <10 µg/L. A standard check was performed after every eight samples analyzed.

Analytical Definitions

Undigested 0.2 µm filtered samples were analyzed with the AA to determine *soluble selenite* concentrations. Usually this procedure is said to reveal the “selenite” concentration, but because the samples were passed through a filter and some results of this project suggest the presence of readily adsorbed/desorbed selenite, we refer the results of this analysis as soluble selenite. Total soluble selenium determined by the HCl-persulfate method minus selenite was defined as “selenate” in this study, although this fraction could also contain Se(-II) forms such as organic or sulfide selenium. The same dilution and standard checks described for total selenium analysis were performed for selenite. Particulate selenium was defined as total unfiltered selenium as determined by alkaline digestion minus total soluble selenium as determined by HCl-persulfate digestion.

Quality Assurance and Quality Control for Selenium Analysis

Analytical accuracy was assured by a quality assurance/quality control (QA/QC) program consisting of matrix spikes, standards, blanks, split samples, and duplicates. These QA/QC samples consisted of 10% to 15% of the samples analyzed. A sample set was considered out-of-control when standards, splits, or duplicates differed by more than 10%; when spike recoveries were less than 85% or greater than 115%; or blanks were higher than recommended by Standard Methods (APHA, 1995). Out-of-control sample sets were re-analyzed to achieve in-control results.

INTRODUCTION TO THE BRINE TREATMENT RESEARCH

The San Joaquin Valley is one of the most productive agricultural regions in the world. However, agriculture in the San Joaquin Valley relies on heavy crop irrigation because of low annual precipitation in the region. Salts from irrigation water accumulate in soils and groundwater over time as irrigation water evaporates. Salt is accumulating at a rate of 2.45 million tons per year in the Central Valley (DWR, 2001). Parallel to the salt accumulation problem in the San Joaquin Valley, is the problem of selenium contamination of drainage and of brines produced in drainage reuse and RO projects. Selenium contamination makes safe management of the drainage salts more difficult and expensive. Accordingly, removal of selenium from brines should facilitate the brine and salt management.

While the ABSR Process has been shown to remove selenium and nitrogen from drainage water with salt concentrations ranging from 6 to 8 g/L, the question addressed in this study was the ability of the ABSR Process to remove selenium and nitrogen from drainage brines. In order to determine whether the ABSR Technology can be used or adapted for this purpose, the effectiveness of nitrogen and selenium removal from brine was examined in special laboratory experiments. In one form of the experiment, primary drainage was evaporated to a dense brine and then diluted with DI water to make solutions with several total dissolved solids (TDS) concentrations. These brine solutions were used in batch bioassays. Dissolved oxygen, pH, and turbidity were monitored as well as nitrate+nitrite, selenate, and selenite. In a second form of the experiment, four different brine solutions were prepared by addition of sodium chloride to achieve TDS concentrations of up to 22 g/L. RO brines would contain 22 g/L salt, for example, when the RO system recovery was 55% and the RO influent contained 10 g/L salt or when recovery was 73% and the RO influent contained 6 g/L salt.

A perceived advantage of the first form of the experiment was that all salts present in the drainage would be concentrated as would be expected in RO treatment. However, controls showed that the oven evaporation and redilution with DI water was in itself detrimental to nitrate and selenium reduction, perhaps due to permanent precipitation of

essential nutrients. The second form of the experiment showed that bacterial denitrification and selenate reduction occurred at the same rate for all four different salinities. These results suggest that the ABSR Technology is appropriate for removal of nitrate and selenium from agricultural drainage brines. Future research can help determine how other constituents such as sulfate and phosphate may affect nitrate and selenium reduction of drainage brines both as nutrients and redox sensitive constituents.

METHODS FOR THE BRINE TREATMENT EXPERIMENTS

EXPERIMENT WITH EVAPORATED DRAINAGE

Drainage Preparation

Subsurface drainage was collected from Drainage Point 25 of the Panoche Drainage District on September 6, 2002. This drainage source was also the influent source for the ABSR Facility. The 20-L drainage sample was brought to LBNL and stored at room temperature. The unmodified drainage is hereafter referred to as "PI" (Panoche Influent). A subsample of the PI water was allowed to evaporate in an oven at 180°C to 240°C over seven hours from 2,550 mL to 840 mL. After evaporation, the concentrated PI solution was divided and diluted with deionized water (DI) to give three beakers with salt concentrations ratios of 98% ("1.0x"), 147% ("1.5x"), or 196% ("2.0x") of the original concentration of the PI water which was 7.9 g/L TDS. A beaker of unconcentrated PI was also prepared for an experimental control.

Substrate and Inoculum

Each of the four concentrations of drainage was dosed with animal feed-grade molasses (76 Brix, Foster Farms, Turlock, California collected on July 31, 2002 and stored at 5°C) to achieve 400 mg/L molasses concentration. The composition of typical feed-grade molasses is shown in **Table 2**. Each beaker of 465 mL of drainage was inoculated with 10 mL of inoculum solution. This solution was 50% effluent from the North Reduction Pond of the ABSR Facility collected on September 11, 2002 and 50% anaerobic culture from high salinity drainage treatment experiments conducted in April 2001. For an inoculum carbon

control, a beaker of 1.0x drainage was inoculated as described but not dosed with molasses.

Table 2. Feed grade molasses constituent analysis (from Liquid Sugar, Inc.) with resulting concentration of constituents in drainage water if dosed with 1.0 g/L molasses. Typically actual molasses doses ranged from 0.2 to 0.7 g/L in the ABSR process experiments.

Constituent	Per 100 g of molasses	Units	Concentration in drainage with 1.0 g/L molasses dose	Units
Water	21.3	g	0.213	g/L
Biochemical Oxygen Demand	270	g	270	mg/L
Calories	297	kcal	2.97	kcal/L
Protein	0.26	g	2.6	mg/L
Ash	8.50	g	85	mg/L
Total Carbohydrates	74.2	g	0.742	g/L
Total Fat	0.09	g	0.90	mg/L
Nitrogen (16% of protein assumed)	42	mg	0.42	mg/L
Sodium	216	mg	2.16	mg/L
Calcium	64	mg	0.64	mg/L
Potassium	150	mg	1.50	mg/L
Copper	0.020	mg	0.20	μ g/L
Iron	10.5	mg	0.105	mg/L
Magnesium	16.2	mg	0.162	mg/L
Phosphorus	4.7	mg	0.047	mg/L
Selenium	not detectable	μ g	not detectable	μ g/L

After addition of substrate and inoculum and mixing, the five drainage solutions were distributed in 65-mL aliquots to 100-mL serum bottles. The serum bottles were wrapped in aluminum foil to prevent photosynthetic oxygen production. Six bottles each of the 1.0x, 1.5x, and 2.0x solutions were prepared, plus three bottles of PI and one bottle for the inoculum control. The total number of bottles was 22. Each bottle was sparged with helium for 2.5 minutes through an airstone to lower the dissolved oxygen concentration. The helium flow was approximately 200 mL/min.

The sparged bottles were transferred into an anaerobic glove box (Bactron Anaerobic Chambers, Sheldon Manufacturing Inc). In the air lock, the bottles were subjected to three cycles of vacuum to 45 cm of Hg followed by flushing with an anaerobic gas mixture (4.87% H₂, 5.05% CO₂, balance N₂) at 25°C. The bottles were sealed with rubber stoppers with sleeves inside the glove box, removed from the box, placed in a tray, and incubated at 35°C beginning September 16, 2002. During incubation, the bottle tray was vigorously shaken once a day and the incubator temperature recorded.

Sampling and Preservation

On day 0, 3, 6, 13, 18, and 31 of the incubation, one bottle of each concentration (1.0x, 1.5x, 2.0x) was sacrificed. The PI bottles were opened on day 0, 6, and 18. Sample pH and turbidity were measured immediately. Next, a 40 mL aliquot from each bottle was filtered through a 0.2- μ m filter (Pall Supor 200) and stored in two 25-mL polycarbonate vials. The subsample in one vial was preserved by lowering the pH to <2 with HCl. This acidified subsample was used in determination of nitrate+nitrite concentrations. The unacidified subsample was used for nitrite, selenite, and total soluble selenium determinations. Nitrite was usually determined within 5 hrs and always within 48 hrs of sampling. Subsamples were stored at 4°C until analyzed.

Another subsample from each bottle was filtered for suspended solids determination according to APHA (1995) using 1.2- μ m pore size Whatman GF/C filters.

SODIUM CHLORIDE ADDITION EXPERIMENT

Selenium removal in the PI bottles was more rapid than in the 1.0x bottles indicating that the oven evaporation caused precipitation of essential nutrients, perhaps phosphorus. To avoid such unintended changes in drainage composition during evaporation and as the objective of the studies was to determine the effect of high salt concentrations on the rate of anoxic biological treatment, we opted to add salt to the drainage rather than remove water by evaporation. As sodium can be detrimental to non-halophytic bacteria (Atlas and Bartha, 1987) and presumably is more detrimental than the other major ions found the drainage at Drainage Point 25, we chose sodium chloride (NaCl) as the salt to supplement.

Drainage Preparation

A 20-L sample of Panoche Influent (PI) was collected on October 26, 2002 and stored unrefrigerated. A 5-L subsample was passed through Whatman 2V fluted paper filter to remove any large particles including precipitates that might have subsequently dissolved during the experiment. Total dissolved solids were found to be 8,824 mg/L for the filtrate. Unaltered PI served as the "100%" salt concentration, labeled "1.0x". Drainage with salinity of 147% of PI ("1.5x") was made by adding 2.255 g of NaCl (Fisher Certified; **Table 3**) to 540 mL of PI. The 204% ("2.0x") salt concentration was achieved by adding 4.955 g of NaCl to 540 mL of PI water. For 249% ("2.5x"), 7.115 g of NaCl was added to 540 mL of PI. Evaporation of drainage was not used in these sodium chloride addition experiments.

Table 3. Lot analysis for Fisher Certified sodium chloride used in experiments (Lot 796274).

Insoluble matter:	0.0025%
Free acid as HCl:	0.002%
Free alkali as NaOH:	none
Br:	0.001%
I:	0.0005%
N compounds as N:	3 ppm
PO ₄ :	2 ppm
SO ₄ :	0.0008%
Ba:	0.001%
Fe:	0.5 ppm
Ca, Mg, R ₂ O ₃ ppt:	0.0035%
Heavy metals as Pb:	1 ppm
K:	0.002%
ClO ₃ :	0.001%
NO ₃ :	0.003%

Nitrate added to the drainage with the NaCl preparation was negligible, amounted to <1 mg/L as N in the highest NaCl solution used.

Substrate, Nutrients, and Inoculum

A nutrient buffer solution was added to each salinity solution (**Table 4**). Each liter of drainage solution received 1 mL of the phosphate buffer and 1 mL of the trace metals solutions prior to distribution to the serum bottles.

Table 4. Phosphate buffer and trace metal solutions recipes.Phosphate Buffer Solution

The following were added to 500 mL of DI water resulting in a pH of 6.6.

KH_2PO_4	2.0 g
K_2HPO_4	2.1 g
NH_4Cl	2.0 g

Trace Metals Solution

The following salts and 2 mL concentrated HCl were added to 1998 mL of DI water.

$\text{MnSO}_4 \cdot \text{H}_2\text{O}$	3.3 mg
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	6.2 mg
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	7.6 mg
$\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$	11.7 mg
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	64.6 mg

Each liter of drainage also received 400 mg/L of molasses (Foster Farms, collected September 28, 2002) prior to distribution to the serum bottles. Seven 100-mL serum bottles for each salt concentration (1.0x, 1.5x, 2.0x, and 2.5x) were prepared, for a total of 28 bottles. Each 100-mL bottle contained 65 mL of solution consisting of drainage, molasses, and nutrient solution.

In this experiment, the inoculum included biomass collected from high salinity drainage at the Red Rock Ranch drainage reuse site near Five Points, California and from the Panoche Drainage District ABSR Facility. The inoculum solution contained a mixture of black sediment from Red Rock Ranch, biofilm from barrels holding drainage at Red Rock Ranch, and effluent from the North Reduction Pond (October 26, 2002 sample). Each serum bottle received 1 mL of inoculum solution while in the anaerobic glove box. In this way, the exposure of the inoculum solution to air was minimized. According to initial volatile suspended solids measurements, each serum bottle received 20 mg/L to 40 mg/L of inoculum solids.

The bottles were passed through three cycles of vacuum upon entering the glove box as described for the previous experiments. After inoculum addition to each serum bottle in the anaerobic glove box, each bottle was vigorously agitated for 30 seconds and then left unstoppered for an additional minute before inserting the stoppers. In this way, DO was decreased in the drainage and the bottle atmosphere was given time to equilibrate with the anaerobic atmosphere. DO measurements in the initial (time=0) samples were all <0.7 mg/L.

The 28 bottles were placed in an automatic orbital shaking incubator at 30°C beginning November 1, 2002. The shaking rate was 100 rpm, causing a slight motion of the liquid in the serum bottles.

Sampling and Preservation

During the second experiment, one bottle of each salt concentration (1.0x, 1.5x, 2.0x, and 2.5x) was sacrificed on day 0, 3, 6, and 9. On the last day of the experiment, day 14, three bottles of each concentration were sacrificed to determine water quality variance among the bottles. Following procedures described for the evaporation experiment, samples from each bottle were filtered and analyzed.

Total nitrate and nitrite, nitrite concentration, and turbidity measurements were tested for correlation. Day 14 results from the NaCl-addition experiment were used for the Tukey Honestly Significant Difference (HSD) test (Zar, 1999). The Tukey HSD test was used to analyze for differences in total NO_3+NO_2 , NO_2^- , and turbidity due to differences in salt concentrations.

RESULTS OF BRINE TREATMENT EXPERIMENTS

EVAPORATION EXPERIMENTS RESULTS

Nitrogen removal occurred for all three salt concentrations of the evaporation experiments. The progression of bacterial denitrification over time can be observed in **Figure 3** and **Figure 4**. Nitrate+nitrite concentrations as N started at 59 mg/L for PI, 67 mg/L for 1.0x, 71 mg/L for 1.5x, and 113 mg/L for 2.0x. After 18 days, the PI bottles had reached <1

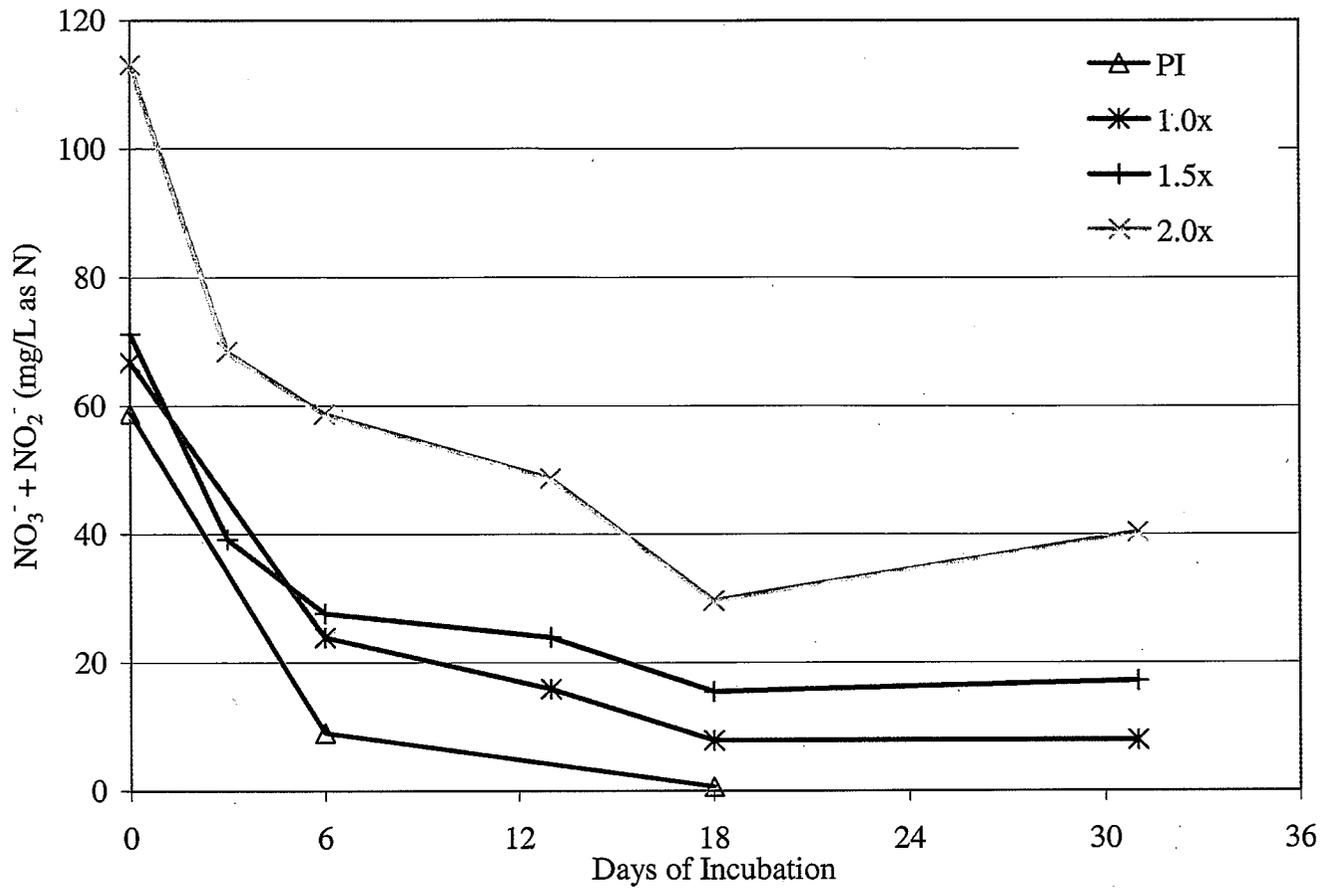


Figure 3. Nitrate+nitrite-N concentration during batch bioassays using evaporation-concentrated drainage. The PI solution was the unaltered drainage control for the 1x solution. Both waters had the same TDS concentration of 7.9 g/L. The greatest TDS concentration (2x) was 15.8 g/L.

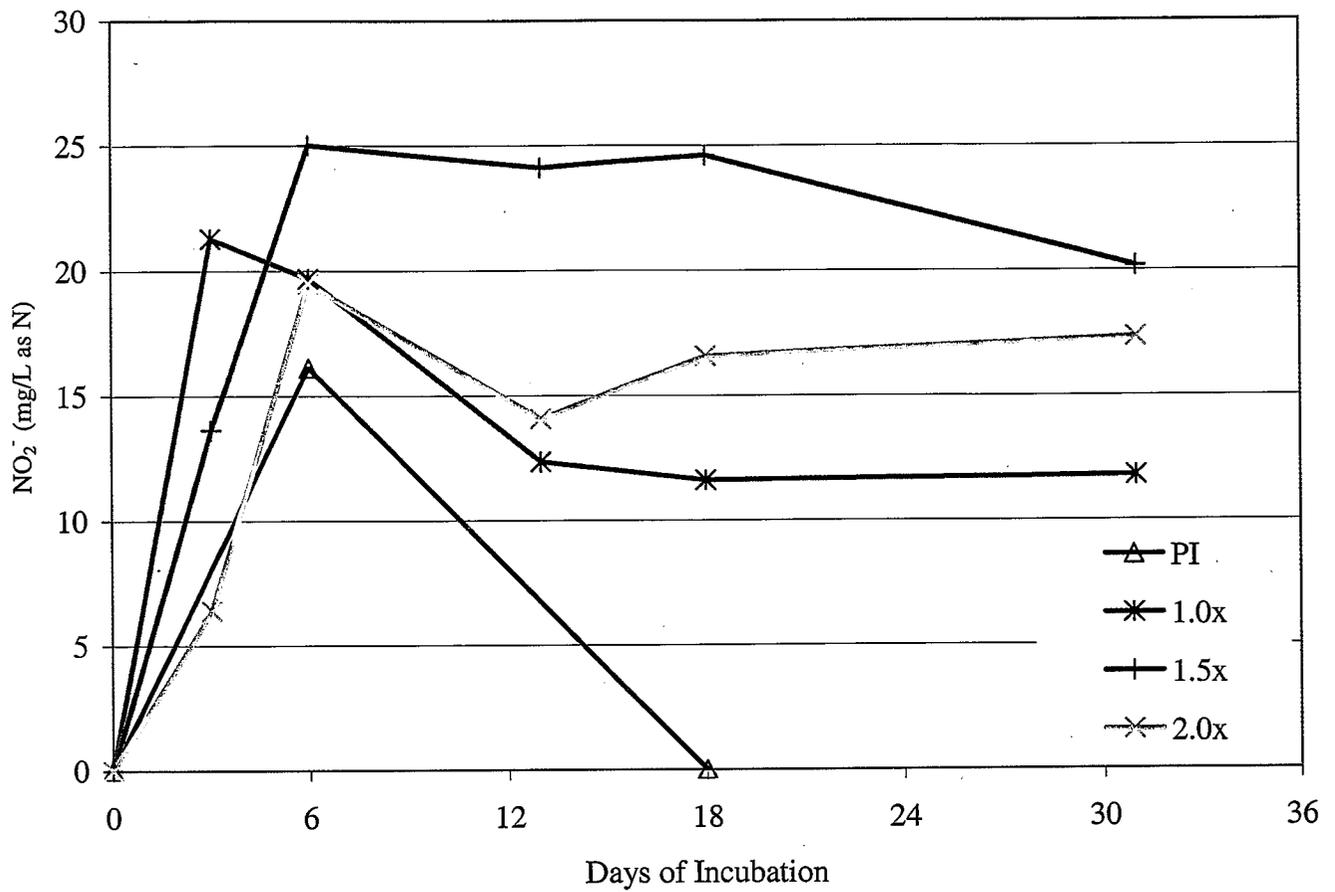


Figure 4. Nitrite-N concentration during batch bioassays using evaporation-concentrated drainage. The PI solution was the unaltered drainage control for the 1x solution. Both waters had the same TDS concentration of 7.9 g/L. The greatest TDS concentration (2x) was 15.8 g/L.

mg/L nitrate+nitrite as N. At both Day 18 and Day 31, the 100% (1.0x) treatment had still 7.9 mg/L as N of nitrate+nitrite remaining. At Day 31, the nitrate+nitrite concentration was about 17 mg/L as N for 150% (1.5x), and 40 mg/L for the 200% (2.0x) TDS concentration.

During the evaporation experiment, little nitrogen removal occurred in any of the treatments after Day 18. Nitrate concentrations and nitrite concentrations were tested for correlation with residual dissolved oxygen concentrations and turbidity. No correlation was found between nitrogen concentration and levels of dissolved oxygen, and there was no significant correlation between nitrogen removal and turbidity.

Complete nitrite removal occurred only the control, PI. In all other treatments, nitrite concentrations reached a plateau ranging from 20-25 mg/L as N for 1.5x to 12 mg/L as N for 1.0x (**Figure 4**).

Total soluble selenium removal was poor (0% to 10%) for 1.0x, 1.5x, and 2.0x. However, total soluble selenium decreased to near non-detectable levels by Day 18 for PI.

Volatile suspended solids (VSS), a measure of cell growth, increased from 17 mg/L initially to 43-48 mg/L in the evaporation treatments by Day 3 (**Figure 5**). Volatile solids then declined throughout the rest of the experiment. PI initially had a higher VSS concentration of 36 mg/L.

Only the 1.5x treatment had low pH in the Day 3 samples (pH 6.2-6.4). By Day 13, the 1.5x pH had increased to 6.9. In all other treatment samples, pH ranged from 6.6 to 7.7 over the course of the experiment.

SODIUM CHLORIDE ADDITION EXPERIMENT RESULTS

In the NaCl-addition experiment, denitrification proceeded at approximately the same rate for all four NaCl concentrations. Almost all nitrate and nitrite were removed from the drainage after 14 days (**Figures 6 and 7**). Less than 1 mg/L of total nitrate+nitrite remained after Day 14 of the experiment. Nitrite concentrations rose sharply on Day 3 due to the conversion of nitrate to nitrite (**Figure 7**). Nitrite concentrations then decreased sharply to Day 6. Further minor decreases of nitrite occurred until the end of the experiment on Day 14.

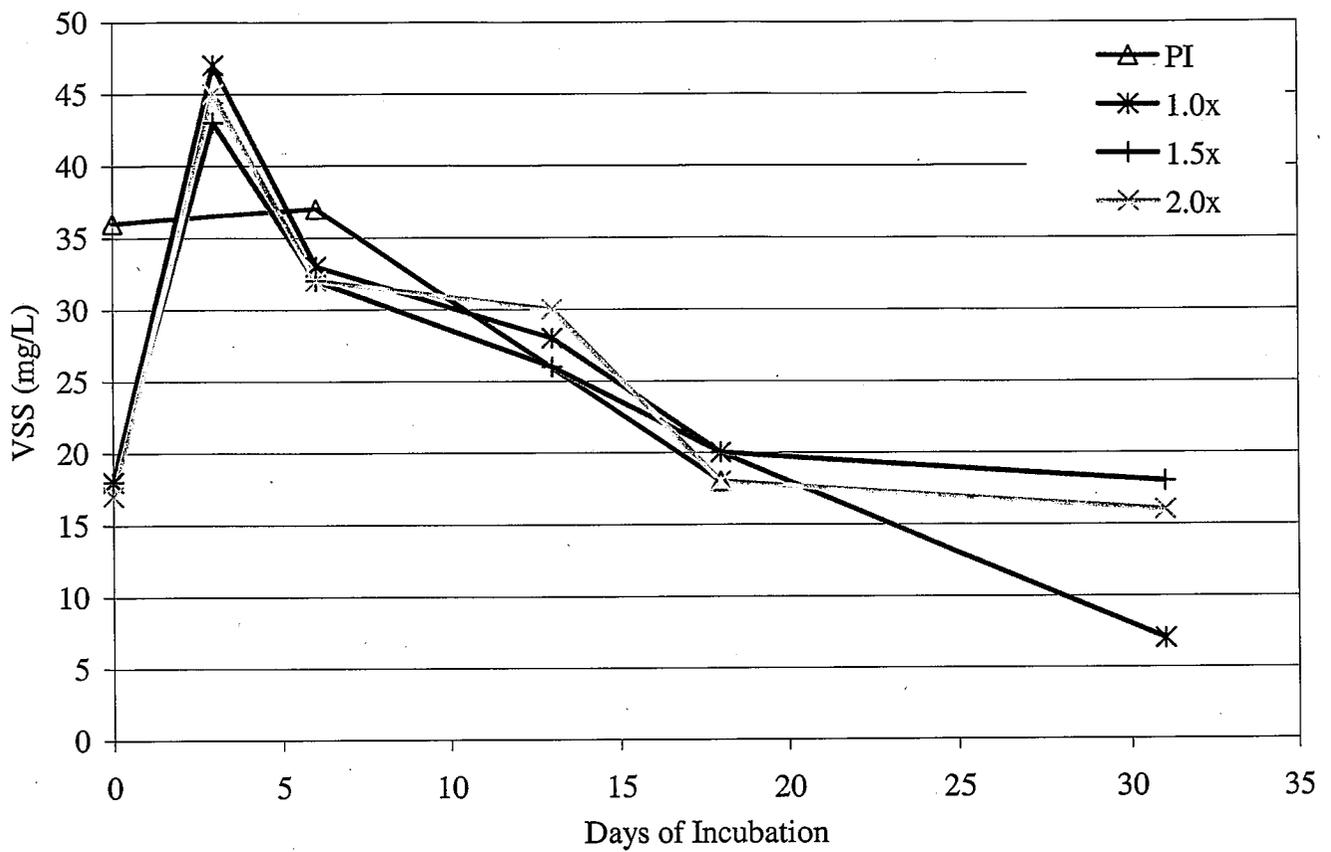


Figure 5. Volatile suspended solids concentration during batch bioassays using evaporation-concentrated drainage. The PI solution was the unaltered drainage control for the 1x solution. Both waters had the same TDS concentration of 7.9 g/L. The greatest TDS concentration (2x) was 15.8 g/L.

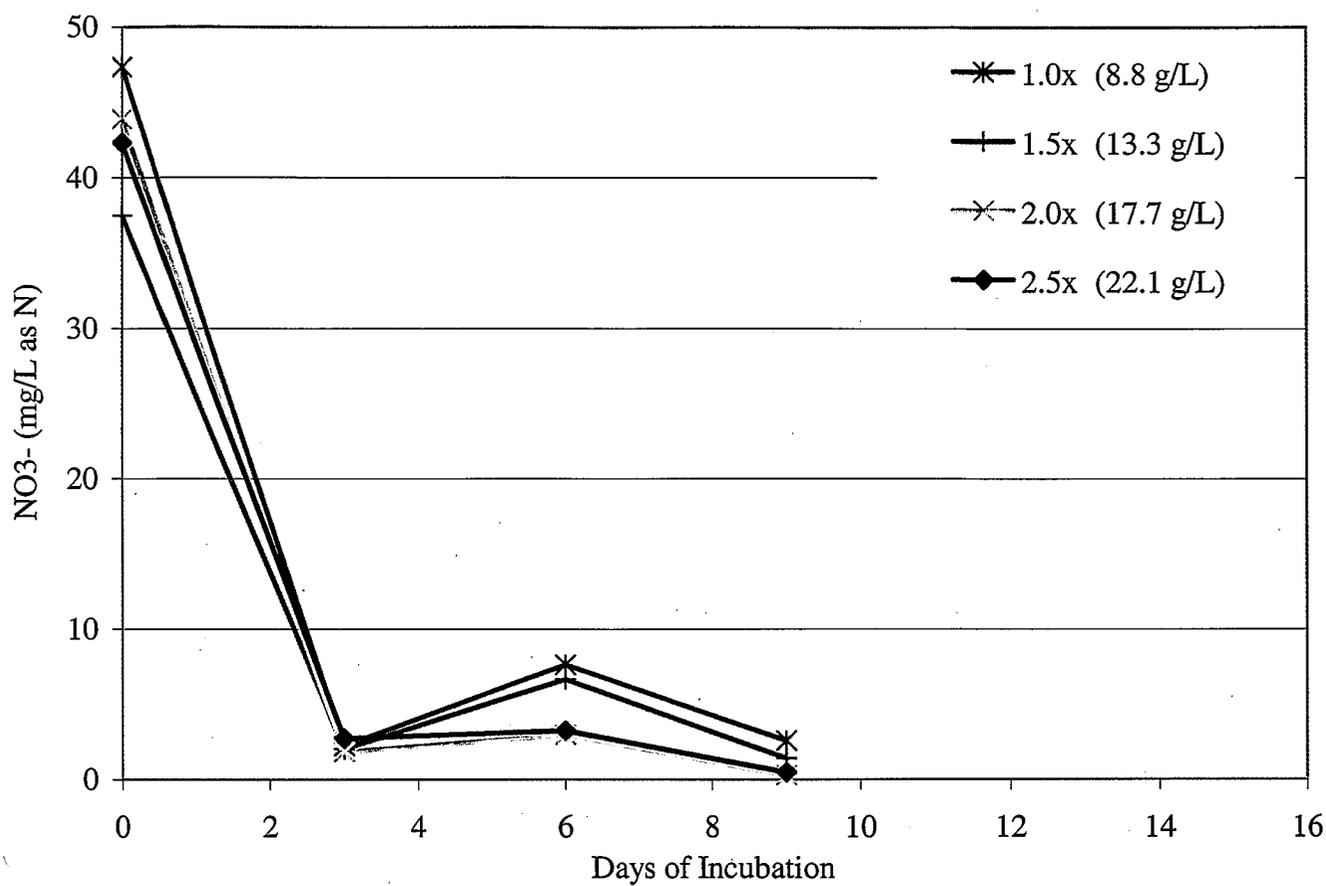


Figure 6. Nitrate-N concentration during batch bioassays with sodium chloride addition.

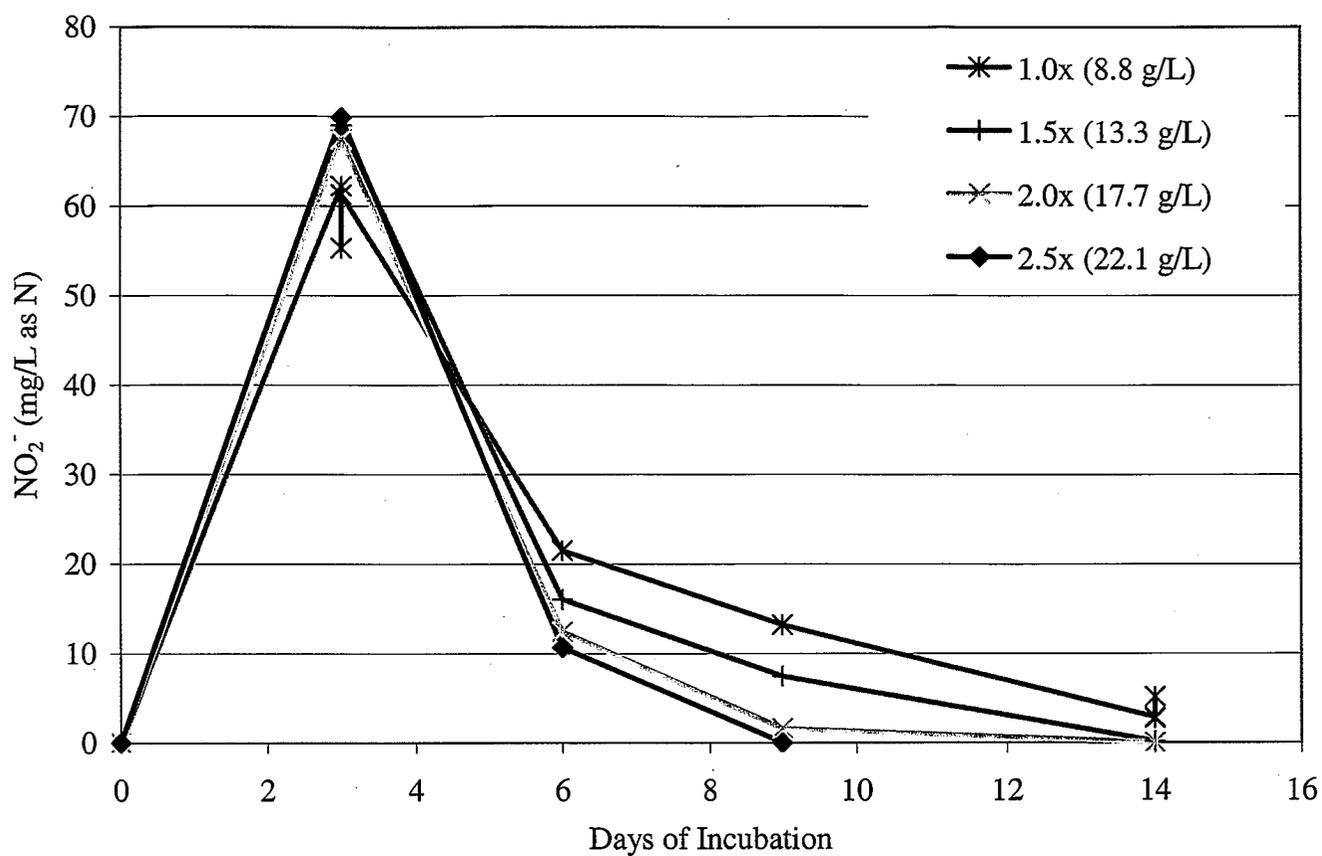


Figure 7. Nitrite-N concentration during batch bioassays with sodium chloride addition. The total dissolved solids (TDS) concentration of the unaltered drainage was 8.8 g/L. Multiple points are the results of replicate samples.

On Day 14, nitrite concentrations were essentially zero for salt concentrations of 1.5x, 2.0x, 2.5x, while there were still 2 mg/L of nitrite left in 1.0x drainage water.

Turbidity, indicating cell growth, increased from 80 NTU to 120-130 NTU by Day 3, as occurred in the evaporate bioassay. Following its initial peak, turbidity gradually declined in all treatments (**Figure 8**). The volatile suspended solids concentrations corresponding to the peak turbidity was 55-71 mg/L, an increase of 20-47 mg/L from Day 0 (**Figure 9**).

The initial non-volatile solids concentrations (i.e., suspended mineral particles) were likely related to the amount of NaCl added (**Figure 10**). This result indicates that some component of the reagent NaCl was not soluble or that some component promoted a precipitation in the drainage. The precipitates were captured on the analytical filters and were measured as non-volatile suspended solids. In future experiments, one should filter drainage treatments after reagent salts are added and before inoculation and incubation.

In statistical treatment of the data, the Tukey Honestly Significant Difference (HSD) test was used to test for whether the different nitrite concentrations on Day 14 were due to different salinities. The Tukey HSD test showed that the differences in nitrite concentration on Day 14 were not significantly related to the different salt concentrations, at 95% confidence. The Tukey HSD test also showed that differences in nitrate+nitrite, dissolved oxygen, and turbidity measurements were not due to salt, at 95% confidence level. In other words, we can be 95% confident that nitrate+nitrite concentrations, dissolved oxygen, and turbidity did not differ significantly between the four different salt concentrations in the NaCl-addition experiment.

During the NaCl-addition experiment, total soluble selenium concentration decreased from 300 $\mu\text{g/L}$ to 50-70 $\mu\text{g/L}$ on Day 6 (**Figure 11**). A delay of three to six days before selenium reduction began coincided with the reduction of nitrate+nitrite to $<20 \text{ mg/L}$ as N. After Day 6, total soluble selenium did not change significantly through Day 14 indicating that either an inhibitory substance had accumulated in the bottles or that the readily available electron acceptors were completely consumed.

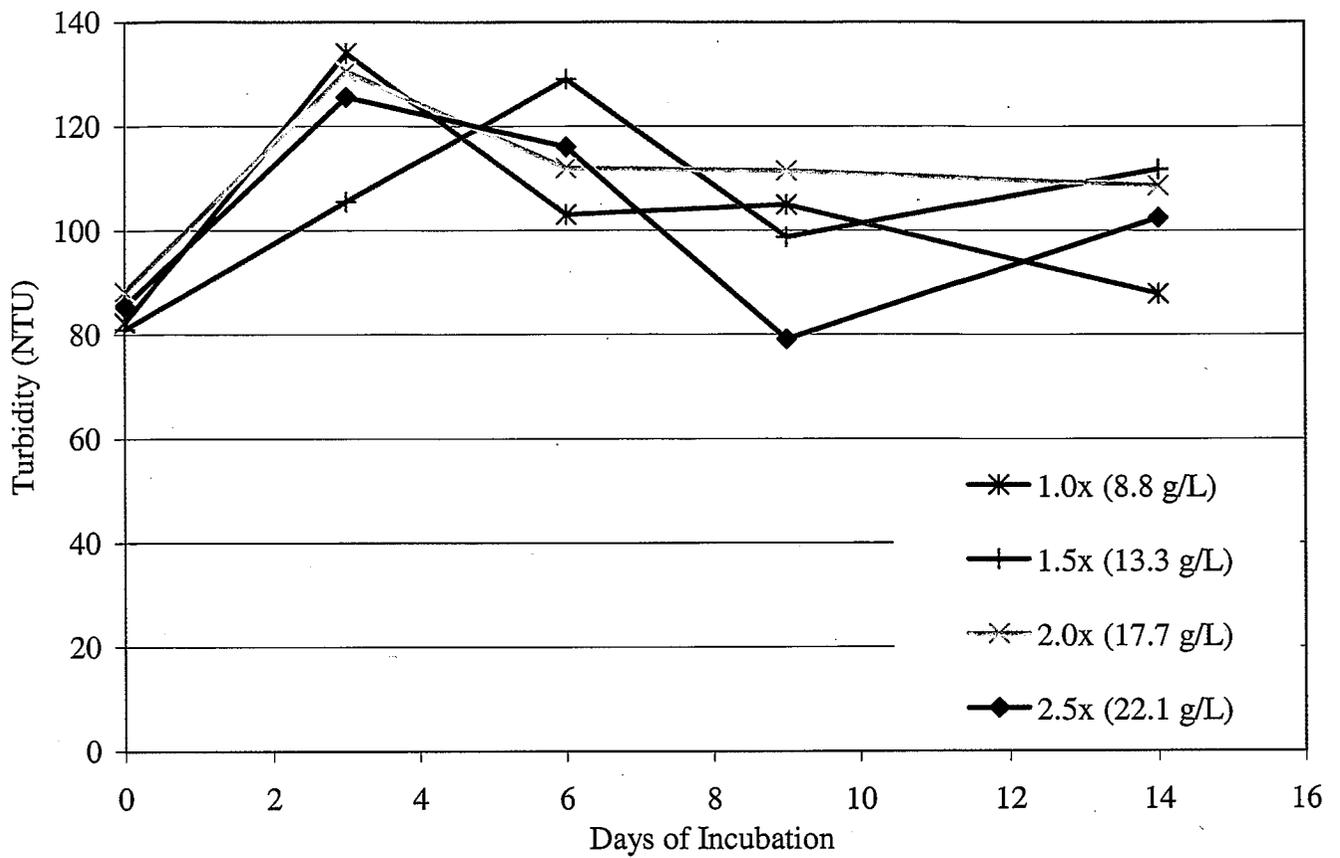


Figure 8. Turbidity (a measure of cell growth) during batch bioassays with sodium chloride addition. Most bacterial cell growth appears to have occurred by Day 3. The total dissolved solids (TDS) concentration of the unaltered drainage was 8.8 g/L.

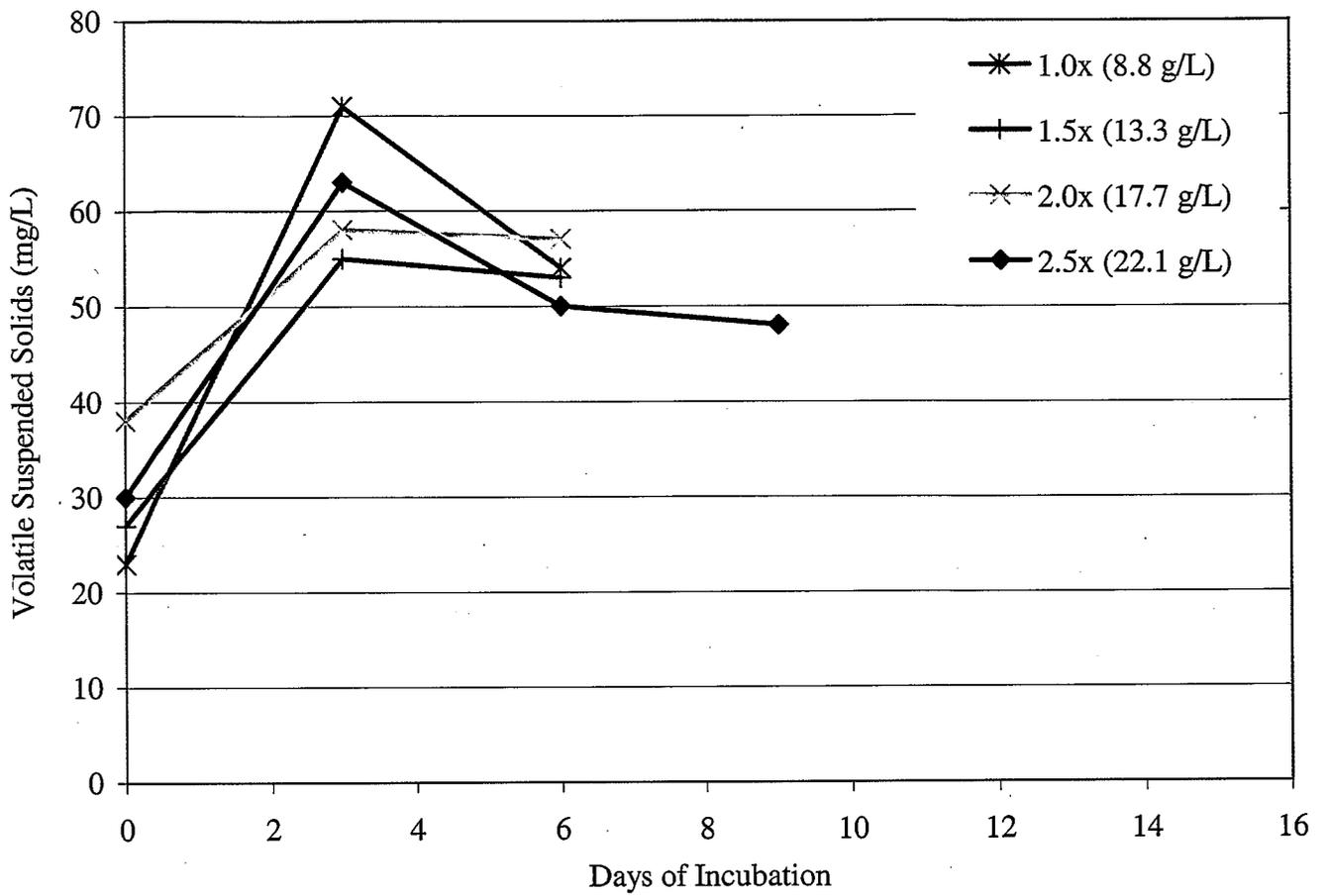


Figure 9. Volatile suspended solids concentration during batch bioassays with sodium chloride addition.

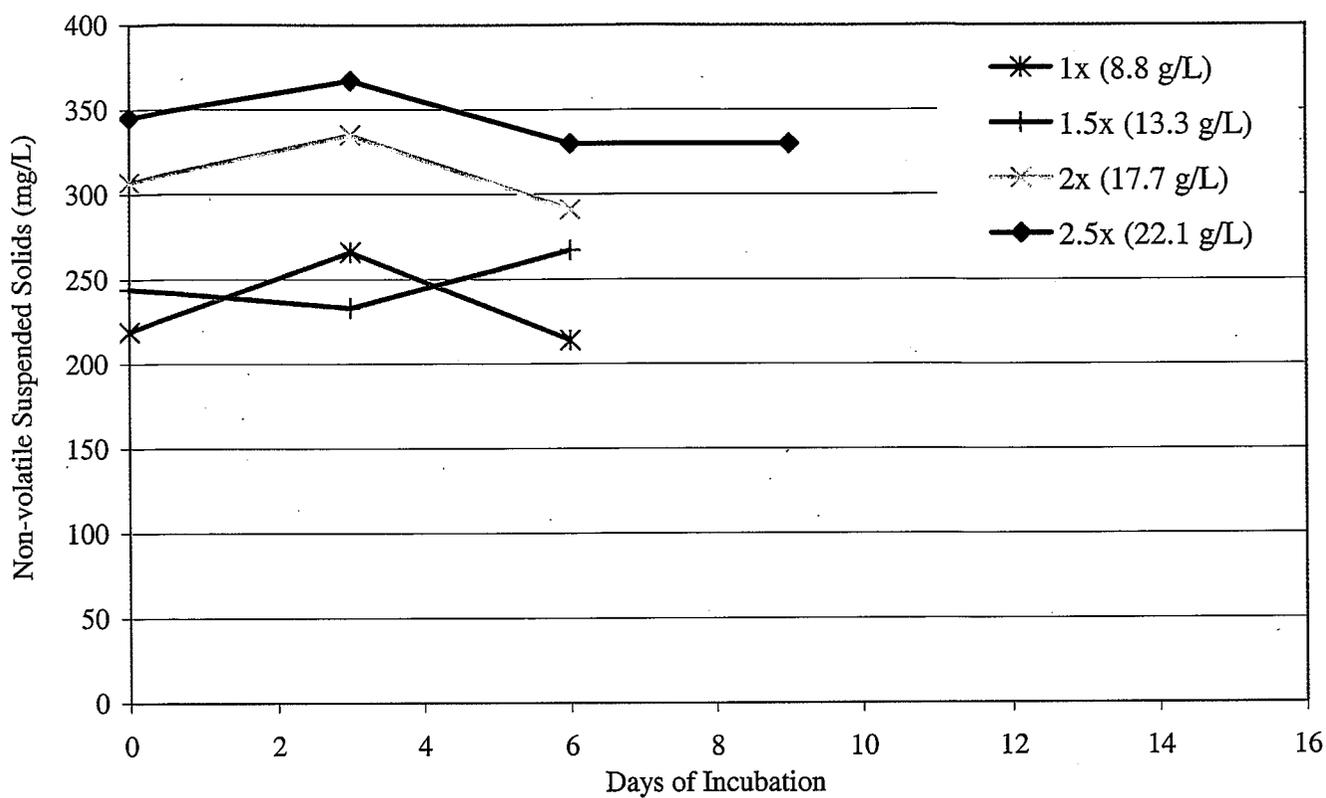


Figure 10. Non-volatile suspended solids concentration during batch bioassays with sodium chloride addition. The initial difference among the treatments indicates that the NaCl used contained NVSS or caused precipitation of mineral on Day 0.

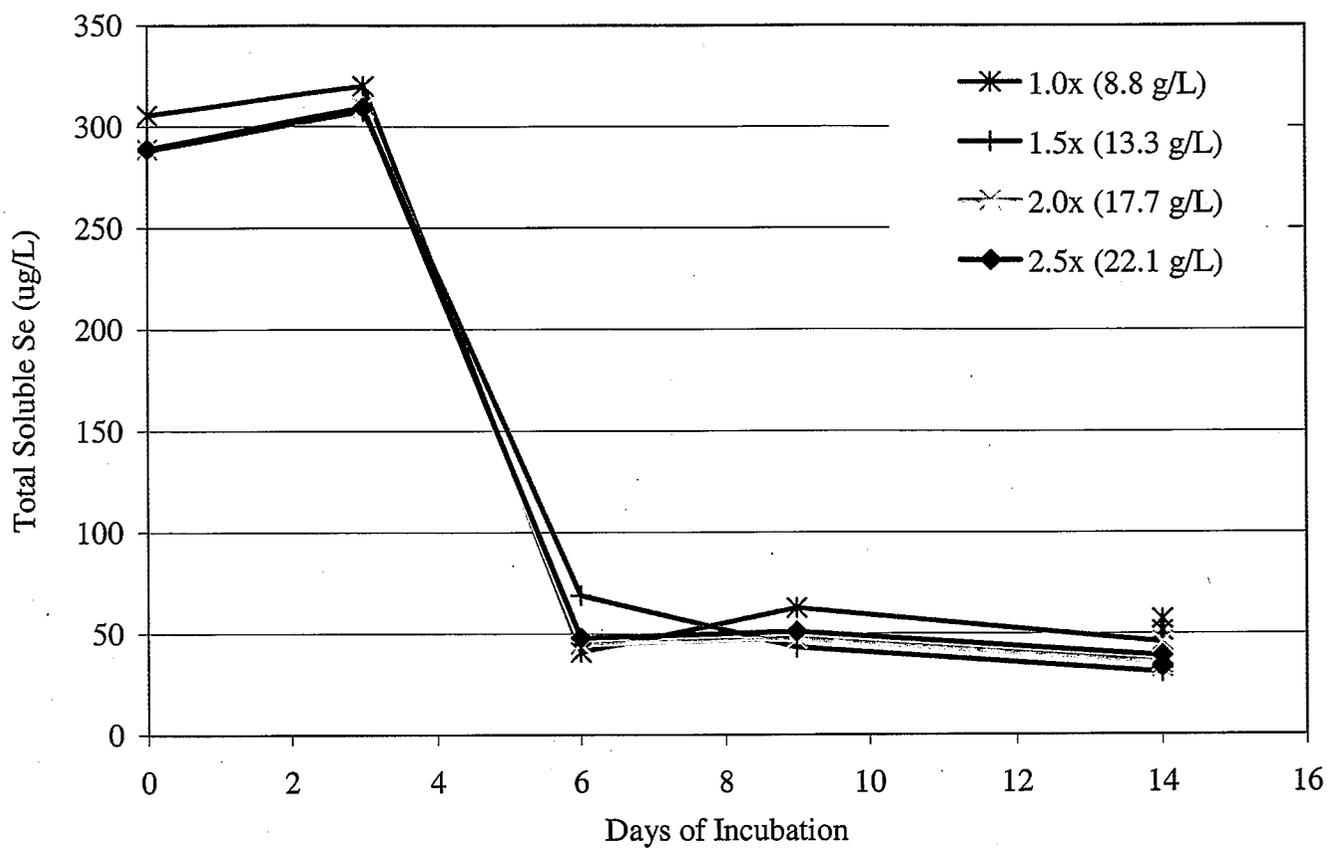


Figure 11. Total soluble Se concentration during batch bioassays with sodium chloride addition. Multiple points on Day 14 are the results of replicate samples.

Figure 12 shows that initial selenite production (Day 3) was in inverse proportion to the NaCl concentration with the 1.0x treatment producing twice as much selenite as the 2.5x treatment. After Day 6, selenite-Se concentrations leveled at 7 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in all treatments except the control (1.0x) which retained 25 $\mu\text{g/L}$ to 30 $\mu\text{g/L}$ of selenite-Se. Presumably, this accumulated selenite was the portion formed during the reduction of selenate that was not subsequently reduced to elemental, organic, or polysulfide Se. As total soluble selenium decreased 250 $\mu\text{g/L}$ (**Figure 11**), selenite was observed to increase from <1 $\mu\text{g/L}$ to ~ 10 $\mu\text{g/L}$ indicating that the difference, approximately 240 $\mu\text{g/L}$ Se, was converted from selenate to insoluble forms such as elemental Se, organic Se, or seleno-polysulfides. Selenate (analytically defined as total soluble Se minus selenite) decreased throughout the incubation with all treatments decreasing to <50 $\mu\text{g/L}$ Se by Day 9 (**Figure 13**). Accordingly, salinity was shown to have no direct influence on the reduction potential within the varying samples.

DISCUSSION OF BRINE EXPERIMENTS

In past studies, increased salinity levels have been shown to decrease the metabolism of certain bacteria including certain facultative heterotrophs. Rael and Frankenberger (1994) found that elevated salt concentrations decreased the specific growth rate of the Se-volatilizing bacteria *A. Veronii*. In another study, Dincer and Kargi (1999) found that nitrification and denitrification of saline wastewater ($>2\%$ salt) resulted in low treatment efficiencies because of plasmolysis or loss of activity of organisms in the presence of salt. In our study, however, salt concentrations up to 250% of the initial 8.8 g/L TDS concentration in the drainage had no effect on the removal of total soluble selenium, selenite, or nitrate. Among the salt concentrations tested, there was little variation in the rate or total amount of nitrate and selenium reduced.

In the NaCl-addition experiment, despite no addition of nitrate, the initial nitrate-N concentrations on Day 0 ranged from 38 mg/L to 48 mg/L. These initial differences must be attributed to measurement errors, although the QA/QC results met the required recoveries in the initial and subsequent analyses. For all four salt concentrations, denitrification occurred

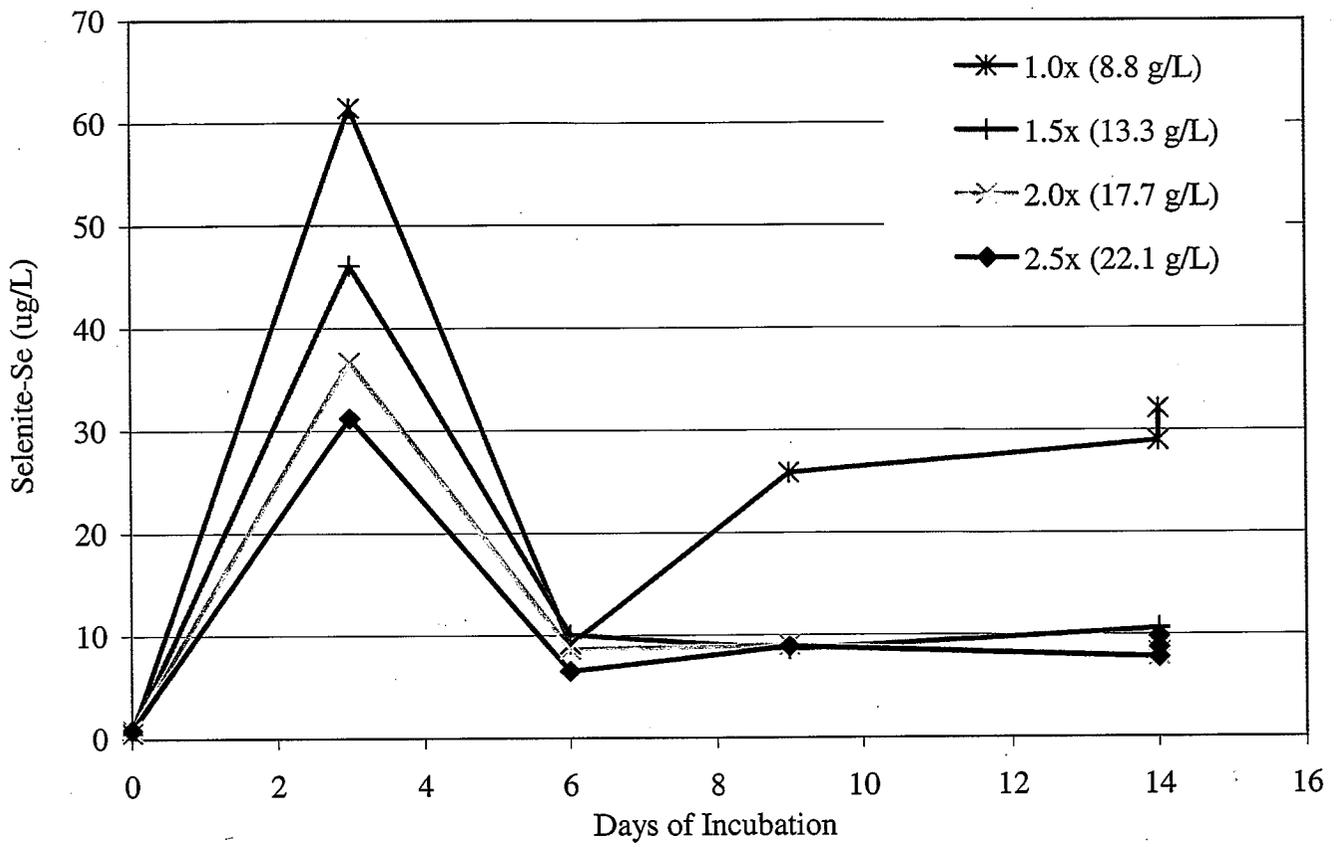


Figure 12. Selenite-Se concentration during batch bioassays with sodium chloride addition.

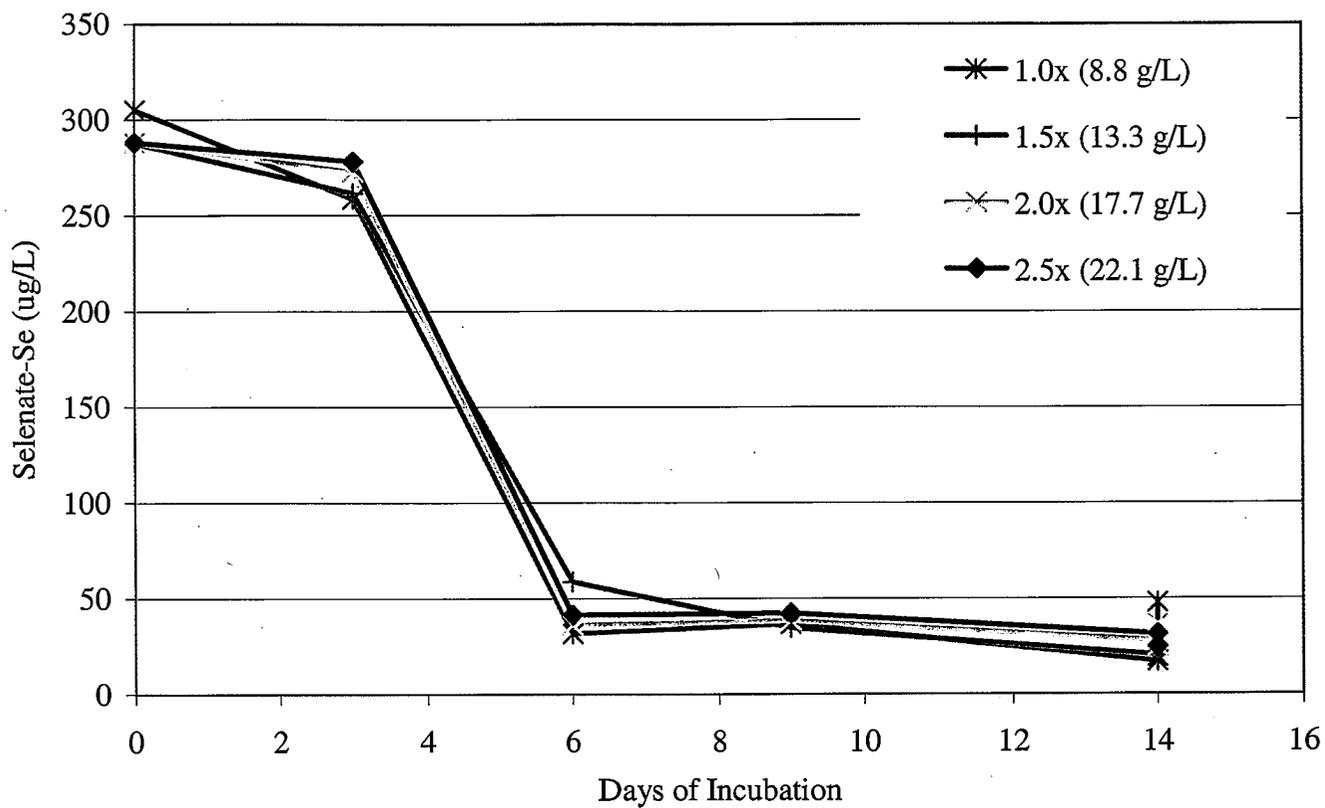


Figure 13. Selenate-Se concentration during batch bioassays with sodium chloride addition. The total dissolved solids (TDS) concentration of the unaltered drainage was 8.8 g/L. The multiple points on Day 14 are the results of replicate samples.

at similar rates over the 14 days of the experiment. By Day 3, nitrate concentrations were <3 mg/L as N, although further subsequent reduction was not clearly seen. The Tukey HSD test provided further evidence that different salt concentration had no significant effect on bacterial denitrification in the NaCl-addition experiment.

This result suggests that the ABSR Process can be used to treat high salty drainage water. However, we can only be confident that nitrogen removal by bacteria will not be hindered by salt at salt concentrations of up to 22 g/L which is about twice as high as the secondary drainage produced at Red Rock Ranch, but less than the 60 g/L that might be produced from an RO plant treating 9 g/L TDS drainage while operating at 85% recovery. Recoveries of 85% have been difficult to sustain at San Joaquin Valley drainage RO pilot plants.

Batch experiments of the type described above may not simulate phenomena that will occur in a series of Reduction Ponds units in which the anoxic microbial flora develops over time. The results shown do provide confidence that successful denitrification and selenium reduction will occur in brines.

It is expected that our forthcoming studies will provide nitrate and selenium level of <2 mg/L and <10 μ g/L, respectively. Such removal might permit direct discharge to the upper Bay near Carquines Strait and eliminate discharge of brines to the San Joaquin River or the operation of evaporation systems in the San Joaquin Valley.

BIOLOGICAL REDUCTION EXPERIMENTS AT THE ABSR FACILITY

OPERATION OF THE ABSR FACILITY

Evaluation of two modes of operation continued at the PDD Facility during this project—the South System was operated in Mode 1 (described above) and the North in Mode 2. The modes are described in “*ABSR Modes of Operation*” section above.

The Mode 2 System was operated to expand the previously tested range of flow and substrate dose, and the Mode 1 System was operated at previously tested flow rates, but under different temperature and algae loading levels.

Drainage Flow

The influent source was the tile drainage sump, PDD Discharge Point 25. At approximately 15-minute intervals a float switch activated a sump pump which discharged drainage water into a waste ditch. A portion of the pumped flow was shunted into an 8,000-gal (30-m³) black, plastic tank with a closed top. This tank provided constant head flow for the ABSR Facility. The constant head tank fed the influent splitter box through a 3-in (76-mm) pipe. Two V-notch weirs in the influent splitter box divided the flow between the North and South ABSR Systems. The V-notch weirs were marked at 5-mm intervals, and a flow vs. gage height curve was developed. One or two times per weekday, PDD personnel recorded the influent gage reading and adjusted the flow as needed to achieve the target flow. Periodically the V-notch calibration was checked using a bucket and stopwatch. RP effluent flows were typically measured weekly using a 20-L pail and stopwatch.

Two different influent flow rates to the Mode 2 North ABSR System were used during the study period—54 m³/d from September 2001 through August 2002 and 72.3 m³/d in September and October 2002 (**Figure 14**). These steps provided RP hydraulic residence times (HRT) of 14.0 d and 10.5 d. The year-long operation at 14.0-days HRT was needed in order to eliminate flow as a variable. Instead, the variables were seasonal temperature, influent selenium and nitrate concentrations, and molasses dose. Fourteen days was chosen so that comparisons could be made to data from previous years when that HRT was used but for which the molasses doses were lower.

The Mode 1 South ABSR System was also operated with two flows—12 m³/d and 19 m³/d (**Figure 15**) corresponding to HRTs of 63 and 40 days, respectively. The Mode 1 System was off-line for 2 months beginning in early December 2001 due to a malfunctioning pump. Both Systems received a large, one-day spike of flow in early October 2001 due to a broken valve.

Substrates Used for Denitrification and Selenium Reduction

Animal feed-grade molasses (**Table 2**) was used as the carbon and energy substrate

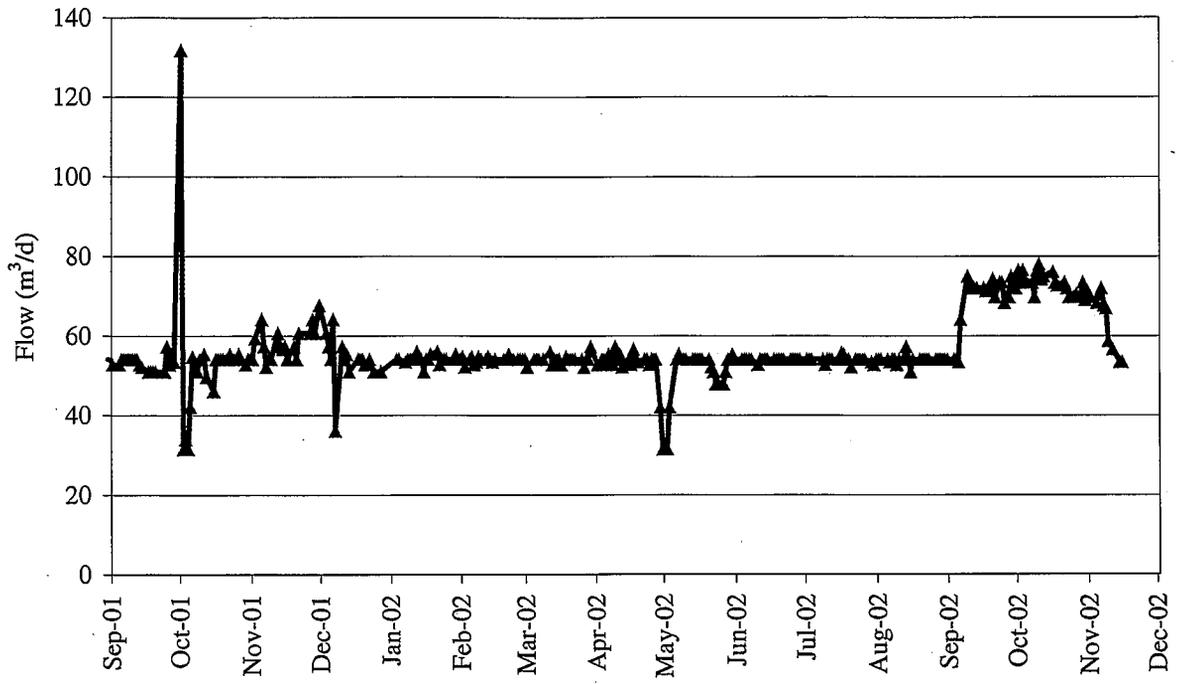


Figure 14. Mean daily influent flow to the Mode 2 North Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

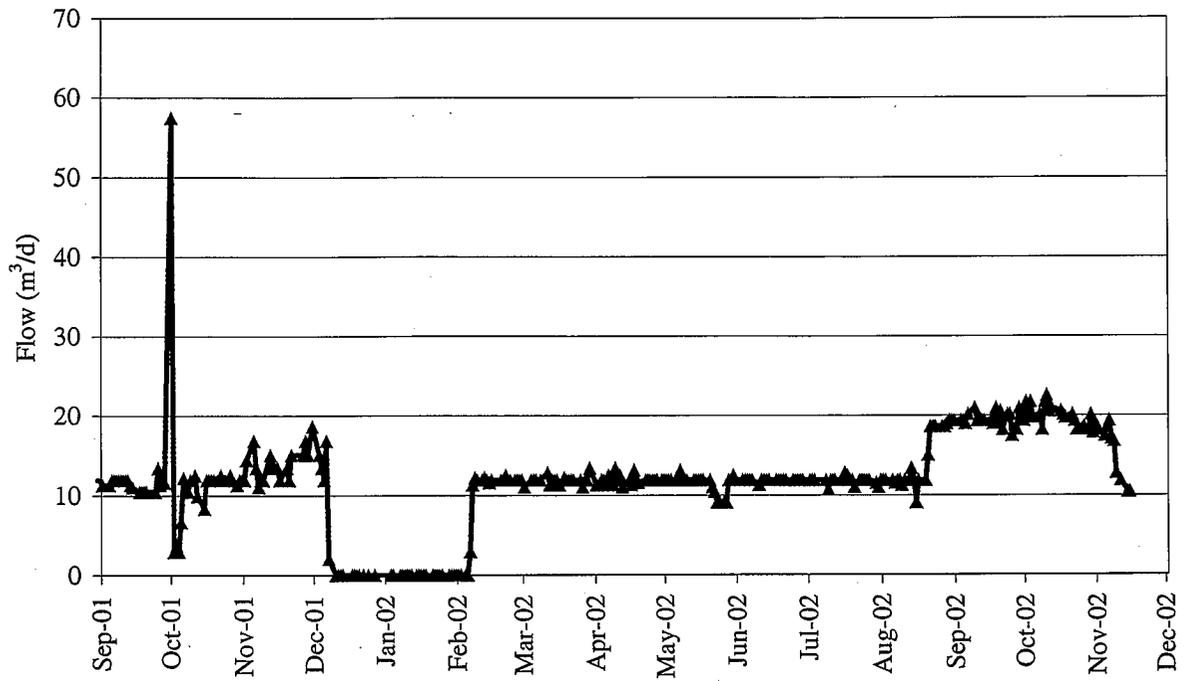


Figure 15. Mean daily influent flow to the Mode 1 South Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

in the North ABSR System. The molasses was supplied by Foster Farms, Turlock, California. Foster Farms is a distributor of Westway Trading Corporation of Stockton, California (cane feeding molasses, brix 76% min., moisture 27% max., sugar (TSI) 48% min.). Every weekday, the quantity of molasses needed to achieve the desired dose for the day's flow was added to the influent weir box of the North ABSR. To provide for the weekends, on Fridays and Mondays, two days' quantity of molasses was added by PDD personnel. A similar approach was taken for 3 or 4-day holidays.

Microalgae grown in the South HRP served as bacterial substrate in the South RP. The algae-rich HRP effluent was pumped to the RP where a great majority of the algae settled, eventually to decompose and provide carbon and energy to denitrifying and selenium reducing bacteria.

High Rate Pond Operations

In the Mode 1 South System, influent tile drainage water was the medium for algae growth. The inorganic carbon source for algal growth was bicarbonate in the drainage influent and atmospheric carbon dioxide which dissolved in the alkaline HRP water (pH 8.4 to 10.4). Influent drainage provided abundant nitrogen and trace amounts of phosphorus and iron.

The Mode 2 North System, the HRP influent was the RP effluent which was rich in dissolved carbon dioxide, phosphorus, and iron from decomposing molasses and algae.

RESULTS AND DISCUSSION

Mode 2 North System: As in past years, the selenate removal performance followed a seasonal pattern apparently related to water temperature. Although December 2001 and January 2002 were the coldest months of the year, selenate removal was the poorest later during the warmer months of February and March. Failure to respond rapidly to warm temperature was also observed in past years (Oswald *et al.*, 2002). While the 2 to 3 week lag of the residence time of the water in the RP may partially explain this phenomenon, the full

explanation will continue to be sought during planned continuing studies.

During April through July 2002, while influent selenate-Se concentrations ranged from 200-300 $\mu\text{g/L}$ and the molasses dose averaged 0.44 g/L, the Mode 2 ABSR System removed 69% of influent selenate (**Figure 16**). During August through October 2002, influent selenate increased sharply to 600 $\mu\text{g/L}$ and then varied from near 200 $\mu\text{g/L}$ to 600 $\mu\text{g/L}$. With the more concentrated influent, selenate removal increased to 76%. The molasses dose, 0.42 g/L, during this time was similar to the earlier period, suggesting that the improved removal was due to the increased influent selenium concentration and the first-order nature of selenate reduction.

From September 1, 2001 to September 8, 2002, the influent flow to the Mode 2 RP was 54 m^3/day giving a HRT of 14 days. From September 9, 2002 through November 6, 2002 the flow was increased to 72.4 m^3/day giving a HRT of 10.5 days. This lower HRT did not appear to decrease selenate removal during the rest of September, but an effluent peak did occur in October. On average in September through October 2002, total soluble selenium removal was 361 $\mu\text{g/L}$ indicating 80% removal.

A first-order decay constant, k , for selenate can be calculated assuming that the RP is a completely mixed flow reactor (CMFR). Although the RPs are not completely mixed (Lundquist *et al.*, 1999), if one assumes that the mixing regimes in the ponds are constant, the CMFR decay constant provides a means to compare current and past results. For September through October 2002, the decay constant was $[(450 \mu\text{g/L} \div 89 \mu\text{g/L}) - 1] \div 10.5 \text{ days} = 0.39$ per day. This decay rate is the highest achieved at the ABSR Facility (Oswald *et al.*, 2002). The daily selenate mass removal rate of 26 g/d (34 $\text{mg}/\text{m}^3/\text{d}$) was also the highest measured, while the selenate-Se removal efficiency of 0.85 g Se/kg molasses added was approximately the 80th percentile of efficiencies measured during 1998 through 2002.

An earlier test of an 11-day HRT was performed in June and July 2000. In that period, the molasses dose was 0.19 g/L, and selenate removal averaged 195 $\mu\text{g/L}$ (59% removal; $k=0.13$). Temperatures in both periods varied about 20°C, so it appears that the Reduction Pond can be operated at shorter hydraulic residence times if the organic substrate

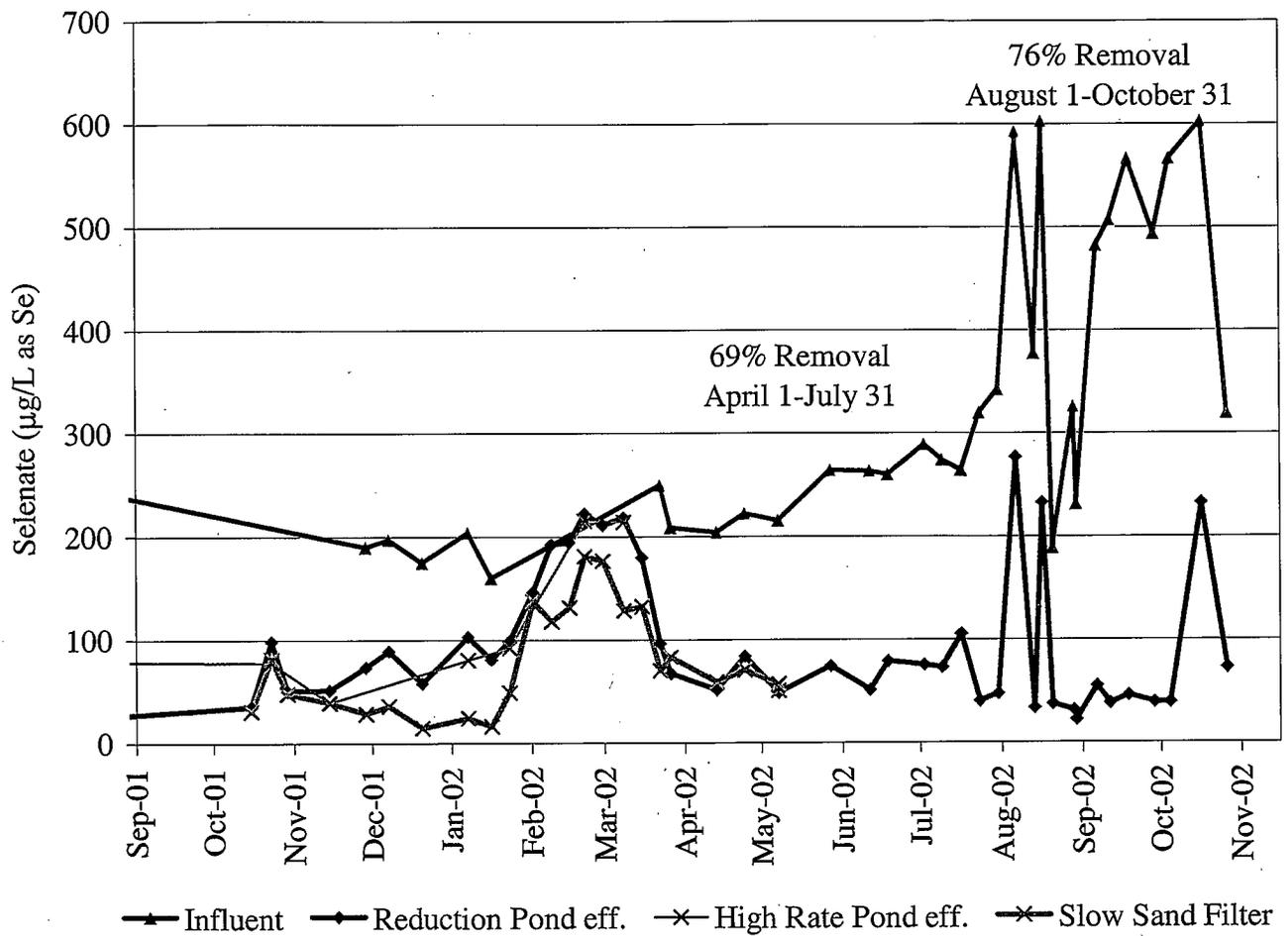


Figure 16. Selenate-Se concentrations in the Mode 2 North Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

dose (molasses, in this case) is increased.

Soluble selenite concentration was $<1 \mu\text{g/L}$ in the influent, as is normal for drainage (Figure 17). The reducing environment of the RP caused an increase of selenite to between $4 \mu\text{g/L}$ and $58 \mu\text{g/L}$. One outlying measurement was $90 \mu\text{g/L}$, but the average concentration was $21 \mu\text{g/L}$. A majority of this selenite can be removed during ferric chloride coagulation and particle removal, as described in the *Pilot-Scale Particulate Selenium Removal* section.

The purpose of the shallow, algae-rich Mode 2 HRP, which was operated through April 2002, was to remove residual biochemical oxygen demand and ammonia in the RP effluent. However, the HRP also caused soluble selenite to increase by as much as $40 \mu\text{g/L}$. This increase may be due to selenite desorbing from particles or by reoxidation of elemental Se, as discussed in the *Brine Treatment* section of this report.

An even more dramatic soluble selenite increase occurred at times in the slow sand filter which also received RP effluent. Spikes as high as $115 \mu\text{g/L}$ selenite-Se occurred suggesting that particulate selenium trapped in the filter was solubilized. During December 2001, however, selenite was removed by the slow sand filter, but during the months proceeding and following December, selenite appear in the effluent of the filter apparently due to reoxidation of particulate selenium trapped in the filter. The October-November 2001 spike in selenite concentration might be explained by the low RP molasses dose provided just prior— 0.22 g/L (g molasses per L influent drainage) during September and 0.19 g/L during October. In November and December 2001, the molasses dose was increased to 0.44 g/L . In January and February 2002, the molasses dose was further increased to 0.53 g/L , and yet the selenite concentration in the slow sand filter effluent continued to increase until April. The molasses doses in March and April were 0.46 g/L . Thus, there is not a simple correlation between molasses dose to the RP and selenite production by the slow sand filter. Instead, the selenite release may be a more complex function of temperature, particulate Se build-up in the filter, and residual BOD in the RP effluent.

Mode 1 South ABSR System: The Mode 1 System, which was not dosed with molasses, removed an average of 53% of influent selenate-Se (Figure 18) during the warm

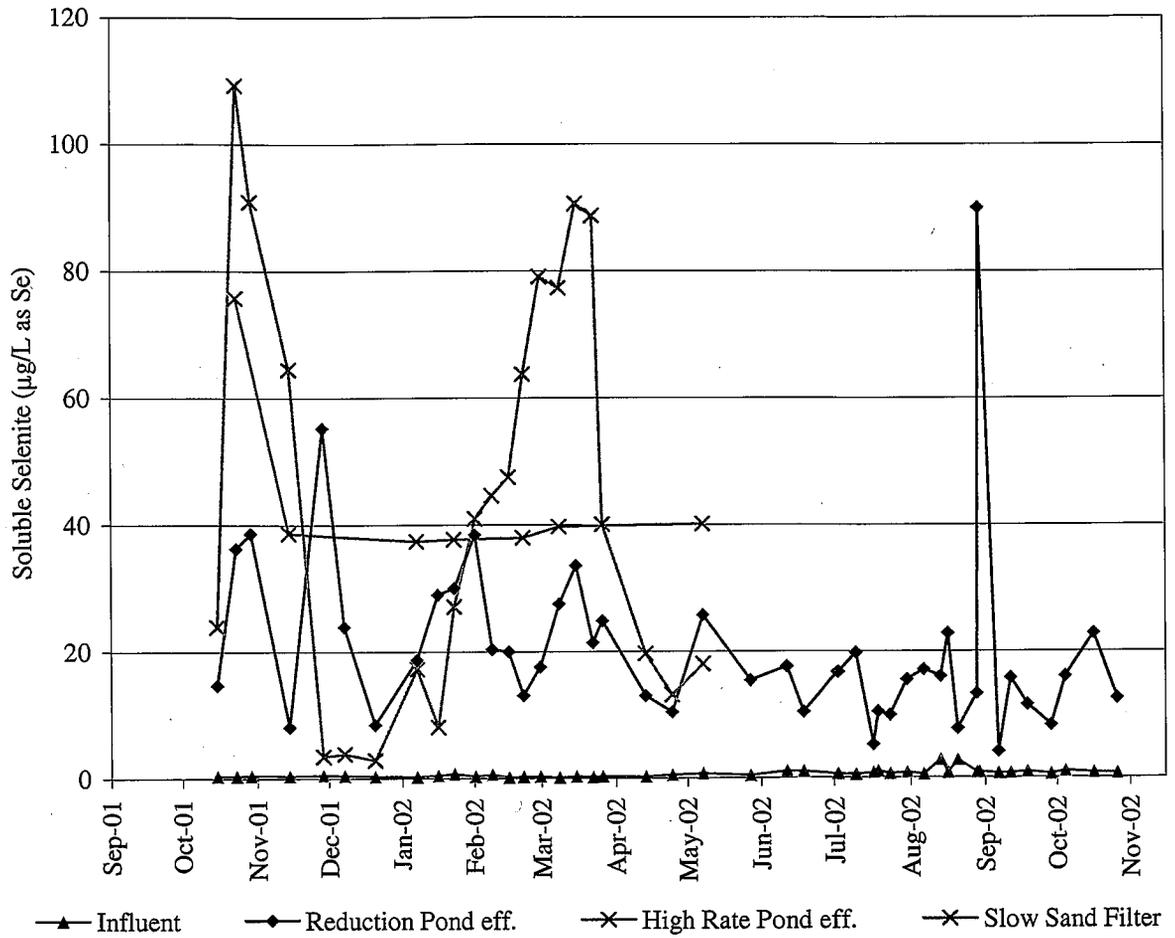


Figure 17. Soluble selenite-Se concentrations in the Mode 2 North Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

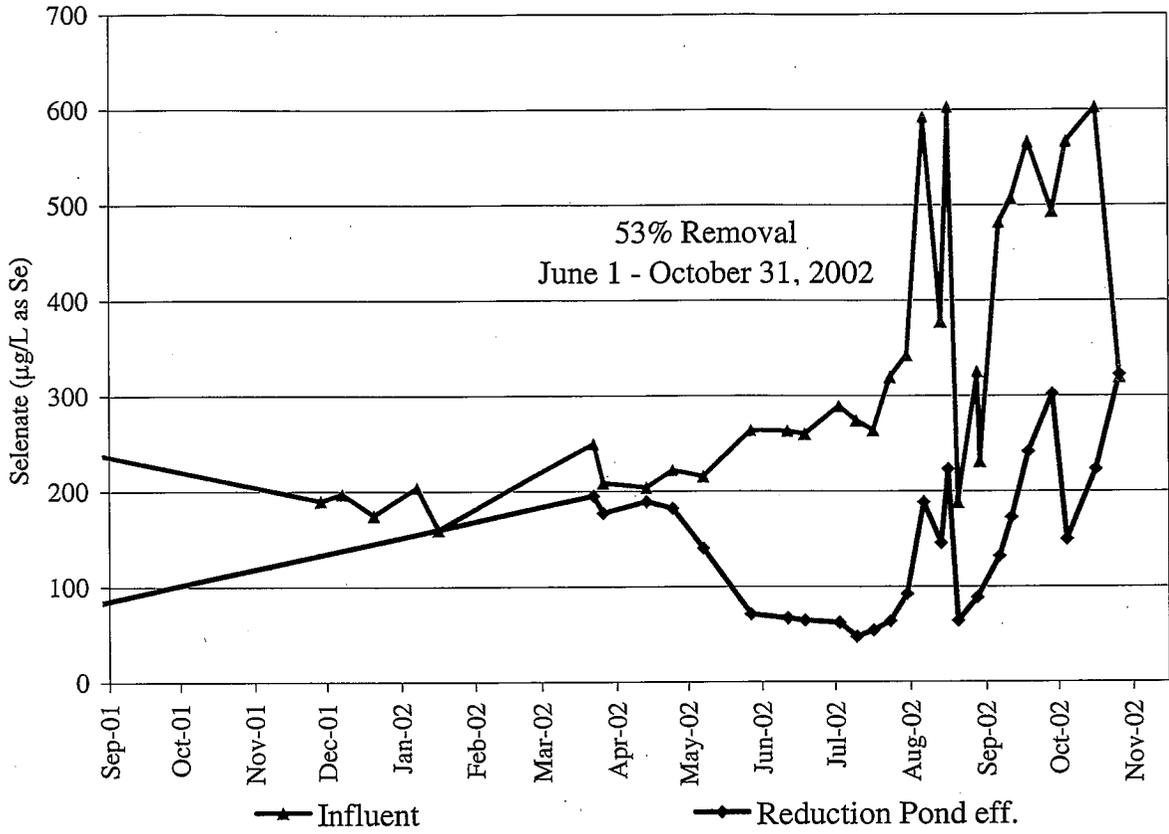


Figure 18. Selenate-Se concentrations in the Mode 1 South Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

weather of June through October 2002. This performance was comparable to past summers which had removals ranging from 31% to 64% (Lundquist *et al.*, 1999; Oswald *et al.*, 2002).

The poor selenate removal performance (<10%) during the cooler months, generally November through April, is also typical of the Mode 1 system. The Mode 1 system relies on the degradation of algae settled in the RP to provide organic substrate for selenate reducing bacteria. The results indicate that cool weather slows this degradation sufficiently to halt selenate reduction. The water clarity through the process is shown in **Photograph 4**. The profuse algal growth in the HRP, and its subsequent efficient settling in the RP are evident in the photograph.

While influent selenite concentration was <1 $\mu\text{g/L}$, levels in the Mode 1 High Rate Pond (HRP) ranged from 10 to 69 $\mu\text{g/L}$ (**Figure 19**). Apparently, some selenate was reduced to selenite in the HRP despite its primarily aerobic nature. The HRP floor was covered with 1 to 15 cm of settled algae, and some of the deeper, consolidated sediments had a sulfide odor and were black indicating metal sulfide precipitates. It is likely that the selenite was produced from selenate in these highly anoxic, unmixed sediments.

Future Work: The Reduction Ponds of the existing ABSR Facility are at most 10 feet deep and have floating plastic covers intended to lessen oxygenation by photosynthesis and wind mixing. Unfortunately, the shallow depth and a peripheral gap around their covers makes these Reduction Ponds less than ideal models of planned full-scale Reduction Ponds since their structural deficiencies provide opportunities for dissolved oxygen to intrude into the intended anoxic zones during windy periods disrupting anoxic treatment. The Intermediate-Scale ABSR Facility, to be constructed during summer 2004, will better model full-scale Facilities. The 20-ft. depth of the planned Reduction Ponds, plus their internal cells and baffles, should prevent destratification and oxygen intrusion into their reduction zones and thereby improve treatment performance.



Photograph 4. Mode 1 South ABSR System influent (left), High Rate Pond effluent (center), and Reduction Pond effluent (right) in September 2002. No chemicals were used during the process, and algae removal was achieved only by sedimentation in the Reduction Pond.

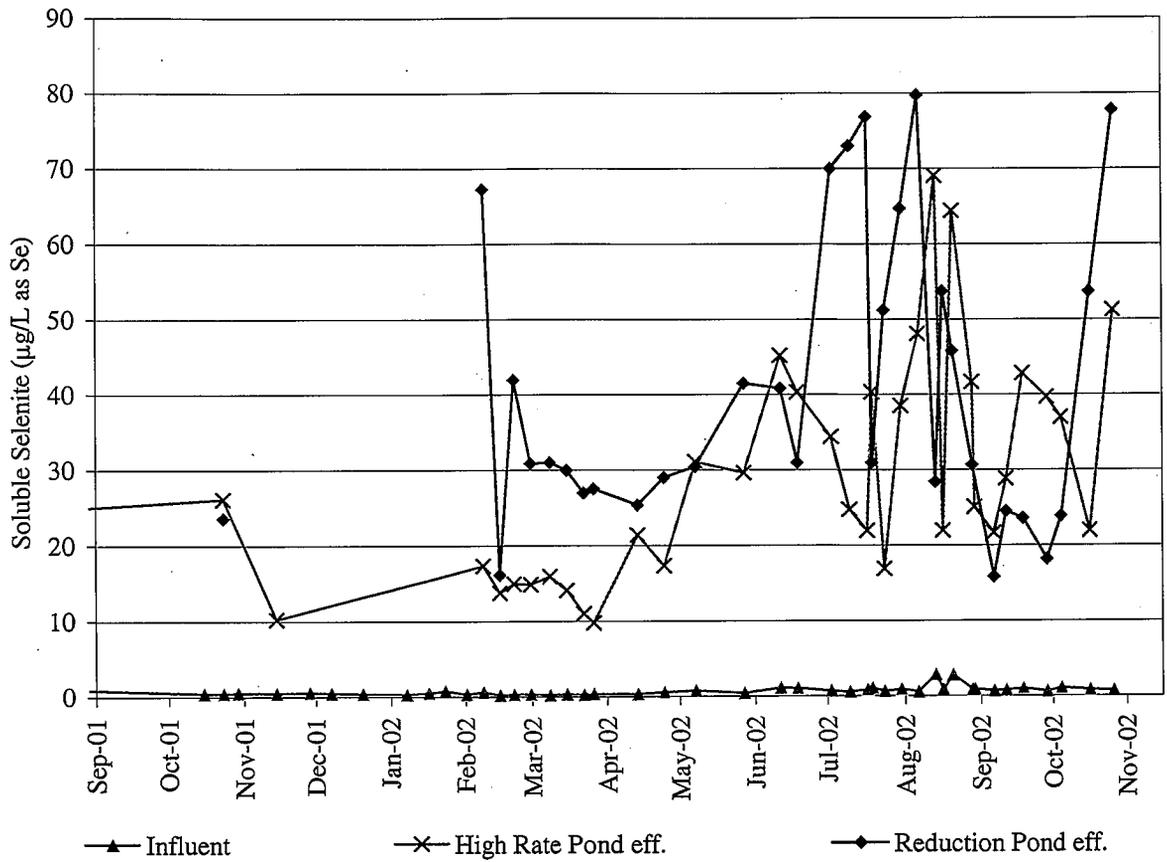


Figure 19. Soluble selenite-Se concentrations in the Mode 1 South Algal-Bacterial Selenium Removal System at the Panoche Drainage District.

PILOT-SCALE PARTICULATE SELENIUM REMOVAL

THE NEED FOR RAPID PARTICLE SEPARATION

As described above in the *Operations* section, in Mode 2, drainage was mixed with biodegradable carbon substrate and discharged near the floor of an anoxic Reduction Pond (RP). There, together with nitrate reduction to nitrogen gas, selenate was reduced to potentially insoluble forms such as selenite, elemental Se, organic Se, and possibly metallic selenium sulfides. We have evidence that the particulate selenium found in the ABSR ponds is a mixture of elemental and organic selenium and selenite, apparently adsorbed to or inside the cells of microorganisms rather than present as free colloidal selenium (Oswald *et al.*, 1999). Organic selenium (at least the in the form of seleno-amino acids and ingestible particles for which studies have been done) and selenite are more bioavailable than selenate. Thus, reduced selenium should be removed from the ABSR Facility effluent before discharge. We have found that selenite and particulate selenium can be removed by ferric chloride coagulation followed by filtration.

Bioavailable Selenite Release during Aerobic Conditions

As described above in the *Operations* section, Mode 2 RP effluent was discharged to an aerobic High Rate Pond (HRP) for removal of residual oxygen demand and for production of algae for use as bacterial substrate. But having consistently measured increases in selenite concentration from the HRP influent to effluent, we discontinued use of the HRP. We suspected that the aerobic and/or alkaline conditions of the HRP caused conversion of other selenium forms to selenite, a bioavailable form of selenium. Similarly, the slow sand filters operated during the Amweg *et al.* (2003) bioavailability study were aerobic, and selenite concentrations were increased in their effluent. In the Amweg *et al.* study, invertebrates were held in microcosms receiving slow sand filter effluent. Since selenite is bioavailable, the high selenite concentrations promoted selenium uptake by the study invertebrates.

Laboratory experiments conducted during the present project revealed that particulate selenium in the Reduction Pond effluent apparently is converted rapidly to selenite under

aerobic conditions (**Figure 20**). An increase of five times the original selenite-Se concentration ($4 \mu\text{g/L}$ increased to $20 \mu\text{g/L}$) could occur during 9 hours of aeration. After 7 days of aeration, the selenite-Se rose to $75 \mu\text{g/L}$. The selenite increase could be due to the release of selenite adsorbed on particles or polysaccharides (Ferri and Sangiorgio, 2001) or from the oxidation of elemental Se (Zhang and Frankenberger, 2003).

Instead of HRP treatment, the RP effluent was subjected to combinations of particle separation processes, namely sedimentation, dissolved air flotation (DAF), slow sand filtration, rapid sand filtration, and diatomaceous earth filtration. By eliminating the HRP with its 3-5 day hydraulic residence time, the RP effluent was exposed to <30 minutes of aerobic conditions during flotation and filtration. This change lessening the time available for selenite production or selenite release from particles.

We also suspected that additional selenite retention by the slow sand filter, rather than selenite release, could be promoted by maintaining anaerobic conditions in the slow sand filter. Anoxia in the slow sand filter was promoted by increasing the molasses dose to the RP prior to filtration. The additional organic matter carry-over in the RP effluent loaded the slow sand filter sufficiently so that atmospheric oxygen entering the filter's open water surface was consumed by bacteria.

METHODS FOR THE PARTICLE SEPARATION RESEARCH

Gravity settling is the simplest of particle separation processes and so was briefly evaluated for application to RP effluent. RP effluent was dosed with ferric chloride coagulant and delivered to a 100-L pilot clarifier providing a hydraulic residence time of 2 hours. The cone-shaped clarifier had a baffled center inlet and a serrated, peripheral outlet weir. Effluent turbidity and suspended solids were monitored.

In slow sand filtration experiments, RP effluent was passed through a biological slow sand filter for particulate removal and further biological selenium reduction. This configuration was tested previously during a microcosm bioaccumulation study in 2001 but under aerobic conditions (Oswald *et al.*, 2002). In the current study, molasses dosing to the

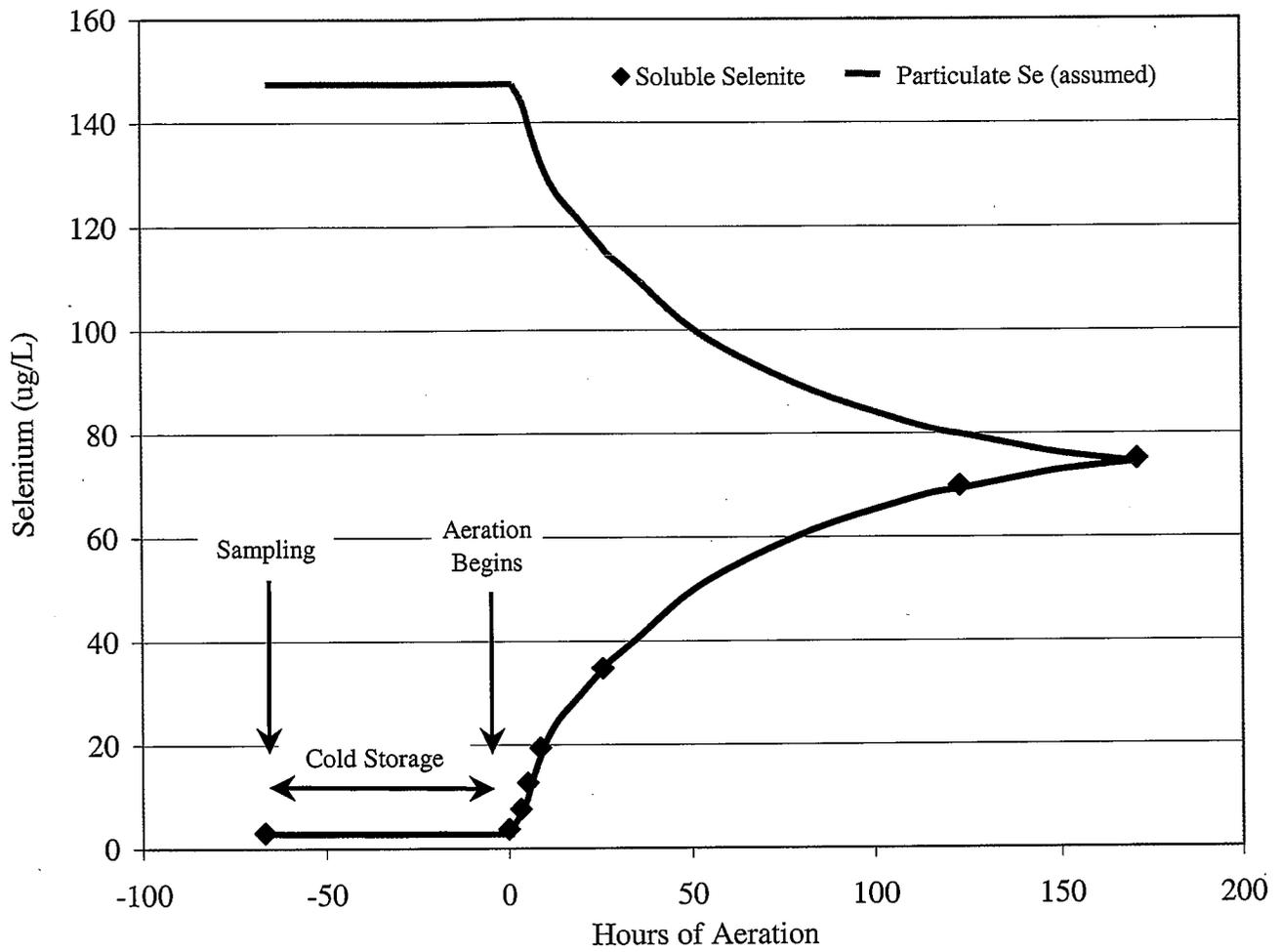


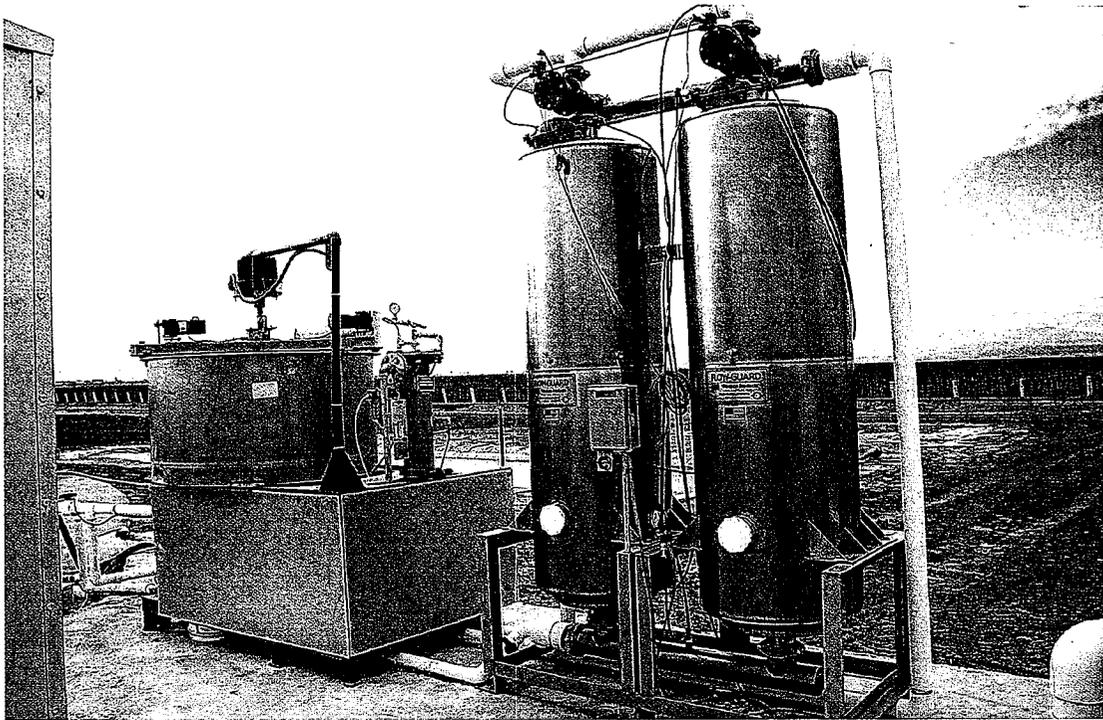
Figure 20. Effect of aeration on soluble selenite concentration in the Mode 2 Reduction Pond effluent. The rapid increase suggests that selenite desorbs from particles under aerobic conditions. The initial particulate selenium concentration was 146 ug/L.

RP was increased until the slow sand filter became anaerobic and allowed further reduction of selenite rather than promoting selenite release as occurred in 2001. Slow sand filtration is attractive for its simplicity and for the possibility of further selenium reduction by bacteria living in the sand bed. It also served as a rough analog for the drain irrigated soils of drainage reuse sites such as the San Joaquin River Water Quality Improvement Project.

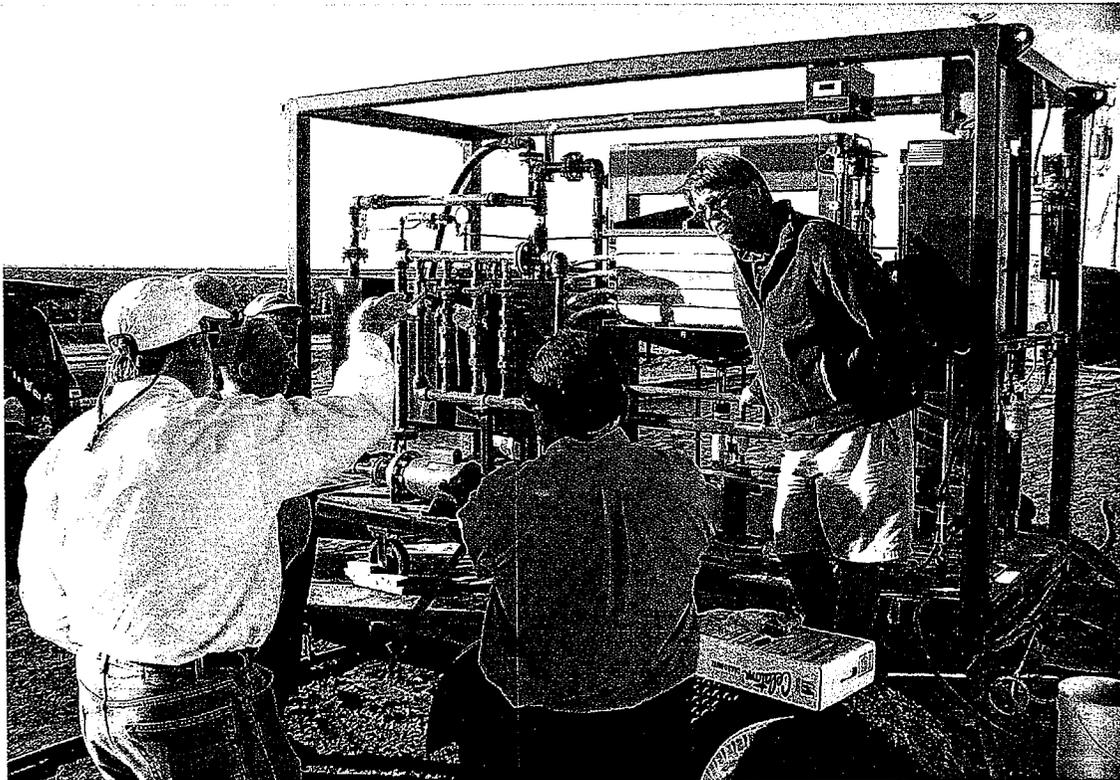
In another configuration, the RP was followed by ferric chloride coagulation for selenite precipitation/adsorption and cationic polymer addition for particulate flocculation. Much of the precipitate and floc was removed by a dissolved air flotation (DAF) unit which was followed by a rapid sand filter (**Photograph 5**). Ferric chloride doses ranged from 50 to 100 mg/L, and the cationic polymer (Cytec Superfloc 255G) doses ranged from 4 to 8 mg/L. The doses were adjusted as needed to produce 2-mm to 4-mm diameter flocs in the DAF tank.

A diatomaceous earth filter following the DAF was also tested. A pilot-scale diatomaceous earth filter manufactured by J.R. Schneider Co. Inc., of Benicia, California was transported to the ABSR Facility and used in two days of trials (**Photograph 6**). Darrel Snell of J.R. Schneider Co. operated the unit with assistance of members of the U.C. Berkeley research group. Since diatomaceous earth (DE) filters are well-known for their ability to produce extremely clear effluent (<1 NTU), we wanted to compare this technology's ability to remove particulate selenium compared to rapid sand filtration.

In DE filtration, porous fabric septa are laid over frames. The frames are stacked and compressed in a hydraulic press. The septa are loaded with a precoat layer of DE, and then the water to be filtered is passed through the DE layers. Additional DE powder is dosed into the water stream. As the water passes through the DE layers, the additional DE collects on the layers providing a new filtering surface. In this way the filter porosity is maintained. When the DE layer builds to about 4 cm thick or the headloss increases beyond specification, filtering is stopped, and the septa and DE layers are replaced. In full-scale DE filters, these operations are automated. The DE grades tested during the study are listed in **Table 5**.



Photograph 5. The Krofta Engineering dissolved air flotation (DAF) unit (left) and the Fresno Valve and Castings rapid sand filters (right) used during the pilot-scale particulate removal study.



Photograph 6. Diatomaceous earth pilot filter used at the ABSR Facility. The white plates at the center hold the fabric septa and diatomaceous earth precoat layers.

Table 5. Diatomaceous earth grades tested in the pilot scale diatomaceous earth filter at the ABSR Facility. The specifications were provided by the manufacturers.

Brand	Product	Median DE Particle Diameter (μm)	Median Pore Diameter (μm)
Celite Corp.	Standard Super Cel	15.4	3.5
Celite Corp.	512	16.4	5.0
Celite Corp.	Hi Flo Super Cel	22.3	7.0
Eagle Picher	Swimming pool grade*	>36.2	>17.0

* Swimming pool grade is an unspecific grade of DE, however, it is coarser than Celite 545. The diameters listed are those for Celite 545 plus ">" symbols indicating that the swimming pool grade diameters are greater than the Celite 545 diameters.

The specifications for the equipment used in the various experimental configurations are given in **Table 6**.

Table 6. Specifications for the particulate removal processes used during 2001-2002 at the ABSR Facility.

Unit	Brand & Model	Dimensions: diameter x height in m	Tank Material; Media Specifications	Hydraulic Loading Rate and Residence Time in Vessel	Coagulant Dose
RP → Coagulation → Gravity Clarifier Configuration					
0.8 L/min.					
100-L conical tank with inlet baffle & peripheral effluent crown weir	Custom	0.7 x 2.4	Painted steel	3 m/d 2 hours	80-100 mg/L FeCl ₃
RP → Slow Sand Filter Configuration					
0.6 L/min.					
Slow Sand Filter	Custom	1.5 x 1.2	Black polyethylene; 60-mesh silica filter sand; 70-cm bed depth	0.8 m/d 1day	none
RP → Coagulation → DAF → RSF Configuration					
24 L/min.					
Dissolved Air Flotation Unit	Krofta SPC4	1.2 x 0.8	Stainless steel	47 m/d 15 minutes	80-100 mg/L FeCl ₃
Rapid Sand Filters	Fresno Valve & Castings deep bed filter	0.8 x 2.4	Stainless steel; 20-mesh silica filter sand; 60-cm bed depth	60 m/d 1 hour	none

Continued.

RP → Coagulation → DAF → Diatomaceous Earth Filter Configuration
24 L/min.

The DAF unit was the same used in conjunction with RSF (see above)

Diatomaceous Earth Filter; dry cake discharge, horizontal plate	J.R. Schneider Co. Inc.	1.3 m ²	Fiberglass-reinforced polypropylene frames; DE grades: Celite 512, Celite Hi Flo Super Cel, and Eagle Picher Swimming Pool grade; Septum 10 μm pore size (see Table 7)	17 - 44 m/d 1 hour	80-100 mg/L FeCl ₃ and 1.3 ppm Cytec 255G cationic polymer
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RESULTS AND DISCUSSION

Gravity Clarifier: When RP effluent was coagulated and delivered to the pilot clarifier, approximately half of the flocculated material floated and half settled. The tendency for the flocs to float makes sedimentation an unworkable process. At times, fine bubbles were visible in the RP effluent. Presumably, these were nitrogen and carbon dioxide, byproducts of the biological reactions in the RP. Although detrimental to sedimentation, the presence of these fine bubbles should enhance dissolved air flotation.

Slow Sand Filtration: Together, the RP and the SSF sequence provided 32% total selenium removal and 43% soluble selenium removal during November 2001 through March 2002. Bacteria living in the SSF reduced 34% of its influent selenate over the water's one-day HRT. However, particulate selenium removal by the SSF was not impressive (**Figure 21**). The SSF influent averaged 83 μg/L particulate Se and the effluent averaged 56 μg/L, a 32% removal.

Over the whole period, selenite increased on average, although at times, selenite decreased. With sufficient molasses dosing to the Mode 2 RP (>0.4 g/L), enough residual oxygen demand passed to the slow sand filter (SSF) to promote anoxic bacterial growth. The growth was apparent in that from November 28, 2001 to January 23, 2002, the SSF removed an average of 17 μg/L of selenite-Se presumably by bacterial reduction. At other times,

Table 7. Specification for the diatomaceous earth filter septum used in the pilot studies at the ABSR Facility.



J.R. SCHNEIDER CO., INC.

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Web:

www.jrschneider.com

S-375LM

S-375LM FILTER SEPTA SPECIFICATIONS

	<u>S.I. Units</u>	<u>U.S. Units</u>
-Basis Weight	93.24g/m ²	2.75 oz./yd. ²
-Grab Tensile MD	191.3 N	52lbf
-Grab Tensile CD	244.6 N	43lbf
NOTE: The above tensile tests are performed at a speed of 0.2 in/sec. or 5.08mm/sec. Range tensile tests +/- 5%.		
-Trap Tear MD	103.2 N	23.2lbf
-Trap Tear CD	70.3 N	15.8lbf
-Air Permeability Range +/- 9cfm/ft. ²	18/m ³ /min./m ²	59cfm/ft. ²
-Mullen Burst Range +/- 4 psi	4.5 Bar	66 psi
-Shrinkage (Kerosine)	0%	0%
-Roll Width	1041mm	41"
-Roll Length	251.46m	275 yds.
-Roll Diameter	<381mm max.	<15" max.

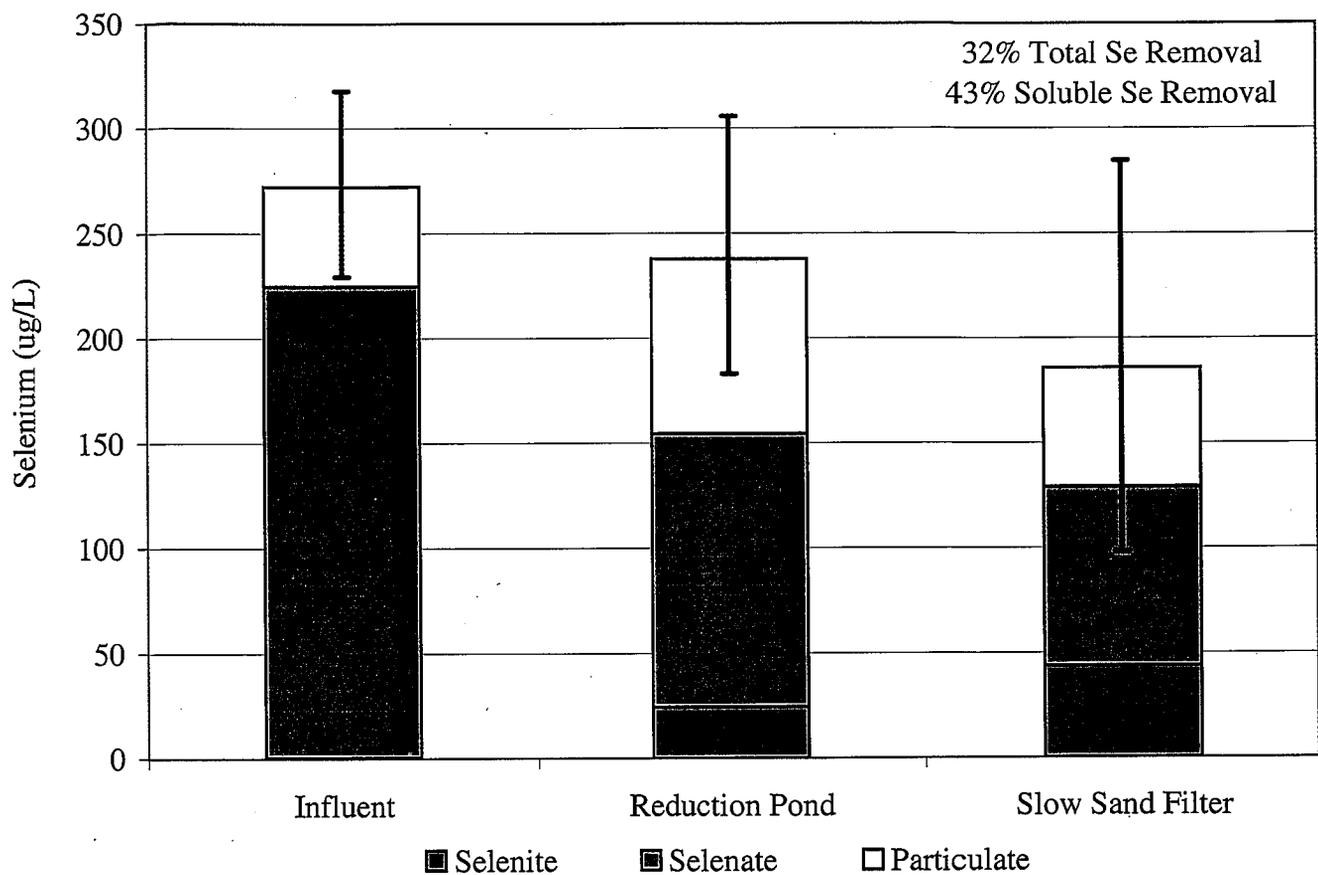
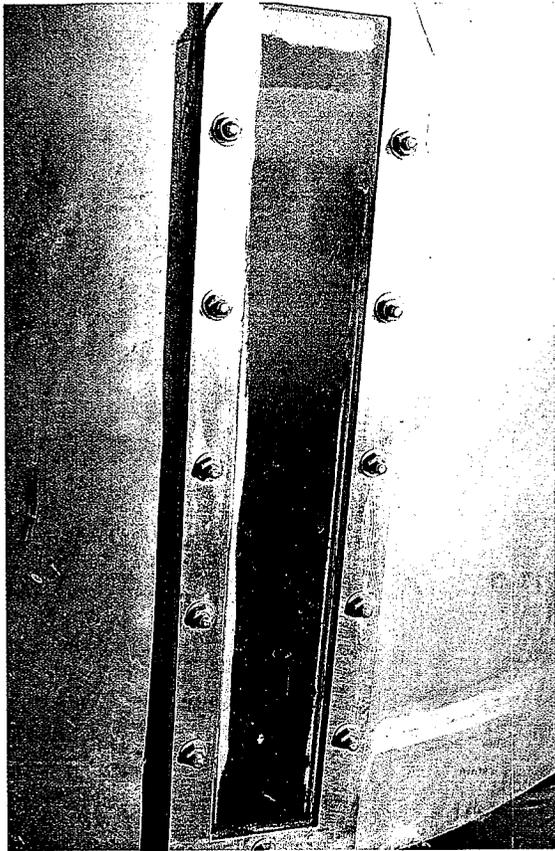


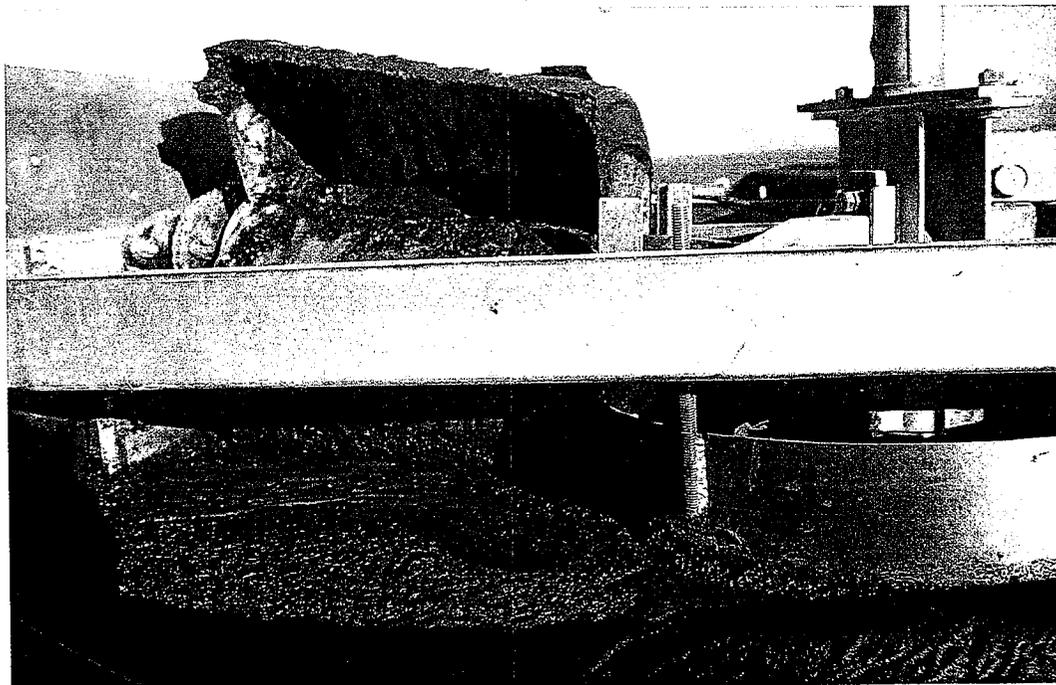
Figure 21. Selenium removal by the Mode 2 Reduction Pond and a Slow Sand Filter at the Algal-Bacterial Selenium Removal Facility in the Panoche Drainage District during November 2001 through March 2002. The error bars indicate the 90th and 10th percentiles in total selenium concentration.

however, during October through early November 2001 and February through April 2002, selenite-Se increased as much as 73 $\mu\text{g/L}$ during SSF treatment. Selenite removal occurred again in one SSF sample taken in early May 2002 just prior to shut-down of the SSF. During October 2001, the molasses dose to the RP was 0.19 g/L. Thereafter, through early May 2002, the dosing was increased to an average of 0.47 g/L. Thus, the increase in molasses dose may explain the onset of selenite removal by the SSF, but does not explain the subsequent return to selenite increase during February to April 2002.

Dissolved Air Flotation: The main purpose of the DAF unit was to remove a substantial mass of suspended solids from the RP effluent so that the filter following it would not become overloaded. The coagulation and DAF operations were successful with formation of suitable flocs and microbubbles being the norm (**Photographs 7 and 8**). During DAF runs in July, August, and November 2001, ferric chloride coagulation and dissolved air flotation removed substantial amounts of selenite and particulate selenium, as expected (**Table 8**). The selenite was not removed as completely as desired (9.1 $\mu\text{g/L}$ remaining) or as completely as expected based on the solubility of ferric hydroxide-selenite complexes. Interference by sulfate, which is present in the drainage at 2,000 to 3,000 mg/L, has been suggested as a possible cause of this incomplete selenite precipitation/absorption (J.J. Morgan, 2002).



Photograph 7. DAF window showing white micro-bubbles and bacterial floc floating to the water surface and clear water below which is discharged from DAF as underflow effluent.



Photograph 8. Floated bacteria at the surface of the DAF tank. The sludge is skimmed off the water by the spiral scoop in the center of the photograph.

Table 8. Mean removal of selenium species from Reduction Pond effluent by pilot-scale ferric chloride coagulation and dissolved air flotation during July, August, and November 2001 at the ABSR Facility.

Site	Total Se	Total Soluble Se	Selenite Se	Particulate Se
RN effluent ($\mu\text{g/L}$)	255	97	16	158
DAF effluent ($\mu\text{g/L}$)	168	88	9.1	80
Concentration Removed ($\mu\text{g/L}$)	87	9	6.8	78
Percent Removal	34%	9%	43%	49%

Diatomaceous Earth Filtration: On November 11, 2002, the diatomaceous earth (DE) filter was setup to accept effluent from the Krofta DAF unit. The 1.3-m² filter was operated with a 36 m/d hydraulic loading. A fine grade of DE, Celite 512, was used initially. The filter runs were of short duration, only about 20 minutes, before pressure losses rose over the specified headloss of 20 psi.

Due to the rapid clogging of the fine DE during the previous day, on November 13, 2002, a coarse DE, Eagle Picher Swimming Pool grade, was used. The flow rate was set at 17 m/d. The initial pressure drop was 8 psi and increased over the course of 15 minutes to 12 psi during a brief upset in the DAF operation that allowed suspended solids to pass. Filter differential pressure remained at 12 psi for 4 hours with a DE bodyfeed rate of 100 mL every 2 minutes. Total filter run time was 5 hours, and this test was terminated after another upset in the DAF allowed poor quality water to plug the filter. The DAF upsets were caused by unintentional interruptions in coagulant or flocculant dosing.

New septa were installed, and a second run was started using a medium-grade DE, Celite "Hi Flo Super Cel". A loading rate of 44 m/d was used. With these parameters, the pressure loss rate was 3 psi per hour. The appearance of the DE filter cakes can be seen in

Photograph 9.

The DAF removed 54% of the total selenium in the RP effluent and the DE Filter removed an additional 39 $\mu\text{g/L}$ to achieve an overall 70% total selenium removal (**Figure 22**). In the DE filter effluent, 5 $\mu\text{g/L}$ of selenite-Se and 31 $\mu\text{g/L}$ of particulate selenium remained in addition to the soluble selenate. The DE filter removed 56% of the DAF effluent particulate selenium. DE filter effluent turbidities ranged from 6-24 NTU which is much higher than normal for this technology. Suspended solids analyses showed that the turbidity was caused by non-volatile suspended solids, presumably DE that passed through the septa. This pass-through can be caused by low hydraulic loading of the filter. A minimum of 59 m/d has been found recently to be the minimum requirement at reclaimed sewage treatment systems (Snell, 2003). Hydraulic loads >59 m/d are also expected to greatly improve the performance of DE filters bringing effluent turbidity to <1 NTU with concomitant decrease in particulate Se removal. Water clarity through the ABSR Process followed by DE filtration on November 13, 2002 is shown in **Photograph 10**.

DE filters may have an advantage over rapid sand filters in terms of final effluent clarity and the perfect cleaning of the filter media by its removal during septa changes. However, DE filters must have filter run times (time between septa changes) of about 10 days to be competitive with sand filters in terms of economy (Snell, 2003). A question that remains to be answered is if, during a 10-day residence on the DE cake, trapped selenium would be released from the DE cake as selenite or degradation products from particulate selenium. Evidence from the rapid sand filter trials (see below) suggests that such Se release would occur.

Rapid Sand Filtration: The Rapid Sand Filters (RSFs) removed a similar amount of particulate selenium as the DE filter (57% vs. 56%; **Figure 23**). The water clarity through the process is shown in **Photograph 11**. Effluent turbidities ranged from 2-13 NTU which is generally higher than the turbidity produced in full-scale rapid sand filter plants filtering treated sewage for reuse. Many of these filters are required by law to produce effluent <2 NTU. **Figure 24** shows the correlation between RSF effluent turbidity and effluent



Photograph 9. The diatomaceous earth filter with its plates opened to reveal the fabric septa with precoat layers and brown, selenium-rich bacteria that have been removed from the effluent.

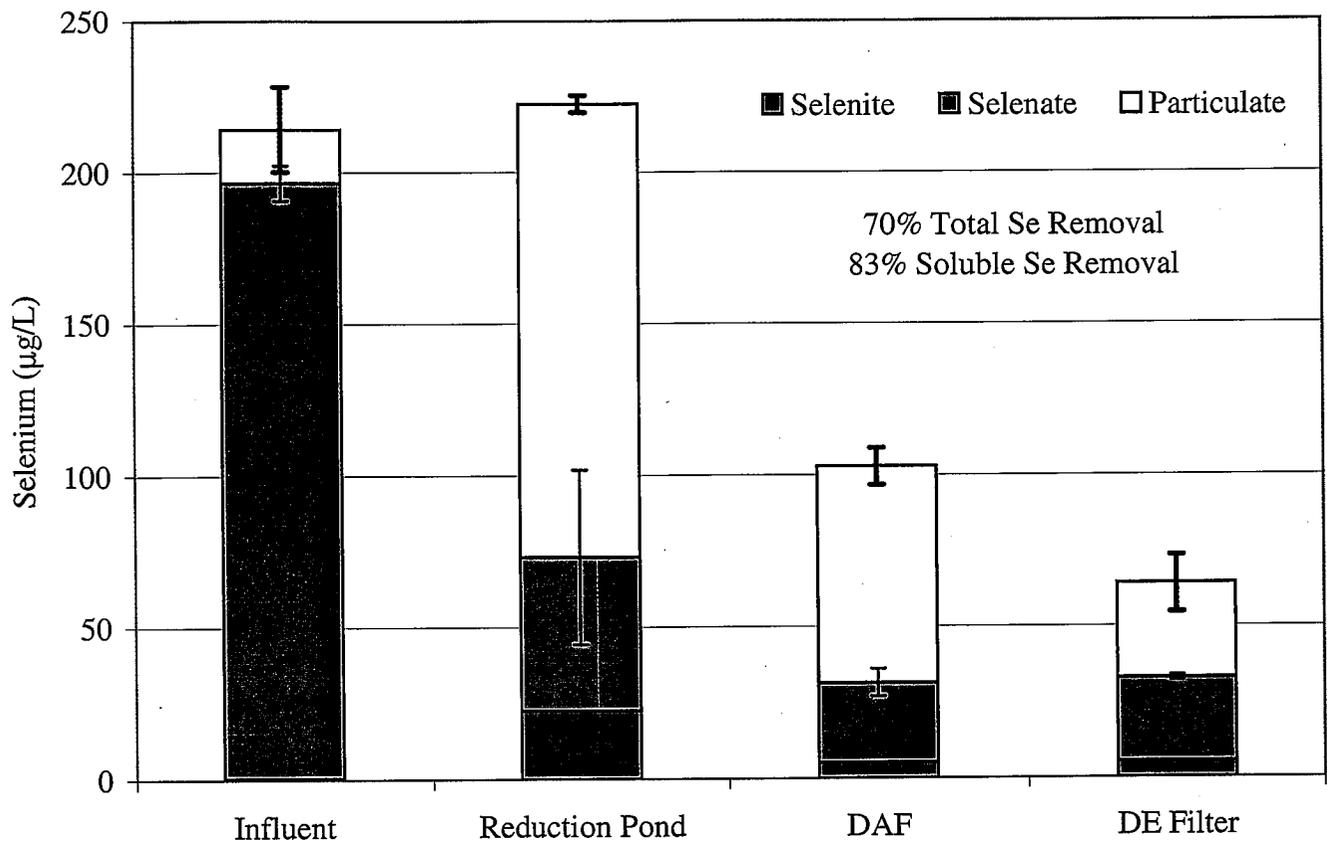
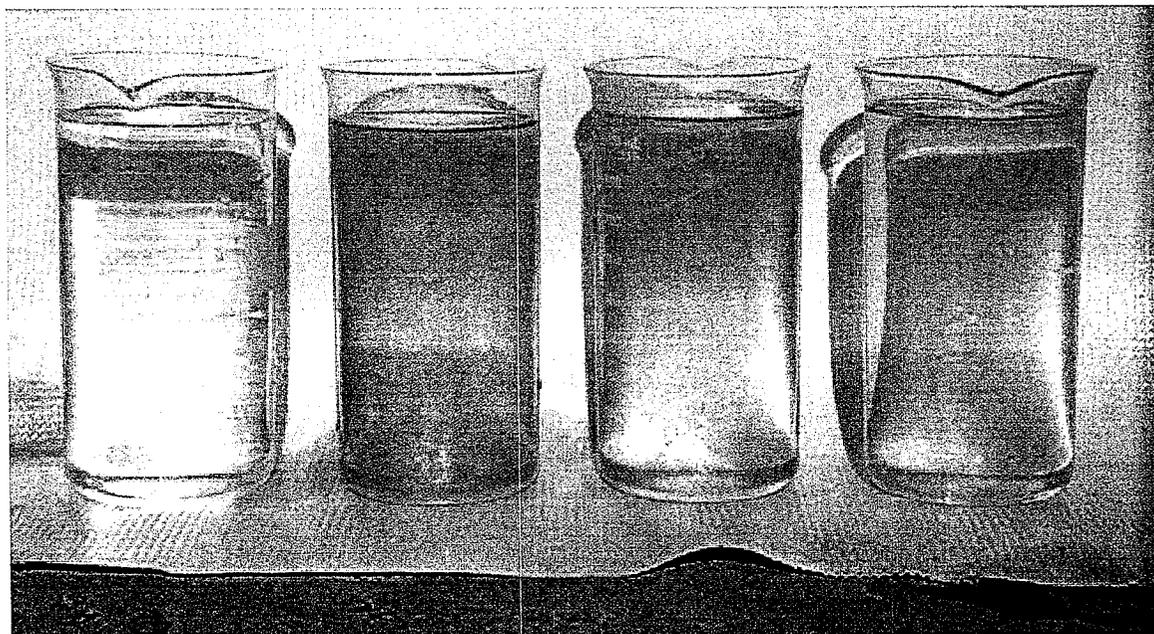


Figure 22. Selenium removal by the Mode 2 Reduction Pond, pilot Dissolved Air Flotation Unit, and pilot Diatomaceous Earth Filter at the Algal-Bacterial Selenium Removal Facility at the Panoche Drainage District, November 11 & 13, 2002. 0.2 µm filters were used in determination of the soluble selenium. Error bars indicate selenium concentration ranges.



Photograph 10. From left, Mode 2 North ABSR System influent, Reduction Pond effluent, dissolved air flotation (DAF) unit effluent, and diatomaceous earth filter effluent on November 13, 2002. Ferric chloride and cationic polymer were added prior to the DAF unit.



Photograph 11. From left, Mode 2 North ABSR System influent, Reduction Pond effluent, dissolved air flotation (DAF) unit effluent, and rapid sand filter effluent in September 2002. Ferric chloride and cationic polymer were added prior to the DAF unit.

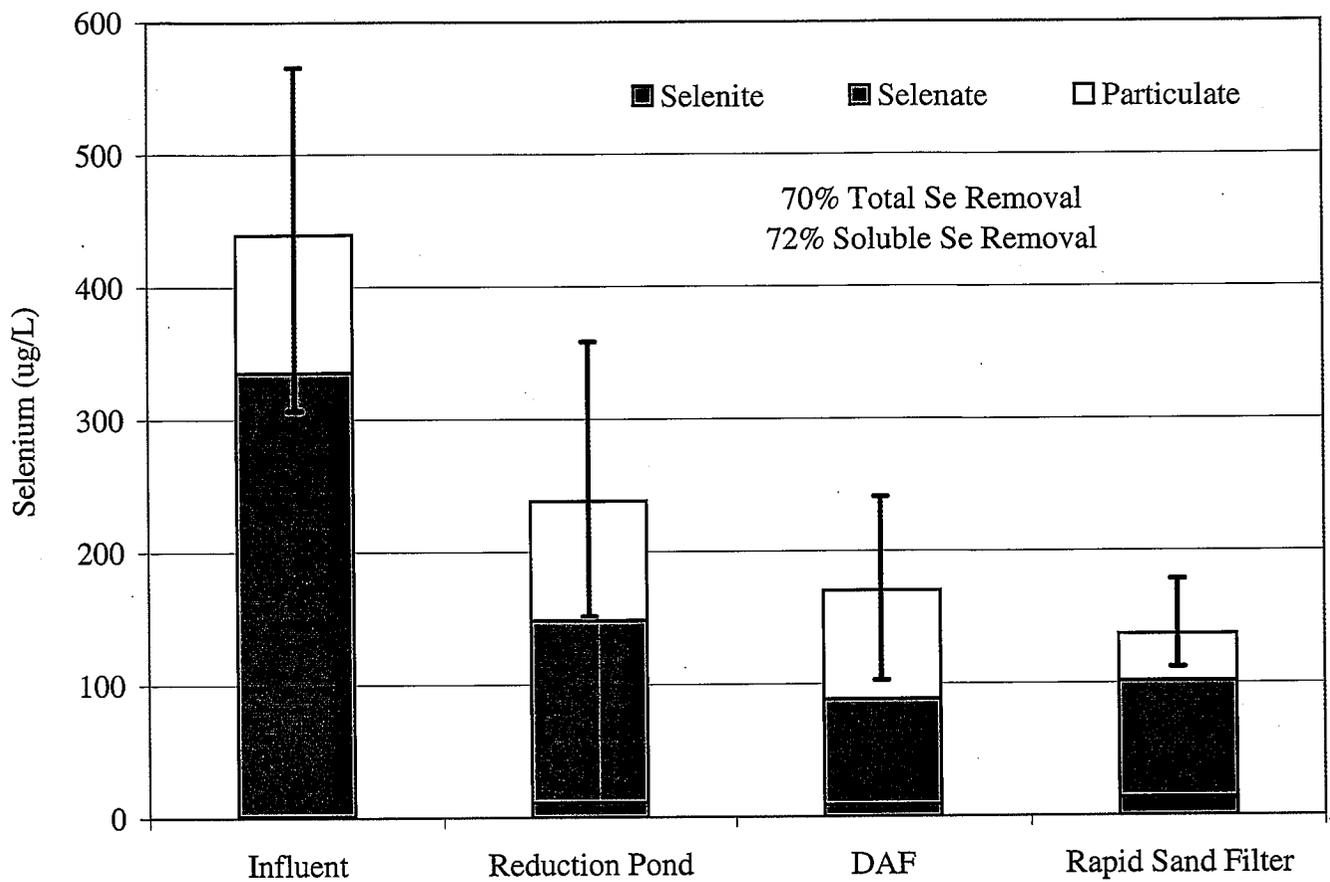


Figure 23. Selenium removal by the Mode 2 Reduction Pond, pilot Dissolved Air Flotation Unit, and Rapid Sand Filters at the Algal-Bacterial Selenium Removal Facility in the Panoche Drainage District during June 2001 and August 2002. Error bars indicate total selenium concentration ranges.

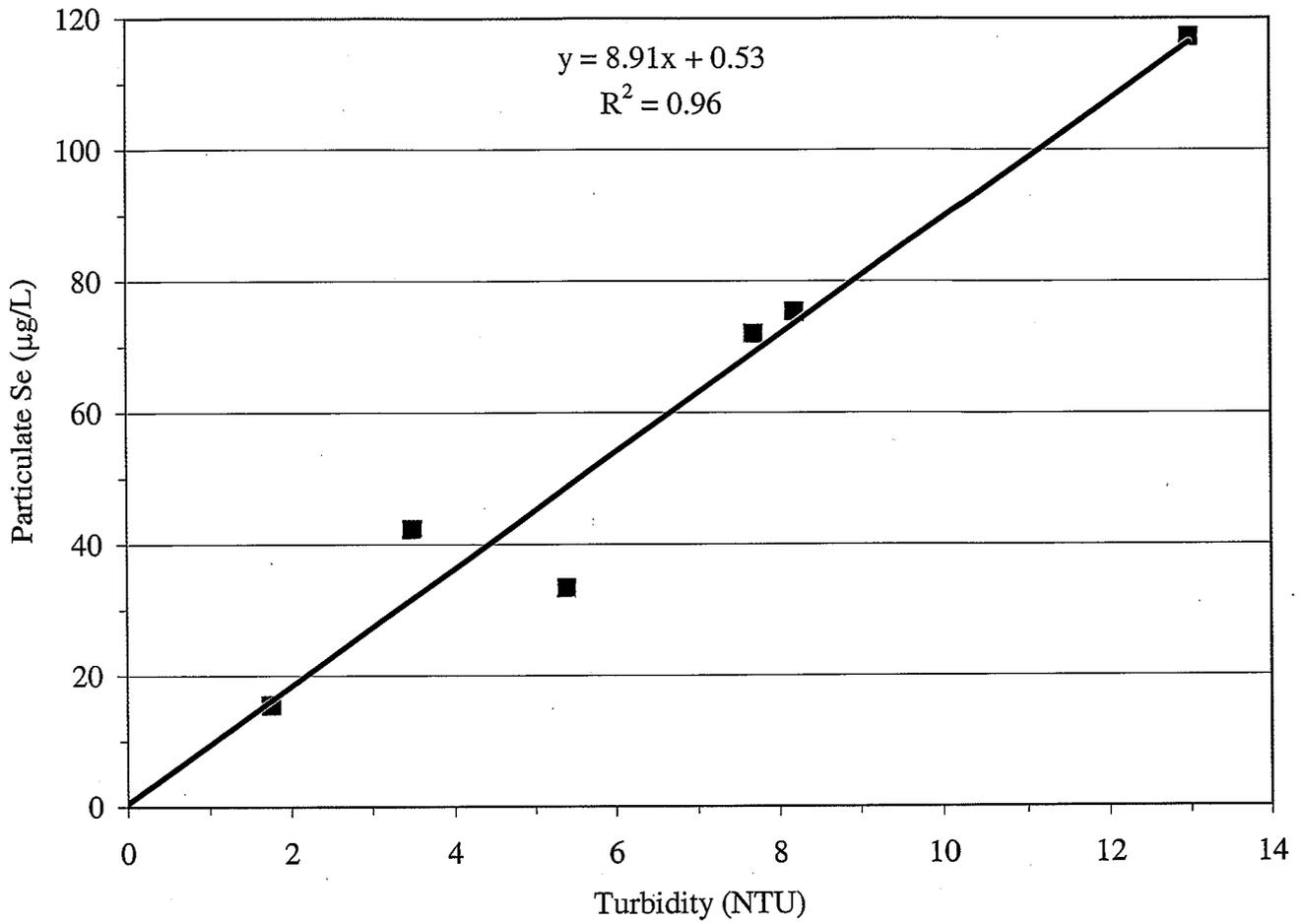


Figure 24. Correlation of particulate selenium and turbidity in the effluent of a rapid sand filter at the Algal-Bacterial Selenium Removal Facility in the Panoche Drainage District. The treatment sequence was Reduction Pond→Dissolved Air Flotation Unit→Rapid Sand Filter. Full-scale wastewater filtering facilities typically achieve turbidity <2 NTU with multimedia filtration and <0.1 NTU with microfiltration.

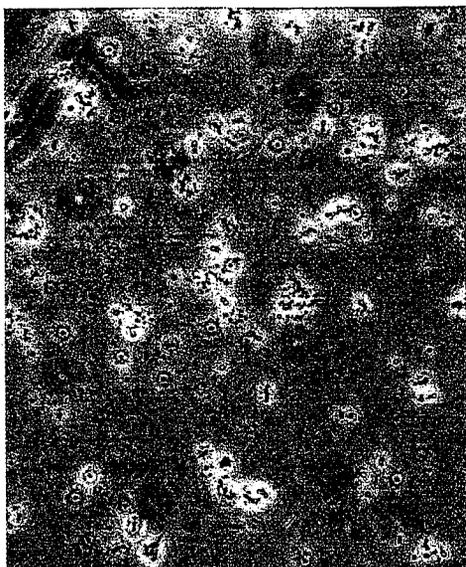
particulate selenium. The linear regression was not forced to pass through the origin, but rather the data points lead to the regression intercepting the origin. This correlation suggests that to achieve $<10 \mu\text{g/L}$ particulate selenium, the filter turbidity will have to be brought below 1 NTU.

At 1000x magnification, the particles visible in the Mode 2 Reduction Pond effluent are primarily disperse bacteria (**Photograph 12**). After coagulation, flocculation, flotation, and sand filtration far fewer bacteria are present (**Photograph 13**). Improved particle separation processes should be capable of removing these remaining bacteria and any associated selenium.

The RSFs were backwashed after each use in order to minimize potential release of selenium from decaying of selenium-laden bacteria. A backflush rate of 0.23 m/minute for 5 minutes was used. This rate was apparently not adequate for cleaning as evidenced by the increase in selenite concentration in the RSFs from $9 \mu\text{g/L}$ in the influent and $14 \mu\text{g/L}$ in the effluent. A backwash sample was determined to contain $150 \mu\text{g/L}$ of total selenium. The effect of longer backwash periods on cleaning particulate selenium from the filter bed and on selenite concentration will be addressed in future studies.

During the RSF trials, the RP effluent had an average of $11 \mu\text{g/L}$ selenite-Se, half as much as during the November 2002 DE filter trials (**Figure 21**). The coagulation, flocculation, and DAF treatment decreased the $11 \mu\text{g/L}$ selenite-Se to $9 \mu\text{g/L}$, whereas in November 2001, the DAF decreased selenite from $23 \mu\text{g/L}$ to $5 \mu\text{g/L}$, a greater removal to a lower value. We plan to continue investigation of this variability in selenite removal.

Although, both rapid sand and diatomaceous earth filtration decreased particulate Se by over 50%, the lowest effluent achieved was $15 \mu\text{g/L}$ particulate Se. The corresponding turbidity for this sample was 1.9 NTU (**Figure 24**). The pilot rapid sand filters at the ABSR Facility did not achieve effluent turbidity levels typical of full-scale filtration facilities. Since sand filters effluents are often required to be <2 NTU at wastewater reclamation facilities, and microfilters achieve <0.1 NTU, particulate Se concentrations of $2 \mu\text{g/L}$ to $10 \mu\text{g/L}$ may be possible with conventional equipment, as suggested by **Figure 24**.



Photograph 12. Micrograph of Reduction Pond effluent (1000x; no scale).



Photograph 13. Micrograph of Reduction Pond effluent after rapid sand filtration (1000x; no scale).

POTENTIAL FOR MICROFILTRATION

Microfilters use membranes with $<1 \mu\text{m}$ pore diameters. These sizes are small enough to remove most individual bacterial cells and inorganic colloids. Consequentially, particulate removal by microfilters is better than most sand filters, and microfilters do not have as great a scaling potential as finer membranes such as nanofilters. Microfilters will not concentrate soluble minerals and so scaling from the high hardness found in drainage should be less of a problem than in nanofiltration or reverse osmosis.

Biofouling of microfilter membranes is expected to be the limiting factor in their use in biological drainage treatment. Microfilters are cleaned by backwashing and by chemical cleanings. Results from a 6-month microfilter pilot project at the Geyserville, California municipal wastewater treatment pond are summarized below (Michelsen and Thayer, 1999).

Effluent turbidity: mean 0.054 NTU; range 0.04-0.12 NTU
Transmembrane pressure difference: 6-16 psi
Backwash interval: 12-15 minutes
Chemical cleaning interval: 7-14 days
Particle removal: 8.4 log

The particles consisted of single cell microalgae and bacteria. The soluble and particulate organic content of this municipal wastewater pond effluent was probable higher than that measured in the effluent of the ABSR Facility. The ABSR Facility effluent has had the following quality:

Total BOD₅: 10-15 mg/L
Soluble BOD₅: 1-5 mg/L
Total suspended solids: 10-40 mg/L

With this relatively high effluent quality, we expect the backwash and cleaning intervals at an ABSR Facility to be longer than those used at the Geyserville pilot study. Despite these promising factors, microfiltration remains an expensive form of filtration, and

the investigation of more conventional multi-media filters should be continued, building on the positive results of the present project.

DRAINAGE IRRIGATION MONITORING

In order to improve water use efficiency and to minimize the volume of drainage discharged, the PDD is now irrigating areas with primary drainage and producing what may be called secondary drainage. The PDD hopes to expand this irrigation to at least 4,000 acres, and if successful, other districts are likely to follow the example.

We have suggested that treatment of secondary drainage may be more economical than treatment of primary drainage for several reasons. First, secondary drainage volume is decreased by evapotranspiration compared to the primary drainage. The smaller volume likely would require smaller treatment pond volumes. Second, evapotranspiration would increase the selenium concentration in the remaining water. Selenium removal rates increase with modest increases in selenium concentration (Oswald *et al.*, 2002). Finally, crop uptake of nitrate would decrease the concentration of this inhibitor of dissimilatory selenium reduction. On the other hand, potential toxicity of the increased salt concentration of secondary drainage may interfere with necessary denitrification and selenium reduction, as discussed in the *Brine Treatment* section of this report.

Prior to the current study, little water quality analysis of secondary drainage in the PDD had been done, so the potentially beneficial changes in water quality caused by drainage irrigation were not well known. Our sampling and analysis of secondary drainage in the PDD's San Joaquin River Water Quality Improvement Project (SJRWQP) drainage reuse area provides initial information useful for evaluating the treatment of secondary drainage, for comparison to the Red Rock Ranch drainage reuse site in Five Points, and suggesting further investigations in both treatment and reuse management.

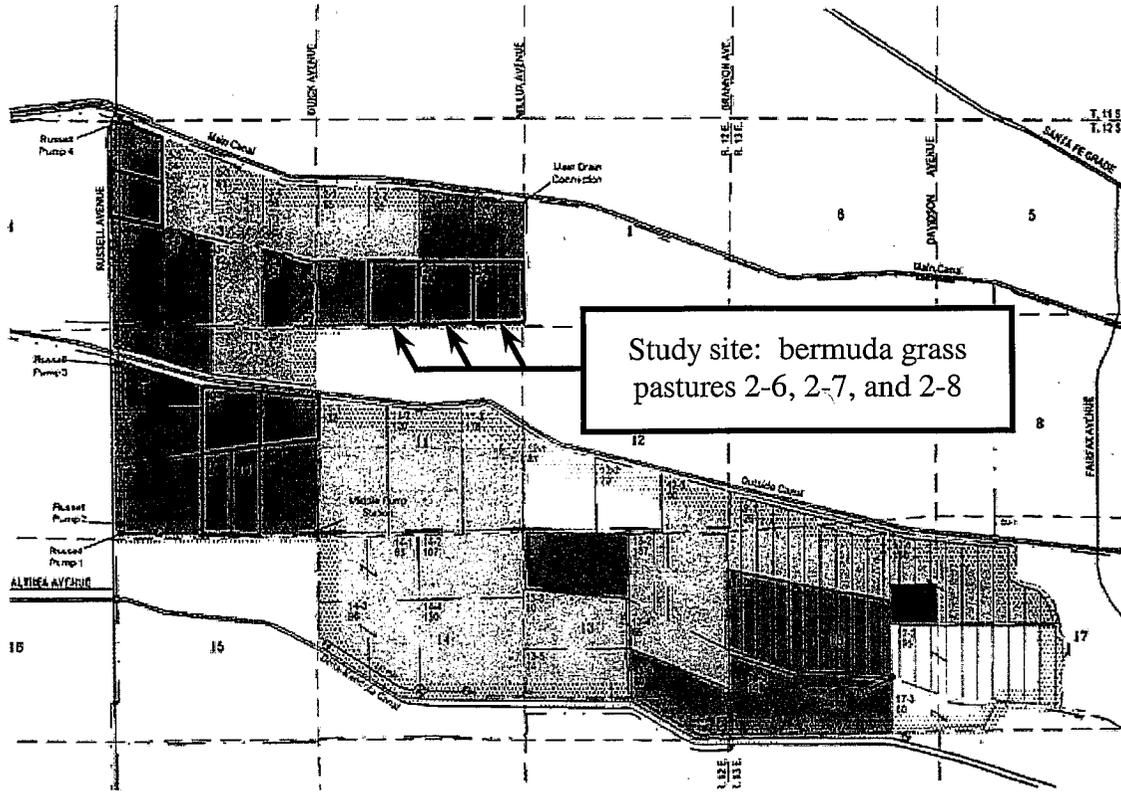
DESCRIPTION OF THE SJRWQIP

The SJRWQIP drainage reuse area is bordered by the Delta-Mendota Canal on the south and the Main Canal on the north and is bordered by Russell Avenue on the west and Fairfax Avenue on the east (**Figure 25**). Within the 4000-acre SJRWQIP, the PDD irrigates alfalfa, bermuda grass pasture, and asparagus fields. A small eucalyptus grove is also irrigated with drainage. The drainage is diverted from the PDD's main drainage channel that leads to the Grasslands Bypass. If needed for a particular crop, fresh well water is blended with the drainage before application.

STUDY SITE SELECTION AND METHODS

Three bermuda grass pastures in the SJRWQIP were chosen for the study of drainage water quality changes caused by reuse. During the study, only approximately 600 acres of the SJRWQIP was underdrained with tile drains. Several other fields were drained by open seepage trenches. The optimal fields for the drainage reuse study would have the following characteristics: (1) they would be underdrained; (2) they would be irrigated with unblended drainage; (3) they would have been irrigated with drainage for many years prior to the study; (4) not recently fertilized with nitrogen in order to promote nitrate uptake; and, (5) not under the influence of leakage from nearby freshwater delivery canals.

The fields that best met these criteria were Fields 2-6, 2-7, and 2-8 (**Photograph 14**). These 144 acres (45 to 50 acres per field) were planted with bermuda grass for onsite cattle grazing. This pasture had been irrigated with unblended drainage beginning in 2000 (B. Hurley, 2002) (**Photographs 15 and 16**). In 1999, the pastures were irrigated with drainage-freshwater blends, and prior to that the fields had been fallow for many years. The disadvantages of these fields for the study were that they were drained by seepage trenches rather than tile drains (**Photograph 17**), and they were fertilized by manure deposited by grazing cattle. The cattle were rotated among the three pastures to accommodate the flood irrigation, spending about a week in a pasture before being moved to the next pasture.



Study site: bermuda grass pastures 2-6, 2-7, and 2-8

LEGEND		
Acreage		Crop
60		Existing Canola / Salado Alfalfa / Salado Grass
72		Existing Alfalfa Seed
122		Existing Alfalfa / Pasture Grass
220		Existing Asparagus
336		Existing Alfalfa Seed / Pasture Grass
752		Existing Alfalfa
457		Existing Pasture
28		New Eucalyptus Trees
1816		Fallow
		Fenced Areas
3863		Total Acres



PANOCHÉ DRAINAGE DISTRICT

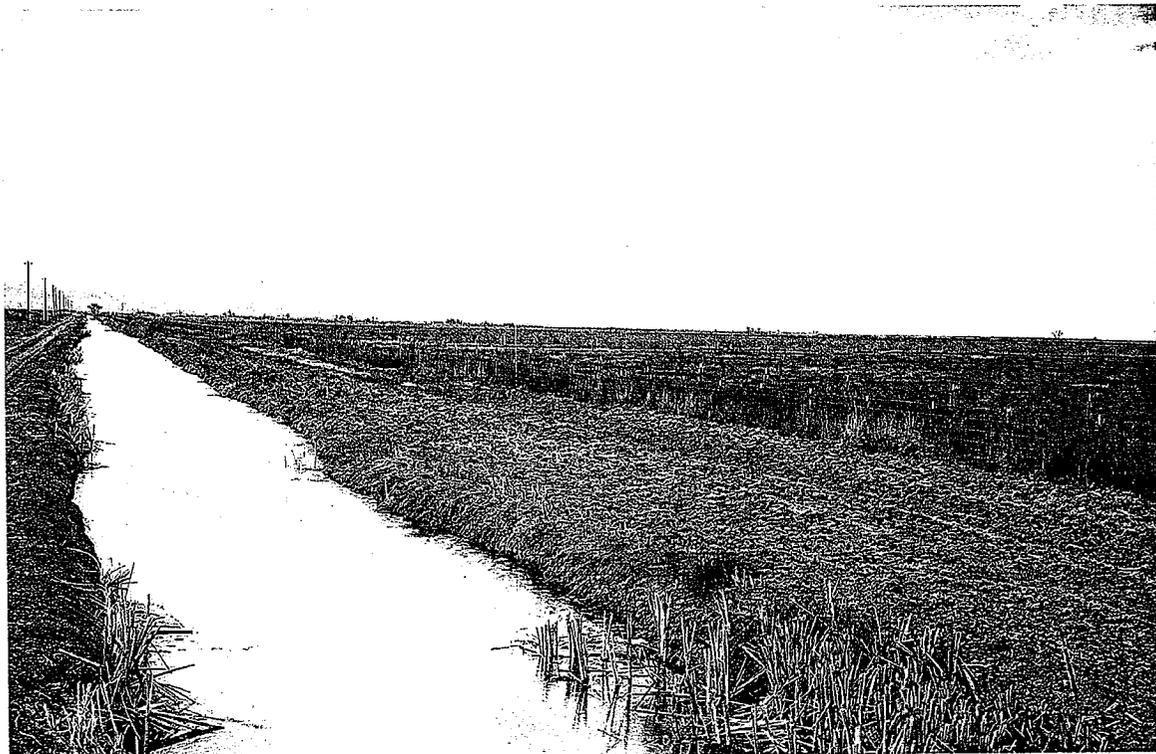
San Joaquin River Water Quality Improvement Project
2001 Crop Map

SUMMERS ENGINEERING, INC.
Consulting Engineers
HANFORD CALIFORNIA
April 2001

Figure 25. Location of the bermuda grass pasture study site in the San Joaquin River Water Quality Improvement Project (SJRWQIP) at the Panoche Drainage District.



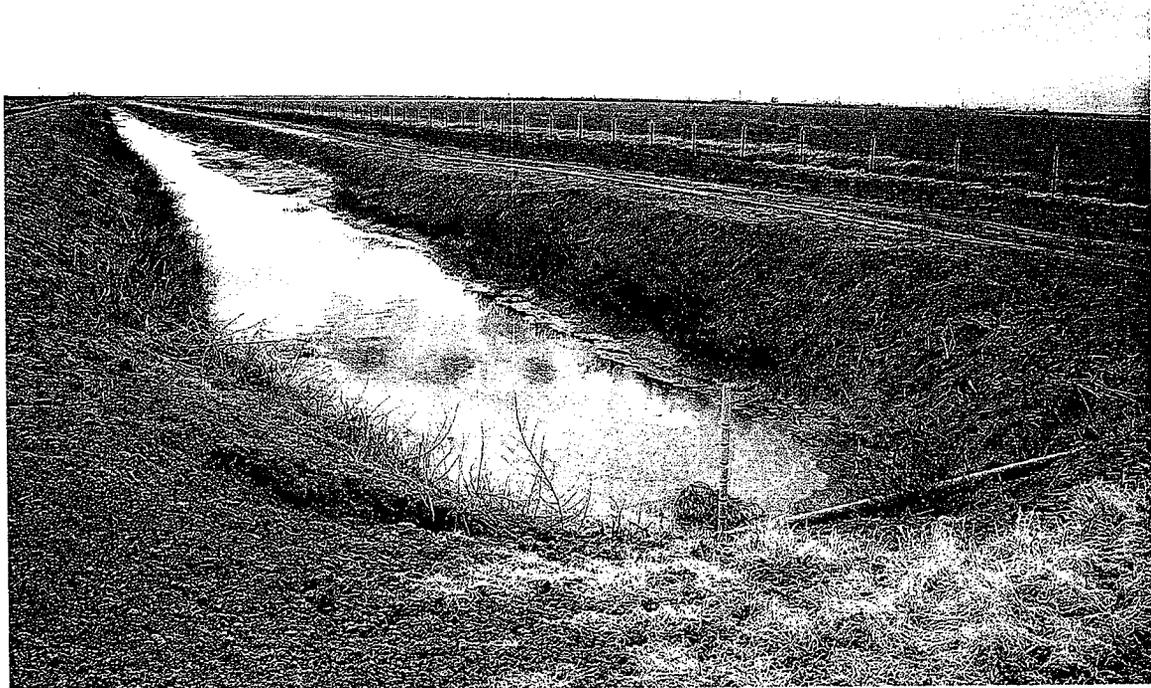
Photograph 14. Field 2-8, one of the bermuda grass pastures that was irrigated with undiluted drainage water.



Photograph 15. Channel that delivered drainage water to the bermuda grass pastures studied.



Photograph 16. Headwater distribution during flood irrigation of Field 2-8.



Photograph 17. Seepage trench between Field 2-7 and Field 2-8 at its lower, discharge end (Sample Site 7/8).

Each of the three fields was separated by a seepage trench, and there were trenches on the outer north-south borders of Field 2-6 and 2-8. Thus, there were four seepage trenches altogether, but samples were collected from only the middle two trenches designated "6/7" (between Fields 2-6 and 2-7) and "7/8" (between Fields 2-7 and 2-8). The floors of the seepage trenches were approximately 6 feet below the pasture grade. The trenches were about 20 feet wide at their tops and 8 feet wide at their floors with 0.5 feet to 2 feet of water depth. Cattle were kept about 25 feet from the seepage trenches by fence, and no surface runoff approached the trenches.

Samples of the applied drainage, field tailwater if present, and seepage trench effluent were collected once in March 2002 and then weekly during July through September 2002. The seepage effluent flow was measured when samples were collected, and the water surface elevation in the two seepage trenches was recorded. This flow and elevation data was compared to irrigation timing and location to show the influence of the irrigation in the adjacent field to the drainage in the seepage trench.

RESULTS

Total Dissolved Solids: The primary drainage applied to the bermuda grass pasture had an average TDS concentration of 2,780 mg/L (range: 1,860 to 3,290 mg/L), and the tailwater samples had similar TDS concentrations. The secondary drainage TDS averaged five-times higher in the 6/7 seepage trench (14,370 mg/L) and nine-times higher in the 7/8 trench (23,850 mg/L). In comparison, the TDS concentrations at the Red Rock Ranch Integrated On-Farm Drainage Management Facility (IODMF) had the concentrations shown in **Table 9**.

Table 9. Water quality at the Red Rock Ranch Integrated On-Farm Drainage Management Facility on May 26, 2000 (top line of each cell) and the average during 1995-1998 (bottom line of each cell). The raw data were provided by K. Buchnoff-Kirn of DWR in 2002.

Sample Site	TDS (mg/L)	Nitrate as N (mg/L)	Cl ⁻ ÷ Nitrate as N (mg/L ÷ mg/L)	Total Se (µg/L)	Cl ⁻ ÷ Se (mg/L ÷ mg/L)
Irrigation water for salt-sensitive crops	245	na	na	1	na
	na	na	na	na	na
Drainage from salt- sensitive crops	7,100	na	na	383	na
	8,800	92	25	870	2238
Drainage from salt- tolerate crops and grasses	8,500	na	na	556	na
	12,000	154	18	1412	1933
Drainage from halophytes	10,700	na	na	625	na
	9,900	192	24	1122	2369
Evaporator contents	5,000	na	na	na	na
	to	na	na	na	na
	33,000 na				

na = not available

At the SJRWQIP, the salt-tolerate grasses were irrigated with much fresher water than at Red Rock Ranch (2,780 vs. ~8,000 mg/L TDS), but the resultant drainage was as concentrated as drainage from the Red Rock Ranch halophytes or evaporator. The high concentration in the SJRWQIP secondary drainage may be due to additional leaching of salt from the soil and evaporation from the seepage trenches, in addition to concentration by crop evapotranspiration.

Nitrogen: The drainage used to irrigate the bermuda grass pasture contained an average of 12.3 mg/L of nitrate+nitrite nitrogen during the March through September 2002 sampling (**Figure 26**). However, the concentrations varied considerably over time—ranging from 0.5 to 20.2 mg/L as N. Tailwater nitrate+nitrite concentrations were also highly variable

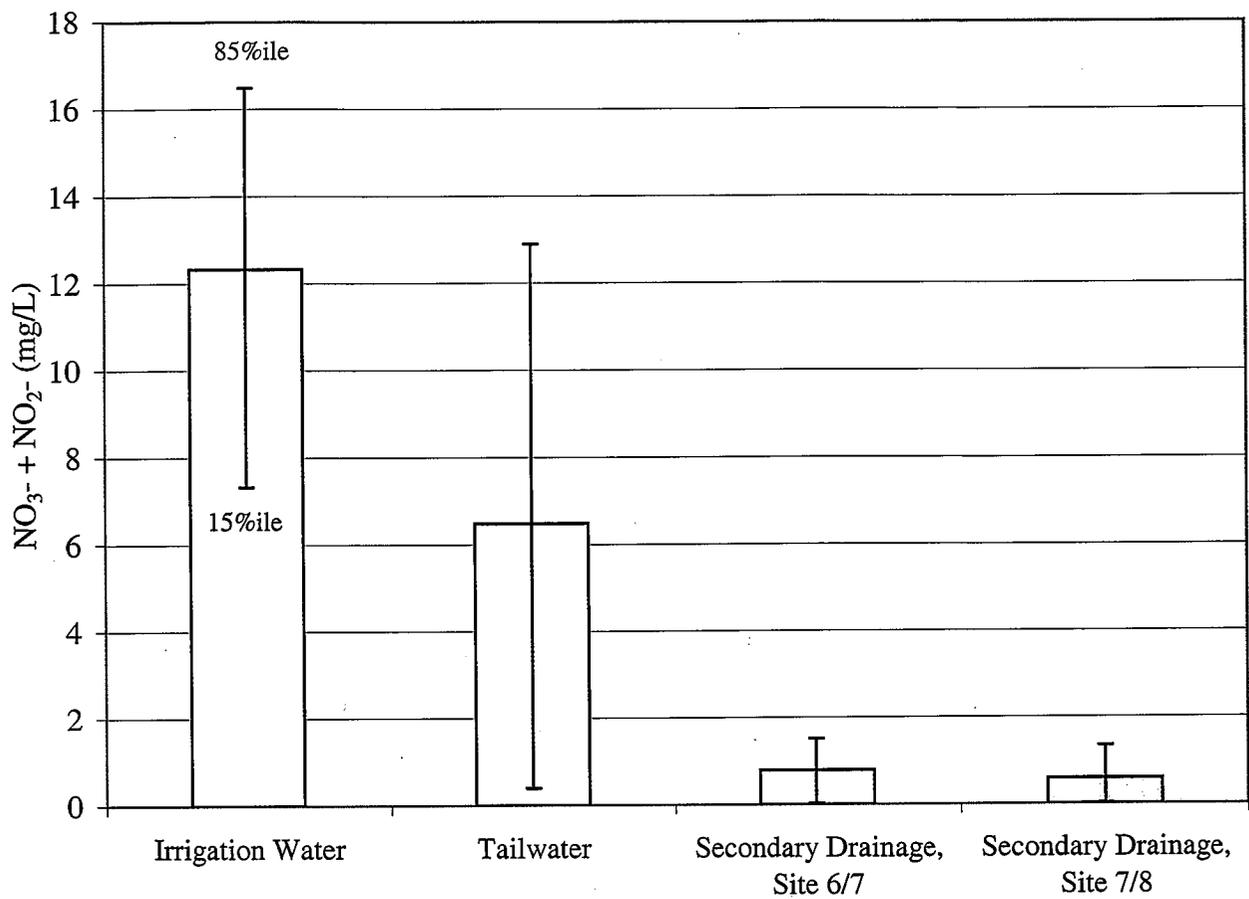


Figure 26. Mean nitrate+nitrite nitrogen concentrations in primary drainage used for irrigation of pasture, in tailwater, and in secondary drainage from two seepage trenches adjacent to the pasture in the San Joaquin River Water Quality Improvement Project during March-September 2002.

and had no correlation to the concentrations of the irrigation water. The secondary drainage from the seepage trenches (Sites 6/7 and 7/8), however, contained considerably less nitrate+nitrite nitrogen than the irrigation water, averaging <1 mg/L oxidized nitrogen. The low concentrations in the seepage trenches could be caused by uptake by the crop, denitrification in the soil, and uptake by periphytic algae growing on the submerged banks of the trenches. These algae were not filamentous, but instead formed a tan film on the submerged earth.

If TDS is assumed to be a conservative tracer, then a considerable N mass was removed during the irrigation process. Using the five-fold increase in TDS of trench 6/7 as an example, the nitrate+nitrite in the secondary drainage should have averaged $(12 \text{ mg/L N})(5)=60 \text{ mg/L N}$ after evapotranspiration. Because it instead averaged 0.8 mg/L, the nitrate+nitrite removed was approximately $(60 \text{ mg/L N})-(0.8 \text{ mg/L N})=59.2 \text{ mg/L N}$. Such a decrease in oxidized nitrogen would greatly lessen the operating cost of the ABSR Process. Oxidized nitrogen inhibits selenium reduction and is often found in drainage at 100-fold higher concentrations than selenium. As such, most of the substrate used in the ABSR Process is required for denitrification.

In contrast to the SJRWQIP, the nitrate concentration more than doubled as drainage passed through the Red Rock Ranch IODMF during 1995 through 1998. The nitrate concentrations were also much higher (92 to 192 mg/L as N) compared to <20 mg/L as N at the SJRWQIP. (Table 9). Assuming that chloride ions were a conservative tracer, the ratio of Cl⁻ to nitrate remained fairly constant as the drainage progressed through the system, indicating that nitrate mass was not significantly changed by the crop and that the doubling was due to evapotranspiration. Selenium behaved similarly to nitrate at the IODMF, increasing in concentration through the system but without mass removal, as indicated by the Cl⁻ to Se ratio.

Selenium: At the SJRWQIP, the concentration of total soluble selenium did not change significantly from primary drainage to secondary drainage (Figure 27), however, the

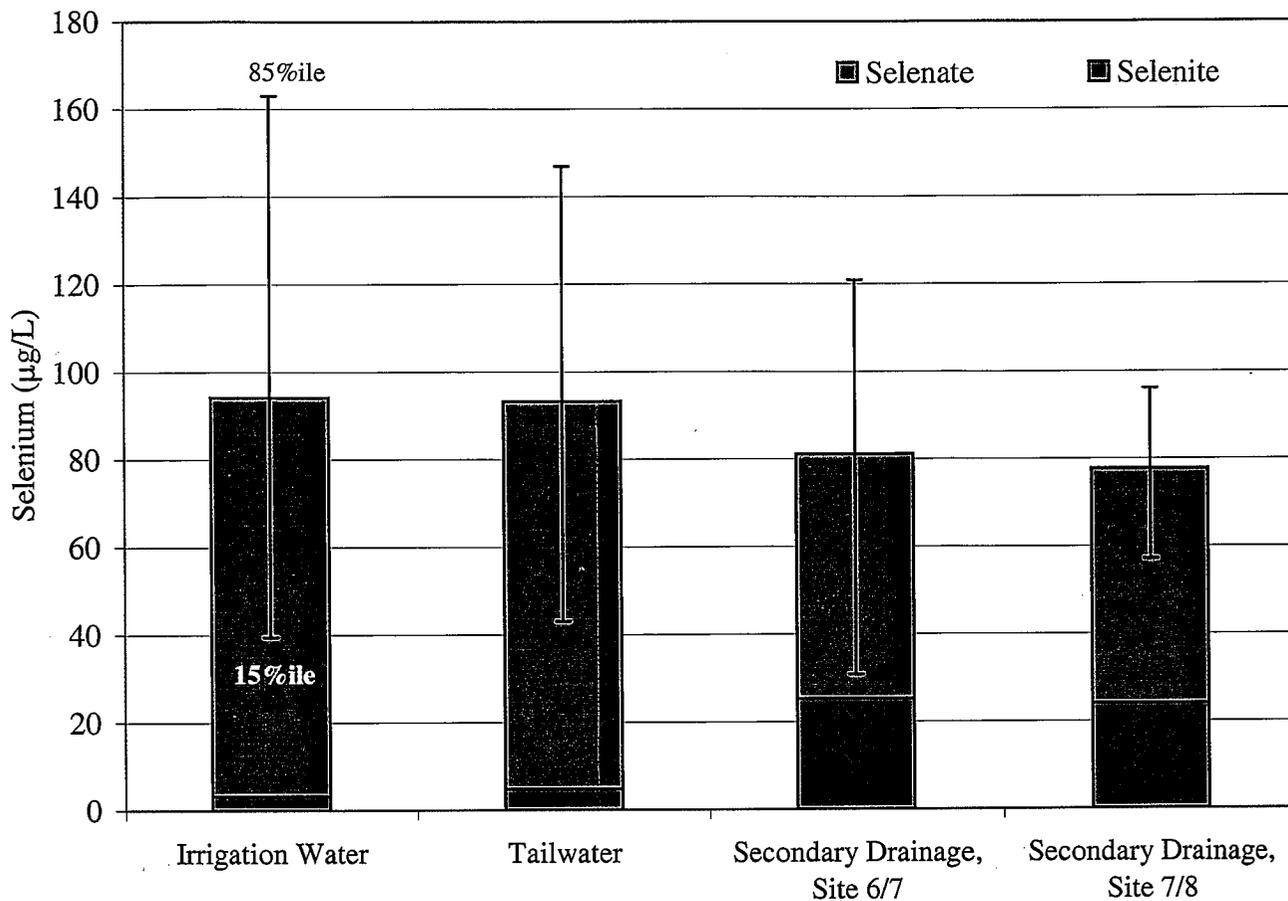


Figure 27. Mean selenate and selenite selenium concentrations in primary drainage used for irrigation of pasture, in tailwater, and in secondary drainage from two seepage trenches adjacent to the pasture at the San Joaquin River Water Quality Improvement Project during March-September 2002.

selenite fraction did increase from an average of 3 $\mu\text{g/L}$ to 25 $\mu\text{g/L}$ indicating reductive processes were present.

Reduced substances such as organic carbon or sulfide are necessary for reduction of selenate to selenite. The most obvious source of organic carbon in the study area was the manure deposited on the pastures from the 75 cow and calf pairs that graze there during April 15th to October 15th of each year. The tailwater from the pastures was tan-colored suggesting high organic content. Indeed, volatile suspended solids (VSS) determined for three tailwater samples were high: 87 mg/L, 224 mg/L, and 1309 mg/L.

The total manure deposited during a grazing season and its organic matter and nitrogen content can be estimated using typical as-excreted manure production rates for beef cows (SCS, 1992). The cows and the calves weighed an average of 825 lbs and 325 lbs, respectively, giving a total of $(825+325 \text{ lbs}) \times (75 \text{ pairs}) = 86,250 \text{ lbs}$ of animals on the pastures (C. Hurley, 2003). At 6.2 lbs of VS per 1,000 lbs of animal, during the 183 days of April 15th to October 15th, a total of 97,859 lbs VS would have been deposited on the 144 acres or 680 lbs VS/acre.

During the 2002 irrigation season, 3.51 feet of drainage was applied to the pastures. Thus, the ratio of manure VS applied to drainage applied was 71 mg VS per liter of drainage applied.

Other sources of organic carbon in the study area were algae in the irrigation water, the bermuda grass itself, and the algae growing in the seepage trenches. VSS in the irrigation water averaged 73 mg/L (range: 46 to 91 mg/L) which is about equal to the manure VS application of 71 mg/L. The two seepage trenches had higher suspended solids content, averaging 142 mg/L (range: 61 to 203 mg/L), but this secondary drainage was not applied to the pastures.

Denitrification, another reduction process, is a precursor to dissimilatory selenium reduction, as mentioned above. The algae-fed Mode 1 ABSR System has removed as much as 0.21 mg nitrate-N per mg of algal VS substrate (Lundquist *et al.*, 2001). If half of the 73 mg/L VSS in the irrigation water were algae and were degraded in anaerobic zones in the soil,

then $(50\%) \times (73 \text{ mg/L VSS}) \times (0.21 \text{ mg N/mg VS}) = 7.7 \text{ mg/L N}$ could have been denitrified in the soil. This quantity is a substantial portion of the average 12.3 mg/L nitrate+nitrite N that remained in the drainage when it was applied to the pastures. A similar amount of denitrification might be expected due to the manure VS deposited on the pastures. The measured nitrate+nitrite removal from the drainage applied to the SJRWQIP pastures seems plausible considering nitrogen uptake by the bermuda grass and the possible denitrification powered by VS applied with the manure and irrigation water algae.

Considering the five-fold increase in TDS in trench 6/7 as compared to the TDS of the irrigation water, the expected total soluble selenium concentration can be estimated as it was for nitrate+nitrite. Assuming TDS as a conservative tracer: $(95 \text{ } \mu\text{g/L total soluble Se})(5) = 475 \text{ } \mu\text{g/L total soluble Se}$ should have been in the secondary drainage. Since an average of $80 \text{ } \mu\text{g/L}$ of soluble selenium was measured in the secondary drainage, approximately $(475 \text{ } \mu\text{g/L}) - (80 \text{ } \mu\text{g/L}) = 395 \text{ } \mu\text{g/L}$ of soluble selenium may have been removed from the flow.

The differences in the Panoche Drainage District and Red Rock Ranch drainage reuse sites are great. The pasture at Panoche's SJRWQIP is fortified with a considerable amount of organic matter from manure and algae, whereas at the IODMF, the crop litter is the prime source of carbon addition. The additional carbon at SJRWQIP may allow the substantial decrease in oxidized nitrogen and increase in selenite observed. Alternatively, because groundwater flows were not monitored in this study, it is possible that the drainage in the seepage trenches was affected by up-gradient groundwater that diluted oxidized nitrogen. Also, the selenite in the seepage trenches could have been produced during bacterial degradation of organic sediment in the trenches.

NEEDED RESEARCH

BIOLOGICAL TREATMENT

The results of our continuing pilot-scale studies at the Panoche Drainage District indicate that our reduction system due to its shallow depth could not be maintained free of

dissolved oxygen intrusion and that selenite, when reduced from selenate in such a semi-anoxic environment, tends to remain in the selenite form binding to negatively charged colloidal particles such as silt, microalgae and bacteria. Such selenite-bearing colloidal particulates can then be taken up by protozoa and invertebrate filter feeders entering the food web and ultimately vertebrate DNA with subsequent teratogenesis. The removal of such selenite-bearing particulates is essential since some selenite may be formed and adsorbed to a negatively charged suspended solid that may be carried forward in the Reduction Pond effluent. On the other hand, it should be possible to avoid production of partially reduced selenite with well designed reduction systems. It follows that our new pair of Reduction Ponds at the intermediate-scale ABSR Facility must be designed to completely and permanently exclude any drainage water containing dissolved oxygen. Selenate and selenite contained in drainage can then be reduced all the way to selenide and rendered permanently insoluble by precipitation by iron or other polyvalent cations. Our work with fermentation cells in sewage treatment has proved that redox potentials in the -0.3 to -0.5 volt range can be attained and sustained through rational design and operation (e.g. organic loading) of these fermentation cells. We have applied this technology and process to the ABSR irrigation drainage treatment process.

In addition to being too shallow, our existing pilot-scale Reduction Ponds, while converting nitrate to nitrogen gas, were being gently mixed by the nitrogen gas bubbles as they emerged and rose through the overlying water. In spite of the Reduction Ponds' opaque plastic surface covers, wind action across these surface covers and the exposed surface water at periphery of the surface covers inevitably resulted in the intrusion of some dissolved oxygen. This intrusion of dissolved oxygen into the deeper more anoxic depths decreased the efficiency and the stability of the oxidation-reduction conditions that are meant to be low (i.e. -0.3 to -0.5 volts) in order to reduce selenate completely avoiding the production of selenite. The indicated solution to this problem is to first reduce most, if not all, of the nitrate present in the drainage in a primary reduction cell followed by a secondary cell where any residual nitrate, selenate, selenite, and elemental selenium can be reduced to selenide. There,

as noted above, selenide can be instantly, permanently fixed in the insoluble, anoxic, bottom sediments by precipitation with polyvalent cations. Accordingly our new intermediate-scale ABSR Facility will have at least two reduction cells in series, the first to reduce nitrate and the second to reduce selenate all the way to selenide. A second identical pair will permit simultaneous controlled studies.

The removal of particulates (colloidal inorganic silts, algae and bacteria) may ultimately be needed to prevent the discharge of any trace amount of selenium, especially particles containing organo-selenium compounds that are bioavailable and concentrate in the food web. According, we have explored during the current study final filtration to further remove suspended solids from the treated drainage effluent of the existing pilot-scale ABSR Facility in which low-cost agricultural molasses has been most successfully used as an available source of carbon. We have obtained turbidities of less than 2 NTU using diatomaceous earth filtration, but we have also found trace amounts of selenite present in the filtered effluent. Of course, both selenate and selenite are so soluble that they must be reduced or precipitated in some way if they are to be removed as suspended particles. Their precipitation or adsorption in aerobic systems is unlikely. Future studies must focus on more efficient use of carbon-rich substrates by determining the precise relationship between the organic loading and redox conditions when treating drainage with various substrate additions and salt concentrations. The use of algae as a carbon-rich substrate for nitrate-reducing bacteria and selenate-reducing bacteria should be continued because of their high productivity compared with other crops such as sugar beets that yield meager amounts of molasses as a carbon-rich substrate. The productivities of microalgae exceed those of most agricultural crops by many fold. Among the problems we find in using green microalgae as a carbon source for nitrate-reducing and selenate-reducing bacteria is the cost of their harvest and their natural ability to hibernate and thus avoid bacterial decomposition for long periods under dark, anoxic conditions. The blue green alga *Spirulina* is easily harvested and, though not as productive as most green algae, *Spirulina* is far more digestible and fermentable than are most green microalgae. *Spirulina* could be grown in the existing pilot-scale ABSR High Rate

Ponds and then used in the intermediate-scale ABSR Facility to determine its availability as a carbon source for nitrate-reducing and selenate-reducing bacteria. The fact that *Spirulina* grows well on nitrate as a source of nitrogen and on carbonate as a source of carbon should not be overlooked as an antecedent to subjecting drainage waters to Reverse Osmosis (RO). As is well known, removal of the carbonate ion can mitigate scale formation on RO membranes. The cultivation of the salt-tolerant green alga *Dunaliella* on drainage RO brine concentrates should also be investigated since *Dunaliella* is a rich source of valuable, natural beta carotene. The growth of green algae in series with *Spirulina* should also be explored in higher salinity drainage.

Improved selenium reduction efficiency and substrate use efficiency are expected in the next generation ABSR Facility design. This intermediate-scale, one acre-foot per day Facility will be constructed during 2004 and will have anoxic treatment zones that are better protected from oxygen intrusion than the existing ABSR Facility. More complete substrate-drainage mixing and improved drainage-bacterial biomass contact in the new Facility should also contribute to increased efficiencies. It will be determined if, together, these design improvements also increase the production of the highly reduced, easily precipitated inorganic selenide form of selenium.

PARTICULATE SELENIUM REMOVAL

While it is expected that <2 NTU effluent can be produced reliably with multi-media filters treating Reduction Pond effluent, filter backwashing efficiency appears crucial to filters' long-term selenium removal performance. Particulate selenium remaining in the media after backwashing appears to be converted to soluble selenite which is release into the final effluent. Future studies should determine more precisely relationship between selenite release and backwash flow rate, frequency, and duration. Microfilters, while potentially vulnerable to biofouling, do not have media to be cleaned during backwashing. As such, microfiltration should be evaluated as an alternative to media filtration.

SECONDARY DRAINAGE CHARACTERIZATION AND TREATMENT

Lysimeter studies should be conducted at the bermuda grass pasture and other crop fields to confirm the results of this study, to explore the use of organic carbon (crop litter, algae, manure, etc) as substrate for nitrate and selenium reduction, and to determine the form and fate of selenium in the field soil. As the slow sand filter study, described in the *Biological Treatment* section, indicates, when soil becomes aerobic, reduced selenium may be remobilized. If nitrate and selenium concentrations can be decreased during drainage irrigation without the crops exceeding safe selenium contents, the size and cost of downstream selenium treatment facilities might be lessened.

BRINE TREATMENT

Besides sodium chloride, other compounds in drainage brine may affect biological treatment. Sulfate is a candidate inhibitor because, even in primary drainage, it's concentration is typically high (c. 2,500 mg/L), and because it can be reduced to toxic hydrogen sulfide, its reduction may compete with and inhibit nitrate and selenium reduction. Sulfate reduction, however, has been minimal at the pilot-scale ABSR Facility. Laboratory studies using sulfate-enriched drainage and actual reverse osmosis brines are recommended. In the near future, such brine is expected to be available from an RO pilot plant located at the ABSR Facility site and operated by the Bureau of Reclamation.

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