Selenium and nitrate removal from agricultural drainage using the AIWPS® technology

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Abstract Monthly Maximum Discharge Limits (MMDL) have been established for selenium in irrigation drainage by the State of California and the U.S. Environmental Protection Agency following observations of avian teratogenesis at the Kesterson Reservoir in the San Joaquin Valley of California. As a result of these and other adverse effects, farmers and drainage districts on the western side of the San Joaquin Valley must reduce selenium concentrations in irrigation drainage discharged to the San Joaquin River. Drainage treatment will be required in the near future to meet existing MMDL and future Total Maximum Discharge Limits (TMDL) for the San Joaquin River. A 0.4-hectare Algal Bacterial Selenium Removal (ABSR) Facility was designed and constructed at the Panoche Drainage District in 1995 and 1996 using the Advanced Integrated Wastewater Pond Systems® or AIWPS® Technology. Each of two physically identical systems combined a Reduction Pond (RP) with a shallow, peripheral algal High Rate Pond (HRP). A Dissolved Air Flotation (DAF) unit and a slow sand filter were used to remove particulate selenium from the effluent of each system. The two systems were operated under different modes of operation and the bacterial substrate varied in each system. The rates of nitrate and selenium removal were compared. Microalgae were harvested using DAF and used as a carbon-rich substrate for nitrate- and selenate-reducing bacteria. Mass removals of total soluble selenium of 77% or greater were achieved over a three-year period. Nitrate and selenate were removed by assimiliatory and dissimiliatory bacterial reduction, and nitrate was also removed by algal assimilation. The final removal of particulate selenium is the focus of ongoing investigations. The removal of particulate selenium is expected to increase the overall removal of selenium to greater than 90% and would allow farmers and drainage districts to discharge irrigation drainage in compliance with regulatory discharge limits.
Keywords AIWPS® technology; algal-bacterial; irrigation drainage; nitrate; selenium

Irrigation and selenium toxicity

A large inland sea once covered the San Joaquin Valley and part of the Coastal Range of California (U.C. Agricultural Issues Center, 1987). About 60 million years ago, the western section of this sea uplifted and formed the Coast Range. More uplifting caused the sea to recede, leaving behind a valley containing ancient marine sediments. Shale in the Coast Range has eroded and oxidized leaving selenium-rich soils in the western San Joaquin Valley where large-scale irrigated agriculture has been practised since the 1940s (Tanji, Lauchli, and Meyer, 1986).

Dams and canals built during the 1940s, 1950s and 1960s provided irrigation for thousands of hectares of cotton, alfalfa, tomatoes, melons, and orchard fruits. Due to the Corcoran Clay layer and other impervious subsurface soil layers, natural drainage in parts of the western San Joaquin Valley is poor. Under flood irrigation conditions, the water table can rise into the crop root zone. Salts accumulate as irrigation water is lost to evapotranspiration forming "alkali soils." Salt accumulation was lessened by the installation of subsurface tile drains and by the application of excess irrigation water to move salts below the crop root zone. Drainage canals have been used to collect and discharge irrigation drainage through the San Luis Drain and Mud Slough to the San Joaquin River. A proposed

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"master drain" to the San Francisco Bay estuary has not been completed. Instead, beginning in 1978, western San Joaquin Valley drainage was discharged and evaporated in a terminal wetlands known as Kesterson Reservoir. Because of its location on the major migratory bird flyway, the area was designated as the Kesterson National Wildlife Refuge (U.C. Agricultural Issues Center, 1987).

Teratogenic effects of selenium on wildlife were observed at Kesterson in the early 1980s. Mosquitofish (*Gambusia* sp.) in Kesterson Reservoir were found to contain unusually high tissue levels of selenium (Saiki and Lowe, 1987), and bird nests in the wildlife refuge were found to contain exceptionally high numbers of deformed or dead embryos (Tanji, Lauchli, and Meyer, 1986). Other studies have shown selenium contamination in wildlife areas in 14 other states (Harris and Morris, 1985). To prevent further contamination of the Kesterson Reservoir, the San Luis Drain was closed in June 1986, and the return irrigation flows have instead been conveyed to the San Joaquin River and thence to the San Francisco Bay estuary. Approximately 350 MLD of selenate- and nitrate-contaminated irrigation drainage is produced by agriculture in California's San Joaquin Valley.

Properties of selenium

Chemical properties

Selenium (Se) is a group VI element, appearing directly below sulfur on the periodic table. As such, it behaves similarly to sulfur. Selenium can exist in the VI, IV, zero, and -II oxidation states. Selenium may substitute for sulfur in the amino acids cysteine and methionine, and it can also exist in volatile methylated species including dimethyl selenide, dimethyl diselenide, and dimethyl selenone (Doran and Alexander, 1977).

Biological properties

Selenium is required by higher animals as a trace nutrient (Garberg and Hogberg, 1986) and by some microbes (Lindblow-Kull, Shrift, and Gherna, 1982; Lindstrom, 1983). In excess, selenium is toxic to all organisms. Shrift (1954) showed that selenomethionine interfered with cell division in the alga *Chlorella* leading to the formation of "giant cells." Toxicity in livestock is seen at dietary levels of 3–5 ppm (Burau, 1985). Single doses are lethal to laboratory animals at 1.5–6 mg/kg body weight (Garberg and Hogberg, 1986). Mechanisms for the toxicity include substitution of Se atoms for S atoms in amino acids resulting in inhibition of protein synthesis and depletion of methyl groups.

Many bacteria can reduce selenate and selenite to Se^0 (Silverberg, Wong, and Chau, 1976), and many organisms have been shown to convert Se(VI) and Se(IV) to organic selenium compounds, in which the selenium is in the -II state, including bacteria (Doran and Alexander, 1977), zooplankton (Cutter, 1982), mice (Ganther, 1966), barley (Zieve and Peterson, 1984), and cabbage (Lewis, Johnson, and Broyer, 1974).

Drainage water composition

The chemical composition of the drainage water to be treated has important implications on potential treatment processes. Because of the sulfate and other components such as sodium, calcium, and chloride, the total dissolved solids (TDS) level in drainage water is quite high, ranging from 5,000 to 20,000 mg/l (Table 1). California has recommended an interim maximum concentration of 5 μg/l for selenium in the San Joaquin River at Crow's Landing and downstream and 2 μg/l in wetlands (SWRCB, 1989), while the U.S. EPA standard for selenium in drinking water is 10 μg/l.

Solutions

Of the many options open for consideration in remedial actions, treatment of drainage waters is high on the list. The many modes of treatment proposed may be categorized as physical, chemical, biological and combinations of the three. This report deals mainly with the potential of biological treatment with algae and bacteria employing advanced forms of high rate, facultative and anaerobic ponds in strategic combinations. The objective is to bring concentrations of selenium and heavy metals in drainage waters into conformity with established water quality standards for fresh water aquatic life.

Nitrate (NO_3^-) is also a major component of the San Joaquin Valley drainage water, and its presence greatly complicates selenium removal. Because most of the selenium is present as Se(VI), the most soluble form, removal by physical means such as sorption or sedimentation requires that the selenium first be reduced to Se(IV) or Se^0. However, the region of oxidation-reduction potential (Eh) in which Se(VI) is reduced to Se(IV) and Se^0 is roughly the same as the region in which nitrate is reduced to elemental nitrogen (N_2), a process called denitrification. Since nitrate in drainage waters may be found in concentrations as high as 150 mg/l as N, two to three orders of magnitude greater than selenium concentrations, NO_3^- competes with Se(VI) for reducing agents. Therefore, nitrate reduction is necessary before selenium reduction in drainage waters.

The ABSR process

A 75 m^3 per day ABSR Facility has been treating agricultural drainage water in the District on the western side of the San Joaquin Valley since 1997. The pilot-scale ABSR Facility consists of two parallel series of ponds designed to promote indigenous microorganisms that remove nitrate and selenium. The ABSR Process is a unique application of the Advanced Integrated Wastewater Pond Systems® or AIWPS® Technology that was developed by Professor W.J. Oswald and his research associates at the University of California, Berkeley over the past five decades. During 1997 and 2000, the ABSR Facility reduced nitrate by over 95% and reduced total soluble selenium mass by 80%. Recent DAF and slow

Table 1 Range of Individual Constituents Reported in San Joaquin Valley Agriculture Drainage Waters[a]

Parameters	Concentration[b] Maximum	Minimum	Average[c]
Calcium	590	55	369
Magnesium	583	54	161
Sodium	5,250	400	1,093
Potassium	7.0	0.9	4.0
Bicarbonate	391	132	214
Sulfate	10,100	607	2,282
Nitrate (NO_3^-)	234	3.2	97
Chloride	2,680	110	987
Manganese	0.36	0.04	–[d]
Iron	12	0.04	2.1
Strontium	4.8	3.6	–[d]
Boron	34	1.4	12
Silica	60	7.2	26
Phosphates (as P)	0.15	0.01	0.04
Total Organic Carbon	14	1.0	4.6
pH (units)	8.0	7.0	7.3
Temperature (°C)	21	7	16
Suspended Solids	715	1	54
Total Dissolved Solids	20,700	1,930	5,342
Electrical Conductivity (µmho/cm)	21,500	2,250	6,462

[a] From Gerhardt *et al.* (1991)
[b] Concentrations of chemical constituents are expressed as milligrams per litre (mg/L) of constituent unless stated otherwise
[c] Average based on 5 to 200+ individual samples
[d] Only two samples

sand filtration studies have shown over 90% removal of total selenium. DAF followed by sand filtration was necessary to remove particulate selenium, the organic fraction that is most bioavailable to aquatic organisms and aquatic food webs. Investigations focused on optimizing operational parameters and determining operational costs and scale-up design requirements. Preliminary capital and operational costs for the ABSR Process were estimated to be between \$200/AF and \$300/AF (\$0.16/m^3–\$0.24/m^3) for full-scale ABSR Facilities with a capacity of 30 AF/d (37,000 m^3/d or 37 MLD) including solids disposal. The literature reflects that the ABSR Process has the longest track record and lowest projected cost of any drainage treatment technology for selenium removal (Quinn *et al*., 1998).

The basic concept underlying the ABSR Process is to grow microalgae in drainage water and to use the algal biomass, together with other supplements, as the carbon sources for indigenous nitrate- and selenium-reducing bacteria, such as *Pseudomonas* and *Bacillus* (Oswald, 1985; Gerhardt *et al*., 1991; Lundquist *et al*., 1994; Green *et al*., 2001; Zarate, 2001). In the near absence of oxygen and nitrate, the bacteria use soluble selenate as an electron acceptor reducing it to selenite and other insoluble forms such as organic and elemental selenium. A portion of the selenite combines with polyvalent cations present in the drainage to form insoluble precipitates that remain in the sediment on the floor of the Reduction Ponds (RPs). Further selenite and particulate selenium removal and clarification has been accomplished by use of DAF and slow sand filtration. Supplemental carbon sources such as molasses and algal biomass are used as bacterial substrates to enhance the rate of nitrate reduction and selenate reduction.

Past and current studies show that DO and nitrate concentrations must be reduced to low levels before selenate reduction can be optimal. In the research-scale ABSR Facility, DO and nitrate are reduced during respiration by microorganisms at the floor of the RPs that were covered to decrease the intrusion of DO. Since nitrate concentrations in drainage water are often as high as 90 mg/L as N compared to <0.5 mg/L of selenium, the carbon requirement for nitrate reduction far exceeded that required for selenate reduction.

If the filter effluent requires reoxygenation or ammonia removal, it can be subsequently treated in a HRP where microalgae produce dissolved oxygen and assimilate ammonia or nitrate. The low-speed paddle wheel mixing of HRPs requires only 5 to 10 kWh/acre/d, and HRPs have been proven to be 2 to 10 times more energy efficient in producing oxygen as compared with mechanically aerated wastewater treatment processes (Green, 1998).

Insoluble selenium removed from the water column accumulated in settled algal-bacterial biomass and inert materials on the floor of the RPs. This biomass was continuously undergoing anaerobic decomposition, so the volume of inert solids increases very slowly over many decades. Based on experience with similar pond designs, removal and disposal of the solids in a landfill should not be required for many decades (Green *et al*., 1995). Alternatively, the dried inert solids that contain nitrogen and phosphorus, as well as selenium, could be used as a soil amendment on the eastern side of the San Joaquin Valley where soils are known to be selenium deficient.

In one mode of operation, the Reduction Pond effluent flows to a High Rate Pond where micro-algae oxygenate the effluent and remove any ammonium prior to the water flowing to the Algae Settling Pond, designed to remove settleable algae and additional semi-colloidal selenium. The residence times in the ponds are as follows: Reduction Pond, 16 days in the winter and 10 days in summer; High Rate Pond, 5 days in winter and 3 days in summer; and the Algae Settling Pond, 2 days in winter and 0.75 days in summer. In another mode, the drainage water is first applied to the High Rate Pond where nitrate and some selenate are incorporated into algae biomass which, following sedimentation and harvest, can be used as a bacterial carbon source in the Reduction Pond in conjunction with other readily available sources such as molasses. In the Reduction Pond, bacteria convert the remain-

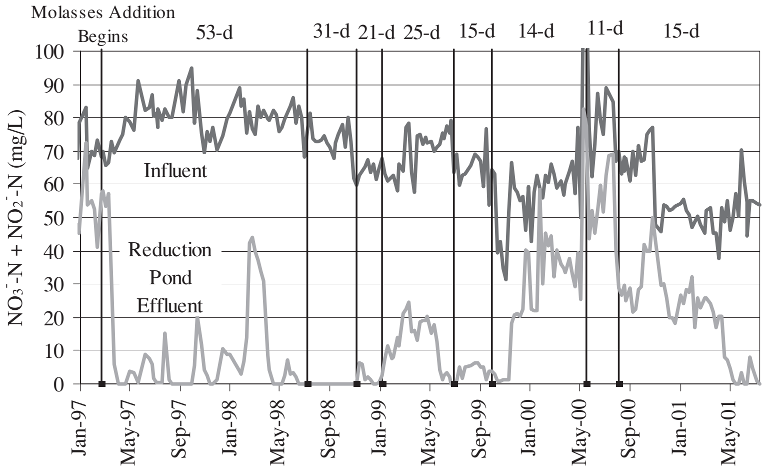

Figure 1 Nitrate+nitrite concentrations in the Mode 2 Reduction Pond. Hydraulic residence times in days are shown

ing nitrate to N_2 while selenium is further precipitated. In either mode, the biomass in the Reduction Pond is continuously undergoing anaerobic decomposition, so the volume of solid residues increases only slowly over many years. Removal and disposal of the selenium-containing solids in a landfill should not be required for many years, if not several decades. Alternatively, the dried inert solids that contain organic nitrogen, potassium, and phosphorus, as well as selenium, might again be useful as a soil amendment and fertilizer in the eastern San Joaquin Valley where the soils are selenium deficient.

Results

From 1997 through 1999, the ABSR Facility at Panoche removed 95% of the influent nitrogen load and 80% of the influent selenium load. Recent results from the ABSR Facility including DAF and slow sand filter units indicated that removals of 90% or greater are possible.

Because of the low cost of methanol and because it, unlike algae or molasses, contains no nitrogen, future laboratory and pilot plant studies are planned to determine the effectiveness of methanol as a carbon-rich bacterial substrate. Preliminary total cost estimates for a proposed 10 acre-feet per day (10-AF/day) or 12,300 m^3/day ABSR Facility using molasses and algae as substrates are less than $200/AF ($0.16/m^3) of treated drainage water. Other cost estimates for a 30-AF/day ABSR Facility are less than $100/AF treated. It was determined that complete anoxia was not consistently maintained due to the relatively shallow depth of 3 m in the Reduction Ponds. The proposed intermediate 10-AF/day ABSR Facility will have deeper Reduction Ponds that should maintain constant redox potentials of at least –0.5 volts and completely anoxic conditions.

Conclusions

Dissolved and particulate forms of selenium, including selenate, selenite, and especially particulate forms of organic selenium, found in irrigation drainage must be removed to prevent selenium bioaccumulation in the environment. The Algal-Bacterial Selenium Removal Process, a special application of the AIWPS® Technology, has been demonstrated to be an effective and economical drainage treatment process at the Panoche Drainage District in the San Joaquin Valley of California. Average total soluble selenium mass removal of >76% was achieved in the Mode 2 Reduction Pond (Figures 1 and 2) for a year with animal-feed-grade molasses used as the main carbonaceous substrate and algal cells as

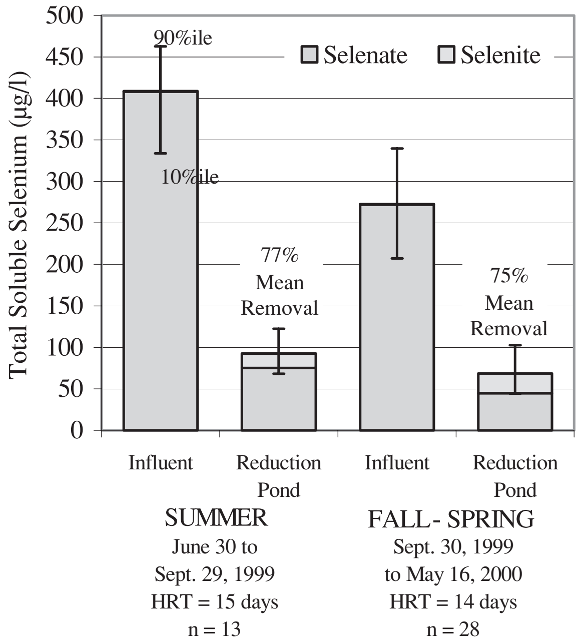

Figure 2 Mean soluble selenium reduction by Mode 2 RP

secondary substrate. Slow sand filtration was shown to be a promising means of removing particulate selenium. Rapid sand filtration, microfiltration, and other types of filtration may also be proven to be effective in removing particulate selenium. The land required for a 10-AF/day (12,300 m^3/day) ABSR Facility is currently estimated to be between 40 and 60 acres. Total costs (capital and O&M) for a 10-AF/day ABSR Facility are likely to be between $200/AF and $300/AF (\$0.16/m^3–\$0.24/m^3) of treated irrigation drainage over a 20-year life and using an interest rate of 7%.

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