APPENDIX E

SELENIUM BIOTREATMENT

TABLE OF CONTENTS

Figures

Acronyms

BOD	biological oxygen demand
BOD_5	biochemical oxygen demand
DO	dissolved oxygen
mg/L	milligram(s) per liter
Se	selenium
TDS	total dissolved solids

Treatment would consist of the biological removal of selenium (Se). Biological removal uses anoxic conditions to convert selenate to elemental Se and other reduced (likely organic) species. Elemental Se has a low solubility and can be separated from solution using standard settling/clarification and filtration methods. Organic Se species are more soluble than elemental Se and more difficult to separate. If nitrate is present, it can be an interfering substance. Bacterial reduction of nitrate is similar to bacterial reduction of selenate although different bacterial species may be involved. Nitrate is preferentially reduced before Se owing to the energetics of the reduction reaction – hence nitrate must often be removed before Se reduction will occur in earnest. Some bacterial species (Macy 1994) such as *thauera selenatis* that will reduce selenate to reduced forms in the presence of nitrate. In addition to Se removal the biotreatment system will remove nitrate and constituents that are associated with particulates (such as some metals and toxic organics, if present) in the treatment system.

Anoxic conditions are typically defined as the condition where no dissolved oxygen (DO) is present and the only oxygen source is chemically bound oxygen such as nitrate. Anaerobic conditions are defined as the absence of both nitrate and free DO. Most Se removal occurs in the region between the practical definition of anoxic and anaerobic conditions. Anoxic conditions can be created readily by adding a carbonaceous source to stimulate the growth of naturally growing bacteria that will reduce nitrate to nitrogen gas. Typical carbonaceous sources like methanol, molasses, whey, etc., will exhibit a biological oxygen demand (BOD) which will drive free oxygen in the water column to low levels. Another method of ensuring low oxygen levels in ponds or other reactors used for selenate reduction is to employ baffles and floating covers to minimize short-circuiting and wind mixing. When adding carbon it is critical to provide only enough substrate for the needs of the bacteria that are responsible for Se assimilatory reduction (Oremland 1994; Frankenberger and Karlson 1994). Nitrate and selenate are both terminal electron acceptors and are used by bacteria in the electron transfer reactions that power their internal machinery allowing them to take in nutrients and grow. Past studies have shown that the rates of Se removal of with lagoon type biological treatment followed by clarification ranged from 68 to 92 percent during a 4-year study (Quinn et al. 2000). For the current planning document, an 80 percent removal rate was estimated.

Two types of biological treatment have been selected for further study: lagoon treatment and high-rate treatment. The description, advantages, disadvantages, and cost assumptions of each of the treatments are described below.

E1 LAGOON TREATMENT FACILITY

E1.1 Description

A schematic of the treatment facility is shown on Figure E-1. The site is assumed to be suitable for gravity flow through the treatment facility. An influent equalization basin is provided. The equalization basin will be used to hold surge flows off-line and the diverted water will be pumped slowly into the treatment facility at no more than 5 percent of the influent flowrate. The volume of the equalization basin was assumed to be 10 percent of the influent flowrate.

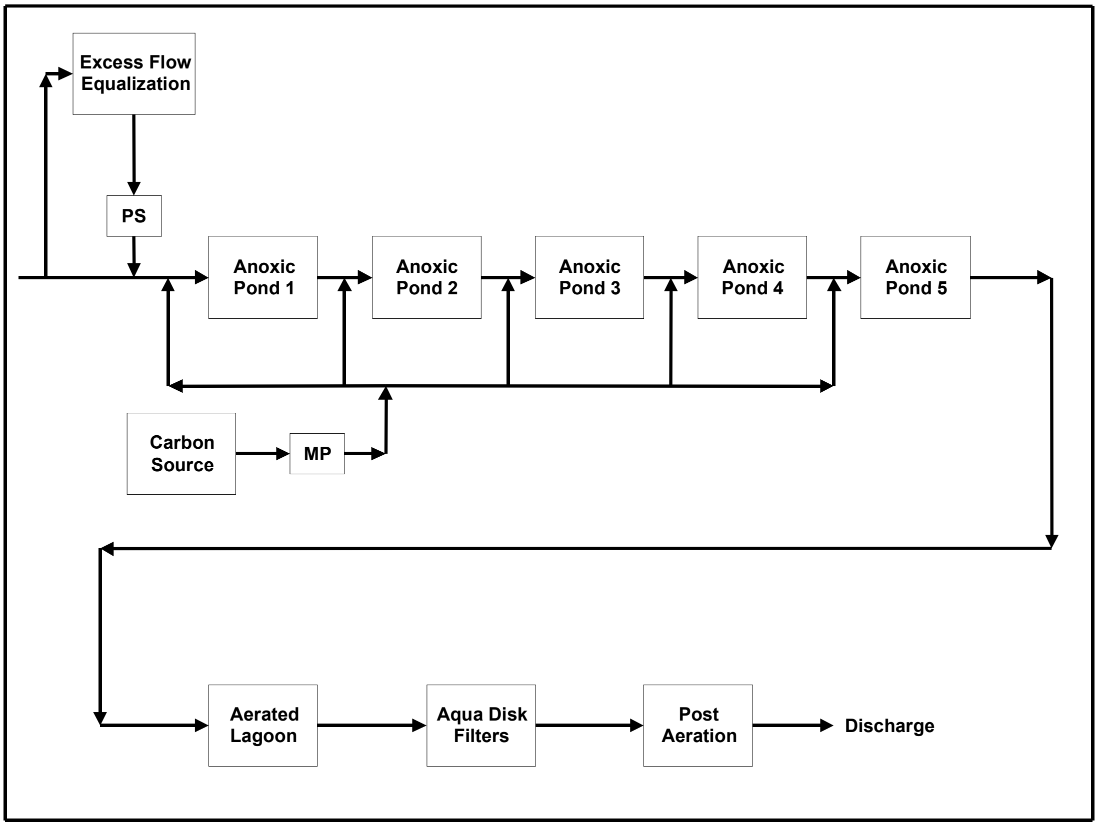

Figure E-1 Lagoon Biological Se Removal Process Flow Schematic

The influent will flow into the first of five lagoon cells in series. The multiple lagoon cell design in series is a typical for lagoon systems to minimize short-circuiting. A 4:1 length to width ratiowas assumed for the lagoons to promote plug flow and minimize short-circuiting. The lagoons are sized with a 20-foot liquid depth to minimize surface area.

Natural aeration will interfere with the process by aerobically consuming the BOD intended to create anoxic conditions. To minimize the effects of wind-inducted aeration, the lagoons will be covered by a floating cover. The pilot tests have been run using molasses as the carbon source. This supplemental organic carbon is one of the major operating costs. For the purposes of this evaluation, methanol was assumed to be used as the carbon source. Other organic materials could be used in place of methanol such as sugar, molasses, or other food processing wastes. The denitrification process can also use a wide range of materials as supplemental organic carbon. Wastes from canning operations, wine production, and soda bottling could easily be used in place of methanol. Domestic sewage or fermented sewage sludge could also provide the substrate needed for this process. It needs to be determined if the Se removal mechanism can use other substrates. If another organic carbon source can be used, operating costs can be significantly reduced. However, the use of any of these alternate sources of organic carbon could not be evaluated until the treatment sites are selected and the final treatment plant capacity is defined. Proximity of the alternate carbon source to the treatment site is a major economic factor.

Methanol is commercially available and is proven to be effective in denitrification systems and is commonly used in nitrate removal systems at conventional wastewater treatment plants.

The feed system was assumed to have the flexibility to feed methanol to any of the five anoxic lagoons. Ninety percent of the methanol is anticipated to be fed to the first lagoon and capacity to feed 10 percent of the total methanol to each of the following four anoxic lagoons. Most of the consumption of methanol and Se removal is expected to take place in the first two lagoons.

The sixth lagoon in the flow schematic is defined as the Aerated Lagoon and this lagoon is intended to be an aerated aerobic system to remove any excess BOD. This lagoon is aerated using coarse bubble diffusers.

Following the Aerated Lagoon is a filtration step to remove any biomass that did not settle in the preceding lagoon and any particulate Se in the effluent. An Aqua Aerobics Aqua Disk Filter or similar could be used in this application. The Aqua Disk Filter is approved for use under Title 22. The disk filter is a compact cloth media filtration system that is typically automated to backwash once head loss exceeds a preset value. To meet the effluent DO permit limit, a Post Aeration basin has been provided. Coarse bubble diffusers are used for efficient oxygen transfer and long diffuser life with little maintenance. An effluent pumping station and forcemain will convey the treated water to the Sacramento-San Joaquin River Delta.

E1.2 Cost Estimates and Assumptions

The following estimates and assumptions were incorporated into the design.

- **Influent water quality.** Influent water quality was estimated based on best available data. In some cases (Westlands Water District) these data were primarily from sampling that occurred in the mid–1980s. New shallow groundwater data are being collected as a part of this Study and will be used to update the costs as they become available. In addition, the effect of reuse facilities on nitrate, Se, and total dissolved solids (TDS) concentrations in drainwater was estimated based on best professional judgment, since long-term monitoring data from such facilities do not exist. This is particularly important because biotreatment system operating costs are largely a function of influent nitrate concentration, which was assumed to be 53 milligrams per liter (mg/L) Nitrate as N. Treatment removal efficiency is based on pilot scale studies conducted for the lagoon system treating drainwater prior to reuse. It is assumed similar removal efficiency would be obtained when treating the more saline reused drainwater.

To account for the above uncertainties inherent in the design assumptions, the contingency factor for developing the costs was increased from 45 to 65 percent.

- **Double Containment for Waste Handling.** After reviewing the process criteria, it became evident that the biological sludge will have a high Se content and may be classified as a hazardous waste. This issue was addressed in the conceptual design by providing each anoxic lagoon with dual containment. The lagoon floor was assumed to consist of a concrete slab. This concrete slab serves as primary containment as well as a hard smooth surface to ensure that the integrity of the lagoon floor is not compromised when the lagoon solids are removed. Other construction options are possible; however, with the need to periodically remove solids with either dredge or a front-end loader, the use of concrete will assure the floor of the lagoon is not damaged and reduce the possibility of primary containment failure. Alternative configurations may be investigated during future design. It was assumed that each lagoon will be taken out of service, the liquid will be pumped over to another operating lagoon, and the sludge will be allowed to air dry. Bobcats or front-end loaders will be used to remove the solids from the lagoon. Lagoon sludge would be hauled off site for disposal as a hazardous material because of the Se content. A second HDPE liner would be placed under each lagoon as secondary containment to prevent loss of Se-laden water to groundwater.

- **Floating Covers for BOD Control.** Pilot testing has shown that the Se removal process is adversely impacted by the introduction of DO. An open lagoon will be naturally aerated and wind action will cause a lagoon to become mixed and will allow oxygen transfer that will stimulate the production of aerobes or facultative anaerobic bacteria that can also remove Se but with the added cost of excessive sludge production. The production of sludge is minimal in a well-designed anaerobic system – the pilot treatment plant at Panoche Water District has accumulated only 12 inches of sludge biomass after more than 4 years of operation. To prevent oxygen interference with the process and to reduce operating costs, the lagoon was assumed to be constructed to have floating covers. The floating cover also has another benefit in that additional mitigation ponds would not be required because the lagoon water surface would not be accessible to wildlife. The covered lagoons will probably go anaerobic and produce hydrogen sulfide. The hydrogen sulfide will be oxidized in the aerated lagoon. If odor emissions become excessive from the aerated lagoon, an iron addition system can be added to chemically precipitate sulfide. For this effort the iron addition system was assumed to not be necessary.

While double containment and floating covers add to the system cost, technical and/or regulatory regions are sufficient for their inclusion into the project.

In a series of experiments conducted at a pilot-scale Se reduction facility within Panoche Water District (Quinn et al. 2000) the researchers reported a retention time needed for selenate reduction of 40 days when using algae as the carbon source. Algae is a low cost substrate for bacterial growth; however, much of the algae that grows on drain water is difficult to kill. Only dead and decaying algae will release the carbon and micronutrients essential for bacterial growth. The researchers therefore turned to molasses as the carbon source for denitrification and selenate reduction. The reported retention time needed for selenate reduction was reduced to 20 days. While the reduction in retention time from 40 to 20 days is a major improvement in the process, from a practical perspective, the lagoon treatment system still requires a large lagoon surface area. An alternative to lagoon treatment is the high-rate treatment described below. The feeding of an organic carbon source such as molasses also adds to the operating cost of the system.

E2 HIGH-RATE TREATMENT FACILITY

E2.1 Description

The Se removal process involves two steps. The first step is denitrification and the second step is Se reduction. Denitrification can be performed at a much higher rate than in the 20-day retention time lagoons through the use of a Moving Bed Bio Reactor system or deep bed denitrification filters. Both processes are fixed film systems that may be suitable for Se reduction also. The reduction of the retention time would significantly decrease the treatment system footprint.

In biological treatment three conditions are currently defined for treatment. Aerobic or oxic conditions are defined as having free DO present in solution. Anaerobic conditions are the other extreme where no DO or other chemical oxygen sources are present. Anoxic conditions fall in between aerobic and anaerobic and are typically defined as only chemically bound oxygen (nitrates) is present in the water with no free DO. Selenate under this definition is a chemical oxygen source similar to nitrate. From a microbial perspective, nitrate is a chemical that is easier to reduce and preferred by more species of bacteria over selenate. Selenate reduction will occur in the presence of nitrate; however, most of the nitrate must be removed to achieve a high degree of Se removal. Some have reported nitrate as an inhibitory substance. Nitrate is not inhibitory in the true sense; rather from a microbial perspective, it is a higher available energy source that is preferred over selenate.

After reviewing the available information on the microalgal and biological Se removal processes, it appears that the basic mechanism is similar to denitrification and that some of the microbes that denitrify may also reduce selenate. The denitrification process is understood and is commonly used in municipal and industrial wastewater treatment. Nitrate removal only requires a retention time of 15 to 60 minutes depending on the nitrate load and final permit limits. At this time, the rate of selenate reduction is not known and would be developed during future design phases. The available information on the mechanism of biological selenate removal was reviewed and the process shown on Figure E-2 was developed. An influent equalization tank is still used to limit peak flow conditions through the selenate biological treatment system.

The lagoon treatment system has been replaced with a high-rate anoxic reactor using the Moving Bed Bio Reactor technology, which is a fixed film biological treatment process that uses a buoyant plastic media to provide a large surface area to volume ratio. For this evaluation, the Kaldnes brand of media was chosen for use. The biomass grows on the media surfaces and sloughs off periodically, much like a trickling filter. Mechanical mixers are used to provide the necessary agitation for the process. A synthetic carbon source is fed to provide the BOD needed to trigger denitrification. It is estimated that nearly 100 percent of the nitrate will be removed in the Kaldnes basin.

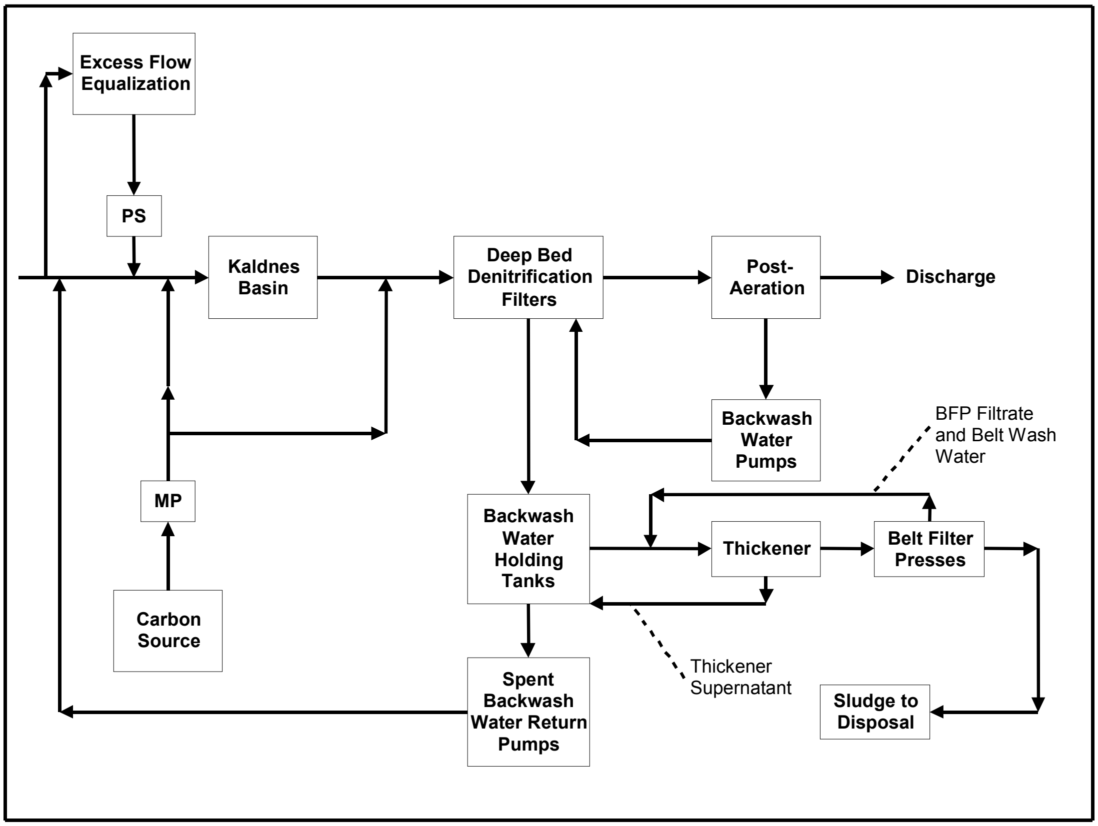

Figure E-2 High-Rate Biological Se Removal Process Flow Schematic

The second biological process step uses deep bed denitrification filters to remove any remaining nitrate and then to remove selenate. The deep bed denitrification filter is also a fixed film process that when lightly loaded produces a long sludge age. The long sludge age is presumed to allow the selenate reducing bacteria to accumulate in concentrations that will allow selenate reduction to occur rapidly. The deep bed denitrification filter will remove the biosolids that slough off the Kaldnes media and should also remove the precipitated Se. Additional process evaluation would need to be conducted in future design phases.

As with the lagoon treatment, it was assumed that methanol will be used as the carbon source for this evaluation. Molasses, waste sugar products, waste syrup from soda bottling, or municipal wastewater or biosolids are some of the materials that could be used as the carbon source for denitrification.

The high-rate system has a short retention time, so the rate of methanol feed can be carefully controlled and eliminate the need for the Post Oxic Basin to remove excess BOD. The post aeration basin is still needed to re-aerate the effluent to meet the 6 mg/L effluent DO limit.

High-rate treatment will require a backwash water management system and solids dewatering. The deep bed denitrification filter is similar to water plant filters and it is envisioned that each filter will be backwashed daily. Backwash water pumps are needed for filter backwashing and spent backwash water holding tanks are also needed to equalize the backwash water for return to the head of the wastewater treatment plant. The backwash water holding tanks are assumed to have sloped bottoms to facilitate the removal of solids. The solids are assumed to thicken to about 1 percent in this basin and would be pumped to a gravity thickener. The backwash water will be pumped to the thickener continuously and the thickener underflow is estimated to be 4 percent solids. The thickened biosolids will be pumped to a belt filter press for dewatering. A spent backwash water pump station will return backwash water to the head of the plant at a continuous rate. The biosolids will have a high Se concentration and will be disposed of as a hazardous waste.

E2.2 Cost Estimates and Assumptions

The following estimates and assumptions were incorporated into the design:

- **Influent water quality.** Influent water quality was estimated based on best available data. In some cases (Westlands Water District) these data were primarily from sampling that occurred in the mid 1980s. New shallow groundwater data were being collected as a part of this study and will be used to update the costs as they become available. In addition, the effect of reuse facilities on nitrate, Se, and TDS concentrations in drainwater was estimated based on best professional judgment, since long-term monitoring data from such facilities does not exist. This is particularly important because biotreatment system operating costs are largely a function of influent nitrate concentration, which was assumed to be 53 mg/L Nitrate as N. Treatment removal efficiency is based on pilot scale studies conducted for the lagoon system treating drainwater prior to reuse. It is assumed that similar removal efficiency would be obtained when treating the more saline reused drainwater with the high-rate system. It is recommended that the removal efficiency for reused drainwater be confirmed in pilot testing.

To account for the above uncertainties inherent in the design assumptions, the contingency factor for developing the costs was increased from 45 to 65 percent.

E3 PROCESS RELIABILITY

The removal of Se by biological systems has been known for decades; however, researchers are attempting to define the biological removal mechanism and the environmental conditions needed for optimum performance. Since all of the factors affecting biological Se removal have not been fully defined, some of the following discussion is based on best professional judgment and would be confirmed during future design of the system. Biological Se removal occurs when chemical conditions for the reduction of oxygenated materials are created. Various microbes can strip oxygen from specific chemicals like nitrate to satisfy their oxygen needs to remain in an aerobic mode of operation. Anoxic conditions are defined as the absence of DO with the presence of oxygen-bearing chemicals that can be reduced through microbial action, such as when nitrate is present in the water. Anaerobic conditions are defined as the absence of dissolved and chemically bound oxygen. Research has shown that Se reduction can occur in the presence of nitrate; however, most of the nitrate must be removed for efficient Se reduction to occur. For all practical purposes, it would appear to be a stepwise process with the removal of most of the nitrate occurring before significant amounts of Se are reduced and precipitated.

Biological Se removal occurs when sufficient 5-day biochemical oxygen demand (BOD_5) is present in the water to create strongly anoxic conditions. While nitrate has been reported to inhibit Se reduction, it is more accurately described as a pollutant that is competing for the available BOD_5. Se reduction to low soluble Se concentrations does not occur until nearly all of the nitrate is removed. It may also be that the microbes that reduce Se also reduce nitrate and obtain more energy from nitrate as an oxygen source over Se. In either case sufficient carbon source (BOD_5) must be added to remove nitrate to create conditions that promote Se reduction.

From a process reliability perspective, the Se reduction process can be interrupted if too little BOD_5 is present either because of a mechanical failure in the methanol addition system or because the BOD_5 demand in the incoming wastewater exceeds the design capacity of the methanol feed system because the nitrate concentration is too high.

The drainwater to be treated will have a high TDS concentration that may approach that of seawater. The activated sludge biological treatment process can function efficiently in seawater. Sudden increases in the TDS concentration will shock a biological treatment system for a day or so but once acclimated to the new condition the process will again function normally. Sudden decreases in the TDS concentration have another effect. Sudden decreases in the water TDS concentration cause microbes to rupture because of osmotic pressure. While nitrate removal will remain unaffected by TDS concentrations in the 20,000 mg/L range, it is not known what if any impact the high TDS concentration will have on the microbes that reduce Se. Further research is needed.

Se removal has been documented in evaporation ponds where the TDS concentration will exceed 100,000 mg/L. However, the rate of Se removal is important in the design of a treatment facility and it is not known if high TDS concentrations affect the rate of Se reduction.

Chemicals related to industrial activity can interfere or inhibit biological activity; however, these materials are not expected to be present in this drainwater except for those materials used on the farms. The accumulation of metals, pesticides and herbicides in the drainwater is a potential concern. As the TDS accumulates through reuse, so will metals that occur naturally in the water supply and chemically stable pesticides and herbicides. The impact of the accumulation of these materials on Se removal is not known. Any inhibition or toxicity from these materials would reduce Se removal efficiency or could possibly stop Se removal altogether.

The lagoon treatment system is probably more susceptible to long-term upsets by the presence of any toxic material. With the large volume of the lagoon, the microbial population is protected from short-term toxic events. However, if enough toxic material enters the lagoon to harm the microbial population, it will take a significant length of time for the system to recover. Conversely, because the lagoon treatment system is a low rate treatment process with a long retention time it can absorb short duration slug loads of inhibitory or toxic material without harm. However, because of the nature of the drainwater, any contaminants that could cause the system to become upset will not be present as transient events. The drainwater to be treated is the shallow groundwater below the reuse facilities. This shallow groundwater will provide a reservoir that will dilute any pulses of toxicants introduced onto the facilities. Instead, contaminants would accumulate on the reuse facilities and gradually percolate into the shallow groundwater where they will be collected over time.

On the other hand, the high rate system will rapidly respond to any short-term event where toxic or inhibitory material is present. Since the microbes are present as a fixed film rather than as suspended material they will be much better able to withstand a short-term transient exposure to toxic material as long as the toxicity is only inhibitory. The toxic material would rapidly wash out of the high-rate system. If the toxic material causes microbial mortality, process failure would occur. Prolonged exposure to toxic material will harm the bacteria and will impair the ability of the process to remove Se. The presence of compounds that are toxic to Se-reducing bacteria in reused drainwater would be investigated in future design phases.

Lower temperatures in the winter will also impact the Se removal process. This is usually a design concern. Normal procedure is to design biological treatment systems for winter operation. Determination of the summer and winter rates for Se removal would be addressed during future design phases.

As long as no material inhibits bacterial reduction of Se present in the drainwater (includes potential impacts of high TDS concentrations, and the accumulation of metals, pesticides and herbicides), the biological treatment process would be a stable system, and the process would be reliable as long as routine maintenance of mechanical items such as pumps, blowers, and chemical feed systems is performed.

In summary the biological Se removal process should provide good reliable service. Additional pilot studies are needed to better define process capabilities in the higher TDS concentrations expected in the drainwater. On-site reuse has proven to be beneficial in reducing project costs by reducing the volume of drainwater to be treated. However, the side effect of on-site reuse is the concentration of TDS, metals, and other persistent and nonbiodegradable material in the drainwater that may interfere with biological Se removal. It should be noted that many wastewater treatment plants in California biologically remove nitrates. These facilities are subjected to influent loads that are much more variable than the drainwater, and with proper operation these facilities are able to meet their strict permit limits. Biological systems, once fully understood, have proven to be reliable treatment systems. However, a biological treatment system relies on living organisms to remove the contaminants from the wastewater and their limitations must be understood to avoid process failures.

E4 REFERENCES

Frankenberger, Jr., W.T. and U. Karlson. 1994. Microbial volatilization of selenium from soils and sediments. In *Selenium in the Environment,* W.T. Frankenberger, Jr. and S. Benson, eds., pp 369-388.

Macy, J.M. 1994. Biochemistry of selenium metabolism by *Thauera selenatis* gen. nov. sp. nov. and use of the organism for bioremediation of selenium oxyanions in San Joaquin Valley drainage water. In *Selenium in the Environment,* W.T. Frankenberger, Jr. and S. Benson, eds., pp. 421-444.

Oremland, R.S. 1994. Biological transformations of selenium in anoxic environments. In *Selenium in the Environment,* W.T. Frankenberger, Jr. and S. Benson, eds., pp. 389-420.

Quinn, W.T., T.J. Lundquist, F.B. Green, M.A. Zarate, and W.J. Oswald. 2000. Algal-bacterial treatment facility removes selenium from drainage water. *California Agriculture* 54 (6): 50-56.