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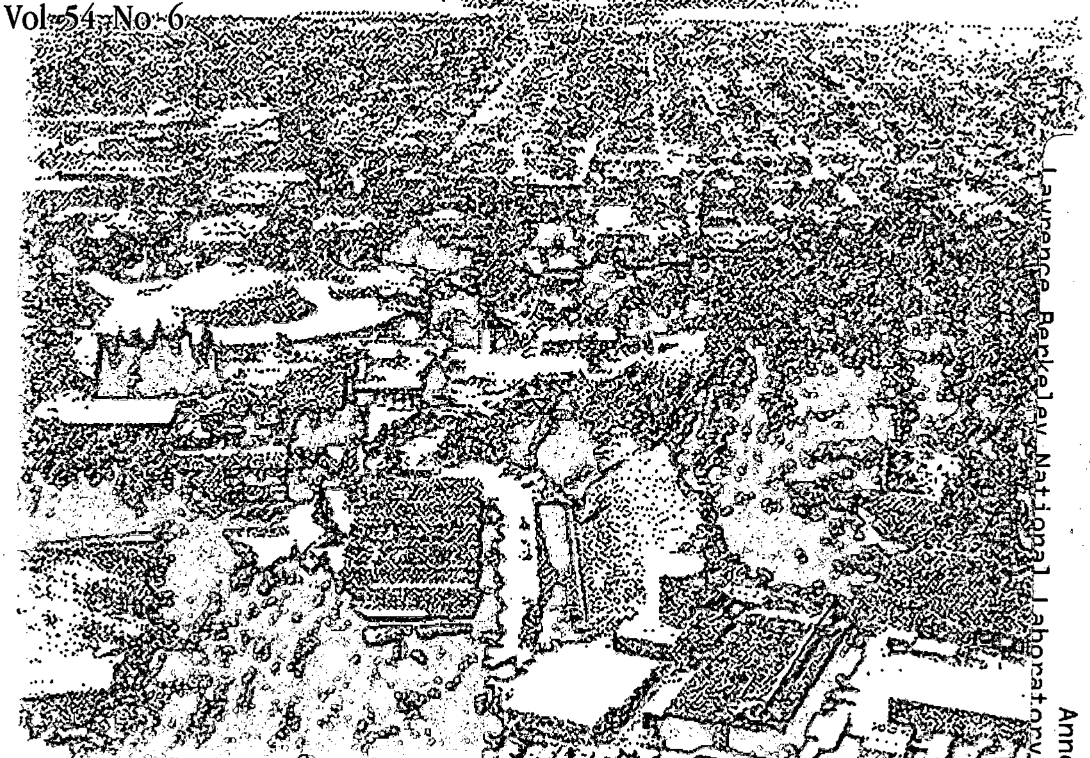

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Abstract

A demonstration Algal-Bacterial Selenium Removal (ABSR) Facility has been treating agricultural drainage water in the Panoche Drainage District on the west-side of the San Joaquin Valley since 1997. The goals of the project are to demonstrate the effectiveness of the ABSR Technology for selenium removal, to investigate potential wildlife exposure to selenium at full-scale facilities, and to develop an operational plant configuration that will minimize the life cycle cost for each pound of selenium removed. The Facility consists of a series of ponds designed to promote native microorganisms which remove nitrate and selenium. Previous treatment research efforts sought to reduce selenium concentrations to less than 5µg/L, but the ABSR Facility demonstration focuses on providing affordable reduction of the selenium load that is discharged to the San Joaquin River. During 1997 and 1998, the best-performing ABSR plant configuration reduced nitrate over 95% and reduced total soluble selenium mass by 80%. Ongoing investigations at the Facility focus on optimizing operational parameters and determining operational costs and scale-up engineering requirements. The preliminary total cost estimate for a 10 acre-ft/day ABSR facility is less than $200 per acre-ft of treated drainage water.

Solutions to Drainage Selenium Problem

Agricultural drainage water treatment for selenium removal has been an active area of research for over a decade since the discovery of deformed waterfowl embryos at Kesterson Reservoir in the western San Joaquin Valley (Ohlendorf *et al.*, 1986). As yet no treatment technology has proven economically feasible for meeting the 5 µg/L State Water Resources Control Board objective for selenium discharged to receiving waters such as the San Joaquin River and Mud Slough (SWRCB, 1989; U.S. EPA, 1987). Agricultural drainage discharged into Mud Slough from the Grasslands Basin exceeds this concentration regularly (CVRWQCB, 1999).

Since the authorization of the Grassland Bypass Project in 1996 (Quinn *et al,* 1998) the regulatory approach of choice has shifted from one of meeting concentration objectives to one of selenium load reduction. The Grassland Bypass Project is a 5-year experiment, currently in its fourth year, involving Grassland Basin water districts, the US Bureau of Reclamation, Department of Fish and Game, Fish and Wildlife Service and the US Environmental Agency which established a schedule of selenium load targets for agricultural tile drainage discharged to Mud Slough and the San Joaquin River. The Grassland Basin farmers agreed to these monthly and annual selenium load targets, which decline by 5% each year after the second year of the project -- exceedences of which could lead to fees levied against the participating drainage districts of up to $500,000 per year (Quinn *et al*, 1998). This policy of monthly and annual load targets has injected new life into the quest for affordable selenium treatment technologies by changing the immediate goals of drainage treatment. The expensive polishing processes required to achieve 5 μg/L are no longer obligatory in treatment systems designed for selenium load reduction. Biological treatment processes may become the most likely cost-effective solution to the selenium drainage problem in the Grasslands Basin after source control if expensive external feedstocks can be minimized (Table 1).

One simple biological treatment technology is the pond-based Algal-Bacterial Selenium Removal (ABSR) Technology which was proposed by Professor William J. Oswald of the University of California, Berkeley (Oswald, 1985), tested on the pilot scale (Gerhardt and Oswald, 1990; Gerhardt *et al.*, 1991; Lundquist *et al.*, 1994) and now operated on the demonstration scale at Enrico Farms within the Panoche Drainage District (PDD) (Figure 1). The current project is a collaboration among the PDD and engineers, microbiologists, and chemists from the University of California at Berkeley and Lawrence Berkeley National Laboratory. The project will show the potential of the ABSR Technology to affordably reduce selenium loads from a single subsurface drainage sump yielding the highest selenium loads of any sump in the PDD.

Full-Scale Experience with Algal-Bacterial Technologies

The ABSR Process is a specialized application of the effective and economical wastewater treatment technology known as the Advanced Integrated Wastewater Pond Systems (AIWPS®) Technology which has been implemented at full-scale for sewage and industrial wastewater treatment by Professor Oswald and his co-workers over the past 32 years. Components of the AIWPS® Technology have also been used for decades at farms that produce algae for pharmaceutical, food dye, and health food markets.

The chemical transformations involved in the reduction of selenium are different than those required for wastewater treatment or for food-grade algae production, but many of the treatment steps and pond designs are similar. Thus, the design, construction, and costs of proposed large-scale ABSR facilities will be similar to those of the well-established AIWPS® Technology.

Treatment Mechanisms

The main components of the ABSR Technology are two types of ponds in series--Reduction Ponds (RPs) and High Rate Ponds (HRPs)–each designed to foster native bacteria and algae needed for drainage water treatment. Additional units for algae harvesting and water clarification may also be required--an Algae Settling Pond (ASP) or a dissolved air flotation (DAF) unit.

Nearly all the selenium (Se) present in drainage water is part of the highly soluble ion selenate (SeO_6^{2-}) in concentrations typically ranging from 100 to 600 μg/L as Se. In the RPs, bacteria convert selenate to insoluble precipitates or take up selenium in their cells. Much of the insoluble selenium settles in the RPs and, if needed, any particulate selenium remaining in the effluent can be removed from the water with DAF.

Selenate cannot be reduced to low levels in the ABSR Process unless dissolved oxygen (O_2), nitrate (NO_3^-), and nitrite (NO_2^-)[1] are also removed (Gerhardt *et al.*,1990). When

[1] Nitrite concentrations were at least ten times lower than nitrate concentrations in the ABSR Facility. Both compounds were determined using a single analytical method hence the term nitrate refers to the sum of NO_3^- and NO_2- in this study)

biodegradable carbon is present, O_2 is converted to carbon dioxide (CO_2) and nitrate is converted to nitrogen gas (N_2) during respiration of microorganisms at the bottom of the RPs. The RPs are sufficiently deep or covered to exclude atmospheric oxygen from a large part of their volume. Since nitrate concentrations in drainage water are often as high as 90 mg/L as N compared to <0.5 mg/L for selenium, the carbon requirement for nitrate reduction far exceeds that for selenium reduction. Despite high sulfate concentrations (2,000 to 4,000 mg/L as SO_4^{2-}) in drainage water, sulfate does not appreciably interfere with nitrate or selenium reduction.

Nitrate also is removed by a second means in the ABSR Technology. Microscopic algae grow in the HRPs using the nitrate as fertilizer. HRPs are shallow, continuously-mixed raceways designed to maximize algal productivity and bacterial oxidation of dissolved organic matter (Oswald, 1988). In HRPs, algal productivities typically range from 15 to 30 tons dry weight per acre per year. In comparison, the productivity of crops such as rice, wheat, corn, and soybeans is rarely in excess of 2 to 3 tons/acre/year of product. Continuous low-speed paddle wheel-mixing of HRPs requires only 5 to 10 kWh/acre/day, and beyond promoting high productivity, the gentle mixing of HRPs enhances the selection of algal species that tend to settle when introduced into the quiescent ASPs. The settled algae form a thick slurry that is pumped into the anoxic zone of the RPs. There the algae become a carbon feedstock for bacteria, decreasing or eliminating the need for supplemental feedstocks imported from offsite.

Although algae can utilize carbon from natural alkalinity, the algal growth rate in HRPs is enhanced by addition of carbon dioxide. There are at least two practical carbon dioxide sources for HRPs treating drainage water: (1) CO_2 produced during bacterial respiration in the RPs and (2) bubbling of exhaust gas from on-site power or heat generation units. Pure CO_2 has been used since 1983 as a carbon source in HRPs used for commercial algal cultivation in the Imperial Valley, California (Naylor, 1993).

Selenium removed from the water column accumulates in settled algal-bacterial biomass and inert materials on the floor of the RPs. This biomass is continuously undergoing anaerobic decomposition, so the volume of solid residues only increases slowly over many years. Removal and disposal of the solids in a landfill should not be required for many years, if not for several decades. Alternatively, the inert solids which contain nitrogen and phosphorus, as well as selenium, might be dried and used as a soil amendment and fertilizer in the eastern Central Valley where the soils are selenium deficient. Data collected so far indicate that the selenium associated with the algal biomass is in the following forms: elemental selenium, organic selenium, and sorbed selenite (SeO_3^{2-}) (Tokunaga, 1998). The organic form is likely to be the most available to selenium-deficient crops (Meyer, 1998). The solids will have to be evaluated for contamination by metals and agricultural chemicals prior to reuse.

Wildlife Protection

Large-scale ABSR Facilities are expected to pose much less hazard to wildlife than the surrounding drainage channels, evaporation ponds, or drainage-contaminated wetlands. The concentration of selenium in the shallow HRPs will be similar to that in the drainage channels themselves, and HRPs will be continuously mixed by paddle wheels to minimize formation of sediment that would harbor invertebrates. Concentrated selenium will be sequestered in the deep sediments of the RPs. With RP depths of 20- to 25-feet, these sediments will be anoxic and would not attract waterfowl since there is little or nothing to forage even if those depths could be reached by diving water fowl. In contrast, wetlands with selenium-contaminated sediments and biota will require special management to prevent use by birds. Residual organic selenium in the ABSR Facility final effluent is a concern, however. Studies in progress will indicate what level of final clarification will be required to minimize this readily bioaccumulated form of selenium in the effluent.

Treatment Plant Configuration

Two treatment plant configurations are being evaluated at the ABSR Facility in the Panoche Drainage District each having potential cost advantages due to nitrate removal mechanism and internal nutrient recovery. In the low cost plant configuration (Mode 1 - Figure 2), drainage water is brought into a HRP where 15 to 30 mg/L of nitrate-nitrogen (nitrate-N) is removed through assimilation by algae. The HRP effluent flows to the RP where the algae settle and become bacterial feedstock. The bacteria remove dissolved oxygen and the remaining nitrate. The advantages of this mode are that an ASP is not needed and less carbon feedstock is required for bacterial nitrate reduction since algae take up a portion of the nitrate. The disadvantage is that carbon dioxide, phosphate, and trace nutrients must be added to the HRP in order to achieve maximum algal growth.

In the high removal efficiency plant configuration (Mode 2 - Figure 3), drainage water and carbon feedstock are added to the RP first. In the RP, the dissolved oxygen, nitrate, and selenium are depleted by bacteria. The RP effluent containing bacterial metabolites such as ammonium, phosphate, and dissolved carbon dioxide passes to the HRP. The metabolites become fertilizer for algae growth thereby reducing the need for supplemental carbon dioxide and nutrients. The HRP algae are removed from the water by the ASP or DAF and are then added to the RP as carbon feedstock. In Mode 2, nitrate is removed by bacterial nitrate reduction only which requires more carbon feedstock than Mode 1. However in Mode 2, the RP influent is drainage water containing 8 to10 mg/L of dissolved oxygen. This oxygen concentration is two to three times lower than that of the HRP effluent pumped to the RP during Mode 1 operation. The lower oxygen level requires less feedstock for oxygen removal. Some operational programs may utilize the diurnal cycle of low oxygen concentration characteristic of HRPs during the hours between midnight and sunrise.

In either treatment plant configuration, supplemental carbon feedstocks such as molasses or other food processing wastes can be utilized in conjunction with the algae feedstock produced onsite. Molasses is commonly used as a cattle feed supplement and is readily available in the San Joaquin Valley at a wholesale price of $60 to $90 per ton (USDA, 1999). Both plant configurations and supplemental molasses addition are being evaluated at the Panoche Drainage District Facility.

The Panoche Drainage District Facility

The ABSR Facility in the PDD consists of two parallel systems each having a RP; a paddle wheel-mixed HRP; and an ASP. So far, the two systems have been used to simultaneously compare the Mode 1 and Mode 2 (low cost and high removal efficiency configurations)using the feedstocks algae and molasses. Having two parallel systems allows the operational parameters of one system to be varied while the other system is operated as a control. A control system is essential to normalize the inevitable changes in drainage composition and weather conditions.

The 0.1-acre RPs are as deep as site constraints allowed–a 10-foot water depth. Greater depth would have helped prevent significant oxygen concentrations in the reaction zone near the floor of the ponds. Floating covers were installed on these relatively shallow RPs to reduce wind-induced mixing and photosynthetic oxygenation by algae. Full-scale RPs would probably not require surface covers due to their 20-ft to 25-ft depth and internal anoxic cells. During the course of the experiments, the RPs have been operated at hydraulic residence times (HRTs) from 14 to 60 days. The 0.1-acre, paddle wheel-mixed HRPs typically have generated algae concentrations of 100 mg/L to 300 mg/L with HRTs from 3 to 9 days . Carbon dioxide has been provided by bubbling the gas into a sump in each HRP. A baffle in the carbonation sump forces the flow of water downward. Against this downward current, the carbon dioxide bubbles are held in suspension as they dissolve into the water. The 1,400-ft^2 ASPs with HRTs of 2 to 7 days provide a quiescent zone for the algae grown in the HRPs to settle. Overflow troughs in the ASPs improve algae sedimentation by removing supernatant from the surface of the pond at a very low overflow velocity. The sloped floor and internal sump in each ASP enables the harvesting of the algal biomass using a diaphragm pump.

Samples for water quality analysis and mass balance calculations are collected weekly and analyzed according to *Standard Methods* (APHA, 1995). Flow rates and site observations are recorded every weekday by Panoche Drainage District personnel.

Results

Both treatment configurations demonstrated a regular seasonal fluctuation in nitrate and selenium removal, but the cumulative, two-year selenate-Se mass removal for 1997-1998 was 45% in the low cost, Mode 1 System and 80% in the high removal efficiency, Mode 2 System. The Mode 1 System removed 70% of influent selenate during June 1998 through November 1998, the most critical season for the Grasslands Bypass Project monthly load limits. During these two years the Mode 1 System received algae feedstock only and the Mode 2 system received algae and molasses feedstocks.

DAF clarification with ferric chloride coagulant is expected to remove residual selenite and particulate selenium, leaving selenate and soluble organic selenium in the effluent. Selenate and soluble organic selenium are measured with a single analytical method and are referred to as "selenate" in this discussion.

In short-term laboratory experiments, algae were about half as effective as molasses as a feedstock for bacterial nitrate reduction. But high selenium removals during the summer of 1998 in the Mode 1 System indicate that in terms of nitrate removed per gram of algae added, the feedstock value of algae increases if they are allowed to undergo bacterial digestion over many months, as is the case in the RPs. The good summer performance also indicates that bacterial breakdown of algae is sensitive to water temperature. But regardless of feedstock, once nitrate-N was reduced to 5 mg/L to 10 mg/L, total soluble selenium was reduced.

Between April 1997 and January 1998, the Mode 2 ABSR System consistently reduced nitrate to less than 10 mg/L NO_3^--N until molasses addition was interrupted during mid-January to mid-February due to wet, impassable roads (Figure 4). During the April 1997 to January 1998 period of high nitrate removal, selenate removal averaged 82% from a mean of 422 µg/L as Se in the influent to a mean of 77 µg/L as Se in the ASP effluent. Selenate removal reached 5 g/day to 6 g/day as Se during this period. Colder winter temperatures and the month of interrupted molasses addition presumably slowed bacterial activity and caused selenate removal to decrease to 68% during October 1, 1997 to March 31, 1998. From April 1, 1998 through December 31, 1998, selenium removal increased to 92% along with increased selenium loading to the System. The average influent selenate concentration was 402 μg/L which was reduced to an average of 32 μg/L.

Between March 1997 and July 1998, the flow to the Mode 2 System was 3,800 gallons per day, giving a hydraulic residence time (HRT) of 66 days. The HRT in the Mode 2 System was reduced to 38 days during July 1998 to November 1998 which increased the influent selenate load from about 5.5 g/day to 9 g/day. Despite the increased load, selenate mass in the effluent rose less than 1 g/day as Se (Figure 5). The flow was further increased at the end of November 1998 to reduce the HRT to 31 days.

After July 1997, the Mode 1 System received only algal feedstock produced onsite. Nitrate-nitrogen was removed from 80-90 mg/L to less than 1 mg/L by September 1997 with a HRT of 49 days (Figure 6). Removal of nitrate decreased from October through March which corresponds to the period of lower selenium removal in the Mode 2 System. Nitrate and selenium removal generally increased from April 1998 through October 1998 (Figures 6 and Figure 7). Selenate-Se mass removal averaged 64% during this period. Influent concentration averaged 431μg/L as Se, and the effluent averaged 155 μg/L as Se. The Mode 1 System produced more sludge biomass per kg of selenium removal. The cost of sludge disposal will be a function of both transportation costs and the volume of biomass requiring removal. After 3 years of continuous operation the Mode 2 system has accumulated less than 6 inches of sludge in the reduction pond. Future expansion and cloning of the current ABSR system to other locations will need to consider the lower operating costs of the Mode 1 System, using only algae feedstock, to the sludge disposal and performance advantages of the molasses-fed system. This trade-off may yield different results in different locations.

Continuing Work

In mid-1999, the flow to the Facility reached 27,000 gallons per day giving an HRT of 25 days in the Mode 1 System and 20 days in the Mode 2 System. The project goal over the next six months is to further increase the flow rates through the ABSR Facility in order to achieve the greatest selenium mass reduction at the lowest cost for the Panoche Drainage District. A real-time, telemetered flow and water quality monitoring and control system is being installed at the Facility to improve the efficiency of feedstock use and maximize throughput without sacrificing selenium removal efficiency. The instrumentation chosen for the ABSR Facility is similar to that used by the District to routinely monitor drainage outflow hence the time and effort to instruct District personnel in the monitoring and control of plant operation will not be significant. Once this transfer of technology to the District is complete, a cost evaluation based on a full-scale facility design will be finalized. This will allow drainage district managers to make informed decisions on future investments in agricultural drainage treatment using the ABSR technology.

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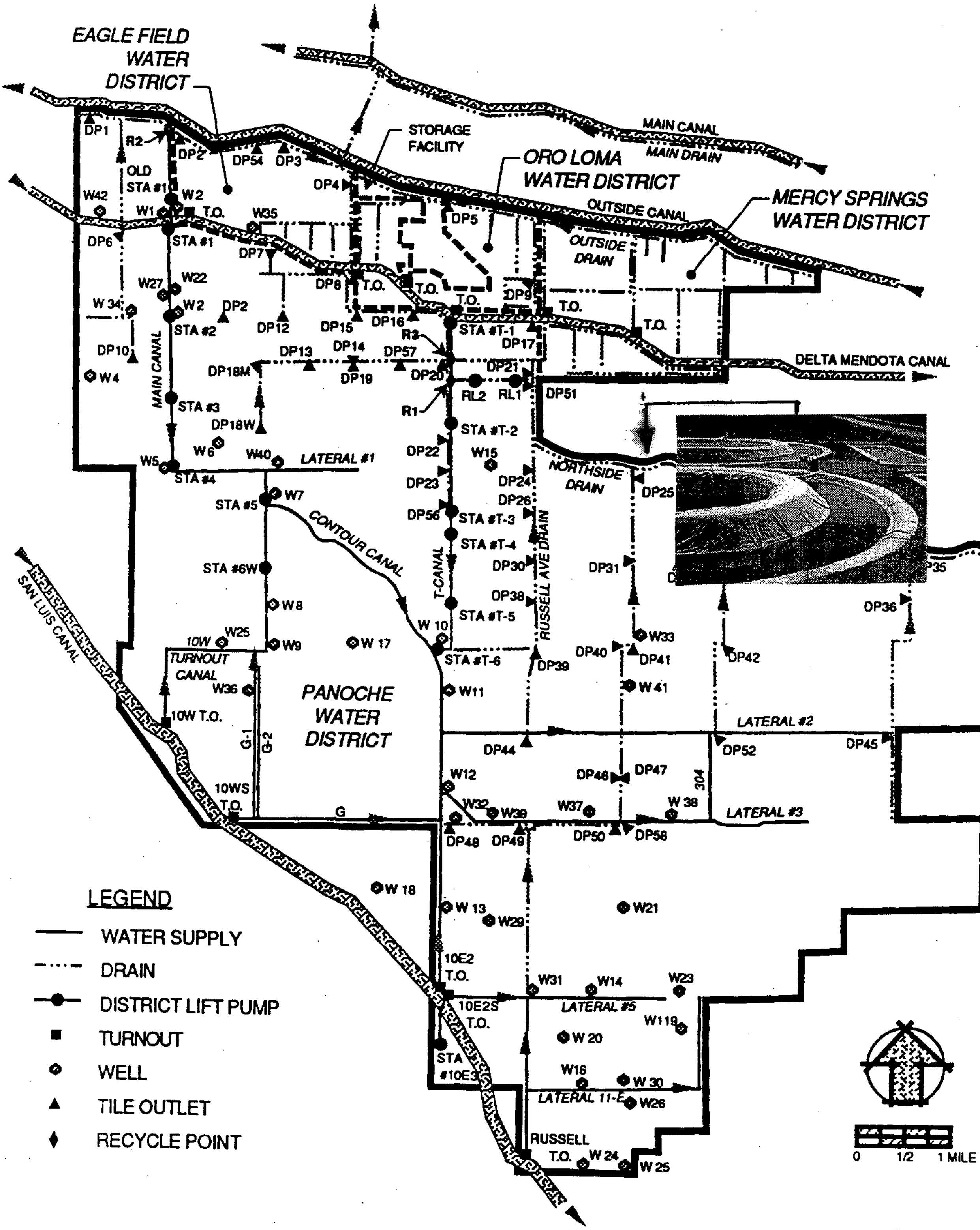

Figure 1. Panoche Algal Bacterial Treatment Facility located at DP-25 in the Panoche Drainage District.

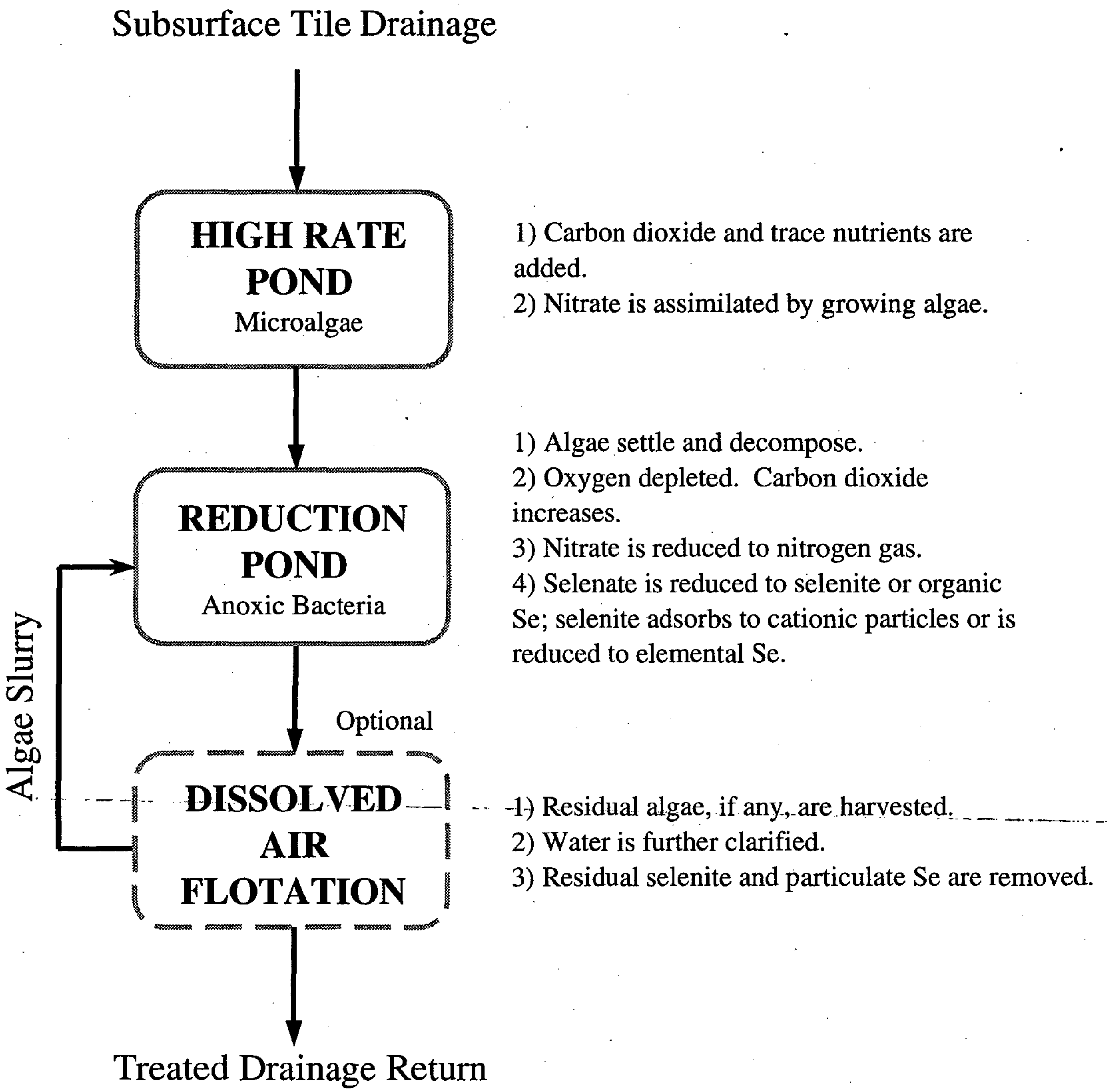

Figure 2. Schematic of the ABSR Technology operated in Mode 1.

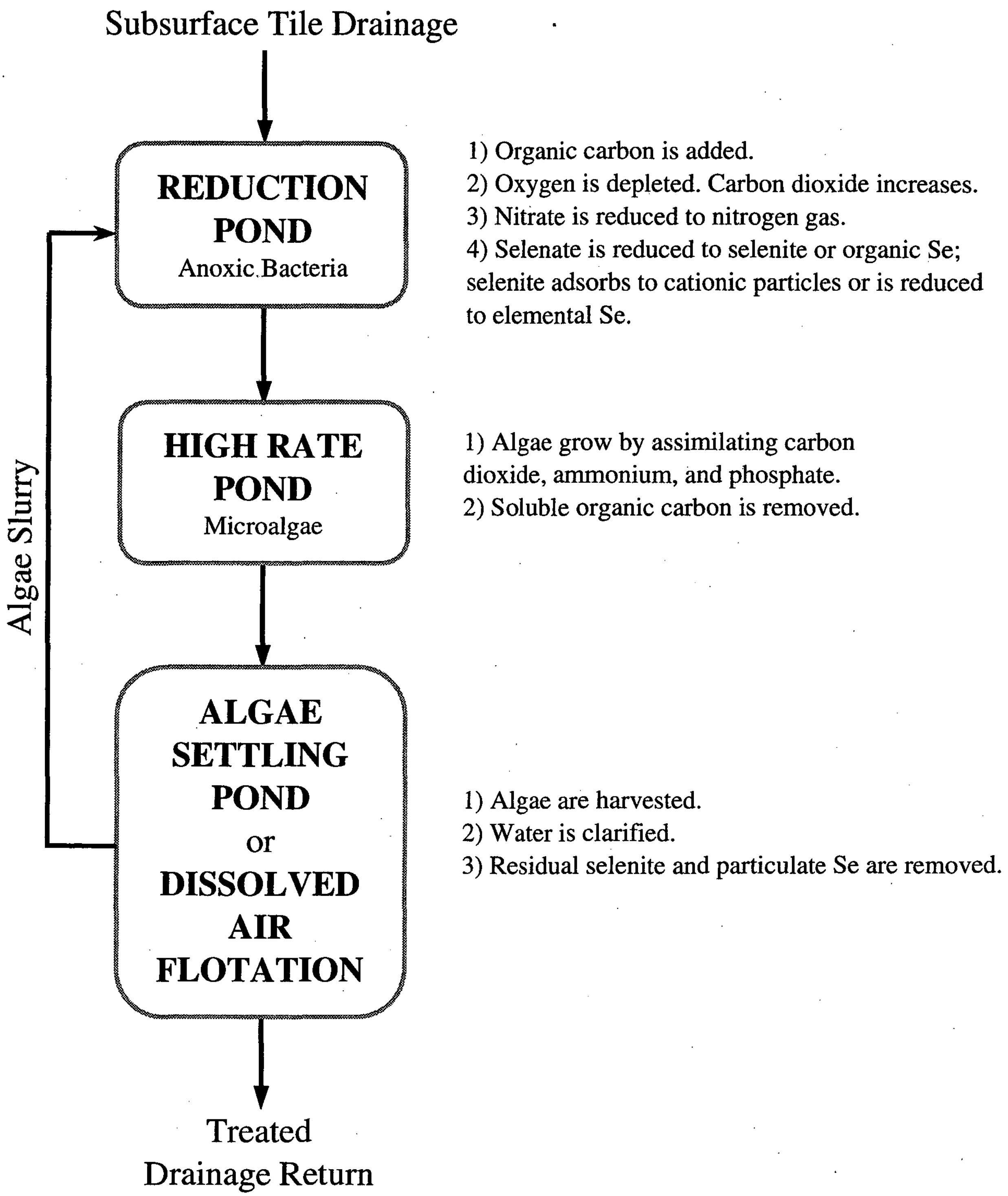

Figure 3. Schematic of the ABSR Technology operated in Mode 2.

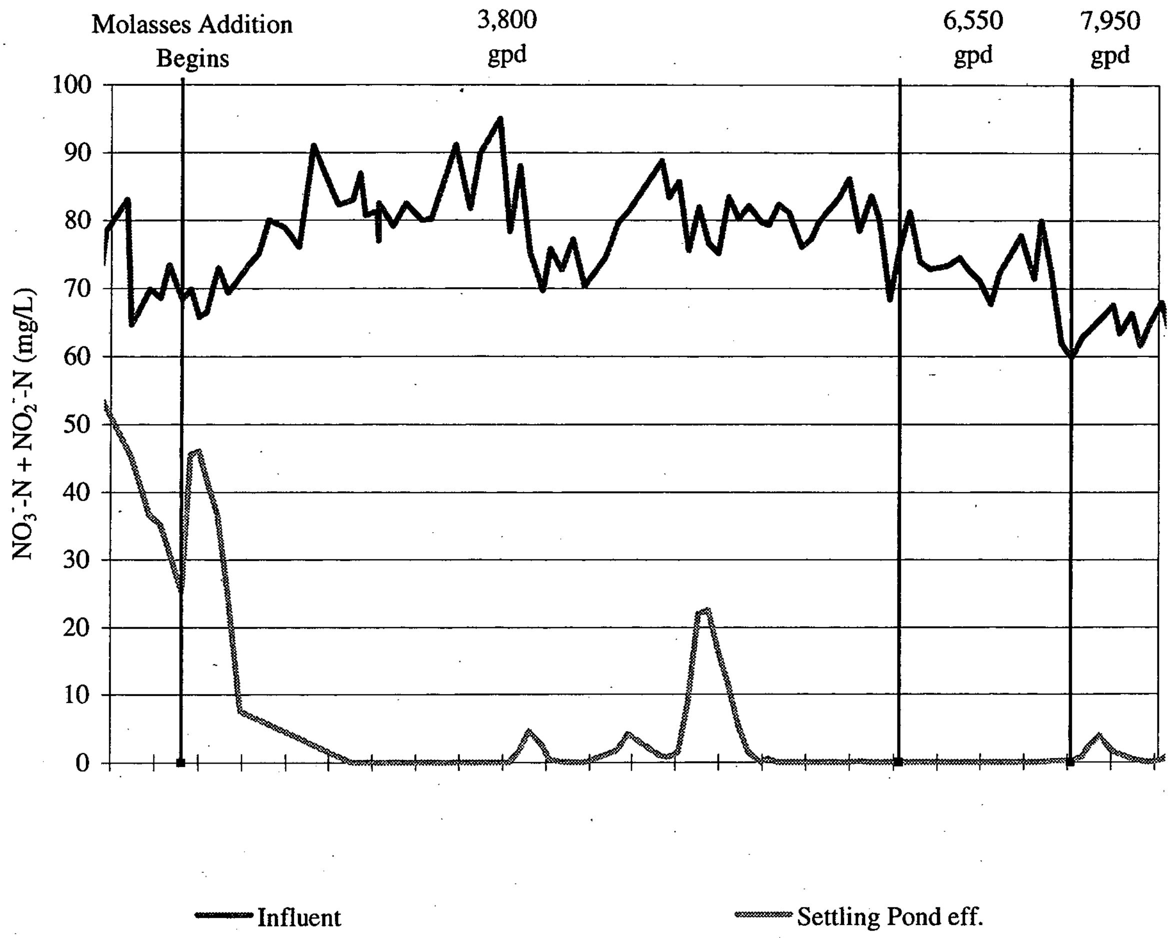

Figure 4. Nitrate+nitrite concentrations in the Mode 2 ABSR System.

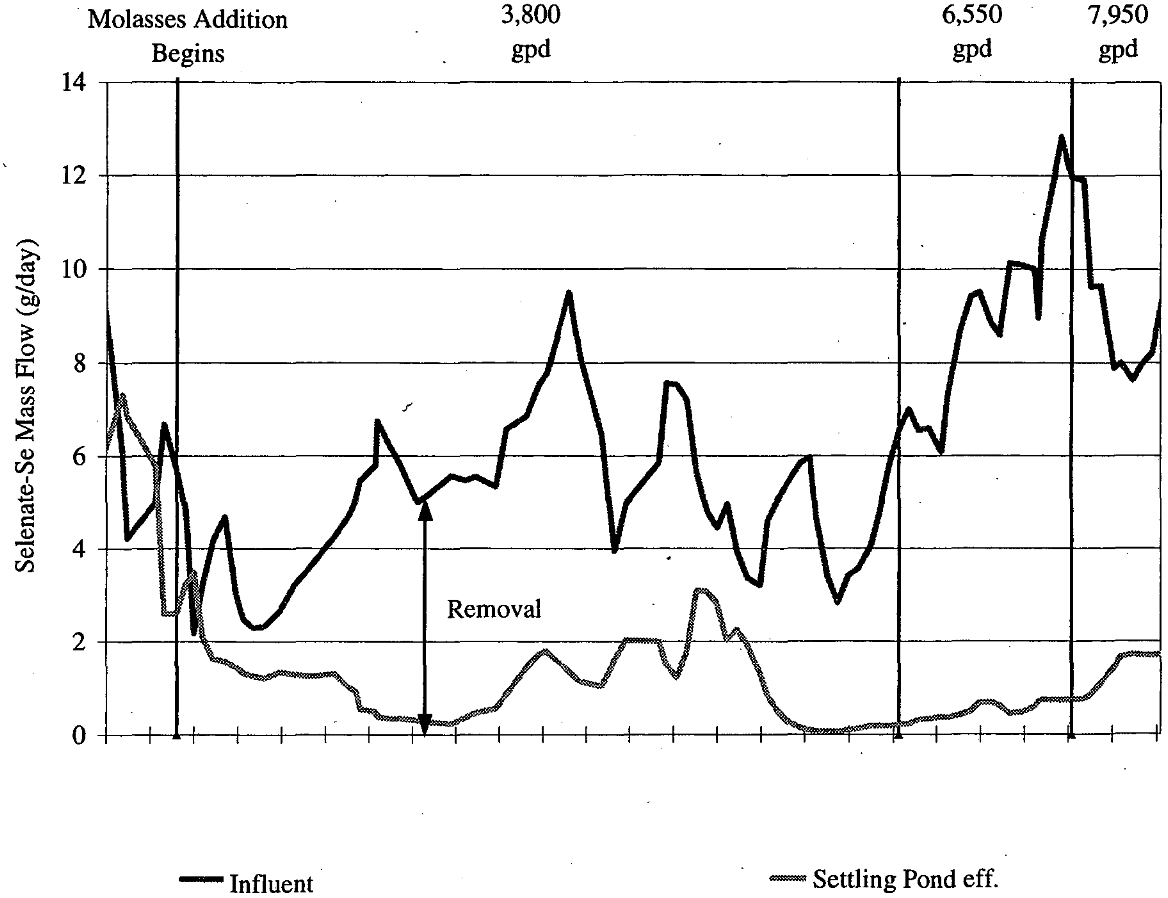

Figure 5. Selenate-Se mass flow in the Mode 2 ABSR System. Mass calculated as a three-week moving average in grams/day. Average drainage water flow in gallons per day.

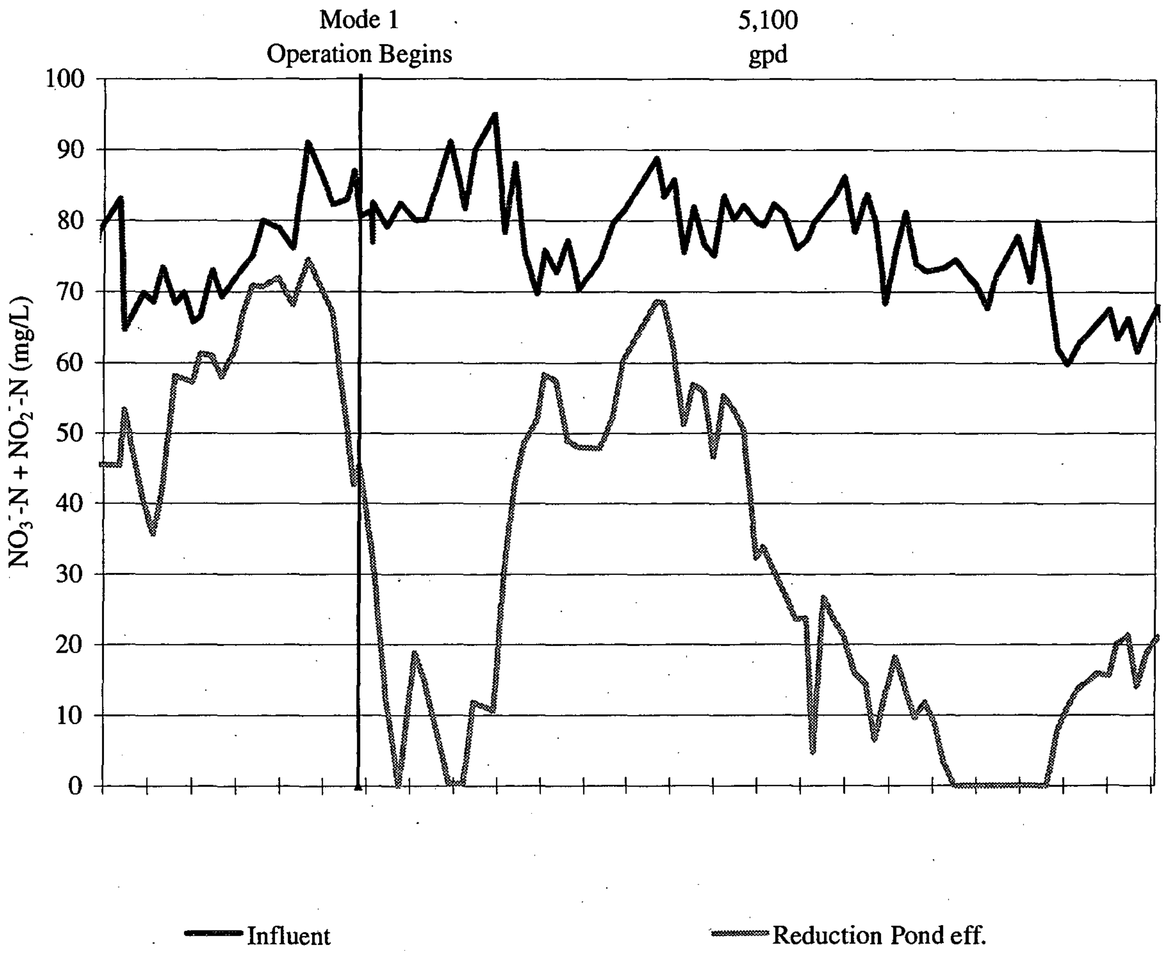

Figure 6. Nitrate+nitrite concentrations in the Mode 1 ABSR System.

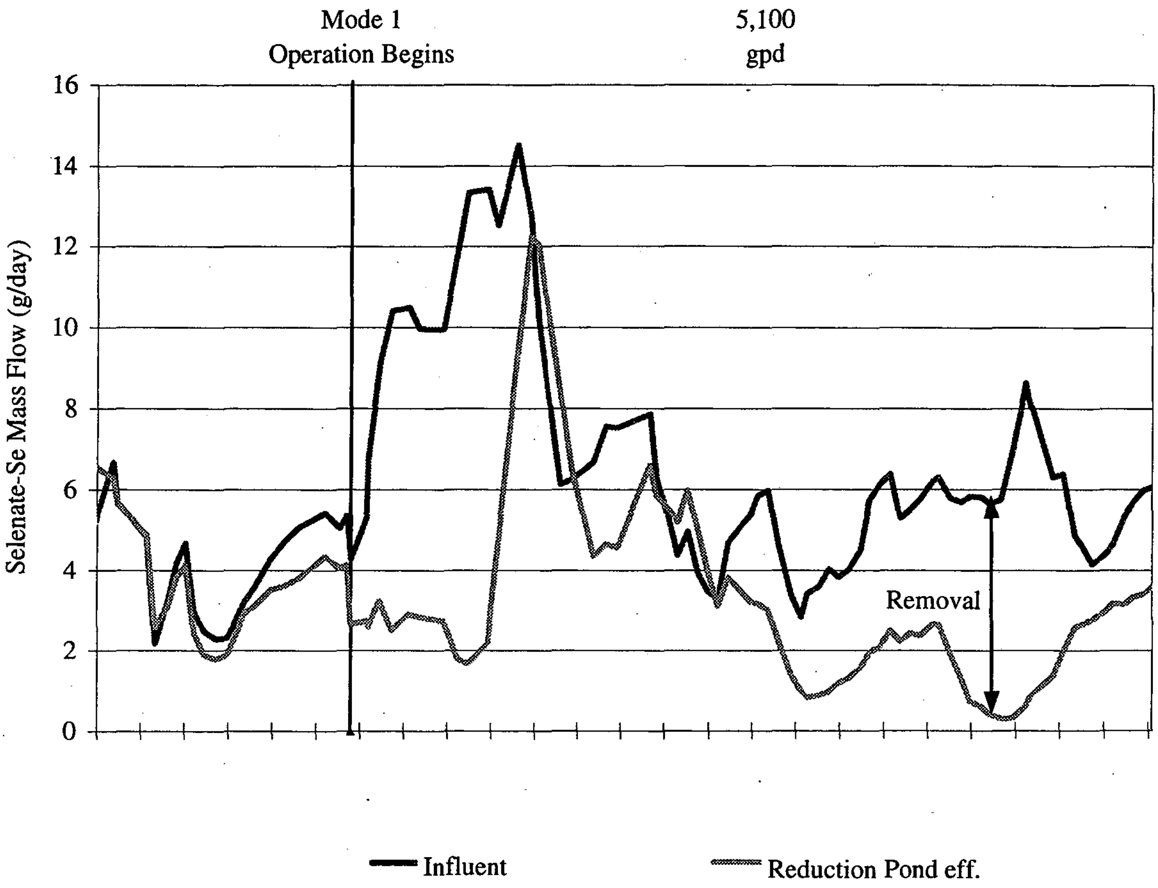

Figure 7. Selenate-Se mass flow in the Mode 1 ABSR System. Mass calculated as a three-week moving average in grams/day. Average drainage water flow in gallons per day.

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