

During the past decade, perchlorate at levels above regulatory standards has become increasingly prevalent in drinking water aquifers. A large pilot-scale biological fluidized bed reactor (FBR) followed by a surface water treatment plant was tested to demonstrate effective treatment of perchlorate-laden groundwater to potable water. At perchlorate concentrations up to 1,000 µg/L, nitrate-nitrogen concentrations of 6.1 mg/L, and flow rates of 95–189 L/min (25–50 gpm), the FBR treatment plant was effective in removing perchlorate and producing potable water that met all drinking water regulations before disinfection. The use of on-line perchlorate and nitrate analyzers allowed for rapid analysis of plant performance and provided continuous electron donor feed control to maintain optimal contaminant treatment rates. Recovery from feed and plant electrical interruptions was rapid in achieving acceptable treatment performance. Study results provided essential design data for a potential full-scale treatment plant.

Fluidized bed bioreactor treatment of perchlorate-laden groundwater to potable standards

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Perchlorate is a highly soluble salt anion that can negatively affect the ability of the human thyroid to adequately uptake iodide (Greer et al, 2002; Wolf, 1998). Since early 1997, perchlorate analytical techniques have significantly improved. As a result, drinking water testing performed throughout the United States has uncovered perchlorate contamination in several regions of the country at levels at or below 1 µg/L (USEPA, 2004).

The majority of the perchlorate contamination in groundwater aquifers is believed to be attributable to historical disposal practices by the aerospace and ordnance industries, the military, and chemical manufacturers. Perchlorate salts have been used in the US defense and space programs for several decades as primary oxidants in the solid propellants that power rocket motors, rocket boosters, and missiles. In past disposal practices, solid perchlorate-containing fuels were often burned in open-detonation areas, and aqueous processing waters or wastewaters were released to surface soils or discharged into evaporation ponds. Given past disposal practices and the mobility of the anion, numerous drinking water aquifers throughout the United States have been contaminated with perchlorate (USEPA, 2004).

No federal drinking water maximum contaminant level (MCL) has been established for perchlorate. However, several states have set their own advisory levels, e.g., 1 µg/L in Maryland and New Mexico, 5 µg/L in New York, 14 µg/L in Arizona, and 18 µg/L in Nevada (Hatzinger, 2005). In July 2006, Massachusetts became the first state to set an MCL of 2 µg/L (MDEP, 2006). California followed in 2007 with the establishment of an MCL of 6 µg/L (CDPH, 2007). In the absence of federal regulation, these states chose to take a proactive approach to remove from service any drinking water well in which these advisory levels or MCLs are exceeded. In many cases, this water must be replaced with other outside sources (i.e., bottled water, imported surface water) at substantially higher costs to the residents in the area. Alternative cost-effective perchlorate remediation technologies are needed to help put these wells back in service.

BIOLOGICAL TREATMENT OF PERCHLORATE

Numerous bacteria capable of biologically degrading perchlorate have been isolated over the past seven years (Coates & Achenbach, 2004; Zhang et al, 2002). Such bacteria appear to be nearly ubiquitous in soil, groundwater, surface water, and sediment environments (Wu et al, 2001; Coates et al, 1999). Through anaerobic respiration, perchlorate-reducing organisms couple the oxidization of an organic substrate—or in some instances, hydrogen gas—to the reduction of perchlorate (Song & Logan, 2004; Zhang et al, 2002; Kengen et al, 1999). This respiratory process, which produces chloride as a degradation product, closely resembles dissimilatory nitrate reduction, in which nitrate is reduced to nitrogen gas.

Biological fluidized bed reactor (FBR) process. In order to ensure that the perchlorate-degrading organisms can effectively treat large volumes of perchlorate-laden groundwater to desired levels, the organisms must be maintained at a high density with sufficient contact time (Webster, 2007; Brown et al, 2005). The FBR is one type of fixed-film system that can meet these requirements. An FBR is a fixed-film reactor in which the biological media, i.e., granular activated carbon (GAC), are suspended or fluidized within the reactor vessel by the upward flow of water through the system (Figure 1). Because the media particles are small and suspended, they present a large surface area for microbial growth and promote a biomass density that is often several times that of other bioreactor designs under similar loading conditions (Sutton et al, 1994; USEPA, 1993a). An electron donor (i.e., acetic acid) is provided to the FBR where, under anoxic conditions, the attached microorganisms perform an oxidation-reduction reaction in consuming all of the dissolved oxygen, nitrate, and perchlorate. The by-products of the process are nitrogen gas, chloride ions, carbon dioxide, heat generation, and additional biomass.

As the microorganisms acclimate and grow, the amount of attached microbes per media particle increases. Because the microbes consist primarily of water, the volume of the microbe-per-media particle increases, but the specific density decreases. This allows the media bed to expand and fluidize at a higher rate such that a longer media bed

hydraulic retention time (defined as the ratio of the expanded bed volume to the feed groundwater flow rate) can be achieved for contaminant removal. The complete destruction of the perchlorate ion ensures that it will no longer be an environmental hazard.

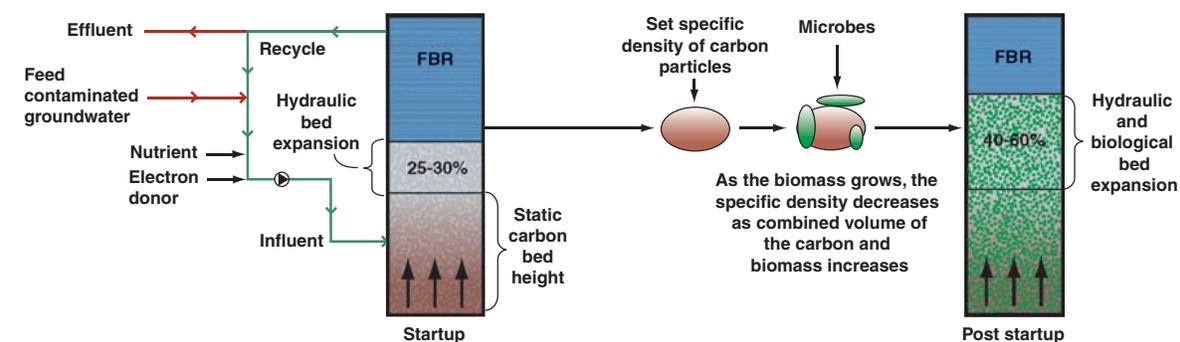
FBR systems in use. To date, six full-scale FBR systems have been designed and implemented for perchlorate treatment to nonpotable standards (Hatzinger, 2005). These systems currently treat more than 9 mgd of groundwater at influent perchlorate concentrations ranging from 1,700 to 400,000 µg/L to effluent concentrations of < 4 µg/L (Evans et al, 2008; Webster, 2007). On the basis of this historical operating experience, the FBR process has been listed in the California Code of Regulations as one of only two treatment technologies considered a best available technology for treating perchlorate-contaminated water to drinking water standards (CCR, 2008). Although the FBR treatment approach is mature, none of the currently operating full-scale systems has been used for drinking water production. Demonstration of a large pilot-scale FBR coupled with a surface water treatment plant to produce perchlorate-free drinking water could provide the necessary design criteria needed to implement the first full-scale FBR drinking water plant in the United States.

Demonstration project objectives. A demonstration of the FBR treatment plant was conducted at the city of Rialto (Calif.) wellhead 2. This well has been inactive for the past decade because of varying levels of perchlorate contamination (Geosyntec Consultants, 2007). A complete treatment system to remediate the perchlorate from the groundwater to produce drinking water (before disinfection) was installed and consisted of the FBR, followed in series by a postaeration tank and a multimedia filter. The FBR and surface water treatment components interacted as one collective unit designated the FBR treatment plant.

In order to generate the necessary data for full-scale design criteria, the primary objectives of the demonstration project were to evaluate

- the nitrate and perchlorate treatment performance of the FBR using only microorganisms indigenous to the local groundwater as the microbial seed,

FIGURE 1 Simple schematic of an FBR showing the hydraulic and biological expansion of media



FBR—fluidized bed bioreactor

- the use of a postaeration vessel and a multimedia filter to produce a potable effluent water stream,
- the effect of feed pump failures (with the FBR remaining in recycle) and complete electrical system shut-downs on treatment performance,
- the operational effectiveness and necessity of the on-line nitrate and perchlorate analyzer systems, and
- the long-term monitoring of system robustness and performance under steady-state and spiking perchlorate concentrations.

EXPERIMENTAL METHODS

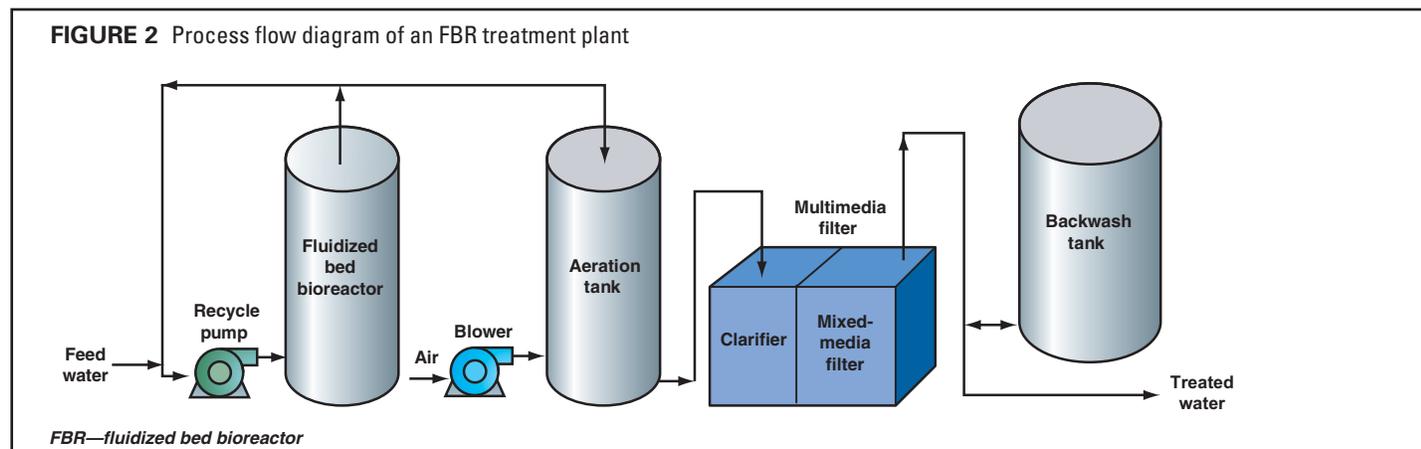
Equipment. For this demonstration, the technology used was based on a number of previously successful FBRs treating higher concentrations of perchlorate-laden groundwater. The FBR vessel was a stainless-steel tank, 0.92 m (3.0 ft) in diameter by 5.2 m (17 ft) high, capable of treating up to 231 L/min (61 gpm) at a maximum feed surface loading of 348 L/min/m² (8.6 gpm/sq ft). The contaminated feed water was pumped from the wellhead typically at a rate of 189 L/min (50 gpm) and fed directly into a recycle line of the reactor. The feed and recycle water entered the vessel through an inlet header manifold at the bottom of the reactor at a combined flow of 348 L/min (92 gpm). The fluid moved upward through the media bed—coconut shell-based GAC¹ (0.9–1.1 mm)—causing the media to hydraulically expand ~28% of the settled bed height (Figure 1).

Through a self-inoculating process from the contaminated feed water, microorganisms attached to the fluidized media. In proportion to the feed flow and the stoichiometric requirements to treat the feed concentrations of dissolved oxygen, nitrate, and perchlorate, a programmable logic controller (PLC) automatically controlled addition to the system influent of an NSF 60–approved 50% acetic acid solution² v/v and a 1.7% phosphoric acid nutrient solution² (diluted from 85 wt% phosphoric acid). The excess acetic acid beyond the stoichiometric requirement was evaluated to account for adsorption and biomass synthesis.

Using these additives, the microbial colonies biologically treated the contaminants in the FBR. The treated water then flowed into a submerged recycle-collection header pipe and

the effluent-collection header pipe at the top of the reactor. A 189-L/min (50-gpm) portion of the fluid exited the FBR system to a postaerator, and 159 L (42 gpm) was recycled back to the suction of the influent pump. Two in-bed biomass separation devices—a biomass separator and an eductor—were used at the top and bottom of the media bed, respectively. The biomass separator used air pressure of 15–25 scfh at the carbon–water interface to separate the biomass from the carbon. The in-bed eductor used pressurized water (10 psig) to physically agitate the biomass off the carbon. Once separated, the carbon settled back into the bed whereas the removed biomass exited through the effluent collection system. A combined hydraulic–biological bed expansion of 40–60% of the settled bed height was targeted.

After the FBR vessel, the water was treated through two posttreatment steps to meet regulatory standards (Figure 2). Through the postaerator vessel, the level of dissolved oxygen was increased from anoxic conditions to 6–8 mg/L via sparging of 10 scfm of ambient air at 9 psig through the water. The stainless-steel vessel was 0.92 m (3.0 ft) in diameter by 4.88 m (16 ft) high, providing an 8-min contact time through the tank at 189 L/min (50 gpm). The effluent from the postaerator passed through a multimedia filter³ where solids were removed through an adsorption clarifier at 407 L/min/m² (10 gpm/sq ft) and a mixed-media chamber at 204 L/min/m² (5 gpm/sq ft). To promote coagulation and flocculation for more efficient suspended solids removal, an NSF 60–approved coagulating agent⁴ (48% aluminum sulfate, alum) and 0.8 % diluted polymer⁵ (stock of 20% cationic polymer) were added to the feed water before the multimedia filter at rates of 1 mL/min (0.4 gpd) and 4 mL/min (1.5 gpd), respectively. Through the adsorption clarifier, an upflow treatment process combined flocculation and clarification. The chemically treated water flowed upward through the adsorption media over a trough weir and onto the mixed-media filter. The adsorption clarifier media consisted of scarified high-density polyethylene plastic beads (2.36–3.35 mm); the mixed-media filter was layered with anthracite, silica sand, and high-density sand. The final product water passed through the filter media into the underdrain system. Turbidity was continuously measured



via an on-line turbidimeter.⁶ The setup also included a back flush–effluent tank system, 1.37 m (4.5 ft) in diameter and 5 m (16.5 ft) tall, capable of storing backwash water for the multimedia filter system. The adsorption clarifier flush was initiated at a bed pressure of 1.8 psig and the mixed-media filter at a vacuum of 3.2 psig. Treated water from the multimedia filter unit was discharged to a local catch basin.

Analysis. Monitoring of the feed groundwater and the effluent from the FBR reactor and downstream equipment was performed throughout the demonstration under various phases of operation in order to evaluate overall treatment effectiveness of the system with respect to the target contaminants of nitrate and perchlorate. The on-line nitrate and perchlorate analytical systems were incorporated into the FBR treatment system using standard USEPA methods 300.0 and 314.0, respectively (*Standard Methods*, 2005). Feed and FBR effluent water continuously passed through two on-line nitrate analyzers⁷ providing continuous monitoring through a universal controller with measurements logged every minute. The minimum detection limit (MDL) of the instrument was 0.1 ppm as nitrate-nitrogen (nitrate-N). To ensure consistently effective nitrate removal, the analyzers were tied into the feed-forward control logic within the system PLC to modify the electron donor pump addition rate as needed. The perchlorate analysis was conducted using an on-line, continuous perchlorate analyzer⁸ with a minimum reporting limit (MRL) of 2.3 µg/L and an MDL of 1 µg/L. Values below the MDL were reported as zero. This complete on-line perchlorate analyzer and sampling system allowed samples of water to be collected at the influent and effluent of the FBR system. Water was pumped using an air-driven double-diaphragm pump⁹ and filtered through a 0.2-µm membrane-sampling filter.¹⁰ A portion of each sample was fed to a multipoint sampling flow-control valve and directed to the perchlorate process analyzer. Within the analyzer, the sample was processed through a guard column (2 × 50 mm), a concentrator (4 × 50 mm), an anion self-regenerating suppressor (92 mm), and an analytical column (2 × 250 mm) to which a 40-mM potassium hydroxide solution as eluent was added via an eluent hydroxide cartridge.¹¹ Individual feed and effluent samples were analyzed by the instrumentation in alternating fashion. With the PLC used to control the sampling and analyzer activity, a maximum of 24 combined samples per day could be collected and analyzed for the influent and effluent of the FBR. From such readings, the PLC controlled the electron donor addition rate to ensure complete removal of the perchlorate by the FBR. A 50-µg/L and a 1,000-µg/L calibration standard¹² were used to calibrate the on-line perchlorate analyzer on a weekly basis as needed.

To meet the five primary evaluation objectives of the study, analysis also included extensive analytical water testing beyond nitrate and perchlorate analysis using onsite measurements and offsite certified analytical laboratories.¹³ Table 1 shows the analyses and methods used.

Self-inoculation. Typically, FBRs are inoculated with a seed population of microorganisms to rapidly initiate the

system operation and increase target contaminant-removal performance. For this experimental study, the natural microbial flora of the incoming groundwater to the FBR was allowed to inoculate the system. The primary objective was to determine the efficiency of the FBR during startup without the addition of an outside microbiological seed. For the first 21 days of the demonstration, the FBR system was operated in batch mode to promote maximum bioactivity. Perchlorate-laden water (~ 50 µg/L) was introduced into the reactor, and the FBR was placed in recycle. Over the course of 21 days, 2 L of 50% acetic acid and 1–2 L of 0.85% phosphoric acid were added in batch to the FBR on an intermittent basis. These quantities met the stoichiometric requirements for the treatment of the concentrations of electron acceptors of oxygen, nitrate, and perchlorate.

With the FBR system in recycle, the natural microbial flora was fostered on the GAC media. Over the last week of batch operation, complete oxygen and nitrate consumption occurred, and visual inspection of the media demonstrated moderate microbial growth on the media. On the basis of historical observations in starting full-scale FBR systems, this bioactivity performance data indicated that the media had sufficient denitrifiers and perchlorate reducers to proceed with feed-forward operation. Therefore, system feed flow was initiated on day 0 at 75.7 L/min (20 gpm) and increased to 189 L/min (50 gpm) stepwise over the first month of operation.

Treatment effectiveness. After reaching steady-state operation in which all oxygen, nitrate, and perchlorate were being completely consumed, the complete FBR treatment plant was monitored to determine the ability of the system to adjust to changes in feed characteristics while continuously producing potable water that met all regulatory requirements. As nitrate and perchlorate treatment effectiveness was demonstrated across the FBR, the downstream systems were also monitored and tested to ensure their ability to effectively perform under varying conditions (i.e., increasing flow rates and concentrations). The postaeration system was tested to effectively and continuously reaerate the water to pre-FBR levels. The requisite coagulant and polymer loading rates for the multimedia filter were established to ensure adequate solids removal and a filter effluent water quality < 0.3 ntu. In addition, the adsorption clarifier and filter backwash frequencies were established. Routine maintenance of the entire plant was conducted to optimize plant performance and chronicle those items that required a preventive maintenance schedule to be developed for full-scale application.

System shutdown scenarios. The robustness of the FBR system to respond to shutdown and restart scenarios was tested. In the first case (repeated twice), a simulated feed pump failure was tested. The FBR system was placed in recycle mode for five days without forward feed flow. This situation simulated a temporary well shutdown scenario for maintenance or a feed pump failure. No electron donor or nutrients were added to the FBR system over the five-day period. Upon restart, electron donor and nutrient addition were reinitiated,

and the plant began receiving full forward feed flow. As the system came back on line, analysis of the FBR feed and effluent water chemical parameters was conducted several times to establish rebound performance from the short-term shutdown. The experiment was repeated after the plant had been operating for 65 days to determine whether the rebound time for system treatment could be affected by the maturation of the FBR biological population.

For the second case (also repeated twice), a complete plant electrical failure scenario was demonstrated by completely shutting the system down. No forward feed of water flow occurred, and the FBR was not in recycle mode. After five days of inoperation, the system was restarted as in the feed pump failure experiment, and the FBR system rebound performance was analyzed. Because most plant shutdowns are generally brief, a second electrical shutdown experiment was conducted for a shorter duration of 8 h, and the system was analyzed for performance rebound upon restart.

On-line analyzer effectiveness. The on-line nitrate and perchlorate analyzers were operated continuously during the year of operation of the FBR treatment plant. Nitrate samples were analyzed every minute whereas perchlorate samples were collected according to the individual experi-

mental requirements. Under typical steady-state operating conditions, however, perchlorate samples were analyzed every 4 h from the effluent and twice per day from the feed to the system. Additional samples were also collected and analyzed off site for comparison.¹³

In addition to daily on-line measurements of nitrate and perchlorate, additional experiments were conducted to assess the necessity for each on-line analyzer for sites with a mixture of nitrate and low concentrations of perchlorate. On the basis of historical practice from other FBR applications, when nitrate concentrations have been substantially higher than perchlorate concentrations in the feed water, nitrate removal across the FBR has shown to be an excellent marker for the removal of perchlorate (Webster et al, 2004). Under steady-state operating conditions, a determination of such a correlation was demonstrated using three separate electron donor reduction experiments such that varying levels of nitrate (up to 1 mg/L as nitrate-N) and perchlorate in the FBR effluent were observed.

During any typical FBR startup, a number of adjustments to the electron donor addition rate are required over the first few months of operation. These various adjustments allow for precise determination of upper and lower

TABLE 1 Partial list of analytes measured, methods used, and California regulatory limits

| Analyte | Method (Reference) | California Regulatory Limit |
|---|--|---------------------------------------|
| Inorganics MCL | | |
| Nitrate (as NO ₃) | 300.0 (USEPA, 1993b) | 45 mg/L |
| Nitrite (as N) | 4500 (Standard Methods, 2005) | 1 mg/L |
| Nitrate-N/nitrite-N | 300.0 (USEPA, 1993b) | < 10 mg/L (combined) |
| Metals | 200.7, 200.8 (USEPA, 1994); 3010A (USEPA, 1992); 6010B (USEPA, 1996); 4500CN, 7470A (Standard Methods, 2005) | Varies per metal |
| Perchlorate | 314.0 (USEPA, 2000) | 6 µg/L |
| DBP MCL | | |
| HAAS | 6251B (Standard Methods, 2005) | 60 µg/L |
| TTHM | 524.2 (Standard Methods, 2005) | 80 µg/L |
| Secondary MCLs | | |
| Aluminum | 200.7 (USEPA, 1994) | 0.2 mg/L |
| Chloride | 300.0 (USEPA, 1993b) | < 250 mg/L (recommended) |
| Color | 2120B (Standard Methods, 2005) | 15 units |
| Copper | 200.8 (USEPA, 1994) | 1.0 mg/L |
| Foaming agents (MBAS) | SM 5540C (Standard Methods, 2005) | 0.5 mg/L |
| Iron | 200.7 (USEPA, 1994); 3010A (USEPA, 1992); 6010B (USEPA, 1996) | 0.3 mg/L |
| Manganese | 200.8 (USEPA, 1994); 3010A (USEPA, 1992); 6010B (USEPA, 1996) | 0.05 mg/L |
| Odor threshold | 2150 (Standard Methods, 2005) | 3 units |
| Silver | 200.8 (USEPA, 1994) | 0.1 mg/L |
| Specific conductance | 2510B (Standard Methods, 2005) | < 900 µS/cm (recommended) |
| Sulfate | 300.0 (USEPA, 1993b) | < 250 mg/L (recommended) |
| TDS | 2540C (Standard Methods, 2005) | < 500 mg/L (recommended) |
| Turbidity | 2130B (Standard Methods, 2005) | < 0.3 ntu |
| Zinc | 200.8 (USEPA, 1994); 3010A (USEPA, 1992); 6010B (USEPA, 1996) | 5.0 mg/L |
| Microbiological requirements | | |
| HPC | 9215B (Standard Methods, 2005) | < 500 cfu/mL (in distribution system) |
| Total coliform/ <i>Escherichia coli</i> | 9223B (Standard Methods, 2005) | < 1 MPN/100 mL |

DBP—disinfection by-product, HAAS—sum of five haloacetic acids, HPC—heterotrophic plate count, MBAS—methylene blue active substances, MCL—maximum contaminant level, MPN—most probable number, N—nitrogen, TDS—total dissolved solids, TTHM—total trihalomethane

electron donor addition requirements for the complete treatment of the feed oxygen, nitrate, and perchlorate. The electron donor reduction experiment 1 (day 54) involved one of these periods of adjustment in operation. During this experiment, the acetic acid rate of addition was decreased stepwise by the PLC such that breakthroughs of both nitrate and perchlorate were observed. For all experiments, the perchlorate analyzer was set up to take samples every 45 min (the most rapid sampling frequency available), whereas the nitrate analyzer measured nitrate-N every minute. For the electron donor reduction experiment 2 (day 116), the acetic acid was cut back rapidly. With the rapid decrease in acetic acid, a coarse correlation between nitrate-N and perchlorate breakthrough could be determined. Finally, to establish a more-refined correlation between nitrate-N and perchlorate breakthrough, experiment 3 (day 138) was conducted by slowly reducing the acetic acid addition rate. On the basis of the experimental results, a full-scale system possibly could be designed using only the nitrate-N analyzers and the established nitrate-N effluent control point at which perchlorate first exceeds the MCL.

Spiking study. Significantly higher perchlorate loading conditions, i.e., 95 L/min (25 gpm) with perchlorate up to 4,000 µg/L, were implemented to determine the treatment robustness and capacity of the FBR treatment plant. The perchlorate spiking experiments occurred via the addition of a solution of potassium perchlorate¹⁴ (99.2% purity, non-NSF certified) using a diaphragm pump¹⁵ downstream of the wellhead but upstream of the FBR treatment plant. Over the course of four months, the feed water perchlorate concentrations were ramped up from the existing groundwater perchlorate concentrations (baseline of 50 µg/L) to 100, 500, 1,000, 1,500, 2,000, and 4,000 µg/L (as measured by the on-line perchlorate analyzer). Short-term perchlorate spiking interruptions of 1–12 h and longer-term interruptions over

weekends occurred that demonstrated the robustness of the treatment system under the most stressful operating conditions. Microbiological, chemical, and disinfection by-product (DBP) potential analyses were conducted for the plant effluent as a function of the spiked perchlorate conditions.

RESULTS AND DISCUSSION

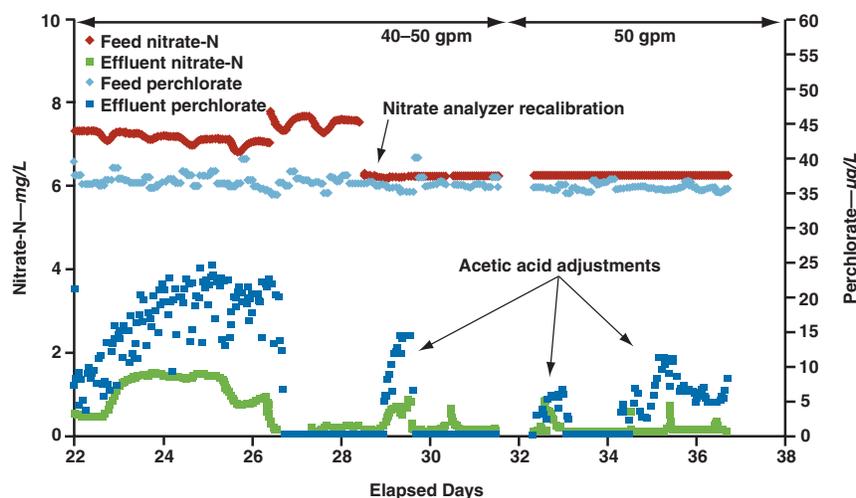
For the FBR treatment plant, the criteria for success were that nitrate-N and perchlorate in the FBR effluent consistently measured at levels < 1 mg/L and 6 µg/L, respectively. At the same time, the downstream equipment was required to meet California surface water treatment regulatory rules for potable water (before disinfection). Table 2 shows the groundwater feed characteristics and the system design criteria established during the demonstration study.

Self-inoculation results. As the forward feed of groundwater was initiated, a number of typical plant startup issues occurred. These issues were primarily related to communication failures between different pieces of equipment. Once these issues were addressed, the actual effectiveness of self-inoculating the system was observed. The plant was operated in continuous forward feed to achieve steady-state performance (day 0). The feed flow was ramped up from 76 L/min to 189 L/min (20 gpm to 50 gpm). Within ~ 30 days (i.e., by day 28), the system was completely removing all nitrate and perchlorate to nondetectable levels (Figure 3). Fine adjustments to the acetic acid addition rate were made from day 28 through day 36 to maximize the nitrate and perchlorate removal while minimizing costs associated with the chemical addition. The optimal addition rates were set at 15 mL/min (16.2 mg/L as carbon [C]) for 50% acetic acid and 10.5 mL/min (0.3 mg/L as phosphorus [P]) for 1.7% phosphoric acid. This electron donor addition of 16.2 mg/L as C included 20% excess electron donor beyond the stoichiometric requirements. Electron-donor addition rates

5–10% below this amount typically resulted in nitrate and/or perchlorate breakthrough, whereas values 10% above this amount unnecessarily wasted electron donor.

Treatment effectiveness results. *FBR.* By day 30 of the plant operation, minimal flow interruptions attributable to mechanical, electrical, and process issues occurred that typically hinder any large-scale water treatment plant startup. Dissolved oxygen was rapidly consumed and was measured to be < 0.5 mg/L in the FBR effluent based on grab-sample analysis in the field. Over the course of the study, the ability of the FBR to completely remove nitrate and perchlorate was readily observed (Figures 4 through 6). The temperature in the reactor averaged 18.5°C,

FIGURE 3 Nitrate-N and perchlorate on-line analytical results (days 22–38), demonstrating contaminant removal within 28 days after self-seeding



nitrate-N—nitrate-nitrogen

and the pH of the feed water dropped slightly from an average of 7.7 to 7.4 in the FBR effluent. Although denitrification promotes bicarbonate alkalinity increase and a subsequent pH increase (as shown by the data), the combined addition of the acetic and phosphoric acid to the FBR promoted a slight decline in pH.

The orthophosphate phosphorus concentration was maintained above 1.0 mg/L in the FBR effluent, whereas dissolved organic carbon (DOC) from acetic acid varied with the experiments but typically ranged between 1.0 and 3.0 mg/L at the FBR effluent. DOC from the acetic acid after the postaeration or multimedia filter was < 0.8 mg/L. The oxidation reduction potential (ORP) in the feed groundwater varied and was generally positive (in the range of 0.0 to +50.0 mV), whereas the ORP in the FBR effluent was shown to be negative (< -150 mV) through both on-line and grab-sample analyses. The negative FBR effluent ORP values provided a general trending tool for the field engineer to understand the health of the FBR system in treating the

nitrate and perchlorate. Negative ORP values to -250 mV generally indicated adequate denitrification and perchlorate reduction conditions. However, an ORP beyond -250 mV indicated potential sulfate-reducing conditions, requiring reductions in electron donor addition.

The FBR media bed growth was excessive because of the saturated oxygen concentrations in the feed groundwater, which promoted robust aerobic bed growth. For the first 120 days of operation, the field engineer assessed the bed height on a daily to weekly basis and set the eductor to operate intermittently for a period of time as needed to control the lower bed expansion (typically a few hours per day). As the denitrifying bacteria grew within the bed, by day 120 it was necessary for the biomass separator to be used in combination with the eductor to control both the aerobic-microbe-dominated lower region of the bed and the denitrifying upper region of the bed. The biomass separator was operated continuously, with intermittent operation of the eductor. This combined controlled opera-

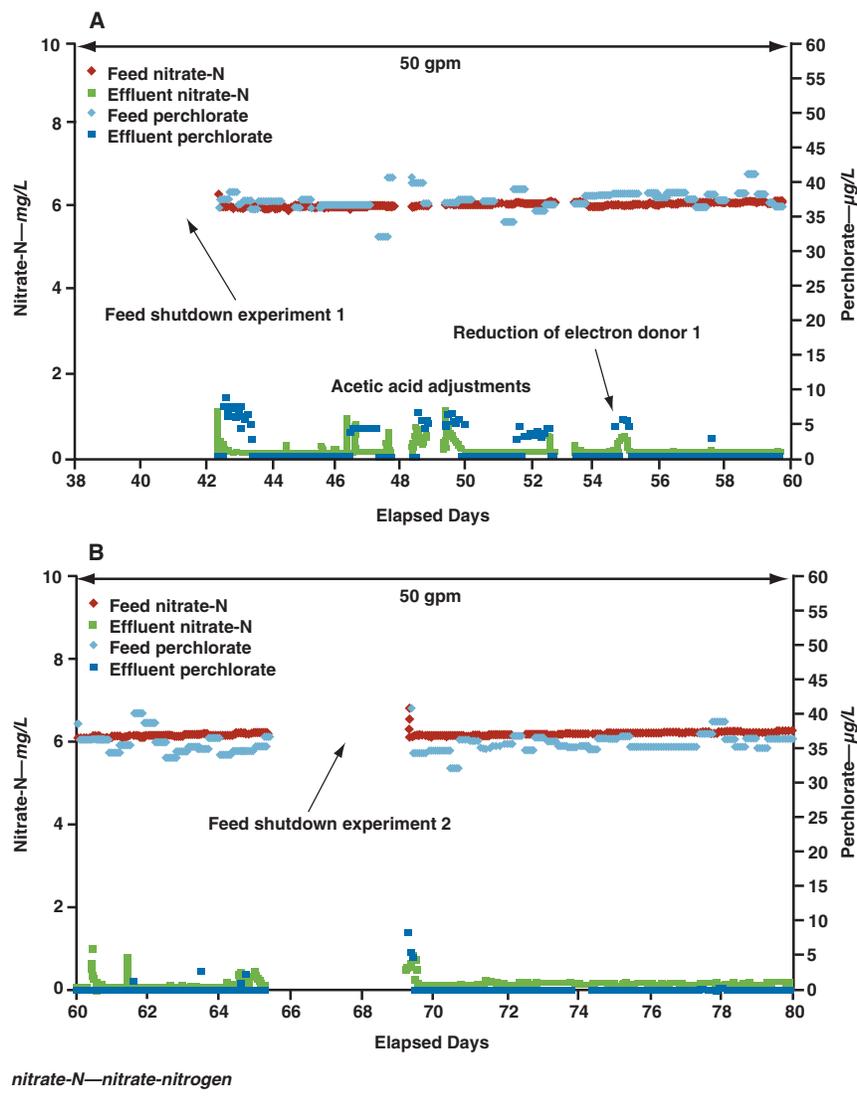
TABLE 2 Select feed water characteristics and associated plant design criteria values

| Feed Water Characteristics | | | | |
|--|--------------|--------------------------|-----------|-----------|
| Primary Electron Acceptors | | Other (In)organics | | |
| Dissolved oxygen—mg/L | 8.1 | Ammonia—mg/L | 0.24 | |
| Nitrate-N—mg/L | 6.1 | Chloride—mg/L | 21.2 | |
| Perchlorate—µg/L | 52.5 | Chlorate—µg/L | < 20.0 | |
| Metals | | Chlorite—µg/L | < 20.0 | |
| Barium—mg/L | 0.0291 | Nitrite-N—mg/L | < 0.05 | |
| Cadmium—mg/L | < 0.001 | Orthophosphate-P—mg/L | < 0.25 | |
| Chromium—mg/L | < 0.0025 | Sulfate—mg/L | 19.1 | |
| Iron—mg/L | 0.0673 (J) | VOCs—µg/L | 3.8 (TCE) | |
| Lead—mg/L | < 0.003 | Physical Characteristics | | |
| Manganese—mg/L | 0.00327 (J) | Color—cpu | < 2.5 | |
| Mercury—µg/L | < 0.1 | pH | 7.7 | |
| Nickel—mg/L | < 0.0025 | TDS—mg/L | 283 | |
| Zinc—mg/L | 0.00726 (J) | TSS—mg/L | < 5.0 | |
| Design Criteria | | | | |
| Parameter | Steady State | Spiking Study | | |
| Perchlorate—µg/L | 52.5 | 500 | 1,000 | 2,000 |
| Nitrate-N—mg/L | 6.1 | 6.1 | 6.1 | 6.1 |
| Feed flow—L/min (gpm) | 189 (50) | 94.5 (25) | 94.5 (25) | 94.5 (25) |
| Recycle flow—L/min (gpm) | 347 (92) | 347 (92) | 347 (92) | 347 (92) |
| Recycle ratio | 0.84 | 2.67 | 2.67 | 2.67 |
| Expanded media bed height—cm (in.) | 371 (146) | 371 (146) | 371 (146) | 371 (146) |
| Media bed HRT—min | 12.2 | 24.3 | 24.3 | 24.3 |
| Elimination capacity—g ClO ₄ /m ³ media × h | 0.25 | 1.2 | 2.4 | 4.8 |
| Elimination capacity—g NO ₃ -N/m ³ media × h | 29.3 | 14.6 | 14.6 | 14.6 |
| Acetic acid dose—mg/L as C | 16.2–17.3 | 18.0–19.3 | 18.0–19.3 | 18.0–19.3 |
| Phosphoric acid dose—mg/L as P | 0.2–0.3 | 0.3–0.4 | 0.3–0.4 | 0.3–0.4 |
| Postaeration HRT—min | 8 | 16 | 16 | 16 |
| Alum dose—mg/L | 2.5 | 5.0 | 5.0 | 5.0 |
| Polymer dose—mg/L | 0.17 | 0.34 | 0.34 | 0.34 |
| Clarifier flushes—number per day | 6 | 6 | 6 | 6 |
| Media backwashes—number per day | 1 | 1 | 1 | 1 |

C—carbon, ClO₄—perchlorate, HRT—hydraulic residence time, N—nitrogen, NO₃—nitrate, P—phosphorus, TCE—trichloroethylene, TDS—total dissolved solids, TSS—total suspended solids, VOC—volatile organic chemical

(J) indicates the analyte was positively identified; value is estimated.

FIGURE 4 Nitrate-N and perchlorate removal (days 38–80) during the first (A) and second (B) feed shutdown experiments and first electron donor reduction experiment (A)



tion, along with occasional manual lancing of the lower portions of the bed, maintained the expanded bed height at between 280 and 381 cm (110 and 150 in.).

Postaeration. The postaeration vessel effectively raised the dissolved oxygen concentrations from < 0.5 mg/L to > 7.5 mg/L consistently. The vessel also provided additional residence time for aerobic consumption for any residual acetic acid that carried over from the FBR. For the first nine months of operation, no blockage or operational issues were observed with the blower used to continuously re-aerate the water. On day 274, the postaeration blower failed in operation. The motor assembly of the blower still functioned correctly, but two of the four impeller vanes cracked. At this point, the FBR was placed into recycle, a repair kit was purchased from the manufacturer, and the blower was repaired after four days

of the FBR operation in recycle mode. The treatment performance of the system upon restart was not affected, but this kind of incident highlighted the necessity for an effective preventive maintenance program at full scale.

Multimedia filter. All of the effluent analytical results from the multimedia filter met the regulatory limits for inorganics and organics for potable water (Table 3). Regardless of the plant operating condition (steady-state operation, restart after shutdown, during spiking experiments), no presence of *Escherichia coli* was ever detected—< 1.0 most probable number (MPN)/100 mL—at the multimedia filter effluent. Total coliform data varied from the multimedia filter effluent per operating condition from a high of 690 MPN/100 mL to < 1 MPN/100 mL. Heterotrophic plate count (HPC) measurements were consistently higher from the FBR effluent (averaging 9×10^6 cfu/mL) compared with the multimedia filter effluent (averaging 4×10^4 cfu/mL). Typically, > 95% removal of HPC was observed across the filter. Nevertheless, HPC values of < 500 cfu/mL were not consistently achieved in the filter effluent. A chlorination study was conducted on samples of the multimedia filter effluent water at chlorine contact times of 5 mg-min/L that demonstrated no presence of total coliform and < 30 cfu/mL of HPC

(data not shown). For this reason, the microbes generated from this biological drinking water plant were not considered problematic to chlorine disinfection.

Total trihalomethane (TTHM) and sum of five haloacetic acids (HAA5) formation potential were measured as DBPs at the multimedia filter effluent during system steady-state operation (days 34, 77, and 96), after the last feed shutdown experiment (day 69), after the plant shutdown experiment (day 89), and during the spiking study (days 301 and 327). The regulatory limits for TTHMs and HAA5 are set at 80 and 60 µg/L, respectively. Regardless of operating condition, the multimedia effluent water values never exceeded 30 µg/L for either TTHM or HAA5. During the initial operation of the plant (day 34), higher DBP concentrations were observed at the multimedia filter effluent as a result of fine-tuning of the chemical addition

(aluminum sulfate and polymer) to the filter. Higher concentrations of DBPs were also observed during the spiking studies (days 301 and 327) and likely were attributable to the larger contaminant loads being treated by the FBR, which resulted in more biomass carryover.

Continuous operation of the in-bed eductor within the FBR resulted in biomass solids being carried over to the postaeration tank and subsequently to the multimedia filter. Initially, the amount of biomass removed from the FBR caused the multimedia filter to produce water with a turbidity > 0.5 ntu. For this reason, 1 mL/min (0.4 gpd) of the NSF 60-approved 48% aluminum sulfate (2.5-mg/L dose) and 4 mL/min (1.5 gpd) of the 0.8% cationic polymer (diluted from 20% stock, 0.17-mg/L dose) were optimally added as coagulating and flocculating agents, respectively. Upon addition of these chemicals on day 55, the effluent turbidity of the multimedia filter was reduced to < 0.1 ntu. The biomass loading and the chemical additions to the filter feed resulted in the requirement of six adsorption clarifier flushes and one multimedia filter backwash per day. For the FBR forward feed of 189 L/min (50 gpm), each flush and backwash gener-

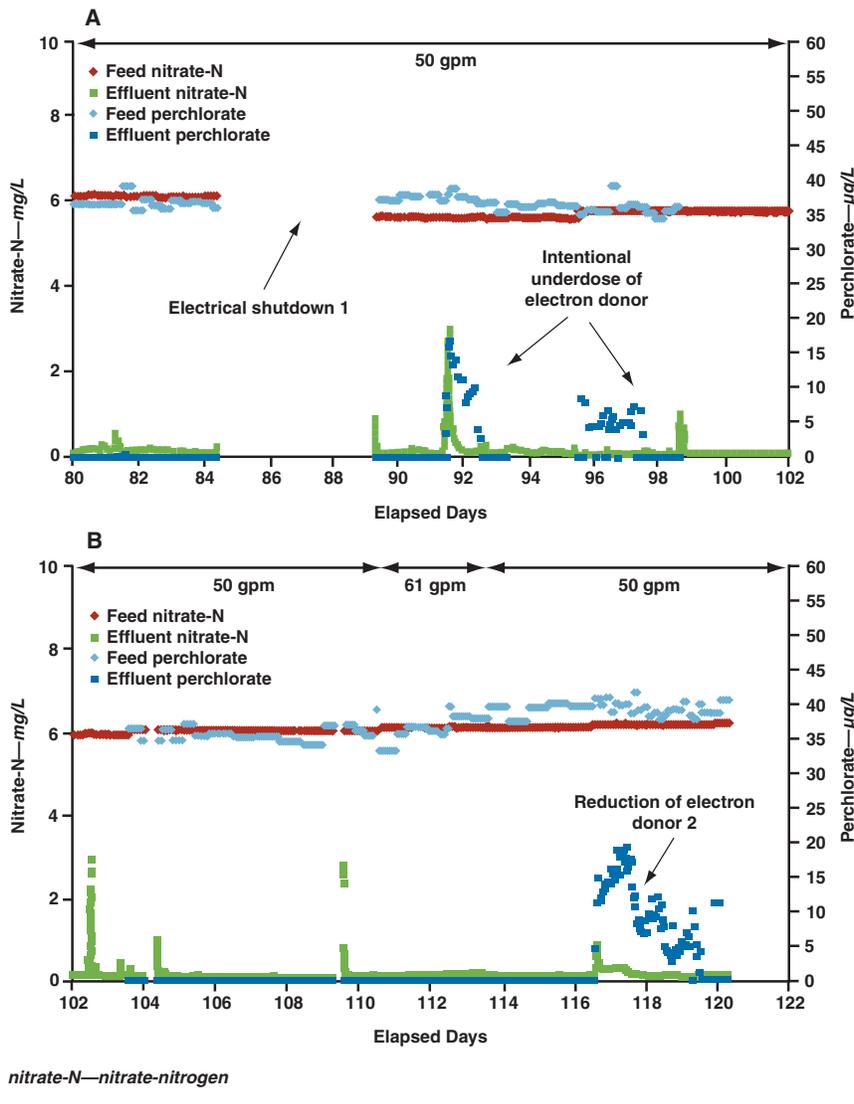
ated 2,460 L (650 gal) and 3,785 L (1,000 gal), respectively. This amounted to a water recovery of more than 93% per day. On the basis of analyses conducted during each flush and backwash, the time-weighted average biological oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS) concentrations were 26.7, 478, and 272 mg/L, respectively, during each flush and 1.78, 69.5, and 128 mg/L, respectively, during each backwash. These results indicated that the adsorption clarifier was primarily responsible for the majority of the solids removal across the multimedia filter. Individual sanitary sewers have unique acceptance criteria for the volume and BOD, COD, and TSS concentrations of accepted wastewater. However, the demonstrated wastewater characteristics resembled a weak to medium wastewater and should be acceptable to most wastewater treatment plants (Metcalf & Eddy Inc., 2002). If desirable at the full-scale plant, the 93% recovery could be significantly enhanced to > 98% by processing the clarifier flush and backwash water through a settling clarifier before discharge to sewer and reprocessing the supernatant through the feed of the FBR treatment plant.

TABLE 3 Multimedia filter effluent water quality for metals, inorganics, and organics under steady-state operating conditions and perchlorate spiking conditions

| Condition | Steady-State 50 µg/L | Perchlorate 1,000 µg/L | Perchlorate 2,000 µg/L | Perchlorate 2,500 µg/L | California Limit |
|-----------------------------|-------------------------|---------------------------|---------------------------|---------------------------|---------------------|
| Days Elapsed | 137 | 301 | 329 | 335 | |
| Metals | | | | | |
| Aluminum—mg/L | 0.053 | 0.064 | 0.062 | 0.076 | 0.2 |
| Antimony—mg/L | < 0.006 | < 0.006 | < 0.006 | < 0.006 | 0.006L |
| Arsenic—mg/L | < 0.002 | < 0.002 | < 0.002 | < 0.002 | 0.01 |
| Barium—mg/L | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 1 |
| Beryllium—mg/L | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.004 |
| Cadmium—mg/L | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.005 |
| Chromium—mg/L | 0.0039 | 0.0033 | 0.0019 | 0.0024 | 0.05 |
| Copper—mg/L | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 1 |
| Cyanide—mg/L | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 0.15 |
| Iron—mg/L | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 0.3 |
| Lead—mg/L | < 0.005 | < 0.005 | < 0.005 | < 0.005 | 0.015 |
| Manganese—mg/L | < 0.02 | < 0.02 | < 0.02 | < 0.02 | 0.05 |
| Mercury—µg/L | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.002 |
| Nickel—mg/L | < 0.01 | < 0.01 | < 0.01 | < 0.01 | 0.1 |
| Selenium—mg/L | < 0.005 | < 0.005 | < 0.005 | < 0.005 | 0.05 |
| Silver—mg/L | < 0.01 | < 0.01 | < 0.01 | < 0.01 | 0.1 |
| Thallium—mg/L | < 0.001 | < 0.001 | < 0.001 | < 0.001 | 0.002 |
| Zinc—mg/L | < 0.05 | < 0.05 | < 0.05 | < 0.05 | 5 |
| Other (In)organics | | | | | |
| MBAS—mg/L | < 0.10 | < 0.05 | < 0.05 | < 0.05 | 0.5 |
| Nitrate—mg/L | < 1.0 | < 1.0 | < 1.0 | < 1.0 | 45 |
| Nitrite—mg/L as N | < 0.1 | < 0.1 | < 0.1 | < 0.1 | 1 |
| Sulfate—mg/L | 16 | 17 | 16 | 17 | < 250 |
| Color—cpu | < 2.5 | < 3.0 | < 3.0 | < 3.0 | 15 units |
| Odor—TON | < 1.0 | < 1.0 | < 1.0 | < 1.0 | 3 units |
| Turbidity—ntu | < 0.2 | < 0.2 | < 0.2 | < 0.2 | < 0.3 |
| Specific condition—µmhos/cm | 430 | 410 | 420 | 430 | < 900 |
| TDS—mg/L | 250 | 230 | 300 | 280 | < 500 |
| VOC—µg/L | ND | ND | ND | NM | Varies |

MBAS—methylene blue active substances, N—nitrogen, ND—nondetect, NM—not measured, TDS—total dissolved solids, TON—threshold odor number, VOC—volatile organic chemical

FIGURE 5 Nitrate-N and perchlorate removal (days 80–122) during the first electrical shutdown experiment (A), the second electron donor reduction experiment (B), and steady-state operation



System shutdown scenario results. The first water feed interruption experiment was conducted on days 37–42 (Figure 4, part A). The FBR was placed in recycle without electron donor and nutrient addition. Upon restart of the feed water (day 42), the nitrate-N and perchlorate breakthrough were observed for ~24-h before the system effluent nitrate-N and perchlorate concentrations returned to nondetect levels. After some maturation of the microbial community in the FBR as the bed height increased 31 cm (12 in.), a second feed-interruption experiment was conducted from days 65 to 69 (Figure 4, part B). Upon restart of the feed water (day 69), the removal recovery of nitrate-N and perchlorate to nondetect levels required <8 h. A denser, robust denitrifier and perchlorate-degrading population colonized the filter bed, providing shorter recovery times.

The first plant electrical shutdown experiment occurred on days 84–89 (Figure 5, part A). This experiment replicated

a long-term electrical outage at the plant. Upon restart of the plant, a breakthrough of nitrate-N was quickly observed, but no corresponding breakthrough of perchlorate occurred. The recovery period for the nitrate-N was <2 h. The lack of perchlorate breakthrough was likely a combination of adsorption and biodegradation and has been observed in other fixed-film reactor studies (Brown et al, 2005). Adsorption of perchlorate on activated carbon, though limited, has been demonstrated previously (Gu & Coates, 2006; Brown et al, 2002; Na et al, 2002). Upon restart, the initial primary mechanism for nitrate-N and perchlorate removal was adsorption, but as the microbes were reactivated by the addition of forward flow, electron donor, and nutrients, the primary removal mechanism of both the nitrate-N and perchlorate shifted to biodegradation. It is postulated that because a perchlorate-degrading population had matured in the bed over the course of the demonstration study (i.e., over the first 80 days), the biological activity was able to rebound quickly and remove the perchlorate before the media bed had reached its adsorptive capacity.

The second plant electrical shutdown experiment was conducted on day 134 for 8 h, replicating a realistic short-term electrical failure and subsequent system restart (Figure 6). Similar to the long-term plant electrical interruption, nitrate-N breakthrough occurred, but perchlorate did not appear in the FBR effluent. Upon restart, the recovery time for the nitrate-N was ~90 min. Again, adsorption coupled with biological treatment allowed the FBR to quickly recover from a short-term electrical outage. Both of these experiments demonstrated that long- and short-term electrical shutdowns for a mature microbiological FBR system do not lead to extensive downtime in performance upon system restart.

On-line analyzer effectiveness results. Nitrate analyzers. The feed and effluent nitrate analyzers worked effectively throughout the demonstration (Figures 3–6). Data registered between the on-line instrumentation and the offsite laboratory analysis for the feed nitrate-N agreed on average within 6.5% (Figure 7, part A). The outside laboratory had an MDL of 0.05 mg/L nitrate-N whereas the on-line instrument MDL was 0.1 mg/L. This difference in MDLs skewed the

FBR effluent data for comparison because the majority of the measured values were at the MDL. The on-line nitrate-N analyzer consistently demonstrated its MDL for the effluent water during steady-state operation. As preventive maintenance, the analyzer sampling chamber typically was wiped off with a cloth to remove solids once a week, with the FBR effluent nitrate analyzer requiring more attention. Nonetheless, on three occasions (days 167, 168, and 317), one or both analyzers failed to read accurate nitrate concentrations, and these instruments were subsequently returned to the manufacturer for repair and recalibration.

Perchlorate analyzer. The operation of the on-line perchlorate analyzer worked effectively in analysis and in providing feed-forward control of the electron donor (Figures 3–6). Initially, the on-line perchlorate analyzer instrument had a consistent, low bias in reportable perchlorate concentrations compared with the offsite laboratory analyses. On average, the on-line instrument reported the feed concentration to be 36.2 $\mu\text{g/L}$, whereas the outside laboratory reported 52.1 $\mu\text{g/L}$.

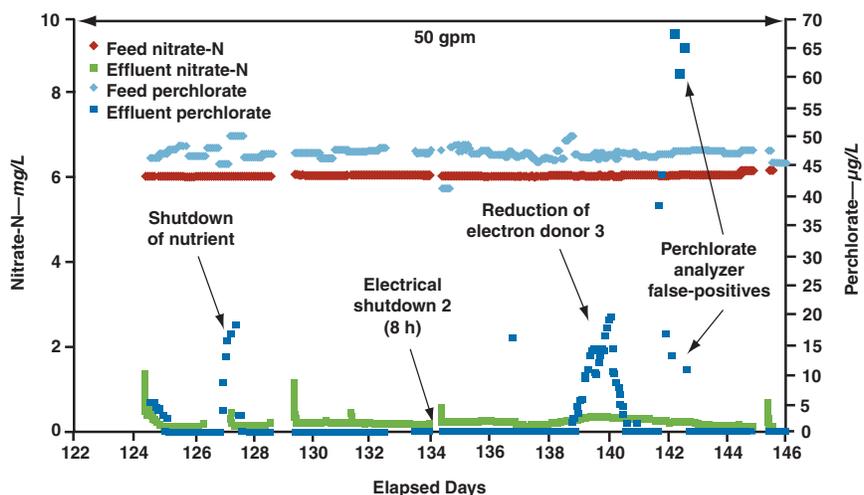
Using a certified 1,000- $\mu\text{g/L}$ perchlorate standard, a 50- $\mu\text{g/L}$ perchlorate standard was prepared and analyzed both on site and at an offsite laboratory.¹³ The onsite analyzer detected the sample at 44.5 $\mu\text{g/L}$, whereas the offsite laboratory result was 53.8 $\mu\text{g/L}$. It was discovered that this difference was attributable to the sample preparation technique within the on-line instrument compared with the outside laboratory analysis. The dilution pump within the on-line perchlorate analyzer delivered a lower volume of water during the internal calibration preparation steps. This caused the FBR feed sample to continually read low.

On day 124, the dilution pump volume and the perchlorate analyzer sampling protocol were adjusted, allowing the onsite instrument and the laboratory analytical FBR feed results to compare within 10–20% (Figures 6 and 7). The outside, offsite laboratory MRL was 2 $\mu\text{g/L}$, and the instrument MDL was 0.5 $\mu\text{g/L}$. Even with the difference observed between the reported onsite and the offsite laboratory feed perchlorate values, the effects on the PLC to adequately control the electron donor were minimal. An excess of electron donor beyond the stoichiometric requirements was always provided to the FBR to account for variabilities in the feed water contaminant composition that absorbed this difference in readings. This inherently low bias was not observed repeatedly for the reported effluent perchlorate concentrations by the on-line instrument.

On-line instrument necessity. Experiments were conducted to correlate nitrate-N and perchlorate removal to determine the necessity of both instruments. During electron donor–reduction experiment 1 (day 54), fine-tuning of the acetic acid between 16.2 and 17.3 mg/L as C was conducted for a week to attempt to minimize the electron donor required (Figure 4, part A). From this experiment, a general observation was made that at FBR effluent nitrate-N concentrations as low as 0.5 mg/L, breakthrough of perchlorate was observed (4.2 $\mu\text{g/L}$) in the FBR effluent water. This perchlorate breakthrough first occurred ~ 1 h after the first indications of nitrate-N breakthrough. Higher concentrations of perchlorate (up to 5.3 $\mu\text{g/L}$) were not observed until almost 5 h after the initial nitrate-N breakthrough. However, these perchlorate concentrations never exceeded the California state MCL of 6 $\mu\text{g/L}$ before the nitrate-N FBR effluent concentrations began to decline again to nondetect levels (13 h from initial breakthrough).

For electron donor reduction experiment 2 (day 116), the excess acetic acid dose was cut back rapidly from 16.2 to 13.5 mg/L as C (Figure 8, part A). This experiment simulated a loss of electron-donor pumping capacity (i.e., a leak in the delivery line). Upon this rapid reduction of electron donor, the nitrate-N concentration increased from 0.1 to 0.8 mg/L within 4 h. The perchlorate analyzer was set up to take samples every 45 min (the most rapid sampling frequency achievable). Within 3 h of the rapid reduction of electron donor, the perchlorate began to quickly increase (above 6 $\mu\text{g/L}$) in the FBR effluent as the nitrate-N exceeded 0.4 mg/L. After this point, the acetic acid was slowly increased from 13.5 to 14.4 mg/L as C, and the increasing perchlorate trend was reversed. Only after a subsequent increase in the acetic acid dose from 14.4 to 16.2 mg/L as C over the next two

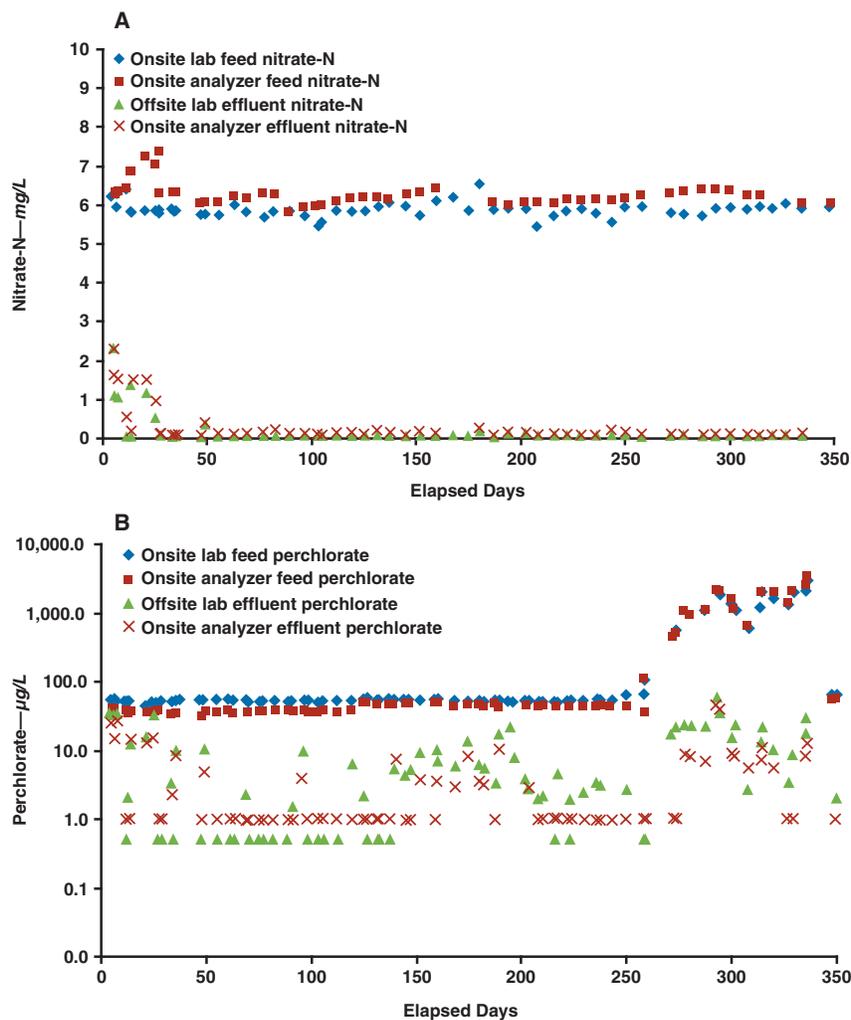
FIGURE 6 Nitrate-N and perchlorate removal (days 122–146) during the second electrical shutdown experiment, the third electron donor reduction experiment, and steady-state operation



nitrate-N—nitrate-nitrogen

Feed perchlorate concentrations were adjusted after a change in the analytical instrument operation.

FIGURE 7 Comparison of offsite lab and onsite feed and effluent nitrate-N (A) and perchlorate data (B), with nondetects reported as the MDLs for each analysis



days did the perchlorate effluent values decrease to nondetect levels. When the effluent nitrate-N decreased below the 0.4-mg/L value, a correlative rapid decline in perchlorate was not immediately observed. This lag may be a function of the lack of bound acetic acid available for perchlorate treatment (as would be present just after the acetic acid is initially reduced) that possibly results in a slower treatment response by the microorganisms. A more rapid recovery of perchlorate treatment may have been observed had much higher loads of acetic acid been continually supplied before the rapid reduction of the electron donor. These higher loads would have provided more adsorbed, stored acetic acid on the carbon from which the microbes could have sequestered the electron donor for perchlorate removal.

For electron donor reduction experiment 3 (beginning of day 138), the acetic acid dose was slowly reduced over a 15-h period from 16.2 to 13.9 mg/L as C (Figure 8, part

B). The FBR effluent nitrate-N gradually increased from 0.22 to 0.34 mg/L over a 23-h period. Within the first 20 h of this 23-h period, when the nitrate-N was 0.31 mg/L, the FBR effluent perchlorate first exceeded the MCL. Upon restart of the acetic acid at the original addition rate of 16.2 mg/L as C, the FBR effluent perchlorate decreased below 6 µg/L ~ 8.5 h later, when the nitrate-N was at a value of 0.29 mg/L. This experiment demonstrated that the actual intersection point for perchlorate breakthrough for this system is closer to 0.3 mg/L of nitrate-N rather than 0.4 mg/L nitrate-N (as demonstrated by experiment 2). At this intersection point for this specific operating scenario in treating lower levels of perchlorate (50 µg/L), the FBR effluent nitrate analyzer could be used as the sole effective determination method of perchlorate concentrations above and below the MCL. However, if the perchlorate load had been significantly higher, a different intersection point might have been observed.

Spiking study. At each spiked perchlorate concentration of 100, 500, and 1,000 µg/L, the FBR effluent water gradually decreased over five days to less than the California state MCL of 6 µg/L. From days 299 to 321, the perchlorate feed concentration was ramped up from 1,000 to 2,000 µg/L. A definitive trend with perchlorate removal over time was

observed for spiked perchlorate concentrations > 1,000 µg/L. As the biomass in the FBR matured and acclimated to the higher perchlorate loading, a declining trend of FBR effluent perchlorate concentration was observed (Figure 9). A similar response to increasing perchlorate concentrations by a maturing perchlorate population had been observed previously in other bioreactors (Nerenberg et al, 2007). A zero-order to first-order removal kinetic regime dominated.

The spiking experiments were conducted for short periods (days to weeks), and a true steady-state operating condition was difficult to achieve. Therefore, the microbiology within the system was still developing under these spiking conditions, and perchlorate removal appeared to be only a function of a temporary reaction limitation attributable to lack of biomass development. When the feed perchlorate concentration was reduced from 2,000 to 1,000 µg/L (days 327–329), a return to complete perchlorate removal was

observed (Figure 10). Under all perchlorate spiking conditions up to 2,000 µg/L, the acetic acid dosages were similar (between 18.0 and 19.3 mg/L as C). This was not an unexpected result because the majority of the supplied acetic acid was used primarily for nitrate-N treatment. Regardless of the perchlorate-feed spiking concentrations, the downstream equipment continued to produce consistent effluent water that met all California Title 22 MCL requirements before disinfection (Table 3). Minimal increase in the adsorption clarifier and mixed media backwash frequency of the multimedia filter was observed under all spiking conditions.

A gradual increase in perchlorate concentration from 1,000 to 4,000 µg/L in the feed water occurred from days 329 to 335. Once the biomass started to acclimate and accrue within the system, perchlorate performance continued to improve. At perchlorate concentrations spiked to 4,000 µg/L, the rate of removal was near first order and > 99.6% removal efficiency. If longer, uninterrupted operation of the spiking study could have been conducted, complete treatment of the perchlorate at concentrations as high as 4,000 µg/L to nondetect values presumably would have been demonstrated.

CONCLUSION

The use of an FBR treatment plant for the effective remediation of perchlorate-laden groundwater to potable water standards before disinfection was demonstrated. A critical issue in applying a full-scale FBR treatment plant is qualifying the system robustness in effectively operating under various scenarios. The FBR system in this research was biologically seeded using only the feed groundwater and demonstrated complete removal of the nitrate and perchlorate to nondetect levels within 28 days of operation under continuous, steady-state feed conditions.

The demonstration highlighted the fact that the FBR treatment plant, like any biological plant, requires careful monitoring during startup. As is typical with the initiation of any water treatment plant, mechanical, electrical, and process issues can arise. For a biological plant, this causes interruptions in feed flow, which ultimately hinders the treatment process. Therefore, every effort should be made to provide a constant feed during startup so that the

microorganisms have an opportunity to rapidly grow and acclimate within the FBR.

At perchlorate concentrations up to 1,000 µg/L, complete perchlorate treatment to below 6 µg/L was demonstrated. The FBR operated at hydraulic residence times of 12.2 and 24.3 min with acetic acid dosing rates ranging from 16.2 to 19.3 mg/L as C. A 20% excess of electron donor was required for adsorption and cell synthesis. The downstream equipment of the postaeration and the multimedia filter operated effectively under all scenarios to continually produce effluent water that met California Title 22 drinking water requirements (before disinfection). *E. coli* was not formed within the system, DBP formation potential did not exceed the regulatory standards, and total HPC effluent concentrations were effectively reduced across the multimedia filter (although further disinfection would be required).

FIGURE 8 Onsite feed and effluent nitrate-N and perchlorate results for electron donor reduction experiments 2 (A) and 3 (B)

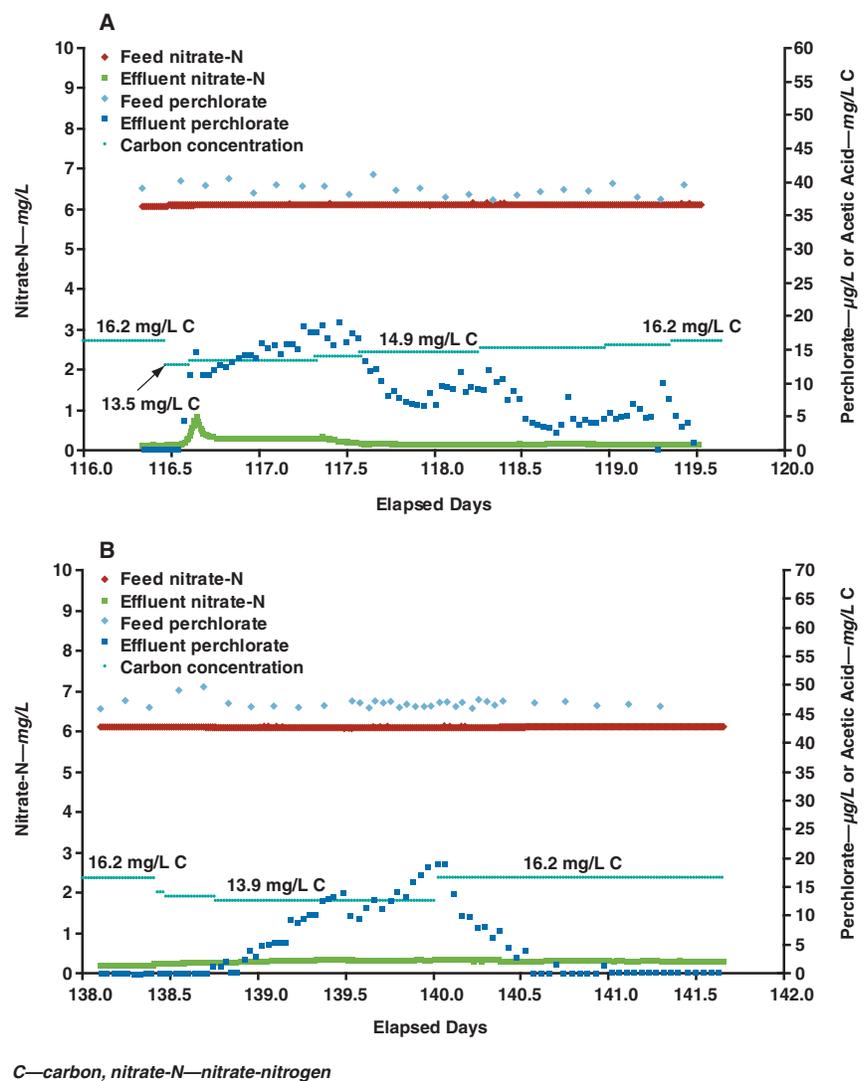


FIGURE 9 Spiked perchlorate concentrations to 2,000 µg/L showing a general improvement in performance over time as the microbial population acclimates to the higher perchlorate loading

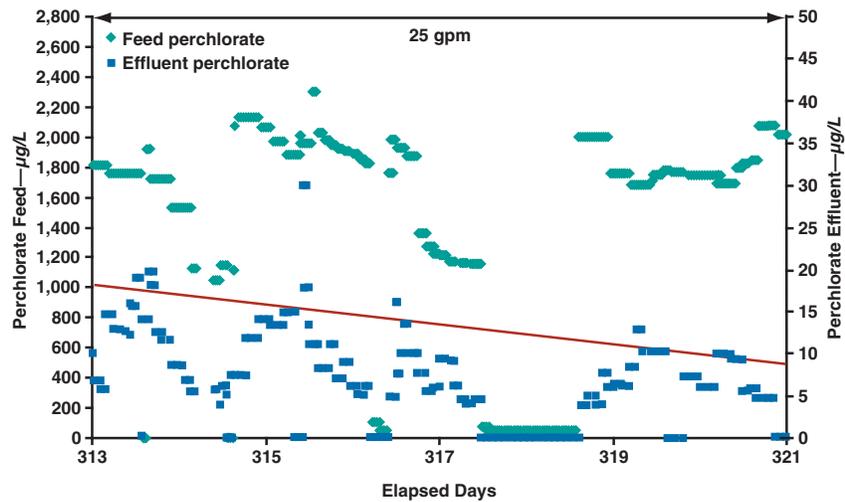
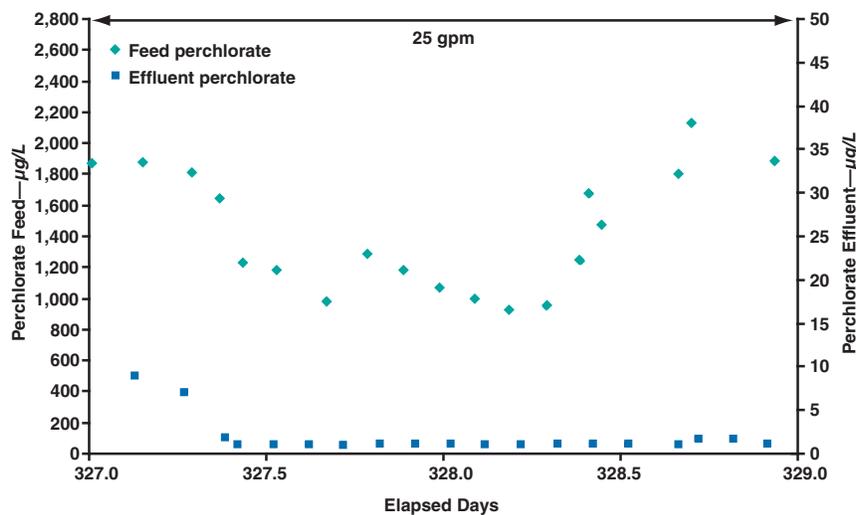


FIGURE 10 From days 327 to 329, complete treatment of perchlorate at a feed concentration near 1,000 µg/L



A rapid recovery pattern was demonstrated for the FBR treatment plant during the feed and plant interruptions after a more mature microbial population developed within the FBR. Within the first 90 days of plant operation, < 2 h were required to achieve acceptable treatment performance upon restart of the plant. Even with such a short recovery period, however, these results underscore the need to design a full-scale plant with the ability to either operate in plant recycle until the required regulatory treatment levels can be met or discharge directly to a sanitary sewer or catch basin.

The use of on-line analytical instrumentation for rapid analysis of the system performance and control of the acetic acid feed rate proved effective and reliable. Reductions in acetic acid indicated that for FBR nitrate-N effluent concentrations at 0.3 mg/L, perchlorate concentrations exceeded

the California state MCL. This point of intersection is a function of the specific operating conditions evaluated at the site, but the results in this study indicated that an FBR can be operated around this point of intersection using only the nitrate effluent analyzer to demonstrate perchlorate treatment. Still, for any future full-scale FBR treatment plant installation, the necessity of each piece of equipment must be evaluated on a case-by-case basis for its cost-effectiveness.

The implementation of such a first-of-its-kind technology to remediate perchlorate-laden contaminated groundwater to drinking water standards (rather than simply rely on phase transfer) can serve as a new paradigm of water treatment of significantly impaired resources. With quality supplies of water rapidly declining and existing supplies often degraded by multiple contaminants, the implementation of such a biological treatment plant can be effective for the removal of multiple contaminants to drinking water standards.

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FOOTNOTES

¹Aquasorb, Jacobi Carbons, Philadelphia, Pa.

²Univar, National City, Calif.

³Trimita TA-50A, Siemens Water Technologies, Ames, Iowa

⁴Sterling Water Technologies, Columbia, Tenn.

⁵Callaway cationic polymer 4080, Kemiron, Fontana, Calif.

⁶FilterTrak 660, Hach Co., Loveland, Colo.

⁷NITRATAX Plus SC, Hach Co., Loveland, Colo.

⁸DX-800, Dionex, Sunnyvale, Calif.

⁹Sandpiper pump, Warren Rupp, Mansfield, Ohio

¹⁰Collins Products, Livingston, Texas

¹¹IonPac AG16 guard column, IonPacAG16 concentrator, ASRS-ULTRA anion self-regenerating suppressor, IonPac AS16 analytical column, EluGen II hydroxide cartridge, Dionex Sunnyvale, Calif.

¹²Accustandard, New Haven, Conn.

¹³EMAX Laboratory Inc., Torrance, Calif., and E.S. Babcock & Sons Inc., Riverside, Calif.

¹⁴Hummel Croton, South Plainfield, N.J.

¹⁵LMI Milton Roy, Ivyland, Pa.

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