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from the Saugus Aquifer, TM 3 Bench and Pilot Test Results
(February 2004)

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engineers

Castaic Lake Water Agency

Treatment of Perchlorate Contaminated
Groundwater from the Saugus Aquifer

TECHNICAL MEMORANDUM NO. 3
BENCH AND PILOT TEST RESULTS

February 2004

CASTAIC LAKE WATER AGENCY

TREATMENT OF PERCHLORATE CONTAMINATED GROUNDWATER FROM THE SAUGUS AQUIFER

TECHNICAL MEMORANDUM
NO. 3

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BENCH AND PILOT TEST RESULTS

1.0 EXECUTIVE SUMMARY

1.1 Background

A 6-month study was performed to evaluate the effectiveness of ion exchange (IX) and biological processes for treating perchlorate-contaminated water from the Saugus aquifer. Three single-pass perchlorate-selective IX resins were evaluated at the bench-scale while fixed-bed biological reactors (FXBs) and fluidized-bed biological reactors (FBRs) were tested at the pilot-scale. These processes were chosen due to their ability to remove perchlorate from groundwater without generating a perchlorate-laden waste stream or brine that needs to be discharged.

1.2 Ion Exchange

Breakthrough of most anions from the IX resins occurred in the first 24 hours of run time. No chromatographic peaking was observed for any of the critical anions. Chloride breakthrough decreased from 325 mg/L to background concentrations (~35 mg/L) after 280 bed volumes. Perchlorate breakthrough (i.e., greater than 1 μg/L) occurred at 25,000 to 76,000 bed volumes (26 to 79 days). This translates to treated water volumes of 187,000 to 569,000 gal/cu-ft resin.

Contacting IX effluent with free and combined chlorine for 2- and 24-hour incubation periods produced no detectable (i.e., < 2 ng/L) N-nitrosdimethylamine (NDMA) concentrations for all three resins tested, indicating that NDMA precursors did not leach from the resins. When 2 mg/L of free chlorine was dosed to the IX feed water, effluent NDMA concentrations were below or just over the detection limit. To evaluate the NDMA precursor leaching potential of the resins, 100 mL batches of fresh resin were incubated for four hours in deionized water and groundwater. NDMA was detected in only one sample, which measured at less than half the 10 ng/L Action Level.

A California Total Threshold Limit Concentration (TTLC) analysis showed that metals were mostly non-detect in all three spent resins. Chromium, vanadium, and zinc were detected in two of the spent resins at levels significantly below the regulatory TTLC threshold concentrations. Uranium levels in the spent resin leachate were significantly below the Title 22 MCL of 20 pCi/L. To investigate whether the spent resins would be classified as hazardous for transportation to an incineration facility, a mass balance of the uranium adsorbed and desorbed from the resin up to 50 percent perchlorate breakthrough was performed. The amount of uranium accumulated on the spent resins is far below the lowest permissible reporting quantity and A-value of the California Department of Transportation.

1.3 Biological Filtration

Consistent perchlorate removal to below detection was achieved in the FXB filter using only organisms indigenous to the Saugus aquifer. With influent DO and nitrate concentrations of 7 and 15 mg/L, respectively, the lowest EBCT and acetic acid concentration that allowed consistent perchlorate removal to below detection was 15 minutes and 7.8 mg/L as carbon, respectively. Run times ranged from 24 hours to several days. Effluent from the FXB filter was biologically stable and contained no fecal coliforms. Challenge tests demonstrated that the FXB filter was robust with respect to backwashing episodes, changes in feed water quality, system shut-downs, and electron donor addition failures. Large step increases in feed nitrate concentration (e.g., 23 mg/L) required a period of bio-acclimation before perchlorate removal to below detection could be reestablished in the FXB filter.

Demonstration testing showed that a submerged membrane bioreactor (SMBR) can meet several post-FXB treatment objectives in a single step: 1) aeration, 2) biomass separation, 3) residual organic carbon removal, and 4) hydrogen sulfide removal.

The FBR did not achieve perchlorate removal to below detection over a period greater than 8 days, in spite of numerous mechanical and operational adjustments made to the system. However, testing did demonstrate that biological perchlorate removal can be achieved using indigenous microorganisms, a feature that had not yet been demonstrated for the FBR system. Because the FBR was not optimized, challenge testing was not performed.

Disinfection by-product formation potential (DBPFP) tests were performed using effluent from the FXB, FBR, and SMBR reactors. After 7 days of incubation with an excess chlorine residual, DBPs were formed in all three streams, though only the FBR stream produced DBPs exceeding the current MCLs of 80 μg/L total trihalomethanes (TTHMs) and 60 μg/L HAA5s. It should be noted that the FBR was not optimized prior to the DBPFP tests. Because the FBR feed acetic acid concentrations were higher than ultimately required, the FBR DBPFP tests are considered conservative. DBPs formed in all three streams consisted primarily of haloacetic acids (HAAs). Seven-day incubation of process effluents with combined chlorine produced only low levels of THMs and HAAs. A follow-up 72-hour simulated distribution system (SDS) DBP formation test was conducted on the FBR effluent. The SDS-THM4 and SDS-HAA5 concentrations were 40 μg/L and 23 μg/L, respectively.

To simulate DBP formation potential of FXB effluent that is post-treated at the Rio Vista Water Treatment Plant (WTP), a blend of 90 percent State Project Water (SPW) and 10 percent FXB effluent was ozonated and contacted with free or combined chlorine. Bromate was formed at concentrations ranging from 1.8 to 8.7 μg/L due to high bromide concentrations (200 μg/L) in the blended water. Aldehydes were formed at moderate levels, even in one sample that was spiked with 7.5 mg/L of acetic acid carbon prior to ozonation. High levels of THMs and HAAs were measured in the ozonated samples following a 7-day incubation with free chlorine. However, residual chlorine concentrations were excessive during incubation and, more importantly, a large fraction of DBP precursors would likely be removed downstream of ozonation, prior to chlorination at the Rio Vista WTP. Seven-day incubation of ozonated water with combined chlorine generated only 23 μg/L TTHM4 and 12 μg/L HAA5.

2.0 INTRODUCTION

2.1 Overview

Castaic Lake Water Agency (CLWA) retained Carollo Engineers (Carollo) to screen available perchlorate treatment alternatives applicable to Saugus Aquifer water, test the most promising alternatives, and select a process train for predesign to treat perchlorate-impacted wells.

Carollo identified the following processes as potential treatment approaches for perchlorate:

- Conventional regenerable IX.
- "Throw-away" perchlorate selective IX.
- FBR biological filtration.
- FXB biological filtration.
- High-pressure membrane separation.

A desktop study was conducted to narrow the treatment alternatives. The benefits and issues related to each one of these approaches were presented at a workshop held at CLWA on February 3, 2003. During the workshop, participants from CLWA, member agencies (Newhall County Water District (NCWD), Valencia Water Company, and Santa Clarita Water Company), Carollo, and Kennedy/Jenks performed a process selection based on the following criteria:

- Effectiveness in treating other potential contaminants such as NDMA, HMX, RDX, TNT, etc.
- DHS approval (fast track implementation).
- O&M costs.
- Capital costs.
- Architectural, siting, and permitting issues.
- Robustness of the process.
- TDS and hardness removal ability.

Workshop participants performed a pair-wise comparison analysis to weight the relative importance of each criterion, and assigned criteria scores to each process. The following alternatives were recommended by the participants for bench and/or pilot testing.

- "Throw-away" perchlorate selective IX.
- FBR biological filtration.
- FXB biological filtration.

These alternatives were selected because they can treat perchlorate with minimal production of perchlorate-laden liquid waste or brine that needs to be discharged.

2.2 Project Objectives

The overall goal of bench and pilot testing at the CLWA was to develop design parameters for a treatment facility that is capable of removing perchlorate to below the action level (AL) at affected Santa Clarita Valley wells. The AL in the State of California is currently 4 µg/L. The method detection limit (MDL) used by the CLWA lab was 1 to 4 μg/L and the minimum reporting limit (MRL) for the standard analytical method (EPA 314.0) is currently 4 μg/L.

The specific objectives of this work were to:

1. Compare the perchlorate removal performance of three commercially available and NSF certified perchlorate-selective IX resins using water from the Saugus Aquifer under identical operational conditions by running a parallel bench-scale flow-through column test.
2. Determine the NDMA formation potential of the three IX resins when subject to pre- or post-chlorination at the bench-scale.
3. Determine characteristics of the spent IX resins.
4. Demonstrate the efficacy of FBR and FXB treatment for perchlorate removal from Saugus aquifer water (i.e., show consistent removal of perchlorate to below the MRL of 4 µg/L).
5. Verify that sufficient perchlorate-reducing biological activity can be developed in the pilot-scale reactors using microorganisms indigenous to the Saugus Aquifer.
6. Using pilot-scale FBRs and FXBs, develop full-scale design criteria for empty-bed contact time (EBCT), backwashing procedures, electron donor (acetic acid) addition, and nutrient addition.
7. Evaluate the robustness of the fluidized- and FXB biological process with respect to system upsets, such as electron donor feed failure, process shutdowns, and changes in the feedwater oxidant concentrations.

8. Compare overall process performance between a FXB and FBR configuration.

9. Demonstrate the efficacy and robustness of the FBR's on-line perchlorate analyzer in comparison to other laboratories.

10. Prepare planning-level capital and O&M cost analyses for biological- and IX-based treatment facilities to be incorporated in the pre-design report.

11. Determine post-treatment requirements for the IX, FBR, and FXB perchlorate removal processes (i.e., characterize process effluent quality and disinfection by-product formation potential).

3.0 BACKGROUND AND TEST SITING

3.1 Test Approach and Siting

The preliminary test program included two main testing protocols:

- Bench-scale IX testing using three perchlorate selective resins.
- Pilot-scale biological testing using two system configurations.

The perchlorate selective resins have a high capacity for perchlorate adsorption and depending on the influent perchlorate and sulfate concentrations, may experience extensive run-times to reach perchlorate breakthrough (i.e., perchlorate > 4 µg/L). To simplify testing logistics, IX testing was conducted at the bench-scale. The test was carried out in the chemical building at the Rio Vista WTP. This site also served as the pilot-scale testing site. Bench-sale IX data are readily scaleable. Factors considered in scaling-up the bench test are water quality, bed volumes until perchlorate breakthrough, EBCT, and separation factors specific to the selected resin. The controlling factor of the contaminants' diffusion into the resin matrix is the selectivity of the resin's positively charged quaternary amine functional group for a specific anion relative to the chloride anion. The order of elution of ions from the resin is determined solely by the selectivity sequence. The species exit the column in reverse preferential order, with the less preferred ions (smallest separation factors) emerging first. Other factors include charge of ion, valence of ion (mono- or divalent), and other resin-specific physical factors.

While the effectiveness of treating perchlorate using biological processes has been demonstrated extensively at the bench-scale, the scalability of these processes is not well established. This project evaluated the removal of perchlorate from Saugus Aquifer water using two pilot-scale biological system configurations (FXB and FBR).

3.2 Feed Water

Perchlorate-contaminated wells were not used for testing due to the complications and costs associated with the discharge requirements and the need for an extensive analysis of influent and effluent waters. Instead, a perchlorate-free operational well (NC-12) located near one of the perchlorate contaminated wells (NC-11) was used as feed water for both bench- and pilot-scale systems. Perchlorate was spiked to achieve a final target concentration of 50 µg/L for most of the study. NC-11 and NC-12 draw water from the Saugus Aquifer and have comparable raw water quality (chemistry). Sulfate was spiked to the feed of the ion-exchange unit to achieve a final target concentration of 300 mg/L. This mimics the highest average sulfate concentration measured in Saugus wells. Sulfate is a critical parameter in the ion-exchange process since it competes with the perchlorate ion. NC-11 and NC-12 were sampled and characterized in February and March 2003, respectively (Table 3.1). NC-12 well water was transferred to four 6,500-gallon storage tanks located outside the chemical building at the Rio Vista WTP via a 6,000-gallon stainless steel tanker truck which was filled at the well site and transferred to the pilot site. The tanker used for transferring the raw feed water was washed with hot water or a caustic solution and then rinsed prior to use, to ensure no impact on the raw water quality. The water stored in the baker tanks at the site was delivered to the test equipment via Schedule 80 PVC. To maintain a consistent water temperature, feed flows were routed through an ITT Standard heat exchanger, Model SX200. The water was used at a rate varying from 2,900 to 5,800 gallons per day (2 to 4 gpm).

Table 3.1 Water Quality Parameters in the Groundwater at Newhall 11 and 12 Wells
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Units	NC-12 (March 2003)	NC-11 (Feb 2003)	NC-11 (Historic)
Perchlorate	µg/L	ND$^{(1)}$	17-20	13-23
Nitrate-NO_3^-	mg/L	14.6	18-20	14-30
Sulfate	mg/L	131	309-330	255-443
Bicarbonate	mg/L	199	220	232-235
Chloride	mg/L	38	28	29-38
Alkalinity	mg/L as $CaCO_3$	163	180	182-280
pH	–	7.5	7.4	7.5-7.7
Conductivity	µhom/cm	846	1,120-1,138	980-1,116
Temperature	degrees C	19	16	
Uranium	pCi/L	0.679	2.887-4.368	NA

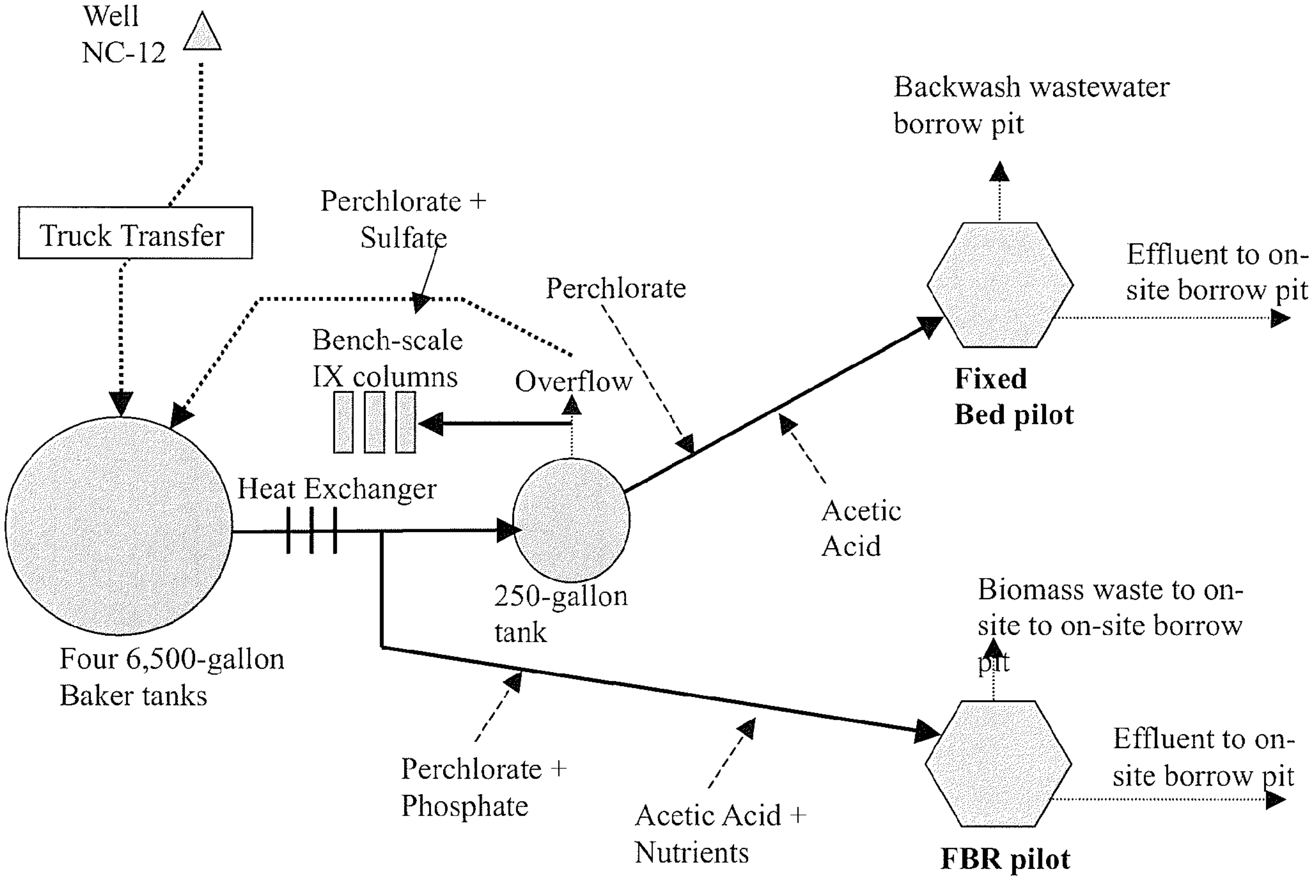
Table 3.1 Water Quality Parameters in the Groundwater at Newhall 11 and 12 Wells
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Units	NC-12 (March 2003)	NC-11 (Feb 2003)	NC-11 (Historic)
Arsenic	µg/L	1.3	<1.0-1.0	<2.0-2.0
TOC(2)	mg/L	<0.7	2.0(3)	N/A(4)

Notes:
(1) Not detected.
(2) Total Organic Carbon.
(3) After approximately three hours of flushing.
(4) Not available.

A process flow schematic for bench- and pilot-testing is provided in Figure 3.1. The water was pumped from the four 6,500-gal tanks to a 250-gallon tank inside the building. The flow was then split two ways into the FXB and the FBR pilots. Schedule 80 PVC was used to hard pipe the baker tank to the feed pump of each biological pilot skid. Perchlorate stock solution was prepared as necessary by spiking reagent grade sodium perchlorate (Fischer Scientific, Hanover Park, Illinois) to 1 liter of deionized, distilled water from the CLWA laboratory. Peristaltic pumps (Ismatec, Northbrook, Illinois) dosed the perchlorate stock solution near the front end of each pilot feed line for adequate mixing. Perchlorate was dosed independently to each pilot skid to maintain flexibility in the pilot testing protocol. For example, using this configuration, perchlorate spiking tests were applied to one pilot without having to be applied to the other. Technical-grade acetic acid (Eastman Chemical Company, Kingsport, Tennessee) was used as the stock electron donor solution and dosed to the pilot feed lines just before entry to the biological reactors using a peristaltic pump. This acetic acid is undergoing ANSI/NSF 60 certification, which should be completed by the mid-2004. ANSI/NSF 60 - certified, food-grade phosphoric acid (Prayon, Inc., Augusta, Georgia) was also dosed to the pilot feed lines using peristaltic pumps. For the FBR system, a micronutrient mixture was added to the phosphoric acid solution for selected tests. The micronutrient mixture contained trace amounts of iron, copper, magnesium, manganese, zinc, boron, sulfur, molybdenum, and cobalt. The main PVC feed pipes were fitted with a static mixer downstream of the chemical injection points.

For the bench-scale IX tests, water was collected from the pilot feed tank in two 55-gallon tanks (approximately 1 week's supply). The tanks were filled from the overflow line of the 250-gallon tank. A 1,000-mg/L perchlorate stock solution was prepared by adding reagent-grade sodium perchlorate salt to distilled deionized water obtained from the CLWA laboratory. This solution was spiked directly into the containers to result in a final concentration of 50 µg/L. Additional sulfate was also added to the containers by dissolving reagent sodium sulfate (Na_2SO_4) in distilled-deionized water to reach a final sulfate concentration of 300 mg/L.



PROCESS FLOW SCHEMATIC FOR BENCH- AND PILOT-SCALE TESTING

FIGURE 3.1

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CASTAIC LAKE WATER AGENCY

3.3 Discharge Streams

All process effluents (i.e., bench-scale effluent, pilot-scale effluents, and backwash wastewater) were pumped to a borrow pit on the Rio Vista plant site. The discharge waters were first directed to off-site GAC drums to remove any residual perchlorate prior to ultimate disposal in the borrow pit. The backwash water from the pilot-scale systems was first directed to a 100-gallon drum to allow for settling, and the decant wastewater was then directed to the feed of the GAC drums. The effluent stream from the GAC drums was analyzed for perchlorate once per week. Additional tanks with approximately 300 pounds of Virgin GAC were installed before the discharge point to treat any perchlorate that may be present in the effluents. If perchlorate was detected in the GAC effluent, the spent GAC was removed and replaced with virgin GAC. The borrow pit has no surface discharge and allows negligible percolation due to the presence of a heavy clay soil lining. There was no discharge to the sewer system or Santa Clara River. Spent resins were sent to a certified laboratory for further characterization and disposal.

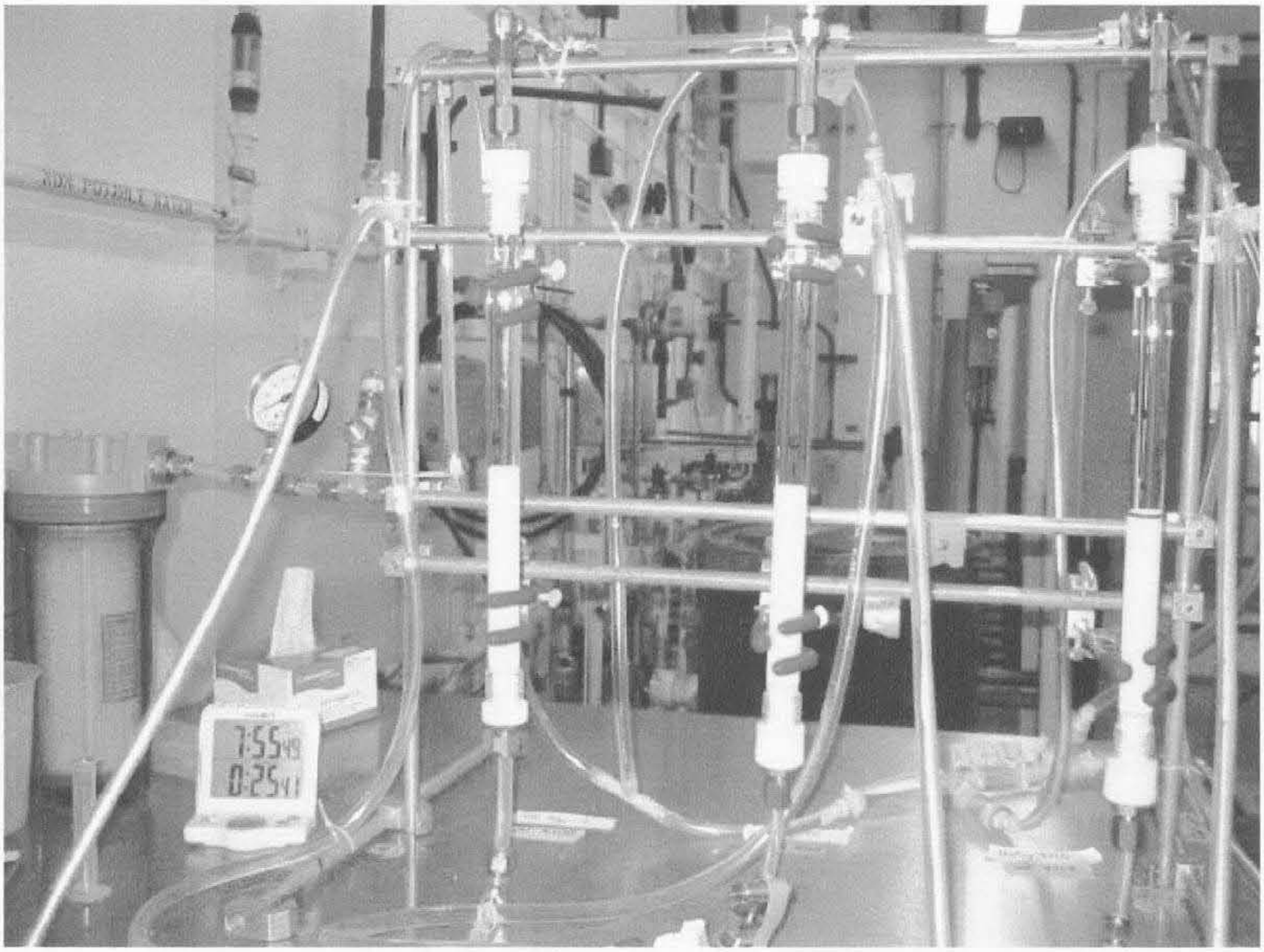
4.0 EQUIPMENT DESCRIPTION AND CAPABILITIES

4.1 Ion Exchange

4.1.1 Bench-Scale Flow-Through Column Testing Unit

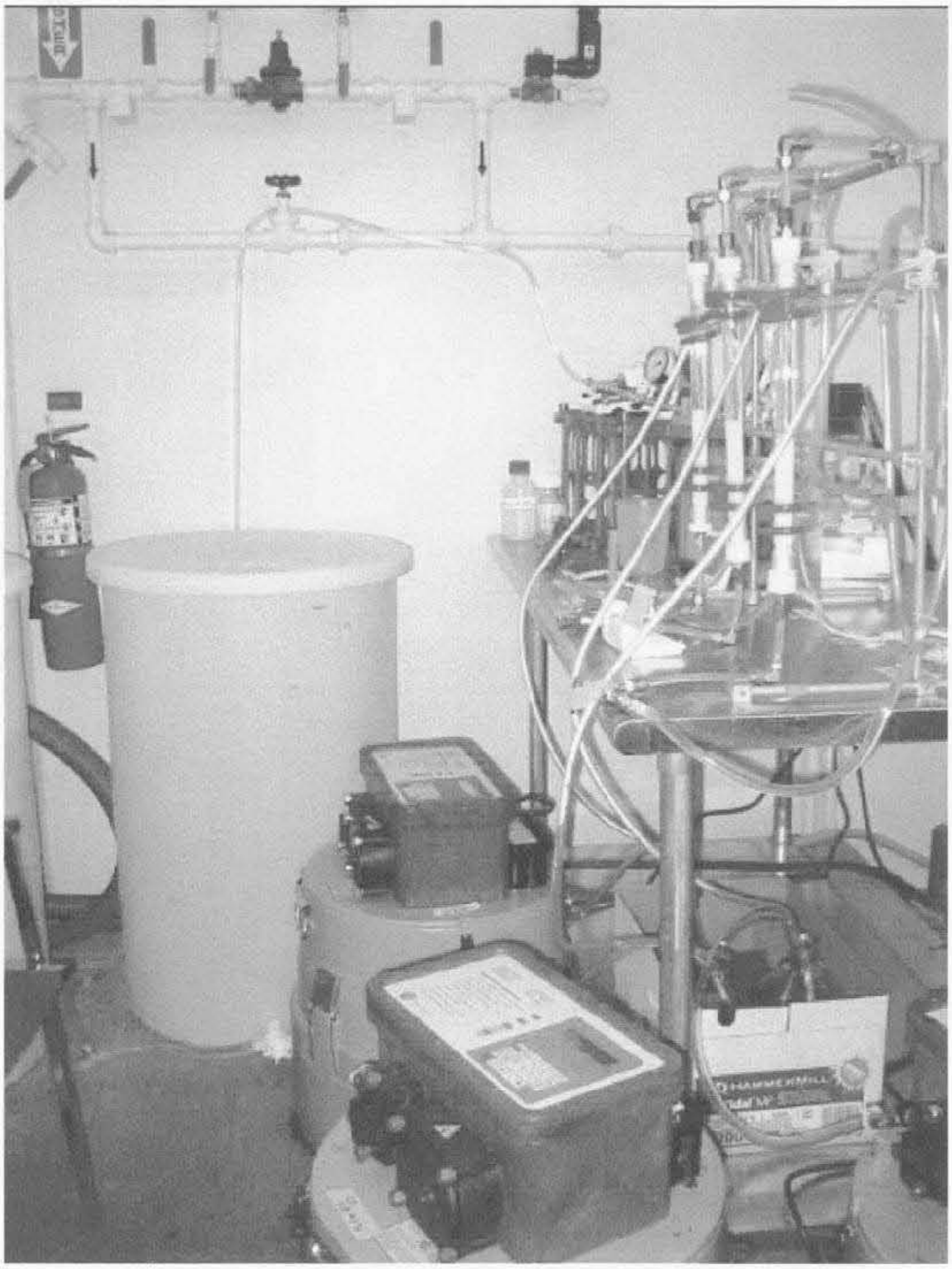
A bench-scale flow-through column apparatus was used to evaluate the removal of perchlorate and other anions by IX (Figures 3.2 and 3.2(a)). This equipment was used to determine performance and cost data for three commercially-available perchlorate-selective, IX resins.

Three glass columns were set up to run in parallel, each with a different resin. The columns are 15 mm in diameter, 30 cm in length, and were filled to a depth of 12.7 cm with resin media (22.5 mL of resin). The media was supported with stainless steel screens. Each column was first half-filled with distilled water. Resin was then added from the top and allowed to settle to the bottom of the column. Resin was added until the settled resin level reached the 12.7-cm mark. Resin was added with excess water in the column to prevent the formation of air-gaps in the packed resin. Once the full amount of resin was added, the column was filled with distilled water. An in-line pre-filter (9.824-inch Osmonics Flotrex-GF pleated 3.0 μm absolute Model FGF031AAS) was installed after the feed pump to remove suspended material from the feed water. To monitor headloss, pressure gauges were installed upstream and downstream of the filter housing unit, and pressure relief valves were used to prevent pressure build-up. A three-way valve was also installed in the effluent line to provide a location for manual sampling.



BENCH-SCALE FLOW-THROUGH ION EXCHANGE EQUIPMENT

FIGURE 3.2



BENCH-SCALE COLUMN SETUP AND AUTOSAMPLERS

FIGURE 3.2(a)

The columns were set up to run in parallel such that perchlorate spiked water was delivered from the two 55-gallon storage tanks to the head of the columns using an LMI model QG 400 piston lab pump. Flow-rates from each column were measured using a stopwatch and a 5-mL graduated cylinder. Volumetric measurements were taken on a daily basis. The flow was adjusted as necessary using a needle valve located at the effluent of each column. Timed effluent water samples were collected by autosamplers (leased from ISCO, Lincoln, Nebraska) during the first week of testing. The autosamplers were used to collect a one-hour composite batch from each column over a period of 24 hours. This process was repeated over the entire first week. The sampling intervals were determined from modeling results provided by the resin suppliers and/or generated by IX Pro Software using the Saugus water quality and separation factors associated with a perchlorate-selective resin as inputs.

4.1.2 Resins

There are several commercial resin manufacturers/suppliers. Based on the raw water quality in the Saugus Aquifer (i.e., perchlorate, sulfate, nitrate, TDS) and the lack of a dedicated line for disposing spent brine produced from conventional ion-exchange systems, perchlorate-selective, throw-away ion-exchange resins were selected for further evaluation using bench-scale testing. The following three resins were tested in parallel based on the availability for use in packaged systems, vendor recommendations and applicability to treating Saugus groundwater based on modeling results:

- US Filter K-9710 (US Filter Corporation, Rockford, Illinois): USF K-9710 is a strong base quarternary amine macroporous anion resin consisting of a styrene divinylbenzene matrix. The resin was tested at the Edwards Air Force Base. This resin, which received on NSF-61 certification in July 2003, can be supplied directly through a system manufacturer (e.g., US Filter, Calgon Carbon). A full-scale system using this resin is operational in the City of Rialto, California. The resin has a unique dual functionality exhibiting very high selectivity for oxy anions, such as perchlorate and pertechnate, that allows for efficient removal in a relatively high TDS background. US Filter recommends the use of this resin for single pass applications.

- Calgon Carbon Cal Resin 2 Resin 2100 Series (Calgon Carbon Corporation, Pittsburgh, Pennsylvania): This resin consists of a trimethylamine functionalized, chloromethylated copolymer of styrene and divinylbenzene in the chloride form. DHS approved packaged treatment systems are located at the City of Riverside and at California Domestic Water Company. Cal 2100 Series resins are NSF certified (NSF/ANSI Standard 61) through WQA.

- US Filter K-9708 resin (US Filter Corporation, Rockford, Illinois): USF K-9708 is a strong base quarternary amine macroporous anion resin consisting of a styrene divinylbenzene matrix. The resin has a special functionality which exhibits high selectivity for perchlorates and nitrates over sulfates. This selectivity allows the resin to remove perchlorates and nitrates preferentially over sulfates with no potential for perchlorate or nitrate dumping. The resin is initially in the chloride form. USF K-9708 is an NSF-certified resin.

4.1.3 Autosamplers

During the first week of testing, sample collection from each column was automated using 3700 Portable Isco autosamplers (Isco, Inc., Lincoln, NE). Effluent samples were drawn every hour from 2-L glass Erlenmeyer flasks into the custom-fit polypropylene bottles located within the autosampler. Selected samples were stored at 4 degrees C in amber glass bottles until they were analyzed by CLWA or MWH laboratories. Samples were preserved by laboratory personnel with the exception of TOC/DOC samples for which 8 drops of 50 percent HCl were added on site to reduce the pH to less than 2.

During the remainder of the weeks, samples were manually collected by allowing the effluent to flow directly into the sampling bottles using three-way valves.

4.1.4 NDMA Formation Potential Testing

Bench-scale NDMA formation potential tests were conducted during the later phases of the ion-exchange testing. Post-chlorination testing with free and combined chlorine was conducted on each column effluent, as well as pre-chlorination testing with free chlorine. In addition, resin leaching testing in groundwater and DI water without the addition of chlorine was conducted for baseline comparison.

4.1.4.1 Post-Chlorination Testing with Free Chlorine

A 2,000 mg/L free chlorine stock solution was prepared from a 17,000 mg/L hypochlorite solution provided by CLWA. Two 1-L samples were collected from each column effluent. A 1-mL volume of chlorine stock solution was added to each of the bottles, resulting in a 2 mg/L free chlorine dose. The bottles were incubated for 24 hours in the dark under ambient room temperature. Free chlorine residuals were measured after 2 hours of incubation and after 24 hours of incubation. Samples were sent to MWH Laboratories for NDMA analysis. All chlorine stock solutions, doses, and residuals were measured on-site using a Hach DPD field test kit.

4.1.4.2 Post-Chlorination Testing with Chloramines

An ammonium chloride stock solution was prepared by dissolving 1.9 g of reagent-grade anhydrous NH_4Cl (also provided by CLWA laboratory) in 500 mL water. A chlorine:ammonia-N ratio of 4.0 on a weight basis was used (i.e., 2 mg/L chlorine and 0.5 mg/L ammonia-nitrogen) and 2-hour and 24-hour incubation periods were used as described above. Free and total chlorine residuals were measured in the bottles at the end of the incubation period. Bottles were sent to MWH Laboratories for NDMA analysis.

4.1.4.3 Pre-Chlorination Testing with Free Chlorine

Toward the end of the study, a 2 mg/L free chlorine dose was added to the 55-gallon drum, which fed the IX columns. Two samples were collected over a 4-day time period from each column effluent for NDMA analysis. Free chlorine residuals were measured in the bottles.

4.1.4.4 Fresh Resin Batch Testing

To evaluate the leaching potential of fresh resin, approximately 100 mL of fresh resin was added to 1 L of DI water and 1 L of feed groundwater. Bottles were allowed to incubate for a period of 4 hours. Samples were shipped to MWH Laboratories for NDMA analysis.

4.1.5 Spent Resin Characterization

TTLC and Soluble Threshold Limit Concentration (STLC) are used when determining the hazardous waste characterization of a substance under California State regulations as outlined in Title 26 of the California Code of Regulations (CCR). The three spent resins were shipped to MWH Laboratories (TTLC analyses were subcontracted to Columbia Labs in Canoga Park, California) for the following characterizations:

- <u>TTLC Analysis for CAM 17 Metals (in California)</u>: This analysis determines the total concentration of each target analyte in a sample. Resin samples were homogenized and 5 grams of each sample were digested and analyzed for the TTLC metals according to standardized EPA methods (EPA Methods 6020 for most metals, 6010B for cooper, lead, and zinc, and 7471A for mercury). When any target analyte exceeds the TTLC limits (Table 3.19 in the Results Section), the waste is classified as hazardous and its waste code is determined by the compound(s) that failed TTLC. The results of this analysis can be used to determine if analysis for STLC level is necessary by comparing 10 times the STLC limit to the TTLC results. A factor of ten is necessary to compensate for a 1:10 dilution factor that is present in one analysis but not the other. If the TTLC results do not exceed 10 times the STLC limit, then normally no further STLC analysis is required.

- <u>STLC Analysis for Perchlorate, Nitrate, and Uranium</u>: This analysis determines the amount of each analyte that is soluble in the "Waste Extraction Test" (WET) leachate. This WET leachate procedure is used for solid samples or for samples containing more than 0.5 percent solids. The sample is tumbled in 10 times its weight of a 0.2 M sodium citrate buffer for 48 hours.

- Approximately 100 mL of STLC extract was obtained from each resin sample. These extracts were returned to MWH Labs for analysis of perchlorate, nitrate, and radioactive uranium.

4.2 Biological Fixed-Bed Filter

4.2.1 Pilot Skid

A photo of the FXB granular media filtration skid is provided in Figure 3.3. Important process components are identified.

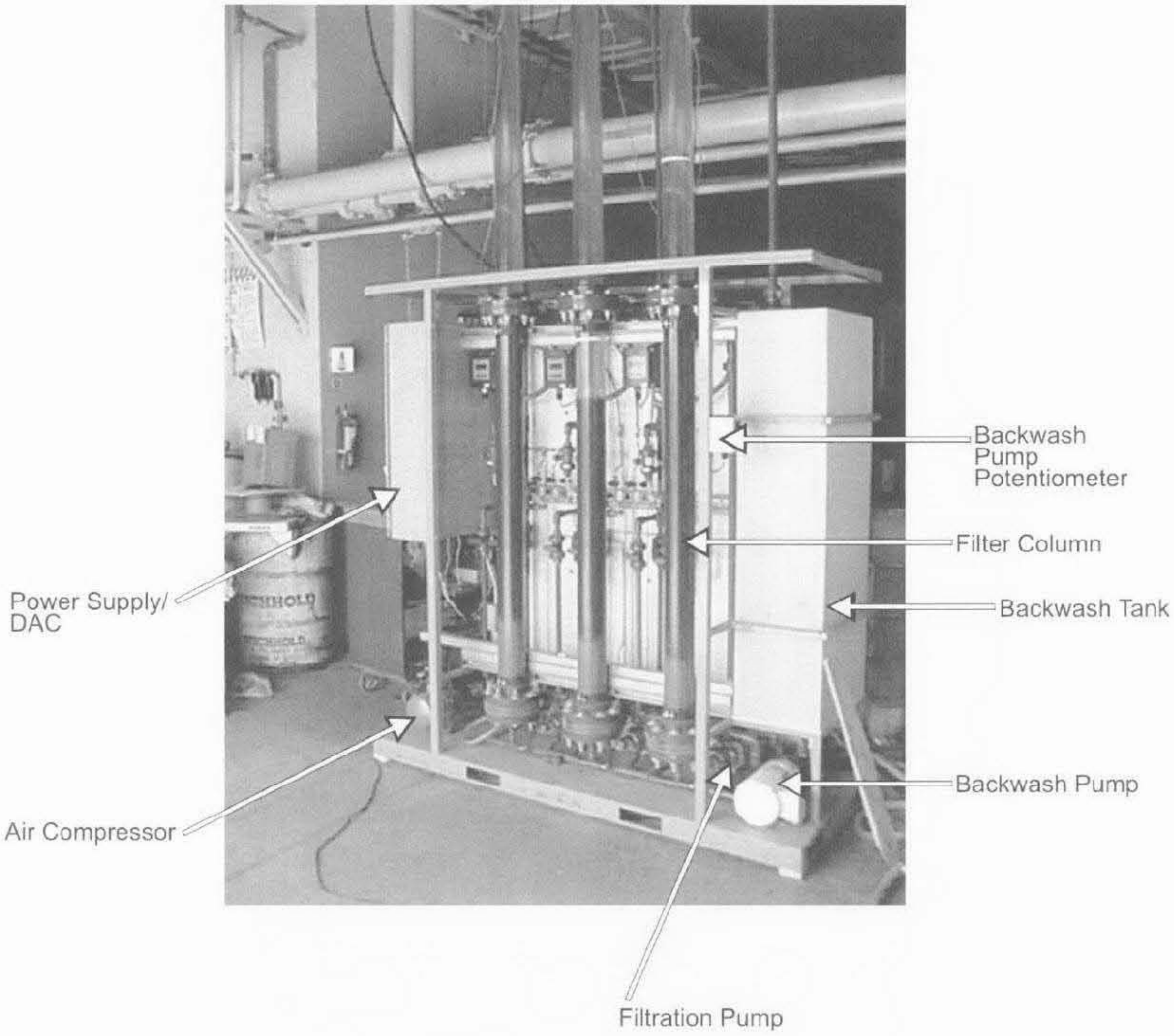
Design criteria and technical specifications for the FXB biological filtration skid are provided in Tables 3.2 and 3.3, respectively.

Table 3.2 Fixed-Bed Filter Design Criteria
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Value/Description
Filter dimensions	4" diameter, 14' tall
Number of filters per skid	3
Number of independent feed pumps	3
Maximum flow per filter	1.5 gpm
Hydraulic loading rate	2-17 gpm/ft^2
Media support mechanism	Retention plate
Backwash type	Air and/or water
Air supply	On-board compressor (with 5 μm filter)
Backwash water tank volume	20 gallons
Parameters measured by in-line meters	Flow Effluent turbidity Effluent particle counts Headloss across the filters

Table 3.3 Fixed-Bed Filter Technical Specifications
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Value/Description
Skid weight	750 lbs
Skid dimensions (LxWxH)	6'6"x2'6"x14'
Electrical requirements	3-phase, 30A, 208-Volt, AC power (Y connection)
Influent, effluent, overflow connections	1" Cam Lock



FIXED-BED BIOLOGICAL FILTRATION PILOT PLANT

FIGURE 3.3

A schematic of the FXB pilot is shown in Figure 3.4. The FXB skid is configured for down-flow operation. Initially, all three columns on the skid were utilized for pilot testing.

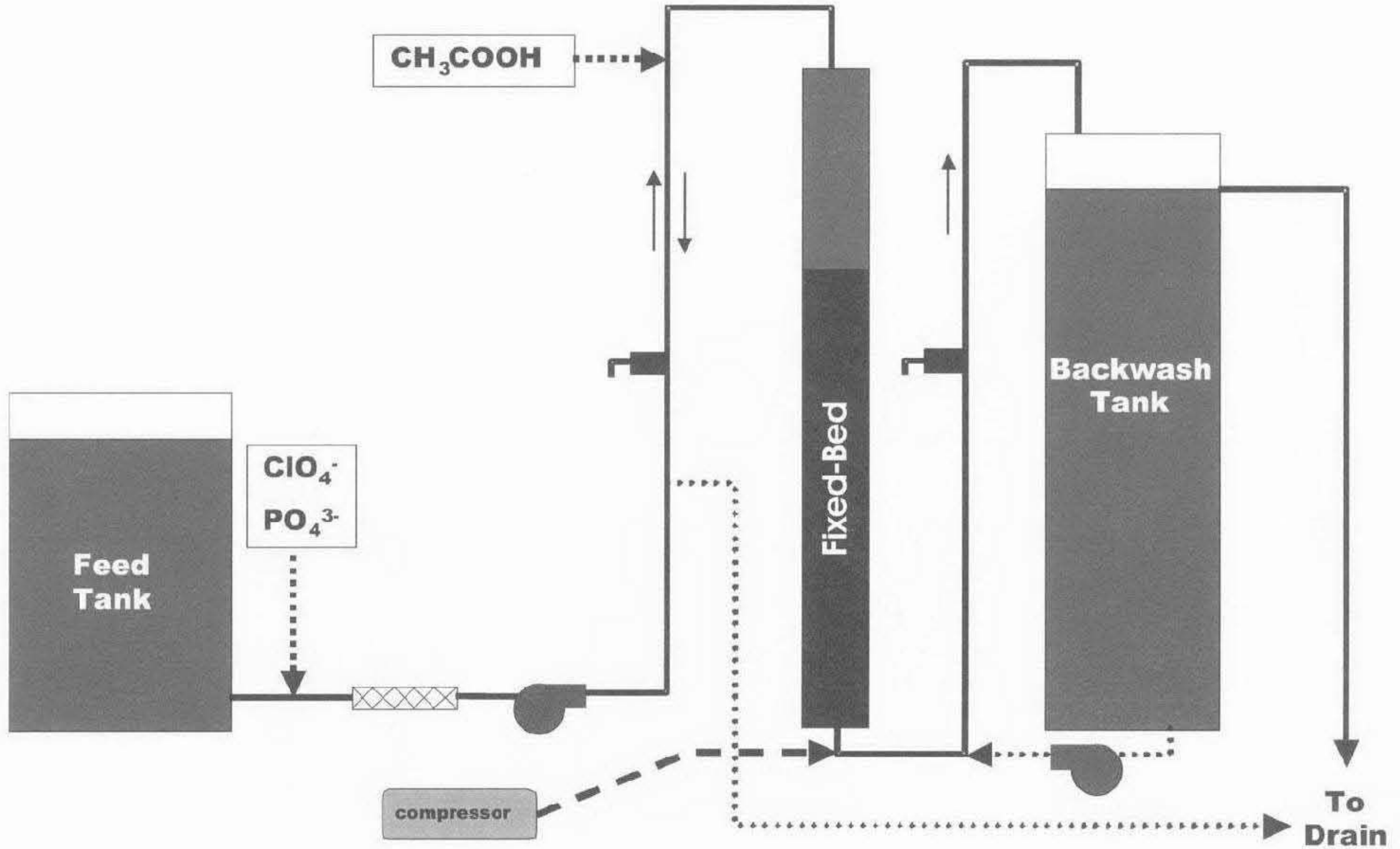
However, because sampling and other daily pilot tasks required for three columns were too onerous for a single operator, two of the columns were shut down one month into the piloting period. Stock perchlorate and (temporarily) phosphate solutions were added upstream of an in-line static mixer using an Ismatec ISM 832B two-channel eight-roller peristaltic pump together with Pharmed 0.020-inch ID peristaltic pump tubing. A second head was added to the peristaltic pump to add acetic acid to the system. Initially, acetic acid was also added at the same location as the perchlorate stock solution. However, excessive growth in the feed lines prompted a relocation of the acetic acid feed to the top of the column one month into the piloting period. Filter effluent turbidity and particle counts were monitored continuously by dedicated turbidimeters and particle counters. A pressure transducer mounted on the pilot skid monitored head loss development across the filter; backwashes, which could include air scour, were initiated manually. The pilot skid is equipped with a data acquisition and control (DAC) system, which stores and manages data. For each filter column, the DAC continuously logs date/time, flow, headloss, effluent turbidity, and effluent particle counts. The skid includes a touch screen interface to monitor and control pilot operations.

4.2.2 Media

The columns were filled to a depth of 7 feet (approximately 0.6 ft^3) with virgin Calgon F-400 granular activated carbon (GAC). This allowed for bed expansion up to 50 percent. F-400 is a bituminous-based carbon commonly used in the United States. The GAC was stored overnight in 5-gallon buckets to wet the surface and internal pores. The filter columns were filled with NC-12 well water and the GAC was dosed slowly into the columns until the 7-foot depth was reached. Once the columns were packed with GAC, they were backwashed for a period of 24 hours at a 45 percent bed expansion to remove carbon fines from the GAC bed.

4.2.3 Stock Solutions

For the biological pilot systems, an intermediate stock perchlorate solution of 136.17 g/L ClO_4^- was made using reagent grade sodium perchlorate salt and distilled deionized water. Individual stock solutions were made as necessary in 2-L glass bottles using the intermediate stock solution. During periods where phosphorus was added to the feed stream, 75 percent pure food-grade phosphoric acid was added directly to the perchlorate stock solution. For the acetic acid stock solutions, technical-grade acetic acid (Eastman Chemical Company, Kingsport, Tennessee) was used. Stock solutions were stored in 2-L glass bottles that were flame sterilized using ethanol.



FIXED-BED BIOLOGICAL FILTRATION PILOT SCHEMATIC (NOT TO SCALE)

FIGURE 3.4

4.3 Biological Fluidized-Bed Reactor

4.3.1 Pilot Skid

The basic components of the pilot FBR system included the bioreactor, bed height control component (when required), biomass separator, a fluid distribution system at the bottom of the reactor, a feed pump, and chemical feed systems (Figure 3.5). The bed of GAC media is hydraulically fluidized to reduce its resistance to flow and to improve substrate/biomass contact by directing liquid flow upward into the bed. The fluidization rate is controlled to maintain a 25 to 30 percent bed expansion over the resting bed height. Feed flow is supplemented with recycle flow to provide the appropriate up-flow velocity for fluidization. When biofilm growth occurs on the GAC media, the particle diameter increases and the effective density of the particle decreases, which causes further expansion of the bed. It is necessary to manage film thickness to control or prevent bed carryover. In full-scale FBR systems, bed height is managed in the top portion of the bed by mechanically shearing the biomass from the GAC through a valve. The "cleaned" GAC particles settle back into the bed, ready to support more biofilm growth, and the sloughed biomass is discharged. In the pilot test unit, mechanical mixing or pump shear was used to perform this task.

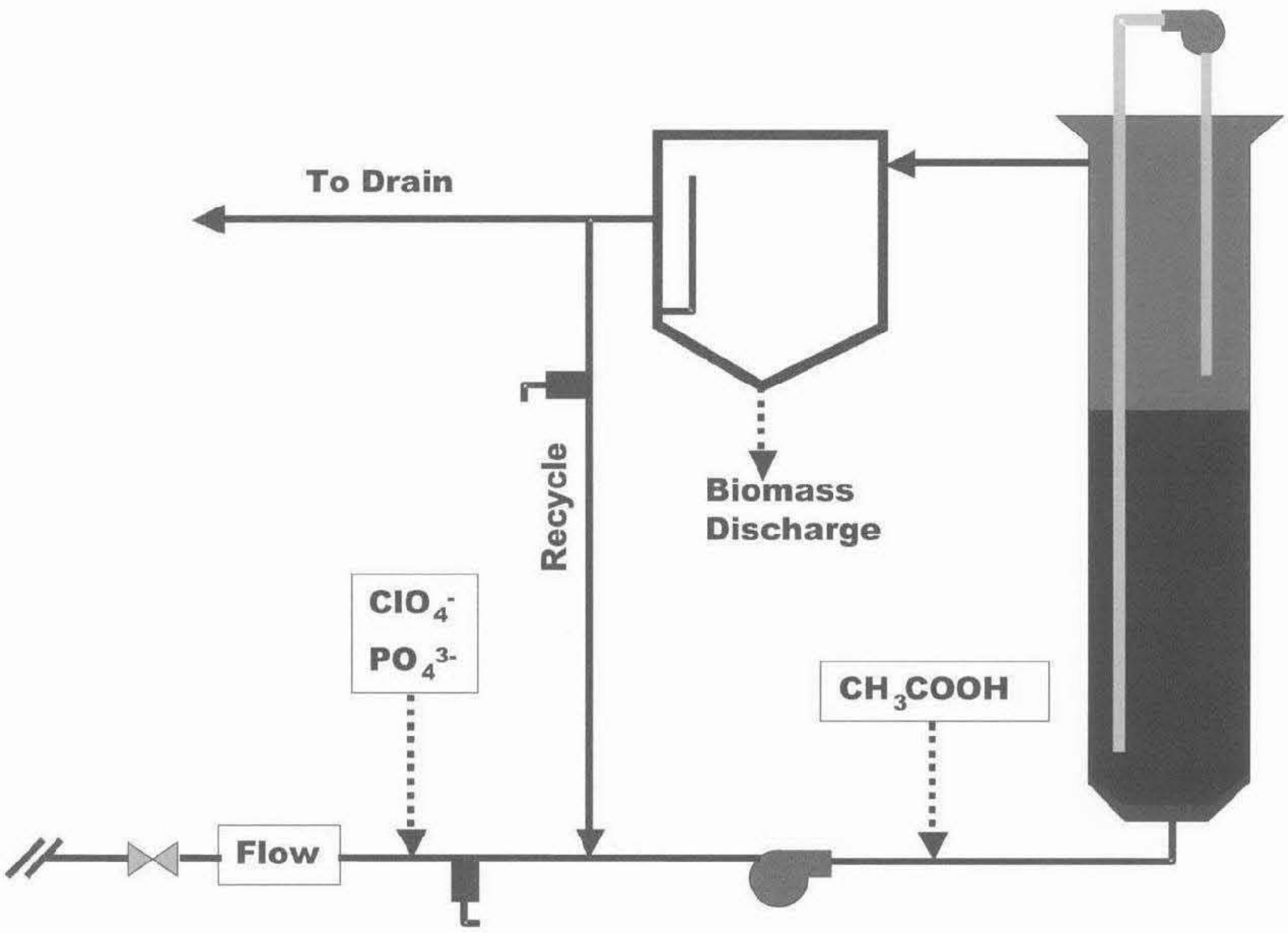
Perchlorate and phosphorous stock solutions were added directly to the feed line upstream of the recycle line connection using a diaphragm metering pump. A second diaphragm metering pump was used to add acetic acid stock solution to the feed line. Initially, the acetic acid was injected just prior to the feed pump, but was later moved closer to the bioreactor to minimize biofouling in the feed lines.

4.3.2 Media

The FBR bioreactor uses a proprietary coconut shell based carbon that meets Shaw Environmental-Envirogen specifications for hardness, apparent density, effective size, iodine number, and uniformity coefficient.

4.3.3 Stock Solutions

For the biological pilot systems, an intermediate stock perchlorate solution of 136.17 g/L ClO_4^- was made using reagent grade sodium perchlorate salt and distilled deionized water. Individual stock solutions were made as necessary in 2-L glass bottles using the intermediate stock solution. Food-grade phosphoric acid (Prayon, Inc., Augusta, Georgia) was added directly to the perchlorate stock solution. Acetic acid stock solutions were prepared using technical-grade acetic acid (Eastman Chemical Company, Kingsport, Tennessee) and were stored in a 10-L polypropylene carboy. Before stock solutions were prepared, these carboys were rinsed with rubbing alcohol for sterilization. For selected tests, a micronutrient mixture (GrowMore, Gardena, California) was added directly to the acetic acid stock solution. The micronutrient mixture contained trace amounts of iron, copper, magnesium, manganese, zinc, boron, sulfur, molybdenum, and cobalt.



FLUIDIZED-BED BIOLOGICAL FILTRATION PROCESS SCHEMATIC (NOT TO SCALE)

FIGURE 3.5

4.4 Submerged Membrane Bioreactor

4.4.1 Objectives

Zenon Zeeweed® membranes, operating in an SMBR configuration, were evaluated as an alternative combined treatment step for post-treatment of effluent from the biological filtration process. The post-treatment process must achieve four treatment goals:

1. Aeration: Since biological perchlorate reduction requires anaerobic conditions, DO must be supplied during the post-treatment process.
2. Residual Organic Carbon Removal: Organic substrate is added to the FXB to achieve perchlorate reduction. Therefore, to prevent regrowth problems and to minimize the formation of DBPs, the effluent water must be stabilized biologically.
3. Sulfide Removal: Under anaerobic conditions, sulfate can be reduced to sulfide, which generates a rotten-egg odor. Therefore, the post-treatment process must be able to remove sulfide, which can be accomplished via biological oxidation or air stripping.
4. Biomass Separation: The post-treatment process must provide a barrier for removal of biological matter (HPC bacteria) that sloughs from the biological filters.

4.4.2 System Description

The ZeeWeed® water treatment process is a proprietary ZENON process technology that involves the production of treated water by drawing water through ZeeWeed® "outside-in" hollow fiber membranes that are immersed in the feed water. The ZeeWeed® ultrafiltration membranes have nominal and absolute pore sizes of 0.04 and 0.10 mm, respectively. The membranes act as a physical barrier that prohibits particulate matter exceeding 0.1 μm in size, including *Giardia* cysts and *Cryptosporidium* oocysts, from entering the treated water supply. The small pore size ensures the removal of a high percentage of impurities, including some viruses (typically 2 to 4.5 log reduction), which are removed by a combination of adsorption onto the solids in the process tank and membrane filtration.

The ZeeWeed® membrane filtration system operates under a low-pressure vacuum that is induced within the hollow membrane fibers by a connection to the inlet (suction) side of a centrifugal permeate pump. The treated water is drawn through the membrane by vacuum, enters the hollow fibers and is pumped out to distribution by the permeate pumps. Airflow is introduced at the bottom of the membrane module to create turbulence that scrubs and cleans the outside of the membrane fibers. This reduces the solids accumulation on the membrane surface, thereby allowing the membrane to operate for extended periods at high permeate fluxes. The air also has the beneficial side effect of oxidizing iron and other organic compounds that may be present. It also provides mixing within the process tank to maintain solids in suspension. The membranes are periodically backwashed which consists of passing permeate through the membranes in the reverse direction to dislodge solids from the membrane surface.

The ZeeWeed® Ultrafiltration system provides a single step process, effectively replacing both the clarification and granular media type (sand) filtration processes found in conventional water treatment plants. The membrane pore size is extremely small and effectively provides a physical barrier to solids present in the water. Therefore, there is no need to create flocculated particles that are large enough to settle in clarifiers or large enough to be captured by granular media filters. Also, as the membranes are immersed directly in the process tank and under only low vacuum, high levels of suspended solids do not foul the membrane.

The ZeeWeed® membranes, operating in an MBR configuration, were considered in this case as an alternative combined treatment step for post-treatment of the effluent from the biological filtration processes. Post-treatment has three main purposes:

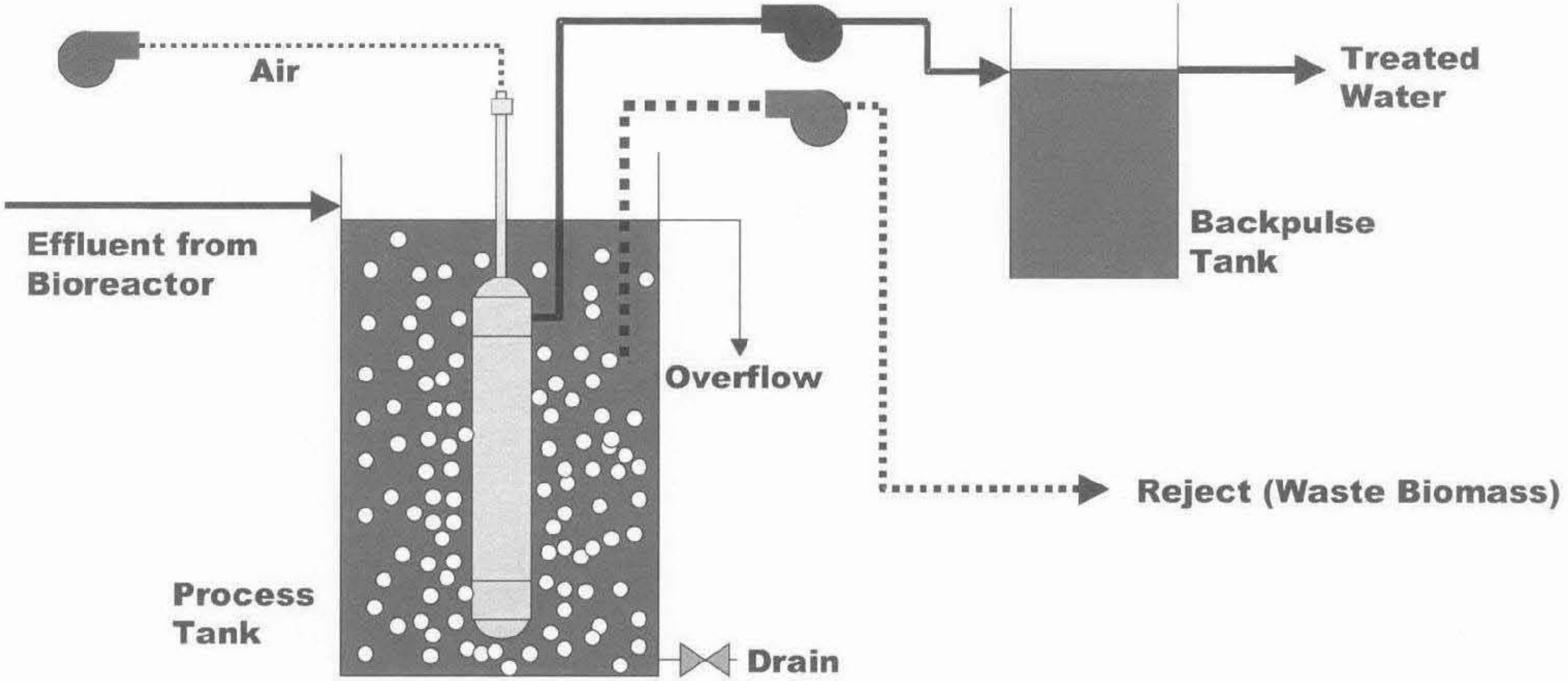
- To provide biological oxidation of excess substrate (acetic acid) fed to the filters;
- To re-oxygenate the water; and
- To provide a barrier for removal of biological matter (HPC bacteria) present in effluent from the biological filters.

A flow schematic for the ZeeWeed®-based post biological FXB filtration process is presented in Figure 3.6.

4.4.3 System Components and Specifications

The unit is equipped with:

- Coagulant Feed Pump and Chemical Tank.
- Cleaning Chemicals.
- Process Tank (hydraulic retention time is 3 to 5 hours).
- Membrane Air Scour Blower.
- Dual head, variable speed, reversible, metering pump for permeate and reject.
- One ZeeWeed®-10 Ultrafiltration Membrane.
- Backpulse Tank.
- Instrumentation and Control Panel.



POST-FXB TREATMENT
MBR SCHEMATIC
(NOT TO SCALE)

FIGURE 3.6

ZW-10 module and system specifications are listed in Tables 3.4 and 3.5, respectively. Table 3.6 lists system operating limits.

Table 3.4 SMBR ZW-10 Module Specifications
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Model	ZW-10, Submersible Module
Configuration	Outside/In Hollow Fiber
Dimensions (length x width x height)	6'x4'x5'
Nominal Membrane Surface Area	0.93 m^2 (10 ft^2)
Absolute Pore Size	0.1 micron
Weight of Module (Drained)	1.9 kg (4.2 lb)
Weight of Module (Wet)	2.1 kg (4.6 lb)
Permeate (Fiber Side) Hold-up Volume	0.13 liters (0.033 gal)

Table 3.5 SMBR ZW-10 System Specifications
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Designation	ZW-10 Bench Test Unit
Electrical service required	115 V, 60 Hz, 2A
Process tank total volume	220 L (58 usg)
Process tank working volume, nominal	190 L (50 usg)
Backpulse tank total volume	20 L (5 usg)
Backpulse tank working volume	15 L (4 usg)
Shipping weight	75 kg (160 lb)
Operating weight	300 kg (660 lb)
Process tank size (with backpulse tank)	75 cm Ø x 160 cm H (30"Ø x 60" H)
Process pump size	40 cm x 15 cm x 15 cm (16" x 6" x 6")
Blower size	40 cm x 25 cm x 25 cm (16" x 10" x 10")
Control panel size	38 cm x 38 cm x 20 cm (15" x 15" x 8")

Table 3.6 SMBR ZW-10 System Operating Limits
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Maximum pump capacity	2 liters/minute (0.53 gpm)
Maximum Transmembrane Pressure	62 kPa (9.0 psig) @ 40°C (104°F)
Typical Operating TMP	10-50 kPa (1.0-7.0 psi) @ 40°C (104°F)
Maximum Operating Temperature	40°C (104°F)
Operating pH range	5-9
Maximum Cleaning Temperature	40°C (104°F)
Cleaning pH Range	2-10.5
Maximum OCl^- Exposure(1)	1,000 mg/L
Maximum TMP Back Wash Pressure	55 kPa (8.0 psi)
Maximum Aeration Flow per Module	3.6 m^3/h (2 scfm)

Notes:
(1) Higher OCl^- concentrations can occasionally be used.

4.5 DBP Formation Potential Testing

4.5.1 Source Waters

DBPFP is defined as the difference between the TTHM or HAA concentration after 7 days of incubation with excess free or combined chlorine residual and the initial TTHM or HAA concentration. Free chlorine and combined chlorine DBPFP tests were conducted using the following source waters:

- FXB and FBR Effluent: This test served as a worst-case scenario test (i.e., no post-treatment downstream to remove excess electron donor).
- SMBR Effluent: This test simulated on-site post-treatment with an aerated SMBR.
- Ozonated FXB and FBR Effluent: This test simulated post-treatment at the Rio Vista WTP.

4.5.2 Formation Potential Method

Test waters were subjected to formation potential evaluation of trihalomethanes and haloacetic acids. The trihalomethane formation potential method (THMFP) is described in the 20th Edition of Standard Methods (Method 5710B). All samples for DBP formation potentials were subjected to the standard methodology for THM formation potential:

"Under standard conditions, samples are buffered at pH 7.0 ±0.2, chlorinated with an excess of free chlorine, and stored at 25 ± 2 degrees C for 7 days to allow the reaction to approach completion. As a minimum, pH is buffered at a defined value and a free chlorine residual of 3 to 5 mg/L exists at the end of the reaction time and THMFP = TTHM at day 7-TTHM at day 0."

In the same manner, HAAFP = THAA at day 7 – THAA at day 0. The same conditions were be used for THMFP and HAAFP with combined chlorine (w:w, chlorine:ammonia = 4).

4.5.3 DBPFP Yield

The THMFP and HAAFP TOXFP yields are a measure of DBP formation potential per mg dissolved organic carbon and are defined as the following:

THMFP yield = THMFP/DOC, where DOC = dissolved organic carbon;

HAAFP yield = HAAFP/DOC and TOXFP yield = TOXFP/DOC.

The yield is a way to estimate the fraction of natural organic matter that is a precursor to formation of halogenated disinfection by-products. It was determined as part of this test.

4.5.4 Chlorine Demand

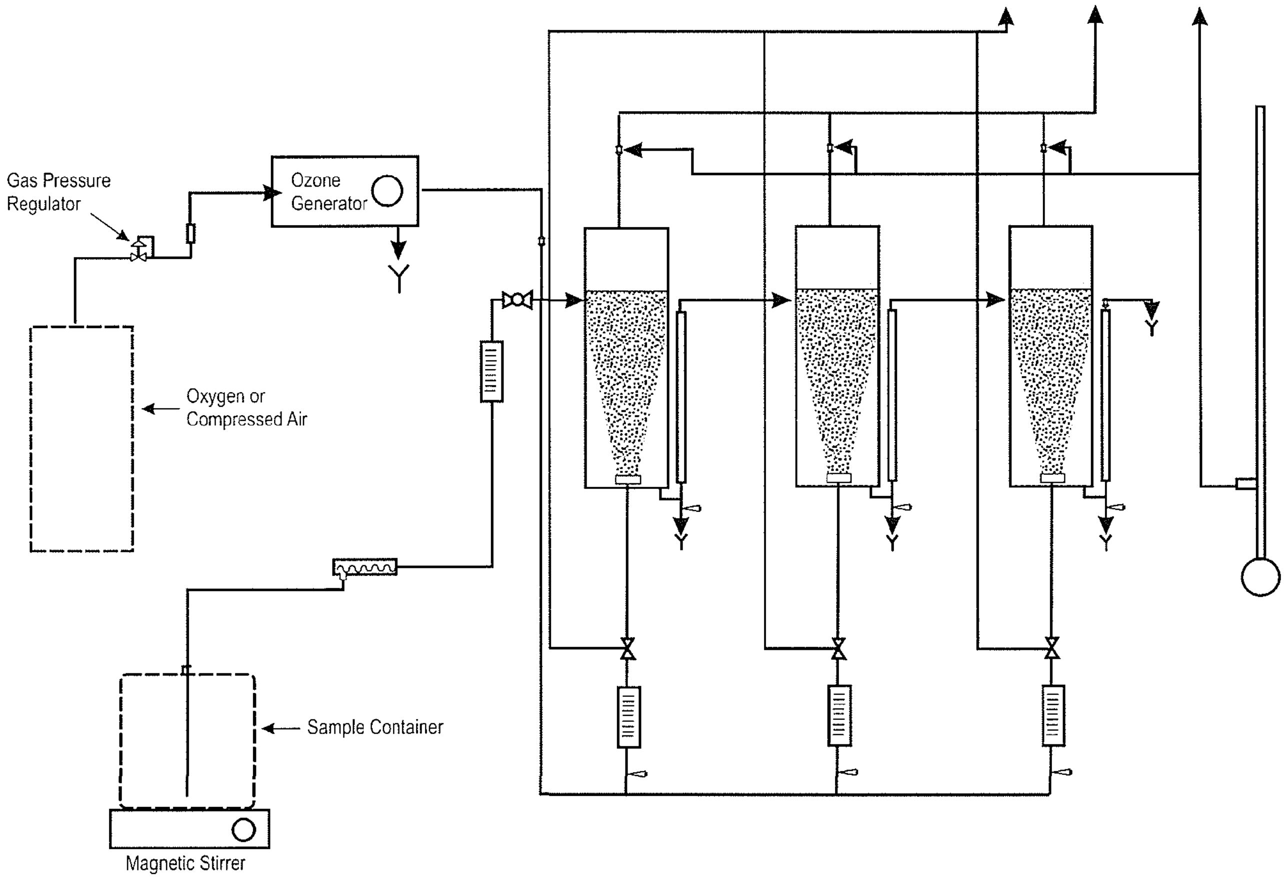
The 7-day chlorine demand was determined by the following procedure:

- Upon receipt of the samples, each sample was analyzed for ammonia, total and free chlorine, and TOC/DOC. The one-hour chlorine demand was measured at day 0. A chlorine:DOC ratio ranging from 2.5 to 5 was used. The results of this preliminary evaluation were used to estimate the required chlorine dose to achieve a 3 to 5 mg/L free chlorine residual at the end of the 7-day incubation period. It was assumed that once the instantaneous free chlorine demand is satisfied, the free chlorine decay would be much slower over the 7-day incubation period.

  A total chlorine residual of 3 to 5 mg/L after the 7-day incubation period was targeted. A chlorine:ammonia ratio of 4 was used.

4.5.5 Ozone Testing

An ozone demand test was conducted on two blended water samples that simulated the feed of the biological effluent to the Rio Vista Surface Water Treatment Plant: 90 percent SPW with 10 percent fixed bed reactor effluent and 90 percent SPW with 10 percent fixed bed effluent spiked with acetic acid. Carollo's bench-scale, continuous-flow, three-chamber ozone contactor was used (Figure 3.7). The hydraulic retention time in the bench-scale contactor was set at 6 minutes, and the test was conducted at ambient water temperature and ambient pH. The applied ozone dose (1.5 mg/L) was equally split between the three chambers. Ozone residuals were measured at the effluent of the third chamber. The



CAROLLO'S CONTINUOUS BENCH-SCALE OZONE REACTOR (NOT TO SCALE)

FIGURE 3.7

20-CLWA204F3.7-6625A10.CDR

effluent of the third ozone chamber was sampled for parameters listed in Table 3.7. Effluent samples were taken after a minimum of three nominal hydraulic retention times (HRTs) were achieved. The ozonated waters were then subjected to chlorine and chloramines for formation potential testing.

Table 3.7 DBPFP Analytical Matrix
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	FXB and FBR BIO Effluent	MBR Effluent	Ozonated Effluent	Lab
TOC/DOC	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
BDOC	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	MWH
AOC	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	MWH
TTHM	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	
HAA5	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
	7-day Cl_2/NH_2Cl	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	
Free/Total Chlorine	After Cl_2/NH_2Cl (time 0 and time 7 day)	After Cl_2/NH_2Cl (time 0 and time 7 day)	After Cl_2/NH_2Cl (time 0 and time 7 day)	On-site
Ammonia	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	On-site
	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	
pH	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	On-site
	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	
UV_{254} Absorbance	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
Alkalinity	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
Bromide	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	Before Cl_2/NH_2Cl	CLWA
	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	After Cl_2/NH_2Cl	
Bromate			Before Cl_2/NH_2Cl	CLWA/MWH
Aldehydes			Before Cl_2/NH_2Cl	MWH

4.5.6 Water Quality Analysis

Each sample was analyzed according to the matrix presented in Table 3.7 for full characterization before the addition of disinfectant and 7 days after addition. Ozonated waters were analyzed for bromate and aldehydes. On day 7 of the test following application of chlorine or chloramines, samples were analyzed for free and total chlorine residual, THM4, HAA5, pH, and bromide.

4.6 Simulated Distribution System Test

A follow-up SDS test was conducted on the FBR effluent with free chlorine to confirm the high THM4 and HAA5 levels measured in the FBR effluent during the DBPFP test. Free chlorine was added to the FBR effluent to satisfy the initial demand (approximately 8 mg/L) and to result in a free chlorine residual of 0.3 to 0.5 mg/L after an incubation period of 72 hours. This free chlorine residual and incubation period mimic the free chlorine residuals and maximum hydraulic residence time in the distribution system served by Newhall County Water District wells. The SDS test was conducted at ambient room temperature.

5.0 ANALYTICAL METHODS

Water quality data were measured on-site using bench-top equipment, on-line instruments, and laboratory analyses. The CLWA lab performed the majority of the laboratory analyses. Initial samples for nitrate, sulfate, chloride and bicarbonate were sent to MWH Laboratories in Monrovia, California, in addition to routine analysis for BDOC, sulfide, AOC, VSS, COD, NDMA, uranium, HAAs, TTHMs, and split perchlorate samples. For laboratory analyses, samples were collected in amber glass or polypropylene bottles. Samples sent to MHW labs were placed in bottles supplied by the laboratory and stored at 4 degrees C until analyzed.

5.1 pH

pH was measured on-site using Standard Method 4500-H + B. The pH meter was an Oakton 300 series with a single junction pH electrode. A 2-point calibration of the pH meter was performed daily.

5.2 Temperature

Temperature was measured in accordance with Standard Method 2550 B. This was done daily to check in-line temperature transmitters on the pilot plants. Temperature measurements were made daily using an Oakton 300 series pH/Conductivity meter with a built-in automatic temperature compensation ATC element.

5.3 Turbidity

Feed and permeate water in-line turbidity measurements were logged continuously on the pilot plant using Hach 1720 D low range process turbidimeters. The feed and permeate turbidimeters were calibrated after each run using primary calibration standards purchased from the manufacturer. Turbidimeter sensor lenses were cleaned every two weeks according to the manufacturer's instructions. Turbidimeter flow rates were checked daily to insure that they were within the range required by the manufacturer. Daily bench-top turbidity analyses were performed using a Hach 2100 P field turbidimeter. The instrument was calibrated before measurements using primary turbidity standards (0, 20, 100, 800 NTU).

5.4 Perchlorate

Perchlorate was measured by the CLWA laboratory using EPA method 3.14.0 with a minimum reporting limit of 4 µg/L.

5.5 Common Anions

Analysis for nitrate, nitrite, sulfate, bicarbonate, chloride, and phosphate were provided by CLWA using EPA method 300.0A.

5.6 Dissolved Oxygen

On-site DO measurements were taken using a YSI 5500 portable dissolved oxygen (DO) meter that was calibrated daily.

5.7 Metals

Calcium, magnesium, iron, chromium, and manganese measurements were analyzed using EPA method 200.7 by the CLWA laboratory.

5.8 Sulfide

Total sulfide measurements were made by MWH laboratories using EPA method 376.2.

5.9 NDMA

Analysis for NDMA was made using EPA method 1625 at MWH laboratory.

5.10 Uranium

Uranium analysis was performed by MWH using EPA method 908.1.

5.11 Total Suspended Solids

Total suspended solids (TSS) were measured at CLWA laboratory according to Standard Method 2540 D.

5.12 Total Alkalinity

Total alkalinity was measured at CLWA laboratory according to Standard Method 2320 B.

5.13 Total Hardness

Total hardness was measured at CLWA laboratory according to EPA Method 200.7 and Standard Method 2340 B.

5.14 Organic Carbon

Total organic carbon (TOC) and dissolved organic carbon (DOC) were measured at CLWA laboratory according to EPA Method 415.1. CLWA uses a Shimadzu TOC-5050 Total Organic Carbon Analyzer. The minimum reporting level was 0.7 mg/L. Biodegradable DOC was measured by MWH using the Servais method.

5.15 UV_{254} Absorbance

UV_{254} absorbance was measured at CLWA laboratory according to Standard Method 5910 B. The instrument used for measurements was a Shumadzu UV-1201 UV-VIS Spectrophotometer.

5.16 Total and Free Chlorine

Total and free chlorine concentrations were measured using an on-site, HACH DR 890 field spectrophotometer. High range measurements (0 to 5 mg/L) for total and free chlorine were made in accordance with HACH methods 10070 and 10069, respectively (adapted from Standard Methods). Measurements for total and free chlorine concentrations from 0 to 2.00 mg/L were made using HACH methods 8167 and 8021, respectively (equivalent to Standard Method 4500-Cl G).

5.17 Microbial Parameters

Heterotrophic plates counts (HPCs) and total and fecal coliform counts were measured according to Standard Methods 9215B and 9221 D, respectively by CLWA and MWH laboratories.

5.18 Particle Counts

FXB in-line particle count measurements of the effluent water were logged continuously using a Hach 2200 PCX particle counter. Continuous maintenance of the particle counter (cleaning and flow adjustment) ensured accurate readings.

5.19 Disinfection By-Products

TTHMs and HAAs were measured by MWH laboratories according to EPA Methods 502.2 and 552.2, respectively.

5.20 Ozone Residual

Ozone residual was measured according to the Indigo Blue Method (Standard Method 4500-O3 B). Hach accuvacs were used that withdraw 10 mL of samples directly reacting with the Indigo Powder in the ampule.

5.21 COD

Chemical oxygen demand (COD) analysis was performed at MWH laboratories using EPA method 410.4.

6.0 OPERATING PROTOCOL

6.1 Ion-Exchange Columns

6.1.1 Experimental Design

The bench-scale IX study was conducted by Carollo. There were four objectives for this work:

1. Evaluate the efficiency of three ion-exchange resins for perchlorate removal under the identical feed water, flow rate, and EBCT.
2. Establish the perchlorate breakthrough curves for Saugus Aquifer water using three perchlorate-selective, throw-away resins.
3. Determine the NDMA formation potential of treating Saugus Aquifer water with these resins.
4. Determine characteristics of the spent resin.

- Phase 1 (Perchlorate Breakthrough: Approximately 2 to 4 Months): The columns were fed at a constant flow rate with perchlorate- and sulfate-spiked groundwater and sufficient influent and effluent samples were taken to establish a complete breakthrough curve for each anion. The columns were shut off once perchlorate breakthrough in all columns reached approximately 20 percent of the feed concentration. This translates into an effluent perchlorate concentration of 10 µg/L.

  The operating conditions for each ion-exchange column are listed in Table 3.8. The columns were operated at a service loading rate of 5 gpm/ft^3. With a resin volume of 22.5 mL in each column, the flow rate to each column was approximately 15 mL/min, which equates to an EBCT of 1.5 minutes.

Table 3.8 Breakthrough of Anions
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Value
EBCT	1.5 min
Service Flow Rate	15 mL/min
Service Loading Rate	5 gpm/ft^3
Surface Loading Rate	2.1gpm/ft^2
Run Length- from Preliminary Modeling	> 20,000 BVs
Batch Feedwater Volume per Column	40 gal/week
Total Batch Feedwater Volume	119 gal/week

The breakthrough profiles of the various anions depend on the resins selected. Breakthrough modeling data (IX Pro Software) for a generic perchlorate selective resin are tabulated and plotted in Table 3.9 and Figure 3.8, respectively. The anticipated anionic breakthrough order was as follows: bicarbonate, sulfate, nitrate, perchlorate. The inputs to the modeling program were: component concentration, component separation factor (or selectivity coefficient); resin capacity; number of plates; and run length. The separation factors were based on the research conducted by Tripp et al. (2003).

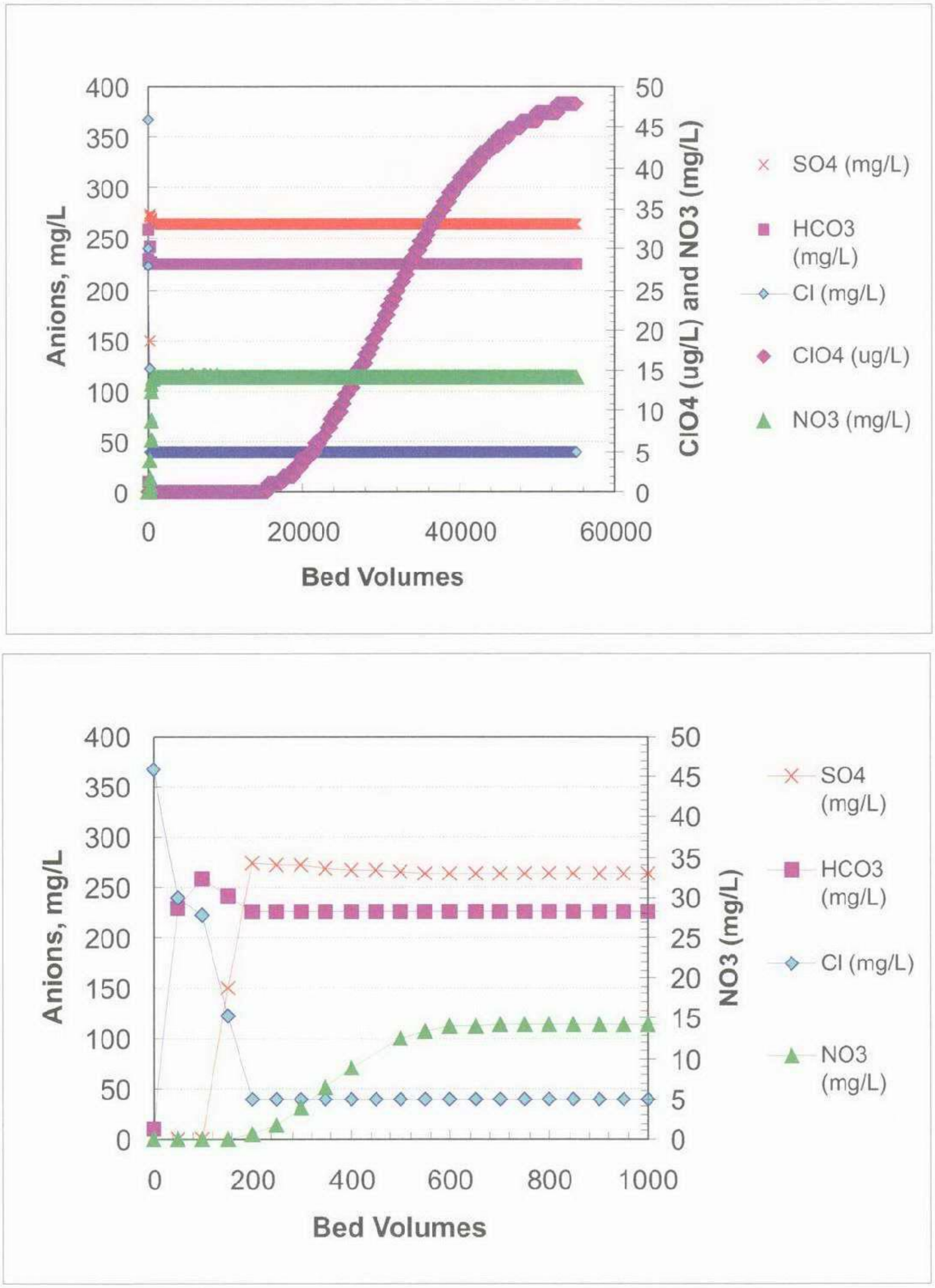
Table 3.9 Breakthrough of Anions for a Generic Perchlorate Selective Resin
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Anions	Bed Volumes (BVs)	Equivalent Time (EBCTxBVs)
Bicarbonate	40 BVs for complete breakthrough	1 hr
Sulfate	200 BVs for complete breakthrough	5 hours
Nitrate	600 BVs for complete breakthrough	15 hours
Perchlorate	>20,000 BVs for breakthrough up to 4 μg/L	21 days

6.1.2 Sampling

Carollo staff was responsible for day-to-day operation and sampling of the bench-scale IX columns during regular weekdays (excluding holidays). CLWA staff checked on the columns during the weekend and holidays. To address emergencies during off-hours, CLWA staff contacted the lead Carollo operator. Operator log sheets were used daily to record flow rates and sample collection times.

Perchlorate-spiked raw water was analyzed once per week for perchlorate, nitrate, sulfate, bicarbonate, chloride, pH, and conductivity.



ANITICIPATED BREAKTHROUGH CURVES FOR KEY ANIONS

FIGURE 3.8

20-CLWA204F3.8-6625A10.CDR

Sampling frequencies for column effluents were established so that breakthrough profiles for sulfate, bicarbonate, chloride, nitrate, and perchlorate were captured. Sampling frequencies were as follows:

- First 48 hours: One sample per hour. Analyzed 12 (every 3 to 4 hours) samples for nitrate, sulfate, chloride, and bicarbonate. Perchlorate was analyzed three times per week.
- After the first two days of operation, sample frequencies were decreased to six samples per day, depending on whether the parameter has broken through. Perchlorate was analyzed three per week.

Table 3.10 lists the sampling frequencies and locations from Day 3 until 20 percent perchlorate breakthrough occurred. This sampling schedule was adequate to capture breakthrough of all anions for all three types of resins. During the first week of operation (i.e., the time-sensitive breakthrough period for bicarbonate, chloride, sulfate, and nitrate), samples were collected with a timed autosampler. Subsequently, all samples were collected manually at the frequencies describe in Table 3.10.

Table 3.10 Testing Matrix for Bench-Scale Ion Exchange Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer Castaic Lake Water Agency

Chemical Parameter	Lab	Sampling Frequency from Each Column Effluent		
		Day 3-Day 7	Weeks 2-5	Weeks 6-10
pH[(1)]	-	1/day	1/day	1/day
Temperature[(1)]	-	1/day	1/day	1/day
Conductivity[(1)]	-	1/day	1/day	1/day
Perchlorate	CLWA & MWH	2/week	3/week	1/day
Nitrate	CLWA	6/day	3/week	1/week
Sulfate	CLWA	6/day	3/week	1/week
Bicarbonate	CLWA	6/day	3/week	1/week
Chloride	CLWA	6/day	3/week	1/week
Alkalinity	CLWA	2/week	1/week	1/week
Hardness	CLWA	1/week	1/week	1/week
Iron	CLWA	1/week	1/week	1/week
Manganese	CLWA	1/week	1/week	1/week
Calcium	CLWA	1/week	1/week	1/week
Magnesium	CLWA	1/week	1/week	1/week

Table 3.10 Testing Matrix for Bench-Scale Ion Exchange Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer Castaic Lake Water Agency

Chemical Parameter	Lab	Sampling Frequency from Each Column Effluent		
		Day 3-Day 7	Weeks 2-5	Weeks 6-10
Turbidity	CLWA	1/week	1/week	1/week
TOC	CLWA	1/week	1/week	1/week
Chromium	CLWA	As needed	As needed	As needed
NDMA	MWH	As needed	As needed	As needed
Bromide	CLWA	As needed	As needed	As needed
Arsenic	CLWA	As needed	As needed	As needed
Uranium	MWH	As needed	As needed	As needed

Note:
(1) Measured on-site.

Table 3.10 also identifies the laboratory that was responsible for analyzing each parameter. The majority of parameters were analyzed at CLWA, while perchlorate checks, NDMA, and uranium were measured at MWH laboratories. All samples not analyzed immediately were stored at 4 degrees C for no more than the recommended holding time before analysis.

6.2 Biological Fixed-Bed Filter

6.2.1 Experimental Design

A 6-month biological FXB filtration pilot study was conducted. The overall objective of this study was to demonstrate the efficacy of biological FXB filtration for perchlorate removal from Saugus aquifer water. A more specific objective was to determine whether biologically acclimating the GAC with indigenous microorganisms would be sufficient to achieve efficient perchlorate reduction in the filter. Once these objectives were achieved, a testing protocol was employed to determine requirements for EBCT, backwashing protocol, and acetic acid addition. A series of short-term experiments were also performed to evaluate the robustness of the process with respect to system upsets.

During the first 2 weeks of pilot-testing, acetic acid was fed to each filter at a concentration twice that required to stoichiometrically reduce all influent DO and nitrate (($O_2 \Rightarrow H_2O$, $NO_3^- \Rightarrow N_2$; for calculation purposes, it was assumed that no electron donor is used for cell synthesis). This ensured that electron donor was not limiting. EBCT and acetic acid feed were optimized during Phase 2 of the FXB pilot study. Perchlorate was spiked to the influent at 50 μg/L except during the perchlorate spiking tests (see Phase 3 of this section). Phosphoric acid was added for a two-month portion of the pilot study. No other chemicals were added to the process system during the pilot study.

- Phase 1 (Biological Acclimation): The purpose of this phase was to determine whether or not efficient perchlorate-reducing biological activity could be developed in the GAC filters using microorganisms indigenous to the Saugus Aquifer. Once the filtration skid was mobilized, the filters began treating Saugus Aquifer water from Well NC-12 spiked with perchlorate. Technical-grade acetic acid (electron donor) was added to the feed water. An EBCT of 15 minutes was used during the first few weeks of the acclimation phase to allow for the rapid saturation of sorption sites on the surface of the GAC and to promote rapid growth of the microbial community in the biological FXB filter.

- Phase 2 (EBCT and Acetic Acid Optimization): The purpose of this phase was to determine the minimum EBCT required to achieve perchlorate removal to below the 4 μg/L reporting limit ($EBCT_{critical}$). Acetic acid was initially added at 100 percent excess relative to the emperical stoichiometric influent DO and nitrate demand (based on an influent DO concentration of 7.0 mg/L and an influent nitrate concentration of 15 mg/L). EBCT was incrementally lowered until perchlorate breakthrough was observed. Once $EBCT_{critical}$ was found, the feed acetic acid concentration was incrementally lowered until perchlorate breakthrough was observed ($AC_{critical}$).

- Phase 3 (Robustness Characterization): The purpose of this phase was to determine how the FXB system responds to various process up-sets. The $EBCT_{critical}$ and $AC_{critical}$ were set as operating parameters throughout this phase of testing. Five process upsets were tested: 1) backwashing, 2) perchlorate spiking, 3) nitrate spiking, 4) electron donor feed failure simulation, and 5) a total system shutdown.
  - Backwashing: These tests were designed to evaluate perchlorate removal performance immediately after backwash episodes. Because backwashes remove perchlorate-reducing biomass from the filter, it is possible that perchlorate breakthrough would occur after backwashes until the biological community in the filter had sufficient time to regrow. This test was performed twice, one-month apart. Samples were taken a 0, 15, 30, 45, and 60 minutes after the filter was put into production following a backwash.
  - Perchlorate Spiking: These tests were designed to evaluate perchlorate removal performance during periods of transient perchlorate loading episodes. Perchlorate was spiked to the feed at 100 μg/L for a 48-hour period and effluent perchlorate concentrations were monitored. Influent perchlorate concentration was then readjusted to 50 μg/L and the system was allowed to stabilize (i.e., reestablish pre-spiking, perchlorate removal performance), if necessary. A 48-hour spiking test was then performed using 300 μg/L perchlorate, followed by a 5 mg/L perchlorate spiking test. The 5 μg/L perchlorate spiking test was designed to: 1) demonstrate perchlorate removal performance at a low-end feed perchlorate concentration, 2) initiate the desorption of perchlorate from the carbon surface (if any) as the bed equilibrated with a lowered feed perchlorate concentration. Along

with the regular daily samples, samples were taken at 0, 15, 30, 45, and 60 minutes after the filter was put into production following a change in feed perchlorate concentration.

  - Nitrate Spiking: This test was designed to evaluate perchlorate removal performance during periods of transient nitrate loading episodes. Over a 48-hour period, nitrate was spiked to the feed to reach a final influent concentration of 30 mg/L (the historical Saugus aquifer maximum concentration) and effluent perchlorate concentrations were monitored. During the first part of the test, EBCT and acetic acid concentration were not adjusted to account for the increased nitrate in the feed. A second nitrate spiking test was performed during which the EBCT and acetic acid were both adjusted to achieve perchlorate removal to below detection. Along with the regular daily samples, samples were taken at 0, 15, 30, 45, and 60 minutes after the filter was put into production following a change in feed nitrate concentration.
  - Electron Donor Feed Failure Simulation: This test was designed to evaluate perchlorate removal performance during a period of simulated electron donor feed system failure. The acetic acid feed was shut off for 48 hours and effluent perchlorate concentrations were monitored. The acetic acid feed was then restarted and the time required to reestablish efficient perchlorate reduction was evaluated. Along with the regular daily samples, samples were taken at 0, 15, 30, 45, 60, 120, 180, 240, and 630 minutes after the filter was put into production following a change in feed perchlorate concentration.
  - System Shutdown: This test was designed to evaluate perchlorate removal performance after the system has been shut down for 1-day, 2-day, and 2-week periods. The time required to reestablish efficient perchlorate reduction in the filters was evaluated.

- Backwashing Protocol: Backwashes were performed using effluent water stored in the pilot backwash tank (see Figure 2.4). Backwashes were performed approximately every 48 hours. If run times did not reach 48 hours due to rapid headloss build-up, operating parameters were adjusted (i.e., EBCT and acetic acid concentration). Backwashes consisted of a 10-minute air scour period using ~0.1-0.2 scfm, followed by a 20-minute backwash at 0.8 gpm (9 gpm/ft^2), which resulted in a 45 percent bed expansion.

6.2.2 Sampling

Table 3.11 lists the various water quality parameters that were measured, sampling location and frequency, and the associated laboratory responsible for the analysis. Increased perchlorate sampling frequencies during the challenge tests are described above.

Table 3.11 Sampling Schedule for Fixed-Bed Biological Pilot Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
ClO_4^-	Feed	Once per 2 days	CLWA and occasional checks with MWH
	Effluent	Daily	
	Backwash	As Needed	
NO_3^-	Feed	2/week	CLWA
	Effluent	3/week	
DO	Feed	Daily	On-site
	Effluent	Daily	
NO_2^-	Feed	1/week	CLWA
	Effluent	1/week	
PO_4^{3-}	Feed	1/week	CLWA
	Effluent	1/week	
SO_4^{2-}	Feed	1/week	CLWA
	Effluent	1/week	
NH_3	Feed	1/week	CLWA
	Effluent	2/week	
H_2S	Feed	1/week	MWH
	Effluent	1/week	
TOC/DOC	Feed	3/week	CLWA
	Effluent	3/week	
BDOC	Feed	2/week	MWH
	Effluent	2/week	
HPC	Feed	2/week	CLWA
	Effluent	2/week	
Total coliforms	Feed	1/week	CLWA & MWH
	Effluent	1/week	
	Backwash	1/backwash	
Fecal coliforms	Feed	1/week	CLWA & MWH
	Effluent	1/week	
	Backwash	1/backwash	
Turbidity	Feed	3/wk	Dedicated in-line HACH 1720D turbidimeters and Bench-top turbidimeter
	Effluent	Continuous	
Total particle counts	Effluent	Continuous	In-line particle counter

Table 3.11 Sampling Schedule for Fixed-Bed Biological Pilot Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
pH	Feed	Daily	On-site
	Effluent	Daily	
Headloss	Across FXB	Continuous	In-line pressure transducer
Backwash volatile suspended solids (VSS)	Backwash water	Once per backwash	CLWA
Assimilable Organic Carbon	Backwash water	Once per backwash	MWH
Chemical Oxygen Demand	Backwash water	Once per backwash	MWH
Total Suspended Solids	Backwash water	Once per backwash	MWH

Given that adjustments to process operation were made based on perchlorate removal performance in the filters, it was important to maintain a short turn-around time for perchlorate samples throughout pilot testing. Therefore, perchlorate samples was taken for analysis at the CLWA laboratory to expedite the acquisition of perchlorate data. However, since the CLWA laboratory has partial certification for perchlorate analysis, duplicate samples were set weekly to MWH for analysis. Bacterial samples, TOC/DOC, and anions were transported to the laboratory every Tuesday. Additional anion samples were transported to the lab every 3 days (i.e., Monday, Wednesday, and Friday) due to the short holding time of nitrate (48 hours).

The on-line ion chromatography perchlorate analyzer (DX-800 Process Analyzer), which was generally used to continuously monitor FBR effluent perchlorate concentrations, was configured to accept manual injections of FXB samples. Thus, near real-time perchlorate removal performance was monitored during the majority of FXB pilot testing.

6.3 Biological Fluidized-Bed Reactor

6.3.1 Experimental Design

A 6-month biological FBR pilot study was conducted using Shaw Environmental-Envirogen/US Filter/Envirex Products' low-flow FBR. The overall objective of this study was to demonstrate the efficacy of an FBR biological process for perchlorate removal from Saugus aquifer water. A more specific objective was to determine whether biologically acclimating the GAC with indigenous microorganisms is sufficient to achieve efficient perchlorate reduction in the FBR. The testing protocol was also designed to optimize HRT and acetic acid addition, and to test the robustness of the process during system upsets.

However, establishing consistent perchlorate removal to below detection required the entire length of the pilot testing period.

The FBR system was monitored using a Dionex On-Line Ion Chromatography Perchlorate analyzer (DX-800 Process Analyzer). The use of the DX-800 analyzer provided a better understanding of the instrument's capabilities in a field setting. The testing of this system also allowed for immediate operational responses based on FBR performance.

- Phase 1 (Biological Acclimation): During start-up, the FBR system was filled with NC-12 groundwater. Carbon was added to provide a desired settled bed height of approximately 5 feet. The system was then started in recycle and the carbon hydraulically fluidized 1.25 to 1.30 times the settled bed height. The feed and recycle rates required to meet this bed expansion were documented and utilized as a baseline for future bed growth measurements. Following this procedure, nutrients and electron donor were added to the reactor in batch mode to allow the microbial consortium to develop over a period of two days. The system was then put into continuous operation mode at a feed flow of 1 gpm and a recycle flow of 8 to 9 gpm. The feed flow was set between 1 and 3 gpm throughout pilot testing and the recycle flow was typically set so that total flow was approximately 10 gpm.

- Phase 2 (Continuous Operation): This phase was initially intended to determine optimal feed and recycle flow rates as well as optimal feed phosphorous and acetic acid concentrations. During the bulk of this phase, Carollo worked with Shaw Environmental (formerly Envirogen) staff to make mechanical and operational changes designed to improve the perchlorate removal performance of the FBR.

- Phase 3 (Robustness Characterization): FBR robustness characterization testing did not occur for the FBR as stable performance was not achieved during the 6-month period.

6.3.2 Sampling

Table 3.12 lists the various water quality parameters that were measured once start-up was completed, the sampling location and frequency, and the associated laboratory responsible for the analysis.

Table 3.12 Fluidized-Bed Sampling Matrix
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
Perchlorate	Feed Effluent	Once per 2 days Daily	CLWA and occasional checks with MWH + on-line ion chromatograph

Table 3.12 Fluidized-Bed Sampling Matrix
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
Nitrate	Feed	3/week	CLWA
	Effluent	3/week	
Nitrite	Feed	1/week	CLWA
	Effluent	1/week	
Phosphate	Feed	1/week	CLWA
	Effluent	1/week	
Sulfate	Feed	-	CLWA
	Effluent	-	
DO	Influent	Daily	On-site analysis
	Effluent	Daily	
H_2S	Influent	1/week	MWH
	Effluent	1/week	
BDOC	Feed	2/week	MWH
	Effluent	2/week	
HPC	Feed	1/week	CLWA
	Effluent	1/week	
Total Coliforms	Feed	1/week	CLWA
	Effluent	1/week	
Fecal Coliforms	Feed	1/week	CLWA
	Effluent	1/week	
TOC	Feed	-	CLWA
	Effluent	2/week	
TSS	Feed	-	CLWA
	Effluent	-	
Ammonia	Feed	1/week	CLWA
	Effluent	1/week	
Total phosphorous	Feed	1/week	CLWA
	Effluent	2/week	

6.4 Submerged Membrane Bioreactor

6.4.1 Experimental Design

Due to the short SMBR testing period, the experimental design focused only on demonstration, not optimization, of the SMBR process. Operational settings for the SMBR are listed in Table 3.13.

Table 3.13 SMBR ZW-10 System Operating Parameters
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Value
Q_{FEED} (mL/min)	300-680
$Q_{PERMEATE}$ (mL/min)	300-680
Recovery (%)	80-99
HRT (hours)	4.7-10.6
Aeration rate (scfm)	1-2

For the majority of SMBR testing, the biological FXB filter was operated using $EBCT_{critical}$ and $AC_{critical}$. SMBR backpulses were initiated every 15 minutes, for a duration of 15 seconds. The system was operated continuously and monitored regularly for two months to determine whether each of the four post-treatment objectives was being met. A three-week acetic acid spiking test was performed after it was observed that biological FXB filter effluent contained non-detect concentrations of TOC. During this test, 3.5 mg/L of acetic acid carbon was continuously spiked to the SMBR process tank using a peristaltic pump to validate residual organic removal efficiency.

6.4.2 Sampling

Table 3.14 lists the various water quality parameters that were measured, sampling location and frequency, and the associated laboratory responsible for the analysis.

Table 3.14 SMBR Sampling Matrix
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
DO	Feed	Daily	On-site
	Effluent	Daily	
H_2S	Feed	1/week	CLWA & qualitative (i.e., by nose)
	Effluent	1/week	

Table 3.14 SMBR Sampling Matrix
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Sampling Location	Sampling Frequency	Lab
TOC/DOC	Feed	3/week	CLWA
	Effluent	3/week	
BDOC	Feed	2/week	MWH
	Effluent	2/week	
HPCs	Feed	2/week	CLWA
	Effluent	2/week	
Total coliforms	Feed	1/week	CLWA
	Effluent	1/week	
Fecal coliforms	Feed	1/week	CLWA
	Effluent	1/week	
Turbidity	Feed	3/week	Bench-top turbidimeter
	Effluent	3/week	
pH	Feed	2/week	On-site probe
	Effluent	2/week	
Process tank volatile suspended solids	Process tank	2/week	CLWA

7.0 TEST RESULTS

7.1 Ion-Exchange Testing Results

7.1.1 Feed Water Quality

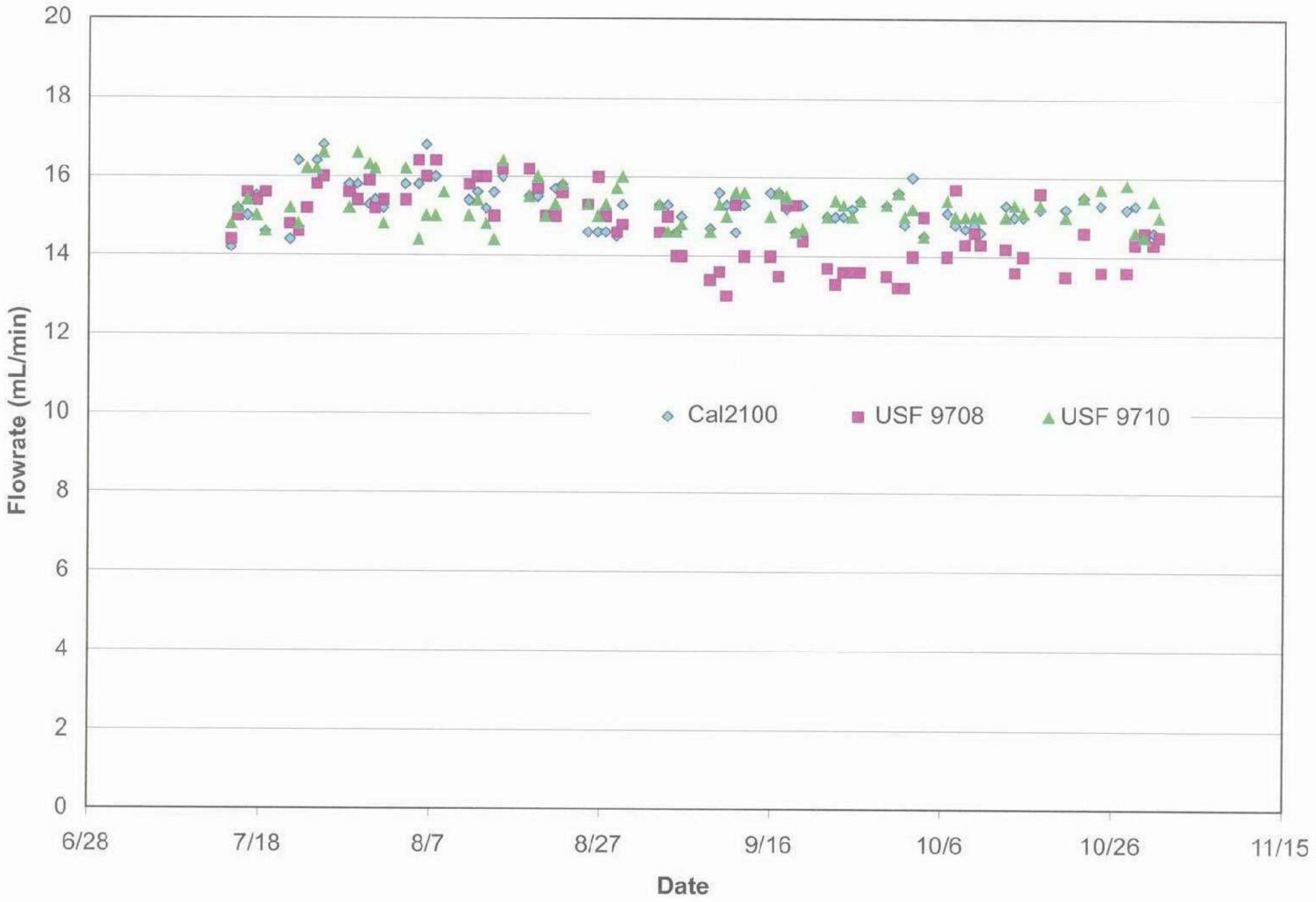
The range of constituent concentrations in the feed water to the ion-exchange columns is presented in Table 3.15. The feed water is characterized as low in organic matter, moderately hard and buffered, and moderate in iron and bromide. It should be noted that during the month of October 2003 the NC-12 groundwater quality was observed to slowly change over a 4-week period before returning to its steady-state quality at the end of the bench-scale study. The nitrate concentration decreased from 3.3 mg/L as N to 1.7 mg/L as N, sulfate increased from 290 mg/L to 373 mg/L (after sulfate spike), and the chloride concentration increased from 35 mg/L to 45 mg/L.

Table 3.15 Range of Constituent Concentration in Feedwater to the IX System
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Chemical Parameter	Unit	Count	Average	Min	Max
Perchlorate	μg/L	18	45.5	42.6	52.9
Nitrate-N	mg/L	18	3.0	1.7	3.4
Sulfate	mg/L	18	301	276	373
Bicarbonate	mg/L	18	199	171	221
Chloride	mg/L	18	37	32	45
pH	—	18	8.1	7.9	8.4
Alkalinity	mg/L as $CaCO_3$	18	165	152	181
TOC	mg/L			<0.7	<0.7
DOC	mg/L			<0.7	<0.7
Arsenic	μg/L			ND	ND
Iron	μg/L	9	15.3	7	27
Manganese	μg/L	9		<1	<1
Hardness	mg/L as $CaCO_3$	2		282	315
Calcium	mg/L	3	84	77	94
Magnesium	mg/L	3	17.7	17	18
Uranium	pCi/L			ND	1.03
NDMA	ng/L			ND	ND
Vanadium	μg/L	3	10.7	2.0	15.0
Bromide	mg/L	2		0.22	0.24
Turbidity	NTU	12	0.337	0.180	0.580
Conductivity	μmhos/cm	15	1043	1003	1158

7.1.2 Operational Data

Two operational parameters were recorded on a daily basis for the ion-exchange setup: flowrate through the columns (Figure 3.9) and pressure buildup. The pump setting and/or the needle valves connected downstream of the columns were adjusted when the measured flow rate deviated by more than 10 percent from the target flow rate of 15 mL/min. The flow rate ranged from 13.5 to 16.5 mL/min during the course of the study, which resulted in an EBCT range of 1.4 to 1.6 minutes. The pressure drop remained constant at 5 psi throughout most of the project duration, and increased to 7 psi during the last two weeks of testing. The level of water in the 55-gal feed tanks was monitored daily. The experimental apparatus was monitored for the presence of air bubbles and leaks.



FLOW RATES MEASURED THROUGH THE THREE ION-EXCHANGE COLUMNS

FIGURE 3.9

7.1.3 Temperature

The temperature, which was measured in the effluent of the three columns over the course of the study, ranged from 32 degrees C (89 degrees F) in the summer months to 16 degrees C (61 degrees F) in the fall (Figure 3.10).

7.1.4 pH Values

pH was measured in the feed and effluent of the three columns, and both ranged from 7.6 to 8.4 (Figure 3.11), indicating only minor impact on pH by the resins.

7.1.5 Breakthrough Curves

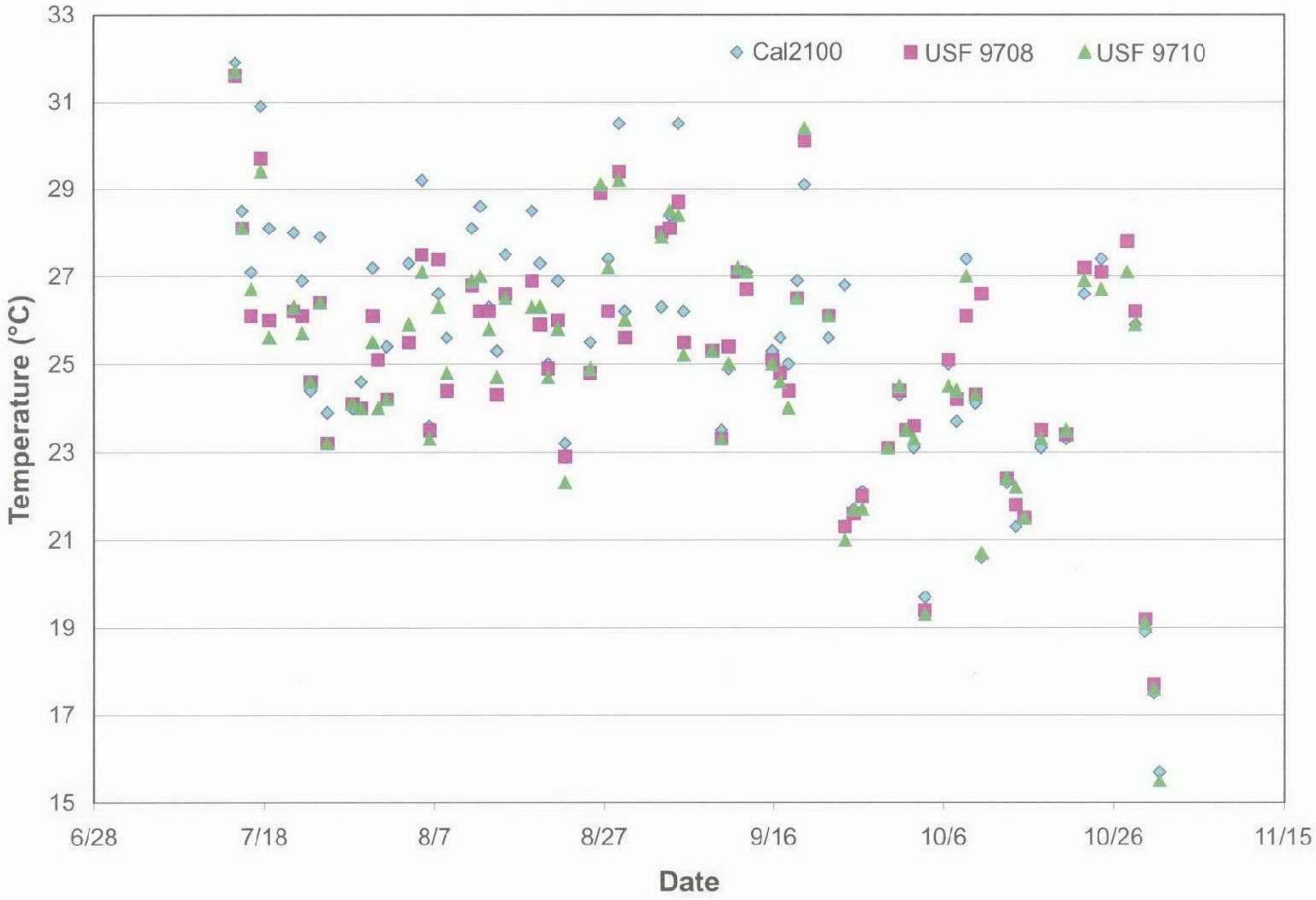
Breakthrough curves of key anions were developed for the ion-exchange resins under identical conditions of water quality, flowrate, and EBCT. The three columns were operated in parallel using one feed pump. The columns ran continuously with minimal shut-down periods. A 45-hour shut-down period was simulated at the end of the study to investigate its potential effect on breakthrough.

7.1.5.1 High-Resolution Breakthrough Curves of Key Anions

As predicted by the IXPro Model, the breakthrough of most anions (with the exception of perchlorate) was very fast and occurred in the first 24 hours of operation. This breakthrough sequence was similar for the three resins tested, as illustrated in Figures 3.12 through 3.14. The figures are plotted for the first 2,000 bed volumes of run time.Bicarbonate was the first anion to break through reaching its background value of 220 mg/L after 80 to120 bed volumes. Sulfate was next to breakthrough after 80 bed volumes and reached its steady-state concentration of 300 mg/L after 280 to 310 bed volumes. The nitrate breakthrough rate was somewhat different for the three columns. Nitrate broke through after 280 bed volumes, 440 bed volumes, and 600 bed volumes from USF 9708, USF 9710, and Cal 2100 resins, respectively. Steady-state concentrations were reached after 1,000 bed volumes for all three tested resins. No chromatographic peaking was observed for any of the critical anions within the test conditions.

Chloride concentration dropped from a high of approximately 325 mg/L to background levels of approximately 35 mg/L after 280 bed volumes. The highest measured chloride levels in the first 280 bed volumes did not exceed the Title 22 Secondary Maximum Contaminant Level of 500 mg/L. However, they did exceed the Los Angeles County Sanitation District (LACSD) maximum acceptable chloride level of 100 mg/L in the Santa Clara Valley Basin.

In a full-scale application, following a resin change-out, the new resin may need to be flushed over a few days to meet DHS requirements. This flushed water, which will contain higher concentrations of chloride during the first few hours of flushing (as illustrated in Figures 3.12 to 3.14), will need to be dealt with by discharge to a sewer, for example. The flushed water will be free of perchlorate.



COLUMN EFFLUENT TEMPERATURE MEASURED OVER THE COURSE OF THE STUDY

FIGURE 3.10

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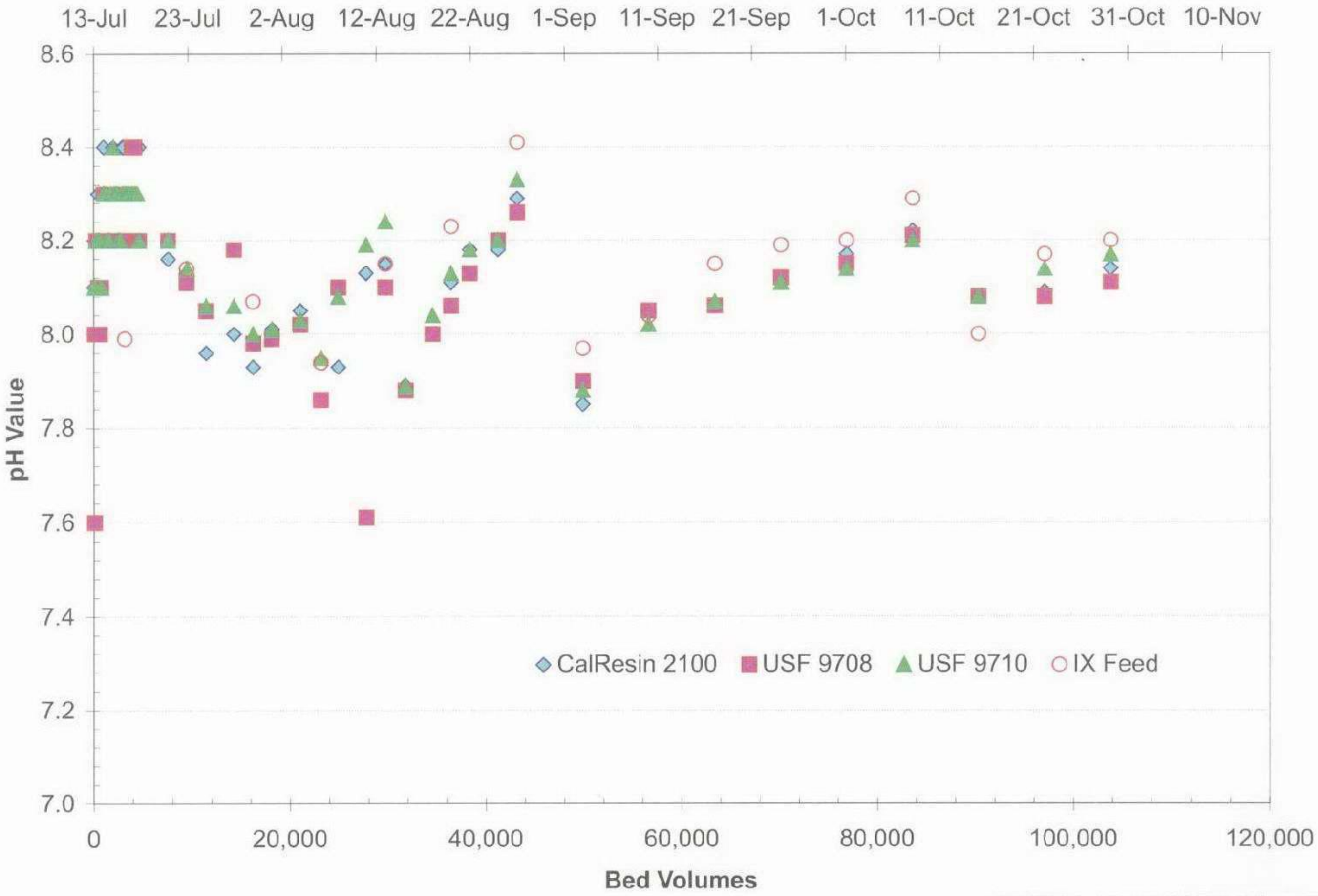
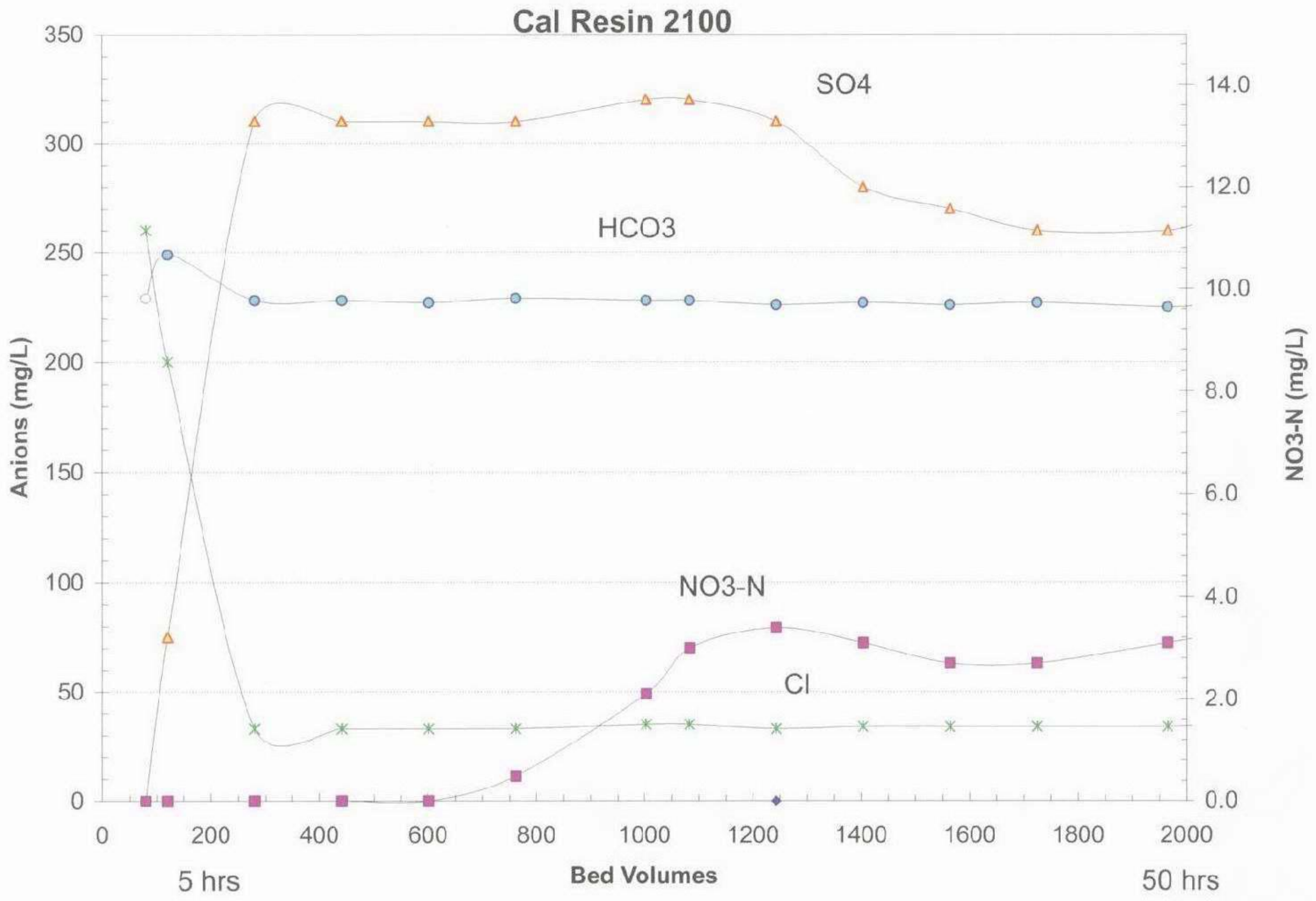


pH VALUES MEASURED IN THE FEED AND IX COLUMN EFFLUENT

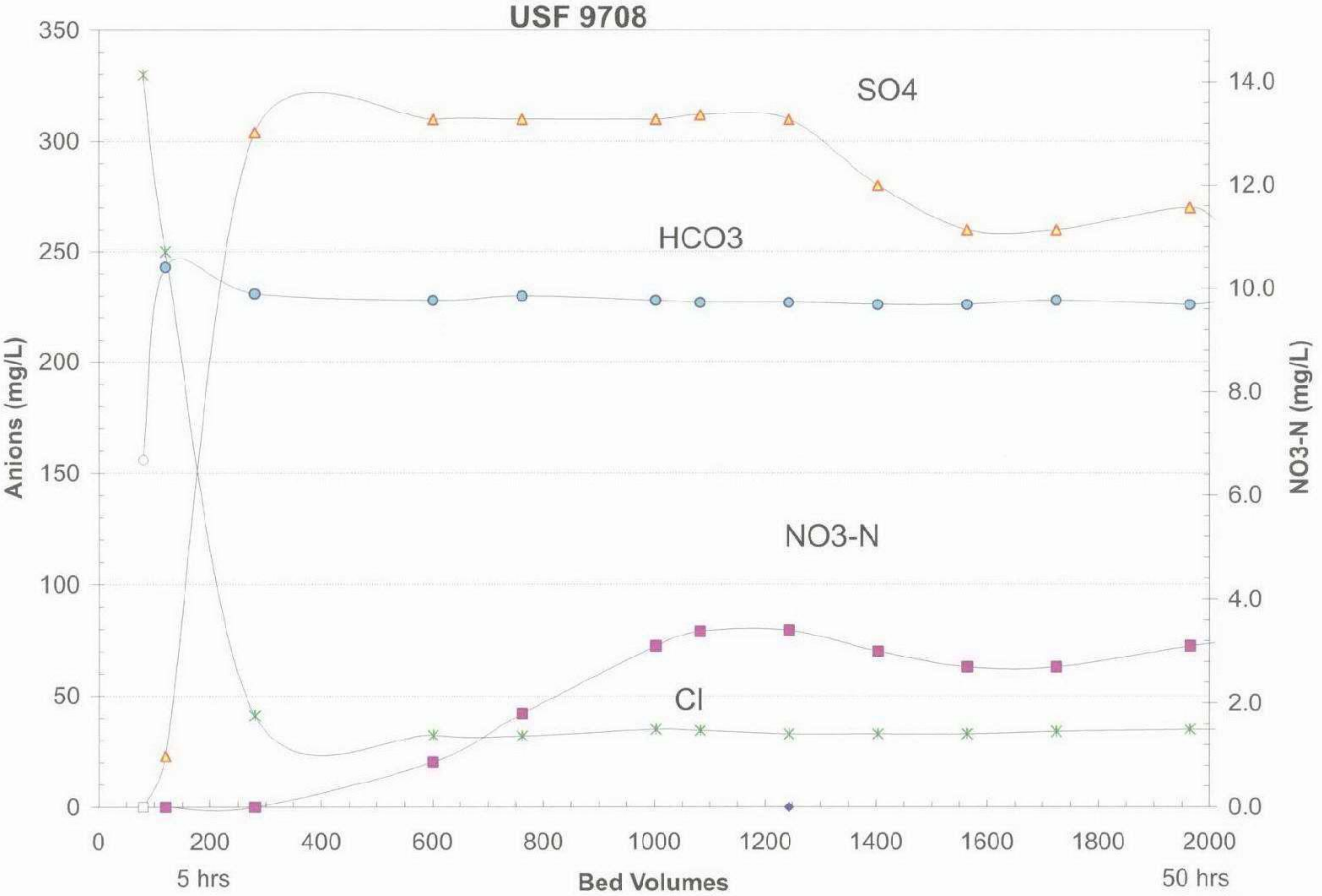
FIGURE 3.11

20-CLWA204F3.12-6625A10.CDR



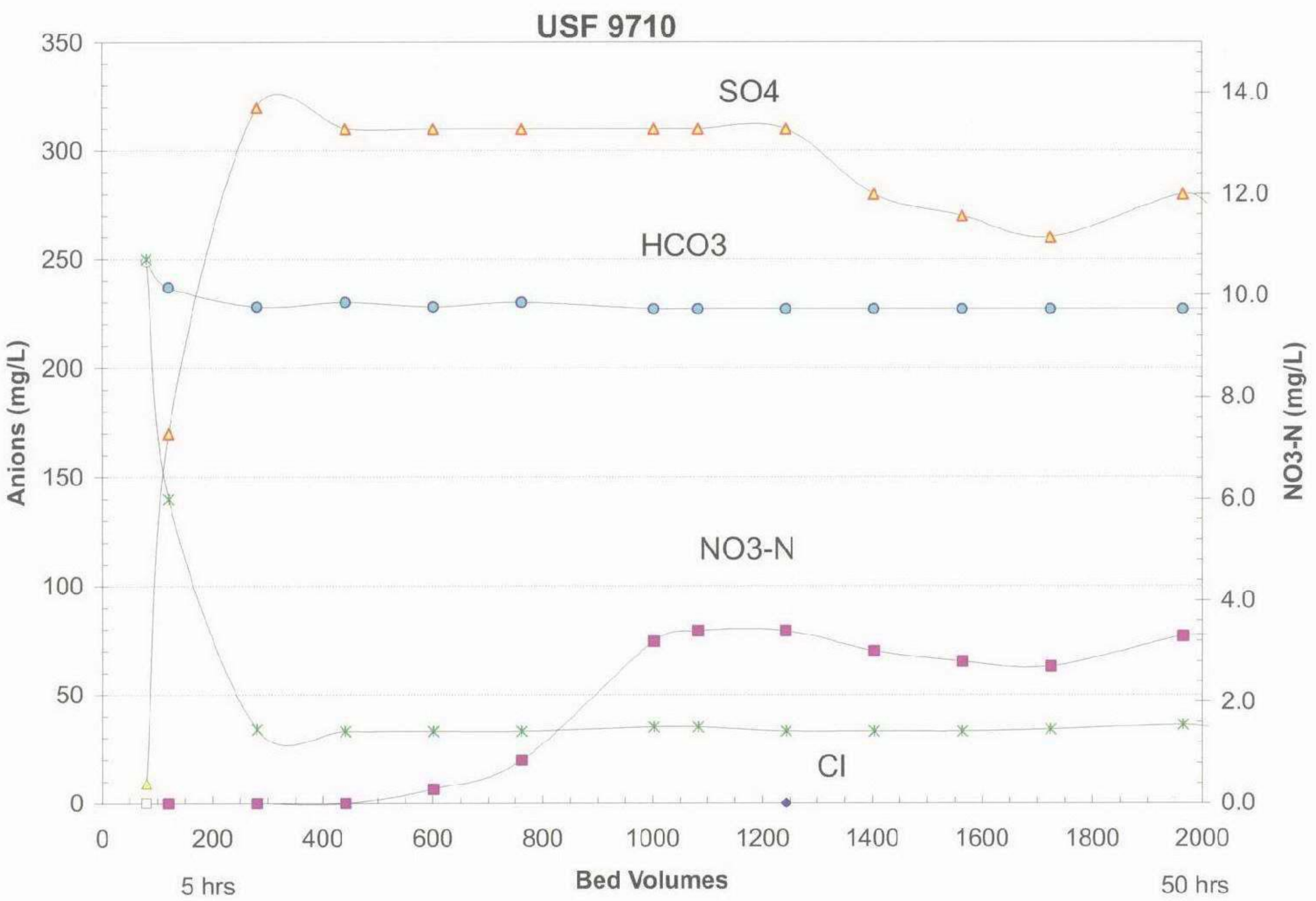
BREAKTHROUGH OF MAJOR ANIONS FROM CAL 2100 SERIES RESIN IN THE FIRST 2000 BVs

FIGURE 3.12



BREAKTHROUGH OF MAJOR ANIONS FROM 9708 RESIN IN THE FIRST 2000 BVs

FIGURE 3.13



BREAKTHROUGH OF MAJOR ANIONS FROM 9710 RESIN IN THE FIRST 2000 BVs

FIGURE 3.14

7.1.5.2 Breakthrough Curves of Perchlorate and Other Anions

Perchlorate breakthrough curves for the three ion-exchange resins are illustrated in Figure 3.15. As expected, perchlorate breakthrough did not occur until several thousand bed volumes had been treated by the resin. Actual run lengths were longer than those predicted by the IX-Pro Model. Bed volumes to perchlorate breakthrough (greater than 1 μg/L) were 25,000 bed volumes (26 days), 72,000 bed volumes (75 days), and 76,000 bed volumes (79 days) for USF 9708 resin, USF 9710 resin, and CalResin 2100, respectively. The details of run lengths until perchlorate breakthrough are presented in Table 3.16.

Table 3.16 Run Lengths Until Perchlorate Breakthrough (1 μg/L)
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Resin	Bed Volumes	Treated Water Volumes (gal)	Treated Volume gal/cu-ft resin
USF 9708	25,000	145.3	187,045
USF 9710	72,000	418.5	538,735
CalResin 2100	76,000	441.7	568,600

A temporal change in raw well water quality occurred between 85,000 and 100,000 bed volumes. However, this did not seem to impact the breakthrough of anions, with the possible exception of the USF 9708 perchlorate breakthrough curve, for which a noticeable drop in perchlorate concentration was measured in the effluent during that period.

At the end of the study, a 45-hour shutdown period was simulated by shutting off the feed pump. During this period, the resins were allowed to sit in the columns containing the groundwater. Critical anions were measured immediately after the shut-down period and breakthrough curves were developed for all key anions after restarting the columns. Breakthrough curves of all major anions for USF 9710 are illustrated in Figure 3.16. An increase in chloride concentration (45 to 72 mg/L) was observed upon column restart. Similar trends were observed for USF 9708 and CalResin 2100, indicating leaching from the IX resins.

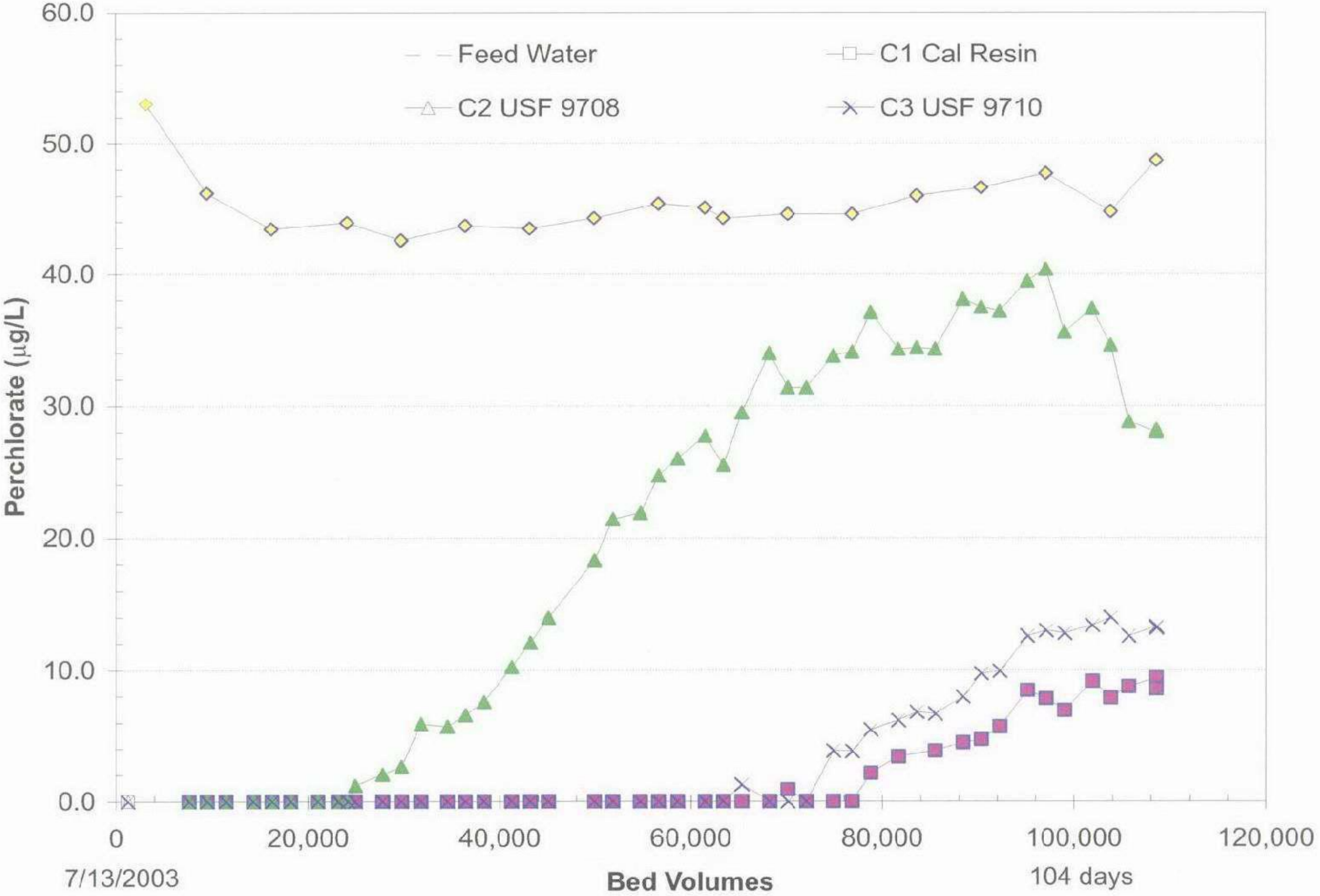
7.2 NDMA Formation Potential Testing

7.2.1 Post-Chlorination Testing

The results from the post-chlorination testing with free chlorine are plotted in Figure 3.17. Free chlorine residuals ranged from 1.8 to 1.9 mg/L after 24 hours of incubation. The 2- and 24-hour NDMA concentrations in all three ion-exchange column effluents were below the 2 ng/L detection limit. Therefore, precursors did not leach from the resin to form NDMA upon post-chlorination with free chlorine.

The results from the post-chlorination testing with combined chlorine are plotted in Figure 3.18. Total chlorine residuals ranged from 1.6 to 2.2 mg/L after 24 hours of

20-CLWA204F3.15-6625A10.CDR



COMPARISON OF PERCHLORATE BREAKTHROUGH CURVES

FIGURE 3.15

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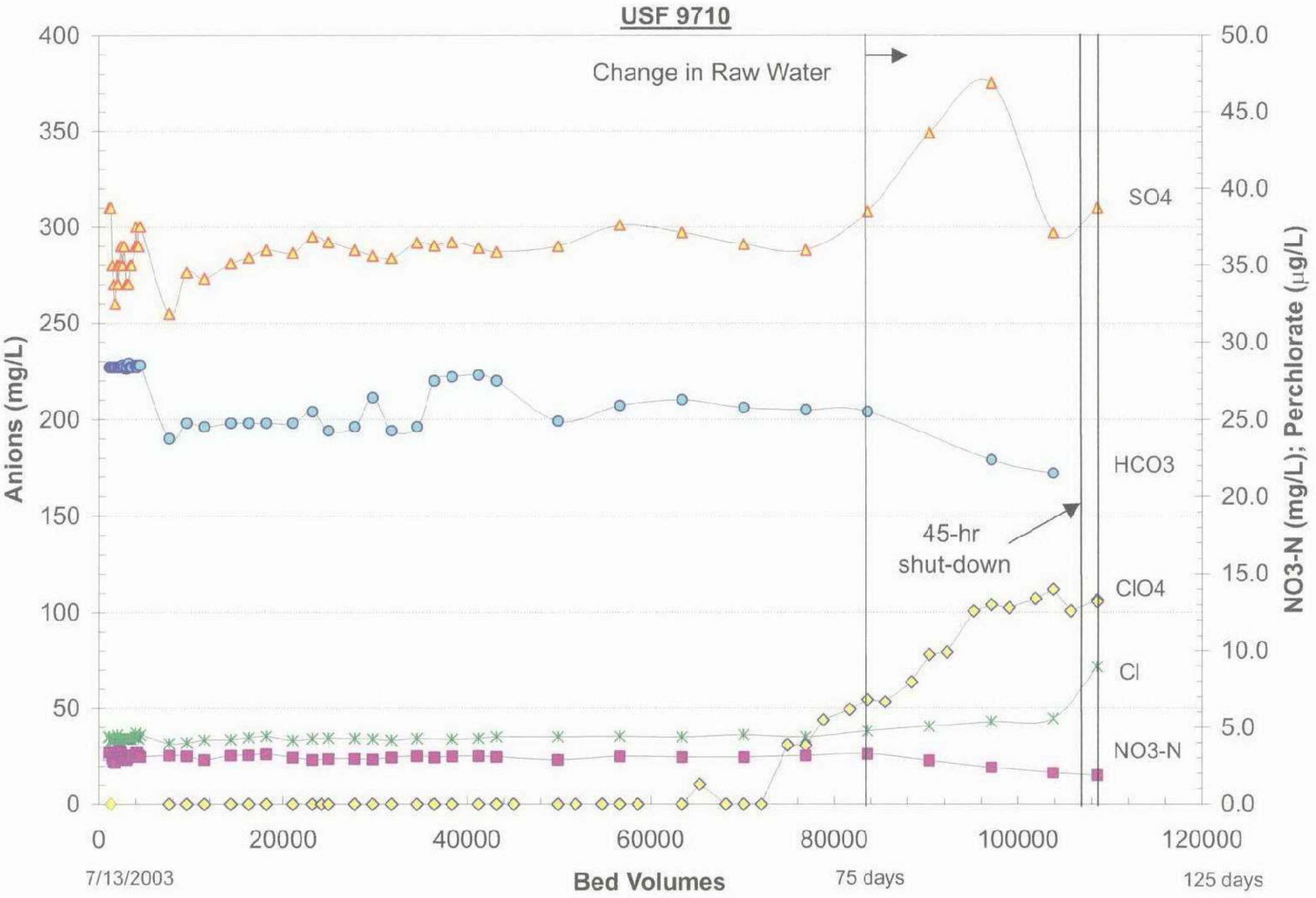
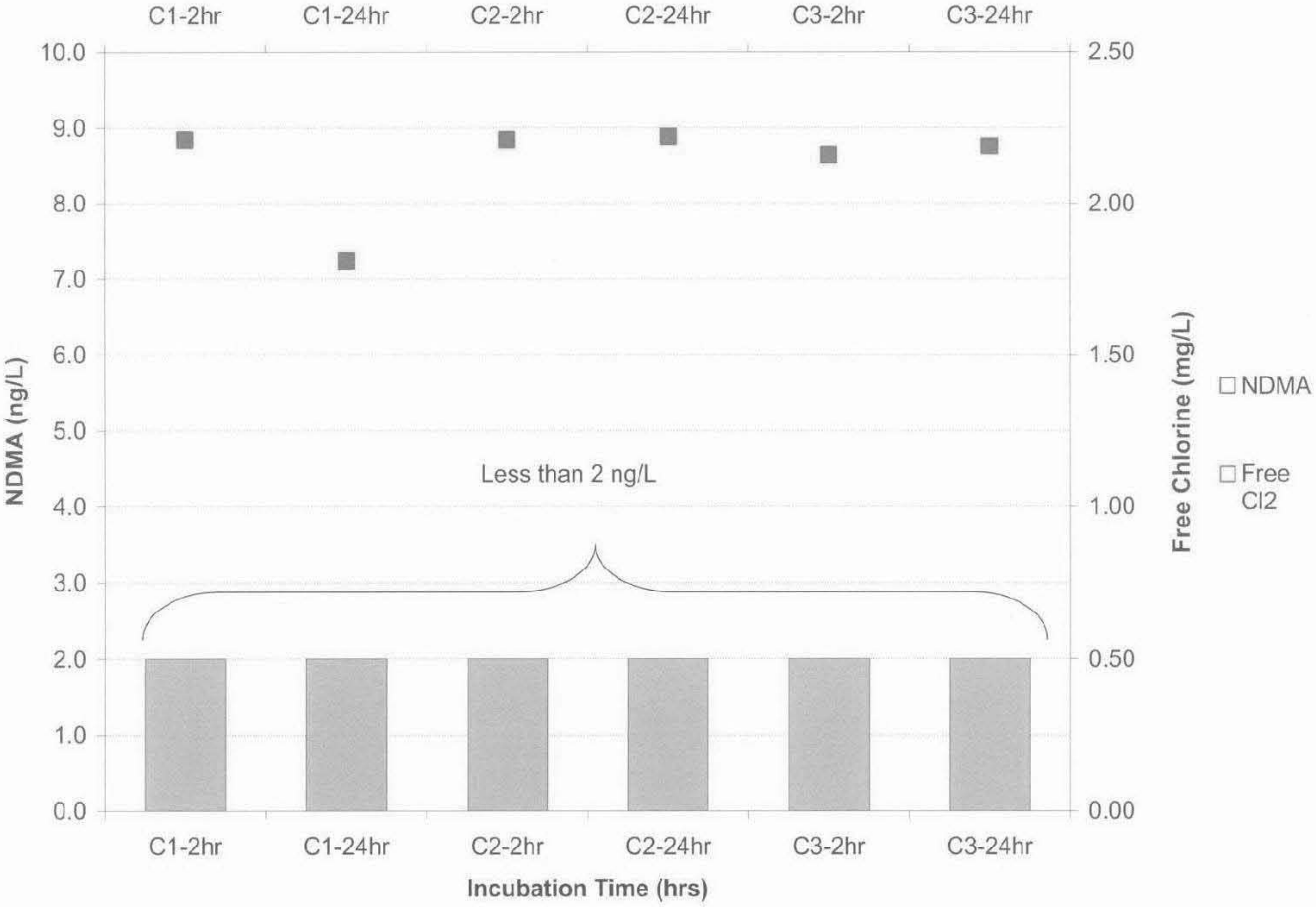


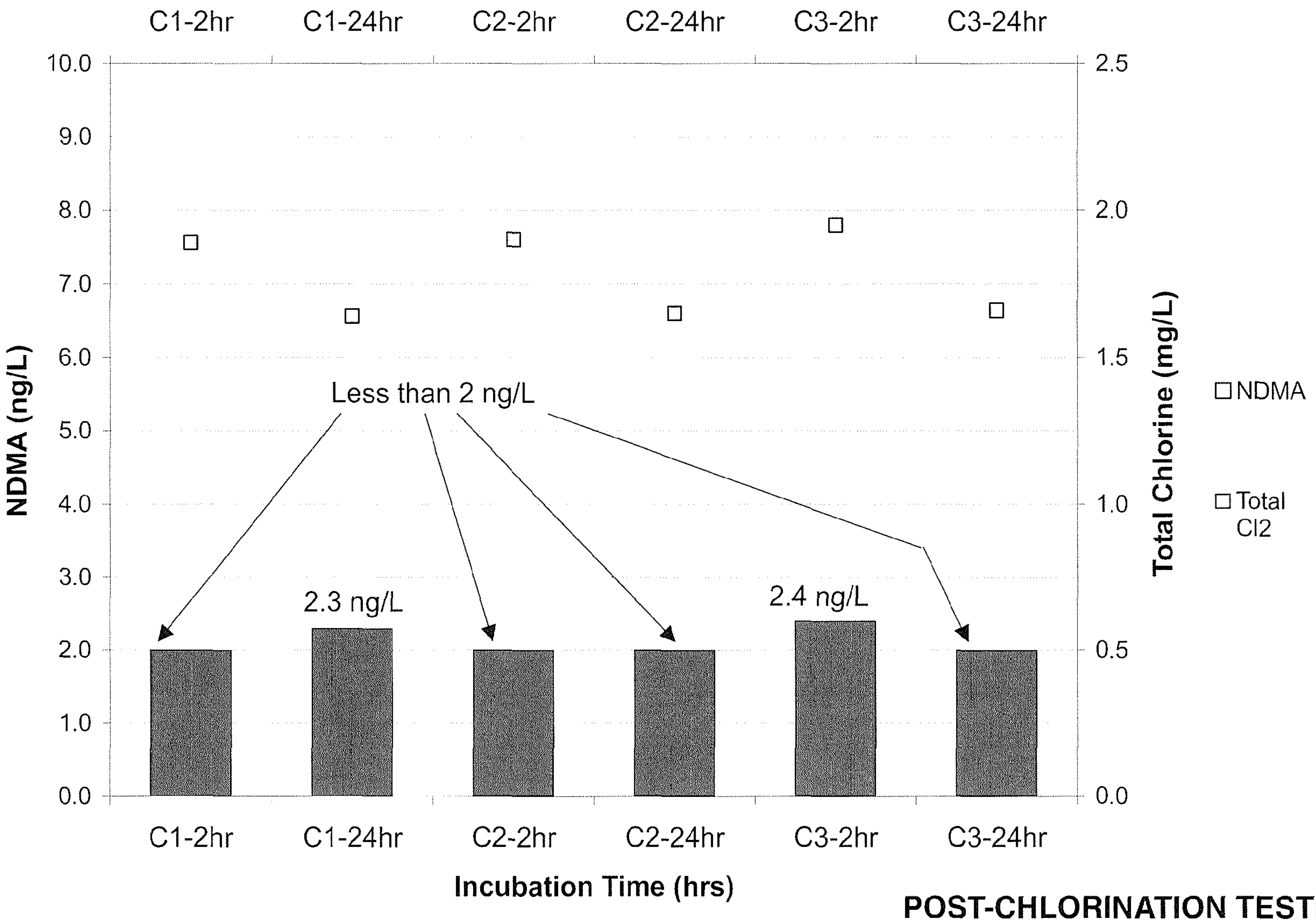
BREAKTHROUGH OF CRITICAL ANIONS FROM USF 9710

FIGURE 3.16



POST-CHLORINATION TESTING WITH FREE CHLORINE NDMA RESULTS

FIGURE 3.17



POST-CHLORINATION TESTING WITH COMBINED CHLORINE NDMA RESULTS

FIGURE 3.18

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incubation. The 2- and 24-hour NDMA concentrations in all three ion-exchange column effluents were below or just above the detection limit of 2 ng/L.

7.2.2 Pre-Chlorination Testing

To test the effect of prechlorinated water on the resins, chlorinated feedwater was allowed to run through the columns for a period of 2 hours. After that time, samples were collected and analyzed for NDMA. No detectable free chlorine residual was measured at the column effluents. This experiment was repeated four days later by adding a second 2 mg/L dose of free chlorine (duplicate samples). NDMA results are plotted in Figure 3.19. Measured levels were below or just over the detectable limit of 2 ng/L. The NDMA concentration in the feedwater (control sample) was non-detect.

7.2.3 Fresh Resin Batch Testing

Each resin was tested to determine if leaching of NDMA occurred from precursors in the resin functional sites. These results are plotted in Figure 3.20. Although NDMA was detected in one sample (CalResin), the result was less than half the current Action Level of 10 ng/L.

7.3 Spent Resin Characterization

7.3.1 Lab Results

Table 3.17 presents the Federal Toxicity Characteristic Leaching Procedure (TCLP) toxicity limits, TTLC, and STLC threshold values defined in the California Code of Regulations, Title 22, Chapter 11, Article 3, Section 66261.24, as well as the results from the actual TTLC metal concentrations measured in the three ion-exchange spent resins. TTLC results indicate the total bulk amount of each constituent per unit mass of solid waste. If the TTLC (or bulk) content is low, then the solid waste when subjected to leaching tests (STLC, TCLP) does not produce significant amounts of contaminants in the leachate. Since TTLC results are very low, there would not be any problem with the STLC or TCLP. These soluble limits, however, are listed in the table for comparison.

Most values for the TTLC analysis were non-detect. Chromium, vanadium, and zinc were detected in USF 9708 and USF 9710 spent resins at levels just above minimum reporting limits, but these values are several orders of magnitude below the regulatory TTLC threshold concentrations. Given that the TTLC metal concentrations were 10 times lower than the STLC limits, no further metals analysis for STLC was needed.

Due to the limited quantity of resin samples, TTLC for uranium, which required separate analysis, was not performed by the lab. However, projected total amount of uranium was calculated to be well below the regulatory limit (see Table 3.21). The leachate from spent resins was further analyzed for perchlorate, nitrate, and uranium (Table 3.18). Uranium levels in the spent resin leachate were significantly below the drinking water Title 22 maximum contaminant limit of 20 pCi/L.

Table 3.17 Comparison of TTLC Metals in Spent Resins to Federal and State Toxicity Limits
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

	Actual TTLC Metals Concentrations Measured in Spent Resins (mg/kg)			Federal and State Regulatory Limits		
Contaminant	**Cal 2100 Series**	**USF 9708**	**USF 9710**	**TTLC Threshold Concentration (mg/kg)**	**STLC Threshold Concentration (mg/L)**	**TCLP Regulatory Level (mg/L)**
Antimony	<4	<4	<4	500	15	
Arsenic	<0.5	<0.5	<0.5	500	5.0	5.0
Barium	<0.3	<0.3	<0.3	10,000	100	100.0
Beryllium	<0.2	<0.2	<0.2	75	0.75	
Cadmium	<0.2	<0.2	<0.2	100	1.0	1.0
Chromium	<0.3	**0.4**	<0.3	2,500	5	5.0
Chromium VI				500	5	
Cobalt	<1	<1	<1	8,000	80	
Copper	<4	<4	<4	2,500	25	
Lead	<10	<10	<10	1,000	5.0	5.0
Mercury	<0.05	<0.05	<0.05	20	0.2	0.2
Molybdenum	<2	<2	<2	3,500	350	
Nickel	<2	<2	<2	2,000	20	
Selenium	<3	<3	<3	100	1.0	1.0
Thallium	<0.2	<0.2	<0.2	700	7.0	
Vanadium	<0.5	**0.6**	<0.5	2,400	24	
Zinc	<4	<4	**7.8**	5,000	250	

Table 3.18 Comparison of Perchlorate, Nitrate and Uranium in Spent Resins Leachates
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

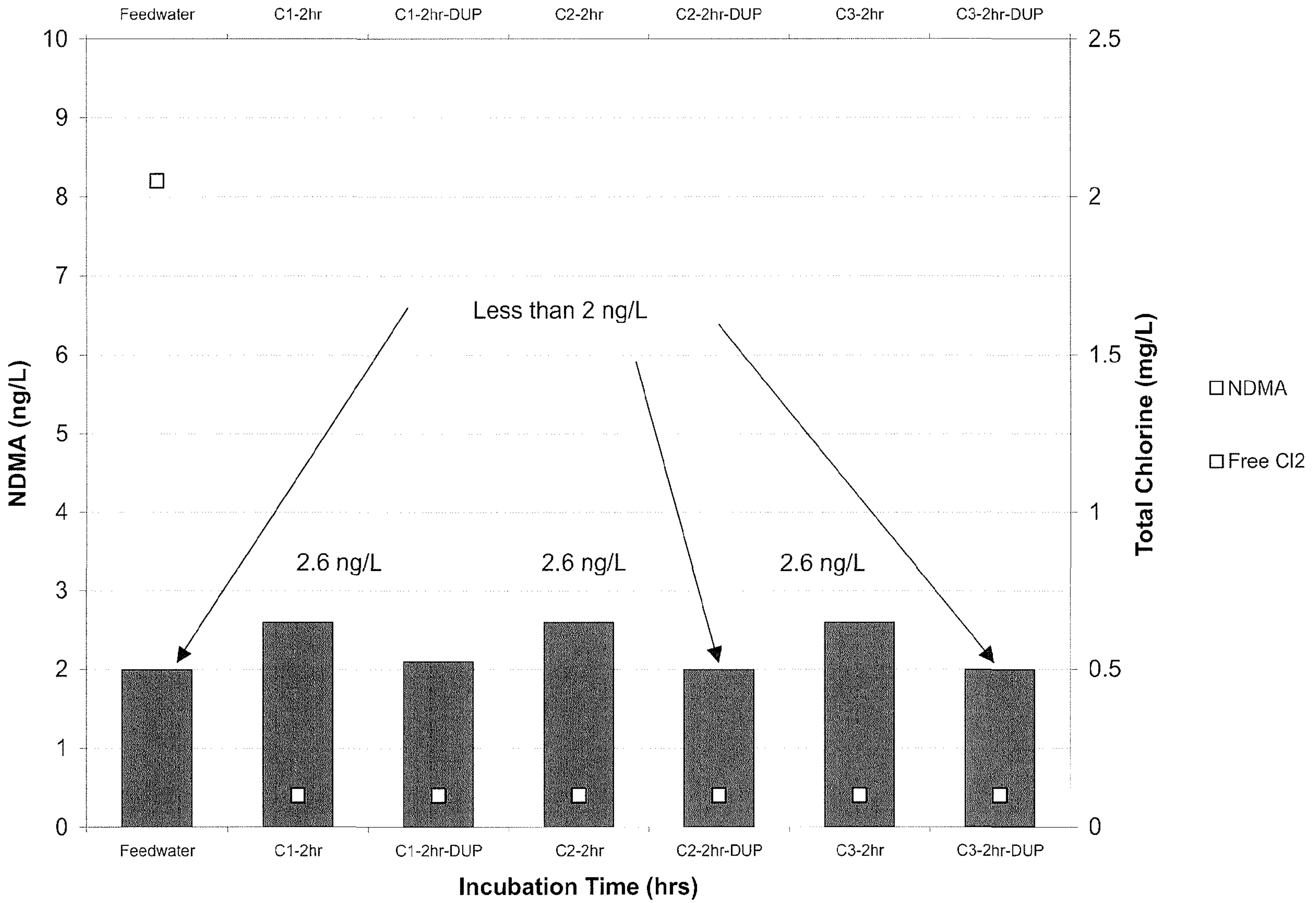
Contaminant	Cal 2100 Series	USF 9708	USF 9710	CA-T22 MCL	DHS Action Level
Perchlorate (μg/L)	< 4,000	< 4,000	< 4,000	—	4
Nitrate-N (mg/L)	21	19	22	10	—
Uranium (pCi/L)	3.0 ± 0.307	7.35 ± 0.752	4.06 ± 0.419	20	—

Table 3.19 Radionuclides Reportable Quantities (Table 2 of Appendix A under CERCLA)
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Radionuclide	Atomic Number	RQ (Ci)
Uranium 230	92	1
Uranium 231	92	1,000
Uranium 232	92	0.01
Uranium 233	92	0.1
Uranium 234	92	0.1
Uranium 235	92	0.1
Uranium 236	92	0.1
Uranium 237	92	100
Uranium 238	92	0.1
Uranium 239	92	1000
Uranium 240	92	1000

7.3.2 Uranium Accumulation

To further assess any challenges of transporting spent resins from the treatment plant to an incineration facility, a mass balance was performed to calculate the amount of uranium accumulated on the resins for comparison to the Department of Transportation's (DOT's) reportable quantities (which define whether or not a substance is hazardous) and A-Values (values used during shipping of hazardous substances).



POST-CHLORINATION TESTING NDMA RESULTS

FIGURE 3.19

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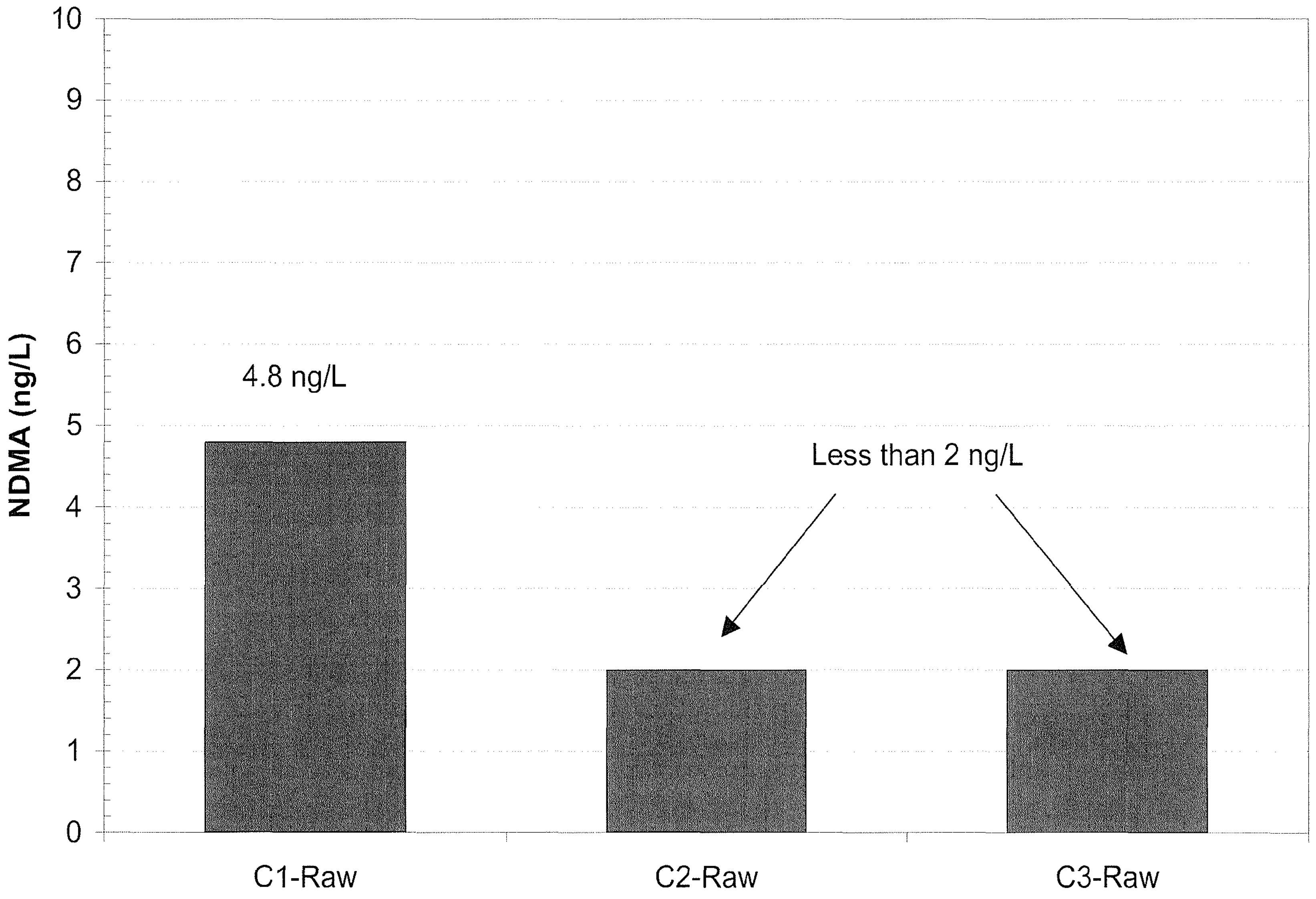

RESIN LEACH TEST RESULTS

FIGURE 3.20

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According to DOT's Hazardous Materials Regulations, 49 Code of Regulation SubChapter C (Hazardous Materials Regulations), subpart §171.8 (Definitions), a hazardous substance means a material, including its mixtures and solutions, that:

1. Is listed in the Appendix A to subpart §172.101 of the subchapter (Purpose and use of hazardous materials table).
2. Is in a quantity, in one package, which equals or exceeds the reportable quantity (RQ) listed in the Appendix A to §172.101 of the subchapter.

Appendix A lists materials and their corresponding RQs that are listed or designated as "hazardous substances" under section 101(14) of the Comprehensive Environmental Response, Compensation, and Liability Act, 42 U.S.C. 9601(14) (CERCLA; 42 U.S.C. 9601 et seq). Table 2 of Appendix A lists radionuclides that are hazardous substances and their corresponding RQs. *The RQs in Table 2 for radionuclides are expressed in units of curies,* and are shown in Table 3.20.

Table 3.20 A1 and A2 Values for Radionuclides- Shipments
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Radionuclide	Atomic Number	A1 (Ci)	A2 (Ci)	Specific Activity (Ci/g)
Uranium 230	92	1,080	0.270	27,000
Uranium 232	92	81.1	0.00811	22
Uranium 233	92	270	0.027	9,700
Uranium 234	92	270	0.027	6,200
Uranium 235	92	Unlimited	Unlimited	0.0000022
Uranium 236	92	270	0.027	0.000065
Uranium 238	92	Unlimited	Unlimited	0.00000034
Uranium Natural	92	Unlimited	Unlimited	0.00000071

As far as transportation of hazardous substances, in Part 173 (Shippers- General Requirements for Shipments and Packaging), Subpart § 173.435, the values of A1 and A2 for radionuclides are defined. A1 means the maximum activity of special form Class 7 (radioactive) material permitted in a Type A package. A2 means the maximum activity of Class 7 (radioactive) material, other than special form, Low-Specific Activity (LSA) or Surface Contaminated Object (SCO), permitted in a Type A package, see Table 3.21.

Table 3.21 Calculated Accumulated Amount of Uranium on the Spent Resins
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Resin	Days Until 50% ClO_4^- Breakthrough	Projected Uranium Accumulation (Ci)	Lowest RQ (Ci)	Lowest A Value (Ci)
Cal Resin	146(1)	1.6E-09	0.01	0.027
USF 9708	60	3.1E-09	0.01	0.027
USF 9710	138(1)	1.2E-09	0.01	0.027

Note:
(1) Extrapolated from perchlorate breakthrough plots

A mass balance of the uranium adsorbed and desorbed from each of the three resins up to 50 percent perchlorate breakthrough was performed based on an influent concentration range of 1.0 to 3.9 pCi/L and measured effluent uranium concentrations from each of the columns. The amount of uranium accumulated on the resins through 50 percent perchlorate breakthrough was calculated and is presented in Table 3.21. Accumulated uranium is far below the lowest permissible reporting quantity and A-value. The resins are thus not classified as hazardous and their transportation and disposal to an incineration facility should not pose a challenge to CLWA.

7.4 Summary of Ion-Exchange Testing Results

7.4.1 Feed Water Quality

The feed water is low in organic matter, has moderate hardness and alkalinity, and contains moderate levels of iron and bromide. The raw water quality was stable over the testing period with the exception of the month of October 2003, during which period pumping rates at the NC-12 well were temporarily reduced, causing a decrease in nitrate concentration, and increases in sulfate and chloride concentrations.

7.4.2 Operational Data

The flow rate ranged from 13.5 to16.5 mg/L during the course of the study, which resulted in EBCTs of 1.4 to 1.6 minutes (the target was 1.5 min).The pressure drop across the column remained constant at 5 psi during most of the project. The water temperature ranged from 32 degrees C (89 degrees F) in the summer months to 16 degrees C (61 degrees F) in the fall. pH ranged from 7.6 to 8.4.

7.4.3 Focused Breakthrough Curves of Nitrate, Sulfate, Chloride, and Bicarbonate

The breakthrough of most anions (with the exception of perchlorate) occurred in the first 24 hours of run time. Bicarbonate broke through immediately, followed by sulfate at 80 bed volumes. Nitrate broke through after 280 bed volumes, 440 bed volumes, and 600 bed volumes from USF 9708, USF 9710, and Cal 2100 resins, respectively. No chromatographic peaking was observed for any of the critical anions. Chloride level dropped from a high of approximately 325 mg/L to background concentrations (~35 mg/L) after 280 bed volumes.

7.4.4 Long-Term Breakthrough Curves of Perchlorate and Other Anions

Bed volumes to reach perchlorate breakthrough (greater than 1 μg/L) were 25,000 (26 days), 72,000 (75 days), and 76,000 (79 days) for USF 9708 resin, USF 9710 resin, and CalResin 2100, respectively. This translates in treated water volumes of 187,000 gal/ft^3, 540, 000 gal/ft^3, and 569,000 gal/ft^3, respectively. A small increase in chloride concentration was observed after a simulated 45-hour shutdown period, likely due to leaching from the resin.

7.4.5 NDMA Results

The results from the post-chlorination testing with free chlorine (residual of 1.8 to 2.2 mg/L after 24 hours) and with combined chlorine (residual of 1.6 to 1.9 mg/L after 24 hrs) showed that NDMA concentrations in all three ion-exchange column effluents after 2- and 24-hour incubation times were below the detection limit of 2 ng/L. Therefore NDMA precursors did not leach from the resin .

To investigate the formation potential of NDMA upon the reaction of chlorine with DBP precursors in the water or leaching from the resin, a 2-mg/L free chlorine dose was added directly to the feed water. Measured NDMA levels were below or just over the detectable limit of 2 ng/L.

To evaluate the NDMA precursor leaching potential of the resins, 100 mL batches of fresh resin were incubated for four hours in deionized water and groundwater. NDMA was detected in only one sample, which measured at less than half the 10 ng/L Action Level.

7.4.6 Spent Resin Characterization

The California TTLC metal concentration values were mostly non-detect in all three spent resins. Chromium, vanadium, and zinc were detected in USF 9708 and USF 9710 spent resins at levels significantly below the regulatory TTLC threshold concentrations. Uranium levels in the spent resin leachate were significantly below the Title 22 MCL of 20 pCi/L. To investigate whether the spent resins would be classified as hazardous for transportation to an incineration facility, a mass balance of the uranium adsorbed and desorbed from the resin up to 50 percent perchlorate breakthrough was performed. The amount of uranium accumulated on the spent resins is far below the lowest permissible reporting quantity and A-value of the California DOT.

7.5 Fixed-Bed Filter

7.5.1 Biological Acclimation

Figure 3.21 shows FXB perchlorate removal performance during the biological acclimation and optimization phases[1]. Perchlorate was initially removed by adsorption onto the virgin GAC, and began to break through after 12 days as the carbon's adsorption capacity diminished. These data are consistent with other perchlorate/GAC breakthrough curves reported in the literature (Na et al., 2002, Brown et.al, 2002). During the subsequent month of biological acclimation, run times were less than 24 hours due to rapid headloss development in the filter. The pilot feed lines were experiencing heavy biological growth, and the biofilm from the feedlines would occasionally detach and clog the bed. The acetic acid feed concentration was lowered during the acclimation phase (Figure 3.22) to minimize growth. However, excessive biogrowth in the feed lines continued to generate rapid headloss build-up. Phosphoric acid was added at 0.2 mg/L PO_4-P to select away from filamentous organisms suspected of causing the overgrowth and clogging problems. Simultaneously, the electron donor feed was repositioned so that acetic acid was fed directly to the top of the filter column instead of upstream of the static mixer, thus minimizing biofilm growth in the feed line. Consequently, biogrowth was isolated to the filter bed, headloss development rates decreased, and 48-hour run times were achieved. Within 10 days of adding phosphoric acid and repositioning the acetic acid feed, steady perchlorate removal to below detection was achieved in the filter. The phosphoric acid feed was removed during the optimization tests without affecting perchlorate removal performance, indicating that phosphorous in the natural water did not limit biological activity in the filter. Therefore, repositioning the acetic acid feed was likely the key to effectively acclimating the FXB filter for biological perchlorate removal. If this electron donor feed configuration had been used from time zero, it is estimated that steady-state biological perchlorate removal to below detection would have required 3 to 4 weeks of operation.

7.5.2 Optimization

During the two months of piloting after the acclimation period, EBCT and acetic acid feed concentrations were optimized (Figures 3.21 and 3.22). The minimal acetic acid concentration that still allowed removal of perchlorate to below detection was 7.8 mg/L as carbon (25% excess).[2] EBCTs as low as 15 minutes allowed for the consistent, complete removal of perchlorate to below detection, although only 24-hour run times were achieved. To lengthen run times, the EBCT was increased to 20 minutes. However, short-circuiting of the filter was observed throughout this period, resulting in perchlorate breakthroughs from 20 to 65 percent. While the 15-minute EBCT operation resulted in rapid headloss development (i.e., < 24-hour run times) but no perchlorate breakthrough, the 20-minute EBCT resulted in short-circuiting and variable perchlorate breakthrough. It appears that the

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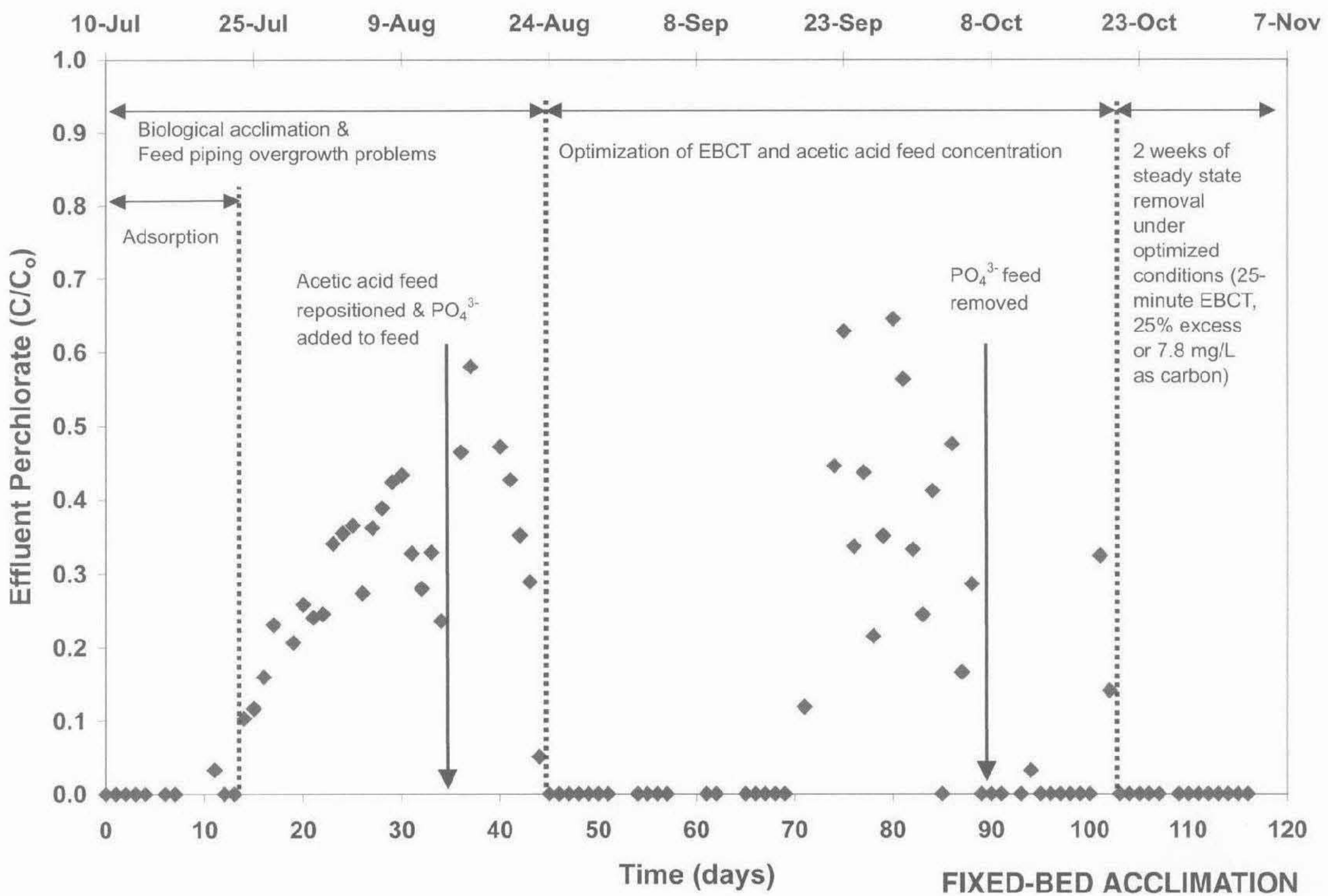
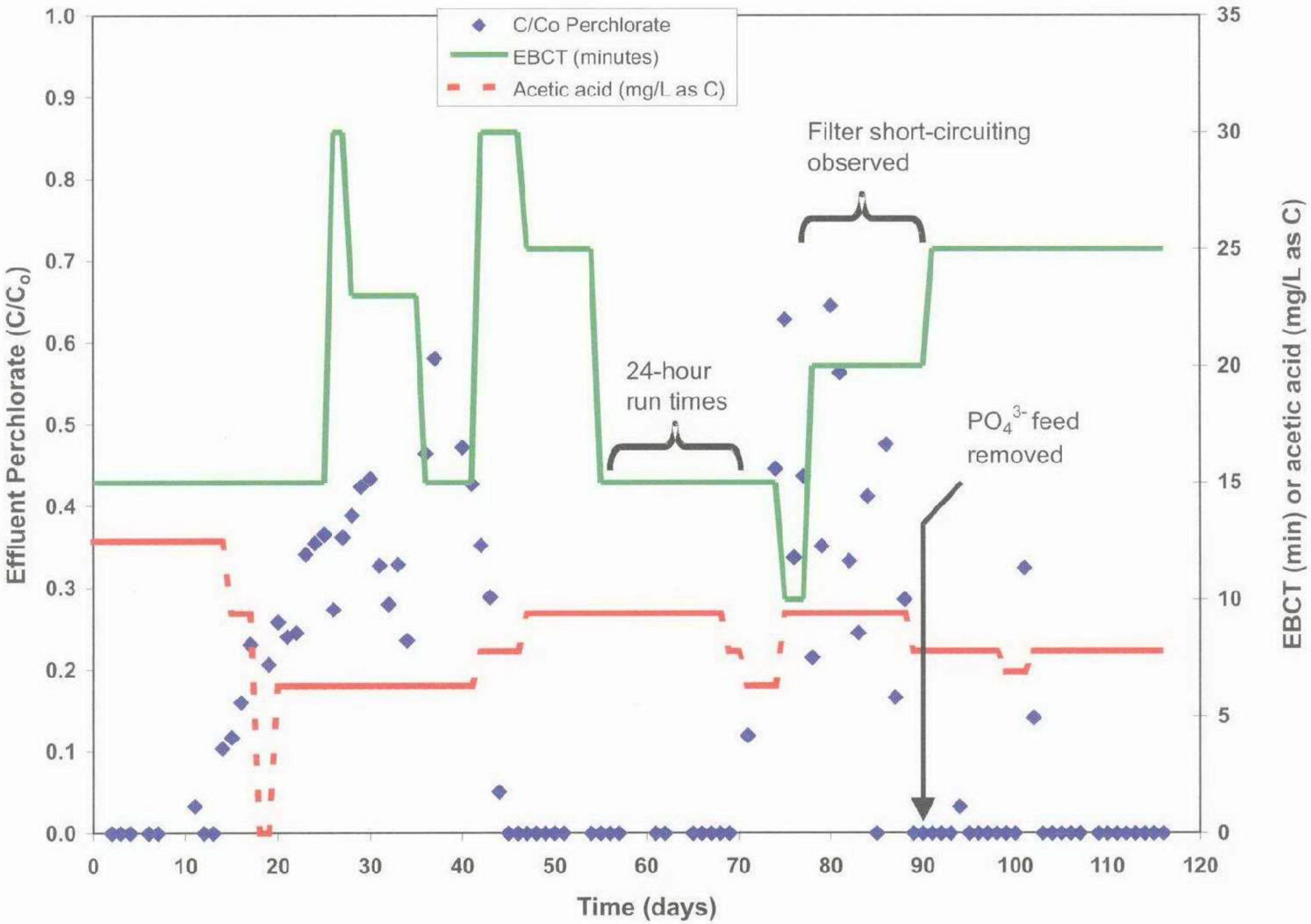
[1] All perchlorate detections (even those lower than the 4 μg/L MRL) are shown in the FXB and FBR figures.

[2] Assumes complete reduction of 7.0 mg/L of feed DO and 15 mg/L of feed nitrate.



FIXED-BED ACCLIMATION AND OPTIMIZATION

FIGURE 3.21



FIXED-BED EBCT AND ACETIC ACID SET-POINTS

FIGURE 3.22

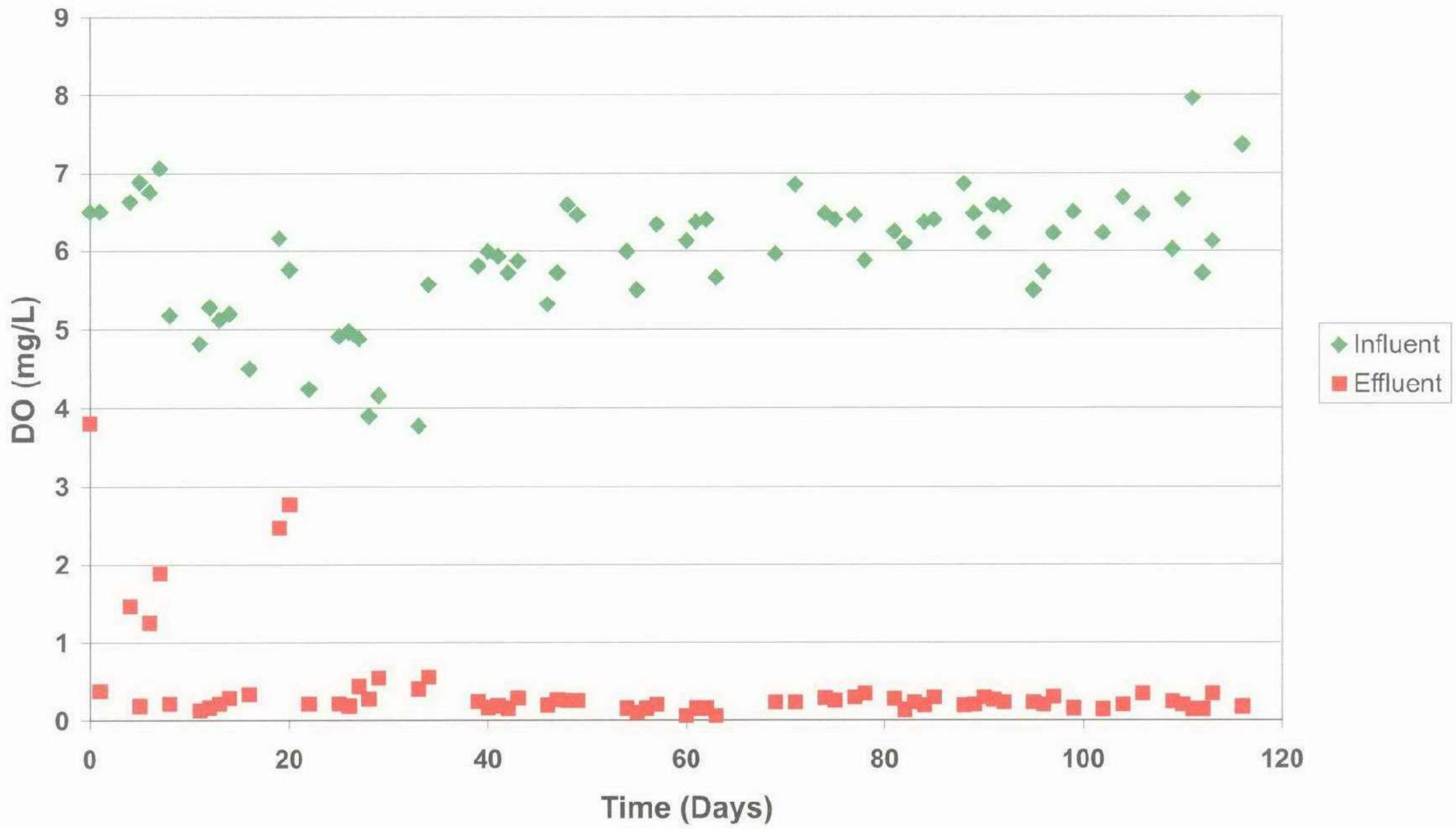
higher flow rate promoted more uniform hydraulic loading in the filter, which distributed growth evenly across the bed. Instead of passing through the filter evenly, feedwater pumped at lower flow rates followed preferential paths that produced the observed channeling. The shortest EBCT that allowed ≥ 48-hour run times while consistently removing perchlorate to below detection was 25 minutes. Though some channeling was observed under 25-minute EBCT conditions, it was less extensive than that observed during 20-minute EBCT operation. After the optimization period, the filter was run for two weeks using a 25-minute EBCT and 7.8 mg/L acetic acid carbon. Removal of perchlorate to below detection was observed throughout this period as well.

7.5.3 Dissolved Oxygen and Nitrate

All perchlorate-reducing bacteria described in the literature are facultative aerobes or microaerophiles. Thus, oxygen can inhibit biological perchlorate reduction by acting as a competing electron acceptor. Similar to oxygen, nitrate has a high redox potential that allows it to compete with perchlorate for use as an electron acceptor. Research has confirmed the occurrence of this competitive inhibition by demonstrating that DO and nitrate concentrations must be very low to achieve efficient perchlorate reduction in biological reactors (Brown et al., 2001, Herman and Frankenberger, 1999). Therefore, influent and effluent DO and nitrate concentrations were monitored closely during pilot testing.

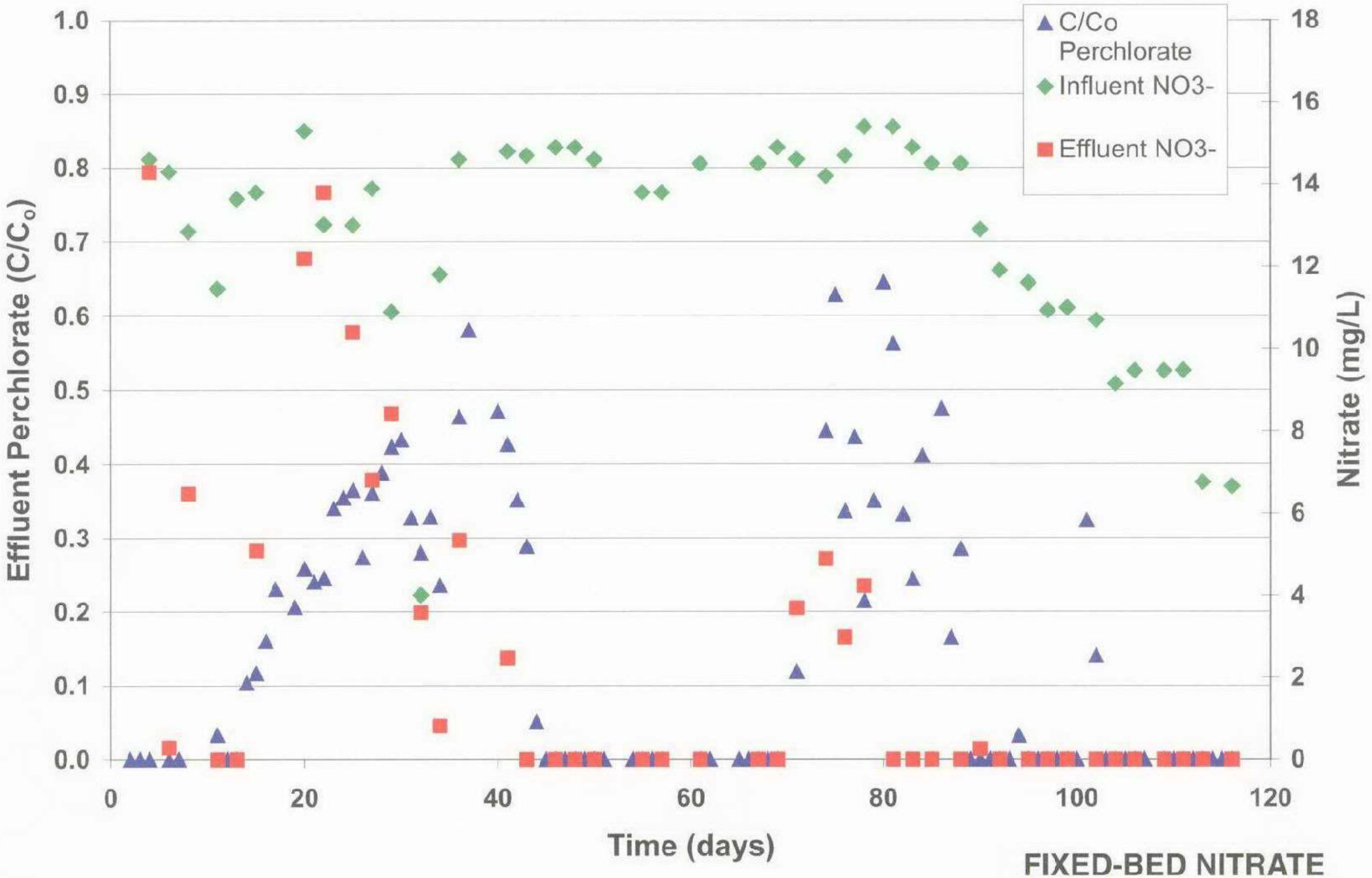
Effluent DO concentrations were generally low during the acclimation phase (Figure 3.23). DO was likely reacting with the surface of the GAC initially, and was being reduced biologically as bacteria colonized the bed. Influent DO concentrations ranged from 4 to 8 mg/L and were reduced to 0.2 percent 0.3 mg/L throughout most of the pilot testing period. While effluent DO concentrations were steady, Figure 3.24 shows that effluent nitrate concentrations were variable. It was also observed that when effluent nitrate concentrations were detected, effluent perchlorate concentrations were also detected. These data: 1) indicate that DO was preferentially reduced over nitrate, and 2) confirm that DO and nitrate inhibit biological perchlorate reduction, as has been widely reported in the literature.

Figure 3.24 also reveals that feed nitrate concentrations gradually declined to approximately 7 mg/L as NO_3 after operating for 80 days at 15 mg/L as NO_3. The decline in feed nitrate concentrations coincided with a change in the NC-12 pumping schedule. After Day 80 of pilot operation, NC-12 was no longer pumped continuously for production, but rather was turned on periodically only to produce water for pilot plant operation. The resultant decrease in NC-12 production may have caused the variable background nitrate as well as sulfate (Figure 3.27).



FIXED-BED DISSOLVED OXYGEN

FIGURE 3.23



FIXED-BED NITRATE AND PERCHLORATE

FIGURE 3.24

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7.5.4 Other Parameters

The following water quality observations were made during acclimation and optimization phases of FXB piloting:

- Effluent TOC concentrations were very low (Figure 3.25); generally non-detect (i.e, ≤ 0.7 mg/L). Effluent BDOC concentrations were non-detect (Figure 3.26). These data indicate that effluent from the FXB filter is biologically stable, and suggest that the post-treatment steps may be somewhat simplified to aeration and disinfection.
- Sulfate concentrations and pH were not significantly impacted across the filter (Figures 3.27 and 3.28, respectively). However, sulfide was occasionally detectable by smell.
- HPCs increased across the filter, resulting in counts between 70,000 and 650,000/mL (Figure 3.29).
- With the exception of two data points, total coliforms were not detected in the feed or effluent of the filter (Figure 3.30). The two detections indicated that coliforms in the feed water were partially removed across the filter. No fecal coliforms were detected.
- Average feed water turbidities were approximately 0.5 NTU. Average effluent turbidities were approximately 0.6 NTU (Figure 3.31). Average effluent particle count (>2 µm) was 99 counts/mL (Figure 3.31). The particle counter malfunctioned after 80 days of operation.
- Headloss across the filter ranged from < 2 feet to 30 feet (Figure 3.32). Under optimal operating EBCT and acetic acid conditions, headloss peaked at 25 feet, but was typically between 5 and10 feet.

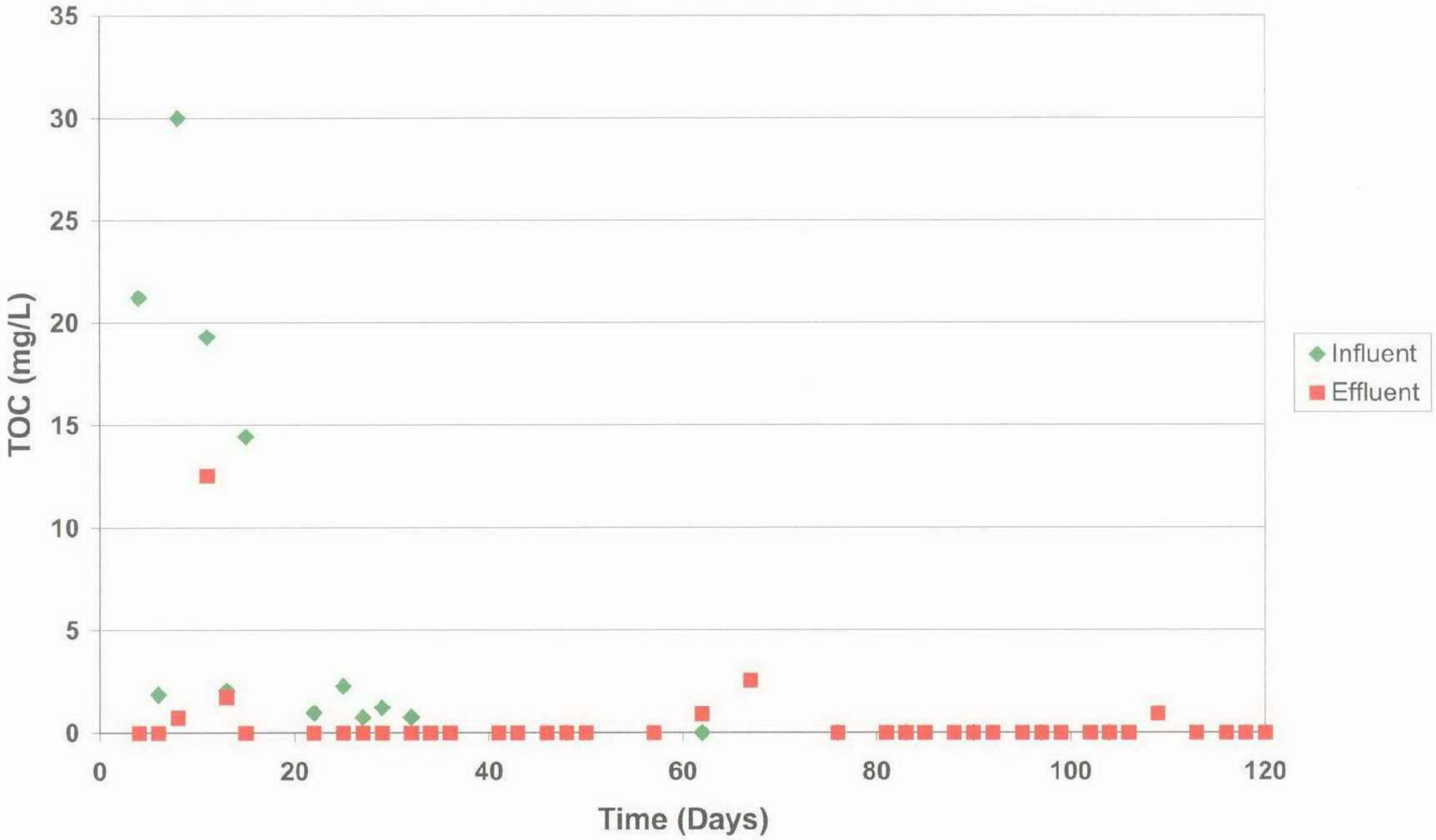
7.5.5 Robustness Characterization

7.5.5.1 Backwashing

The results of the backwash challenge tests are shown in Figure 3.33. After the filter was put back into production following a backwash event, samples were taken every 15 minutes for an hour. No perchlorate was detected. This experiment was repeated one month after the first backwash challenge test with the same result.

7.5.5.2 Perchlorate Spiking

Transient perchlorate loading episodes did not impact perchlorate removal performance in the FXB filter (Figure 3.34). The feed perchlorate concentration was varied from 50 μg/L to 100 μg/L to 50 μg/L to 300 μg/L to 5 μg/L while EBCT and feed acetic acid concentration were maintained at 25 minutes and 7.8 mg/L as carbon, respectively. No perchlorate was detected in the effluent, even for the high resolution samples (i.e., samples taken at 0, 15, 30, 45, and 60 minutes) taken immediately after the influent perchlorate concentration was changed.



FIXED-BED TOTAL ORGANIC CARBON

FIGURE 3.25

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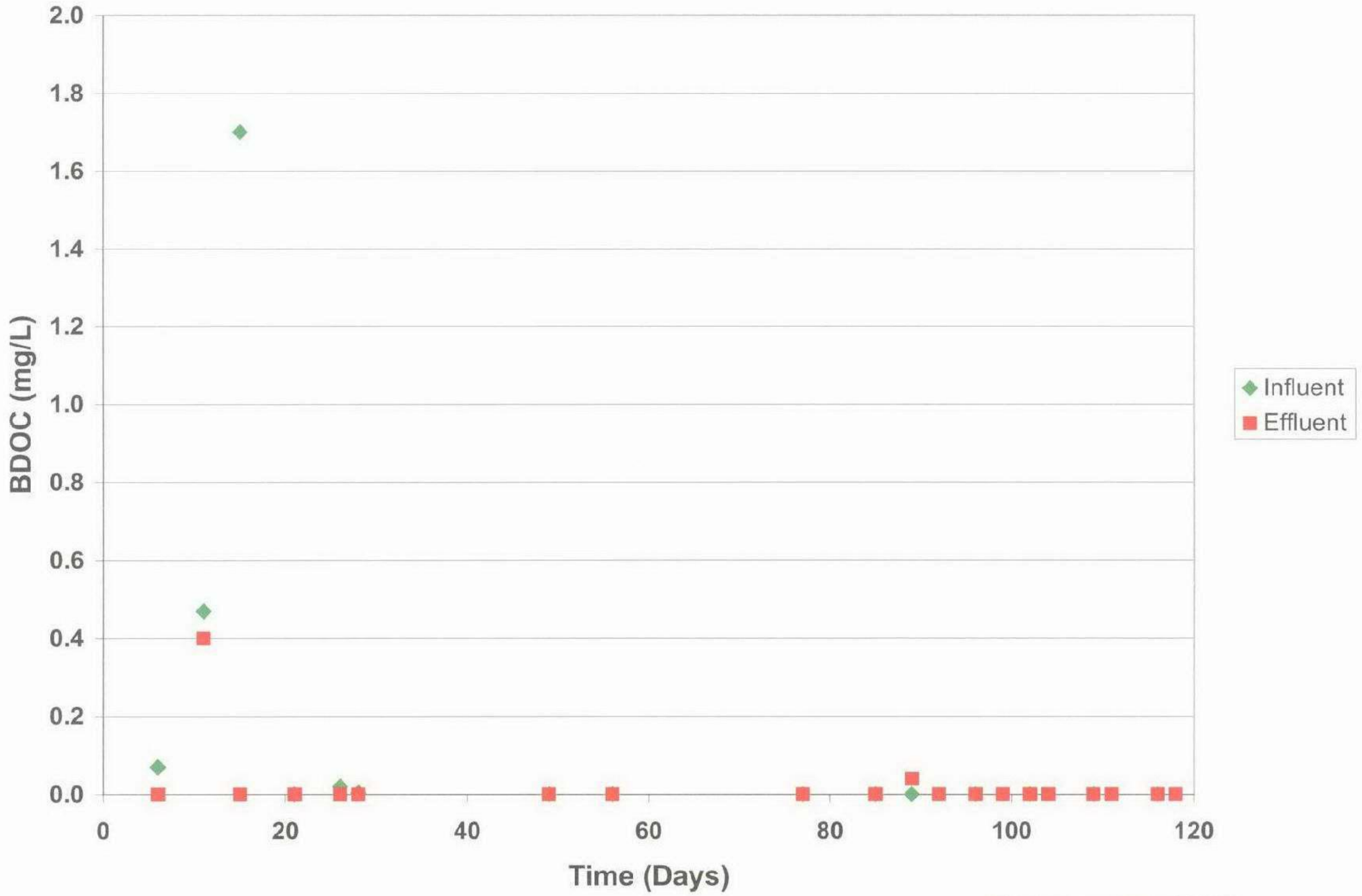
20-CLWA204F3.26-6625A10.CDR



FIXED-BED BDOC

FIGURE 3.26

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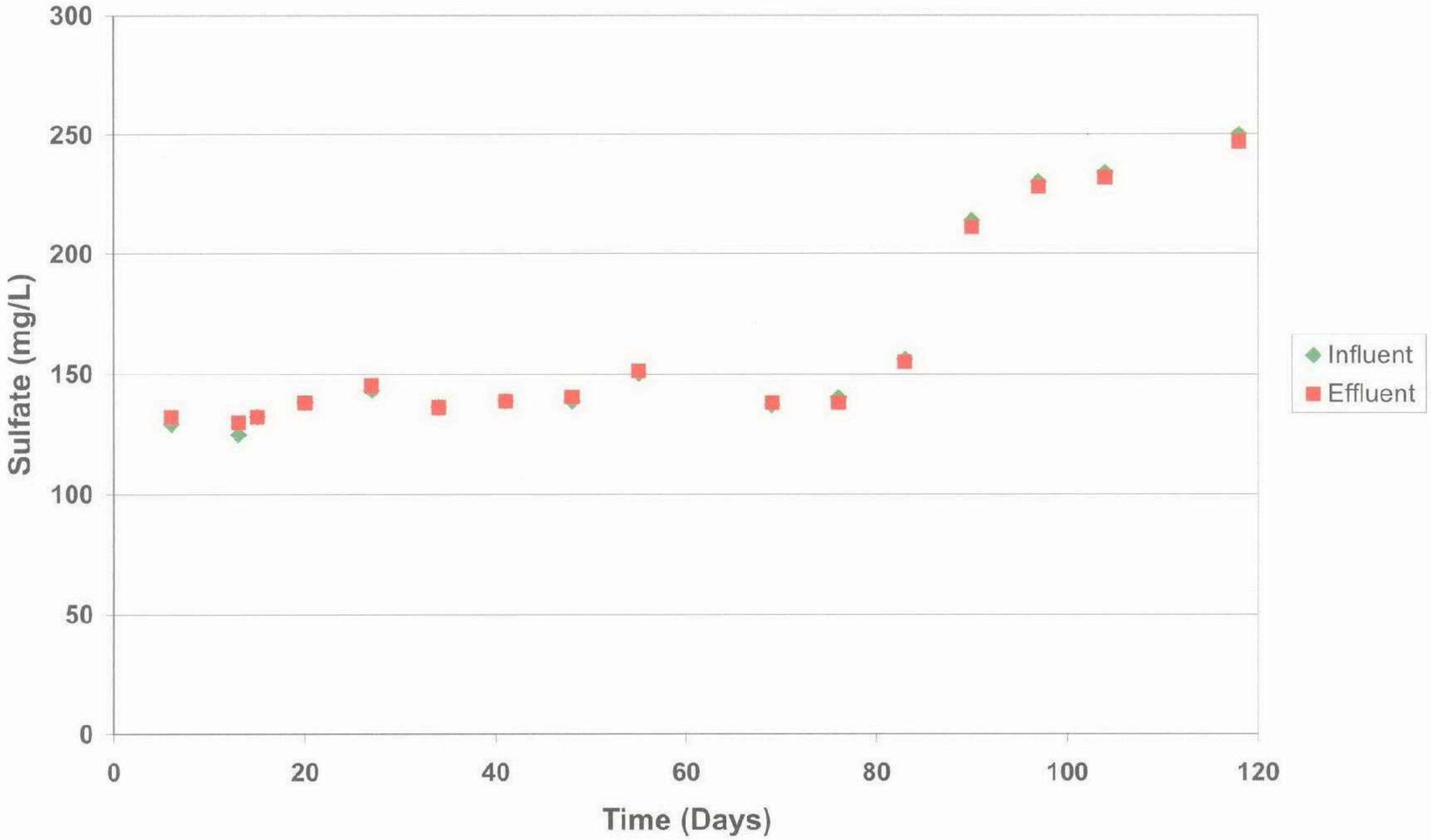
20-CLWA204F3.27-6625A10.CDR



FIXED-BED SULFATE

FIGURE 3.27

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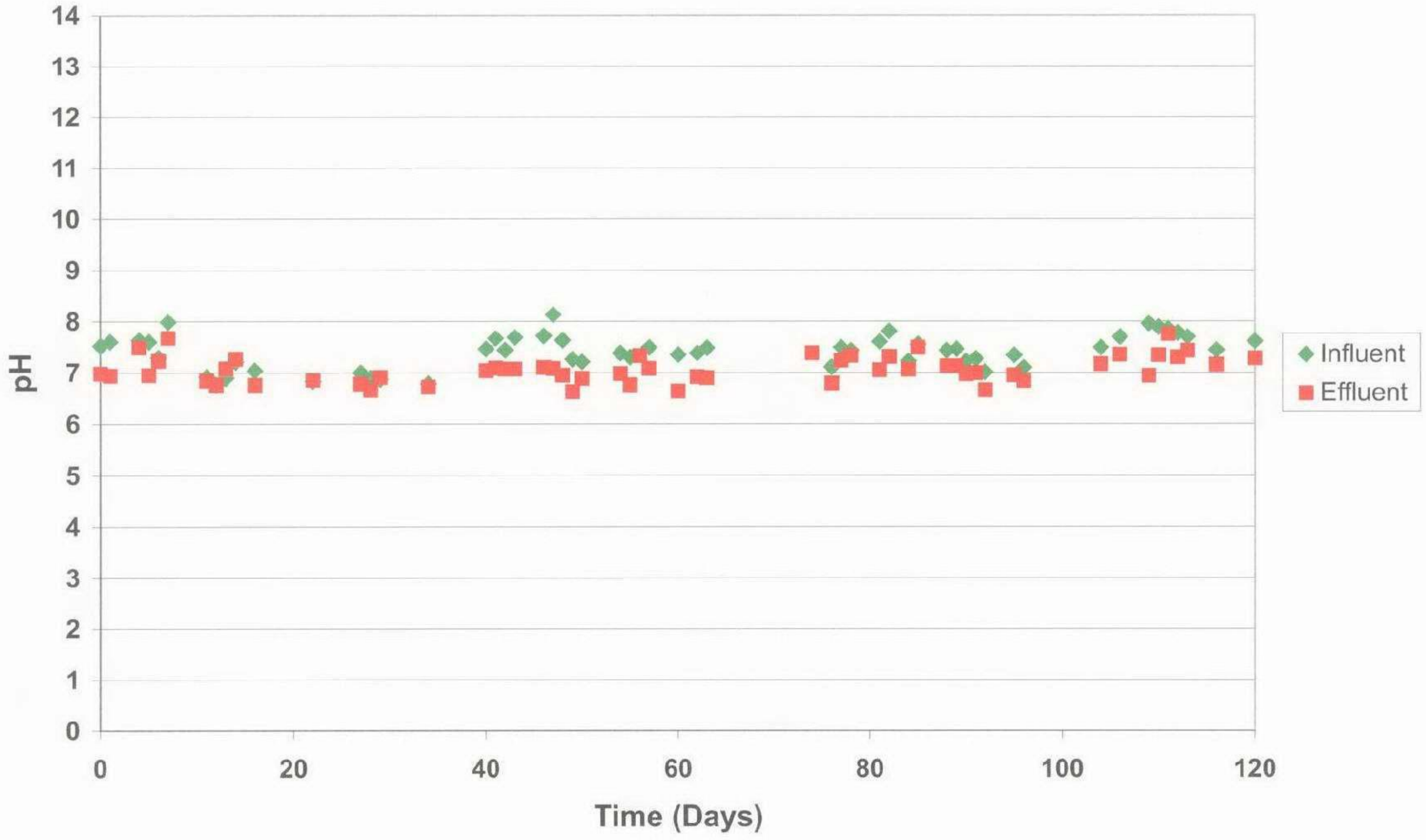

FIXED-BED pH

FIGURE 3.28

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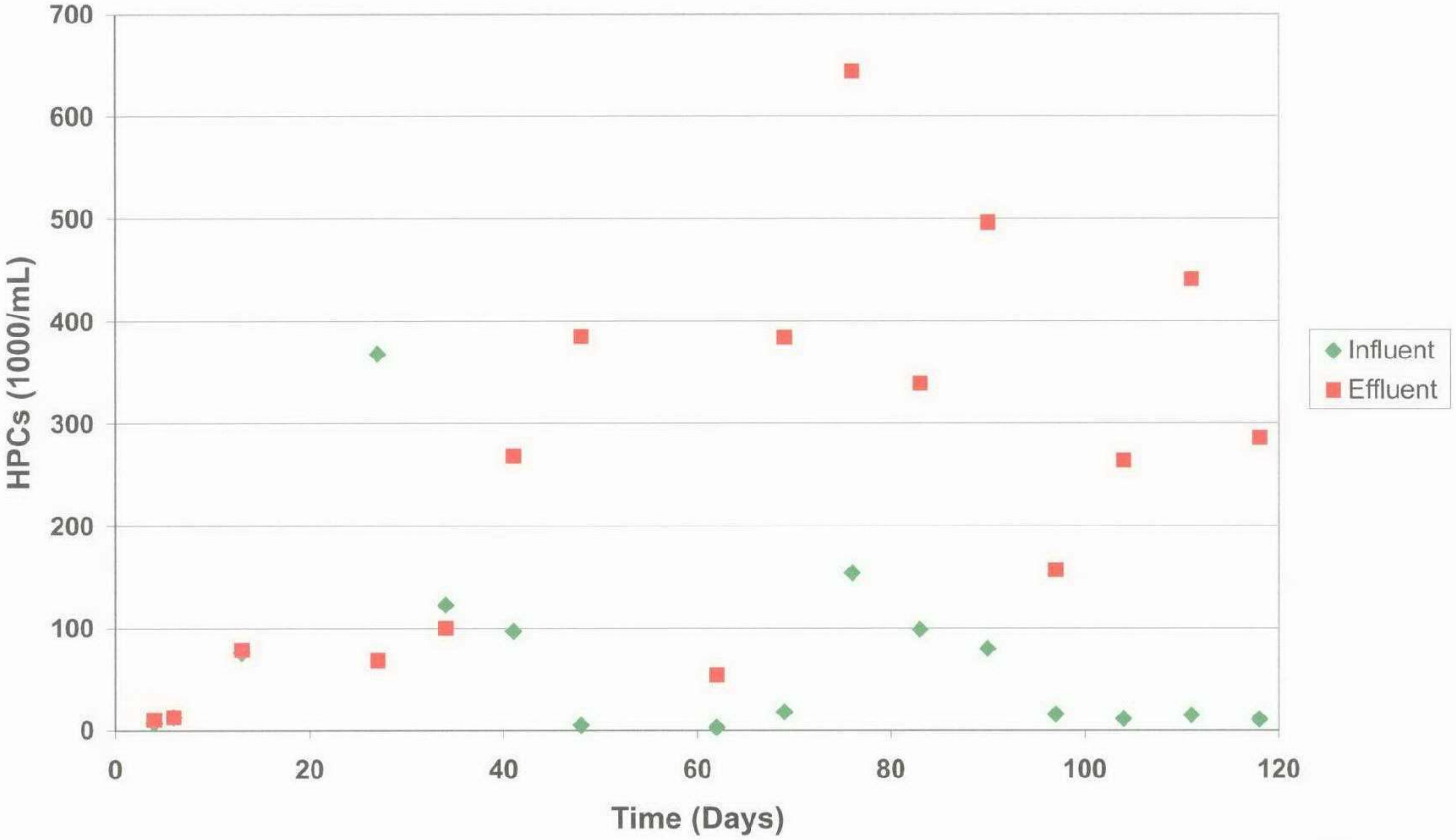

FIXED-BED HETEROTROPHIC PLATE COUNTS

FIGURE 3.29

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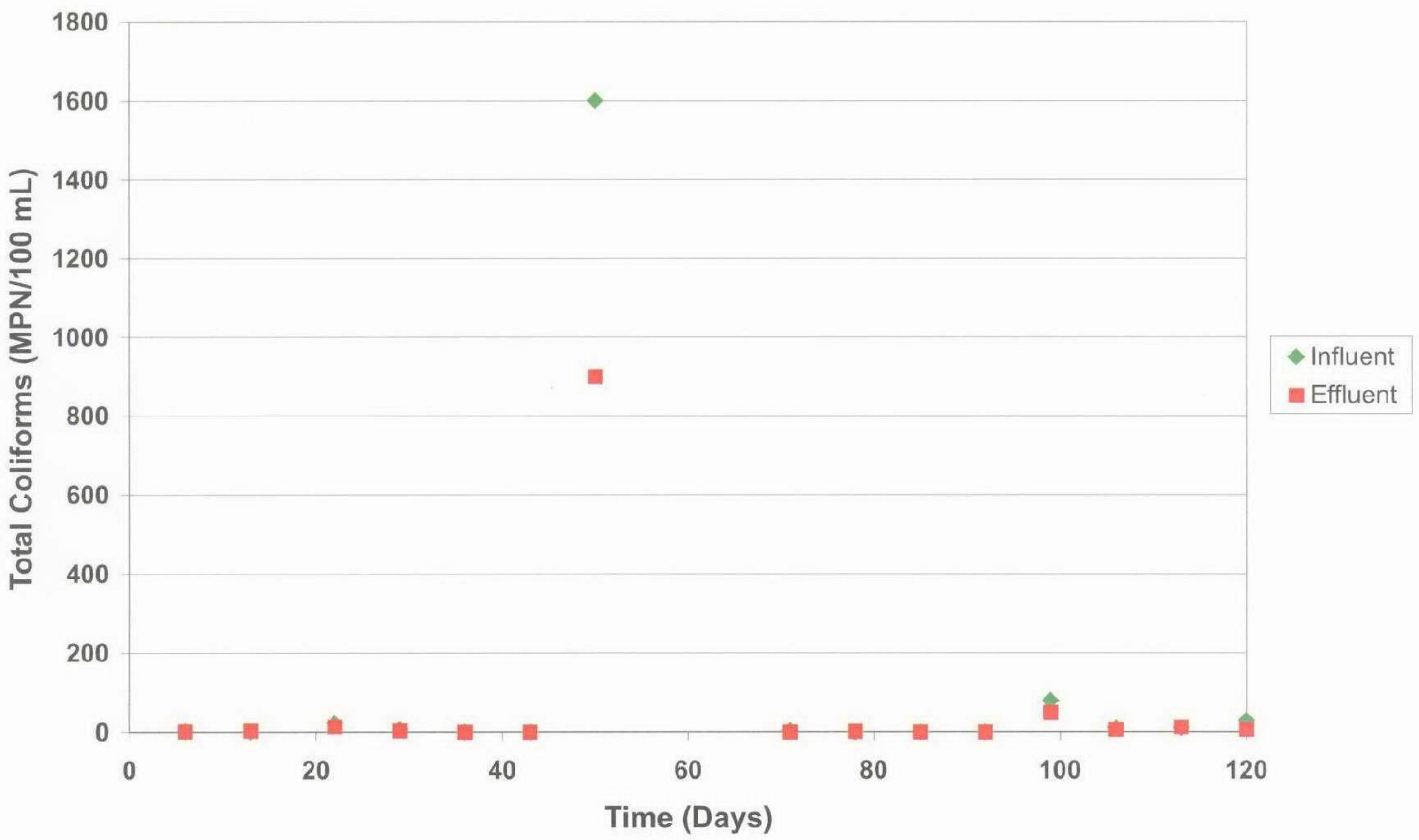
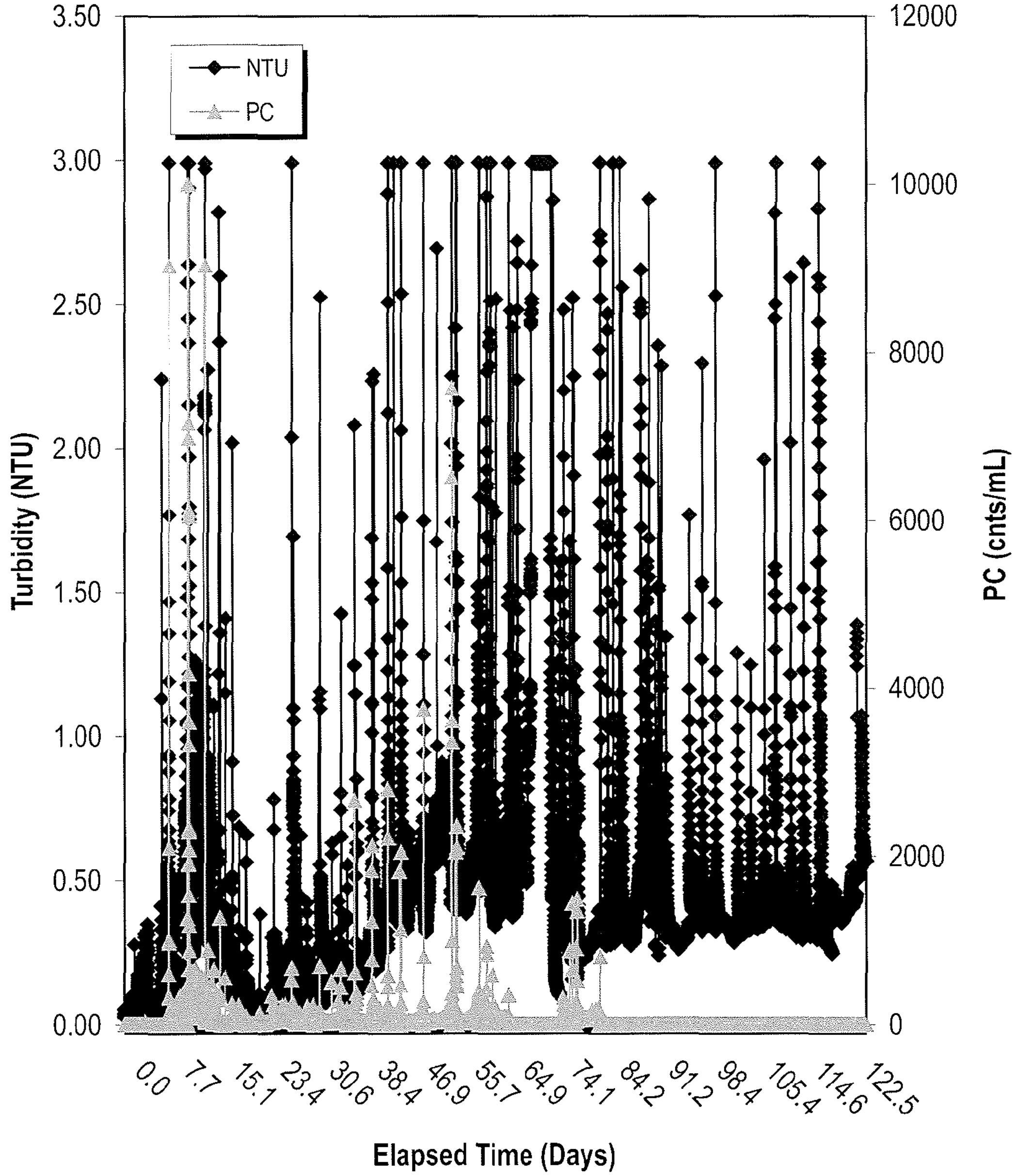


FIXED-BED TOTAL COLIFORMS

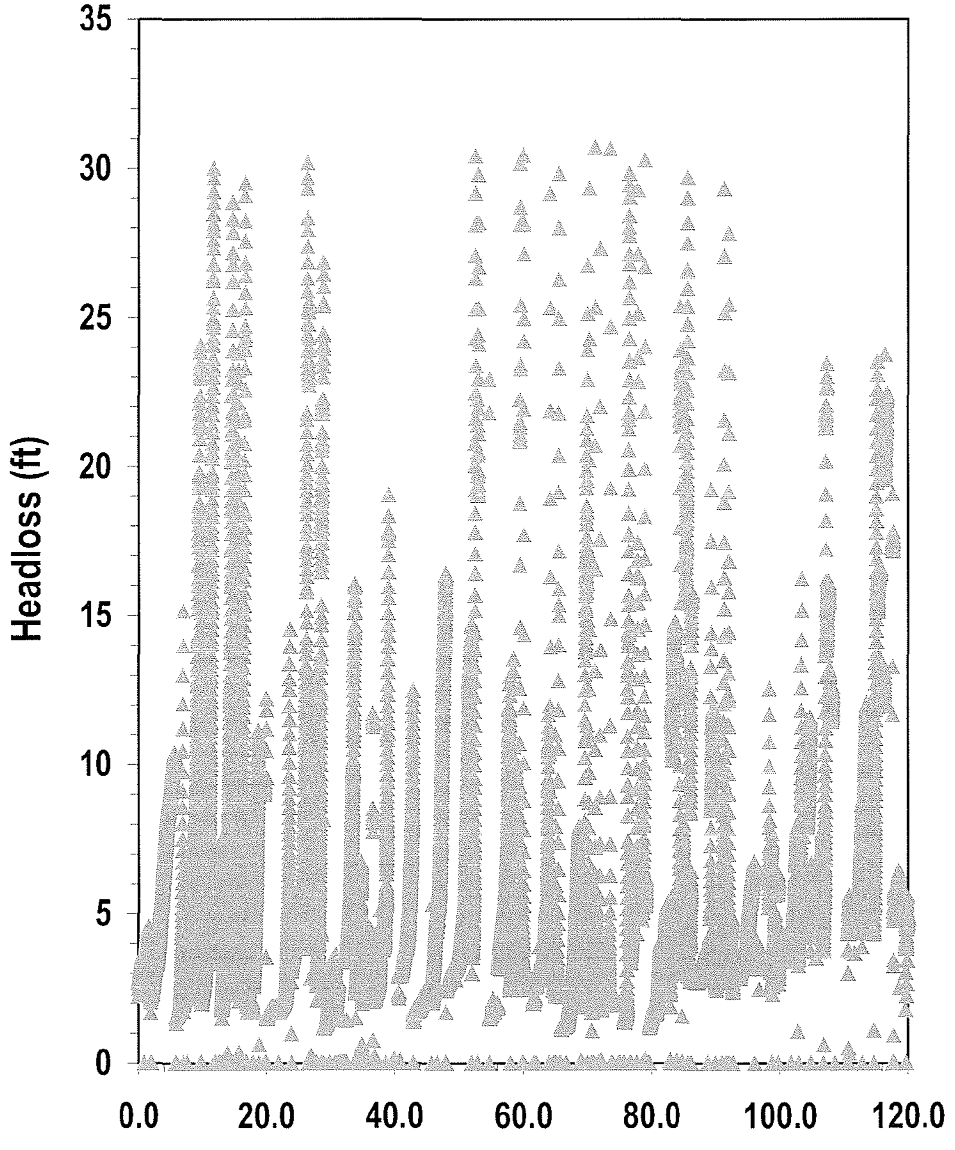
FIGURE 3.30



FIXED-BED EFFLUENT TURBIDITY AND PARTICLE COUNTS

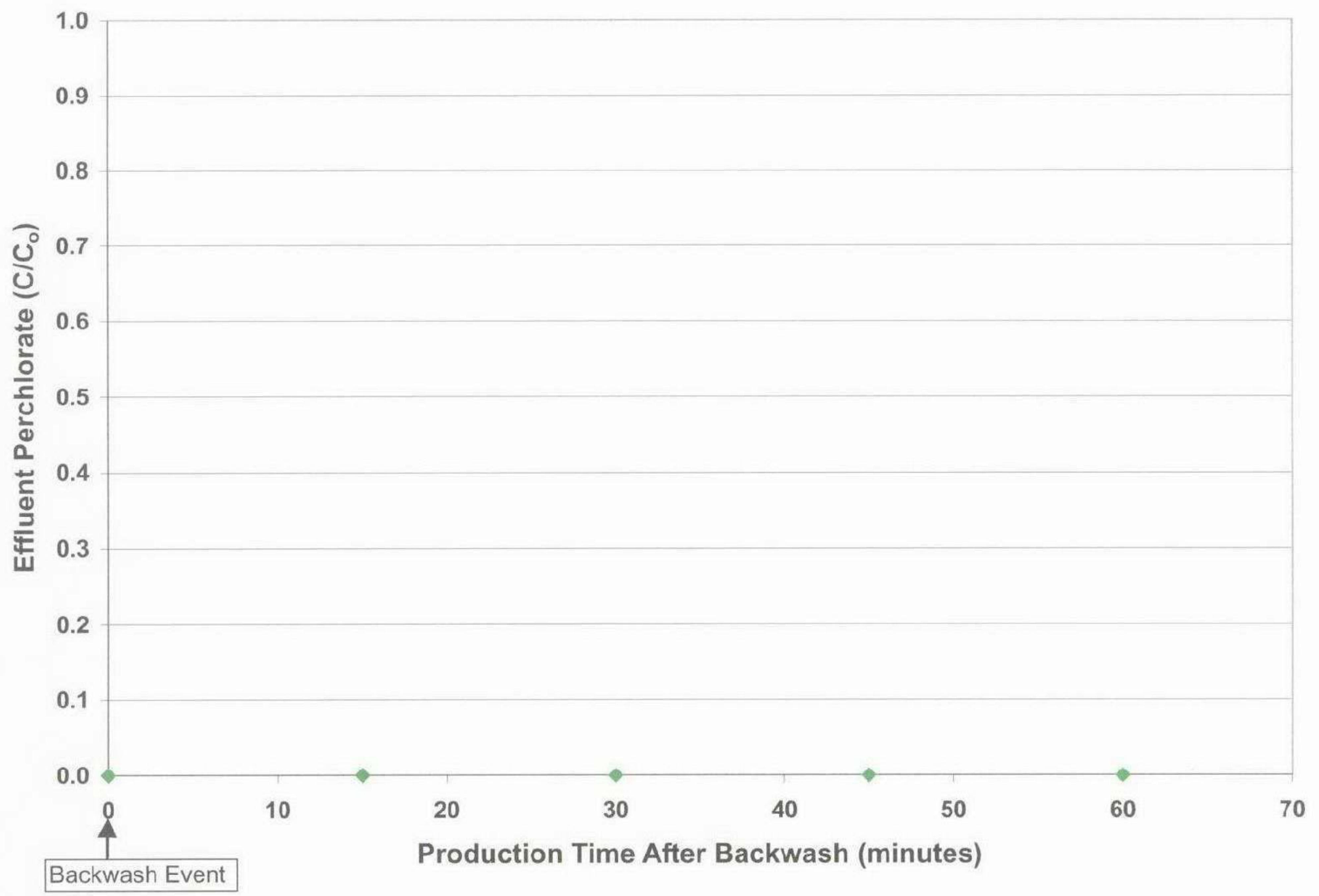
FIGURE 3.31

20-CLWA204F3.31-6625A10.CDR



FIXED-BED HEADLOSS

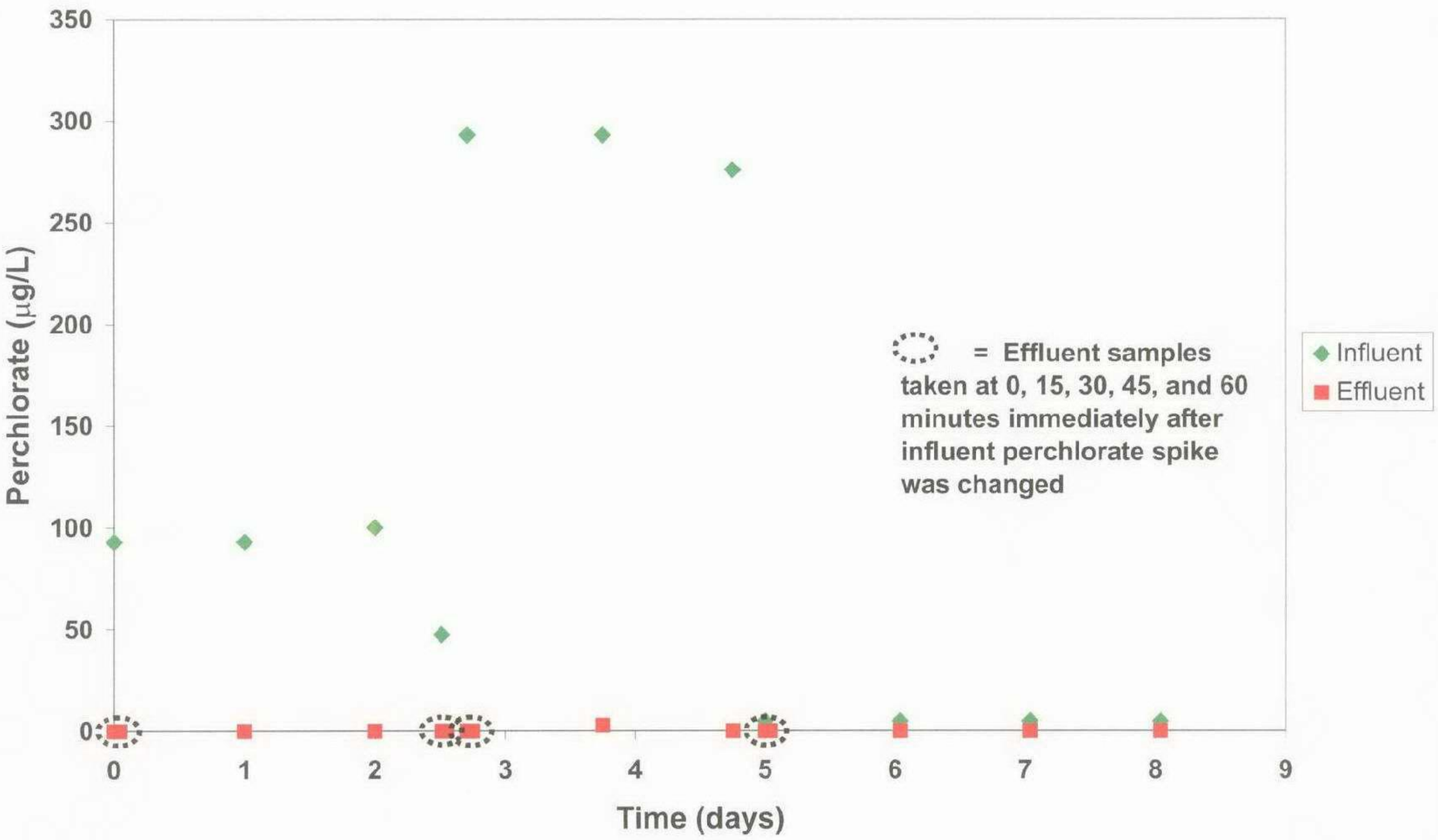
FIGURE 3.32



FIXED-BED BACKWASH CHALLENGE TEST

FIGURE 3.33

CASTAIC LAKE WATER AGENCY



FIXED-BED PERCHLORATE SPIKE CHALLENGE TEST

FIGURE 3.34

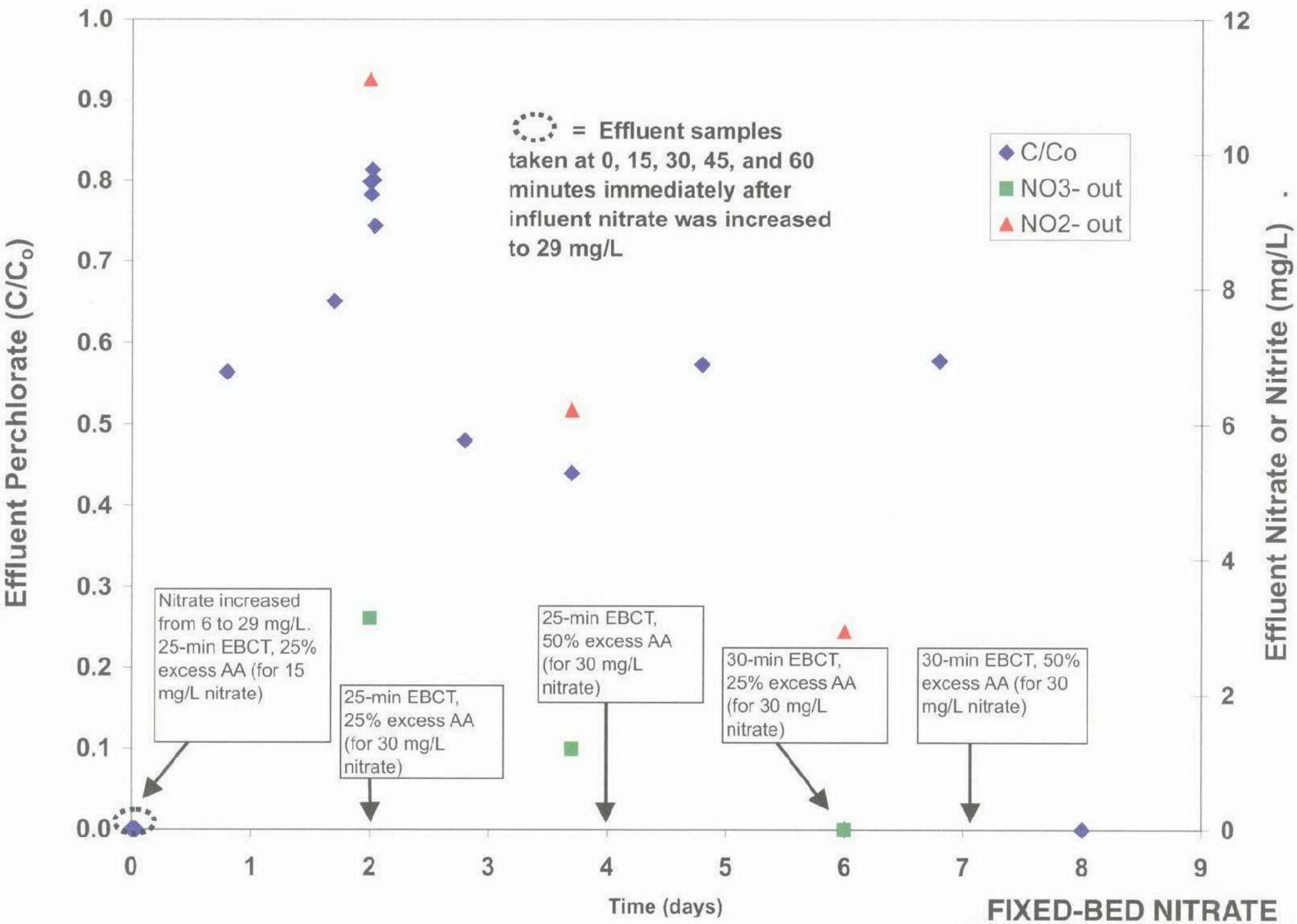
7.5.5.3 Nitrate Spiking

When the feed nitrate concentration was increased stepwise from 6 mg/L as NO_3 to 29 mg/L as NO_3, perchlorate was not detected in the high resolution samples taken up to an hour after the event (Figure 3.35). However, samples taken ≥ 24 hours after the step increase showed perchlorate, nitrate, and nitrite breakthrough. Increasing the acetic acid feed concentration and EBCT did not immediately recover perchlorate removal performance to below detection. Eight days after the feed nitrate concentration was increased by 23 mg/L as NO_3^-, complete removal of nitrate, nitrite, and perchlorate was again observed in the FXB. These data suggest two important phenomena:

1. When large step increases in feed oxidant concentrations occur, the biological FXB requires a period of bioacclimation before perchlorate removal to below detection can be reestablished and maintained. In other words, the bacterial mass in the FXB, which was equilibrated to a feed nitrate concentration of 6 mg/L as NO_3^-, was insufficient to handle a sudden increase in feed nitrate concentration of 23 mg/L as NO_3^-. The bacterial community had to grow and equilibrate with a much higher nitrate concentration before it could produce the redox conditions necessary for complete perchlorate removal.

2. Via adsorption, GAC provides a safety factor with respect to perchlorate removal in the FXB. This is supported by the lack of perchlorate detections immediately following the step nitrate increase. The primary perchlorate removal mechanism in the biological FXB is biological reduction. However, if the microbial activity in the filter is insufficient to remove perchlorate, the GAC can adsorb perchlorate for a period of time to prevent breakthrough. If perchlorate diffusion through the biofilm is fast, adsorption could be occurring near the top of the GAC bed, where the biological activity is highest. If perchlorate diffusion through the biofilm is slow, adsorption could be occurring in the lower portions of the GAC bed, where there is little biological activity. Sorption sites may be biologically regenerated when perchlorate reducing conditions return to the FXB. This may be the case even for adsorption sites in the lower portions of the bed, as GAC tends to migrate toward the top of the column during a backwash event, positioning it at depths of increased biological activity. This hypothesis explains why there might be perchlorate adsorption capacity available on the GAC after five months of pilot testing.

Large step changes in nitrate concentration, like the one tested during this experiment, are not typical for a groundwater system. Unintentional, gradual nitrate fluctuations were observed throughout pilot testing and did not impact perchlorate removal performance in the FXB.



FIXED-BED NITRATE SPIKE CHALLENGE TEST

FIGURE 3.35

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7.5.5.4 System Shut-Down

Figure 3.36 shows the results of the 24- and 48-hour shut-down tests. The pilot plant was turned off for 24 hours and then restarted using a 25-minute EBCT and 7.8 mg/L acetic acid carbon. No backwash was performed prior to restarting the FXB. Samples taken at 0, 15, 30, 45, and 60 minutes and 24 hours after the pilot was restarted showed no perchlorate breakthrough. However, 26 percent and 40 percent breakthrough occurred 48 and 72 hours after the pilot was put back into production. After the 72-hour sample, the pilot was turned off for a period of 48-hours and then restarted without a backwash. Samples taken at 0, 15, 30, 45, and 60 minutes, 24 hours, and 48 hours after the pilot was restarted showed no perchlorate breakthrough. The 72-hour sample showed 24 percent breakthrough and the 96-hour sample again showed perchlorate removal to below detection.

The 24-hour shut-down experiment was repeated, but included a backwash prior to restarting the system. As Figure 3.36 indicates, no perchlorate was detected in the effluent in the high resolution samples or in subsequent samples taken daily for five days. A review of previous data also revealed four periods over which the biological FXB pilot system was shut down unintentionally. These periods ranged from 12 to 62 hours, the biological FXB was backwashed prior to restarting after each period, and production EBCTs were 15 or 25 minutes. No effluent perchlorate was detected following the shut down periods (Figure 3.37).

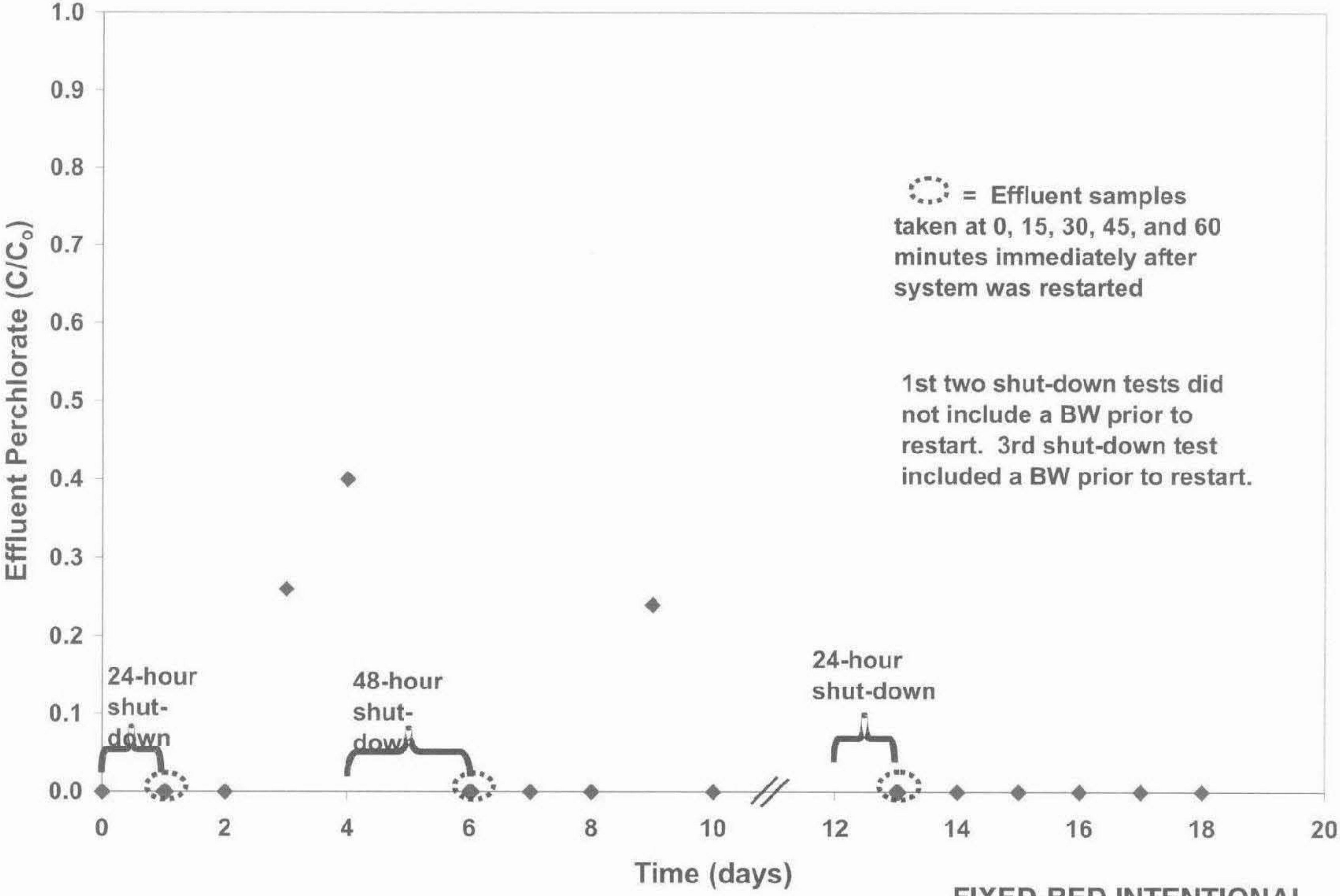
The biological FXB was also shut down for a two-week period in December 2003. It was backwashed and restarted at a 25-minute EBCT. Consistent perchlorate removal was immediately observed and sustained; no effluent perchlorate was detected.

7.5.5.5 Electron Donor Feed Failure Simulation

To investigate the impact of the future of the electron donor addition on perchlorate removal performance in the FXB, the acetic acid feed was shut off and effluent perchlorate concentrations were monitored. Samples taken at 0, 15, 30, 45, and 60 minutes and 2, 3, 5 and 24-hours after the acetic acid pump was turned off showed no perchlorate breakthrough (Figure 3.38). The acetic acid pump was then restarted and perchlorate continued to be removed to below detection. The following hypothesis may account for the exceptional perchlorate removal performance in the biological FXB while no exogenous electron donor was being added to the system:

1. The bacterial community in the biological FXB was respiring endogenously. That is, bacteria were metabolizing their own cells for use as an electron donor. This often occurs when food sources are scarce.

2. Via adsorption, GAC was providing a safety factor with respect to perchlorate removal in the FXB. When the acetic acid pump was turned off, biologically reductive activity likely slowed in the filter, allowing adsorption to become a more active mechanism for perchlorate removal.

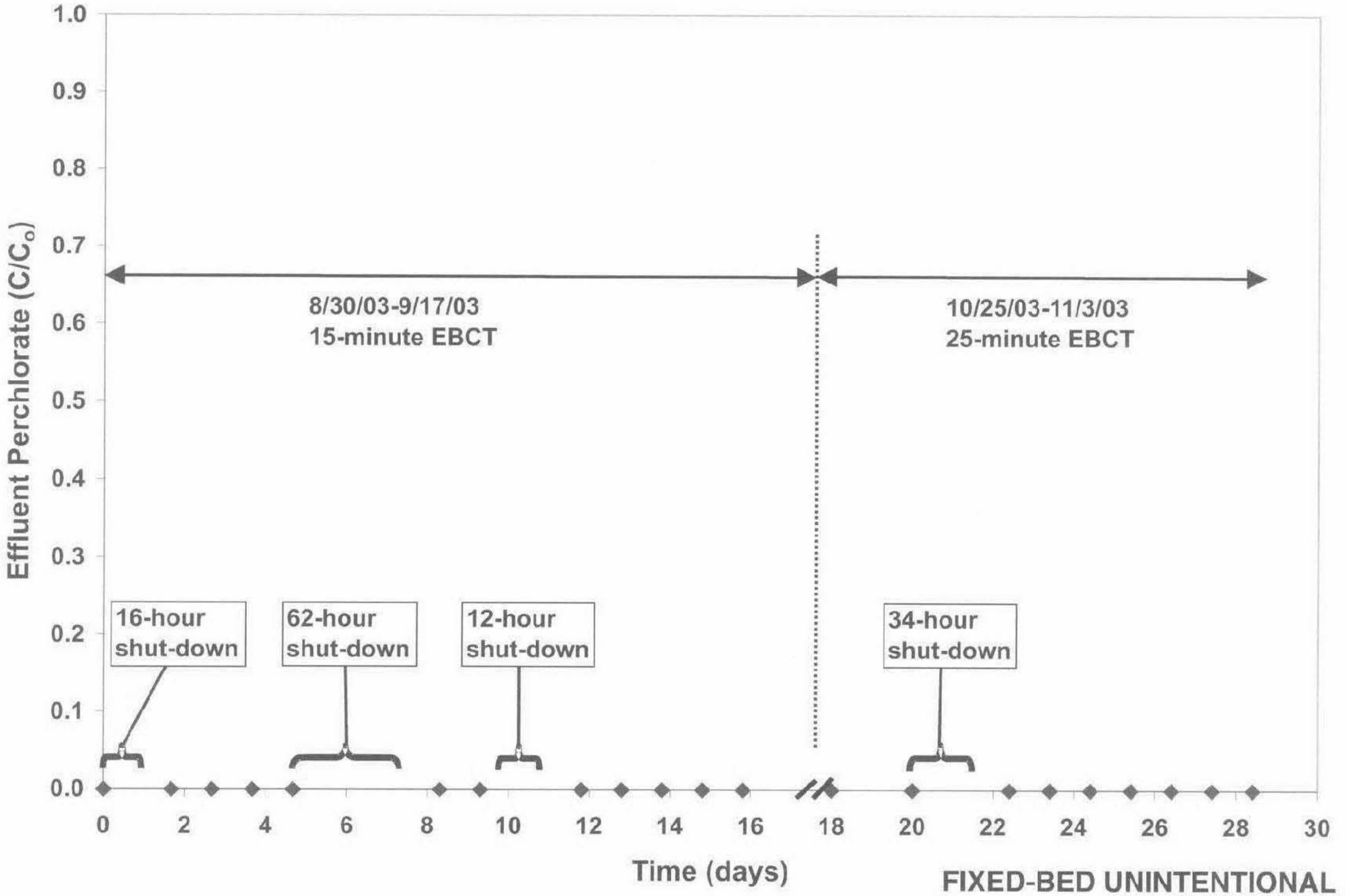


⬭ = Effluent samples taken at 0, 15, 30, 45, and 60 minutes immediately after system was restarted

1st two shut-down tests did not include a BW prior to restart. 3rd shut-down test included a BW prior to restart.

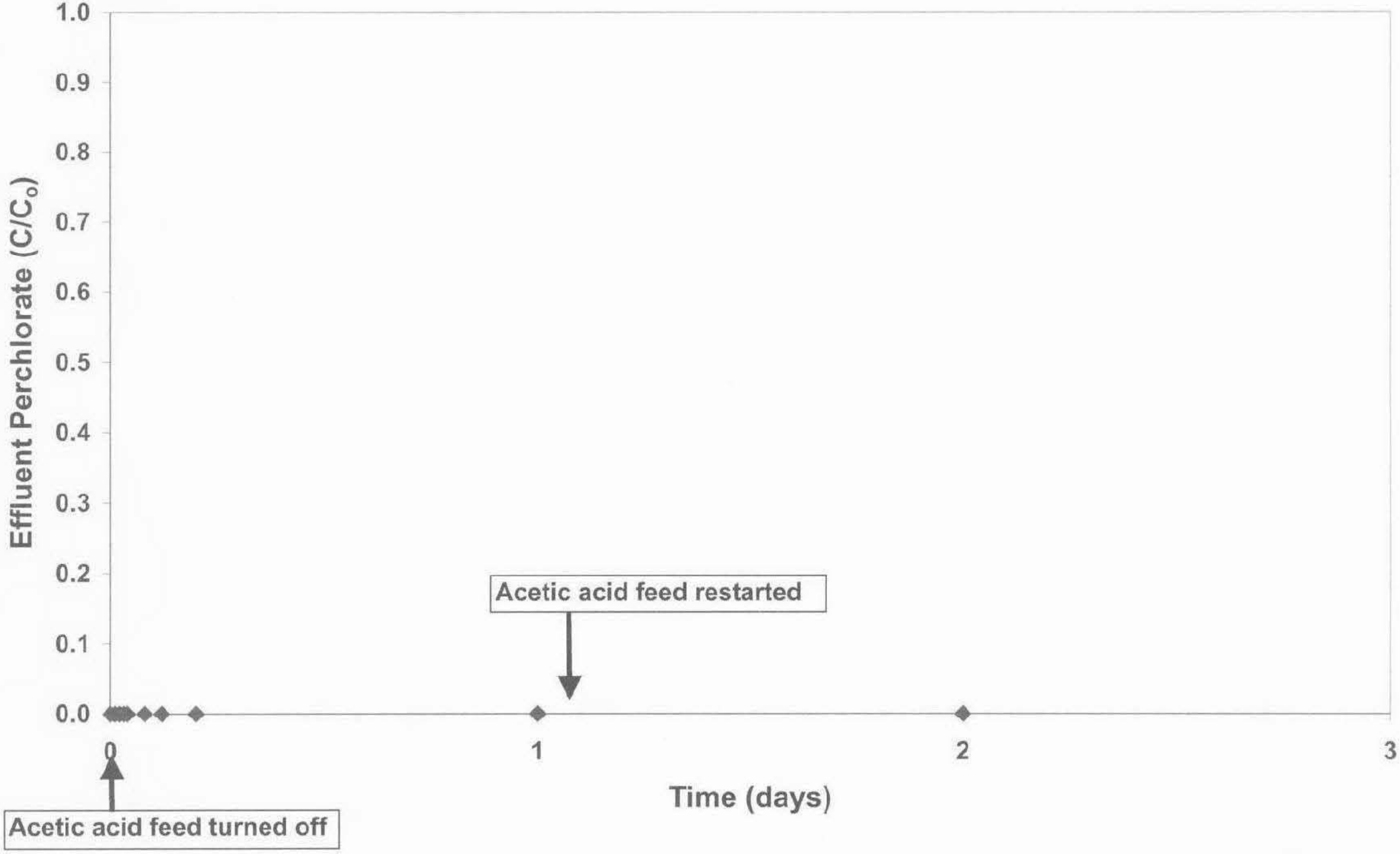
FIXED-BED INTENTIONAL SHUT-DOWN CHALLENGE TEST

FIGURE 3.36



FIXED-BED UNINTENTIONAL SHUT-DOWN PERFORMANCE

FIGURE 3.37



FIXED-BED ACETIC ACID FEED FAILURE CHALLENGE TEST

FIGURE 3.38

It is possible that both of the above phenomena contributed to the 24-hour removal of perchlorate to below detection in the biological FXB while the acetic acid feed was shut off, though no experiments were performed to confirm this.

7.5.6 Backwash Water Quality

Table 3.22 lists backwash water quality data, as determined using composite samples of backwash water.

Table 3.22 Backwash Water Quality
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Parameter	Range
Perchlorate (μg/L)	ND (two points)
AOC (mg/L)	1.0-2.5
COD (mg/L)	63-250
VSS (mg/L)	41-140
TSS (mg/L)	39
Total coliforms (MPN/100 mL)	4-110
Fecal coliforms (MPN/100 mL)	ND - 4

The level of perchlorate in the backwash water (ND) is below the Los Angeles County Sanitation District (LACSD) Phase I limit of 4 ppb. The values for COD and TSS are used in obtaining discharge permits for the disposal of the backwash water if the water is being discharged into LACSD lines.

7.5.7 Summary

Consistent perchlorate removal to below detection was achieved in the FXB filter using only organisms indigenous to the Saugus aquifer. With influent DO and nitrate concentrations of 7 and 15 mg/L, respectively, the lowest EBCT and acetic acid concentration that allowed consistent perchlorate removal to below detection was 15 minutes and 7.8 mg/L as carbon, respectively. Run times ranged from 24 hours to several days. Effluent from the FXB filter was biologically stable and contained no fecal coliforms. Challenge tests demonstrated that the FXB filter was robust with respect to backwashing episodes, changes in feed water quality, system shutdowns, and electron donor addition failures. Large step increases in feed nitrate concentration (e.g., 15 mg/L) required a period of bio-acclimation before perchlorate removal to below detection could be reestablished in the FXB filter.

7.6 Fluidized Bed Reactor

7.6.1 Perchlorate Removal Performance

Over the course of pilot testing, the FBR achieved perchlorate removal to below detection for periods of up to 8 days. However, perchlorate removal performance generally fluctuated and sustained (i.e., ≥ 2 weeks) removal to below detection was not achieved (Figure 3.39).

7.6.1.1 Mechanical & Operational Adjustments

Numerous mechanical and operational adjustments were made throughout pilot testing to establish sustained perchlorate removal to below detection. A detailed list of these adjustments is provided in Table 3.23 followed by a description of the main mechanical and operational changes, reasons for their implementation, and their impact on perchlorate removal performance. Throughout the course of the study, changes made to the system were done under the direction of representatives from Shaw Environmental.

Table 3.23 FBR Mechanical and Operational Adjustments
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

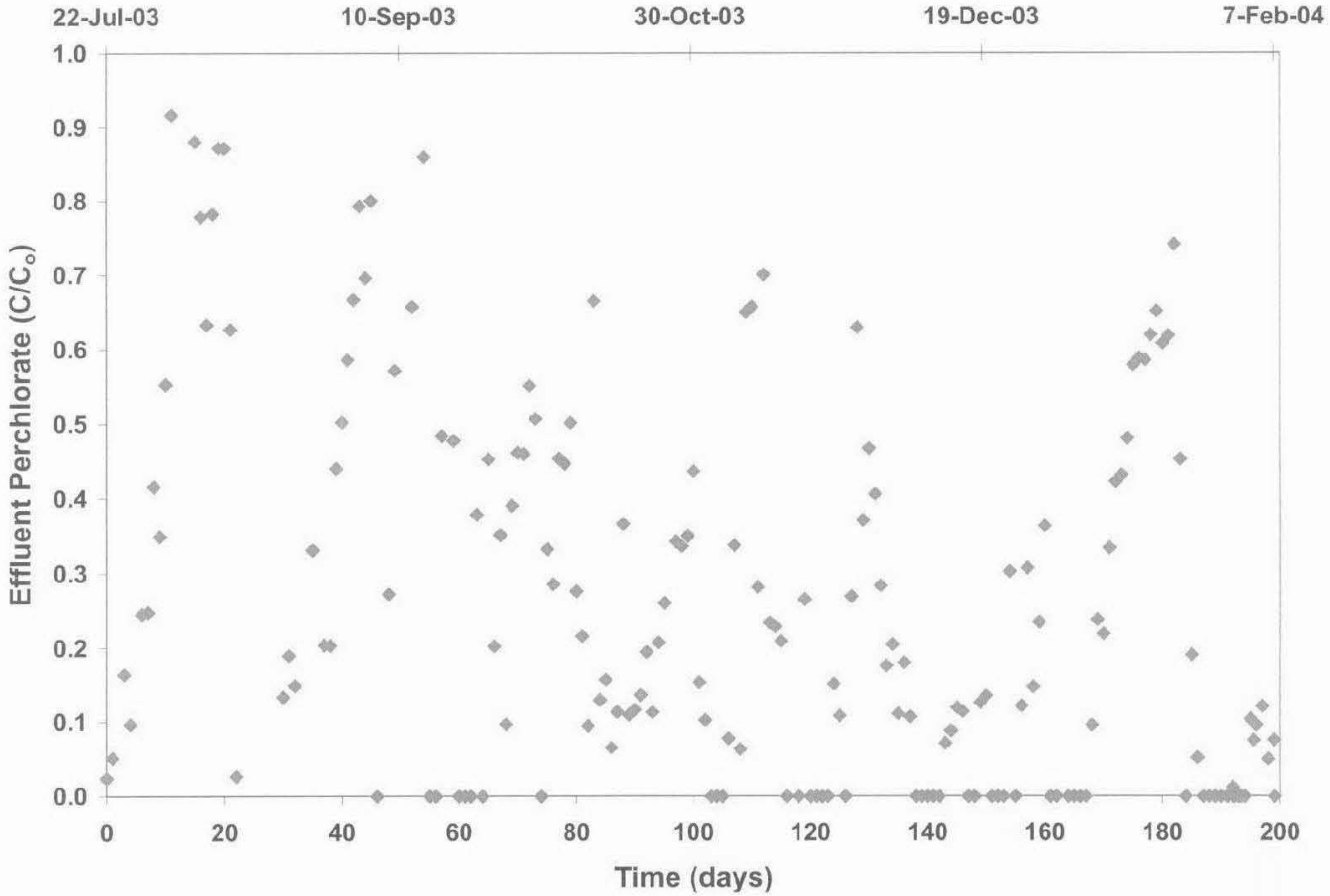
Date (Day of operation)	Event
7/21/03 (0)	System started. 3 gpm.
8/2/03 (11)	Power outage at pilot caused system shutdown
8/4/03 (13)	System restarted, causing carbon to blow out top of reactor.
8/6/03 (15)	Phosphorous added to feed at 0.2 PO_4–P
8/11/03 (20)	Carbon ball-like mass observed in reactor.
8/13/03 (22)	Mechanical mixer observed to be missing
8/14/03 (24)	System put in recycle to scour carbon.
8/19/03 (29)	Carbon manually cleaned with PVC pole and air scour. Carbon/biomass mats broken up and biomass removed.
8/26/03 (36)	Biomass separator installed with 3/8" SS. Top of reactor removed to insert tubing. Designed to operate continuously by drawing carbon from the bottom of the reactor and place carbon back to top of bed.
8/28/03 (38)	Biomass separator clogged, shut down.
8/29/03 (39)	Biomass separator system changed to 3/4" PVC. Configuration changed to draw from top and put carbon back to bottom.
9/1/03 (41)	Solids recovery tank overflowed. Lowered flow to 1 gpm. Large mat of biomass observed in tank, possibly due to aerobic growth. Large amounts of growth in pump.
9/2/03 (42)	Feed and recycle lines and pump cleaned of biomass.
9/9/03 (49)	Nitrogen blanket added to the top of the reactor to minimize re-entrainment

Table 3.23 FBR Mechanical and Operational Adjustments Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer Castaic Lake Water Agency

Date (Day of operation)	Event
	of oxygen.
9/16/03 (56)	Reconfigured system piping to bypass oxygenation vessel. Moved acetic acid injection point closer to bioreactor vessel. Biomass separator system to be operated for 1 hour per day.
9/17/03 (59)	Solids recovery tank overflowing, system shut down for 1 hour (recycle).
9/18/03 (58)	Acetic acid pump replaced. It had lost prime several times.
9/24/03 (64)	Phosphorous feed concentration increased to 3 mg/L PO_4-P
9/25/03 (65)	Excessive biogrowth in effluent line causing back-up of the solids recovery tank. Effluent line cleaned out.
9/26/03 (66)	Flow decreased to 2 gpm
9/29/03 (69)	Flow increased to 3 gpm. Large amounts of biomass floating on water surface in solids recovery tank. Mat removed from tank.
10/1/03 (71)	Water observed in nitrogen line. Water removed and nitrogen restarted. Flow decreased to 2.5 gpm.
10/3/03 (73)	Phosphorous feed concentration increased to 3.5 mg/L PO_4-P.
10/6/03 (76)	Small carbon ball mass observed in reactor. Ball broken up manually and with biomass separator.
10/8/03 (78)	Feed flow reduced to 1.5 gpm.
10/17/03 (87)	Feed flow reduced to 1.0 gpm.
10/21/03 (91)	Feed flow reduced to 0.8 gpm.
10/23/03 (93)	Samples sent to Shaw lab for analysis. Results corroborate results seen from CLWA lab.
10/24/03 (94)	Biomass separator to remain off to promote bed expansion.
10/30/03 (100)	Carbon removed from reactor and bottom of bioreactor removed to check for distribution header clogging. No clogging observed. Added 2 feet of carbon to the reactor for settled bed of 72" and expanded of 92". Flow changed to 2 gpm.
10/31/03 (101)	Flow increased to 3 gpm.
11/3/03 (104)	More carbon added to reactor for settled bed of 82" and expanded of 106".
11/5/03 (106)	Phosphorous feed concentration decreased to 2.5 mg/L PO_4-P
11/13/03 (114)	Micronutrients added to the feed water through electron donor feed.
11/26/03 (127)	Second dose of micronutrient added to system
11/28/03 (129)	Third dose of micronutrient added to system
12/3/03 (134)	Flow decreased to 1.5 gpm and mircronutrient eliminated from feed.

Table 3.23 FBR Mechanical and Operational Adjustments
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Date (Day of operation)	Event
12/5/03 (136)	Flow increased to 3 gpm and acetic acid feed concentration lowered to 13.9 mg/L as C (15% dilution)
12/10/03 (141)	Plant shutdown for 3 hours. Electron donor decreased (94 grams/day).
12/15/03 (146)	Acetic acid feed concentration increased to 20% dilution (125 grams/day)
12/19/03 (150)	Acetic acid feed concentration increased to 30% dilution (185 grams/day)
12/22/03 (153)	Rapid bed expansion noticed in reactor.
12/23/03 (154)	Biomass separator pump turned on for 1 hour due to rapid bed expansion
12/27/03 (158)	Biomass separator pump turned on for 2 hours
12/30/03 (161)	Biomass separator pump turned on for ½ hour
12/31/03 (162)	System placed in recycle due to rapid bed expansion
1/2/04 (164)	System restarted at 3 gpm.
1/7/04 (169)	Acetic acid feed solution decreased to 20% dilution (125 grams/day)
1/9/04 (171)	Suspended biomass removed from top of the reactor Phosphate addition reduced by 50% to 1.25 mg/L PO_4-P
1/12/04 (174)	Acetic acid feed solution increased to 25% dilution (155 grams/day)
1/16/04 (178)	Due to phosphoric acid supply limitations, phosphate addition was reduced to 25 mL in 1 L total volume.
1/19/04 (181)	Flow decreased to 2 gpm w/ current donor addition remaining the same (25% dilution at 1 mL/min).
1/20/04 (182)	System reconfigured to bypass solids recovery tank due to high DO in recycle. New perchlorate stock solution mixed incorrectly, causing influent concentrations to be 20-25 ug/L. Increase of phosphate concentrations back to previous levels (>2 mg/L).
1/21/04 (183)	Flow increased to 3 gpm (1 mL/min 25% dilution for donor) and increased ClO4 back to 50 ug/L. Increased flow of donor to 7 strokes/min from 6 (160 grams/day).
1/24/04 (186)	Increased electron donor to 33% dilution. (210 grams/day)
2/2/04 (195)	Increased flow of donor to 8 strokes/min from 7 (225 grams/day).
2/3/04 (196)	Added micronutrient (~50 mL to 8 L)
2/4/04 (197)	Reduced flow of donor to 5 strokes /min from 8 (180 grams/day).
2/5/04 (198)	Reduced flow to 2 gpm.
2/6/04 (199)	System shutdown (recycle).



FLUIDIZED-BED PERCHLORATE

FIGURE 3.39

Mechanical Adjustments:

- Concern: Excessive clumpy biogrowth was observed in the FBR, potentially causing clogging or short-circuiting. The mechanical mixer, which was designed to control overgrowth in the system, did not function properly.

  Adjustment: A biomass separator system was installed (Day 35) and used intermittently throughout pilot testing.

  Impact: The biomass separator was effective at controlling bed expansion and overgrowth. However, perchlorate removal performance did not appear to improve by the installation of the biomass separator system.

- Concern: Excessive biogrowth was observed across the entire FBR system, which was clogging pumps and piping and may have been causing short-circuiting in the reactor.

  Adjustments: On Day 29, the GAC was manually scoured using a PVC pipe and aeration. Piping and pumps were cleaned out on Days 42 and 65. Biomass clumps were removed from the solids recovery tank (Day 69) and from the reactor (Day 171). The acetic acid feed point was moved closer to the base of the reactor on Day 56.

  Impact: These adjustments were effective at controlling excessive biogrowth, though they did not appear to positively impact perchlorate removal performance.

- Concern: DO was being entrained between the top of the reactor and the recycle line. This could cause aerobic growth in the system and inhibit perchlorate reduction by increasing the redox potential.

  Adjustments: A nitrogen blanket was added to the top of the reactor on Day 49. The effluent/recycle piping was reconfigured to completely bypass the solids recovery tank on Day 182.

  Impact: Adding the nitrogen blanket and bypassing the oxygenation vessel lowered DO entrainment, and perchlorate removal performance improved slightly with each adjustment. Bypassing the solids recovery tank eliminated DO entrainment and appeared to improve perchlorate removal performance substantially. Four days after the system was reconfigured, perchlorate removal to below detection was achieved and sustained for eight days. However, electron donor was also being adjusted during this period and, after eight days of removal to below detection, perchlorate breakthrough was observed. Therefore, though controlling DO entrainment did appear to improve perchlorate removal performance in the FBR, it did not completely eliminate perchlorate breakthrough.

- Concern: The turbulent zone near the base of the FBR is essentially abiotic due to the high shear stresses generated by the feed jets. If this abiotic zone is a significant fraction of the overall bed depth, then the depth of the anaerobic zone within the carbon bed might be insufficient to allow for the removal of perchlorate to below detection.

- Adjustment: Two feet of carbon were added to the top of the GAC bed on Day 100. An additional 10 inches of carbon were added to the top of the GAC bed on Day 104.

  Impact: Perchlorate removal performance appeared to improve for about a week after the carbon was added to the bed, though this may have been due to adsorption. Regardless, this improvement in perchlorate removal performance was not sustained beyond one week.

Operational Adjustments:

- Concern: Low phosphorous concentrations may be limiting biological activity in the FBR.

  Adjustment: Phosphorous was added to the feed at 0.2 mg/L PO_4-P beginning on Day 15. Phosphorous addition was increased to 3.0 mg/L PO_4-P on Day 64. Phosphorous addition was increased to 3.5 mg/L PO_4-P on Day 73 (Figure 3.40).

  Impact: Adjusting the concentration of phosphorous being added to the feed did not appear to impact perchlorate removal performance in the FBR. Feed PO_4-P was later reduced to 2.5 mg/L and then 1.25 mg/L for short periods of operation, without impacting perchlorate removal performance.

- Concern: The contact time may be insufficient to allow for sustained perchlorate removal to below detection.

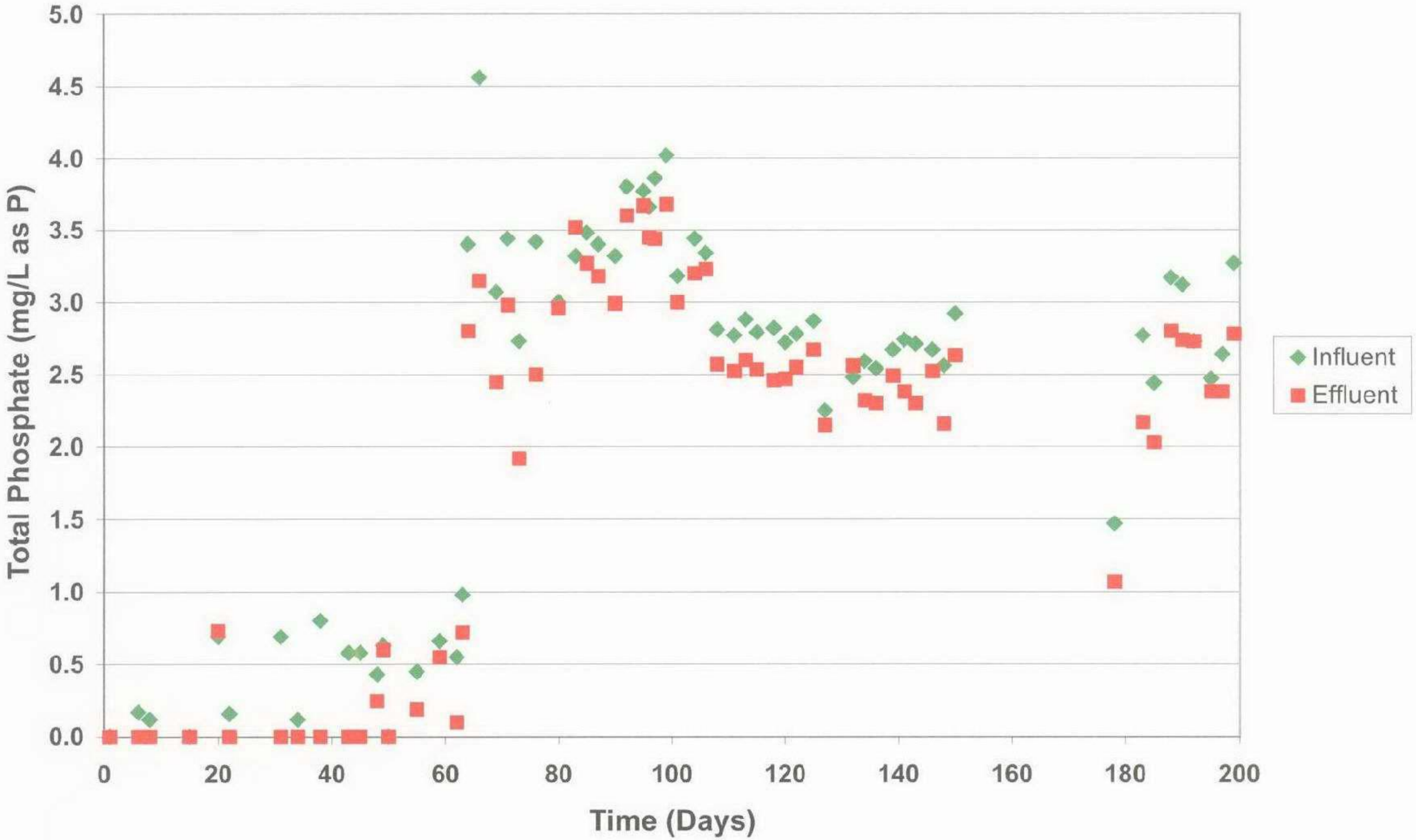
  Adjustment: The feed flow was reduced gradually from 3.0 gpm to 0.8 gpm over a four-week period (Days 71 through 99).

  Impact: While increasing the HRT did appear to improve perchlorate removal performance initially, it did not effect perchlorate removal to below detection, and, eventually, perchlorate removal performance declined at the lower feed flow rates.

- Concern: Low concentrations of micronutrients may be limiting biological activity in the FBR.

  Adjustment: A micronutrient solution was added to the feed from Day 114 to Day 134. It was again added on Day 196 through the end of pilot testing. The micronutrient contained low concentrations of iron, copper, magnesium, manganese, zinc, boron, sulfur, molybdenum, and cobalt.

  Impact: The addition of the micronutrient feed might have caused improved perchlorate removal performance initially, though the impact was confounded due to the nearly simultaneous addition of fresh carbon to the bed. Regardless, perchlorate removal performance eventually declined in spite of the micronutrient feed.



FLUIDIZED-BED PHOSPHOROUS

FIGURE 3.40

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- Concern: Over-excess acetic acid concentrations in the feed may have been selecting away from perchlorate-reducing bacteria and toward sulfate-reducing bacteria. As the feed nitrate concentration decreased during the pilot test period, the acetic acid concentration was not adjusted to account for the decreased oxidant demand in the system. It was theorized that this could help explain why only partial perchlorate removal was observed in spite of very low redox conditions (down to –200 mV). In other words, though complete DO and nitrate reduction and partial sulfate reduction was occurring in the reactor, only partial perchlorate reduction was observed (Figures 3.41 and 3.42), suggesting that the perchlorate-reducing community in the reactor was being depressed.

  Adjustment: Feed acetic acid concentration was lowered on Day 136.

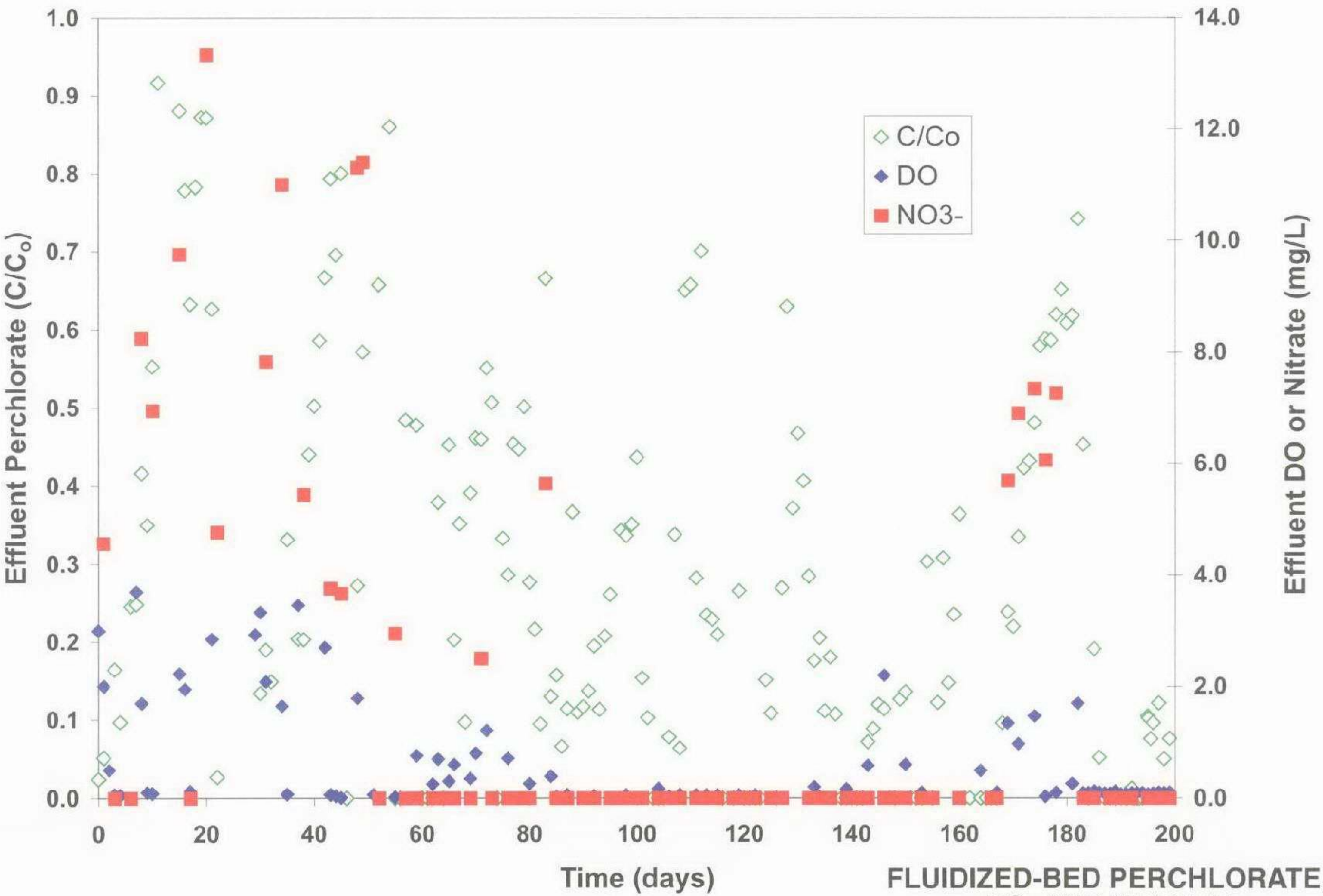
  Impact: Perchlorate was removed to below detection for about a week after the acetic acid feed concentration was lowered. Subsequently, feed acetic acid concentrations were adjusted up and down as feed nitrate concentrations fluctuated. Though perchlorate removal was generally ≥ 90% during this period, sustained perchlorate removal to below detection was not achieved.

7.6.2 Other Parameters

The following non-anionic water quality observations were made during the course of FBR piloting:

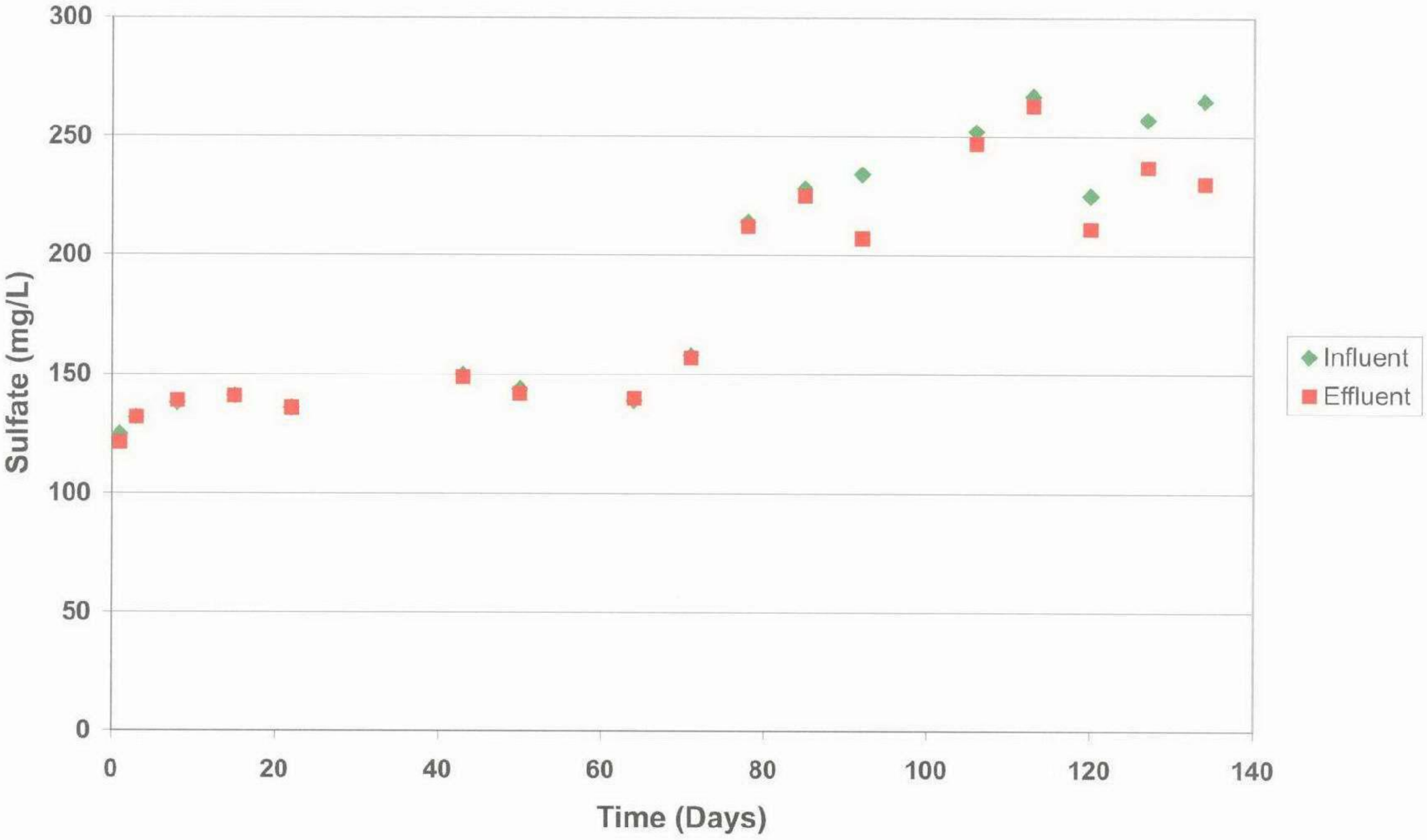
- Effluent TOC concentrations were typically 1 to 9 mg/L (Figure 3.43).
- Effluent BDOC concentrations ranged from non-detect to 1.3 mg/L (Figure 3.44).
- On average, pH decreased by 0.5 units across the FBR bed (Figure 3.45). This was likely due to the addition of CO_2 to the water as acetic acid was oxidized.
- HPCs increased across the filter, resulting in counts between 50,000 and 870,000/mL (Figure 3.46).
- Total effluent coliforms ranged from non-detect to 900 MPN/100 mL, but were typically 300 MPN/100 mL or less (Figure 3.47). No fecal coliforms were detected.
- Average feed water turbidities were approximately 0.5 NTU. Effluent turbidities ranged from 2 to 70 NTU (Figure 3.48).

20-CLWA204F3.41-6625A10.CDR



FLUIDIZED-BED PERCHLORATE, DO, AND NITRATE

FIGURE 3.41



FLUIDIZED-BED SULFATE

FIGURE 3.42

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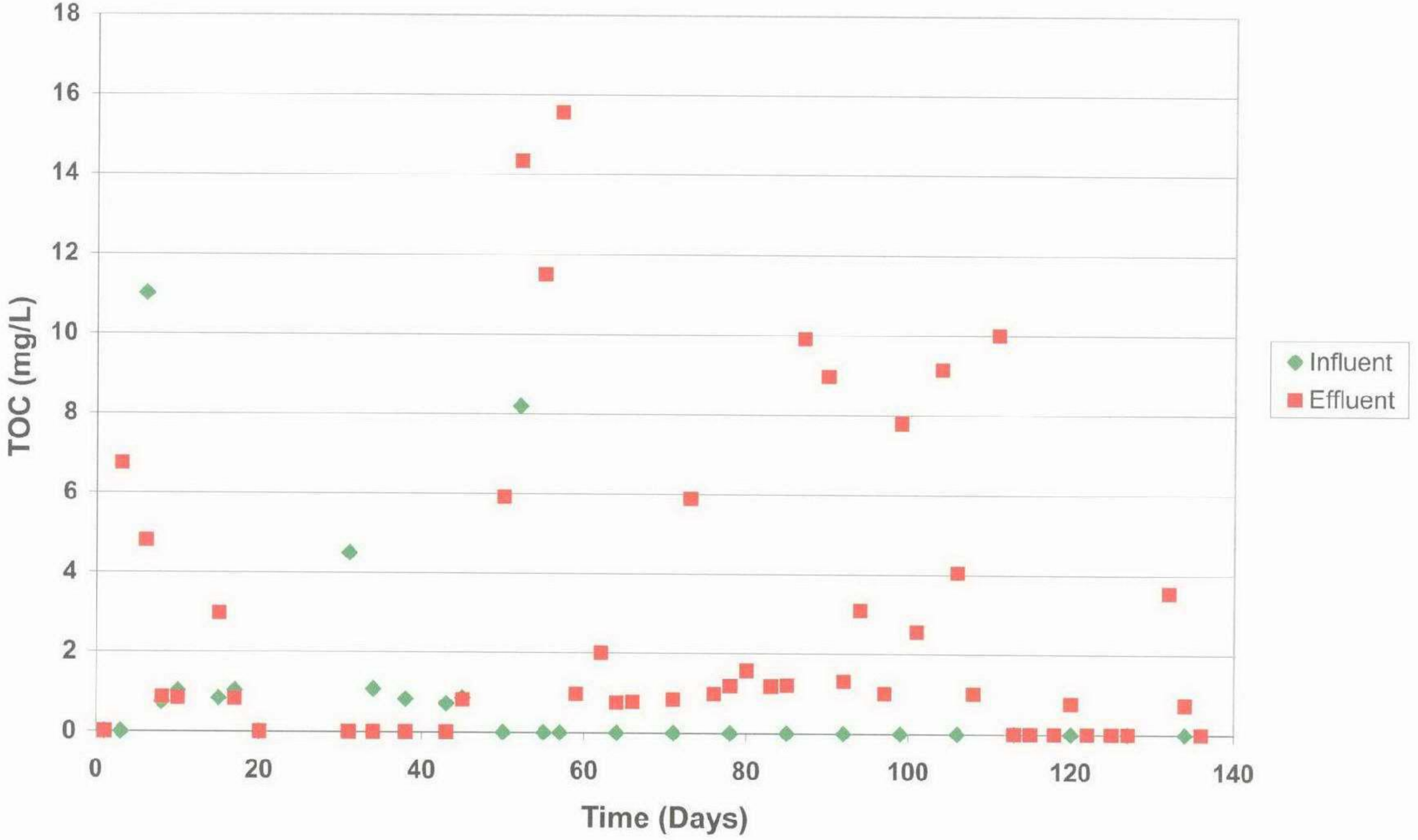
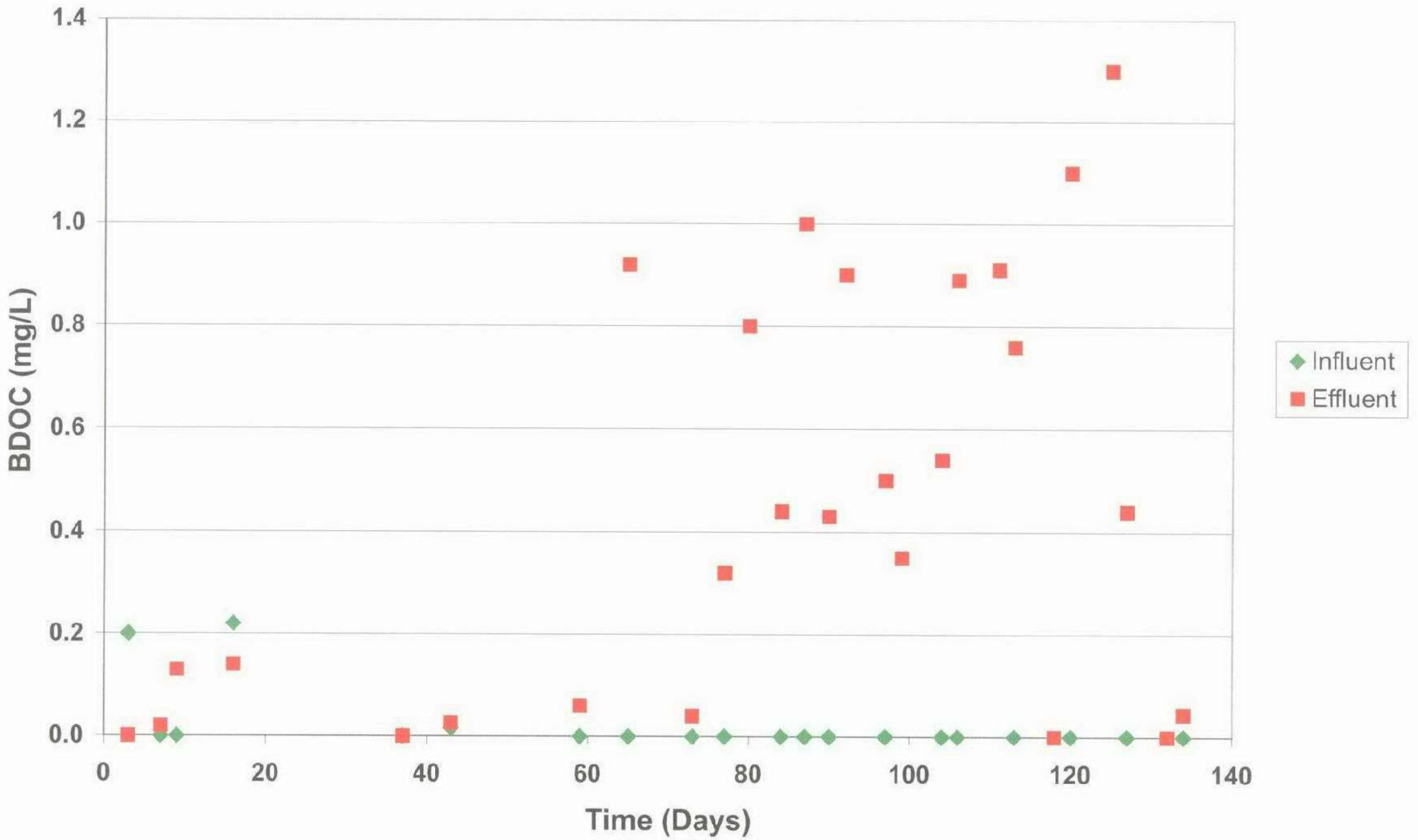


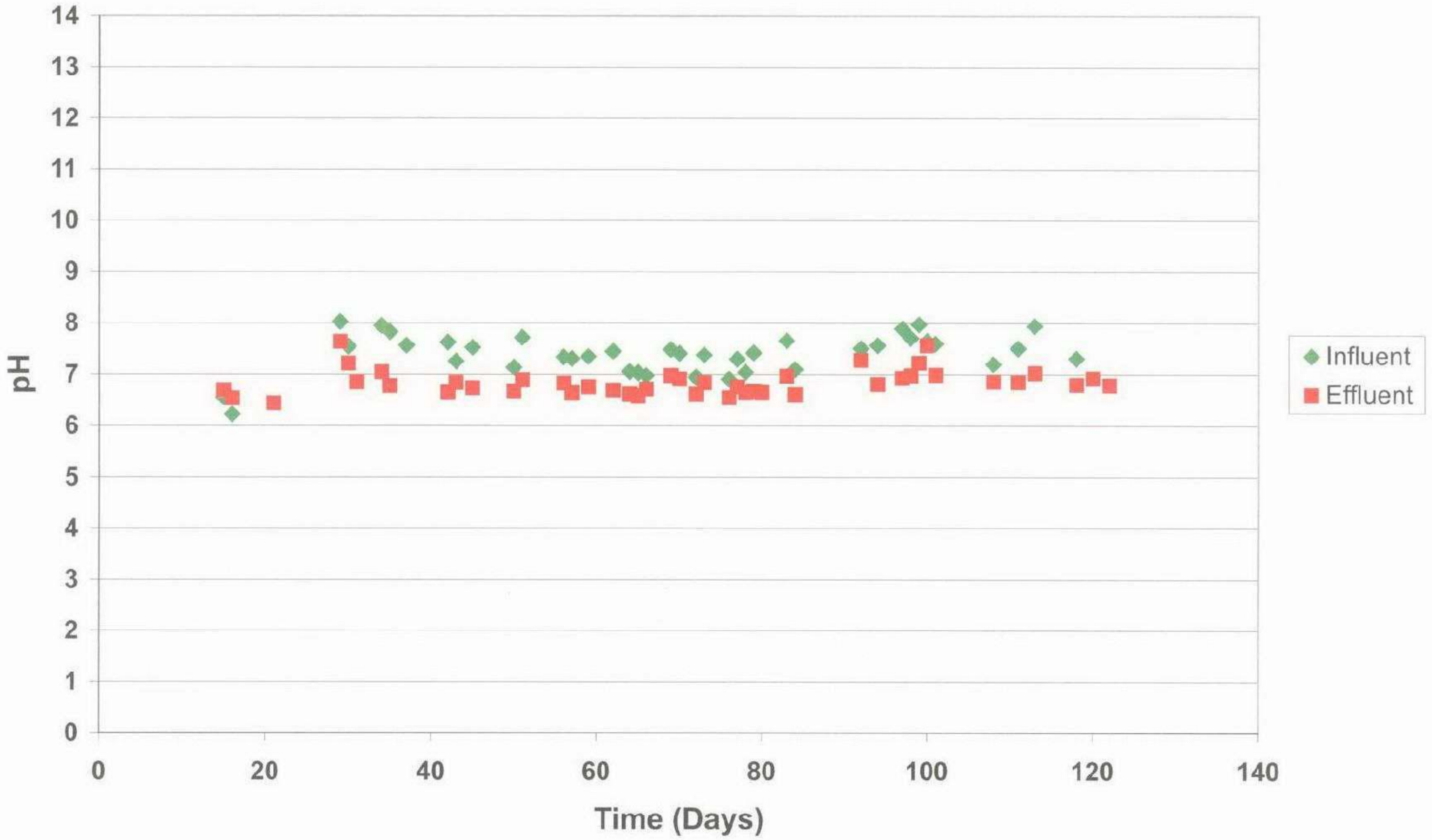
FLUIDIZED-BED TOC

FIGURE 3.43



FLUIDIZED-BED BDOC

FIGURE 3.44



FLUIDIZED-BED pH

FIGURE 3.45

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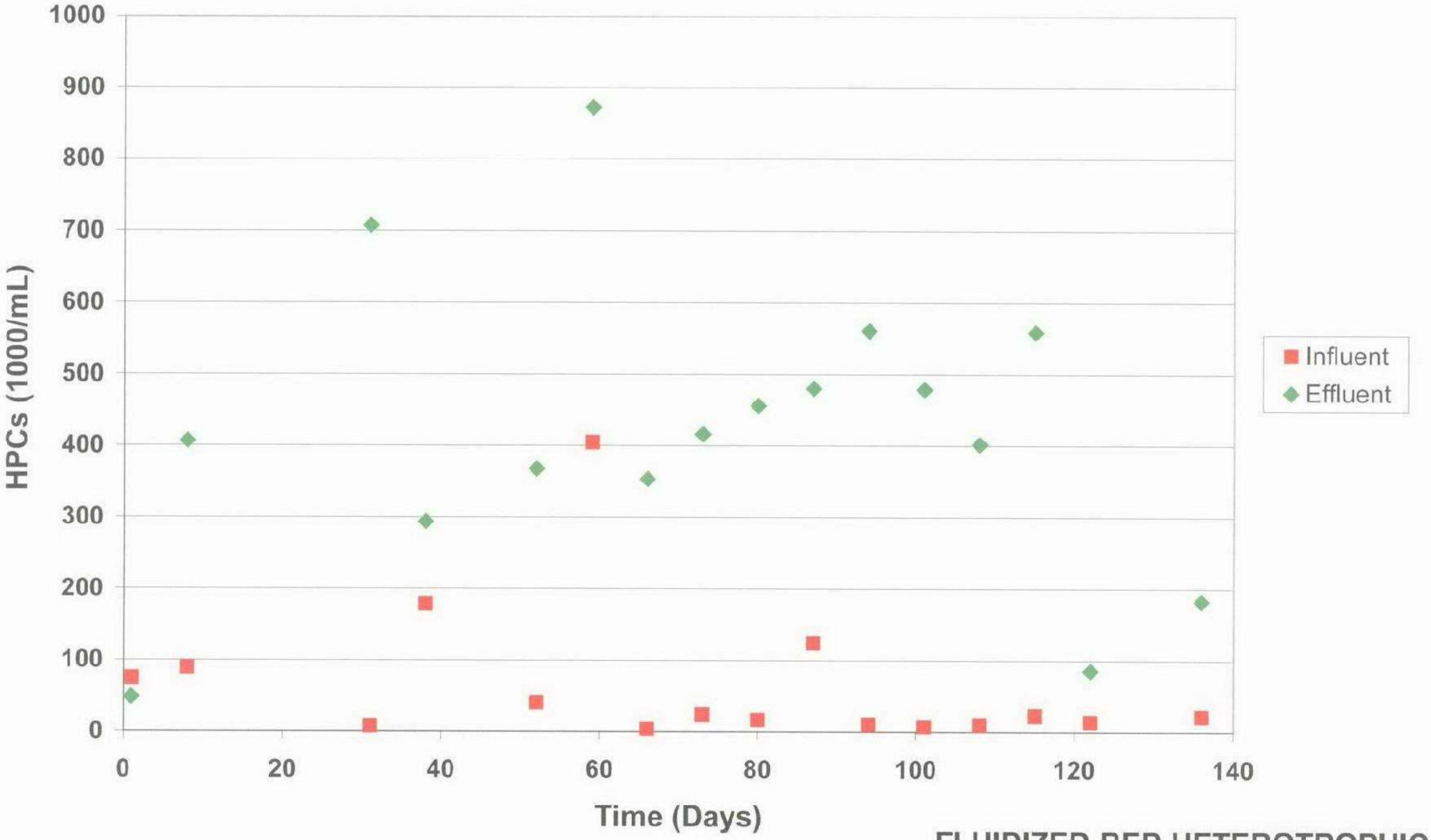
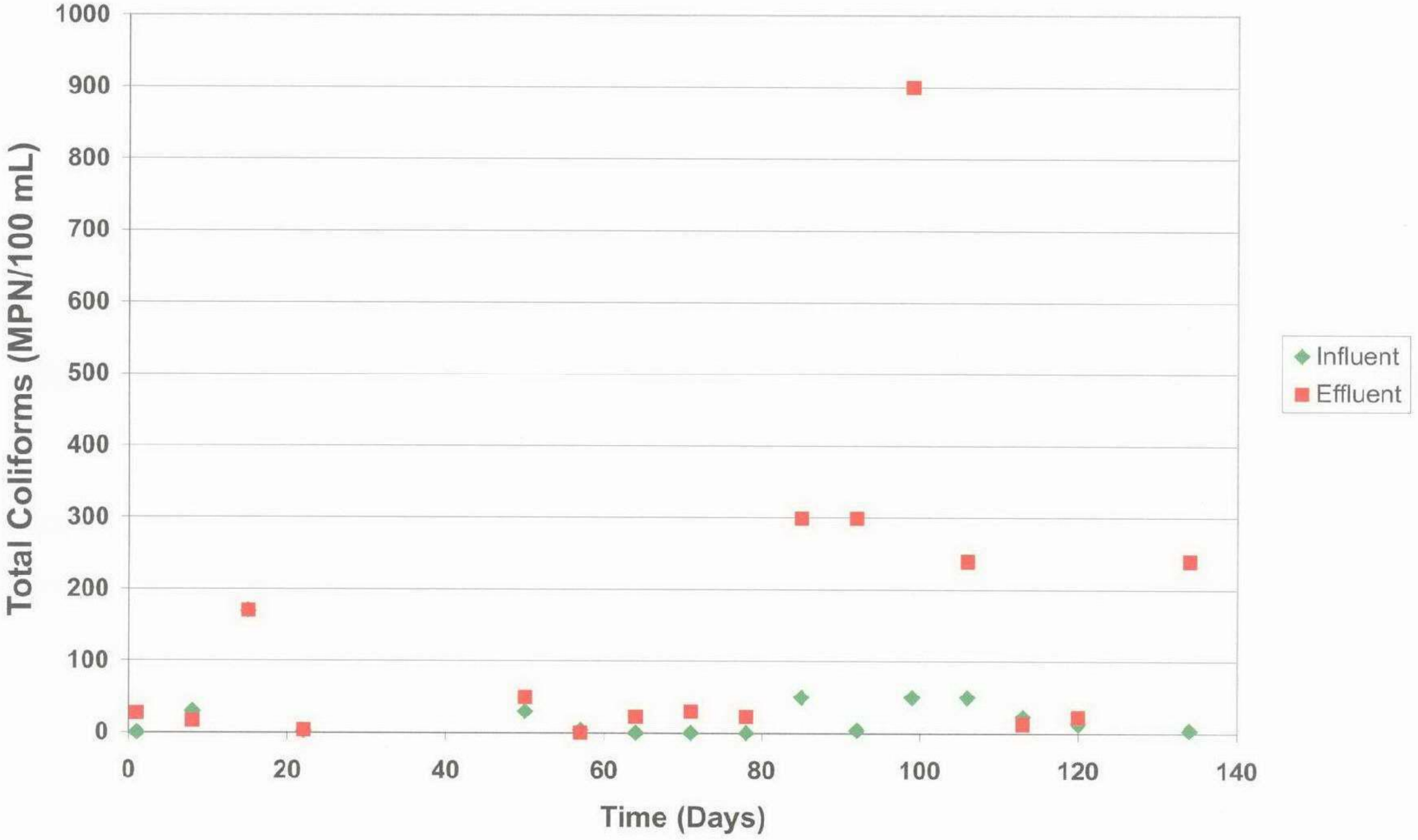


FLUIDIZED-BED HETEROTROPHIC PLATE COUNTS

FIGURE 3.46



FLUIDIZED-BED TOTAL COLIFORMS

FIGURE 3.47

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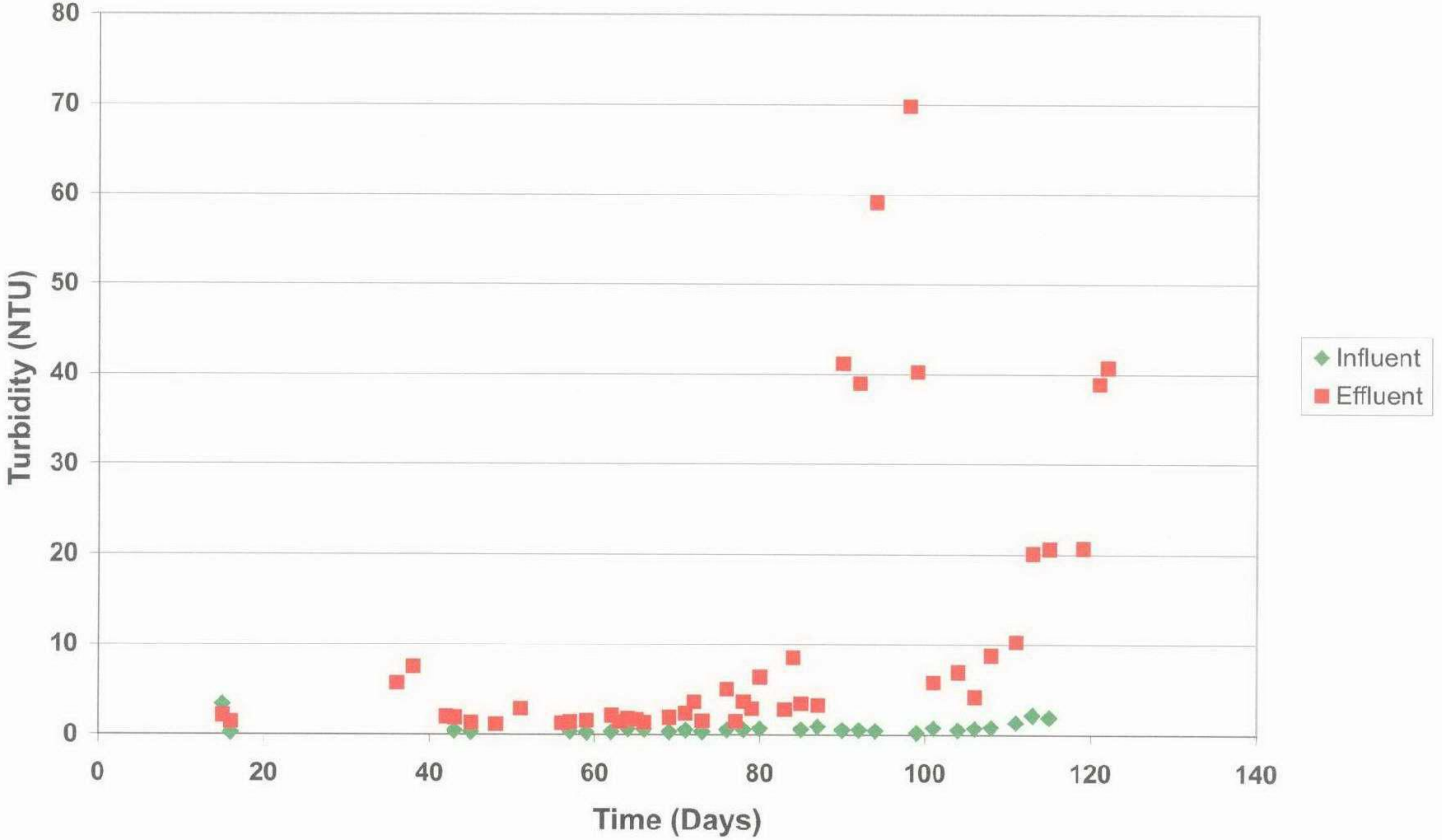

FLUIDIZED-BED TURBIDITY

FIGURE 3.48

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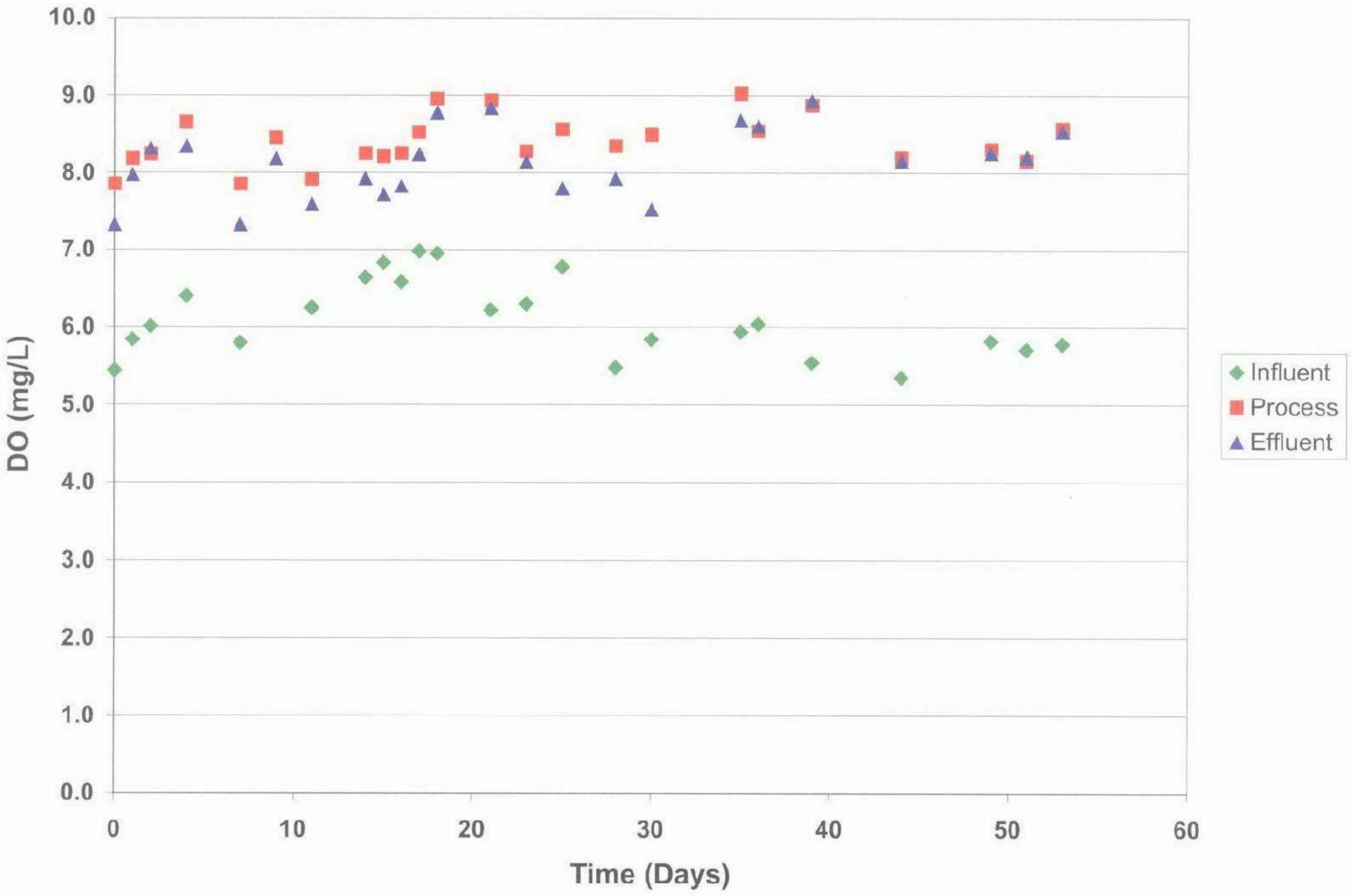

SMBR DISSOLVED OXYGEN

FIGURE 3.49

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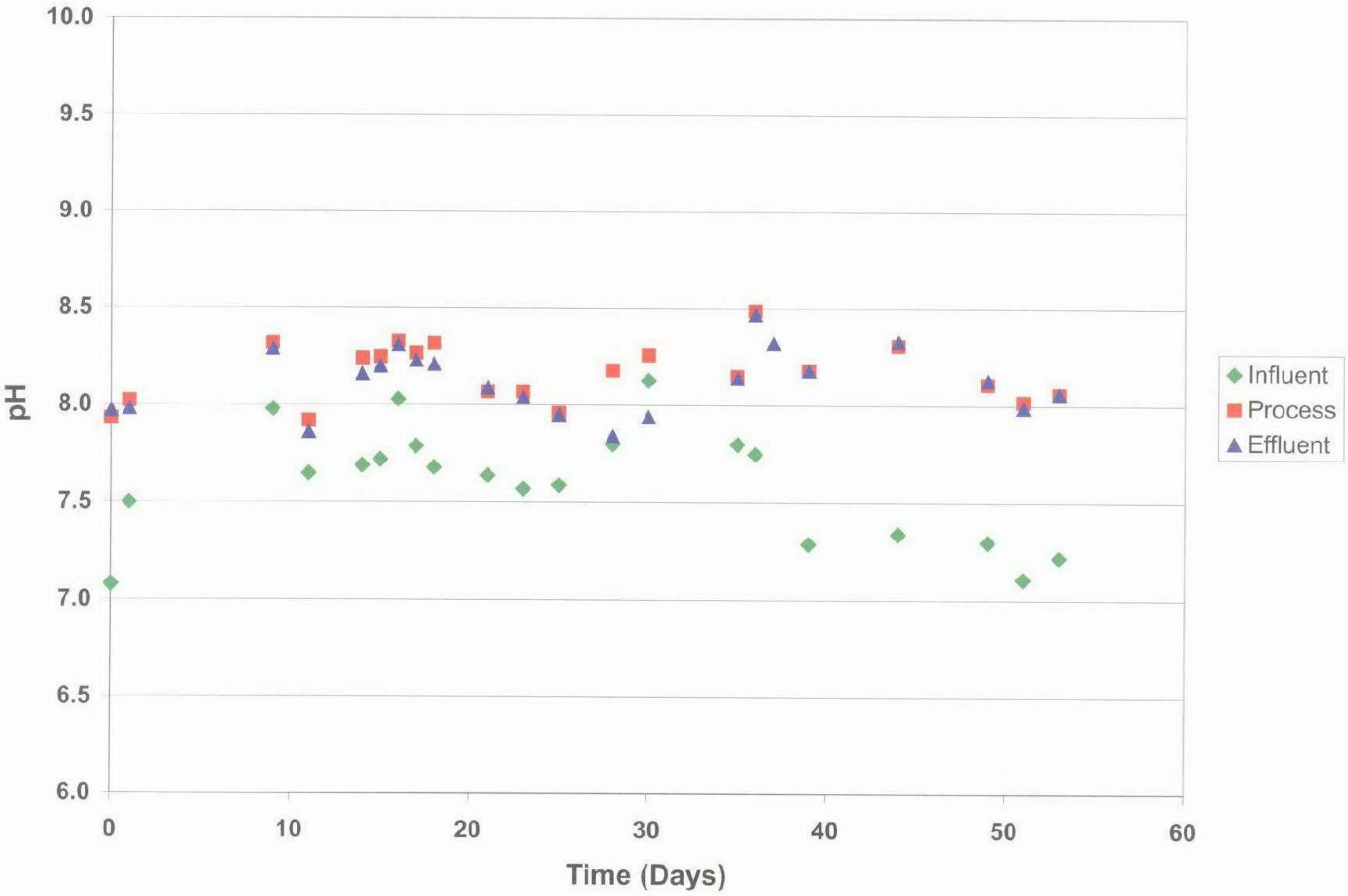

SMBR pH

FIGURE 3.50

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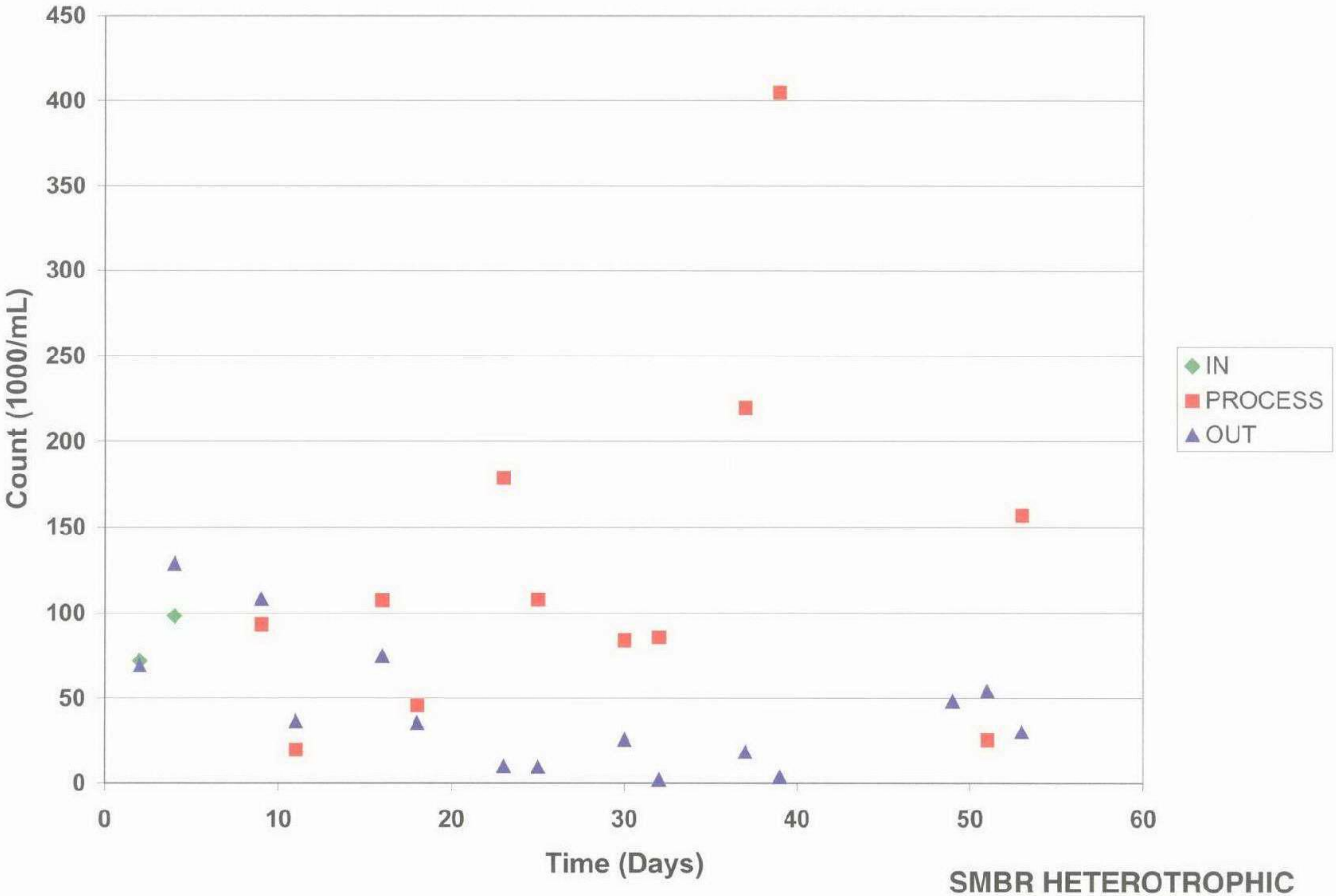

SMBR HETEROTROPHIC PLATE COUNTS

FIGURE 3.51

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7.6.3 Summary

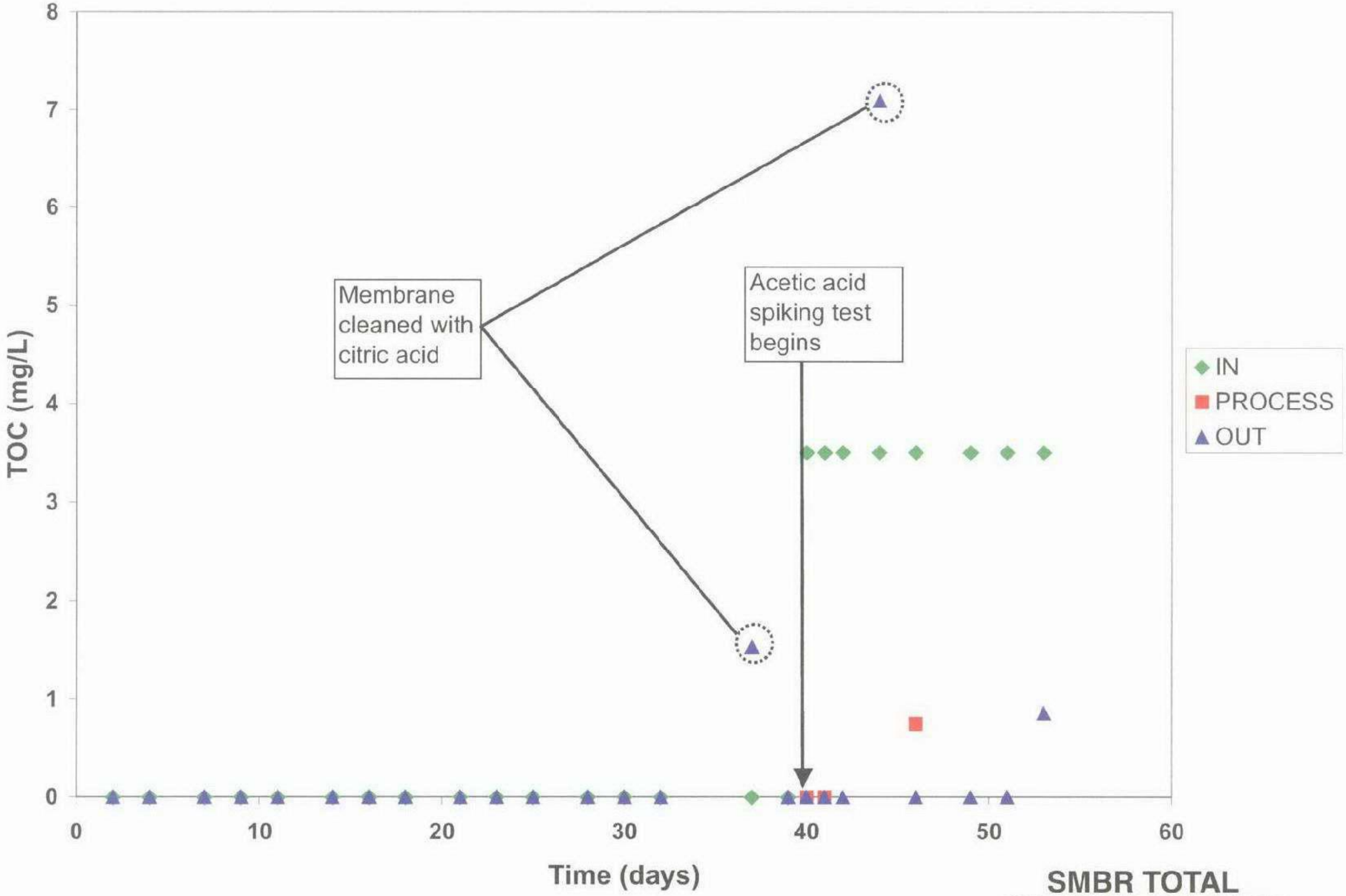
The fluidized-bed reactor did not achieve perchlorate removal to below detection over a period greater than 8 days, in spite of numerous mechanical and operational adjustments made to the system. However, testing did demonstrate that biological perchlorate removal can be achieved using indigenous microorganisms, a feature that had not yet been demonstrated for the FBR system. Because the FBR was not optimized, challenge testing was not performed.

7.7 Submerged Membrane Bioreactor (Post-Treatment of FXB Effluent)

The SMBR was set up to provide post-treatment for the FXB effluent, as required by DHS, i.e., aeration, filtration, and biological degradation of excess BDOC. The SMBR was fed with effluent from the FXB biological filter, which was already partially reaerated due to exposure to atmospheric conditions in the backwash tank. As expected, DO concentrations further increased in the SMBR process tank (Figure 3.49). pH also increased during the post-treatment process (Figure 3.50). The water entering the process tank is likely supersaturated with CO_2, produced by the oxidation of acetic acid in the FXB. Aeration within the process tank volatilizes supersaturated CO_2, thus bringing the water into equilibrium with atmospheric conditions and increasing the pH. Figure 3.51 shows that HPCs were being reduced across the ultrafiltration membrane. The effluent HPC concentrations are typically lower than the values observed in the raw well water. (See Figure 3.29.) Additional removal of heterotrophic bacteria can be achieved through disinfection following the SMBR. Batch experiments were performed to assess chlorine demand and HPC reduction using SMBR effluent. The chlorine demand of SMBR effluent was < 1 mg/L in all but one case, and only low doses of chlorine were required to reduce HPCs below 500 counts/mL (Table 3.24).

Table 3.24 Testing Matrix for Bench-Scale Chlorination of SMBR Effluent
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Chlorine Dose (mg/L)	12/1/03		12/3/03		12/5/03	
	Residual (mg/L)	HPCs (counts/mL)	Residual (mg/L)	HPCs (counts/mL)	Residual (mg/L)	HPCs (counts/mL)
0	0	48,450	0	54,150	0	30,400
0.5	0	69,250	0.15	250	0.08	4
1.0	0.17	271	0.31	100	0.60	52
2.0	0.88	10	1.15	450	1.58	2



SMBR TOTAL ORGANIC CARBON

FIGURE 3.52

Organic carbon concentrations in the effluent of the biological FXB were typically below detection throughout pilot testing. Therefore, 3.5 mg/L of acetic acid carbon was spiked to the SMBR process tank to evaluate the ability of the SMBR system to remove residual organic carbon. Figure 3.52 shows that in all but one instance, TOC concentrations were below detection in the SMBR effluent. Though some of the acetic acid may have volatilized, the lack of acetic acid smell in the vicinity of the process tank suggests that biological oxidation was the dominant mechanism of organic carbon removal in the SMBR.

Hydrogen sulfide odor was rarely detected in the feed to the SMBR and was never detected in the SMBR effluent. Analytical measurements resulted in no detectable sulfide (MRL = 0.1 mg/L). Any observed removal may have been due to volatilization. However, given a $pK_{a,1} = 7.1$ and an average process tank pH of 8.2, approximately 92 percent of the sulfide was in the HS^- form, thus minimizing the contribution of volatilization to sulfide removal. It is also possible that sulfide oxidation was occurring in the reactor, either spontaneously or via microbial catalysis. No effort was made to isolate the sulfide removal mechanism.

7.7.1 Summary

Demonstration testing showed that a submerged membrane bioreactor can meet several post-FXB treatment objectives in a single step: 1) aeration, 2) biomass separation, 3) residual organic carbon removal, and 4) hydrogen sulfide removal.

7.8 In-Line Ion Chromatographic Analysis

In addition to perchlorate analyses performed by CLWA and MWH labs, an in-line perchlorate analyzer was installed to provide real time perchlorate data. A Dionex DX-800 in-line ion chromatograph was used that can sample, analyze, and store data from up to 21 process streams. The system uses a 2 x 250 mm IonPac® AS16 analytical column (Dionex P/N 055378) with a 2 x 50 mm AG16 guard column. The sample volume was 1,000-mL with a flow rate of 0.4 mL/min. The effluent was an EG50-generated 50 mM potassium hydroxide (KOH) solution with a back pressure of approximately 2,500 psi. A 2-mm AMMS III suppressor operated in the chemical suppression mode and a CD20-PA Conductivity Detector was used for detection. The system was controlled by a CC81 controller. Run times for the samples were 30 minutes.

The instrument was initially connected directly to the FBR with samples being continuously drawn into the analyzer every 30 min for analysis. This created a problem due to the high amount of biomass being sloughed from the system. A rough prefilter was installed to complement the 20-µm pre-sample loop filter. This provided some removal of biomass but clogging continued to occur in the instrument, thus causing high excessive pressure build-up in the system. As a result, the system was configured to analyze only occasional grab samples for remainder of the project. This was beneficial in that the results were obtained in 30 minutes rather than 2 or 3 day for the CLWA lab or up to 1 month for MWH labs.

To test the accuracy of the instrument, split samples of raw water, spiked raw water, and effluents from each of the treatment alternatives were analyzed using the instrument. These samples were also sent to the CLWA lab and two different DHS labs. The results from the tests are provided in Table 3.25.

Table 3.25 Comparison of Perchlorate Results (μg/L)
(<MRL indicates less than method reporting limit of 4 μg/L)
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Sample	CLWA	DHS-LA	DHS-Berkley	In-Line Instrument
Raw water	<MRL	<MRL	<MRL	<MRL
IX-Spike	45.1	54.4	47.5	48.5
IX-C1	<MRL	<MRL	<MRL	<MRL
IX-C2	27.7	32.8	29.1	27.3
IX-C3	<MRL	<MRL	<MRL	<MRL
FXB-Spike	42.1	48.6	44.5	38.9
FXB-Out	<MRL	<MRL	<MRL	<MRL
FBR-Spike	41.8	50.2	43.2	42.4
FBR-Out	<MRL	34.2	26.8	<MRL

The results for the Dionex DX-800 were acceptable in most cases and correlated well with results from the other 3 labs. One sample, FBR out, read 27 and 34 mg/L from the two DHS labs, where the CLWA lab and the in-line monitor read below the reporting limit. This may be due to the lack of sample preservation of samples from the FBR. These samples were not preserved, therefore perchlorate degradation could have been an issue. In general, the Dionex instrument showed good correlation with measurements from other laboratories.

7.9 DBP Formation Potential Testing

7.9.1 Experimental Matrix

7.9.1.1 DBPFP Testing on FXB, FBR, and MBR Effluents

Conditions applied during the DBPFP testing conducted on the FXB effluent, the FBR effluent, and the MBR effluent are presented in Table 3.26. For each experiment, three samples were dosed with a range of free and combined chlorine concentrations in order to reach the target free and combined chlorine residual of 3 to 5 mg/L after an incubation period of 7 days. At the end of the incubation period, the sample with the chlorine residual closest to the target was used for DBP analysis and the other two samples were discarded.

Table 3.26 Conditions Applied during DBPFP testing
Treatment of Perchlorate Contaminated Groundwater from the Saugus Aquifer
Castaic Lake Water Agency

Free Chlorine Testing					
Stream	**Free Cl_2 Dose (mg/L)**	**$[Cl_2]_{Free,0}$ (mg/L)**	**Initial Demand (mg/L)**	**$[Cl_2]_{Free,7}$ (mg/L)**	**7-day Demand (mg/L)**
FXB Effluent	10	7.4	2.6	8.6	0
FBR Effluent	24	15.5	8.5	8.0	7.5
MBR Effluent	12	7.4	4.6	7.6	0

Combined Chlorine Testing					
Stream	**Free Cl_2 Dose (mg/L)**	**NH_3-N Dose (mg/L)**	**$[Cl_2]_{Total,0}$ (mg/L)**	**$[Cl_2]_{Total,7}$ (mg/L)**	**7-day Demand (mg/L)**
FXB Effluent	8	2.0	6.3	3.0	3.3
FBR Effluent	12	3.0	5.1	3.1	2.0
MBR Effluent	6	1.5	6.4	3.2	3.2

Free chlorine demand was slightly overestimated, resulting in free chlorine residuals ranging from 7.6 to 8.6 mg/L after 7 days of incubation, which was considerably higher than expected. Instantaneous free chlorine demands ranged from 2.6 mg/L in the FXB effluent to 8.5 mg/L in the FBR effluent. This was expected, since the FBR effluent contained higher levels of organic matter relative to the FXB effluent. The free chlorine demand in the FXB effluent and the MBR effluent was satisfied immediately and no decay of free chlorine was measured thereafter. In the case where the initial free chlorine concentration for the fixed bed effluent was lower than after 7-days of incubation, this was most likely due to the error in the measurements. Sample above 5 mg/L free chlorine had to be diluted to fall within the linear range of the method. In contrast to the other systems, free chlorine continued to decay over the 7-day incubation period in the FBR effluent.

As expected, combined chlorine residuals were more stable, measuring at 3 mg/L after 7 days of incubation in all three streams. The initial combined chloramine demand was greater in the FBR effluent relative to the other two streams.

7.9.1.2 DBPFP Testing on Ozonated FXB Effluent

The ozone test was conducted on a blend of 90 percent SPW and 10 percent FXB effluent to simulate the feed of the biological reactor effluent into the Rio Vista WTP. Conditions applied during ozone testing are presented in Table 3.27. Ozone demand ranged from 1.2 to 1.4 mg/L.

Table 3.27 Conditions Applied During Ozonation Testing
Perchlorate Treatment from Saugus Aquifer
Castaic Lake Water Agency

Stream	Transferred Ozone Dose (mg/L)	Ozone Residual (mg/L)	HRT (min)
FXB Effluent	1.76	0.37	5.4
FXB Effluent + Acetic Acid (AA)	1.72	0.54	5.3

Ozonated streams were further analyzed for critical parameters and subjected to DBPFP testing with free and combined chlorine. DBPFP conditions applied during ozone testing are presented in Table 3.28. Seven-day free chlorine residuals were higher than the target residual of 5 mg/L. Due to the limited availability of ozonated water, multiple bottles could not be incubated. Therefore, the DBP formation potential results are conservative. The free chlorine residual at time zero was not measured. Combined chlorine residuals ranged from 3.4 to 4.3 mg/L, falling within the target range of 3 to 5 mg/L.

Table 3.28 Conditions Applied During DBPFP Testing of Ozonated Waters
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Free Chlorine Testing					
Stream	**Free Cl_2 Dose (mg/L)**	**$[Cl_2]_{Free, 0}$ (mg/L)**	**Initial Demand (mg/L)**	**$[Cl_2]_{Free, 7}$ (mg/L)**	**7-day Demand (mg/L)**
Ozonated FXB Effluent	16	NA	NA	11.4	NA
Ozonated FXB Effluent+ AA	16	NA	NA	10.4	NA
Combined Chlorine Testing					
Stream	**Free Cl_2 Dose (mg/L)**	**NH_3-N Dose (mg/L)**	**$[Cl_2]_{Total, 0}$ (mg/L)**	**$[Cl_2]_{Total, 7}$ (mg/L)**	**7-day Demand (mg/L)**
Ozonated FXB Effluent	8	2	NA	4.3	NA
Ozonated FXB Effluent+ AA	8	2	NA	3.4	NA

7.9.2 Analytical Results

7.9.2.1 DBPFP Testing on FXB, FBR, and MBR Effluents

Control samples of each stream were analyzed for critical parameters (Table 3.28). Prior to chlorination, the FBR effluent contained a DOC concentration of 6 mg/L, whereas the other two streams contained negligible quantities of organic matter. It should be mentioned that DBPFP samples were collected from the FBR at a time before feed acetic acid concentration had been optimized. Since the acetic acid feed concentration was later reduced, the NOM and DBP results are conservative. A BDOC of 1.1 mg/L was measured in the FBR effluent. This BDOC level is higher than the 0.15 to 0.3 mg/L range of acceptable BDOC level for microbial growth in the distribution system. The AOC level in the FBR effluent of 178 µg/L is higher than the suggested 50 µg/L level to control coliform growth in distribution systems. The AOC concentration in the MBR effluent was higher than the AOC concentration in the MBR feed (i.e., FXB effluent), reflecting the fact that the MBR system was still being optimized at the time of the DBPFP tests. As expected, background THM4 and HAA5 levels (prior to chlorination) were non-detect.

Following free chlorine addition with an excess 7-day residual of 7.6 to 8.6 mg/L, THM4 and HAA5 levels were detected in all three streams. TTHM and HAA5 concentrations in the chlorinated FBR stream exceeded Stage 1 and Stage 2 D/DBP maximum contaminant levels of 80 µg/L and 60 µg/L, respectively. HAAs were the dominant DBPs in the biological and MBR effluents. All four TTHM species and all five HAA5 species were detected during the DBPFP testing with FBR effluent.

The reported 7-day TTHM and HAA concentrations are equivalent to formation potential levels since the concentrations on day zero (controls) were non-detect. It should be noted that a detectable level of DOC was measured in the FXB effluent, resulting in a BDOC of 0.23 mg/L. This is unexpected because the DOC in the control FXB effluent sample (i.e., prior to chlorination) was non-detect. THMs and HAAs in the MBR were below the Stage 1 and Stage 2 MCLs.

As expected, chloramination resulted in low levels of TTHMs and lower levels of HAA5 relative to free chlorination.

Table 3.29 DBPFP Testing Results
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Prior to Chlorination (Control)					
Stream	**DOC (mg/L)**	**BDOC (mg/L)**	**AOC (µg/L)**	**$THM4_0$ (µg/L)**	**$HAA5_0$ (µg/L)**
FXB Effluent	<0.5	ND	47	ND	ND
FBR Effluent	6.0	1.1	178	ND	ND
MBR Effluent	<0.5	ND	95	ND	ND

Table 3.29 DBPFP Testing Results
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Following DBPFP with Free Chlorine- Day 7

Stream	DOC (mg/L)	BDOC (mg/L)	AOC (μg/L)*	THM4,$_7$ (μg/L)	HAA5,$_7$ (μg/L)
FXB Effluent	NA	NA	NA	20	26
FBR Effluent	NA	NA	NA	110	140
MBR Effluent	NA	NA	NA	24	39

Following DBPFP with Combined Chlorine- Day 7

Stream	DOC (mg/L)	BDOC (mg/L)	AOC (μg/L)*	THM4,$_7$ (μg/L)	HAA5,$_7$ (μg/L)
FXB Effluent	NA	NA	NA	ND	17
FBR Effluent	NA	NA	NA	2.2	24
MBR Effluent	NA	NA	NA	ND	13

Notes:
NA: not analyzed

The DBPFP yields are presented in Table 3.30. The highest DBP formation yields were observed for the tests using FBR effluent. HAA formation yields were higher than THM yields for the same samples. Even though the DOC was non-detect in the MBR effluent, an HAA concentration of 13 μg/L was measured after chloramination, resulting in a yield of > 26 μg/mg DOC.

Table 3.30 DBPFP Yields
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

	THM4FP Yield (μg/mg DOC)		HAA5FP Yield (μg/mg DOC)	
Stream	Free Chlorine	Combined Chlorine	Free Chlorine	Combined Chlorine
FXB Effluent	5.0	0	6.6	4.3
FBR Effluent	32.0	2.1	40.7	7.0
MBR Effluent	0.2	0	0.4	>26(1)

Notes:
(1) DOC was ND

A follow-up 72-hr SDS test was conducted on the FBR effluent. A free chlorine dose of 2.6 mg/L was used, which resulted in a 3-day residual of 0.4 mg/L. The SDS-TTHM4 and SDS-HAA5 concentrations were 40 and 23 μg/L, respectively.

7.9.2.2 DBPFP Testing on Ozonated FXB Effluent

Following ozonation of the FXB effluent and the acetic acid-spiked FXB effluent samples, DBPFP testing was conducted with both free and combined chlorine (Table 3.32).

Bromate was formed at concentrations ranging from 1.8 to 8.7 μg/L. The bromide levels of 200 μg/L for the blended water (i.e., 90 percent SPW and 10 percent FXB effluent) are on the higher side. For comparison, bromate concentrations measured following ozonation at the Rio Vista WTP are less than 5 μg/L.

Aldehydes were formed at moderate levels when the FXB effluent was ozonated. As expected, total aldehydes (acetaldehyde, formaldehyde, glyoxal, pyruvic aldehyde, and pentanal) were slightly higher in the ozonated FXB effluent spiked with acetic acid relative to the unspiked FXB effluent. It should be noted that the filtration process at the Rio Vista WTP downstream of ozonation may further reduce the aldehyde levels in the finished water.

Ozonation increased the concentration of BDOC and AOC, a phenomenon widely reported in the literature. In a full-scale treatment process, the biodegradable organic matter would be reduced through the filters prior to final chlorination by biological oxidation. Chlorination and chloramination of the samples resulted in a decrease in the BDOC concentration, probably as a direct result of NOM oxidation by the disinfectant.

High concentrations of TTHMs and HAAs were measured in the ozonated samples following DBP formation testing with free chlorine. It should be noted that since the measured free chlorine residuals after 7 days of incubation were higher than the target residual range of 3 to 5 mg/L, these DBP results are conservative. In addition, in a full-scale treatment process, the preozonated water would be filtered prior to final chlorination. This filtration process would be expected to remove some of the DBP precursors by biological oxidation, resulting in lower DBP levels than those shown in Table 3.31.

Table 3.31 DBPFP Testing Results-Ozone Test
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Raw Samples					
Stream	**TOC (mg/L)**	**DOC (mg/L)**	**BDOC (mg/L)**	**AOC (μg/L)**	**Bromide, low (mg/L)**
FXB Effluent	2.4	2.5	0.53	200	200
FXB Effluent+AA	9.2	8.8	2.5	1266	200

Table 3.31 DBPFP Testing Results-Ozone Test
Treatment of Perchlorate Contaminated Groundwater
from the Saugus Aquifer
Castaic Lake Water Agency

Ozonated Samples Prior to Chlorination (Control)

Stream	DOC (mg/L)	TOC (mg/L)	BDOC (mg/L)	AOC (μg/L)	Br (μg/L)	BrO_3 (μg/L)	Aldehyde (μg/L)	THM4,$_0$ (μg/L)	HAA5,$_0$ (μg/L)
FXB Effluent	2.6	2.4	3.7	240	190	8.7	40	ND	ND
FXB Effluent +AA	3.2	8.8	5.6	1,446	200	1.8	54	ND	ND

Following DBPFP with Free Chlorine- Day 7

Stream	TOC (mg/L)	DOC (mg/L)	BDOC (mg/L)	THM4,$_7$ (μg/L)	HAA5,$_7$ (μg/L)
FXB Effluent	2.0	1.9	0.22	200	56
FXB Effluent+AA	8.6	8.5	1.5	180	65

Following DBPFP with Combined Chlorine- Day 7

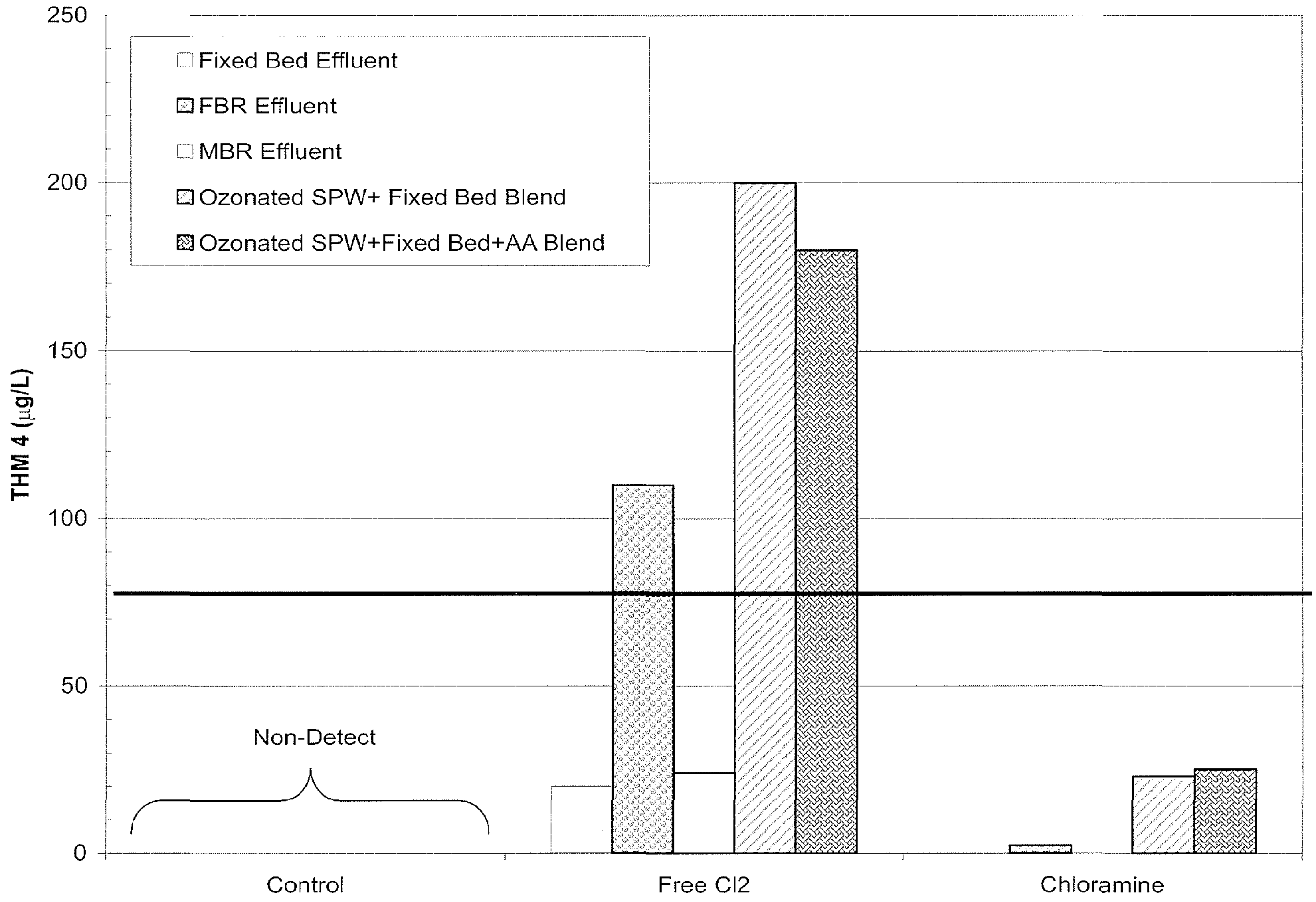
Stream	TOC (mg/L)	DOC (mg/L)	BDOC (mg/L)	THM4,$_7$ (μg/L)	HAA5,$_7$ (μg/L)
FXB Effluent	2.3	2.2	0.38	23	12
FXB Effluent+AA	8.8	9.0	0.50	25	13

While HAAs were the dominant DBPs in the chlorinated FXB, FBR, and MBR effluents, TTHMs were the dominant DBPs in the blended FXB effluent samples, which is confirmed by typical DBP concentrations measured in the full-scale Rio Vista WTP distribution System (i.e., approximately 65 μg/L for THMs and 15 μg/L for HAAs).

7.9.3 Comparison of DBP Formation Results

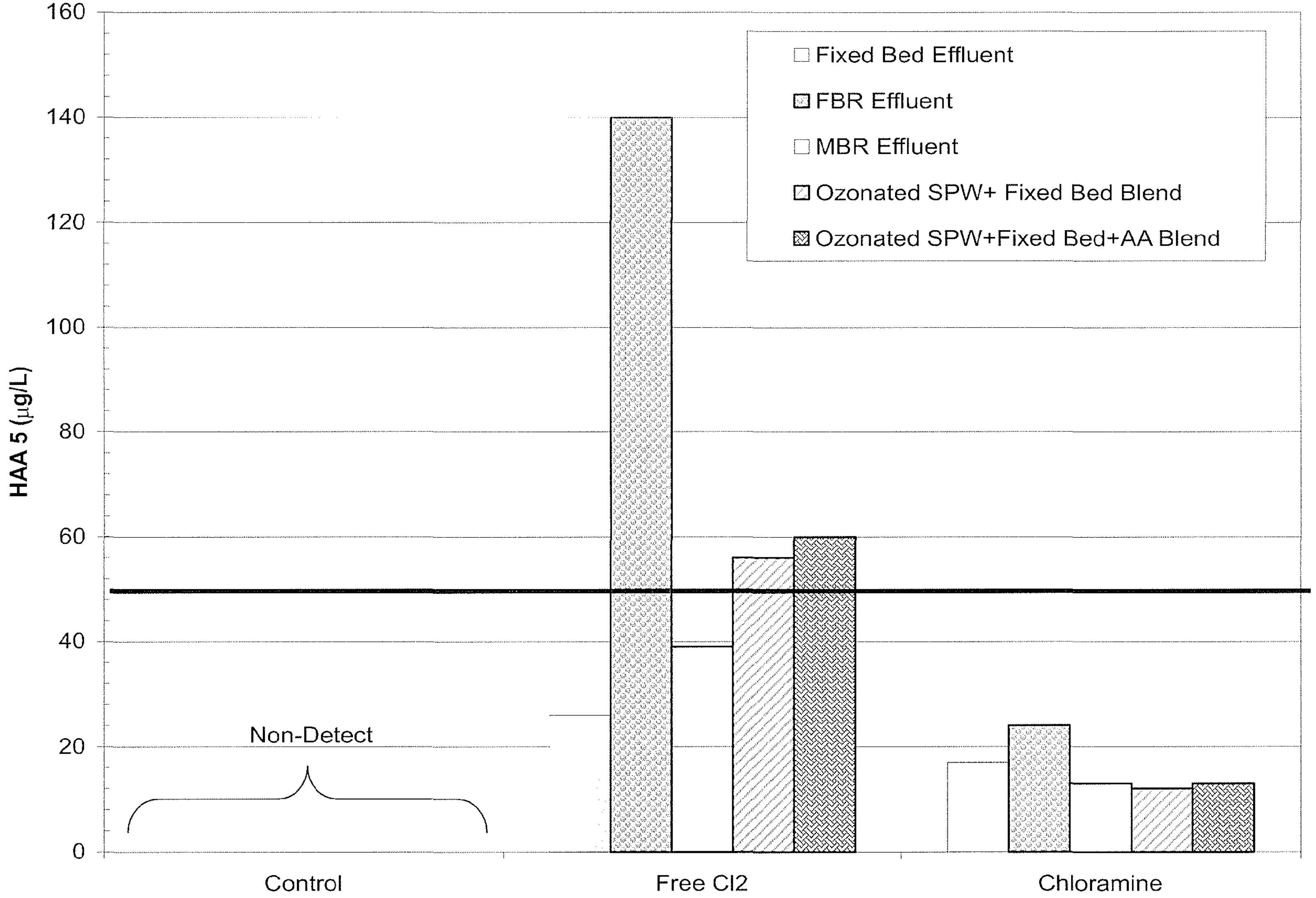
THMFP and HAAFP results for all streams are plotted in Figures 3.53 and 3.54. It must be emphasized that the chlorination and ozone results are conservative. The HAA concentrations in the ozonated samples are lower than the TTHM concentrations, suggesting that the SPW water favors the formation of THMs over HAAs. Non-blended water tended to form HAAs over THMs.

In summary THMs and HAAs tend to form in the effluent of the biological systems upon the addition of free chlorine. The THMs and HAAs in the FXB effluent (which was already at steady-state operation) were lower than the current Stage MCLs. Higher DBP concentrations measured in the chlorinated and ozonated FBR effluent are premature since the FBR was not optimized.



COMPARISON OF DBPFP THM4 SAMPLES FROM SEVERAL STREAMS

FIGURE 3.53



COMPARISON OF DBPFP HAA5 SAMPLES FROM SEVERAL STREAMS

FIGURE 3.54

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As expected, chloramination results in THM and HAA levels significantly lower than the Stage 2 MCLs.

7.10 Summary of DBPFP Results

7.10.1 DBPFP Testing on Fixed Bed, Fluidized Bed, and MBR Effluents

Following free chlorine addition with an excess residual after 7 days of incubation, DBP levels were formed in all streams, with levels in the FBR stream exceeding current MCLs of 80 μg/L and 60 μg/L for THMs and HAAs, respectively. It should be noted that the FBR was not optimized prior to the DBPFP tests. Because the FBR feed acetic acid concentrations were higher than ultimately required, the FBR DBPFP tests are considered conservative. HAAs were the dominant DBPs in the three samples. As expected, chloramination resulted in low levels of THMs and lower levels of HAAs as compared to free chlorination. Higher DBP formation yields were calculated in the FBR effluent relative to the FXB effluent. A follow-up 72-hour SDS test was conducted on the FBR effluent. The SDS-THM4 and SDS-HAA5 concentrations were lower than the D/DBPR Stage 2 MCLs, measured at 40- and 23-μg/L, respectively.

7.10.2 DBPFP Testing on Ozonated Fixed Bed Effluent

To simulate DBP formation potential of FXB effluent that is post-treated at the Rio Vista Water Treatment Plant (WTP), a blend of 90 percent State Project Water (SPW) and 10 percent FXB effluent was ozonated and contacted with free or combined chlorine. Following ozonation, bromate was formed at concentrations ranging from 1.8 to 8.7 μg/L due to high bromide levels of 200 μg/L for the blended water. Aldehydes were formed at moderate levels, even in the effluent spiked with acetic acid. The ozonation of the samples resulted in an increase in the BDOC and AOC concentrations. It should be noted that the filtration process at the Rio Vista WTP downstream of ozonation may further reduce the aldehydes and BDOC levels in the finished water. High levels of THMs and HAAs were measured in the ozonated samples following DBP formation testing with free chlorine. THM4 concentrations were two times the Stage 2 MCL. However, residual chlorine concentrations were excessive during incubation and, more importantly, a large fraction of DBP precursors would likely be removed downstream of ozonation, prior to chlorination at the Rio Vista WTP. The HAA concentrations in the ozonated samples, although relatively high, were lower or equal to the Stage 2 MCL. Seven-day incubation of ozonated water with combined chlorine generated only 23 μg/L TTHM4 and 12 μg/L HAA5.

8.0 CONCLUSION

All three ion-exchange resins removed perchlorate to below detection for run times exceeding model predictions. Preliminary NDMA formation potential tests with pre- and post-disinfection, as well as spent resin characterization tests suggest that the operation and disposal of these resins under the conditions tested should not raise any concern. It should be noted however that in a full-scale process, the temporal discharge of groundwater following a resin change-out may pose a challenge due to potential restrictions in chloride level imposed by the relative agency (e.g., county sanitation district or regional water quality control board).

Consistent perchlorate removal to below detection was achieved in the FXB filter using only organisms indigenous to the Saugus aquifer. With influent DO and nitrate concentrations of 7 and 15 mg/L, respectively, the lowest EBCT and acetic acid concentration that allowed consistent perchlorate removal to below detection was 15 minutes and 7.8 mg/L as carbon, respectively. Run times ranged from 24 hours to several days. Effluent from the FXB filter was biologically stable and contained no fecal coliforms. Challenge tests demonstrated that the FXB filter was robust with respect to backwashing episodes, changes in feed water quality, system shut-downs, and electron donor addition failures. Large step increases in feed nitrate concentration (e.g., 15 mg/L) required a period of bio-acclimation before perchlorate removal to below detection could be reestablished in the FXB filter. A short-term post-treatment test performed on the FXB system with an SMBR demonstrated that the SMBR would be able to meet regulatory requirements in terms of aeration and filtration in a single step. DBP formation tests for the fixed bed reactor resulted in THM and HAA levels lower than the Stage 2 MCLs.

The fluidized-bed reactor did not achieve perchlorate removal to below detection over a period greater than 8 days, in spite of numerous mechanical and operational adjustments made to the system. However, testing did demonstrate that biological perchlorate removal can be achieved using indigenous microorganisms, a feature that had not yet been demonstrated for the FBR system. Because the FBR was not optimized, challenge testing was not performed.

A number of critical design parameters have been established based on the test results. These will be used during the pre-design of a selected system. Based on the performance of these systems, preliminary budget level costs have been developed, which will be presented in the pre-design report.

9.0 REFERENCES

Na, C., Cannon, F.S., and Hagerup, B. 2002. "Perchlorate Removal via Iron-Preloaded GAC and Borohydride Regeneration." Journal AWWA, 94(11): 90-102.

Brown, J.C., V.L. Snoeyink, and M.J. Kirisits. 2002. “Removal of Perchlorate at Low µg/L Concentrations by Sorption and Biological Reduction in an Activated Carbon Filter.” Journal AWWA, 94(2): 70-79.

Herman, D.C. and Frankenberger Jr., W.T. 1999. "Bacterial Reduction of Perchlorate and Nitrate in Water." Journal of Environmental Quality, 28: 1018-1024.