FINAL REPORT

Tailored Granular Activated Carbon Treatment of Perchlorate in Drinking Water

ESTCP Project ER-200546

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List of Acronyms

AA	Atomic Absorption
AFB	Air Force Base
AFIT	Air Force Institute of Technology
ANSI	American National Standards Institute
ANSI/NSF	American National Standards Institute/National Sanitary Foundation
ARAR	Applicable or Relevant and Appropriate Requirements
AWWA	American Water Works Association
BGS	Below Ground Surface
BV(s)	Bed Volume(s)
CERCLA	Comprehensive Environmental Response Compensation and Liability Act
CFU	Colony Forming Units
ClO_4^-/NO_3^-	Nitrate
COC	Chain of Custody
CPC	Cetylpyridinium Chloride
CTAC	Cetyltrimethylammonium Chloride
CUR	Carbon Utilization Rates
DHS	Department of Health Services
DI	Deionized
DO	Dissolved Oxygen
DoD	Department of Defense
DOT	Department of Transportation
DPD	N,N′-diethyl-p-phenylenediamine
DPH	Department of Public Health
DTAB	Decyltrimethylammonium Bromide
DTSC	Department of Toxic Substances Control
DWEL	Drinking Water Equivalent Level
EBCT	Empty Bed Contact Time
EI	Electrical and Instrumentation
EPA	Environmental Protection Agency
ESC	Excavation, Site Work, and Concrete
ESTCP	Environmental Security Technology Certification Program
FDA	Food and Drug Administration
FWC	Fontana Water Company
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
GPD	Gallons per Day
GPM	Gallons per Minute
HCL	Hydrogen Chloride
HCO_3	Bicarbonate
HHA	Haloacetic Acids
HMX	Octahydro-1,3,5,7-Tetranitro-1,3,5,7-Tetrazocine

HPLC	High Pressure Liquid Chromatography
HRL	Health Reference Level
IC-MS/MS	Ion Chromatography Tandem Mass Spectrometry
ID	Identification
ITRC	Interstate Technology and Regulatory Council
IX	IX
LC/MS/MS	Liquid Chromatography Tandem Mass Spectrometry
MCL	Maximum Contaminant Level
ME	Manufactured Equipment
MPN	Most Probable Number
MS	Mass Spectrometry
MTAB	Myristyltrimethylammonium Bromide
MW	Molecular Weight
NAS	National Academy of Science
NCP	National Contingency Plan
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NDPA	N-Nitrosodi-n-propylamine
NFESC	Naval Facilities Engineering Services Center
NL	Notification Level
NPDES	National Pollution Discharge Elimination System
NSF	National Sanitary Foundation
NWIRP	Naval Weapons Industrial Reserve Plant
O&M	Operations and Maintenance
OEHHA	Office of Environmental Health Hazard Assessment
OMB	Office of Management and Budget
ORP	Oxidation Reduction Potential
PCE	Perchloroethylene
PHG	Public Health Goal
polyDADMAC	Poly(Dimethyldiallylammonium Chloride)
PPE	Personal Protective Equipment
PPV	Pumps, Piping and Valves
PRG	Preliminary Remediation Goal
PSU	Pennsylvania State University
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance and Quality Control
QMDL	Quantitative Minimum Detection Limit
RCRA	Resource Conservation and Recovery Act
RDX	Hexahydro-1,3,5-Trinitro-1,3,5-Triazine
RfD	Reference Dose
RSD	Relative Standard Deviation
RSSCT	Rapid Small Scale Column Tests
RWQCB	Regional Water Quality Control Board
$S_2O_3^{2-}$	Thiosulfate
SAI	Superior Adsorbents, Inc.
SCADA	Supervisory Control and Data Acquisition

SDS	Simulated Distribution System
SDWA	Safe Drinking Water Act
TBC	To Be Considered
TCE	Trichloroethene
TDS	Total Dissolved Solids
TGAC	Tailored Granular Activated Carbon
THAB	Tributylheptylammonium Bromide
THM	Trihalomethane
TNT	Trinitrotoluene
TOC	Total Organic Carbon
TOX	Total Organic Halides
USGS	U.S. Geological Survey
VOC	Volatile Organic Compounds

Acknowledgement

The help and support of the Fontana Water Company in the conduct of this work is greatly appreciated.

Executive Summary

Perchlorate is a drinking water concern because of its high solubility and mobility, its effects on thyroid hormone production, and its relatively high treatment cost. Although perchlorate removal technologies suitable for wellhead application such as ion exchange (IX) are in service, there is a need to develop additional economical perchlorate removal technologies. In an Environmental Security Technology Certification Program (ESTCP)-funded technology validation project, ARCADIS, Siemens, Pennsylvania State University (PSU), and the Air Force Institute of Technology (AFIT) demonstrated the application of "tailored" granular activated carbon (TGAC) for the removal of perchlorate for a drinking water application. The tailoring process adsorbs surfactants with quaternary ammonium groups to granular activated carbon (GAC), which dramatically increases the perchlorate removal capacity of the GAC, while still allowing the GAC to remove volatile organic compounds (VOC).

The primary objectives of the project were to demonstrate the following: (1) a reliable, cost-effective treatment technology for removing perchlorate from drinking water, (2) removal of both perchlorate and TCE simultaneously, and (3) simple system operation and maintenance with minimal monitoring. The major activities/scales of testing performed under the ESTCP project are summarized in Table E1 along with the major results of each phase of the project. Additional data sets collected under other funding, but used to help interpret the results of this Fontana demonstration, are summarized in Table E2. The 38-gallons per minute (gpm) field-scale TGAC demonstration system operated nearly continuously between January 11, 2007, and December 5, 2007. During that period, the system operated for approximately 318 days and treated over 16.2 million gallons of perchlorate-impacted groundwater. Six parallel pilot-scale test beds, including a chlorinated solvent (trichloroethene [TCE]) as a co-contaminant, were operated in Fontana for approximately 6 months each (challenging the technology with varied influent conditions). Field data were supplemented with seventeen rapid small-scale column tests (RSSCT) performed in the laboratory with Fontana groundwater.

For these Fontana pilot scale and bench-scale trials, an anthracite-based GAC was preloaded with cetylpyridinium chloride (CPC). The TGAC system was effective in removing perchlorate to below current regulatory standards for approximately 15,000 bed volumes (BV) (4- to 5-month bed life). Data from two different scales of testing suggest that increases in nitrate and perchlorate influent concentrations reduce breakthrough time, as expected. Increases in the concentrations of other anions appear only to moderately decrease performance, at worst.

Performance data have been obtained for unamended Fontana groundwater at three different scales: laboratory-scale and two field-scale systems. TGAC testing with Fontana groundwater showed a lower bed life to initial perchlorate breakthrough than proportional-diffusivity-based RSSCT tests predicted. Laboratory studies conducted after the Fontana demonstration indicate that when using RSSCT tests to predict perchlorate removal by TGAC, the best fit to field-scale data relative to initial breakthrough can be obtained using a mathematical approach intermediate between proportional (exponent = 1) and that with an exponent =1.5.

Field-scale TGAC operations showed an absence of problems directly attributable to the technology. During drinking water treatment with TGAC, the operations and maintenance activities are likely to be very similar to those required for a similarly-sized IX system. However, since IX systems using currently available resins are likely to have a longer time to breakthrough, a greater frequency of monitoring is likely to be required for the TGAC system.

As a result of recent technological and process improvements, the general cost of conventional IX systems used to remove perchlorate has declined steadily between 2000 and 2009. This makes it difficult for an innovative technology to displace this accepted alternative. The cost analysis conducted in this project suggests that TGAC is not currently able to economically displace conventional IX resins. There are, however, several options that may improve TGAC cost effectiveness. Studies conducted after the completion of the Fontana field-scale work show that the anthracite-based GAC used in tailoring is inferior in performance to bituminous-based GAC because of differences in porosity structure. Bench scale studies showed the bituminous-based GAC could achieve nearly twice the bed life to perchlorate breakthrough. The change in carbon type alone would not have been enough to economically displace perchlorate selective resins. The particular cetylpyridinium chloride (CPC) tailoring agent used was selected for this field test based on previous data and because the permitting of CPC for drinking water applications is straightforward (CPC is an ingredient in mouthwash). However, other tailoring agents such as Arquad 2C-75 may provide better perchlorate selectivity over competing anions like nitrate. Based on the results available to date, the TGAC technology may be best suited for use on aerobic waters with low nitrate concentrations and with a VOC(s) as a co-contaminant(s). Additional research to optimize tailoring agents to particular groundwater chemistries may be warranted.

Table E1: Major Project Activities/Scales of Testing

Scale of Testing	Location, Source Water	Major Data Sets Developed	Major Results	Location in Report
Field **37 gpm** **Three beds in series**	Fontana Well 17B/17C	Perchlorate elution curve, major anion and cation concentrations, operational performance, economics. Tailoring agent leaching analysis.	Bed A (Lead Bed) reduced perchlorate concentrations below 6 µg/L for ~15,000 BVs. The tailoring agent was not detectable after the guard bed. Achieved an operational uptime of approximately 97%.	Main body of report, example results in Section 5.7.2
Field **1.5 to 3 gpm** **Six sets of two beds in series**	Fontana Well 17B/17C	Perchlorate elution curve during challenge with various influent amendments. Tailoring agent leaching analysis.	The perchlorate spike had the most dramatic effect on performance, followed by total dissolved solids (TDS), nitrate and TCE. The predisinfectant/oxidant train also performed more poorly than the control. Most trains displayed substantial evidence of a chromatographic roll-over effect. At the concentration ratio tested, TCE broke though after perchlorate.	Main body of report, example results in Section 5.7.3
RSSCTs **17 columns** **2.5 ml/min**	At PSU using water from Fontana Well 17B/17C	Perchlorate elustion cuve during challenge with various influent ammendments at multiple concentration levels. Mass perchlorate loading per gram TGAC. Performance as a function of pH.	The capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7. Sulfate, thiosulfate, chloride, and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites.	Discussed briefly in main report body, but primarily in Appendix B
Electronic cost and performance model	Based primarily on Fontana RSSCT data to model sensitivity to different competing anions	Sensitivity of costs to various competing anions. Major cost components within lifecycle cost. Effect of flow rate on unit cost of treatment.	Estimated capital and operating cost of $261 per acre foot, which is likely to be higher than IX under many treatment scenarios. Technology is more cost competitive with organic co-contaminants present.	Report Section 7, AFIT thesis documents.
Simulated distribution system tests	Batch tests at ARCADIS labratory using water from Fontana Well 17B/17C	Disinfection byproducts from chlorination of TGAC treated water	Disinfection byproducts essentially unchanged by use of TGAC	Report Section 5.7.4
Tracer testing of 37-gpm field-scale system	Fontana tap water (treated) spiked with magnesium sulfate as a tracer	Conductivity vs. flow volume curves	The 37-gpm beds had minimal potential for bypassing but some potential for fluidizing the upper layer of TGAC	Introduced in report Section 5.5.2, detailed in Appendix I, refered to in report section 6.8.2

Table E2: Supplementary Studies Used in Demonstration Interpretation

Scale of Testing	Location, source water	Major Data Sets Developed	Major results	Location in Report
RSSCT tests and comparison to field-scale results at another site (Redlands)	Redlands, CA, groundwater and deionized distilled water control	Parametric RSSCT study producing perchlorate elution curves wth various combinations of water age, perchlorate concentration and thiosulfate concentration. Some conditions were tested with and without prechlorination before TGAC treatment.	Under some conditions, unstable reduced sulfur compounds such as thiosulfate can compete effectively with perchlorate for sorption sites on TGAC. These compounds are not stable in long-term storage, making laboratory testing for technology performance prediction difficult. Prechlorination can remove these compounds.	Redlands study introduced in Sections 2.2.3. Appendix C presents the RSSCT study. Section 6.8.2 uses it in interpreting the Fontana data.
RSSCT tests comparing GAC source materials	Redlands, CA, groundwater	Perchlorate elution curves with anthracite vs. bituminous based GAC. Pore size analysis of these GACs.	Bituminous-based GAC substantially better then anthracite-based GAC for perchlorate removal. Particle size distribution analyses show a dramatically different porosity structure for anthracite-based carbons than for bituminous-based carbons.	Appendix J, briefly discussed in report Sections 6.8 and 7.4
RSSCT tests and slow bench-scale test comparison	State College PA water, spiked with perchlorate	Perchlorate elution curves using RSSCT protocol, compared to a bench pilot test run under directly field mimicing conditions.	RSSCT tests for perchlorate TGAC will best fit field-scale data using a mathematical scaling approach intermediate between proportional and constant diffusivity.	Detailed in Appendix J and discussed in report Section 6.8.1

1. INTRODUCTION

This final report describes the results of an Environmental Security Technology Certification Program (ESTCP) Environmental Restoration project evaluating the use of tailored granular activated carbon (TGAC) in wellhead treatment of perchlorate in drinking water.

Several large perchlorate plumes have impacted at least 20 large municipal drinking water supply wells in California's Inland Empire, resulting in their removal from service or installation of costly treatment systems. Perchlorate is a drinking water concern because of its high solubility and mobility, effects on thyroid hormone production, and relatively high treatment cost. The need for perchlorate treatment is nationwide and especially acute in the southwestern United States, including the Southern California Inland Empire region. Throughout the United States, state standards or advisory levels are still evolving, and currently range from 1 to 18 micrograms per liter (µg/L) (http://www.epa.gov/swerffrr/pdf/stateadvisorylevels.pdf).

Although perchlorate removal technologies suitable for wellhead application exist, there is a need to develop additional economical perchlorate removal technologies. In addition, conventional wellhead technologies are specific for perchlorate only and are unable to effectively treat VOCs that are often co-contaminants.

In ESTCP-funded technology validation project ER-0546, ARCADIS, Siemens Water Technologies (Siemens), Pennsylvania State University (PSU), and the Air Force Institute of Technology (AFIT) (hereafter referred to as the Project Team) demonstrated the application of TGAC for the removal of perchlorate from drinking water. Points of contact for the project team are listed in Appendix A. The demonstration site was an operating drinking water treatment plant in Fontana, California, a city located in the Inland Empire region of southern California. The tailoring process to convert granular activated carbon (GAC) to TGAC attaches surfactants with quaternary ammonium groups to conventional-GAC, which increases the perchlorate removal capacity by up to 35 times, while still allowing the GAC to remove VOCs. During this project, data to achieve regulatory and water purveyor acceptance were generated using pilot-scale equipment and perchlorate impacted groundwater in Fontana, California.

Two field test installations were implemented and are discussed below. The first installation consisted of three vessels in series treating 37 gallons per minute (GPM) (0.14 m^3/minute), and the second installation consisted of six smaller scale treatment trains treating 1.5 GPM (0.0057 m^3/minute).

For the larger scale treatment train, approximately 38 GPM (0.14 m^3/minute) of water was processed. The 38 GPM (0.14 m^3/minute) passed through three demonstration vessels connected in series. Six smaller scale treatment trains were operated to permit the determination of TGAC performance under different groundwater chemistry conditions.
The induced changes in water chemistry on a per treatment train basis are listed below and described in more detail later in this document:

- Increased total dissolved solids (TDS)/sulfate
- Trichloroethene (TCE) addition
- Increased perchlorate
- Increased nitrate
- Stratified beds control – no spiking agent
- Predisinfectant/oxidant

Funding and oversight was provided by ESTCP and the Naval Facilities Engineering Services Center (NFESC). The project was funded under a special congressionally directed program to ESTCP for wellhead perchlorate treatment. This work was contracted through the Corps of Engineers in Alexandria, Virginia, and overseen by the NFESC. The program involved field activities at a municipal perchlorate treatment facility and TGAC production at a Siemens Water Technologies facility.

1.1 BACKGROUND

Perchlorate is an issue in drinking water due to its high solubility and mobility, known effects on thyroid hormone production, and treatment cost. The need for perchlorate treatment is nationwide and especially acute in the southwestern United States, including the Southern California Inland Empire region. Throughout the United States, state standards or advisory levels are still evolving, and currently range from 1 to 18 µg/L. The need for cost effective treatment is especially pressing in the Inland Empire, a two-county region, whose population of 3.4 million is larger than that of many states (City of Mecula 2003). The Inland Empire is California's fastest growing area, and has a rapidly increasing demand for water. The area's perchlorate plumes are at least six-miles long and impacts four towns' water supplies, resulting in impairment of approximately 62,000 acre-feet (7.6×10^7 m^3) per year of potable water (Doyle and Enterprises, 2003).

GAC has been used successfully at least 28 years for the removal of organic contaminants from drinking water systems. In 1977, GAC was reported to be used by several hundred American municipalities as a substitute for powdered activated carbon because of its high organic removal efficiency (American Water Works Association [AWWA] Committee, 1977). The most common applications of activated carbon in drinking water systems are to remove taste and odor causing compounds and to remove organic contaminants including pesticides and chlorinated solvents.

PSU has developed a surfactant/activated carbon technology that can cost-effectively remove perchlorate from water to concentrations below 1 µg/L (Parette and Cannon, 2005[a], 2005[b], 2005[c] and 2006). PSU has teamed with Siemens Water Technologies to further develop the technology and move it toward commercialization. This technology has not yet been permitted for use in drinking water applications but has been tested at field scale for environmental remediation applications (Graham et al., 2004; Graham 2006). The technology involves pre-treating, or *tailoring*, GAC with cetylpyridinium chloride (CPC), or other compounds containing active quaternary ammonium, identified herein as N-surfactants. This tailoring extends GAC bed life for removing perchlorate up to 35 times compared to conventional, non-tailored GAC (Parette and Cannon 2005a). This finding indicated that TGAC could potentially be cost competitive with established perchlorate treatment technologies such as ion exchange (IX). However, more data are needed to validate these projections for the water quality conditions that exist in Fontana and elsewhere in the Inland Empire. This validation required pilot-scale field tests and was made more robust and broadly applicable by conducting additional rapid small-scale column tests (RSSCTs) at PSU under varying groundwater chemistry conditions.

Perchlorate removal by TGAC represents the technical expansion of a previously widely accepted drinking water treatment technology (GAC) to accommodate an emerging contaminant of great interest to both California's Inland Empire and the Department of Defense (DoD). The fact that TGAC can also be utilized to simultaneously treat perchlorate and regulated organics, such as TCE, further distinguishes it from other perchlorate only treatment options as a novel, standalone option for implementation on mixed contaminant plumes. Perchlorate and TCE are known co-contaminants at several sites, including Vandenberg Air Force Base (AFB), California, Naval Weapons Industrial Reserve Plant (NWIRP) McGregor, Texas, Aerojet Corporation, California, and in a regional-sized plume in Riverside and San Bernardino, California (which are located in the southern California Inland Empire area.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall goal of this project was to evaluate the technical and economic performance of the TGAC technology for wellhead treatment of groundwater supplies.

Tests were conducted to provide information valuable to water purveyors who draw groundwater from the Colton-Rialto plume and the regulatory community that is overseeing perchlorate wellhead treatment and remediation in this heavily populated area. In addition, the demonstration design addressed ESTCP's goal of offering accurate cost projections for a broad range of perchlorate contaminant and competing species concentrations that allow cost evaluations for other groundwater applications worldwide.

Specifically, the technical objectives for this project included the following:

- Demonstrate that the TGAC technology is a cost-effective treatment method for removing perchlorate from drinking water to effluent concentrations of µg/L, the current California drinking water standard or less.
- Demonstrate that the TGAC technology does not cause significant secondary water quality issues. Specifically, the potential for interactions between disinfection processes and the TGAC system will be assessed.

- Demonstrate that the TGAC technology requires low capital, operating, and energy costs.
- Develop treatment costs for a range of water chemistry conditions determining performance after varying TDS, nitrate, perchlorate in the small-scale field pilot treatment trains and the presence and absence of TCE.
- Demonstrate that the TGAC technology's operation and maintenance (O&M) requirements are simple.
- Demonstrate that the TGAC technology minimizes residual waste streams for the host municipalities.
- Obtain performance data for water that contains varying concentrations of TCE during RSSCT or isotherm studies at PSU and in the small-scale field pilot treatment train.
- Demonstrate that the performance of the TGAC technology is predictable so that monitoring can be minimized.

1.3 REGULATORY DRIVERS

Throughout the United States., perchlorate standards or advisory levels are still evolving (https://www.denix.osd.mil/portal/page/portal/denix/environment/MERIT/EC/ECAL/Perchlorate/StatesReg) and currently range from 1 to 18 µg/L. The California Department of Public Health (DPH), formerly the Department of Health Services (DHS), established a notification level (NL) (formerly referred to as an action level) for perchlorate of 6 µg/L. This NL was based on the public health goal (PHG) for perchlorate as determined by the California Office of Environmental Health Hazard Assessment (OEHHA). The PHG is the concentration of a substance that is considered not to pose a significant health risk, which OEHHA established as 6 µg/L for perchlorate in March 2004. OEHHA later reviewed the National Academy of Sciences' (NAS) report on perchlorate (NAS 2005), and determined that no revision to the PHG was required. As required by California statute, DPH must establish a maximum contaminant level (MCL) for drinking water as close to the PHG as technically and economically feasible. In August 2006, the DPH proposed a MCL for perchlorate in drinking water of 6 µg/L, which became the MCL on October 18, 2007.

No enforceable federal standard has yet been set. However, the United States Environmental Protection Agency (EPA) established an official reference dose (RfD) of 0.0007 mg/kg/day of perchlorate in February 2005. This level is consistent with the recommended RfD included in the NAS report (NAS 2005). An RfD is a scientific estimate of a daily exposure level that is not expected to cause adverse health effects in humans. EPA's new RfD translates to a Drinking Water Equivalent Level (DWEL) of 24.5 µg/L. A DWEL, which assumes that all of a contaminant comes from drinking water, is the concentration of a contaminant in drinking water that will have no adverse effect with a margin of safety. In practice many water purveyors are conservative and consider treatment whenever perchlorate is found even if only a tentative detection (J-value).

EPA derived a perchlorate HRL of 15 µg/L for pregnant women and other sub-populations, including fetuses. In January 2009 EPA issued an interim health advisory for perchlorate in drinking water at 15 µg/L (http://www.epa.gov/safewater/contaminants/unregulated/pdfs/healthadvisory_perchlorate_interim.pdf), stated that it intends to seek further NAS' comment, and issue a "final regulatory determination as soon as possible". EPA also addressed the issue of cleanup levels:

> "***How does this decision impact clean up of perchlorate at Superfund sites?*** *As a result of the publication of the Interim Health Advisory for perchlorate, the Agency is formally withdrawing the January 26, 2006 guidance it issued regarding perchlorate and sites addressed under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the National Oil and Hazardous Substances Contingency Plan (National Contingency Plan or NCP). The January 2006 guidance recommended that Regions consider using a preliminary remediation goal (PRG) of 24.5 ppb (or µg/L). In its place, the Agency now recommends that Regions consider using the interim health advisory level of 15 µg/L as a PRG; consistent with the NCP, the Agency often considers health advisories as "to be considered" (TBC) values for setting cleanup levels. Also, where state regulations establish applicable or relevant and appropriate requirements (ARARs) for perchlorate, these standards should be used as the cleanup level at Superfund sites, unless the ARAR is waived at the site". http://www.epa.gov/safewater/contaminants/unregulated/perchlorate.html #questionsandanswers*

In addition to the above guidelines, that are used to determine where perchlorate treatment is required, the California DPH requires that any treatment technology used in drinking water applications must have National Sanitary Foundation (NSF) 61 certification.

2. TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

2.1.1 Properties of GAC and Tailoring Process

GAC has a long and successful history of use in drinking water treatment settings. For example in 1977, GAC was reported to be used by several hundred municipalities as a substitute for powdered activated carbon due to its high organic removal efficiency (American Water Works Association [AWWA] Committee, 1977). In the United States, GAC is generally used to combat taste and odor problems or to remove volatile organic compounds (VOCs) from groundwater. Its usual operation geometry is as a filter; both gravity and pressure filters are used. Filter performance depends on pre-treatment, concentration of contaminant applied, presence of competing species, and hydraulic residence time. Spent GAC can be regenerated thermally, which is usually performed off-site. The technology we focus on here is to use GAC as a substrate upon which a surfactant such as CPC can be preloaded, so as to remove the inorganic ionic species perchlorate which would not normally be highly adsorbed by GAC.

Activated carbon is created by thermally and chemically treating carbon-based solids, such as bituminous coal, anthracite coal, lignite coal, coconut shells or wood. The pyrolysis step creates narrow fissures between graphene planes; and the oxidation step facilitates the gasification of some graphene layers so as to create slightly wider spaces between the layers. The carbon layer surfaces are generally uncharged (hydrophobic), and they thus repel water and charged inorganic species such as perchlorate. However, the outer edges of the carbon layers (graphene planes) can carry a charge (Leon y Leon and Radovic, 1994), which is why conventional activated carbons can adsorb a limited amount of perchlorate (Na et al., 2002, Chen et al., 2005[a], 2005[b]; Chen and Cannon, 2005). Significantly, the uncharged carbon surfaces are ideally suited to sorb surfactants. Surfactants consist of an uncharged tail (alkyl chain) plus a charged head (in this case a quaternary ammonium or pyridinium). The uncharged alkyl tails attract to the uncharged carbon surface; and they also align with each other as micelles. The charged heads face away from the carbon surface and away from the other alkyl tails, as shown in Figure 2-1(a). The structure of the CPC molecule before association with the GAC is shown in Figure 2-1(b). At the high concentrations that occur within GAC pores, the surfactant micelles can congregate as hexagonal liquid crystals shown as H1 in Figure 2-2. In Figure 2-2, each white dot represents a positively charged head that can bind with perchlorate. Thus, by preloading the activated carbon with N-surfactant that consists of alkyl quaternary amines or other active nitrogen groups, a non-charged surface is converted into a highly plus-charged matrix. This creates a unique rigid material, which offers properties that are well suited for capturing the perchlorate anion.

Several authors have explored the sorption and binding of cationic surfactants onto graphite (Xu et al., 2002; Kiraly and Findenegg, 1998); and onto cellulose, clay, quartz, titanium dioxide, zeolites, soils and membranes (Baillarger et al., 1994; Biswas and Chattoraj, 1997[a] and 1997[b]; Churaev et al., 2000; Esumi et al., 1998; Gzara and

Dhahbi, 2001; Haggerty and Bowman, 1994; Sheng et al., 1998; Wang et al., 1999 and 1999a). However, the Project Team is not aware of others who have explored pre-loading activated carbons with N-surfactants to enhance anion removal. To date, PSU and Siemens Technology have used tallowtrimethyl ammonium chloride (Arquad T-50), dicocodimethylammonium chloride (Arquad 2C-75), and CPC and cetyltrimethylammonium chloride (CTAC) successfully as GAC tailoring agents for the perchlorate sorption during bench- and field pilot-scale technology development. CPC was chosen as the tailoring agent for this project due to previous performance and the fact that it is an approved ingredient in many commercially available brands of mouthwash (Food and Drug Administration [FDA] in 2003 reviewed more than 55 years of adverse event data for these mouthwashes and concluded it was safe at concentrations from 0.045 to 0.1% in mouthwash). This fact should facilitate obtaining American National Standards Institute (ANSI)/NSF certification of the tailoring agent, which is required by the DPH for full-scale application of a drinking water treatment technology. Siemens has begun the ANSI/NSF certification process.

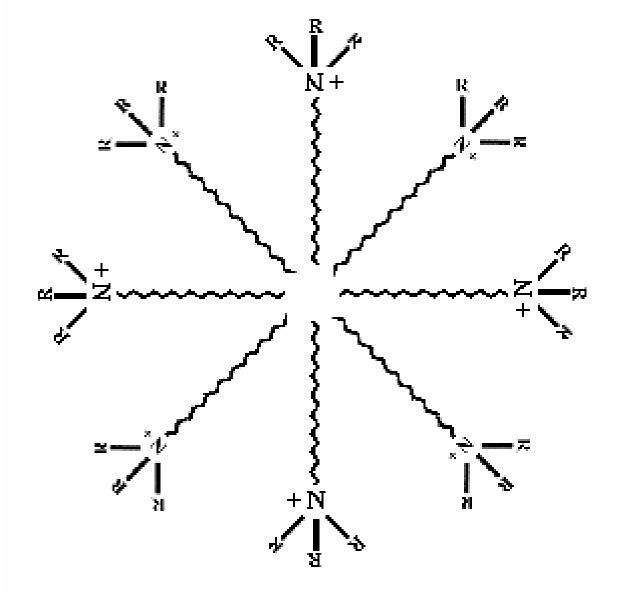


Figure 2-1(a). Hypothesized Micelle Alkyl Quaternary Amine Configuration within Activated Carbon Pores: Planer, Spherical or Cylindrical; or Half-Cylinder on Carbon Surface

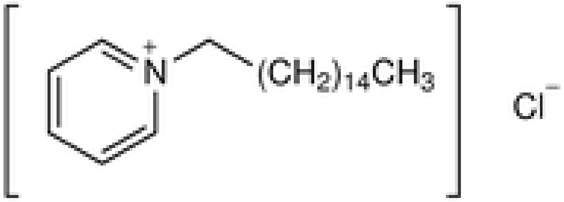


Figure 2-1(b). Structure of an Individual CPC Molecule (from http://www.medicinescomplete.com/mc/martindale/current/images/CLK0318C001.gif)

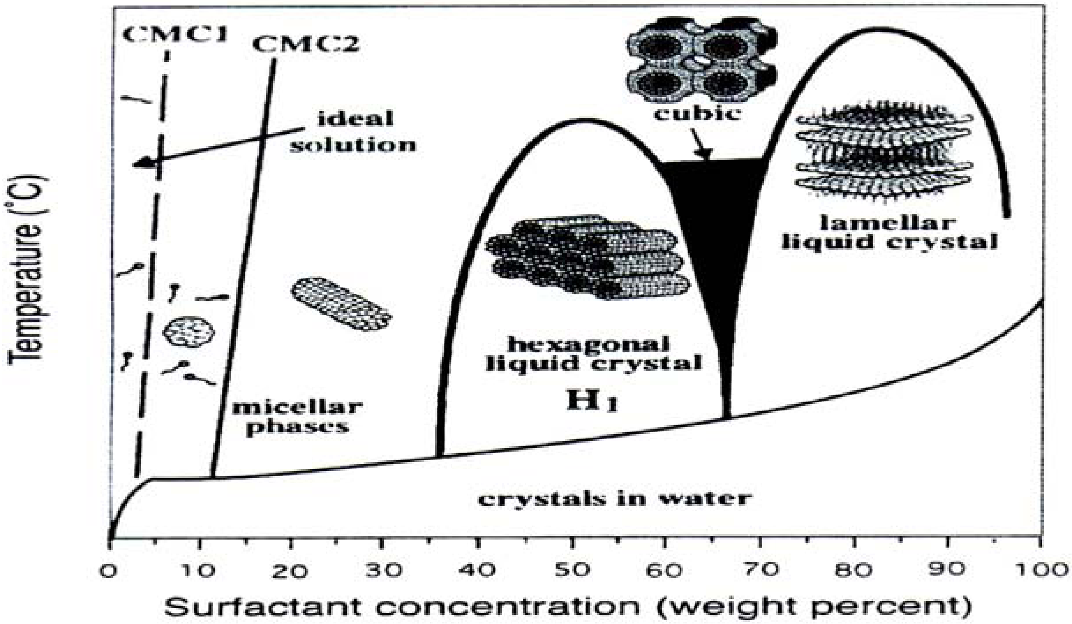


Figure 2-2. Micellar Configuration as a Function of Surfactant Concentration and Temperature in the Aqueous Phase (Brinker et al., 1999)

CPC is known to serve as a mild antimicrobial agent (Lobene et. al., 1979), its ability to serve in this role while attached to TGAC may depend on how physically recessed it is within the pore structure of the GAC. Previous bench and pilot-scale tests have not shown any media being clogged during 6-10 months of operation; this then indicates that microbial growth had not proliferated excessively (if at all) (Na et al., 2002; Parette 2005, 2005a, 2005b, 2006).

The N-surfactant arrangement offers distinct differences from conventional IX resins, where functional groups rigidly reside in structured positions within the resin framework. Within TGACs, the perchlorate removal mechanism can behave in accordance with an electric double layer type phenomenon (Rosen 1989), rather than via the Langmuir-type bonding in IX resins. The N-surfactants are pre-loaded onto GAC by pumping a concentrated surfactant-water solution cyclically through a GAC bed. Heating the surfactant (40 to 70 °C (104 to 158 °F)) increases its solubility in water to facilitate the pre-loading process. The solution cycles through the bed multiple times until the surfactant has been adsorbed to such a point that its water-phase concentration drops below a pre-selected threshold (approximately 0 to 10 milligrams/liter [mg/L]). The GAC bed is then rinsed several times to remove the water-phase surfactant residual and prepare the bed for water treatment service. Siemens produced the TGAC for this project at its Los Angeles California facility, which may ultimately be ANSI/NSF certified for TGAC production. This facility has capabilities for processing waste waters, including wastewaters that contain CPC.

This technology is expected to be especially cost-effective and suitable for applications where conventional GAC is already in use for taste and odor or organic contaminant removal.

In proof-of-concept bench-scale trials performed thus far at PSU and during a field-pilot demonstration at Redlands, California, it has been shown that bituminous GAC can be pre-loaded with N-surfactants in a manner that dramatically increases its capacity to remove perchlorate. The cationic surfactants used in this project contain a quaternary ammonium or pyridinium functional group (Parette 2005[a], 2005[c]). These same functional groups have been shown to remove perchlorate in IX resins technology (Clifford et al., 2004). These quaternary ammonium based cationic surfactants have a high pK_a value and this characteristic renders their charge to be independent of pH in natural waters (Laughlin 1991). Once the cationic surfactant is pre-loaded onto the GAC, it then acts as an exchange site where perchlorate can be captured.

Siemens and PSU have tested other carbons for use in the manufacture of TGAC. The bituminous coal based carbons have shown to be the best performing of all of the carbons tested in this role. It was observed that the conventional coconut carbon, with its predominance of micropores, could not become loaded with as much of the surfactant, so run times were shorter. At the other extreme, the conventional wood based carbon, with its predominance of mesopores, could become preloaded with more surfactant, but a higher fraction of the surfactant leached off during water treatment operations (Parette 2009). It is anticipated that a more microporous coconut shell based carbon will be used as the polishing or secondary barrier carbon to prevent CPC from being leached from the system.

For a number of liquid phase organic adsorption applications anthracite and bituminous coal based GACs can be used pretty much interchangeably and achieve the same results with respect to contaminant removal and service life. Acid washed GAC manufactured from a high purity anthracite coal (i.e. AC2050AW) has significantly lower ash content and a lower level of water leachables when compared to bituminous coal based carbons. When initially placed in water AC2050AW exhibits a contact pH near neutral as compared to a highly alkaline pH observed for non-acid washed bituminous carbons.

This makes anthracite carbons, for example, more suitable for use in critical applications such as hemodialysis and the remove of chlorine from water to be used in beverage manufacture.

The choice of coal used in the manufacture of an activated carbon does affect somewhat its total pore volume and pore size distribution. Anthracite coal based carbons tend to have a slightly lower total pore volume and a more microporous pore size distribution (See Appendix J). Bituminous coal based carbons tend to have more meso and macroporosity. has a significantly lower ash content and a lower level of water leachables when compared to bituminous coal based carbons. When initially placed in water AC2050AW exhibits a contact pH near neutral as compared to a highly alkaline pH observed for non-acid washed bituminous carbons.

PSU has also measured the selectivity of TGACs prepared with various tailoring agents against nitrate (ClO_4^-/NO_3^-). The values measured were 33.6 for CPC TGAC, 41.2 for Arquad T-50 TGAC, and 51.0 for Arquad 2C-75 TGAC. (Parette 2007) To put those numbers into perspective, comparative selectivity values for trimethylamine functionalized IX resin was 10, triethylamine IX resin was 40, tripropylamine IX resin was 70, and bifunctional IX resin was 100.

2.1.2 Schematic Diagram of the Technology

During the demonstration project two field tests were conducted:

- 38 GPM beds
- Six (1.5 to 3 GPM) beds designed to challenge the system with various additives to the influent

The 38 GPM system comprised three vessels operating in series Figure 2-3. The treatment train included a lead and lag TGAC vessel and a third conventional GAC vessel for tailoring agent polishing. All three vessels were operated in a down-flow configuration, and contained approximately 375 gallons (1.4 m3) of media (either TGAC or conventional GAC). This system was designed to treat water at a flow rate of approximately 37.5 GPM (0.14 m3/min), which corresponds to a 10 minute empty bed contact time (EBCT) in each vessel (total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC). Each of the three beds were 4 feet (1.22m) in diameter, with a 4 foot depth (1.22m) of GAC media

The second major element of the field test program consisted of six sets of three vessels operating in series as shown in figures 2-4 and 2-5. The first two vessels in each set were stratified with TGAC overlying conventional GAC in the same chamber. They contained 2.0 cubic feet of TGAC in the lead chamber (on top), and 1.0 cubic feet of conventional GAC in the second chamber (on bottom) to remove residual TCE (from spiking) and/or tailoring agent, if present. The third vessel in each series contained 3.1 cubic feet of conventional GAC. These smaller vessels were also designed to operate in a down-flow configuration with a 10 minute TGAC EBCT and 5-minute conventional GAC EBCT, which corresponds to a flow rate of approximately 1.5 GPM. Thus with two stratified beds in series the system had a total design EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC), which was designed to be the same as the 38 gpm system. These were implemented to test varying arrays of common competitive species such as nitrate, sulfate and TCE.

In both the 38 GPM system and the six condition field pilot scale test it is possible that tailoring agent that leached off the tailored beds would provide additional perchlorate capacity after being adsorbed to the conventional GAC polishing beds. But this is not anticipated to be a significant effect. To minimize the possibility of reverse flow multiple check valves and a pressure sensing actuated valve were incorperated into the demonstration systems.

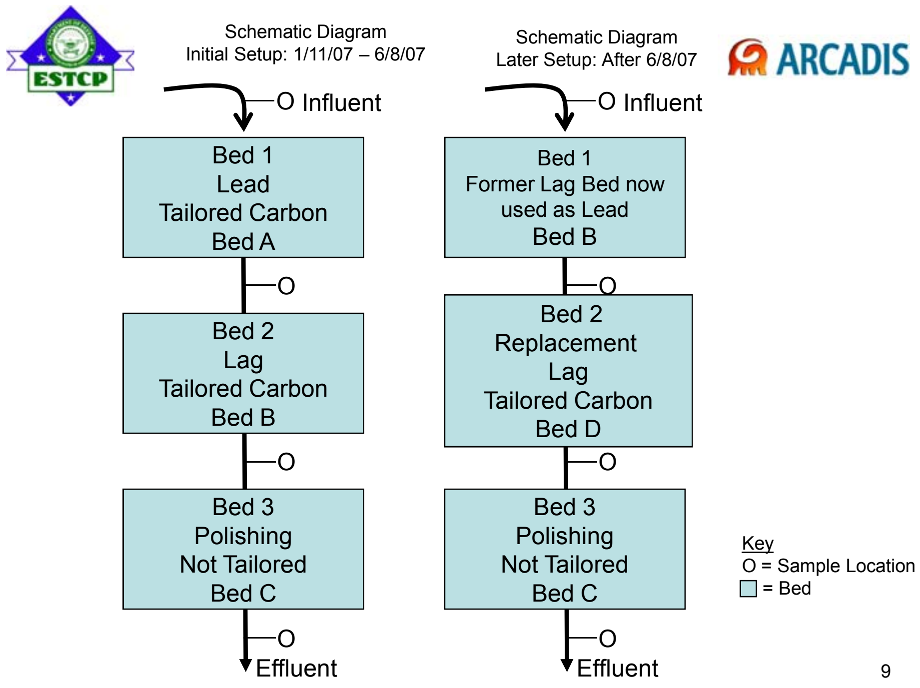


Figure 2-3. Bed Ordering/Operational Diagram of 38 GPM Systems at Fontana, California

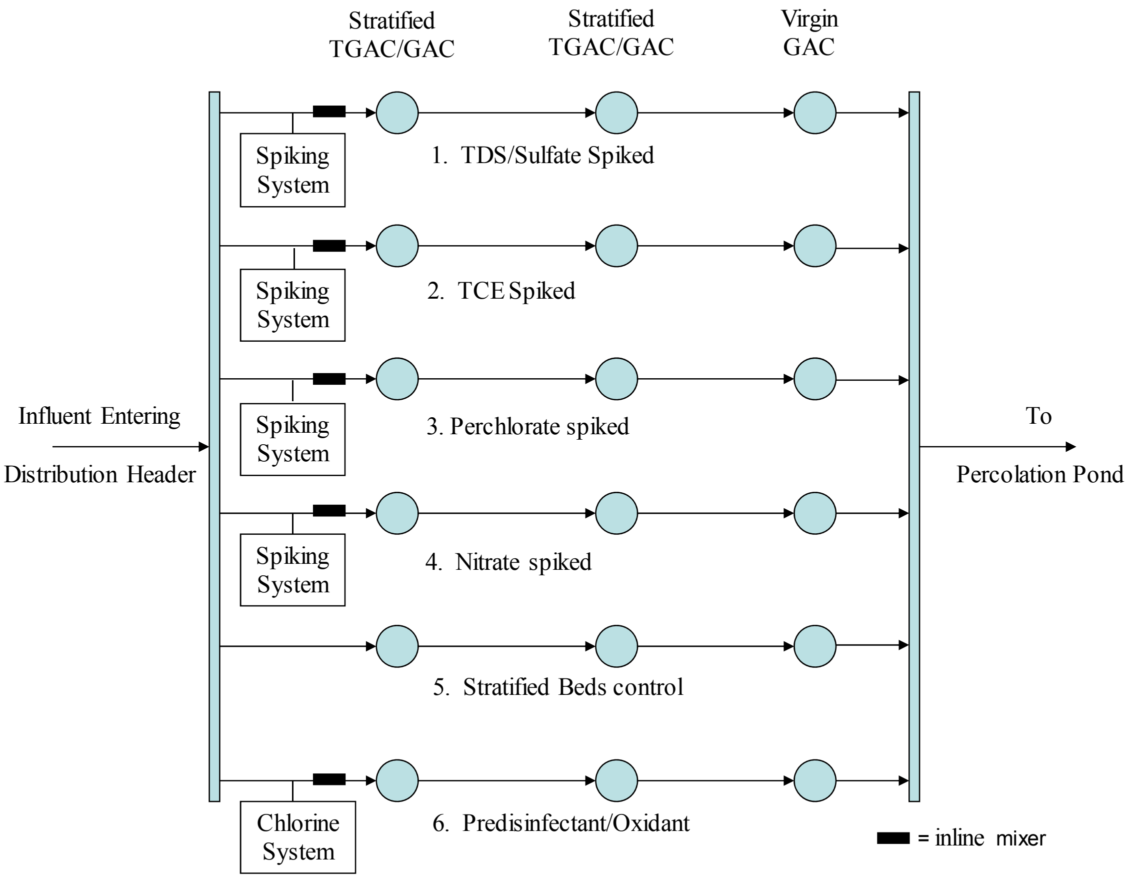


Figure 2-4. Flow Path Schematic for Six Small-scale TGAC Treatment Trains

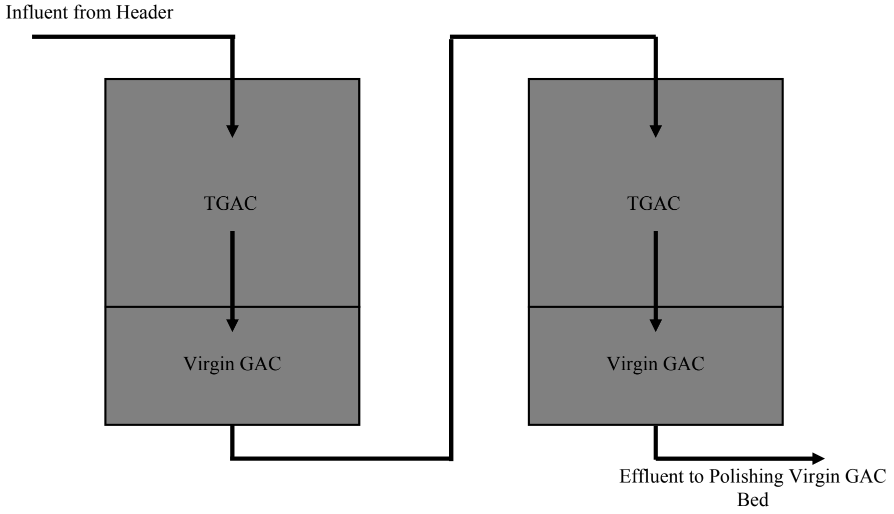


Figure 2-5. Cross Section of a Single Small-Scale TGAC Treatment Train Illustrating the Stratified Bed Approach

2.1.3 Chronological Summary of TGAC Technology Development to date

Recognizing a need to improve the removal of perchlorate in GAC systems, PSU started looking at cationic surfactants as a tailoring agent, first starting with a polymer known as poly(dimethyldiallylammonium chloride) (PolyDADMAC). These surfactants were selected for initial testing because they were already used in treatment facilities as well as being NSF approved. Results using Redlands water and polyDADMAC tailored Superior Adsorbents, Inc. of Emlenton, Pennsylvania, (SAI) carbon showed perchlorate breakthrough at 4,200 bed volumes (BVs) which is 3.5 times more than virgin carbon. It was noted that tailoring with low molecular weight blends of polyDADMAC led to greater perchlorate capacity in GAC than with their high molecular weight counterparts. (Parette 2004). After these initial results PSU worked to improve the tailoring process of the carbon as well as to find smaller molecule cationic surfactants. Thus tailoring with quaternary ammonium monomer species was investigated. These alkyl monomers contain the same functional group as polyDADMAC. However due to their small size (molecular weight of a few hundred Daltons vs. in the tens of thousands for polyDADMAC), the monomers should have access to the micropores of the GAC, whereas the polymer was only expected to enter the meso and macropores. The micropores contain the majority of surface area for the GAC (Bansal et al., 1988). A number of quaternary ammonium monomers were used and the adsorption capacity for GAC after they were pre-loaded with any one of these monomers was as great as 34,000 BVs (33 times that of virgin carbon) when using Redlands, California groundwater. After this discovery more studies were conducted and these were reported by Parette (2004, 2005, 2005[a] and 2005[b]). More extensive discussion of these recent studies is presented in Section 2.2.

A comparison of the various tailoring agents used by PSU is given in Table 2-1:

Table 2-1. Characteristics of Surfactant Tailoring Agents Used (www.inchem.org)

Surfactant	Surfactant	Molecular Weight (MW)	Number of Long Alkyl Chains	Carbon Atoms in Chain	Applications for Use
Decyltrimethylammonium Bromide	DTAB	280.3	1	10	NA
Myristyltrimethylammonium Bromide	MTAB	336.4	1	14	NA
Tributylheptylammonium Bromide	THAB	364.5	1	7	NA
Cetyltrimethylammonium Chloride	CTAC	320	1	16	NA
Tallowtrimethylammonium Chloride	T-50	350	1	16-18	NA
Dicocodimethylammonium	2C-75	450	2	12-14	NA

Surfactant	Surfactant	Molecular Weight (MW)	Number of Long Alkyl Chains	Carbon Atoms in Chain	Applications for Use
Chloride					
Cetylpyridinium Chloride	CPC	358	1	16	Antiseptic in mouth wash
Poly (Dimethyldiallylammonium Chloride)	Poly-DADMAC	150,000-200,000 g/mol	2 per monomer	3	Coagulant, flocculant in waste water and water treatment technologies

There have been some prior applications of GAC to perchlorate treatment at field scale. Interstate Technology and Regulatory Council (ITRC) has recently summarized them in a report titled "Remediation Technologies for Perchlorate Contamination in Water and Soil" (2008). Table 5-5 of this ITRC report is titled "Effectiveness of tailored granular activated carbon", and would probably have been better titled "Effectiveness of conventional granular activated carbon and tailored granular activated carbon." This Table 5-5 addresses five studies with activated carbon:

- The first, at the City of Redlands, California, was a full-scale operational system that employed conventional GAC for drinking water, as was permitted by the State of California. The GAC bed was regenerated every 6 weeks during this period of treatment.
- At Camp Edwards (part of the Massachusetts Military Reservation, Cape Cod, Massachusetts) a two-stage system included conventional GAC and IX. The GAC was primarily included to remove organic compounds, while the IX was primarily for removing perchlorate.
- At Edwards AFB, California, Site 133, a conventional GAC system was constructed to remove VOCs, and conventional GAC alone was also monitored. The ITRC notes that the system was "ineffective for perchlorate." At the same site TGAC tailored with Arquad 2C-75 was also tested in water with a TCE concentration at 1,200 µg/L and perchlorate at 7-18 µg/L (Graham 2007; DTSC 2004; Lang et al., 2007). This system had a conventional GAC lead bed, so that the TGAC only treated perchlorate; 24,000 bed-volumes (BVs) were treated before the 6 µg/L effluent goal was exceeded. But after the system was reconfigured with the TGAC bed leading and thus treating both VOCs and perchlorate, the target value of 6 µg/L was exceeded after only 8,500 BVs. The effect of tailoring on TCE treatment performance was also studied. With an influent TCE concentration of 1,200 µg/L complete saturation (effluent = influent) occurred at approximately 6,800 BVs for conventional GAC and about 3,500 BVs for TGAC. Note that

the level of TCE in this system is much higher than would reasonably be expected in drinking water treatment applications.

- At Monterrey Park, California, conventional coconut GAC was used to remove low levels of perchlorate while also removing VOCs.
- The final entry in the ITRC Table 5-5 is the surfactant-tailored GAC used at Redlands, California, which is addressed in Section 2.2.3 below.

2.2 TECHNOLOGY DEVELOPMENT

2.2.1 Redlands, California Bench-Scale Studies

Using impacted groundwater from Redlands, California as an experimental water source, GAC tailored with CTAC removed perchlorate for 30,000 to 35,000 bed volumes (BVs) during laboratory experiments using Rapid Small Scale Column Tests (RSSCTs) before initial perchlorate breakthrough. In these experiments the influent perchlorate concentration was 60 to 70 µg/L and the empty bed contact time (EBCT) was 10.8 minutes (simulated for a 20 x 40 mesh GAC). The impacted groundwater used for this laboratory proof-of-concept contained 16 mg/L nitrate (all references to nitrate in this report are as NO_3 not as nitrogen unless otherwise noted), 30 mg/L sulfate, 0.5 to 0.7 mg/L total organic carbon (TOC), and had a conductivity of 330 micromhs per centimeter (µmho/cm). Additional RSSCTs also employed different surfactants example Arquad T-50, Arquad 2C-75, or CPC to compare the removal of perchlorate and to find the most cost effective surfactant. These tests with Redlands water simulated a 3.2 minute EBCT for 20 x 40 mesh GAC (0.85 x 0.40 mm). For these cases, initial perchlorate breakthrough occurred at 28,000-30,000 BVs (Parette and Cannon 2005, 2005a, 2005b). By contrast, virgin bituminous GAC experienced initial perchlorate breakthrough after 1,200 BVs."

2.2.2 Eastern Massachusetts Site Bench-scale Studies

Additional laboratory based RSSCT screening of TGAC took place utilizing groundwater from eastern Massachusetts that contained perchlorate at a concentration of 5.6 µg/L. With this water, perchlorate was removed to below 1 µg/L for approximately 220,000 bed volumes (BVs). Also, other RSSCTs appraised performance with groundwater from an adjacent well that contained 1 µg/L of perchlorate. In this case, perchlorate was removed to below 0.3 µg/L for approximately 270,000 BVs. The eastern Massachusetts water contained 0.1 to 0.4 mg/L nitrate, 6 mg/L sulfate, and had a conductivity of 50 to 60 µmho/cm. These RSSCTs simulated a 2.1 minute EBCT for a 20 x 40 mesh GAC; and the 220,000 to 280,000 BVs correspond to a 2 to 2.5 year service life at a 4 minute EBCT (Parette et al., 2005[b]). PSU also observed during these RSSCTs experiments with eastern Massachusetts groundwater, that the two beds together offered the same bed life for removing the nitrogen-containing explosives hexahydro-1,3,5-trinitro-1,3,5-triazine

(RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) as they did for perchlorate (Parette et al., 2005[b]).

2.2.3 Redlands, California Field Scale Studies and Bench-field Scale Correlation

As a follow-up to the RSSCTs, pilot-scale field demonstration tests were conducted in Redlands, California Texas Street plant, with water that contained 50-70 µg/L perchlorate and 16 mg/L nitrate. The first employed conventional GAC, and the second is employing Arquad T50 and Arquad 2C-75 tailoring agents. In this study, the bed volumes to initial breakthrough was 17,000 bed volumes; and this compared to 30,000-35,000 bed volumes to initial breakthrough in rapid small scale column tests (section 2.2.1). However, the Redlands water composition has important distinctions from Fontana groundwater, and thus this demonstration is crucial to commercializing this technology in a manner that is useful to Fontana and other the Inland Empire municipalities (Parette, 2004, Graham 2004, Graham 2006). In follow up work, we have observed that at least some of the limitation to demonstration-scale bed life could be attributed to thiosulfate and other reduced sulfur species. This issue is addressed in appendix C to this report.

Demonstration and pilot-scale studies that were conducted in the field at the Redlands, California, Texas Street Water Treatment Plant show that the results that were observed at the laboratory RSSCT scale were not the same at field scale. There was a 50% decrease in the TGAC capacity to remove perchlorate from the groundwater from what was predicted based on laboratory scale tests. A paper in preparation (Patterson et al., 2009, Appendix C) shows that this could be attributable to reduced sulfur species such as thiosulfate ($S_2O_3^{2-}$), competing with perchlorate for sorption sites on TGAC. These reduced sulfur species had become fully oxidized during shipment, and thus did not affect the original RSSCT tests for the Redlands site. Thiosulfate was not a significant competitor for perchlorate at 30 µg/L perchlorate and 40 µg/L $S_2O_3^{2}$. Thiosulfate concentrations of 250, 500 and 1000 µg/L did significantly compete. Prechlorination is able to remove the interfering thiosulfate but the dose must be carefully controlled because chlorine also reduces the effectiveness of TGAC in perchlorate removal. (Patterson et al., 2009, Appendix C).

The scaling of this technology has employed the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). If this proportional diffusivity model holds, then a properly designed RSSCT will accurately predict field scale performance. This model works even though the test period is dramatically shorter since RSSCT uses a smaller GAC particle size and its performance is governed by the same adsorption capacity and kinetics factors that govern larger scale adsorption performance (Crittenden et al., 1986 and 1991). In this project both demonstration-scale tests and RSSCTs were conducted with the same Fontana water so as to appraise whether the proportional diffusivity model fits for perchlorate sorption here. PSU has demonstrated with virgin GAC that proportional diffusivity is indeed the proper model. However, when employing TGAC, there are some possible distinctions: the proportional diffusivity model addresses how to scale-up diffusion effects in small grains that are simulating full-sized grains. However, similitude with regard to the reduction/oxidation level of the water may be difficult to achieve in RSSCTs, and the proportional diffusivity model may not comprehensively simulate full-scale TGAC performance from RSSCT testing.

2.2.4 Effects of TCE on GAC and the removal of Perchlorate

TCE is used widely as a solvent for the industrial degreasing of metal products and has also seen such varied uses as food processing and textile cleaning. The presence of TCE in drinking water can frequently be attributed to historic waste disposal practices. The molecular structure of TCE is shown in Figure 2-6 and the physical/chemical properties are contained in Table 2-2.

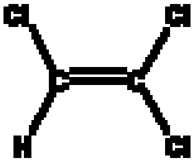


Figure 2-6. Structure of TCE

Table 2-2. Physical and Chemical Properties of TCE (from http://www.inchem.org)

Molecular Weight (D)	131.4
Melting Point (°C)	-73
Boiling Point (°C)	87
Density (g/cm^3) @ 20°C	1.47
Aqueous Solubility (g/L)	~1.19
Log Octanol/Water Partition Coefficient	2.42
Vapor Pressure (atm) @ 25 °C	1.01
Henry's Law Constant (atm•L/mol) @ 25 °C	1.03
Odor Threshold in Air (ppm)	82
U.S. EPA MCL (µg/L)	5

The mechanism by which GAC removes TCE from water involves liquid phase adsorption where the adsorbate, TCE, is held to the carbon surface via hydrogen bonds, dipole-dipole interactions, or van der Waals forces (Snoeyink 1990). This mechanism is thus different from the mechanism of removal of perchlorate by TGAC discussed in Section 2.1. This adsorption will progress until an energetic equilibrium has been achieved such that the rate of adsorption equals the rate of desorption. At this point, the carbon is termed "exhausted" and no additional removal of the compound from the liquid phase is observed. As with other hydrophobic compounds, a given carbon's affinity for TCE is a combination of surface chemical structure, surface area, and pore size distribution. The nature of TCE, its polarity and molecular size, is accordingly important in the adsorption mechanism (Karanfil and Dastgheib, 2004).

Methods and results for the bench-scale studies carried on in parallel with the Fontana field scale demonstration are discussed in Sections 5.3 and 5.7.1 of this report.

2.2.5 CPC Leaching

During RSSCTs and demonstration scale trials, the PSU team have observed that a small fraction of the CPC could leached out of the first TGAC bed (below 1 mg/L for most of the runs). However, when the CPC pre-loaded bed was followed by a conventional GAC bed, no CPC has been detected in the polishing bed effluent (less than 60 parts per trillion, as monitored via a high pressure liquid chromatography – mass spectrometry (HPLC-MS) method. At full-scale, the N-surfactant that migrates to the polishing bed, or through GAC in a two-chambered or mixed media (GAC and TGAC) vessel, will aid in perchlorate removal through the second bed when it becomes the lead bed following a TGAC change-out. Additionally, when CPC TGAC bed is followed by a conventional polishing GAC bed (or the GAC in a two-chambered or mixed media vessel), both beds can remove organic contaminants. (Parette 2005b)“

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Reviews of currently available technologies for perchlorate in drinking water and for ex-situ treatment of groundwater have been published recently (ITRC, 2005 and 2008; U.S. EPA 2005). Although IX and bioremediation methods have been shown to be effective technologies to treat perchlorate contaminated water, the use of TGAC to treat microgram per liter concentration of perchlorate has some advantages over these methods.

When considering a new technology, advantages and limitations must be evaluated and addressed. TGAC technology has several potential advantages and limitations when compared to other perchlorate treatment technologies. Of the currently widely used methods, TGAC is most similar to IX, the most common technology being applied for perchlorate treatment in drinking water.

2.3.1 Advantages

Tailored GAC has several potential advantages over other perchlorate treatment technologies. These advantages include:

- Ability to simultaneously treat both perchlorate and organic co-contaminants (e.g., VOCs, pesticides etc.).
- There is the potential cost savings when compared to IX, particularly in mixed perchlorate/VOC applications that are common in the Inland Empire.

- Simple installation and operations and maintenance.
- Can be implemented at existing VOC and perchlorate treatment facilities.
- May be possible to reactivate spent TGAC by destroying perchlorate and/or VOCs, re-tailor, and reuse the TGAC.
- Does not have secondary water quality concerns associated with IX (e.g., nitrate and/or sulfate sloughing during start up).
- In comparison, microbial treatment processes are less favorable for processing low-concentrations of perchlorate, as another stable food supply must be added to the water such that perchlorate can be a secondary substrate. Also, a number of utilities are not currently comfortable with using microbial methods for treating drinking water.
- TGAC may be less likely to leach nitrosamines than IX. Most water purveyors have the resin pre-rinsed by their vendor or run to waste for a period of one hour, or both, to prevent this.

Another inherent reason for the favorability of the TGAC is that it can be potentially thermally reactivated, while IX systems cannot (although chemical regeneration processes are available for IX systems) (Chen et al., 2005[a]). Chen et al., showed that thermal treatment of ammonia TGAC at 600-800C restored essentially all the perchlorate adsorption capacity while preserving the nitrogen content and positive surface charge. From that Chen et al., inferred that the perchlorate had been removed from the carbon or destroyed. Note however that thermal regeneration was not tested in this demonstration. With surfactant based TGAC the approach that would be used is to thermally reactivate, during which time the quaternary ammonium surfactant would be either volatilized or charred; and then reapply a new round of quaternary ammonium surfactant after reactivation. In order for IX systems to be regenerated using the conventional process, a brine solution, or another chemical reentrant such as Ferric chloride – hydrogen chloride (HCL) has to be used, which in turn will have to be handled and dispose of.

2.3.2 Disadvantages

TGAC also has several perceived or potential limitations not found with other treatment technologies. These limitations include the following:

- TGAC has a lower perchlorate capacity than most IX resins and will require more frequent change-outs because a smaller volume of water is treated prior to perchlorate saturation. This limitation may become more pronounced as new, higher perchlorate capacity IX resins are developed.
- TGAC requires a lower hydraulic loading rate (GPM per square foot), or a longer contact time (EBCT) than IX, and thus more or larger vessels (additional capital cost) are required to treat a given flow rate of water. Additionally, if TGAC were to be implemented at an existing IX facility,

additional vessels would need to be installed or more frequent change-outs would be required to accommodate the existing water flow rate.

- TGAC has less selectivity over certain competing anions such as nitrate than the most advanced selective IX resins.
- If applied on a mixed-contaminant water (e.g., perchlorate and VOCs, etc.) perchlorate or the VOCs may reach breakthrough at different times, which would require an early change-out, and thus a reduced capture efficiency for VOCs or perchlorate than with two separate media (such as found at existing perchlorate and VOC treatment facilities that utilize both conventional GAC and IX resin).
- TGAC may leach small concentrations of tailoring agent into treated water although testing to date has shown that a polishing GAC bed is very effective in removing these trace concentrations.
- Perchlorate may be released after the bed has reached perchlorate saturation. Specifically, a minor perchlorate “roll-over” effect has been observed in some circumstances when the bed is kept in service for longer than would be recommended in practice. This phenomenon is consistent with the performance of ion exchange media and conventional GAC media, when a more strongly adsorbed (but less concentrated) species somewhat displaces the target species.
- Perchlorate is typically at concentrations that are orders of magnitude below nitrate and sulfate concentrations. This holds true for Fontana groundwater (see Section 4-2). Therefore, should all incoming perchlorate displace previously adsorbed nitrate or sulfate, the concentration of nitrate/sulfate in the effluent would not be significantly higher than the influent concentration for any significant time period. While a chromatographic “peak” of nitrate or sulfate is theoretically possible, it would be likely masked for the user by mixing from multiple parallel treatment trains or in the distribution system. Such nitrate roll-over would thus likely be undetectable.
- A potential issue for any exchange based media including TGAC is the impact of some reduced species (i.e., thiosulfate) on performance; see section 2.2.3 and Appendix C.

2.3.3 Evaluation Factors

When evaluating the potential cost and performance of a TGAC system for the treatment of perchlorate-contaminated water, several important factors are considered, these include the following:

- Site-specific water chemistry, particularly the presence of competing anions such as chloride, sulfate, and nitrate, and the presence of volatile organic compounds (VOCs)
- Adsorption kinetics

- Breakthrough volume (i.e., TGAC change-out frequency)
- Pre-treatment requirements (e.g., pre-filters, etc.)
- Perchlorate, VOC, and other end-user discharge/treatment requirements
- Generation of secondary waste streams
- Regulatory requirements
- Anticipated effects of TGAC on other water quality constituents and co-contaminants (e.g., VOCs, tailoring agent, etc.)
- Total capital and operational costs that are dependent on the factors listed above.

When comparing the empty-bed contact times and head losses through TGAC beds versus IX beds, a number of operational factors should be compared. These relate to the grain sizes and number of beds in series. By convention, GAC grains are commonly larger than IX grains, because GAC technology initially emerged for open-to-atmosphere beds, while IX technology initially emerged for pressure vessel beds. When the grain sizes and number of vessels in series are the same, the head losses will be the same for TGAC and IX.

2.3.4 Best Applications of the Technology

The combined experience at bench-scale and field-scale at the Redlands and Fontana sites indicates that the surfactant-tailored GAC will be most suitable for removing perchlorate when the nitrate levels are low. The dual surfactant tailored/ conventional GAC combination is likely to be the more economical when removing both perchlorate and volatile organic compounds. This technology has potential applications both to drinking water treatment and groundwater remediation.

The experience at Fontana and at other locations where this approach to perchlorate removal has been applied indicate that the surfactant-tailored GAC will be most suitable for removing perchlorate when the nitrate levels are low; and the dual surfactant / conventional GAC combination will be the more economical when removing both perchlorate and volatile organic compounds. The TGAC system is less selective vs. nitrate as an interference than the most advanced IX systems currently in use. Therefore, in retrospect, although the Fontana demonstration site provides a useful test of the system, it is not an ideal location for the TGAC technology to be cost competitive because of the elevated nitrate concentrations.

3. PERFORMANCE OBJECTIVES

The performance objectives for the perchlorate system are listed in Table 3-1.

Table 3-1. Performance Objectives for TGAC Perchlorate Treatment Train

Type of Performance Objective	Performance Criterion	Performance Metric	Actual Performance Objective Met?
Quantitative	Ability of TGAC to meet California DHS NL for perchlorate (DHS changed to DPH and NL changed to MCL during demonstration).	Treatment of typical Fontana concentrations of perchlorate to <6 µg/L (Note however that many utilities will target treatment to <4 µg/L, or below detection limits, to provide an additional safety factor).	Yes, for 15,000 BV
	Time to saturation of TGAC/GAC unit.	Observance of volumes to breakthrough and saturation for perchlorate and co-contaminants.	No, data showed 4 to 5 months of treatment
	Pressure drop across system	Differential pressure drop of less than 10 pounds per square inch (psi) (69 kilopascals [kPa)) from startup to breakthrough, across three-bed demonstration system.	No, pressure drops were typically higher (average ~20 psi, 138 kPa).
	Cost of TGAC and GAC	Cost per pound of TGAC and per acre-foot (cubic meter) of water treated.	Cost not reduced compared to current IX prices.
	Demonstrate TCE removal in laboratory RSSCT studies	TCE is the most likely co- contaminant to be expected. For a balanced system, perchlorate and TCE breakthrough would occur at approximately the same time through a GAC train. TCE metric is 4 µg/L.	Yes, plan was changed and TCE removal was demonstrated in field scale testing as part of six condition pilot-scale test. TCE removal was also measured in a laboratory isotherm test.
	Removal and competition of other anions – nitrate, sulfate, chloride, bicarbonate, and other sulfur species.	Should be quantitatively measured but no performance metric established because removal of nitrate for example can be a benefit in some applications (e.g., where influent concentrations are above standards) and a detriment in others (e.g., when nitrate competes with perchlorate for TGAC adsorption wites).	Yes

Type of Performance Objective	Performance Criterion	Performance Metric	Actual Performance Objective Met?
	Removal of TCE present as a co-contaminant	below MCL.	Yes
	Scalability	Identify and assess scaling parameters for TGAC system.	Yes
	Operator time spent	Man-hours and cost to operate the 38 GPM system per acre-foot of water treated.	Yes
	Reliability	Down time. Time required for adjustments and restarts of the 38 GPM system.	Yes, considering only down time attributable to the technology reliability was 98.2%. Some additional downtime was attributable to the Fontana Water Company's (FWC) well operations.
Qualitative	Reduced treatment costs	Reduce treatment costs significantly over conventional IX technology by reducing adsorbent media costs.	No, cost of conventional IX treatment has decreased substantially and TGAC had a lower treatment capacity during field-scale operation than anticipated.
	Flow and Pressure Fluctuations	Determine how the TGAC system responds to flow and pressure fluctuations.	Yes
	Ease of operation & maintenance	From the perspective of the municipal operator, O&M same as or better than current IX systems. Assessed based on 38 GPM system.	Yes
	Waste generation	Spent TGAC will be shipped off- site. Information on how the spent TGAC is disposed and any other potential waste streams will be documented.	Not yet completed.

3.1 QUANTITATIVE PERFORMANCE OBJECTIVES

3.1.1 Ability of TGAC to Meet California DPH NL for Perchlorate

The data provided in this report will document that the TGAC technology reliably met the former California DPH NL, now MCL, for at least 10,000 BVs per bed treating unamended Fontana groundwater. Multiple data points over months of operation confirming this performance objective were collected at the 38 GPM scale and the 1.5 GPM scale. Perchlorate analysis was performed by Methods 314 and in confirmation by Method 332.0.

3.1.2 Time to Saturation of TGAC/GAC Unit

The number of BVs to saturation was measured multiple times at the 38 GPM and 1.5 GPM scales. Saturation was interpreted as the volume of impacted groundwater treated before perchlorate concentration in the effluent to a treatment vessel was equal to 90% of the perchlorate concentration in the influent of the same treatment vessel.

3.1.3 Pressure Drop across the System

Figures 5-28 through 5-30 provides a graphic presentation of pressure drop across the lead and lag TGAC beds. Pressure drop across the lag bed is representative of pressure drop across the entire system. This pressure drop was 6-12 psi initially, then rose to 14-28 psi ultimately with some clogging (compared to 50 psi for comparable IX).

The evaluation of pressure drop data must include specifics about what well pumping configuration was in place at the time of measurement. Since the test was conducted at a full-scale drinking water supply facility, the wells used was dependant on the water demands of the utility's customers and was not controlled by the demonstration team. Only well FWC-17B was operational at start-up and well FWC-17C became operational later, so that two wells were providing groundwater starting in early April of 2007. Towards the end of the demonstration, only well FWC-17C was operational. Each change in well configuration produced variable pressure drop data because of the increased pressure in the demonstration system's influent manifold until the new configuration stabilized and flow rates were reset. In addition, fluctuation in pressure drop occurred in late May/early June of 2007 when the configuration of the TGAC treatment beds was altered to change-out the lead bed that had reached perchlorate saturation. Pressure drop is a function of flow rate. Therefore, flow rate is plotted along with pressure drop data in Figures 5-28 to 5-30. Increased pressure drop across the TGAC system indicates an increase in the amount of energy needed to pump water through the TGAC beds, which directly correlates with increased booster pump/electrical costs to implement the technology. Therefore, economic considerations justify the evaluation of pressure drop during the demonstration. While the pressure drop of between 6-28 psi recorded is higher than the 10 psi goal set prior to the demonstration, it is significantly less than the 50 psi that would be expected for a comparable IX system.

3.1.4 Cost of TGAC and GAC

The TGAC utilized during the demonstration was manufactured by Siemens from virgin GAC. The virgin GAC was priced at $1.00/pound (lb) and the cost of the TGAC was $5.99/lb. Should TGAC be manufactured in larger quantities than needed for this demonstration, it is possible that economy of scale factors could decrease the cost per lb. Media cost was estimated at $200 per acre-foot of water treated (section 7). It should be noted that during the demonstration, GAC prices increased significantly because of import tariffs on Chinese GAC, which would also correspond with increased TGAC prices.

3.1.5 Demonstrate TCE Removal in Laboratory RSSCT Studies

The initial plan to demonstrate TCE removal with RSSCT was changed. TCE removal with TGAC was demonstrated for approximately 12,000 BV before breakthrough at the 1.5 GPM field-scale (see report Section 5.7.3.6). Bench-scale isotherm testing showed minimal influence of the tailoring agent on the capacity of the TGAC to adsorb TCE (Section 5.3).

3.1.6 Removal and Competition of Other Anions – Nitrate, Sulfate, Chloride, Bicarbonate, and Other Sulfur Species

Removal of other anions by TGAC can be considered either a positive or negative attribute of the technology on an ion specific basis. For instance, the removal of nitrate, if above drinking water limits, would be considered positive to the extent that it renders the water safe for consumption. Conversely, nitrate is documented to compete with perchlorate for sorption sites on the TGAC. The anions nitrate, sulfate, chloride, bicarbonate and other sulfur species have been examined during this demonstration through a combination of means and are dealt with separately below.

Nitrate was examined during the 38 GPM system operation, at bench-scale with RSSCT, and was evaluated as a spiked contaminant during the 1.5 GPM system operation. Nitrate is present in wells FWC-17B and FWC-17C that provided groundwater for this demonstration. Operation of the 38 GPM system shows nitrate sorption between BVs zero and 1000 for the initial start-up and the TGAC bed replacement in June of 2007 (See Section 5.6.2). The RSSCT conclusion pertaining to nitrate was that nitrate spiked as sodium nitrate competed with perchlorate thus reducing the perchlorate sorption capacity (See Section 5.3 and PSU Bench-Scale RSSCT Report in Appendix B). The nitrate spiked small-scale column was found to break through at significantly lower BVs than the control small-scale column thus indicating that nitrate does compete with perchlorate on the TGAC media.

The sulfate anion was monitored during 38 GPM system operation and was tested during the 1.5 GPM small-scale system TDS treatment train through the use of magnesium sulfate as the salt used to increase TDS concentration. At ambient concentrations of approximately 15 mg/L, sulfate appears to have little effect on TGAC perchlorate capacity. When tested at much higher concentrations during the 1.5 GPM small-scale TDS treatment, a reduction in the number of BVs treated prior to perchlorate breakthrough was noted.

Chloride removal and competition was examined during the 38 GPM system operation and during RSSCT experimentation at PSU. During 38 GPM system operation, with chloride at an ambient concentration of approximately 11 mg/L, it appeared to have little effect on TGAC perchlorate capacity. PSU found that chloride (as sodium chloride) actually appeared to extend the TGAC's to perchlorate breakthrough.

Bicarbonate removal and competition was examined through alkalinity measurement during the 38 GPM system operation and through measured bicarbonate dosing during the laboratory-scale RSSCT experimentation. A reduction in alkalinity was measured in the initial BVs passing through the 38 GPM system from system start up through approximately 7,500 BVs. This trend suggests initial bicarbonate sorption that reached breakthrough. PSU RSSCT experimentation with spiked bicarbonate suggests that bicarbonate spiked to 550 mg/L actually increased TGAC's perchlorate adsorption capacity (see Appendix B).

PSU investigated the effect of thiosulfate on TGAC's perchlorate capacity during RSSCT experimentation. Thiosulfate was dosed at 1 mg/L and 10 mg/L. Both concentrations induced significant decreases in TGAC's perchlorate capacity (see Appendix B and C).

3.1.7 Removal of TCE Present as a Co-Contaminant

The removal of TCE was demonstrated at the 1.5 GPM scale. TCE and perchlorate breakthrough was quantified at the 1.5 GPM scale. Breakthrough is defined as the volume of impacted groundwater treated prior to measurement of perchlorate/TCE in the effluent of the lead treatment vessel (thus breakthrough is defined as the reporting limit of the analytical technique). TCE breakthrough occurred at approximately 12,000 BVs after perchlorate breakthrough (see section 5.7.3.6).

3.1.8 Scalability

Scaling TGAC systems during design is typically done using RSSCT protocols as described elsewhere in this document. RSSCT application does not always result in a perfect correlation with field-scale systems. In this instance, RSSCT appears to have overpredicted the mass of perchlorate that would be sorbed by the TGAC at field-scale prior to initial breakthrough and saturation. There was reasonably close agreement between the BVs treated prior to perchlorate saturation at the 1.5 GPM and 38 GPM scales during the demonstration. Section 6.8 contains more information on these findings.

3.1.9 Operator Time Spent

This section makes comparisons between the operator time spent for the 38 GPM TGAC system demonstrated during this project to the time expenditure that would be expected for a similar sized system that is in a routine “production” setting. Operator time spent attending to the six small-scale TGAC treatment trains where groundwater chemistry was altered for research purposes is not considered representative of real world well head treatment equipment operation and thus will not be discussed.

The EPA document “Design Manual: Removal of Arsenic from Drinking Water by IX” (EPA/600/R-03/080, June 2003, http://www.epa.gov/nrmrl/pubs/600r03080/600R03080.pdf) identifies operating labor as the most difficult cost to quantify for systems such as IX (and thus TGAC by association). This EPA document provides guidance on page 48 for the computation of an annual labor budget for a 620 GPM system. The estimate for an automated IX arsenic treatment is 465 hours per year.

Another pertinent comparison can be found in “Arsenic Removal from Drinking Water by IX, USEPA Demonstration Project at Fruitland, Idaho, Six-Month Evaluation Report” (EPA/600R-07/017, April 2007; http://www.epa.gov/nrmrl/pubs/600r07017/600r07017.pdf). This 250 GPM IX system consumed “about 30 minutes per day in “routine, non-demonstration related labor activities”.

The system size is a variable that impacts the cost of operation. Operating labor requirements generally do not vary significantly with the scale of the system within scales from tens to thousands of GPM. Therefore, the smaller the system, the greater the labor cost per unit of water treated. ARCADIS believes that the arsenic IX systems discussed above provide a reasonable baseline for operational labor against which to compare the 38 GPM TGAC system. Table 3-2 summarizes the number of operations and maintenance (O&M) visits required by the 38 GPM TGAC system. Table 3-2 provides O&M in terms of man hours for the project and man hours per acre-foot of water treated. ARCADIS estimates in its Systems Operations & Maintenance Summary that an actual TGAC system would require a 0.5 hour visit each day similar to the arsenic removal IX system discussed by EPA.

Table 3-2. 38 GPM System Operations & Maintenance Summary

Estimated for an Actual System Checked Daily		
Treated acre-feet	Number of O&M visits because of sampling and repairs	O&M Visits per Week
42.99	59	7
Approximate months of operation	Man Hours Per Visit	Man Hours Per Visit
9.8	1	0.5
Approximate required O&M visits	Total Man Hours	Total Man Hours per week
39	59	3.5
Man Hours Per Visit	Man Hours per Treated acre-foot	Total Man Hours per month
1	1.37	14
Total Man Hours		Treated acre-feet per month
39		4.39
Man Hours per Treated acre-foot		Man Hours per Treated acre-foot
0.91		3.19

3.1.10 Reliability

The assessment made in this section pertains to the reliability of the 38 GPM system only. The six smaller-scale spiked columns are not evaluated since spiking made these systems significantly more complex to operate than real world systems.

The 38 GPM TGAC system achieved an operational uptime of approximately 98.2 percent during the demonstration, excluding downtime caused by FWC (e.g., shutting their wells down, stopping the demonstration flow, etc.) that was unrelated to the TGAC system. Considering only down time attributable to the TGAC technology reliability was 98.2%. Some additional downtime was attributable to the FWC well operations.

The 38 GPM TGAC system was installed on January 3, 2007. Siemens and ARCADIS consider the period between installation and January 15, 2007 (12 calendar days) to be an initial "shake-down" period. During the "shake-down" period, the system required installation of manual air release valves and repair of two of the three manual release valves. In addition, the 38 GPM system was shut down between January 13, 2007 and January 15, 2007. The shutdown was needed to repair leaking pressure gauge assemblies and to allow the polyvinyl chloride (PVC) cement to cure prior to re-pressurization. The 38 GPM TGAC system was re-started on January 15, 2007 when minor foaming was noted from the open manual air release valves immediately after re-start; no foam was observed following the re-start. A prefilter element was changed on January 20, 2007 and the flow rate was adjusted on January 23, 2007. On January 24 and January 25, 2007, the 38 GPM TGAC system was shut down by Siemens for 90 minutes and 60 minutes respectively to facilitate routine maintenance of the FWC IX system. Flow rate adjustments were made on February 2, 2007. On February 7, two leaks on the system prefilter were repaired with the system down for 68 minutes. FWC took the 38 GPM system off line for 30 minutes on February 8 for routine maintenance. On February 12, severe leaks were again noted in the prefilter pressure gauge and Siemens was contacted to effect repairs. FWC took the 38 GPM system off-line for 40 minutes on February 13 for routine maintenance.

Following February 13, the TGAC system required only flow rate adjustment and change-outs of the disposable pre-filters, and did not require any significant maintenance until June 21, 2007 when excessive leakage from Vessel #2 was observed and repaired. Following the repair of Vessel #2, the 38 GPM system demonstrated another lengthy interval of reliable performance extending until December 7, 2007 when FWC shut both of their wells down. The TGAC system did not operate through December 26, 2007 at which time it was shut down after analytical data revealed that perchlorate saturation had occurred and demonstration objectives had been met.

3.2 QUALITATIVE PERFORMANCE OBJECTIVES

3.2.1 Reduced Treatment Costs

The cost of conventional IX treatment has decreased substantially since this demonstration project was conceived (Figure 7-4). TGAC did not operate as long in field-scale tests as anticipated based on RSSCT results. In order for the TGAC technology to be cost competitive with next-generation IX resin technologies, TGAC production costs would have to be significantly reduced. Research is ongoing at PSU under other funding sources to achieve this goal. Cost issues are covered in detail in Section 7 and specifically Section 7.3.3.

3.2.2 Flow and Pressure Fluctuations

Flow rate and pressure fluctuations experienced during the demonstration interval were minimal during the operation of the 38 GPM TGAC system. These reductions in flow/pressure did not significantly affect TGAC operations. The experimental design did not permit a determination of whether flow rate or pressure fluctuations negatively influenced TGAC effluent quantity.

3.2.3 Ease of Operation & Maintenance

TGAC system O&M was considered routine, thus comparing favorably with other means of perchlorate well head treatment technologies. Once oriented to the demonstration system, all levels of ARCADIS and FWC staff could operate the TGAC system. The predominant system need was to monitor effluent for perchlorate breakthrough and subsequent saturation so that TGAC columns could be changed-out once spent. Routine monitoring of pressure drop is also recommended to facilitate optimal operation and to ensure proper pre-filtration. During the demonstration interval, maintenance was only required on ancillary systems such as pressure gauges, that were mainly caused by the PVC materials of construction – these repairs would not likely occur in full-scale systems. The O&M costs are discussed above and in Section 7.

3.2.4 Waste Generation

Waste disposal activities for the demonstration have not yet been completed, however there are no indications that the waste generation profile of the technology will be significantly different than planned.

4. SITE DESCRIPTION

The field demonstration was performed at the FWC existing perchlorate treatment facility located in Fontana, California, adjacent to groundwater production wells FWC-#17B and FWC-#17C. The site was selected by ESTCP in consultation with local municipalities and the project team

4.1 SITE LOCATION AND HISTORY

The field demonstration was performed at FWC existing perchlorate treatment facility located in Fontana, California, adjacent to groundwater production wells FWC-17B and FWC-17C. FWC is a subsidiary of the San Gabriel Valley Water Company, which uses a drinking water source mix of approximately 85 percent groundwater, 14 percent surface water, and 1 percent purchased water (FWC, 2004). The demonstration site has several characteristics that made it suitable for the demonstration:

- Water chemistry that was representative of the California Inland Empire.
- Adequate supply of water for testing.
- Piping infrastructure available for relatively easy connection.
- Nearby electrical source for the booster pump.
- National Pollution Discharge Elimination System (NPDES)-permitted percolation pond for discharge of treated demonstration water.
- FWC had 12 DPH-certified water treatment system operators that inspected the demonstration system on a near-daily basis.

The FWC full-scale perchlorate treatment system at the same site utilizes one-pass (non-regenerable) IX that is comprised of five parallel trains of lead-lag vessel pairs (a total of 10 IX vessels), and has a maximum treatment capacity of approximately 5,000 GPM (0.3 m^3/s). Production wells FWC-17B and FWC-17C pump water through the treatment system and then to the FWC's distribution system reservoir. Currently, the IX system utilizes Purolite A-530E resin. The site also has an NPDES-permitted percolation pond that is used to discharge water generated during resin change-outs and testing, and was used to discharge the treated demonstration water. A site location map is provided as Figure 4-1.

Figure 4-1. Site Map

4.2 SITE GEOLOGY, HYDROGEOLOGY AND CONTAMINANT DISTRIBUTION

Several large perchlorate plumes have impacted at least 20 large municipal drinking water supply wells in California's Inland Empire, resulting in their removal from service or installation of costly treatment systems. The demonstration site houses two groundwater production wells, a drinking water reservoir, a percolation pond, and a perchlorate treatment system. The site sits above a large regional perchlorate plume (illustrated on Figure 4-2) that is unrelated to past or current site operations, and is located in a light industrial/residential area of Fontana, California. Groundwater from the two production wells is representative of perchlorate-impacted water in the Inland Empire of Southern California.

Groundwater chemistry for both production wells is summarized in Table 4-1. Historical trends in two contaminants, perchlorate and nitrate, over time are shown in Figures 4-3 and 4-4 based on data provided by FWC and graphed by ARCADIS. FWC provided data for nitrate spanning the demonstration time period is shown in Figure 4-5.

Table 4-1. Historical Production Well Groundwater Chemistry (multiple data points divided with slash mark)

Well Identification (ID):	FWC-17B	FWC-17C	Average
Production Rate (GPM):	1,290	1,850	3,150 (Total)
Production Rate (m3/min):	4.9	7.0	11.9
Average Water Quality Parameters:			
Perchlorate (µg/L)	18/12	8.6/7.7	11.6
Nitrate (mg/L as nitrate)	36/30	33/32	32.8
Chloride (mg/L)	11/8.9	11/12	10.7
Sulfate (mg/L)	14/16	14/15	14.8
Carbonate/Bicarbonate (mg/L)	ND/192 & ND/210	ND/186 & ND/180	ND/192
pH	7.5/6.94	7.5/8.17	7.5
TDS (mg/L)	250/250	238/270	252
Specific Conductance (µmho/cm)	415	388	401
Volatile Organic Compounds (µg/L)	ND	ND	ND

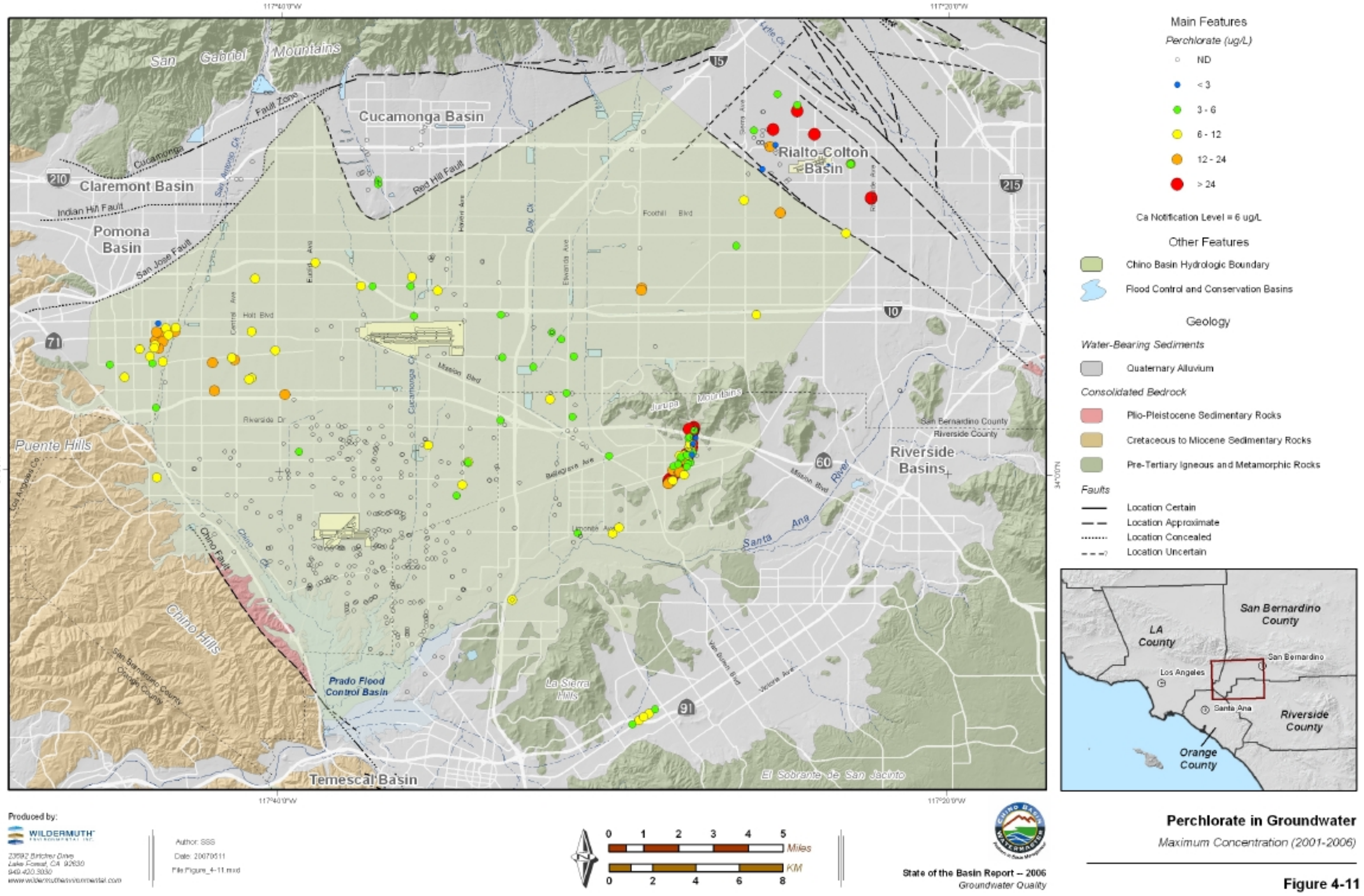


Figure 4-2. Perchlorate in Groundwater in Chino Basin

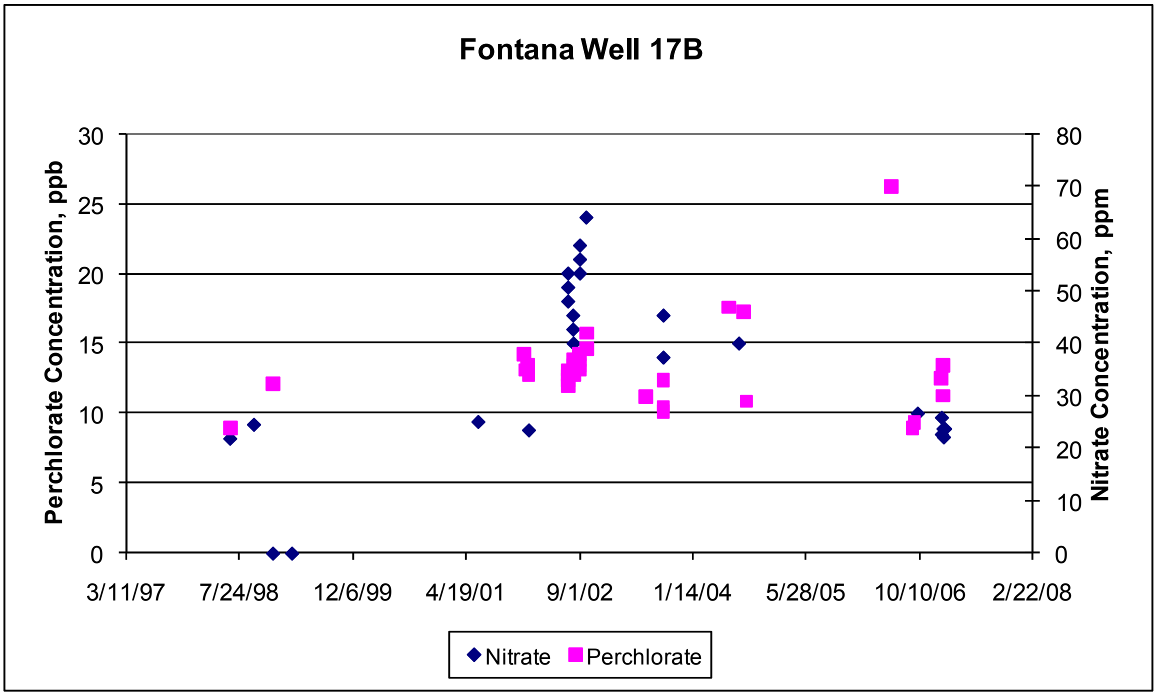


Figure 4-3. Historical Trends in Nitrate and Perchlorate in well FWC-17B (Nitrate in units of ppm and perchlorate in units of ppb)

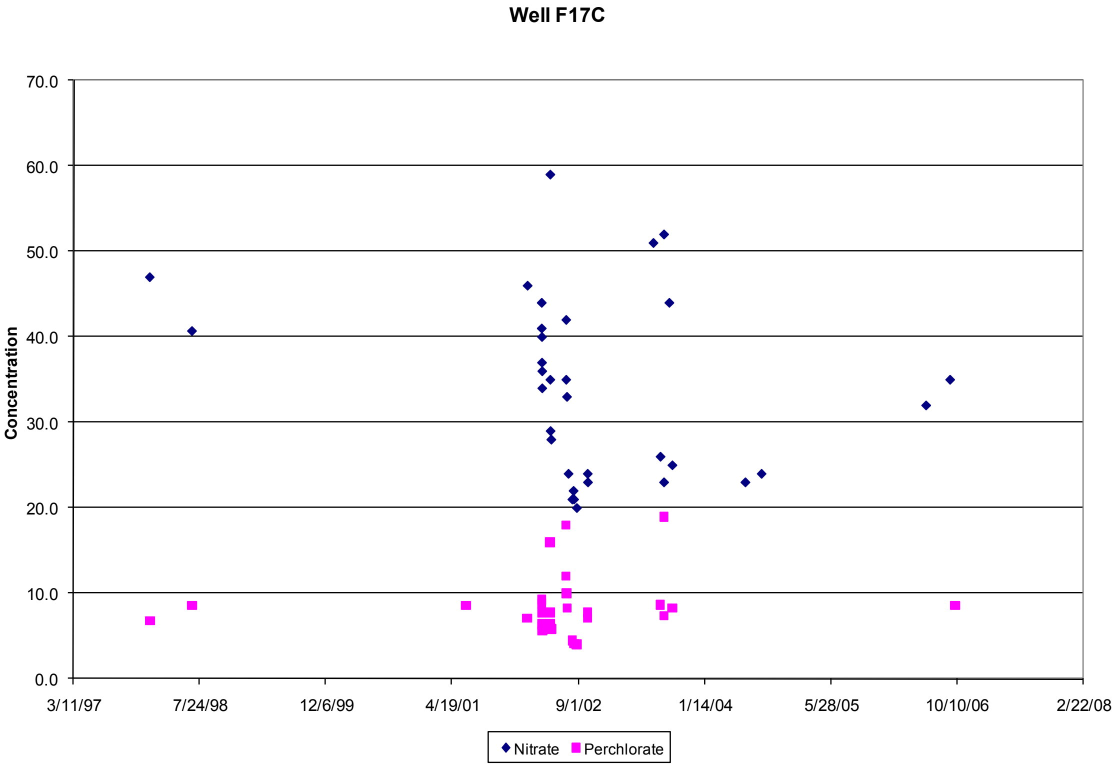


Figure 4-4. Historical Trends in Nitrate and Perchlorate in well FWC-17C (Nitrate in units of ppm and perchlorate in units of ppb)

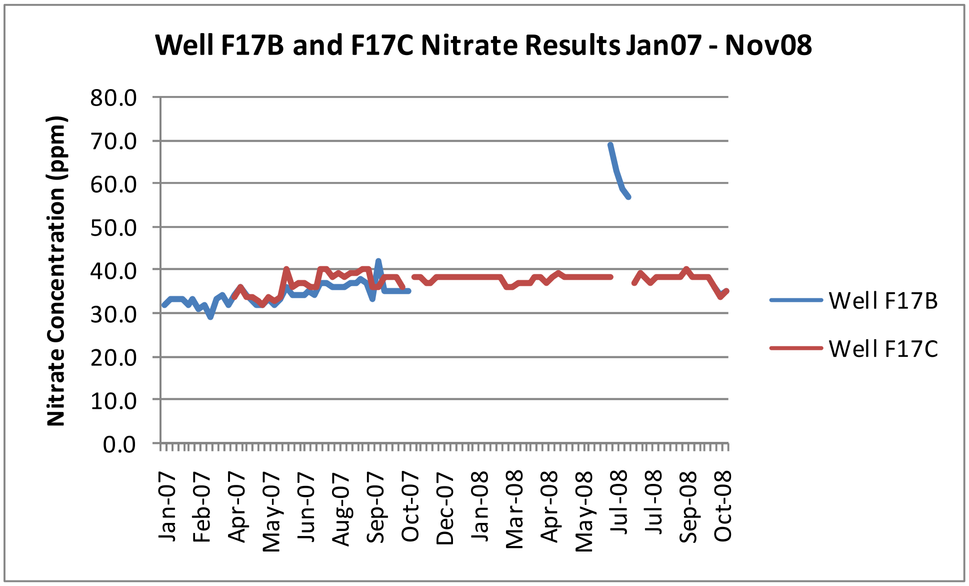


Figure 4-5. Nitrate Concentration for Wells FWC-17B and FWC-17C during 2007 and 2008, Data from FWC

These particular wells extract from the Chino formation. The water chemistry of the Chino formation as a whole has been extensively studied by the Chino Basin Watermaster http://www.cbwm.org/ov_engineering.htm and by the United States Geological Survey (USGS) in their report on the Santa Ana watershed http://pubs.usgs.gov/wri/wri02-4243/text.html. From these documents it is clear that these wells are likely to be quite high in dissolved oxygen (DO) (>50% of saturation), with dissolved organic carbon below 1 mg/L, phosphorous below 0.04 mg/L and have alkalinities between 130-180 mg/L as $CaCO_3$.

The pumping times for the wells at the Fontana 17 location are limited by the demand in the pressure zone into which they pump and the ability to vacate water from this zone in order to keep at least one of the wells running at all times. In the winter operation is typically on one well. In the summer it will typically be two wells. Fall and spring operations are based on demand.

The FWC is observing some fluctuation in nitrate levels that they attribute to operation of both wells at the same time. Their Supervisory Control and Data Acquisition (SCADA) system is set to automatically trip off the wells if they exceed an established level of nitrate. However they normally see nitrate increases coming and respond before this takes place.

Packers (permanent or tempory sealing devices to isolate portions of the well) are used in wells FWC-17B and FWC-17C to select for waters low in nitrate, because nitrate concentrations have historically approached the MCL in these wells.

The following are the specifications of well FWC-17B:

- Originally drilled to 870' (265 m) below ground surface (BGS).
- The screened interval is from 500' to 860' (152 m to 262 m).
- The casing is 16" (0.4 m) steel.
- The static level as of April 2006 was 326' (99 m).
- The pumping level was 349' (106 m) in 3-06.

In well FWC-17B is as follows: The original K-Packer was installed July 2002. It was set at 650' (198 m) BGS. It was removed in October 2004, and the equipment changed to increase the flow rate. The nitrate levels at that time were suitable to do so. As of early 2006 the nitrate levels in FWC-17B were 59 mg/L and thus a new inflatable packer was installed in June 2006.

The following are the specifications of well FWC-17C:

- Screened interval: 500' to 920' (152 m to 280 m) BGS
- Total depth: 930' (283 m) BGS
- Slot Size: 3/32" (0.23 cm)
- Packer Depth: 610' (186 m) BGS (approximately 40' (12 m) above the clay barrier)
- Water Level: 359' (109 m) BGS (standing level in March 2006)
- Pumping Level: 363' (111 m) BGS (pumping level in April 2006)

FWC had originally installed a K-Packer in FWC-17C also. It was set at 650' (198 m) BGS and the flow rate was reduced from 2800 GPM (10.5 m^3/min) to < 2,000 GPM (7.6 m^3/min). FWC decided they could allow some of the water from the upper strata to pass an inflatable packer, increasing the flow rate and still yielding an acceptable level of nitrate. They now are producing close to 3000 GPM (11.3 m^3/min) at 26 mg/L of nitrate, as nitrate. The packer is now completely inflated.

5. TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design associated with this project was intended to transition the TGAC technology from laboratory testing to field implementation. During this project, a series of TGAC experiments were implemented with sufficient performance monitoring to delineate the functional lifetime of the media and generate data for the California regulatory approval process. From an experimental design perspective, the demonstration consisted of three main experimental components discussed in detail below. The output from these three experimental components was then coupled to a predictive model that will expedite the screening of future sites for the practicality and economics of TGAC implementation.

The demonstration study experimental design focused on consistently conducting analyses aimed at delineating TGAC performance over the long time period of operation typically seen for adsorptive technologies in drinking water service. Accordingly, this demonstration had an twenty-month overall duration (12 months of testing at 38 GPM scale overlapping with 12 months of testing at 1.5-3 GPM scale). The project team also designed the project to gather data on the scalability of the system. The scaling of this technology has previously employed the RSSCTs and scaling equations for proportional diffusivity by Crittenden et al. (1991). Additional information used in the experimental design and pertaining to scaling relationships for adsorption technologies is provided in Weber et al. (1975 and 1983) as well as in Section 5.3.

A 38 GPM scale field pilot system was a major component of the TGAC demonstration designed to evaluate performance over an extended demonstration interval. With greater than 50 samples of influent water conducted over the demonstration interval, an accurate assessment of the perchlorate influent flux and other general groundwater chemistry parameters such as nitrate was developed. The long operational interval permitted the project team to evaluate the system's ability to accommodate temporal variation in groundwater chemistry found in FWC's production wells FWC-17B and FWC-17C. Groundwater chemistry varied modestly over the demonstration interval with some variability in nitrate concentration likely associated with repositioning of well packers within well FWC-17C which was conducted by FWC during the demonstration period. In addition, operation at 38 GPM was utilized to better understand and document TGAC's reliability and operations and maintenance requirements. Lastly, the effectiveness of TGAC treatment and its longevity in service were documented.

An additional component of the experimental design for this demonstration project was PSU evaluation of water quality parameter effects on TGAC performance through the application of RSSCTs. PSU conducted RSSCTs with groundwater that had been spiked to an array of concentrations of perchlorate, nitrate, sulfate, chloride, thiosulfate, bicarbonate and adjusted to more acidic and basic conditions. This RSSCT data provides information on how the technology's critical design and operating factors vary with differing influent concentrations. The RSSCT procedure is fully described in Crittenden et al. (1986 and 1991). The effect of the influent water quality on the perchlorate treatment performance has been mathematically modeled by AFIT. The results of the RSSCTs and Field Sensitivity tests have been intercompared and used to support AFIT's model development. The intent of varying each water quality parameter during RSSCT is briefly documented below:

- Perchlorate was varied to demonstrate the effect on TGAC performance and longevity so that performance at sites with higher perchlorate influent concentrations could be projected
- Nitrate is known to compete with perchlorate for sorption sites on TGAC. Therefore, variation of nitrate concentrations during RSSCT permits the project team to predict performance over a range of nitrate concentrations.
- Sulfate content in groundwater varies widely across the western geography where perchlorate groundwater contamination is widespread. Sulfate RSSCT analysis was conducted to document that sulfate does not compete with perchlorate for TGAC sorption sites.
- Increases in chloride and bicarbonate ions were studied to document TGAC performance in the presence of variable anion concentrations.
- Thiosulfate was studied during RSSCT testing as a potential detriment to TGAC sorption capacity.
- Acidic and basic groundwater pH values were investigated during RSSCT to generate a more complete understanding of TGAC response to pH variation and to provide insight into the sorption mechanisms behind TGAC functionality.

Six additional smaller-scale field column tests were performed in addition to the 38 GPM TGAC field-pilot demonstrations to confirm the system response to variations of selected groundwater chemistry parameters. These sensitivity tests were included so as to identify the overall performance impacts of changes to influent TDS, TCE, perchlorate, nitrate, and residual chlorine. An additional baseline test (Small-scale Treatment Train 5 – stratified bed control) was performed to provide a direct comparison of elevated concentrations of these components and to provide a direct comparison to the field-pilot test.

Compilation and analysis of the data resulting from the 38 GPM system, the RSSCT results, and the small-scale field pilot tests in this report document TGAC performance and reliability over a broad range of contaminant concentrations and realistic groundwater chemistries. The resulting data contained in this report can be used for future evaluations of TGAC performance and economic feasibility over at a broad range of groundwater chemistries.

Lastly, the results of this demonstration at Fontana may be compared to the results of previous TGAC demonstrations at Redlands and the Massachusetts site previously described. This will provide further insight into how the technology's critical design and operating factors vary with differing combination of general influent chemistry.

5.2 BASELINE CHARACTERIZATION

This demonstration project was conducted on groundwater that was pumped from a perchlorate-impacted aquifer that is contaminated on a regional-scale (see Section 4.2). The perchlorate plume is a very large plume that affects the region where the demonstration was conducted, and the production wells have a high yield, thus the local demonstration site cannot be feasibly characterized using the same tools as a remediation project. In the previous section however, the physical elements of the demonstration site were described—two groundwater extraction wells, perchlorate treatment system, distribution reservoir, percolation pond—as well as the location of the site. The demonstration site can be described as a "typical" example of a site where a drinking water perchlorate treatment system might be located even though the baseline perchlorate concentration only modestly exceeds California's 6 µg/L MCL. The chemistry of the groundwater that was used in the demonstration is typical of groundwater that is treated in the California Inland Empire, however, the average perchlorate concentration is slightly lower, and the average nitrate concentration is slightly higher than at other perchlorate treatment systems in the area.

For the purposes of this project, the baseline was defined as the untreated water as pumped during routine operation from wells FWC-17B and/or FWC-17C. Which wells were operated at which times were controlled by the needs of the FWC. As shown in Figures 4-3, 4-4 and 4-5 history shows there is some variability in the levels of nitrate and perchlorate in these wells, which is likely a function of regional hydrogeology and the pumping rate and depth adjustments made to these supply wells. A statistical analysis of the influent concentration during the demonstration is presented in Table 5-1.

Table 5-1: Influent Perchlorate concentration Statistical Analysis.

Mean	8.3
Standard Error	0.2
Median	8.3
Standard Deviation	1.7
Minimum	5.1
Maximum	12.6
Count	58

During the demonstration itself, influent water quality was routinely monitored by ARCADIS using the same methods used for effluent quality as discussed in Section 5.6.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

In parallel with the field scale work, the Penn State team conducted a number of RSSCTs. These focused on how other anions compete with perchlorate in a manner that diminishes the capacity of the cationic surfactant-tailored GAC for removing perchlorate. The anions appraised include nitrate, sulfate, chloride, and bicarbonate. In addition, they conducted extensive work regarding the competition of thiosulfate for perchlorate removal; and whether this thiosulfate competition can be diminished by prechlorinating the groundwater. A detailed report of these experiments can be found in Appendix B and C. Additionally, they have appraised whether the cationic surfactant tailoring has impacted TCE removal, as appraised by bench-scale isotherms.

The design of the bench scale experiments employed the RSSCT scaling equations for proportional diffusivity by Crittenden et al. (1991). If this proportional diffusivity model holds, then a properly designed RSSCT will accurately predict field-scale performance. This approach is effective even though the test period is dramatically shorter since the RSSCT uses a smaller particle size and its performance is governed by the same adsorption capacity and kinetics factors that govern larger scale performance (Crittenden et al., 1986 and 1991) Both demonstration-scale and RSSCTs were conducted with the same Fontana water so as to appraise whether the proportional diffusivity model is appropriate for perchlorate sorption here. A discussion of the scale-up to larger columns is included in this report in Section 6.8. When employing virgin GAC, PSU has demonstrated that that proportional diffusivity is indeed the proper model. However, when employing TGAC, there was some possible distinction. Significant modeling differences between virgin GAC and TGAC will also be discussed in this final technical report. As per its name, the proportional diffusivity model addresses how to scale-up diffusion effects in small grains that are simulating full-sized grains. However, since the RSSCTs reach breakthrough in time scales of weeks, one weakness is that they may not mimic the biological population dynamics that can occur in full-scale systems, even those that are not intentionally biological, since they are not perceived to achieve well-developed microbial populations. Moreover, similitude with regard to the oxidation/reduction potential (ORP) of the water may be difficult to achieve in RSSCTs.

There were several problems with running RSSCTs with TCE and perchlorate concurrently during this work. The largest problem was that an RSSCT designed for perchlorate works on proportional diffusivity, while an RSSCT designed for TCE works on constant diffusivity. This means that an RSSCT cannot be compatibly run on both constituents simultaneously. Thus we chose to evaluate the effects of the concurrent operation using the field-scale 1.5 GPM beds and isotherm information.

Seventeen rapid small scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment of pH 4 was 50% greater than the natural occurring pH of the groundwater at 8, and 75% greater than at a pH of 10. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration (60mg/L) reduced the removal of perchlorate by 17%; and a nitrate concentration of 100mg/L reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level. Also the bench scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7 (Table 5-20***).***

Table 5-20 Results Summary of Laboratory Scale experiments

Conditions	**Spiked concentration**	**Bed Volumes to Breakthrough**
pH	8 (no addition of acid or caustic solution)	18,500
	4	30,000
	10	6,500
Nitrate	32 mg/L (native concentration of water	18,500
	60 mg/L	15,600
	100 mg/L	8, 500
Sulfate	5 mg/L (native concentration of water)	18,500
	50 mg/L	20,000
	250 mg/L	20,000
Thiosulfate	None (native concentration of the water)	18,500
	1 mg/L	16,700
	10 mg/L	14,500
Chloride	12mg/L (native concentration of the water)	18,500
	250mg/L	23, 000
Bicarbonate	250 mg/L (native concentration of the water)	18,500
	550 mg/L	23,000

The effects of the tailoring agent on carbons ability to remove TCE have been studied in the form of sorption isotherms. These experiments were conducted to determine whether the presence of a tailoring agent (in this case CTAC) would inhibit the sorption of TCE. These isotherms compared activated carbon that had been preloaded with CTAC versus virgin (i.e. unloaded) activated carbon. As presented in Figure 5-43, the CTAC exhibited minimal influence on TCE adsorption. These experiments showed there were no differences in the capacity of TGAC and ordinary GAC to adsorbed TCE when there were high concentrations of TCE present.

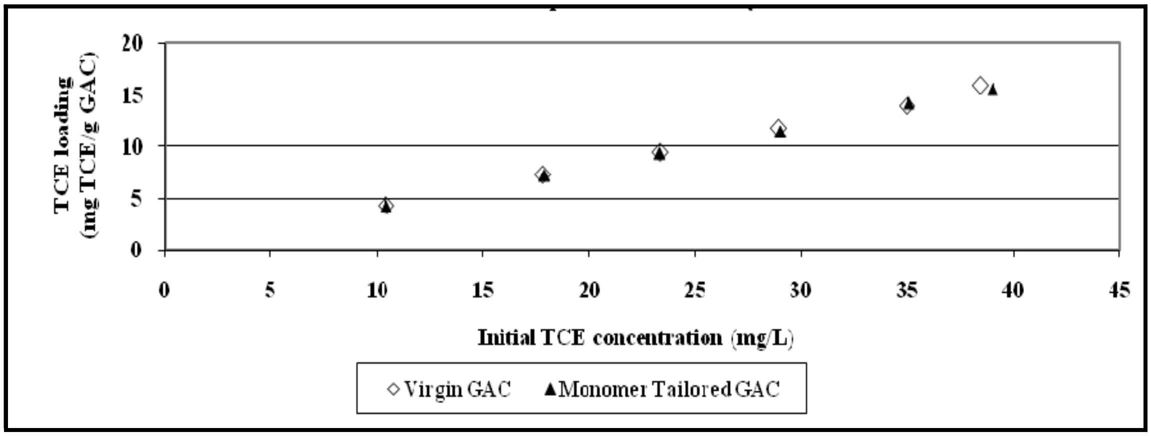
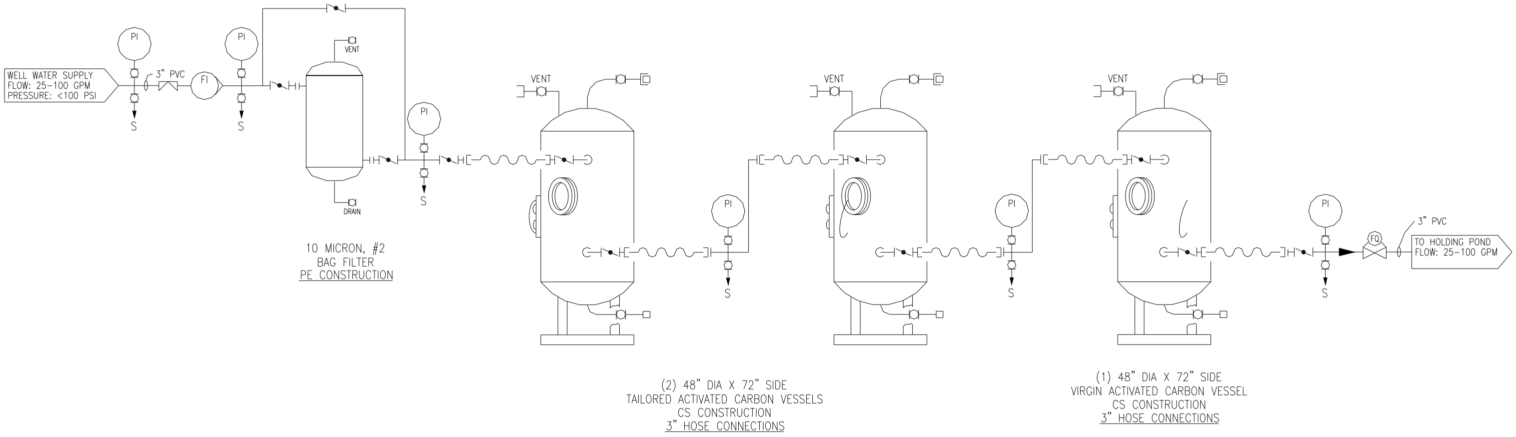


Figure 5-43. Isotherm Test for Effect of CTAC Preloading on Co-adsorption of TCE

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

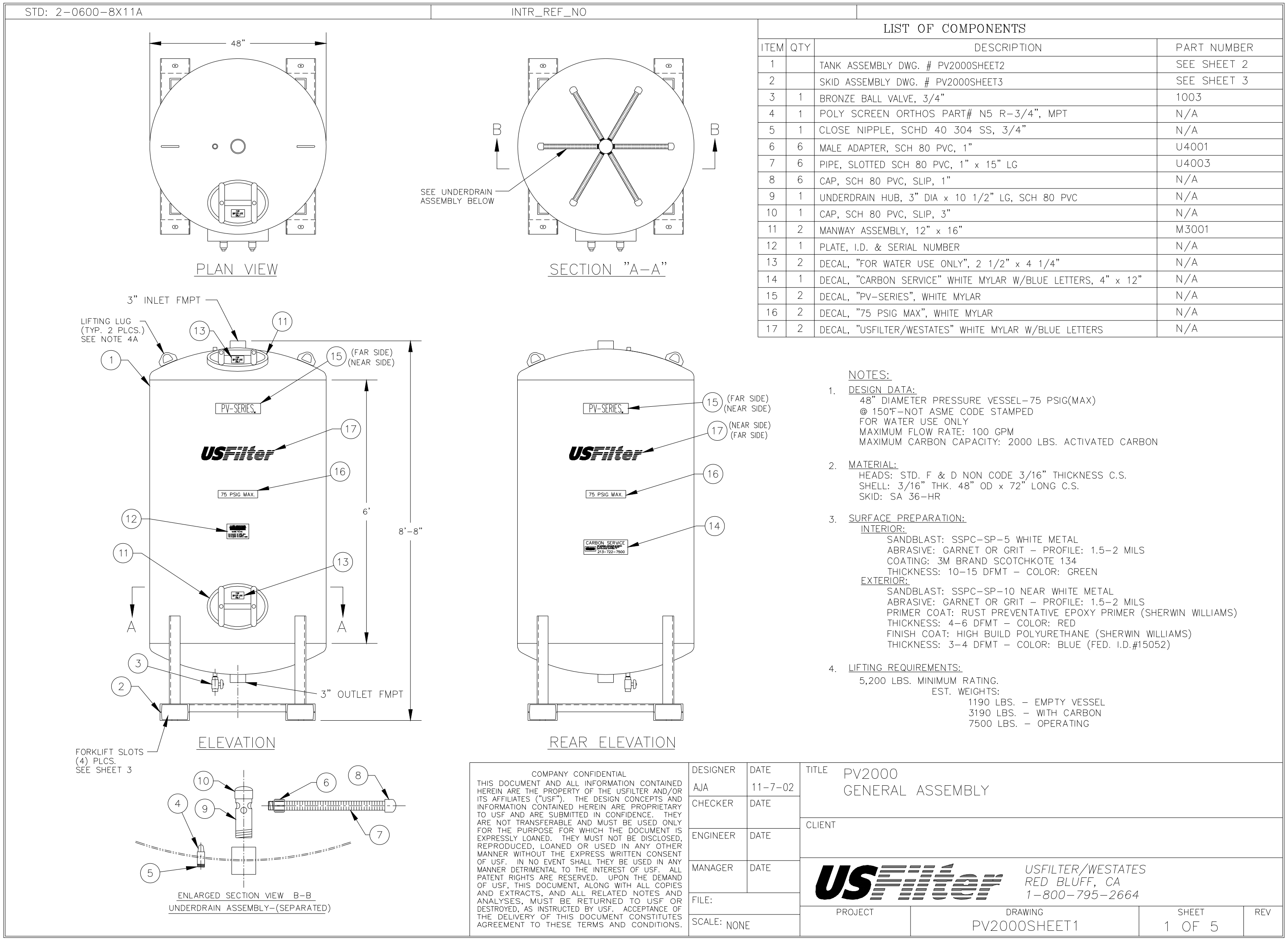
5.4.1 Overview of Design and Layout

The field-scale demonstration included testing on a 38 GPM TGAC system (Figure 5-1A and B) and testing on a Six-Condition Pilot-Scale Field System (Figure 5-2), that was comprised of six parallel systems to study TGAC performance at different influent water quality chemistries. The demonstration systems were designed by Siemens and ARCADIS and were operated at FWC wells, FWC-17B and FWC-17C, because the wells deliver an adequate supply of water, and the site could accommodate the discharge flow rate of the two systems.



PI = Pressure Gauge FI = Flow Meter S = Sampling Port

Figure 5-1A. Process Schematic of 38 GPM TGAC System



LIST OF COMPONENTS

ITEM	QTY	DESCRIPTION	PART NUMBER
1		TANK ASSEMBLY DWG. # PV2000SHEET2	SEE SHEET 2
2		SKID ASSEMBLY DWG. # PV2000SHEET3	SEE SHEET 3
3	1	BRONZE BALL VALVE, 3/4"	1003
4	1	POLY SCREEN ORTHOS PART# N5 R-3/4", MPT	N/A
5	1	CLOSE NIPPLE, SCHD 40 304 SS, 3/4"	N/A
6	6	MALE ADAPTER, SCH 80 PVC, 1"	U4001
7	6	PIPE, SLOTTED SCH 80 PVC, 1" x 15" LG	U4003
8	6	CAP, SCH 80 PVC, SLIP, 1"	N/A
9	1	UNDERDRAIN HUB, 3" DIA x 10 1/2" LG, SCH 80 PVC	N/A
10	1	CAP, SCH 80 PVC, SLIP, 3"	N/A
11	2	MANWAY ASSEMBLY, 12" x 16"	M3001
12	1	PLATE, I.D. & SERIAL NUMBER	N/A
13	2	DECAL, "FOR WATER USE ONLY", 2 1/2" x 4 1/4"	N/A
14	1	DECAL, "CARBON SERVICE" WHITE MYLAR W/BLUE LETTERS, 4" x 12"	N/A
15	2	DECAL, "PV-SERIES", WHITE MYLAR	N/A
16	2	DECAL, "75 PSIG MAX", WHITE MYLAR	N/A
17	2	DECAL, "USFILTER/WESTATES" WHITE MYLAR W/BLUE LETTERS	N/A

NOTES:

1. DESIGN DATA:
   48" DIAMETER PRESSURE VESSEL-75 PSIG(MAX)
   @ 150°F-NOT ASME CODE STAMPED
   FOR WATER USE ONLY
   MAXIMUM FLOW RATE: 100 GPM
   MAXIMUM CARBON CAPACITY: 2000 LBS. ACTIVATED CARBON

2. MATERIAL:
   HEADS: STD. F & D NON CODE 3/16" THICKNESS C.S.
   SHELL: 3/16" THK. 48" OD x 72" LONG C.S.
   SKID: SA 36-HR

3. SURFACE PREPARATION:
   INTERIOR:
   SANDBLAST: SSPC-SP-5 WHITE METAL
   ABRASIVE: GARNET OR GRIT - PROFILE: 1.5-2 MILS
   COATING: 3M BRAND SCOTCHKOTE 134
   THICKNESS: 10-15 DFMT - COLOR: GREEN
   EXTERIOR:
   SANDBLAST: SSPC-SP-10 NEAR WHITE METAL
   ABRASIVE: GARNET OR GRIT - PROFILE: 1.5-2 MILS
   PRIMER COAT: RUST PREVENTATIVE EPOXY PRIMER (SHERWIN WILLIAMS)
   THICKNESS: 4-6 DFMT - COLOR: RED
   FINISH COAT: HIGH BUILD POLYURETHANE (SHERWIN WILLIAMS)
   THICKNESS: 3-4 DFMT - COLOR: BLUE (FED. I.D.#15052)

4. LIFTING REQUIREMENTS:
   5,200 LBS. MINIMUM RATING.
   EST. WEIGHTS:
   1190 LBS. - EMPTY VESSEL
   3190 LBS. - WITH CARBON
   7500 LBS. - OPERATING

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DESIGNER: AJA
DATE: 11-7-02
CHECKER:
DATE:
ENGINEER:
DATE:
MANAGER:
DATE:
FILE:
SCALE: NONE

TITLE: PV2000
GENERAL ASSEMBLY
CLIENT:

USFilter
USFILTER/WESTATES
RED BLUFF, CA
1-800-795-2664

PROJECT:
DRAWING: PV2000SHEET1
SHEET: 1 OF 5
REV:

Figure 5-1B. Detailed diagram of Vessels of the Type Used in 38 GPM System

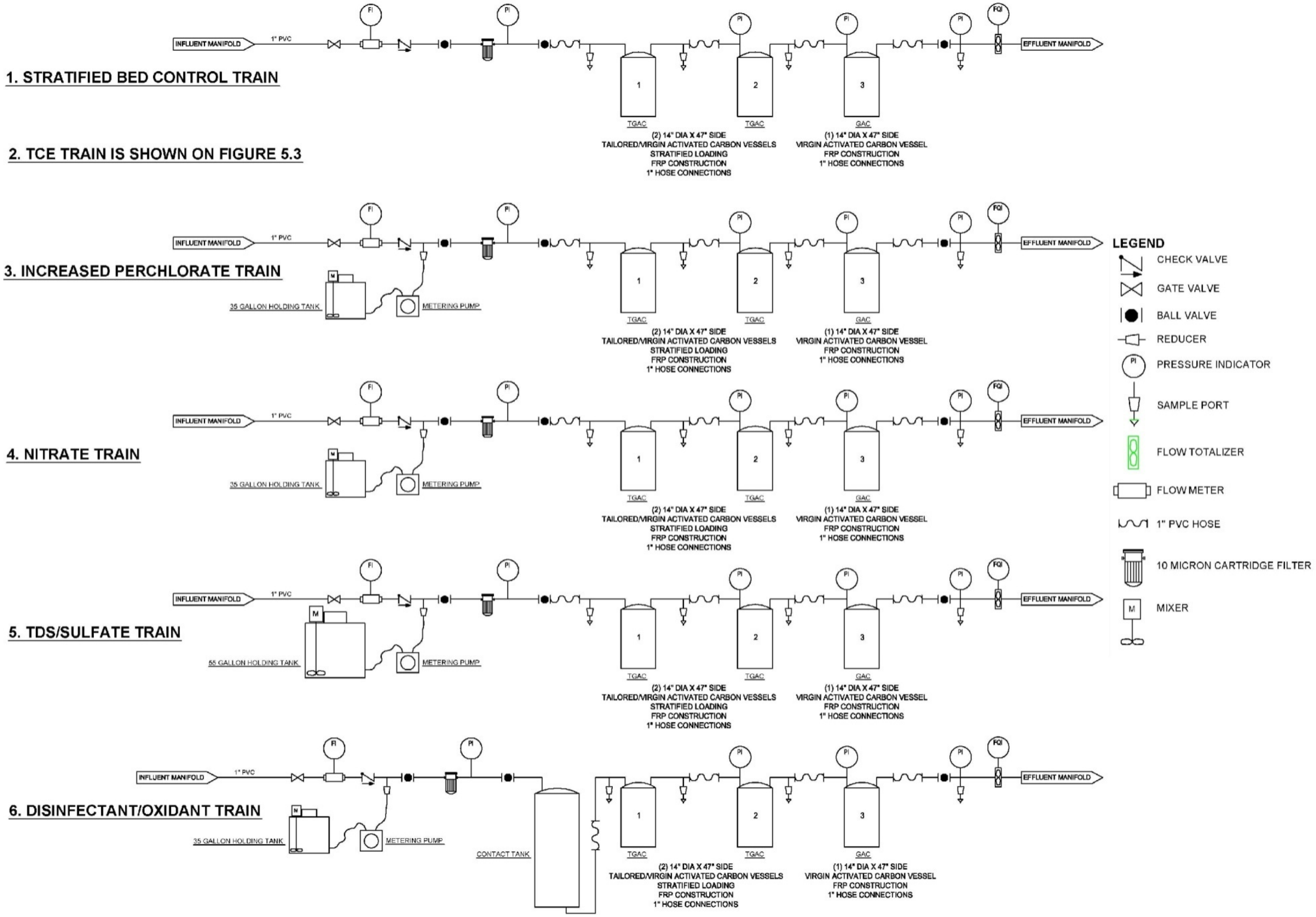


Figure 5-2. Process Schematic of Six-Column Pilot-Scale TGAC System

5.4.2 38 GPM System

The larger-scale (38 GPM) portion of the field-scale test was comprised of one set of three vessels operating in series. The first two vessels of the treatment train each contained approximately 50 cubic feet (1.4 cubic meters [m^3]) of TGAC, while the third contained the same volume of conventional GAC, to remove residual tailoring agent, if any, in the treated water. This system treated water at a target design flow rate of approximately 37.5 GPM (0.14 m^3/min), which corresponds to an approximate 10 minute EBCT in each vessel (a total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC). Each of the three beds was 4 feet in diameter, with a 4 foot depth of GAC media. The influent water was pre-filtered to remove particulates using a 10 micron bag filter. Figure 5-1 provides a process schematic of the 38 GPM TGAC System and Figure 5-5 is a photograph of this system.

Materials of construction for the 38 GPM TGAC System included steel vessels with four inch, schedule 80 PVC pipe and fittings and four inch industrial, chemical-resistant rubber hoses connected the TGAC/GAC vessels to each other and connected to/from the influent and effluent manifolds. Piping was supported by steel slotted-hole C-channel (i.e., unistrut).

5.4.3 Six Condition Field Pilot-scale System

The smaller Six-Condition Pilot-Scale System consisted of six parallel, pilot-scale beds that challenged the technology with different influent water chemistries, including TCE as a co-contaminant. These six pilot-scale treatment trains consisted of three down-flow vessels operating in series (similar to the 38 GPM System described above). Both the first and second vessels in each series were stratified TGAC/GAC beds that contained 2.1 cubic feet of TGAC in the lead layer (on top), and 1.0 cubic feet of conventional GAC in the second layer (on bottom) to remove residual TCE (from spiking) and/or tailoring agent, if present. Similar to the field-scale system, a third vessel containing 3.1 cubic feet of conventional GAC was utilized as a guard bed. Figure 5-2 shows the process schematic for the Six-Column Pilot-Scale TGAC System. Figure 5-3 shows the process schematic for the TCE Pilot-Scale Treatment Train. Figure 5-4 illustrates the cross section of a typical Pilot-Scale TGAC Treatment Train Illustrating the stratified beds. Figure 5.5 is a photograph of the 38 system and Figure 5-6 is a photograph of the six-condition system.

Table 5-2 summarizes the nomenclature, spiking levels and achieved EBCT for these trains.

The influent water for the pilot-scale tests was pre-filtered to remove particulates using 10 micron bag filters. This pre-filtration reduces particulate accumulation that can lead to excessive pressure drop across the TGAC/GAC beds. Mechanical totalizers were installed in the effluent piping of each treatment train.

Materials of construction for the Six-Column Pilot-Scale treatment trains included polyethylene lined fiberglass tanks with one inch flexible PVC hoses connecting the stratified-bed TGAC and GAC vessels to each other and to/from the influent/effluent pipe manifolds that were constructed with one inch schedule 80, PVC pipe and fittings. Piping was supported by steel unistrut. The stratified-bed TGAC/GAC vessels were 14 inches in diameter by 47 inches in height.

Table 5-2. Summary of Spiking Levels and EBCT in Six Condition Pilot-Scale Test

Train Name	Compound Spiked	Mean EBCT[1]	Standard Deviation of EBCT[1]	Mean Concentration Unspiked Influent	Standard Deviation Unspiked Influent	Mean `Concentration Spiked Train Influent	Standard Deviation Spiked Train Influent	% Relative Standard Deviation (RSD) in Spiked Train Influent
Stratified bed control	None	11.2/5.5	3.28/0.73	NA	NA	NA	NA	NA
TCE Spiked	TCE	11.5	1.51	<0.5 µg/L	NA	35.7 µg/L	16.2	45
Perchlorate Spiked	Sodium perchlorate	11.7	3.42	8.0 µg/L	1.7	314.7 µg/L	134.9	43
Nitrate Spiked	Sodium nitrate	11.6	2.51	40.5 mg/L	3.3	60.9 mg/L	12.1	20
Predisinfectant/oxidant	Sodium hypochlorite	12.0/5.57	6.28/1.48	NA	NA	0.28 mg/L	0.33	118
TDS/Sulfate Spiked	Magnesium sulfate	13.2	6.37	274.3 mg/L	30.6	995.0 mg/L	511.7	51

Note 1: TCE EBCT was only calculated for the final spiking system. When two values are shown these correspond to the 1.5 and 3.0 GPM target flow rates respectively.

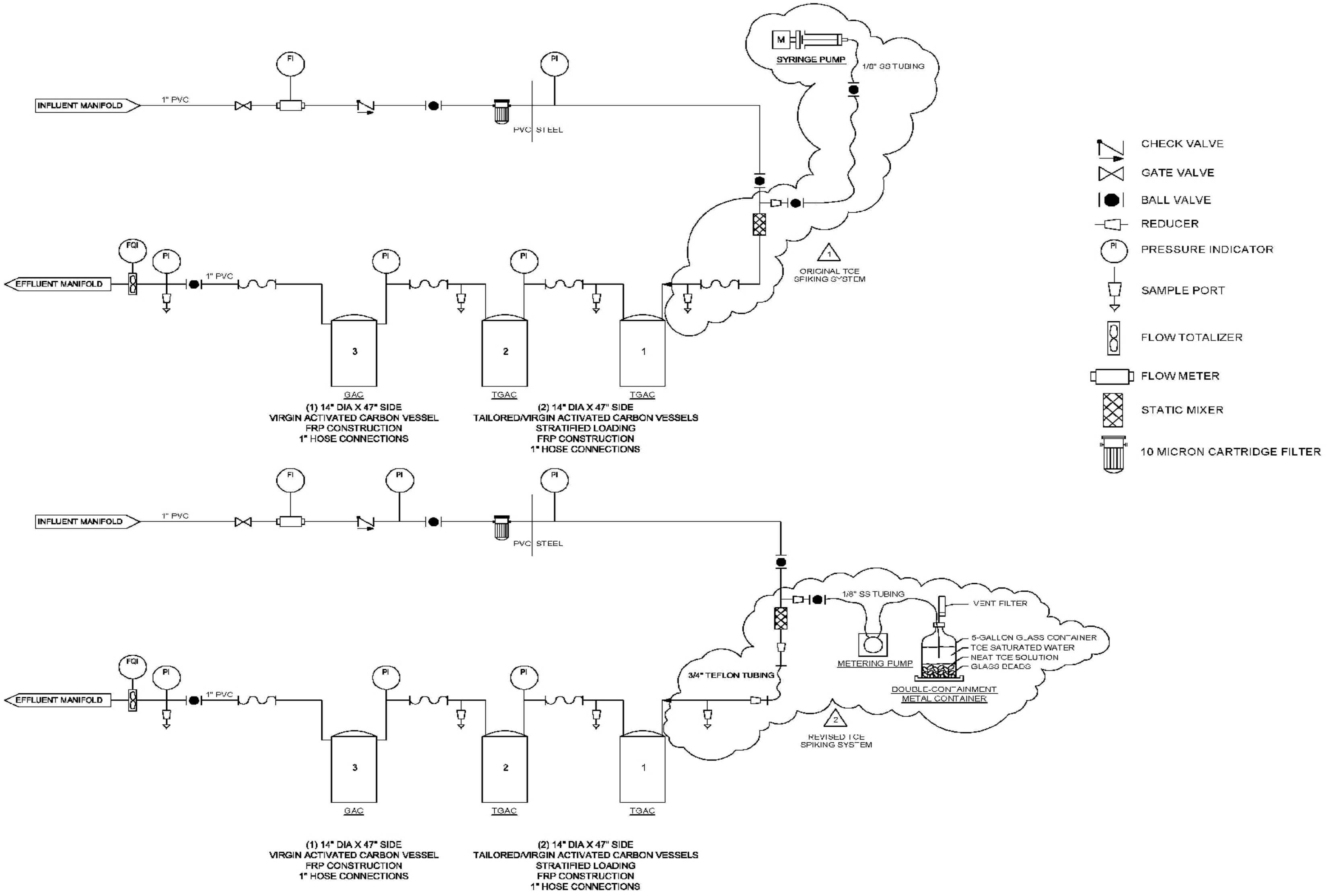


Figure 5-3. Process Schematic of the TCE Pilot-Scale TGAC System

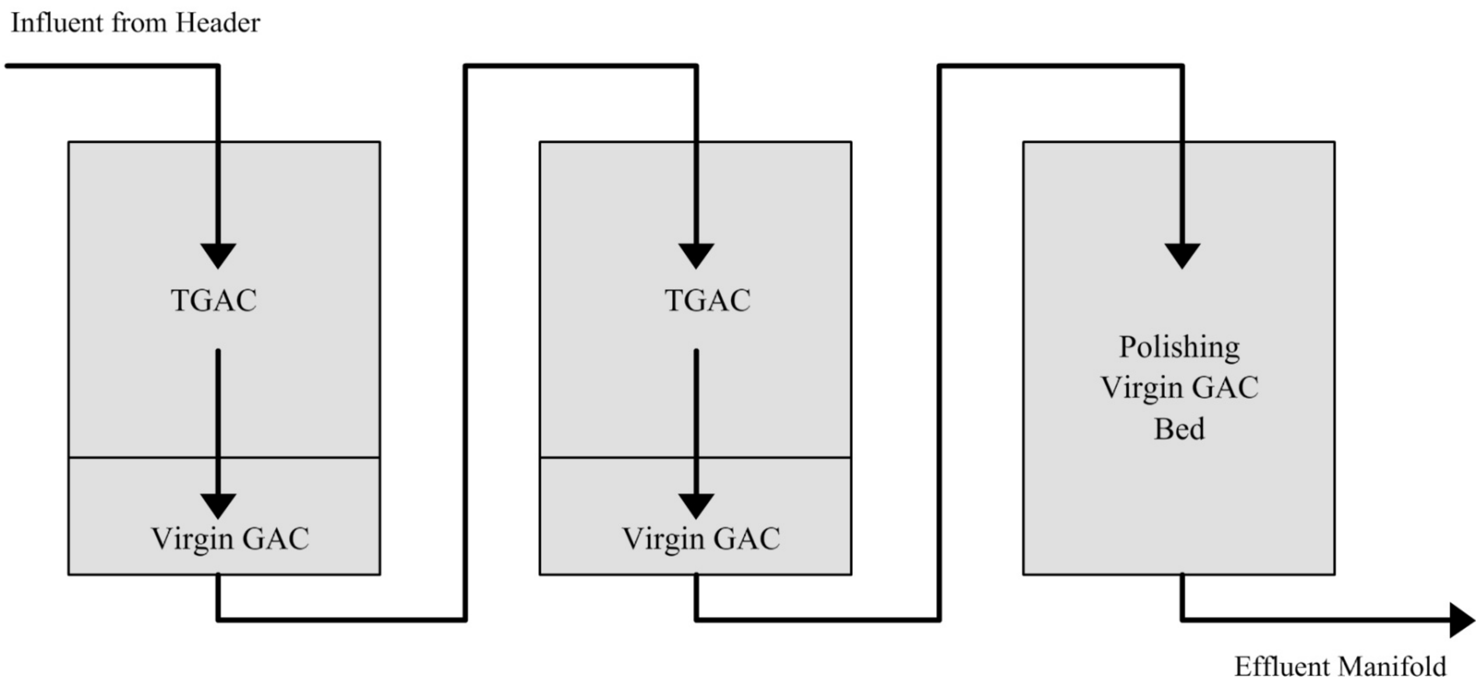


Figure 5-4. Cross Section of a Typical Pilot-Scale TGAC Treatment Train Illustrating the Stratified Beds

Figure 5-5. 38 GPM Field-Scale System

Figure 5-6. Six-Condition Pilot-Scale Field System

A PVC sample port was located upstream of the influent to the first stratified TGAC vessel for all six treatment trains. Effluent sample ports were located downstream of each of the two stratified TGAC tanks and after the final conventional GAC tank in each of the six treatment trains. The influent PVC sample port for the TCE spiking train was a stainless steel sample port because of TCE/PVC chemical compatibility concerns. Battery-powered digital flow meters were installed in the influent pipe manifold of each train, but never operated correctly because of the low flow rates. Flow rates were obtained using the mechanical flow totalizers and a stopwatch.

The spiking and operation of the smaller Six-Condition Pilot-Scale System trains are summarized below:

Stratified Bed Control: The Stratified Bed Control train provided the baseline for comparison for the other field six-condition tests. This treatment train was fed un-amended Fontana site water and did not have a spiking system.

TCE: The TCE spiked train was used to determine the effect of TCE on TGAC performance. The train originally had a spiking system that consisted of a syringe pump, a glass syringe filled with "neat" (i.e., pure solvent) TCE, and stainless steel tubing that connected to the influent manifold. The TCE and influent water were mixed with a static mixer before entering the first TGAC bed. The spiking system was revised because of problems achieving a constant TCE concentration in the influent water, which was caused by the extremely slow TCE injection flow rate from the syringe pump. The revised spiking system consisted of a metering pump and a 5-gallon glass carboy jar installed inside a metal container that provided double-containment. The carboy contained glass beads, a "neat" TCE phase, and an aqueous phase that was TCE-saturated. A GAC vent filter was installed in the carboy to prevent fugitive emissions of TCE vapors. Stainless steel tubing was used to connect the carboy to the metering pump and the metering pump to the piping upstream of the static mixer. The 1-inch PVC tubing that originally connected the influent manifold to the first TGAC bed was replaced with 3/4-inch Teflon$^{©}$ tubing to ensure that TCE was not being absorbed by the PVC pipe. Figure 5-3 shows the original spiking system and the revised spiking system.

Increased Perchlorate Concentration: The Increased Perchlorate Concentration train was used to determine the effect of increased perchlorate concentration on TGAC performance. This train had a spiking system that consisted of a holding tank for the perchlorate solution, an electric tank mixer, and a metering pump.

Nitrate: The Nitrate spiked train was used to determine the effect of increased nitrate concentration on the TGAC performance. This train had a spiking system that consisted of a holding tank for the nitrate solution, an electric tank mixer, and a metering pump.

TDS/Sulfate: The TDS/Sulfate train was used to determine the effect of increased TDS on TGAC performance. This train had a spiking system that consisted of a holding tank for the magnesium sulfate solution, a mixer, and a metering pump.

Disinfectant/Oxidant: The Disinfectant/Oxidant train was used to determine the effect of an oxidant on TGAC performance. This train had a spiking system that consisted of a holding tank for the sodium hypochlorite (NaOCl) solution, an electric tank mixer, and a metering pump. The influent to this treatment train was be pre-treated with between 0.15 and 0.3 mg/L free chlorine to simulate a subset of a full-scale drinking water treatment system. Free chlorine was monitored using Hach test kit, Model CN-66F (N,N′-diethyl-p-phenylenediamine [DPD] Method) by ARCADIS. A polyethylene lined fiberglass mixing tank was installed in this train to provide 30 minutes of chlorination contact time prior to entering the first TGAC bed.

The project team selected chemical dosing pumps to spike the individual chemicals or mixes of chemicals into the Six-Condition Treatment Train influents that required spiking. The chemical dosing pumps were designed to provide the requisite concentration of spiking chemical into each influent stream. Each train had a reservoir that was large enough to provide spiking solution for a period of at least four days.

5.4.4 Production and Loading of TGAC

5.4.4.1 TGAC Manufacturing

The TGAC used was produced by Siemens at their production facility on Washington Blvd in Los Angeles, California. Its perchlorate capacity was tested at bench-scale on June 30, 2006, and July 11, 2006, at the Siemens Rockford Illinois facility as shown in Table 5-3.

Siemens and PSU developed a tailoring protocol for GAC that was implemented for this project. The protocol is briefly described below. Tailoring was carried out using a 20x50 mesh GAC and enough CPC tailoring agent to give a 30 wt.% loading on the carbon if all the CPC were adsorbed. The concentration of the CPC in the tailoring recycle stream was monitored using a two-phase titration technique until the concentration of CPC in the recycle stream approached equilibrium. At this point washing of the TGAC was initiated, and was continued until the CPC concentration in the wash water was less than 5 mg/L. All of the TGAC manufactured for use at the Fontana test site was made using this procedure. See Figure 5-7 for a schematic of the manufacturing setup that was used.

5.4.4.1.1 Vessel Configuration and GAC Soaking and Backwashing

The following procedures were followed to soak and backwash the TGAC at the Siemens Los Angeles facility

- Two PV2000 vessels were configured such that the vessels operated in a parallel/up-flow configuration. A drinking water supply was connected to the vessels in an up-flow direction with the discharge from the vessels going to the facilities chemical waste drain.
- Each vessel was filled to approximately 1/3rd full with drinking water and then one 1,100 pound super sack of AC2050aw (1,100 pounds per vessel) anthracite coal-based GAC was loaded into each vessel. The anthracite based granular activated

carbon, AC2050AW, was inadvertently used by Siemens to manufacture the 20x50 mesh TGAC for use in the Fontana ESTCP pilot project. The same anthracite based carbon was supplied to Penn State in untailored form, and then tailored by Penn state for the bench scale tests performed there (Appendix B). The principle investigators had originally intended that a bituminous coal based GAC be used. Results of QA/QC testing of the TGAC after manufature using a perchlorate isotherm and a batch selectivity test with perchlorate and nitrate were reviewed and did not provide an indication of any performance issue (see section 5.4.4.1.2). Neither isotherm testing, RSSCTs nor any other known bench scale protocol is able to perfectly predict field scale performance in a rapid laboratory test.

- Each vessel was filled with water until both vessels were full. The GAC was allowed to soak overnight before beginning the backwashing process.
- Each vessel was backwashed starting with a flow rate of ~35 GPM. The flow rate was slowly increased until a small amount of the 20x50 mesh GAC began to appear in the discharge water, at which time the backwash flow rate was reduced by approximately 3 - 5 GPM. Backwashing continued until the water ran clear and was free of GAC fines. The backwash water which contained carbon fines and an elevated pH was treated to remove the fines and the pH was adjusted to meet the water discharge standards established by the City of Los Angeles before being discharged into the sanitation sewer.
- The manifold valves were reconfigured for parallel/down-flow operation. Some water was drained from each vessel and the top manway was opened. Additional water was drained from each vessel until the water level was 36” below the top manway (as measured from the lowest outside point of the manway lip). This was done to make room in the vessel for the tailoring agent solution.

The GAC used in the polishing bed was not processed at the Los Angeles facility. The conventional carbon was taken directly from inventory and soaked and backwashed at the site.

5.4.4.1.2 Quality Assurance Testing of TGAC

Two production lots of tailored carbon were tested for perchlorate capacity. A simple jar test with material balance was used to evaluate the carbon samples. A stock perchlorate solution was reacted with the lots of carbon as received. The goal of the test design was to have enough residual perchlrate to be sure perchlorate occupied all the IX sites while maintaining a significant difference between the initial and equilibrium concentrations to minimize the effect of analytical error. The evaluation was performed with three differently massed subsamples of carbon to ensure these conditions were met.

Procedure:

1. Make 750 mg/l perchlorate solution from deionized (DI) water and $NaClO_4 \cdot H_2O$.
2. Weigh approximately 3, 4, and 5 gram samples of carbon. Record weight.
3. Transfer carbon to 500 ml polyethylene sample bottles.
4. Add 300 ml perchlorate solution by pipette.

5. Place bottles on shaker for 3 days. (bottles turned end over end)
6. Remove approximately 4 ml supernatant with syringe and filter through a 0.1 µm syringe filter.
7. Pipette 1 ml filtered supernatant into a 100 ml volumetric flask and dilute to volume with DI water.
8. Pipette 1 ml diluted filtered supernatant into a 100 ml volumetric flask and dilute to volume with DI water.
9. Repeat dilutions for 750 mg/l perchlorate solution.
10. Perchlorate was analyzed by Weck Laboratories.

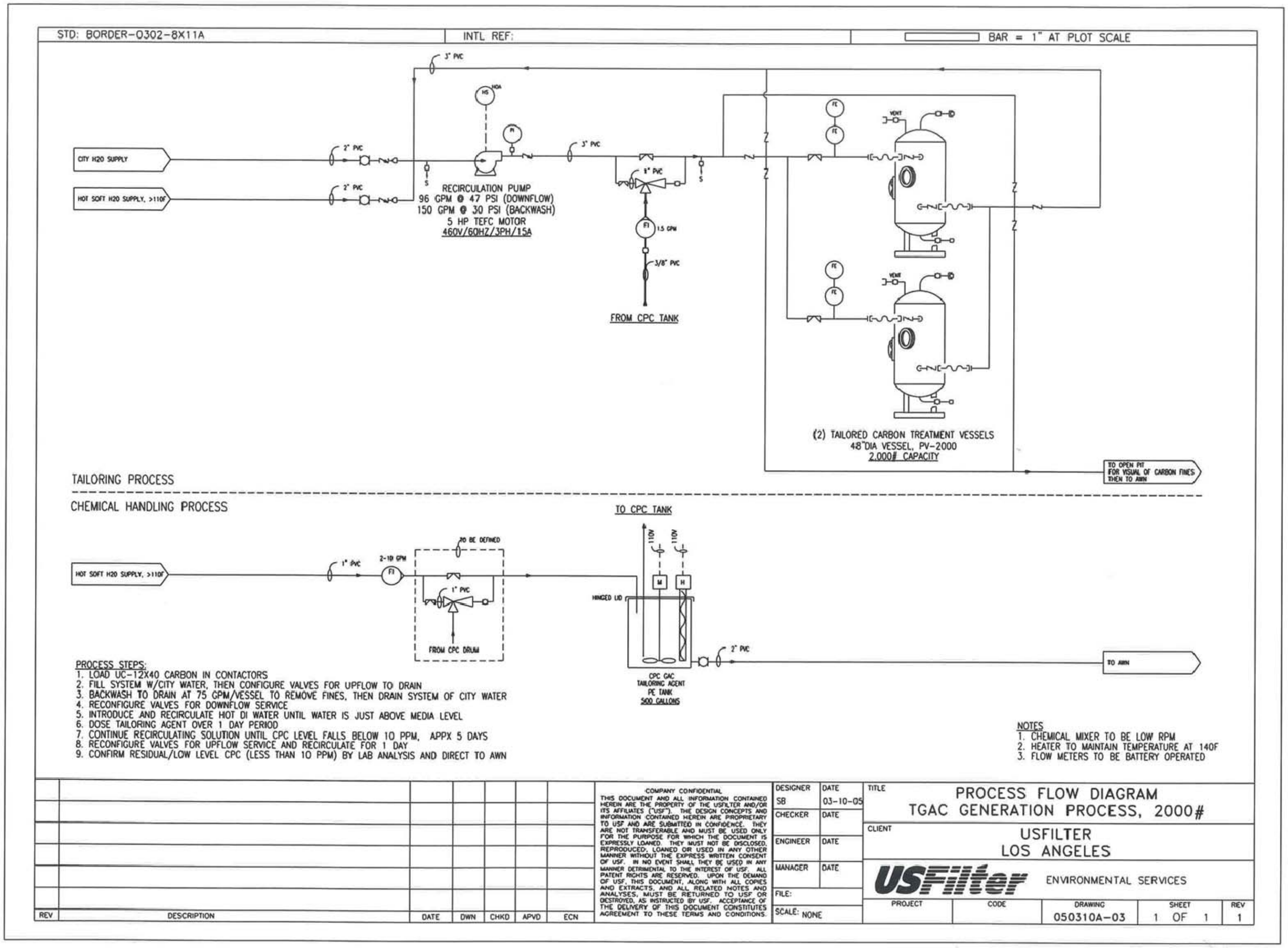
Calculations:

Solution Conc. = Analytical Result × 100 × 100 × 0.001 mg/µg

As shown in Table 5-3 the results show a reproduceable perchlorate capacity of approximately 0.34 miliequivalents/gram.

Table 5-3. TGAC Quality Assurance Testing – perchlorate Isotherm, Performed by Siemens

		Wet		Initial	Final	ClO_4	ClO_4
		TGAC	Solution	ClO_4	ClO_4	Capacity	Capacity
6/30/2006		grams	Ml	g/L	g/L	mg/g	Miliequivalents (meq)/g
	B1-3	3	300	0.75	0.40	35	0.35
	B1-4	4	300	0.75	0.31	33	0.33
	B1-5	5	300	0.75	0.18	34	0.34
	Average						**0.34**
7/11/2006							
	B2-3	3	300	0.75	0.43	32	0.32
	B2-4	4	300	0.75	0.28	35	0.35
	B2-5	5	300	0.75	0.20	33	0.33
	Average						**0.34**



PROCESS STEPS:
1. LOAD UC-12X40 CARBON IN CONTACTORS
2. FILL SYSTEM W/CITY WATER, THEN CONFIGURE VALVES FOR UPFLOW TO DRAIN
3. BACKWASH TO DRAIN AT 75 GPM/VESSEL TO REMOVE FINES, THEN DRAIN SYSTEM OF CITY WATER
4. RECONFIGURE VALVES FOR DOWNFLOW SERVICE
5. INTRODUCE AND RECIRCULATE HOT DI WATER UNTIL WATER IS JUST ABOVE MEDIA LEVEL
6. DOSE TAILORING AGENT OVER 1 DAY PERIOD
7. CONTINUE RECIRCULATING SOLUTION UNTIL CPC LEVEL FALLS BELOW 10 PPM, APPX 5 DAYS
8. RECONFIGURE VALVES FOR UPFLOW SERVICE AND RECIRCULATE FOR 1 DAY
9. CONFIRM RESIDUAL/LOW LEVEL CPC (LESS THAN 10 PPM) BY LAB ANALYSIS AND DIRECT TO AWN

NOTES
1. CHEMICAL MIXER TO BE LOW RPM
2. HEATER TO MAINTAIN TEMPERATURE AT 140F
3. FLOW METERS TO BE BATTERY OPERATED

DESIGNER SB DATE 03-10-05
CHECKER DATE
ENGINEER DATE
MANAGER DATE
FILE:
SCALE: NONE

TITLE PROCESS FLOW DIAGRAM
TGAC GENERATION PROCESS, 2000#

CLIENT USFILTER
LOS ANGELES

USFilter ENVIRONMENTAL SERVICES

PROJECT	CODE	DRAWING	SHEET	REV
		050310A-03	1 OF 1	1

Figure 5-7. TGAC Manufacturing Schematic

5.4.4.1.3 Preparation of CPC Tailoring Solution

1. During the handling of the CPC powder and the preparation of the CPC solution, personal protective equipment (PPE) including rubber gloves, apron and full face dust mask were used.

2. Approximately 250 gallons (about ½ full) of hot softened City drinking water was added to the 500 gallon CPC make-up tank. A heating coil and a mechanical stirrer were used to keep the water hot and fully agitated.

3. 660 lbs (6 drums) of CPC powder was slowly added to the tank, using water spray to control CPC dust. The CPC was added at a slow enough rate to prevent significant clumps of undissolved powder from forming in the tank. After the addition of each 110 pound drum of CPC powder to the make-up tank, stirring was continued to make sure most of the CPC had dissolved before addition of the next drum was initiated. The water temperature was maintained at about 120 ^{o}F (or higher) to facilitate dissolving of the CPC. The CPC solution was found to be clear with no undissolved solids at the end of the preparation period. Some additional hot soft water was added to the CPC makeup tank at the end of the preparation so that the final volume was 450 +/-25 gallons.

5.4.4.1.4 Tailoring Process

1. The top manway was next closed and sealed and the top vent valve was opened. A 1" hose was run from the top vent valve to the CPC make-up tank where it was submerged into the CPC solution. This vent line was careful routed to prevent it from coming in contact with the mixing blade.

2. A re-circulation rate of ~40 GPM was established through each vessel and an eductor was used to begin introducing the hot CPC solution into the re-circulation stream.

3. The CPC tailoring solution was added at a rate of between 0.4 and 1.5 GPM. The eduction rate was judged so that the CPC tank was empty at a time when an operator was present to close the eductor valve and prevent air from being introduced into the system. During the period when the CPC was being educted into the GAC vessels excessive foam was occasionally observed being discharged from the 1" vent hoses. When this happened, the\ CPC solution eduction rate was reduced to minimize this foaming.

4. Once all of the CPC tailoring solution had been added to the system, a re-circulation rate of ~40 GPM through each vessel was maintained.

5. This recirculation was maintained while monitoring the CPC concentration in the recirculation loop. Monitoring of the CPC concentration was done twice daily until the CPC concentration stabilized and had dropped in the recirculation loop to less than 350 mg/L. This process took approximately three days of recirculation to complete

5.4.4.1.5 Washing Process

1. With the system configured for parallel/down-flow operation and the discharge from each vessel directed to the chemical waste drain, drinking water at a flow rate of 40 – 50 GPM was used to begin the TGAC washing process.
2. The washing process was continued until the CPC concentration in the discharge decreased to below 10 mg/L. This took 6 – 8 hours. The CPC washout rate was tracked by taking water samples every 30 minutes for the first two hours and then every hour until the washing cycle was complete. Siemens' laboratory personnel monitored the CPC concentration in the discharge water using the 2-phase titration method (Tsubouchi et al., 1981).
3. Next the system was reconfigured for parallel/up-flow operation and washing of the TGAC at ~50 GPM with no GAC particles being carried over was continued for an additional three hours using drinking water. The volume of water used in this phase of the washing cycle was recorded.
4. Once the tailoring process had been completed, the water was drained from each vessel.
5. The finished TGAC was removed by vacuum from the tailoring vessels and placed into lined super sacks for transport to storage at Siemens warehouse in La Mirada prior to shipment to the Fontana test site. The super sacks were labeled with the product name, weight of TGAC in the super sack (based on the dry virgin GAC weight used), and the date manufactured.

5.4.4.2 38 GPM System

The TGAC and GAC media was loaded into the beds on January 3 and 4, 2007, at Fontana, California, approximately 50 cubic feet (Ft^3) in each vessel. The TGAC was 20 X 50 mesh, and the conventional GAC was 8 X 30 mesh. Both media were backflushed at Fontana.

Backflushing of the lead, or primary, TGAC vessel (#1) was performed at 28-35 GPM for approximately 3,010 gallons or 8 BVs. The initial backflush water was black and foamy and had a faint "solvent like" odor. Some foaming was noticed but started to dissipate after 100 gallons.

Backflushing of the lag, or secondary, TGAC vessel (#2) was performed at 35 GPM for approximately 3,540 gallons or 9.5 BVs. Composite backflush samples were obtained after approximately 1/3 of the total volume, 2/3, and at completion of the process.

Dr. James Graham of Siemens collected effluent samples from TGAC #1 and TGAC #2 flowing in their normal down-flow direction immediately following the backflush process. The samples were analyzed for CPC by titration by Siemens with the following results:

- TGAC-#1 effluent: 2.1 mg/L CPC
- TGAC-#2 effluent: 0.6 mg/L CPC.

The conventional GAC vessel (Bed C) was backwashed with approximately 2,600 gallons of water. Then, on January 6 through January 11, Siemens installed manual air release valves on each of the three vessels. System operation began on January 11.

As shown in Figure 2-3 dated June 8, 2007, Bed A, which had become perchlorate-saturated was removed from the system and replaced with the former lag vessel, Bed B. A new TGAC vessel (Bed D) was installed in the lag position. The same batch of TGAC was used to fill this new bed that was used for the original two beds. The field team observed foaming from Bed D effluent, but no odor was observed in the Bed D effluent.

5.4.4.3 Six Condition Field-scale Pilot System

The TGAC used for the 6 condition testing was manufactured at a later date using the same procedure that was used to manufacture the initial TGAC batch. These smaller vessels were backwashed at the Siemens facility prior to delivery to Fontana. This system was brought on line September 7, 2007. Some operational difficulties were experienced during startup and shakedown of some these systems such as the wrong size syringe was provided for the TCE train, a malfunctioning Y-check valve for the Nitrate train, a stuck ball valve for the TDS/Sulfate train, and the battery-operated flow meters for all trains would not accurately measure the low flow rates.

5.5 FIELD TESTING

5.5.1 Installation and Startup

The treatment systems were anchored on a concrete pad at the site. Once the systems were installed, the following activities were performed:

- The piping systems were pressure tested to check for leaks.
- The battery-powered flow meters were checked for proper operation with a bucket and stopwatch.
- The entire piping system was disinfected with chlorine prior to installing the Siemens pre-loaded, fresh TGAC and GAC vessels. The disinfection process followed AWWA-approved procedures.

The system start-up entailed opening and closing process valves to allow groundwater to flow from Fontana’s treatment system influent manifold to the demonstration system influent manifold, pre-filter, instrumentation (e.g., flow meters and pressure gauges, etc.), TGAC/GAC vessels, and the percolation pond. System valves were then adjusted to maintain a flow rate of approximately 37.5 GPM for the field-scale vessels and 1.5/3.0 GPM for the pilot-scale systems.

5.5.2 38 GPM system Operations

The 38 GPM field-scale TGAC system operated nearly continuously between January 11, 2007 and December 5, 2007—approximately 318 days, treating over 16.2 million gallons of perchlorate-impacted groundwater during this period. Approximately 38 GPM (0.14 m^3/minute) of Fontana groundwater was processed through the three demonstration vessels—the primary TGAC vessel (Bed A), the secondary TGAC vessel (Bed B), and the polishing conventional GAC vessel (Bed C)—corresponding to a 10 minute design EBCT per vessel (a total EBCT of 20 minutes for TGAC and 10 minutes for the conventional GAC). The configuration of the vessels is indicated schematically in Figure 2-3.

Initial perchlorate breakthrough on Bed A was observed at ~12,400 BVs. This bed continued operating until perchlorate saturation (defined as an effluent perchlorate concentration of 90 percent, or more, of the influent perchlorate concentration) was observed at ~17,300 BVs. On June 8, 2007, Bed A's spent TGAC was transported off-site for incineration and disposal, Bed B was re-configured as the lead vessel, and fresh TGAC was placed in service as the new lag bed—Bed D. Following the change-out and reconfiguration (Figure 2-3), Bed B (now in the lead position) reached initial perchlorate breakthrough after ~8,300 additional BVs (~25,600 BVs total) and perchlorate saturation at ~16,000 additional BVs (~33,300 BVs total). Following perchlorate breakthrough in Bed B, Bed B remained in service but Bed D provided the primary perchlorate removal. Initial perchlorate breakthrough in Bed D was detected at ~7,100 BVs and perchlorate saturation at ~20,000 BVs.

The operational up-time efficiency of this system is displayed in Figure 5-8 and the flow rate vs. time is plotted in Figure 5-9. Overall the system operated at 97% uptime. The flow rate was maintained at approximately 38 GPM throughout the demonstration. The primary causes of downtime were not directly attributable to the TGAC media. The primary causes of downtime that were attributable to the TGAC demonstration system are summarized in the following Table 5-4:

Table 5-4: Downtime Occurrences on 38 GPM TGAC System

Date	System Down-Time (Minutes)	Reason for System Down-Time
1/15/2007	3,000	Repaired leaking pressure gauge assemblies. System remained off to allow PVC cement to dry and cure.
2/7/2007	68	Repaired two leaks on system pre-filter pressure gauge connections.
2/14/2007	75	Repaired leak on broken sample port fitting on Bed C.
2/16/2007	140	Repaired leaking pressure gauge connections near pre-filter.
6/28/2007	1,400	Repaired leak on Bed B gasket.
9/27/2007	3,379	Repaired leaking 4-inch valve.

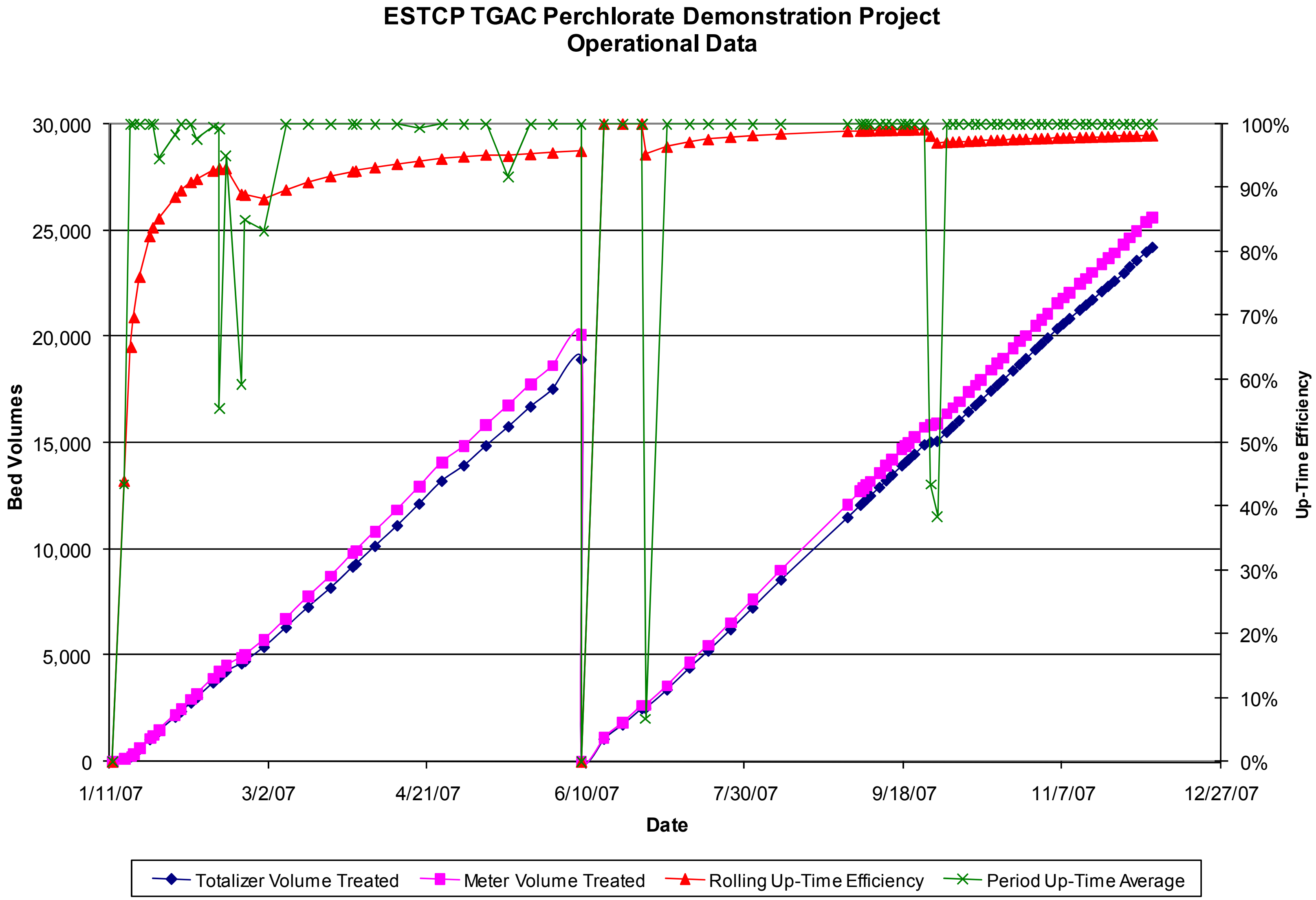


Figure 5-8. Operational Data: BVs and Up-time Efficiency vs. Time, 38 GPM System

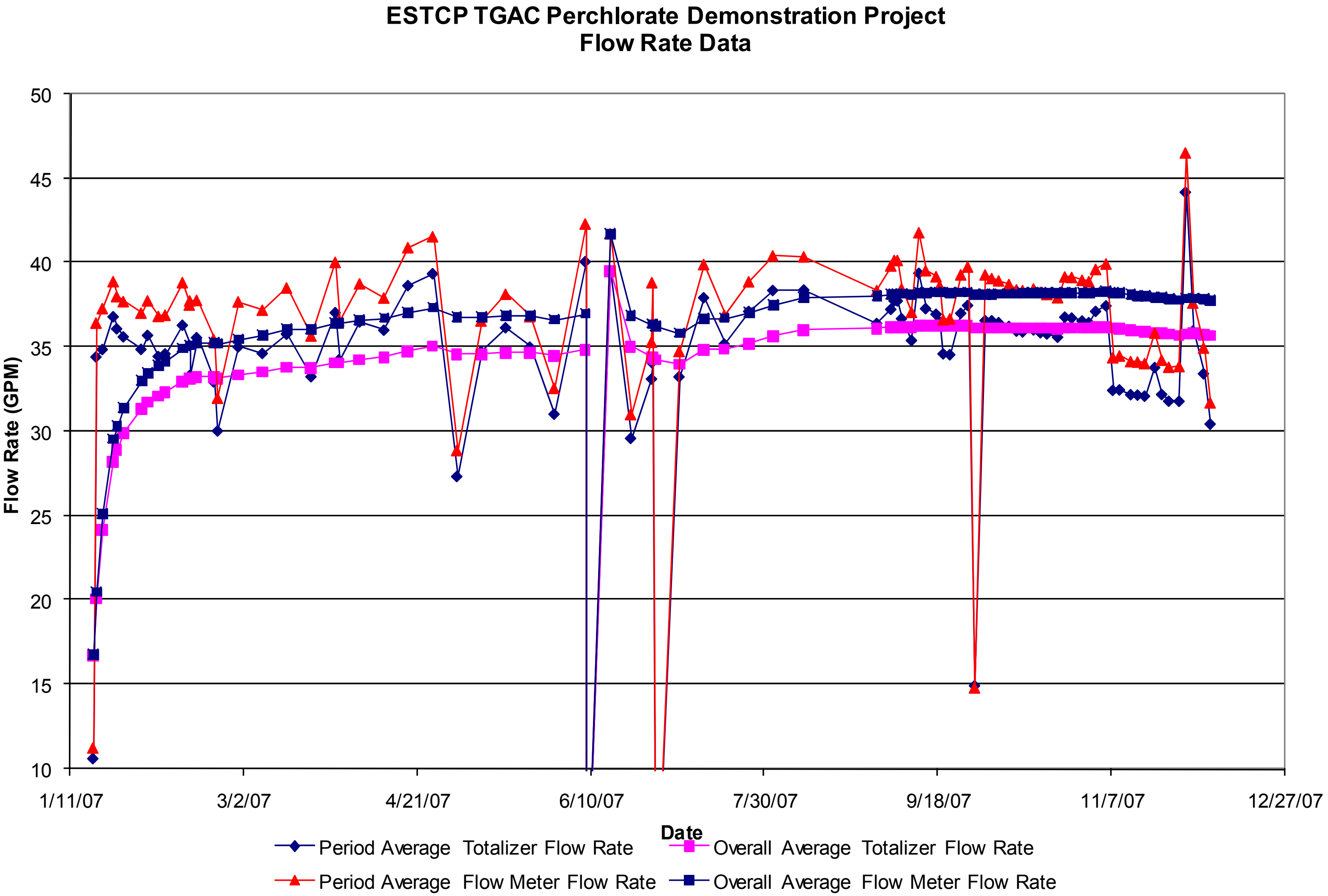


Figure 5-9. Flow rate of 38 GPM System vs. Time

The primary causes of downtime that were not related to the TGAC demonstration system were caused by FWC (or others such as utilities) operations, and included pumping interruptions of the supply wells, media change-outs on the site's full-scale treatment system, and routine or non-routine maintenance activities. While the demonstration system was installed in parallel with FWC's full-scale treatment system, not in series with it, whenever the Fontana system was down, the wells supplying both it and the demonstration system were shut off. The system was shut down during a FWC system IX resin change-out (1/26/07), FWC preventative maintenance (2/14/08), FWC telemetry system failure and repair (2/21/07 through 2/28/07), and a power failure (5/16/07). Ignoring non-TGAC system related downtime, the uptime efficiency would be 98%.

The actual EBCT operated at was calculated at 10.2 minutes on a one bed basis with a standard deviation of 1.81 minutes.

Operational logs are provided in Appendix D. TGAC demonstration system hydraulic data is discussed in Section 5.7.2.

Routine activities performed during O&M of the 38 GPM system included the following:

- Monitoring and recording of process data including pressures, flow rates, water and ambient air temperatures, and cumulative volume treated—performed by ARCADIS' personnel and FWC's California DPH (formerly California DHS)-certified water treatment system operators.
- Obtaining influent, midpoint, and effluent water samples for process performance monitoring—performed by ARCADIS' personnel.
- Replacing bag filters in the pre-filter system (based on a maximum differential pressure as specified by the filter manufacturer) on February 18, 2007, March 29, 2007, May 9, 2007, and August 31, 2007—performed by ARCADIS personnel.
- Removing spent TGAC from the demonstration system for shipment to the Covanta destruction facility—performed by Siemens.
- Re-installing fresh TGAC into the demonstration system—performed by Siemens.
- Inspecting the system for water leaks and process upsets—performed by ARCADIS' personnel when on site (approximately weekly) and FWC personnel on a daily basis.

At the completion of the project, the TGAC was sampled from the vessels. The TGAC was examined microscopically for observable evidence of microbial growth, and compared to control samples obtained prior to system startup. Additionally, Weck laboratories analyzed the TGAC slurry for heterotrophic plate count and total coliform.

At completion of the study a tracer test was performed to independently estimate the EBCT and in an attempt to evaluate the possibility of short circuiting (see Appendix I).

5.5.3 Six Condition Pilot-scale System Operation

The six parallel trains of the Six-Condition Pilot-Scale System began operation in September 2007, and the last train (TCE spiked train) was shutdown in September 2008. The Stratified Beds Control, Perchlorate spiked, and Nitrate spiked trains were started on September 6, 2007. The TDS/Sulfate spiked Train and Predisinfectant/Oxidant Train were started on September 7, 2007. On September 10, 2007 the TDS/Sulfate and Nitrate trains were shutdown because of metering pump and valve failures; they were re-started on September 24, 2007 and October 1, 2007, respectively.

The last train—TCE Train—was started on September 14, 2007, after addressing equipment issues with the syringe pump (subsequent to replacing the incorrectly sized syringe). The TCE Train was shutdown on January 30, 2008 because of inconsistent TCE spiking concentrations caused by the extremely low TCE injection rate (which was approximately 0.2 microliters per minute—the syringe pump's minimum injection rate). The train was operated intermittently between January 30, 2008, and May 22, 2008, in an effort to re-design the system without consuming the TGAC's TCE (and perchlorate) capacity. Between September and January, multiple potential causes of the inconsistent TCE spiking were evaluated including absorption to system piping components (e.g., PVC hoses), volatilization losses, incomplete mixing, sampling variability, and the potential problems with the syringe pump. Among the approaches used to evaluate the TCE spiking problem were additional sampling (including passive and active integrating samplers), system modifications, and extensive technical reviews of the TCE spiking system. The TCE Train with restarted on May 22, 2008, after consultation with ESTCP, re-designing the TCE spiking system (see Section 5.4.3), and removing the first (lead bed) of the two stratified beds from the TCE Train. The original and re-designed TCE spiking system was described in Section 5.4.3. TCE spiking performance between May 22, 2008, and system shutdown on September 4, 2008, was greatly improved.

The six pilot-scale vessels were originally designed to operate at the same 10 minute TGAC EBCT as the larger 38 GPM system, which corresponded to a flow rate of approximately 1.5 GPM (0.0057 m^3/minute). On 2 January 2008, the flow rate was increased to approximately 3.0 GPM in the Stratified Bed Control and Disinfectant/Oxidant Train to decrease the TGAC EBCT to ~5 minutes in each bed because a preliminary analysis of bench-scale data had suggested that a higher flow rate could provide a longer bed life (see Appendix B, Figure 12, data from 10,000 to 20,000 BVs). There was a question as to whether higher flow rates the beds would be less subject to short circuiting. One reason why very slow flow rates in media systems might incur channeling is a lack of friction head to distribute flow. The flow rate data for these trains is displayed in Figures 5-10 through 5-15.

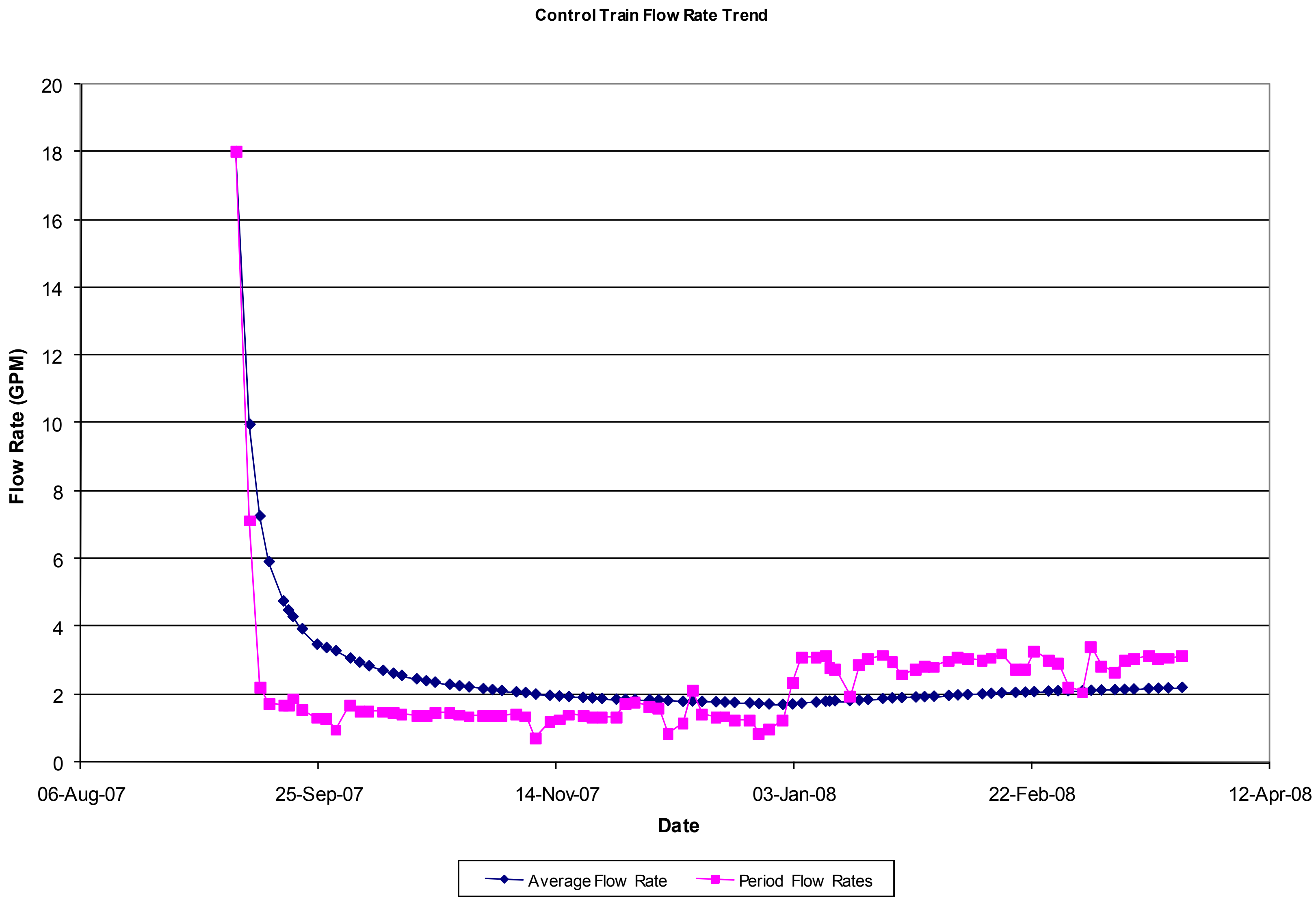


Figure 5-10. Flow Rate vs. Time Stratified Bed Control Train

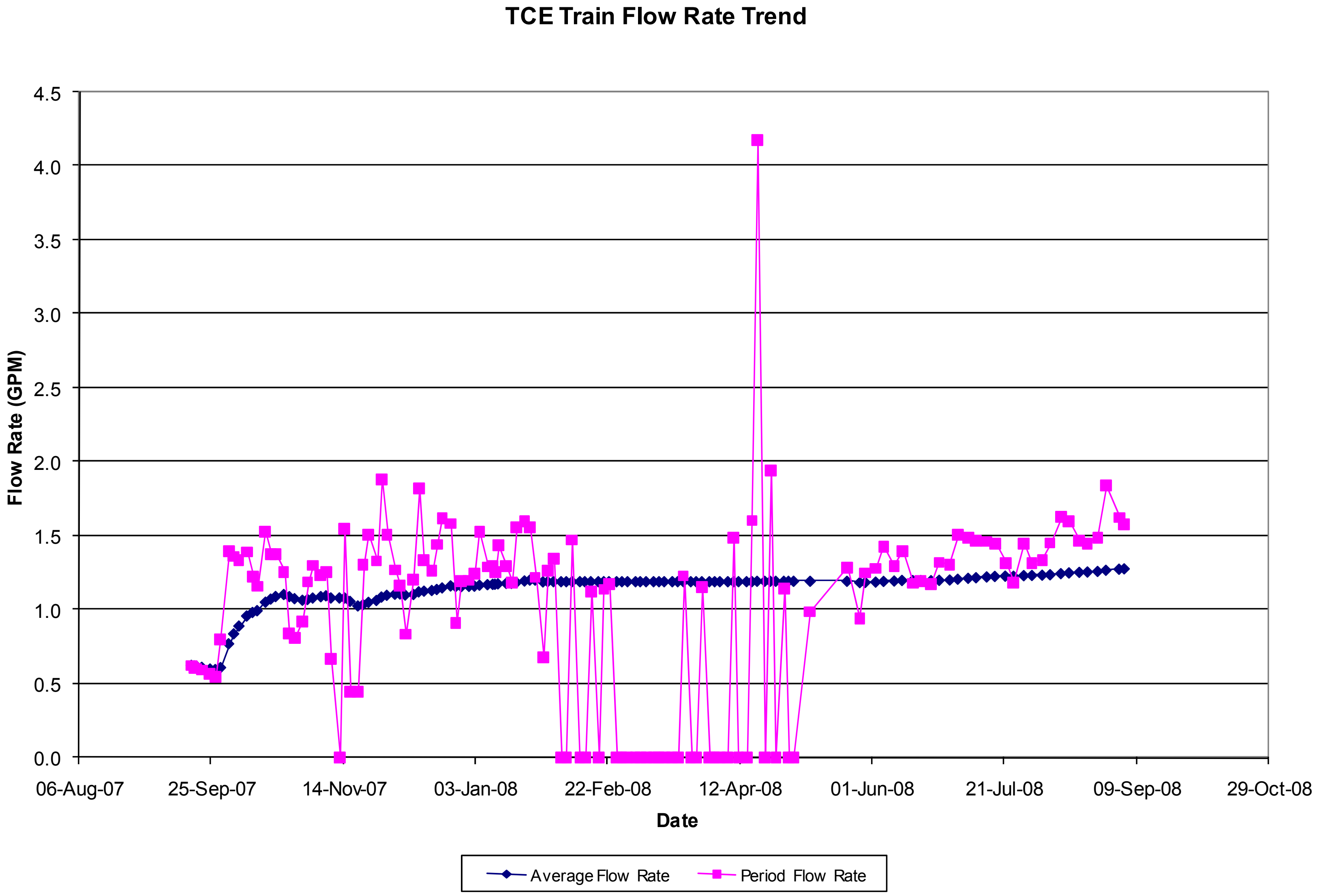


Figure 5-11. Flow Rate vs. Time TCE Spiked Train

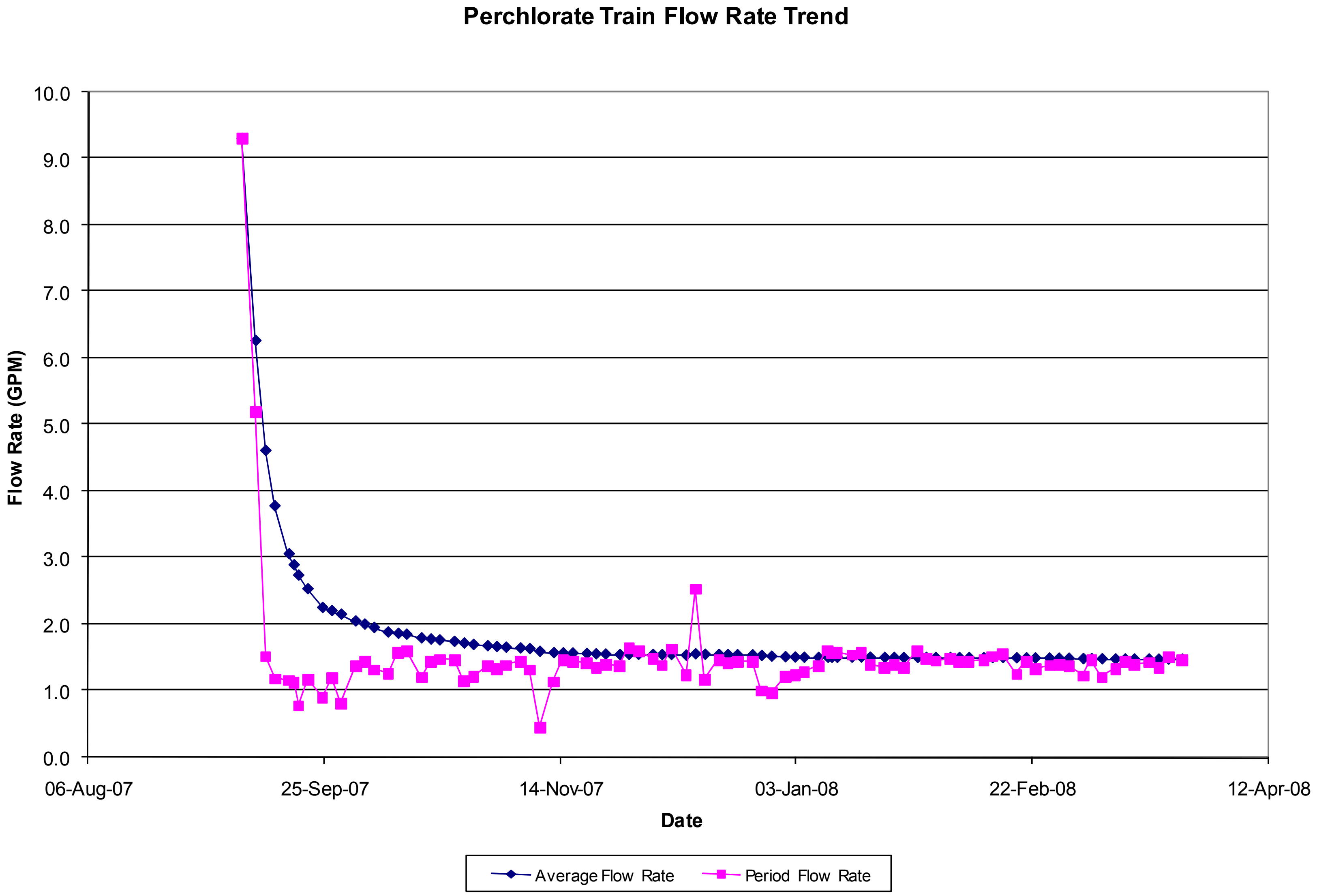


Figure 5-12. Flow Rate vs. Time Perchlorate Spiked Train

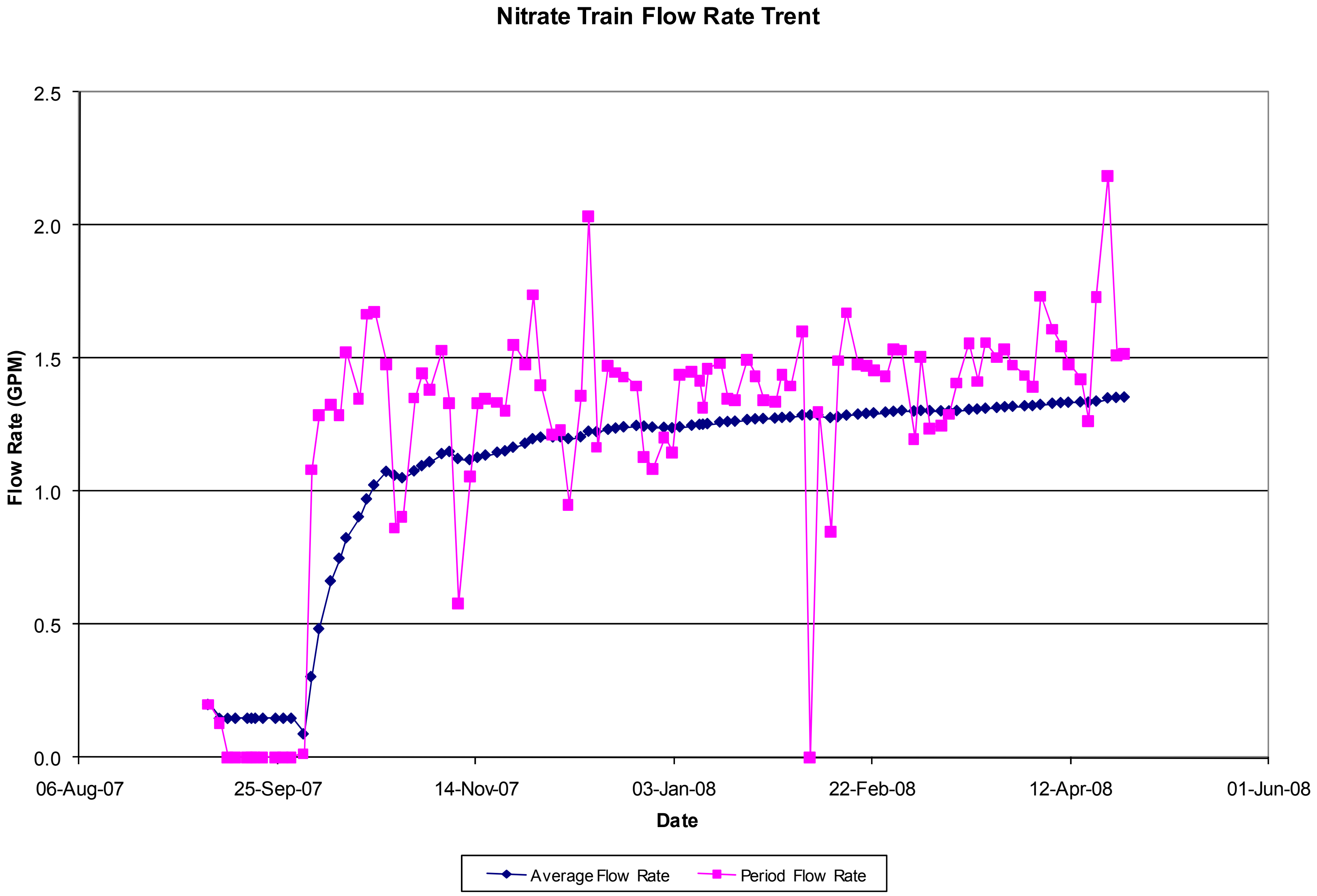


Figure 5-13. Flow Rate vs. Time Nitrate Spiked Train

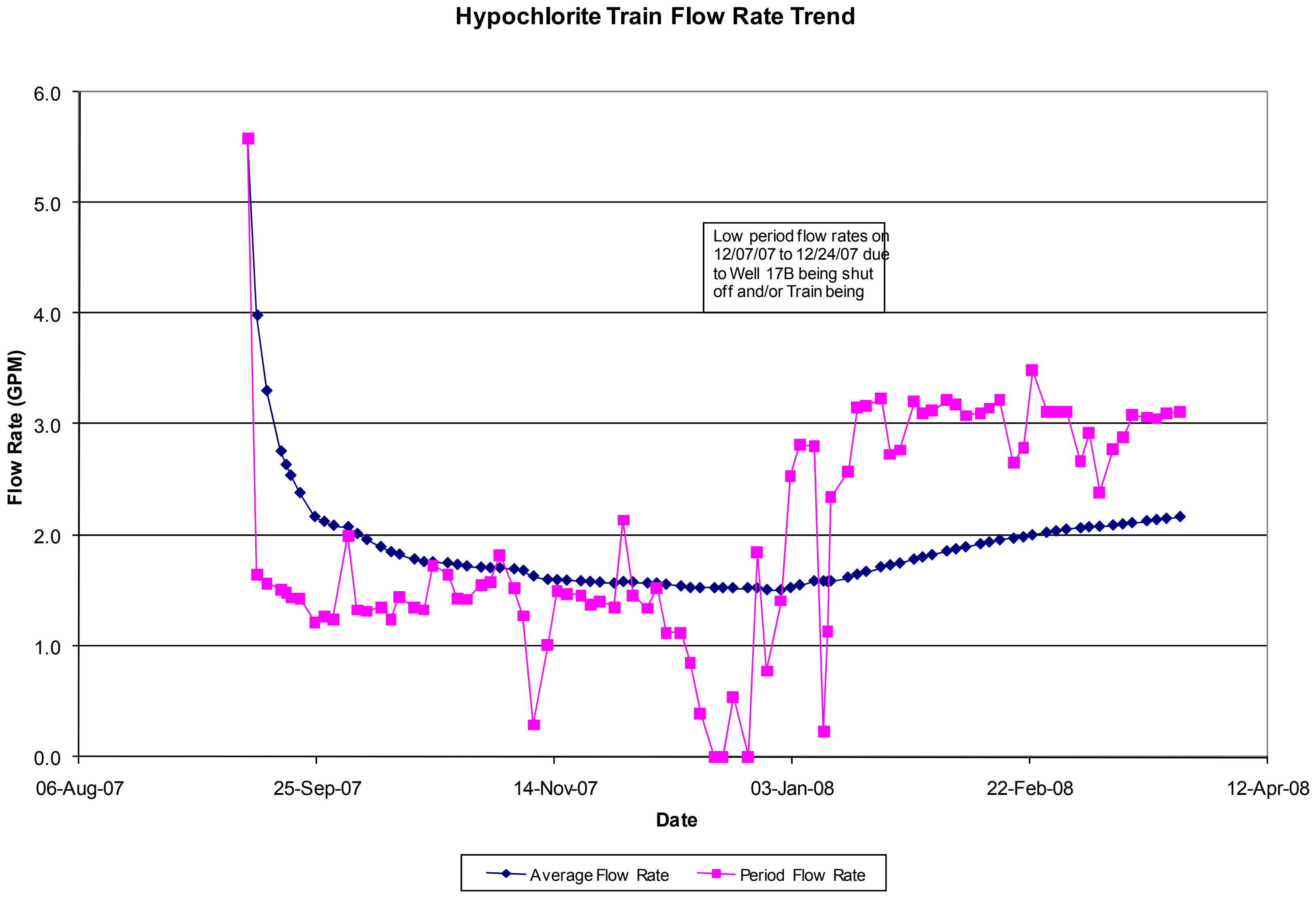


Figure 5-14. Flow rate vs. time Six Condition Predisinfectant/Oxidant Train

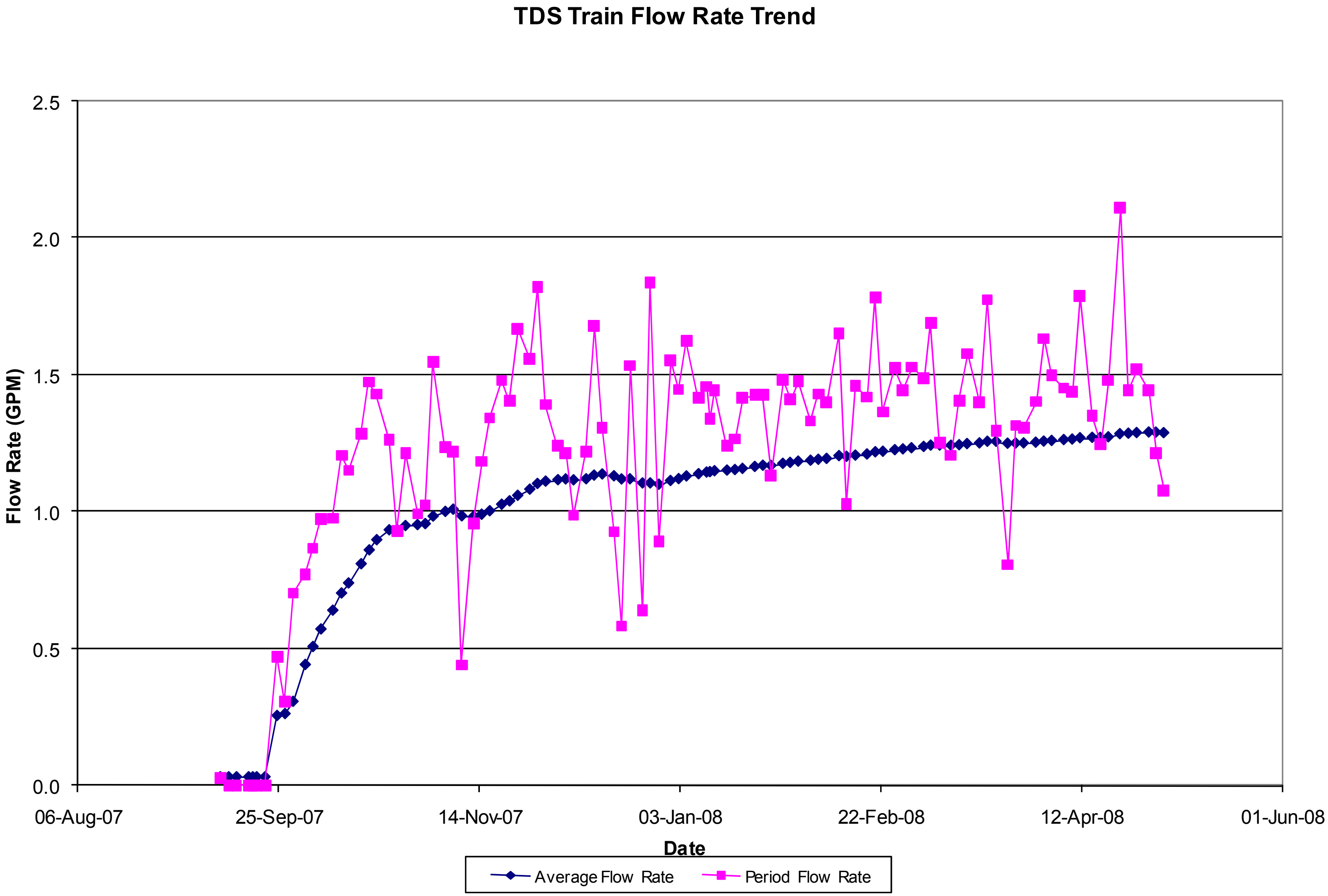


Figure 5-15. Flow Rate vs. Time TDS/Sulfate Train

As can readily be seen from a comparison of Figures 5-10 through 5-15 to Figure 5-9, flow rate control was significantly more difficult in these smaller pilot-scale systems than in the 38 GPM systems. This is mainly attributed to the lower flow rates of the systems that required more precise flow control, the battery-operated flow meters that were not as accurate as they needed to be at the lower flow rates, the layout of the influent and effluent manifolds, and the lower pressure drops that dictated flow rates. Flow rate readings were obtained by taking timed readings from the flow totalizer.

Routine O&M activities for the Six-Condition Pilot-Scale System included the following:

- Monitoring and recording pressures, flow rates, cumulative volume treated, and water and ambient air temperatures, and adjusting flow rates, if needed—performed by ARCADIS and FWC personnel.
- Mixing and adding spiking reagents to the metering pump tanks and carboy jug—ARCADIS personnel.
- Obtaining influent, midpoint, and effluent water samples for process performance monitoring—performed by ARCADIS personnel.
- Replacing filter bags in the pre-filter system (based on a maximum differential pressure as specified by the filter manufacturer)—performed by ARCADIS personnel.
- Inspecting the system for leaks and equipment malfunctions—ARCADIS and FWC personnel.

5.5.4 Spiking of the Six-Condition Pilot-Scale System

The water chemistries that were tested are described in this section. In this and all subsequent sections, the BVs are as measured through one activated carbon bed.

5.5.4.1 Stratified Beds Control – No Spiking Agent

This treatment train was designed to provide the baseline for comparison with the other field tests and RSSCT results. The Stratified Beds Control Train operated nearly continuously between September 7, 2007, and March 24, 2008, —approximately 197 days. The average flow rate for this train was 1.8 GPM (11.2 min EBCT) until January 2, 2008, (18,200 BVs) when the flow rate was increased to a target of 3.0 GPM (5.5 min EBCT). After January 2, 2008, the average flow rate was 2.9 GPM. The average flow rate for the entire period of operation was 2.2 GPM. The average influent water temperature was 74.7 °F and the average effluent water temperature was 73.9 °F.

5.5.4.2 TCE Spiked

Perchlorate and TCE are common co-contaminants in the Inland Empire of southern California. This treatment train was spiked with TCE with a target concentration of 50 µg/L. Because of the volatility of TCE and low target concentration, this train originally had a spiking system that consisted of a syringe pump, a glass syringe filled with "neat" (i.e., pure solvent) TCE, and stainless steel tubing that connected to the influent manifold. The variability of TCE concentration was extreme during the period of operation of this first spiking system but no TCE breakthrough was noted through the first bed.

The spiking system was revised (see discussion in Section 5.4.3) because of operational difficulties in achieving the TCE target concentration. The revised spiking system consisted of a metering pump, five-gallon glass carboy jar containing glass beads, a "neat" TCE layer, and TCE-saturated water phase. The metering pump was set to pump the TCE-saturated water at a flow rate of 0.2 ml/min. This pumping rate was verified by conducting intake tests using a graduated cylinder and a stopwatch. The first bed was taken off line when the revised spiking system had proven its reliability. The average TCE concentration in the influent water to the beds was 42.5 µg/L after revising the spiking system with a 45% RSD. The influent TCE concentration for the period of operation after May 22, 2008, is shown in Figure 5-45.

After replacing the spiking system the train ran continuously between May 22, 2008, and September 4, 2008 (approximately 105 days). The average flow rate for the original spiking system was 1.2 GPM and the re-designed spiking system flow rate was 1.4 GPM (11.5 min EBCT). The average influent water temperature during the original spiking system operation was 74.7 °F and the average effluent water temperature was 75.9 °F. The average influent water temperature during the re-designed spiking system operation was 77.7 °F and the average effluent water temperature was 79.0 °F.

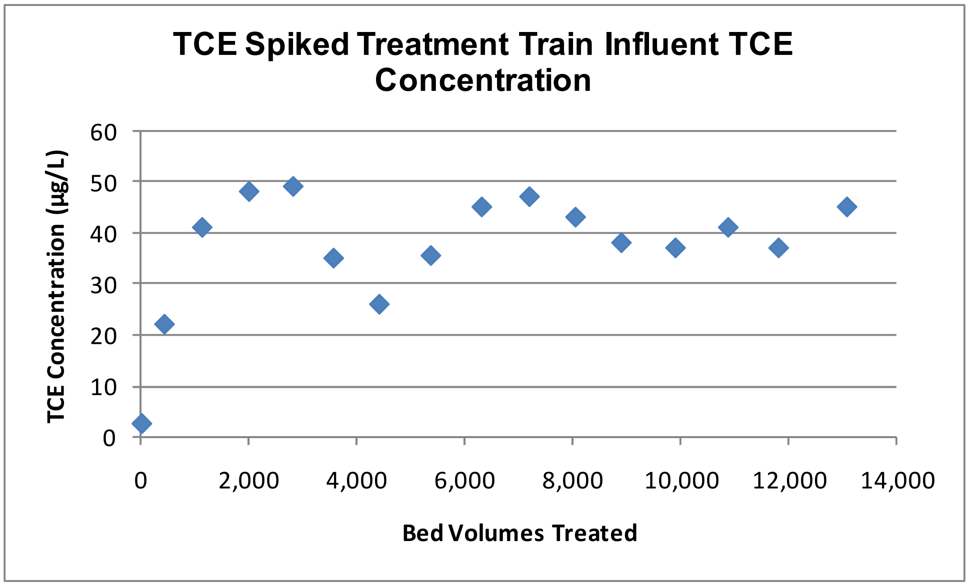


Figure 5-45. TCE Spiked Treatment Train Influent TCE Concentration (BVs as measured through one bed), after May 22, 2008

5.5.4.3 *Perchlorate Spiked*

This train increased the perchlorate concentration with a target concentration of 200 µg/L in order to demonstrate the technology's response to a higher concentration of this key contaminant. This treatment train had a spiking system that consisted of a holding tank for the perchlorate solution, an electric tank mixer, and a five gallons per day (GPD) chemical metering pump. The perchlorate solution was prepared by mixing 16 gallons of water with 12.12 grams of sodium perchlorate monohydrate ($NaClO_4 \bullet H_2O$). The metering pump was programmed to deliver the solution at 2.9 GPD to achieve the target perchlorate concentration of 200 µg/L. The flow rate was reduced to 2.5 GPD on October 10, 2007, to reduce the spiking concentration after analyzing influent sample results. The spiked perchlorate concentration averaged 315 µg/L for the duration the demonstration. The achieved EBCT overall was 11.7 min.

The Increased Perchlorate Concentration Train operated nearly continuously between September 7, 2007, and March 24, 2008–approximately 197 days. The average flow rate for the system was 1.5 GPM. The average influent water temperature was 74.7 °F and average effluent water temperature was 75.0 °F.

5.5.4.4 *Nitrate Spiked*

Nitrate is a competitive anion with perchlorate for sorption sites on TGAC and is known from bench-scale testing to significantly decrease perchlorate capacity. The target concentration was 50 mg/L (vs. a typical value of approximately 32 µg/L in unspiked and untreated Fontana groundwater). This treatment train had a spiking system that consisted of a holding tank for the nitrate solution, an electric tank mixer, and a five GPD metering pump. The nitrate solution was prepared by mixing 15 gallons of water with 1.14 kilograms of sodium nitrate ($NaNO_3$). The metering pump was programmed to deliver the solution at 2.9 GPD, for a target nitrate concentration of approximately 50 mg/L (as nitrate). The metering pump flow rate was decreased to 2.6 GPD on October 10, 2007, and then to 2.5 GPD on October 29, 2007, to attain the target nitrate concentration. This treatment train was spiked to an average concentration of 61 mg/L of nitrate (as nitrate). The achieved EBCT overall was 11.6 min.

The Nitrate Train was started on September 7, 2007, but was shutdown on September 10, 2008, to address flow rate control problems that were caused by a Y-check valve. The system ran continuously between October 1, 2007, and April 25, 2008–approximately 212 days. The average flow rate for the system during this period was 1.4 GPM. The average influent water temperature was 74.7 °F and the average effluent water temperature was 75.1 °F.

5.5.4.5 *Pre Disinfectant/Oxidant*

A number of drinking water treatment systems disinfect groundwater with an oxidant (typically chlorine based) prior to the application of GAC. The effect(s) of upstream chlorination on perchlorate removal by TGAC is unknown. The influent of this pilot-scale treatment train was designed to pre-treat with between 0.15 and 0.3 mg/L free chlorine as sodium hypochlorite (NaOCl) to simulate a full-scale drinking water treatment operation. It has also been hypothesized that in some systems, pre-chlorination could improve TGAC performance by removing interfering reduced sulfur species (Appendix C).

This treatment train had a spiking system that consisted of a chlorination contact tank, an electric tank mixer, and a metering pump. Because of the requirement for chlorination contact time prior to being pumped through the TGAC bed, this train also included a tank downstream of the spiking solution injection point. This tank provided ~30 minutes of contact time prior to the first TGAC bed. The hypochlorite solution was prepared by mixing 15 gallons of water with 75 to 310 milliliters of household bleach that contained 6 percent sodium hypochlorite (NaOCl) by weight. The metering pump was programmed to deliver 2.9 GPD of hypochlorite solution, which created the target free chlorine residual of between 0.15 and 0.3 mg/L. The metering pump flow rate was increased to 3.0 GPD on October 10, 2007, and then reduced to 2.5 GPD on October 29, 2007. The average free chlorine concentration averaged 0.28 mg/L after the metering pump flow rate adjustments and adjustments to the volume of bleach used for the hypochlorite solution (average from 10/12/07 through 3/19/08) were made. The predisinfectant/oxidant train influent free chlorine is shown in Figure 5-44.

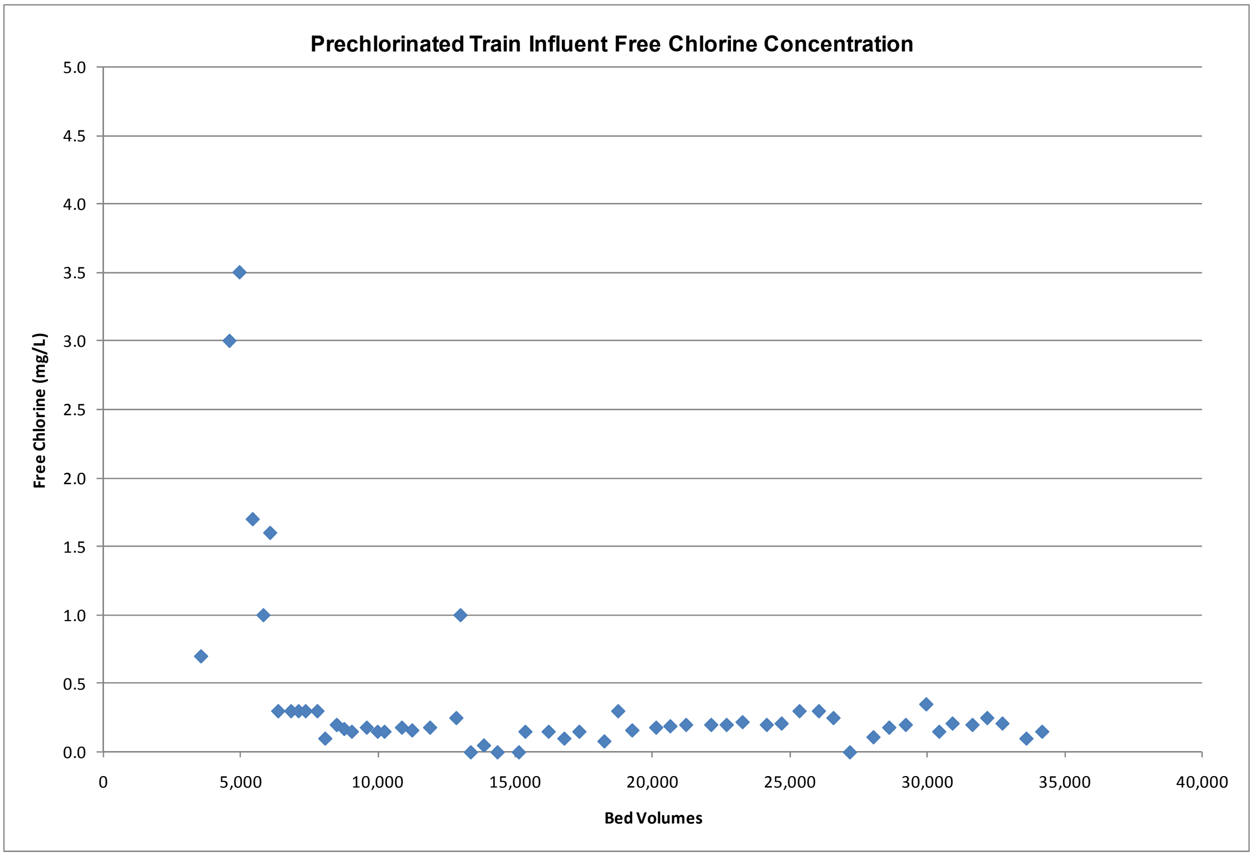


Figure 5-44. Influent Free Chlorine Concentration Predisinfectant/oxidant Train (BVs as measured through one bed)

The Disinfectant/Oxidant Train operated nearly continuously (with the exception of approximately two weeks in December 2007 when the train was down because of low flow rates) between September 10, 2007, and March 24, 2008, with—approximately 179 days. The average flow rate for the system was 1.5 GPM until January 2, 2008 (12.0 min EBCT), when the flow rate was increased to a target of 3.0 GPM, as discussed earlier. After January 2, 2008, the average flow rate was 2.8 GPM (5.6 min EBCT). The average influent water temperature was 74.7 °F and the average effluent water temperature was 75.1 °F.

5.5.4.6 TDS/Sulfate Train

TDS may compete with perchlorate for TGAC sorption sites, and thus impacts perchlorate capacity. This treatment train was spiked with magnesium sulfate heptahydrate ($MgSO_4 \cdot 7\ H_2O$) to approximately 1,200 mg/L TDS. This treatment train had a spiking system that consisted of a holding tank for the sulfate solution, an electric tank mixer, and an 18 GPD metering pump. The spiking solution was prepared by mixing 100 pounds of magnesium sulfate heptahydrate with water until 23.8 gallons of solution was prepared. The metering pump was programmed to deliver 11 GPD of sulfate solution, for a target TDS concentration of approximately 1,200 mg/L. The metering pump flow rate was decreased to 9 GPD on October 10, 2007, to reduce the spiking concentration after analyzing influent sample results. This treatment train was spiked with an average TDS concentration of 969 mg/L. The influent TDS trend is shown in Figure 5-46.

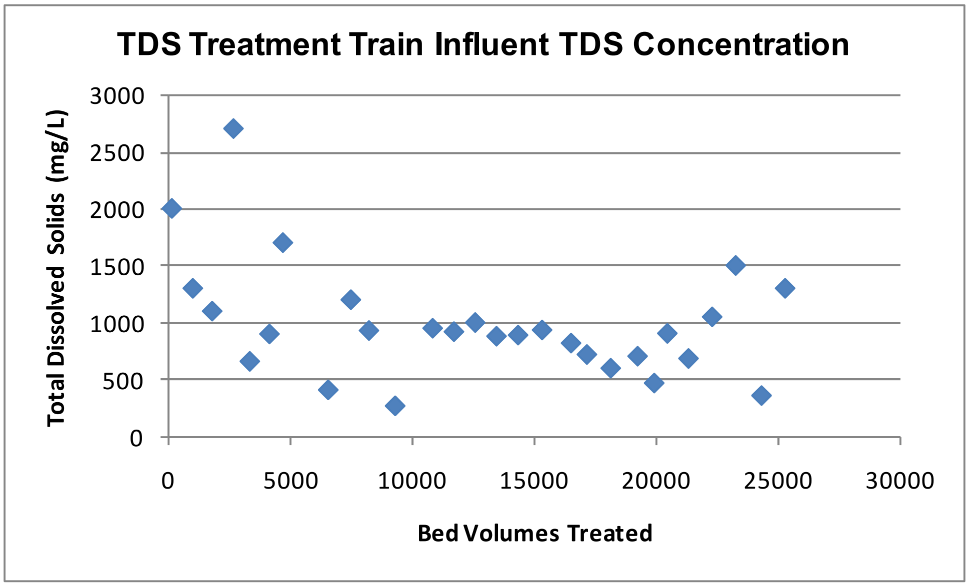


Figure 5-46: TDS/Sulfate Spiked Train, Influent TDS Concentration (BVs as measured through one bed)

The operator reported that the TDS train spiking was by far the most difficult of the spiking trains to operate other than the TCE train. This was caused by the large amounts of magnesium sulfate needed (compared to the other train spiking agents). The operator reported that the mixer was difficult to use, that it was hard to get the water and magnesium sulfate to dissolve completely, and that the transfer pump became clogged with scale. Finally, the tubing from the spiking tank to the system sometimes posed problems such as being clogged with scale, breaking (because of ultraviolet radiation to the tubing), and leaking.

The TDS Train operated nearly continuously between October 1, 2007, and May 2, 2008, — approximately 218 days. The average flow rate for the system was 1.3 GPM (13.2 min EBCT). The average influent water temperature was 74.7 °F and the average effluent water temperature was 74.5 °F.

5.5.5 Simulated Distribution System (SDS) Testing

ARCADIS conducted SDS testing on the TGAC system effluent as a one-time event to determine the potential for disinfection byproduct generation following disinfection treatment with bleach only or bleach combined with CPC.

5.5.5.1 Treatment set-up

The ARCADIS' Durham, North Carolina, Treatability Laboratory (Durham Treatability Laboratory) received three 2.5 gallon containers of TGAC effluent, TGAC-EFF3-07-09-26. The three containers were consolidated into two twelve-liter glass jugs and the pH was adjusted as follows, see Table 5-21.

Table 5-21. Samples collected for SDS Testing

Consolidated Vessels	Initial pH	End pH
Jug 1	7.15	8.02
Jug 2	7.15	7.99

Six treatments were prepared from the consolidated effluent; each in 4-L amber jugs with Teflon lined caps and filled to zero headspace. Each treatment was then dosed with bleach and or CPC according to the following (Table 5-5).

Table 5-5. Treatments for SDS Testing

SDS Sample Name	Bleach Dose	CPC spike	Description
SDS-TGAC-1	1.25 mg/L	0.3 ml	Chlorinated + spiked
SDS-TGAC-2	1.25 mg/L	0.3 ml	Chlorinated + spiked duplicate
SDS-TGAC-3	1.25 mg/L	0	Chlorinated
SDS-TGAC-4	1.25 mg/L	0	Chlorinated duplicate

SDS Sample Name	Bleach Dose	CPC spike	Description
SDS-TGAC-5	0	0	Control
SDS-TGAC-6	0	0.3 ml	Un-chlorinated + spiked

Among the treatments, two controls were established. Treatment SDS-TGAC-5 received no disinfection treatment and treatment SDS-TGAC-6 was treated with only CPC. All treatments were incubated in the dark at 20ºC for 24 hours.

5.5.5.2 Analysis of Treatments

At the end of the test incubation each treatment was analyzed for the following:

By the Durham Treatability Laboratory for:

- Free chlorine by HACH DPD Free Chlorine test program #9

By Weck Laboratories for:

- Total organic halides (TOX) by Method SM5320B
- Haloacetic acids 6 compounds + HHA5 (HHAs) by EPA Method 552.2
- Trihalomethane (THMs) by EPA method 524.2
- Nitrosamines (including N-nitrosodimethylamine [NDMA], N-nitrosodiethylamine [NDEA], and N-nitrosodi-n-propylamine [NDPA]) by EPA method 521

5.5.6 Demobilization

Spent TGAC and GAC were transported off-site for destruction at the Covanta Stanislaus Waste-to-Energy facility in Crows Landing, California. The Covanta Stanislaus facility routinely disposes of spent perchlorate IX resins.

All piping and equipment will be removed from the site, and will be either properly disposed of, or returned to Siemens Water Technologies, at their discretion. The concrete pad will either be left in place or demolished and removed from the site, as directed by FWC. If the concrete pad is demolished, the ground surface will be returned to pre-demonstration condition.

5.5.7 Schedule

An overall project Gantt chart is provided as Figure 5-16.

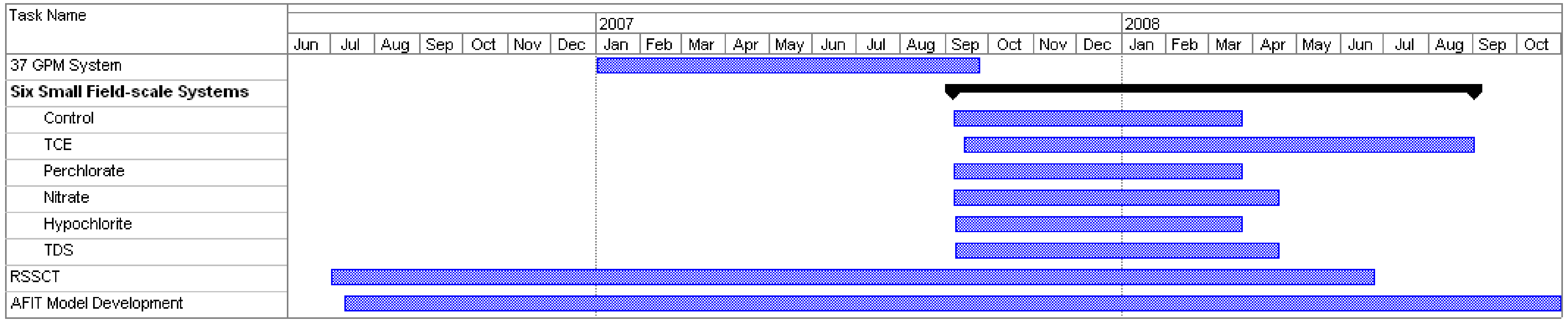


Figure 5-16. Testing Schedule

5.6 SAMPLING AND ANALYSIS METHODS

5.6.1 Sampling Methods:

Locations of sample ports are shown in Figures 5-1 and 5-2. Essentially all samples were discrete grab samples. The primary sample locations for the 38 GPM system were:

- Influent (taken before the pre-filter)
- Effluent 1 (after first TGAC bed)
- Effluent 2 (after second TGAC bed)
- Effluent 3 (after third conventional GAC bed)

The primary sample ports used in the six condition pilot-scale system were:

- SIX-INF – Common six column influent manifold
- Individual bed influents
- Effluent 1 (after first stratified bed)
- Effluent 2 (after second stratified bed)

Each train was given an individual code:

- CTRL – stratified bed control
- TDS – TDS/magnesium sulfate spiked
- NO3 – Nitrate spiked
- CLO – Prechlorinated
- PERC – perchlorate spiked
- TCE – TCE spiked

5.6.2 Analysis Methods

Throughout the demonstration, the primary chemical analyses required for performance assessment were performed off-site by Weck Laboratories (with the exception of the primary perchlorate method 314.0 analyses, which was conducted at PSU). The analysis for anions and cations was performed at AFIT. The analysis for CPC was conducted by Exygen Research. Confirmatory analyses for perchlorate were conducted by STL Inc./TestAmerica and Weck laboratories. Matrices of analyses performed are given in Table 5-6 for the 38 GPM system and Table 5-7 for the 6 condition field-scale trains.

Data verification/validation was performed on selected key datasets as discussed in Appendix F. These summaries discuss in depth results from duplicates and blanks for the selected analyses. Blank and duplicate results are also discussed for each data set interpreted in Section 5.7.

5.6.2.1 Perchlorate Analysis Methods

There are several recognized limitations in the use of EPA Method 314.0 for perchlorate analysis. The analysis is 1) subject to false positives due to the unspecific nature of the conductivity detector; 2) can be subject to matrix interferences, especially in the presence of high concentrations of other anions; and 3) is inappropriate for use in samples with high TDS because of interference problems.

For this project, possible method limitation associated with Method 314.0 included:

- (a) The TDS affect on the perchlorate analysis, and
- (b) The presence of CPC affecting the perchlorate analysis.

With regard to (a), higher levels of salts and TDS can cause the quantitative minimum detection limit (QMDL) to be a higher value, as determined by the peak area-to-peak width ratio as discerned for a ion chromatography peak for perchlorate. With regard to (b) PSU also screened samples for CPC as needed to ensure that the levels of CPC were not sufficient to cause a significant interference.

Because of possible Method 314.0 limitations, five percent of the perchlorate samples were submitted to STL/TestAmerica/Weck for confirmatory analysis by EPA Method 332.0 (ion chromatography tandem mass spectrometry [IC-MS/MS]). This method provides a much greater sensitivity, eliminates matrix interferences (false positives), and provides for high confidence in compound identification. The use of MS/MS in lieu of MS allows for structural information from fragmentation (not just the analyzing of molecular ions), quieter background, and better chromatography (separation) for difficult samples. There have been no reports of false positive results using this technique.

5.6.2.2 Anion and Cation Analysis Methods

AFIT provided analyses for anions and cations for both laboratory and field portions of the project. Cation analyses were performed using atomic absorption (AA) spectrometry and followed Quality Assurance/Quality Control (QA/QC) procedures detailed in Part 3000 of Standard Methods for the Examination of Water and Wastewater, 20th Edition.

5.6.2.3 CPC Analysis Methods

Exygen Research performed CPC analyses by direct injection liquid chromatography tandem mass spectrometry liquid chromatography tandem mass spectrometry LC/MS/MS with a 7 point calibration curve.

PSU screened samples for CPC and provided additional data for high concentration samples using the titration method of Tsubouchi et al. (1981). Siemens also used this method in the field on one occasion during system startup.

There are several analytical methods that have been reported for analyzing surfactants, the general class of compounds to which CPC belongs. There are two major approaches for determining surfactants, Chromatographic and Spectrophotometric. Spectrophotometric techniques are the basis of the most common standard procedures for analyzing surfactants in the environment. One major disadvantage for these methods is that they are more susceptible to interference than chromatographic procedures. Table 5-21 summarizes available analytical methods that are used for surfactant analysis.

Table 5-21 Surfactant Analysis Methods (Adapted from Schmitt, 2001; Tsubouchi et al., 1981)

Analytical Methods	**Type of Surfactants**		**Separation Mechanism**	**Detection**	**Adv. and Disadv.**
	Anionic	**Cationic**			
Colorimetric	X	X	N/A	N/A	Rapid method of detecting surfactants
High Performance Liquid Chromatography	X	X	Reverses-Phase, Normal Phase, Ion Exchange chromatography	Ultraviolet Absorbance, Post column	
Thin Layer chromatography	X	X	Normal and /or reversed phase techniques		Rapid and inexpensive method for analyzing surfactants
Gas Chromatography	X	X	Hoffmann elimination, extraction, hydrogenation	Direct Analysis, Derivatization,	Coupled with Mass Spectrometry makes it suitable for analyzes of unknown products
Capillary Electophoresis	X	X	N/A	Conductivity, cathodic and UV and indirect UV	Quantification is difficult due to variable migration times. Care should be taken not to form micelles

Analytical Methods	**Type of Surfactants**		**Separation Mechanism**	**Detection**	**Adv. and Disadv.**
	Anionic	**Cationic**			
Ultraviolet and Visible Spectrophotometry	X	X	Ion exchange chromatography	Formation by ion pairs detected by:- Disulfine Blue, Picric Acid, Tetraiodobismuthate and Orange II	Susceptible to interference from other surfactants, fatty matter; insensitive to low concentration
Mass Spectrometry	X	X	Gas chromatograpgy, liquid chromatography	Chemical or electron Impact Ionization.	Cannot directly analyze cationic surfactants, has to coupled with a separation method. Suitable for low concentration of surfactants

The two methods that were employed in this project were the two-phase titration method and the Liquid Chromatography Tandem Mass Spectrometry (LC/MS/MS) method. A brief description is given below.

Mass Spectrometry (MS) has become a method of testing organic compounds. It is a very sensitive and specific method for both mixtures and pure cultures. If used properly with the appropriate separation method, this technique can quantify surfactants in the low ug/L and ng/L concentration. MS without prior separation is not a suitable method for determining surfactants (Schmidt, 2001). Common separation techniques are Gas and Liquid Chromatography. Ionization techniques that are required with MS procedures usually require large excess of surfactant of which only a small portion volatilized and ionized. To acquire true quantification of the surfactant tested, internal standards of isotope-labeled compounds of the precise surfactant to be determined, this is a costly step.

Colorimetric methods such as the two-phase titration method employ indicators for visual end point detection. This method provides a means for rapid determination of cationic surfactants without the need for complex instrumentation. According to Tsubouchi et al., 1981, the two phase titration end point detection can be a problem due to color reflectance and differences in shade or hue of the color. The detection limit is 0.2 mg/L per titration method. This method gives a rough idea of the surfactant concentration in the water. For a more precise method then instrumentation methods such as chromatography and spectrophotometry is needed.

Intercomparision of the two CPC analysis methods was not a project objective. The titration method was used for the samples suspected of potentially containing higher concentrations of CPC for two reasons: 1) to ensure that CPC concentrations were not high enough to cause problems with the perchlorate analysis instrumentation and 2) because this titration method was considerably more cost effective then the LC/MS/MS method.

Table 5-6. Demonstration: Analytical Matrix – 38 GPM System

CONSTITUENT	ANALYTICAL METHOD	SAMPLING FREQUENCY (INFLUENT, EFFLUENT, BED 1, BED 2)	PERFORMER
Perchlorate	314.0	Weeks 1-52 Weekly[1]. Influent Bed 1, Weekly Effluent Bed 1 Weekly Effluent Bed 2 Weekly Effluent Bed 3	PSU (1/20 were sent to another laboratory for confirmatory analysis)
Perchlorate	332.0	Confirmatory sampling of 1/20 of the perchlorate samples collected above Weeks 1-3 Weekly for Effluent Bed 2	STL/Test America or Weck Laboratories
pH	150.1	Weekly. Influent Bed 1 and Effluent Bed 1 & Bed 2	Weck Laboratories
Alkalinity	A2320	At startup and monthly thereafter. Influent Bed 1 and effluent, Bed 2.	Weck Laboratories
Common anions (including chloride sulfate, nitrate, bromide)	RSSCT 300.0	At startup and monthly Influent Bed 1 and Effluent Bed 2. (*Except – at least three times per week during the first 3,000-5,000 BVs (21 to 35 days of operation*))	AFIT
Common cations (sodium, and calcium, potassium; and metals such as iron and aluminum)	300 and 6010B	At startup and monthly Influent Bed 1 and Effluent Bed 2.	AFIT
Conductivity	120.1	Once weekly at Influent Bed 1 and Effluent Bed 2.	Weck Laboratories
NDMA, NDEA, and other nitrosamines	521.0	At startup and monthly on Influent Bed 1 and Effluent Bed 2.	Weck Laboratories
TDS	160.1	At startup and monthly at Influent Bed 1 and Effluent Bed 2.	Weck Laboratories
CPC	Tsubouchi et al, (1981) & triple quad gas chromatography/mass spectrometry (GC/MS)	5 times in first week with at least one analysis of Bed 3 effluent, then 3 more times during run with at least one analysis of Bed 3 effluent.	Exygen Research http://www.exygenresearch.com
Heterotrophic Plate Count	Standard Methods 9215 C	Up to 4 analyses in GAC slurry at conclusion of demonstration	Weck Laboratories

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[1] All weekly samples were collected at startup and then weekly thereafter.

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Table 5-7. Demonstration: Analytical Matrix – Six-Condition Pilot-Scale Field System

SIX-COLUMN STUDY			
Perchlorate	314.0	At start up and weekly for all small-scale treatment trains at common influent header, specific influent to perchlorate spiked train, specific influent to disinfectant/oxidant train and in effluent of bed 2 for each treatment train.	PSU (1/20 will be sent to another laboratory for confirmatory analysis)
pH	150.1	At start up and four times a month for 2 months; then twice a month for all small-scale treatment trains in common influent header and each treatment train effluent for all small-scale treatment trains	Weck Laboratories
Alkalinity	A2320	At start up and monthly in influent header and each treatment train effluent for all small-scale treatment trains	Weck Laboratories
Common anions	300.0	At start up and weekly in influent header and each treatment train effluent for all small-scale treatment trains. Additionally testing will include sulfate in TDS Treatment Train spiked influent and effluent. Nitrate in Nitrate Treatment Train spiked influent and effluent.	AFIT
Conductivity	120.1	At startup and 2 times per month in influent header and for individual small-scale treatment train's effluent	Weck Laboratories
NDMA, NDEA, and other nitrosamines	521.0	At startup and monthly in the specific influent and treatment train effluent of small-scale Control Treatment Train and Disinfectant/Oxidant Treatment Train Pre-disinfected Beds.	Weck Laboratories
TDS	160.1	At start up and monthly in common influent header and all individual small-scale treatment train's effluent. Weekly in influent and effluent to TDS/chloride train.	Weck Laboratories
TCE	8260/524.0	Weekly in Treatment Train #2 spiked influent and effluent.	Weck Laboratories
Temperature	Thermometer	At least twice Weekly in influent header and Polishing Vessel Effluent	ARCADIS
Redox Potential	ORP Meter	At least weekly in influent header and individual treatment train effluents.	ARCADIS
CPC	Tsubouchi et al, (1981) & triple quad GC/MS	CPC testing done on at least 6 occasions at intervals to be defined in the demonstration plan. Testing will be performed on the common influent, the effluent from the stratified bed train and the effluent from the pre-disinfected train.	Exygen Research

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5.6.2.4 *Calibration of Field equipment:*

Calibration of the majority of analytical equipment is described in the cited methods.

The ORP meter used in the field was calibrated weekly with DI water prior to obtaining ORP readings. The ORP meter probe was also pre-soaked in water for at least 30 minutes (pursuant to the manufacturer's recommendations) before ORP reading was taken.

The sample volumes required for a complete analysis were obtained. Samples were chilled with ice after samples were taken. Sample holding times varied depending on the sample and the parameter analyzed—all samples, unless otherwise discussed, were analyzed within the required holding time. New sample bottles and containers were used during the demonstration.

All samples were labeled and documented following proper chain-of-custody (COC) procedures. ARCADIS chains of custody forms were used for all samples that were sent to PSU and AFIT. Copies of the COCs were sent with the samples and via e-mail to PSU and AFIT.

Field logs were used to track ORP and temperature data, as well as other system parameters such as flow rates, volumes, etc.

5.7 SAMPLING RESULTS

5.7.1 Bench-scale Tests Sampling Results

The sorption of perchlorate to TGAC was studied at bench-scale. Seventeen rapid small scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment of pH 4 was 50% greater than the natural occurring pH of the groundwater at 8, and 75% greater than at a pH of 10. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration (60mg/L) reduced the removal of perchlorate by 17%; and a nitrate concentration of 100mg/L reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level. Also the bench scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7. Details of the bench scale results are given in Appendix B.

5.7.2 – 38 GPM Demonstration Scale Tests Sampling Results.

5.7.2.1 Perchlorate Results, 38 GPM

Results for perchlorate for the 38 GPM system is shown in Figure 5-17 and 5-18. Figure 5-17 shows just the primary perchlorate dataset. Figure 5-18 compares PSU results to those of certified laboratories. Figure 5-19 shows individual bed breakthrough curves. Perchlorate breakthrough was observed at 12,000 BVs for bed A which was used in the lead position (the term breakthrough is defined for this report in section 3.1.7). Breakthrough was observed at 20,000 BVs for bed B which was the initial lag bed. Saturation was observed at approximately 16,000 BVs for bed A (measured through one bed) and 27,000 BVs for Bed B (measured through one bed).

Bed D was placed in service at 18,000 BVs as the new lag bed while bed B became the lead bed. A low level of perchlorate breakthrough from Bed D was observed between 21,000 and 26,000 BVs into the demonstration before the concentration reverted to nondetect. Breakthrough clearly occurred at 35,000 BVs and saturation was reached by 40,000 BVs.

Bed C was not tailored, and thus was intended only to treat any CPC that leached from the TGAC beds, not to provide significant perchlorate removal. As expected bed C breaks through soon after Bed D. This is consistent with the low capacity of conventional GAC for perchlorate that has been shown in other experiments (see Section 2 and Appendix B).

During the later periods of operation, beds B, C and D all reached perchlorate effluent concentrations that exceeded the influent. Thus they showed some evidence of a chromatographic roll-over effect.

Perchlorate results were also confirmed by splitting samples with an outside laboratory. Figure 5-18 shows that results both from PSU and Weck Laborataory were generally similar. Blank values were nondetect for both field and method blanks. Replicate results showed acceptable reproducibility (see Appendix F for more details).

5.7.2.2 CPC Results, 38 GPM

5.7.2.2.1 <u>CPC Result – field samples</u>

CPC leaching was also monitored from beds A, B, C and D (Figure 5-20). The lead bed—Bed A—showed substantial leaching of CPC immediately after being placed in service, which rapidly declined. The maximum concentration observed from any bed was observed from the lag bed—Bed B—at 4,600 µg/L. CPC was never detected in the effluent of the final polishing bed C, suggesting that the provision of a polishing bed was an adequate precaution against the release of the tailoring agent to the treated water.

The CPC concentration for backwash water showed 1.3 mg/L for the colorimetric method and 5.8 mg/L for the LC/MS/MS method.

5.7.2.2.2 CPC Results – Quality Control

Extraction blanks, calibrations, laboratory control spikes and matrix spikes for project samples analyzed by Exygen/MPI were acceptable (see Appendix F for more details).

Only a limited number of samples were run by both CPC analysis methods since method intercomparision was not a project objective. While the agreement between the two methods was poor for some individual samples, the overall trends shown by both methods are the same – CPC is released from the tailored beds early in their service life at concentrations up to 4000 ug/l but it is adquately captured by the polishing beds.

The CPC concentration for backwash water showed 1.3 mg/L for the colorimetric method and 5.8 mg/L for the GC/MS method. As discussed in the section 5.6.2.3., the LC/MS/MS method is expected to be more sensitive and quantitative then the titration method.

5.7.2.2.3 Evaluation of possible CPC Biodegradation

As discussed in section 2.1.1 since CPC has mild antimicrobial activity it was not expected to biodegrade. The biodegradability of the CPC on the carbon is likely to depend on its mode of binding to the bulk carbon matrix. If the amine group is bonded directly to the carbon (figure 2-1(a)), then although microbial attack along the alkyl chain of CPC is likely, this would not be expected to reduce the effectiveness of the media in perchlorate sorption. In this configuration the aromatic hetercyclic portion of the CPC molecule would be expected to be resistant to microbial attack. If however the alkyl chain of the CPC formed the bond with the carbon, then cleavage along the alkyl chain would have released the heterocyclic aromatic portion of the molecule which would then could have been washed out. Such a biodegradation product would not necessarily been detected by the analytical methods used. Thus the possibility of biodegradation of the CPC cannot be ruled out. However if biodegradation was occuring at field scale it would also be expected to occur in the bench scale test run at a slow flow rate (Appendix B, experiment 15, Figure 12). However saturation occurred at a similar number of bed volumes in the slow bench scale test as in the RSSCT.

Heterotrophic plate counts indicated that in some cases, microbial growth was present; and this were more prevalent in the top portion of the bed, where they could have accumulated via filtering action by the granular media. The results herein neither confirm nor discount microbial action as a factor in the perchlorate removal performance. A thorough appraisal of microbial affects was beyond the scope of this study, particularly in light of the other numerous studies that have focused on microbial-perchlorate treatment. This project was designed as a technology demonstration, not a mechanistic study. As we discuss further in section 6.8.2 it would be methodologically difficult to directly observe biological degradation of CPC bonded to GAC at field scale.

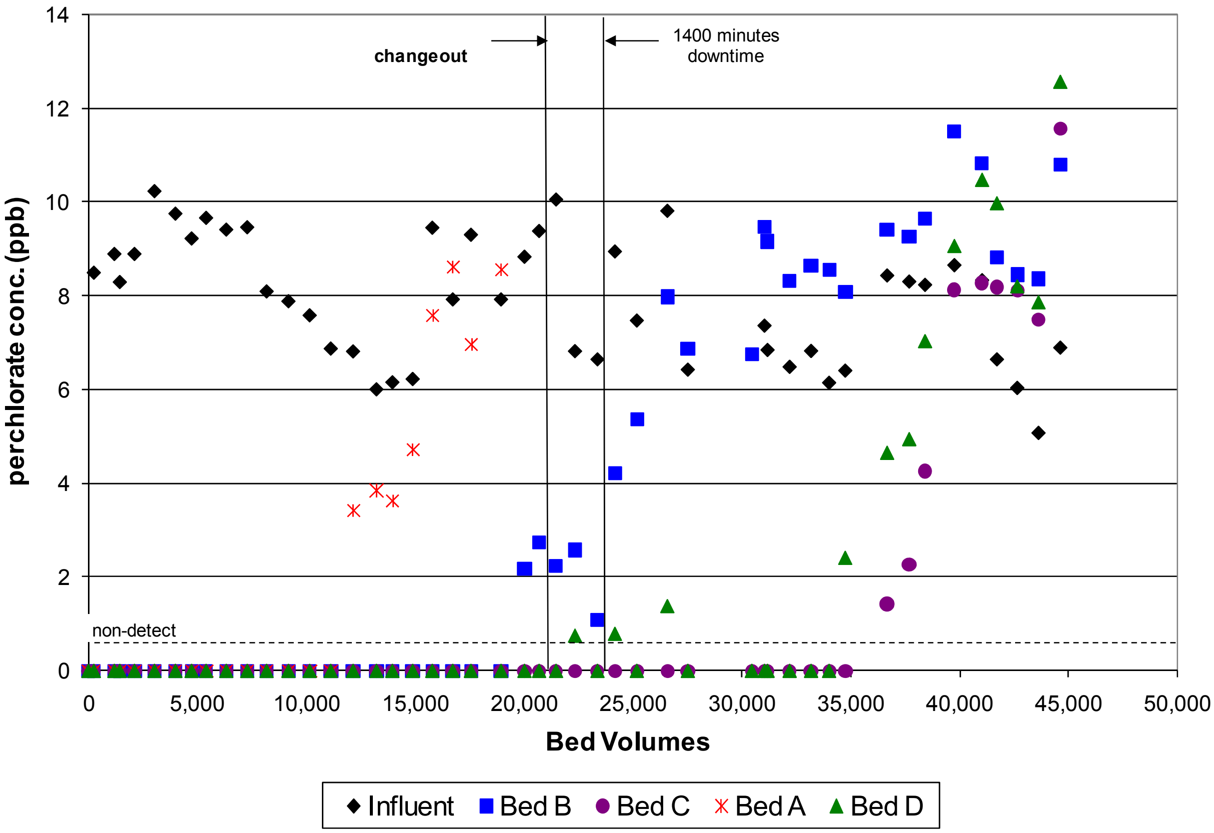


Figure 5-17. Breakthrough Curves for All Beds in 38 GPM System, BVs are Cumulative for the Entire Demonstration, Primary PSU Analytical Dataset Only, BVs as Measured Through One Bed

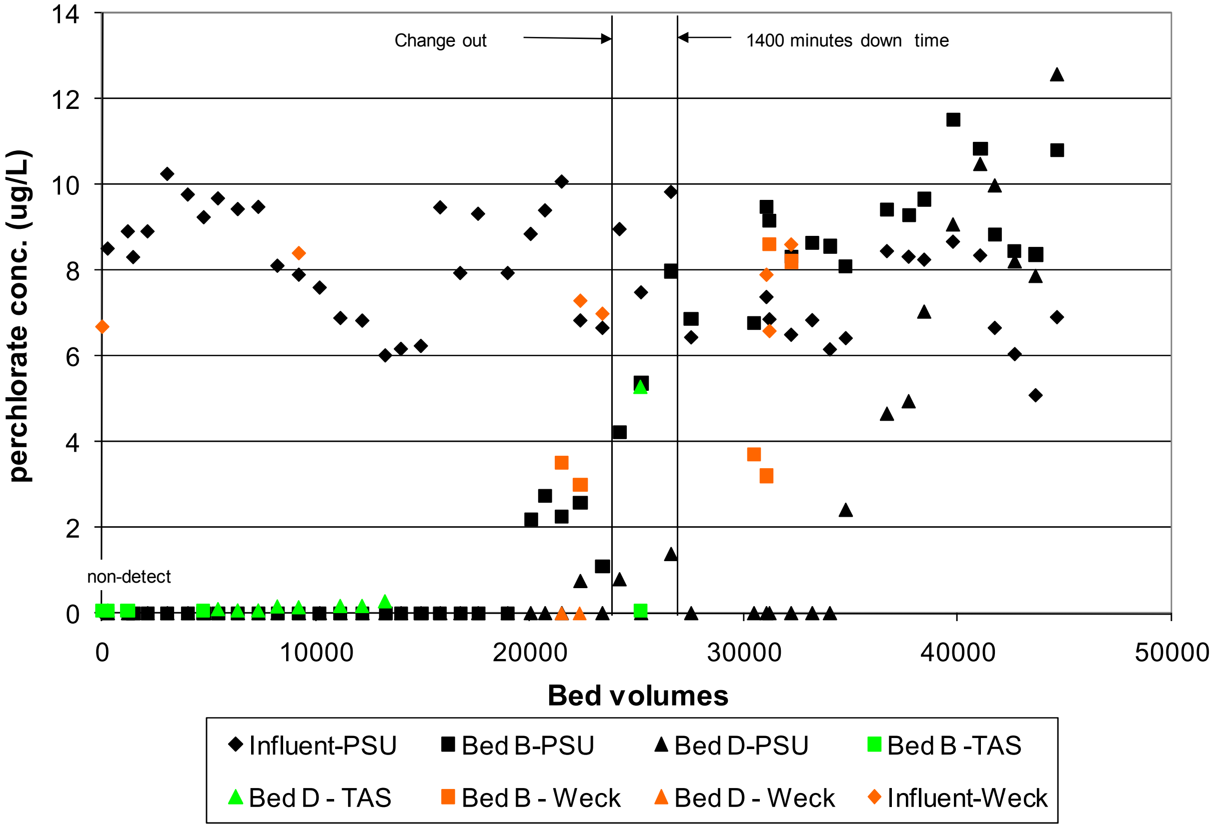


Figure 5-18. Comparison of Results from PSU with Certified Laboratories, 38 GPM Bed Data, BVs as Measured Through One Bed

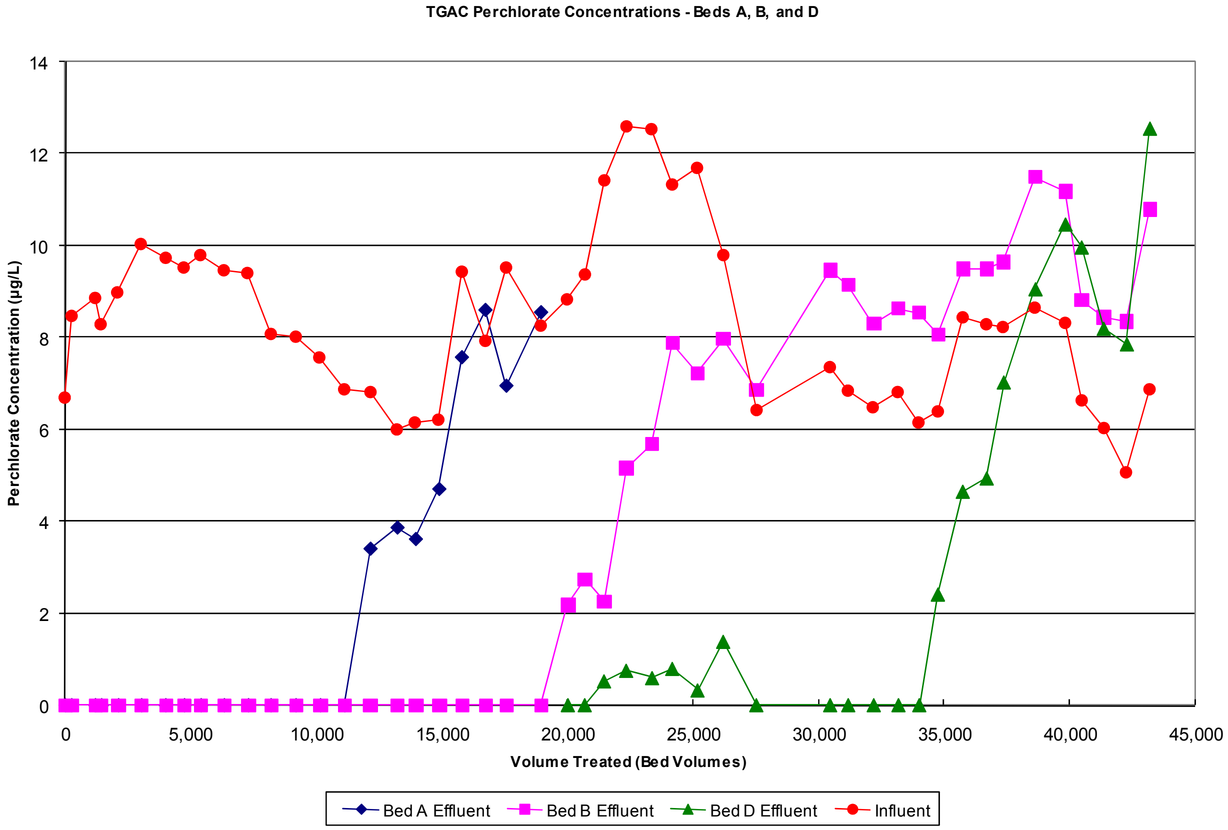


Figure 5-19. Individual Bed Breakthrough Curves, BVs as Measured Through One Bed

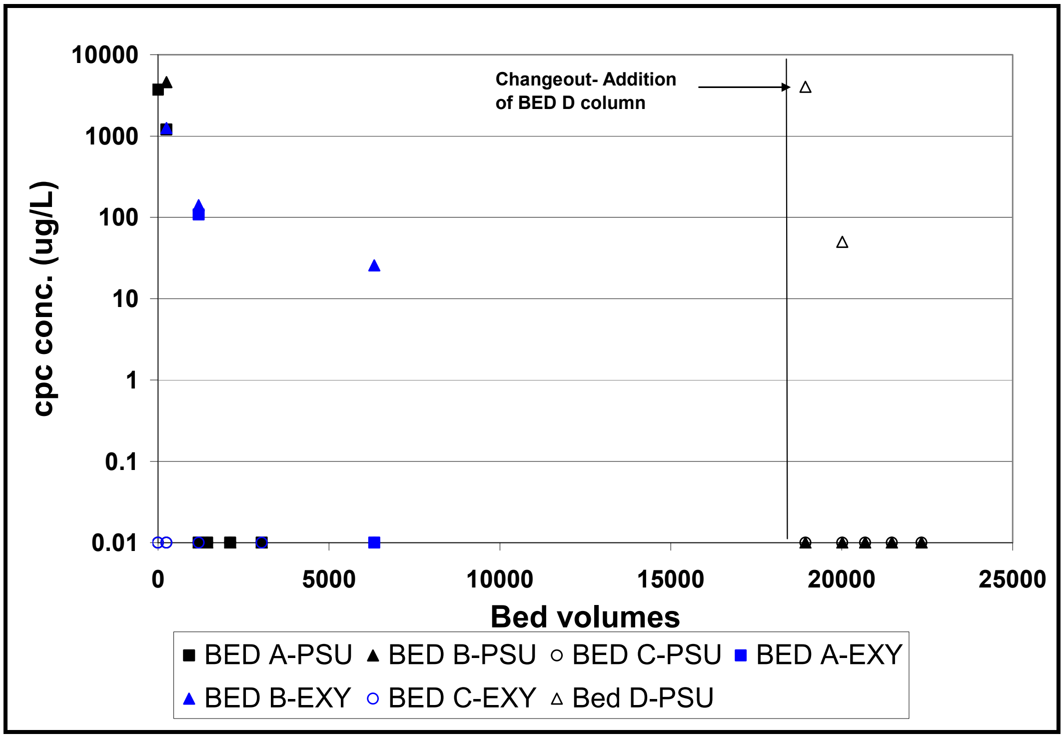


Figure 5-20. CPC Leaching, Including Data from Two Laboratories - PSU and Exygen, Note Beds A, B and D are TGAC, Bed C is a Polishing Bed (BVs as measured through one bed)

5.7.2.3 Nitrosamine Results, 38 GPM

Nitrosamines were sampled on a monthly basis throughout the course of the test, beginning in January 2007 through November 2007. No nitrosamines were detected in the influent water in any sampling event above the reporting limit of 2 ng/L.

Nitrosamines were sampled also from the effluent 2 port on a monthly basis throughout the course of the test, beginning in January 2007 through November 2007. On January 11, 2007 at system start-up N-Nitrosodimethylamine (NDMA) was measured at 39 ng/L. No other nitrosamines were detected in any other sampling event above the reporting limit of 2 ng/L.

Selected nitrosamine reports were validated by ARCADIS (Appendix F) – the identified issues were quite minor (see Appendix F).

5.7.2.4 General Chemistry Results, 38 GPM

5.7.2.4.1 Influent General Chemistry

Figure 5-21 shows influent pH, alkalinity, conductivity and TDS data collected from the 38 GPM influent collected from the first period of operation, BVs 0 through 20,104. All of these parameters were relatively stable with no clear trends. The average pH value was 7.82 s.u., with a standard deviation of 0.20 s.u. The average alkalinity was 154.00 mg/L with a standard deviation of 11.40 mg/L, the average specific conductance was 401.48 µmhos/cm with a standard deviation of 11.67 µmhos/cm and the average TDS was 256.00 mg/L with a standard deviation of 26.08 mg/L.

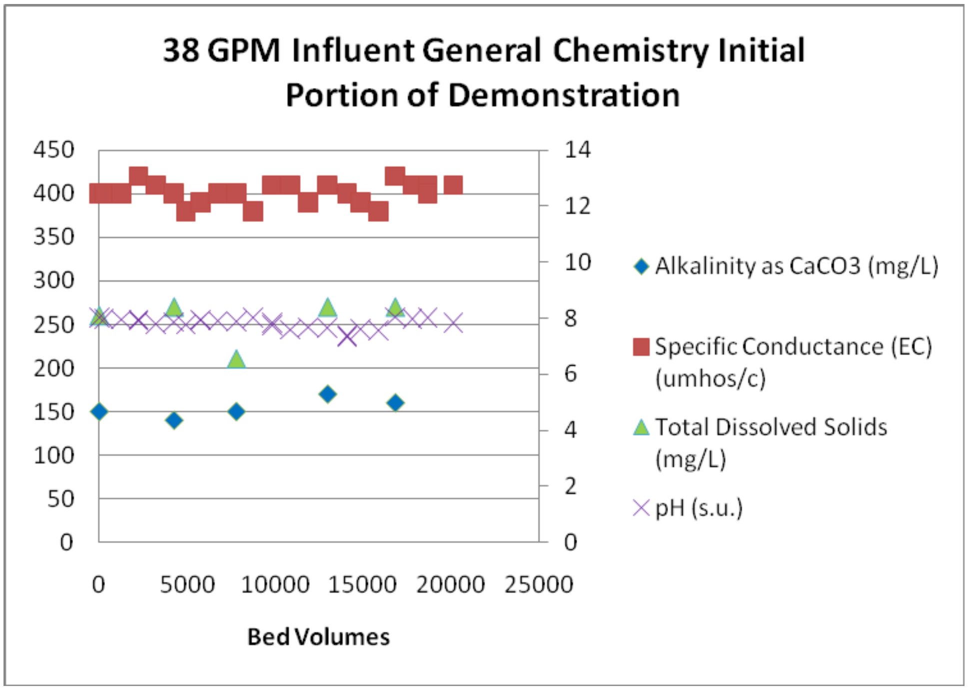


Figure 5-21. 38 GPM Influent General Chemistry, Initial Portion of Demonstration, BVs as Measured Through One Bed

Figure 5-22 shows the pH, alkalinity, conductivity and TDS data collected from the 38 GPM influent collected during the second period of operation (after bed D was introduced and bed B moved to the lead position). Again most of these general chemistry parameters were stable but there may be a general trend of increasing TDS during this period. The average pH value was 8.0 0s.u. with a standard deviation of 0.18 s.u. The average alkalinity as $CaCO_3$ was 150 mg/L with a standard deviation of 0.00 (four measurements gave an identical result), the average alkalinity as bicarbonate (HCO_3^-) was 188.33 mg/L with a standard deviation of 4.08 mg/L the average specific conductance was 418.00 µmhos/cm with a standard deviation of 10.64 µmhos/cm and the average TDS was 242.86 mg/L with a standard deviation of 76.31mg/L.

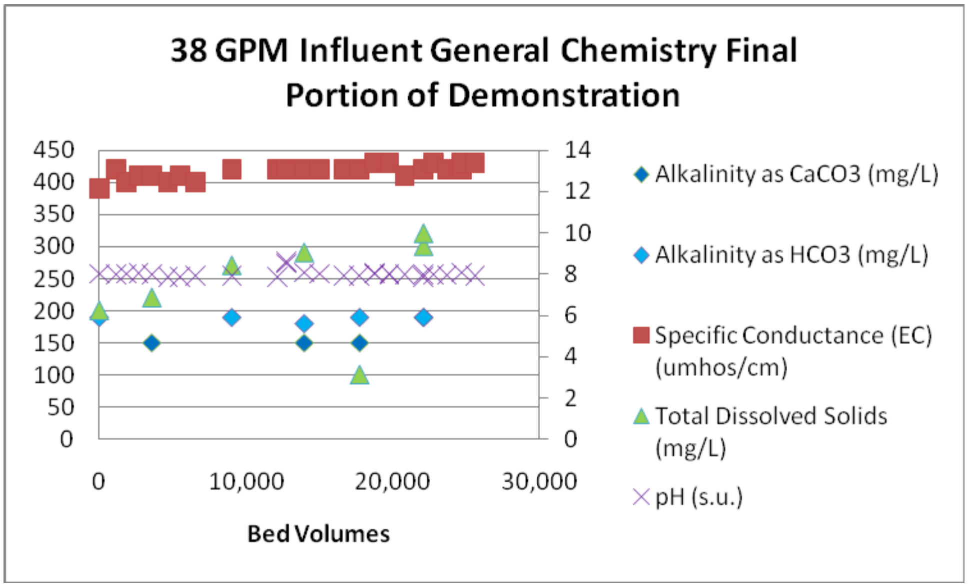


Figure 5-22. 38 GPM Influent General Chemistry, Final Portion of Demonstration (BVs as measured through one bed)

5.7.2.4.2 Effluent Port 1 General Chemistry

For the 38 GPM mid train sampling point (Effluent 1) during the first portion of the demonstration (BVs 0 through 20,104) pH was the only parameter monitored. The average pH value was 7.70 s.u. with a standard deviation of 0.29 s.u.

During the second cycle (BVs 0 through 25,625) pH and specific conductance were monitored. The average pH was 7.91 s.u. with a standard deviation of 0.21 s.u. and the average specific conductance was 412.0 0µmhos/cm) with a standard deviation of 10.95 µmhos/cm.

5.7.2.4.3 Effluent Port 2 General Chemistry

Figure 5-23 displays the pH, alkalinity, conductivity and TDS data collected from the 38 GPM effluent 2 port during the initial portion of the demonstration, BVs 0 through 20,104. The general pattern is again of stability although alkalinity appears to begin substantially below the influent concentration and then rise gradually until it equals the influent concentration. This may suggest that bicarbonate is initially sorbed by the TGAC and then saturates. The average pH value was 7.61 s.u., with a standard deviation of 0.34 s.u. The average alkalinity was 137.40 mg/L with a standard deviation of 40.91 mg/L, the average specific conductance was 403.48 µmhos/cm with a standard deviation of 15.84 µmhos/cm and the average TDS was 270.00 mg/L with a standard deviation of 36.74 mg/L.

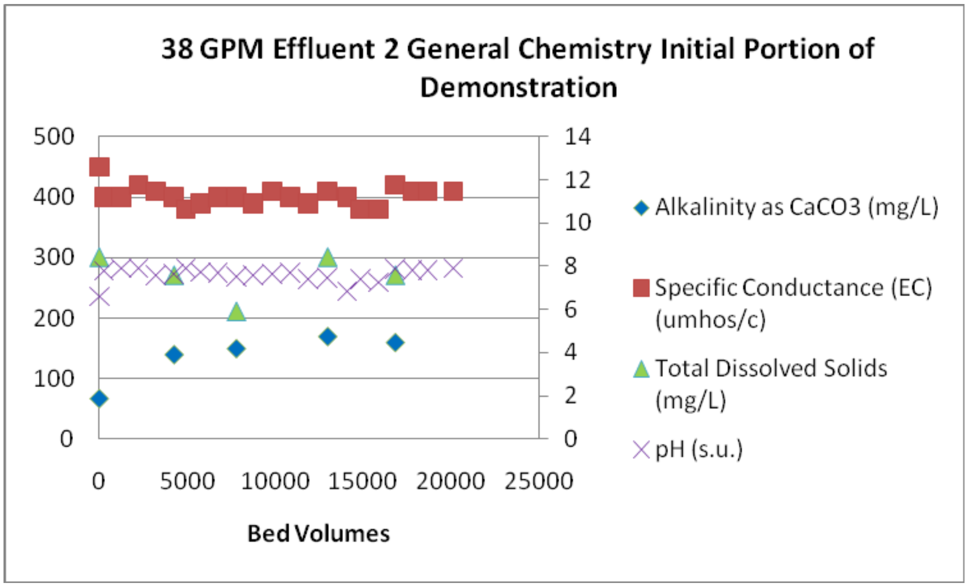


Figure 5-23. 38 GPM Effluent 2 General Chemistry Initial Period of Demonstration (BVs as measured through one bed)

Figure 5-24 shows the pH, alkalinity, conductivity and TDS data collected from the 38 GPM effluent 2 port during the later part of the demonstration (after bed B was moved to the lead position and bed D was installed. As was seen with the first portion of the demonstration the general pattern is of stability although alkalinity appears to begin substantially below the influent concentration and then rise gradually until it equals the influent concentration. This may be attributable to bicarbonate sorption. The average pH value was 7.73 s.u. with a standard deviation of 0.37 s.u. The average alkalinity when reported as $CaCO_3$ was 150.00 mg/L with a standard deviation of 0.00, and the average alkalinity when reported as HCO_3 was 160.00 mg/L with a standard deviation of 61.64 mg/L the average specific conductance was 425.79 µmhos/cm with a standard deviation of 13.05 µmhos/cm and the average TDS was 292.00 mg/L with a standard deviation of 34.21 mg/L.

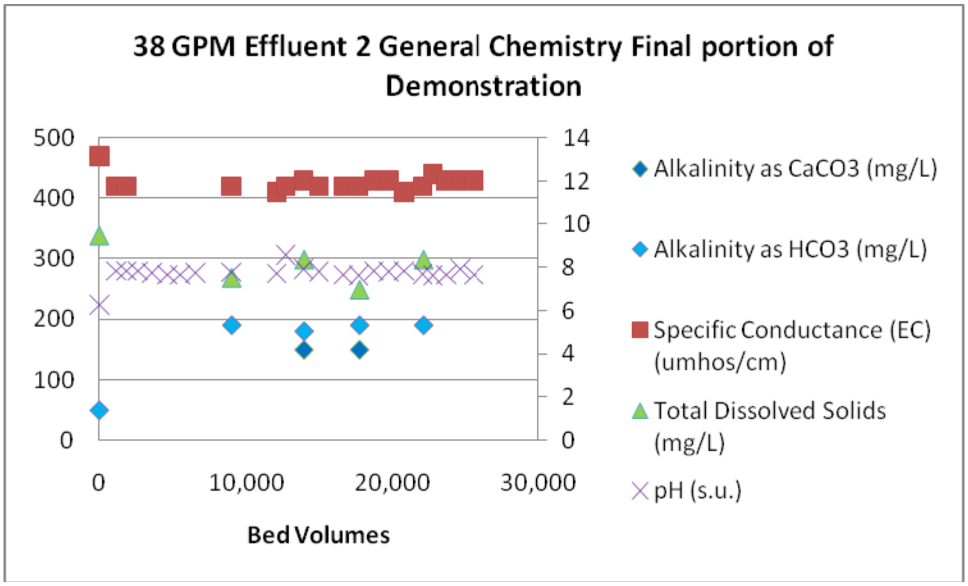


Figure 5-24. GPM Effluent 2 General Chemistry Final Period of Demonstration (BVs as measured through one bed)

5.7.2.5 Anion and Cation Results, 38 GPM System

AFIT analyzed for anion and cation concentrations in the influent and effluent of the 38 GPM TGAC column. Results are reported below.

5.7.2.5.1 <u>Anion Data</u>

Influent and effluent concentrations of chloride, nitrate, sulfate, and bromide were measured over the course of the evaluation. Bromide concentrations were all below detection limits. The mean and standard deviation of influent and effluent concentrations measured after initial column startup are indicated in Table 5-8. There was no statistical difference between the influent and effluent concentrations of the anions measured after initial startup. However during startup there are relevant differences, which are expected.

Table 5-8. Influent and Effluent Concentrations of Anions after Initial Startup for the 38 GPM TGAC Column

Analyte	Number of Samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	19	10.7	2.9
Effluent chloride	19	10.7	2.8
Influent nitrate	19	34.5	4.6
Effluent nitrate	19	34.8	5.2
Influent sulfate	19	16.7	1.1
Effluent sulfate	19	17.0	1.4

Figures 5-25 and 5-26 show how anion concentrations varied during the TGAC startup periods.

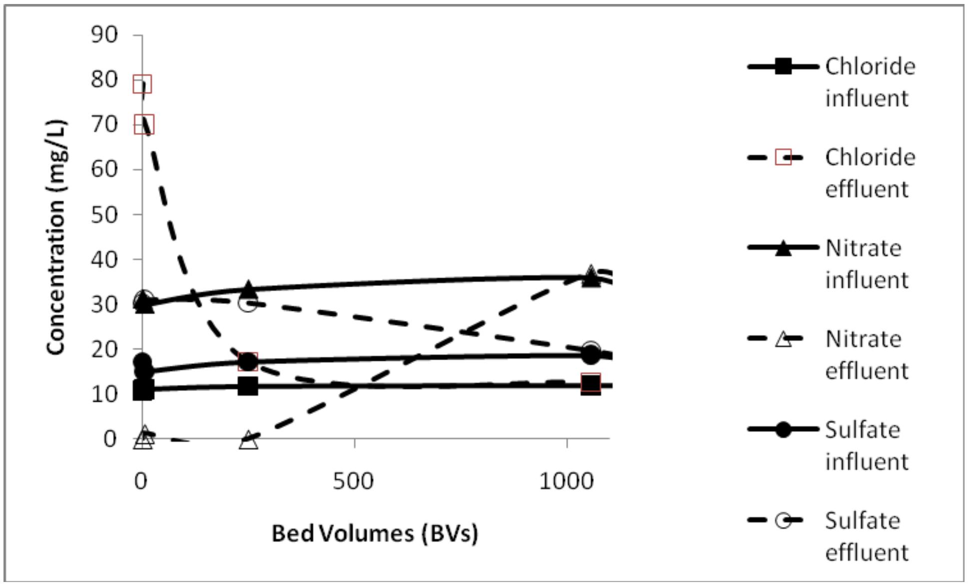


Figure 5-25. Influent and Effluent Anion Concentrations at Initial Startup of 38 GPM TGAC Column (Zero BV Corresponds to January 7, 2007)

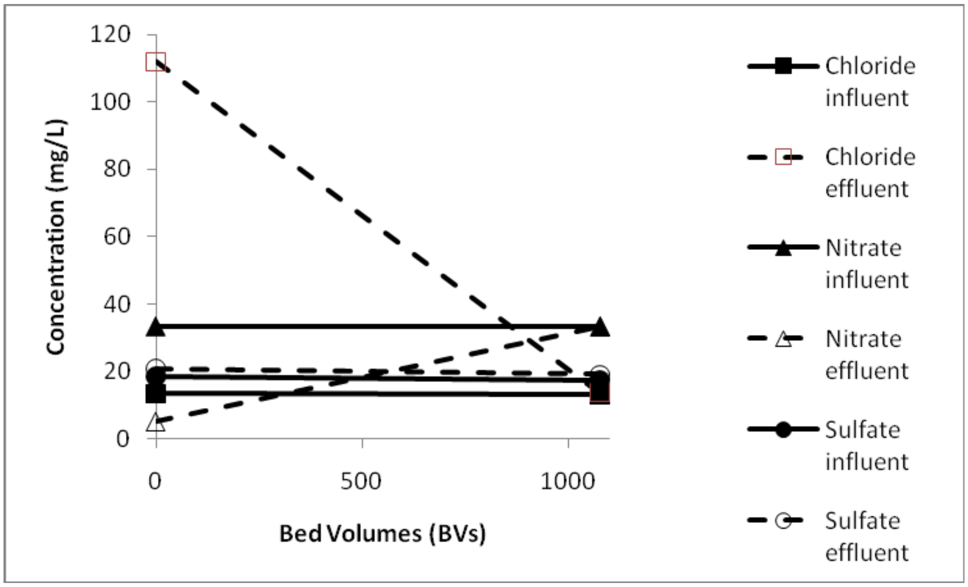


Figure 5-26. Influent and Effluent Anion Concentrations Right After TGAC Replacement in 38 GPM TGAC Column (Zero BV Corresponds to June 8, 2007)

Both figures show consistent behavior for key anions. Initially, chloride effluent concentrations are higher than the influent concentrations. This may indicate early sloughing off of the counterion of the CPC surfactant used to tailor the GAC. At startup (less than 500 BVs treated) nitrate effluent concentrations are less than influent, indicating nitrate sorption by the TGAC. Thus it is possible that initially nitrate and chloride are exchanging. Sulfate influent and effluent concentrations appear about equal during startup. As noted above in Table 5-8, after these initial effects there is no statistically significant difference between influent and effluent anion concentrations.

5.7.2.5.2 Cation Data

Influent and effluent concentrations of potassium, sodium, calcium, magnesium, iron, aluminum, vanadium, and uranium were measured over the course of the evaluation. Iron, aluminum, vanadium, and uranium concentrations were all below detection limits. The mean and standard deviations of measured influent and effluent concentrations are indicated in Table 5-9. There was no statistically significant difference between the influent and effluent concentrations for each of the cations. High frequency cation data were not obtained during the 38 GPM TGAC column startup.

The anion behavior seen at early startup times (<500 BVs) that was distinct from the anion long-term behavior in the 38 GPM TGAC system, was not observed when looking at the cation data. This is not surprising, as we would anticipate that cation concentrations would be unaffected by the TGAC media. However, it may be because the cations were sampled less frequently than anions during the course of the evaluation, so very short-term effects might be missed.

Table 5-9. Influent and Effluent Concentrations of Cations for the 38 GPM TGAC Column

Analyte	Number of samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent potassium	15	2.1	0.6
Effluent potassium	15	2.2	0.5
Influent sodium	8	23.3	5.0
Effluent sodium	8	23.5	5.1
Influent calcium	15	39.4	8.4
Effluent calcium	15	39.8	8.2
Influent magnesium	8	9.9	3.7
Effluent magnesium	8	9.7	3.3

5.7.2.6 Microbiological Testing of TGAC Media

Unused TGAC was submitted for microbiological testing on June 8, 2007; refer to Table 5-10 for complete results. The test confirmed that the new TGAC had no contamination with coliform bacteria and a very low heterotrophic plate count with only 20 colony forming units (CFU) per gram of material (CFU/g).

Spent TGAC was removed from the system after 6 months of operation in which it had filtered 7,539,098 gallons of site water and was also submitted for microbiological testing on 6/8/2007. The spent TGAC measured very low total coliform levels at 22 most probable number (MPN) per gram of material (MPN/g) and no contamination with fecal coliform bacteria. The heterotrophic plate count on the other hand was quite high with greater than 57,000 CFU/g.

On January 21, 2009, a second spent TGAC sample from Bed B was submitted for microbiological testing. The TGAC carbon sample had no contamination with coliform bacteria, but again had a high hetertrophic plate count with greater than 5,700 CFU/g.

Table 5-10. TGAC Microbiological Data

Sample Name	Total Coliform (MPN/g)	Fecal Coliform (MPN/g)	Heterotrophic Plate Count (CFU/g)
TGAC-New-07-06-08	<20	<20	20
TGAC-Spent-070608	22	<20	>/=57000
TGAC1-Carbon-09-01-21	<2	<2	>/=5700

5.7.2.7 38 GPM System Pressure Data

The data collected during system operations was examined to determine if the pressure drop across the beds changed during the demonstration. The lead bed pressure drop data shows a slow, steady increase in pressure drop during the January through July 2007 initial operational period, with only slight increases after that (Figure 5-28). At the beginning of April the system went from one well operation to two wells pumping, this substantially increased the inlet pressure to the system (Appendix D). But this doesn’t seem to have affected the lead bed pressure drop.

The lag bed pressure drop (Figure 5-29) increased fairly dramatically from January through August 2007, then dropped off and held steady. The changes do not seem to be correlated with the well operational change or the change-out in the lag bed.

Bed B is the only bed that served in both positions – lag, and then lead. Bed B pressure drop (Figure 5-30) increased rapidly through June while it is in the lag position, then immediately dropped when it was moved to the lead position. While it is in the lead position it did not appear to increase markedly.

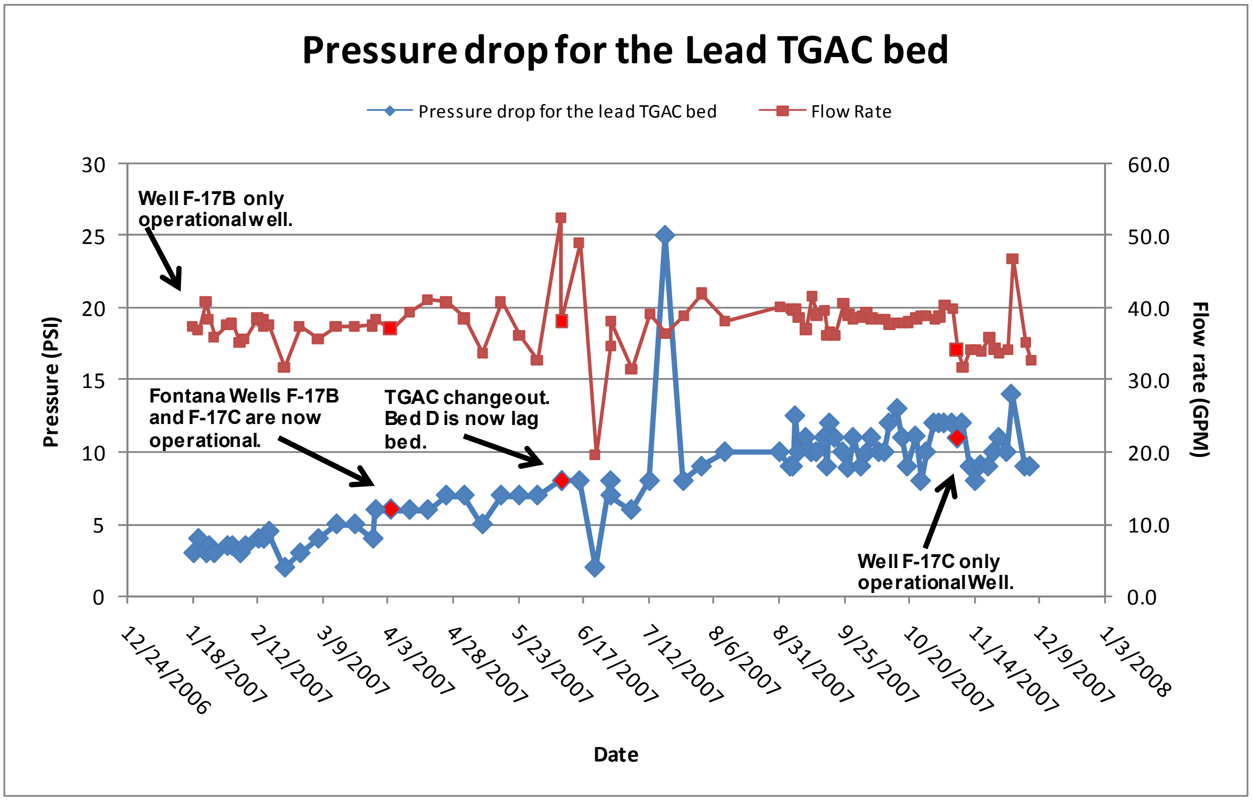


Figure 5-28. Pressure Drop across the Lead 38 GPM TGAC Bed vs. Time

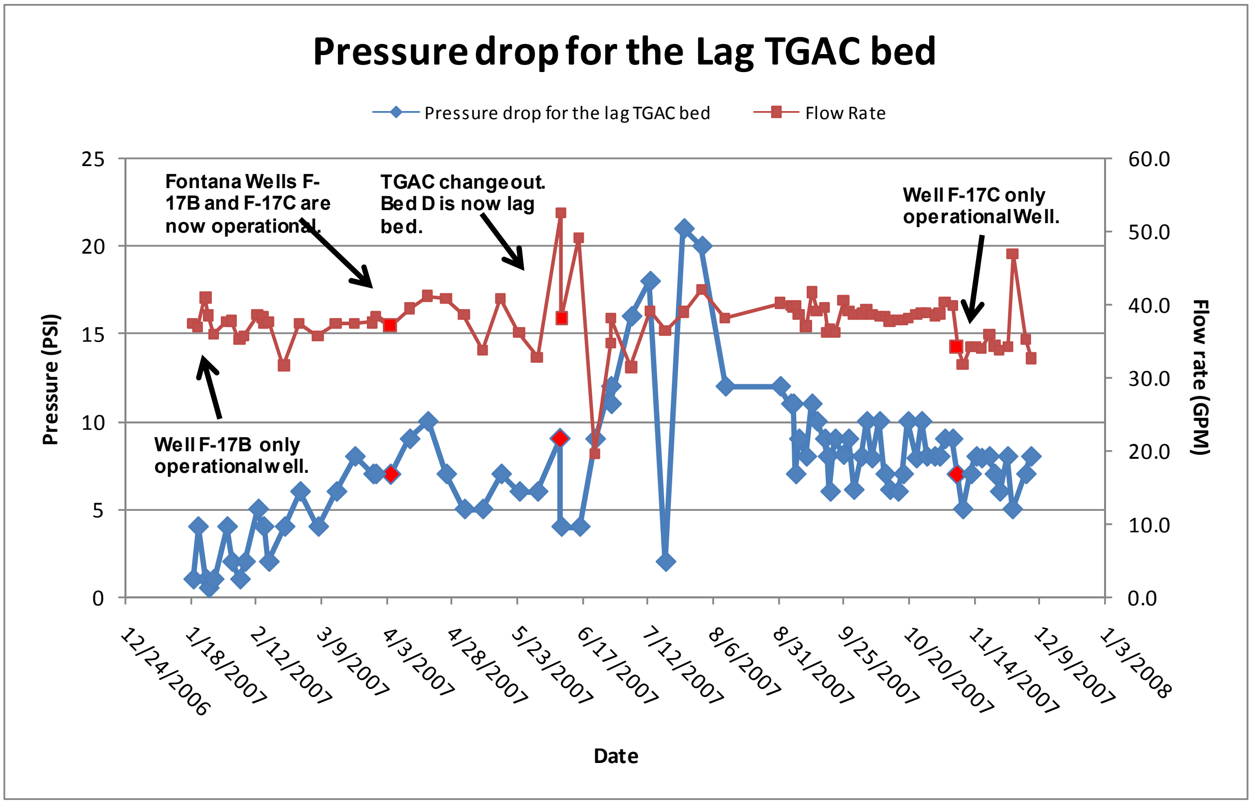


Figure 5-29. Pressure Drop over the Lag 38 GPM TGAC Bed vs. Time

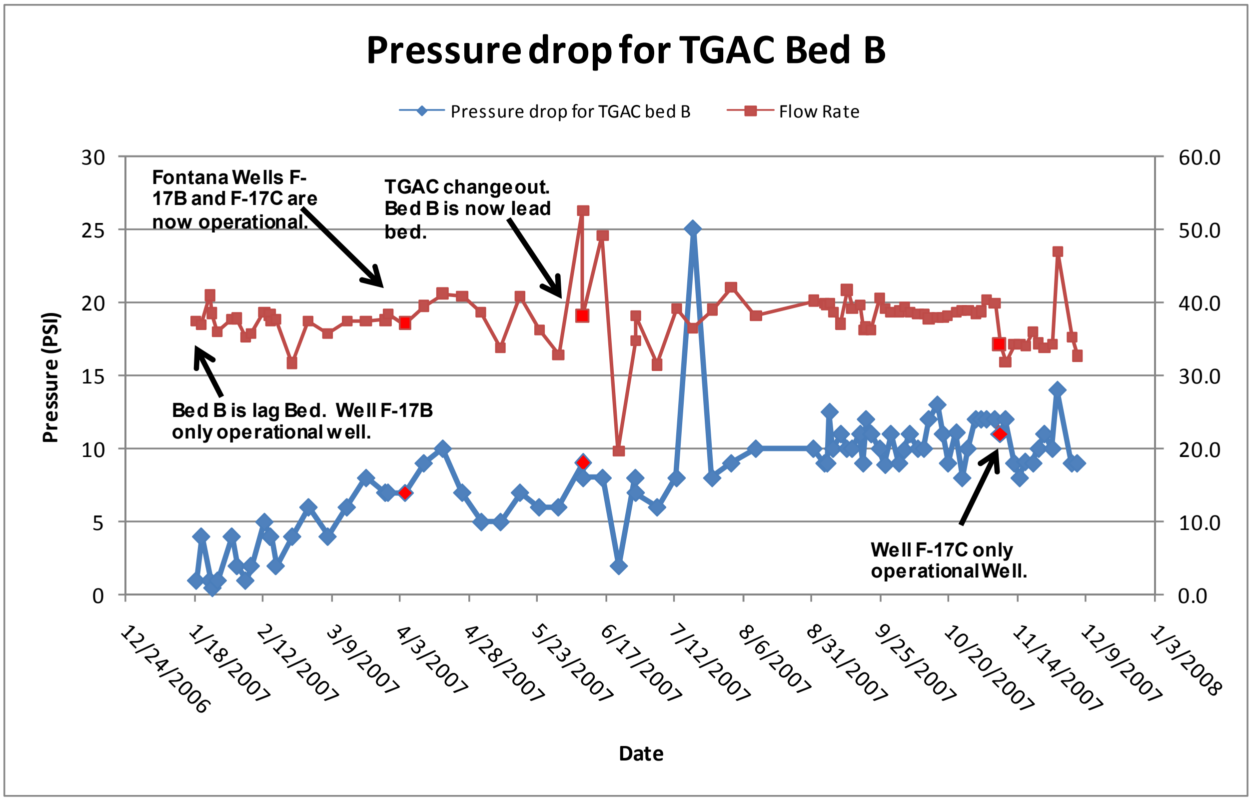


Figure 5-30. Pressure Drop for TGAC Bed B (38 GPM)– in Lag and later in Lead Position

5.7.2.8 Tracer Test Data, 38 GPM

After completion of the field scale testing for perchlorate, a tracer test was performed on one of the beds, as discussed in appendix I.

5.7.3 Six Condition Pilot-scale Sampling Results

The effects of different water chemistry parameters on perchlorate sorption to TGAC were evaluated through the six condition pilot test. The target and actual spiked influent concentrations of these pilot-scale systems is discussed in Section 5.5.4 and are summarized in Table 5-11. The achieved mean EBCTs for these six condition pilot scale beds, operated at 1.5 GPM were slightly longer then for the 38 GPM system (which averaged an EBCT of 10.2 minutes with a standard deviation of 1.81 minutes).

Table 5-11. Summary of Spiking Levels and EBCT in Six Condition Pilot Scale Test

Train Name	Compound Spiked	Mean EBCT (EBCT, Minutes)[2]	Standard Deviation of EBCT	Mean Concentration Unspiked Influent	Standard Deviation Unspiked Influent	Mean Concentration Spiked Train Influent	Standard Deviation Spiked Train Influent
Stratified bed control	None	11.2 / 5.50	3.28 / 0.730	NA	NA	NA	NA
TCE Spiked[1]	TCE	11.5	1.51	<0.5 µg/L	NA	35.7 µg/L	16.2
Perchlorate Spiked	Sodium perchlorate	11.7	3.42	8.0 µg/L	1.7	314.7 µg/L	134.9
Nitrate Spiked	Sodium nitrate	11.6	2.51	40.5 mg/L	3.3	60.9 mg/L	12.1
Predisinfectant/oxidant	Sodium hypochlorite	12.0 / 5.57	6.82 / 1.48	NA	NA	0.28 mg/L	0.33
TDS/Sulfate Spiked	Magnesium sulfate	13.2	6.37	274.3 mg/L	30.6	995.0 mg/L	511.7

Notes to Table:

1. TCE EBCT calculated only for final spiking set-up.
2. Where two values are shown indicates the EBCT @ ~1.5 GPM and ~3 GPM after major flow rate adjustments were made.

Effluent concentrations were monitored after each of the two stratified beds that comprised each of the six condition systems (effluent 1 and effluent 2).

5.7.3.1 Perchlorate Results, Six Condition Pilot-scale System

Table 5-12 lists the BVs to breakthrough for perchlorate in each of the 6 systems. The breakthrough curves for each condition are shown as Figures 5-31 (Effluent port 1) and 5-32 (Effluent port 2).

In the effluent 1 results the perchlorate spike had the most dramatic effect on performance, followed by TDS, Nitrate, and TCE. The predisinfectant/oxidant train also under-performed the control. All of the trains except the TCE spiked train display substantial evidence of a chromatographic roll-over effect.

When perchlorate concentration was 40 times that of the control, a 39% reduction in the TGAC capacity was observed for effluent 1. This was also observed in the bench-scale experiments (Appendix B) and at the effluent 2 port (31% reduction, Table 5-11).

The magnitude of the nitrate effect at the effluent 1 port was approximately a 22% reduction in breakthrough volume when influent nitrate increased from 41 to 61 mg/l. This is consistent with the bench-scale data (Appendix B, Table 2 and Figures 5 and 9) and with the behavior at the effluent 2 port (Table 5-1).

As discussed in Sections 5.4.3 and 5.5.4.2 substantial problems were experienced with the initial design of the TCE spiking system. Therefore our analysis of the effect of TCE in the influent water will focus on the data collected from that train with the second spiking system – after May 22, 2008. In Figure 5-34 that data is compared to the behavior of the lead bed of the control stratified bed train. That figure shows that the range and variance of the perchlorate influent concentration were similar in the two periods of operation. Breakthrough and saturation both occurred in 8-22 percent less BVs with the TCE spiked system than with the control system.

Comparing the effluent 2 dataset to the effluent 1 data set, the greatest inconsistency in terms of tabulated breakthrough time was seen with the predisinfectant/oxidant system, which reduced performance 15% at Effluent 1 and 40% at effluent 2. However a close examination of Figure 5-32 will show that while pre-chlorination had a substantial effect on the time of initial breakthrough at effluent 2, it had much less of an effect on the overall shape of the breakthrough curve. Another possible explanation for this difference in behavior is that the pre-chlorinated train and control train were operated at higher water flow rates during the second half of their operational period than the first (see Section 5.5.3 and Figures 5-10 and 5-14).

The average influent perchlorate concentration during the six column operational period was calculated to be 8.15 µg/L; with most of the data in the range of 6 µg/L and 10 µg/L (Figure 5-33). Blank values at Penn State were nondetect for both field and method blanks. Replicate results showed acceptable reproducibility (see Appendix F for more details).

Table 5-12. BVs to Perchlorate Breakthrough in Six Condition Pilot-scale Test (BVs as Measured Through One Bed)

	BVs to Breakthrough		Difference from Control (%)	
Train	**Effluent 1**	**Effluent 2**	**Effluent 1**	**Effluent 2**
Control (Stratified)	12,794	23,191	NA	NA
TCE Spiked	9,942	21,266	-22	-8.3
TDS Spiked	9,145	19,940	-29	-14
Nitrate Spiked	9,966	17,986	-22	-22
Perchlorate Spiked	7,767	15,894	-39	-31
Pre-disinfectant/ Oxidant	10,881	13,863	-15	-40

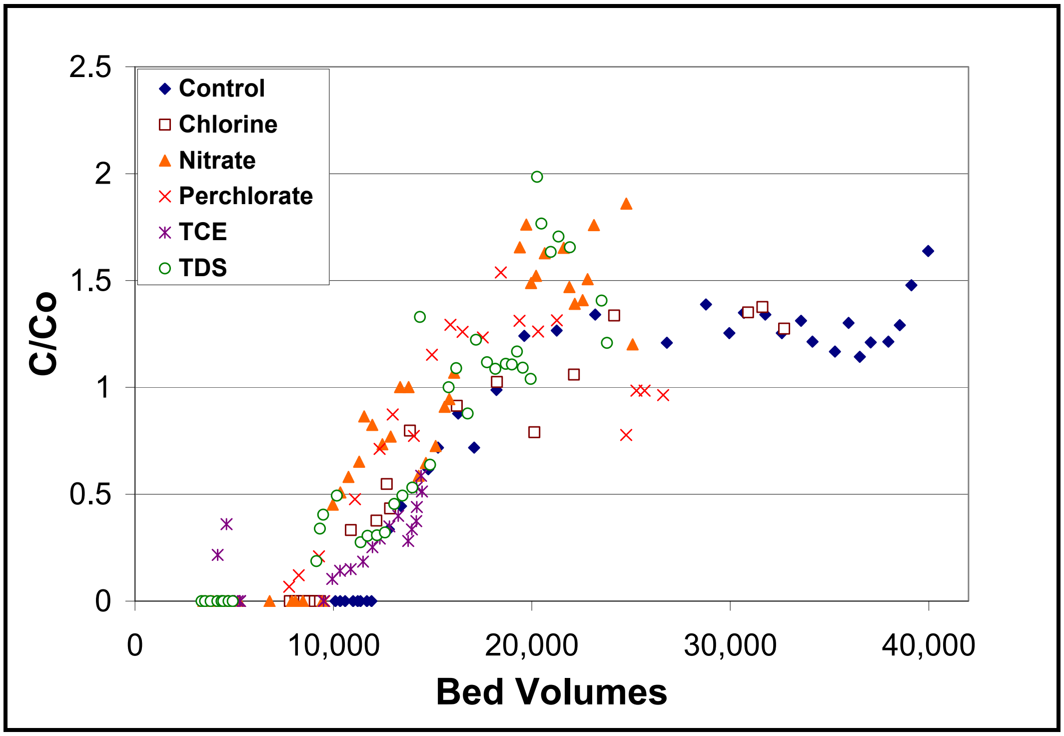


Figure 5-31. The Effects on Perchlorate Breakthrough from Effluent Port 1 of Different Water Chemistries in Six Condition Pilot-Scale Test - Y Axis is Effluent Perchlorate Concentration over Influent Perchlorate Concentration Legend Identifies the Species that was Spiked into the Water (BVs as measured through one bed)

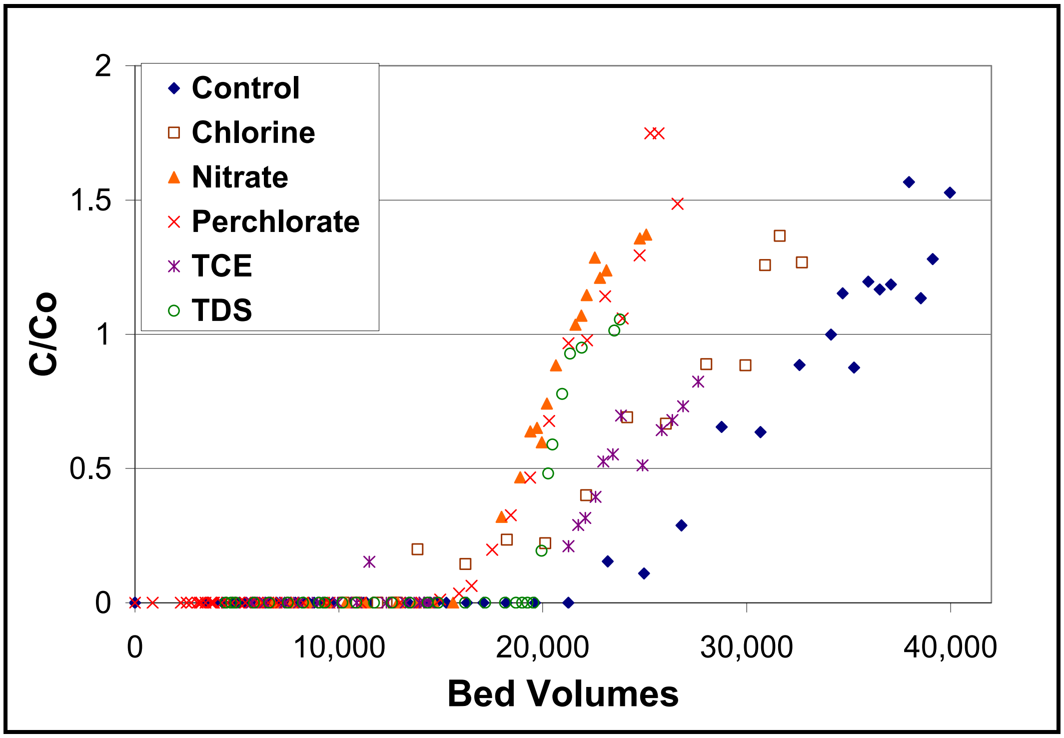


Figure 5-32. The Effects on Perchlorate Breakthrough from Effluent Port # 2 of Different Water Chemistries in Six Condition Pilot-Scale Test - Y Axis is Effluent Perchlorate Concentration over Influent Perchlorate Concentration Legend Identifies the Species that was Spiked into the Water (BVs as measured through one bed)

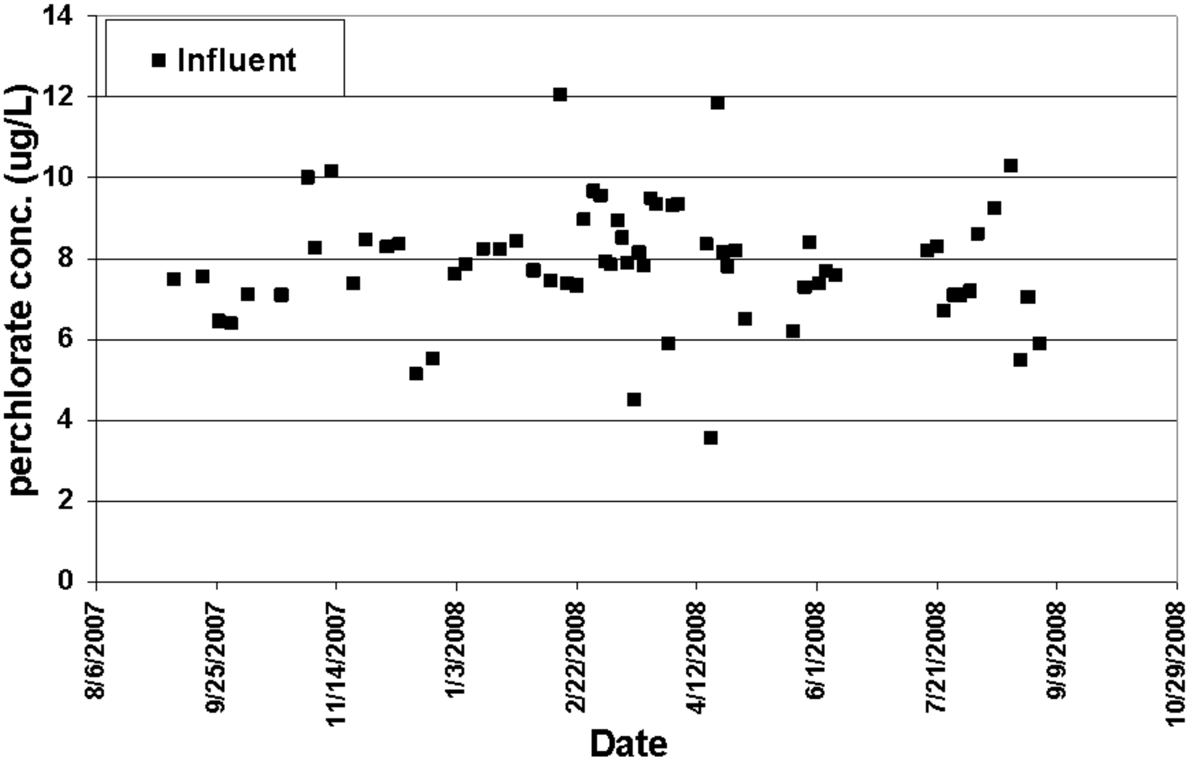


Figure 5-33. Influent Perchlorate Concentration during Six Condition Pilot-scale Tests

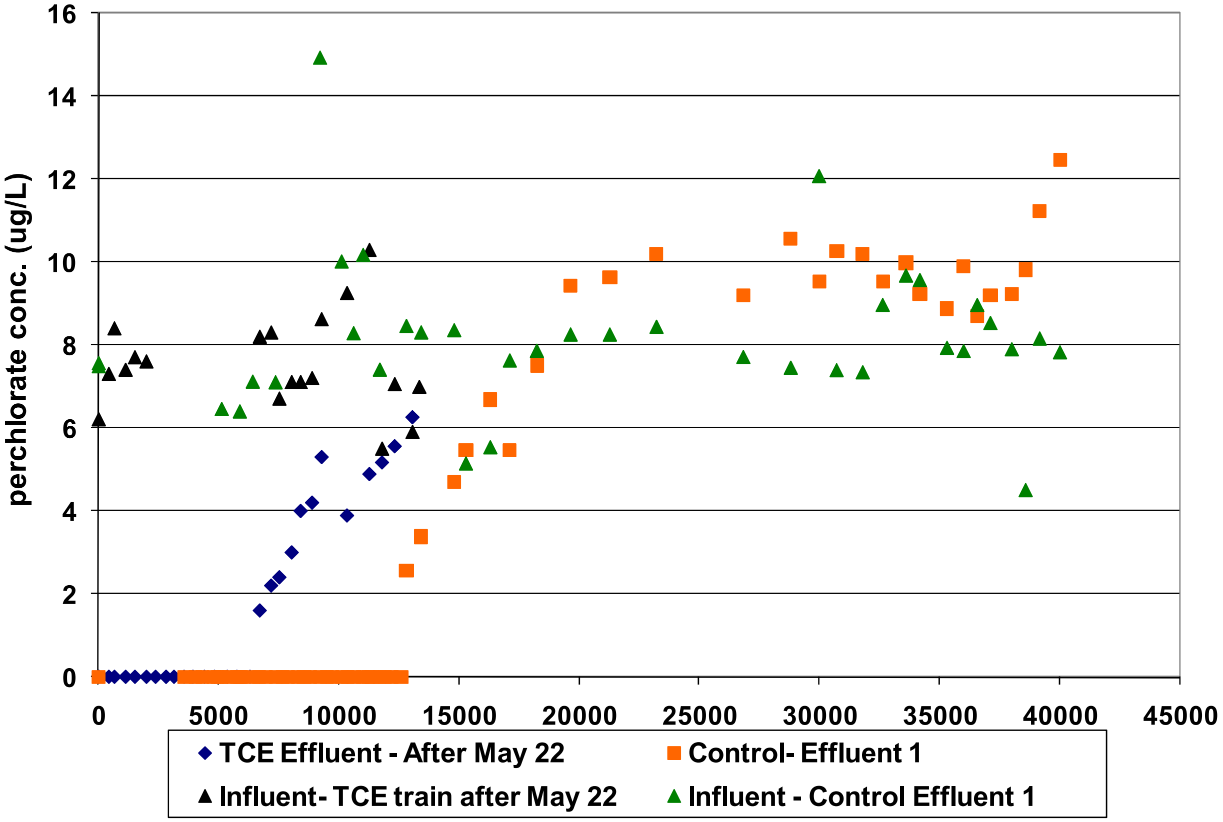


Figure 5-34. Comparison of TCE Spiked Train with Second Spiking System to Control Train (X axis BVs as measured through one bed)

5.7.3.2 CPC Results, Six Condition Pilot-scale Test

Influent and effluent samples for all conditions in the 1.5GPM column demonstration were tested for CPC using the titration method at PSU. Results indicated that no CPC was detected for all samples tested. Samples were tested using water from the effluent 2 ports.

Samples were also tested using the LC/MS/MS method by Exygen Laboratory. Results showed that unlike the titration method that 42.3 Ng/mL of CPC was detected from the stratified bed control Effluent 2 port and 16.5 Ng/mL from the predisinfectant/oxidant train during the first 2,000 BVs. All other conditions tested for the six condition pilot-scale tests were nondetect (i.e., < 0.4 Ng/mL).

Extraction blanks, calibrations, laboratory control spikes and matrix spikes for project samples analyzed by Exygen/MPI were acceptable (see Appendix F for more details).

5.7.3.3 Nitrosamine results, Six Condition Pilot-scale Test

5.7.3.3.1 Six Condition Common Influent

Nitrosamines were sampled on a monthly basis throughout the course of the test, beginning in October 2007, through March 2008. No nitrosamines were detected in any sampling event above the reporting limit of 2 ng/L.

5.7.3.3.2 Stratified Bed Control Train Effluent 2

Nitrosamines were sampled on a monthly basis throughout the course of the test, beginning in October 2007, through March 2008. No nitrosamines were detected in any sampling event above the reporting limit of 2 ng/L.

5.7.3.3.3 TCE, Nitrate, Perchlorate and TDS Spiked Trains

Nitrosamines were not sampled from the effluent of these trains.

5.7.3.3.4 Nitrosamine Quality Assurance Results

Nitrosamines were analyzed for twice from a field blank sample. On January 21, 2008, no nitrosamines were detected above the detection limit of 2 ng/L. On March 3, 2008, N-Nitrosodimethylamine (NDMA) was measured at 2.3 ng/L, all other nitrosamines were below the reporting limit of 2 ng/L.

Selected nitrosamine reports were validated by ARCADIS– the identified issues were quite minor (see Appendix F).

5.7.3.3.5 Pre-Chlorination/Oxidant Train

Nitrosamines were sampled on an appxorimate monthly basis throughout the course of the test, beginning in October 2007, through March 2008 in the specific influent and effluent of this train. No nitrosamines were detected in any sampling event above the reporting limit of 2 ng/L in the influent to this specific train. On December 26, 2007, N-Nitrosodimethylamine (NDMA) was measured at 6.3 ng/L in the effluent. No other nitrosamine was detected in any other sampling event above the reporting limit of 2 ng/L in the effluent.

5.7.3.4 General Chemistry Results,

5.7.3.4.1 Influent General Chemistry for Six Condition Pilot-scale Test Common Influent

Refer to Figure 5-35 for the pH, alkalinity, conductivity and TDS data collected from the six column influent throughout the course of the test. The average pH value was 7.91 s.u., with a standard deviation of 0.10 s.u. The average alkalinity was 182 mg/L with a standard deviation of 24 mg/L, the average conductivity was 424 µmhos/cm with a standard deviation of 6.7

µmhos/cm and the average TDS was 273 mg/L with a standard deviation of 32 mg/L. There was little variance in these conditions over the test period.

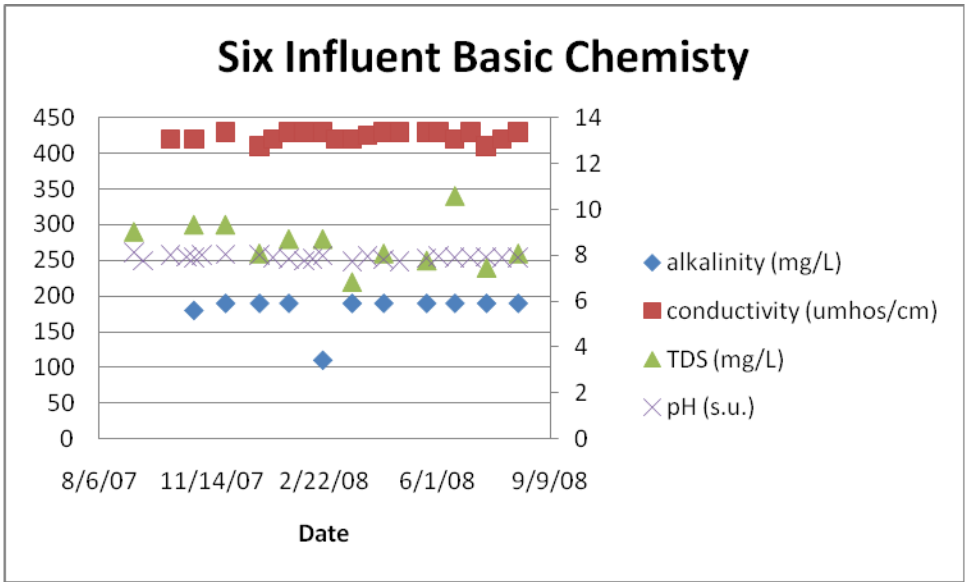


Figure 5-35. Common Influent General Chemistry during Six Condition Pilot-scale Tests

5.7.3.4.2 Stratified Bed Control Train Effluent 2

Refer to Figure 5-36 for the pH, alkalinity, conductivity and TDS data collected from the control train effluent 2 collected from 0 through 37,962 BVs. The average pH value was 7.68 s.u. with a standard deviation of 0.16 s.u. The average alkalinity was 181 mg/L with a standard deviation of 18 mg/L, the average conductivity was 428 µmhos/cm with a standard deviation of 6.5 µmhos/cm and the average TDS was 278 mg/L with a standard deviation of 26.7 mg/L. As with the 38 GPM system, the primary trend of interest is that alkalinity in the effluent starts well below the influent concentration and gradually rises so that effluent becomes approximately equal to influent, suggesting that bicarbonate may be being sorbed initially.

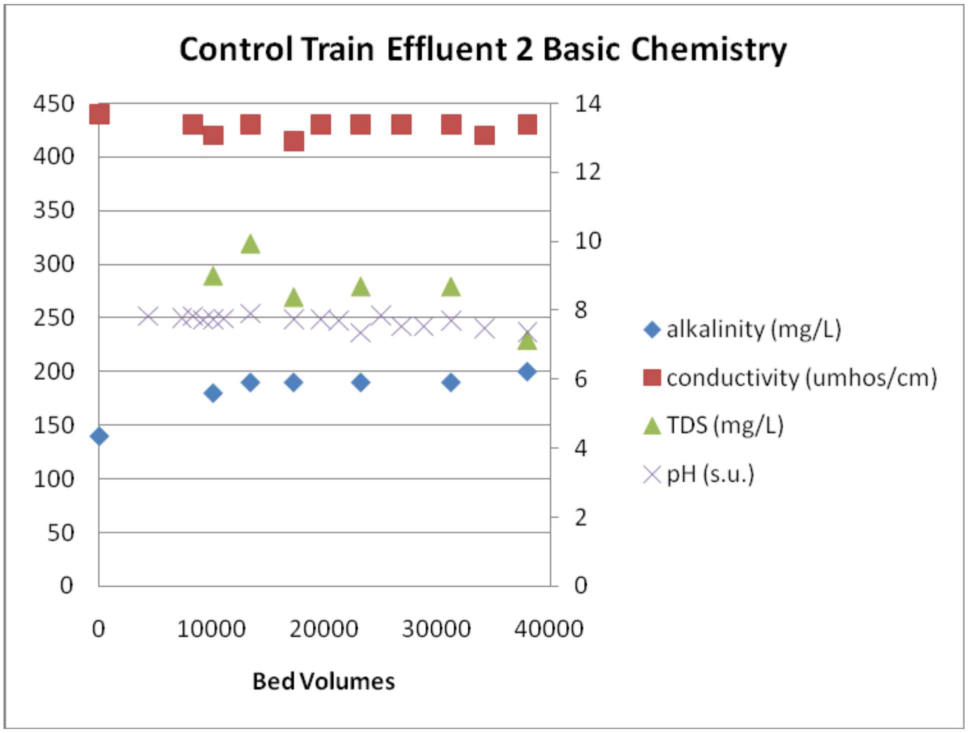


Figure 5-36. Effluent General Chemistry – Stratified Bed Control, Six Condition Pilot-Scale Test (BVs as measured through one bed)

5.7.3.4.3 <u>TCE Train</u>

Refer to Figure 5-37 for the pH, alkalinity, conductivity and TDS data collected from the TCE train effluent, collected from 14,562 through 26,355 BVs. The average pH value was 7.77 s.u. with a standard deviation of 0.10 s.u. The average alkalinity was 193 mg/L with a standard deviation of 5 mg/L, the average conductivity was 426 µmhos/cm with a standard deviation of 5.0 µmhos/cm and the average TDS was 263 mg/L with a standard deviation of 47 mg/L. There were few clear trends in these datasets.

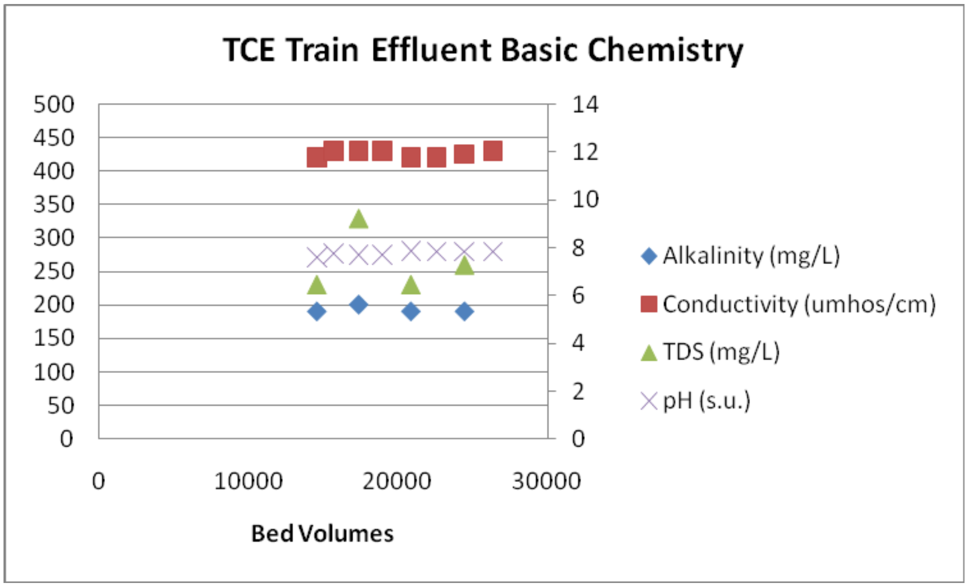


Figure 5-37. Effluent General Chemistry, TCE Spiked Train, Six Condition Pilot-scale System (BVs as measured through one bed)

5.7.3.4.4 Perchlorate Spiked Train Effluent 2

Refer to Figure 5-38 for the pH, alkalinity, conductivity and TDS data collected from the perchlorate train effluent 2, collected from 0 through 26,613 BVs. The average pH value was 7.71 s.u. with a standard deviation of 0.16 s.u. The average alkalinity was 175 mg/L with a standard deviation of 27 mg/L, the average conductivity was 431 µmhos/cm with a standard deviation of 12 µmhos/cm and the average TDS was 272 mg/L with a standard deviation of 33 mg/L. As with other general chemistry data sets, the primary trend was an increase in alkalinity during the run.

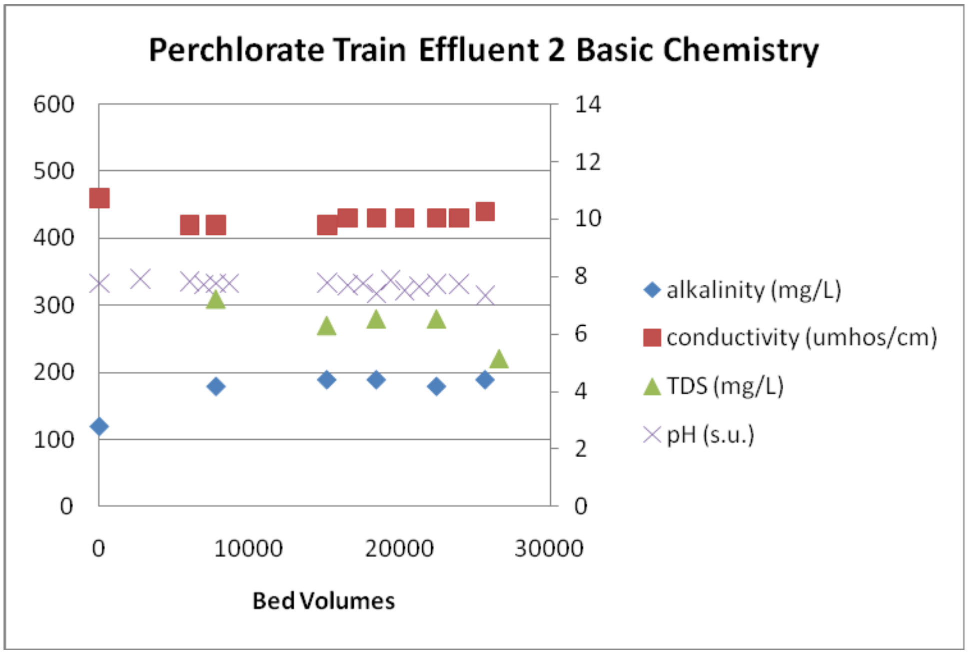


Figure 5-38. Effluent General Chemistry Perchlorate Spiked Train, Six Condition Pilot-scale Test (BVs as measured through one bed)

5.7.3.4.5 <u>Nitrate Train Effluent 2</u>

Refer to Figure 5-39 for the pH, alkalinity, conductivity and TDS data collected from the nitrate train effluent 2, collected from 0 through 24,522 BVs. The average pH value was 7.70 s.u. with a standard deviation of 0.24 s.u. The average alkalinity was 185 mg/L with a standard deviation of 15 mg/L, the average conductivity was 499 µmhos/cm with a standard deviation of 113 µmhos/cm and the average TDS was 317 mg/L with a standard deviation of 63 mg/L. There is one notable outlier in the dataset–conductivity at startup–which likely reflects the system adjustments being made during that time.

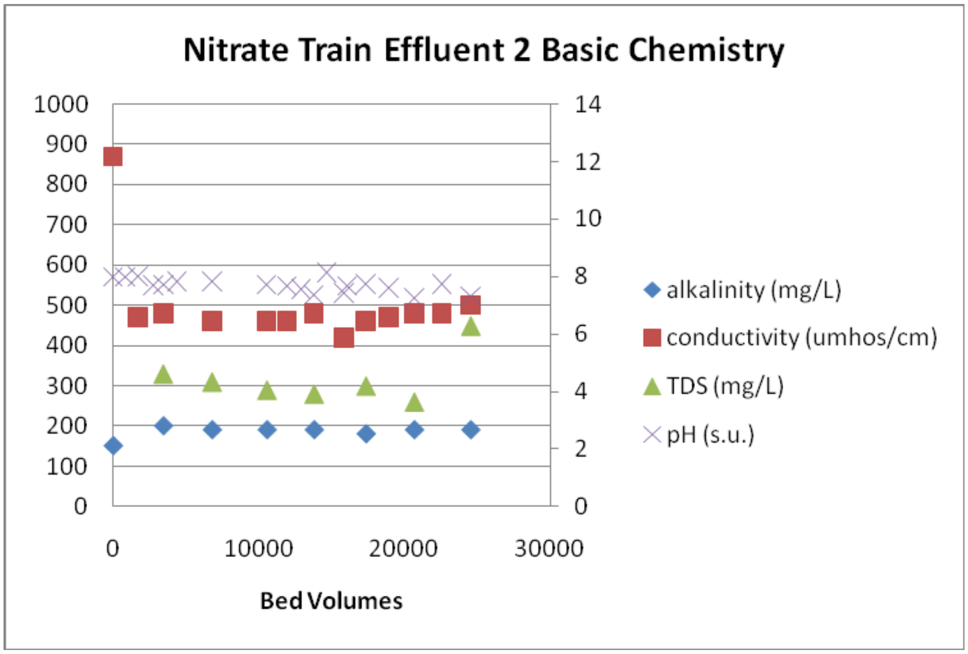


Figure 5-39. Effluent 2 General Chemistry, Nitrate Spiked Train, Six Condition Pilot-scale Test (BVs as measured through one bed)

5.7.3.4.6 Pre-Chlorination/Oxidant Train

TDS were monitored in the specific influent to this train from 0 through 35,753 BVs on a near weekly basis. (Figure 5-40). The average TDS concentration was 271 mg/L with a standard deviation of 40.

Refer to Figure 5-40 for the pH, alkalinity, conductivity and TDS data collected from the disinfectant train effluent 2, collected from 0 through 33,573 BVs. The average pH value was 7.74 s.u. with a standard deviation of 0.15s.u. The average alkalinity was 179 mg/L with a standard deviation of 19.5 mg/L, the average conductivity was 430 µmhos/cm with a standard deviation of 12 µmhos/cm and the average TDS was 284 mg/L with a standard deviation of 49 mg/L.

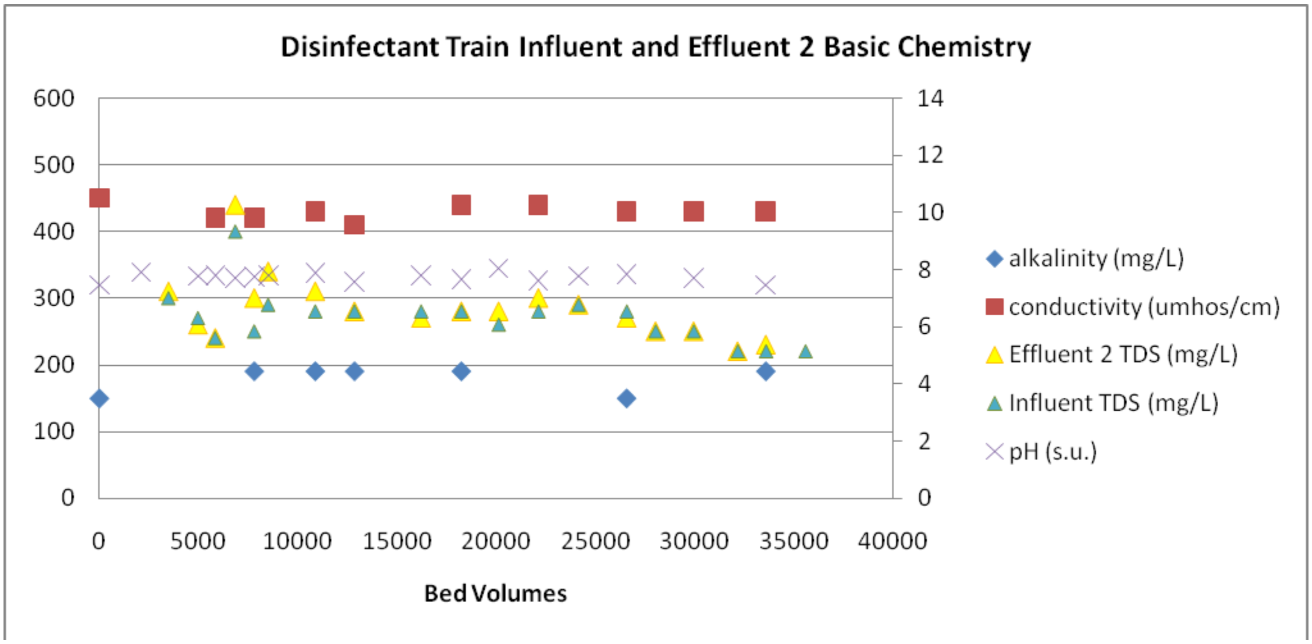


Figure 5-40.Influent and Effluent General Chemistry, Pre-Chlorination/Oxidant Train, Six Condition Pilot-scale Test (BVs as measured through one bed)

5.7.3.4.7 TDS/Sulfate Spiked Train

Refer to Figure 5-41 for TDS data collected from the TDS spiked train influent, collected from 0 through 25,308 BVs on a near weekly basis. The average TDS in the influent was 969 mg/L with a standard deviation of 493 mg/L.

Refer to Figure 5-41 for the pH, alkalinity, conductivity and TDS data collected from the TDS train effluent 2, collected from 0 through 25,308 BVs. The average pH value was 7.68 s.u. with a standard deviation of 0.24 s.u. The average alkalinity was 193 mg/L with a standard deviation of 47 mg/L, the average conductivity was 1266 µmhos/cm with a standard deviation of 502 µmhos/cm and the average TDS was 953 mg/L with a standard deviation of 452 mg/L.

As shown in Appendix E and discussed further in Section 5.4.6 there was substantial variability in the general chemistry of this train because the spiking system for this train was difficult to control.

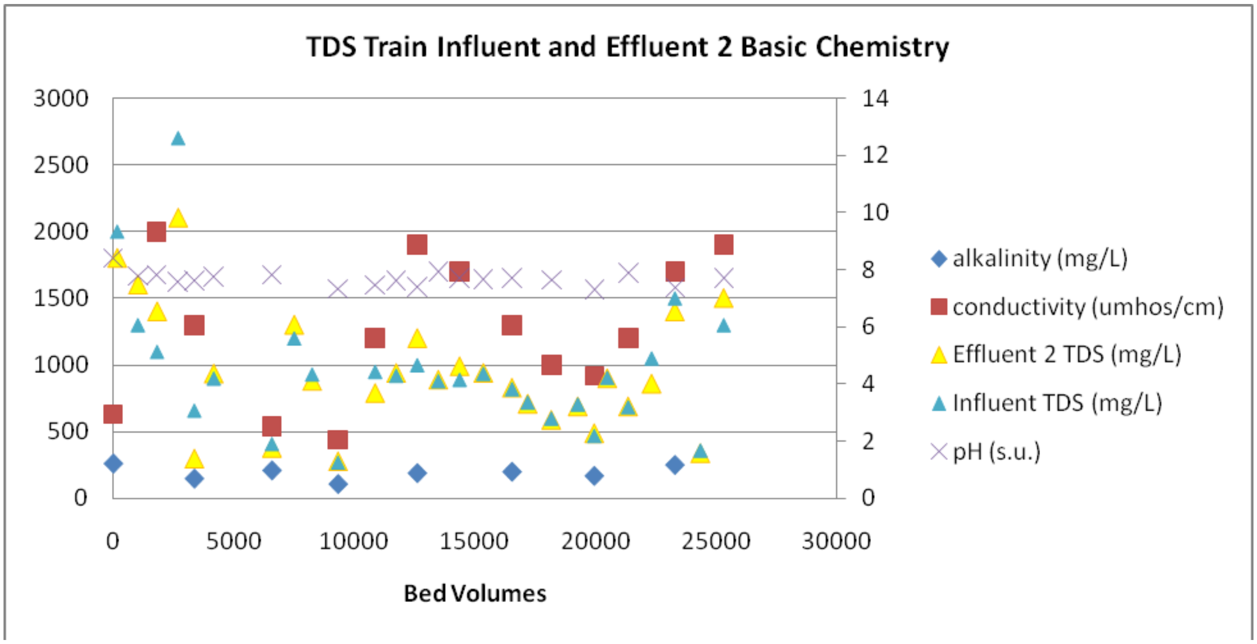


Figure 5-41. Influent and Effluent General Chemistry, TDS/Sulfate Spiked Train, Six Condition Pilot-scale Test (BVs as measured through one bed)

5.7.3.4.8 General Chemistry Field Blanks

A field blank was analyzed for alkalinity three times during the course of the study for an average value of 8.67 mg/L. A field blank was analyzed for conductivity nine times with all results below the detection limit of 2 µmhos/cm. TDS was analyzed for eight times with an average value of 10.88 mg/L. These values for field blanks were well below all of the field samples.

5.7.3.5 Anion and Cation Results, Six Condition Pilot-scale Test

5.7.3.5.1 Anion Results, Six Condition Pilot-scale Test

AFIT analyzed for bromide, chloride, nitrate, and sulfate concentrations in the influent and effluent of the 1.5-3 GPM six-condition field studies. Results are reported in Tables 5-13 to 5-18.

Table 5-13. Influent and Effluent Concentrations of Anions for the Nitrate Spiked Train in the 1.5-3 GPM Six-Column Field Studies

Analyte	Number of Samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	20	12.1	2.11
Effluent chloride	20	12.3	2.17
Influent nitrate	19	63.9	17.0
Effluent nitrate	19	60.5	11.6
Influent sulfate	20	16.8	2.46
Effluent sulfate	20	16.2	3.30

Table 5-14. Influent and Effluent Concentrations of Anions for the Perchlorate Spiked Train in the 1.5-3 GPM Six-Column Field Studies

Analyte	Number of samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	17	11.9	0.63
Effluent chloride	17	11.9	0.44
Influent nitrate	17	40.5	2.06
Effluent nitrate	17	41.4	1.93
Influent sulfate	17	17.0	1.50
Effluent sulfate	17	16.9	1.62

Table 5-15. Influent and effluent concentrations of anions for the TDS/Sulfate Spiked train in the 1.5-3 GPM six-column field studies.

Analyte	Number of samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	20	12.2	0.64
Effluent chloride	20	12.7	6.18
Influent nitrate	21	40.7	3.39
Effluent nitrate	21	49.9	25.7
Influent sulfate	15	444	200
Effluent sulfate	15	405	208

Table 5-16. Influent and effluent concentrations of anions for the TCE Spiked train in the 1.5-3 GPM six-column field studies.

Analyte	Number of samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	31	13.6	2.27
Effluent chloride	31	13.5	2.27
Influent nitrate	31	40.1	3.03
Effluent nitrate	31	36.8	7.38
Influent sulfate	29	17.6	1.43
Effluent sulfate	29	16.8	2.49

Table 5-17. Influent and effluent concentrations of anions for the predisinfectant/oxidant train in the 1.5-3 GPM six-column field studies.

Analyte	Number of samples	Mean (mg/L)	Standard Deviation (mg/L)
Influent chloride	16	11.9	0.65
Effluent chloride	16	12.9	1.47
Influent nitrate	16	40.4	2.07
Effluent nitrate	16	42.1	2.04
Influent sulfate	15	16.9	1.51
Effluent sulfate	15	17.2	1.73

Table 5-18. Influent and effluent concentrations of anions for the control train in the 1.5-3 GPM six-column field studies.

Analyte	Number of samples	Mean (mg/L)	Standard deviation (mg/L)
Influent chloride	17	11.9	0.63
Effluent chloride	17	11.8	0.56
Influent nitrate	17	40.5	2.06
Effluent nitrate	17	40.8	2.34
Influent sulfate	16	16.9	1.46
Effluent sulfate	16	16.5	1.70

Except for the nitrate concentrations in the TDS train and the chloride concentrations in the pre-disinfectant/oxidant train, there was no statistically significant difference between influent and effluent anion concentrations. The statistical significance of the predisinfectant/oxidant train and nitrate/TDS train results was caused by a small number of outliers, and no meaning is attributed to it.

The anion behavior just after startup (approximately the first 500 BVs) of the six-column field study mirrored their behavior during startup of the 38 GPM TGAC column. That is, nitrate effluent concentrations were less than influent (signifying initial sorption of nitrate), chloride effluent concentrations were higher than influent (possibly suggesting exchange of chloride with nitrate), and sulfate influent and effluent concentrations exhibited no trend.

5.7.3.6 TCE Results, TCE Spiked Train

Since the TCE concentration in the Fontana groundwater was low, typically below laboratory detection limits, extensive VOC testing was only performed on the TCE spiked train, at its specific influent port and effluent port. All of the TCE data is included in Appendix D, but this discussion will only focus on the operation of the TCE train with the second spiking system, after May 22, 2008, because of the operational difficulties with the first spiking system discussed in Section 5.5.4.2. As shown in Figure 5-42 TCE breakthrough occurred after perchlorate breakthrough, near the very end of the operation of the TCE train. An estimate made by James Graham of Siemens, using the modeling program IsoCalc predicted breakthrough for TCE at 87,500 BV for virgin carbon under these circumstances.

5.7.4 SDS Results

SDS testing was conducted as discussed in Section 5.5.4. At the end of the test period, all the treatments dosed with hypochlorite still contained free chlorine at approximately 0.2 mg/L. The un-dosed control treatments contained no free chlorine. All samples measured below detection limits for total organic halides and nitrosamines. Only sample SDS-TGAC-1 measured above the detection limit for haloacetic acid (HHA) at 1.8 µg/L Several samples had low concentrations of the volatile organic compounds; bromoform, dibromo-chloromethane, and TCE. The complete results can be found in Table 5-19:

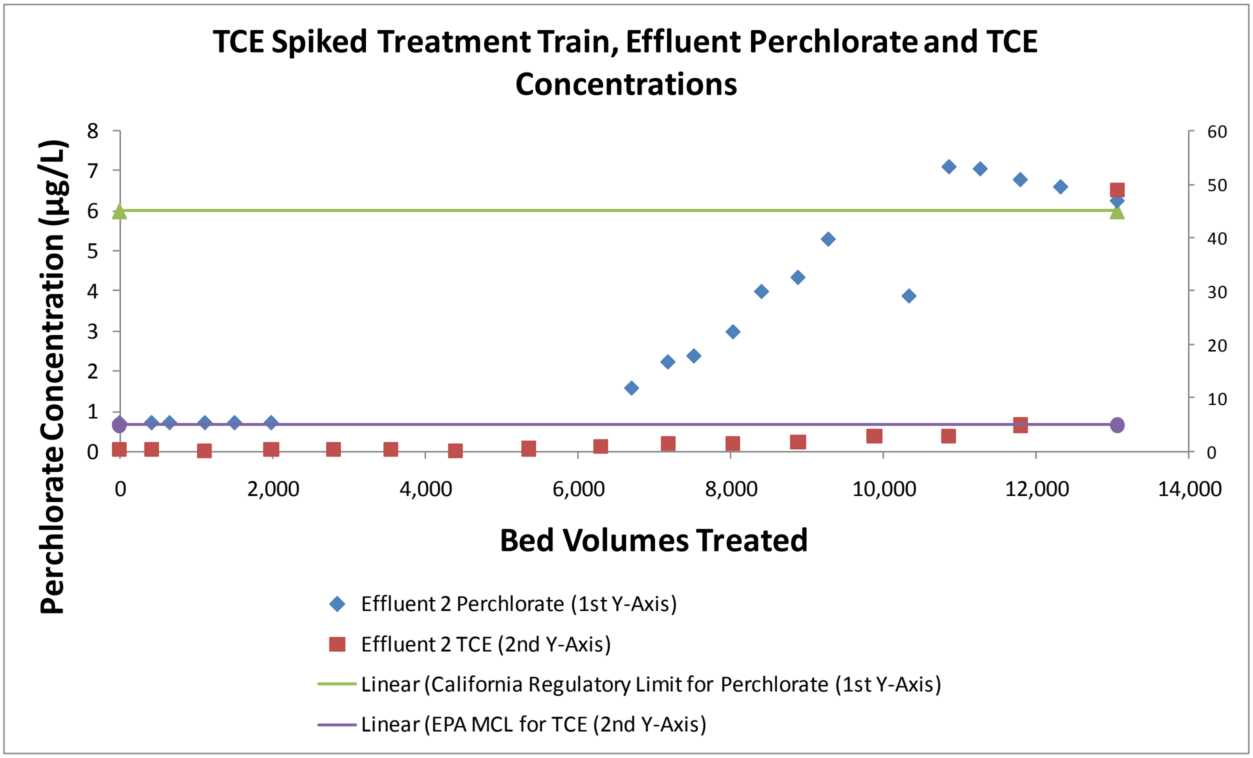


Figure 5-42. TCE and Perchlorate Breakthrough Curves, Six Condition Pilot-scale Train (BVs as measured through one bed), TCE spiked Train

Table 5-19. Results of SDS Test

			HHAs		**THMs (VOCs)**		
Sample ID	**Free Chlorine**	**TOX**	**Dibromoacetic Acid**	**Nitrosamines**	**Bromoform**	**Dibromo-chloromethane**	**TCE**
Units	**mg/L**	**µg/L**	**µg/L**	**ng/L**	**µg/L**	**µg/L**	**µg/L**
SDS-TGAC-1	0.18	ND	1.8	ND	0.76	ND	ND
SDS-TGAC-2	0.20	ND	ND	ND	0.58	ND	0.58
SDS-TGAC-3	0.20	ND	ND	ND	0.74	0.52	ND
SDS-TGAC-4	0.21	ND	ND	ND	0.70	ND	0.52
SDS-TGAC-5	0.01	ND	ND	ND	ND	ND	0.52
SDS-TGAC-6	0.01	ND	ND	ND	ND	ND	ND

This test showed that the potential for the generation of disinfection byproducts following treatment with hypochlorite in the TGAC system is minimal, with the possible exception of the formation of a low concentration (< 1 µg/L L) of bromoform. There was no greater potential for disinfection byproducts following treatment with hypochlorite combined with CPC.

6. PERFORMANCE ASSESSMENT

The performance objectives for the perchlorate systems are listed in Section 3, Table 3-1. Assessment of those objections:

6.1 PERCHLORATE CONCENTRATION REDUCTION

Performance Criterion: Ability of TGAC to Meet Former California DPH NL for Perchlorate

The perchlorate concentration reduction objective was to demonstrate that TGAC could reduce perchlorate concentrations below the California DPH NL, now MCL, of 6 µg/L. TGAC successfully reduced perchlorate concentrations in FWC water below the California NL/MCL of 6 µg/L. Bed A (Lead Bed) of the 38 GPM TGAC system, reduced perchlorate concentrations below 6 µg/L for ~15,000 BVs. Perchlorate concentration was below the detection limit of 2 µg/L in the Bed B (Lag Bed) and Bed C (conventional GAC guard Bed) while Bed A continued operating to perchlorate saturation (defined as an effluent perchlorate concentration of 90 percent or more of the influent perchlorate concentration). After Bed B became the lead bed, the reduction of perchlorate to less than 6 µg/L continued for an additional ~12,000 BVs for a total treated volume of ~30,500 BVs. In the new lag bed (Bed D) a reduction of perchlorate to less than 6 µg/L continued for ~18,000 BVs as measured through one bed. TGAC successfully achieved the perchlorate concentration reduction objective of the demonstration.

6.2 PERCHLORATE MASS REMOVAL AND BREAKTHROUGH VOLUME

Performance Criterion: Ability of TGAC to Meet California DPH NL for Perchlorate for a Consistent Period of at Least Six Months

The perchlorate mass removal and breakthrough volume objective was to demonstrate that the of mass of perchlorate removed per unit volume of TGAC would be sufficient to allow at least six months of treatment with a reasonably sized vessel in a typical application. During the demonstration of the 38 GPM TGAC system, the first lead vessel operated for a period of approximately five months. Bed B operated for approximately four months as the lead bed before perchlorate saturation. Bed D, the lag bed for Bed B, operated for approximately five months. The TGAC approached the perchlorate mass removal and breakthrough volume objective, but did not achieve it during the demonstration.

6.3 AVOIDANCE OF SECONDARY IMPACTS TO DRINKING WATER

Performance Criterion: Ability of TGAC to meet DHS NLs or MCLs for nitrate, metals, NDMA, NDEA, other nitrosamines and tailoring agent

The intent of this objective was to demonstrate that the technology does not cause significant secondary water quality issues.

As discussed in Section 5.7.2.5 and 5.7.3.5 the effect of TGAC on nitrate concentrations was limited to the very initial period of each beds operation when nitrate was adsorbed. Thus the ability of a TGAC system to comply with MCLs for nitrate is primarily controlled by influent quality.

As discussed in Section 5.7.2.5.2 there was no discernable effect of the TGAC technology on metals concentrations, as expected. Therefore the ability of a TGAC system to comply with MCLs for metals is controlled by influent quality or other treatment processes.

For the 38 GPM TGAC system, nitrosamines above the reporting limit of 2 ng/L were detected only in a single sampling event – at startup on January 11, 2007. The Stratified Bed Control train and predisinfectant/Oxidant train from the Six-Condition Pilot-Scale System were also tested for nitrosamines. Nitrosamines above the reporting limit of 2 ng/L were not detected during any sampling event, with the exception of one detection of N-Nitrosodimethylamine (NDMA) of 6.3 ng/L from the effluent of the lag bed of the predisinfectant/Oxidant train. This detection of NDMA however, was below the DPH NL of 10 ng/L.

CPC leaching was also monitored from the 38 GPM TGAC system beds. CPC concentrations were observed during startup of the system, but were non-detect (< 0.2 mg/L by the titration method) after 1,200 BVs of operation for Effluent A and B. There was no CPC detection in effluent of Bed C, the guard bed. After the introduction of Bed D, CPC was observed initially but was non-detect after 20,700 BVs. The guard bed prevented CPC from being leached into the treated water.

6.4 EFFECT OF SECONDARY ANALYTES - TIME TO SATURATION

The effects of different water chemistry parameters on TGAC perchlorate removal were monitored in both bench scale and the six condition field-scale tests as discussed in Sections 5.3 and 5.7.3.

Seventeen rapid small scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results (Appendix B) show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment of pH 4 was 50% greater than the natural occurring pH of the groundwater at 8, and 75% greater than at a pH of 10. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration (60mg/L) reduced the removal of perchlorate by 17%; and a nitrate concentration of 100mg/L reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level. Also the bench scale experiments showed that the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7 (Appendix B).

In the six condition pilot scale tests, focusing on the effluent port 1 results, the perchlorate spike had the most dramatic effect on performance, followed by TDS, Nitrate and TCE. The predisinfectant/oxidant train also performed more poorly than the control. All of the trains except the TCE spiked train display substantial evidence of a chromatographic roll over effect.

When perchlorate concentration was 40 times that of the control, a 39% reduction in the TGAC capacity to absorbed perchlorate was observed for effluent 1. As measured through the effluent 2 port there was a 30% reduction in the TGAC capacity when there is an increased in perchlorate concentration of 40 times. Effects of a similar magnitude were observed in the bench scale experiments when the perchlorate concentration was increased (Appendix B, Table 4 and Figures 5-7).
Breakthrough and saturation both occurred sooner with the TCE spiked system then with the control system. For example the breakthrough occurred 8 to 22 % sooner in the TCE spiked system.

6.5 EASE OF USE - EASE OF OPERATION & MAINTENANCE

Performance Metric: From the perspective of the municipal operator, O&M labor hours would be the same as or better than current IX systems. Level of skill required compared to existing IX systems.

Routine activities that were performed during O&M of the Pilot-Scale treatment Systems included the follow:

- Monitoring and recording of process data including pressures, flow rates, water and ambient air temperatures, and cumulative volume treated.
- Obtaining influent, midpoint, and effluent water samples for process performance monitoring.
- Replacing bag filters in the pre-filter system.
- Removing spent TGAC from the demonstration system for shipment to the Covanta destruction facility.
- Installing fresh TGAC into the demonstration system.
- Inspecting the system for water leaks and process upsets.

The O&M for the pilot 38 GPM TGAC system required approximately two hours for a weekly visit, and approximately 10 to 15 minutes on a daily basis to obtain routine process readings (e.g., temperatures, pressures, flow rates, etc.). The O&M for a three bed, full-scale TGAC system would be similar to the 38 GPM demonstration system. If more than three beds were utilized in a full-scale TGAC treatment system, additional O&M time would be required to obtain the additional monitoring samples.

During the period of operation these activities are likely to be very similar to those required for a similarly sized IX system. However since IX systems using currently available resins are likely to have a longer time to breakthrough, a greater frequency of monitoring is likely to be required for the TGAC system. A faster breakthrough time will also require more operator attention to the breakthrough curve.

6.6 RELIABILITY/ROBUSTNESS - PERCENTAGE OF TIME IN OPERATION

Performance Metric: Operability 98% or greater.

The 38 TGAC system achieved an operational uptime of approximately 97 percent during the demonstration, including causes of downtime that had little or nothing to do with the TGAC technology itself. For the first phase of operation with Bed A, Bed B, and Bed C, the system had an operational uptime of approximately 96 percent. For the second phase of operation with Bed B, Bed D, and Bed C, the system had an operational uptime of approximately 98 percent.

The reasons for the downtime include the shutdown of FWC extraction wells caused by high nitrate concentrations or replacement of the FWC IX resin, maintenance on the FWC extraction wells, leaks from piping and broken pressure gauges for the 38 GPM TGAC system, and a leak on one of the TGAC vessels. PVC piping was used for the 38 GPM field-scale TGAC system. A full-scale treatment system would use steel for all above-ground piping, which would reduce the frequency of piping leaks and increase operational uptime.

6.7 COST REDUCTION - REDUCED TREATMENT COSTS

Performance Metric: Reduce treatment costs significantly over IX technology by reducing waste disposal and/or use of lower priced TGAC compared to Resin.

Please see Section 7 and the cost and performance report for a full discussion of economic issues.

6.8 SCALING

Although no specific performance metric was developed for scalability, the experimental design of the project was intended to allow this to be qualitatively evaluated. Specifically three scales were compared:

- RSSCT
- 1.5 to 3 GPM (six condition pilot scale test)
- 38 GPM (main demonstration)

6.8.1 RSSCT

The RSSCT is a scaled-down version of a full-scale GAC water treatment system that can be used to determine model parameter values to predict full-scale performance within a short period of time. Crittenden et al. (1986 and 1991) pioneered this use of RSSCTs as a rapid method for the design of large-scale fixed-bed GAC adsorbers, and developed and tested scaling equations for designing full-scale adsorbers based upon the results obtained from small column RSSCTs. To apply RSSCT results to simulate a large-scale adsorber, particle size (of the medium), hydraulic loading, and EBCT must be properly upscaled.

Crittenden et al. (1991) found that if the void fractions, bulk densities, and capacities are identical for the GAC used in both the RSSCT and full-scale process, scaling of the EBCT can be determined from:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} = \frac{t_{SC}}{t_{LC}} \qquad (6\text{-}1)$$

Where: SC = Small Column, LC = Large Column
d_p = adsorbent particle size [cm]
t = elapsed time in the respective column test [min]
X = the parameter defining dependence of the intraparticle diffusion coefficient on particle size

Crittenden et al. (1991) note that when internal diffusion controls the adsorption rate so that the intraparticle diffusivity is a linear function of particle size (referred to as proportional diffusivity), exponent = 1 in equation (6-1). For some other applications where the exponent =2 (i.e. X=0), a relationship known as constant diffusivity is simulated. Also other exponents have been employed. For proportional diffusivity the ratio of superficial velocities (*v*, cm/s), of the small and large columns is given by (Crittenden et al, 1991). :

$$\frac{v_{SC}}{v_{LC}} = \left[\frac{d_{p,LC}}{d_{p,SC}}\right] * \frac{\mathrm{Re}_{SC\,\min}}{\mathrm{Re}_{LC}} \qquad (6\text{-}2)$$

Where $\mathrm{Re}_{SC\ min}$ is the minimum Reynold's Number (Re) that guarantees the effects of dispersion and external mass transfer in the small column do not exceed those of the large column. The Reynold's number is defined as (Droste, 1997):

$$\mathrm{Re} = \left[\frac{\rho v \psi d_p}{u}\right] \qquad (6\text{-}3)$$

Where: ρ = density of water [g cm^{-3}]
v = superficial velocity [cm s^{-1}]
u = viscosity of water [g cm^{-1} s^{-1}]
d_p = media grain diameter [cm]
ψ = sphericity of filter media [unitless]

RSSCT results are then used to design a full-scale system. The EBCT for the full-scale system is found by using equation 6-1. The EBCT and the influent flow rate are then used to size the system. The operating time until breakthrough for the full-scale system is found using equation 6-1 where t_{LC} and t_{SC} are the times to breakthrough for the large and small column respectively, and the time to breakthrough of the small RSSCT column is used as with $t_{SC.}$

6.8.2 RSSCT to Demonstration Scale Comparison

In addition to the field-scale tests, this technology has been tested at a demonstration scale at Fontana. The 38 GPM system used at Fontana was much smaller than the full scale FWC system, but the equipment used could be considered full scale if used in a much smaller community. For example given an adequate storage capacity to allow 24x7 treatment operation, no industrial demand or fire flow demand, such a system could supply approximately 500 residents.

Results from the 38 GPM scale showed a lesser capacity for TGAC to adsorb perchlorate than what was observed using the RSSCT. Perchlorate breakthrough was observed at 12,000 BVs for bed A which was used in the lead position (the term breakthrough is defined for this report in section 3.1.7). Breakthrough was observed at 20,000 BVs for bed B which was the initial lag bed. Saturation was observed at approximately 16,000 BVs for bed A (measured through one bed) and 27,000 BVs for Bed B (measured through one bed). Bed D was placed in service at 18,000 BVs as the new lag bed while bed B became the lead bed. A low level of perchlorate breakthrough from Bed D was observed between 21,000 and 26,000 BVs into the demonstration before the concentration reverted to nondetect. Breakthrough clearly occurred at 35,000 BVs and saturation was reached by 40,000 BVs.

With regard to these Fontana trials, these results from the 38 GPM scale showed a lesser capacity for TGAC to adsorb perchlorate than what was observed when using the RSSCT that employed proportional diffusivity similitude. There are several possibilities as to why there could be such a distinction: (a) there could be redox-sensitive species in this water that when in an intermediate-valent state pose considerable competition with perchlorate, but when yet further oxidized pose less competition. (b) proportional diffusivity is not the appropriate similitude to use when sorbing perchlorate onto surfactant tailored media. (c) The pore volume distribution of the GAC used in the pilot scale tests was enough different from those in the RSSCTs to pose considerable difference. (d) Microorganisms decomposed the surfactant and rendered it unable to sorb perchlorate (e) downtime that was experienced at field scale was not experienced at bench scale effected performance (f) perhaps a portion of the field scale beds bypassed/short-circuited. These issues are of continuing interest to the PSU-Arcadis-Siemems team; and some of our appraisal of this issue is presented in Appendix C.

With regard to (a) intermediate-valent species, the PSU team has conducted a comprehensive study of thiosulfate as a surrogate for a number of sulfur-based intermediate species. Hydrogen sulfide is reduced (S_{-2} valence), sulfate is oxidized (S^{+6} valence), and in between are a number of intermediate species such as thiosulfate (S^{+2} valence), persulfates, etc. Our results show that thiosulfate indeed competes with perchlorate, whereas sulfate competes far less. In continuing work at Redlands, California, we also observed thiosulfate or other sulfur intermediates in that water, and observed that these indeed competed with perchlorate sorption in RSSCTs. Moreover, with the proper (stoicheometric) dose of chlorine oxidation, this thiosulfate competition could be alleviated. But if too high a chlorine dose was used, the chlorine could degrade the GAC, and thus render the TGAC less able to remove perchlorate This is further discussed in Section 2.2.3 and Appendix C. However it is unclear that thiosulfate is the cause of the more rapid breakthrough observed at Fontana, as this water when pumped from the ground appears to be more oxidized than the Redlands water. In order to test whether preoxidation improved performance, we operated one small field scale column with prechlorination. We did not see improved performance through this column; and this could either mean that such oxidation was not needed and/or did not help, or that the oxidation dose selected was higher or lower than would be appropriate. Also, the thiosulfate effect seen at bench-scale in Redlands Water (Appendix C) was not seen in one Fontana RSSCT test (Appendix B, Test 11).

With regard to (b) the proportional diffusivity effect, we have observed in Penn State pilot column tests and RSSCTs that for arsenate removal, proportional diffusivity is the correct similitude. Specifically, we have found that when we preload activated carbons with hydrous ferric oxide, then use them to sorb arsenate, the proportional diffusivity RSSCT results match quite closely to the full-grain size pilot tests. Arsenate ($H_2AsO_4^-$) is an oxyanion just as perchlorate (ClO_4^-) is an oxyanion; and it would stand to reason that if proportional diffusivity is the correct similitude to use for the one, it should likewise correct for the other. In this light, the Penn State team recently compared pilot columns to RSSCTs when using University Park groundwater that had been spiked with perchlorate. These trials showed that Proportional Diffusivity overestimated bed life, Constant Diffusivity far underestimated bed life, and a bed designed in between, with d-small / d-large raised to the 1.5 exponent, exhibiting somewhat similar results to the pilot scale (See new Appendix J).

With regard to (c) pore volume distribution, in preparing the material we have aimed to maintain a balance between sorbing a larger amount of surfactant that is arranged with accessible quaternary ammonium heads, and limitating the amount of surfactant that desorbs during operation. Most of our RSSCTs prior to the Fontana study had been conducted with bituminous-based Ultracarb. One test that compared bituminous-based Ultracarb to bituminous-based Aquacarb exhibited nearly the same breakthrough results when using eastern Massachusetts water (Parette et al. 2005b). However, when coconut-based carbon was used, the breakthrough occurred far sooner. Retrospective analysis has shown that the pore volume distribution of the anthracite based Aquacarb that was used at Fontana was quite similar to conventional coconut GAC, in that both of these are primarily microporous with almost no mesopores. The Aquacarb used at Fontana hosts some pores in the 20-30 A range, as shown in the Appendix J. Surfactant confined within narrow micropores may be sorbed in ageometry where the quaternary ammonium head is hidden from access by the perchlorate. Surfactants accumulated in large micropores and mesopores may align in mycellar arrangements, where the quaternary ammonium heads are more accessible to perchlorate. But then the surfactants accumulated in larger pores may be more likely to leach out during water treatment operations. Several of these pore volume distributions appear in new Appendix _J.

With regard to (d) biological decomposition of the surfactant, this was beyond the scope of this study to evaluate; and indeed it would be quite difficult to evaluate. Heterotrophic plate counts indicated that in some cases, microbial growth was present; and these were more prevalent in the top portion of the bed, where they could have accumulated via filtering action by the granular media. The CPC is known as a mild antimicrobial agent; and this is what renders it attractive in its application to mouth washes. The results herein neither confirm nor discount microbial action as a factor in the perchlorate removal performance.

To discern whether such microbial action had decomposed the quaternary ammonium surfactants, one would need to determine how much less surfactant was on the GAC grains after the pilot testing than before. The tests to do this would be methodologically disfficult. If one attempted to do so by weighing the media, other substances besides CPC could have loaded or leached. If one attempted to test by extraction, the CPC could (and surely would) migrate to more recessed pores where it would not be as extractible. Such recessed surfactant could also be less available for removing perchlorate and could thus contribute to lower bedlife observed with long term testing of full scale operations. If one attempted to do this by nitrogen mass balance, other substances could contribute to nitrogen mass, including: the nitrate adsorbed, the partially decomposed surfactant, microbial mass, nitrogen-containing NOM, etc. which would make data interpretation difficult.

With regard to downtime (e), we lack hard data, but do not believe that this would prolong or diminish the bed life to the extent at issue.

With regard to short-circuiting (f) the data presented in appendix I suggests that short circuiting did not occur to a significant degree, although some fluidization of the 38 gpm bed probably did occur.

As discussed above recent tests using perchlorate spiked into Penn State University water suggest that a simultude intermediate between constant and proportional diffusivity, one where exponent=1.5 may be the most appropriate way to use RSSCTs to predict field scale perchlorate performance for TGAC. Thus this difference in simultude would appear to best explain the lack of RSSCT to field scale correlation observed here (See appendix J).

6.8.3 Comparison Between Two Field-scales Tested

Comparing Figures 5-17 through 5-9 (38 GPM system) to the data for the stratified bed control in figures 5-31 and 5-32 we can conclude that semi quantitatively the 1.5-3 GPM tests in the six condition pilot scale test reasonably agreed with the 38 GPM system performances at Fontana. This is an expected result since these two scales were run at essentially the same EBCT thus the simultude approach of Crittenden is not required for this comparision. Since the influent concentrations varied somewhat and the two tests were not conducted simultaneously a more in-depth comparison was not made. A comparision of the stratified bed control (figure 5-31 and table 5-12) to the 38 gpm results (figures 5-17 to 5-19) suggests that the use of stratified beds did not produce significantly different results when compared to the design in which the tailored and untailored carbon were in separate beds.

6.8.4 Scalability Summary

Unexpectedly, the RSSCT did not accurately predict the full scale performance in either the Redlands (Section 2.2.3) or Fontana cases. However the comparison between the two field scales tested does suggest that full scale performance can be predicted from small pilot tests. However these small-scale pilot tests would have the disadvantage of requiring a time equivalent to the full scale EBCT for performance. Thus it is desireable to improve the ability of the RSSCTs to predict full scale performance for this technology which can be done as follows:

- In waters known to be at least mildly reducing (negative redox potentials), and thus to potentially contain unstable reduced sulfur species; perform the RSSCTs at the field site or with very fresh samples (Appendix C).
- Use X=1.5 in the Crittenden simultude to relate RSSCT data to full scale data for TGAC applications (Appendix J)

7. COST ASSESSMENT

Any innovative technology, in order to successfully transition to commercial use, must be cost competitive with established technologies. This section describes a model that was developed to predict the cost of using the TGAC technology to treat water of a specified quality. The model accounts for the presence of anions that compete with perchlorate for sorption sites on the TGAC. The model is then applied to help identify key factors that drive TGAC technology cost. The section concludes with an analysis of an example water, where TGAC treatment costs are calculated using the cost model, and compared with the cost of treating the water using IX, the technology that is conventionally used to treat perchlorate-contaminated water.

7.1 COST AND PERFORMANCE MODEL

A number of isotherms are used to characterize adsorption; the two most commonly used are the Freundlich and Langmuir isotherms (Seader and Henley, 1998). The Langmuir isotherm is derived from simple mass-action kinetics and assumes chemisorption. Parette and Cannon (2005[a]), based on RSSCT trials, concluded that perchlorate adsorption on quaternary ammonium TGAC was associated with charge attraction rather than covalent bonding. Moreover, Chen et al. (2005[b]) effectively used the Freundich adsorption isotherm to characterize perchlorate adsorption on ammonia-tailored GAC, observing that perchlorate adsorption was highly related to change in carbon surface charge; therefore, they concluded that perchlorate adsorption is principally a function of charge rather than a physical interaction.

A TGAC cost model was developed during this project to predict TGAC performance and life-cycle costs to treat perchlorate-contaminated water for various influent water quality and technology operating conditions (Powell 2007; Craig 2008). Using inverse modeling, the model's design parameters were obtained from the laboratory rapid RSSCTs discussed in Section 5.3 and Appendix B. Cost data used in the model were based on conventional GAC installations, modified to account for tailoring.

Due in part to the issues encountered up-scaling the RSSCT results (discussed in Section 6.8), the cost and performance sub-models described in the sections below should not be viewed as fully quantitative design tools, but rather screening models that can be applied to help a user qualitatively understand how the cost and performance of the T-GAC system will vary in response to changes in environmental and operational conditions. In the future, model parameters can be adjusted as additional data become available from pilot- and field-scale operations. However the results of further laboratory testing conducted after the cost model and Fontana field testing were completed suggest that:

- The anthracite based TGAC used in the bench and full scale testing for Fontana probably performed worse than bituminous based TGAC would have and
- the use of exponent=1.5 in the simultude of Crittenden may have better predicted the midpoint of the perchlorate breakthrough curve then the proportional diffusivity assumption (exponent=1) used in designing the RSSCTs in this project. For the conditions proportional diffusivity exponent = 1 overpredicted initial breakthrough performance. Constant diffusivity exponent =2 would have substantially

underpredicted initial breakthrough performance. So the authors tested an interim exponent=1.5 and this slightly underpredicted initial breakthrough but matched the midpoint of the breakthrough cuve. For predicting initial perchlorate breakthough an exponent between 1 and 1.5 would be best.

- our analysis suggests that the full scale performance prediction inaccuraccies caused by these differences roughly cancel each other, therefore the economic analysis presented here should be reasonably reliable for use in technology screening.

7.1.1 Performance sub-model

Craig (2008) utilized the multi-component Freundlich adsorption equation, which incorporates the effect of competing anions on perchlorate sorption (Faust and Aly, 1998):

$$q_e = K_{ClO4} C_{ClO4} \left(\sum_{j=1}^{n} a_{ClO4,j} C_j \right)^{\frac{1}{n_{ClO4}} - 1}$$

where:

q_e = Mass of adsorbed perchlorate per mass of TGAC adsorbent at equilibrium [mg g^{-1}]

K_{ClO4} = Freundlich adsorption coefficient, (mg/g) $(L/mg)^{1/n}$

$1/n_{ClO4}$ = Freundlich adsorption exponent (unitless)

C_{ClO4} = Dissolved perchlorate equilibrium concentration (mg/L)

$a_{ClO4,j}$ = competition coefficient that quantifies the inhibition of adsorption of perchlorate due to the presence of anion j [dimensionless]

C_j = contaminant/competing anion species j concentration [mg L^{-1}]

Parameter values were established based on a best fit of the model to experimental results obtained from 12 RSSCTs conducted at PSU (Craig 2008). The model (originally developed by Powell (2007)) minimizes "total error" to obtain the best fit. The total error is defined as the sum of the percent differences between the model-predicted and observed BVs to breakthrough for the different RSSCT runs. Table 7-1 shows the parameters that were estimated.

Table 7-1. Best-Fit Model Parameters

<table>
<tr><th colspan="6">Freundlich Adsorption Coefficients</th></tr>
<tr><td colspan="3">K_{ClO4}</td><td colspan="3">30.07</td></tr>
<tr><td colspan="3">$1/n_{ClO4}$</td><td colspan="3">0.148</td></tr>
<tr><th colspan="6">Competition Coefficients
($a_{ClO4,\ j}$)</th></tr>
<tr><td>Perchlorate</td><td>Thiosulfate</td><td>Nitrate</td><td>Bicarbonate</td><td>Sulfate</td><td>Chloride</td></tr>
<tr><td>1.00</td><td>0.028</td><td>0.021</td><td>0.00</td><td>0.00</td><td>0.00</td></tr>
</table>

From these results, it was possible to conclude that the presence of bicarbonate, sulfate, and chloride, at the typical concentrations that were studied in the RSSCTs, did not inhibit perchlorate sorption on TGAC. The results also indicate that TGAC is 47.6 times more selective for perchlorate than nitrate (Craig 2008). However, since nitrate is often present in water at concentrations several orders of magnitude higher than perchlorate, it would be expected that perchlorate sorption would be significantly inhibited by the presence of nitrate. On the other hand, thiosulfate, which is typically not detected in water at high concentrations, would not be expected to inhibit perchlorate sorption on TGAC.

Also included in the performance sub-model is allowance for improved performance by configuring two TGAC columns in series (Craig 2008). This improved performance occurs because if only a single bed is being operated, it's necessary to take the bed off-line as soon as breakthrough begins. However, with two beds in series, the first bed can be operated until the GAC is totally exhausted. The extent of performance improvement through series operation is based on the 38 GPM study at Fontana, which used such a configuration (see Section 5.7.2).

Using the performance sub-model, and given a design flow rate, an EBCT for a TGAC column, column configuration (series or stand-alone) and concentrations of perchlorate and competing anions in the influent water, it is possible to predict BVs of water that can be treated before TGAC replacement is needed. Details of the calculation may be found in Powell (2007) and Craig (2008).

7.1.2 Cost Sub-model

The cost model was based on a series of EPA (1979) reports that were developed to estimate costs of various water treatment technologies; these reports were revised and updated by Craig (2008) to apply to the TGAC technology. In particular, Craig used cost data for GAC installations. In the original EPA (1979) reports, cost curves were developed based on manufacturer data, real-world plant construction data, published data, and “unit takeoffs from actual and conceptual designs”. Based on these curves, Craig developed empirical expressions for cost as a function of treatment capacity in GPM. The cost curves were divided into two categories: construction cost curves and O&M cost curves. The construction costs were subdivided into the following subcategories: excavation, site work, and concrete (ESC);

manufactured equipment (ME); labor; pumps, piping, and valves (PPV); electrical and instrumentation (EI); and housing.

The U.S. EPA report also includes several O&M subcategories (EPA 1979). These are: energy, maintenance material, and labor. Energy can be broken into two categories: building-related energy and process energy. If a building/housing unit is not required, this cost can be ignored and only the process energy taken into account. If a building/housing unit is required, the energy cost is the sum of the building and process energies. Maintenance material costs include the cost of replacing unit components periodically in order to keep the system running. Labor includes O&M labor.

Additional cost elements specific to TGAC were included in the model to ensure a thorough cost analysis. In addition to the capital costs listed above, the cost of tailoring the GAC was included in the capital cost. Additional O&M costs include media costs, disposal and transport. The media costs include the cost of replacing the spent TGAC (these costs are dependent on the water chemistry that dictates the TGAC utilization rate, as predicted by the performance model) and the cost of annual replacement of conventional GAC in the polishing "guard" bed, which is assumed to be operated in series after the TGAC bed(s) to remove the tailoring agent and other organic contaminants from the water.

In our analysis, the capital cost in 2007 dollars was converted into equivalent annual payments using the capital recovery factor over a 20-year planning horizon. This annualized cost was then added to the annual O&M costs to derive a total annual cost. The analysis assumed the annual O&M costs would be constant over the years. Additionally, the model used a 2.8% real interest rate as specified by the Office of Management and Budget (OMB) Circular A-94 (OMB 2009). The real interest rate represents the time value of money adjusted for inflation.

Although not directly tested in this demonstration, the potential for GAC reactivation was considered in the economic analysis presented in this section. The concept of reactivation of GAC that has been tailored for perchlorate removal has been tested at bench scale (Chen and Cannon, 2005[b]). Resulting material losses from the reactivation process range from 10% to 20% each cycle (Marve and Ryan, 2001). The source of this attrition is caused from transport losses and carbon burn-off (Clark and Lykins, 1989). It is envisioned that spent TGAC would be thermally reactivated. During reactivation, the quaternary ammonium group would be either volatilized or charred; necessitating reapplication of the surfactant following reactivation (Cannon 2009). The cost model permits the user to specify whether or not the media is to be reactivated. If reactivated, cost savings over using new media of $0.30 per pound are assumed.

Additional information on development of this cost model is available in Powell (2007) and Craig (2008).

7.1.3 Combined cost and performance model

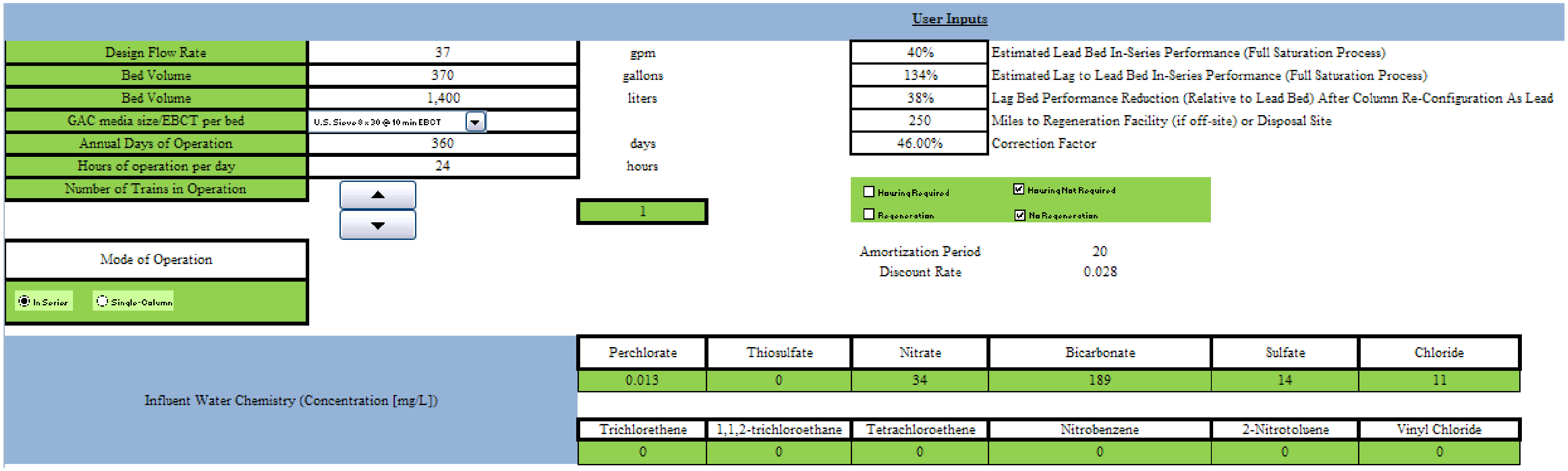
The cost and performance model is an Excel program that is provided with this report. User inputs to the model include: design flow rate, GAC media size, EBCT per bed, annual days of operation, hours of operation per day, the mode of operation (in-series or single-column), the number of trains in operation, if housing is required, miles to the regeneration facility, and if TGAC regeneration will be conducted. Also required are concentrations of the following anions: perchlorate, thiosulfate, nitrate, bicarbonate, sulfate, and chloride. In addition, the assumed amortization period and discount rate are needed. Figure 7-1 shows the user input screen for the cost and performance model.

Based on the input, the performance sub-model determines the BVs of water that can be treated, which is then used as input for the cost sub-model. The final output of the cost and performance model is the cost of treatment per acre-ft of water (Figure 7-2). The output includes both the total O&M cost and the capital cost (both total and annualized based on the amortization period and the given discount rate).

7.1.4 Application of model to predict 38 GPM field demonstration costs at Fontana

The cost and performance model was used to simulate the capital and O&M costs of the 38 GPM field demonstration at Fontana. Table 7-2 shows the model predictions and the actual Fontana 38 GPM pilot study costs. The difference between the model prediction and the actual capital costs was approximately 0.6%.

O&M cost elements of the 38 GPM demonstration were also modeled and compared with actual costs (Table 7-3). The difference between the model estimated annual costs and the Fontana experimental site actual annual costs was 27.6%.



User Inputs

Design Flow Rate	37	gpm
Bed Volume	370	gallons
Bed Volume	1,400	liters
GAC media size/EBCT per bed	U.S. Sieve 8 x 30 @ 10 min EBCT	
Annual Days of Operation	360	days
Hours of operation per day	24	hours
Number of Trains in Operation	1	

40%	Estimated Lead Bed In-Series Performance (Full Saturation Process)
134%	Estimated Lag to Lead Bed In-Series Performance (Full Saturation Process)
38%	Lag Bed Performance Reduction (Relative to Lead Bed) After Column Re-Configuration As Lead
250	Miles to Regeneration Facility (if off-site) or Disposal Site
46.00%	Correction Factor

☐ Housing Required ☑ Housing Not Required

☐ Regeneration ☑ No Regeneration

Amortization Period	20
Discount Rate	0.028

Mode of Operation

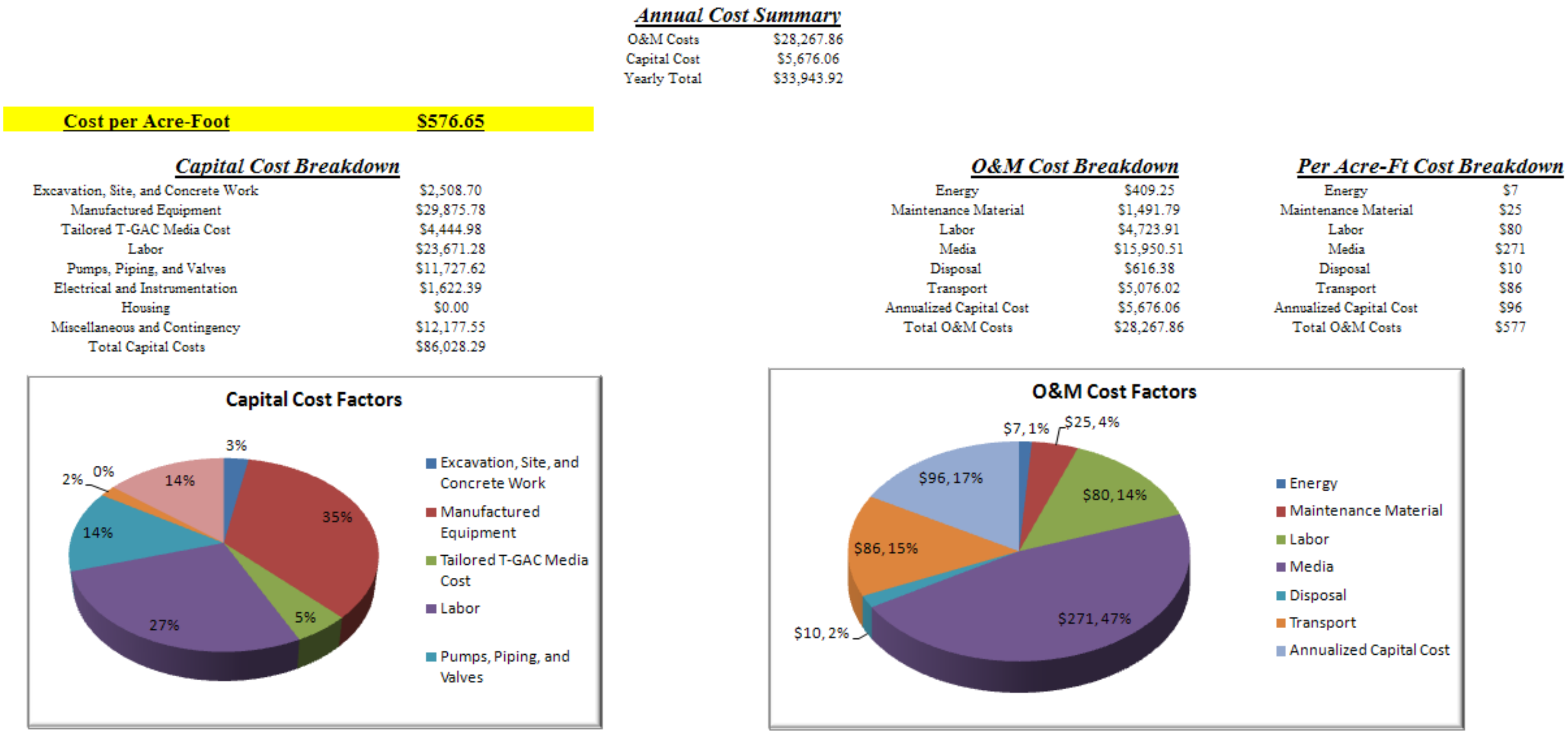
● In Series ○ Single-Column

Influent Water Chemistry (Concentration [mg/L])

Perchlorate	Thiosulfate	Nitrate	Bicarbonate	Sulfate	Chloride
0.013	0	34	189	14	11

Trichlorethene	1,1,2-trichloroethane	Tetrachloroethene	Nitrobenzene	2-Nitrotoluene	Vinyl Chloride
0	0	0	0	0	0

Figure 7-1. Input Screen of Cost and Performance Model.



Annual Cost Summary

O&M Costs	$28,267.86
Capital Cost	$5,676.06
Yearly Total	$33,943.92

Cost per Acre-Foot **$576.65**

Capital Cost Breakdown

Excavation, Site, and Concrete Work	$2,508.70
Manufactured Equipment	$29,875.78
Tailored T-GAC Media Cost	$4,444.98
Labor	$23,671.28
Pumps, Piping, and Valves	$11,727.62
Electrical and Instrumentation	$1,622.39
Housing	$0.00
Miscellaneous and Contingency	$12,177.55
Total Capital Costs	$86,028.29

O&M Cost Breakdown

Energy	$409.25
Maintenance Material	$1,491.79
Labor	$4,723.91
Media	$15,950.51
Disposal	$616.38
Transport	$5,076.02
Annualized Capital Cost	$5,676.06
Total O&M Costs	$28,267.86

Per Acre-Ft Cost Breakdown

Energy	$7
Maintenance Material	$25
Labor	$80
Media	$271
Disposal	$10
Transport	$86
Annualized Capital Cost	$96
Total O&M Costs	$577

Figure 7-2. Cost Result Screen of Excel based Cost and Performance Model

Table 7-2. Capital Cost Elements, Model Predictions, Actual Costs and Notes for Fontana 38 GPM Field Demonstration (Craig 2008)

Capital Cost Elements	Model Estimated	Fontana Experimental Site Actual Costs	Explanation of Field Expenses
Site Preparation	$2,500.	$5,530.	Based on 50-50 split of 38 GPM and 6-Condition Column costs[1]
Manufactured Equipment	$30,140.	$76,840	Includes all expenses needed to produce, transport, install, and start-up the system on-site.[2]
Tailoring GAC Media Cost (CPC)	$15,600[4].		
Pumps, Piping, and Valves	$11,810.		
Miscellaneous and Contingency	$12,240.	$12,240	Engineering and design drawings
Electrical and Instrumentation	$1,630.	$3,630.	Based on 50-50 split of 38 GPM and 6-Condition Column costs[3]
Labor	$23,730.		Labor costs were included in expenses and not broken out separately
Total Capital Costs	$97,650.	$98,240.	Deviation of 0.6%

Note 1: Total site preparation expense was $11,050 for the entire Fontana demonstration. Site preparation cost for the 37GPM plant is considered to be half.

Note 2: Complete cost to furnish the TGAC system was $86,200. This cost includes media change-out and installation of Bed D. To discount this media-change-out, $9,356 was subtracted; bed volume: 375 gallons (approximately 1,562 pounds of TGAC media in vessel); $5.99/lb CPC-tailored TGAC media (Peschman 2007); 1,565 lb x $5.99/lb = $9,356).

Note 3: Total electrical and instrumentation expense was $7,250 for the entire Fontana demonstration. Electrical and instrumentation cost for 37GPM plant was considered to be half.

Note 4: Tailoring media cost is based on demonstration media expenses ($5.99/lb) minus estimated conventional GAC cost ($1.00/lb) (Cannon 2007); 1,565 lb/bed x $4.99/lb x 2 beds = $15,619.

Table 7-3. O&M Cost Elements Model Estimates of Fontana 38 GPM Field Demonstration

O&M	Model Estimated Annual Costs	Fontana Experimental Site Actual Annual Costs	Explanation of Field Expenses
Energy Costs	$500	$500	Model electricity costs estimated at $0.0616 per kW-hr and actual Fontana electricity costs estimated at $0.0633 per kW-hr.
Maintenance Material Costs	$1,200	$9,800	Maintenance material costs assumed to be 10% of the capital cost.
Labor Costs	$8,500	$8,300	Model predicted 161 hours per year and actual hours per year was 156. Hourly wage rate of $53 per hour used.
Total Media Costs	$35,000	36,025	Model predicted carbon utilization rates (CURs) utilized. TGAC cost was $5.99 per cubic foot for both estimates. Actual GAC cost estimated at $1.68 based on several real-world site costs.
Disposal	$600	$15,000	Actual cost based on contract costs.
Transport	$4,600		
Total O&M Cost	$50,400	$70,209	
	Deviation = 27.6%		

7.2 COST DRIVERS

Sensitivity analyses were conducted using the cost and performance model to estimate how individual parameter values affected overall cost. The effects of the following parameter values and operational characteristics on cost were evaluated: flow rate, influent water quality, parallel versus series operation, media regeneration versus replacement, housing, media size, and EBCT.

The first parameter considered was flow rate. It was found there are significant economies of scale, and as the flow rate increased, treatment costs per unit ($ per acre-ft) decreased. However, as shown in Table 7-4, above 400 GPM, the decreases in unit costs with increases in flow rate were greatly diminished.

Table 7-4. Effect of Flow Rate on Relative Unit Costs to Treat Fontana Water

Flow Rate (GPM)	10	25	50	200	400	1600
Relative Unit Cost	3.03	1.84	1.42	1.16	1.06	1.00

Similar analyses were conducted for other parameters and operating conditions (Craig 2008). As an example of these analyses, Tables 7-5 and 7-6 show the effect of influent water quality and EBCT on unit treatment costs, respectively. Table 7-5 was developed using influent water quality data from three sites where the TGAC technology has been tested. Note that relative costs were determined using the model and are not based on actual cost data from the sites. Table 7-5 shows the strong effect of nitrate concentration on relative unit costs.

Table 7-5. Effect of Influent Water Quality on Relative Unit Treatment Costs

Water Source	Perchlorate Concentration	Nitrate Concentration	Relative Unit Cost
Fontana	13 ppb	34 ppm	1.0
Redlands	75 oob	16 ppm	0.75
Massachusetts	5.6 ppb	0.4 ppm	0.41

Table 7-6. Effect of EBCT* on Relative Unit Costs to Treat Fontana Water

EBCT (min)*	2.0	3.0	3.5	4.5	5.0	10.
Relative Unit Cost	2.19	1.29	1.16	1.04	1.03	1.00

*EBCT = reactor volume/water flow rate

The effect of EBCT on unit costs that is shown in Table 7-6 is typical of GAC adsorbers, because true equilibrium is not achieved during operation (Faust and Aly, 1998). Figure 7-3 from Faust and Aly (1998) shows how carbon usage rate (and, therefore, cost) increases with decreasing EBCT in a typical GAC operation.

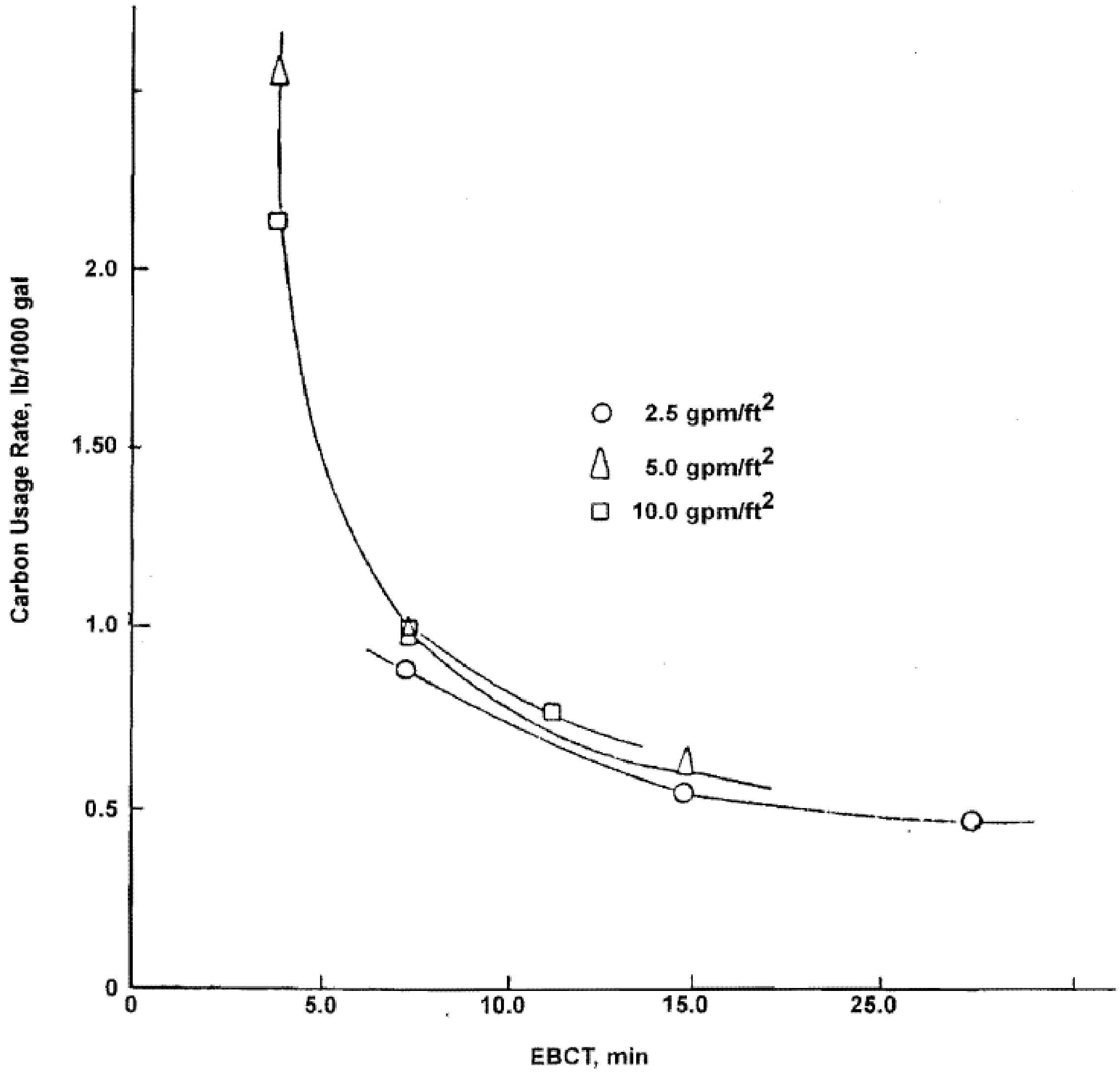


Figure 7-3 Carbon Usage Rate vs EBCT (Faust and Aly, 1998)

7.3 FULL SCALE COST ANALYSIS

7.3.1 Cost of Competing Technology

As a result of recent technological and process improvements, the general cost of IX water treatment for perchlorate has declined steadily since its early use. Siemens (2007) estimates IX treatment costs for perchlorate removal (including cost of resin, pre-installation rinses, vessel loading and unloading, vessel sanitization, transportation, final resin disposal, and certificate of destruction) for 2007 to be in the range of $75 to $100 per acre-foot; a significant decline from cost estimates in 2000, where treatment costs ranged from $450 to $650 per acre-foot (see Figure 7-4). This treatment cost decline is attributed to improved resin selectivity and regulatory acceptance of selective resin technology.

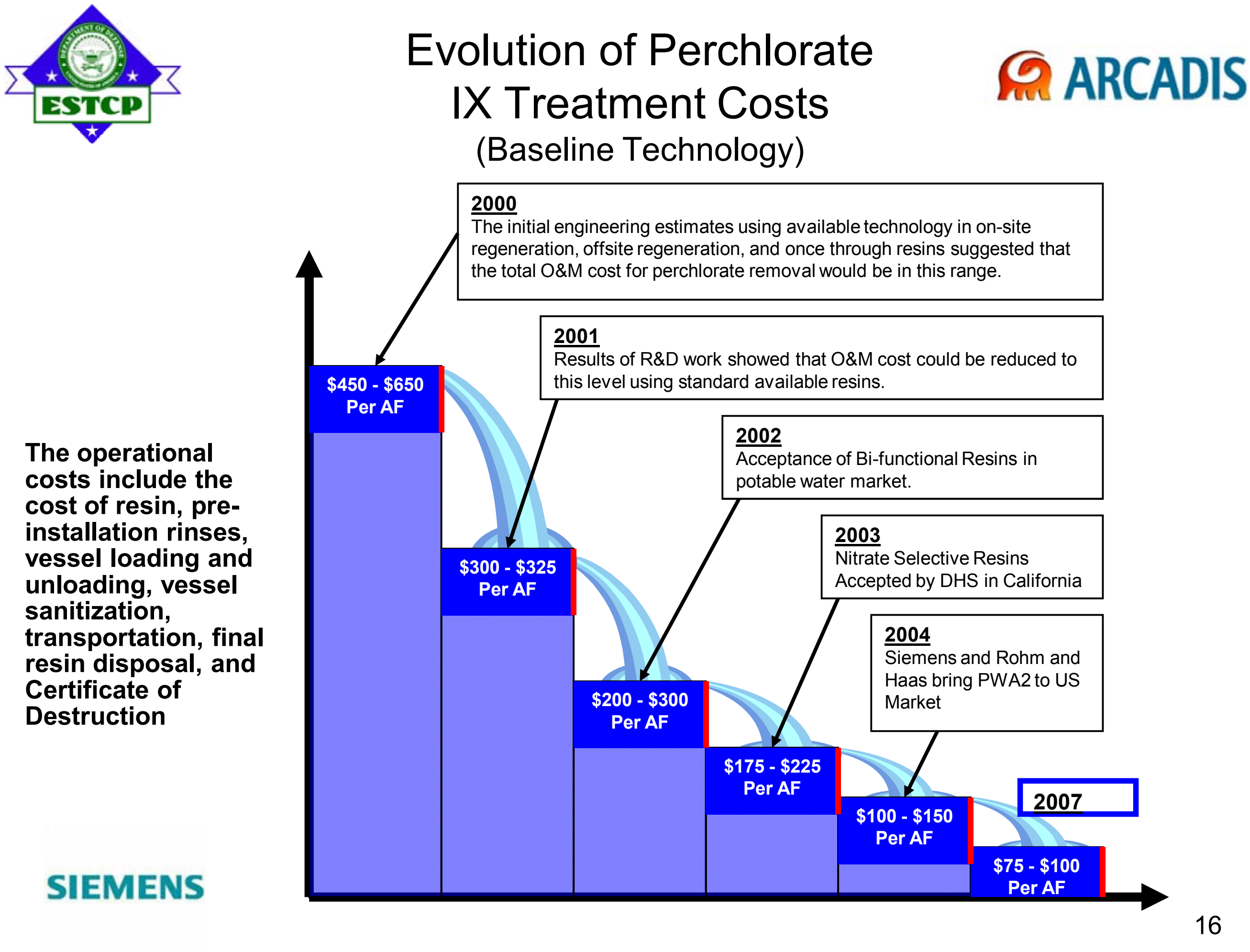
It is especially important to understand this figure to provide interpretative context for this project which was:

- Based on bench scale research in modifying the properties of GAC for the removal of perchlorate that began at PSU circa 2001
- First proposed to ESTCP in 2004
- Funded by ESTCP in 2005
- Completed in the field in 2008
- Reported in 2009

Thus during the technology development timeline for the TGAC technology the cost of competing technologies has dropped approximately five fold. This has made the task of developing a less costly solution for perchlorate treatment then IX much more difficult.

7.3.2 Fontana California Full Scale TGAC Cost Analysis

After making various operating assumptions (e.g., 8.4 min EBCT, 2000 GPM water flow, series operation, media regeneration) the cost and performance model was applied to estimate costs to treat Fontana water (Figure 7-5) at large-scale using TGAC. Figure 7-5 shows that the major cost driver for the TGAC technology is media costs. After the media, capital and labor costs are the next most important. As shown in Table 7-2, TGAC media costs are relatively high ($5.99 per lb). It should be noted that TGAC is currently produced on a very small-scale. As the cost per pound of TGAC decreases with expanded production, it would be anticipated that the overall cost of the TGAC technology would decrease to a similar extent.



Evolution of Perchlorate
IX Treatment Costs
(Baseline Technology)

2000
The initial engineering estimates using available technology in on-site regeneration, offsite regeneration, and once through resins suggested that the total O&M cost for perchlorate removal would be in this range.

2001
Results of R&D work showed that O&M cost could be reduced to this level using standard available resins.

2002
Acceptance of Bi-functional Resins in potable water market.

2003
Nitrate Selective Resins Accepted by DHS in California

2004
Siemens and Rohm and Haas bring PWA2 to US Market

2007

The operational costs include the cost of resin, pre-installation rinses, vessel loading and unloading, vessel sanitization, transportation, final resin disposal, and Certificate of Destruction

Figure 7-4. Historical Evolution of IX Treatment Costs for Perchlorate

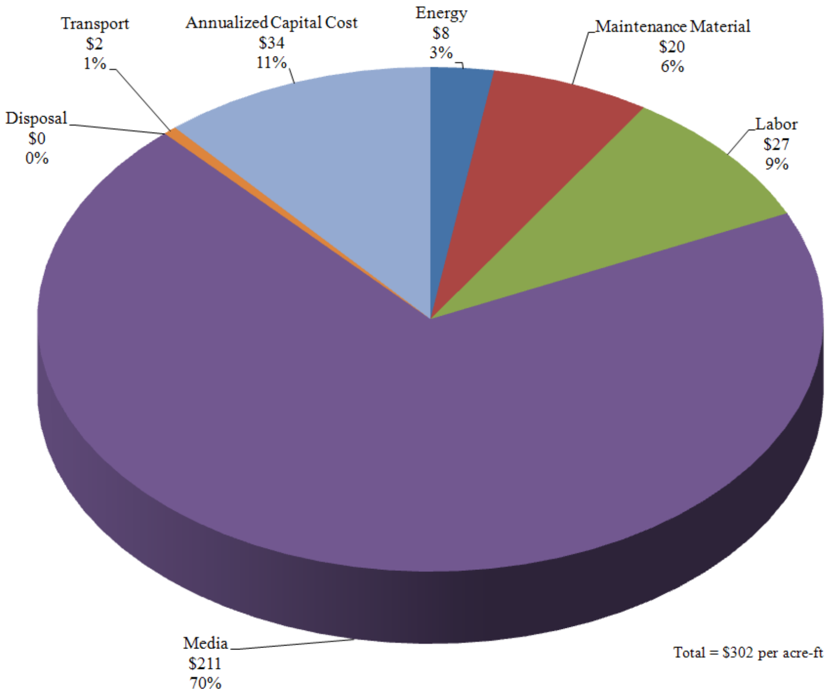


Figure 7-5. Relative and Absolute Costs for TGAC Treatment of Fontana Water by Cost Element

7.4 COST ANALYSIS

To illustrate use of the cost and performance model, a typical treatment scenario will be assumed and costs calculated (Table 7-7).

Table 7-7. Example Treatment Scenario

Model Input Parameter	Base Value	Unit
Flow	1000	GPM
GAC Media Size	80 x 30	
EBCT	20	min
Annual Days of Operation	360	days
Hours of Operation per day	24	hours
# of trains in operation	2	
Mode of operation	Series	
Perchlorate	0.01	mg/L
Thiosulfate	2	mg/L
Nitrate	10	mg/L
Bicarbonate	10	mg/L
Sulfate	10	mg/L
Chloride	10	mg/L
Miles to Regeneration Facility (if off-site) or Disposal Site	250	miles
Process Housing Required?	Yes	-
Regenerate Carbon?	No	-
Amortization Period or Useful Life (years)	20	years
Discount Rate (Bond Rate)	2.8%	-
O&M Cost (total)	$685,000.	
Capital Cost (total)	$2,200,000.	
Cost per acre-ft	$261	

As shown in the table, the capital and operating costs for treating this water by TGAC is $261 per acre-ft. The IX estimated capital cost for this system is $295,000 and the estimated resin cost is $62 per acre-ft (Berrum 2009). When these values are substituted into the model for the capital and media costs and all other parameters in the model are held constant, the resulting cost estimate is $135 per acre-ft. costs, transport costs, etc. In order for TGAC technology to be cost competitive with IX, technology costs would have to decrease significantly. As indicated in the previous section, such decreases may result from significant decreases in the cost of TGAC media.

As discussed above, the presence of nitrate inhibits perchlorate adsorption on TGAC. Thus a higher nitrate concentration should result in an increased treatment cost. Table 7-8 provides an example of this effect. Doubling the nitrate concentration in the water increases the treatment cost per acre-ft by 34%.

Table 7-8. Effect of Increased Nitrate Concentration on TGAC Treatment Costs

Model Input Parameter	Base Value	Value Variations (highlighted yellow)	Unit
Flow	1000	1000	GPM
GAC Media Size	80 x 30	80 x 30	
EBCT	20	20	min
Annual Days of Operation	360	360	days
Hours of Operation per day	24	24	hours
# of trains in operation	2	2	
Mode of operation	Series	Series	
Perchlorate	0.01	0.01	mg/L
Thiosulfate	2	2	mg/L
Nitrate	10	20	mg/L
Bicarbonate	10	10	mg/L
Sulfate	10	10	mg/L
Chloride	10	10	mg/L
Miles to Regeneration Facility (if off-site) or Disposal Site	250	250	miles
Process Housing Required?	Yes	Yes	-
Regenerate Carbon?	No	No	-
Amortization Period or Useful Life (years)	20	20	years
Discount Rate (Bond Rate)	2.8%	2.8%	-
O&M Cost (total)	$685,000.	$890,000.	
Capital Cost (total)	$2,200,000.	$2,200,000.	

Model Input Parameter	Base Value	Value Variations (highlighted yellow)	Unit
Cost per acre-ft	$261	$325	

A number of caveats need to be added to the above analyses. Note that the cost and performance model is based on 12 proportional diffusivity based RSSCTs using FWC water spiked with perchlorate at various concentrations and model validation was based on a single pilot study at Fontana. Both the RSSCTs and pilot testing at Fontana used anthracite based GAC, which was later shown to be a nonoptimal choice. Subsequent to the study and the development of the cost model it was shown that bituminous based GAC and the use of exponent=1.5 in the simultude of Crittenden would have been preferable Our analysis suggests however that the distinctions caused by these two factors roughly cancel, so that the current cost model r would still be useful as a screening modelfor the X=1.5, bituminous based GAC, optimum case.

Another caveat is that the TGAC media, which is the single largest cost driver, had costs based on the pilot-scale study. Presumably, full-scale production costs will be considerably less. The field scale testing used TGAC prepared from anthracite based carbon. Although bituminous based carbon would have been more effective, that change alone would not have been enough to economically displace perchlorate selective resins.

Further analysis was conducted by AFIT to determine if TGAC is an economically viable technology to treat plumes of perchlorate co-mingled with other organic contaminants (e.g., nitroaromatic compounds such as HMX, RDX, and Trinitrotoluene (TNT), and/or chlorinated solvents like TCE, perchloroethylene (PCE), and VOC. A survey that was conducted as part of this study indicates that such co-mingled plumes are relatively common (Downen 2009). In these plumes, the conventional treatment technology is to use a treatment train, with IX to remove perchlorate, and typically GAC to remove the non-polar organic contaminants. Operation of a treatment train is relatively costly. Additionally, skills for operating both systems must be developed and maintained.

Performance data from the TCE column of the six-column study were analyzed in order to determine if TGAC could effectively treat co-mingled chlorinated solvents and perchlorate. Based on these data, the model predicted costs for the treatment of 0.01 mg/L perchlorate and TCE concentrations between 0.01 µg/L and 70 µg/L ranged from $260 to $970 per acre-ft. When the model was run with additional organic compounds, it was shown that the model-predicted costs of treating other, more hydrophobic, compounds like PCE and the nitroaromatics were less than the cost to treat TCE. Thus, the model predicted cost range for TGAC treatment of about $200 to $1000 per acre-ft to treat perchlorate-contaminated water with an organic co-contaminant is conservative. The analysis also showed that these costs are comparable to the costs of using conventional technologies to treat water with co-contaminants (Downen 2009).

The Excel model, which is available as an addendum to this report, has the capability of estimating costs of treating co-mingled plumes with perchlorate, competing anions, and various organic compounds (nitroaromatics, chlorinated solvents) as contaminants. The model, which is described in detail in Downen (2009), uses a recently published correlation (Shih and Gschwend, 2009) to estimate the Freundlich isotherm parameters that are used to predict organic sorption.

8. IMPLEMENTATION ISSUES

8.1 REGULATORY REQUIREMENTS

The water produced and treated during the pilot testing was disposed of in the FWC percolation pond at the site using an existing NPDES discharge permit (because the water from the demonstration was not used as drinking water). Application of the TGAC technology to treat drinking water would not require a NPDES permit; however, a discharge permit may be required for the disposal of backwash water and other process water (e.g., water used during disinfection of the vessels and piping, etc.) that is generated during normal operation of the treatment system. A TGAC drinking water treatment system would need to be permitted through the appropriate permitting agency as required in the state of operation prior to being used as a drinking water treatment technology. For example, in California, all drinking water treatment systems must be permitted through the DPH.

Disposal of the spent TGAC was conducted in accordance with Department of Transportation (DOT) and Resource Conservation and Recovery Act (RCRA) regulations. These regulations would also need to be adhered to in a full-scale application of the treatment technology.

Siemens Water Technologies produced the TGAC for this project at their Los Angeles, California facility. This facility was equipped to process waste waters such as those that contain CPC—the tailoring agent used during this demonstration. The only CPC discharge from the tailoring process occurred during the final rinsing process. During the rinsing operation, CPC that was present in the rinse water was removed by pumping the rinse water through a bed of virgin GAC prior to being discharged. This partially tailored bed could be used in the manufacture of subsequent batches of TGAC. The spent 10-micron particulate filters generated during the demonstration were air dried on-site, and then disposed of as municipal waste since no VOCs were present in the influent water. A TGAC treatment system that is used to treat both perchlorate and a VOC may require disposing of spent particulate filters as a solid waste that may require characterization. No other residuals requiring disposal were generated.

8.2 OTHER REGULATORY ISSUES

Building permits for the construction of the demonstration system were not required by the City of Fontana. Depending on the jurisdiction, building and safety permits may be required for construction of a full-scale TGAC treatment system.

Because this project was a demonstration of a drinking water treatment technology, the DPH was presented with information regarding the project and the results of the project. Copies of this report, and other project information, will be forwarded to the appropriate personnel at DPH with ESTCP approval and guidance. Other interested regulatory agencies such as the California Regional Water Quality Control Board (RWQCB), California Department of Toxic Substances Control (DTSC), and the NSF will also be provided with applicable documents as approved or requested by ESTCP, or other involved agency. Public participation was not included in the demonstration.

8.3 END-USER ISSUES

The California DPH is believed to be the state regulatory agency in the United States with the most experience with perchlorate issues in drinking water. Stakeholders for this technology included water utilities, water purveyors, and potentially responsible parties for any given perchlorate plume. End-users are the general public (drinking water customers), agricultural (crop irrigation and livestock) operations, and commercial, industrial and government facilities. From a stakeholder/end-user perspective, the economic costs/issues are important; based on current full-scale estimates, the TGAC and perchlorate destruction will cost more than current methods, for example, single-use IX with incineration of spent resin as the predominant disposal technique.

The results of this project showed that:

- Bituminous based carbons are superior to anthracite based carbons in preparing TGAC for perchlorate treatement.
- Neither isotherm testing, RSSCTs nor any other known bench scale protocol is able to perfectly predict field scale performance in a rapid laboratory QC or treatability test.
- A simultude intermediate between constant and proportional diffusivity, one where exponent=1.5 may be the most appropriate way to use RSSCTs to predict Field scale perchlorate performance for TGAC.

TGAC also has several perceived or potential limitations not found with other treatment technologies. These limitations include the following:

- TGAC has a lower perchlorate capacity than most IX resins and will require more frequent change-outs because a smaller volume of water can be treated prior to perchlorate breakthrough/saturation. This limitation may become more pronounced as new, higher perchlorate capacity IX resins are developed.
- TGAC requires a lower hydraulic loading rate (GPM per square foot), or a longer contact time (EBCT) than IX, and thus more or larger vessels (additional capital cost) will be required to treat a given flow rate of water. Additionally, if TGAC were to be implemented at an existing IX facility, additional vessels would need to be installed.
- If applied on a mixed-contaminant water (e.g., perchlorate and VOCs, etc.) perchlorate or the VOCs may reach breakthrough at different times, which would require an early change-out, and thus a reduced capture efficiency for VOCs or perchlorate than two separate media (such as found at existing perchlorate and VOC treatment facilities that utilize both conventional GAC and IX resin).
- TGAC may leach small concentrations of the tailoring agent into treated water. Some state agencies may require the addition of a “guard” bed to capture residual tailoring agent.

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APPENDICES

Appendix A: Points of Contact

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Appendix B:
PENNSYLVANIA STATE UNIVERSITY FINAL REPORT, PERCHLORATE REMOVAL FROM FONTANA, CALIFORNIA, GROUNDWATER USING RAPID SMALL-SCALE COLUMN TESTS

June 23, 2008

By: Judodine Patterson, Bob Parette, Fred S. Cannon,

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Collaborators:

Trent Henderson, Chris Lutes, David Liles, (ARCADIS), Jim Graham (Siemens Water Technologies), Mark Goltz (AFIT)

Abstract

The adsorption of perchlorate to tailored granular activated carbon (TGAC) was studied at bench scale. Seventeen rapid small-scale column tests (RSSCT) were conducted with groundwater from Fontana, California under different operational variables and water chemistry solutions. Results show that the adsorption of perchlorate is pH dependent. The removal efficiency in an acidic environment was 50% greater than neutral pH, and 75% greater than at an alkali pH. Nitrate also affects the removal of perchlorate from groundwater using TGAC. A doubling of the nitrate concentration reduced the removal of perchlorate by 17%; and a tripling of nitrate concentration reduced removal by 53%. Sulfate, thiosulfate, chloride and bicarbonate did not affect the adsorption of perchlorate to the TGAC sites up to the maximum contaminant level.

Introduction

Virgin GAC (i.e. without tailoring) has only been conditionally effective in removing perchlorate from water (Parette et al., 2005). However, our Penn State team has hypothesized that virgin carbon could be pre-loaded with cationic surfactants so as to increase the GAC capacity for removing perchlorate from water. The cationic surfactants used in this project contain a quaternary ammonium functional group (Parette et al., 2005). These same functional groups have been shown to remove perchlorate in IX resins technology (Clifford et al., 2004). These quaternary ammonium based cationic surfactants have a high pK_a value and this characteristic renders their charge to be independent of pH in natural waters (Laughlin, 1991). Once the cationic surfactant is pre-loaded onto the GAC, it then acts as an exchange site where perchlorate can be adsorbed.

The Pennsylvania State University has developed a technology that uses a cationic surfactant to tailor activated carbon. This has been shown to efficiently remove perchlorate from water at concentrations below 1 ppb (Parette and Cannon, 2005). This tailoring of GAC with cationic surfactants extends its bed life for adsorbing perchlorate up to 34 times that of virgin GAC when testing Redlands, California water (50-75 ppb) in rapid small-scale column tests (RSSCTs). This technology has not been permitted for use in drinking water systems; and it has also not been commercialized yet, although we are actively pursuing this.

This earlier work by Parette et al. (2005) also showed that the pyridinium cationic surfactant will also efficiently remove perchlorate from water. The loading of the quaternary ammonium or pyridinium (as a subset of quaternary ammonium) surfactants produces positively charged groups that act as IX sites where perchlorate can be adsorbed.

The purpose of the study herein has been to evaluate the use of GAC that was tailored with a cationic surfactant (cetylpyridinium chloride) for the removal of perchlorate, under different water chemistry parameters, from groundwater. Previous work has shown that virgin GAC was ineffective in the removal of perchlorate for concentration ranging between 50 - 75 ppb, as breakthrough was detected at 1100 BV of water treated. By tailoring with cationic surfactants, positively charged groups can be used as exchange sites for the adsorption of perchlorate as well as other anions.

Experimental

In all experiments, the GAC was ground and sieved to a size range of US Mesh #200 x 400 mesh (0.074 x 0.037 mm). The tailoring protocol used was as discussed in section 5.4.4.1 of the main report except that distilled water was used without heating in the application of the tailoring agent. The laboratory columns used were manufactured to withstand high pressure that is required with the use of the small GAC grains. The columns were designed according to the RSSCT (Figure 1) proportional diffusivity equations; and the columns measured 0.5 cm in diameter and 13.5 cm in length (Figure 2). Therefore 1 bed volume (BV) was equal to 2.65 mL. HPLC pumps (Waters models 501 and 510) were used to provide flow in the experiments (Figure 3). The flow rates of the RSSCTs were 2.5 ml/min which corresponds to a 10 minute empty bed contact time (EBCT) at the field-scale level for US mesh #20 x 50 GAC, or to a 17 minute EBCT for #12 x 40 mesh GAC. Perchlorate measurements were conducted with the use of Dionex DX-120 ion chromatograph using method 314.0 and a laboratory specific QAPP.

The stock solutions used in these experiments were prepared using reagent grade chemicals as well as deionized distilled water. The Fontana water for the RSSCT tests was obtained from well FWC-17C, and was collected on 9/1/06 by ARCADIS in 10, 55-gallon, polyethylene drums. Field conductivity readings were obtained and recorded (written with a Sharpie pen) on each drum. The drums were wrapped with plastic and strapped to pallets (four drums per pallet). They were shipped via Fed Ex Freight (unrefrigerated) to PSU. PSU periodically monitored the perchlorate concentration in the stored barrels and found it to be stable. RSSCT testing began 9/18/06. To check the stability of perchlorate concentration in the barrels that constituted this sample, we checked the influent concentration of perchlorate every time a new barrel was open to run laboratory tests. On average the concentration was 7.1 ppb for all the barrels used in the tests.

Table1. Perchlorate Concentrations for Barrels of Fontana Well 17 C Water used in Bench Scale Test

Barrel	Perchlorate Concentration (µg/L)
1	7.1
2	6.9
3	7.2
4	7.6
5	6.8
6	7.3

Table 2. Statistics Summary of Perchlorate Concentrations Found in Six Barrels of Fontana Well 17C Water used in the Bench-scale Test

Mean	7.15
Standard Error	0.117615
Median	7.15
Standard Deviation	0.288097
Sample Variance	0.083
Range	0.8
Minimum	6.8
Maximum	7.6

Table 3 shows all the experiments that were conducted and the concentrations of perchlorate and anions that were employed. With the exception of experiment 1 all other experiments were conducted using tailored carbon. The concentration of perchlorate in the Fontana groundwater was 7 µg/L and with the exception of experiment 3 and 5 all other experiments were conducted using that concentration. The Fontana groundwater used was also monitored for other background species such as nitrate, sulfate and chloride concentration. Results showed 32 mg/L nitrate as nitrate, 5 mg/L sulfate, and 12 mg/L chloride.

In order to test the effect on TCE removal of the tailoring agent, the Penn State team conducted isotherm experiments. These experiments are reported here, because of their relevance to the questions of this report, and because they have not been previously reported, even though Redlands water was used for the experiments. The isotherm experiments were used in lieu of RSSCTs, to examine this effect because of similitude issues. The perchlorate RSSCTs behaves according to the proportional diffusivity similitude equations, whereas the TCE RSSCTs was expected to behave according to the constant diffusivity similitude equations. Since these dictated considerably different RSSCT column designs, it was discerned that more useful information would be obtained by using isotherms. To perform the isotherm test 0.1 grams of 8x30 mesh UltraCarb was placed in a 40 mL glass vial. 25 mL of distilled water was added to the carbon. After one day, 0.03 grams of cetyltrimethylammonium chloride was added and the vials were placed on a shaker table at 20 oC for 8 days. The liquid in the vials was then exchanged 5 times over 4 days with 25 mL of Redlands water. TCE (1% in methanol) was then spiked into the vials and the vials were filled to the top (no headspace) with Redlands water. The vials were placed on a shaker table for one day and then placed on a rotary tumbler (5 RPM) for six days prior to analysis.

Results and Discussion

For the virgin carbon test, 1.27 grams of AquaCarb 2050AW (an Anthracite based GAC manufactured by Siemens Water Technologies) was placed in the column; and this corresponded to a bed density of approximately 0.48 g/mL. Perchlorate breakthrough in this column was observed at 1100 to 1150 BV. The result shown in Figure 4 compares favorably to RSSCT results obtained with bituminous GAC in the January 2003 study with Fontana groundwater prior to the development of cationic surfactant tailored GAC.

Table 3. List and Description of Rapid Small-scale Column Tests (RSSCTs) conducted with Fontana water.

Experiment	Tests
1	Virgin Carbon
2	Tailored carbon by Siemens
3	Water spiked to 50 ppb perchlorate
4	Carbon Tailored by Penn State
5	Water spiked to 500 µg/L of perchlorate
6	Nitrate concentration increased to 100 mg/L
7	Sulfate concentration increased to 50 mg/L
8	Sulfate concentration increased to 250 mg/L
9	Carbon tailored with Arquad 2C-75
10	Nitrate concentration increased to 60 mg/L
11	Water spiked with 1 mg/L thiosulfate (thiosulfate nondetectable in starting water)
12	Chloride concentration increased to 250 mg/L
13	Water spiked with 10 mg/L Thiosulfate
14	Bicarbonate concentration increased to 500 mg/L
15	Flow rate decreased to 0.25 mL/min
16	pH lowered to 4.2
17	pH increased to 10

The time to perchlorate breakthrough was 18,700 BVs for tailored carbon. Two sources of origin for tailored carbons were used in these experiments: those prepared by Penn State, and that prepared by Siemens Water Technologies. This was done to compare the breakthrough for both carbons. Figure 5 shows that there were no differences in performance between the carbon that was tailored at Penn State and the carbon that was tailored by Siemens Water Technologies. The loading was 0.30 g CPC/g GAC for the carbon tailored at Penn State tailored carbons; and 0.29 g CPC / g GAC for the carbon tailored by Siemens.

Experiments were also conducted where perchlorate concentration was spiked to 50 μg/L and 500 μg/L. These were approximately six and 60 times greater than the concentration found in the native Fontana ground water. Breakthrough occurred at 16,000 BVs for 50 μg/L-spiked water and at 10,000 BVs for the 500 μg/L-spiked water (Figure 6 and 7). This showed that there would be about a 14% decrease in the tailored carbon bed life for removing perchlorate from the groundwater if the concentration was 6x higher. This result highlights that it was the background competing anions that dictated breakthrough performance, more than the level of perchlorate present (see further discussion as follows).

Activated carbon that was loaded with dicocoalkyldimethylammonium chloride (Arquad 2C-75) was also tested to observe if there would be a difference in perchlorate adsorption. Arquad 2C-75 was chosen since it has two long alkyl chains instead of the one found on the CPC molecule. This property of the Arquad 2C-75, facilitated lower leaching of the surfactant off of the carbon. The loading for Arquad 2C-75 was 0.245 g/g GAC compared to 0.30 g/g GAC for CPC. It can be seen from Figure 8, that even though CPC had a greater concentration loading, there were no significant difference for BVs to break through between the Arquad 2C-75 and CPC. Breakthrough of perchlorate when using Arquad 2C-75 as the surfactant occurred at 19,500 BVs while for CPC, it was 18,500 BVs.

Figure 9 shows the results of experiments that were conducted using an array of concentrations of potentially competing anions (nitrate, sulfate, and thiosulfate). When the nitrate concentration was 100 mg/L as nitrate, which is three times the concentration of nitrate found in Fontana groundwater, the breakthrough for perchlorate occurred at 8,500 BVs. In comparison, when the nitrate concentration was two times the initial concentration (60 mg/L as nitrate), breakthrough for perchlorate occurred at 15,600 BVs. It could be seen from the graph that nitrate was the one anion that greatly diminished the effectiveness of the tailored carbon to remove perchlorate from Fontana groundwater when using CPC as the surfactant.

Sulfate concentration was increased to (a) 50 mg/L, which is 10 times the initial concentration of Fontana water, and (b) 250 mg/L, which corresponds to the maximum contaminant level (250 mg/L). For each of these cases, perchlorate breakthrough was unaffected, and occurred at 20,000 BVs. This showed that there was no change in the performance of the tailored carbon to remove perchlorate when sulfate concentration is increased.

As discussed in section 2.2.3 although thiosulfate is not a typical parameter measured in geochemical analysis of drinking water, it is expected that reduced sulfur species similar to Thiosulfate may be a significant competitor for sorption sites on the TGAC. Thiosulfate at 1 mg/L and 10 mg/L concentration was also added to Fontana water to observe any effects on the removal of perchlorate by the tailored carbon. Breakthrough of perchlorate occurred at 16,700 and 14,500 BVs respectively, which is a 10 and 19 percent decrease in the performance of the carbon to remove perchlorate from the groundwater when thiosulfate is added.

From ion activity tables for quaternary ammonium IX media, the sulfate anion (formal charge -2) would have been more competitive than nitrate anion (formal charge -1) for adsorption sites, if the CPC tailored carbon followed the quaternary ammonium pattern. These results show the opposite of this expected pattern when pyridinium is the perchlorate-exchanging functional group. From this it can be hypothesized that the sulfate anion cannot simultaneously access two charged pyridinium sites. Sulfate is a tetrahedral species and only has a covalent diameter of approximately 0.500 nm. Thus it appears that the sulfate anion cannot simultaneously effectively bond with the two charged pyridinium sites needed to balance its charge. So instead of adsorption of sulfate anion to the charge sites on the carbon, it could pass through the column, therefore not affecting perchlorate removal. Nitrate on the other hand only needs one pyridinium site to balance its formal charge so the steric issue would be lessened.

The effect of pH (Figure 10), bicarbonate and chloride (Figure 11) was also evaluated to observe the effects of perchlorate adsorption on CPC-tailored GAC. Fontana groundwater was spiked with sodium bicarbonate to the amount equivalent to 550 mg/L as bicarbonate.

In another test, hydrochloric acid was added to lower the pH of Fontana groundwater to approximately 4.2; and in yet another column, the pH was increased to approximately 10 by adding sodium hydroxide.

Lowering the pH to approximately 4.2 increased the bed life of CPC-tailored GAC to remove perchlorate from Fontana groundwater, to where initial perchlorate breakthrough occurred at between 30,000-34,000 BVs. Figure 10 also depicts that for the unammended Fontana water the bed life was 20,000 BVs to initial perchlorate breakthrough (3 μg/L perchlorate in effluent). Thus a 42% increase in bed life of the CPC-tailored GAC was achieved with the lower pH. This shows that perchlorate breakthrough is more gradual in a moderately acidic environment compared to an environment with more normal groundwater pH. Since the pKa of quaternary ammonium surfactants is approximately 11, we would not have expected this pH change to have a significant effect in protonating CPC. However the pH change could have influenced the charge balance of the carbon surface itself.

Increasing the pH to 10 showed results opposite of what was observed when the pH was lowered. Breakthrough for perchlorate was observed at 8,500 BVs. This indicated that a higher pH will diminish the capacity of the TGAC to adsorb perchlorate. There was a 54% lower CPC-tailored GAC capacity for adsorbing perchlorate at pH 10 than at the natural pH for the Fontana groundwater. The background pH for Fontana groundwater ranges from 7-8.

From Figure 11 it can be seen that a bicarbonate concentration that is almost twice the secondary drinking water quality standard set by the state does not affect the adsorption of perchlorate to granular activated carbon tailored with CPC. Breakthrough of perchlorate occurred at 24,000 BVs. This is approximately 5,000 BVs more or approximately 25% more than for Fontana groundwater that is not spiked with sodium bicarbonate. The Fontana groundwater already has a background bicarbonate concentration of 330 mg/L.

The mass of sorbed perchlorate and the percent of surfactant sites occupied by perchlorate were also calculated, as shown in Table 4 for each experiment. When preparing these calculations, we estimated (based on prior experience) that 10% of the CPC and 1% of the Arquad 2C-75 desorbed. With native levels of perchlorate and competing anions, the mass of perchlorate adsorbed per gram of carbon was about 0.33 mg perchlorate g GAC, which corresponded to about 0.44% of the active sites exchanging with perchlorate. The loadings under other circumstances appear in Table 4. In general in Table 4 the efficiency of the TGAC media expressed as % of CPC sites occupied by perchlorate is greatest when the waters have higher influent perchlorate concentrations and is least when nitrate concentrations are higher.

In an attempt to understand differences between bench sale and field-scale performance, an experiment (test 15) was conducted in which the RSSCT apparatus was used, but at a flow rate more typical of the field application (0.25 ml/min). As shown in Figure 12 breakthrough in this more slowly operating train initially occurred at approximately the same number of BVs as the field-scale train. However the 0.25 ml/min bench scale train did not follow a typical curve, rather than proceeding to saturation, the effluent returned to the baseline and then reached saturation much later – approximately 25,000 BVs.

Examining Figures 5, 7, 8, 9, 10, 11 and 12, we can observe several cases where if the TGAC system is operated beyond saturation, a chromatographic roll-over effect is observed, in which the effluent concentration exceeds the influent concentration for at least a brief period. This is a common phenomenon in sorption systems; and beds are normally removed from operation at full-scale before such perchlorate roll-over would occur.

Conclusion

Activated carbon tailored with cationic surfactants has a greater capability to remove perchlorate from Fontana groundwater than activated carbon not tailored with cationic surfactants. Nitrate was the only interfering anion tested that greatly diminished the CPC-tailored GAC to remove perchlorate from Fontana groundwater; and thiosulfate diminished capacity slightly. It was also observed that at alkaline pH, the CPC-tailored GAC capacity was diminished, while at pH 4.2, the capacity is increased. It can be concluded that activated carbon tailored with CPC can significantly remove perchlorate concentration ranging from 7-50 μg/L. Also the capacity to remove perchlorate can be greatly enhanced if nitrate concentrations are low and the pH is below 7.

Table 4. Mass of Perchlorate Adsorbed and Percent CPC Sites Occupied for Each Experiment

EXP. #	Condition	BVs*	Total Mass of ClO_4^- (mg)	$mgClO_4^-$ /gGAC	% of CPC sites occupied by ClO_4^-
1	Virgin Carbon	640	0.0258	0.0204	0.027
2	Tailored carbon by Siemens	17,700	0.403	0.32	0.42
3	Water spiked to 50 µg/L perchlorate	15,200	2.65	2.08	2.7
4	Carbon Tailored by Penn State	16,500	0.422	0.33	0.44
5	Water spiked to 500 µg/L perchlorate	9,200	14.5	11.4	15.0
6	Nitrate concentration increased to 100 mg/L	7,900	0.204	0.16	0.21
7	Sulfate concentration increased to 50 mg/L	18,800	0.436	0.34	0.45
8	Sulfate concentration increased to 250 mg/L	19,000	0.45	0.358	0.46
9	Carbon tailored with Arquad 2C-75	19,000	0.429	0.338	0.67#
10	Nitrate concentration increased to 60 mg/L	15,200	0.251	0.198	0.26
11	Water spiked with 1 mg/L thiosulfate	15,800	0.359	0.283	0.37
12	Chloride concentration increased to 250 mg/L	22,500	0.473	0.372	0.49
13	Water spiked with 10 mg/L thiosulfate	13,700	0.378	0.298	0.39
14	Bicarbonate concentration increased to 500 mg/L	23,300	0.565	0.445	0.58
15	Flow rate decreased to 0.25 ml/min	10,800	0.275	0.217	0.28
16	pH Lowered to 4.2	28,700	0.638	0.502	0.66
17	pH Increased to 10	5,500	0.315	0.248	0.0002

BVs is defined here as the last undetectable perchlorate before Breakthrough.

#Arquad 2C-75 was used instead of CPC to calculate the percent sites occupied by perchlorate.

Figure 1. Rapid Small-scale Column Tests in the Laboratory

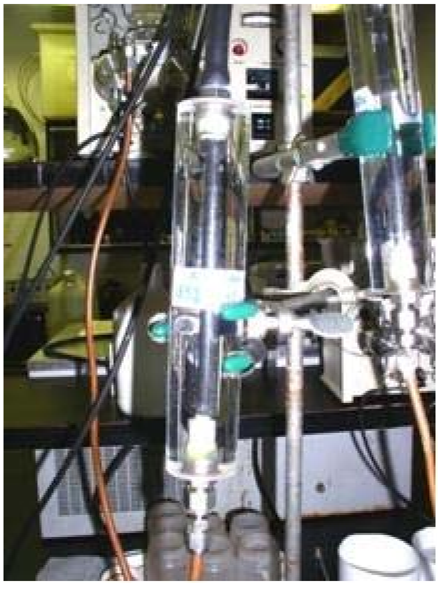

Figure 2. Picture Showing 13.5cm x 0.5cm Columns

Figure 3. High Pressure Liquid Chromatography Pumps used in RSSCT Experiments

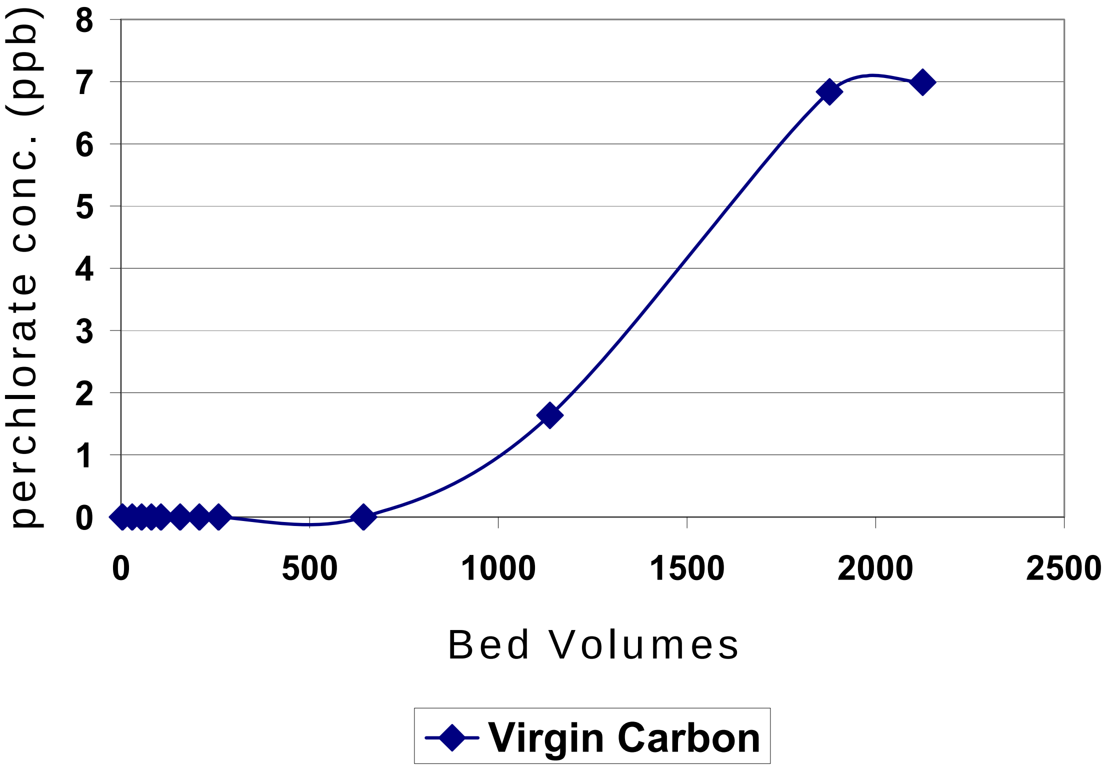

Figure 4. Graph Shows Perchlorate Adsorption to Activated Carbon that is Not Tailored

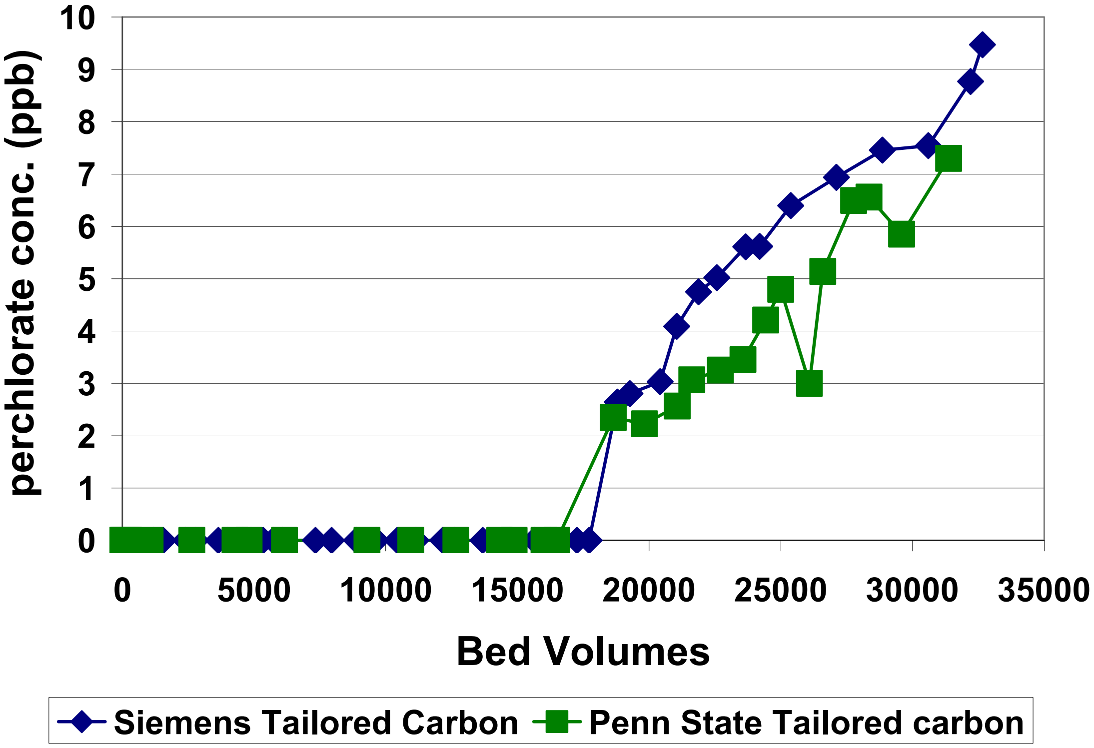

Figure 5. Graph Showing Perchlorate Breakthrough for Carbon that was Tailored by PSU and Siemens Technology

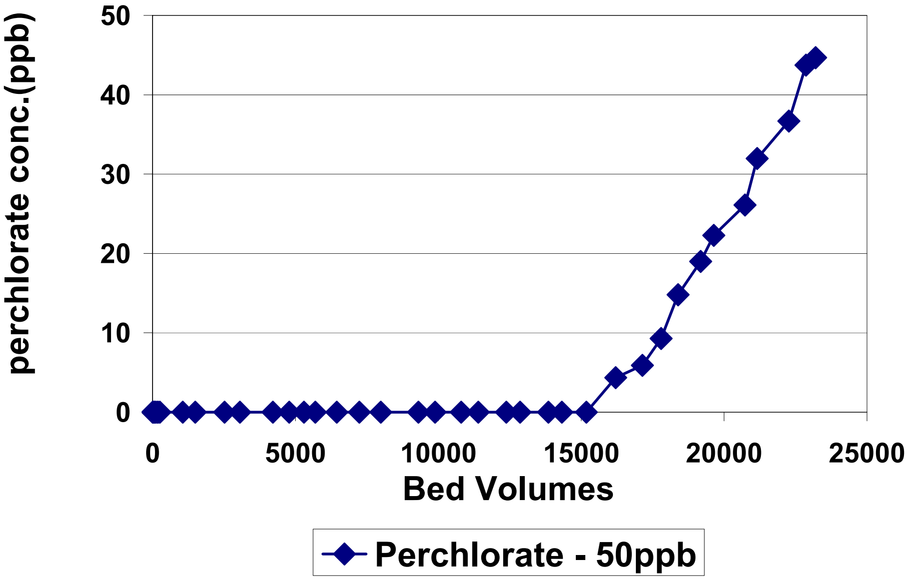

Figure 6. Graph Showing Perchlorate Breakthrough when Fontana Water had a 50 Ppb Concentration of Perchlorate

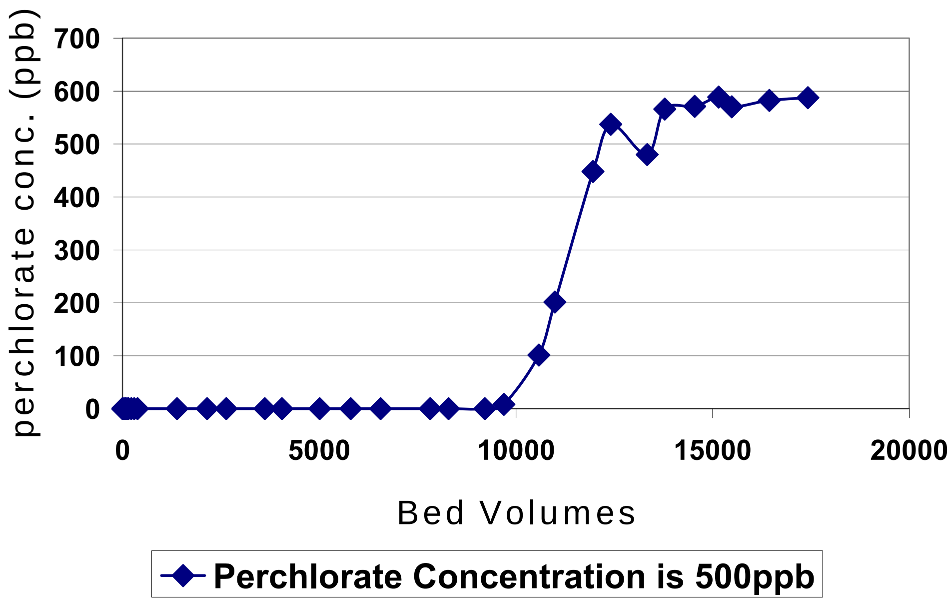

Figure 7. Perchlorate Breakthrough when Fontana Water is Spiked to 500 Ppb Perchlorate

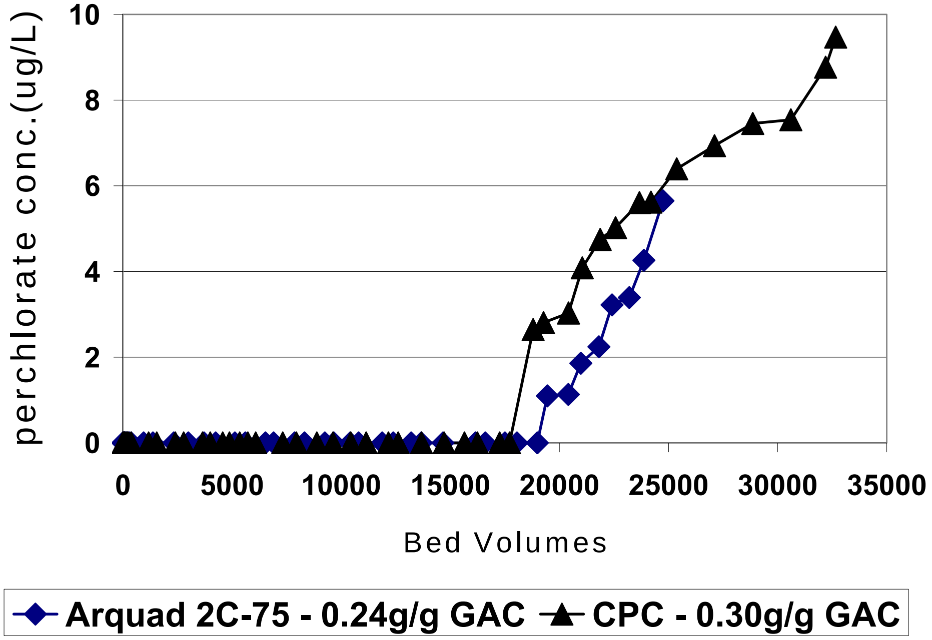

Figure 8. Graph Showing Perchlorate Adsorption Results with Different Tailoring Agents

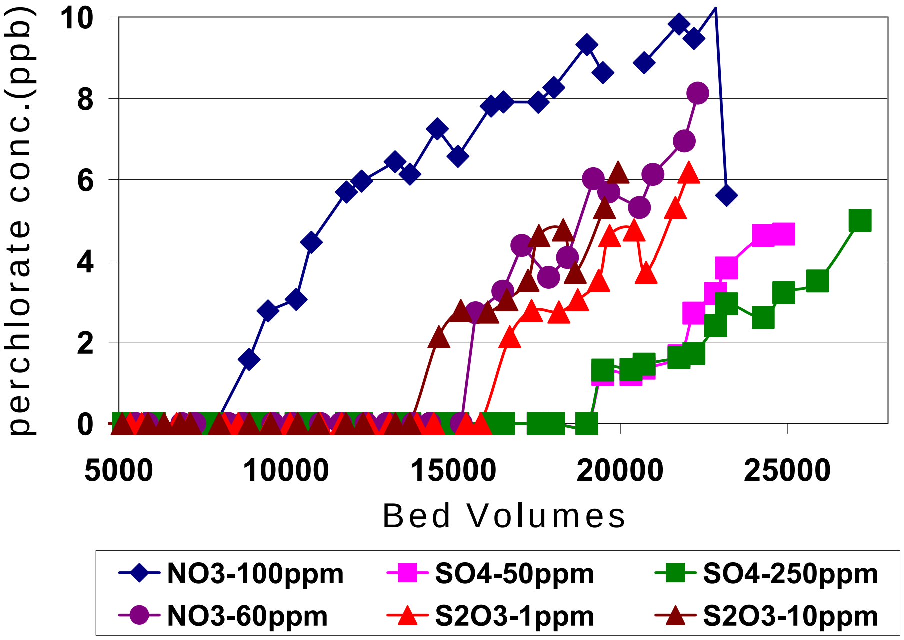

Figure 9. Graph Showing the Effects of Increased Concentration of Anions On Perchlorate Removal, Notations: NO_3 –Nitrate, SO_4-Sulfate, S_20_3-Thiosulfate

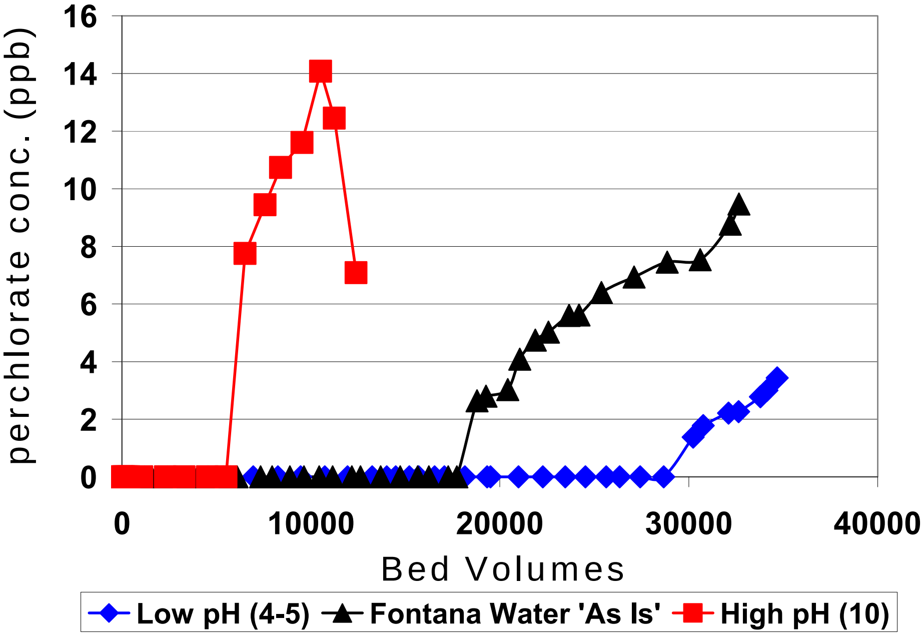

Figure 10. The Effects of Ph on Perchlorate Adsorption to TGAC

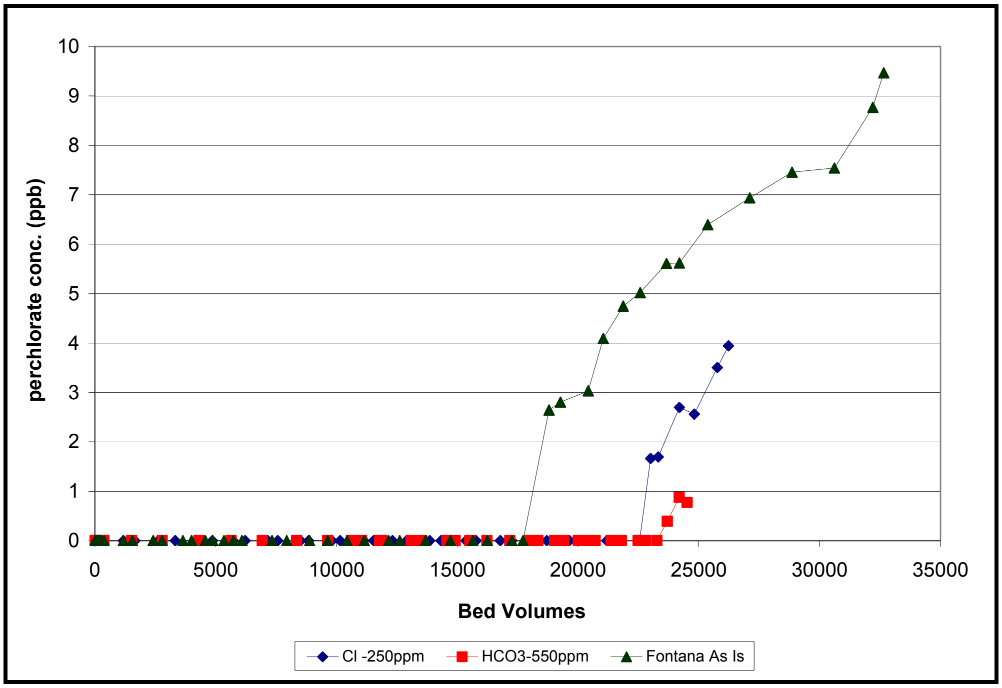

Figure 11. Graph Depicting the Effects of TDS on Perchlorate Adsorption to TGAC. Notation: - Cl- Chloride, HCO_3- Bicarbonate

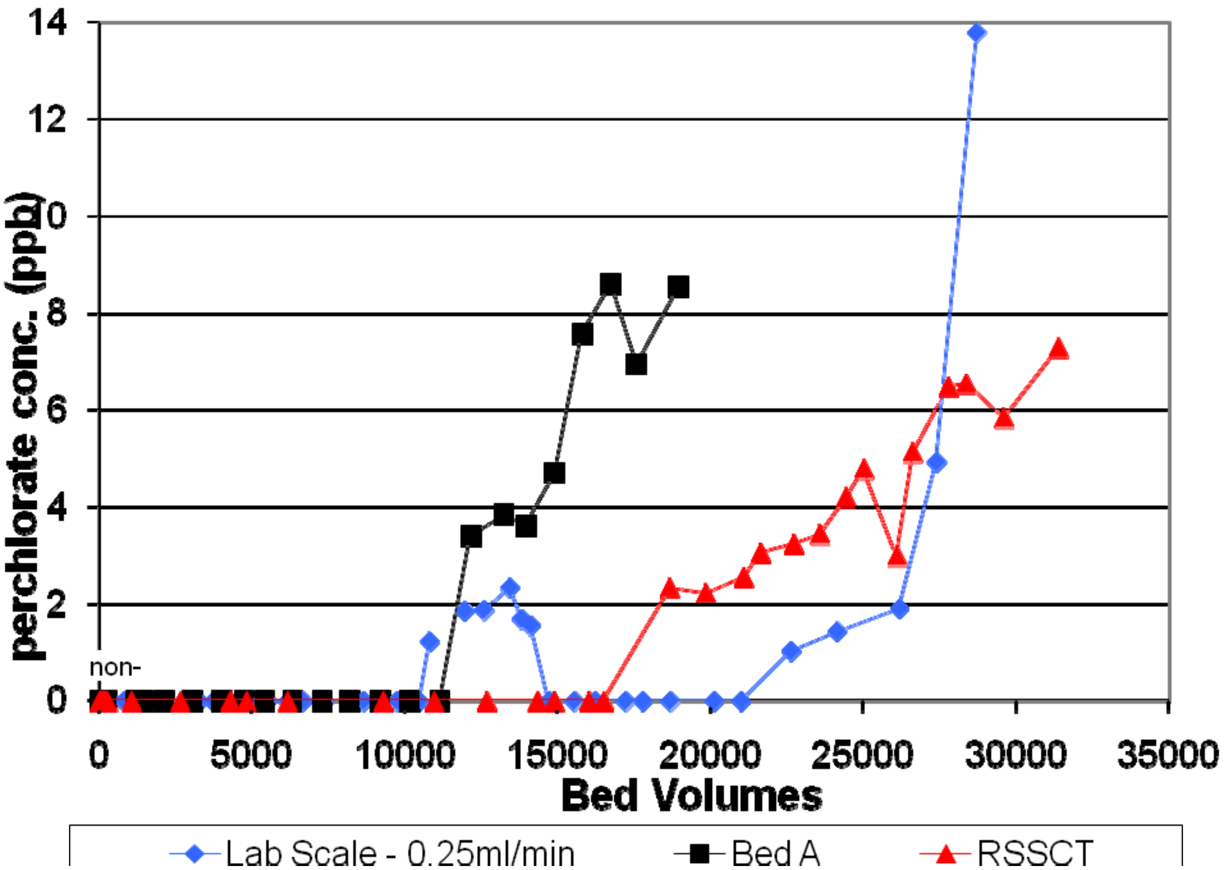

Figure 12. The Effect of Flow Rate Change on Perchlorate Breakthrough

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Appendix C:
PSU Paper Submitted for Referreed Journal PublicationDiscussing Thiosulfate Effects on Removal of Perchlorate

Oxidation of Reduced sulfur species (Thiosulfate) by Free Chlorine to increase the bed life of Tailored GAC to remove Perchlorate.

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ABSTRACT

This research determined that the oxyanion thiosulfate ($S_2O_3^{2-}$) competed with perchlorate (ClO_4^-) for sorption onto activated carbons that had been pre-loaded with a quaternary ammonium surfactant. Thiosulfate is an anoxic sulfur species that served as a surrogate for a number of intermediate - valence sulfur oxyanions that could be present in groundwaters during the brief time frames of treatment processes. Specifically, $S_2O_3^{2-}$ hosts redox stability in time frame of days, rendering it as a candidate ion exchange competitor in anoxic groundwaters. When pre-chlorination oxidized this $S_2O_3^{2-}$ to sulfate (SO_4^{2-}), this competition was diminished. When Rapid Small Scale Column Test (RSCCT) employed Redlands, CA groundwater that contained a native 30 µg/L ClO_4^-, this exhibited a 6 µg/L ClO_4^- breakthrough after 33,000 bed volumes (BV) when processed through bituminous- based GAC that had been preloaded with 0.24 g/ g Arquad 2C-75. When this same water was spiked with 1000 µg/L $S_2O_3^{2-}$, 6 µg/L of ClO_4^- broke through at 17,000 BV. However, when $S_2O_3^{2-}$-spiked Redlands groundwater was also spiked with 2,500 µg/L chlorine, this reactant stoichiometrically oxidized the $S_2O_3^{2-}$ so as to diminish this competition, such that 6 µg/L ClO_4^- broke through at 31,000 BV. Similar RSSCT trends were exhibited when using deionised distilled water that had been spiked with ClO_4^-, $S_2O_3^{2-}$ and chlorine.

Keywords: thiosulfate, perchlorate, granular activated carbon, quaternary ammonium, ion exchange

INTRODUCTION

Sulfur Redox Species

Intermediate sulfur species can exist in anoxic waters that have a redox level between those of H_2S and sulfates (SO_4^{2-}). These intermediate species could include polythionates, thiosulfate ($S_2O_3^{2-}$), and tetrathionate with sulfur valences of +1.67 and +2.5 (Table). Intermediate sulfur species can derive from reduced sulfur species such as sulfides, can occur naturally in reduced groundwaters and hydrothermal waters and aqueous systems where hydrogen sulfide (H_2S) and bisulfide (HS^-) are present (Druschell et al., 2003a.b; Jorgensen, 1990).Research indicates that thiosulfate ($S_2O_3^{2-}$) appears in hydrothermal waters (Webster, 1987; Barnes, 1979; Veldeman et al., 1991; Xu et al., 1998, 2000) and is an important intermediate in the sulfur cycle between H_2S and SO_4^{2-}. Also, polythionates are abundant in many different systems such as acid carter lakes (Veldeman et al., 1991) and gold ore leaching solutions (O'Reilly et al., 2002). Schoonen 1989 stated that the concentrations of $S_2O_3^{2-}$ and other intermediate-valent sulfur species in natural waters should thermodynamically be less that 0.01% of the total dissolved sulfur. However concentrations have been observed considerably above this percentage (Boulegue, 1978; Webster, 1987, 1989; Veldeman, 1991). Concentration of $S_2O_3^{2-}$ in anoxic environments can range up to a few hundred micromoles per liter (Druschel et al. 2003a). Thiosulfate can constitutes sixty-seven to seventy-five percent of the intermediate oxidation products from HS^- (Jorgensen, 1990). Thus, $S_2O_3^{2-}$ has a kinetically dynamic relationship to H_2S and HS^- in anoxic environments, and $S_2O_3^{2-}$ is an important intermediate product of gradual oxidation reactions as H_2S oxidizes to SO_4^{2-}. In the aqueous environment, intermediate sulfur species are formed due to the gradual oxidation process of HS^- in the presence of low dissolved oxygen (DO). The oxidation of sulfides in a basic environment similar to that of groundwater has been postulated to yield intermediate products such as polysulfides, sulfites, and $S_2O_3^{2-}$ as well as the oxidized species SO_4^{2-} (Lyn and Taylor, 1992; Siu and Jia, 1999; Thompson et al., 1995; Sharma et al., 1997). In a basic environment $S_2O_3^{2-}$ is relatively stable when formed from the oxidation of sulfides (Siu and Jia, 1999). Allen and Day (1927, 1934, 1935) reported concentrations of $S_2O_3^{2-}$ in alkaline hot springs water in the Yellowstone Natural Park and the geysers of California. Thiosulfate can also be formed from the fast oxidation of inorganic polysulfide that can be found in near - neutral and basic aqueous systems (Kamyshny et al., 2006). Thus, per redox reactions, $S_2O_3^{2-}$ appears as an important intermediate – valence sulfur oxyanion in groundwaters.

Table Species of sulfur based ions and their valence state

SPECIES	**FORMULA**	**S VALENCE**	**Relative Stability/ Oxidation rate at near neutral pH in aqueous systems (in times of Days)**	**Observed IC (DX 12O) Peak time (mins)***
Hydrogen Sulfide	H_2S	-2	Unstable. Oxidized to form SO_4^{2-}, $S_2O_3^{2-}$, and other intermediate valence species. (Thompson et al., 1996; Senning, 1972)	3
Elemental Sulfur	S	0	Stable in the form of S8 ring. Slow oxidation (Steudel, 1996)	not tested
Hexathionate	$S_6O_6^{2-}$	+1.67	Unstable. Oxidized in minutes to form $S_2O_3^{2-}$. (Miura and Kawaoi, 200; Senning, 1972)	not tested
Pentathionate	$S_5O_6^{2-}$	+2	Unstable. Fast oxidation to $S_2O_3^{2-}$ (Miura and Kawaoi, 2000; Iguchi, 1958)	not tested
Thiosulfate	$S_2O_3^{2-}$	+2	Stable. Oxidize slowly to $S_4O_6^{2-}$, SO_4^{2-} (Siu and Jia, 1999; Iguchi, 1958; Rolia and Chakrabarti, 1982; Senning, 1972)	7.4
Tetrathionate	$S_4O_6^{2-}$	+2.5	Unstable. Decompose to form $S_2O_3^{=}$ and $S_3O_6^{=}$ (Druschel, 2003; Rolia and Chakrabarti, 1982; Senning, 1972).	not tested
Dithionite	$S_2O_4^{2-}$	+3	Unstable. Oxidize in seconds to SO_2^{-} radical, $S_2O_3^{2-}$ and HSO_3^{-}, in the presence of oxygen	Not tested
Trithionate	$S_3O_6^{2-}$	+3.33	Unstable. Decompose to $S_2O_3^{2-}$ (Druschel, 2003; Rolia and Chakrabarti, 1982)	Not tested

Sulfite	SO_3^{2-}	+4	Unstable, reacts with air to form SO_4^{2-} (Senning, 1972)	6.2
Dithionate (Hydrosulfite)	$S_2O_6^{2-}$	+5	Stable. Low oxidation rate with forced oxygen at room temperature. Oxidize to SO_4^{2-}, with strong oxidizing agents (Wang and Zhao, 2007; Senning, 1972)	3.9
Sulfate	SO_4^{2-}	+6	Stable	5.4

*** Peak times shown are for 1 IC run. Peaks times may vary due to eluent concentration, and age of column and ionic strength of water.**

Sulfur intermediates can persist for times measured in hours and days and this constitutes significant durations, relative to the time that water resides within a water treatment facility. Amongst the sulfur intermediate shown in Table 1, $S_2O_3^{2-}$ is one that can persists for times measured in days when in the presence of incidental air contact (Senanayake, 2004; Rolia and Chakrabarti, 1982; Zhang and Dreisinger ,2002; Lam and Dresinger ,2003; Breuer and Jeffrey 2003a,b; Millano et al., 1983) Chu et al. 2003 showed that intensely oxygen sparging $S_2O_3^{2-}$ solution with 200 ml O_2 per min, the $S_2O_3^{2-}$ had decreased only by 10% after 10 minutes sparging and 40% after an hour of oxygen sparging. Thus, even intense oxygen sparging would not offer a practically rapid means of transforming $S_2O_3^{2-}$ to SO_4^{2-} in water treatment applications.

It can also be noted that when the oxidation rate of HS^- to $S_2O_3^{2-}$ is higher than the oxidation rate of $S_2O_3^{2-}$ to SO_4^{2-} in a system, then there will be an accumulation of these competitive intermediate species in a treatment system.

Several research papers have appraised the use of $S_2O_3^{2-}$ for leaching of gold (Byerley et al., 1973; Byerley et al., 1975; Breuer and Jeffrey, 2003; Chu et al., 2003). Intermediate products of $S_2O_3^{2-}$ oxidation during gold leaching can also affect the adsorption of anions to exchange sites (Senanayake, 2004; Nicol and O'Malley, 2001; 2002; Zipperan et al., 1988; Abbruzzese et al., 1995; Muir and Aylmore, 2004). It was observed by Chu et al., (2003) that disulfite, a polythionate formed in the oxidation of $S_2O_3^{2-}$ reduced the effect of gold leaching due to the competition of copper (II), $S_2O_3^{2-}$ and gold. Nicol and O'Malley (2002) showed that during the leaching of gold, the trithionate that is oxidized from $S_2O_3^{2-}$ will compete strongly with the gold -

thiosulfate complex for exchange sites on ion exchange resins. Moreover, these species exhibited stabilities of several days duration when an aqueous solution contained 4,000 mg/L $S_2O_3^{2-}$ plus ammonia, a fifth of the $S_2O_3^{2-}$ had converted to trithionate after two days (Nicol and O'Malley, 2002). But tetrathionate was less stable.

Motivation for Hypothesis Regarding Intermediate-Sulfur Oxyanions

Our Penn State team has developed a water treatment technology where granular activated carbon (GAC) has been tailored with quaternary ammonium surfactants or ammonia to increase the bed life of the carbon for removing ClO_4^- and other oxyanions (Parette and Cannon 2005a,b; Parette et al., 2005; Chen and Cannon, 2005; Chen et al., 2005a,b). The surfactant tailored GAC increased the carbon bed life 33 times when removing 70 µg/L of the ClO_4^- from Redlands groundwater at the rapid small scale column test (RSSCT) level (Parette and Cannon 2005a,b; Parette et al., 2005). Demonstration and pilot scale studies that were conducted at the Texas Street Water Treatment Plant depicted ClO_4^- breakthrough earlier than in RSSCT trials that employed barrels of the Redlands water that had been stored in Penn State for a month or longer. However, when RSSCTs employed Redlands groundwater that was employed as soon as it reached Penn State, ClO_4^- breakthrough occurred considerably sooner than when employing this same groundwater after it had been stored for a month. This led our team to suspect that the gradual oxidation of a competing oxyanion intermediate was playing a role. The authors also noticed that the Redlands groundwater that was tested at the source showed a negative redox value of -125 mV which inferred that this water was in a reduced form. In contrast, Redlands groundwater that had been shipped to our Penn State lab and stored for several months showed positive redox values ranging from +150 to 200 mV. These two redox probes may not have been normalized to the same redox solution; and some scientists question the quantitative value of any redox measurements. None the less these results together raised the intriguing hypothesis that the Redlands groundwater contained a species that in its reduced form competed quite significantly with ClO_4^-, but in its oxidized form did not compete as prominently. Such could be the case with sulfur oxyanions which could represent transition species between the reduced sulfides and the oxidized sulfate. In time frames that would be significant relative to water treatment operations, the sulfur could appear as $S_2O_3^{2-}$, polythionate, or other intermediate sulfur oxyanions. We further hypothesized that these intermediate sulfur oxyanions (including $S_2O_3^{2-}$) competed with the adsorption of ClO_4^- to the tailored GAC when fresh Redlands Water was employed. In concurrence with this hypothesis, background analysis of several fresh samples of Redlands water depicted an anion with the known retention time of $S_2O_3^{2-}$ and perhaps some other intermediate valence sulfur oxyanion via ion chromatography (see discussion of Figures 1 and 2 below). Thus, it was anticipated that $S_2O_3^{2-}$ specifically could be at least one of the intermediate sulfur species that competed with ClO_4^- for adsorption sites. Also $S_2O_3^{2-}$ served as a surrogate for other anoxic / reduced sulfur based oxyanions that had a sulfur valence between that of H_2S and SO_4^{2-}.

Objective and Hypothesis

In light of this background, our specific objective was to test the hypothesis that $S_2O_3^{2-}$ competitively diminished ClO_4^- sorption on GAC that had been preloaded with quaternary ammonium surfactant. Moreover we hypothesized that stoichiometrically designed chlorination dosing could oxidize $S_2O_3^{2-}$ to SO_4^{2-}; and then the SO_4^{2-} would not extensively diminish the bedlife for ClO_4^- sorption.

Chlorine Oxidation of Intermediate-valence sulfur oxyanions

Oxidants that effectively oxidize reduced and intermediate sulfur species to SO_4^{2-} include chlorine, ferrate, hydrogen peroxide, permanganate and ozone (Levine et al., 2004; Suidan et al., 1977). Chlorine is often the less expensive oxidant; and it has been commonly used to oxidize hydrogen sulfide to SO_4^{2-}. Sodium thiosulfate can be routinely used as a dechlorinating agent in analytical labs (Tchobanoglous et al., 20003). However, we are aware of very few refereed journal papers that appraise the oxidation of other native intermediate valence sulfur oxyanions such as tetrathionate, dithionate and polythionates. Also we are not aware of any other researchers who have appraised the competition of $S_2O_3^{2-}$ with ClO_4^- or other oxyanions for adsorption sites onto media that employ quaternary ammonium functional groups.

This paper appraises chlorine as an oxidant for converting $S_2O_3^{2-}$ to SO_4^{2-} so the sulfur species incurs less sorption competition for ClO_4^-. As background, Penn State experiments that were carried out with SO_4^{2-} (the most oxidized compound in the sulfur cycle) showed that 250 mg/L SO_4^{2-} incurred only slight competition with ClO_4^- for adsorption sites (Patterson, 2009).

Stoichiometrically, a molar ratio of 4 moles of chlorine to 1 mole of $S_2O_3^{2-}$ will result in complete oxidation of $S_2O_3^{2-}$ to SO_4^{2-} as per equation 1-3.

$4Cl_2 + 4H_2O \longrightarrow 4HOCl + 4H^+ + 4Cl^-$ **Equation**

$4HOCl + S_2O_3^{2-} + H_2O \longrightarrow 2SO_4^{=} + 4Cl^- + 6H^+$ **Equation**

$4Cl_2 + S_2O_3^{2-} + 5\ H_20 \longrightarrow 2\ SO_4^{=} + 8Cl^- + 10\ H^+$ **Equation**

With groundwater pH ranging between 7-8.5 and intermediate-valence sulfur oxyanions concentration in micromoles per liter, chlorination of these sulfur species will favor the formation of SO_4^{2-} as opposed to elemental sulfur (Levine et al., 2004). And this outcome is desirable in water treatment systems.

Chlorination treatment processes are also influenced by activated carbon since the activated carbon serves as a redox surface that can reduce chlorine to chloride (Collivignarelli, et al., 2006; Dixon and Lee, 1991; Gonce and Voudrias, 1994; Hassler, 1967; Snoeyink et al., 1981; Hwang et al., 1989). Hassler, 1967 and Martin and Shackleton (1990) observed that activated carbon can dechlorinate water through a combination of adsorption and catalysis processes. Moreover, as an unfavorable side effect incurred via excessive chlorination, the activated carbon surface can experience oxidative degradation, yielding oxygenated substituents (Snoeyink et al., 1981) such as carboxyls whose negative charge could repel the ClO_4^- anion. Also, under the conditions herein, there was a possibility that chlorine could oxidize the reduced – N in the quaternary ammonium functionality. If this occurred it could inactivate the quaternary ammonium's ability to exchange with perchlorate. However, tests showed that this did not occur for the conditions herein as described below.

EXPERIMENTAL

Materials

The granular activated carbon (GAC) that was used in these experiments was bituminous based UltraCarb unless otherwise identified. This activated carbon was obtained from Siemens Water Technologies (formerly USFilter) of Los Angeles CA. One experiment employed activated carbon. This bituminous – based activated carbon was obtained from Superior Adsorbents Inc. of Emlenton, PA. The carbon was ground and sieved to a mesh size of US # 200 x 400, which was 38 x 75 µm.

Unless otherwise listed , the groundwater for these experiments originated Redlands California, Texas Street Well 31A.This native groundwater contained 30 µg/L ClO_4^-, 55 mg/L SO_4^{2-}, and 38 mg/L nitrate as NO_3^- (Table). When fresh, this Redlands groundwater also contained some intermediate sulfur species, as discussed below. The Redlands water was stored in 55 gallons polyethylene barrel at ambient temperature and they were sealed with polyethylene caps that were not airtight.

Several initial experiments employed Redlands groundwater that was sampled earlier (identified as earlier vintage herein), and this contained 52 µg/L ClO_4^- and 10 mg/L nitrate as NO_3^-.

Table Water Chemistry of Redlands Groundwater from Well 31A at the Texas Street Plant* used herein unless otherwise identified.

Contaminants/ Specie	**Concentration**
Perchlorate	30 µg/L
Sulfate	55 mg/L
Chloride	14 mg/L
Nitrate as NO_3^-	38 mg/L
Total dissolved solids	250 mg/L
Total Alkalinity	160 mg/L as CaCO3
Bicarbonate	210 mg/L

***Some tests employed vintage Redlands groundwater that contained 52µL ClO_4^- and 10 mg/L nitrate as NO_3^-.**

The cationic surfactant used was dicocoalkyldimethylammonium chloride (Arquad 2C-75). Arquad 2C-75 was chosen because its two long carbon chains that facilitates low leaching of the surfactant from the carbon (Parette and Cannon, 2005, Parette et al. 2005). The $S_2O_3^{2-}$ source was sodium thiosulfate by Fisher Scientific. Arquad 2C-75 were prepared from analytical grade reagents that were dissolved in deionized distilled water.

Methods

Sodium Thiosulfate Solution Preparation

Thiosulfate spiking concentrations and analysis standards was prepared from1g/L as $S_2O_3^{2-}$ the stock solution. During RSSCT experiments, to ensure that a relatively uniform thiosulfate concentration was used at all times, stock solutions and influent solutions were prepared every 3 days in a given RSSCT run period. All other solutions were prepared from analytical grade reagents and deionized distilled water.

To test the rate of thiosulfate degradation with incidental air contact 1 mg/L of $S_2O_3^{2-}$ was mixed into 200 mL of deionized distilled or Redlands water and let stand without further agitation in capped bottles. Thiosulfate was tested at T=0 day and daily until 50% of $S_2O_3^{2-}$ remained in the solution after 5 days.

Rapid Small Scale Column Tests

The rapid small scale column tests (RSSCTs) were designed for proportional diffusivity according to Parette and Cannon, (2005a). The RSSCT columns were dry- packed with UltraCarb; and glass wool was packed at both ends. 1.27 g of UltraCarb GAC was used and tailored with 33 bed volumes of 0.4% Arquad 2C-75 solution that was recirculated through the bed for 3 days, during which the surfactant solution was pumped and recirculated at a rate of 2 mL per minute through the carbon media. The surfactant tailored GAC was not washed before the introduction of the ClO_4^- contaminated influent water solution. This protocol had been observed to pre-load 0.24 g Arquad 2C-75/ g GAC, which correspond to 0.56 meq of active N functionality / g GAC (Parette et al., 2005a).

The RSSCTs were conducted at ambient temperatures, which were measured at $20 \pm 2^{o}C$; and the flow rate was maintained at 2.5 mL/min through a 2.65 mL bed, giving a 1.1 minute empty bed contact time (EBCT) through the RSSCT. Per proportional diffusivity, this would simulate an EBCT of 10 minutes for the US# 12 x 40 mesh size GAC (0.55 mm x 0.75 mm) that could be used at the field scale level. Pumps (Waters models 501 and 510) were used to provide flow; and these had been disengaged from prior HPLC analytical instruments.

Chlorine Gas Preparation and Application

Because of heightened security issues, US university labs cannot readily acquire chlorine gas directly. Thus, we produced chlorine gas by reacting 1.5 g of potassium permanganate with 3.5

mL of concentrated HCl (Equation 4), then bubbled the resultant chlorine gas into a plastic polyethylene collapsible container that contained deionized distilled water. This formed a mixture of HOCl and hydrochloric acid (Equation 5). Dilutions were carried out when necessary to get the correct concentrations that were needed stoichiometrically, to oxidize $S_2O_3^{2-}$ but not more or less. HOCl solution was monitored daily to ensure the correct concentration of free chlorine was present to oxidize $S_20_3^{2-}$.

$6HCl + KMNO_4 + 2H^+ \longrightarrow 3Cl_2 + 2MnO_4 + 4H_20 + 2K^+$ Equation

$H_20 + Cl_2 \longrightarrow HOCl + HCl$ Equation

Operation of RSSCTs with concurrent perchlorate/thiosulfate spiking and chlorine oxidation

During RSSCT operations, one pump supplied water that was spiked with the $ClO_4^-$and or $S_2O_3^{2-}$ while the second pump supplied the HOCl solution separately when included (Figure 1). This was done to control the contact time between the free chlorine and $S_2O_3^{2-}$ solution. Collapsible plastic containers were used to store the solutions to ensure that the $S_2O_3^{2-}$ did not oxidize before use and that the HOCl did not dissipitate before use. Also the $S_2O_3^{2-}$ solution was replaced every 3 days, so as to maintain its proper concentration. Both solutions were covered with a dark plastic to also ensure no reactions with light.

Various concentrations of chlorine, $S_2O_3^{2-}$ and ClO_4^- were appraised using deionized distilled water or Redlands, CA groundwater. Spiked concentration of $S_2O_3^{2-}$ included 40, 250, 500 and 1000 µg/L as $S_2O_3^{2-}$. The chlorine dose ranged from 0 – 3.5 mg/L as Cl_2 (Table); and was paced to offer either the stochiometric amount needed to oxidize the $S_2O_3^{2-}$ per equations 1-3 (in most cases); or to offer an excessive amount.

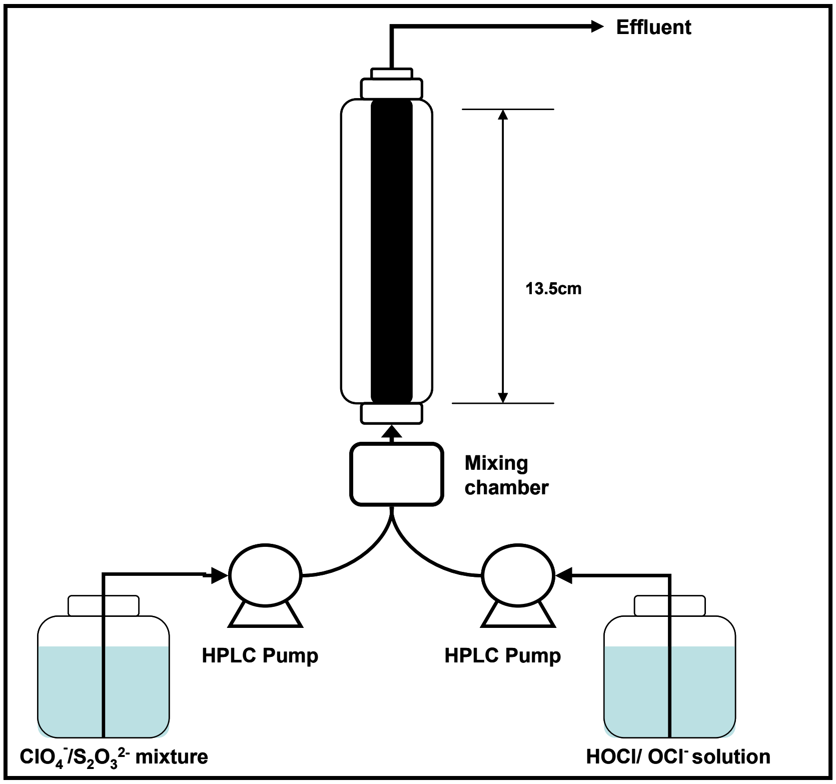

Figure - Schematic of the RSSCT experimental set-up when concurrently spiking perchlorate/thiosulfate and oxidizing with chlorine.

These experiments employed a mixing chamber when reacting the $S_2O_3^{2-}$ with HOCl. The chamber had a 5 minute detention time with a stir bar mixing at 250 rpm, and a velocity gradient G of 348 sec^{-1}. Preliminary mixing test conducted showed that this achieved sufficient mixing to achieve $S_2O_3^{2-}$ oxidation before the water flow entered the column. The presence of thiosulfate was tested after the 5 minute retention time and it found that no $S_2O_3^{2-}$ was present.

Effluent water samples were collected 2 times per day from the RSSCT effluent until at least 50% of the influent ClO_4^- concentration was observed in the effluent.

Monitoring Perchlorate, Thiosulfate Anion and Surfactants

Perchlorate and $S_2O_3^{2-}$ were monitored by use of Dionex 120 ion chromatograph system, which was equipped with an AS40 auto sampler, a 4 mm AS16 column, and a 4 mm AG16 guard column. The DS4 suppressor was set at 300 mA and a temperature of 35°C. Sodium hydroxide solution either at 25 mM or 30 mM was used as the eluent. When 25 mM of NaOH was employed, the relative peak time for thiosulfate ranged between 7.0 and 7.8 minutes, while for perchlorate peak times ranged between 14.0 and 15 minutes. Shorter peak times are observed at a higher eluent concentration, at 30 mM, thiosulfate range from 5.5 to 6 minutes and perchlorate 10 to 11 minutes. Other anions were also monitored with Dionex 120 ion chromatograph system, while using the proper eluent concentration.

The concentrations of surfactants were monitored by a colorimetric method (Tsubouchi et al., 1981; Parette et al. 2005). This method has a detection limit of 0.1-0.2 mg/L.

Quality assurance analyses were conducted to discern the accuracy to which ClO_4^- could be measured at Penn State. Experimental quality was conducted at all stages of the experiments and data handling protocols. A formal quality assurance program was practiced to ensure that the Penn State laboratory was operating according to the requirements of EPA method 314.0. Table 3 shows a list of our quality control checks and the acceptable criterion that was met. The Minimum Detection Level (MDL) was also calculated and estimated to be 1µg/L for our instrument. The author noted that the chromatographic time for ClO_4^-, $S_2O_3^{2-}$ and other anions to elute will vary due to factors such as age of the column, eluent concentration and the type of water tested. It is observed that deionized distilled water has a shorter retention time than water that has an ionic strength. Also as the column gets older the retention time of anions will be longer. Eluent concentration affects elution time in that a higher concentration depicts shorter retention time.

Table Quality control check criteria

QC Check	**Frequency**	**Acceptable Criterion**	**Results**
Calibration Curve	1	R^2 - ≥0.997	0.9995
Check Sample	1/10 samples	±15%	3%
Matrix conductivity	Each sample	< 6400 µs/cm	Criterion met for all samples
Method Blank	2 per IC run	No trace	No trace
Replicate	1 per 10 samples	±20%	<5%
Matrix	1/20 samples	80%-120%	111%

Spike/Duplicate			

EXPERIMENTAL RESULTS AND DISCUSSION

Initial Comparisons of Fresh versus Aged Redlands Water

In early work that compared various RSSCTs and field scale operations, the team had observed variations in bedlife performance. Specifically, when RSSCTs employed freshly received Redlands water within one week storage in a 55 gallon closed barrel), the ClO_4^- broke through sooner than when RSSCTs employed Redlands water that had been aged (stored) for longer than a month. Likewise, when full-scale tests were demonstrated at Redlands with very fresh water, the initial ClO_4^- breakthrough was sooner than when using Redlands water that had been aged for longer than a month (Figure). These initial RSSCTs and full-scale demonstrations used the earlier vintage Redlands water, with ClO_4^- at 52 μg/L and nitrate at 10 mg/L as NO_3^-; and the surfactant tailoring agent was cetylpyridinium chloride (CPC). Some of these differences could be attributed to inherent distinctions between RSSCTs and full-scale operations, for example, others have observed that RSSCTs can often exhibit sharper breakthrough profiles than do full-scale beds when using conventional GAC; and that is the pattern observed here, where the full scale bed exhibited earlier initial breakthrough, but the same BV to half breakthrough as did the RSSCT. Also some compounds behave according to proportional diffusivity, while others do not (Patterson, 2009). Also, the field scale GAC hosted slightly less surfactant loading by10-15% than did the RSSCTs.

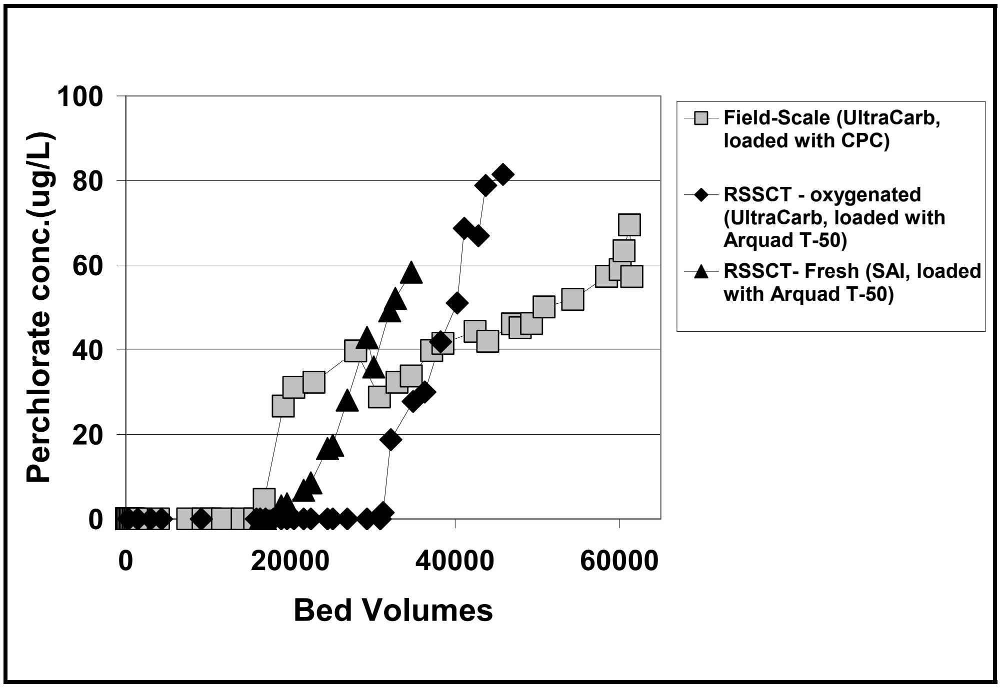

Figure – Comparison of RSSCTs with Fresh versus aged Redlands water and with full-scale performance. These tests used Redlands groundwater with 52 µg/L ClO_4^- and 10mg/L nitrate as NO_3^-

None-the-less, the distinctions between the RSSCTs with fresh versus RSSCT with aged Redlands Water had to be attributed to something other than similitude considerations. The authors hypothesized that these distinctions were associated with competitive oxyanions whose concentrations were redox sensitive. For the work herein we particularly appraised suspected sulfur based oxyanions that were intermediate between sulfide and sulfates.

As a substantiation of this hypothesis, ion chromatograms of fresh Redlands water exhibited peaks that just preceded the ClO_4^- peak; and these peaks disappeared in the aged Redlands Water. For example, when the raw Redlands groundwater was sampled into a sealed vial and mailed overnight to Penn State, our team observed a distinct ion chromatograph peak at 6.1 minutes (Figure), and for eluent and column conditions; this corresponded to the $S_2O_3^{2-}$ peak.

It is note worthy that these peaks occur just before the ClO_4^- peak. Since ion chromatogram resin media often employ quaternary ammonium functionality, this similar time to peak breakthrough behavior inferred that likewise in the quaternary ammonium tailored GACs these same intermediate sulfur species would likewise compete with ClO_4^- relative to RSSCT bed life.

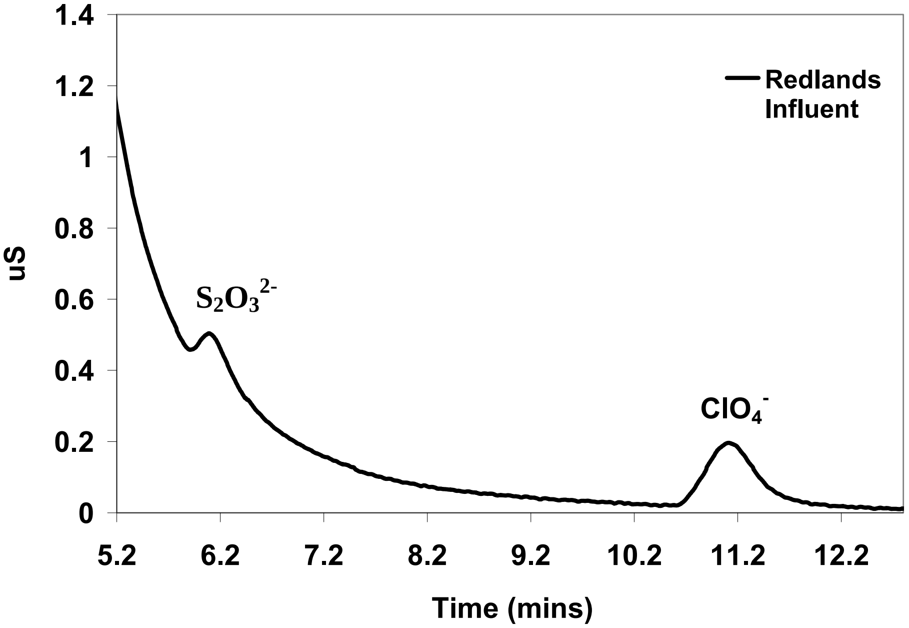

Figure - Conductivity Chromatogram for Redlands groundwater that was sampled on-site and shipped overnight to be tested, shows retention times of ClO_4^- and an unknown peak that corresponds to when thiosulfate or other intermediate-valence sulfur oxyanions would elute using the DX 120 ion chromatogram instrument.

Stability of Sulfur Species in the Presence of Indicated Air Contact

In follow-up to this observation, the authors tested the stability that sulfides and intermediate sulfur oxyanions could have in a reduced groundwater when it becomes exposed to incidental air. To simulate this, the authors spiked 1 mg/L S^{2-} into deionized / distilled water that was exposed to incidental air contact. This water was held in a container that was closed but not air tight, or that was open to air on top with no lid—and these two configurations yielded the same results. Within an hour exposure to this incidental air contact, much of the S^{2-} oxidized to SO_4^{2-}. But ion chromatograph analyses revealed that some S^{2-} oxidized only partially to $S_2O_3^{2-}$ (Figure 4). These analyses employed 25mM NaOH eluent, for which the IC thiosulfate peak appeared at 7.4 minutes. Additionally, the chromatogram showed two other peaks that exited the IC after the $S_2O_3^{2-}$ had; and these were taken to be other intermediate valence sulfur species. The chromatogram at 20 hours was essentially the same as the chromatogram at 1 hour. Then, after 10 days, neither the S^{2-} nor the $S_2O_3^{2-}$ appeared; although a sulfur intermediate with a longer retention time still remained (Figure 4). It should be noted to the readers that intermediate valence sulfur compounds are very reactive and therefore unstable; as mentioned previously these compounds can react with each other and will undergo decomposition as was observed in Figure 4. As a consequence of this the analytical determination of intermediate sulfur species can be quite difficult.

The authors sought to discern how long the spiked $S_2O_3^{2-}$ would remain in a stock water supply. For this test, 1 mg/L sodium thiosulfate was spiked into distilled water, which remained in a closed 5 gallon container that allowed for incidental surface contact with air, but no mixing. After 3 days the $S_2O_3^{2-}$ concentration in solution decreased by a mere 5% and after 5 days by 50% (Figure). When this experiment was repeated with Redlands groundwater, the same results occurred. There were no significant difference between Redlands groundwater and deionized distilled water.

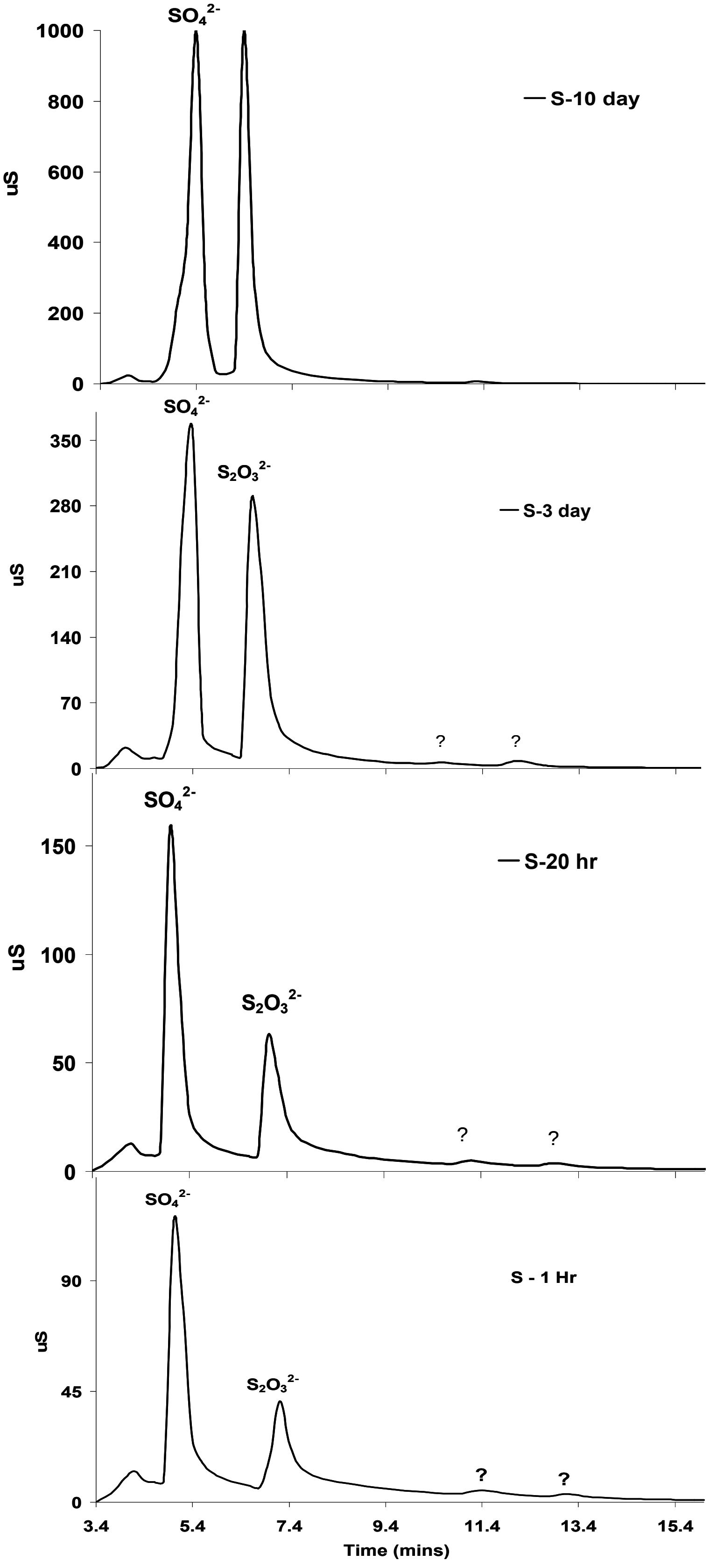

Figure - Conductivity chromatogram showing sulfide oxidation by incidental contact with air, after 1 hour 20 hr, 3 days and 10 days. Initial concentration was 1 mg/L of sulfide in deionized distilled water

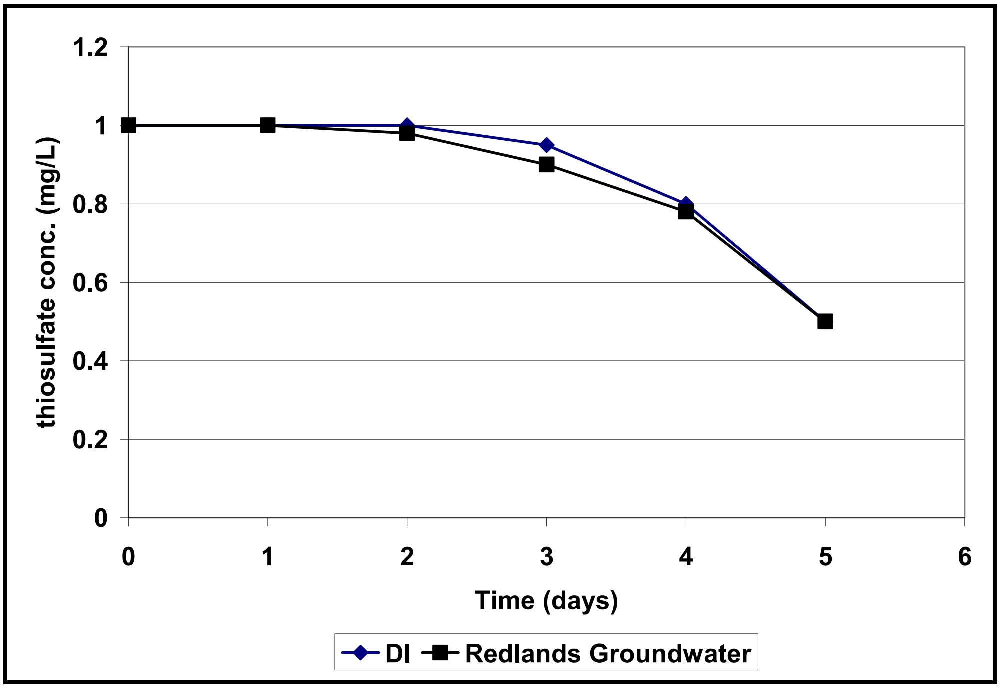

Figure - Rate of $S_2O_3^{2-}$oxidation in deionized distilled and Redlands groundwater, when the water source experienced incidental surface contact with air but with no mixing. Initial $S_2O_3^{2-}$ is 1 mg/L.

Competition by Thiosulfate for Perchlorate Sorption and Chlorine Oxidation

Rapid Small Scale Column Tests (RSSCT) was conducted to test the hypothesis that intermediate valence sulfur species competed with ClO_4^-, for sorption onto GAC that had been preloaded with quaternary ammonium surfactants. In light of the literature, and the availability of operational and chromatographic protocols, the authors chose to appraise $S_2O_3^{2-}$, served as a surrogate for both itself and other sulfur intermediates. To appraise such competition, the authors spiked either deionized distilled water or Redlands groundwater with various doses of $S_2O_3^{2-}$; and the RSSCT experiments that were conducted to test this hypothesis are listed in Table . Also the authors sought to test the hypothesis that chlorine could diminish this competition by oxidizing the $S_2O_3^{2-}$. All these RSSCTs employed GAC that was tailored with Arquad 2C-75; and the Redlands groundwater source contained 30 µg/L ClO_4^- and as 38 mg/L nitrate as NO_3^-.

Table List of experiments conducted using both deionized distilled water and Redlands groundwater

Water source	**RSSCT start time: # of days after receipt of barrel**	**ClO_4^- Conc. (µg/L)**	**$S_2O_3^{2-}$ conc. (µg/L)**	**Free Chlorine dose (mg/L)**	**Bed Volumes to 6 µg/L ClO_4^-**
Deionized distilled Water	-	1000	-	-	15,000
	-	1000	100		9,500
	-	1000	1000		8,000
	-	1000		2.5	9,000
	-	1000	100	0.25	13,000
	-	500	-	-	20,000
	-	500	500	-	10,000
	-	500	500	3.5	16,000
Redlands Groundwater, 38 mg/L nitrate as NO_3^-	***Fresh***	***52***	**-**	**-**	***22,000***
	Aged	***52***	**-**	**-**	***35,000***
	Aged (60 days)	30	-	-	33,000
	Aged (30 days)	30	-	-	33,000
	Fresh (1 day)	30	-	-	24,000
	Aged (120 days)	30	1000	-	25,000
	Aged (30 days)	30	40	-	33,000
	Aged (135 days)	30	250	-	33,000
	Aged (240 days)	30	-	-	38,000
	Aged (10 days)	30	1000	-	17,000
	Aged (44 days)	30	1000	-	18,000
	Aged (150 days)	30	1000	2.5	31,000
	Aged (210 days)	30	1000	2.5	31,000
	Aged (60 days)	30	500	-	17,000
	Aged (120 days)	30	500	1.25	>28,000
	Aged (132 days)	30	500	1.25	>28,000

***Perchlorate did not breakthrough by 28,000 bed volumes, the duration of these tests**

***"Fresh" Experiments employed Redlands groundwater that had aged less than a week. Otherwise Redlands RSSCT experiments employed groundwater that had aged for at least 10 days.**

RSSCT with Synthetic Deionised Distilled Waters

The first array of these RSSCTs discussed herein employed deionized distilled water that was spiked with 1000 µg/L ClO_4^- plus various levels of $S_2O_3^{2-}$ (0 – 1000 µg/L) and free chlorine (0 – 3.5 mg/L), as presented in Table . When 1000 µg/L ClO_4^- alone was present in deionized distilled water, surfactant tailored GAC removed ClO_4^- to below 6 µg/L for 15,000 bed volumes (BVs). However, when the deionized distilled water also contained 1000 µg/L $S_2O_3^{2-}$, the tailored GAC removed ClO_4^- to below 6 µg/L for only 8,000 BVs (Figure). Thus $S_2O_3^{2-}$ did indeed compete with ClO_4^- for adsorption sites.

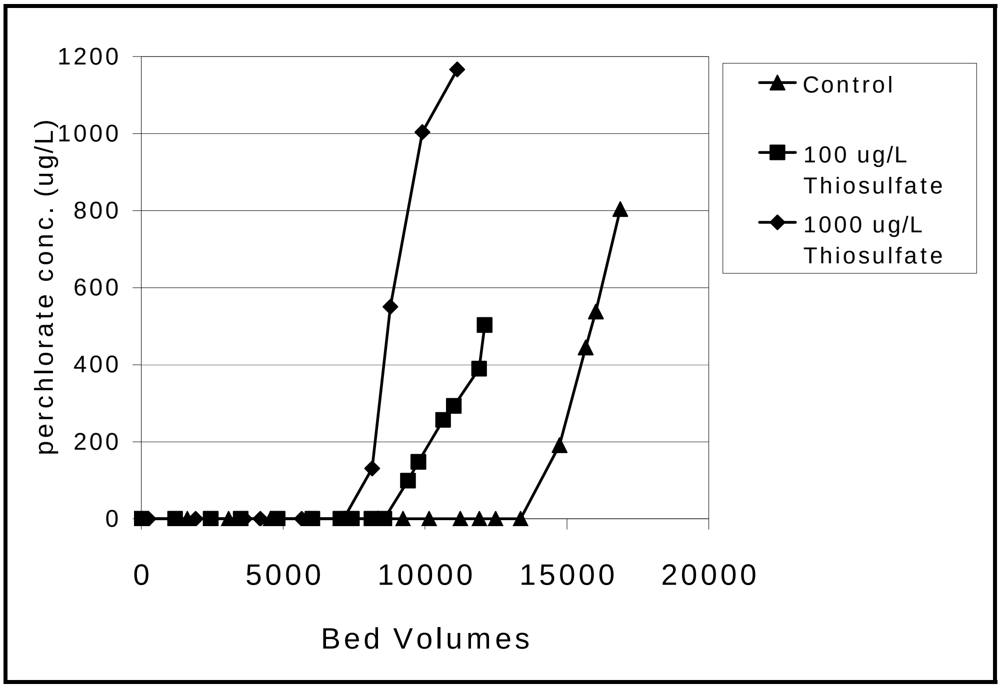

Figure - The effects of $S_2O_3^{2-}$ on ClO_4^- adsorption to TGAC using deionized distilled water

Next we sought to discern the effects of adding 2,500 µg/L chlorine to deionized distilled water that contained 1,000 µg/L ClO_4^- but no $S_2O_3^{2-}$. In this case, the chlorine diminished bed life to 9,000 BV, as shown in Figure . Thus the chlorine either oxidized the carbon surface to create negatively charged oxygenated substituent that hindered ClO_4^- diffusion through the GAC grain; or the chlorine oxidized the quaternary ammonium active exchange site or both. To test whether chlorine was oxidizing the quaternary ammonium surfactant, the authors conducted an experiment where chlorinated water - 2.2 g/L Cl2 concentration in deionized distilled - was used as the tailoring solution instead of deionized distilled water. The surfactant loading was 0.25 g / g GAC and at 1000 µg/L ClO_4^-, breakthrough of ClO_4^- occurred at 16,000 bed volumes. From these results the authors concluded that there was no significant difference between the experiments that used a tailoring solution that used chlorinated water and the solution that employed only deionized distilled. It was concluded from this result that chlorine does not affect the quaternary ammonium active exchange site for perchlorate.

The authors note that the conventional carbon surface offers little sorption capacity for perchlorate. Thus these results indicate that the chlorine was oxidizing the carbon surface in a manner that rendered it more negatively charge; and it was this negative charge that imposed a reverse Donnan effect (Jang et al., 2009) that precluded the perchlorate from penetrating the pores to where the resident surfactant quaternary ammonium could sorb it.

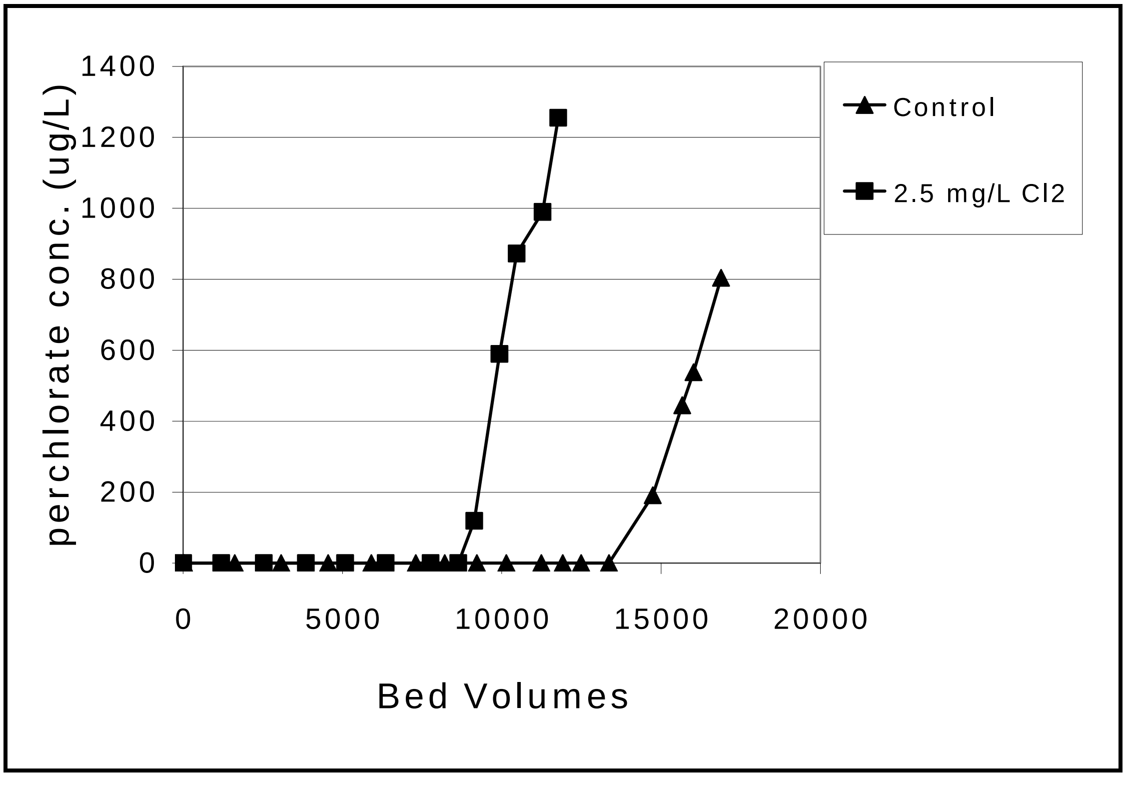

Figure - The effects of chlorination on ClO_4^- adsorption to the surfactant tailored GAC. The influent ClO_4^-concentration was 1,000 µg/L with deionized distilled water

We next conducted three experiments with deionized distilled water where we included 1,000 µg/L ClO_4^-. For the control (spiked with only ClO_4^-), breakthrough occurred at 15,000 BV. However, when 100 µg/L of $S_2O_3^{2-}$ was also included, 6 µg/L breakthrough occurred at 9,500 BV (Figure). In contrast, when the stoichiometric amount of 0.25 mg/L chlorine was used to oxidize the $S_2O_3^{2-}$ to SO_4^{2-}, bed life reverted to 13,000 BV. Thus, this prechlorination process sustained the capacity of GAC to remove ClO_4^- when the spiked $S_2O_3^{2-}$ was oxidized by the chlorine. It is noted that SO_4^{2-} competed far less than did $S_2O_3^{2-}$ with ClO_4^- in this surfactant tailored GAC, even when the SO_4^{2-} concentration was as high as 250 mg/L (Patterson et al. 2009; Patterson, 2009).

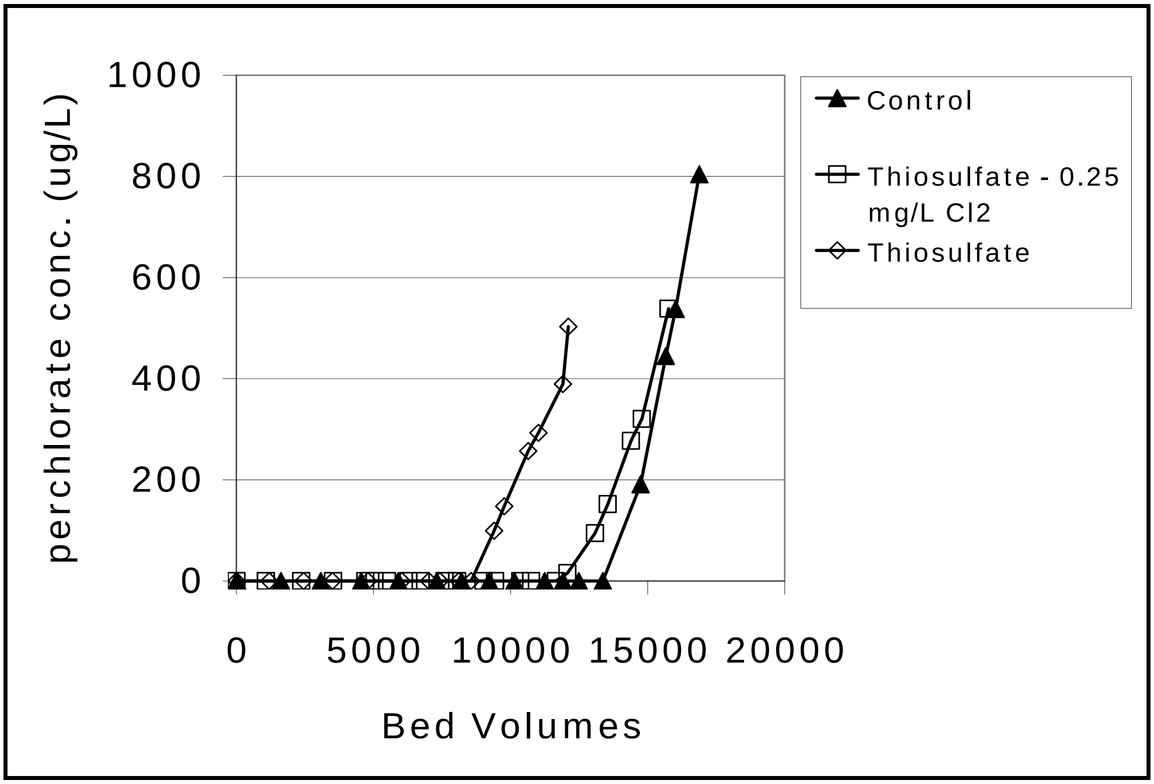

Figure - The effects $S_2O_3^{2-}$concentration and pre-chlorination on ClO_4^- adsorption. Influent concentration is 1000 µg/L ClO_4^- and 100 µg/L $S_2O_3^{2-}$, with deionized distilled water

Similarly we conducted three experiments with deionized distilled water that was spiked with 500 µg/L ClO_4^-. The control exhibited breakthrough at 20,000 BV. Then when 500 µg/L $S_2O_3^{2-}$ was also added, bed life dropped to 10,000 BV. When pretreated with 3.5 mg/L chlorine the bed life reverted to 16,000 BV (Figure). With this result it can be observed that the chlorine usefully oxidized $S_2O_3^{2-}$ and thus sustained the bed life of the GAC. These results using deionized distilled water showed that there was an affect for ClO_4^- adsorption when $S_2O_3^{2-}$ was present, and properly mixed pre chlorination oxidized this species, thus restoring to some degree the bed life of the surfactant tailored GAC. Next, the authors tested this same chlorination strategy using groundwater from Redlands, California.

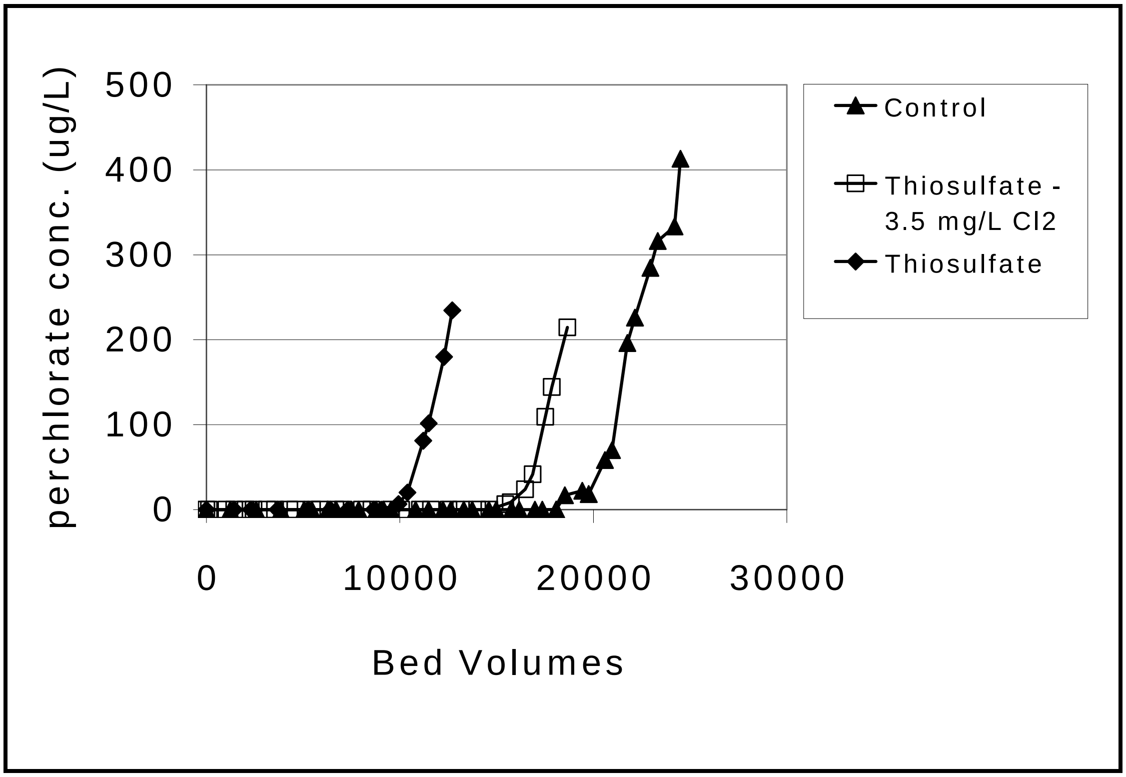

Figure - The effects of $S_2O_3^{2-}$ concentration and pre-chlorination on ClO_4^- adsorption. Influent concentration was 500 µg/L ClO_4^- and 500 µg/L $S_2O_3^{2-}$ with deionized distilled water.

Redlands Groundwater

The first of these Redlands experiments involved validating the fresh versus aged distinctions in RSSCT performance that was discussed above relative to figure 2, while using the most recent Redlands water source that contained 38 mg/L nitrate as NO_3^- and 30 µg/L ClO_4^-. As shown in Figure , this fresh Redlands groundwater exhibited 6 µg/L ClO_4^- breakthrough at 24,000 BV. In contrast, this water after aging (by storage in barrels for more than a month) exhibited breakthrough at 33,000 BV. This result was quite similar to Figure trends discussed above. Next, the authors sought to mimic the hypothesized effect of the sulfur intermediate oxyanions by adding 1000 µg/L $S_2O_3^{2-}$ to aged Redlands water. As observed in Figure , 6 µg/L ClO_4^- breakthrough occurred at 25,000 BV, virtually the same as when fresh Redlands groundwater had been used. This result concurs with the notion that when the Redlands groundwater was fresh, it contained sulfur oxyanion intermediates species that exerted the same level of competition as 1,000 µg/L of $S_2O_3^{2-}$.

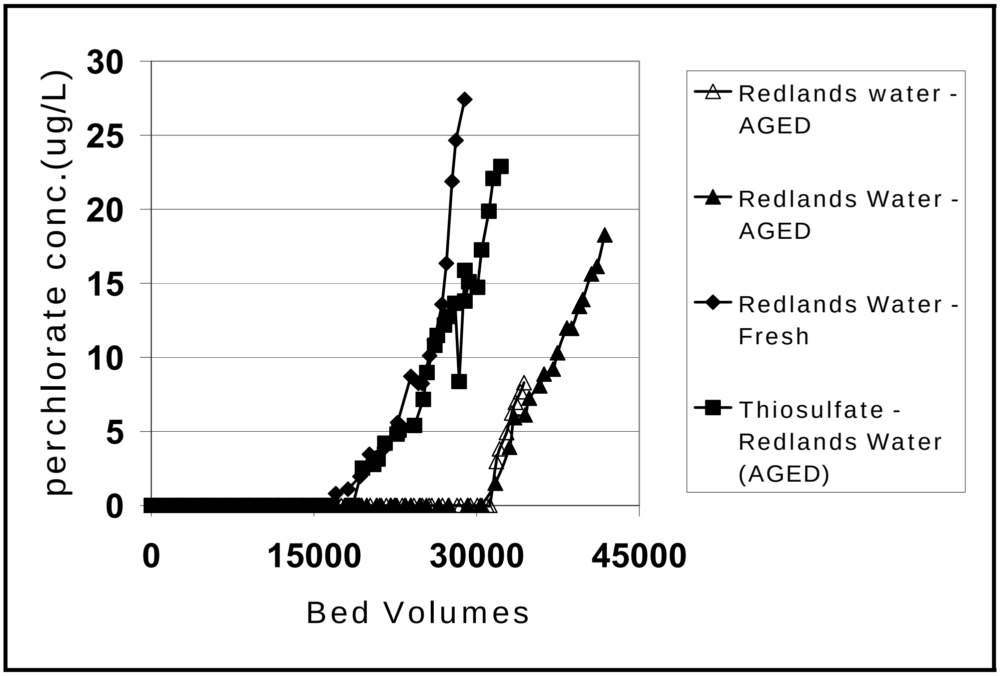

Figure - Comparing the effects of ClO_4^- adsorption to surfactant tailored GAC when spiked with $S_2O_3^{2-}$ using Redlands water that was aged versus Redlands groundwater that was relatively fresh

The aged Redlands water was spiked with other levels of $S_2O_3^{2-}$, including 40, 250, 500 and 1,000 µg/L of $S_2O_3^{2-}$ (Figure). As shown, even 250 µg/L $S_2O_3^{2-}$ exerted competition for perchlorate sorption.

The authors' note that the competition of $S_2O_3^{2-}$ and other intermediate sulfur valence oxyanions may have eluded prior appraisal in the literature, because the relatively short lives of these species dictate the need for real time analytical protocols to discern their presence. As a further complication when using granular activated carbon as the structural matrix for hosting these quaternary ammonium surfactants, the GAC surface itself can serve as a redox reactant. Thus, in all these RSSCTs the authors never observed $S_2O_3^{2-}$ presence in the tailored GAC effluent.

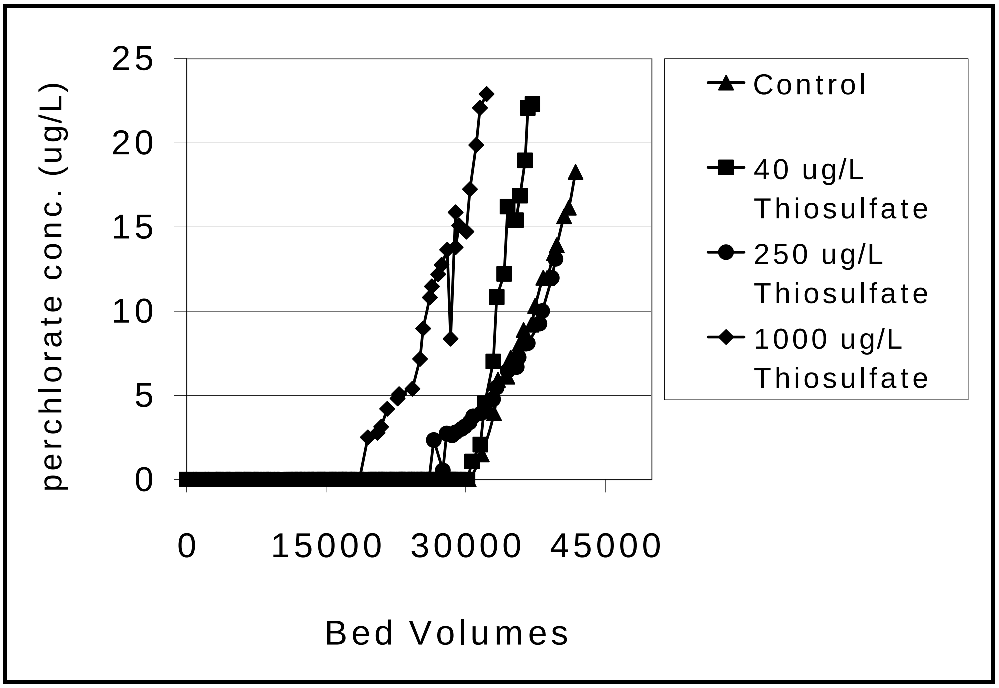

Figure - The effects of ClO_4^- adsorption to tailored GAC when spiked with 40, 250 and 1000 µg/L of $S_2O_3^{2-}$, when using Redlands water where the native ClO_4^- influent is 30 µg/L.

With this information regarding how $S_2O_3^{2-}$ affects ClO_4^- adsorption when using this native groundwater, the authors next looked at whether $S_2O_3^{2-}$ could be oxidized with chlorine, so as to diminish its competition with ClO_4^- sorption. These RSSCTs were all conducted with aged Redlands groundwater that contained 38 mg/L nitrate as NO_3^- and 30 µg/L ClO_4^-. Figure depicts the effects of chlorination on the oxidation of $S_2O_3^{2-}$ to SO_4^{2-}. With no pre-chlorination, the bed volumes to ClO_4^- breakthrough was 33,000 BV. The capacity was further diminished by 30% when 1,000 µg/L of $S_2O_3^{2-}$ was spiked into this groundwater. However, when the stochiometric amount of 2.5 mg/L chlorine (needed to oxidize $S_2O_3^{2-}$) was mixed in, the BV to 6 µg/L ClO_4^- breakthrough increased to 31,000 BV. Thus the chlorine again diminished the $S_2O_3^{2-}$ competition by oxidation.

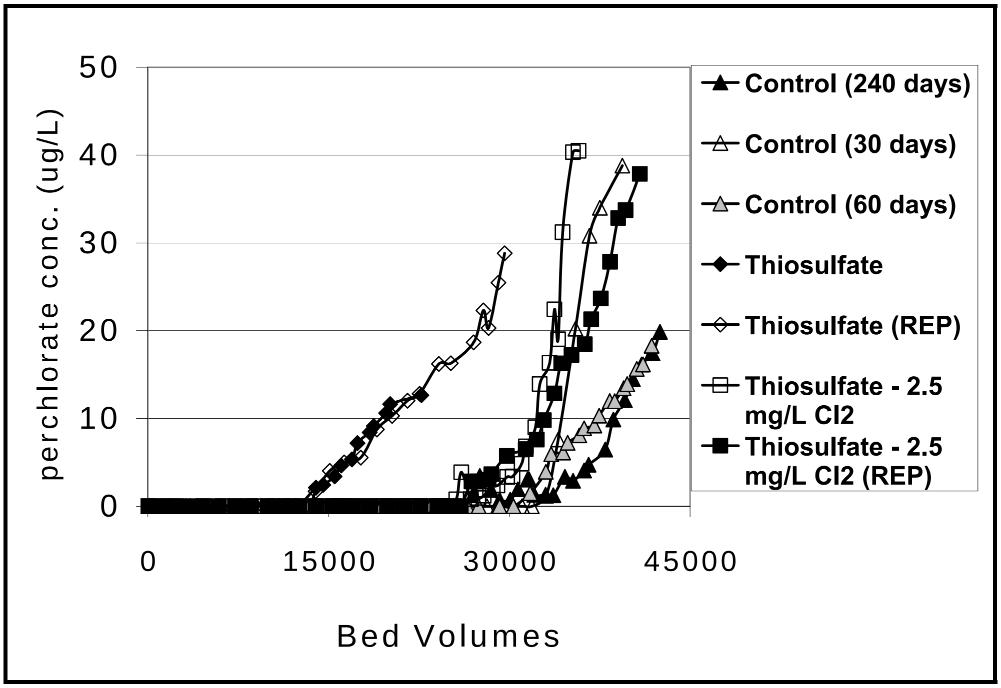

Figure - The effects of $S_2O_3^{2-}$ and chlorine on the adsorption of ClO_4^- to surfactant tailored GAC when using Redlands groundwater. Native influent ClO_4^- 30 µg/L. Spiked with 1000 µg/L $S_2O_3^{2-}$.

Similar favorable results were observed when 500 µg/L of $S_2O_3^{2-}$ was oxidized by completely mixing with 1.25 mg/L chlorine, (Figure). Whereas mere spiking with 500 µg/L $S_2O_3^{2-}$, diminished the capacity of TGAC to remove ClO_4^-, pre chlorinated restored that capacity for the duration that these runs proceeded.

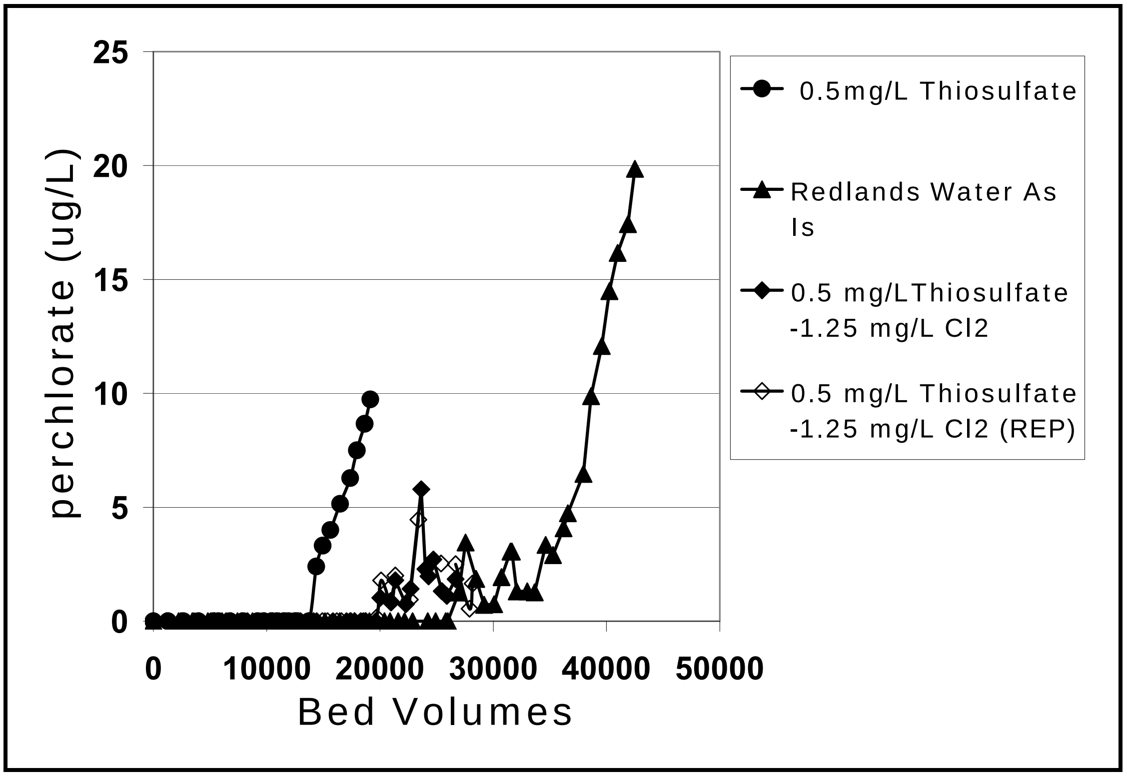

Figure - The effects of $S_2O_3^{2-}$ and chlorine on the adsorption of ClO_4^- to surfactant tailored GAC when using Redlands water. Native ClO_4^- influent was 30 µg/L and Influent $S_2O_3^{2-}$ spiked with 500µg/L.

The authors would like to briefly point out that the mixing of chlorine with the water source is important. It was observed that there was no improvement in the surfactant tailored GAC performance to remove ClO_4^- when added chlorine was not mixed in with the thiosulfate-containing water.

SUMMARY AND CONCLUSIONS

It was shown in RSSCT experiments with GAC that had been pre-loaded with quaternary ammonium surfactants (TGAC) that thiosulfate greatly diminished the effectiveness of this tailored GAC to remove ClO_4^- from a deionized distilled water source, and also from Redlands groundwater. Also when thiosulfate concentration equaled 1,000 µg/L for both cases, the extent of ClO_4^- interference was comparable to the diminished ClO_4^- bed life that has been observed with fresh Redlands groundwater in RSSCTs. Also, chlorine oxidation of the thiosulfate increased the bed life of the carbon to adsorb ClO_4^- when the chlorination was conducted in the proper stochiometric proportion and with complete mixing. However, when the chlorine was added in an unbalanced and incompletely mixed manner such that HOCl or OCl^- entered the GAC vessel, this chlorine could react with the carbon surface in an unfavorable manner. With these results, it can be seen that stoichiometrically applied chlorination with proper mixing offers a technically useful means of oxidizing thiosulfate and other intermediate –valent sulfur species that it mimics; so that these species would not compete as extensively with ClO_4^- for adsorption to surfactant tailored granular activated carbon.

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Appendix D:
38 GPM Operational Log and Data

ESTCP TGAC Demonstration Project Field Activity Log and Notes (see pdf)

TGAC Flow Data (see pdf)

TGAC Pressure Data (see pdf)

Chemical Data Influent (see pdf)

Chemical Data Effluent 1 (see pdf)

Chemical Data Effluent 2 (see pdf)

Appendix E:
Six Condition Field Test Operational Log and Data

Six Column Operational Data (see pdf)

Stratified Bed Control

TCE Spiked

Perchlorate Spiked

Nitrate Spiked

Predisinfectant/Oxidant

TDS/Sulfate Spiked

Six Column Spiking Data (see pdf)

Six Condition Common Influent

Stratified Bed Control

TCE Spiked

Perchlorate Spiked

Nitrate Spiked

Predisinfectant/Oxidant

TDS/Sulfate Spiked

Field Blank

Appendix F:
Data Validation/Verification Reports

Validation of CPC Analysis by Exgen MPI by ARCADIS

Validation of PSU Perchlorate Data by ARCADIS

Validation of Weck Nitrosoamine & VOC Data by ARCADIS

Validation of CPC Analysis by Exgen MPI by ARCADIS

Exygen Research (a division of MPI Research) in State College, Pennsylvania, used a liquid chromatography/tandem mass spectrometry (LC/MC/MC) method to analyze for cetylpyridinium chloride (CPC).

There is no holding time for this method. To establish an allowance for the holding time criteria, TGAC BACKFLUSH (sampled 1/4/07) was analyzed four times on two occassions over a eight month period It was originally analyzed 2/16/07 at 33 days with a result of (6000 ng/mL) and then eight months later on 10/10/07 with a result of 9930 ng/mL. Thus the concentration had changed significantly with storage. Because of this result both the sample containers were reprepared and reanalyzed in October, with dissimilar results: container "2/16/07" (3710 ng/mL) and container "10/10/07" (12,500 ng/mL). The relative percent difference (RPD) between the samples analyzed 8 month apart was 47-49%, indicating that the CPC concentration may change with extended aging (8 months) beyond the 30% RPD criteria. The RPD between the 10/10 sample results was 23%, within the expected range of 30%. Most of our samples were analyzed from day 9 to 33, with a few extending as far as 65 days. It is unlikely that this issue had a significant impact on our results.

Laboratory duplicates , both ND = 0.4 ng/mL. Other RPD <30%

7-point calibration run at the beginning and dispersed throughout the analytical sequence (acceptable if r^2 >0.985).

Extraction blanks were prepared and analyzed with the samples. All did not detect CPC at or above the detection limit.

Laboratory Control Sample (LCS) recoveries were all between 70 and 130%.

Matrix Spike (MS) recovery of our sample was 93%.

An experiment was run on sample CLO-EFF2-07-09-07 to see if one of our representative samples would stick to the autosampler vial. An aliquot was added to autosampler vial then dumped out. Methanol was added and vortexed, then analyzed. The result was 0.638 ng/mL – so although this is an indication that there is some "sticking" to the vial, the results was very low and just slightly above the MDL of 0.4 ng/mL.

Listed below are issues noted for specific Exygen reports:

L0010533 – no QC, results only
L0010574 – no QC, results only
L0010643 – MS spike result only
L0010685 – no QC, results only
L0011004 – MS spike result only

L0011004a – no QC, results only

L0010917 (HT = 19 to 33 days)
L0014069 (HT = 14 days)
L0012663 (HT = 9 to 65 days)

Validation of PSU Perchlorate Data by ARCADIS

PSU analyzed the perchlorate samples according to the EPA Method 314.0 and the QAPP entitled, “Tailoring of Granular Activated Carbon to Remove Perchlorate for ESTCP.” Samples were analyzed within the 28 day hold time, with the following exceptions: samples collected on 6/27/07 (analyzed on day 30), collected on 8/10/07 (analyzed on day 40), and collected on 8/20/07 (analyzed on day 30). These results should be considered estimated “J” if detected and “UJ” if nondetect.

The method detection limit for all samples was 0.74 ppb, below the QA objective of 1 ppb. When there was no ion chromatograph (IC) area, the result was listed as “0 ppb.” This equates to a commercial laboratory result of 0.74 U, or nondetect at the MDL.
The field blanks (FB) collected on 3/28/07, 6/27/07, 7/25/07, 10/10/07, 10/17/07, 10/22/07, 10/31/07, 11/9/07, 11/14/07, and 11/21/07 were nondetect for perchlorate. A method blank was run with each batch of samples and percholorate was not deteted in any of these blanks.

Calibration curves were run with a minimum of five standards prior to sampling and met the minimum correlation coefficients (r^2) of 0.997 except for samples collected 2/22/07 (r^2 = 0.9948), 3/2/07 (r^2 = 0.9954) and 6/8/07 (r^2 = 0.9935). The standard laboratory procedure when the r^2 fell below the 0.997 criteria is to rerun the standards. If the calibration then met the minimum correlation coefficient, then the samples were rerun. Although the column was replaced, the samples in question were too old to retest. Therefore, these results should be considered estimated “J” if detected and “UJ” if nondetect. Check samples were run with every batch and the QA criteria of ±15% was met.

Table F-1 gives the r^2 values, laboratory control standard checks and the QC/QA criteria calculated for these laboratory control sample checks. The table shows that when the r^2 values were slightly below the 0.997 linearity criteria, the corresponding standard checks were nevertheless within the QC/QA criteria. There are no discontinuities in the pattern of perchlorate breakthrough on the dates when the linearity was slightly below the criteria.

Table F-1 PSU Perchlorate Calibrations

Date	Standard Check Value	Date Received	Date Analyzed	IC Area	Perchlorate Concentration (ppb)	Detection Limit (ppb)	# Samples in Batch	Criteria (+/- 15%)	Equation	R2
1/17/2007	20ppb			19521	22.95	0.74	16	14.77	y = 853.58x - 72.317	R2 = 0.9985
2/7/2007	10ppb	2/16/2007	2/17/2007	6255	9.25	0.74	10	-7.48	y = 710.98x - 322.75	R2 = 0.9985
2/22/2007	10ppb	3/1/2007	3/2/2007	9837	9.07	0.74	11	-9.31	y = 998.46x + 781.49	R2 = 0.9948
3/7/2007	10ppb	3/15/2007	3/15/2007	10656	10.70	0.74	9	6.96	y = 967.35x + 308.8	R2 = 0.9997
3/21/2007	10ppb	4/5/2007	4/5/2007	10156	9.28	0.74	16	-7.19	y = 1071.8x + 208.28	R2 = 0.9954
4/11/2007	10ppb	4/26/2007	4/27/2007	10960	10.63	0.74	14	6.27	y = 1015.3x + 170.62	R2 = 0.9994
5/2/2007	10ppb	5/11/2007	5/14/2007	9646	9.05	0.74	9	-9.55	y = 1023.4x + 389.34	R2 = 0.9968
5/16/2007		5/18/2007	5/20/2007			0.74	4		y = 1165.4x - 158.26	R2 = 0.9995
5/23/2007		5/24/2007	5/24/2007			0.74	4		y = 1181.4x - 425.33	R2 = 0.9981
5/30/2007	5ppb	5/31/2007	6/3/2007	6991	4.83	0.74	6	-3.33	y = 1028.6x + 2019.2	R2 = 0.9983
6/8/2007	7ppb	6/22/2007	6/26/2007	7905	7.93	0.74	9	13.23	y = 1097.7x - 795.8	R2 = 0.9935
6/15/2007	10ppb	6/22/2007	6/26/2007	8904	10.67	0.74	9	6.72	y = 896.8x - 666.72	R2 = 0.9972
6/27/2007	7ppb	7/19/2007	7/27/2007	5387	7.13	0.74	26	1.84	y = 709.62x + 328.45	R2 = 0.998
	5ppb			3836	4.94			-1.14		
8/1/2007		8/3/2007	8/22/2007			0.74	4		y = 950.07x - 256.4	R2 = 0.9991
8/10/2007	10ppb	9/15/2007	9/19/2007	11004	10.13	0.74	12	1.35	y = 1091.3x - 56.3	R2 = 0.9993
9/19/2007	10ppb	10/1/2007	10/3/2007	10569	10.19	0.74	10	1.87	y = 1001.7x + 364.94	R2 = 0.9997
10/3/2007		10/5/2007	10/10/2007			0.74	4		y = 523.56x - 34.62	R2 = 0.9999
10/10/2007	10ppb	10/19/2007	10/24/2007	11925	9.50	0.74	15	-4.98	y = 1223.4x + 300.76	R2 = 0.999
10/22/2007	20ppb	10/26/2007	10/29/2007	21403	17.60	0.74	9	-12.02	y = 1186.3x + 528.99	R2 = 0.998
10/31/2007	10ppb	11/13/2007	11/15/2007	10501	10.17	0.74	14	1.69	y = 1062.7x - 305.15	R2 = 0.9992
11/14/2007	10ppb	11/28/2007	11/30/2007	10987	9.70	0.74	12	-3.01	y = 1096.5x + 325.08	R2 = 0.9992
12/5/2007		12/7/2007	12/112007			0.74	4		y = 1133.3x + 333.45	R2 = 0.9996
11/28/2007		12/19/2007	12/20/2007			0.74	4		y = 1285.1x + 371.69	R2 = 0.9992

Replicates were only run for large data sets. The influent sample was usually used and replicates were denoted with a D or DUP to show that it was a replicate. Matrix Spike/Matrix Spike Duplicates were run for influent samples when provided. All samples met the

80-120% recovery criteria. A number of duplicates were run using our samples and all RPD were <15%, indicating an acceptable reproducibility for this method and our sample matrix.

Split samples were analyzed by the certified laboratory (STL Savannah) and these results are discussed in the main body of the report.

Validation of Weck Nitrosoamine & VOC Data by ARCADIS

Weck Laboratories, Inc. of Industry, California, analyzed the samples for nitrosoamines by EPA Method 521 and volatile organic compounds (VOCs) by EPA 524.2. Samples were hand delivered shortly after being collected, so that in some cases the temperature upon receipt by the lab was above the ≤10 C specified by Method 521. However, given the close proximity of the time of delivery to their time of collection, no action was taken (samples were hand delivered by ARCADIS staff directly to the lab in most instances).

Selected reports were validated, representing samples collected at various times throughout the study:

Nitrosoamines:	April 18, 2007	Work Order (WO)	7041815
	October 10, 2007	WO	7101057
	October 29, 2007	WO	7102949
	December 26, 2007	WO	7122650
	January 21, 2008	WO	8012137
	March 17, 2008	WO	8031725
VOCs:	January 21, 2008	WO	8012137
	July 21, 2008	WO 8072117	

Samples were received in good condition and were analyzed within the required analytical hold times. Surrogate recoveries were within control limits, with one exception. The surrogate recovery for sample CTRL-EFF2-08-03-17 (collected 3/17/08) was below the control limit. All results for this sample were nondetect and were qualified as estimated "UJ."

The method blanks did not detect any of the target analytes at concentrations above the reporting limit. In several Method 521 reports, one or more analytes were qualified as having been detected in the method blank at a concentration below the reporting limit, but above the method detection limit. All associated samples were either nondetect for those analytes, or were detected at a concentration of more than twice the reporting limit (the method blanks must not detect any analyte at more than 1/3 of the reporting limit; anything more than five times the blank concentration is considered a valid detection). No action was required.

The Laboratory Control Sample (LCS)/ LCS Duplicate (LCSD) recoveries and/or relative percent differences (RPD) were within control limits, with the following exceptions. In several cases, the RPD was above the control limit, but the analyte was not detected in the associated samples and no action was taken.

Sample TGAC-EFF2-07-10-10 (collected 10/10/07) was used for the Matrix Spike (MS)/MS Duplicate (MSD) analysis. One recovery for Nitrosomethylethylamine (NMEA) was slightly below the control limit, but the other recovery was acceptable as was the RPD. One recovery for N-Nitrosodi-n-butylamine (NDBA) was slightly below the control limit, and the RPD exceeded the control criteria. As neither of these analytes was detected in this sample, no action was taken.

Sample SIX-INF-07-12-26 (collected 12/26/07) was used for an MS/MSD analysis. Both recoveries for NDMA were above the control limit. However, as this analyte was not detected in this sample, no action was taken.

Appendix G:
Pennsylvania State University Laboratory QAPP

QAPP Plan for EPA, Category IV Quality Assurance Project Plans

Tailoring of Granular Activated Carbon to Remove Perchlorate, for ESTCP

Fred S. Cannon, P.I., The Pennsylvania State University

SECTION 1.0 PROJECT DESCRIPTION

Project Description is as listed above.

1.2 EXPERIMENTAL DESIGN

The purpose of this research is to evaluate the use of granular activated carbon (GAC) that has been tailored with organic monomer or polymer for removing perchlorate from groundwater. Measurements will be taken to determine the concentration of perchlorate.

The measurement of certain parameters is critical to the success of this study. Critical parameters are defined as those measurements necessary to achieve the project objectives. Table 1 presents the critical analytical chemistry measurements of the above species.

Table 1. Summary of Critical Water Quality Measurements (may want to add a column for Influent Measurement Frequency – extract information from Table 1 in Letter SOW).

Measurement	Measurement Description	Effluent Measurement Frequency
ClO_4^-	raw water, treated water	As received

1.3 PROJECT ORGANIZATION AND RESPONSIBILITIES

The Principal Investigator for this project will be Dr. Fred S. Cannon of the Pennsylvania State University (814-863-8754). The perchlorate analyses will be conducted in the laboratories of Dr. Fred Cannon at The Pennsylvania State University (Penn State) located in State College, PA. Periodically, split-samples will be supplied to another certified lab of ESTCP's choosing, funded as a separate subcontractor service. These split samples will be analyzed at both the certified lab and Penn State, and this will facilitate quality assurance/quality control within the Penn State laboratories.

SECTION 2.0 QUALITY ASSURANCE OBJECTIVES

2.1 DETERMINING QA OBJECTIVES

The quality assurance objectives for this study are presented in terms of the ability to accurately measure perchlorate. The experimental quality of results that are obtained during this study will be ensured at all stages of the experimental and data handling protocols, including the collection of samples, performing the experiments, analyzing samples, entering data, verifying data and reporting data.

2.2 QUANTITATIVE QA OBJECTIVES: PRECISION, ACCURACY, METHOD DETECTION LIMIT, AND COMPLETENESS

The QA objectives for this study are presented in terms of the ability to accurately measure the critical parameter perchlorate in 1) laboratory standards, 2) untreated raw water, and 3) treated water. Specific QA objectives outlined in this section must be met for the analyses to be considered valid. Among the QA objectives for the critical perchlorate parameter are (a) method detection limits (MDL) at the 1 ppb level for perchlorate, and the values listed below for the other species, (2) a percent relative standard deviation (% RSD) of less than 20 percent (±20% stated in Table 3) (precision), (3) sample check standards that are less than 20 percent different from the known check sample value (accuracy), and 4) a completeness of 95 percent.

<u>Minimum Detection Level</u> The MDL for perchlorate will be computed by injecting 7 samples of a given ppb into the IC unit and computing the peak area given by the 7 injections. The standard deviation of the 7 corresponding peak areas will be calculated and subsequently, the MDL will be calculated as:

$$MDL = (SD * t * C) / Am$$

where:

SD = the standard deviation of the 7 areas recorded
t = student t distribution for n = 7
C = perchlorate concentration
Am = the mean area of the 7 peak areas measured

The above method for determining the perchlorate MDL follows Standard Method 1030-E (Standard Methods 19th edition, 1995).

<u>Precision</u> Precision of an analytical method will be measured by calculating the relative standard deviation (RSD) for at least triplicate measurements.

<u>Accuracy</u> The accuracy of a perchlorate measurement will be determined based on the recovery of the individual calibration standards and a check sample. A minimum of a five calibration points are used to develop a calibration curve. The validity of the calibration curve is determined using a linear least squares analysis. The accuracy of the method is determined using check samples other than calibration standards.

Completeness Completeness is a measurement of the amount of valid data obtained compared to the total amount of data collected. The degree of completeness is the number of samples with acceptable data divided by the total number of samples collected and tested, and multiplied by 100. The QA objective for the degree of completeness is 95 percent. Table 2 presents the QA objectives for this study.

Table 2. QA Objectives for Precision, Accuracy, and Method Detection Limits

Critical Parameter	**Matrix**	**Method**	**MDL (ppb)**	**Precision (% RSD)**	**Accuracy (% Recovery)**
ClO_4^-	DI, Raw and Treated Water	Ion Chromatography (IC)	1*	± 20%	80-120%

#
*For the Dionex 120 instrument that is at Penn State, we anticipate, based on prior experience, that the perchlorate MDL of this instrument will be 1 ppb. With more competition, the MDL may be higher; and with less competition, the MDL may be lower.

Average effluent perchlorate concentrations will have to satisfy the QA objectives outlined in the above table. If the QA objectives are not met, adjustments will be made to the experimental conditions and the measurements will be conducted again.

2.3 QUALITATIVE QA OBJECTIVES: COMPARABILITY AND REPRESENTATIVENESS

Comparability is a quantitative parameter that expresses the degree of confidence that data are equivalent for a specific parameter or group of parameters. Comparability will be addressed through the collection of samples in the exact same manner every time. Test conditions will be replicated by using the same procedures in order to directly compare results.

Representativeness expresses the degree to which sample data accurately and precisely represent the characteristics of a population, parameter variation at a sampling point, or an environmental condition. The sampling technique is standardized, thereby ensuring the representativeness of the relative performance test results.

Specifically, qualitative representativeness will be achieved by employing groundwater from the subject water that has been spiked with perchlorate. Since at full-scale, it is this very same water that will need to be treated, this is the best way to represent full-scale conditions of competitive adsorption, etc.

2.4 WHAT IF THE QA OBJECTIVES ARE NOT MET?

The QA/QC efforts discussed in this project plan focus on controlling measurement error within the precision, accuracy and detection limits discussed above. The precision of replicate samples are to be used to establish background data. If replicate analyses are outside of the acceptable range for this work, corrective measures will be taken to identify the source of any discrepancy in the data. If the data quality achieved is well-documented and known, the project's technical objectives can still be met although with decreased certainty depending upon the variability of the data.

As soon as available, data for all critical measurements will be evaluated in relation to the QA objectives of this study so that the appropriate corrective action(s) can be immediately implemented. Examples of corrective actions include repeating the experiment in question, reanalyzing samples, checking the validity of calculations, examining the equipment and instruments for malfunctions, or modifying the method to meet project objectives.

If the QA objectives are not met after the corrective action has been implemented, the data will be qualified and a discussion will be included in the project summary report that outlines the overall impact to the project of not meeting the objectives. The discussion will address, as appropriate: 1) possible sources of bias or variability that affect the data, 2) inadequacies of the techniques used to assess precision and accuracy, or 3) limitations of the measurement methods used.

2.5 Approach to QA

The analysis methods used in this study conform to the USEPA and American Water Works Association (AWWA) accepted methodologies when applicable and appropriate. In cases where new or improved methods have been developed, sufficient data to support the method will be included in the required reporting. Data will be entered into computer spreadsheets for comprehensive data storage and backup. Hard copy of the spreadsheets is to be verified by the Principal Investigator or their designee.

The data quality objectives for this project are based upon project requirements and are designed to ensure that the data generated during the project are of known and acceptable quality to achieve the project's technical objectives.

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SECTION 3.0 SAMPLING AND ANALYTICAL PROCEDURES

#

3.1 Sampling ProcedureS

The sample volume required for a complete analysis is generally 50- 200 mL per test. This volume is adequate for analysis, spike solutions, duplicates, and blanks.

Samples for perchlorate, need not be cooled during transport. Sample holding times will vary depending on the nature of the experiment and the parameter to be measured. Sample bottles will be new. Maximum holding times, starting from the time of sample collection, (as listed in the Federal Register 40 CFR) for the critical parameters, namely perchlorate, are listed in Table 3.

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Wdeoh#61#Vdpsoh#Frqwdlqhuv/#Suhvhuydwlrq/#dqg#Kroglqj#Wlphv##

#

# Sdudphwhu#	# Frqwdlqhu# W|sh2Vl}h#	# Suhvhuydwlrq#	Pd{lpxp# Kroglqj#Wlph# +Gd|v,#
FoR$_{7}^{0}$#	KGSS273(433#po O#	Qr#suhvhuydwlrq#	5;#gd|v#
#	#	#	#

#

HDPP is high density polypropylene

#

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3.1.1 Sample Custody

A chain of custody will be used by the ESTCP team for the samples that are sent to Penn State. Via e-mail to Arcadis, Penn State will confirm receipt of samples and verify number/condition of samples after each shipment is received.

A Sample Identification protocol should be established between Arcadis and Penn State. The protocol should be consistent throughout the project. This will be beneficial for sample tracking and reviewing data deliverables.

3.2 process measurements

For the demonstration scale units, process measurements will include flow rate, water pressure, and temperature. Perchlorate analyses will be conducted in the Penn State lab and the certified laboratory when split-sampling is required.

3.3 ANALYTICAL PROCEDURES AND CALIBRATION

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3.3.1 EPA-Approved or Other Validated Standard Methods

A listing of EPA-approved or validated standard methods are presented in Table 4. Perchlorate will be measured according to the EPA method 314.0. Prior to its use in the IC unit, the sodium hydroxide eluent will be vacuumed to de-gas the solution. A 1-L solution of sodium hydroxide can be used for up to a month (Dionex, 1998), but will likely be used much more rapidly. Based on prior experience, we anticipate that the perchlorate can be measured down to concentrations of 1 ppb using a Dionex DX-120 with an AS-l6 column, with a 30 mM NaOH solution, sparged with helium gas, as eluent, and a 1000 microliter sample loop. The Penn State team has observed a 1 ppb lower detection limit when monitoring Redlands, CA groundwater.

3.3.2 Calibration Procedures and Frequency

Calibrations will be performed for all measurements. Three-to-five calibration standards will be prepared in solutions similar to those of the experiment. Calibration standards will be prepared using materials of the highest grade purity available. To determine the linearity of the measurements, the detector signal will be calculated for the standard concentrations and graphed against the concentration of the species to be measured. Calibration curves will be prepared prior to initiation of testing. A check standard will be analyzed with each batch of samples so as to establish calibration stability.

Table 5. EPA-Approved/Standard Methods

#

Sdudphwhu#	#	Phwkrg#	#	Uhihuhqfh#
FoR$_{7}^{(}$# \#	Lrq#fkurpdwrjudsk|# \# \#		XVHSD#Phwkrg#64713#	

#

Our ion chromatograph (IC) has an autosampler. The following calibration procedure will be used before each day's sample analysis. Each step represents a run through the IC unit.

#

1. Deionized water sample
2. Calibration standards of 1.0 µg/L, 5.0 µg/L, 10 µg/L, 20 µg/L, 30 µg/L.
3. Run samples, matrix spike and matrix spike duplicate per Table 6
4. Run Quality Control (QC) and mid-standard check per Table 6.

This procedure will be repeated provided that the QC and mid-standard check have accurate results. A QC sample is a sample prepared by a member of the research group, different from the person who prepared the calibration standards. A mid-standard check consists of injecting one of the standards after every 20 samples, to check the accuracy of the calibration.

If the R^2 value of the ClO_4^- standard curve is not ≥ 0.997, the calibration standards will be reanalyzed, and a new calibration curve constructed. If the criterion of $R^2 \geq 0.997$ is again not met, new standards will be prepared and the process repeated. The IC will also be examined to make sure that it is functioning properly.

SECTION 4.0 APPROACH TO QA/QC

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4.0.1 Data Reduction, Validation, and Reporting

Reporting, validating, and reducing the data generated are all critical to meeting the QA objectives for this study. To ensure accurate data collection, a data reduction and a validation process is in place.

Each of the methods used to calculate the critical parameters listed in this QAPP is based on instrument calibration against known standards or defined by volumetric equations described in the method operating procedure. The unit of the calibration is generally mg/L or µg/L. Whenever possible, the initial data reduction will be computerized to reduce the frequency of transcript errors and calculation errors. Where data reduction is not computerized, calculations will be performed in permanently bound laboratory notebooks or on preprinted data reduction pages. Any corrections to the data will be made by lining out inaccurate information, and adding the revised information next to the line-out.

Raw data will be recorded in a bound project logbook. All analytical results will be calculated by the appropriate equations and reported in the appropriate concentration units. Data reduction of analytical results will be performed by the analyst and checked by the principal investigator. Raw data from the tests will be transcribed to computer spreadsheets for data calculations.

Data validation begins with the analyst and continues until the data are reported. The principal investigator or the consultant subcontractor will be responsible for validation of the quality of the data generated by the laboratory with respect to the QA objectives. The principal criteria that will be used to validate the integrity of the data during collection and reporting are:

- Weekly verification by the laboratory analyst that all raw data generated in the preceding week have been stored on hard copy and storage locations have been documented in the laboratory records.

- Ongoing verification of instrument calibration data.

- Confirmation that all calibration standards are within the range of expected values.
- Analysis and reporting of all calibration checks, blanks, and replicates for each batch of samples.

- Presentation and interpretation of data for samples with no values rejected as outliers.

Quality control outlier data are defined as those data outside of the specific QC objective window for precision or accuracy for a given analytical method. Should QC data be outside of the control limits, the analyst will investigate the cause of the problem, have the QC data flagged with a data qualifier, and notify the principal investigator; who will rectify the issue.

4.1 CALCULATION OF RESULTS

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Analytical results will be calculated by the appropriate equations and be reported in appropriate units. In addition to the analytical results and QA/QC data, details regarding the corrective actions taken and a discussion of any necessary modifications to the protocols established in the methods will be reported. Generally, aqueous concentrations will be presented in units of mg/L or µg/L, and solid-phase concentrations will be presented in units of mg/kg GAC. These units will carry through in mass balances as well.

#

4.2 Internal Quality Control Checks

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An internal quality system is a set of routine internal practices for assuring that the data output of a measurement system meets prescribed criteria for data quality. The analytical quality control program for this study will use results for the following QC sample analyses to control and assess data quality:

#

Calibration standard data
Method blank data
Check sample
Replicate measurements

#

4.2.1 Calibration Standards

Calibration standards are prepared by using the same methods as used to prepare the samples in order to reduce bias from the preparation method. The linearity of the calibration curves will be established by comparing the detector response for the individual calibration standards with the mean detector response for those calibration standards having readings above the background detector response of a method blank over the method's linear range. The acceptance criteria for the individual detector readings must be less than 25 percent different from the mean detector reading in order to establish an acceptable instrument calibration.

A check sample will be analyzed prior to analyzing samples. The acceptance criterion for the check sample is the same as that for the calibration. Additional calibration checks will be performed after every 10 samples.

An experimental method blank will be analyzed at a minimum of one analysis per experimental set. An experimental method blank is an analyte-free matrix that includes all components and reagents in the same volumes or proportions as used in real sample analyses. Method blanks will be used to indicate whether or not the test equipment is free from contamination.

4.2.3 Check Sample

The stability of all analytical instruments will be determined by analyzing a check sample independent of the calibration standards for every batch of samples. The acceptance criteria for the check standard is a detector response of less than 10 percent from the calculated detector response for the check sample.

4.2.4 Replicate Measurements

Replicate measurements will be performed periodically as a QC check on the analytical measurement. The acceptance criteria for the replicate measurements is a relative standard deviation (RSD) of less than 20 percent.

Table 6. Quality Control Check Program

QC Check	Frequency	Acceptance Criteria	Corrective Action
Calibration Curve	1/day	$r^2 \geq 0.997$	Correct, Rerun*
Continuing Calibration Check Sample	1/10 samples	±15%	Correct, Rerun*
Matrix Conductivity Check	Each sample	<6400 microS/cm**	Dilute according to EPA 314.0 if necessary
Method Blank	1 Per IC run	No trace of ClO_4^-	Correct, rerun*
Replicate	1 Per 10 samples	± 20%	Correct, rerun*
Matrix Spike/Matrix Spike Duplicate	1 Per 20 samples	80% - 120%	Correct, rerun*

Note: Batch size is less than 20. Method 314 specifies that "values that exceed ½ the MRL indicate a laboratory or regent contamination is present."

*Identify problem, take appropriate measures, re-run all samples in question.

**Matrix conductivity threshold for the Penn State Dionex 120 instrument has been measured to be 6400 microS/cm.

4.3 CALCULATION OF DATA QUALITY INDICATORS

Two of the criteria by which the methods used in this project will be evaluated are the precision and accuracy of the results. Precision refers to the variability, or spread, of the data around its mean. Accuracy refers the closeness of the final result to the actual value. Therefore, to be accurate, the method must also be precise. However, a precise method is not necessarily accurate due to the possibility of bias introduced by the method. Bias refers to a consistent lack of correspondence between the mean of the data (the sample mean) and the actual value (the population mean). Bias is commonly the result of systematic error, such as from mis-calibrated equipment, nonlinearities in conversion factors, or the loss of material during processing. Bias is controlled through the quality control procedures, but its quantification is difficult unless an independent method of deriving the same result is available that is more accurate than the test method. In the present case, mass balance is an approach to assessing bias.

Precision is the result of cumulative random error in the process. Random error will occur at every step in the procedure. The greater the number and magnitude of the errors, the less precise will be the final result. Unlike bias, precision is easily quantified, but is difficult to control beyond the limits of laboratory quality control procedures and proper technique. Precision can be separated into two components: repeatability and reproducibility. Repeatability describes the variability of the results from replications of the method under the same laboratory conditions (identical operator, equipment, and test material). Reproducibility refers to the variability of the results when the process is performed under varying laboratory conditions and materials. Precision can be quantified by one or more standard statistics. These are generally based on the calculation of the variance for a set of replicate sample measurements. The square root of the variance (the standard deviation) quantifies the random error in the same units as the data. The ratio of the standard deviation and the mean (the coefficient of variation [CV]) allows for the comparison of the relative precision between data groups of differing means.

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4.3.1 Precision

The calculation of relative percent difference (RPD) for duplicate measurements will be calculated as outlined in Category IV Prep Aids (Simes, 1991).

4.3.2 Accuracy

The calculation of matrix spike percent recovery will be calculated as outlined in Category IV Prep Aids (Simes, 1991).

4.3.3 Completeness

# #

Completeness will be calculated as outlined in Category IV Prep Aids (Simes, 1991)

4.3.4 Method Detection Limit (MDL)

The MDL for the determination of perchlorate concentrations will be calculated as per Standard Method 1030-E (Standard Methods, 19th edition).

4.3.5 Performance and System Audits

A laboratory audit will be performed periodically by the principal investigator to ensure that 1) the proper calibration methods are being used, 2) the sampling techniques are appropriate for this study and are being performed in accordance with the project QAPP, 3) the samples are appropriately handled, 4) the study is being conducted as described in the QAPP, and 5) the laboratory staff are familiar with the test procedures and equipment.

4.3.6 Corrective Action

There are two known incidents that warrant corrective action in this study: 1) one or more of the calibration standards has a detector response greater than 20 percent from the mean detector response, 2) the RSD for replicate samples is greater than the values listed in Table 3.

1) If one or more of the calibration standards has a detector response greater than 20 percent from the mean detector response, several corrective actions will be applied:

a) Check for calculation errors.

b) Immediately reanalyze the standards that are out of the control limits and recalculate the detector response for the reanalysis.

c) If the standard detector response is still outside of the control limits, immediately reprepare the standard(s) that are outside of the control limits, reanalyze the standards, and recalculate mean detector response and individual detector responses. If the standards are still outside of the control limits, the laboratory technician will contact the Principal Investigator to discuss alternative corrective actions.

2) If the RSD is greater than the values listed in Table 3 for replicate sample measurements, the following corrective actions will be employed:

a) Reanalyze the samples.

b) If the RSD is greater than allowed after reanalyzing the samples, split another sample and analyze it to determine if there is a problem with the first sample or some other problem.

c) If the second split sample is within the RSD control limits, repeat the test in question and analyze the samples.

d) If the second split sample is not within the RSD control limits, check for instrument malfunctions.

e) If no equipment malfunctions can be detected, the laboratory supervisor will contact the Principal Investigator to discuss alternative corrective actions

All problems meeting the QA objectives set forth for this study will be documented in the project logbook along with the corrective actions taken and the results of the corrective actions. The problems encountered during the study and the corrective actions employed will be reported in the deliverable packages to the Project Team.

SECTION 5.0 REFERENCES

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Appendix H:
AFIT Cost and Performance Model for TGAC (see Excel File)

Appendix I:
Tracer Test of Field Scale Vessel

Motivation:

The full scale breakthrough occurred before it was predicted to based on RSSCT data (for example bed A at 12,000 BV vs. bench scale data at 17,000). Thus we conducted a tracer test to evaluate the hypothesis that breakthrough might have been occurring more rapidly at full scale, because there might be significant channeling, and thus inefficient use of the TGAC media.

Field Methods:

A tracer test was conducted in one of the beds used for the 38 gpm field scale system (Siemens Model PV2000) after completion of all of the perchlorate testing. The system was initially flushed with clean water to remove tracer residual from a previous abortive tracer test, first at an average 37. gpm for 14 minutes and then at approximately 55 gpm for a further 23 minutes. The tap water used for flushing had a conductivity of 45 mS/m The flushing period ran from 10:04 to 1:42 AM local time. During that period conductivity was recorded once per minute (Figures 1 and 2).

The tracer was a very nearly full 500 gallon tank with turbid $MgSO_4$ solution. A baseline reading of the conductivity of the tracer was 6,600 mS/m. Tracer feed began at 11:25 AM and continued uniformly at an average 32 gpm until 11:40 AM. Conductivity data was collected every minute starting at 11:30 and every 30 seconds starting at 11:37 (Figures 1 and 3) until 12:22. At 11:40, the peak conductivity had not clearly been seen but the tank was nearly empty, 479 gallons of tracer having been fed. Additional water was added to the 500 gallon tank diluting the remaining solution and undissolved MgSO4. Tracer feed continued uninterrupted until 12:22 when the pump stopped for lack of fuel. After refueling the pump, tracer feed was continued from 14:00 to 15:00 with conductivity data collection was continued at less frequent intervals. ,

Data interpretation:

The vessels used for the 38 gpm system are 4 ft diameter with a side shell height of 72” and domed heads. They have a total volume of approximately 88.2 cubic feet or 660 gallons. However in this application they only contained ~48” feet of bed depth or 50 cubic feet (374 gallons) of TGAC (design was for 375 gallons @ 37.5 gpm = 10 minute EBCT). The vessels were operated in a downflow mode. The vessels were operated with a significant water filled headspace – approximately 38.2 cubic feet (286 gallons). Since it was not possible to eliminate this headspace from the spiking or sampling system for the tracer test the results have to be interpreted in terms of two sequential units within the one reactor. In our analysis we found the data to be consistent with treating the headspace as a Continuously Stirred Tank Reactor (CSTR) followed by the carbon bed acting as a plug flow (PF) reactor. Then in data analysis we also attempted to estimate the percentage of the total flow bypassing the CSTR and PF reactors The data was analyzed based on a tanks in series model[2].

In order to maximize the utility of the available data we analyzed both data from the washout period prior to the start of the tracer test and from the increasing portion of the tracer test curve,

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[2] Levenspiel, O. “Chemical Reaction Engineering 2nd Edition”; John Wiley & Sons, New York, 1072.

after the tracer injection began. The washout period was first operated at 37 gpm and then at 55 gpm. The conductivity response, the effluent conductivity minus the flush water conductivity was plotted against the cumulative flush volume in Figure 4. Portions of the elution curve were fitted to an exponential model; the exponent representing the reciprocal of the CSTR volume. The data from the two washout periods yield estimates of CSTR volume of 329 gallons and 350 gallons respectively. The data from the rising portion of the EBCT tracer test was plotted in Figure 5 as the conductivity response, effluent conductivity minus conductivity at the beginning of the test, divided by the maximum response, maximum observed conductivity minus conductivity at the beginning of the test. A portion of the EBCT tracer test response was fitted to an exponential model; the exponent respresenting the reciprocal of the CSTR volume. The EBCT tracer test led to an estimate of volume for the CSTR at 278 gallons. The log of the pre-exponential factor provides an estimate of the ratio of plug flow volume to CSTR volume. The EBCT plug flow volume is an estimated 260 gallons. Less weight should be attached to the EBCT tracer test since MgSO4 could dissolve from the turbid influent tracer in the test vessel.

The fact that the CSTR volumes determined from the washout periods are higher than the design freeboard significantly diverges from the two tank model. This suggests either entrainment or fluidization of a portion of the media The high CSTR volumes are associated with high average flow rates of 37 and 55 gpm. The CSTR volume associated with the EBCT tracer test is in line with the anticipated freeboard at a modestly lower flow rate of 32 gpm. This suggest a transition to a disturbed bed at flows between 32 and 37 gpm.

The EBCT tracer test produced a plug flow volume, 260 gallons, consistent with expectations for the carbon bed. A 375 gallon carbon bed with a porosity of 0.69 (Clements and Haarhoff[3]) would have pore volume of 259 gallons. Thus the data suggests that the tracer water is interacting with most of the volume of the carbon bed.

Based on a limited amount of data we calculate that 0.15 % of the tracer flow may be bypassing the CSTR and PFR at a 32 gpm flow rate. This estimate of minimal bypassing can also be corroborated to some extent from the full scale operational data. Since the concentration of the effluent perchlorate during the initial operational period was consistently <0.74 ppb, and the typical inlet concentration was approximately 8 ppb, we can conclude that only <10% of the flow could be bypassing the CSTR and PFR from that data set.

Conclusions:

The conductivity responses of the TGAC vessel rinse and the EBCT tracer test are consistent with treating the freeboard as a CSTR and the TGAC bed as a PFR The conductivity response of the TGAC vessel rinse prior to conducting the EBCT tracer tests suggests that the TGAC bed is fluidized to some extent at influent flow rates of 37 gpm and higher. The conductivity response to the EBCT tracer test suggest the TGAC bed is quiescent at 32 gpm. The conductivity response to the EBCT tracer test suggest PFR volume correlates to the pore volume of the bed with minimal bypassing.

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3 "Practical Experiences with Granular Activated Carbon (GAC) at the Rietvlei Water Treatment Plant; Water SA, 2004, Vol 30, No 1 Pp89-95.

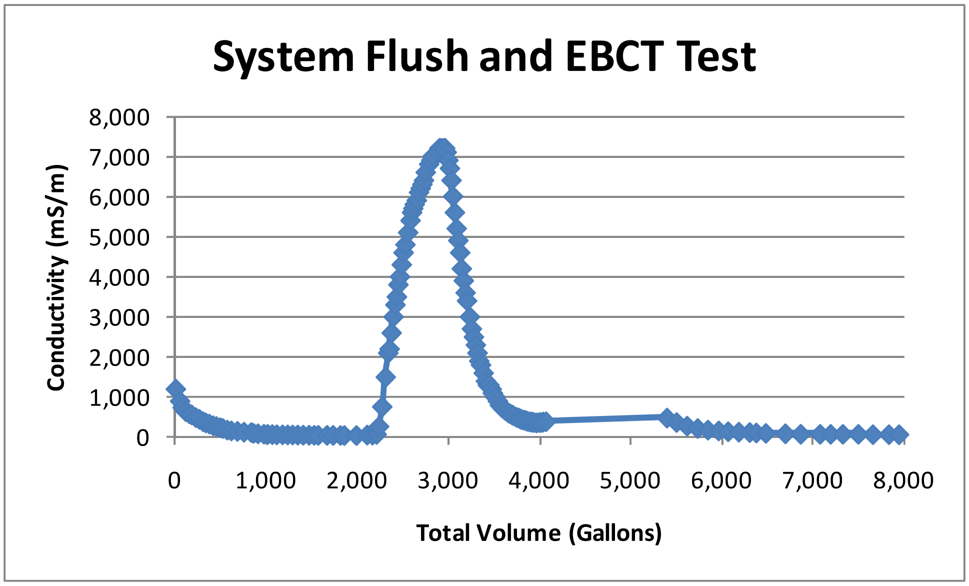

Figure 1: Conductivity vs. Volume during flushout period and tracer test volume zero is the start of flushout period as described in text

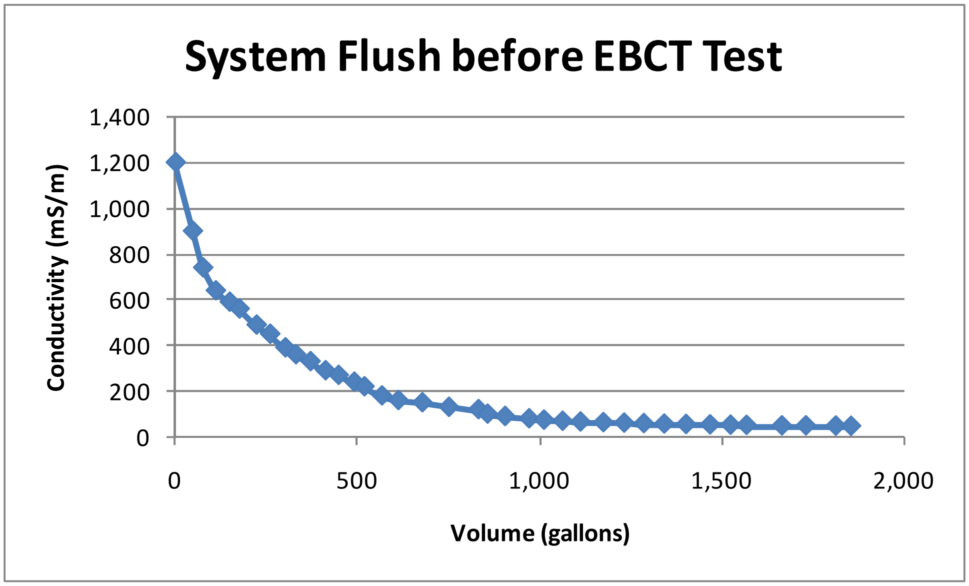

Figure 2: Expanded View of Conductivity vs. Volume during flushout period – volume zero is the start of flushout period as described in text

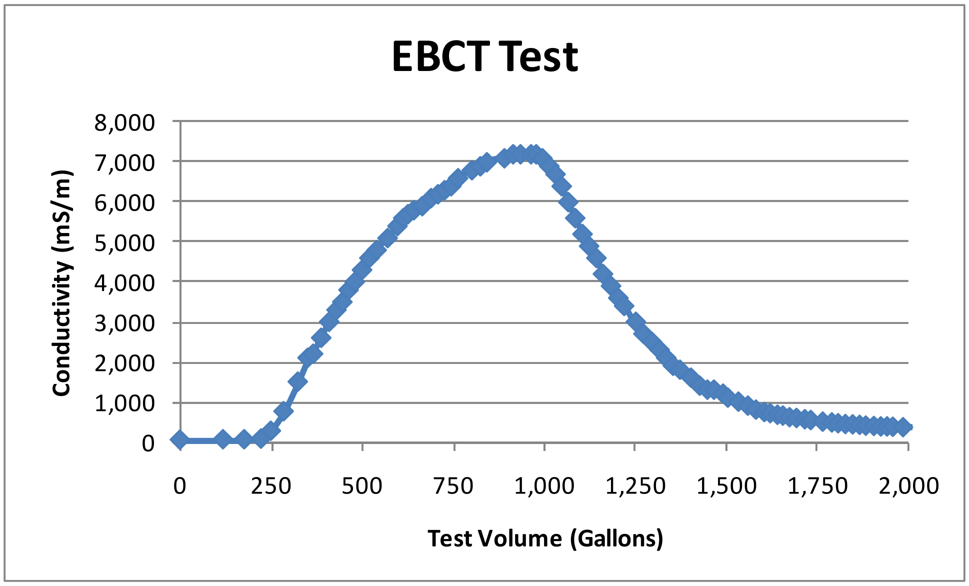

Figure 3: Expanded View of Conductivity vs. Time during tracer test (gallon zero is the start of tracer introduction)

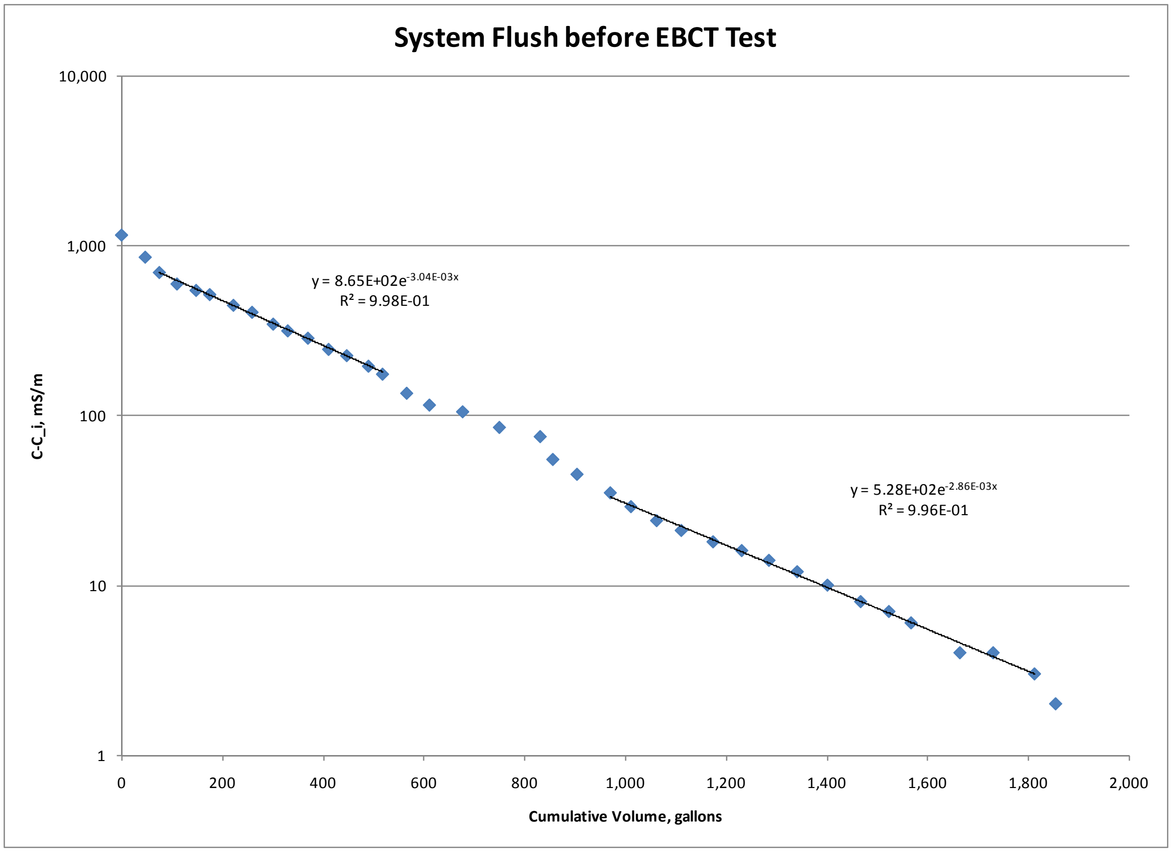

Figure 4: Data Analysis during Flush-out period

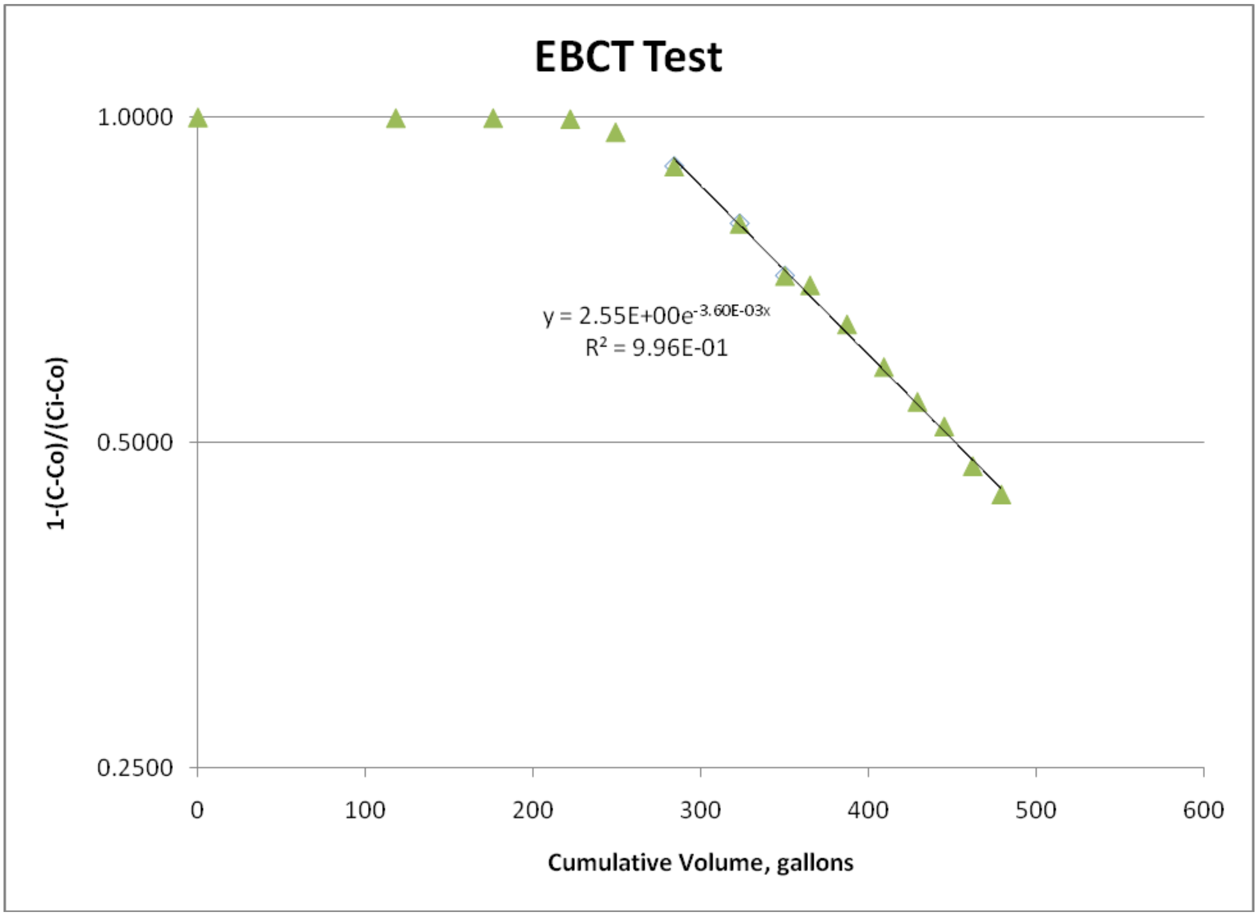

Figure 5: Data Analysis during Tracer Test

Appendix J:
Selection of Similitude Equation Exponent for RSSCT Design; and Affect of Carbon Source on Perchlorate Sorption onto Surfactant Tailored GAC

This appendix J addresses two issues pertaining to the performance of the surfactant-tailored GACs for removing perchlorate at Fontana. The first issue pertains to the most appropriate similitude equation exponent for designing the RSSCTs so that they scale accurately to field scale systems operated over long time periods. The second pertains to what impact the carbon source and its particular pore volume distributions have on perchlorate removal by surfactant tailored GAC. Pore volumes were measured using two methods argon adsorption and mercury porosimetry.

With regard to the rapid small scale column tests (RSSCTs), Crittenden (1991) poses the similitude equation:

$$\frac{EBCT_{SC}}{EBCT_{LC}} = \left[\frac{d_{p,SC}}{d_{p,LC}}\right]^{2-X} = \frac{t_{SC}}{t_{LC}}$$

Equation 1

Where: SC = Small Column, LC = Large Column
d_p = adsorbent particle size [cm]
t = elapsed time in the respective column test [min]
X = the dependence of the intra-particle diffusion coefficient on particle size.

When the exponent is 2 in this equation (i.e. x = 0), constant diffusivity prevails, which means that the rate of the targeted compound diffusion through the GAC pores is constant regardless of the grain size. When the exponent is 1 in this equation (i.e. x = 1), proportional diffusivity prevails. In a proportional diffusivity case internal diffusion controls the adsorption rate, so that the intra-particle diffusivity is a linear function of particle size. The conventional wisdom is that large organic molecules or charged molecules would behave in accordance with proportional diffusivity, while small uncharged organic molecules would behave in accordance with constant diffusivity. Perchlorate is a charged oxyanion, and so one might anticipate that since the ClO_4^- anion it is expected to have associated with it a cluster of four-to six water molecules, it could behave in accordance with proportional diffusivity. Indeed, in early Penn State work, with conventional GACs (i.e. no tailoring agent), proportional diffusivity appropriately characterized perchlorate sorption, as presented in Figure 1 (end of Appendix J). Moreover, when our Penn State team has used iron-tailored GAC to sorb arsenic oxyanions ($HAsO_4^=$ or $H_2AsO_4^-$), proportional diffusivity appropriately simulated full-sized-grain pilot performance, as presented in Figure 2.

When comparing Redlands full-scale performance to RSSCTs that were designed on proportional diffusivity, the picture was less clear. In this case the tests employed an Ultracarb bituminous-based carbon with cetylpyridinium chloride (CPC) as the surfactant. When processing Redlands, CA water that contained 65 µg/L perchlorate, breakthrough of 32 µg/L (half) occurred at 37,000 BV for proportional-based RSSCT's; and at 23,000-37,000 BV for full-size-grained pilot studies (Figure 3). It is this halfway point on the breakthrough curve that the RSSCTs are fundamentally designed to simulate. However, the proportional RSSCTs provided longer bed life to initial breakthrough (31,000 BV) than did the pilot beds (16,000 BV). It is the bed life to initial breakthrough that is the more important threshold for the work herein.

A distinction in the Redlands water, is that it may contain thiosulfate and other intermediate sulfur species when it is first pumped out of the ground. These intermediate sulfur species are oxyanions that we found competed, with perchlorate, as discussed at length in Appendix C. Indeed, when fresh Redlands water was processed through Penn State RSSCTs immediately after a closed barrel of this water had reached Penn State, the proportional-based columns exhibited initial perchlorate breakthrough at about 17,000 BV—much like was observed for full-scale grain performance (Appendix C).

At the other extreme, when constant diffusivity RSSCT design was used with Redlands water, perchlorate breakthrough occurred within 600 BV, and thus this RSSCT design yielded a far under-predicted response, relative to the full-size-grain behavior (Parette thesis, 2005c—data not shown herein).

In comparison to the above results, a number of pilot-scale tests and RSSCTs were compared when using either Fontana water (6-9 µg/L perchlorate) or Penn State groundwater that was spiked with either 50 or 500 µg/L perchlorate. All these trials employed the same acid washed anthracite-based activated carbon (AC 2050 AW) that was also used in the Fontana pilot studies; and these had all been preloaded with 0.29 g CPC / g GAC. Unless otherwise noted, the bench scale preloading occurred within a couple days of the time of RSSCT testing.

When using Fontana water, both initial breakthrough and half-breakthrough occurred earlier for the pilot studies with #20 x 50 mesh GAC, than with the proportional-diffusivity based RSSCTs with #200 x 400 mesh GAC (Figure 4). Likewise, when using Penn State water that was spiked with 50 or 500 µg/L perchlorate, initial perchlorate breakthrough was later in proportional-based RSSCTs than with Penn State pilot columns that employed #20 x 50 mesh anthracite GAC (500 µg/L data in Figure 5).

In light of these results, the Penn State team also appraised RSSCT performance when employing a design based on a 1.5 exponent (i.e. $X = 0.5$), with a 500 µg/L perchlorate spike. Such a design would presume that the perchlorate diffusion behavior was somewhere between constant and proportional. As presented in Figure 5, the RSSCT with a 1.5 exponent exhibited initial perchlorate breakthrough at 2,500 BV, which compared to 8,000 BV for the pilot units. This meant that the 1.5 exponent design far-underpredicted initial perchlorate breakthrough. In yet further comparison, the RSSCT with 1.5 exponent exhibited 250 µg/L the halfway point on the perchlorate breakthrough curve at 8,700 BV, as compared to 9,400 BV for the pilot-scale which was about the same.

Thus, when considering initial perchlorate breakthrough in RSSCTs that have used CPC-tailored anthracite GAC, proportional diffusivity (exponent = 1) over predicted full grain initial perchlorate breakthrough. Constant diffusivity (exponent = 2) dramatically under predicted initial breakthrough performance. Design with the intermediate exponent of 1.5 also underpredicted initial perchlorate breakthrough, but matched the midpoint of the perchlorate breakthrough curve. It thus appears that for predicting initial perchlorate breakthrough, an exponent somewhere between 1 and 1.5 would be the more suitable.

As a second issue, it became known after the completion of the field scale study that the activated carbon used in the Fontana studies was inadvertently anthracite-based. The team's prior experience had been primarily with bituminous-based tailored activated carbons. In order to discern the significance of this, the Penn State team conducted both pore volume distributions and RSSCTs for these two carbon sources. These were also compared to a third GAC type – coconut shell based carbon.

The cumulative pore volume distribution of the bituminous-based Ultracarb appears in Figure 6; and this is compared to the pore volumes for the anthracite-based AC 2050 AW in Figure 7. Both of these results are for GACs with no surfactant loading. Ultracarb is the carbon that the Penn State team had extensively used prior to the Fontana Study. Figures 6 and 7 present pore size data garnered by employing argon adsorption from 4 to 1000 Å; and for this method, it is the data up to 500 Å that is the most useful. For pore sizes above 500 Å, small differences in the argon bath temperature makes a considerable difference in the pore volumes that are computed.

For Ultracarb, the argon method pore size adsorption data exhibited 0.34 mL / g pores with < 30 Å width; and then its pore volume distribution continuously increased up to 0.43 mL / g at <500 Å. In contrast, the anthracite-based carbon exhibited 0.41 mL / g pores with width < 30 Å; and then essentially no more mesoporosity was present up to 500 Å. To place the observation that most of the porosity in AC2050AW is less then 30 Å in perspective, recall that a single bond length in an organic molecule is typically 1 to 2 Å and that CPC contains a 16 carbon chain and a hetrocyclic aromatic ring.

In the mercury porosimetry protocol, mercury is forced into pores at increasingly higher pressure, starting at about 10-20 psi corresponding to 10,000-100,000 Å widths; and then ramping up to 30,000-50,000 psi, which corresponds to 10-30 Å widths. The implied interpretation is that at yet higher pressure, mercury can wedge itself into yet smaller pores. However, the carbon grains surely also collapse under such high pressures; and as an artifact, this collapse can be misconstrued as pore volume. Thus for the purposes of the analysis here, we compare the mercury porosimetry data sets primarily for pores above 100 Å width and use the Argon adsorption for the smaller pore volume sizes. The mercury and argon pore size distributions have been computationally merged in such manner that employs Argon-based pore volumes less than 100Å, and then adds the mercury porosimetry data to this for pores larger than 100 Å(Figures 6 and 7). The bituminous Ultracarb contained 0.17 mL / g of pores with width of 100 to 10,000 Å. In contrast, the anthracite GAC offered only 0.07 mL / g pores in this range. The mercury volumes above 10,000 Å for the anthracite GAC reflect voids between one carbon grain and its neighbor.

In summary, both carbons offered about the same pore volume up to 10,000 Å width (0.5 to 0.57 mL / g). However, for the Ultracarb, much more of this volume occurred in the 30-10,000 Å range – a range in which the anthracite based AC2050AW had little porosity. To place this analysis in perspective, the surfactant could probably wedge its way into pores as small as 4-8 Å. Thus, the two carbons could be anticipated to sorb about the same volume (and mass) of surfactant. This is consistent with the loadings that we observed. However, the surfactant could have adsorbed in a more micellar geometry in the Ultracarb GAC than in the anthracite-based carbon (see further discussion below).

We also include the argon pore volume distributions for two additional carbons in this appendix (neither sample was surfactant-tailored). The first of these is for bituminous based

Aquacarb[4] AC 1240 (Figure 8), which exhibited some mesoporosity (20 Å < pore width < 500 Å). The second is for coconut-based carbon AC 1230 AWC (Figure 9), which exhibited no mesoporosity. We had learned from earlier work that when bituminous based Aquacarb AC 1240 was preloaded with surfactant, RSSCTs with Redlands water exhibited about the same favorable performance as if Ultracarb had been used. However, when coconut based GAC was preloaded with the same amount of surfactant, its bed life was about half as long as when the bituminous-based carbons were used (Parette, 2005).

After the anthracite GAC was loaded with surfactant (0.29 g CPC / g GAC), its argon pore volume distribution was markedly altered as show in Figure 10 from the pore size distribution for the same carbon without surfactant (figure 7). As shown, no pores that were smaller than 10 Å were present, which we interpret as a result of them filling with the surfactant. All but 0.045 mL / g of pores smaller than 500 Å had become filled. We hypothesize that this left little room for the chloride to diffuse out of the pores while perchlorate diffused in during the exchange process. However note that the surfactant-tailored carbons are dried as a precursor step to analyzing pore volumes, thus the surfactants may not retain their micellar character.

Next, we sought to test directly with RSSCTs whether different perchlorate removal performance would be achieved when the CPC surfactant was preloaded onto anthracite-based AC 2050 AW as compared to bituminous-based GAC. These experiments employed aged Redlands site water from barrels which contained 30 μg/Lperchlorate. As shown in Figure 11, with the anthracite GAC, initial perchlorate breakthrough occurred at 13,500 BV, whereas with the bituminous-based Ultracarb, breakthrough occurred at 31,000 BV. Thus the carbon source was shown to be a major influence on performance. Our tentative interpretation is that more of the surfactant that loaded within the anthracite carbon wedged into tight micropores that were not as readily accessible for the larger perchlorate molecules to diffuse into so as to exchange at the quaternary ammonium site. In comparison, for the bituminous carbon, more of the surfactant loaded perhaps as micelles in the mesopores, where it was more accessible to the perchlorate. Both of these carbons had been freshly pre-loaded with the surfactant in-situ within the RSSCT column, just several days before the RSSCT water-processing commenced.

We also sought to discern whether the surfactant became more recessed and inaccessible with prolonged residence within the pores. To test this, we subsampled some of the same CPC-preloaded GAC that had been used in the Fontana pilot columns. This AC 2050 AW anthracite sample had been extracted from the pilot units just after they had been back washed at start-up more than a year before they were tested at Penn State. The sample was shipped to Penn State, where it had remained refrigerated at 4^{o}C until the time of this testing. We crushed and sieved this TGAC subsample, then inserted it into the RSSCT columns, and conducted RSSCT with Redlands groundwater that had an influent perchlorate of 30 μg/L. This carbon exhibited a perchlorate breakthrough curve that was nearly the same as for the AC 2050 AW that had been freshly preloaded (Figure 12).

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[4] AquaCarb is Siemens trade name for granular activated carbons that are used in aqueous applications. The AquaCarb (AC) name can apply to bituminous, anthracite or coconut shell carbons. These different raw materials are differentiated for one another in the naming. UltraCarb (UC) are differentiated from the AC carbons in that they are more meso and macro porous than the standard AquaCarbs.

In summary, the carbon source and the pore volume distributions perculiar to particular carbon types give markedly different performance in TGAC applications to perchlorate. In bench scale tests the anthracite based AC 2050 AW performed considerably less well than the bituminous based Ultracarb GAC. Thus it appears that GACs used to prepare TGAC should be selected to have a high mesoporosity(20 Å < pore width < 500 Å).

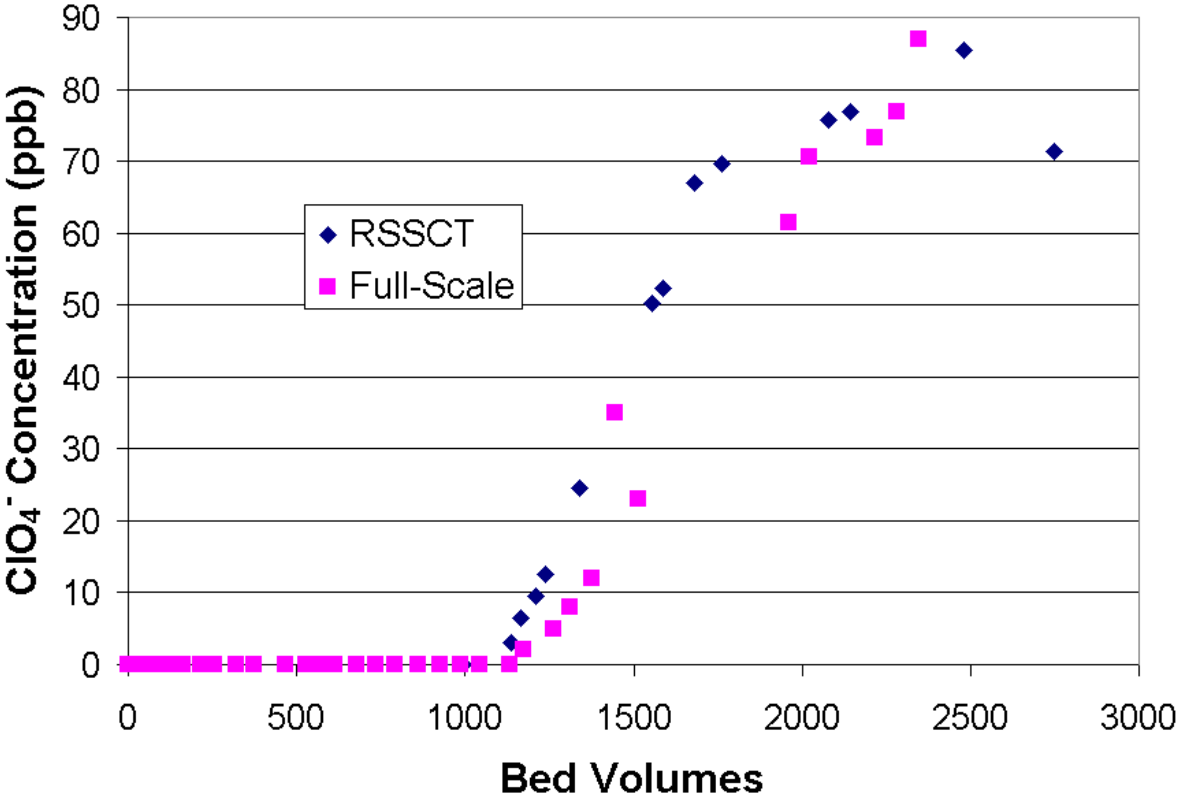

Figure 1: Comparison of Full-Scale versus Proportional-based RSSCT with conventional activated carbons. Redlands groundwater with 80 ppb perchlorate.

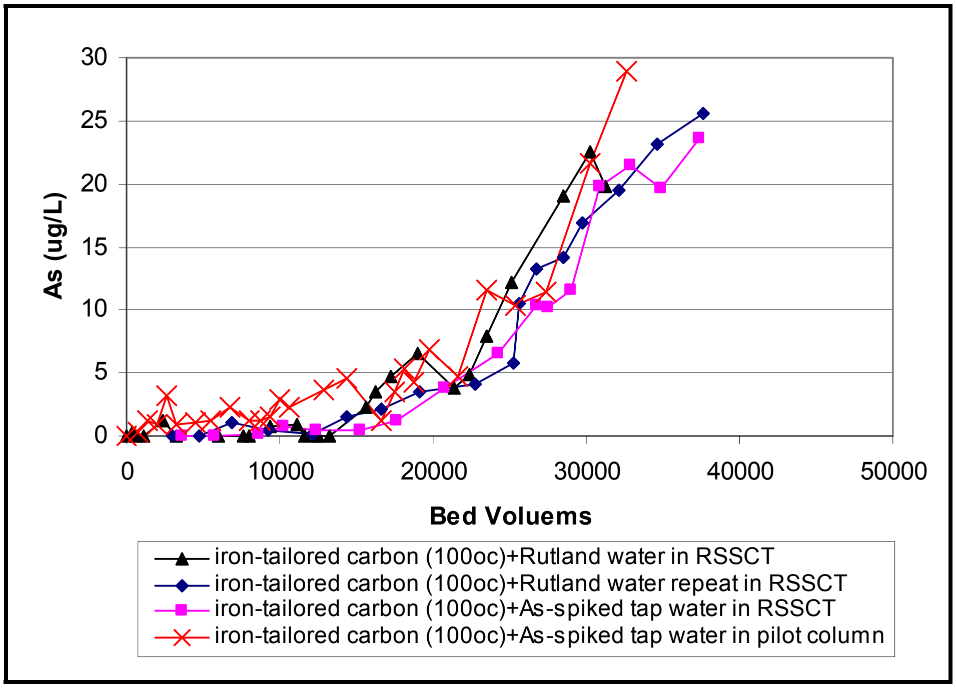

Figure 2: Arsenic breakthrough for iron-tailored (100^{o}C) carbon in proportional-based RSSCTs and Pilot Column

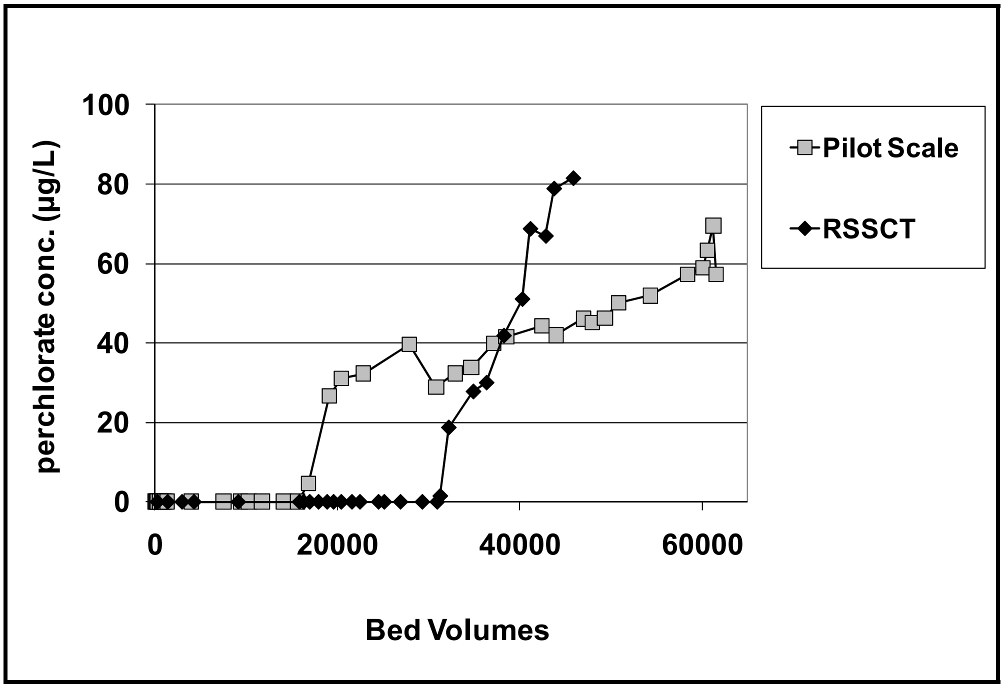

Figure 3: Pilot-Scale versus Proportional-based RSSCT for Redlands Water, when using Ultracarb GAC.

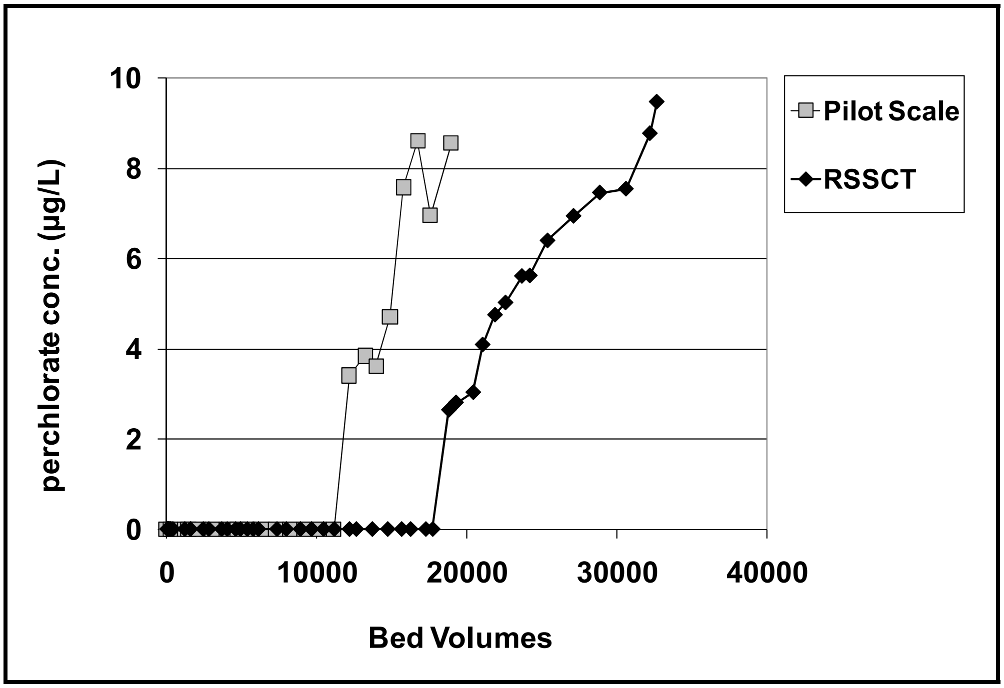

Figure 4: Pilot scale versus proportional-based RSSCT for Fontana Groundwater, when using anthracite-based AC2050 AW.

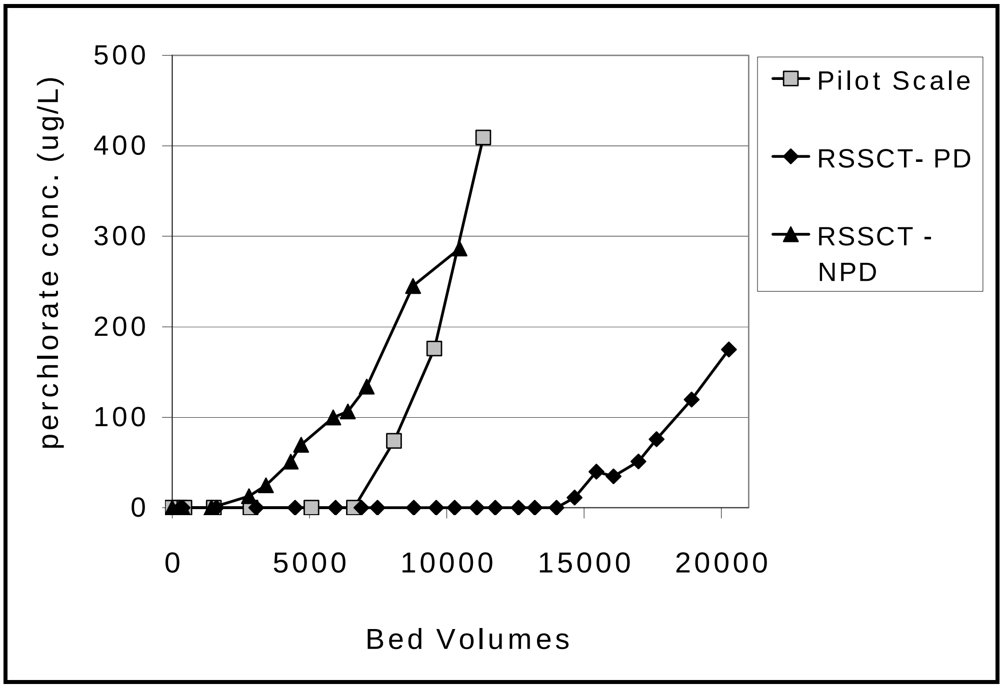

Figure 5. Comparison of RSSCT and pilot scale experiment for Perchlorate adsorption on TGAC using Penn State University tap water spiked with 500 µg/L perchlorate, using different intraparticle diffusion coefficients. PD is denotes that proportional diffusivity (exponent=1) was employed, while NPD denotes an exponent of 1.5

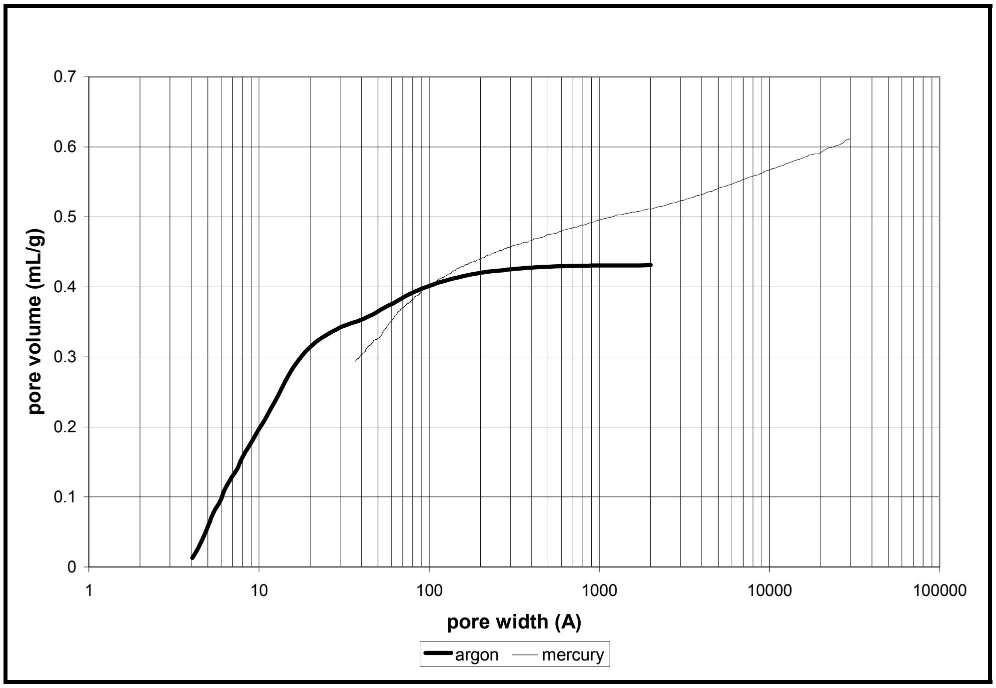

Figure 6. Pore Volume distribution for UltraCarb, a bituminous based carbon using the mercury porismetry and argon adsorption methods.

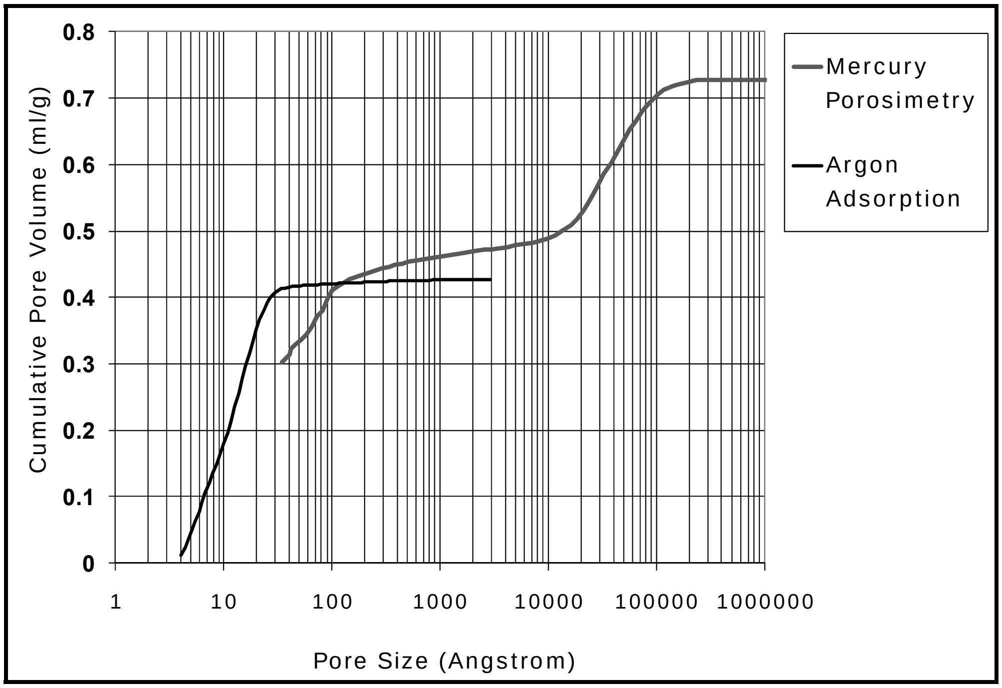

Figure 7. Pore Volume Distribution for non tailored AC2050 AW (acid washed, anthracite based) using the mercury porismetry and argon adsorption methods.

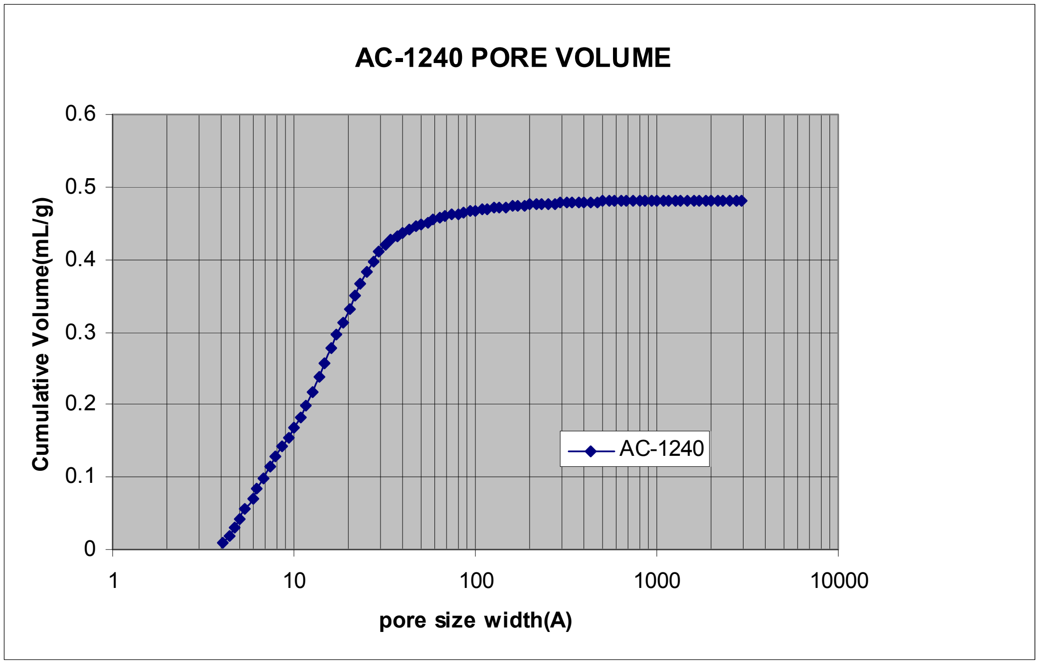

Figure 8. Pore volume distribution for bituminous based AquaCarb AC 1240 – Not tailored

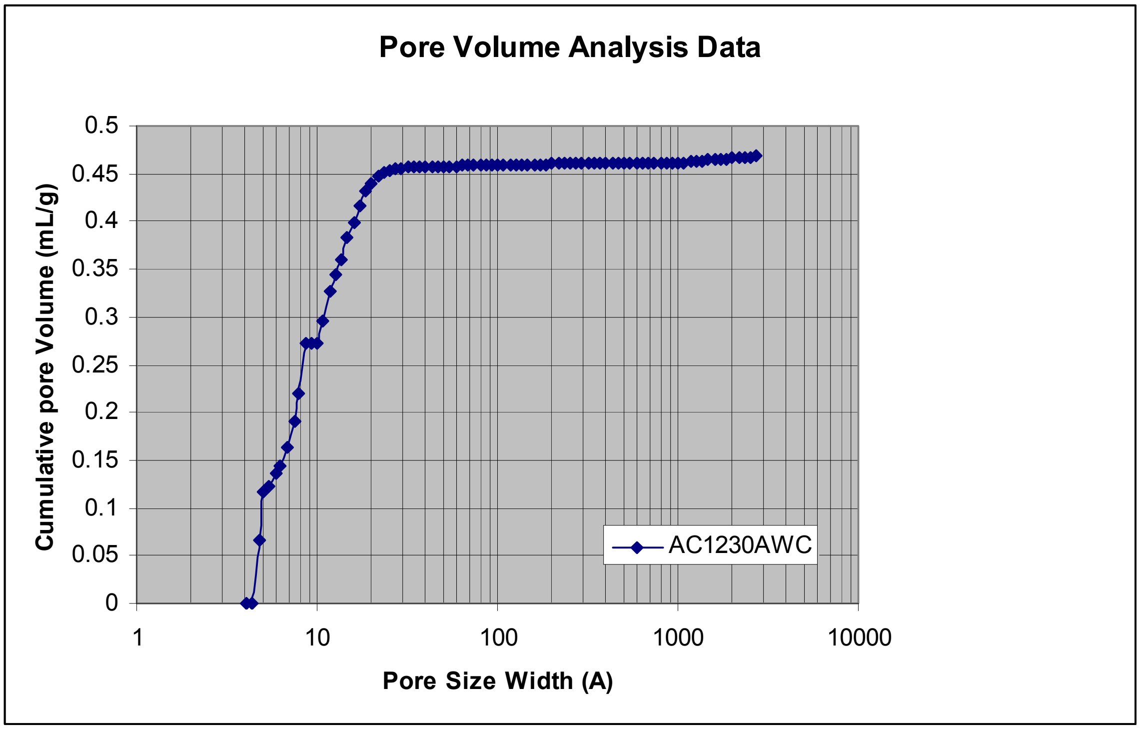

Figure 9. Pore volume distribution for coconut-based AC 1230 AWC (not pre-loaded with surfactants)

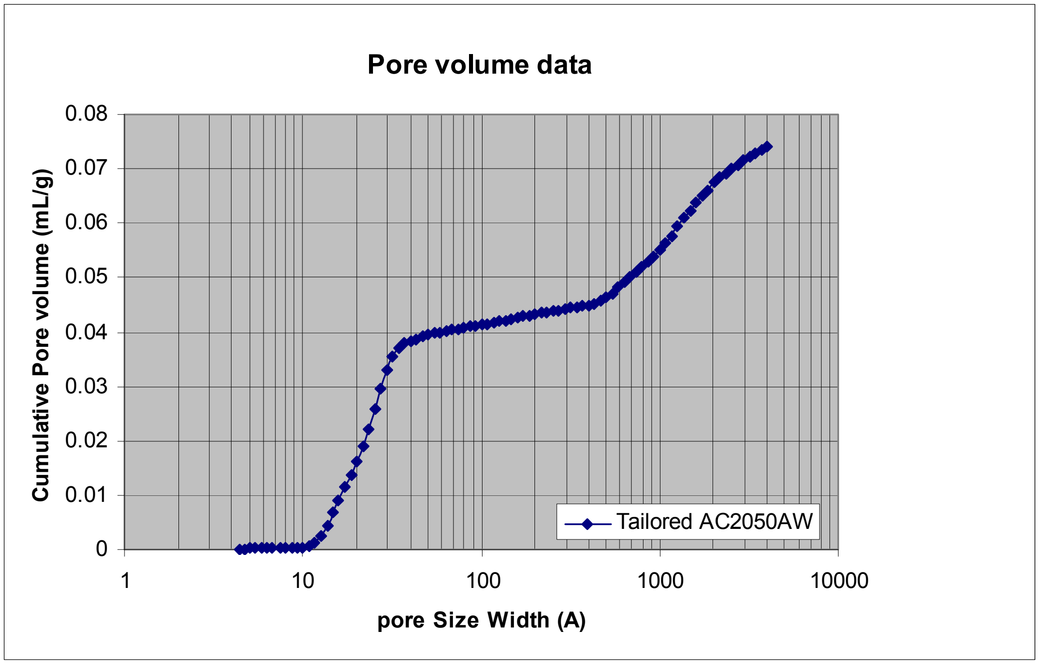

Figure 10. Anthracite-based AC 2050 AW Tailored with CPC for Fontana on site – Ground to 200x 400 mesh size for RSSCT conducted at Penn State

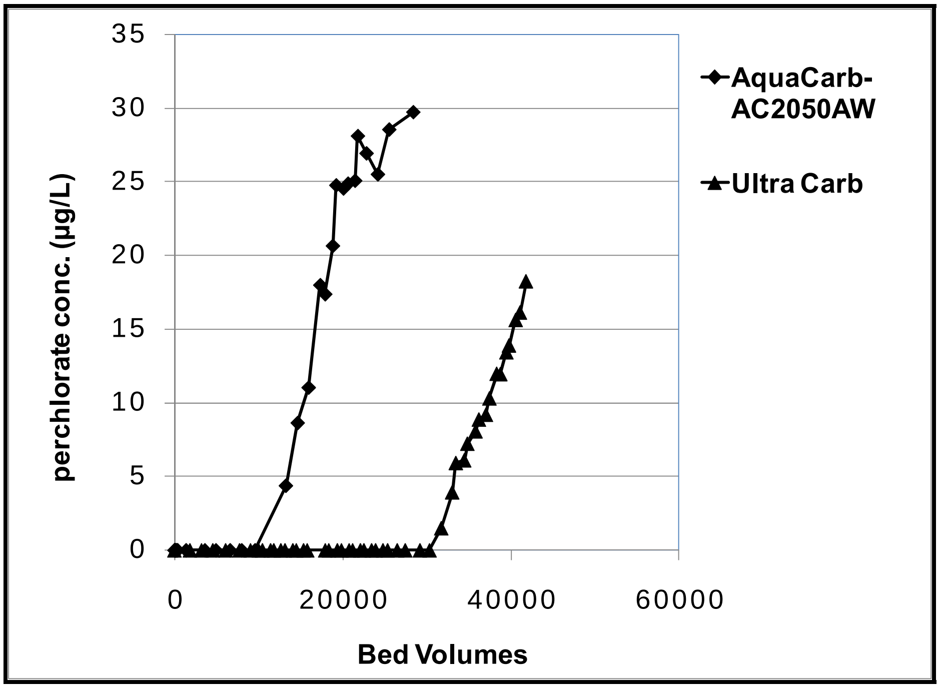

Figure 11 – Comparison of perchlorate breakthrough for two carbons, Ultracarb, a bituminous based carbon and Aquacarb AC 2050 AW, an anthracite carbon (both carbons freshly-tailored). Redlands groundwater was used for both RSSCT with an influent perchlorate concentration of 30 µg/L.

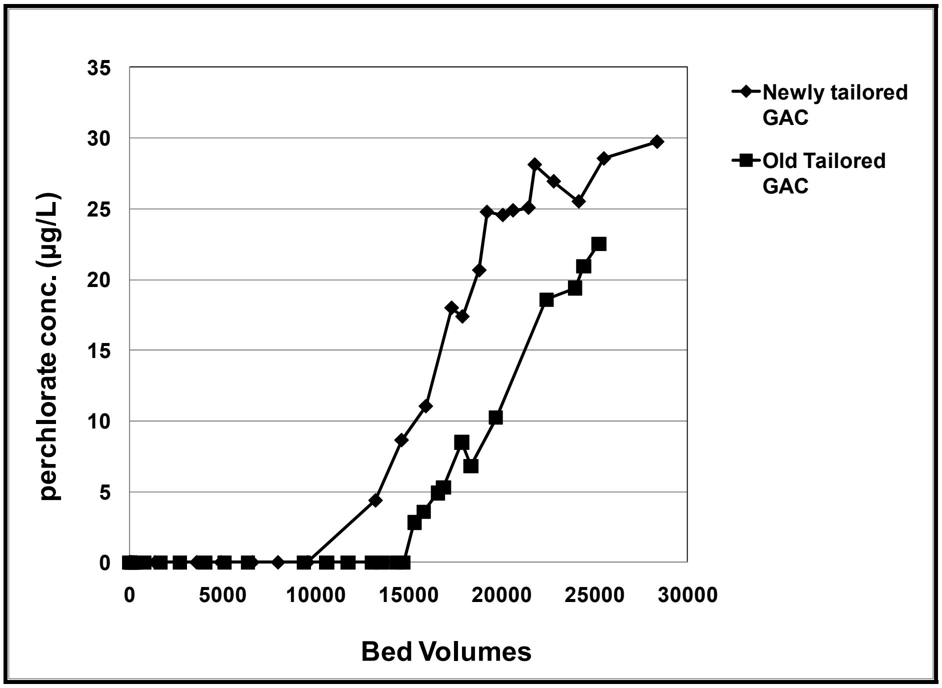

Figure 12 – Comparison of newly tailored anthracite carbon (diamond) versus anthracite carbon that was tailored in Fontana, sampled after backwashing, refrigerated, then employed in Penn State RSSCTs a year later. Redlands groundwater was used for both RSSCT with an influent perchlorate concentration of 30 µg/L.