



**EVALUATION OF AN INNOVATIVE TECHNOLOGY FOR TREATMENT OF
WATER CONTAMINATED WITH PERCHLORATE AND ORGANIC
COMPOUNDS**

THESIS

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AFIT/GEM/ENV/09-M04

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Abstract

Drinking water sources contaminated with both perchlorate and organic compounds have frequently been found in the U.S. Tailored granular activated carbon (T-GAC) is an innovative technology that is being evaluated to determine if it can more cost effectively remove perchlorate than conventional technologies. A question that has been raised is whether T-GAC can economically treat perchlorate-contaminated water that also has organic co-contaminants present.

During a field study, trichloroethylene, an organic compound, and perchlorate were successfully removed by adsorption using a T-GAC/GAC system. These results motivated development of a model that could be applied to predict the cost and performance of a T-GAC/GAC system to treat water with perchlorate and organic co-contaminants.

Correlations developed to predict organic compound adsorption onto GAC were incorporated into a T-GAC/GAC system performance model. These predictions were then used as input to a technology cost model. The predicted T-GAC/GAC system costs were similar to actual costs of conventional technologies that are being used to treat perchlorate and organic contaminated waters at a number of sites. Due to other advantages of the technology (e.g., ease of implementation) it appears the T-GAC/GAC technology has the potential to cost effectively treat water contaminated by perchlorate and organic compounds.

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To D.A.D.

and

My family

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EVALUATION OF AN INNOVATIVE TECHNOLOGY FOR THE TREATMENT OF WATER CONTAMINATED WITH PERCHLORATE AND ORGANIC COMPOUNDS

1.0. Introduction

1.1. Problem Background

Perchlorate-contaminated drinking water is of concern in the United States. Perchlorate (ClO_4^-) has been identified in groundwater, surface water, soil, and food. Studies are being conducted throughout the United States to determine if perchlorate is present, and at what concentration, in drinking water by the United States Environmental Protection Agency (U.S. EPA), in food by the Food and Drug Administration (FDA), and in soil by the United States Geological Survey (USGS) (U.S. GAO, 2005a). Perchlorate contamination is of particular concern within the Department of Defense (DoD) as ammonium perchlorate is a major component of solid rocket propellant, which is used at numerous DoD installations (U.S. GAO, 2005a). Industrial uses of perchlorate include fireworks, flares, automobile airbags, and commercial explosives (U.S. GAO, 2005a). The United States Government Accountability Office (U.S. GAO) has reported that perchlorate has been found throughout the United States. As of 2005, perchlorate contamination has been identified at 400 sites in 35 states, the District of Columbia, and two United States commonwealths (Figure 1-1) (U.S. GAO, 2005a). There is currently

no national standard regulating perchlorate levels in drinking water, although several states have established enforceable standards (U.S. EPA, 2004). Exposure to perchlorate can result in negative health effects including hypothyroidism and various other thyroid disorders (NRC, 2005). Ion Exchange (IX) is currently the most frequently used method for the treatment of perchlorate-contaminated drinking water (Baruth, 2005). Perchlorate removal using IX has proven to be effective due to its simplicity and the ability to regenerate the resin (Lehman et al., 2008). Removal of perchlorate is done by using anion exchange (Gu et al., 2007).

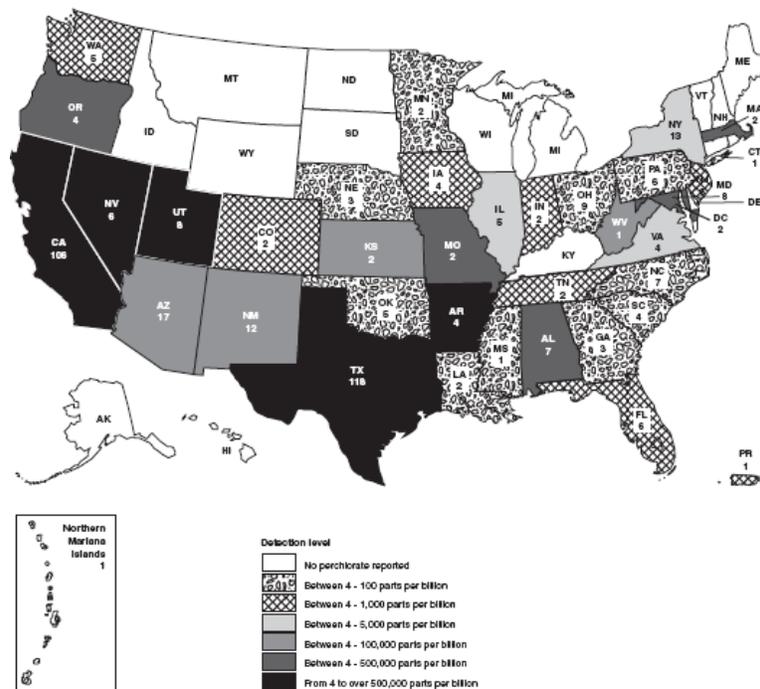


Figure 1-1: Maximum Perchlorate Concentrations Reported in any Media and Number of Sites, January 2005 (U.S. GAO, 2005)

Tailored granular activated carbon (T-GAC) is an innovative technology that is currently being evaluated through laboratory, pilot scale, and field scale tests to determine if it can perform better (i.e., more efficiently and economically) than conventional IX. T-GAC has been shown to remove perchlorate as effectively as IX; however, it has not been shown to be cost-effective when compared to IX (Craig, 2008). Although T-GAC may not be cost competitive with IX for the treatment of only perchlorate, it may be cost effective for the treatment of contaminated waters that contain perchlorate and organic co-contaminants (Craig, 2008). This is particularly important at DoD installations as many DoD sites have plumes with multiple contaminants (U.S. GAO, 2005b).

In addition to perchlorate contamination, contamination of drinking water by organic compounds is also quite common and of great concern. The EPA currently regulates many of these organic compounds, which include chlorinated solvents like trichloroethylene (TCE), tetrachloroethylene (PCE), vinyl chloride (VC), and carbon tetrachloride (EPA, 2008b). Within the DoD, these solvents are widely used for cleaning and metal degreasing. The DoD is also concerned with cleaning up water contaminated by nitroaromatic compounds, like HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and TNT (2,4,6-trinitrotoluene) which are used as explosives. GAC is a conventional technology that is used to treat water contaminated with these non-polar organic contaminants. Research has been done to investigate technologies to treat water containing perchlorate and chlorinated solvents as

co-contaminants (Borden, 2007). Many DoD sites have perchlorate plumes where chlorinated solvents and/or nitroaromatics are co-mingled.

Previous laboratory research conducted at Pennsylvania State University (PSU) has shown that T-GAC can be used to remove perchlorate from drinking water (Parette and Cannon, 2005). Powell (2007) developed a costing model based on GAC modeling techniques using data provided from Rapid Small Scale Column Tests (RSSCTs) that were run at PSU. Craig (2008) attempted to validate Powell's model through the use of results from a field-scale T-GAC pilot test in Fontana, CA. Craig was unable to incorporate Fontana operations and maintenance (O&M) data into his analysis as they were not available before the conclusion of his research.

Additional testing is currently being conducted using six medium-scale columns at the Fontana site. The individual columns are being used to test the impact of varying influent water chemistries on T-GAC performance. The first column, labeled the control column, treated "Fontana water," i.e., the perchlorate-contaminated water that was being extracted by the Fontana Water Company wells and treated in the field-scale pilot test. The second column, labeled the TCE column, treated Fontana water spiked with TCE at a concentration of approximately 40 µg/L. The third column, labeled the perchlorate column, treated Fontana water spiked with perchlorate to a concentration of 200 µg/L. The fourth column, labeled the nitrate column, treated Fontana water spiked with 70 mg/L of nitrate (as nitrate). The fifth column, the disinfectant/oxidant column, treated Fontana water that had received between 0.15 and 0.3 mg/L free chlorine as sodium hypochlorite. Finally, the sixth column, labeled the total dissolved solids/sulfate column,

treated Fontana water spiked with approximately 1,200 mg/L total dissolved solids (TDS) (Henderson et al., 2007). Of particular interest is the TCE column. Operation of this column will provide insight into the efficacy of using T-GAC to treat water where TCE and perchlorate are co-contaminants.

1.2. Problem Statement

There are several treatment technologies that cost effectively remove perchlorate from drinking water. Additionally, there are a number of technologies that can cost effectively remove non-polar organic compounds from water. Specifically, as noted above, IX and T-GAC have both been shown to effectively remove perchlorate and GAC has been shown to cost-effectively remove non-polar organic compounds. However, perchlorate is rarely found to be the sole contaminant in a plume, and it frequently co-exists with other non-polar organic compounds. In these co-mingled plumes, the conventional treatment technology is to use a treatment train, with IX to remove perchlorate and typically GAC to remove non-polar organics. However, operation of a treatment train which uses two completely different technologies is relatively costly. Therefore, the research problem is to identify and evaluate a technology that can cost effectively treat water contaminated with both perchlorate and non-polar organic contaminants to required standards.

1.3. Research Objective

The main focus of this research will be to evaluate the effectiveness of T-GAC at treating water where perchlorate and organic compounds are present as co-contaminants. Additional focus will be to update the existing T-GAC performance and cost model to

account for water chemistry that includes chlorinated and nitroaromatic compounds and to incorporate the O&M data from the Fontana site. Assuming T-GAC proves to be a viable technology to treat water with perchlorate and organic co-contaminants, a secondary objective will be to develop a cost and performance screening tool that can be used to facilitate technology transfer.

1.4. Scope/Limitations of Research

Chlorinated solvents, nitroaromatic compounds, and perchlorate have been identified as contaminants of concern by the DoD (U.S. GAO, 2005b). There are currently many technologies that exist for treatment of these individual contaminants. Both *ex situ* and *in situ* water treatment methods exist. The focus of this research is wellhead treatment for drinking water. Thus, this research will focus on *ex situ* treatment methods for comparison. Additionally, both biological and non-biological treatment methods exist. Biological drinking water treatment methods are not greatly accepted in the U.S. due to health concerns. Thus, this research will focus on non-biological treatment methods for comparison.

Many sites currently have plumes that have both perchlorate and organic contaminants. However, there is not a single database that tracks where these sites are, what has been found at the sites, and what steps are being taken to treat contamination at these sites. Also, it is rare for site remediations to be reported in the peer-reviewed literature. Thus, personal correspondence with individual site managers was relied upon for this portion of the research.

1.5. Methodology Outline

The first step will be to conduct a literature review. This will include a review of the existing T-GAC cost and performance models developed by Powell (2007) and Craig (2008), as well as a review of the T-GAC technology. Additionally, the frequency that organic compounds and perchlorate are found in water as co-contaminants will be investigated. Additional research will involve gathering data and costs from sites that currently have co-mingled plumes and are using technologies to treat these plumes. Capital costs, O&M treatment costs, and treatment performance data will be gathered from these sites for comparison to T-GAC cost and performance data. Further literature review will focus on identifying technologies that may be used to treat organic compound- and/or perchlorate-contaminated water.

Following the literature review, analysis of the six additional Fontana column tests and the Fontana O&M costs will be conducted. Insight gained from these data will be incorporated into the performance and cost models developed by Powell (2007) and Craig (2008). These additional analyses will account for the effect of water chemistry on the effectiveness of perchlorate and organic compound removal using T-GAC.

The final deliverable from this research will be a user-friendly cost and performance model. The model will provide the user with an estimate of capital and operation and maintenance costs for operating a T-GAC/GAC system to treat water with organic compounds and perchlorate as co-contaminants for varying influent water chemistry. Model estimated costs will be compared with the costs of alternative technologies that may be used to treat perchlorate- and organic compound-contaminated

water. The model will provide technology end-users and regulators with an understanding of how T-GAC treatment can be applied to manage water that has organic compounds and perchlorate as co-contaminants, and hopefully facilitate transfer of this innovative technology to these users and regulators.

2.0. Literature Review

2.1. Introduction

Perchlorate is often found in water along with non-polar organic compounds as co-contaminants. Numerous negative health effects can result when these contaminants are present in drinking water supplies. Currently, the conventional approach is to treat these waters with multiple contaminants by using a treatment train. This involves the use of one technology to remove perchlorate and another technology to remove the non-polar organic compounds. Application of a technology train introduces additional logistical difficulties (e.g., need for personnel trained on multiple technologies, different operation and maintenance requirements for each technology) and may not be as cost effective as using a single technology to simultaneously treat multiple contaminants. This section will begin with an explanation of contaminant sources and health impacts. Then, contaminant regulations will be covered. Following that, data showing the frequency of occurrence of groundwater plumes with both perchlorate and other co-contaminants will be presented. Information on conventional technologies that are available for treating these contaminants, and their respective technology costs, will then be summarized. Case studies will be presented showing how plumes having perchlorate and co-contaminants were managed. The section will conclude with a description of tailored granular activated carbon (T-GAC) technology, a summary of data sources that have been used to evaluate T-GAC performance, and an overview of previous models that were developed to predict the cost effectiveness of T-GAC to treat perchlorate-contaminated water.

2.2. Contaminant Sources and Health Impacts

Perchlorate contamination of drinking water is of great concern. Perchlorate (ClO_4^-) is a negatively charged ion that does not easily break down. Perchlorate salts, such as ammonium perchlorate or potassium perchlorate, are commonly used in solid rocket propellant and in missiles within the Department of Defense (DoD) and as fireworks, flares, automobile airbags, and commercial explosives within industry (U.S. GAO, 2005a). Eleven million people have perchlorate present in their drinking water at concentrations greater than or equal to 4 parts per billion ($\mu\text{g/L}$) (NRC, 2005).

Perchlorate has potential negative health effects on human thyroid function because it inhibits iodide uptake by the thyroid (NRC, 2005). Perchlorate-contaminated drinking water is of particular concern in people who have thyroid disorders, women who are pregnant, unborn children, and infants (NRC, 2005). A complete list of health effects associated with perchlorate ingestion can be found in the National Research Council's 2005 report entitled: "*Health Implications of Perchlorate Ingestion.*" In addition to water, perchlorate contamination has been found in soil and food (U.S. GAO, 2005a). The Food and Drug Administration (FDA) has identified that over all ranges of age and sex groups that were monitored, perchlorate consumption through food is approximately 0.08-0.39 micrograms per kilogram of body weight per day ($\mu\text{g/kg bw/day}$) (Murray et al., 2008).

Additional drinking water contaminants of concern include chlorinated solvents such as trichloroethylene (TCE), tetrachloroethylene (PCE) and vinyl chloride (VC). TCE is released primarily from metal degreasing sites (U.S. EPA, 2008b). TCE is also

used in items such as varnishes and paint strippers, and it has been used in dry cleaning operations in the past (U.S. GAO, 2007). The DoD has used TCE in many industrial and maintenance processes (U.S. GAO, 2007). TCE and VC have been regulated by the Environmental Protection Agency (EPA) since 1987 and PCE has been regulated since 1991 (U.S. EPA, 2001a). TCE has the potential to cause liver damage and cancer, while PCE can have negative health effects on the liver, kidney, and central nervous system when lifetime exposure occurs (U.S. EPA 2006b; 2006c). VC can affect the liver when there is lifetime exposure and it is considered a carcinogen through oral exposure routes (U.S. EPA 2006d).

Additional contaminants of concern that are frequently found, especially at DoD sites, are nitroaromatic compounds such as HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane), RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), and TNT (2,4,6-trinitrotoluene). The major source of these contaminants is explosives. Health effects of TNT were studied and a reference dose for chronic oral exposure was established at 0.0005 milligrams per kilogram per day (mg/kg/day) based on negative effects on the liver (EPA, 2008d). RDX has also been studied and a reference dose for chronic oral exposure of 0.003 mg/kg/day was established based on inflammation of the prostate (U.S. EPA, 2008e). Additionally, the EPA identified RDX as a potential carcinogen following a study done in mice (Boyer et al., 2007). For HMX, a reference dose for chronic exposure of 0.05 mg/kg/day has been established based on hepatic lesions (U.S. EPA, 2008f). TNT and RDX are listed under the USEPA's Unregulated Contaminant Monitoring Rule (UCMR) (Boyer et al., 2007). The UCMR calls for monitoring of contaminants with potential health effects

that are suspected to be present in drinking water but that are not currently regulated under the Safe Water Drinking Act (SDWA). Data are stored in the National Contaminant Occurrence Database (NCOD) (U.S. EPA, 2008a) for future regulatory use.

2.3. Contaminant Regulations

Drinking water contaminants are monitored federally under the Safe Water Drinking Act (SWDA). In addition to federal law, individual states have created standards to regulate individual contaminants which state regulators feel pose a public health hazard to state residents. The DoD has also established guidelines for managing individual contaminants that enter the water as a result of DoD operations and which may pose a risk to the base or local populace. The Air Force Center for Engineering and the Environment (AFCEE) has implemented tracking methods to help the USAF ensure that all federal, state, and DoD regulations and requirements with respect to water contaminants are met.

2.3.1. Federal Regulations

To date, perchlorate is not regulated at the national level. Although the EPA has not formally developed a standard, following the NRC (2005) recommendations, the EPA established a reference dose of 0.0007 mg/kg/day of perchlorate. This reference dose corresponds to a drinking water equivalent level (DWEL) of 24.5 µg/L (U. S. EPA, 2006a). This dose is based on a 154-pound adult consuming 2 liters of water per day that contains 24.5 µg/L of perchlorate (U.S. GAO, 2005a). This calculation assumes that perchlorate exposure is from drinking water only. As a requirement under the SDWA, the EPA is required to publish the Contaminant Candidate List (CCL). The CCL lists

contaminants that are present in or may be present in drinking water systems and which may require future regulation (U.S. DoD, 2007). Perchlorate was one of the contaminants listed on the first CCL (CCL 1) in 1998 (U.S. EPA, 2008c). It was then listed on the CCL 2 in 2005 (U.S. EPA., 2008c). Perchlorate is currently listed in the CCL 3 draft published on Feb 21, 2008 (U.S. EPA, 2008c). The CCL 3 draft built on the previous two lists but also took into account recommendations of the National Academy of Science's National Research Council (NRC) and the National Drinking Water Advisory Council (NDWAC) (U.S.EPA, 2008c). Perchlorate was monitored from 2001-2005 under the Unregulated Contaminant Monitoring Rule (UCMR) (U.S. DoD, 2007).

In the winter of 2008, the subcommittee on Environment and Hazardous Materials proposed legislation to amend the SWDA to include a drinking water standard for perchlorate ("Healthy Communities," 2008). On July 31, 2008, the Senate Environment and Public Works Committee passed S. 24 and S. 150. S. 24 was entitled the Perchlorate Monitoring and Right to Know Act and requires the EPA to reinstate its monitoring rule for perchlorate in drinking water until a drinking water standard is established (U.S. EPW Committee, 2008). It also requires that the public be informed regarding perchlorate in their drinking water. S.150, entitled the Protecting Pregnant Women and Children from Perchlorate Act, requires the EPA to develop a health advisory standard followed by the development of a drinking water standard. Both of these are aimed at protecting sensitive populations (U.S. EPW Committee, 2008). These bills have not yet been enacted into law; however, they are aimed at forcing the U.S. EPA to monitor perchlorate in drinking

water and to pursue the development of a health advisory standard and eventually a drinking water standard.

Many chlorinated solvents are regulated by the federal government. The EPA has set a maximum contaminant level (MCL) of 0.005 mg/L for TCE and the maximum contaminant level goal (MCLG) for this chemical is zero (U.S. EPA, 2008b). A complete list of organic solvents regulated by the government is available for public viewing on the EPA's drinking water webpage.

RDX was present on both the CCL 1 and CCL 2 health advisory lists (U.S. EPA, 2008c). It is currently present on the CCL 3 (U.S. EPA, 2008c). Table 2-1 shows current EPA water Health Advisory Levels (HALs) which serve as guidelines for RDX, HMX, and TNT.

Table 2-1: EPA Health Advisory Levels for Selected Nitroaromatic Compounds in Water (Boyer et al., 2007)

Constituent	HAL [mg/L]
RDX	0.002
HMX	0.400
TNT	0.002

2.3.2. State Perchlorate Regulations

Several individual states have developed perchlorate advisory or MCL levels. Table 2-2 is a table that illustrates which states have established requirements. The table outlines the established levels that have been set for each state.

Table 2-2: State Perchlorate Regulations

<u>State</u>	<u>Level</u>	<u>Notes</u>
Arizona	14 µg/L	1998 Health Based Guidance based on child exposures ¹
California	6 µg/L	MCL effective October 18, 2007 ²
Maryland	1 µg/L	Advisory Level ¹
Massachusetts	2 µg/L	MCL effective July 28, 2006 ³
Nevada	18 µg/L	Public Notice Standard ¹
New Jersey	5 µg/L	MCL ⁵ expected to take effect in early 2009
New Mexico	1 µg/L	Drinking Water Screening Level ¹
New York	5 & 18 µg/L	5 µg/L – Drinking Water Planning Level 18 µg/L – Public Notification Level ¹
Oregon	4 µg/L	Action Level ⁴
Texas	17 & 51 µg/L	17 µg/L – Residential Protective Cleanup Level (PCL) 51 µg/L – Industrial Commercial PCL ¹

1. United States EPA (2004)

2. California Department of Public Health (2008)

3. Massachusetts Department of Environmental Protection (2008)

4. Oregon Department of Environmental Quality (2008)

5. Environmental Science and Technology (2008) and AWWA (2009)

2.3.3. DoD Perchlorate Policy

The Under Secretary of Defense signed an official memorandum on January 26, 2006, which outlines the DoD perchlorate policy (USD, 2006). According to this memorandum, a level of concern of 24 µg/L was established for the DoD unless or until EPA or state regulations impose more stringent standards. The memorandum clearly outlines that if either the EPA or individual states establish maximum contaminant levels (MCLs), DoD must follow the established regulations. Perchlorate will be sampled for in accordance with the National Contingency Plan, and if a concentration in water of greater than 24 µg/L is discovered at a site, site remediation should follow the Comprehensive Environmental Response Compensation Liability Act (CERCLA) and Defense Environmental Restoration Program (DERP) requirements (USD, 2006).

DoD is also required to test for off-site migration of perchlorate from range sites. At DoD sites where independent drinking water systems are operated, the site is required to test for perchlorate. If the perchlorate level exceeds 24 µg/L, higher headquarters are to be notified and actions taken as directed. Quarterly sampling is to occur until the major command is satisfied that the perchlorate level is below 24 µg/L. Those sites that do not find perchlorate at concentrations greater than 4 µg/L for two consecutive testing quarters are permitted to stop sampling unless regulations or permits require them to continue sampling. DoD sites where perchlorate is known to be used in the “manufacture, maintenance, processing, recycling or demilitarization of military munitions” must also monitor for perchlorate in the wastewater effluent (USD, 2006). This testing is to be done semi-annually at the point where routine testing is conducted.

If perchlorate is detected, higher headquarters is to be notified and required actions will be taken. The DoD perchlorate handbook released in August 2007 further outlines DoD actions related to perchlorate identification and treatment (U.S. DoD, 2007).

A memorandum was issued in September of 2007 titled Actions in Response to Perchlorate Releases which outlined perchlorate remediation goals for active bases, closed bases, and formerly used defense sites (FUDS) (USD, 2007). These goals require that sites that were sampled at the end of fiscal year 2006 and that had perchlorate detections greater than 24 µg/L or “an applicable regulatory standard” are required to “ensure that appropriate actions have been initiated, programmed, or determined not required by the end of fiscal year 2008 (USD, 2007).” Additionally, perchlorate was placed on the DoD’s Emerging Contaminant (EC) Action List (USD, 2008), indicating that perchlorate has been found to pose a significant potential threat to people or the mission of the DoD. A number of potential risk management options, such as research and development of less harmful substitute materials, are initiated for chemicals on the EC list (DUSD, 2008).

2.3.4. Air Force Perchlorate Policy

In June of 2006, the Air Force implemented a policy on perchlorate entitled “Air Force Guidance on Actions Related to Perchlorate.” This outlined the specific Air Force actions that must be taken in order to comply with the “Policy on DoD Required Actions Related to Perchlorate” (DAF, 2006). Data calls are conducted annually at all stateside and overseas installations. Air Staff directs the Air Force Center for Engineering and the Environment (AFCEE) Remedial Program Management Office (PMO) to initiate the data

calls at the Major Command (MAJCOM) levels (Anders, 2008). Individual base-level program managers receive guidelines from their MAJCOMs regarding the data calls (Anders, 2008). In addition to perchlorate releases detected at installations by complying with the Air Force perchlorate policy, perchlorate is frequently identified at individual sites due to state- or EPA- regulator requests for perchlorate sampling (Anders, 2008). Data gathered by the installations are entered into the Air Force perchlorate database. The accuracy of the data gathered increased from 25% in 2006 to 90% in 2007 (Anders, 2008).

2.4. Frequency of Co-Contaminated Plumes

Groundwater plumes which have perchlorate, organic compounds, and nitroaromatic compounds present as co-contaminants are found throughout the United States. Table 2-3 shows the location, contaminant type, and treatment technology used for a number of these plumes. This list includes many sites where co-contaminants exist, but it is not all inclusive. There is currently no centralized tracking system for comprehensively identifying sites that contain multiple contaminants. Thus, this list was built using various sources. The sites included on this list were determined to have co-contaminated water through personal communications with personnel at AFCEE, project managers at individual sites, and through use of the U.S. EPA website.

Table 2-3: Contaminated Sites, Contaminant Types, and Treatment Systems

<u>Site</u>	<u>Contaminant Types</u>	<u>Type of Treatment</u>
Massachusetts Military Reservation (MMR) ¹	RDX plumes & RDX/perchlorate plumes	IX/GAC/GAC
Edwards Air Force Base (EAFB) ²	TCE & perchlorate	Selective IX/GAC
Stringfellow Superfund Site ³	Predominant compounds: para-chlorobenzenesulfonic acid (pCBSA), TCE, heavy metals, sulfate, chloroform, chlorobenzene, and perchlorate	1) Pre-treatment plant (PTP): uses precipitation for pesticide removal and GAC for VOC removal 2) Lower Canyon Treatment Facility (LCTF): removes gasoline-related compounds 3) Community Wellhead Treatment System (CWTS) uses GAC/IX
National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) ⁴	Perchlorate, carbon tetrachloride, chloroform, and minor NACs	IX/GAC and GAC/FBR

1. *Forbes, 2008 and Nixon, 2008*

2. *Duong, 2008*

3. *California DTSC, 2008, Kenoyer et al. 2008, and Paulson, 2008*

4. *NASA, 2008*

2.5. Conventional Technologies for Perchlorate Treatment

The most common technology in use for perchlorate treatment is ion exchange (IX). This treatment method has been evolving over the last decade and the cost of perchlorate treatment by IX has decreased greatly.

2.5.1. Ion Exchange (IX) Treatment

Ion exchange (IX) is the most frequently used method for removing perchlorate from drinking water. In IX, water is passed over a resin and innocuous ions present on the resin are exchanged for the undesirable target ions (e.g., perchlorate ions) that are present in the water. The primary IX methods for perchlorate treatment use are: (1) selective, non-regenerable, resins and (2) nonselective resins with NaCl regeneration (Gu et al., 2007). The non-regenerable resin, which is selective for the perchlorate anion (that is, it minimally adsorbs competing anions that may be in solution) must be disposed of when the bed reaches its full sorption capacity (Gu et al., 2007). Because the resin contains perchlorate, it must be managed as a hazardous waste (Gu et al., 2007). The nonselective resin can be regenerated (Gu et al., 2007). However, the perchlorate sorption capacity of this resin is extremely limited since the resin will also absorb competing anions such as sulfate and nitrate which may be present in the water (Gu et al., 2007). In fact, these anions typically occupy >99% of the IX sites (Gu et al., 2007). Frequent regeneration of this resin is required, resulting in the production of high quantities of hazardous brine water that must be properly disposed of (Gu et al., 2007).

To address these problems of non-selective/regenerable and selective/non-regenerable resins to treat perchlorate, Gu et al. (2007) investigated the potential of IX treatment using highly selective, yet regenerable resins. This process used ferric chloride-hydrochloric acid ($\text{FeCl}_3\text{-HCl}$) regeneration. The $\text{FeCl}_3\text{-HCl}$ solution was used to form FeCl_4^- ions. The FeCl_4^- ions were then used to displace the ClO_4^- ions from the spent media. Following this, a FeCl_2 thermoreactor was used to destroy the perchlorate.

This resulted in 92-97% reduction of the perchlorate and allowed for the $\text{FeCl}_3\text{-HCl}$ to be reused. The study determined that the use of these highly selective technologies was possible, although cost effectiveness was not evaluated in the paper (Gu et al., 2007).

2.5.2. Cost of IX

The cost of using ion exchange to treat perchlorate-contaminated water has decreased significantly over the last seven years. Figure 2-1, which was developed by Siemens (2008), clearly shows this decrease. In 2000, the cost to treat an acre-foot was \$450-\$650. As of 2007, the cost had decreased to \$75-\$100 per acre-foot (Figure 2-1). Figure 2-1 costs include the resin cost, pre-installation rinses, vessel loading and unloading, vessel sanitation, transportation, resin disposal and the Certificate of Destruction (Lutes, 2008).

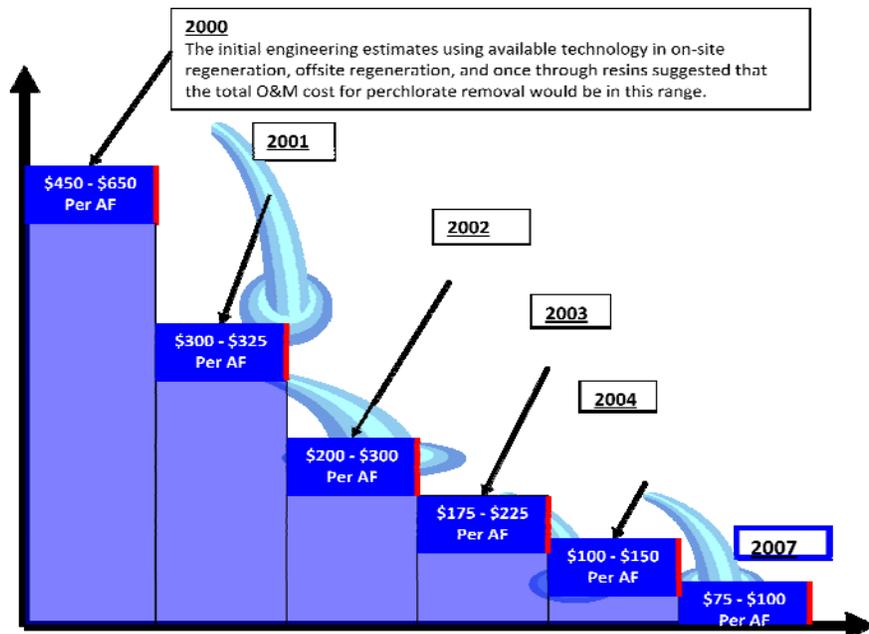


Figure 2-1: Evolution of Perchlorate Costs (After Lutes et al., 2008)

2.6. Conventional Technologies for Chlorinated Solvent Treatment

Conventional treatment technologies for the removal of chlorinated solvents include the use of Granular Activated Carbon (GAC) and air stripping. These technologies rely on the fact that chlorinated solvents are hydrophobic (as non-polar compounds, they are thermodynamically more stable in the presence of other nonpolar molecules—water, of course, is very polar). Hydrophobic compounds are readily removed by GAC, since GAC is a nonpolar phase that hydrophobic compounds will preferentially partition into. The Henry's constant (H) is a measure of a compound's concentration in the gaseous phase divided by its concentration in the aqueous phase at equilibrium. A hydrophobic, volatile compound with a high Henry's constant is easily removed by air stripping, as discussed below.

2.6.1. Air stripping

Air stripping is a technology that can be used to remove volatile organic compounds (VOCs) such as TCE from water (Baruth, 2005). Air stripping involves the transfer of a substance from the liquid phase to a gas phase (Adams and Clark, 1991). Transfer occurs due to a concentration gradient between the air (low concentration of the substance) and the water (high concentration of the substance) (Adams and Clark, 1991). Substances with higher Henry's constants are more likely to partition into the gas phase (Adams and Clark, 1991). Counter-current air stripping within a packed tower is the technology most frequently used to treat VOC-contaminated water (Dzombak et al., 1993). This typically involves the use of a tower in which water flows from the top to the bottom and air flows through the tower from the bottom to the top (Dzombak et al.,

1993). Small-diameter packing material is present in the column to increase the contact surface area between the water and the air (Dzombak et al., 1993). The volatile contaminants are removed from the water and enter the air stream as they travel through the column. Treatment of the air, often by GAC, may occur following the stripping process to remove the contaminants before the air is released into the atmosphere (Dzombak et al., 1993).

2.6.2. Granular Activated Carbon (GAC)

GAC treatment technology has been used for many years to treat industrial and municipal wastewater (Clark and Lykins, 1989). It has also been used for many years to treat drinking water in Europe. GAC relies on the process of adsorption to remove chemical species from water. There are many different varieties of granular activated carbon, each having its own chemical and physical properties. These properties include adsorption capacity, selectivity, and the ability to undergo thermal reactivation. As the carbon is used, its adsorptive capacity is exhausted and this requires that the material be regenerated so that it can once again adsorb the target chemical. One regeneration method is to thermally reactivate the carbon. During this process, the carbon is heated until the adsorbed materials are removed from the carbon by burning them off. The process is optimized to ensure that minimal carbon mass is lost. Once this process is complete, the carbon is reused again in the treatment process (Clark and Lykins, 1989). GAC can be used for the treatment of nonpolar organic compounds (Letterman, 1999). In 1996, approximately 1,700 contaminated groundwater sites with volatile organic compounds were treated by granular activated carbon (Nakano et al., 2000). Okawa et al.

(2007) identified GAC as the most common method for treating TCE-contaminated groundwater.

GAC adsorption isotherms have been developed for various VOCs. Urano et al. (1991) developed adsorption isotherms for several contaminants onto different carbons. All the contaminants studied were represented by the Freundlich adsorption isotherm. Table 2-4 shows various sorbed concentrations onto six GACs (q) for TCE dissolved concentrations (C) equal to 40 µg/L. The q values in table 2-4 were measured experimentally.

Table 2-4: Urano et al. (1991) Sorbed Concentrations

GAC Type	q [µg TCE/g carbon] for C = 40 µg/L
A - Turami HC-30 Coconut Shell	10,000
B – Hokuetu Y-20 Coconut Shell	6,000
C – Mitubisi 005-S Coal	10,250
D – Mitubisi 007-S Coal	9,000
E – Calgon F-400 Coal	6,500
F – Fujisawa ACW Coal	10,250

Urano et al. (1991) showed that for a TCE concentration of 40 µg/L, sorbed concentrations onto various GACs ranged from approximately 6,000 µg TCE/g carbon to 10,250 µg TCE/g carbon. Complete adsorption isotherms are available in Urano et al.

(1991). Data in MWH (2005) showed that for Calgon F400 GAC, for a dissolved TCE concentration of 24.5 µg/L, the sorbed concentration, q [µg/g], was equal to approximately 16,500 and for a dissolved concentration of 74.3 µg/L the sorbed concentration [µg/g] was equal to approximately 19,400. Interpolating these data yields an estimate for a sorbed concentration (q) of 17,400 µg/g corresponding to a dissolved concentration of 40 µg/L. Thus, based on experimental data presented in Urano et al. (1991) and MWH (2005), for a dissolved TCE concentration of 40 µg/L, sorbed concentrations on various GACs range from about 6,000 to 18,000 µg/g.

Based on sorption data, values for the Freundlich isotherm parameters, K_f and $1/n$, have been developed to estimate adsorption of TCE onto GAC. Table 2-5 shows several of these values. The parameters are used to calculate sorbed concentration (q) for a dissolved TCE concentration of 40 µg/L. Examination of Tables 2-4 and 2-5 shows that for a dissolved TCE concentration of 40 µg/L, sorbed concentrations onto various GACs range from about 4,000 to 18,000 µg/g.

Table 2-5: Freundlich Parameters (K_f and $1/n$) and Corresponding Sorbed Concentrations (q) for TCE onto GAC with $C_o = 40$ µg/L

	Kf min	Kf max	1/n min	1/n max	C_o	q range	
Source	[(mg/kg)/(mg/L) ^{1/n}]		[-]		[mg/L]	[µg TCE/g GAC]	
Shih and Gschwend (2009) ¹	34.04	36.98	0.414	0.446	0.04	8,979	8,800
Faust and Aly (1998)	28		0.62		0.04	3,805	

1- 19 data points were used

2.6.3. Costs of GAC and Air Stripping

Economies of scale play a large role in water treatment technology costs. As more units of water are produced, unit costs decrease. Typical capital costs for GAC treatment vary according to the quantity of GAC that is required (Kawamura, 2000). The quantity of GAC required is affected by the quality of the water that is to be treated.

The Air Force developed the Remedial Action Cost Engineering and Requirements program (RACERTM). RACER is a “Windows-based environmental remediation/corrective action cost-estimating system” (WBDG, 2008). One component of this model is a parametric GAC costing model which can be used to determine, based on several input parameters, the installation cost of a GAC system of a given size (Claypool, 2008). The RACERTM software input parameters are: flow, system redundancy, and system configuration, as well as total organic carbon (TOC) and total volatile organic compounds (VOCs) in the influent water. The program is applicable for 1-1000 gallon per minute (gpm) permanent units and for 1-200 gpm modular units.

Adams and Clark (1991) provided costs for the treatment of selected organics by using packed-tower aeration (PTA). They considered systems that were to operate both with and without emission control. The emission control used as a comparison measure was vapor-phase GAC. The authors explain that this technology is the most common and is usually the most cost-effective. Tables 2-6 and 2-7 show costs for the treatment of various compounds by PTA, for effluent concentrations of 5 µg/L and 1 µg/L, respectively. The costs have been updated to 2008 dollars assuming a discount rate of 2.8% per annum compounded monthly for 17 years. This rate is recommended by the

Office and Management and Budget (OMB) for “discounting constant-dollar flows, as is often required in cost-effectiveness analysis” (OMB, 2009). Since this study does a cost-effectiveness analysis, the 20-year discount rate recommended for this type of analysis (2.8%) was chosen. Additionally, this was the rate used by Craig (2008) so the use of this rate provides a common ground between the Craig (2008) model and the new model that will be developed. As one can see, the cost of PTA treatment with air emission control is substantially higher than without air emission control. Additionally, the cost increases as the treatment goal increases. Also note the economies of scale; as the flow increases, the treatment cost per acre-foot treated decreases.

Table 2-6: Packed Tower Aeration (PTA) Costs in \$/acre-foot where Influent Concentration = 100 µg/L and Effluent Concentration = 5 µg/L (Adams and Clark, 1991)

	Flow in million gallons per day (mgd)							
	0.1		1		10		100	
Compound	PTA*	With Emissions Control	PTA	With Emissions Control	PTA	With Emissions Control	PTA	With Emissions Control
Trichloroethylene	204	414	68	129	42	82	34	70
Vinyl chloride	180	1247	50	981	29	937	23	928
Tetrachloroethylene	199	386	63	110	38	65	30	53

Table 2-7: Packed Tower Aeration (PTA) Costs in \$/acre-feet where Influent Concentration = 100 µg/L and Effluent Concentration = 1 µg/L (Adams and Clark, 1991)

	Flow in million gallons per day (mgd)							
	0.1 mgd		1 mgd		10 mgd		100 mgd	
Compound	PTA*	With Emissions Control	PTA	With Emissions Control	PTA	With Emissions Control	PTA	With Emissions Control
Trichloroethylene	228	438	86	147	54	94	44	80
Vinyl chloride	197	1256	61	984	35	936	28	925
Tetrachloroethylene	221	408	80	127	48	76	39	62

Air stripper design models are available for estimating how much it will cost to remove contaminants from water using PTAs. One such model is the Air-Stripper Design and Costing Computer Program developed by Dzombak et al. (1993) at Carnegie Mellon University. This program can generate up to 144 air-stripper designs based on user inputs. User inputs include: water flow rate, water temperature, packing material, contaminants to be removed, and removal efficiencies. A value of ranges must also be specified for the stripping factor and the gas pressure drop (Dzombak et al., 1993). The stripping factor is the ratio between the air-to-water ratio of the designed air stripper and the theoretical air-to-water ratio needed to achieve complete stripping under the assumption of gas phase/liquid phase equilibrium. Typically, the stripping factor, which is essentially a safety factor, is approximately 3 (Ram et al., 1990). Pressure drop is the decrease in pressure across the column. Capital costs can be estimated based on the

designed packing height, tower diameter, and air flow rate (Dzombak et al., 1993).

Operating costs can be estimated based on pump and blower characteristic curves built into the program (Dzombak et al., 1993). The design is based on mass transfer theory and the program's goal is:

...to determine the packed-tower configuration (diameter and height of the packing material) and air and water loading rate (mass/area x time) that will enable reduction of a given influent concentration C_i of a volatile contaminant to a desired effluent concentration C_e at minimum cost for a specific inflow rate Q and a set of environmental conditions (e.g., air and water temperatures, atmospheric pressure). (Dzombak et al., 1993)

Process equipment costs including pumps, blowers, and packing materials are based on per-unit prices that are built into the database (Dzombak et al., 1993). Process equipment costs including the column shell, column internals are based on empirical equations that correlate cost and size. Support equipment costs for items such as electrical equipment and piping are developed as a percentage of the process equipment costs. Indirect capital costs are estimated based on a percentage of the total support equipment costs. Power estimates are based on pump and blower characteristics. Labor and maintenance costs are estimated based on assumptions developed through the use of user input information. The costs in the program are in 1990 dollars. The dollars can be updated within the program to allow for inflation by using the Engineer News Record (ENR) Construction Cost Index (Dzombak et al., 1993). The model was verified by comparing the output to case study data. The combined costs estimated by the program were typically within 25 percent of the actual costs (Dzombak et al., 1993). The author notes that some individual items varied by over 50 percent, but that the capital cost estimate was within 15 percent of the actual cost (Dzombak et al., 1993). Dzombak et al.

(1993) also note that the primary use of this program is to compare the costs of different design outputs and that the estimates developed by the program can vary greatly based on site-specific requirements. Many air stripping technology vendors have also developed cost models which are available commercially (Nyer, 1993).

2.7. Conventional Technologies for Nitroaromatic Compound (NAC) Treatment

Conventional technologies for the removal of dissolved TNT from wastewater include both concentration and destruction methods (Marinović et al., 2005). Currently, TNT-contaminated water is typically treated with granular activated carbon (Marinović et al., 2005). GAC is commonly used to remove RDX and HMX from water as well (Morley et al., 2005). Other destruction technologies exist for the treatment of nitroaromatics; however, for the purposes of this research, GAC will be focused on as the most commonly used technology for NAC treatment.

2.7.1. GAC

Henke and Speitel (1998) reported in a case study at the Amarillo National Resource Center that activated carbon adsorption has been demonstrated to remove explosives from groundwater. Activated carbon adsorption has been applied at explosive handling facilities to remove >99.5% of nitroaromatic compounds present in pink water (Sublette et al., 1992). Pink water is wastewater that is a by-product of explosive manufacture and handling (Card and Autenrieth, 1998). TNT and RDX are the major contaminants present in pink water and HMX is a minor contaminant (Card and Autenrieth, 1998). When carbon adsorption is the chosen treatment method, Burrows (1982) determined that TNT will absorb first, then HMX, and then RDX. As treatment

continues, TNT will begin to displace the HMX and RDX. GAC was shown to effectively and concurrently remove TNT, RDX, HMX, and additional contaminants at the Milan Army Ammunition Plant (MAAP) (Wujcik et al., 1992). One of the main disadvantages of using GAC for treatment of these explosives is the poor efficiency for regenerating the GAC (Oh et al., 2004). Several different thermal regeneration technologies exist; however, following regeneration, the GAC must typically be mixed with a substantial quantity of virgin GAC because the thermally regenerated GAC loses approximately 15-50% of its adsorption capacity (Oh et al., 2004).

2.7.2. Costs of GAC

The purchase cost of GAC for treating pink water is approximately \$4,314 per acre-feet of water (Sublette et al., 1992). The disposal costs for the GAC are approximately \$6,771 per acre-foot (Sublette et al., 1992). The cost is estimated to be less for the treatment of ground and surface water contaminated with these compounds due to significantly lower contaminant concentration (Card and Autenrieth, 1998). The parametric costing model RACERTM can be updated in order to take into account nitroaromatic compounds (Claypool, 2009). Although several of the technologies in RACERTM have nitroaromatic compounds incorporated into their contaminant lists (e.g., advanced oxidation processes), these contaminants have not yet been built into the carbon adsorption (liquid) model (Claypool, 2009). These contaminants could be added to the carbon adsorption (liquid) model if their addition is reviewed and approved by the RACER Technical Review Group (TRG) (Claypool, 2009).

2.8. Co-Mingled Plumes – Case Studies

2.8.1. Edwards AFB

Edwards Air Force base has plumes contaminated with both perchlorate and TCE (Duong, 2008). The site of interest where perchlorate is currently being treated is referred to as site 285 and is located within operable unit (OU) 5/10. Figure 2-2 shows the site location. Other OUs are shown as well to provide a perspective on where the site is located.

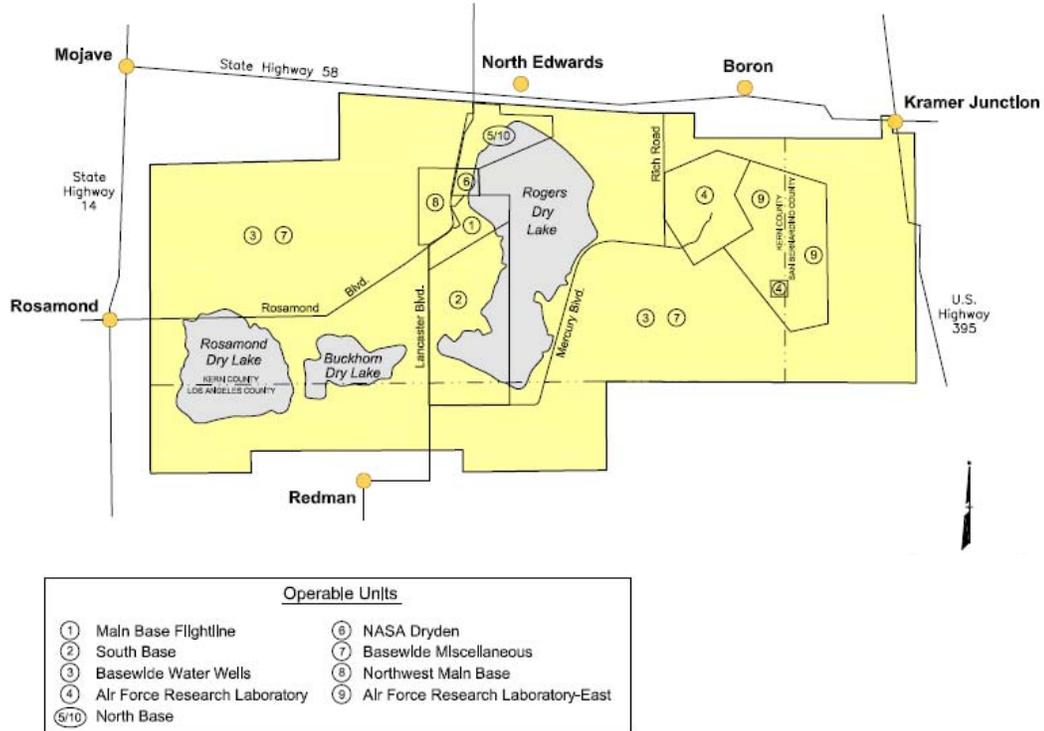


Figure 2-2: Edwards Air Base Operable Units (95th Air Base Wing, 2008)

A treatability study was started in March of 2003 at site 285. This study examined three different technologies (95th Air Base Wing, 2008):

- “Regenerable ion-exchange resin technology to treat extracted groundwater
- Soil flushing infiltration to mobilize perchlorate from vadose zone soils to underlying groundwater
- Enhanced bioremediation for the *in situ* remediation of perchlorate in groundwater”

Prior to full-scale studies at the site, a bench-scale test was conducted. Results of this pilot scale test determined that the “bifunctional (IX) resin has five times the treatment capacity as the commercially available, conventional, monofunctional resins” (95th Air Base Wing, 2008). Additionally, ferric chloride regeneration was shown to be effective at regenerating the resin.

In order to conduct these studies, a global extraction and treatment system (GETS) was installed. The current treatment train is made up of a perchlorate-selective bifunctional ion exchange resin, a granular activated carbon system to remove organics, and the use of carbon dioxide to regulate pH (Duong, 2008). Once the water is pumped above ground and treated, it is reinjected into the ground. The treatability study conducted at the base also looked at regenerating the used IX resin through the use of FeCl₃ solution (Duong, 2008). This solution effectively removes the perchlorate from the spent resin (Duong, 2008). The Oak Ridge National Laboratory (ORNL) has been instrumental in the development of the ion exchange resin and the regeneration solution (Duong, 2008). On-site regeneration was discontinued in November of 2005 as resin replacement was determined to be more economically feasible (95th Air Base Wing, 2008). It is estimated that resin replacement is 40% cheaper than on-site regeneration

(95th Air Base Wing, 2008). However, with a larger treatment scale, off-site regeneration may become economically advantageous (95th Air Base Wing, 2008).

TCE was detected in the past and is still tested for in both the influent and effluent streams (Oshita, 2009). However, the influent and effluent TCE concentrations were non-detect as of March 2009 (Oshita, 2009). The influent perchlorate concentration was 100 µg/L and the effluent concentration was non-detect (Oshita, 2009). The influent flow varied between 9 gpm and 30 gpm. From March 11, 2003, to December 31, 2007, the site had successfully removed 140.7 lbs of perchlorate and extracted 37.5 million gallons of water (95th Air Base Wing, 2008).

The O&M costs for the GAC systems, “which includes procuring and overseeing a subcontractor to profile, replace and dispose of spent GAC is approximately \$8k/year at this site” (Oshita, 2009). The O&M Costs for the IX system which includes the “cost to procure, replace, characterize and dispose of spent resin is \$30-35k/year” (Oshita, 2009). At the time of this report, capital costs were not available.

2.8.2. Stringfellow

The Stringfellow Superfund site in California was used as an industrial waste site and as a munitions and explosives test site (California DTSC, 2008). The site had releases of explosives, rocket propellants, metal finishing products, electroplating material, and pesticides from 1956 through 1972 (Kenoyer et al., 2008). The site has many contaminants including: trichloroethylene (TCE), heavy metals, sulfate, chloroform, chlorobenzene, and perchlorate (California DTSC, 2008). Perchlorate levels have been measured into the thousands of µg/L at the source (Kenoyer et al., 2008).

Groundwater extraction wells have limited the plume spread and have been successful at removing some contamination (California DTSC, 2008). Beyond Freeway 60, the only contaminants in the plume are TCE, chloroform, and perchlorate (California DTSC, 2008). Outside the plume, perchlorate levels have been measured between 1 and 12 µg/L. Testing is being done to determine if these background levels of perchlorate may be due to the use of Chilean nitrate fertilizer in the area or some other human releases. The perchlorate concentrations are reduced before the groundwater plume discharges into the Santa Ana River due to anaerobic conditions created as the geology changes which allows for attenuation of the contaminant (Kenoyer et al., 2008). The site also had a leaking gas station tank that released methyl-tert-butyl-ether (MTBE) into the ground.

The site currently has three treatment systems. The first is a pre-treatment plant (PTP). This treatment process involves two precipitation steps which both use lime. In the first step, pesticides are precipitated by raising the pH from 4 to 4.4 (Paulson, 2008). The second step removes metals through the use of a filter press, once the pH has been raised to approximately 7.5 or 8. Following this step, GAC is used to remove volatile organic compounds (VOCs) including TCE. The second system is the Lower Canyon Treatment Facility (LCTF) which primarily controls VOCs from entering the community (Paulson, 2009). Once water is treated at the LCTF, it is pumped to the PTP where the two waste streams are mixed (Paulson, 2008). The mixed water is tested and then released to the Santa Ana Regional Interceptor (SARI) where it is sent to the secondary wastewater treatment facility in Orange County, CA, for treatment before discharge (Paulson, 2008). The third treatment system is the Community Wellhead Treatment

System (CWTS), which is a standalone system. This system is used to remove low levels of TCE and perchlorate. The TCE is removed through the use of carbon filters and the perchlorate is treated through the use of a resin-bed IX unit. Figure 2-3 shows the location of the treatment sites to provide a perspective on the site location (U.S. EPA, 2009).

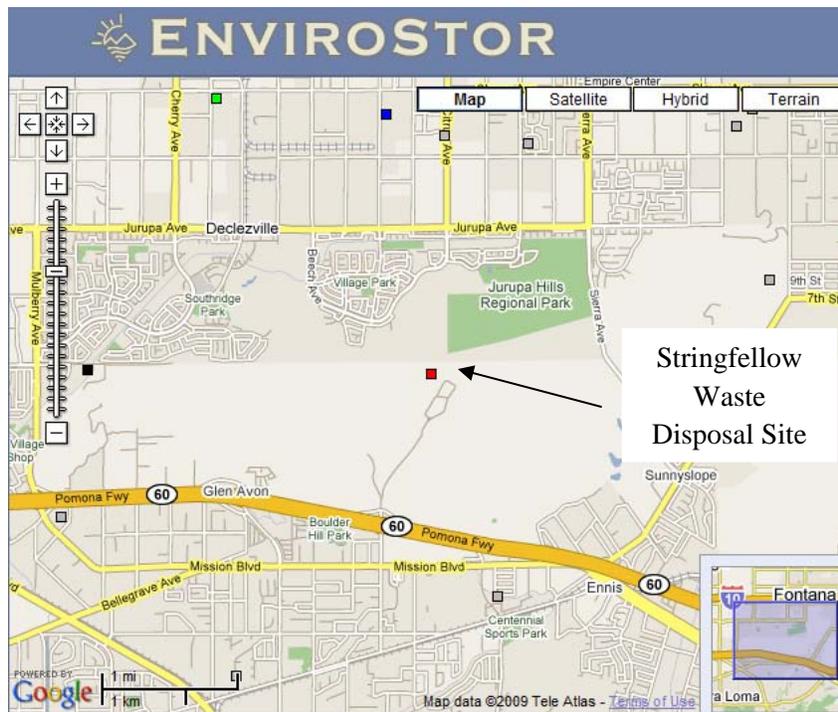


Figure 2-3: Stringfellow Hazardous Waste Site (U.S. EPA, 2009)

The CWTS operates at a flow of 25 gallons per minute (gpm). The cost for GAC replacement is \$1.75/lb. The vessel holds 1000 lbs and is changed out once per year. The cost for resin replacement is \$0.0067 per acre-foot (Paulson, 2008). Each vessel holds 10 ft³ and there are four vessel change-outs per year. The capital cost for the

installation of two extraction wells and the treatment system was \$250,000 (Paulson, 2009). Influent and effluent concentrations for TCE, perchlorate, several anions, and TDS are shown in Table 2-8.

Table 2-8: Stringfellow Influent and Effluent Compound Concentrations

Compound	Influent Concentration	Effluent Concentration
TCE	1.1 µg/L	ND
Perchlorate	29.3 µg/L	ND
Sulfate	150 mg/L	150 mg/L
Nitrate	84 mg/L	84 mg/L
TDS	950 mg/L	950 mg/L

The costs listed in Table 2-9 are actual O&M costs. The way in which the contract was bid results in a higher than normal cost per acre-ft when the actual fixed O&M portion of the contract is taken into account (Paulson, 2009). It is estimated that the actual O&M costs are closer to \$25,000 per year (Paulson, 2009). This estimate will be used for the calculation of the cost per acre-ft at Stringfellow.

Table 2-9: Stringfellow Actual O&M Costs

Line Item	Cost (\$/yr)
GAC	1,750.00
Selective ion exchange resin	14,571.00
Additive cost for GAC treatment based on volume	2,252.00
Additive cost for ion exchange treatment based on volume	2,252.00
Fixed O & M costs	334,815.00

2.8.3. JPL

The National Aeronautics and Space Administration (NASA) Jet Propulsion Laboratory (JPL) is located near Pasadena, CA. The site carries out research and

development (R&D) on “robotic exploration of the universe” and conducts research for other federal agencies in areas such as remote sensing and astrophysics (NASA, 2008). The site is located in the Raymond Basin watershed which is estimated to serve approximately 44,000 people within 3 miles of JPL. In the 1940s and 1950s, liquid and solid wastes were leached into the ground and the deep groundwater aquifer from brick-lined seepage pits. Many chemicals leaked into the ground. The primary chemicals include: carbon tetrachloride, TCE, and perchlorate. The laboratory is still operational and current treatment and disposal of contaminants follows both California and federal regulations. The plume of VOCs and perchlorate has moved to some wells owned by the Lincoln Avenue Water Company (LAWC) and some owned by Pasadena Water and Power.

The site has been broken into three operable units (OUs): OU-1 for on-facility groundwater, OU-2 for on-facility soil, and OU-3 for off-facility groundwater. Several technologies were considered. Program managers developed cost curves for IX and fluidized bed reactor (FBR) treatment of perchlorate in the drinking water. Fluidized bed reactor treatment is a method that results in the perchlorate being destroyed rather than concentrated (Morss, 2003). The method relies on microorganisms attached to a “hydraulically fluidized bed of sand or GAC media” to reduce perchlorate, oxygen, and nitrate (Morss, 2003). The process has been accepted by the California Department of Health Services for drinking water treatment (Morss, 2003). These cost curves plot the cost of treatment for IX and FBR vs. perchlorate concentration. The IX and FBR cost curves crossed at 100 µg/L (Slaten, 2008). The program managers determined that IX is

more cost effective at lower concentrations (e.g., below 100 µg/L) and FBR is more cost effective at higher concentrations (e.g., above 100 µg/L) (Slaten, 2008).

There are several treatment plants in operation at the site (NASA, 2008). The first, which started running in July 2004, is a 2,000 gpm facility that treats water that comes from two of the LAWC wells. The treatment system includes both an IX system for perchlorate removal and a GAC system to remove VOCs. Another plant became operational in early 2005 and it is located at the site of the plume and removes contaminants from the groundwater below JPL. This system can treat 300 gpm and consists of a GAC system to remove VOCs and a biological fluidized bed reactor (FBR) to remove high levels of perchlorate. Six pilot-scale tests were conducted on the site prior to the construction of the GAC/FBR system. Advantage and disadvantages were identified for each of the six methods tested and, as was explained above, a cost comparison accomplished for different perchlorate concentrations before the GAC/FBR system was chosen (NASA, 2008).

The influent perchlorate concentration on-site (at the plume) is approximately 200 µg/L and the influent perchlorate concentration off-site (at the wells) is 20-40 µg/L (Slaten, 2009). The effluent from both plants is non-detect (the method detection limit is 4 µg/L) (Slaten, 2009). A third plant is planned for Pasadena, CA, that can treat 7,000 gpm and it is scheduled to begin in March of 2009 and will take over one year to finish (Slaten, 2009). This system will have an IX system for perchlorate removal and a GAC system to remove VOCs. The IX option was chosen because this unit is located at mid-plume where the perchlorate concentration has decreased by an order of magnitude from

the source area (Slaten, 2008). Additionally, the use of IX over FBR in drinking water treatment is typically more acceptable as biological treatment of drinking water is generally undesirable (Slaten, 2008). Table 2-10 shows the capital costs for the GAC/FBR treatment plant. The annual O&M cost is \$900K and includes the cost of injecting the water back into the aquifer which is a significant portion of the costs (Slaten, 2008).

Table 2-10: JPL GAC/FBR Treatment Plant Capital Costs

<u>Capital Cost Line Item</u>	<u>Cost (\$K)</u>
Design and Planning	350
Well Installation	1,500
Pipeline/Electrical Installation	500
Concrete Pad Installation	700
Construction Oversight	200
Treatment Equipment	1,500
Capital Cost	4,750

2.8.4. Massachusetts Military Reservation

Massachusetts Military Reservation is located on Cape Cod. It covers an area of approximately 21,000 acres. There are currently 11 groundwater plumes containing perchlorate and/or RDX in the northern section of MMR. (Nixon, 2008). The southern portion of the site does not have any co-mingled plumes (Forbes, 2008). HMX and TNT

are also present in some locations; however, they are present in much lower concentrations than RDX. Figures 2-4 and 2-5 show influent water concentration levels from June 2007-October 2008 for Frank Perkins Road Treatment Facility and Pew Road Treatment Facility.

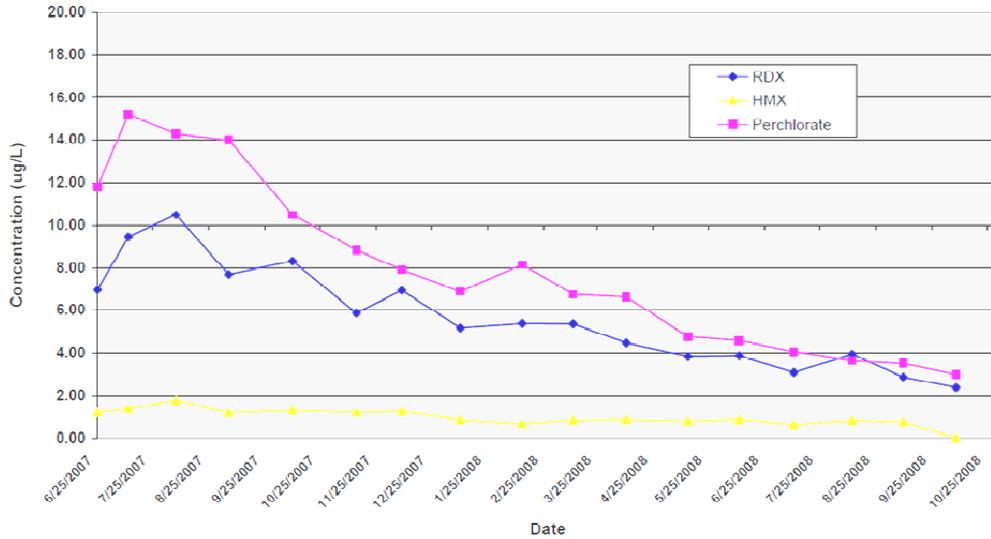


Figure 2-4: MMR Influent Concentrations for Frank Perkins Treatment Facility

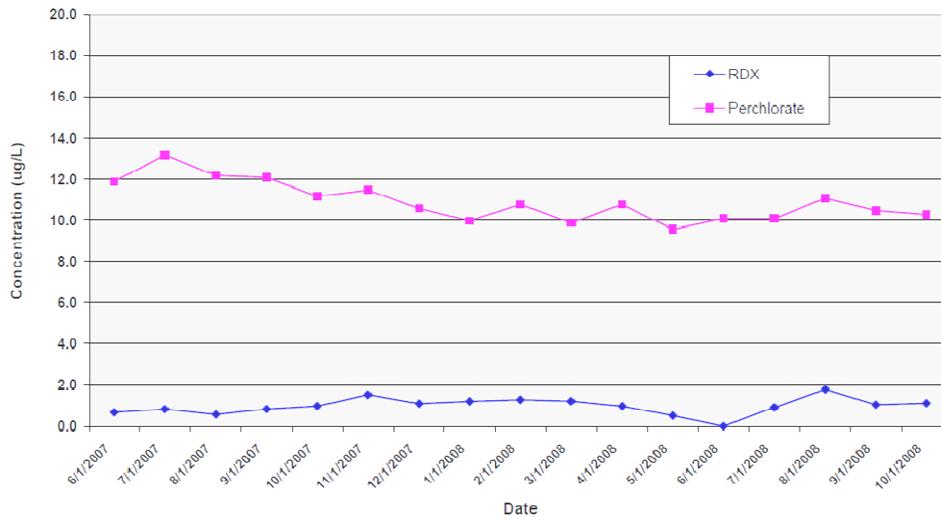


Figure 2-5: MMR Influent Concentrations for Pew Road Treatment Facility

At both of these plants, IX is used to treat the perchlorate first, followed by the use of one GAC bed to remove the RDX followed by a GAC guard bed. RDX and HMX are treated to the reporting limit of 0.25 µg/L and perchlorate is treated to the minimum detection limit of 0.35 µg/L (Nixon, 2008). A 2004 study by AMEC evaluated the use of a couple of different IX resins (styrenic resin and nitrate selective resin), and monomer tailored carbon for the removal of perchlorate and RDX from the drinking water. The study concluded that all three would effectively treat the water (AMEC, 2004). However, due to the decreasing cost of the IX resins discussed earlier, the IX/GAC/GAC configuration was chosen and is now in operation at both the Frank Perkins Road System site and the Pew Road System site (Nixon, 2008). The resin currently in use is SIR-110-HP, which is a strong base anion exchange resin (Resintech, Inc., 2008). The cost for resin at MMR is \$0.0057 per acre-foot and the cost for virgin GAC was \$1.61 per lb. The site now uses reactivated GAC which costs \$1.00 per lb. The reactivated GAC cost for the Frank Perkins Road System may be lower than this as more GAC is used at this site (Nixon, 2008). However, the GAC has not yet been changed out at this site so actual costs are not yet known (Nixon, 2008).

Capital costs for the Frank Perkins Road site were \$4 million and capital costs for the Pew Road site were \$750,000 (Nixon, 2008). The O&M cost of running both plants is \$350,000; \$180,000 of this cost is for electricity of which \$164,000 is used at the Frank Perkins Road site and \$16,000 is used at the Pew Road Site (Nixon, 2008). Based on the ratio of flow rates (100 gpm at the Pew Road Plant and 808 gpm at the Frank Perkins Road Plant), the remaining \$170,000 can be split between the two plants. This results in

an additional cost of \$19,000 for the Pew Road Plant and \$151,000 for the Frank Perkins Road Plant (Nixon, 2008). It should be noted that this is an estimate only because the O&M cost for these plants is under one contract (Nixon, 2008). The O&M costs include the cost of reinjecting the water into the ground (Nixon, 2008). The site managers predict that this cleanup will be completed in ten years (Nixon, 2008). The electricity cost at this site is higher than in other parts of the country at \$0.18 per Kw-hr (Nixon, 2008).

2.9. Overview of Innovative Technology (T-GAC)

Tailored Granular Activated Carbon (T-GAC) is an innovative technology that is being evaluated for treatment of perchlorate- and organic compound-contaminated drinking water. Research in this area is funded under the Environmental Security Technology Certification Program (ESTCP). ESTCP is “a Department of Defense (DoD) program that promotes innovative, cost-effective environmental technologies through demonstration and validation at DoD sites” (ESTCP, 2008). This research is a joint effort between the Air Force Institute of Technology (AFIT), Pennsylvania State University (PSU), ARCADIS, SIEMENS, and the Fontana Water Company.

T-GAC involves pre-loading GAC with cationic surfactants (Parette and Cannon, 2005). Many of these cationic surfactants can be found in personal care products including mouthwash (Parette and Cannon, 2005). Through the use of RSSCTs, it was determined that T-GAC removed perchlorate more effectively than traditional GAC (Parette and Cannon, 2005). The cationic surfactant used throughout this research had a quaternary ammonium functional group (Parette and Cannon, 2005). This group has one

nitrogen atom surrounded by and bound to four carbon atoms as shown in Figure 2-6 (Parette and Cannon, 2005).

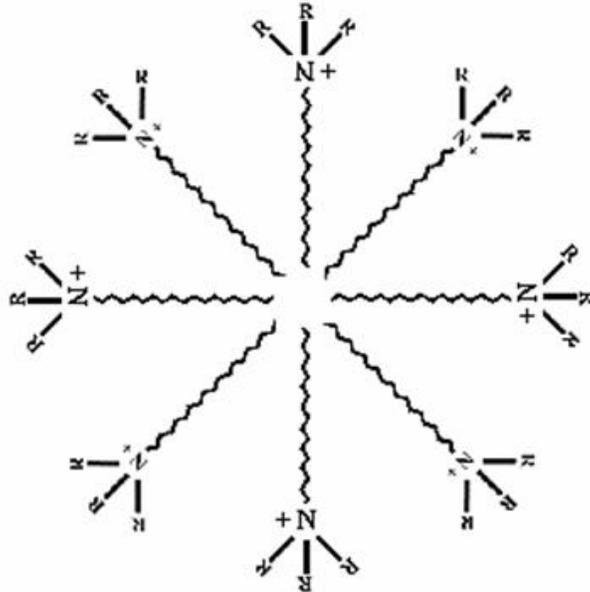


Figure 2-6: T-GAC Structure

Initial T-GAC tests involved the use of several different cationic surfactants including decyltrimethylammonium bromide (DTAB), tributylheptylammonium bromide (THAB), cetyltrimethylammonium chloride (CTAC), and myristyltrimethylammonium bromide (MTAB), and cetylpyridinium chloride (CPC). Research on the technology currently uses CPC. One concern raised through initial testing of T-GAC was the potential that the cationic surfactant would leach off of the GAC during treatment. Following this leaching, it would then enter the treated water stream. As a result of this concern, a GAC guard bed is typically added to the treatment system to remove the

leached surfactant. The use of this guard bed has been shown to effectively remove any leached surfactant to below 0.1 mg/L (Parette and Cannon, 2005).

The effectiveness of removing two nitroaromatic compounds, RDX and HMX, in the presence of perchlorate was studied through the use of additional RSSCT tests (Parette et al., 2005). The authors determined that the tailoring process did reduce the effectiveness for GAC adsorption of organic materials. The authors concluded that all three contaminants could be successfully removed if a 1:1 ratio of T-GAC bed to GAC bed was utilized. At this ratio, perchlorate and RDX both breakthrough after approximately the same number of bed volumes (BVs) have been treated (Parette et al., 2005). A BV is a dimensionless quantity, defined as volume of water treated divided by volume of the GAC treatment bed. Bed volumes to breakthrough is defined as volume of water treated before the effluent concentration reaches a specified concentration divided by volume of the GAC treatment bed. This study involved the use of a virgin bed that had been exhausted with perchlorate which was then tailored with surfactants. This bed was followed by a virgin guard bed. The influent contaminant concentrations were: 0.6 µg/L for HMX, 6 µg/L for RDX, and 1 µg/L for perchlorate. The use of this setup allowed 256,000 BVs of RDX to be treated before breaking through with an effluent concentration of 0.6 µg/L. The HMX effluent concentration remained non-detect throughout the duration of the test, which ran for 320,000 BVs. Perchlorate was first detected in the effluent after 195,000 BVs were treated, with full breakthrough (considered 1 µg/L) at 322,000 BV (Parette et al., 2005).

Parette et al. (2005) also showed that virgin GAC (Ultracarb) could remove RDX with an average influent concentration of 6.0 µg/L for 308,000 BVs before RDX was detected at 0.36 µg/L in the effluent stream. HMX with an influent concentration of 0.6 µg/L was non-detect in the effluent stream throughout the experiment, which was run for 404,000 BVs. Once the same GAC was tailored with surfactants, the adsorptive capacity was reduced. RDX was detected at 7,800 BVs at a concentration of 0.4 µg/L and at 90,000 BVs, the concentration was 6 µg/L. HMX was detected at 116,000 BVs at a concentration of 0.3 µg/L and remained at this level until the experiment was stopped at 140,000 BVs.

Additionally, in this study, it was determined that an effluent concentration of 1 µg/L for RDX was detected after treating 375,000 BVs on virgin GAC and 16,667 BVs for CTAC tailored GAC. This study also showed that HMX treated with virgin GAC did not break through for an entire run. HMX treated with CTAC tailored GAC broke through at a concentration of 1 µg/L after 116,000 BVs were treated.

The effect on TCE adsorption of tailoring GAC with cetyltrimethylammonium chloride (CTAC) was also studied (ESTCP, 2009). It was determined that there was only a minimal difference between TCE adsorption onto GAC and TCE adsorption onto T-GAC (ESTCP, 2009). It was also found that the presence of TCE as a co-contaminant at high concentrations had no noticeable effect on perchlorate adsorption to T-GAC (ESTCP, 2009).

2.10. T-GAC Studies

Initial studies of this new technology included determining the time to breakthrough of virgin GAC compared with the time to breakthrough of ammonia-tailored GAC and numerous cationic surfactant-tailored activated carbons (T-GACs) (Chen et al., 2005). For virgin GAC, breakthrough is observed after only 1100 bed volumes (BVs) and for ammonia-tailored GAC, the number of bed volumes to breakthrough was increased to 4400 (Chen et al., 2005). Parette et al. (2005) conducted research on alternative methods for modifying GAC to treat perchlorate-contaminated water. They found that by pre-tailoring GAC with cetyltrimethylammonium chloride (CTAC), perchlorate breakthrough was not observed until 34,000 BVs.

2.11. Data Sources

Multiple data sources were available to evaluate the effectiveness in treating perchlorate-contaminated water with T-GAC. These data sources will be detailed in the following sections. They include: PSU RSSCTs, Fontana, CA Pilot Study, and six medium-scale columns at Fontana, CA.

2.11.1. PSU RSSCTs

Pennsylvania State University has been running RSSCTs to study T-GAC. RSSCTs are based on “fixed-bed mass transfer models” (Crittenden et al., 1991). These models are used to predict full-size GAC absorber performance by observing the performance of small lab-scale RSSCTs. In order to ensure that the small column is representative of the full-size absorber, particle size, hydraulic loading, and empty bed contact time (EBCT) of the small column are specially chosen. The EBCT is the amount

of time it takes water to travel through the column when it is empty (Faust and Aly, 1998). It is equal to the volume of the contactor bed divided by the flow of water through the column, as shown in equation 2-1 (Clark and Lykins, 1989).

$$\text{EBCT} = \frac{V_c}{Q} \quad \text{Eq 2-1}$$

where:

$$\begin{aligned} V_c &= \text{volume of contact bed [L}^3\text{]} \\ Q &= \text{flow through the column [L}^3\text{/T]} \end{aligned}$$

The volume of carbon is equal to the mass of carbon divided by the bulk density of the carbon as is shown in equation 2-2 (Powell, 2007).

$$\text{Volume of Carbon} = \frac{m_c}{\rho_c} \quad \text{Eq 2-2}$$

where:

$$\begin{aligned} m_c &= \text{mass of carbon [M]} \\ \rho_c &= \text{carbon bulk density [M/L}^3\text{]} \end{aligned}$$

As the EBCT is increased, the number of bed volumes (BVs) to breakthrough will increase (Letterman, 1999).

Three major benefits to using RSSCTs are: it takes less time to run the small column than a larger scale column, extensive isotherm or kinetic studies are not needed, and only a small volume of water is needed to run the test. The relationship between the empty bed contact time (EBCT) for the RSSCT and for the full-scale column is shown in equation 2-3.

$$EBCT_{SC}/EBCT_{LC} = [d_{p,SC}/d_{p,LC}]^{2-x} = t_{SC}/t_{LC} \quad \text{Eq 2-3}$$

where:

$EBCT_{SC}$ = empty bed contact time of small column [T]
 $EBCT_{LC}$ = empty bed contact time of large column [T]
 $d_{p,SC}$ = adsorbent particle size for small column [L]
 $d_{p,LC}$ = adsorbent particle size for large column [L]
 t_{SC} = elapsed time in small column [T]
 t_{LC} = elapsed time in large column [T]
 X = a factor whose value is a function of the dependence of the intraparticle diffusion coefficient on particle size [-]
 (Crittenden et al., 1991).

If we define RSSCT bed life ($Bed\ life_{SC}$) as the amount of time that the RSSCT could treat water until the treatment objective was no longer met (Crittenden et al., 1991), the number of bed volumes that could be treated in the full-scale column before breakthrough (BV_{LC}) is shown by equation 2-4.

$$BV_{LC} = Bed\ life_{SC}/EBCT_{SC} \quad \text{Eq 2-4}$$

The specific throughput is the volume of water treated in the small column up to breakthrough divided by the mass of GAC in the small column. Another term typically used, the carbon usage rate, is the reciprocal of the specific throughput.

Although the benefits of using RSSCTs are numerous, their use has some limitations. One major limitation is that proportional diffusivity is assumed when using RSSCTs. This assumes that “intraparticle diffusion causes most of the spreading in the mass transfer zone and the intraparticle diffusivity is proportional to the particle size” (Crittenden et al., 1991). In this case, the X in equation 2-3 is 1. If this assumption is not valid, equation 2-4 is not valid for use in scaling results to- full scale.

2.11.2. Fontana Pilot-Scale Field Study

A pilot-scale system was run in Fontana, CA, between January 11, 2007, and December 5, 2007 (Henderson, 2008). The flow of water on the site was 37 gpm. Prior to treatment, a 10 micron cartridge filter was used in order to remove particulate matter that could result in clogging of the treatment vessels (Craig, 2008). The treatment set-up consisted of 3 vessels, two filled with 50 cubic feet of T-GAC and one filled with 50 cubic feet of GAC. The GAC used was 8 x 30 mesh GAC (AquaCarb 830AW). The T-GAC used was 20 x 50 mesh. The T-GAC beds were operated in series and the GAC bed was used as a guard bed for the removal of leached surfactant. The EBCT was 10 minutes in each bed and the water flowed downward through each. Following the treatment train, the water is sent to a holding pond. The lead bed ran until perchlorate breakthrough at 6.5 million gallons treated (17,000 bed volumes) on June 8, 2008 (Craig, 2008). At that point, the second bed was moved to the primary position and a new bed was placed in the second location. Figure 2-7 shows the treatment configuration. The average influent perchlorate concentration was 13 ug/L. Complete influent water chemistry data is available in Appendix A (Craig, 2008).

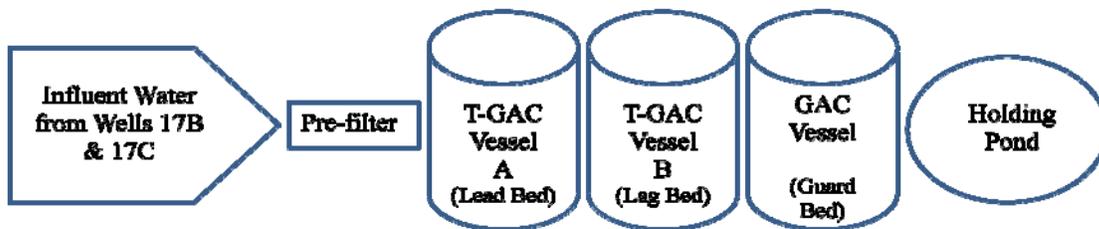


Figure 2-7: Schematic of Fontana T-GAC Treatment System

2.11.3. Fontana Performance Data

Performance data were reported by Craig (2008). Figures 2-8 through 2-10 show the effluent perchlorate concentrations at the Fontana site. Vessel A represents the bed that operated in the lead initially. Vessel B represents the bed that initially operated in the lag position and then moved to the lead position when the lead bed saw breakthrough. Vessel D is the bed that was placed in the lag position when vessel B was moved to the lead position.

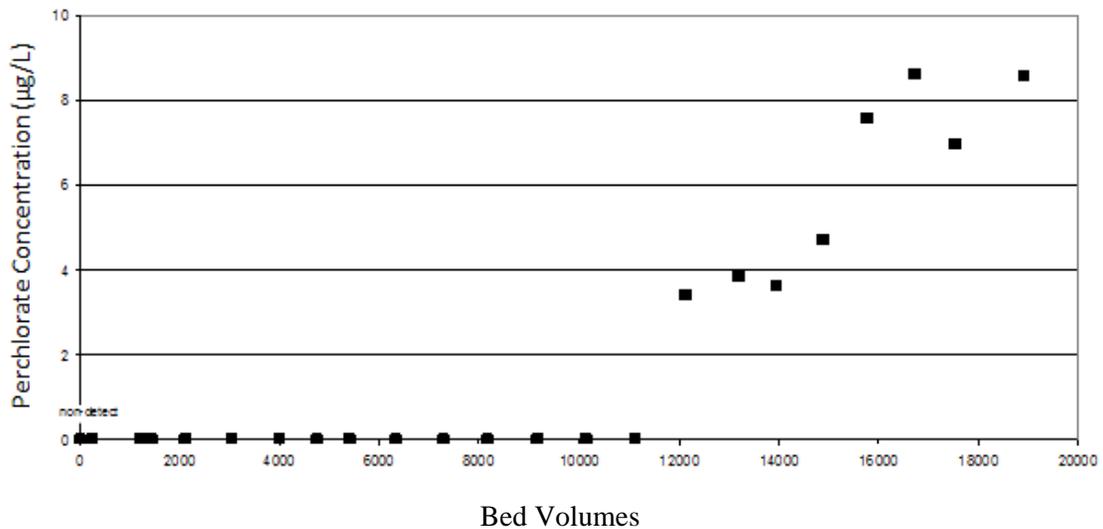


Figure 2-8: Fontana Pilot-Scale Vessel A Breakthrough Curve (Perchlorate Effluent Concentrations) (ESTCP, 2007 and Craig, 2008)

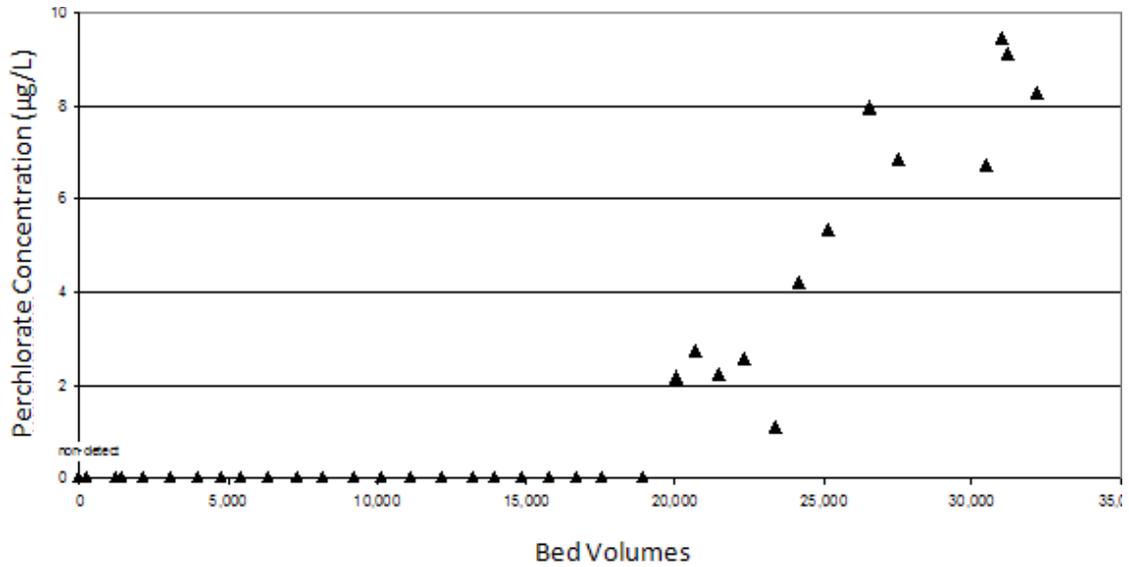


Figure 2-9: Fontana Pilot-Scale Vessel B Breakthrough Curve (Perchlorate Effluent Concentrations) (ESTCP, 2007 and Craig, 2008)

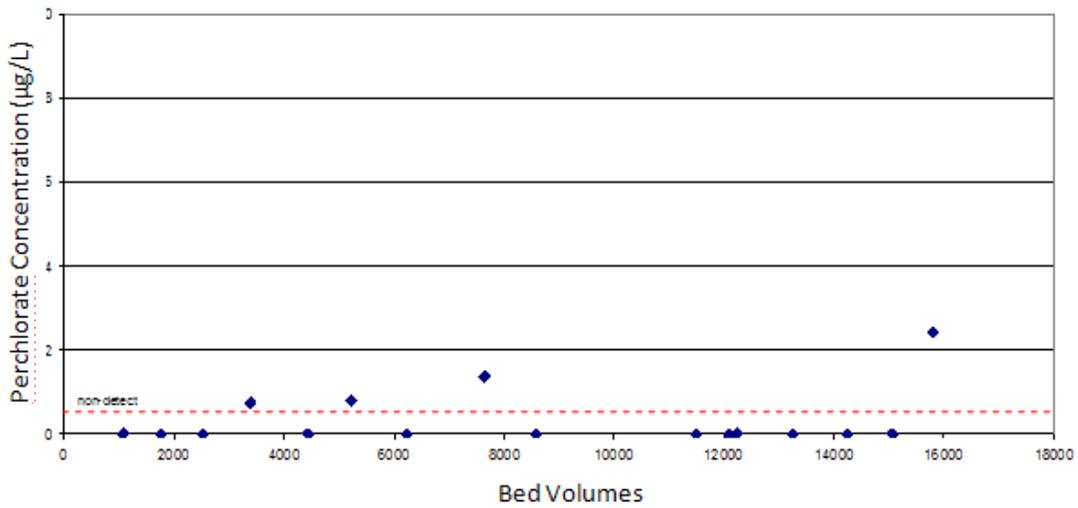


Figure 2-10: Fontana Pilot-Scale Vessel D Breakthrough Curve (Perchlorate Effluent Concentrations) (ESTCP, 2007 and Craig, 2008)

2.11.4. Fontana Cost Data

Craig (2008) reported capital costs for the Fontana site. Table 2-11 shows the costs and assumptions made in order to determine these costs. The total model predicted capital costs for the Fontana, CA pilot scale experimental system was determined to be \$98,240.

Table 2-11: Craig Model Predictions for Fontana Capital Costs

Capital Cost Factors	Fontana Expenses	Explanation of Expenses
Site Preparation	\$5,530.00	Assumes site prep for 37 gpm plant is equal to site prep for 6-column test with a total expense of \$11,050
Manufactured Equipment Tailoring GAC Media Cost (CPC) Pumps, Piping, and Valves	\$76,840	Includes all expenses needed to produce, transport, install, and start-up the system on-site. ¹
Miscellaneous and Contingency	\$12,240	Engineering and design drawings
Electrical and Instrumentation	\$3,630.00	Assumes site prep for 37 gpm plant is equal to site prep for 6-column test with a total expense of \$7,250
Labor	--	Labor costs were included in expenses
Total Capital Costs		\$98,240.00

“Note 1: Complete cost to furnish the T-GAC system is \$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 T-GAC media in vessel); \$5.99/lb CPC tailored T-GAC media (Peschman, 2008); 1,565 lb x \$5.99/lb = \$9,356) (Craig, 2008).”

At the time of his research, Craig (2008) was able to determine how accurately his model predicted capital costs. This was done through a comparison of the T-GAC model outputs with Fontana capital cost data (Table

2-10). Table 2-12 shows capital costs determined by the Craig model and Fontana expenses broken down by capital cost factors. The same assumptions from Table 2-11 apply. Craig determined that there was a 0.6% deviation in the overall capital cost between the model predicted capital cost (\$97,650) and the Fontana actual capital cost (\$98,240). At the time of Craig’s (2008) study, Fontana O&M cost data were not available to compare with model predictions.

Table 2-12: Craig Model Predicted Costs Compared to Actual Fontana Results

Capital Cost Factors	Model Predicted	Fontana Experimental Sites Actual Expenses
Site Preparation	\$2,500.00	\$5,530.00
Manufactured Equipment	\$30,140.00	\$76,840
Tailoring & GAC Media Cost (CPC)	\$15,600.00	
Pumps, Piping, and Valves	\$11,810.00	
Miscellaneous and Contingency	\$12,240.00	\$12,240
Electrical and Instrumentation	\$1,630.00	\$3,630.00
Labor	\$23,730.00	-
Total Capital Costs	\$97,650.00	\$98,240.00
Deviation = 0.6%		

2.12. Additional 6-column tests

Additional research was conducted at the Fontana site. This research included 6 medium-scale columns treating water with varying chemistries. A 10-micron cartridge

filter preceded all of the treatment trains in order to remove any particulate matter that might clog the vessels (Henderson, 2007). The first column, labeled the control column, treated “Fontana water,” i.e., the perchlorate-contaminated water that was being extracted by the Fontana Water Company wells and treated in the field-scale pilot test. The second column, labeled the TCE column, treated Fontana water spiked with TCE at a concentration of approximately 40 µg/L. The third column, labeled the perchlorate column, treated Fontana water spiked with perchlorate to a concentration of 200 µg/L. The fourth column, labeled the nitrate column, treated Fontana water spiked with 70 mg/L of nitrate (as nitrate). The fifth column, the disinfectant/oxidant column, treated Fontana water that had received between 0.15 and 0.3 mg/L free chlorine as sodium hypochlorite. Finally, the sixth column, labeled the total dissolved solids/sulfate column, treated Fontana water spiked with approximately 1,200 mg/L TDS (Henderson, 2007). A three-vessel set-up is used for the 6-column tests to simulate the large scale system. As explained above, the flow is downward through the vessels. The first two beds were stratified horizontally and were filled with 2.1 cubic feet of T-GAC on the top and 1.0 cubic feet of GAC on the bottom (Henderson, 2007). Figure 2-11 shows the six-column set-up and Figure 2-12 shows the individual train set-up.

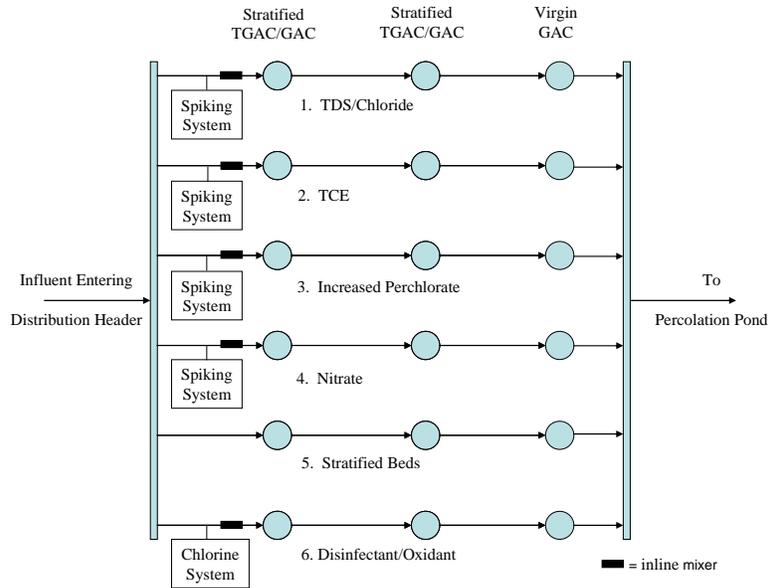


Figure 2-11: Six-Column Test Operational Set-up (ESTCP, 2007)

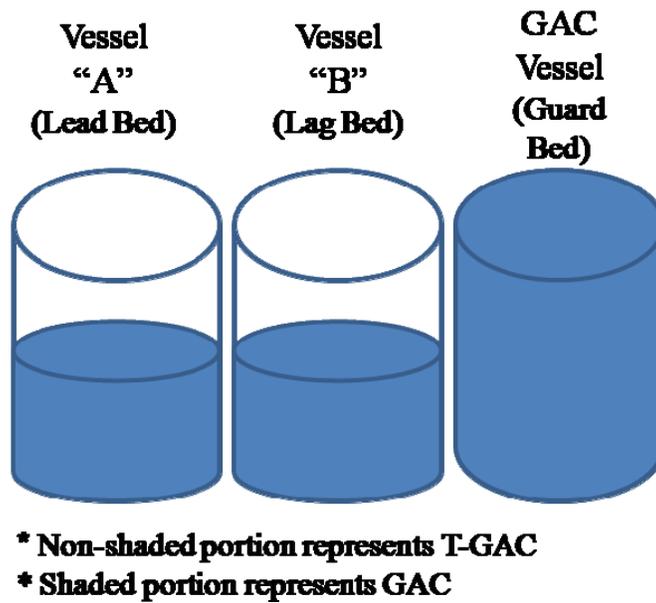


Figure 2-12: Six-Column Test Individual Train Set-Up

Issues encountered with the TCE column resulted in this column being run with only one 3.1 cubic feet stratified vessel (2.1 cubic feet of T-GAC followed by 1.0 cubic feet of GAC) and the guard bed. The columns were initially operated with a 10 min EBCT (approximately 1.5 gpm) in each bed (corresponding to the large 37 gpm system) when operation started in September of 2007 (Henderson, 2007). However, on January 2, 2008, the flow rate was increased in the control and the disinfectant/oxidant column to 3.0 gpm to achieve a 5 min EBCT in each bed. This was done at a point where complete breakthrough of perchlorate had been reached in the first bed (Lutes, 2007). This allowed for a similar flow to be maintained in both the six-column tests (through the first bed) and the 37 gpm system (which operated with a 10 min EBCT). Switching to a faster EBCT following breakthrough in the first bed allowed for an examination of the effects of the shorter EBCT on the system (Lutes, 2007). The data from column two, the TCE column, will be the main focus of this study, since both perchlorate and TCE were treated.

The six column effluent 1 and effluent 2 breakthrough curves are shown in Figures 2-13 and 2-14. Effluent 1 measurements were taken when the water exited the first stratified bed. Effluent 2 measurements were taken when the water exited the second stratified bed. C/C_0 , on the y-axis, is the normalized perchlorate concentration and is equal to the concentration of the effluent sample divided by the concentration of the influent sample. These samples were taken on the same date. TCE column results are not included as they are presented individually in the following sections.

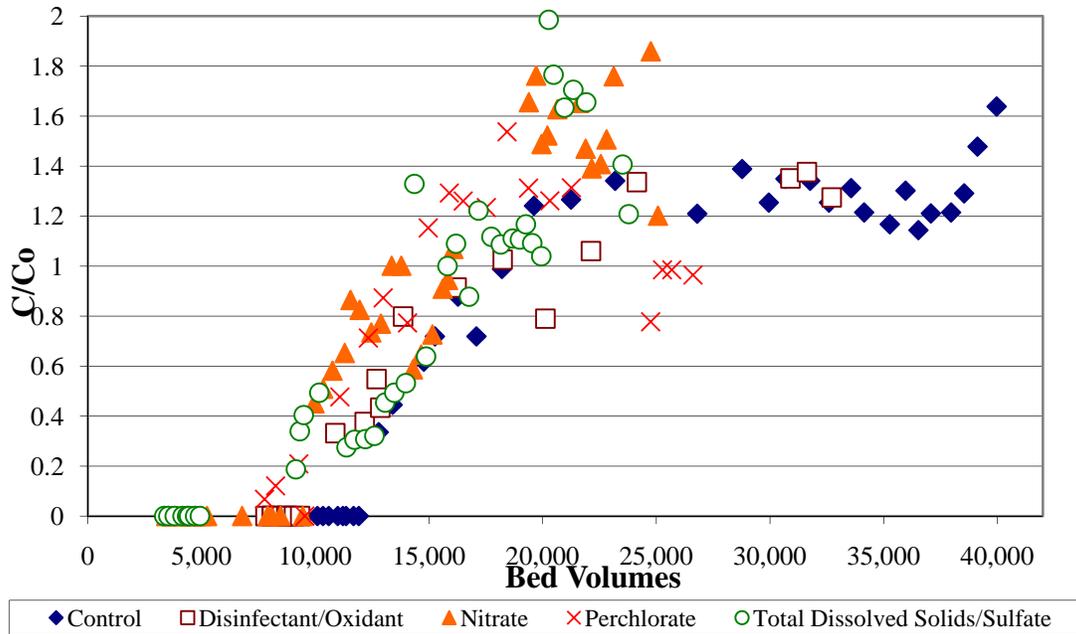


Figure 2-13: Breakthrough Curves for Effluent 1 for Six-Column Study, Fontana, CA as Measured Through Bed A (After ESTCP (2009))

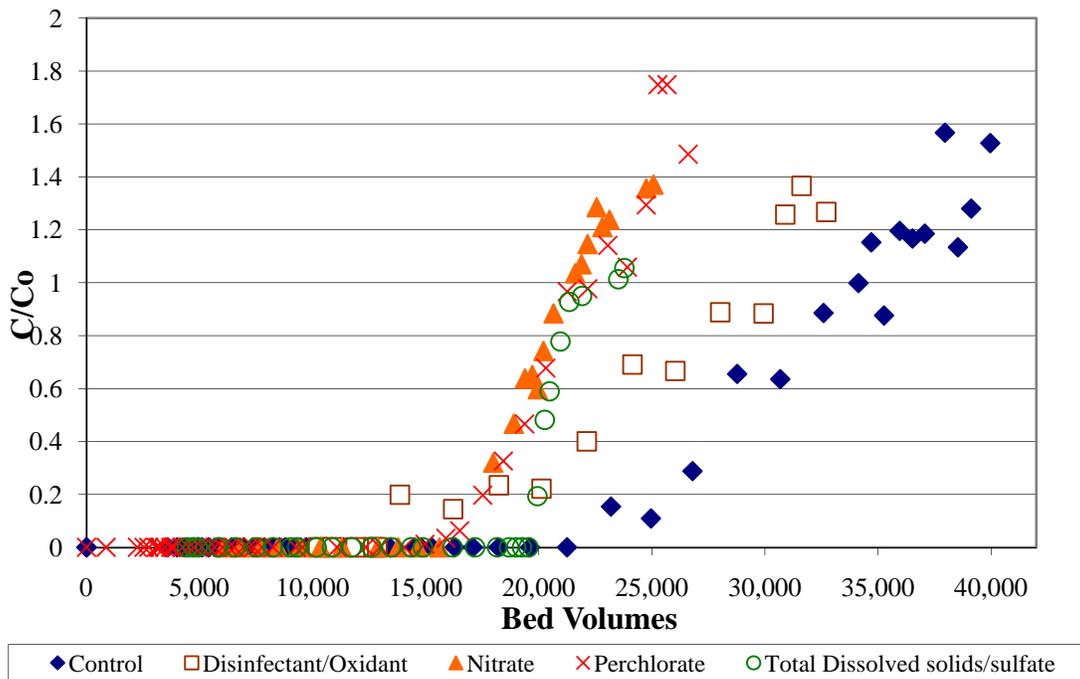


Figure 2-14: Breakthrough Curves for Effluent 2 for Six-Column Study, Fontana, CA as Measured Through Bed A and B (After ESTCP (2009))

These figures show the breakthrough curves for five of the six columns run in the six-column experiment. The breakthrough curves for the TCE column are not included. These curves will be discussed further in chapter 3.

2.13. Powell Model Development

Powell (2007) developed a T-GAC performance and costing model. The performance model was based on traditional GAC design principles and was developed to determine how data from RSSCTs could be used to design a full size T-GAC perchlorate treatment system. Powell (2007) utilized a multi-component Freundlich isotherm in order to show how perchlorate adsorbs to GAC in the presence of competing anions, such as nitrate and sulfate. The model indicated that T-GAC adsorption of perchlorate is very sensitive to the presence of competing ions. Model simulations showed that T-GAC technology would be effective when the perchlorate concentration is low and few competing ions are in solution.

Powell (2007) based his model on the Freundlich isotherm. The Freundlich isotherm is simple to apply and is conventionally used to simulate adsorption onto GAC (Powell, 2007). The Freundlich adsorption isotherm is expressed as shown in equation 2-5 (Faust and Aly, 1998).

$$\frac{x}{m} = K_f C_e^{\frac{1}{n}} \quad \text{Eq 2-5}$$

where:

x = mass of solute absorbed at equilibrium [M]

m = mass of adsorbent [M]

K_f = Freundlich adsorption capacity parameter [(M/M)(L³/M)^{1/n}]

C_e = solute equilibrium concentration [M/L³]

The Freundlich adsorption isotherm only accounts for sorption of a single compound. To account for sorption competition, Powell (2007) utilized the Freundlich-type multi-component isotherm equation which is shown in equation 2-6 (Faust and Aly, 1998).

$$\left(\frac{x}{m}\right)_i = K_i C_i \left(\sum_{j=1}^k a_{ij} C_j \right)^{n_i-1} \quad \text{Eq 2-6}$$

where:

- a_{ij} = competition coefficient [-]
- C_j = contaminant j concentration [M/L³]
- K_i, n_i = Freundlich adsorption parameters for contaminant i
- C_i = contaminant i concentration [M/L³]

In this equation, K_i and n_i are determined through the use of a single component adsorption isotherm, as explained above (Faust and Aly, 1998). The a_{ij} variables are competition coefficients which describe how the adsorption of compound i is affected by the presence of compound j (Faust and Aly, 1998). The multi-component Freundlich isotherm was chosen because it has been shown to work in the past, it is simple and easy to use, and it does not require determination of any difficult to measure parameters (Powell, 2007). Powell (2007) optimized values for K , $1/n$, and the ion competition coefficients. A mean error of 3.99% was calculated between the simulated and observed data. The standard deviation was determined to be 6.41% (Powell, 2007). Since pilot-scale data were not available, Powell (2007) did not attempt to predict pilot-scale performance using his model.

2.14. Craig Model Development

Craig (2008) also utilized a multi-component Freundlich isotherm for his study. At the time of his research he had data from the pilot-scale study at the Fontana site that he attempted to use to validate the Powell model. In order to develop his model, he developed a series of equations that predicted the benefits of operating beds in series, the performance of a lag-bed that is moved to the lead position following breakthrough, and the column bed-life. He proposed a three stage process when operating a treatment system in series. Figure 2-15 shows the first stage of the treatment process.

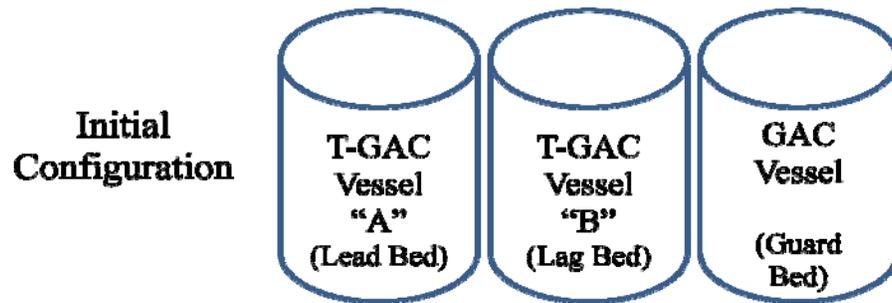


Figure 2-15: Treatment System Operating in Series

In this stage, T-GAC vessel "A" operates as the lead bed, T-GAC vessel "B" operates as the lag bed, and the GAC vessel operates as the guard bed to remove leached surfactant. The next stage occurs when perchlorate breaks through in the effluent of vessel "A." Figure 2-16 shows this configuration.

**Following
Breakthrough
of Vessel “A”**

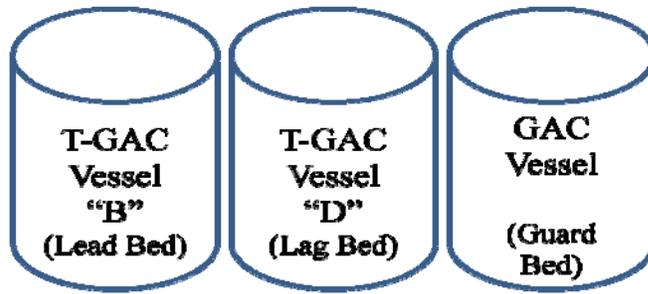


Figure 2-16: Treatment System Following Breakthrough of Vessel “A”

In this second stage, T-GAC vessel “A” has been removed, T-GAC vessel “B” has been moved from the lag to the lead position, T-GAC vessel “D” has become the new lag bed, and the GAC vessel remains. In the third stage, T-GAC vessel “B” becomes exhausted. Figure 2-17 shows this set-up.

**Following
Breakthrough
of Vessel “B”**

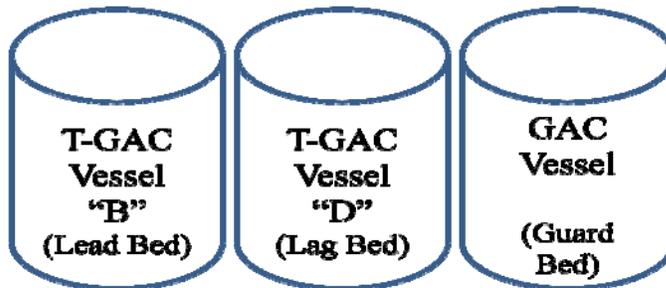


Figure 2-17: Treatment System Following Breakthrough of Vessel “B”

In this final set-up, T-GAC vessel “B” remains but is no longer removing any perchlorate. T-GAC vessel “D”, the lag bed, is now removing perchlorate. The GAC vessel remains the guard bed. Based on this three-stage set-up, which was used at Fontana, Craig (2008) developed several equations. The first, equation 2-7, predicts the estimated benefit of operating in series (Craig, 2008).

Benefits of Series Configuration

$$= \frac{BV(\text{Final}) - BV(\text{Initial})}{BV(\text{Initial})} \quad \text{Eq 2-7}$$

where:

BV(Final) = # BVs treated to full breakthrough (i.e., influent concentration equals effluent concentration)

BV(Initial) = # BVs treated to reach initial breakthrough

Craig (2008) explained that this formulation quantifies the ratio of additional bed volumes that can be treated by using the series configuration instead of the single-column configuration. In a single-column configuration, as soon as initial breakthrough occurs, the column must be replaced. In a series configuration, the lead bed can be used to remove contaminant until the contaminant completely breaks through (influent and effluent concentrations are equal). The second equation that Craig (2008) developed, equation 2-8, compared the performance of a bed that operated in the lead position from treatment start to full breakthrough with the performance of a bed that moved from the lag position to the lead position. A bed that originally operated in the lag position and was then moved to the lead position has a decreased capacity for adsorption compared to a bed that originally operated in the lead position. This is the case because the bed that was moved from the lag to lead position already had some of its adsorptive capacity used while it operated in the lag position (Craig, 2008).

$$\gamma = 1 - \frac{BV(\text{Lag} - \text{to} - \text{Lead})}{BV(\text{lead only})} \quad \text{Eq 2-8}$$

where:

γ = reduction in performance as a result of bed initially holding the lag position
BV (Lag-to-Lead) = #BVs treated to reach initial breakthrough for a lead bed that was initially in the lag position
BV (Lead Only) = # BVs treated to reach initial breakthrough for a bed that is initially in the lead position

The third equation that Craig presented, equation 2-9, was used to calculate the column bed life in days. Equation 2-9 can be used directly in the case of a single column.

$$\text{Bed Life} = \frac{\text{BV (Capacity)}}{\text{BV (Treatment Rate)}} \quad \text{Eq 2-9}$$

where:

BV (Capacity) = Number of BVs treated to reach initial breakthrough [-]
BV(Treatment Rate) = Water flow through the column [/T]

For a series configuration, equation 2-9 still applies; however, the definition of BV(capacity) varies depending on the bed being referred to (Craig, 2008). For bed A, it is the number of BVs treated to reach full breakthrough. For bed B, it is the number of BVs treated to reach full breakthrough (after having been re-configured to the lead position) and for bed D, it is the number of BVs treated to initial breakthrough (Craig, 2008).

For his cost analysis, Craig utilized a 1979 study conducted by the U.S. EPA which investigated different water treatment technology costs (U.S. EPA, 1979). In addition, he utilized personal correspondence with various personnel in the field in order

to determine additional cost parameters. A breakdown of these different costs is shown in Table 2-13.

Table 2-13: Capital and O&M Cost Categories

<u>Capital Cost Category</u>	<u>O&M Cost Category</u>
Excavation, site work, and concrete (ESC) ¹	Energy ¹
Manufactured equipment (ME) ¹	Maintenance Material (MM) ¹
Labor ¹	Labor ¹
Pumps, piping, and valves (PPV) ¹	Media ²
Electrical Instrumentation (EI) ¹	Disposal ²
Housing ¹	Transport ²
Miscellaneous and Contingency (MC) ¹	
Tailored T-GAC Media Cost ²	

1. U.S. EPA (1979)

2. Craig (2008)

Cost curves presented in the 1979 U.S. EPA series of reports were developed based on: manufacturer data, real-world plant construction data, published data, and “unit takeoffs from actual and conceptual designs” (U.S. EPA, 1979). The cost curves in the paper were divided into two categories: capital cost curves and operation and maintenance (O&M) cost curves. For each subcategory of capital cost (e.g., manufactured equipment, electrical, and instrumentation), Craig (2008) developed an empirical expression for the capital cost as a function of treatment flow rate in gallons per minute (gpm). The capital cost categories used were: excavation, site work, and concrete (ESC); manufactured equipment (ME); labor; pumps, piping, and valves (PPV); electrical and instrumentation (EI); housing, and miscellaneous and contingency (MC). Appendix B provides the graphs that were developed in order to determine the empirical

relationships between flow and cost used to develop Table 2-13. The equations provided in Table 2-14 take into account if multiple trains (T) are used, or if multiple columns (C) are operating.

Table 2-14: Capital Cost Equations

ESC capital cost (\$) = T x C x (127.03 x gpm ^{0.3175})
ME capital cost (\$) = T x C x (74.14 x gpm + 1382.5)
Labor capital cost (\$) = T x C x (928.9 x gpm ^{0.455})
PPV capital cost (\$) = T x [329.2 x (gpm x C) ^{0.565}]
EI capital cost (\$) = T x [2.073 x (gpm x C) + 635.6]
Housing capital cost (\$) = T x C x 4638 x gpm ^{0.154}
M&C capital Cost (\$) = 918.3 x (gpm x T x C) ^{0.377}

The U.S. EPA series of reports also includes several O&M categories (U.S. EPA, 1979). These are: energy, maintenance material, and labor. The equations presented in table 2-14 were developed and take into account the train and column configuration that will be used. Appendix B provides the graphs that were developed in order to determine the empirical relationships between flow and energy (kw-hr/yr), labor (hr/yr), and maintenance material (\$/yr) used to develop Table 2-15.

Table 2-15: O&M Cost Equations

$\text{Building Energy (kw-hr/yr)} = T \times 5170 \times \text{gpm}^{0.389}$
$\text{Process Energy (kw-hr/yr)} = T \times C \times (67.62 \times \text{gpm} - 287.4)$
$\text{Labor (hr/yr)} = T \times (0.469 \times \text{gpm} \times C) + 108.4$
$\text{MM} \left(\frac{\$}{\text{yr}} \right) = T \times \left(\frac{C}{3} \times 13.9 \times \text{gpm} \right) + 74.89$

Additional cost categories not covered by the U.S. EPA reports include the capital cost of tailoring the T-GAC media and the O&M costs of media replacement, disposal, and transport. The T-GAC media cost was estimated by Craig (2008) based on the costs presented in Table 2-16. These costs were estimated based on personal correspondence between Craig and Cannon (2007).

Table 2-16: Virgin GAC and T-GAC Replacement and Regeneration Costs (Craig, 2008)

	Virgin GAC	T-GAC
Replaced (new)	\$1.00/lb	\$2.50/lb
Regenerated	\$0.50/lb	\$2.00/lb

Disposal and transport costs developed by Craig (2008) will be used in the updated model. A disposal cost of \$170 per ton will be used (Craig, 2008). A transportation cost of \$2 per mile will be used. In addition to the transportation cost, a trailer fee of \$760 will be used (Craig, 2008). The trailer fee is charged only once per disposal event.

2.15. Craig (2008) Model Interface Overview

The cost and performance model is an Excel program. User inputs to the model include: design flow rate, GAC media size, empty bed contact time (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 for the treatment facility is required, miles to the regeneration facility, and if GAC regeneration will be conducted. Also required are concentrations of the following anions: perchlorate, thiosulfate, nitrate, bicarbonate, sulfate, and chlorine. In addition, the assumed amortization period and discount rate are needed. Figure 2-18 shows the user input screen for the model.

Water Quality					
ClO4-	Thiosulfate	NO3-	Bicarb	SO4-	Cl-
0.013	0	34	189	14	11

****Note: Input mg/liter (ppm)**

Figure 2-18: Craig Model Input Parameter Screen

Based on the input, the performance sub-model determines the bed volumes of water that can be treated before regeneration or replacement of the T-GAC media. This value 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 2-19). The output

includes both the total O&M cost and the capital cost (both total and annualized based on the amortization period and the assumed discount rate). An example application of the Craig (2008) model is located in Appendix C.

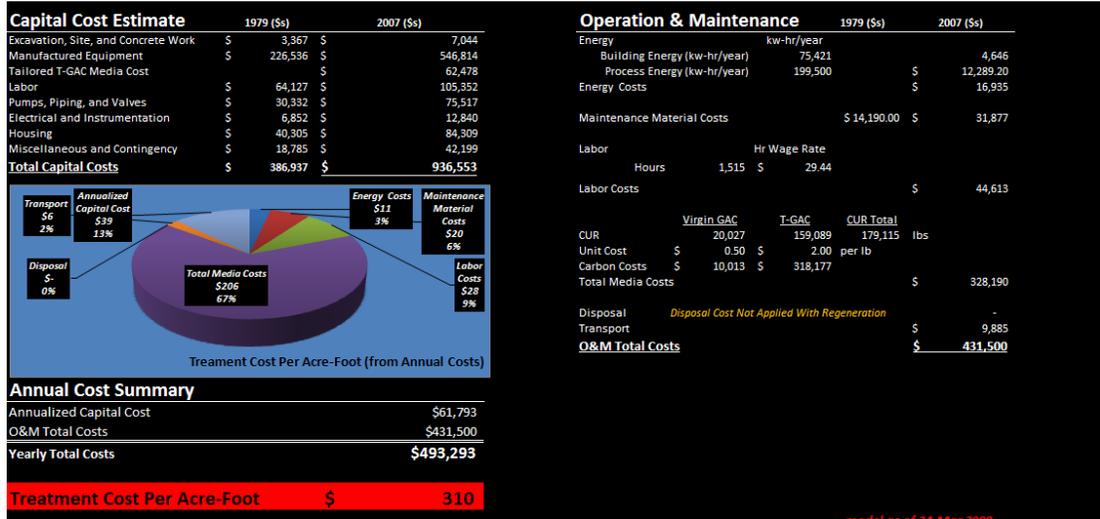


Figure 2-19: Craig (2008) Model Output Screen Showing Capital Cost, Operations & Maintenance Cost and Treatment Cost Per Acre-Foot

2.16. Predicting Sorption of Organic Compounds on GAC

Freundlich isotherms (equation 2-5) are typically used to predict adsorption in aqueous systems (Faust and Aly, 1998). For this reason, these isotherms can be used to predict sorption of organic compounds onto GAC from water. There have been a number of models developed that use chemical and carbon properties to determine the values of the Freundlich isotherm parameters, thereby facilitating the prediction of sorbed concentration as a function of aqueous concentration. The motivation to develop such models was summarized by Otake et al. (2004):

The lack of a procedure to predict the Freundlich coefficients poses a several limitation to the application of Freundlich isotherms in process design. It is, therefore, desirable to develop a predictive tool capable of estimating the values of coefficients based on appropriate properties of the adsorbate and adsorbent. When the goal is accomplished, the predictive correlation will become an efficient tool to replace time-consuming and costly laboratory tests.

Similarly, Crittenden et al. (1999) noted:

...there are relatively few experimental adsorption isotherms available for the approximately 70,000 organic compounds currently in use...In addition, cost, time, and toxicity may prevent the development of experimental adsorption equilibrium isotherms. Consequently, a correlation capable of predicting adsorption equilibrium capacities from commonly available physical properties would be very useful.

Several models that have been developed will now be discussed.

Lohmann et al. (2005) developed a model that relates the Freundlich coefficient (K_f) for polyaromatic hydrocarbon (PAH) adsorption onto black carbon to the aqueous activity coefficient at saturation (γ_w^{sat}). Equation 2-10 shows this relationship.

$$\log K_f \approx 0.83 \log \gamma_w^{\text{sat}} - 1.58 \qquad \text{Eq 2-10}$$

This useful relationship provides a simple way to relate a physical parameter of the contaminant of interest to K_f . Additional correlations for polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) were outlined by Lohmann et al. (2005). These relationships related the octanol-water partition coefficient (K_{OW}), the organic carbon-water partition coefficient (K_{OC}), the polyethylene-water partition coefficients (K_{PEW}), and the aqueous activity coefficient at saturation (γ_w^{sat}). K_{OW} is an

equilibrium parameter that provides information on the relative partitioning of an organic solute into the octanol and water phases (Domenico and Schwartz, 1998). K_{OC} is the partition coefficient that represents the relative partitioning of an organic solute into the organic carbon and water phases (Domenico and Schwartz, 1998). K_{PEW} is an additional partition coefficient that represents the relative partitioning of the PAHs studied into the polyethylene (PE) and water phases that were used in this study (Lohmann et al., 2005).

Otake et al. (2004) developed a relationship between molecular orbital properties and the Freundlich coefficient (K_f) for phenolic compounds. This study examined two adsorbents, a coal based GAC and a synthetic resin adsorbent, and eight phenolic compounds including four chlorophenols, three nitrophenols, and phenol. The authors identified relationships between the total highest occupied molecular orbital HOMO [-] of the adsorbate and the adsorbent and $1/n$ [-]. An additional relationship was noted between K_f/n [-] and the energy difference [eV] between the “adsorbent surfaces and adsorbate molecules” (Otake et al, 2004). Both the HOMO density and energy difference values were obtained by using the CAChe program. The CAChe computer program is chemical modeling software. It allows people to “search for conformation, analyze chemical reactivity and predict properties of compounds with an easy-to-use, award-winning interface on desktop computers” (Fujitsu, 2009). Disadvantages of this study were that it was limited to two types of carbon and only a limited analysis of the developed relationships is provided. An advantage to this study is that it allows for a prediction of the K_f and $1/n$ values from known molecular information.

Polanyi theory can be used in order to determine adsorption parameters (MWH, 2005). Polanyi theory assumes there is only a fixed space around the adsorbent particle where adsorption occurs and focuses primarily on van der Waals forces. The theory was introduced by Polanyi and developed by Dubinin (1966) and Manes and Wohleber (1971) (Xu et al., 2008). The theory has been shown to work for vapor and gas adsorption onto GAC and zeolite “for nonpolar and weakly polar substances” (Xu et al., 2008). Additionally, Manes and Wohleber (1971) showed that the theory applies to adsorption in aqueous solutions (Xu et al., 2008). In *Water Treatment Principles and Design*, the authors outline a method for determining a value for the sorbed concentration (q) based on several adsorbent and adsorbate properties. One benefit to the use of this method is that based only on chemical parameters the sorbed concentration (q) can be determined. This estimated sorbed concentration can then be compared with values determined experimentally through the use of adsorption isotherms.

Crittenden et al. (1999) identified many studies that have been conducted in the past that have separately applied either Polanyi theory or linear salvation energy relationships (LSERs) to estimate adsorption parameters. As noted earlier, studies that use Polanyi theory primarily account for van der Waals forces. Studies that apply LSERs account for dipole-dipole, induced-dipole, and hydrogen-bonding donor-acceptor forces (Crittenden et al, 1999). Crittenden et al. (1999) combined Polanyi theory with LSERs in order to take into account all the relevant forces. Using sorption isotherm data for 8 adsorbents and 56 organic compounds, Crittenden et al. (1999) combined Polanyi theory

and LSERs to develop correlations that allow calculation of adsorbed concentration (q) for a given aqueous concentration (C), based on sorbent and chemical parameter values.

Shih and Gschwend (2009) conducted an analysis similar to Crittenden et al. (1999), although they used LSER theory. Noting that the Crittenden et al. (1999) model required seven adjustable fitting parameters, their goal was to determine a generalized equation to predict organic sorption from water onto GAC. The chemicals studied were a diverse group of organics: benzene, toluene, *n*-hexane, *n*-heptane, 1-hexanol, 1-heptanol, diethyl ether, methy *tert*-butyl ether, diisopropyl ether, 3-hexanone, 2-heptanone, trichloroethene, 1,1,2-trichloroethane, and nitrobenzene. The activated carbon utilized was 20-40 mesh Darco. Only one adsorbent, 20-40 mesh Darco, was used in order to “capture the effects of diverse intermolecular interaction” (Shih and Gschwend, 2009). The data obtained were fit to the Freundlich isotherm with favorable results. Ultimately, equations 2-11 and 2-12 were developed which allow determination of Freundlich parameters from adsorbate properties:

$$\log K_f [(mg/kg)/(mg/L)^{1/n}] = (3.76V - 4.47B - 0.80S + 0.73) \quad \text{Eq 2-11}$$

$$+ (0.20V - 0.16B + 0.48S + 0.24)\log C_{i,w}^{sat}$$

$$1/n = -0.20V + 0.16B - 0.48S + 0.76 \quad \text{Eq 2-12}$$

where: V = McGowan’s characteristic volume for the adsorbate [$cm^3 mol^{-1}/100$]
 S = the compound’s polarity/polarizability [-]
 B = the compound’s electron-donation basicity [-]
 $C_{i,w}^{sat}$ = the aqueous solubility (mg/L)
 K_f = adsorption capacity parameter (mg/g)(L/mg)^{1/n}

The values of V, S, and B can be found in the works of M. H. Abraham, a professor at the University College London. Abraham worked in conjunction with Sirius Analytical Ltd. in order to develop “a software package that includes the prediction of solute descriptors, and thence the prediction of physiochemical and biological properties, as well as including an extensive data base of solute properties” (University College London, 2009). In addition to this database, these values have been published for many compounds in several journal articles. One disadvantage to this method is that the experiment was run on 20-40 mesh Darco. One advantage is that the Freundlich parameters can be predicted from several adsorbate and adsorbent parameters.

3.0. Methodology

3.1. Introduction

In this section, the steps that will be taken in order to meet the primary and secondary objectives of this study will be outlined. These steps include: validating the current cost and performance model, incorporating new performance data into the model by analyzing the Fontana study six-column results, comparing costs obtained by using the modified model to simulate tailored granular activated carbon (T-GAC) treatment of water with perchlorate and organic co-contaminants with costs from case studies, and developing a user-friendly interface for the model. Details of these steps are provided in the following sections.

3.2. Validate Current Cost and Performance Model

The full set of Fontana, CA cost and performance data will be used in order to fully validate the Craig model (Craig, 2008). As discussed in Chapter 2, the cost model was developed based on a 1979 study by the Environmental Protection Agency (EPA) which was based upon data from water treatment plants ranging in capacity from 2,500 gallon per day (gpd) to 1 million gallons per day (mgd) (U.S. EPA, 1979). In order to fully validate the model, a comparison will be made between the operations and maintenance (O&M) model-predicted costs and the actual O&M treatment costs from the Fontana pilot study. Actual costs will be developed by surveying site operators and analyzing contract costs at the Fontana site. Model-predicted costs will be developed by running the Craig (2008) model for the Fontana water.

3.3. Analyze and Incorporate New Performance Data

Once the current model is validated, the additional 6-column data will be analyzed and incorporated into the model. These data will be analyzed to develop a method for predicting the costs to treat both perchlorate and organic co-contaminants. The performance data from the trichlorethylene (TCE) column will provide a baseline that will be used to develop correlations, based on organic contaminant properties, to predict T-GAC system performance for removal of other organic compounds (e.g., chlorinated solvents and nitroaromatic compounds). The TCE column from the six-column study provides operational data which quantify simultaneous perchlorate and TCE removals when T-GAC and GAC columns are run in series. The six-column analysis that will be conducted is outlined below.

The first step will be to determine how much TCE was removed in the GAC and T-GAC portions of the TCE column from the six-column study. The estimate will be made using GAC adsorption isotherms that have appeared in the literature to determine the sorbed concentration (q) based on the known influent concentration of TCE (C_o), which was originally intended to be approximately 50 $\mu\text{g/L}$, but actually averaged 40 $\mu\text{g/L}$. Figure 3-1 shows a graph of the TCE influent concentration over time while the system was run in configuration 2 (configurations will be discussed below).

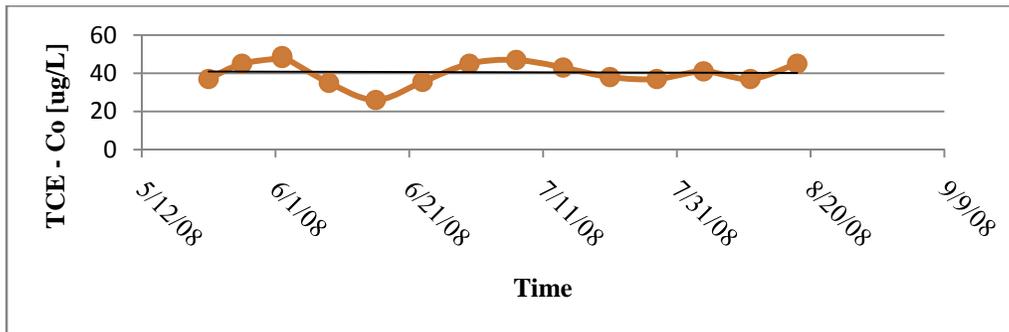


Figure 3-1: Graph of Influent TCE Concentration [µg/L] over Time for Configuration 2

Due to experimental issues encountered while running the TCE column, it is necessary to explain several assumptions that were made in order to conduct data analysis. Figure 3-2 shows the experimental setups that were used during this study. Configuration 1 was run during the first part of the study. When the system was operating under configuration 1, the effluent from vessel “A” was the influent to vessel “B.” However, when it was noted that the column was not operating correctly, as discussed below, the experiment was stopped and restarted using configuration 2.

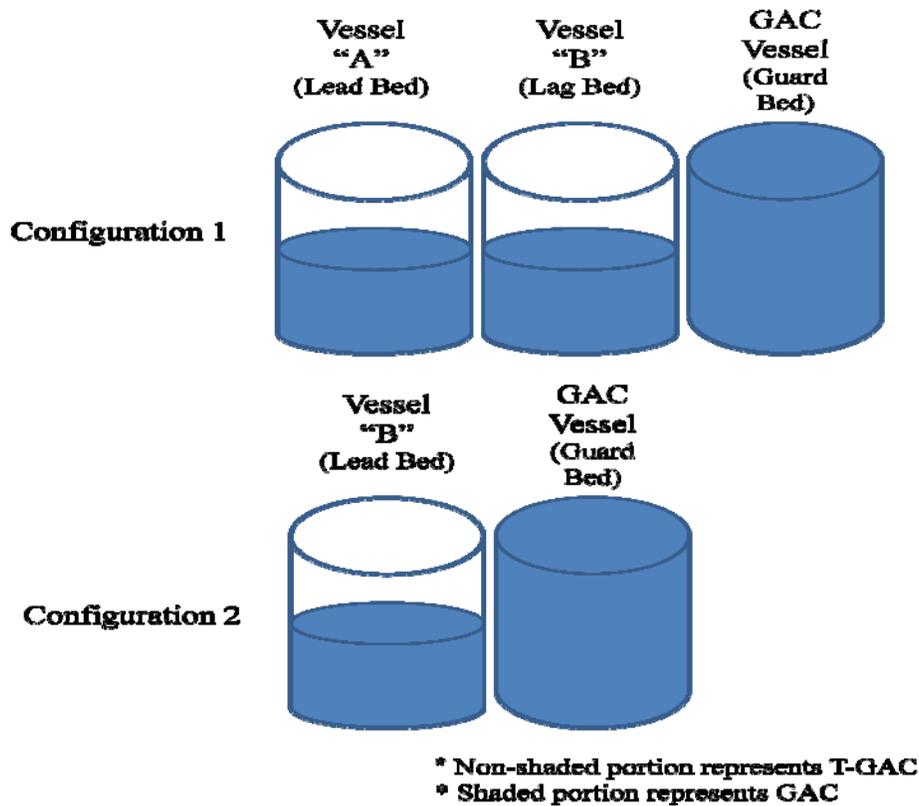


Figure 3-2: TCE Column Configurations

When the six-column experiment began, using Configuration 1, the TCE column was constructed using a syringe pump to inject the TCE with a static mixer to dissolve the TCE in water (Henderson, 2009). However, TCE concentrations were lower than anticipated, indicating one of two things was potentially happening. The first possibility was that the TCE was leaking past the seal on the syringe pump and the second was that the flow of TCE was too low (at approximately 0.2 $\mu\text{L}/\text{min}$). Either of these resulted in lower than expected TCE concentrations. To remedy the problem, a new technique for getting the TCE into the influent water stream was implemented. This method involved the use of a glass container into which the TCE was pre-mixed with water to saturation.

TCE was added each week to ensure the solution remained saturated. Once the solution was saturated, a chemical metering pump was used in order to inject the solution into the influent water stream. The switch from configuration 1 to 2 occurred at approximately the same time that the switch from the syringe system to the glass container solution was made (Henderson, 2009). The data that will be used will come from the results obtained using configuration 2. However, in order to account for the fact that vessel “B” may have adsorbed both TCE and perchlorate while operating in the lag position, one of two assumptions will be made. One assumption we can make is that vessel “B” did not adsorb any perchlorate or TCE while it was in the lag position. That is, the assumption will be made that vessel “A” was adsorbing all the contaminants while the system operated in configuration 1.

Making this assumption, mass balance can be applied while the system operated in configuration 2 to determine q_{T-GAC} and q_{T-GAC} (equation 3-1).

$$TCE_{T-GAC} + TCE_{GAC} = TCE_{Total} \quad \text{Eq 3-1}$$

where: TCE_{T-GAC} = The amount of TCE removed in the T-GAC portion of the bed
 TCE_{GAC} = The amount of TCE removed in the GAC portion of the bed
 TCE_{Total} = The total amount of TCE removed in the bed

If the assumption is made that TCE sorption onto GAC can be described by a Freundlich isotherm, and that the TCE concentration in the column effluent is negligible, Equation 3-1 can be rewritten as:

$$q_{T-GAC} \times m_{T-GAC} + K_f C_o^{\frac{1}{n}} \times m_{GAC} = Q \times C_o \times t \quad \text{Eq 3-2}$$

or

$$q_{T-GAC} \times m_{T-GAC} + q_{GAC} \times m_{GAC} = Q \times C_o \times t \quad \text{Eq 3-3}$$

where:

q_{T-GAC} = adsorbed TCE concentration on T-GAC [mg TCE/g T-GAC]

q_{GAC} = adsorbed TCE concentration on GAC [mg TCE/g GAC]

m_{T-GAC} = mass of T-GAC in the column [g]

K_f = Freundlich isotherm adsorption capacity parameter [(mg/g)(L/mg)^{1/n}]

m_{GAC} = mass of GAC in the column [g]

Q = flow [L/min]

C_o = influent TCE concentration [mg/L]

T = time the system operated in configuration 2 [min]

A second assumption that can be made is that while the column was operating in configuration 1, there was a certain amount of TCE adsorption in vessel “B” that must be accounted for. However, based on the data available for the TCE column, it is possible to see that this is not the case. Figure 3-3 shows the perchlorate and TCE effluent concentrations from vessel “A” for the TCE six-column while it was operating under configuration 1.

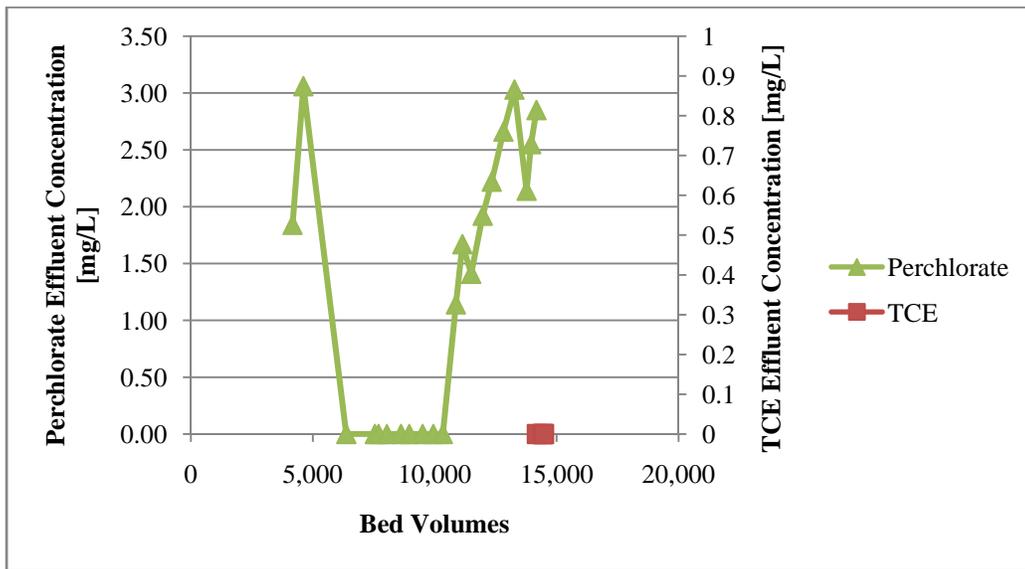


Figure 3-3: Perchlorate and TCE Effluent Concentrations while the TCE Column Operated under Configuration 1

As can be seen from Figure 3-3, there was no TCE breakthrough from vessel “A” during the time that the column was operating under configuration 1, so the assumption can be made that vessel “B” adsorbed no TCE during that time. For completeness, Figure 3-4 shows the perchlorate and TCE effluent concentration from vessel “B” for the TCE six-column while it was operating under configuration 1.

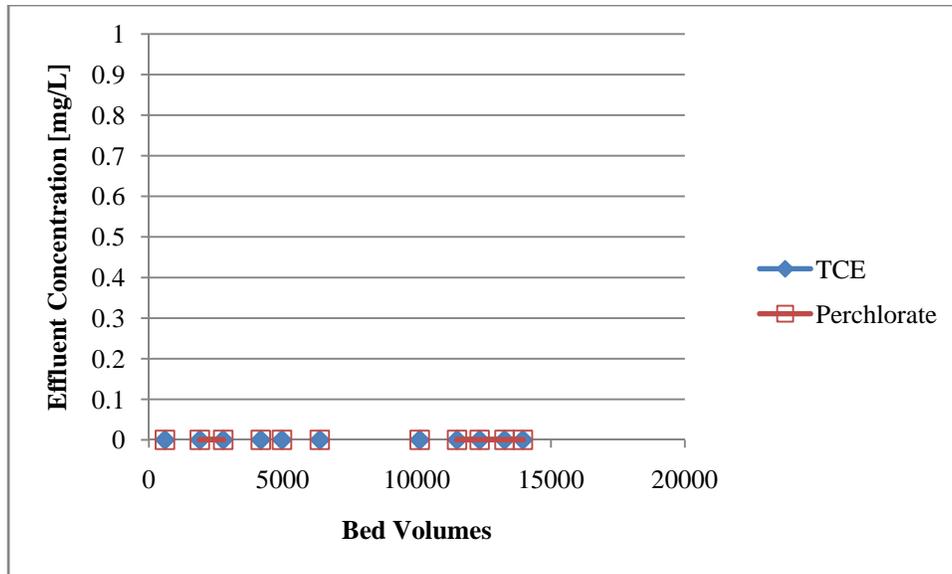


Figure 3-4: Perchlorate and TCE Effluent Concentrations while the TCE Column Operated under Configuration 2

As one can see from Figure 3-4, there was no TCE or perchlorate breakthrough from vessel “B” during the time that the column was operating under configuration 2. It should be noted, however, that perchlorate did break through from vessel “A” while operating under configuration 1. Hence, one must consider the reduction in perchlorate adsorption capacity in vessel “B” when it operated as the lead bed in configuration 2, due to its previous service (and adsorption of perchlorate) when it operated as the lag bed in configuration 1.

3.4. Compare Model-Predicted Costs of T-GAC Treatment to Case Study Data

Costs for Treatment of Perchlorate with Organic Co-contaminants

As was previously discussed, there are many sites in the U.S. where perchlorate and organic contaminants are found to co-mingle. Information on the type of

contaminants present, the concentrations of contaminants present, treatment technologies in use at the individual sites, and the cost for treatment of the water at many of these sites has been gathered through correspondence with program managers and was presented in Chapter 2. Based on the information and data gathered from these various sites, comparisons can be made between the cost of treating a unit volume of water at a specific site using T-GAC and the cost of treating a unit volume of water using competing technologies. T-GAC costs will be determined by utilizing the T-GAC cost model and case study costs will be determined from site cost data and/or the use of conventional technology costing models such as RACER™. This analysis will be both qualitative and quantitative. Qualitative comparisons will include information on the types of contaminants present and the types of treatment technologies being used at the individual sites. Quantitative comparisons will include information on the treatment level achieved for perchlorate and the individual organic compounds and the costs of operating the systems. Comparisons will take into account the site characteristics including information on flow and quality of the influent water. The goal of this section is to compare T-GAC to other systems by comparing the cost to treat a unit volume of water using the different systems.

In order to determine the cost to treat a unit volume of water, total capital cost will be converted to annualized costs. Equation 3-4 will be used in order to complete this calculation

$$A = P \times i \times \left[\frac{(1 + i)^N}{(1 + i)^N - 1} \right] \quad \text{Eq 3-4}$$

where:

A = Annual cost
P = Present cost
i = Interest rate (%)
N = Number of years over which the annual cost will occur

Equation 3-4 calculates an annual cost from a present value cost. For purposes of this research, an interest rate of 2.8% will be used (OMB, 2009). The time frame assumed will be equal to 20 years.

3.5. Update Performance and Costing Model

In chapter 2, the Shih and Gschwend (2009) model was presented. This model predicts Freundlich parameters (K_f and $1/n$) for sorption of organic contaminants onto GAC. This model will be utilized in order to predict adsorption for various organic contaminants. This model was chosen for several reasons. The first is that the equations developed for the prediction of organic sorption from water onto GAC were generalized and do not require fitting parameters. An additional reason that this model was chosen was that the study included a wide variety of organics which allows for the model to be extended to additional organics more easily. There are, however, several disadvantages to using this method. The first is that only one activated carbon, 20-40 mesh Darco, was utilized. This requires the assumption that the GAC used in this study behaves equivalently. The appropriateness of this assumption will clearly affect the ability of the performance model to simulate observations.

Ultimately, Shih and Gschwend (2009) developed equations 2-12 and 2-13 which allow determination of Freundlich parameters from adsorbate properties:

$$\log K_f [(mg/kg)/(mg/L)^{1/n}] = (3.76V - 4.47B - 0.80S + 0.73) + (0.20V - 0.16B + 0.48S + 0.24)\log C_{i,w}^{sat} \quad \text{Eq 2-11}$$

$$1/n = -0.20V + 0.16B - 0.48S + 0.76 \quad \text{Eq 2-12}$$

where: V = McGowan's characteristic volume for the adsorbate [$\text{cm}^3 \text{mol}^{-1}/100$]
 S = the compound's polarity/polarizability [-]
 B = the compound's electron-donation basicity [-]
 $C_{i,w}^{sat}$ = the aqueous solubility (mg/L)
 K_f = adsorption capacity parameter (mg/g)(L/mg) $^{1/n}$

The values of V , S , and B can be found in the works of M. H. Abraham, a professor at the University College London. Abraham worked in conjunction with Sirius Analytical Ltd. in order to develop “a software package that includes the prediction of solute descriptors, and thence the prediction of physiochemical and biological properties, as well as including an extensive data base of solute properties” (University College London, 2009). In addition to this database, these values have been published for many compounds in several journal articles. These equations (including all relevant variables) will be included in the model. These equations will allow for a prediction of BVs to breakthrough in a column when specific organic contaminants are present.

3.6. Develop a User-Friendly Interface

Finally, a user-friendly interface will be developed for the cost and performance model to facilitate technology transfer. The interface will be based on the interface built by Craig (2008). Input parameters will include: treatment flow, influent water quality

(including perchlorate, thiosulfate, nitrate, bicarbonate, sulfate, and chloride and organic contaminant concentrations), T-GAC mesh size, system configuration (series or parallel), and the number of treatment trains in operation. Output will be the treatment cost per acre-ft of water. The interface will be designed in order to assist decision-makers in determining if T-GAC is a suitable option for their treatment system.

4.0. Results and Discussion

4.1. Introduction

In this chapter, the Fontana, CA pilot study and the six-column study will be analyzed from both performance and cost viewpoints. First, actual Fontana operations and maintenance cost data will be compared with model-predicted values. Next, trichloroethylene (TCE) and perchlorate breakthrough curves from the Fontana six-column TCE tailored granular activated carbon (T-GAC)/granular activated carbon (GAC) column will be developed. These will be compared with the TCE breakthrough behavior that would be expected when using conventional GAC treatment. Comparison of the breakthrough data obtained from the six-column T-GAC study with the breakthrough behavior predicted for conventional GAC treatment will permit estimation of the inhibition of TCE adsorption onto GAC due to tailoring. Next, the assumption that the presence of TCE as a co-contaminant does not impact perchlorate adsorption will be verified by examining the six-column data and comparing perchlorate breakthrough in the control column with perchlorate breakthrough in the TCE column. Based on these analyses, a model, based on the Shih and Gschwend (2009) model, will be applied to predict T-GAC/GAC performance for removal of organic compounds. Following this, the performance model for simultaneous perchlorate and organic contaminant treatment will be incorporated into the cost model to allow for the prediction of the cost of removing co-mingled contaminants. Next an analysis of case study data will be conducted. The chapter will conclude with a comparison of the unit costs of actual treatment at the different case study sites to predicted treatment scenario costs.

4.2. Actual Fontana Operations and Maintenance (O&M) Cost Compared to Craig Model Predictions

Craig (2008) validated the capital cost portion of his performance and cost model. However, due to the availability of limited data, he was not able to validate the O&M portion of the model. Thus, this section will provide an analysis of the O&M cost model. Craig (2008) broke operations and maintenance costs down into six categories. Three of these categories were included in the 1979 US EPA cost estimating guide. These three were energy, maintenance material costs, and labor (U.S. EPA, 1979). The remaining three categories were added to account for replacement and regeneration, disposal, and transport of the T-GAC media (Craig, 2008). At the time of his research, Craig (2008) did not have O&M data available for the Fontana site. Thus, he presented only the model predictions. The model predictions as well as actual Fontana annual cost are shown in Table 4-1.

Table 4-1: Fontana Model Predictions and Actual Annual O&M Costs

Operation and Maintenance	Model Estimated Annual Costs	Fontana Experimental Site Actual Annual Costs
Energy Costs	\$500	\$500
Maintenance Material Costs	\$1,200	\$9,800
Labor Costs	\$8,500	\$8,300
Total Media Costs	\$35,000	36,025
Disposal	\$600	\$15,000
Transport	\$4,600	
Total O&M Cost	\$50,400	\$70,209
Deviation = 27.6%		

The Craig (2008) model assumed an energy cost of \$0.0616 per kW-hr and that 7,482 kW-hr/yr were needed to run the technology. This results in a cost of approximately \$500. Unfortunately, the Fontana pilot system did not have a dedicated electrical meter, thus the same energy usage estimated by Craig (7,482 kW-hr/yr) will be utilized. Actual Fontana electricity costs are estimated at \$0.0633 per kW-hr which results in no significant variation between the model predicted costs and the actual Fontana experimental site costs (Henderson, 2008).

According to Henderson (2009), maintenance material costs can be estimated as approximately 10% of the capital costs which is approximately \$9,800. At the Fontana site, maintenance material costs included replacement of the pre-filter approximately every 6-8 weeks (Henderson, 2009). Additionally, it included “minor repairs to leaking piping” (Henderson, 2009).

Craig (2008) was able to validate the labor portion of the operations and maintenance costs to within 5%. The model predicted 161 labor hours per year and the Fontana study actually involved 156 labor hours of work per year (3 hours per week by a senior technician) (Craig, 2008). Craig (2008) based his cost estimate on the assumption that each wage hour of work for a “senior technician grade-level” was \$53.00. Assuming the rate of \$53.00 per hour, the “actual” cost estimate for the Fontana site, obtained by multiplying actual labor hours by \$53 per hour, was \$8,300, while the model predicted \$8,500.

Total media costs were based on the mass of virgin GAC and T-GAC used per year (Craig, 2008). Virgin carbon is used in the guard bed and Craig (2008) assumed that the

virgin carbon was replaced annually, resulting in carbon usage of 1,502 lb/yr. Craig (2008) assumed that the media was not regenerated. He projected that the T-GAC usage was 5,593 lb/yr (Craig, 2008). Based on these estimates and the Fontana actual T-GAC media costs of \$5.99 per lb of CPC tailored GAC (estimated through personal correspondence between Craig and Peschman in 2007) and \$1.68 per pound of GAC (estimated based on known costs from MMR and Stringfellow), the actual cost was determined to be \$33,502 for the T-GAC and \$2523 for the GAC. The total actual media cost is then determined to be \$36,025. Note that the same value of \$5.99 was used in both the model predicted costs and the actual costs. This was the case because the T-GAC media pricing was directly from the company that produced the media. Other estimates (Table 2-15) were provided; however, these were not used by Craig in 2008.

Disposal and transportation costs, although broken out in the Craig (2008) model, were combined in the contract that was let to operate the Fontana pilot study. According to the initial contract, the “completion of all required disposal of residuals, as attested by furnishing proper certificates of destruction” was to cost \$15,000 for labor, services and materials (Arcadis, 2006). When this is compared to the model predicted costs of transport (\$4,600) and disposal (\$600), the predicted costs deviate from the actual costs by 65%. It is necessary to note however, that transportation and disposal costs vary depending on location. For example, if the ultimate disposal site is close to the treatment site, the cost will likely be low; however, if the ultimate disposal site is far from the treatment site, the cost will likely be high.

4.3. Fontana Six-Column Performance Evaluation of T-GAC where Perchlorate and TCE are co-mingled

Samples from the six-column tests were analyzed by the Air Force Institute of Technology (AFIT), Pennsylvania State University (PSU), WECK laboratories, STL Savannah Laboratories, and Exygen Research (ESTCP, 2007). Analyses for common anions were completed at AFIT. Analyses for perchlorate and confirmatory analyses for CPC, the tailoring agent, were conducted at PSU. Analyses for alkalinity, conductivity, total dissolved solids (TDS), TCE, N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), TDS, total organic halogens, halogenated acetic acids (HAAs), nitrosamines, and total trihalomethanes (THMs) were conducted by WECK laboratories. Analysis for the tailoring agent, CPC, was conducted by Exygen Research. Temperature and redox potential were measured on-site by ARCADIS. STL provided confirmatory analysis for perchlorate results and conducted pH measurements. Quality assurance and quality control measures were conducted as outlined in the ESTCP contract (ESTCP, 2007). The bed volumes to breakthrough (defined as the point where effluent concentration begins to rise) were determined. Influent readings were taken at the header for all of the six columns. Readings were also taken following each of the stratified beds. Table 4-2 and 4-3 show the approximate BVs to breakthrough for five of the six columns. The TCE column bed volumes to breakthrough will be discussed in detail later in Chapter 4.

Table 4-2: Six Column Approximate Bed Volumes to Perchlorate Breakthrough for Effluent 1 as Measured Through Bed A

<u>Column Name</u>	<u>Approximate BVs at Breakthrough for Perchlorate</u>
Control	11,900-12,600
Perchlorate	7,800
Nitrate	9,500-9,900
Disinfectant/oxidant	9,500-10,900
Dissolved solids/sulfate	4,700 – 9,100

Table 4-3: Six Column Approximate Bed Volumes to Perchlorate Breakthrough for Effluent 2 as Measured Through Both Bed A and Bed B

<u>Column Name</u>	<u>Approximate BVs at Breakthrough for Perchlorate</u>
Control	21,300-23,200
Perchlorate	15,000-15,900
Nitrate	15,600-18,000
Disinfectant/oxidant	12,900-13,900
Dissolved solids/sulfate	19,600-19,900

Figure 4-1 shows the breakthrough curves for perchlorate and TCE obtained from the TCE column in the six-column study while the column was operated under configuration 2. The y-axis shows the normalized perchlorate concentration which is a ratio of the effluent concentration (C) to the influent concentration (C₀). The x-axis shows bed volumes from the time the experiment began, using configuration 1. The TCE column was switched to configuration 2 at approximately 14,600 BVs which is where the data begins (since the configuration 1 data are suspect, as discussed in Section 3-3).

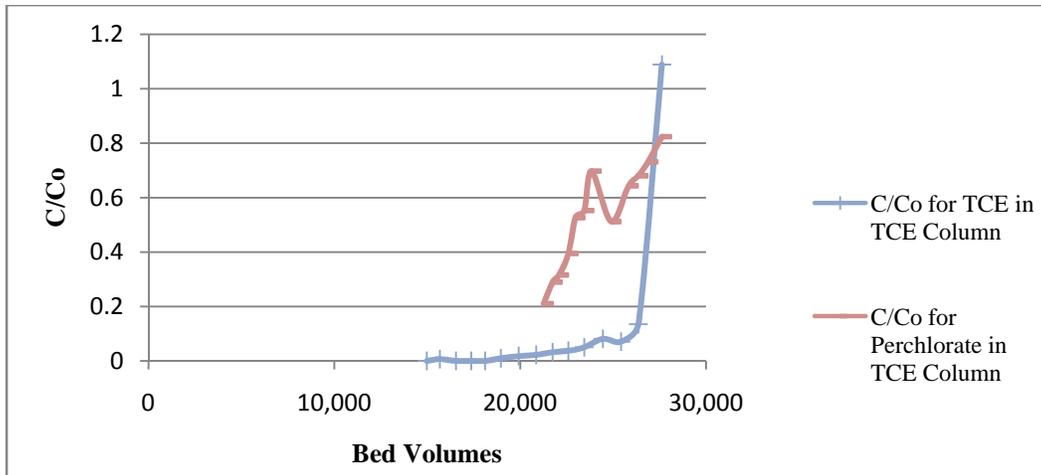


Figure 4-1: C/Co versus Bed Volumes for the TCE Column of the Six-Column Study, Fontana, CA for Configuration 2

As one can see from Figure 4-1 for the TCE column, perchlorate breakthrough occurred at approximately 20,000 total bed volumes and TCE breakthrough began somewhere between 19,000 and 20,000 total bed volumes. The actual bed volumes to breakthrough which takes into account the time the system ran in configuration 1 will be discussed later. Figure 4-2 shows the influent and effluent TCE concentrations for the TCE column during operation under configuration 2. From this figure, it is possible to once again see the TCE influent concentration fluctuations that were discussed in Chapter 3. This figure also shows that TCE breakthrough started to occur at approximately 19,000-20,000 total BVs.

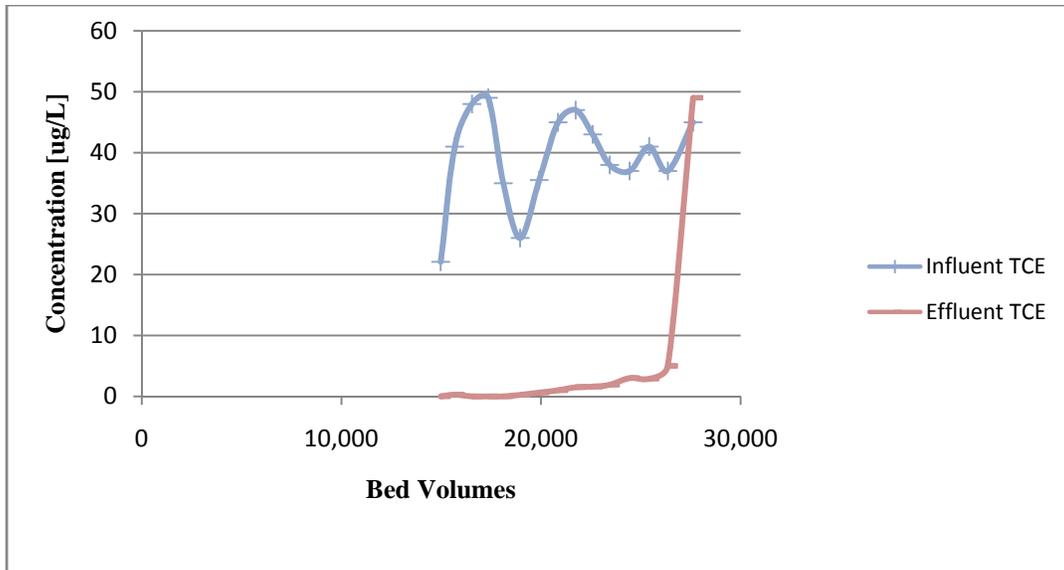


Figure 4-2: TCE Influent and Effluent Concentration [µg/L] versus Bed Volumes for the TCE Column of the Six-Column Study, Fontana, CA for Configuration 2

4.3.1. Predicted T-GAC and GAC TCE Adsorption and Evaluation of Effect of Tailoring on TCE Adsorption

The first step will be to determine how much TCE was removed in the GAC and T-GAC portions of the stratified TCE six-column. Figure 4-3, which was first presented in Chapter 3, shows the experimental setup that was used during this study. Configuration 1 was run during the first part of the study.

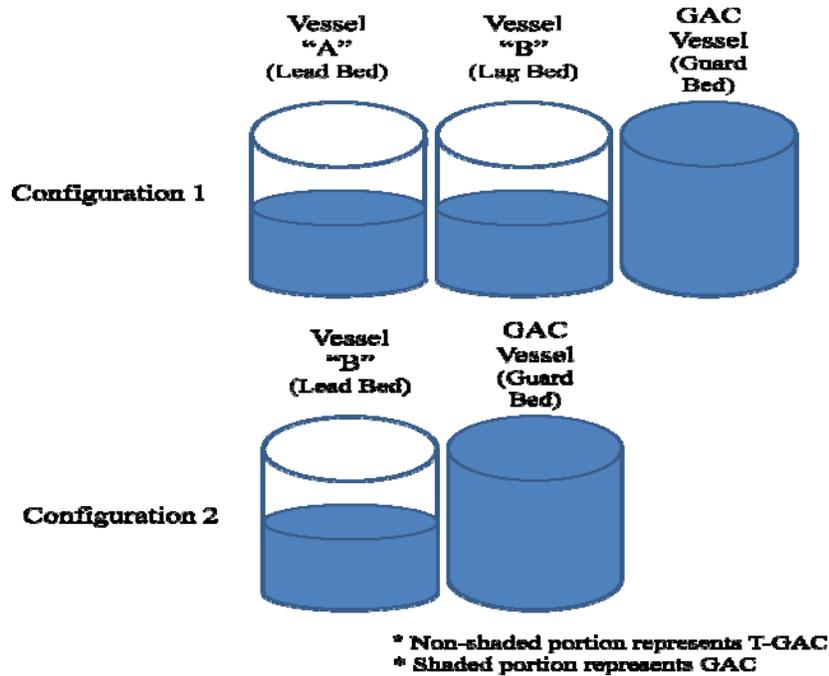


Figure 4-3: TCE Column Configuration

As was discussed in Chapter 3, the assumption will be made that vessel "B" did not adsorb any TCE while it was operating in the lag position under configuration 1. Equation 4-1 will be used in order to determine how much TCE was adsorbed onto the GAC and onto the T-GAC.

Eq 3-3

where:

- q_{T-GAC} = adsorbed TCE concentration on T-GAC [$\mu\text{g TCE/g T-GAC}$]
- q_{GAC} = adsorbed TCE concentration on GAC [$\mu\text{g TCE/g GAC}$]
- m_{T-GAC} = mass of T-GAC in the column [g]
- m_{GAC} = mass of GAC in the column [g]
- Q = flow [L/min]
- C_0 = influent TCE concentration [$\mu\text{g/L}$]
- t = time the system operated in configuration 2 (from 22 May 08 through 2 Sep 08, or approximately 15,000 BVs until breakthrough) [min]

The value for q_{GAC} was approximated using the Shih and Gschwend (2009) model, discussed in Chapter 2, which allowed for the prediction of q_{GAC} values for many compounds (including TCE). Additionally, the value determined by the method was compared to experimental values for TCE sorption onto GAC (Tables 2-4 and 2-5). From the Shih and Gschwend (2009) model (Equations 2-12 and 2-13), the value of q_{GAC} was determined to be 11,421 $\mu\text{g TCE/gram carbon}$ for an influent concentration of 40 $\mu\text{g/L}$. As shown in Tables 2-4 and 2-5, the sorbed concentration (q) for TCE on GAC for a dissolved concentration (C_o) of 40 $\mu\text{g/L}$ ranges from 4,000 $\mu\text{g TCE/g carbon}$ to 18,000 $\mu\text{g TCE/g carbon}$. Thus, the prediction of the Shih and Gschwend (2009) model appears to be reasonable. Additional parameters for use in equation 4-1 are listed in Table 4-4.

Table 4-4: Parameters for Calculation of q_{T-GAC} in Equation 4-1

Parameter	Value	Notes
m_{T-GAC}	28,536 g	$2.1 \text{ ft}^3 \times 480\text{g/L} \times 28.31 \text{ L/ft}^3$
m_{GAC}	11,890 g	$1.0 \text{ ft}^3 \times 420 \text{ g/L} \times 28.31 \text{ L/ft}^3$
Q	5.3 L/min	1.4 gpm x 3.785 L/gal where 1.4 gpm is the average flow through the column
C_o	40 $\mu\text{g/L}$	Equal to the median influent concentration to the column
t	149,760 minutes	The amount of time the TCE column was run in configuration 2: $5/22/08-9/2/08 = 104 \text{ days}$

Application of Eq 4-1, with the parameters in Table 4-4, results in a negative value for q_{T-GAC} . In other words, the predicted capacity of GAC to adsorb TCE is significantly greater than the TCE which entered the column up to breakthrough. There are two explanations for this observed early breakthrough of TCE: 1) an experimental artifact or error (e.g., short-circuiting; misinterpretation of Figure 4-1 and 4-2 data) resulted in early TCE breakthrough or 2) an unaccounted for chemical or physical process occurring in the column (e.g., presence of perchlorate or CPC) that reduced the capacity of GAC to adsorb TCE.

The first explanation, that there was some type of experimental error that resulted in earlier TCE breakthrough, is a possibility. As was discussed above and in Chapter 2, experimental problems were encountered with the TCE column. This resulted in the column being run under two different configurations. The first configuration involved the operation of two stratified columns and one guard bed. The second configuration involved the operation of only one stratified column (after the first column was removed). Based on these issues, and on data from the column, the assumption was made that no TCE sorbed to the GAC while the system was run under configuration 1. However, if this assumption was not valid, and TCE did adsorb to the column while it was run under configuration 1, it is possible that the adsorption capacity was reduced. Another possible explanation for the difference between predicted and observed TCE adsorption is short circuiting of the water through the column. This could have resulted in earlier than anticipated breakthrough. This means that although effluent measurements were correct,

the water was not in full contact with all the GAC in the column. Thus, only a small portion of the adsorptive capacity of the GAC may have been used.

An additional assumption that may be based upon an experimental error is that full TCE breakthrough occurred at 28,000 BVs. This value is based on only one data point. If this data point is in error, the GAC may have additional adsorptive capacity that was not accounted for.

The second explanation, that there is some unaccounted for process occurring in the column, is also possible. CPC surfactant could leach off of the T-GAC. This could possibly increase the solubility of TCE in the water, thereby reducing TCE adsorption to the GAC. Testing was done by Exygen in January 2007 which showed that the CPC from the third vessel (the GAC guard vessel) for the 37 gpm study was non-detect. The CPC readings from the first two T-GAC vessels was also conducted in January of 2007. The effluent CPC concentration from the first T-GAC vessel was 0.108 $\mu\text{g/L}$ and from the second T-GAC vessel, the concentration was 0.139 $\mu\text{g/L}$. Since the concentration of TCE utilized in the six column study was approximately 40 $\mu\text{g/L}$, it is unlikely that the concentrations of CPC seen in the effluent, which were lower by two orders of magnitude, had a large effect on the TCE adsorption onto the GAC. Additionally, there is no chemical reason to expect that the presence of perchlorate would affect TCE sorption onto the GAC.

Hence, based upon the six-column data and the literature, two assumptions can be made with respect to how the tailoring process affects adsorption onto GAC. The first assumption, which is based on the six-column data, would be that the tailoring process

completely inhibits organic adsorption onto the tailored GAC. Based on the observed early breakthrough of TCE in the T-GAC/GAC column, it does seem to be a safe assumption that TCE adsorption onto T-GAC is insignificant. This assumption is supported by the earlier study of Parette et al. (2005), who showed that tailoring reduced adsorption of both HMX and RDX onto GAC by over 95% (see section 2-9). Note, however, that another study reported in ESTCP (2009) showed contradictory results. The ESTCP (2009) study showed that tailoring GAC with cetyltrimethylammonium chloride (CTAC) had no effect on TCE adsorption. However, based on the findings of the Fontana six-column tests, as well as the Parette et al. (2005) study, we conservatively assume that no organics adsorb onto T-GAC.

4.3.2. Evaluation of the Effect of TCE's Presence on Perchlorate Adsorption

Another question that can be answered by evaluating the data from the TCE column is what effect does the presence of TCE have on perchlorate adsorption. In order to determine this effect, a comparison can be made between the control column and the TCE column data. As was discussed in Section 4.3, the control column had perchlorate breakthrough from the first stratified bed (vessel "A") between 11,900 and 12,600 BVs.

There are two approaches that can be taken in order to analyze the perchlorate breakthrough in the TCE column. The first approach is to consider perchlorate breakthrough in the TCE column while the system ran in configuration 1. As was shown in Figure 3-3, perchlorate breakthrough occurred at approximately 10,000 BVs in vessel A of the TCE column while the system ran in configuration 1. However, as discussed in Section 3-3, when the system was running in configuration 1, the TCE influent was

unexpectedly low due to experimental problems. Thus, the use of data from the configuration 1 results to investigate how the presence of TCE affects perchlorate breakthrough would not be meaningful.

A second approach is to compare perchlorate breakthrough for the TCE column while the column was run in configuration 2 with perchlorate breakthrough in effluent 1 of the control column. The perchlorate breakthrough curve for the TCE column while the column was run in configuration 2, with vessel B as the lead vessel, shows a breakthrough time of approximately 19,000 BVs (see Figure 4-1). Accounting for the fact that the system was run in configuration 1 for 14,600 BVs, the BVs to breakthrough in vessel B would be approximately 4,400 BVs (equal to 19,000 – 14,600). However, Fig 3-3 shows perchlorate breakthrough in configuration 1 at approximately 10,000 BVs. Full breakthrough (considered 1 mg/L) occurred at approximately 10,700 BVs. Thus, it will be assumed that vessel B was operating as the lead bed starting at 10,700 BVs. This indicates that vessel B operated as the lead bed for 8,300 BVs (equal to 19,000- 10,700). Craig (2008) found that the reduction in adsorptive capacity of a lag-to-lead bed was equal to at most 38%. Thus, the 8,300 BVs that the bed operated for could be considered at least 62% of the overall bed's performance. Hence, if the bed had not been operated in the lag position prior to being moved into the lead position, the bed might have been expected to treat at most 13,400 BVs.

When 13,400 BVs to breakthrough is compared to the 11,900 to 12,600 BVs to breakthrough for the control column (see Figure 2-13 and Table 4-2), the difference is only 6 - 12%. This difference will be considered insignificant for purposes of this

research. Thus, the conclusion will be made that the presence of TCE does not have a large effect on the adsorption of perchlorate. This conclusion can also be supported by the fact that the adsorption of perchlorate should not be affected by TCE as the chemical mechanisms of sorption for each are different. This conclusion should be readdressed in the future in order to provide the best estimate possible.

4.4. Performance Model to Predict T-GAC System Removal of Organic Compounds

As noted earlier, water contaminated with perchlorate is typically found to have other organic co-contaminants present. Thus, it is important to develop a cost and performance model that incorporates how well the T-GAC system removes these organic co-contaminants. Here, the results of the TCE column are applied and the literature relevant to adsorption of organics on activated carbon is considered to develop such a model. The TCE column data were utilized in order to determine the effect that tailoring of GAC has on organic sorption. As noted earlier, we will conservatively assume that tailoring completely inhibits organic sorption.

The Shih and Gschwend (2009) model will be utilized in order to determine when organic breakthrough would occur in a GAC column for a given influent organic concentration (C_0), flow (Q), and GAC mass (m_{GAC}). By mass balance, and based on the assumption that there is no spreading of the concentration front,

$$\begin{aligned}
Q \left[\frac{\text{L}}{\text{min}} \right] \times C_o \left[\frac{\mu\text{g}}{\text{L}} \right] \times t \text{ [min]} \\
= \text{mass TCE adsorbed in } [\mu\text{g}] \\
= q_{\text{GAC}} \left[\frac{\mu\text{g}}{\text{g}} \right] \times m_{\text{GAC}} \text{ [g]}
\end{aligned}
\tag{Eq 4-1}$$

where:

$$\begin{aligned}
t &= \text{time to breakthrough [min]} \\
q &= \text{mass organic adsorbed per mass GAC } \left[\frac{\mu\text{g}}{\text{g}} \right] \\
C_o &= \text{initial contaminant concentration } \left[\frac{\mu\text{g}}{\text{L}} \right] \\
Q &= \text{column flow } \left[\frac{\text{L}}{\text{min}} \right] \\
m_{\text{GAC}} &= \text{mass of GAC in the column [g]}
\end{aligned}$$

Solving for the time to breakthrough yields equation 4-3.

$$t \text{ [min]} = \frac{q \left[\frac{\mu\text{g}}{\text{g}} \right] \times m_{\text{GAC}} \text{ [g]}}{C_o \left[\frac{\mu\text{g}}{\text{L}} \right] \times Q \left[\frac{\text{L}}{\text{min}} \right]}
\tag{Eq 4-2}$$

In chapter 2, equation 2-11 and 2-12 were first presented.

$$\log K_f [(\mu\text{g/g})/(\text{mg/L})^{1/n}] = (3.76V - 4.47B - 0.80S + 0.73) + (0.20V - 0.16B + 0.48S + 0.24)\log C_{i,w}^{\text{sat}}
\tag{Eq 2-11}$$

$$1/n = -0.20V + 0.16B - 0.48S + 0.76
\tag{Eq 2-12}$$

where:

- V = McGowan's characteristic volume for the sorbate [$\text{cm}^3 \text{ mol}^{-1}/100$]
- S = the compound's polarity/polarizability
- B = the compound's electron-donation basicity
- $\log C_{i,w}^{\text{sat}}$ = the aqueous solubility [mg/L]
- K_f = adsorption capacity parameter [$(\mu\text{g/g})(\text{L}/\text{mg})^{1/n}$]

When these two equations are inserted into the Freundlich isotherm, q_{GAC} can be determined as is shown in equation 4-4.

$$q_{GAC} = [(3.76V - 4.47B - 0.80S + 0.73) + (0.20V - 0.16B + 0.48S + 0.24) \log C_{i,w}^{sat}] \times C_o^{\frac{1}{n}} \quad \text{Eq 4-3}$$

where:

- V = McGowan's characteristic volume for the sorbate [$\text{cm}^3 \text{mol}^{-1}/100$]
- S = the compound's polarity/polarizability
- B = the compound's electron-donation basicity
- $\log C_{i,w}^{sat}$ = the aqueous solubility (mg/L)
- K_f = adsorption capacity parameter ($\mu\text{g/g})(\text{L/mg})^{1/n}$)
- C_o = compounds initial concentration [mg/L]

Once q_{GAC} is determined, the time to breakthrough can be determined through the use of equation 4-3. The number of bed volumes to breakthrough is then defined using equation 4-5.

Bed Volumes to Breakthrough

$$= \frac{Q \left[\frac{\text{L}}{\text{min}} \right] \times t \text{ [min]}}{\text{Volume adsorbent (GAC) [L]}} \quad \text{Eq 4-4}$$

The number of GAC bed regenerations per year will then be calculated through the use of equation 4-6.

$$\text{GAC Bed Regenerations per Year} = \frac{1 \text{ [year]}}{t \text{ [days]}}$$

Eq 4-5

Equations 4-4 and 4-5 will be used to determine the time to breakthrough given different contaminant concentrations. Equations 4-6 will be incorporated into the performance model. A decreased time to breakthrough will result in a increased number of GAC bed regenerations per year. An increased time to breakthrough will result in an decreased number of GAC bed regenerations per year.

4.5. Incorporate Organic Co-contaminant Treatment into Cost Model

This section will detail how the Craig (2008) model was modified in order to incorporate additional organic compounds to predict costs for treating water with organic co-contaminants. Comparisons will be made of the bed volumes to breakthrough predicted by the Craig (2008) model (which accounts for only anions and perchlorate) with bed volumes to breakthrough predicted by a model that incorporates treatment of organic co-contaminants. The configurations will be analyzed as was discussed in Section 2.13 (two T-GAC beds followed by one guard GAC bed). The bed volumes to breakthrough will be calculated independently for both the perchlorate (using the method outlined by Craig (2008)) and for organic co-contaminants (using the Shih and Gschwend (2009) model described in Section 4-3 to predict bed volumes to breakthrough of organic compounds on GAC). The assumption is made that perchlorate adsorption only occurs on the T-GAC vessels and organic adsorption occurs only on the GAC vessel.

For a series configuration, which includes two T-GAC vessels and one GAC vessel, the time to breakthrough for perchlorate will be considered the point at which the second T-GAC vessel (vessel D) has initial breakthrough. The time to breakthrough for the organic compounds will be the point at which the guard GAC bed has initial breakthrough for any organic compound. This will allow the model to predict when the T-GAC and GAC beds need to be changed. The change out does not necessarily have to be simultaneous for both the T-GAC and GAC beds. For the single-column configuration, which includes one T-GAC vessel and one GAC guard vessel, the bed volumes to breakthrough will be considered the point at which the sole T-GAC bed shows breakthrough for perchlorate. The bed volumes to breakthrough for the GAC guard bed will be the point at which the first organic co-contaminant breaks through.

The bed volumes to breakthrough for both the T-GAC and GAC beds will be used in order to calculate the carbon utilization rates (CUR) which will determine the media costs for the system. The rest of the equations presented in Section 2.14 are dependent only on the plant flow. Thus, these will remain the same for the new model. The only new addition is that the CUR for the GAC vessels will vary depending on whether these organic compounds are present.

Considerations should be made in the future for the use of stratified beds run in the single column and/or series configuration. This would be particularly helpful if the influent concentrations are determined to breakthrough on each portion of the stratified bed (perchlorate on the T-GAC bed and organics on the GAC bed) at approximately the same time. Additionally, it might be beneficial to run an additional guard bed in order to

remove the organic compounds in series so that the benefit of series operations (discussed in Chapter 2) can be realized.

4.5.1. Craig (2008) Model Predictions Compared to Predictions of the Revised Model Accounting for Organic Co-contaminants

The Craig (2008) model provides performance and cost predictions for treating perchlorate-contaminated water in the presence of competing anions. The revised model also accounts for the presence of organic co-contaminants. Since all organic compound parameters are not readily available without obtaining the Abraham dataset from Sirius Analytical Ltd., a sensitivity analysis will be performed on one of the contaminants of interest, TCE, in order to provide insight into how the presence of organics affects performance and overall treatment cost. Initial model parameters that were used in the Craig (2008) study are shown in Table 4-5. Demonstration base values have been added so the scenario can be conducted.

Table 4-5: Perchlorate and Organic Model Sensitivity Analysis Parameters

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)	\$690,432	
Capital Cost (total)	\$2,199,094	
Cost per acre-ft	\$263	

Note, costs of \$2.50 per lb of T-GAC, \$1.50 per lb of GAC tailored, and an hourly wage rate of \$29.44 was used for this analysis. These values were used as they likely take into account the economy of scale. The cost per acre-ft determined through the use of the Craig model was \$263. Due to minor variations in densities and empirically developed cost formulas, the revised model, assuming no organic co-contaminants, predicts the cost at \$261 per acre-ft treated.

When TCE is added to the model at a concentration of 40 µg/L, the new cost per acre-ft becomes \$775, an increase of \$514. This increase is due to the need to regenerate

the GAC guard bed 10.7 times per year. The cost is also higher as the media disposal and transport costs are increased.

Table 4-6 shows the influent TCE concentrations, treatment cost per acre-ft, BVs treated, and train regenerations per year required for the same demonstration scenario. The table shows that at very low concentrations of TCE, increased concentrations do not affect the cost of treatment. This is because the Craig model (2008) assumed an annual change out of the GAC bed. Thus, one complete regeneration of the guard GAC bed will be completed annually regardless of whether this is required by the organic load. This same assumption is made in the new model.

Table 4-6: Perchlorate and Organic Model Demo Influent TCE Concentrations, Overall T-GAC System Cost per Acre-Ft, GAC BVs Treated, and GAC Train Regenerations/Year

TCE Co [µg/L]	Cost Per Acre-ft (\$/Acre-ft)	GAC BVs Treated	GAC Train Regenerations/Year
0.01	\$260.80	246,762	1.0
0.1	\$260.80	68,624	1.0
0.5	\$260.80	28,054	1.0
1	\$280.54	19,084	1.4
10	\$470.29	5,307	5.0
20	\$593.67	3,610	7.3
30	\$691.21	2,882	9.1
40	\$775.03	2,456	10.7
50	\$849.93	2,170	12.1
60	\$918.41	1,961	13.4
70	\$981.98	1,800	14.6

From Table 4-6, it is possible to see that as the influent TCE concentration increases, the cost per acre-ft of treatment increases. Additionally, the table illustrates that as the influent TCE concentration is increased, the bed volumes treated decreases as does the number of train regenerations required per year. Figure 4-4 shows the treatment cost per acre-ft [\$/acre-ft] versus influent TCE concentration (Co) in $\mu\text{g/L}$. The figure helps to clearly illustrate that the treatment cost per acre-ft of water increases as the influent TCE concentration increases.

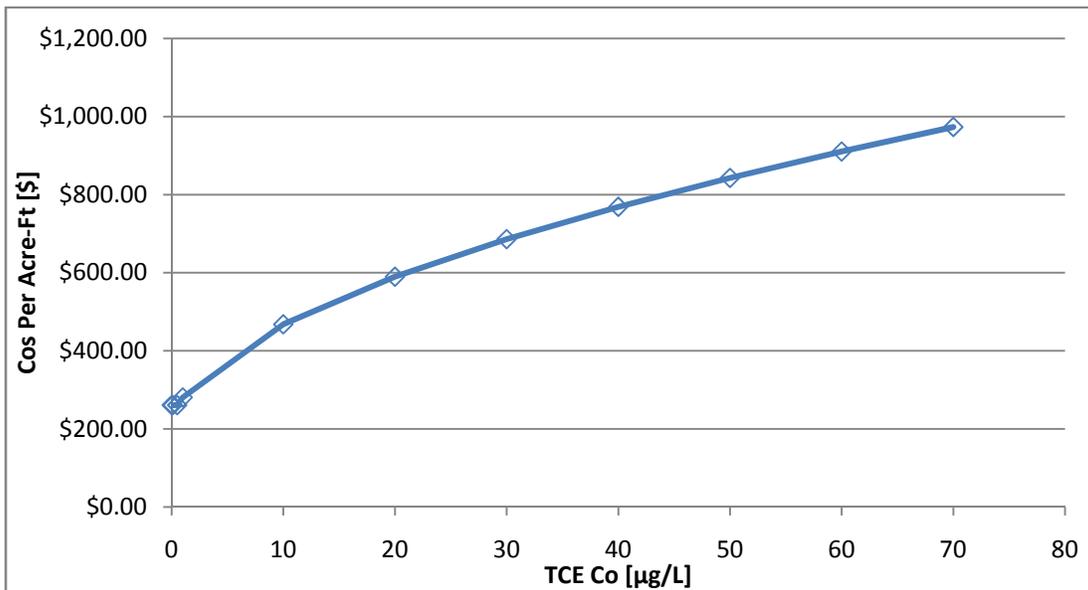


Figure 4-4: Relationship between Influent TCE Concentration [$\mu\text{g/L}$] and Overall T-GAC System Treatment Cost per Acre-ft [\$/acre-ft]

Similar analyses cannot be conducted for some of the nitroaromatic compounds of interest outlined in Chapter 2 due to the limited availability of Abraham's data.

However, data are available for a number of compounds of interest, and costs will be predicted for those compounds. Table 4-7 shows the chemicals that were added to the

model. It also shows the Freundlich parameters that were determined through the use of the Shih and Gschwend (2009) model.

Table 4-7: K_f and $1/n$ Values for Several Organic and Nitroaromatic Compounds

Chemical	Solubility [mg/L]	K_f [(mg/kg)/(mg/L) ^{1/n}]	1/n
Vinyl chloride (VC)	8800	9,442.24	0.4916
TCE	1100	47,720.62	0.4442
PCE	150	74,344.71	0.3814
Nitrobenzene	2000	85,497.49	0.0938
2-Nitrotoluene	650	140,704.15	0.064

Compounds with similar values for $1/n$ will have higher sorbed concentrations (q) for higher values of K_f (Eq 4-4). The higher the sorbed concentration, the longer water can be treated before breakthrough (Eq 4-3). This results in a decrease in the treatment cost because less GAC regenerations are required per year (Eq 4-7).

Figure 4-5 shows the relationship between the influent organic co-contaminant concentration and the overall T-GAC system treatment cost per acre-ft of perchlorate-contaminated water for several compounds. Each compound was examined with perchlorate as the only other compound in the water. The parameters in Table 4-5 were utilized for all scenarios.

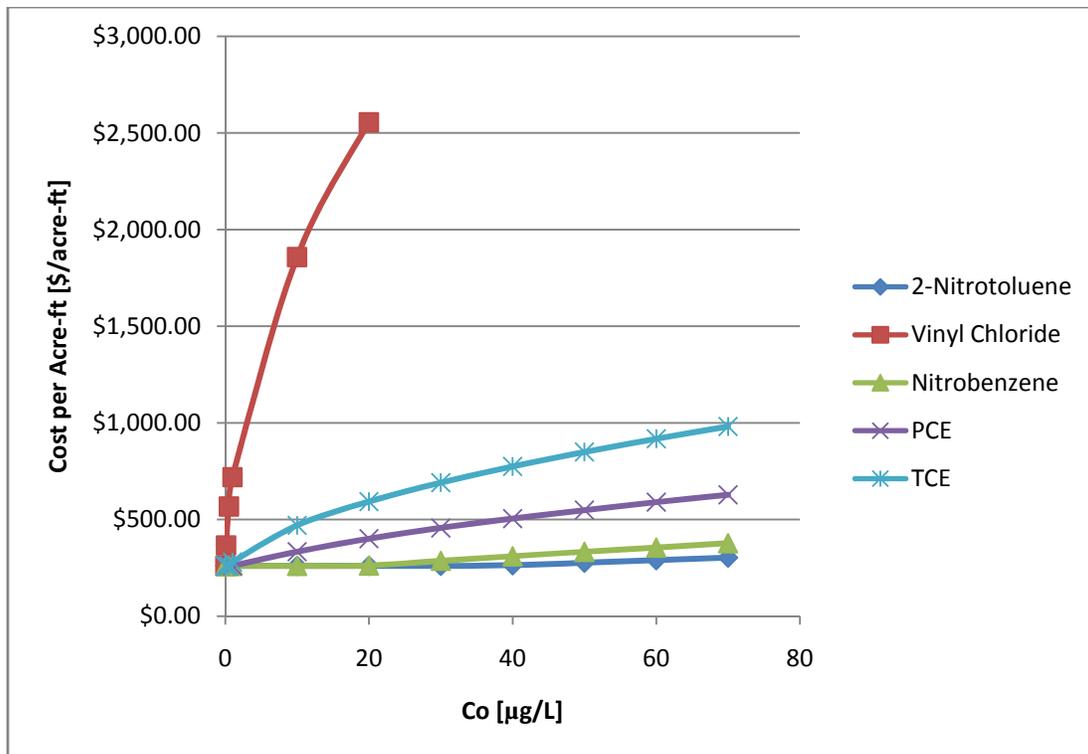


Figure 4-5: Relationship between Influent Concentrations [µg/L] for 2-Nitrotoluene, VC, Nitrobenzene, PCE, and TCE and Overall T-GAC System Treatment Cost per Acre-ft [\$/acre-ft]

From this figure, it is possible to see that the treatment cost is higher for compounds with higher K_f values. It is necessary to note that the solubility alone is not enough information to predict which compounds will cost less or more to treat through the use of the T-GAC/GAC system. The Shih and Gschwend (2009) model must use the compound solubility along with the McGowan's characteristic volume for the adsorbate (V), the compound's polarity/polarizability (S), and the compound's electron-donation basicity (B). These parameters play an important role in determining the Freundlich parameters that are used to predict the contaminant sorbed concentration.

4.6. Summary of Site Cost Information

The following section will provide a summary of the capital and O&M cost information from the different sites discussed in Chapter 2. In order to compare the costs of treatment processes utilized by the sites identified in Section 2.8.2, a common measurement must be used. Based on capital and operations and maintenance costs from the sites a cost to treat the water on an acre-feet basis is presented in table 4-9. This estimate assumes that the treatment lifetime for all of the technologies is 20 years. Capital costs are annualized using equation 3-4.

$$A = P \times i \times \left[\frac{(1 + i)^N}{(1 + i)^N - 1} \right] \quad \text{Eq 3-4}$$

There are a number of caveats associated with the costs that are presented in Table 4-9. The treatment costs are greatly dependent on the water chemistry at the site, the flow of water treated (economies of scale must be taken into account), and the site characteristics (e.g. surface water vs. groundwater, hydrogeology). Other considerations include the distance from the treatment site to the disposal site, local cost considerations, regulatory requirements, etc. Table 4-8 provides a summary of the site contaminant concentrations. Many of the effluent concentrations are either non-detect or below the minimum detection limit.

Table 4-8: Site Data Summary

Site	Contaminants	Approximate Influent Concentration [µg/L]	Effluent Concentration [µg/L]
Edwards	Perchlorate	100	Non-detect
	TCE	Non-detect	Non-detect
Stringfellow	Perchlorate	29.3	Non-detect
	TCE	1.1	Non-detect
JPL - GAC/FBR plant	Perchlorate	200	Non-detect
MMR - Frank Perkins Road Site	RDX	4	< 0.25**
	HMX	1	< 0.25**
	Perchlorate	4	< 0.35*
MMR - Pew Road Site	RDX	1	< 0.25**
	Perchlorate	10	< 0.35*
* Minimum Detection Limit			
** Reporting Limit			

Table 4-9 shows the acre-ft treated per year, the annual O&M costs, the annualized capital cost, and the overall cost of treatment per acre-ft. A broad range of flows is represented from 32.3 acre-ft per year (at Edwards) to 1,300 acre-ft per year (at MMR – Frank Perkins Road Site). The capital costs are annualized over a 20-year period through the use of a discount rate of 2.8% (OMB, 2009). Adding O&M cost (\$K) and annualized capital cost (\$K) gives an estimate of the cost per acre-ft treated (\$/acre-ft).

Table 4-9: Site Information Including Acre-Ft Treated per Year, O&M Costs, Annualized Capital Costs, and Cost of Treatment per Acre – Ft

Site	Acre-ft Treated Per Year	O&M Costs (\$K/yr)	Annualized Capital Costs (\$K) ¹	Cost of Treatment per Acre -Ft (\$)
Edwards	32	38-43	-	-
Stringfellow	40	28 ³	16	1,103
JPL - GAC/FBR plant ³	484	900 ²	313	2,508 ²
MMR - Frank Perkins Road Site	1,303	315	264	444
MMR - Pew Road Site	161	35	49	524

1- Annualized Capital Cost is based on an interest rate of 2.8% and a 20 year life-span

2- Includes cost of reinjecting water into aquifer

3 - Estimated (not actual) O&M cost

A sensitivity analysis was conducted to see what effect the assumed discount rate has on the cost per acre-ft. Figure 4-6 shows the cost per acre-ft for the GAC/FBR plant at JPL, Stringfellow, and the Frank Perkins Road Site and Pew Road Sites at MMR. The figure shows the cost per acre-ft versus the discount rate. As expected, as the discount rate increases, the cost per acre-ft increases. It is important to note that the JPL cost per acre-ft of treated water is high due to the cost of reinjection of the treated water. Additionally, for purposes of the sensitivity analysis, the estimated O&M cost was utilized and not the actual O&M cost from the contract. The Stringfellow cost per acre-ft of treated water is high as a result of the way the contract was bid.

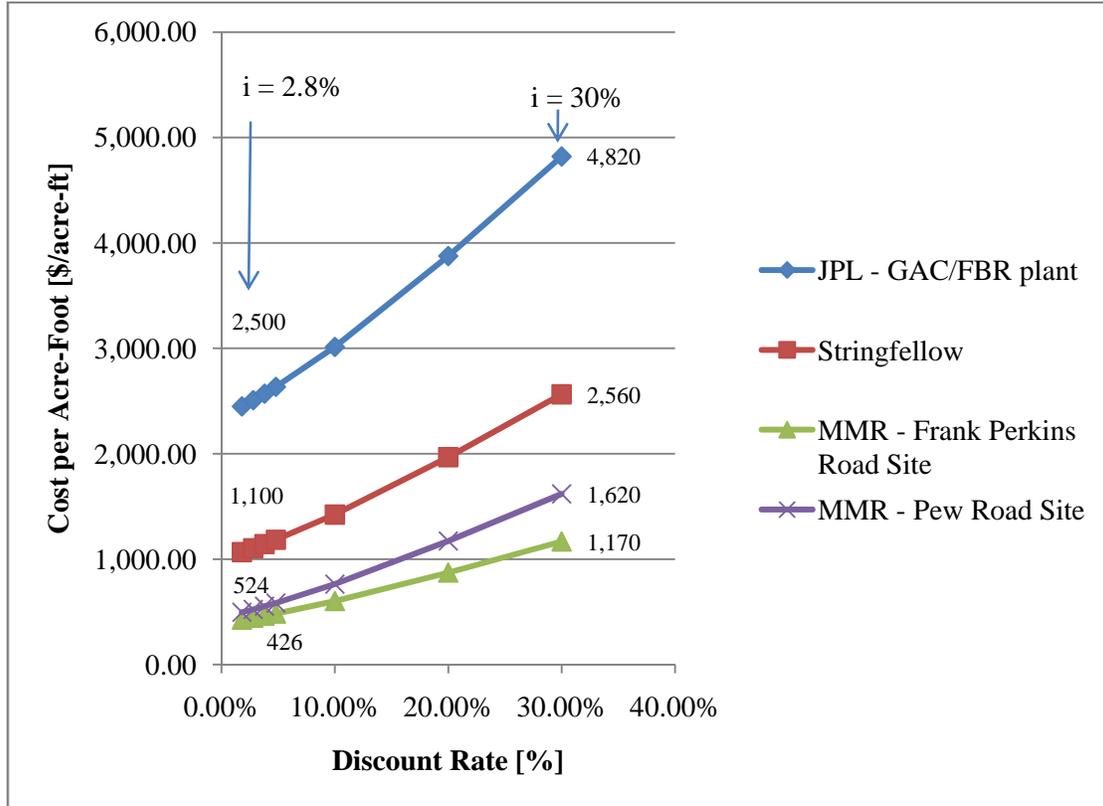


Figure 4-6: Cost Per Acre-Ft [\$/acre-ft] versus Discount Rate [%] for Four Co-Mingled Plumes

4.7. Cost Comparison of T-GAC System and Current Technologies to Treat Water

In order to compare the costs of using a T-GAC/GAC system to treat water with perchlorate and organic co-contaminants with the costs of technologies currently in use, the T-GAC/GAC system cost model predictions are compared to the treatment costs at the sites reviewed in Section 4.6. 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. The cost of treatment at both of the MMR sites (\$426 per acre-

ft at Frank Perkins Road and \$524 per acre-ft Pew Road) falls within this range. The costs of treatment at Stringfellow (\$1,100 per acre-ft) are just outside of this range. The cost of treatment at JPL (\$2,500 per acre-ft) site was higher than this range. Reasons for this high number are outlined in Section 4.6. It is likely that an “apples to apples” comparison of costs at this site, if detailed cost information could be obtained, would show that costs would be in the range of less than \$1,000 per acre-ft. From Figure 4-5 it is possible to see that the model-predicted costs to treat TCE as a co-contaminant are greater than the costs of treating other, more hydrophobic, compounds like PCE and the nitroaromatics. Thus, the model predicted cost range for T-GAC treatment of about \$200 to \$1000 per acre-ft to treat perchlorate-contaminated water with an organic co-contaminant is conservative and on the same order as costs of using conventional technologies at actual sites.

An additional benefit of the T-GAC/GAC system is that GAC is already a widely accepted and understood technology. Site personnel are familiar with operating and maintaining GAC systems. Utilizing T-GAC will require no further training and will allow for utilities that already use GAC to easily transition to T-GAC. Personnel will not have to be trained on multiple treatment technologies in order to treat a single water.

5.0. Conclusions and Recommendations

5.1. Summary

There are many sites where chlorinated solvents, nitroaromatic compounds, and perchlorate are co-mingled. This study examined a technology, tailored granular activated carbon (T-GAC), that has been shown to successfully treat perchlorate-contaminated drinking water. This thesis showed that both TCE and perchlorate can be successfully removed by using a T-GAC system with a T-GAC bed configured in series with a GAC bed. Correlations that had been developed to predict organic compound adsorption onto GAC, assuming a Freundlich isotherm, were incorporated into a T-GAC/GAC system performance model in order to predict bed volumes to breakthrough and carbon utilization rate for the GAC portion of the T-GAC/GAC treatment system. These predictions were then used in a T-GAC/GAC system cost model, in order to estimate the cost per acre-ft of treating water containing perchlorate along with organic co-contaminants at specified concentrations.

5.2. Conclusions

5.2.1. Objective #1

The main focus of this research was to evaluate the effectiveness of the T-GAC/GAC system at treating water where perchlorate and organic compounds are present as co-contaminants. As was demonstrated by data from the six-column Fontana study, both TCE and perchlorate can be successfully removed during drinking water treatment which utilizes a T-GAC bed followed by a GAC bed. When water with influent perchlorate and TCE concentrations of 13 and 40 µg/L, respectively, was treated by the TCE column,

perchlorate was treated for 8,300 BVs and TCE was treated for 4,400 – 5,400 BVs.

Based on experimental results and the literature, it was assumed that no TCE was sorbed to the T-GAC, and that no perchlorate was sorbed to the GAC. The bed volumes of TCE-contaminated water that were treated by the TCE column were significantly less than would be predicted using conventional adsorption isotherms. This may be due to an experimental artifact or error, or it may be due to some characteristic of the T-GAC/GAC system (e.g., tailoring agent leaching off of the T-GAC, resulting in inhibited TCE adsorption onto GAC).

5.2.2. Objective #2

The O&M data from the Fontana site were used in order to validate the Craig (2008) cost model. It was shown that modeled O&M costs were within 27.6% of actual costs at the evaluation site. Modeled total costs (annualized capital plus O&M) were \$947 per acre-ft (assuming \$5.99 per lb of T-GAC, and an hourly wage rate of \$53), within 25% of the actual costs of \$1,268 per acre-ft. The updated model predicted cost for Fontana (assuming \$2.50 per lb of T-GAC, , and an hourly wage rate of \$29.44) was determined to be \$545.

5.2.3. Objective #3

The Shih and Gschwend (2009) model was incorporated into the Craig (2008) model in order to predict the cost and performance of the T-GAC/GAC system to treat perchlorate and organic co-contaminants simultaneously. This model was used in order to predict the Freundlich parameters (K_f and $1/n$) which were then used to calculate the sorbed concentration and ultimately the carbon usage rate and number of annual GAC

regeneration/replacements. Application of the model demonstrated that the more hydrophobic the contaminant, the less costly the treatment.

5.2.4. Objective #4

The model discussed above was built into a user-friendly Excel platform to facilitate technology transfer. The model predicted that the cost per acre-ft for the scenario described in section 4.5 was \$263 per acre-ft. When 40 µg/L of TCE was added, the cost increased to \$769 per acre-ft. For the Stringfellow site, the actual cost using conventional technologies was \$1,103 per acre-ft which is much higher than the model-predicted T-GAC system cost. For the JPL site, the cost using conventional technologies was \$2,508 per acre-ft which is still much higher than the predicted cost for applying the T-GAC system. The actual cost for the MMR Frank Perkins Site was \$444 per acre-ft and for the MMR Pew Road Site the cost was \$524 per acre-ft which were both within the range of \$263-\$769 per acre-ft modeled assuming only perchlorate contamination (\$263 per acre-ft) and when the system had perchlorate and TCE (\$769 per acre-ft). The T-GAC/GAC system model predicted cost per acre-ft were of the same magnitude as the cost per acre-ft determined for both the MMR sites as well as the Stringfellow site which suggests that the T-GAC/GAC system could be cost competitive with conventional treatment train technologies. A benefit to the use of T-GAC is that GAC is already in use at many sites. A T-GAC system operating in conjunction with a GAC system is likely to be easy for operators to run and maintain and will require little training. Additionally, maintenance of the T-GAC system will be similar to GAC system maintenance, thereby reducing the need for maintenance supplies to operate two completely different systems.

5.3. Recommendations for Future Study

5.3.1. Additional Data Collection

Due to experimental problems with the TCE column in the six-column study at Fontana, data interpretation relied on a number of assumptions (e.g. how much TCE was sorbed to the GAC in the B Vessel prior to moving the vessel into the lead column position). In order to fully validate this performance model, more accurate TCE data should be collected. Additionally, data should be collected on additional organic and nitroaromatic compound adsorption onto T-GAC. This will provide vital information so that use of the T-GAC/GAC system to remove these compounds can be further studied and proven as a method that can treat co-mingled plumes in an economically feasible manner.

5.3.2. Site Capital and O&M Costs

Cost data from Fontana and the other sites that could be used for comparison were hard to gather based on various “real-world” vagaries. These include multiple contracts being bid, contract modifications during construction, the use of pre-existing systems on some sites, and different methods of residuals disposal. Additional information should be gathered as more sites with perchlorate and co-contaminants are treated. This information will be critical if the T-GAC/GAC system is to be considered economically competitive with conventional technologies.

5.3.3. Shih and Gschwend (2009) Model Parameters Assumptions

The Shih and Gschwend (2009) model utilized only one type of activated carbon for analysis, 20-40 mesh Darco. For purposes of this model, the activated carbon used was

assumed to be the same. The actual carbon used was 8 x 30 mesh GAC (AquaCarb 830AW). Future work should be done in order to predict if the Shih and Gschwend (2009) model parameters predict sorption onto AquaCarb 830AW, as well as other GAC types.

5.3.4. Model Validation

Data is needed in order to validate the model. In order for the model to be fully validated, real world cost and performance data with co-mingled plumes containing chlorinated and nitroaromatic compounds is required. This data should include plumes with varying contaminants. Also, various GACs should be studied in order to determine if there is a difference in adsorption of the particular contaminants as a result of GAC characteristics.

Appendix A: Fontana Water Characteristics

Well	#17B	#17C	Average
Perchlorate (µg/L)	18	8.6	13
Nitrate (mg/l)	36	33	34
Chloride (mg/l)	11	11	11
Sulfate (mg/l)	14	14	14
Carbonate (mg/l)	Non-detect	Non-detect	Non-detect
Bi-Carbonate (mg/l)	192	186	189
pH	7.5	7.5	7.5
Total Dissolved Solids (mg/l)	250	238	244
Specific Conductance (µmho/cm)	415	388	401
Volatile Organic Compounds (µg/L)	Non-detect	Non-detect	Non-detect

Appendix B: Capital and O&M Cost Curves Developed from 1979 U.S. EPA Study

The excavation, site work, and concrete (ESC) category does not include general site work such as roadways and landscaping. It includes only the site work necessary to install the treatment system under consideration. Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R^2) value of 0.9945.

$$\text{ESC capital cost (\$)} = 127.03 \times \text{gpm}^{0.3175}$$

Eq B-1

For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used (Craig, 2008).

$$\text{ESC capital cost (\$)} = T \times C \times (127.03 \times \text{gpm}^{0.3175})$$

Eq B-2

Manufactured equipment (ME) includes the cost of pumps, drives, process equipment, specific controls, and other items that are sold with the equipment. Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R^2) value of 0.9978. For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used.

$$\text{ME capital cost (\$)} = 74.14 \times \text{gpm} + 1382.5$$

Eq B-3

$$\text{ME capital cost (\$)} = T \times C \times (74.14 \times \text{gpm} + 1382.5)$$

Eq B-4

Labor costs include installation of manufactured equipment, piping and valves, and concrete labor.

Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R²) value of 0.9923. For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used.

$$\text{Labor capital cost (\$)} = 928.9 \times \text{gpm}^{0.455}$$

Eq B-5

$$\text{Labor capital cost (\$)} = T \times C \times (928.9 \times \text{gpm}^{0.455})$$

Eq B-6

The pumps, piping, and valves (PPV) category includes cast iron pipe, steel pipe, valves, and fittings.

Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R²) value of 0.9761. For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used. This equation assumes that the pumps make up the largest fraction of the PPV cost and that pumping “x” gpm through C columns is equivalent to pumping “C*x” gpm through a single column.

$$\text{PPV capital cost (\$)} = 329.2 \times \text{gpm}^{0.565}$$

Eq B-7

$$\text{PPV capital cost (\$)} = T \times [329.2 \times (\text{gpm} \times C)^{0.565}]$$

Eq B-8

For the electrical and instrumentation (EI) costs, Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R²) value of 0.9335. For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used. Equation x uses the same assumptions that were used to develop equation x.

$$\text{EI capital cost (\$)} = 2.073 \times \text{gpm} + 635.6$$

Eq B-9

$$\text{EI capital cost (\$)} = T \times [2.073 \times (\text{gpm} \times C) + 635.6]$$

Eq B-10

The housing costs include all building, heating, ventilation and cooling (HVAC), outlets, slab and foundation. Equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R^2) value of 0.9944. For multiple treatment trains (T) consisting of “C” columns per train, equation X should be used.

$$\text{Housing capital cost (\$)} = 4638 \times \text{gpm}^{0.154}$$

Eq B-11

$$\text{Housing capital cost (\$)} = T \times C \times 4638 \times \text{gpm}^{0.154}$$

Eq B-12

The miscellaneous and contingency (M&C) category includes an allowance for contingency items. The percentage allowed for in this category was 15% of the sum of the other capital costs (accounted for above). For the M&C category, equation X was empirically developed from the data in the U.S. EPA (1979) report, and has a coefficient of determination (R^2) value of 0.984. Equation X represents the equation that should be used when the number of trains (T) and columns per train (C) are taken into account. This equation assumes that the M&C costs relate to the total flow through all the columns in the system and thus gpm is multiplied by T and C.

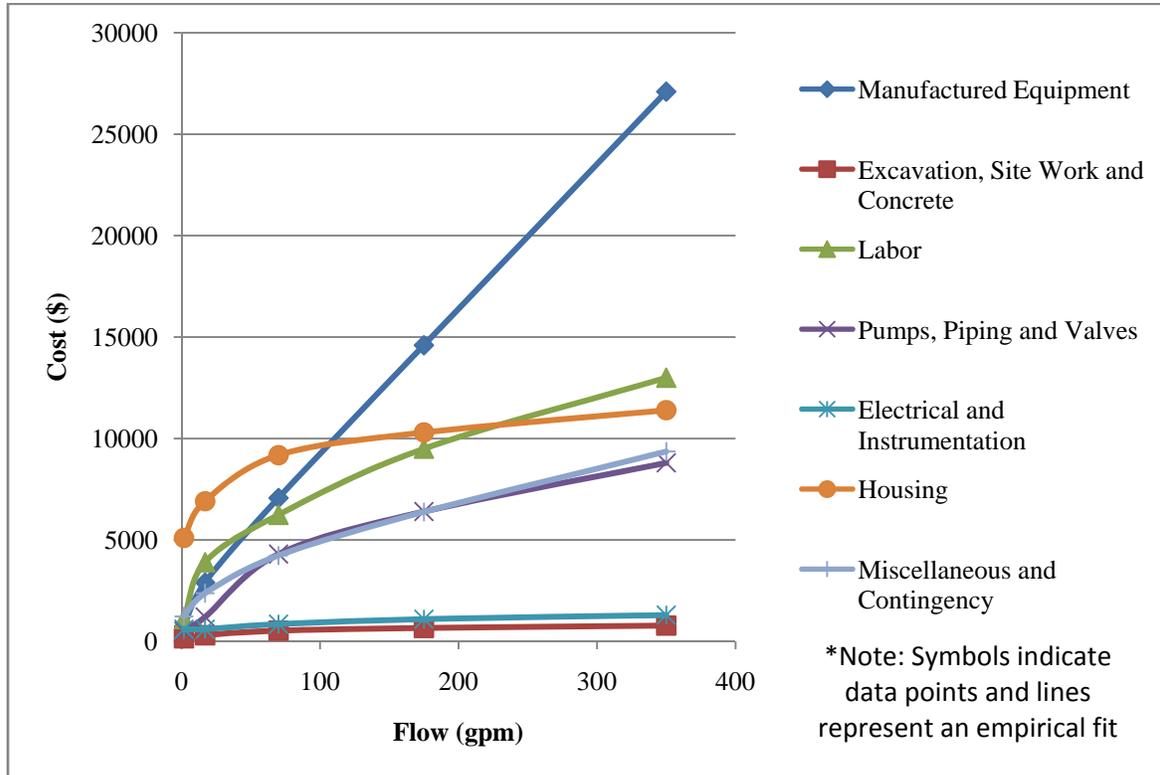
$$\text{M\&C capital Cost (\$)} = 918.3 \times \text{gpm}^{0.377}$$

Eq B-13

$$\text{M\&C capital Cost (\$)} = 918.3 \times (\text{gpm} \times \text{T} \times \text{C})^{0.377}$$

Eq B-14

Figure X shows the curves that were developed for each of the above capital cost categories. Data points are shown by symbols and lines show the empirical fit for the data.



Graph of Flow (gpm) vs. Cost (\$) for Different GAC Capital Cost Categories (U.S. EPA, 1979)

Appendix C: Craig (2008) Model Application Example

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

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)	\$690,432	
Capital Cost (total)	\$2,199,094	
Cost per acre-ft	\$263	

Example Treatment Scenario

As shown in the table, the cost for treating this water by T-GAC is \$263 per acre-ft. Thus in order for T-GAC 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 T-GAC media.

As was discussed above, the presence of nitrate inhibits perchlorate adsorption on T-GAC. Thus a higher nitrate concentration should result in an increased treatment cost.

Table X provides an example of this effect. Doubling the nitrate concentration in the water results in a significantly higher treatment cost per acre-ft.

Effect of Increased Nitrate Concentration on T-GAC Treatment Costs

<u>Model Input Parameter</u>	<u>Base Value</u>	<u>Value Variations (highlighted yellow)</u>	<u>Unit</u>
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)	\$690,432	\$978,547	
Capital Cost (total)	\$2,199,094	\$2,199,094	
Cost per acre-ft	\$263	\$353	

A number of caveats need to be added to the above analyses. Note that the cost and performance model is based on 12 RSSCTs using Fontana water spiked with perchlorate at various concentrations and model validation was based on a single pilot study at Fontana. The T-GAC medium, which is the single largest cost driver, had costs based on the pilot-scale study. Presumably, full-scale production costs will be considerably less.

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14. ABSTRACT Drinking water sources contaminated with both perchlorate and organic compounds have frequently been found in the U.S. Tailored granular activated carbon (T-GAC) is an innovative technology that is being evaluated to determine if it can more cost effectively remove perchlorate than conventional technologies. A question that has been raised is whether T-GAC can economically treat perchlorate-contaminated water that also has organic co-contaminants present. During a field study, trichloroethylene, an organic compound, and perchlorate were successfully removed by adsorption using a T-GAC/GAC system. These results motivated development of a model that could be applied to predict the cost and performance of a T-GAC/GAC system to treat water with perchlorate and organic co-contaminants. Correlations developed to predict organic compound adsorption onto GAC were incorporated into a T-GAC/GAC system performance model. These predictions were then used as input to a technology cost model. The predicted T-GAC/GAC system costs were similar to actual costs of conventional technologies that are being used to treat perchlorate and organic contaminated waters at a number of sites. Due to other advantages of the technology (e.g., ease of implementation) it appears the T-GAC/GAC technology has the potential to cost effectively treat water contaminated by perchlorate and organic compounds.				
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