

4.0 Granular Activated Carbon

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4.1 Background

4.1.1 Nature of Problem

Past use of GAC to treat MTBE-impacted water resulted in difficulties due to the physical and chemical characteristics of MTBE. Results of several full-scale applications suggest that some GACs perform poorly when MTBE is present in the water to be treated (e.g., McKinnon and Dyksen, 1984; Creek and Davidson, 1998). In consideration of this, an in-depth evaluation is needed to identify the most promising GACs for MTBE removal and to define conditions under which GAC is most likely to be a cost-effective treatment alternative for MTBE.

4.1.2 Objectives

The primary objective of this chapter is to provide a detailed feasibility analysis regarding the use of GAC to remove MTBE from drinking water. This feasibility analysis includes determining the conditions (e.g., MTBE influent concentrations, background water quality) under which GAC is most likely to cost-effectively remove MTBE. Other specific objectives include the following:

- Clarify causes of the wide variability in existing data for MTBE removal using GAC.
- Determine state-of-knowledge regarding mass transfer parameters for different types of GAC.
- Evaluate the impact of NOM and SOCs (e.g., benzene) on the adsorption of MTBE.
- Present state-of-knowledge regarding desorption of MTBE from GAC.

To address these objectives, this chapter presents general and detailed evaluations of GAC for treating MTBE-impacted water. The general evaluation includes a focused literature review and a compilation of vendor information to determine the benefits and limitations of GAC, key variables and design parameters, current usage of GAC for MTBE removal, etc. The detailed evaluation includes computer modeling results and cost estimates prepared to determine the impacts of influent MTBE concentrations, background organic matter, and the presence of other organic compounds upon the removal of MTBE using GAC.

4.2 General Evaluation of GAC Technology

This section presents a general evaluation of using GAC for the treatment of MTBE. A brief description of carbon adsorption and its applications are presented, followed by discussions of advantages and disadvantages; key variables and design parameters; GAC vendors; developmental status of technology; ease of installation and operation; permitting; and current usage of technology. This section also presents brief reviews of related research for MTBE treatment with GAC.

4.2.1 Description of Technology

Carbon adsorption technology is implemented by passing contaminated water through a vessel (or vessels) containing GAC. Intermolecular attraction between molecules of a dissolved chemical (adsorbate) and the GAC (adsorbent) surface results in adsorptive forces that physically attract the adsorbate to the GAC as the water passes through the vessel. As such, the adsorbate remains attached to the GAC matrix and the water leaves the system with a decreased contaminant concentration. Chapter 5 presents further discussion of the primary processes that govern adsorption.

GAC for drinking water applications is created from carbonaceous source materials, such as bituminous coal, coconut shell, petroleum coke, wood, and peat. GAC is produced by grinding, roasting, and then activating the source materials with high temperature steam (water-gas reaction). This processing results in a porous material with very high internal surface area. Processing each of the different source materials results in GACs with significantly different adsorption properties. The adsorption potential of a given carbon is dependent on numerous factors, including the adsorption structure (i.e., pore sizes) and the characteristics of the adsorbate. Detailed discussions of these important GAC characteristics are presented in numerous references (e.g., Sontheimer et. al., 1988; Lehr, 1991; and, Nyer, 1992).

To design an efficient carbon adsorption system for water treatment, a set of bench-scale and/or pilot-scale tests using the site-specific water is typically performed. These test results allow designers to optimize the type of GAC used and to estimate operating parameters for the full-scale system. Common types of bench-scale methods include isotherm tests (batch equilibrium tests) and dynamic column tests. These testing methods are discussed separately below.

Isotherm Testing

Isotherm testing is performed to determine the relationship between adsorption capacity of a GAC and concentration of an adsorbate under specific background water conditions. The results of isotherm tests can be used to select the most effective GAC for specific water conditions and to develop preliminary design parameters.

Isotherm testing, a static testing process, is performed by placing a measured amount of GAC into an aqueous solution containing a measured concentration of adsorbate. After equilibration, the adsorbate concentration in the water is measured, allowing the adsorption capacity of the GAC to be calculated. The procedure is performed several times at varying initial adsorbate concentrations in order to develop the relationship between carbon capacity and adsorbate concentration at a constant temperature. This relationship can be described using the well-established Freundlich Isotherm Equation:

$$q = K_F C^n$$

where q is the mass of adsorbate per dry unit weight of carbon [mg/g] and C is the concentration in the bulk solution of the adsorbate at equilibrium. The Freundlich isotherm parameters, K_F and n , are experimentally determined constants at a given temperature. In general, it has been shown that the value of K_F is related to the adsorbent capacity while the value of n is related to the strength of adsorption (Weber, 1972). Specific procedures for isotherm testing are presented in American Society for Testing and Materials (ASTM) Designation D 5919-96 (ASTM, 1996).

Isotherm testing can be performed using distilled-deionized water or site-specific water that includes NOM and competing SOCs. The impacts of carbon fouling by NOM and competitive interaction between SOCs are discussed later in this chapter (Section 4.2.2). It is important to note that in full-scale applications of carbon adsorption, the GAC adsorption capacity for dissolved contaminants typically is lower than the maximum adsorption capacity determined from isotherm testing.

Dynamic Column Testing

Although analytical models that incorporate parameters determined from isotherm testing can be used to predict full-scale results, it usually is better to perform dynamic testing to quantify kinetic effects with site-specific water. Because of this, the design of carbon adsorption systems may be preceded by dynamic column testing with the selected GAC and the site water. These tests can also determine the need for pretreatment of the water prior to carbon adsorption.

Dynamic testing is performed with a set of GAC columns connected in series, using either the rapid small-scale column test (RSSCT) method or the accelerated column test (ACT) method. Samples taken at the effluent end of the columns allow development of concentration breakthrough curves that are dependent on flow conditions in addition to GAC type and influent adsorbate concentration. These test results can be used for full-scale design through the use of scaling relationships and allow for evaluation of EBCT, length of the mass transfer zone (MTZ), and other critical design variables impacted by dynamic effects. Crittenden et al. (1989) present procedures and scaling relationships for the RSSCT method, which is currently being refined for presentation as an ASTM standard test method that is expected to

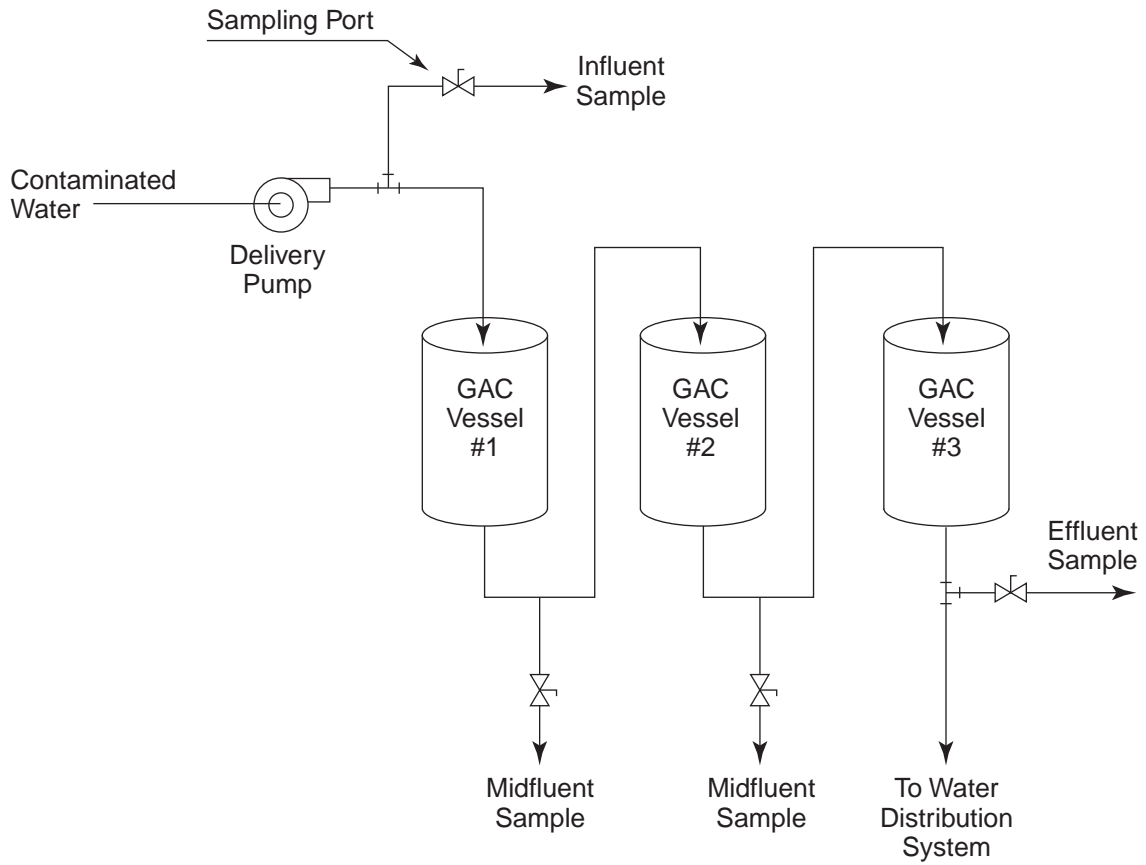
be finalized in the year 2000 (Graham, personal communication, 1999). Detailed discussions of column testing are presented in numerous references (Stenzel and Merz, 1988; Crittenden et al., 1991; and, Hand et al., 1989).

Full-scale Operations

Carbon adsorption systems can be used in various configurations (e.g., in-series, in-parallel, upflow, downflow). In general, adjusting the system configuration allows designers to optimize the adsorption characteristics and cost-effectiveness of the system based on the influent water conditions (e.g., adsorbate properties, flow rate), effluent treatment criteria, and regeneration/replacement methods. These design considerations for full-scale GAC systems are discussed in numerous references (e.g., Sontheimer et al., 1988; Hand et al., 1989; Nyer, 1992).

Single vessel treatment systems are the simplest applications of GAC technology. These systems are often used in situations with low flow rates, low influent concentrations, or less stringent effluent criteria. In single vessel treatment systems (or in the lead vessel of an in-series system), the MTZ (see Figure 5-11 in Chapter 5) of the adsorbate moves down gradient as the GAC at the influent end of the vessel becomes saturated with adsorbate. Eventually, the MTZ of the adsorbate moves far enough into the vessel that measurable concentrations of adsorbate are observed in the effluent (i.e., “breakthrough”). When the effluent from a single-vessel system reaches a specified adsorbate concentration, the vessel is taken off-line and the carbon is replaced. As shown in Figure 5-11, not all of the GAC will be saturated at breakthrough because of the shape of the MTZ. This limits the removal effectiveness of single-vessel systems and necessitates shutdown of the treatment system until new or regenerated carbon can be replaced into the single vessel.

Figure 4-1 presents a schematic of in-series operation, which is often used for public drinking water systems. In-series operation allows the secondary, or “lag,” vessel(s) to maintain final effluent quality while GAC in the lead vessel is used to remove the majority of the adsorbate dissolved in the influent water. Once effluent concentrations from the lead vessel reach a specified level (e.g., 50 percent or more of the influent concentration), the lead vessel is taken off-line, replaced with fresh carbon, and then put back on-line as the lag vessel. Proper change-out of an in-series GAC system ensures that the MTZ of the adsorbate does not reach the effluent end of the lag vessel, thereby ensuring non-detectable concentrations in the system effluent at all times. In-series operation is typically required for weakly adsorbing compounds, such as MTBE, or in situations where effluent criteria are stringent (e.g., drinking water systems). Vessels can be used in series with more than two vessels, particularly with weakly adsorbing contaminants with long MTZs. Longer series can also optimize the cost-efficient use of the adsorptive capacity of a carbon batch, allowing almost complete saturation of the lead vessel without risking a breakthrough in the effluent, exceeding the effluent criteria.



Note: Pretreatment May Be Required
In Some Cases

Figure 4-1. Schematic for GAC using series operation.

Operation of vessels in parallel allows for larger flow rates to be treated and/or for increased EBCTs to be used. Because the adsorbate must be kept in contact with the GAC for a sufficient amount of time, it is sometimes necessary to split the influent flow into more than one series of carbon vessels. This effectively lowers the volumetric flow rate going through a given vessel (or series of vessels), increasing the residence time of the contaminated water in the GAC matrix.

An important aspect of full-scale GAC operation is regeneration or replacement requirements. Carbon regeneration or replacement is necessary when the effluent from the lead vessel or one of the lag vessels in a series reaches a specified concentration. At that time, the lead vessel is taken off-line for either on-site regeneration or replacement with reactivated or virgin GAC. Because of stringent effluent standards, many drinking-water treatment applications will require replacement with virgin carbon, particularly for weakly adsorbing compounds such as MTBE.

Another aspect of full-scale operation of GAC systems is pretreatment. In general, pretreatment is performed to modify the influent water stream in order to maximize the efficiency of the adsorption process for the primary adsorbate(s). Common pretreatment requirements, which are described briefly below, include filtration, precipitation, pH adjustment, and disinfection.

Filtration is performed to remove suspended particles that would otherwise clog the pore structure of the GAC matrix in addition to taking up adsorption sites in the matrix. Influent water may require precipitation pretreatment in order to maximize the GAC adsorption efficiency by minimizing metal precipitation (and associated carbon fouling) within the GAC vessels.

Research has shown that the pH of the influent water can impact carbon column performance (Semmens et al., 1986); thus, pH adjustment is another possible pretreatment requirement. With respect to pH, Semmens et al. (1986) concluded that “conditions employed during pretreatment may have a profound influence on the subsequent performance and useful life of the GAC.” However, Calgon Carbon Corporation (Pittsburgh, PA) has found that pH “will not have an effect on [the adsorption of] compounds such as MTBE, BTEX, etc” (Megonnell, personal communication, 1999).

Disinfection is performed to reduce the growth of bacteria, which — similar to suspended particles — can clog the GAC matrix and take up adsorption sites. However, biological growth within the GAC matrix is sometimes beneficial, as bacteria can utilize organic contaminants as substrates for further growth. Consideration should be given to the potential beneficial effects of biological growth within the GAC vessels when designing pretreatment systems. This topic, which is currently being researched by University of California, Davis, is beyond the scope of this evaluation.

4.2.2 Benefits and Limitations

Benefits

Carbon adsorption has several advantages over other water treatment methods. The primary advantage is that it is a very simple technology that generally has stable operations. In addition, GAC is very well established for removing organic compounds (although, to date, its field application for treating MTBE in large-scale drinking water systems is limited). Carbon systems are very easy to implement due to wide commercial availability; numerous vendors can supply GAC and full-scale systems. Because of the simplicity of the equipment and materials, capital and installation costs are relatively low compared to more innovative technologies. Carbon systems require no off-gas treatment and the creation of by-products is limited to spent carbon that requires regeneration or disposal. In summary, the benefits of GAC for MTBE treatment are as follows:

- Simple technology/stable operations
- Well-established equipment and methods
- Easy to implement/commercially available
- Low capital and installation costs
- No off-gas treatment required

The reader should note that there are other removal/destruction mechanisms that occur within the GAC matrix. Evaluation of these beneficial processes, which include biological activity, is beyond the scope of this report.

Limitations

The limitations of GAC effectiveness for the treatment of MTBE can be separated into the following primary categories, each of which is discussed separately below:

- MTBE characteristics
- Impact of NOM
- Impact of other SOCs
- Desorption
- **MTBE Characteristics**

The physical and chemical characteristics of MTBE are generally considered poor for adsorption. In particular, MTBE's high solubility (48,000 mg/L at 25°C) causes the compound to preferentially remain in solution (API, 1994). This effect is also indicated by

MTBE's low octanol:water distribution coefficient ($\log K_{ow} = 1.2$), which demonstrates its high affinity for water (API, 1994).

The poor adsorptive characteristics of MTBE can cause early breakthrough and/or frequent carbon changeout requirements. Research of small-scale point-of-entry (POE) treatment systems indicated that removal of BTEX compounds by GAC far exceeded that of MTBE, resulting in MTBE controlling GAC life in the systems (Malley et al., 1993). Isotherm studies of the widely utilized Calgon Filtrasorb 300 indicate that the adsorption capacity is approximately an order of magnitude lower for MTBE than for toluene, on an equivalent mass basis (Dobbs and Cohen, 1980).

Because of the low adsorption capacity of carbon for MTBE, system design may require use of three or more vessels in series to contain the MTZ and to maximize carbon usage efficiency. As such, treatment of MTBE-impacted water using GAC may result in higher upfront capital costs and higher O&M costs due to frequent carbon changeout.

- **Impact of NOM**

Numerous studies have shown that the presence of NOM in the source water to be treated can significantly reduce the adsorption capacity of GAC for SOCs (Summers et. al., 1989; Zimmer et al., 1988; and Speth, 1991). Based on these studies, it appears that GAC adsorption capacity decreases with increasing carbon exposure time to NOM. The magnitude of the capacity decrease is also dependent on variables such as type of NOM, type of carbon, and the SOC to be removed.

The NOM fouls GAC in several ways: 1) NOM can take up adsorption sites within the MTZ of the SOC (i.e., competitive adsorption); 2) NOM can preload the GAC by moving more quickly than the SOC (i.e., ahead of the MTZ of the SOC); and, 3) NOM can physically clog the pore space of the carbon. Studies for several SOCs have shown that the Freundlich isotherm parameter, K_F , generally decreases with increasing NOM exposure time (Zimmer et. al., 1988; Hand et. al., 1989). This indicates that the overall capacity of GAC for an SOC will decrease with time as more water is passed through the GAC matrix. Research has also shown that the decrease of K_F varies significantly for different SOCs, different source waters (i.e., different types and concentrations of NOM), and different carbons (Sontheimer et. al., 1988). Because of this, it is difficult to predict the decrease of adsorption capacity without site-specific testing.

Because of the kinetics of NOM adsorption, NOM fouling should have less effect on weakly adsorbing compounds that move relatively quickly through carbon. Based on laboratory data, Speth (1991) speculated that for dichloroethylene (DCE) and other weakly adsorbing compounds, the effects of NOM preloading in a carbon column are less significant on adsorption capacity than for strongly adsorbing compounds. Thus, for the weakly adsorbing MTBE, the impact of NOM may be less severe than for other SOCs.

At this time, there is no measurable water quality parameter that is clearly and consistently indicative of NOM fouling potential (Hand, personal communication, 1998). To date, NOM concentrations have been estimated by using DOC or TOC as surrogate parameters. However, it is unclear how the measured DOC or TOC concentrations in the water relate to the extent of GAC fouling. Although logic suggests that higher DOC or TOC loads will result in greater fouling, contradictory results have been found in research (Zimmer et. al., 1988; Summers et. al., 1989). Experience has shown that measured DOC or TOC concentrations are not always accurate indicators of GAC fouling potential (Hand, personal communication, 1998). This discrepancy is attributed to the fact that NOM fouling is controlled at least in part by the specific types of NOM present (e.g., humic acids, fulvic acids). These specific types of NOM are not quantified by measurements of DOC or TOC. At this time, there is no standard method for determining specific NOM types and concentrations present in a given water. As such, there currently is no readily measurable parameter that is clearly and consistently indicative of NOM fouling potential.

No specific studies on the impact of NOM on MTBE removal by GAC were identified during this evaluation. However, based on the studies described above, NOM fouling is likely to decrease GAC capacity for MTBE to a lesser degree than for more strongly adsorbing chemicals such as the BTEX compounds. Testing under site-specific conditions (e.g., water characteristics, SOC concentrations, GAC characteristics, etc.) is needed to accurately assess the impact of NOM on MTBE removal by carbon adsorption.

- **Impact of Other SOCs**

Similar to the effects of NOM, competitive adsorption due to the presence of other SOCs can reduce GAC capacity for MTBE. The capacity reduction depends on type and concentration of competing SOCs and the type of GAC being used. Because MTBE has relatively low affinity for adsorption onto carbon, other compounds with higher affinities will preferentially take up adsorption sites on the carbon. It should be noted that for strongly adsorbing SOCs, the MTZ will be established as a thin zone near the influent end of the lead vessel. As such, other SOCs may have limited impact on MTBE adsorption in the majority of the downgradient GAC matrix.

Prediction of adsorption effectiveness for multi-component systems is complex, particularly in the presence of NOM. Similar to single component systems, competitive adsorption systems will be affected by NOM and other water quality characteristics. Although isotherm testing can be used to qualitatively assess competitive effects, dynamic column testing under site-specific conditions is generally required to accurately predict the impact of competitive adsorption on full-scale GAC capacity for MTBE. This topic has been researched extensively for numerous organic compounds (e.g., Kong and DiGiano, 1986), though no studies specifically evaluating competitive adsorption effects on MTBE were found for this evaluation. Further discussion of this topic is presented in Section 4.2.8.

- **Desorption**

Since MTBE is only weakly adsorbed by GAC, other more preferentially adsorbed SOCs in the contaminated water will tend to displace previously sorbed MTBE from the GAC matrix. This effect, which is known as desorption, can also occur when influent MTBE concentrations decrease, allowing previously sorbed MTBE molecules to enter back into solution (re-equilibration). Evidence of MTBE desorption (i.e., effluent concentrations higher than influent concentrations) has been observed for several GAC systems designed to remove MTBE, including a service station in Massachusetts at which 33 MTBE desorption events occurred over a 6-year period (compared to seven benzene desorption events) (Creek and Davidson, 1998). Although desorption of MTBE (or other compounds) does not always constitute system failure (e.g., effluent concentrations may still be below treatment goals), it does signal that carbon changeout may be needed.

Desorption is a critical variable in planning O&M efforts for GAC systems treating weakly sorbing compounds such as MTBE. The potential for desorption contributes to the need for design and operational variations such as multiple vessels in series and higher frequency sampling of midfluent and effluent. It should be noted that for a properly designed and maintained GAC system, desorption is a manageable problem.

4.2.3 Key Variables and Design Parameters

This section reviews key variables and design parameters relative to the use of GAC for MTBE removal.

GAC Type

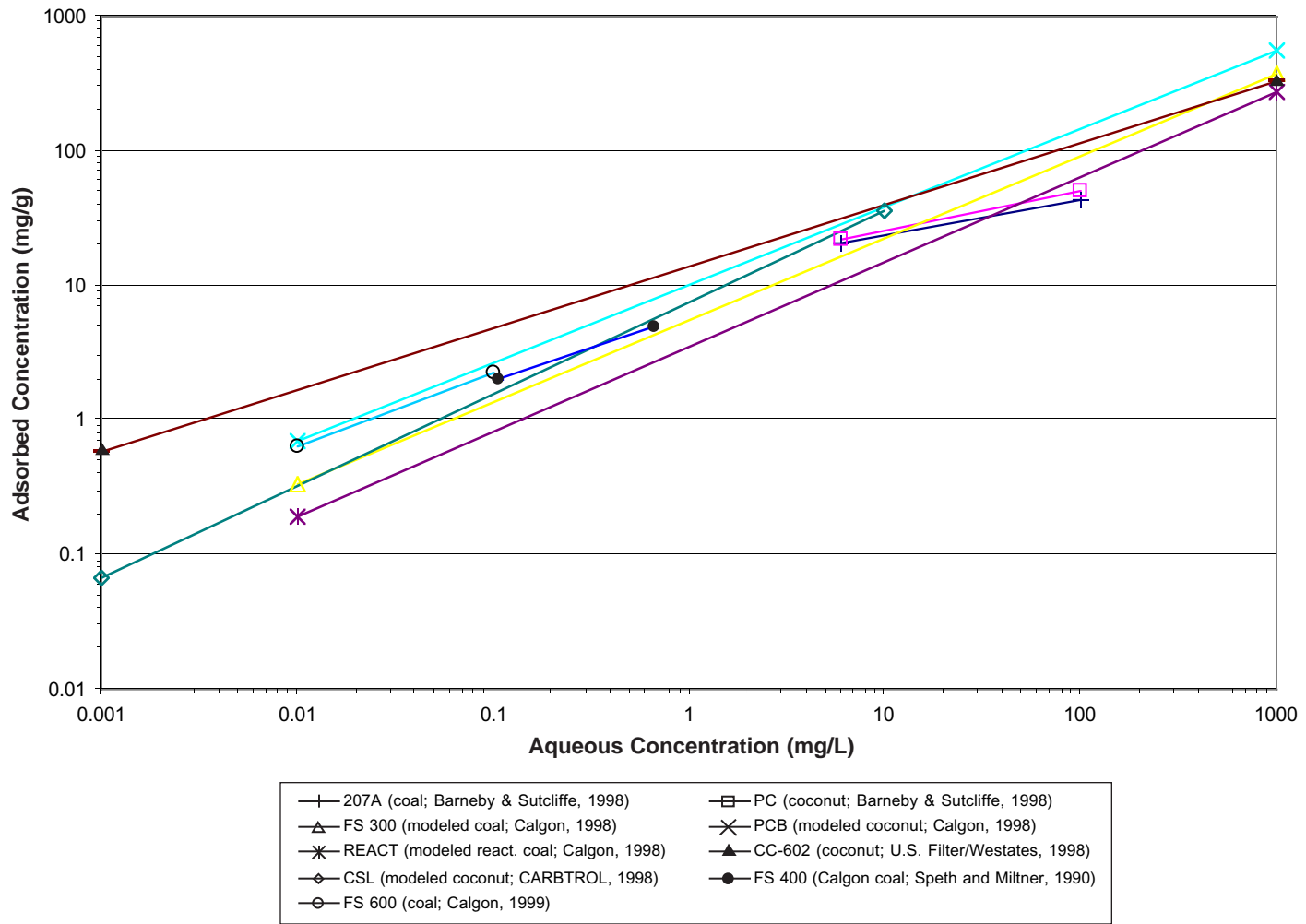
Different types of GAC have widely varying adsorptive properties for MTBE. Freundlich isotherm parameters, in addition to other relevant information for several GAC products, are presented in Table 4-1. Isotherm data for these products, including coal-based, coconut shell, and reactivated coal-based carbons, are plotted in Figure 4-2. It is important to note that not all of the isotherm data presented in Figure 4-2 and Table 4-1 were developed from laboratory testing. Computer models were used to generate the data for CARBTROL's (Westport, CT) CSL carbon and Calgon's (Pittsburgh, PA) Filtrasorb 300, PCB, and REACT carbons. However, the data for Barneby & Sutcliffe's (Columbus, OH) 207A and PC carbons, Calgon's (Pittsburgh, PA) Filtrasorb 400 and Filtrasorb 600 carbons, and U.S. Filter/Westates (Los Angeles, CA) CC-602 carbon were developed using laboratory isotherm testing methods.

A Units of K_F are (mg/g)(L/mg)ⁿ

Vendor/Source	Product Name	Carbon Source	Freundlich Parameters K_F n		Modeling/ Testing Conditions	Range of MTBE Concentrations ($\mu\text{g/L}$)
Barneby & Sutcliffe Corporation	207A	coal	12.9	0.26	laboratory tests T = 25°C	6,000 - 100,000
	PC	coconut	13.2	0.29	distilled water	
Calgon Carbon Corporation	FS 300	coal	5.6	0.61	computer model T = 25°C "pure" water	10 - 1,000,000
	PCB	coconut	10	0.58		
	REACT	reactivated coal	3.5	0.63		
	FS 600	coal	7.8	0.54	laboratory tests T = 25°C distilled water	10 - 100
CARBTRON	CSL	coconut	7.5	0.68	computer model distilled water	1 - 10,000
U.S.Filter/Westates	CC-602	coconut	13.9	0.46	laboratory test T ~ 20°C organic-free water	1 - 1,000,000
Speth and Miltner, 1990	FS 400 (Calgon)	coal	6.0	0.48	laboratory test T = 24°C dist./deion. water	102 - 628

Table 4-1
Summary of MTBE Isotherm Data for Activated Carbons

Figure 4-2. MTBE isotherms for GAC.



Based on the isotherm data available for MTBE, coconut shell carbons appear to have a higher adsorptive capacity for MTBE than coal-based carbons. Figure 4-2 shows that for MTBE concentrations ranging from 1 µg/L to 1,000,000 µg/L, coconut shell carbon (U.S. Filter/Westates CC-602 or Calgon PCB) has consistently higher adsorption potential than the coal-based carbons. As shown on Table 4-1, the Freundlich adsorption capacity parameter, K_F , is 10 for Calgon's PCB coconut shell carbon. In contrast, the K_F values are 5.6 and 7.8 for Calgon's Filtrasorb 300 and Filtrasorb 600, both coal-based carbons. Calgon predicted carbon costs for removal of MTBE from pure water and found that using coconut shell carbon (PCB) was significantly more cost-effective than using coal-based carbon (Filtrasorb 300) for MTBE concentrations below 100 mg/L (McNamara, personal communication, 1998). U.S. Filter/Westates (Los Angeles, CA) also recommended coconut shell carbon based on extensive isotherm testing and in-house computer modeling of performance (Graham, personal communication, 1998). However, it is important to note that properties of GAC will vary from lot to lot, depending on the source material. It is likely that a given coconut shell carbon will vary in quality more than a coal-based carbon due to the less uniform nature of the source materials.

Another possible advantage to coconut shell GAC is that research has shown that it may be less vulnerable to immediate fouling effects due to NOM. Zimmer et al. (1988) tested three different GACs for adsorption of TCE in the presence of NOM. The results of the study showed that the microporous coconut carbon maintained a greater capacity for TCE up to NOM preloading times of 25 weeks. However, after about 25 to 50 weeks, all three of the carbons were measured to have approximately the same capacity for TCE. This research suggests that the adsorption of MTBE may be less likely to be impacted by NOM fouling if coconut shell carbon is used.

Calgon has recently introduced a high quality coal-based carbon (Filtrasorb 600) that reportedly performs very well for removal of MTBE. As shown on Table 4-1, the model-derived K_F -value for Filtrasorb 600 is 7.8. This GAC is produced by carefully screening particle sizes to maximize the quantity of micropore sizes that are most effective for adsorption of MTBE. This GAC is still in early stages of development and, as such, it does not yet have extensive use in full-scale operations.

For drinking water applications, the use of virgin carbon may be necessary in order to meet the low treatment goals for weakly adsorbing compounds like MTBE. As shown on Table 4-1, reactivated carbon (Calgon REACT) has a relatively low K_F value (i.e., 3.5) in comparison to those for virgin coal and coconut shell carbons. Although reactivated carbon is generally less expensive per pound, higher usage rates and associated carbon changeout requirements — and an increased risk of contaminant breakthrough — are expected to outweigh the unit cost advantages of using reactivated GAC for MTBE removal from drinking water.

Background Water Quality

Background water quality can significantly impact the removal efficiency for SOCs. As discussed in Section 4.2.2, NOM and the presence of competing SOCs can significantly reduce carbon capacity for MTBE (*note*: the impact of these variables are evaluated in detail in Section 4.3). In addition, other compounds, such as iron, manganese, and calcium carbonate, can precipitate in the carbon bed, changing the flow structure and limiting diffusion of organics into the micropores (Hall and Mumford, 1987). Because of undesirable background water quality, it may be necessary at some sites to pretreat influent water going into carbon systems in order to optimize treatment efficiency (see Section 4.2.1).

Process Flow Configuration and Operating Parameters

Proper design of a carbon adsorption system is critical for maximizing removal effectiveness. The primary design variables include empty bed contact time (EBCT) and process flow configuration. Other operating parameters include hydraulic loading and carbon bed depth.

The EBCT, calculated as bed volume (BV) divided by flow rate, is proportional to the residence time of water in a GAC vessel (residence time is determined by multiplying EBCT by the porosity of the GAC). The optimum EBCT for a system depends on the length of the MTZ, which is affected by numerous factors including carbon type, concentrations of SOCs present in the water, and background water quality. For many contaminants, municipal water treatment systems have EBCTs ranging from a few minutes to more than 10 minutes, with 15 minutes being a relatively safe upper limit for most groundwater contaminants (Lehr, 1991). However, for weakly adsorbing compounds such as MTBE, longer EBCTs (up to approximately 20 minutes) may be required. As mentioned previously, the optimum EBCT for specific water conditions can be evaluated by performing dynamic column tests with the water in question.

The configuration of a GAC system can be used to increase the volume of water treated per mass of carbon used (i.e., the “specific volume”). As discussed in Section 4.2.1, the use of multiple carbon beds in-series allows for more complete saturation of the lead bed(s) prior to changeout, with the secondary (lag) bed(s) in the series used as a polish or guarantee against total system breakthrough. The potential increase in specific volume due to in-series operation depends on the shape of the MTZ, which varies for different compounds (and different influent conditions). For TCE and PCE, in series operation was found to increase specific volume by 35 to 50 percent in comparison to single-bed operations (Hand et. al., 1989; Zimmer et. al., 1988). Of course the added cost for multiple beds is only justified if the savings in carbon consumption compensates for the higher capital and labor cost associated with the in-series operation.

Other operating parameters that will impact the effectiveness of carbon adsorption systems include hydraulic loading (i.e., linear flow rate) and bed depth. Typical hydraulic loadings

(calculated as volumetric flow rate divided by the cross-sectional area of the GAC vessel) for GAC systems range from 2 to 6 gpm/ft². Bed depth for a given vessel determines the overall volume of GAC available in the treatment zone. Deeper bed depths provide larger treatment zones and also enhance the flow distribution and water contact within the vessel.

Carbon Changeout Requirements

For weakly adsorbing compounds such as MTBE, frequent carbon changeouts may be required. This is a critical variable to account for in cost analyses and system design. As discussed previously, most drinking water treatment applications will require virgin carbon in order to achieve stringent effluent standards, particularly for weakly adsorbing compounds such as MTBE. Because of this, operations will include periodic replacement with virgin carbon and off-site regeneration or disposal of the spent carbon.

4.2.4 Carbon Vendors

Table 4-2 presents product information for the vendors that were contacted for this study, including:

- Barneby & Sutcliffe (Columbus, OH)
- Calgon Carbon Corporation (Pittsburgh, PA)
- Carbon Link Corporation (Columbus, OH)
- CARBTROL (Westport, CT)
- U.S. Filter/Westates (Los Angeles, CA)

Each of these vendors was solicited for data pertaining to promising carbons for MTBE treatment. The carbon products listed in Table 4-2 were those recommended by the responding vendors for treatment of MTBE. As shown, most of the vendors recommended coconut shell carbon. Also included are other carbon products (i.e., coal-based and reactivated coal-based) that have established isotherms for MTBE. It should be noted that several other carbon vendors were contacted for this study, but either did not respond or the response was too limited to include in this report.

The unit costs presented in Table 4-2 are based on price quotes given by the respective vendors in 1998. It is important to note that unit costs for GAC will vary as a function of quantity purchased and location.

4.2.5 Level of Development of Technology

Carbon adsorption is a very well-established technology with decades of practical experience and research. As such, this technology has well-defined methods and widely available

equipment. There currently are numerous systems operating for drinking water treatment for a variety of SOCs.

Knowledge and experience with carbon systems for treatment of MTBE are limited. As presented in Section 4.2.3, MTBE adsorption isotherms for several GACs are available. However, very little detailed information and data regarding full-scale performance, impact of NOM, and competitive adsorption effects specific to MTBE removal were encountered in the literature reviewed for this chapter.

Table 4-2
Vendor Information

Vendor Name	Address/Phone	Product Name	Carbon Source	Unit Cost
Barneby & Sutcliffe Corporation	P.O Box 2525 Columbus OH 43216 614-258-9501	207A	coal	-
		PC	coconut shell	\$1.10/lb
Calgon Carbon Corporation	P.O Box 717 Pittsburgh, PA 15230 412-787-6621	FS 300	coal	-
		PCB	coconut shell	\$1.25/lb
		REACT	reactivated coal GAC	-
		FS 600	coal	-
Carbon Link	4174 Fisher Road Columbus, OH 43228 800-858-6889	Microcarb SXO	coconut shell	-
CARBTRON	51 Riverside Avenue Westport, CT 06880 203-226-5642	CSL	coconut shell	\$0.65/lb
U.S.Filter/Westates	5375 South Boyle Ave. Los Angeles, CA 90058 213-277-4160	CC-602	coconut shell	\$1.35/lb ^A

Note:

^A Includes changeout labor and transport to local regeneration facility.

4.2.6 Technical Implementability

The implementation of carbon adsorption technology is expected to be straightforward because the methods and equipment are very well established. The following is a list of important issues related to implementation of GAC for MTBE removal:

- Many vendors supply GAC and treatment equipment. These vendors have extensive knowledge of installation and operation of carbon systems.
- Activated carbon technology can be implemented quickly due to its commercial availability. Site-specific bench- and/or pilot-scale testing is recommended for most treatment scenarios to allow for efficient design.
- Carbon adsorption systems are mechanically simple (i.e., very few moving parts).
- Pretreatment may be required (e.g., filtration, disinfection) to maximize removal efficiency and limit biofouling, though the presence of MTBE does not cause the need for any specialized pretreatment.
- Power costs are relatively minor; water flow can be gravity- or pump-driven.
- The primary maintenance requirements are associated with carbon changeouts (i.e., regeneration or disposal of spent carbon), which may be frequent due to MTBE characteristics. Periodic backflushing of carbon vessels may be required to remove accumulated biological growth.
- Careful monitoring of influent, midfluent, and effluent streams is required to assess system effectiveness and limit breakthrough events. In addition to monitoring for dissolved-phase MTBE, sampling plans need to include analyses for DOC, metals such as iron and manganese, and other site-specific variables that can cause carbon fouling and limit adsorption efficiency. Monitoring frequency should be based on site-specific conditions such as expected breakthrough time and regulatory requirements.

4.2.7 Permitting

The permitting of carbon adsorption systems is generally straightforward. Standard permitting required for any type of on-site treatment system may be needed as required by local regulatory authorities. No off-gas is produced from carbon adsorption systems therefore no air discharge permits are needed. This is a significant advantage in some areas. Permitting for drinking water applications is discussed in Chapter 1.

The carbon adsorption method does produce a significant amount of byproducts/residuals in the form of spent carbon. As such, transport and disposal permits may be needed. If spent carbon is regenerated onsite, permits for the regeneration facility will be required and may include air discharge permits. In general, permitting for application of carbon adsorption systems should be relatively simple in comparison to other technologies.

4.2.8 Current Usage of Technology

As described previously, GAC is a well-established and widely used technology for removing organic compounds from water. Unfortunately, documentation of full-scale applications for MTBE removal is limited. Creek and Davidson (1998) compiled carbon treatment data from six confidential MTBE point-source remediation sites (i.e., not drinking water treatment). Relevant results from these sites are presented as part of Table 4-3. This table also presents results of a recent application of carbon adsorption at the Arcadia well field in Santa Monica, California (for extracted water from an aquifer pump test; per Komex H₂O Science, 1998) and results of a well-documented drinking-water treatment case study in Rockaway Township, New Jersey (McKinnon and Dyksen, 1984).

As shown in Table 4-3, the performance of GAC for MTBE removal varied widely. For the eight sites reviewed, estimated carbon usage rates ranged from less than 0.4 lbs/1,000 gallons to over 20 lbs/1,000 gallons treated. At the two sites where carbon performed most effectively (i.e., lowest carbon usage rates), influent MTBE was less than approximately 50 µg/L, BTEX was not present, and other contaminants were present at low concentrations. Conversely, the two sites where GAC performed least effectively (i.e., highest carbon usage rates) had relatively high MTBE and BTEX concentrations. In addition to SOC concentrations, other variables that can affect usage rates include variations in GAC type and quality, background water quality, and system operating parameters (e.g., EBCT).

At the well-documented Rockaway site, coal-based carbon (Calgon Filtrasorb 300) was used for removal of MTBE, di-isopropyl ether (DIPE), and TCE (McKinnon and Dyksen, 1984). Based on carbon usage rates, the system at this site appears to have performed better for MTBE removal in comparison to most of the remediation sites reviewed. However, five complete carbon changeouts were required during the first 15 months of operations, causing the system operators to switch to air stripping as the primary treatment method.

For the five sites at which BTEX compounds were present, estimated usage rates ranged from 2 to 23 lbs/1,000 gallons. Influent MTBE concentrations at these five sites varied widely but were always greater than 270 µg/L. It is unknown what type of GAC was used for these systems.

For treatment of the extracted water from the pump test at the Arcadia well field, reactivated coal-based carbon (Calgon REACT) was used. As indicated on Table 4-3, the system performed very poorly, with an estimated usage rate of 4.9 lbs/1,000 gallons for an average influent concentration of 37 µg/L MTBE. This system used EBCTs ranging from 12 to 20 minutes, which is an adequate range for removal of most organic compounds. Based on the data available from this site, it appears that the primary cause of the poor performance is the type of carbon used (i.e., reactivated coal-based carbon).

Table 4-3
Estimated Carbon Usage Rate for Full-scale Systems

Site/Project Description	System Design	Influent MTBE (µg/L)	Other Contaminants Present	Estimated ^A Usage Rate (lb/1000 gal)
Aquifer Pump Test ^B , Arcadia Well Field, Municipal Drinking Water Supply, Santa Monica, California	2-15,000 lb vessels in series avg flow rate = 260 gpm EBCT = 12-20 minutes reactivated coal GAC Calgon REACT	9.5 - 43 average 37	none	4.9
Municipal Drinking Water Treatment System ^C , Rockaway Township, New Jersey	2-20,000 lb vessels in parallel avg flow rate = 800 gpm EBCT = 10 minutes bituminous coal GAC Calgon F-300	25 - 35	DIPE: 35-80 µg/L TCE	0.4
Service Station Remediation ^D , California	2-1,000 lb vessels in series avg flow rate = 1 gpm unknown carbon	15,000 - 23,000	BTEX present benzene: 23,000 µg/L	23
Leaking UST Remediation ^D , Vermont	3-600 lb vessels in series avg flow rate = 3 gpm unknown carbon	400 - 2,720	BTEX present benzene: 1,270 to 3,970 µg/L	13
Service Station Remediation ^D , Massachusetts	2 vessels in-series (2000 lb, 500 lb) avg flow rate = 5 gpm unknown carbon	1,100 - 5,000	BTEX present benzene: 1,200 to 2,100 µg/L	3
Service Station Remediation ^D , Massachusetts	2-300 lb vessels in series flow rate = 1-2 gpm unknown carbon	272 - 34,400	BTEX present benzene: 636 to 11,000 µg/L	2.3
Service Station Remediation ^D , New Jersey	GAC used for air stripper polish single 500 lb vessel avg flow rate = 0.5 gpm unknown carbon	<0.5 - 28 estimated	TBA: up to 630 µg/L	<0.4
Service Station Remediation ^D , Massachusetts	3-1,000 lb vessels in series avg flow rate = 21 gpm unknown carbon	up to 14,700	BTEX present	2.2

^A Carbon usage rates estimated based on approx. breakthrough time/changeout frequency and average flow rate. It is important to note that usage rates are affected by numerous variables including GAC type and quality, concentrations of SOCs, background water quality, and system operating parameters such as EBCT.

^B See Komex H2O Science, 1998.

^C See McKinnon and Dyksen, 1984.

^D See Creek and Davidson, 1998.

An example of desorption of MTBE occurred at a service station site in Massachusetts, where a 2 gpm GAC system (two 300-lb vessels in-series) was used to remove MTBE and BTEX from a contaminated groundwater source (Creek and Davidson, 1998). At this site, desorption caused effluent MTBE concentrations from the first carbon vessel to be higher than influent concentrations in 22 of 73 monthly sampling events. In addition, effluent MTBE concentrations from the second vessel exceeded influent concentrations 11 times over the 6 years of operation. Other examples of MTBE desorption are presented elsewhere (e.g., three field sites in API, 1990).

4.2.9 Summary of Ongoing Research

The University of California, Los Angeles (UCLA) and Calgon Carbon Corporation (Pittsburgh, PA) are currently performing parallel research projects with GAC and MTBE. The scopes of these projects, which are being performed under contract with the MTBE Research Partnership, are presented below. In the year 2000, the California MTBE Research Partnership plans to publish a report that summarizes the results of these studies in addition to revised computer modeling and cost analyses.

UCLA Research

On behalf of the California MTBE Research Partnership, UCLA is currently performing a series of RSSCTs using MTBE influent concentrations ranging from 20 µg/L to 2,000 µg/L. Two different coconut shell carbons are being tested, including Calgon's PCB carbon and U.S. Filter's CC-602 carbon. Three different background water sources are being tested to evaluate the effects of NOM on carbon adsorption. The waters being tested include groundwater from the Arcadia well field in the City of Santa Monica (California), groundwater from South Lake Tahoe Public Utility District (California), and water from Lake Perris, a drinking water source for the Metropolitan Water District (Los Angeles, California). For several of the tests, influent water is being spiked with BTEX compounds or TBA to quantify the effects of competitive adsorption. The results of this study are expected to be ready for publication in the year 2000.

Calgon Research

On behalf of the California MTBE Research Partnership, Calgon Carbon Corporation (Pittsburgh, PA) is performing a study that parallels the work being performed by UCLA. Calgon is running a series of column tests using PCB coconut shell carbon and the ACT method. Calgon is evaluating the same range of MTBE influent concentrations for the same source waters as the UCLA research. Several of the tests will incorporate spiking of BTEX compounds or TBA. Similar to the UCLA study, results of this project are expected in the year 2000.

4.3 Detailed Evaluation of GAC

This section presents a detailed evaluation of carbon adsorption technology for the treatment of MTBE-impacted water. The results of computer modeling and cost estimates for various MTBE treatment scenarios are presented in order to determine the most cost effective applications for GAC. The treatment scenarios considered for this evaluation were based on the following range of conditions:

- Flow Rates: 60 gpm, 600 gpm, and 6,000 gpm.
- Influent MTBE: 20 µg/L, 200 µg/L, and 2,000 µg/L.
- Effluent MTBE Targets: 20 µg/L, 5.0 µg/L, and 0.5 µg/L.

Section 4.3.1 presents a discussion of the computer modeling including a description of the AdDesignS model (Mertz et al. 1994) and the primary assumptions used. Detailed evaluations of flow rate (Section 4.3.2), removal efficiency (Section 4.3.3), and other characteristics (reliability, flexibility, and adaptability) that may influence the selection of GAC technology for MTBE removal (Section 4.3.4) are then presented. Section 4.3.5 presents results of the cost estimates based on carbon usage rates estimated from the computer modeling. Section 4.3.6 discusses sensitivity analyses performed for varying background water-quality conditions (NOM, BTEX loading) and other variables that impact the cost estimates.

4.3.1 Computer Modeling

In order to evaluate GAC under the range of conditions listed above, computer modeling was performed using the Michigan Technological University AdDesignS model (Mertz et al., 1994). This model consists of equilibrium and mass transfer models that can be used to simulate multi-component adsorption in fixed-bed adsorbers. The primary mass transfer model used for this study (the Pore Surface Diffusion Model, or PSDM) accounts for both surface diffusion and pore diffusion as intraparticle mass transfer mechanisms. These mechanisms are modeled using a series of well-established analytical equations, as presented in the program manual (Mertz et al., 1994). The PSDM can account for carbon fouling due to NOM and competitive effects due to the presence of multiple SOCs. The model accounts for the effects of competitive adsorption using the Ideal Adsorbed Solution Theory (Fritz and Schundler, 1981). The AdDesignS modeling package also includes several databases that allow the user to access compound physical properties, adsorbent properties, manufacturer fixed bed adsorber specifications, adsorption equilibrium properties, and kinetic properties. Further information regarding the computer model, which has recently become commercially available, is presented in the program manual (Mertz et al., 1994).

Assumptions Used in Computer Modeling

Numerous assumptions were required in order to utilize the AdDesignS computer model for predicting carbon performance. In addition to the primary assumptions regarding flow rates and concentrations of MTBE in the influent water, detailed assumptions of carbon characteristics, background water quality, etc., were used for the modeling. These assumptions are discussed below.

• Carbon Specifications

The carbon specifications for the modeling were selected in order to be representative of a high-grade coconut shell carbon. The specifications listed below match those of U.S. Filter/Westates CC-602 carbon, as presented in product literature.

Mesh size:	12x30
Apparent density:	0.495 g/cm ³
Porosity:	0.641
Particle radius:	0.0625 cm

• Freundlich Parameters

Although complete isotherm data for MTBE and BTEX with U.S. Filter/Westates CC-602 were available, adjusted parameters for MTBE were used to better reflect typical values found for coconut-based carbons. The values used in the modeling are as follows:

$$K_F = 11.0 \text{ (mg/g)(L/mg)}^n$$
$$n = 0.50$$

These selected parameters are mid-range for the values reported by the vendors for coconut-based carbons (see Table 4-1 for the range of Freundlich parameters). Based on the values reported by Barneby & Sutcliffe (Columbus, OH), U.S. Filter/Westates (Los Angeles, CA), and Calgon Carbon Corporation (Pittsburgh, PA), these values are considered representative of high-grade, virgin coconut shell carbon.

• Background Water Quality

The AdDesignS model can simulate time-dependent fouling that occurs due to the presence of NOM in the water being treated. The model has several waters available, representing a range of fouling effects. As recommended in the AdDesignS manual, Karlsruhe (West Germany) groundwater was used to represent the background water quality for the modeling scenarios. The moderate-level fouling parameters for this water were determined by preloading isotherm studies using Calgon F-100 carbon (equivalent to Filtrasorb 400). The

carbon fouling for MTBE was represented by the chemical correlation for “aromatic” compounds. Although it is recognized that MTBE is not an aromatic, none of the other chemical correlation types available describe MTBE and, based on an abbreviated sensitivity analysis performed for this study (not presented), the correlation for aromatic compounds gives conservative results.

- **Temperature**

The assumed temperature for the modeling was 20°C. Variations in GAC capacity can be expected for different temperatures. However, these variations are considered to be within the accuracy of the evaluations reported here.

- **Vessel Specifications**

The AdDesignS model has standard specifications available for several Carbonair fixed-bed adsorbers, including the following types: PC-20 (2,500 lb capacity), PC-28 (5,000 lb capacity), and PC-78 (20,000 lb capacity). For each of the flow rate/influent concentration scenarios, one of the vessel types listed above was selected for modeling based on flow rate capabilities and/or preliminary modeling. The vessel was then modeled at the appropriate flow rate/influent conditions in order to determine the carbon usage rate and breakthrough time for each of the effluent criteria (i.e., 20 µg/L, 5.0 µg/L, and 0.5 µg/L). The vessel specifications for each of the treatment scenarios are listed in Table 4-4.

- **EBCTs**

As shown on Table 4-4, the EBCTs for the modeling ranged from 10.7 minutes to 22.4 minutes. The effect of optimizing EBCTs was briefly evaluated by varying bed depths for vessels under specific flow rate/influent conditions. Based on the modeling, it was determined that decreases in carbon usage rate due to EBCT optimization were minor and within the accuracy of the evaluations. Therefore, standard EBCTs were selected for each flow rate/influent concentration scenario (constant regardless of the effluent treatment goal).

- **System Configuration**

For the higher flow rate scenarios (600 gpm and 6,000 gpm), it was necessary to assume in-parallel operations because of limited flow capacities of the carbon vessels available. For example, the maximum listed flow capacity of the Carbonair PC-78 is 550 gpm. Detailed assumptions for these scenarios are as follows:

600 gpm systems - two parallel lines of PC-78 vessels operating at 300 gpm per line.

6,000 gpm systems - 12 parallel lines of PC-78 vessels operating at 500 gpm per line.

Table 4-4
Results of AdDesignS Modeling

Flow Rate (gpm)	Influent (µg/L)	Effluent (µg/L)	Adsorber Type/ Specifications	EBCT (min)	MTZ Length (cm)	VTM (m ³ /kg)	Modeled Single-Vessel Breakthrough (days)	Modeled Single-Vessel Usage Rate (lb/1000gal)
60	2000	20	Carbonair PC-28 mass = 5300 lbs bed depth = 6.4 ft int. area = 28 ft ²	22.4	43.9	4.45	31.1	1.85
		5.0		22.4	43.9	4.41	30.8	1.87
		0.5		22.4	43.9	4.35	30.4	1.89
60	200	20	Carbonair PC-28 mass = 5300 lbs bed depth = 6.4 ft int. area = 28 ft ²	22.4	46.7	13.4	93.3	0.61
		5.0		22.4	46.7	12.8	89.6	0.64
		0.5		22.4	46.7	12.6	88.0	0.65
60	20	5.0	Carbonair PC-20 mass = 2500 lbs bed depth = 4.6 ft int. area = 20 ft ²	11.1	66.5	37.2	129	0.22
		0.5		11.1	66.5	31.6	110	0.26
600 ^A	2000	20	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	17.8	75.0	4.39	24.4	1.88
		5.0		17.8	75.0	4.35	24.1	1.89
		0.5		17.8	75.0	4.31	23.9	1.91
600 ^A	200	20	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	17.8	77.1	13.4	74.6	0.61
		5.0		17.8	77.1	12.8	70.9	0.64
		0.5		17.8	77.1	12.5	69.3	0.66
600 ^A	20	5.0	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	17.8	93	35.3	196	0.23
		0.5		17.8	93	31.4	174	0.26
6000 ^B	2000	20	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	10.7	117	4.08	13.6	2.02
		5.0		10.7	117	4.03	13.4	2.04
		0.5		10.7	117	3.97	13.2	2.07
6000 ^B	200	20	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	10.7	132	12.7	42.2	0.65
		5.0		10.7	132	11.6	38.4	0.71
		0.5		10.7	132	11.2	37.3	0.74
6000 ^B	20	5.0	Carbonair PC-78 mass = 20,000 lbs bed depth = 9.1 ft int. area = 78.5 ft ²	10.7	135	37.5	125	0.22
		0.5		10.7	135	31.9	106	0.26

^A Maximum flow capacity of PC-78 is 550 gpm; modeling assumed two vessels in-parallel at 300 gpm each.

^B Modeling assumed twelve vessels in-parallel at 500 gpm each.

EBCT = empty bed contact time.

MTZ = mass transfer zone.

VTM = water volume treated per carbon mass.

Results of Computer Modeling

Results of the computer modeling are summarized in Table 4-4. As shown on this table, the estimated carbon usage rate for single-vessel systems varies from approximately 0.2 lbs/1,000 gallons of water treated (lb/1,000 gallons) to approximately 2.1 lb/1,000 gallons, depending primarily on the influent concentrations and treatment goals. Detailed discussion of the results, as they pertain to flow rate (Section 4.3.2), removal efficiency (Section 4.3.3), and other characteristics (Section 4.3.4), is presented below.

Comparison of the modeling results to data from the full-scale applications presented in Table 4-3 indicates that the modeling predicts significantly better GAC performance than realized under field conditions. However, it is important to note that the modeling was performed assuming favorable conditions with respect to the presence of other SOCs. In contrast, most of the full-scale applications reviewed had BTEX or other organic compounds in the water. In addition, the modeling assumed use of high-grade coconut shell carbon, which is expected to perform better than the coal-based carbons used in many of the full-scale applications reviewed. It should also be noted that the results of the computer modeling for MTBE in natural water compare well to modeling results prepared by Calgon Carbon Corporation (Pittsburgh, PA) and CARBTROL (Westport, CT). In summary, the carbon usage rates predicted by AdDesignS are considered reasonable and accurate within the limitations of computer modeling.

4.3.2 Flow Rate

Table 4-4 presents predicted carbon usage rates for carbon adsorption systems ranging from 60 gpm to 6,000 gpm. As mentioned previously, the predicted usage rates for all the scenarios vary from approximately 0.2 lb/1,000 gallons to approximately 2.1 lbs/1,000 gallons. However, as shown in Table 4-4, the variation in usage rates is not impacted by system flow rate. For example, at an influent concentration of 2,000 $\mu\text{g/L}$ and treatment goal of 5.0 $\mu\text{g/L}$, the carbon usage rate varies from 1.9 lb/1,000 gallons (60 gpm system) to 2.0 lb/1,000 gallons (6,000 gpm system). The slight difference in usage rate noted here is attributable to variations in treatment system parameters such as EBCT and vessel configuration.

Carbon adsorption for MTBE treatment is not technically limited to any range of flow rates. However, in order to treat high flow rates within an acceptable range of EBCTs, it may be necessary to operate carbon beds in parallel, thereby reducing the flow rate that goes through a given bed. For weakly adsorbing compounds that require relatively long EBCTs, it may not be feasible to install high flow rate systems (i.e., capital costs for numerous parallel lines of several beds in-series may be prohibitive). Detailed discussion of cost-effectiveness as a function of system size is presented in Section 4.3.5.

It should be noted that the capacity of the largest, standard carbon vessel is 20,000 lbs. For modeling of the 600 gpm and 6,000 gpm systems, multiple parallel lines of 20,000-lb vessels were used.

4.3.3 Removal Efficiency

Carbon adsorption for MTBE treatment is not technically limited to a specific range of influent concentrations or treatment goals. For any given treatment scenario, removal of MTBE to a non-detectable concentration can be achieved if enough carbon and adequate contact time are used. However, as discussed below, carbon usage rates (hence cost effectiveness) are highly dependent on influent MTBE concentrations and, to a lesser degree, on effluent treatment goals.

Figure 4-3 and results of computer modeling presented in Table 4-4 show that carbon usage rates are closely related to influent MTBE concentrations. For influent concentrations of 20 µg/L MTBE (with no other SOCs and NOM fouling for typical groundwater), the estimated carbon usage rate for single-vessel systems varies from 0.2 to 0.3 lb/1,000 gallons. In contrast, for influent concentrations of 2,000 µg/L, the estimated carbon usage rate under the same conditions varies from approximately 1.9 to 2.1 lbs/1,000 gallons.

Table 4-4 shows that carbon usage rates of single-vessel systems are only mildly impacted by effluent treatment goals ranging from 20 µg/L to 0.5 µg/L. For influent MTBE of 20 µg/L, predicted usage rates vary from 0.22 lbs/1,000 gallons (effluent goal = 5.0 µg/L) to 0.26 lbs/1,000 gallons (effluent goal = 0.5 µg/L). For the higher influent concentrations (200 µg/L and 2,000 µg/L), the predicted usage rates vary by even less.

It is important to note that most carbon adsorption systems are operated such that effluent remains at non-detectable concentrations. This is accomplished by utilizing multiple beds in-series. As discussed in Section 4.2.1, the lead vessel is taken off-line and replaced with new carbon prior to breakthrough of the lag vessel(s). The lead vessel is then reinstalled as the lag vessel, ensuring that contaminant breakthrough of the overall system is avoided.

The carbon usage rate for treatment of MTBE is strongly dependent on the influent MTBE concentration (Figure 4-3). Although it is possible to operate multiple large carbon beds in-series to remove high MTBE concentrations, the carbon usage rate increases significantly with increasing influent MTBE concentrations. This suggests that GAC is more likely to be cost-effective in situations where influent MTBE concentrations are relatively low (e.g., as a polishing step).

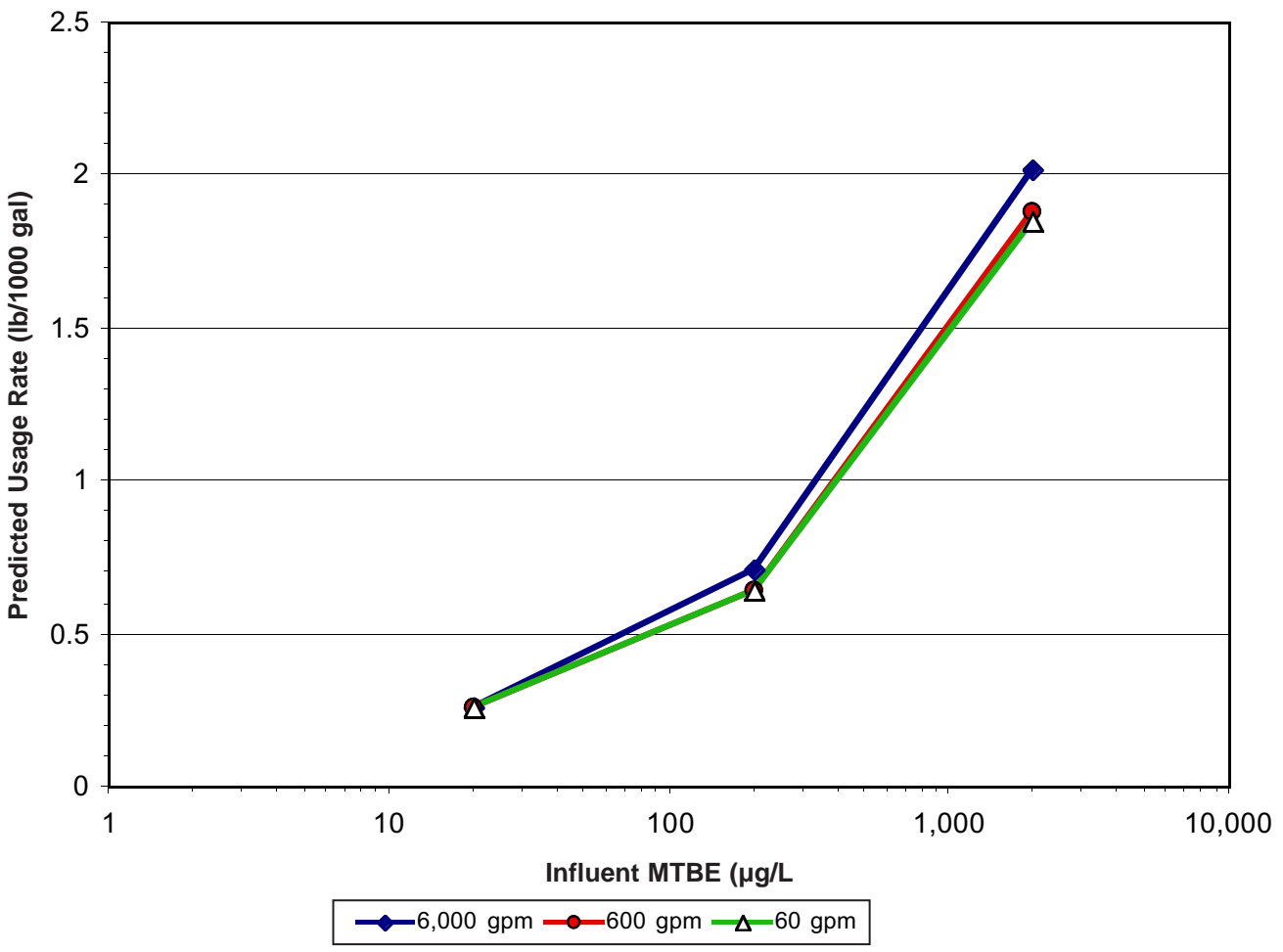


Figure 4-3. Predicted carbon usage rate vs. influent MTBE concentration. Single vessel; removal efficiency = 97.5 to 99 percent.

4.3.4 Other Characteristics

Reliability

The mechanical reliability of GAC technology is very high due to the simple nature of the systems. The primary concerns include pump O&M and tank/line leakage. Continuity of operations is typically very high because of the mechanical simplicity of the systems. Although carbon changeout requirements can cause delays in system operation, these stoppages should be predictable as long as influent water conditions are relatively consistent. Also, with the expected multiple vessel designs for MTBE applications, one vessel can usually be taken out of use for changeout while the system operates with the remaining vessels. The duration of a carbon changeout event typically is less than 1 day. The adsorption process is expected to be reliable for removal of MTBE as long as influent conditions are relatively consistent.

Flexibility

As discussed above, carbon adsorption technology can be implemented for any flow rate, though prohibitively high costs may be encountered at higher flow rates due to equipment size and O&M efforts associated with carbon changeout. Based on results of the adsorption modeling, the primary site factors that determine the effectiveness of GAC for MTBE removal include influent MTBE concentrations, background NOM, and the presence of other SOCs in the influent stream. Although systems can be designed for most influent conditions, the cost-effectiveness of carbon systems may be severely impacted by any one of these factors. This is further discussed in Section 4.3.5.

Adaptability

The adsorption process for MTBE is sensitive to the presence of other more readily adsorbed SOCs (e.g., xylene). If concentrations of other SOCs begin to increase in the influent water, competitive adsorption effects may reduce the removal efficiency for MTBE. Results of the sensitivity analyses (Section 4.3.6) for varying BTEX loads show that carbon usage rates increase significantly if competing SOCs are present. In comparison to natural water with only MTBE (at 20 µg/L), water with a modest additional load of 80 µg/L Total BTEX increases the predicted carbon usage rate by about 17 percent (see Table 4-5). Water with a higher additional load of 800 µg/L Total BTEX increases the predicted usage rate by greater than 50 percent. This conclusion is consistent with data from full-scale applications (see Table 4-3) that show high carbon usage rates at sites with both MTBE and BTEX present.

Arrival of other SOCs in the influent water can also cause an additional problem — the desorption of MTBE already adsorbed onto the carbon. Desorption of MTBE can occur due to displacement of MTBE molecules from GAC by preferentially adsorbed SOCs, resulting in higher effluent MTBE concentrations. Desorption can also occur from MTBE-loaded

carbon as influent MTBE concentrations of the extracted water naturally decrease (which changes the equilibrium of the solid-liquid partitioning). If the influent conditions change in either of these manners, desorption of MTBE can happen quickly. Because of the potential for desorption of the weakly adsorbed MTBE, frequent monitoring of influent, midfluent, and effluent waters is critical to assess the process effectiveness. The arrival of other more strongly adsorbed compounds in the influent stream should be taken as a warning that removal efficiency for influent MTBE will decrease and that desorption of previously adsorbed MTBE may begin very soon. Because of desorption and the effects of competitive adsorption, frequent sampling is critical to monitor system effectiveness and limit the potential for MTBE breakthrough.

The feasibility of carbon adsorption technology for MTBE is not expected to be impacted by regulatory requirements for drinking water. Based on the computer modeling, it appears that variation in effluent treatment goals from 0.5 µg/L to 20 µg/L has only a mild effect on the carbon usage rate (hence the cost-effectiveness). In addition, GAC treatment systems generally are operated such that no detectable contaminants are present in the effluent, particularly in drinking water applications. Because of this, changing regulatory requirements for MTBE effluent standards are not expected to significantly impact the feasibility of GAC for MTBE treatment.

Table 4-5
Results of AdDesignS Modeling for Sensitivity Analyses

Water Type ^A	VTM (m ³ /kg)	Modeled Single-Vessel Breakthrough (days)	Modeled Single-Vessel Usage Rate (lb/1000gal)	Predicted ^B Usage Rate (lb/1000gal)	Predicted ^B Vessel Life (days)	Predicted ^B Changeouts Per Year
Rhine River water (high fouling)	26.9	149	0.31	0.20	223	1.6
Karlsruhe ground water (moderate fouling)	35.3	196	0.23	0.16	294	1.2
Wausau ground water (low fouling)	40.0	223	0.21	0.14	334	1.1
Organic-Free Water	55.2	306	0.15	0.10	459	0.8

Moderate BTEX ^C each at 200 µg/L	22.6	125	0.36	0.24	187	1.9
Low BTEX ^C each at 20 µg/L	30.8	171	0.27	0.18	257	1.4
No BTEX ^C each at 0 µg/L	35.3	196	0.23	0.16	294	1.2
Organic-Free Water	55.2	306	0.15	0.10	459	0.8

EBCT - empty bed contact time

VTM - volume treated per carbon mass

^A Water types are those available in the AdDesignS model (Mertz et al., 1994); calculated values are based on time-dependent fouling correlations determined for coal-based GAC and other organic compounds (not MTBE).

^B Values estimated using assumed capacity increase of 50% due to in-series operation.

^C BTEX and MTBE in Karlsruhe groundwater. Breakthrough, VTM, and calculated usage rate based on equilibrium column modeling using the AdDesignS model.

Assumptions:

Influent MTBE = 20 mg/L; effluent contains no detectable MBTE (<0.5 mg/L).

Total flow rate = 600 gpm; two parallel lines with 2 vessels in series (300 gpm per line)

System type: Carbonair PC-78, bed mass = 20,000 lbs, bed depth = 9.1 ft

EBCT = 17.8 minutes

4.3.5 Cost Estimates

The purpose of this section is to present the estimated costs for carbon adsorption technology under a range of MTBE treatment scenarios. The cost estimates were developed for direct comparison with the estimated costs developed for air stripping (Chapter 2), advanced oxidation (Chapter 3), and resins (Chapter 5). Comparing the relative costs of the technologies allows for determination of the most promising applications for GAC. In addition to estimates for the range of MTBE treatment conditions discussed at the beginning of Section 4.3, cost estimates for several other scenarios are presented to investigate the cost impact sensitivity of varying degrees of NOM fouling and BTEX loading, and of different system design lifetimes.

Cost Estimating Methods and Assumptions

Feasibility-level cost estimates were developed using vendor-supplied costs and standardized assumptions for design/engineering, contractor overhead and profit (O&P), and contingency. Preliminary design configurations and results of computer modeling were used to predict carbon usage rates and vessel changeout frequencies. The primary assumptions used in development of the cost estimates include:

- Flow rates: 60 gpm, 600 gpm, and 6,000 gpm.
- Influent MTBE concentrations: 20 µg/L, 200 µg/L, and 2,000 µg/L.
- No detectable MTBE in effluent (<0.5 µg/L).
- Preliminary system designs established based on computer modeling and engineering judgement; in-series operation (three vessels in-series) assumed for all scenarios; number of parallel lines varies.
- Carbon usage rates and vessel breakthrough times determined by computer modeling using the AdDesignS model by Michigan Technical University (Tables 4-4, 4-6). It was assumed that adsorption efficiency is increased by 50 percent due to in-series operation (see *Note*).
- Modeling used NOM fouling correlations for groundwater from Karlsruhe, West Germany. This water type is considered to cause moderate carbon fouling and is recommended by the authors of AdDesignS as representative of typical groundwater conditions.
- Unit costs for carbon and system capital/installation costs based on 1998 vendor quotes from Calgon Carbon Corporation (Pittsburgh, PA), U.S. Filter/Westates (Los Angeles, CA), CARBTROL (Westport, CT), and Carbonair (New Hope, MN).
- Standard percentage rate assumptions for design/engineering, contractor overhead and profit, and contingency.
- Standard system design life of 30 years with seven percent interest rate for capital amortization.

Note: The adsorption capacities and breakthrough times calculated by the AdDesignS model for single-vessel systems were increased to account for the benefits of in-series operation. As mentioned previously, in-series operation was found to increase specific volume for compounds with long MTZs (i.e., TCE and PCE) by up to 50 percent in comparison to single-bed operations (Hand et. al., 1989; Zimmer et. al., 1988). Preliminary results of bench-scale column testing by UCLA (Suffet, personal communication, 1999) show that MTBE adsorption requires a relatively long MTZ. These results indicate that in-series operation is capable of significantly increasing specific GAC volume for MTBE. As presented in Table 4-6, the single-vessel breakthrough times predicted were increased by 50 percent for in-series operation with effluent having no detectable MTBE (<0.5 µg/L). Similarly, the volume treated per carbon mass was increased by 50 percent. These assumptions are supported by field experience and industry expertise (Graham, personal communication, 1998).

Table 4-7 presents summaries of the cost evaluations for the MTBE treatment scenarios. Further details of methods and assumptions used for the cost estimates are presented in Appendix 4A. Individual costs for each of the scenarios are presented in a series of spreadsheets (Table 4A-3 in Appendix 4A). Discussions regarding critical parameters that impact the costs for GAC are presented below.

Effect of Flow Rate

Figure 4-4 shows the relationship of unit treatment cost (i.e., \$/1,000 gallons) vs. system flow capacity for varying influent MTBE concentrations. Based on this figure and the costs presented in Table 4-7, it is clear that there is economy of scale, particularly for the lower range of flow rates (600 gpm and lower). In this lower range, unit costs decrease significantly as system flow capacity increases. However, the differences in estimated unit costs for the 600 gpm and the 6,000 gpm systems are small to negligible. This lack of economy of scale is primarily because the largest standard carbon vessels are designed for maximum flow rates of approximately 500 to 600 gpm. Flow rates above this level are handled by operating multiple vessels in parallel; hence, there are no significant capital savings for higher flow rates. In addition, as discussed in Section 4.3.2, carbon usage rates (lbs/1,000 gallons) are not impacted by flow rate; as such, O&M costs (and unit treatment costs) increase proportionally with flow rate.

Table 4-6

Predicted Carbon Usage Rates and Breakthrough Times Using In-series Operation

System Flow Rate = 60 gpm; single vessel EBCT = 22.4 minutes

Influent MTBE (µg/L)	Modeled		Predicted ^B Usage Rate (lb/1000gal)	Predicted ^B Vessel Life (days)	Predicted ^B Changeouts Per Year
	Single-Vessel Breakthrough ^A (days)	Single-Vessel Usage Rate ^A (lb/1000gal)			
2000	30.8	1.87	1.25	46	7.9
200	89.6	0.64	0.43	134	2.7
20 ^C	129	0.22	0.15	194	1.9

System Flow Rate = 600 gpm; single vessel EBCT = 17.8 minutes

Influent MTBE (µg/L)	Modeled		Predicted ^B Usage Rate (lb/1000gal)	Predicted ^B Vessel Life (days)	Predicted ^B Changeouts Per Year
	Single-Vessel Breakthrough ^A (days)	Single-Vessel Usage Rate ^A (lb/1000gal)			
2000	24.1	1.89	1.26	36	10.1
200	70.9	0.64	0.43	106	3.4
20	196	0.23	0.15	294	1.2

System Flow Rate = 6000 gpm; single vessel EBCT = 10.7 minutes

Influent MTBE (µg/L)	Modeled		Predicted ^B Usage Rate (lb/1000gal)	Predicted ^B Vessel Life (days)	Predicted ^B Changeouts Per Year
	Single-Vessel Breakthrough ^A (days)	Single-Vessel Usage Rate ^A (lb/1000gal)			
2000	13.4	2.04	1.36	20	18.2
200	38.4	0.71	0.47	58	6.3
20	125	0.22	0.15	188	1.9

^A Results of AdDesignS computer model for effluent containing 5 mg/L MTBE.

^B Values estimated using assumed capacity increase of 50% due to in-series operation.

^C For this 60 gpm scenario (20 mg/L influent), smaller GAC vessels used with EBCT = 11.1 minutes.

Table 4-7
Summary of Cost Estimates

Flow Rate (gpm)	System Configuration	Influent MTBE (µg/L)	Capital Cost (\$)	Annual O&M (\$)	Total Annual Cost (\$)	Unit Cost (\$/1,000 gal)
60	2500 lb beds, 3 in series	20	\$150,000	\$61,000	\$73,000	\$2.30
60	5000 lb beds, 3 in series	200	\$234,000	\$79,000	\$98,000	\$2.92
60	5000 lb beds, 3 in series	2,000	\$234,000	\$127,000	\$146,000	\$4.43
<hr/>						
600	20,000 lb beds, 2 parallel lines, 3 in series	20	\$1,019,000	\$161,000	\$243,000	\$0.77
600	20,000 lb beds, 2 parallel lines, 3 in series	200	\$1,019,000	\$282,000	\$364,000	\$1.15
600	20,000 lb beds, 2 parallel lines, 3 in series	2,000	\$1,019,000	\$665,000	\$747,000	\$2.37
<hr/>						
6,000	20,000 lb beds, 12 parallel lines, 3 in series	20	\$5,979,000	\$1,091,000	\$1,573,000	\$0.50
6,000	20,000 lb beds, 12 parallel lines, 3 in series	200	\$5,979,000	\$2,575,000	\$3,056,000	\$0.97
6,000	20,000 lb beds, 12 parallel lines, 3 in series	2,000	\$5,979,000	\$6,526,000	\$7,008,000	\$2.22

Note:

1. Cost estimates developed from results of adsorption modeling using the AdDesignS model (Mertz et al., 1994).
2. Detailed cost estimates and assumptions presented in Appendix 4A.
3. Cost estimates developed for in-series operation; effluent contains no detectable MTBE (<0.5 mg/L).

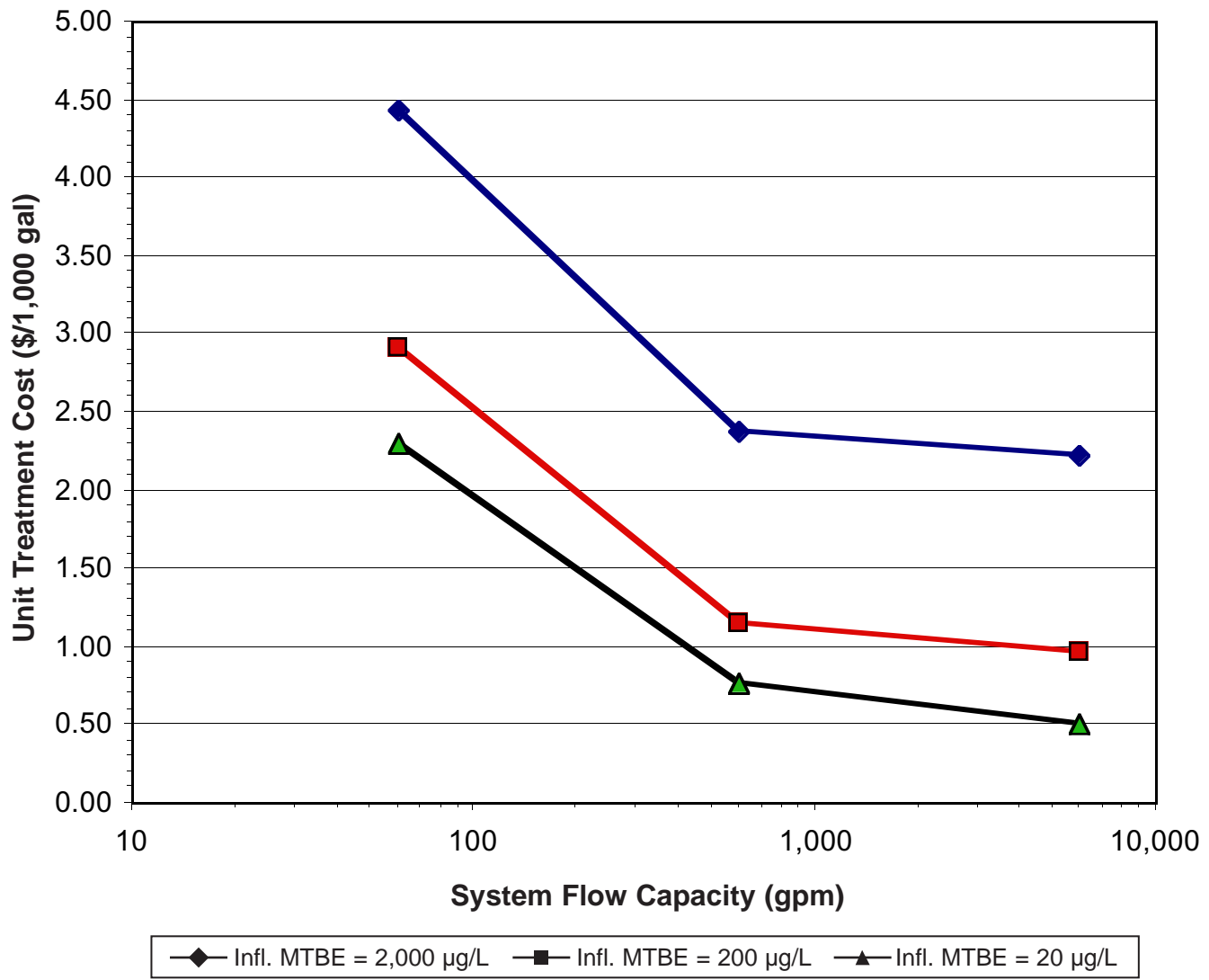


Figure 4-4. Estimated unit treatment cost vs. system flow capacity for in-series operation.

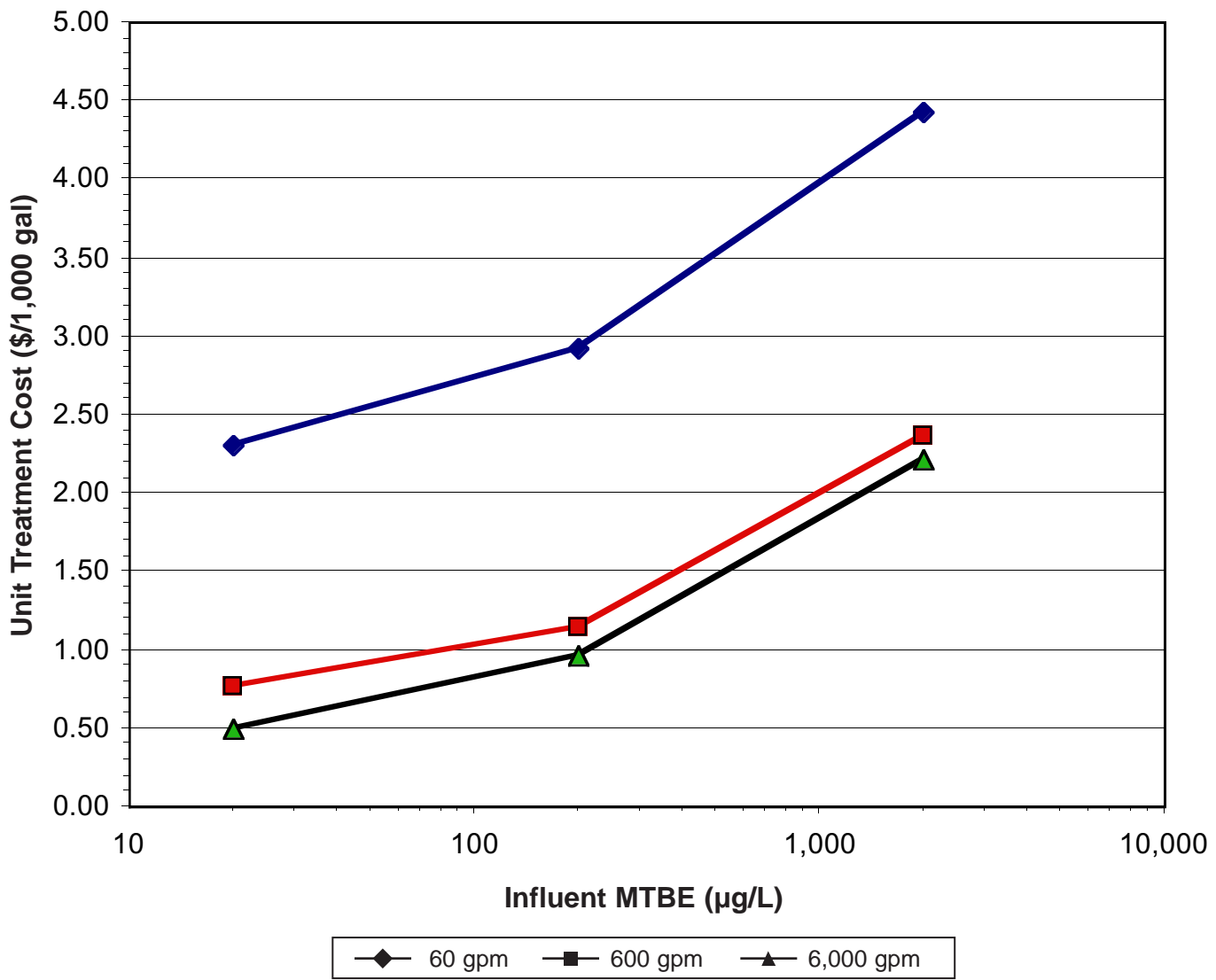


Figure 4-5. Estimated unit treatment cost vs. influent MTBE concentration for in-series operation.

Effect of Influent MTBE Concentration

Figure 4-5 presents unit treatment cost vs. influent MTBE concentration for in-series operation. This figure illustrates that unit costs increase significantly with increasing influent concentrations. As shown on Table 4-7, for the 60-gpm systems, the estimated unit costs vary from \$2.30/1,000 gallons to \$4.43/1,000 gallons. For the 600-gpm and 6,000-gpm systems, estimated unit costs vary from \$0.77 to \$2.37/1,000 gallons, and from \$0.50 to \$2.22/1,000 gallons, respectively.

Effect of Removal Efficiency

As discussed previously, computer modeling indicates that effluent treatment goals between 20 µg/L and 0.5 µg/L result in minimally different carbon usage rates. Therefore, it appears that removal efficiency will have only a minor impact on treatment costs for a single-vessel system. Because in-series operation with no detectable MTBE in the effluent were assumed for the cost estimates, no further conclusions can be drawn regarding cost effectiveness for varying removal efficiencies.

4.3.6 Sensitivity Analyses

Sensitivity analyses were performed for several critical parameters using the AdDesignS computer model and the cost estimating methods described in Section 4.3.5 and Appendix 4A. The parameters evaluated using the adsorption model include NOM and BTEX loading (Table 4-8). These parameters were varied to determine their relative impact on carbon usage rates and cost effectiveness. In addition, system design life was varied to evaluate impacts to unit treatment costs. This section summarizes assumptions used in the sensitivity analyses and presents discussions of the modeling results (Table 4-5) and associated cost estimates (Table 4-8).

Assumptions Used in Sensitivity Analyses

All sensitivity analyses were performed for a single treatment scenario (influent MTBE of 20 µg/L, flow rate of 600 gpm) using the same general assumptions discussed in Section 4.3.1. Brief discussions of additional assumptions used in these sensitivity analyses are presented on the following pages.

Table 4-8
Cost Estimates for Sensitivity Analyses

Sensitivity Parameter	Changeouts per Year ^A	Capital Cost (\$)	Annual O&M (\$)	Total Annual Cost (\$)	Unit Cost (\$/1,000 gal)
NOM Fouling					
Wausau ground water (low fouling)	1.1	\$1,019,000	\$156,000	\$238,000	\$0.75
Karlsruhe ground water (moderate fouling)	1.2	\$1,019,000	\$161,000	\$243,000	\$0.77
Rhine River water (high fouling)	1.6	\$1,019,000	\$183,000	\$265,000	\$0.84
BTEX Load					
No BTEX present each at 0 µg/L	1.2	\$1,019,000	\$161,000	\$243,000	\$0.77
Low BTEX each at 20 µg/L	1.4	\$1,019,000	\$172,000	\$254,000	\$0.81
Moderate BTEX each at 200 µg/L	1.9	\$1,019,000	\$199,000	\$281,000	\$0.89
Design Life					
2 years	1.2	\$1,019,000	\$161,000	\$701,000	\$2.22
10 years	1.2	\$1,019,000	\$161,000	\$287,000	\$0.91
30 years	1.2	\$1,019,000	\$161,000	\$243,000	\$0.77

^A Predicted based on AdDesignS modeling; see Table 4-5.

Primary Assumptions for cost estimates given above:

- 600 gpm systems
- 2 parallel lines of 3 beds in-series
- Influent MTBE = 20 mg/L
- Effluent contains no detectable MTBE (<0.5 mg/L)
- NOM fouling for Karlsruhe groundwater unless otherwise noted.

NOM

The impact of varying background NOM in water was evaluated by changing the carbon fouling parameters during the adsorption modeling. The AdDesignS model has fouling correlation data for several different water types with varying degrees of fouling potential. The different water types used in the modeling, and their relative fouling effects, are as follows:

Surface water from Rhine River, Germany	High fouling
Groundwater from Karlsruhe, Germany	Moderate fouling
Groundwater from Wausau, WI	Low fouling

As discussed in Section 4.3.1, groundwater from Karlsruhe, West Germany was used to model the majority of the treatment scenarios because it is considered representative of typical groundwater. Crittenden et al. (1989) report further details on the characteristics of these waters.

Presence of Other SOCs

Two different scenarios were modeled to evaluate the effects of competitive adsorption from other SOCs. The compounds evaluated, and their concentrations, are as follows:

BTEX at 20 µg/L each (Total BTEX = 80 µg/L).

BTEX at 200 µg/L each (Total BTEX = 800 µg/L).

The assumed Freundlich isotherm parameters used for the BTEX compounds were those reported by U.S. Filter (Los Angeles, CA) for CC-602 GAC (Graham, personal communication, 1998). These values are as follows:

Benzene: $K_F = 50 \text{ (mg/g)(L/mg)}^n$
 $n = 0.53$

Toluene: $K_F = 97 \text{ (mg/g)(L/mg)}^n$
 $n = 0.43$

Ethylbenzene: $K_F = 163 \text{ (mg/g)(L/mg)}^n$
 $n = 0.41$

Xylene: $K_F = 184 \text{ (mg/g)(L/mg)}^n$
 $n = 0.47$

System Design Life

Cost estimates for three system design life durations (2 years, 10 years, and 30 years) were completed to evaluate the effects on unit treatment costs. Cost estimates were prepared by amortizing capital costs over each of these different system design periods.

Impact of NOM

Results of computer modeling and cost estimates using the predicted carbon usage rates for the three different water types are summarized in Tables 4-5 and 4-8. These results show that the carbon usage rate for MTBE removal varies by as much as approximately 50 percent, depending on the degree of NOM fouling (Table 4-5). This difference in carbon usage rate results in differences in unit treatment costs of up to 12 percent for in-series operation under the assumed treatment conditions. For example, Table 4-8 shows that estimated unit treatment costs vary from \$0.75/1,000 gallons to \$0.84/1,000 gallons for water with low and high fouling, respectively.

Impact of BTEX Loading

The impact of BTEX loading on the adsorption of MTBE was investigated by varying influent BTEX concentrations from Total BTEX loads of 80 µg/L (each of the four components at 20 µg/L) to 800 µg/L (each of the four components at 200 µg/L). Results of adsorption modeling and the cost estimates using the predicted carbon usage rates for the BTEX loading scenarios are summarized in Tables 4-5 and 4-8. The adsorption modeling predicts that the carbon usage rate is increased by more than 50 percent if Total BTEX loads of 800 µg/L are added to the water being treated. This difference in carbon usage rate results in increased unit treatment costs of up to 16 percent. Table 4-8 shows that predicted unit costs range from \$0.77/1,000 gallons to \$0.89/1,000 gallons as Total BTEX loads increase from non-detect up to 800 µg/L (for the assumed treatment scenario used in the sensitivity analysis).

Impact of System Design Life

In order to investigate how the assumed design life affects unit treatment costs, the assumed design life was varied between 2 years and 30 years. Using the selected treatment scenario discussed above (i.e., 600 gpm, 20 µg/L MTBE influent, 0.5 µg/L effluent), unit costs were estimated for 2-year and 10-year design periods, in addition to the 30-year period used for the majority of the estimates. The results of these estimates, which are presented in Table 4-8 and Appendix 4A, indicate that the unit treatment cost increases by almost 200 percent when design period is changed from 30 years to 2 years. Specifically, as shown on Table 4-8, predicted unit costs increase from \$0.77/1,000 gallons for a 30-year design life to \$2.22/1,000 gallons for a 2-year design life. Although this may seem to be a dramatic change, it is less than the unit cost increases expected for more capital-intensive technologies such as resins and AOP. Because the total annual costs for GAC systems are highly dependent on O&M costs, the assumed system design life does not impact the unit treatment cost as much as for higher capital technologies. As such, expected project duration is an important variable to consider when comparing costs of treatment technologies.

4.4 Conclusions and Research Recommendations

4.4.1 Conclusions

Based on the literature review, the computer modeling, and the cost analyses, conclusions regarding the feasibility of GAC for aqueous-phase treatment of MTBE are as follows:

1. As indicated by isotherm data (Table 4-1 and Figure 4-2), activated carbons from different source materials have a wide range of adsorption capacities for MTBE. Coconut shell carbon, which often has a slightly higher cost per pound, generally has better adsorption characteristics for MTBE than coal-based carbon. However, carbon quality is more difficult to control for coconut shell carbon than coal-based carbon due to the heterogeneity of the source material (coconut husks).
2. As shown on Table 4-4 and Figure 4-5, carbon usage rates and unit treatment costs are highly dependent on influent MTBE concentrations. As influent MTBE concentrations are increased, carbon usage rate and unit treatment costs increase significantly. This suggests that GAC is most likely to be cost-effective for removal of relatively low MTBE concentrations (e.g., less than 2,000 $\mu\text{g/L}$).
3. Carbon usage rates and unit treatment costs are highly dependent on the characteristics of the background water. As shown on Table 4-5, computer modeling predicts that carbon fouling from NOM can cause up to 50 percent increases in carbon usage rates for removal of low MTBE concentrations (i.e., 20 $\mu\text{g/L}$). Due to this sensitivity, GAC is more likely to be cost-effective for waters that are relatively clean with respect to NOM (e.g., some groundwaters). Research suggests that there is no single water quality parameter (e.g., DOC) that is clearly indicative of fouling potential. As such, isotherm and column testing on site-specific waters should be performed to predict fouling effects on carbon usage rates.
4. Carbon usage rates and unit treatment costs are also highly dependent on the presence of other SOCs. Adsorption modeling shows that moderate loads of Total BTEX (800 $\mu\text{g/L}$) can cause greater than 50 percent increases in carbon usage rates for GAC systems treating influent with 20 $\mu\text{g/L}$ MTBE.

4.4.2 Recommendations for Future Research

Based on the literature review, the computer modeling, and the cost analyses, there are several topics that require more research before GAC usage for MTBE removal from drinking water is fully understood. These topics are: 1) reproducible isotherms for different GAC types; 2) dynamic GAC adsorption capacities for different background water qualities; and, 3) full-scale performance of GAC under field conditions.

Reproducible Isotherms

Although there are MTBE isotherms available for various GAC products, these isotherms were produced using a variety of laboratory testing conditions (e.g., temperatures, background waters). As such, comparisons between these isotherms are of limited value. In addition, based on documented use of GAC for removing MTBE, performance of different GAC types varies widely (Table 4-3). For these reasons, it is recommended that standardized testing be performed to obtain comparable and reproducible isotherms for a range of GAC types, including high-grade coconut shell carbon and coal-based carbon. Prior to testing, consideration should be given to the variability in specific GAC products in order to ensure that isotherm data are developed for representative samples of GAC.

Dynamic GAC Adsorption Capacities

Dynamic column tests should be performed to determine GAC usage rates, optimum EBCTs, and other operating parameters for a variety of background-water conditions and GAC types (i.e., coconut shell and coal-based). Several waters with differing NOM characteristics (e.g., surface water and groundwater) should be tested under a range of MTBE influent concentrations to allow for better prediction of full-scale performance of GAC for removing MTBE. In addition, more information is needed on MTBE desorption from GAC systems and on the competitive effects of other SOCs (e.g., BTEX, TBA) in the impacted water. Dynamic column testing is currently being performed by UCLA and Calgon Carbon Corporation to investigate several of the issues listed above.

Full-scale Performance

To date, there are limited data regarding the successful use of full-scale GAC systems for removing MTBE from drinking water. As such, it is recommended that GAC performance for MTBE removal be evaluated under full-scale, field conditions. Collection of cost and operational data, including long-term NOM fouling effects and pretreatment requirements, will allow for meaningful comparison with results of dynamic column testing and cost analyses.

4.5 References

- American Petroleum Institute, 1990. "A Compilation of Field-Collected Cost And Treatment Effectiveness Data For The Removal of Dissolved Gasoline Components From Groundwater," API Document 4525, November.
- American Petroleum Institute, 1994. "Transport and Fate of Dissolved Methanol, Methyl-Tertiary-Butyl-Ether, and Monoaromatic Hydrocarbons in a Shallow, Sand Aquifer." API Publication 4601.
- American Society for Testing and Materials, 1996. "Standard Practice For Determination of Adsorptive Capacity of Activated Carbon By A Micro-Isotherm Technique For Adsorbates At ppb Concentrations," *ASTM Designation D 5919-96*.
- Creek, D.N., and Davidson, J.M., 1998. "The Performance and Cost of MTBE Remediation Technologies," *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals In Ground Water; Prevention, Detection, and Remediation Conference*, November, 1998, pp.560-568.
- Crittenden, J.C., Reddy, P.S., Aroro, H, Trynoski, J., Hand, D.W., Perram, D.L., and Summers, R.S., 1991. "Predicting GAC Performance With Rapid Small-Scale Column Tests," *Journal AWWA*, January, pp. 77-87.
- Crittenden, J.C., Reddy, P.S., Hand, D.W., and Arora, H., 1989. "Prediction of GAC Performance Using Rapid Small-Scale Column Tests," *AWWA Research Foundation*, September.
- Dobbs, R.A., and Cohen, J.H., 1980. "Carbon Adsorption Isotherms For Toxic Organics," *EPA Document EPA-600/8-80-023*, April.
- Fritz, W. and Schundler, E.U., 1981. "Competitive Adsorption of Two Dissolved Organics Onto Activated Carbon," *Chemical Engineering Science*, Vol. 36, No. 3.
- Graham, J., 1998. Technical director for activated carbon, U.S. Filter/Westates, Los Angeles, CA. Personal communication with D. Creek, Alpine Environmental, Inc., Fort Collins, CO. May 1998.
- Graham, J., 1999. Technical director for activated carbon, U.S. Filter/Westates, Los Angeles, CA. Personal communication with D. Creek, Alpine Environmental, Inc., Fort Collins, CO. October 1999.
- Hall, D.W. and Mumford, R.L., 1987. "Interim Private Water Well Remediation Using Carbon Adsorption," *Ground Water Monitoring Review*, p. 77-83.

Hand, D., 1998. Senior Research Engineer, Environmental Engineering Center for Water and Waste Management, Michigan Technological University, Houghton, MI. Personal communication with D. Creek, Alpine Environmental, Inc., Fort Collins, CO. May 1998.

Hand, D.W., Crittenden, J.C., Arora, H., Miller, J.M., and Lykins, B.W. Jr., 1989. "Designing Fixed-Bed Adsorbers to Remove Mixtures of Organics," *Journal AWWA*, p. 67-77.

Komex H2O Science, 1997. "Literature Review of Technologies for Treatment of Methyl Tertiary Butyl Ether (MTBE) in Drinking Water." Prepared for City of Santa Monica, CA. April 1997.

Komex H2O Science, 1998. Tom Browne, personal Communication with D.Creek, Alpine Environmental, Inc. Fort Collins, CO. May 1998.

Kong, E.J. and DiGiano, F.A., 1986. "Competitive Adsorption Among VOCs on Activated Carbon and Carbonaceous Resin," *Journal AWWA*, April, p. 181-188.

Lehr, J.H., 1991. "Granular-Activated Carbon (GAC): Everyone Knows of It, Few Understand It," *Ground Water Monitoring Review*, Vol. XI, No. 4, p. 5-8.

Malley, J.P., Eliason, P.A., Wagler, J.L., 1993. "Point-of-Entry Treatment of Petroleum Contaminated Water Supplies," *Water Environment Research*, Vol. 65, No. 2, p. 119-128.

McKinnon, R.J. and Dyksen, J.E., 1984. "Removing Organics From Groundwater Through Aeration Plus GAC," *Journal AWWA*, May, p. 42-47.

McNamara, D., 1998. Carbon application specialist, Calgon Carbon Corporation, Pittsburgh, PA. Presentation to California MTBE Research Partnership. February, 1998.

Mertz, K.A., Gobin, F., Hand, D.W., Hokanson, D.R., and Crittenden, J.C., 1994. "Adsorption Design Software for Windows (AdDesignS)," Michigan Technical University.

Megonnell, N., 1999. Carbon specialist, Calgon Carbon Corporation, Pittsburgh, PA. Submittal to California MTBE Research Partnership, October, 1999.

Munz, C., Walther, J-L, Baldauf, G., Boller, M., and Bland, R., 1990. "Evaluating Layered Upflow Carbon Adsorption For The Removal of Trace Organic Contaminants," *Journal AWWA*, March, p. 63-76.

Nyer, E., 1992. *Groundwater Treatment Technology*, Van Nostrand Reinhold Press, New York.

Randtke, S.J. and Snoeyink, V.L., 1983. "Evaluating GAC Adsorptive Capacity," *Journal AWWA*, August, p. 406-413.

Semmens, M.J., Norgaard, G.E., Hohenstein, G., and Staples, A.B., 1986. "Influence of pH on the Removal of Organics by Granular Activated Carbon," *Journal AWWA*, May, p. 89-93.

Snoeyink, V.L., 1990. "Adsorption of Organic Compounds," *Water Quality and Treatment. American Water Works Association*. Editor: F.W. Pontius. McGraw-Hill, New York, 1990.

Sontheimer, H., Crittenden, J.C., and Summers, S., 1988. *Activated Carbon For Water Treatment*, DVGW-Forschungsstelle & AWWA Research Foundation.

Speth, T.F. and Miltner, R.J., 1990. "Technical Note: Adsorption Capacity of GAC for Synthetic Organics," *Journal AWWA*, February, p. 72-75.

Speth, T.F., 1991. "Evaluating Capacities of GAC Preloaded with Natural Water," *Journal of Environmental Engineering*, January/February, Vol. 117, No. 1., p. 66-79.

Stenzel, M.H. and Merz, W.J., 1988. "Use of Carbon Adsorption Processes In Groundwater Treatment," *Proceedings of American Institute of Chemical Engineers, 1988 Summer National Meeting*, Denver, Colorado, August, Paper No. 6c.

Suffet, I. H., 1999. Personal communication with California MTBE Research Partnership, June, 1999.

Summers, R.S., Haist, B., Koehler, J., Ritz, J., Zimmer, G., and Sontheimer, H., 1989. "The Influence of Background Organic Matter on GAC Adsorption," *Journal AWWA*, May, p. 66-74.

Weber, W.J. Jr., *Physicochemical Processes for Water Quality Control*. Wiley Interscience, John Wiley and Sons Inc., New York, NY. 1972.

Zimmer, G., Crittenden, J.C., Sontheimer, H., and Hand, D., 1988. "Design Considerations For Fixed-Bed Adsorbers That Remove Synthetic Organic Chemicals In The Presence of Natural Organic Matter," *Proceedings of AWWA Conference*, Orlando, Florida, June, p. 210-219.

