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EPA

Engineering Bulletin
Granular Activated Carbon Treatment

Purpose

Section 121(b) of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) mandates the Environmental Protection Agency (EPA) to select remedies that "utilize permanent solutions and alternative treatment technologies or resource recovery technologies to the maximum extent practicable" and to prefer remedial actions in which treatment "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants as a principal element." The Engineering Bulletins are a series of documents that summarize the latest information available on selected treatment and site remediation technologies and related issues. They provide summaries of and references for the latest information to help remedial project managers, on-scene coordinators, contractors, and other site cleanup managers understand the type of data and site characteristics needed to evaluate a technology for potential applicability to their Superfund or other hazardous waste site. Those documents that describe individual treatment technologies focus on remedial investigation scoping needs. Addenda will be issued periodically to update the original bulletins.

Abstract

Granular activated carbon (GAC) treatment is a physicochemical process that removes a wide variety of contaminants by adsorbing them from liquid and gas streams [1, p. 6-3]. This treatment is most commonly used to separate organic contaminants from water or air; however, it can be used to remove a limited number of inorganic contaminants [2, p. 5-17]. In most cases, the contaminants are collected in concentrated form on the GAC, and further treatment is required.

The contaminant (adsorbate) adsorbs to the surfaces of the microporous carbon granules until the GAC becomes exhausted. The GAC may then be either reactivated, regenerated, or discarded. The reactivation process destroys most contaminants. In some cases, spent GAC can be regenerated, typically using steam to desorb and collect concentrated contaminants for further treatment. If GAC is to be discarded, it may have to be handled as a hazardous waste.

Site-specific treatability studies are generally necessary to document the applicability and potential performance of a GAC system. This bulletin provides information on the technology applicability, technology limitations, a technology description, the types of residuals produced, site requirements, latest performance data, status of the technology, and sources for further information.

Technology Applicability

Adsorption by activated carbon has a long history of use as a treatment for municipal, industrial, and hazardous waste streams. The concepts, theory, and engineering aspects of the technology are well developed [3]. It is a proven technology with documented performance data. GAC is a relatively nonspecific adsorbent and is effective for removing many organic and some inorganic contaminants from liquid and gaseous streams [4].

The effectiveness of GAC as an adsorbent for general contaminant groups is shown in Table 1. Examples of constituents within contaminant groups are provided in "Technology Screening Guide for Treatment of CERCLA Soils and Sludges" [5]. This table is based on current available information or professional judgment when no information was available. The proven effectiveness of the technology for a particular site or waste does not ensure that it will be effective at all sites or that the treatment efficiency achieved will be acceptable at other sites. For the ratings used for this table, demonstrated effectiveness means that, at some scale, treatability was tested to show that, for that particular contaminant and matrix, the technology was effective. The ratings of potential effectiveness and no expected effectiveness are based upon expert judgement. Where potential effectiveness is indicated, the technology is believed capable of successfully treating the contaminant group in a particular matrix. When the technology is not applicable or will probably not work for a particular combination of contaminant group and matrix, a no-expected-effectiveness rating is given.

The effectiveness of GAC is related to the chemical composition and molecular structure of the contaminant. Or-

* [reference number, page number]

Table 1
Effectiveness of Granular Activated Carbon on General Contaminant Groups

	Contaminant Groups	*Liquid /Gas*
Organic	Halogenated volatiles	■
	Halogenated semivolatiles	■
	Nonhalogenated volatiles[a]	■
	Nonhalogenated semivolatiles	■
	PCBs	■
	Pesticides	■
	Dioxins/Furans	■
	Organic cyanides [a]	▼
	Organic corrosives [a]	■
Inorganic	Volatile metals[a]	■
	Nonvolatile metals [a]	■
	Asbestos	❑
	Radioactive materials [a]	■
	Inorganic corrosives	❑
	Inorganic cyanides [b]	■
Reactive	Oxidizers[b]	■
	Reducers	❑

■ Demonstrated Effectiveness: Successful treatability test at some scale completed

▼ Potential Effectiveness: Expert opinion that technology will work.

❑ No Expected Effectiveness: Expert opinion that technology will not work

[a] Technology is effective for some contaminants in the group; it may not be effective for others.

[b] Applications to these contaminants involve both adsorption and chemical reaction.

ganic wastes that can be treated by GAC include compounds with high molecular weights and boiling points and low solubility and polarity [6]. Organic compounds treatable by GAC are listed in Table 2. GAC has also been used to remove low concentrations of certain types of inorganics and metals; however, it is not widely used for this application [1, p. 6-13].

Almost all organic compounds can be adsorbed onto GAC to some degree [2, p. 5-17]. The process is frequently used when the chemical composition of the stream is not fully analyzed [1, p. 6-3]. Because of its wide-scale use, GAC has probably been inappropriately selected when an alternative technology may have been more effective [7]. GAC can be used in conjunction with other treatment technologies. For example, GAC can be used to remove contaminants from the offgas from air stripper and soil vapor extraction operations [7] [8, p. 73] [9].

Table 2
Organic Compounds Amenable to Adsorption by GAC [1]

Class	*Example*
Aromatic solvents	Benzene, toluene, xylene
Polynuclear aromatics	Naphthalene, biphenyl
Chlorinated aromatics	Chlorobenzene, PCBs, endrin, toxaphene, DDT
Phenolics	Phenol, cresol, resorcinol, nitrophenols, chlorophenols, alkyl phenols
Aromatic amines and high molecular weight aliphatic amines	Aniline, toluene diamine
Surfactants	Alkyl benzene sulfonates
Soluble organic dyes	Methylene blue, textile dyes
Fuels	Gasoline, kerosene, oil
Chlorinated solvents	Carbon tetrachloride, perchloroethylene
Aliphatic and aromatic acids	Tar acids, benzoic acids
Pesticides/herbicides	2,4-D, atrazine, simazine, aldicarb, alachlor, carbofuran

Limitations

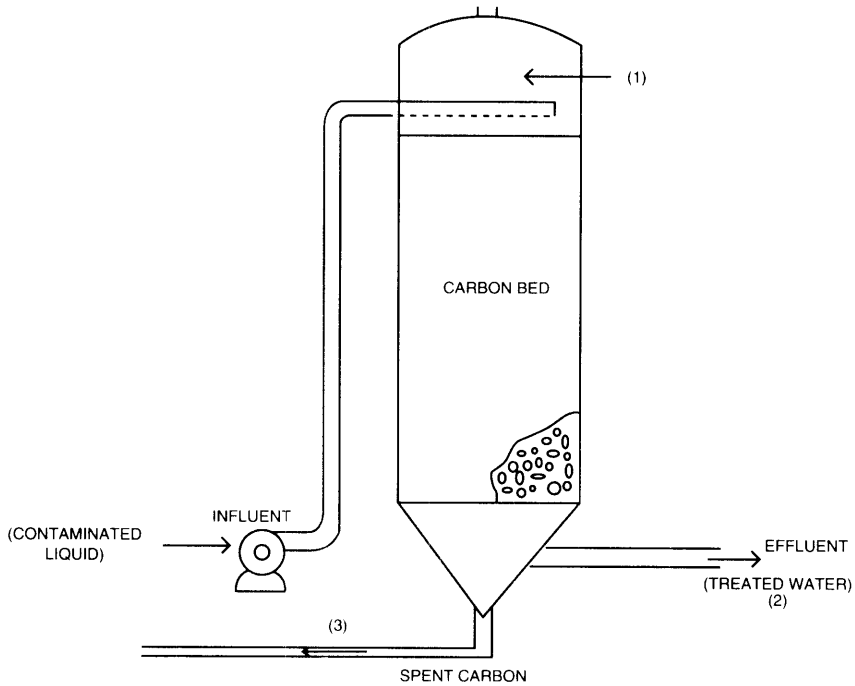
Compounds that have low molecular weight and high polarity are not recommended for GAC treatment. Streams with high suspended solids (≥ 50 mg/L) and oil and grease (≥ 10 mg/L) may cause fouling of the carbon and require frequent backwashing. In such cases, pretreatment prior to GAC, is generally required. High levels of organic matter (e.g., 1,000 mg/L) may result in rapid exhaustion of the carbon. Even lower levels of background organic matter (e.g., 10-100 mg/L) such as fulvic and humic acids may cause interferences in the adsorption of specifically targeted organic contaminants which are present in lower concentrations. In such cases, GAC may be most effectively employed as a polishing step in conjunction with other treatments.

The amount of carbon required, regeneration/reactivation frequency, and the potential need to handle the discarded GAC as a hazardous waste are among the important economic considerations. Compounds not well adsorbed often require large quantities of GAC, and this will increase the costs. In some cases the spent GAC may be a hazardous waste, which can significantly add to the cost of treatment.

Technology Description

Carbon is an excellent adsorbent because of its large surface area, which can range from 500-2000 m^2/g, and because its diverse surfaces are highly attractive to many different types of contaminants [3]. To maximize the amount of surface available

Figure 1. Schematic Diagram of Fixed-Bed GAC System



for adsorption, an activation process which increases the surface-to-volume ratio of the carbon is used to produce an extensive network of internal pores. In this process, carbonaceous materials are converted to mixtures of gas, tars, and ash. The tar is then burned off and the gases are allowed to escape to produce a series of internal micropores [1, p. 6-6]. Additional processing of the GAC may be used to render it more suitable for certain applications (e.g. impregnation for mercury or sulfur removal).

The process of adsorption takes place in three steps [3]. First the contaminant migrates to the external surface of the GAC granules. It then diffuses into the GAC pore structure. Finally, a physical or chemical bond forms between the contaminant and the internal carbon surface.

The two most common reactor configurations for GAC adsorption systems are the fixed bed and the pulsed or moving bed [3]. The fixed-bed configuration is the most widely used for adsorption from liquids, particularly for low to moderate concentrations of contaminants. GAC treatment of contaminated gas streams is done almost exclusively in fixed-bed reactors. The following technical discussion applies to both gas and liquid streams.

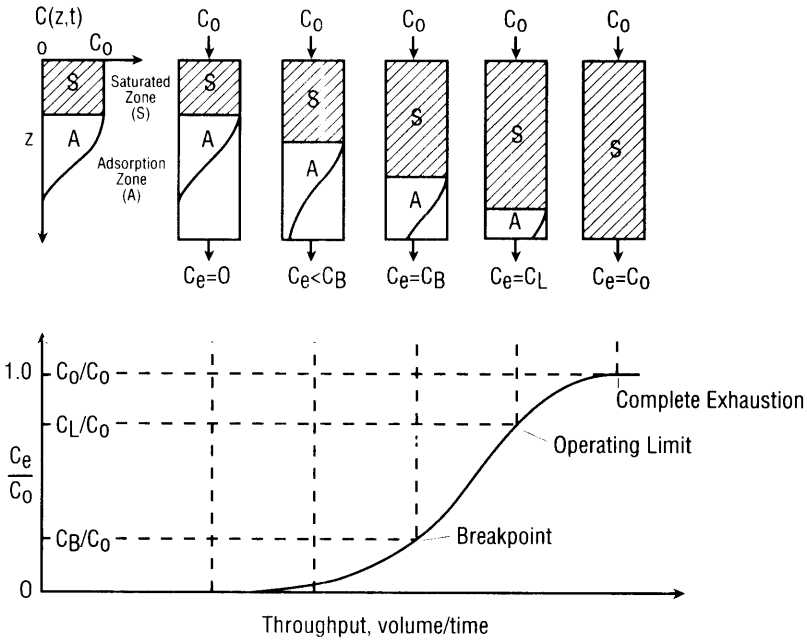
Figure 1 is a schematic diagram of a typical single-stage, fixed-bed GAC system for use on a liquid stream. The contaminant stream enters the top of the column (1). As the waste stream flows through the column, the contaminants are adsorbed. The treated stream (effluent) exits out the bottom (2). Spent carbon is reactivated, regenerated, or replaced once the effluent no longer meets the treatment objective (3). Although Figure 1 depicts a downward flow, the flow direction can be upward, depending on design considerations.

Suspended solids in a liquid stream or particulate matter in a gaseous stream accumulate in the column, causing an increase in pressure drop. When the pressure drop becomes too high, the accumulated solids must be removed, for example by backwashing. The solids removal process necessitates adsorber downtime, and may result in carbon loss and disruption of the mass transfer zone. Pretreatment for removal of solids from streams to be treated by GAC is, therefore, an important design consideration.

As a GAC system continues to operate, the mass-transfer zone moves down the column. Figure 2 shows the adsorption pattern and the corresponding effluent breakthrough curve [3]. The breakthrough curve is a plot of the ratio of effluent concentration (C_e) to influent concentration (C_o) as a function of water volume or air volume treated per unit time. When a predetermined concentration appears in the effluent (C_B), breakthrough has occurred. At this point, the effluent quality no longer meets treatment objectives. When the carbon becomes so saturated with the contaminants that they can no longer be adsorbed, the carbon is said to be spent (C_e=C_o). Alternative design arrangements may allow individual adsorbers in multi-adsorber systems to be operated beyond the breakpoint as far as complete exhaustion. This condition of operation is defined as the operating limit (C_e=C_L) of the adsorber.

The major design variables for liquid phase applications of GAC are empty bed contact time (EBCT), GAC usage rate, and system configuration. Particle size and hydraulic loading are often chosen to minimize pressure drop and reduce or eliminate backwashing. System configuration and EBCT have an impact on GAC usage rate. When the bed life is longer than 6 months and the treatment objective is stringent ($C_e/C_o < 0.05$),

Figure 2
Breakthrough Characteristics of Fixed-Bed GAC Adsorper [3]



a single adsorber or a combination of single beds operating in parallel is preferred. For a single adsorber, the EBCT is normally chosen to be large enough to minimize GAC usage rate. When less stringent objectives are required ($C_e/C_o > 0.3$), blending of effluents from partially saturated adsorbers can be used to reduce GAC usage rate. When stringent treatment objectives are required ($C_e/C_o < 0.05$) and GAC bed life is short (less than 6 months) multiple beds in series may be used to decrease GAC usage rate.

For gas-phase applications, the mass transfer zone is usually very short if the relative humidity is low enough to prevent water from filling the GAC pores. The adsorption zone (Figure 2) for gas-phase applications is small relative to bed depth, and the GAC is nearly saturated at the breakpoint. Accordingly, EBCT and system configuration have little impact on GAC usage rate and a single bed or single beds operated in parallel are commonly used.

GAC can be reactivated either onsite or offsite. The choice is usually dictated by costs which are dependent on the site and on the proximity of offsite facilities that reactivate carbon. Generally onsite reactivation is not economical unless more than 2,000 pounds per day of GAC are required to be reactivated. Even so, an offsite reactivation service may be more cost effective [10].

The basic evaluation technique for initial assessment of the feasibility of GAC treatment is the adsorption isotherm test. This test determines if a compound is amenable to GAC adsorption and can be used to estimate minimum GAC usage rates. More detailed testing such as small-scale column tests and pilot tests should be conducted if the isotherms indicate GAC can produce an effluent of acceptable quality at a reasonable carbon usage rate [10].

Process Residuals

The main process residual produced from a GAC system is the spent carbon containing the hazardous contaminants. When the carbon is regenerated, the desorbed contaminants must be treated or reclaimed. Reactivation of carbon is typically accomplished by thermal processes. Elevated temperatures are employed in the furnace and afterburners to destroy the accumulated contaminants. If the carbon cannot be economically reactivated, the carbon must be discarded and may have to be treated and disposed of as a hazardous waste. In some cases, the influent to GAC treatment must be pretreated to prevent excessive head loss. Residues from pretreatment (e.g. filtered suspended solids) must be treated or disposed. Solids collected from backwashing may need to be treated and disposed of as a hazardous waste.

Site Requirements

GAC equipment generally has small space requirements and sometimes can be incorporated in mobile units. The rapidity of startup and shutdown also makes GAC amenable to mobile treatment. Carbon beds or columns can be skid-mounted and transported by truck or rail [2, p. 5-19].

As previously stated, spent carbon from the treatment of streams containing hazardous substances is generally considered hazardous, and its transportation and handling requires that a site safety plan be developed to provide for personnel protection and special handling measures. Storage may have to be provided to hold the GAC-treated liquid until its acceptability for release has been determined. If additional treatment is required, adequate space must be provided for these systems.

Performance Data

Performance data on full-scale GAC systems have been reported by several sources including equipment vendors. Data on GAC systems at several Superfund sites and other cleanup sites are discussed in this section. The data presented for specific contaminant removal effectiveness were obtained from publications developed by the respective GAC system vendors. The quality of this information has not been determined; however, it does give an indication of the efficiency of GAC.

A GAC system was employed for leachate treatment at the Love Canal Superfund site in Niagara Falls, New York. The results of this operation are listed in Tables 3 and 4 [11].

Table 5 summarizes a number of experiences by Calgon Corporation in treating contaminated groundwater at many other non-Superfund sites. Table 5 identifies the sources of contamination along with operating parameters and results [12]. While these sites were not regulated under CERCLA, the type and concentration of contaminants are typical of those encountered at a Superfund site.

The Verona Well Field Superfund site in Battle Creek, Michigan used GAC as a pretreatment for the air stripper. This arrangement reduced the influent concentrations which allowed the air stripper to comply with the National Pollution Discharge Elimination System (NPDES) permit. The system had two parallel trains: a single unit and two units in series. Approximately one-third of the total flow was directed to the first train while the remaining flow went to the other train. Performance data for removal of total volatile organic compounds (TVOC) on selected operating days are given in Table 6 [13].

A remediation action at the U.S. Coast Guard Air Station in Traverse City, Michigan, resulted in GAC being used to treat contaminated groundwater. The groundwater was pumped from the extraction well system to the GAC system. The treated water was then discharged to the municipal sewer system. Concentrations of toluene in the monitoring wells were reduced from 10,329 parts per billion (ppb) to less than 10 ppb in approximately 100 days [14].

Technology Status

GAC is a well-proven technology. It has been used in the treatment of contaminated groundwater at a number of Superfund sites. Carbon adsorption has also been used as a polishing step following other treatment units at many sites. In 1988, the number of sites where activated carbon was listed in the Record of Decision was 28; in 1989, that number was 38.

Costs associated with GAC are dependent on waste stream flow rates, type of contaminant, concentrations, and site and timing requirements. Costs are lower with lower concentration levels of a contaminant of a given type. Costs are also lower at higher flow rates. At liquid flow rates of 100-million gallons per day (mgd), costs range from $0.10 - 1.50/1,000 gallons treated. At flow rates of 0.1 mgd, costs increase to $1.20 - 6.30/1,000 gallons treated [12].

Table 3
Love Canal Leachate Treatment System[a] (March 1979) [11]

Priority Pollutant Compounds Identified	*Carbon System Influent* µg/l	*Carbon System Effluent* µg/l
Hexachlorobutadiene	109	<20
1,2,4-trichlorobenzene	23	<20
Hexachlorobenzene	32	<20
α-BHC	184	<0.01
γ-BHC	392	0.12
β-BHC	548	<0.01
Heptachlor	573	<0.01
Phenol	4,700[b]	<5[b]
2,4-dichlorophenol	10	<5
Methylene chloride	180	<10
1,1-dichloroethylene	28	<10
Chloroform	540	<10
Carbon tetrachloride	92	<10
Trichloroethylene	240	<10
Dibromochloromethane	21	<10
1,1,2,2-tetrachloroethylene	270	<10
Chlorobenzene	1,200	<10

[a] Samples were analyzed by Recra Research, Inc., according to EPA protocol dated April 1977 (sampling and analysis procedures of screening for industrial effluents for priority pollutants).
[b] The data represent phenol analysis conducted by Calgon in June 1979, as earlier results were suspect.

Table 4
Love Canal Leachate Treatment System[a] (June 1979) [11]

Priority Pollutant Compounds Identified	*Raw Leachate* µg/l	*Carbon System Effluent* µg/l
2,4,6-trichlorophenol	85	<10
2,4-dichlorophenol	5,100	N.D.
Phenol	2,400	<10
1,2,3-trichlorobenzene	870	N.D.
Hexachlorobenzene	110	N.D.
2-chloronaphthalene	510	N.D.
1,2-dichlorobenzene	1,300	N.D.
1,3 & 1,4-dichlorobenzene	960	N.D.
Hexachlorobutadiene	1,500	N.D.
Anthracene and phenanthrene	29	N.D.
Benzene	28,000	<10
Carbon tetrachloride	61,000	<10
Chlorobenzene	50,000	12
1,2-dichloroethane	52	N.D.
1,1,1-trichloroethane	23	N.D.
1,1-dichloroethane	66	N.D.
1,1,2-trichloroethane	780	<10
1,1,2,2-tetrachloroethane	80,000	<10
Chloroform	44,000	<10
1,1-dichloroethylene	16	N.D.
1,2-trans-dichloroethylene	3,200	<10
1,2-dichloropropane	130	N.D.
Ethylbenzene	590	<10
Methylene chloride	140	46
Methyl chloride	370	N.D.
Chlorodibromomethane	29	N.D.
Tetrachloroethylene	44,000	12
Toluene	25,000	<10
Trichloroethylene	5,000	N.D.

[a] Samples were analyzed by Carborundum Corporation according to EPA protocol dated April 1977 (sampling and analysis procedures for screening of industrial effluents for priority pollutants).
N.D. = nondetectable.

Table 5
Performance Data at Selected Sites [12]

Source of Contaminants	*Typical Influent Conc. (mg/l)*	*Typical Effluent Conc. (µg/l)*	*Carbon Usage Rate (lb./1000 gal.)*	*Total Contact Time (min.)*
Truck spill				
Methylene chloride	21	<1.0	3.9	534
1,1,1-trichloroethane	25	<1.0	3.9	534
Rail car spills				
Phenol	63	<1.0	5.8	201
Orthochlorophenol	100	<1.0	5.8	201
Vinylidine chloride	2-4	<10.0	2.1	60
Ethyl acrylate	200	<1.0	13.3	52
Chloroform	0.020	<1.0	7.7	160
Chemical spills				
Chloroform	3.4	<1.0	11.6	262
Carbon tetrachloride	130-135	<1.0	11.6	262
Trichloroethylene	2-3	<1.0	11.6	262
Tetrachloroethylene	70	<1.0	11.6	262
Dichloroethyl ether	1.1	<1.0	0.45	16
Dichloroisopropyl ether	0.8	<1.0	0.45	16
Benzene	0.4	<1.0	1.9	112
DBCP	2.5	<1.0	0.7–3.0	21
1,1,1-trichloroethane	0.42	<10	1.5	53
Trichlorotrifloroethane	5.977	<10	1.5	53
Cis-1,2-dichloroethylene	.005	<1.0	0.25	121
Onsite storage tanks				
Cis-1,2-dichloroethylene	0.5	<1.0	0.8	64
Tetrachloroethylene	7.0	<1.0	0.8	64
Methylene chloride	1.5	<100	4.0	526
Chloroform	0.30-0.50	<100	1.19	26
Trichloroethylene	3-8	<1.0	1.54	36
Isopropyl alcohol	0.2	<10.0	1.54	36
Acetone	0.1	<10.0	1.54	36
1,1,1-trichloroethane	12	<5.0	1.0	52
1,2-dichloroethylene	0.5	<1.0	1.0	52
Xylene	8.0	<1.0	1.0	52
Landfill site				
TOC	20	<5000	1.15	41
Chloroform	1.4	<1.0	1.15	41
Carbon tetrachloride	1.0	<1.	1.15	41
Gasoline spills, tank leakage				
Benzene	9-11 }		<1.01	214
Toluene	5-7 }	<100 Total	<1.01	214
Xylene	6-10 }		<1.01	214
Methyl t-butyl ether	0.030-0.035	<5.0	0.62	12
Di-isopropyl ether	0.020-0.040	<1.0	0.10-0.62	12
Trichloloethylene	0.050-0.060	<1.0	0.62	12
Chemical by-products				
Di-isopropyl methyl phosphonate	1.25	<50	0.7	30
Dichloropentadiene	0.45	<10	0.7	30
Manufacturing residues				
DDT	0.004	<0.5	1.1	31
TOC	9.0		1.1	31
1,3-dichloropropene	0.01	<1.0	1.1	31
Chemical landfill				
1,1,1-trichloroethane	0.060-0.080	<1.0	<0.45	30
1,1-dichloroethylene	0.005-0.015	0.005	<0.45	30

Table 6
TVOC Removal with GAC at Verona Well Superfund Site [13]

Operating Day	Influent Feed Concentration (ppb)	Effluent Train (1) Concentration (ppb)	Effluent Train (2) Concentration (ppb)
1	18,812	NA	25
9	12,850	11	7
16	9,290	41	17
27	6,361	260	426
35	7,850	484	575
42	7,643	412	551
49	7,577	405	524
57	5,591	452	558
69	10,065	377	475
92	6,000	444	509
106	3,689	13	702
238	4,671	246	263

NA = not available

EPA Contact

Technology-specific questions regarding GAC treatment may be directed to:

Dr. James Heidman
U.S. Environmental Protection Agency
Risk Reduction Engineering Laboratory
26 West Martin Luther King Drive
Cincinnati, Ohio 45268
FTS 684-7632 or (513) 569-7632

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Dr. John C. Crittenden	Michigan Technological University
Mr. Clyde Dial	SAIC
Mr. James Rawe	SAIC
Dr. Walter J. Weber, Jr.	University of Michigan
Ms. Tish Zimmerman	EPA-OERR

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