EL AGUA POTABLE

IV

An Evaluation of Activated Carbon for Drinking Water Treatment

This chapter contains the findings of the Subcommittee on Adsorption of the National Research Council's Safe Drinking Water Committee, which studied the efficacy of granular activated carbon (GAC) and related adsorbents in the treatment of drinking water. Some attention is given to an examination of the potential health effects related to the use of these adsorbents, but detailed toxicological and epidemiological implications resulting from the presence of organic compounds in drinking water are considered in separate chapters of *Drinking Water and Health,* Volume 3. The development of standards for GAC and the economic aspects of its use was not a part of this study.

The subcommittee defined "activated carbon" as a family of carbonaceous substances that are characterized primarily by their surface area, pore size distribution, and sorptive and catalytic properties. Different raw materials and manufacturing processes produce final products with different adsorption characteristics.

The use of GAC under specified conditions was proposed by the U.S. Environmental Protection Agency (EPA) as the option of choice for the control of "synthetic organic chemicals" in drinking water. During the subcommittee's study, the EPA held hearings and received written comments regarding this treatment.

The subcommittee reviewed the pertinent literature and rigorously assessed the scientific data base. Its scope of work included a review of work on:

adsorption efficiency

microbial activity on adsorbents

physiochemical interactions

regeneration of ads6rbents

analytical methods to monitor adsorption processes

The subcommittee considered the ability of adsorbents to remove organic compounds of concern to health and the possible products of the adsorption process. A large and diverse segment of the scientific literature, particularly that concerning recent European experience, was scrutinized. Studies that met established criteria for quality assurance and completeness of data were used as primary sources by the subcommittee. Where possible, stress was placed on studies of chemicals at nanogram to microgram per liter concentrations, which are typically found in drinking water. The subcommittee was confronted by a continual flow of new data and the need for postulation and interpretation. To ensure a thorough review of each topic, the data for each type of adsorbent were considered and reported separately.

Carbon and other adsorbents in various forms have been used for the treatment of water and as detoxifying pharmaceutical agents in medicine for many centuries. There has been an uninterrupted use of carbonaceous adsorbents since biblical times (Old Testament, Num. 19:9; Maimonides, 1185) and there have been marked changes in the nature of the adsorbent since that time (Kunin, 1974a,b).

During the twentieth century, GAC and powdered activated carbon (PAC) have been used in the United States to control taste and odors in drinking water (U.S. Environmental Protection Agency, 1978a). During the past 20 yr, research on the use of adsorbents to treat drinking water has emphasized the removal of specific organics. The removal of organic compounds from drinking water has been based primarily on the measurement of organic matter as measured by carbon chloroform extract (CCE), total organic carbon (TOC), or other group parameters. However, it has long been recognized that these group parameters provide only estimates of performance for target compounds. Studies beginning with those of Middleton and Rosen *(1956)* began to identify the specific organic compounds in drinking water and their removal by the carbon adsorption.

Over 700 volatile organic compounds have been identified in drinking water (U.S. Environmental Protection Agency, 1978c). These compounds make up only a small fraction of the total organic matter National Academy of Sciences, 1977). Approximately 90% of the volatile organic compounds that can be analyzed by gas chromatography have been analyzed, but this represents no more than 10% by weight of the total organic material. Only 5%-10% of the nonvolatile organic compounds that comprise the remaining 90% of the total organic matter have been identified.

The EPA (1978c) has categorized the organic compounds in drinking water into five different classes. Each class has distinctly different characteristics of concern to those involved in water treatment.

Class 1: organic compounds that cause taste and odor and/or color problems;

Class II: synthetic organic chemicals that are present in source waters from upstream discharges or runoff;

Class III: organic. compounds (precursors) that react with disinfectants to produce "disinfectants by-products";

Class IV: organic chemicals that are the disinfectants by-products themselves; and

Class V: natural (non-Class III) organic compounds of little direct toxicological importance.

Today there are GAC beds in U.S. water treatment plants for removal of Class I compounds. Consideration is being given to the use of GAC for removal of Class II, III, and IV compounds as data become available. Class V compounds are of interest because they may compete for adsorption sites, thereby lessening the removal of other compounds.

This report identifies the compounds that may be removed and/or added to drinking water by the adsorption process with its attendant chemical and microbial processes. It focuses on recently published lists of organic chemicals of concern to health (Interagency Regulatory Liaison Group, 1978; National Academy of Sciences, 1977, 1979; National Cancer Institute, 1978).

Each section deals with complex subjects in which there are uncertainties, inconclusive or incomplete data, and, thus, conflicting opinions. The length of each section represents only the number of studies reviewed and does not reflect the relative importance of the subjects.

ACTIVATED CARBON-A DEFINITION

"Activated carbon" comprises a family of substances, whose members are characterized primarily by their sorptive and catalytic properties. Different raw materials and manufacturing processes produce final products with different characteristics.

Activated carbon can be made from a variety of carbonaceous materials and processed to enhance its adsorptive properties. Some common materials that are used to make activated carbon are bituminous coal, bones, coconut shells, lignite, peat, pecan shells, petroleum-based residues, pulp mill black ash, sugar, wastewater treatment sludge, and wood (Weber, 1972). As is true with any production process, the quality of the final product is influenced by the staring material. In the past, activated carbons that were used for industrial applications were commonly produced from wood, peat, and other vegetable derivatives. Today, lignite, natural coal, and coke are the most frequently used sources of activated carbon due to their availability and attractive price.

The basic structural unit of activated carbon is closely approximated by the structure of pure graphite with only slight differences. The structure of activated carbon is quite disorganized compared with that of graphite because of the random oxidation of graphite layers. The regular array of carbon bonds in the surface of the crystallites is disrupted during the activation process, yielding free valences that are very reactive. The structure that develops is a function of the carbonization and activation temperatures. During the carbonization process, several aromatic nuclei with a structure similar to that of graphite are formed. From X-ray spectrographs, these structures have been interpreted as microcrystallites consisting of fused hexagonal rings of carbon atoms. The diameter of the planes making up the microcrystallite is estimated to be 150 A, and the distance between microcrystallites ranges from 20 A to *50A(Wolff, 1959).*

The presence of impurities and the method of preparation influences the formation of interior vacancies in the microcrystallite. The ringed structures at the edges of the planes are often heterocyclic, resulting from the nature of either the starting material or the preparation process. Heterocyclic groups would tend to affect both the distance of adjacent planes and the sorptive properties of the carbon.

As a rule, the structure of the usual types of active carbon is tridisperse, i.e., they contain micropores (effective radii of l8-20 A), transitional pores (40-200 A), and macropores (500-20,000 A). According to Dubinin (1966) only a few of the micropores lead directly to the outer surface of the carbon particle. Most of the pore structures of the particles are arranged in the following pattern: the macropores open directly to the external surface of the particle; transitional pores branch off from macropores; and micropores, in turn, branch off from the transitional pores. The specific area of the micropores usually amounts to at least 90% of the total surface area.

THE WATER TREATMENT PROCESS

GAC is typically used in a water treatment plant after the coagulation and sedimentation processes and, commonly, following preliminary disinfectants steps during which chemical reactions can occur. Moreover, water is often disinfected before it passes through the GAC adsorbers in order to prevent nuisance biological growths. In many instances, the activated carbon functions as a granular filter medium for removing particulates, although in a few cases in the United States and in most instances in Europe the GAC adsorbers are preceded by filters for particulate removal.

Water is usually passed downward through packed beds of GAC. The frequency of backwashing is dependent on the amount of particulates being removed and the extent of microbial growth. Some intermixing of the GAC granules takes place during this step, although this tendency is countered by particle size stratification during backwash. Wile packed-bed downflow adsorbers in parallel are most commonly used, many other flow patterns, such as operation in series, upflow packed bed, and upflow expanded bed, may be used.

Regeneration of GAC is not generally practiced at water plants in the United States as it is in Europe. If the objective of GAC use is to include the removal of organic compounds in addition to those that cause taste and odor, regeneration is likely to become more common in the United States. The type of contactor selected for the GAC will be influenced by the frequency of regeneration.

After treatment of a water supply with GAC, postdisinfection is generally used to reduce the total number of bacteria, some of which may be present because of the microbial growths in adsorbers. Sufficient disinfectant is usually applied to ensure a residual in the distribution system to prevent contamination of the water. Postdisinfection is used in addition to predisinfection because aqueous oxidants that are used in preliminary disinfectants steps will generally be eliminated by reaction with the GAC.

In certain instances, some synthetic resins may serve as replacements for GAC or they may be used in conjunction with GAC to provide the desired quality of water. The major difference between resins and GAC is that the resins are regenerated by application of aqueous solutions of acids, bases, and/or salts, or of nonaqueous solvents or steam, while GAC is usually thermally regenerated. In general, resins usually require a pretreatment step that is dependent upon the nature of the resins.

Powdered activated carbon (PAC) is now more commonly used in the United States than is GAC. It generally added to control taste and odor at points in the water treatment plant, ranging from the water supply intake to just before the rapid sand filter. PAC is removed either in the sedimentation basin or by the rapid sand filter. No attempt is made to regenerate it during the water treatment. Whether PAC can be used to remove organics other than those that cause offensive taste and odor requires closer examination.

Various types of GAC and PAC are commercially available as a result of variations in the raw materials and manufacturing processes. Because the types of organic contaminants vary widely from location to location, the best carbon for one application may not be the best in another. Consequently, comparative testing for a particular water source is mandatory.

The chemical compounds entering an adsorption water treatment process consist of high-molecular-weight humic materials, lower-molecular-weight organic compounds of natural or industrial origin, and the products of previous treatment such as chlorination or ozonization. A portion of the chemicals can be removed by the clarification process and/or sorbed by the adsorbent or any microbial floc within the adsorbent bed. Some compounds may be nonadsorbable or only very weakly adsorbable.

The chemical compounds leaving the adsorption treatment process can be the same chemicals that entered the plant, or they may be products of chemical reaction or microbial action within the system. Organic compounds may appear in the effluent of an adsorption column because available adsorption sites are saturated or because they are displaced from the adsorption sites by other organics. Because adsorption is often reversible, adsorbed compounds may desorb and appear in the effluent when the influent concentrations of those compounds decrease. These phenomena may lead to the appearance of a larger concentration of a compound in the effluent than is in the influent. Thus, both the qualitative and quantitative variability of the mixture of organics entering an adsorption process affect the quality of water that can be produced by it.

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Raw water sources and disinfected water supplies may contain organic compounds that have been demonstrated to be carcinogenic or otherwise toxic in experimental animals or in epidemiological studies. Also present are a large number of compounds that either have not been identified or their effects on health have not been characterized. Properly operated GAC systems can remove or effectively reduce the concentration of many of the compounds described above. Less is known about synthetic resins than about GAC, but it is known that they can be applied to remove certain types of organic contaminants.

The information available as of this date on the treatment of water with GAC provides no evidence that harmful health effects are produced by the process under proper operating conditions. However, there are incomplete studies on the possible production of such effects with virgin or regenerated carbon through

reactions that may be catalyzed by the GAC surface;

reactions of disinfectants with GAC or compounds adsorbed on it;

reactions mediated by microorganisms that are part of the process; or

by the growth of undesirable microorganisms on GAC.

Studies are also needed on the properties of regenerated activated carbons and on the adsorption of additional contaminants with potential health effects. The frequency of GAC regeneration is determined by the organic compounds in the water and their competitive interactions. The types and concentrations of organic compounds may vary widely among different locations and seasons of the year. Competitive interactions are complex and presently cannot be predicted without data from laboratory and/or pilot scale tests on the water to be treated.

While there is ample evidence for the effectiveness of GAC in removing many organics of health concern, more data are needed in the quantification of any harmful health effects related to the use of GAC. This need, however, should not prevent the present use of GAC at locations where analysis of the water supply clearly indicates the existence of a potential health hazard greater than that which would result from the use of GAC

Clarification processes (coagulation, sedimentation, filtration) remove significant amounts of some organics, especially some types of THM precursors and relatively insoluble compounds that may be associated with particulates. In some cases, the removal of THM precursors by clarification may be sufficient to eliminate the need for an adsorption process.

ADSORPTION EFFICIENCY OF GAC

The trace organic compounds that can be removed by GAC are usually present at ug/liter quantities or less. The subcommittee considered the GAC adsorption efficiency for individual compounds and the competitive adsorption of mixtures. Since GAC is used in conjunction with other water treatment processes, the effect of pretreatments for removing trace organic compounds and their precursors were examined in depth. Hence, the following questions were addressed:

1. How efficiently does GAC adsorb individual trace organic compounds, particularly those of concern to health?

2. When processes such as coagulation, sedimentation, filtration, aeration, disinfectants, oxidation, and PAC adsorption precede GAC adsorption, how is the efficiency of the GAC affected?

3. Can water that has been treated by GAC be disinfected more or less easily than water that has not been treated by GAC?

4. What is the potential for effectively using PAC to remove organics?

5. What reactions take place between oxidants that are applied as predisinfectants and the activated carbon or the compounds that are adsorbed on the activated carbon? Do these reactions result in potentially hazardous compounds that would not be present if activated carbon were not used?

6. To what extent does competitive adsorption between trace organics with potential health effects and the large concentrations of background organics, generally characterized as humic substances, influence the effectiveness of GAC?

7. To what extent does competitive adsorption among similar concentrations of trace organics with potential health effects influence the effectiveness of GAC?

8. How significant is the effect of competitive adsorption when it is compared to the effect of the reequilibration that is produced by the variable nature of the composition and concentration of trace organics in the feedwater to the GAC bed?

Removal of Selected Organic Compounds

Adsorption isotherms and small column studies that are performed in the laboratory using GAC are useful tools that have been developed to

describe how specific organic chemicals can be removed in large-scale GAC applications. A considerable amount of adsorption research describing the affinities of pure compounds for the activated carbon surface has been reported in the literature during the last 15 years. Improved analytical tools have made it possible both to detect the organics at trace levels in the environment and to follow their removals in adsorption studies in the laboratory. This section of the chapter evaluates the efficiency of GAC adsorption of individual trace organic compounds, particularly those with potential health effects.

Removals of organic chemicals are discussed in the literature on the basis of laboratory and pilot-scale studies and large-scale applications. Laboratory studies are by far the most useful for describing specific organic removals since environmental factors can be more carefully controlled in them than in field evaluations. The problem of competitive adsorption is significant when environmental samples are used in experiments in which specific organic compounds are removed by adsorption. A later section of this chapter addresses this problem exclusively.

Adsorption data obtained in the laboratory are normally reported as percent removed, adsorption isotherms, kinetics of adsorption, and the results of small-scale column studies. In the following sections, these data are reviewed and the utility of each method is evaluated.

Percent Removals

Giusti *et al.* (1974) made extensive use of percent reduction as a measure of the effectiveness of activated carbon for removing organic chemicals. They added 93 petrochemicals individually at one level to one type of activated carbon and used the subsequent calculated percent reductions to test several hypotheses concerning the removal of different classes of organics by activated carbon.

There are several problems associated with using percent removal data exclusively to describe how well a particular organic compound is removed from water. The single value study results in a single point on an isotherm. Unfortunately, this single point gives no indication of how capacity varies with concentration, i.e., by the isotherm slope and shape. To be truly representative, the amounts of adsorbed compound per gram of carbon for individual organic compounds must be compared on an equal equilibrium concentration basis, which is not possible if only a single percent removal value is available.

Adsorption Isotherms

Adsorption isotherms are plots of the equilibrium relationship between the amount of organic compound that is left in solution (equilibrium concentration, *Ce)* and the amount of compound that is on the surface of the activated carbon (surface concentration, q).

Few studies describe the adsorption isotherms of a wide variety of organic compounds over several orders of magnitude. An EPA publication (U.S. Environmental Protection Agency, 1978c) tabulated references on the removals of some *50* organic compounds by GAC. While there are some useful data among the references cited in this work, a large fraction of the reported data is fragmentary. Generally, information is omitted, such as the number of data points used to define the isotherm or the equilibrium concentration range over which the slope and intercept of the linear isotherm are valid. Dobbs *et al.* (1978) have made significant efforts to standardize the reporting of isotherm data.

Table IV-l lists a series of compounds for which detailed isotherms are available. No attempt has been made to list all studies that have been published. Instead, Table IV- I presents a sample of available studies. The compounds in the table represent a wide variety of organic chemicals, including naturally occurring chemicals, industrial solvents, and compounds that have been identified in surface waters and waste streams in the United States. Dobbs *et al.* (1978) and Fochtman and Dobbs (1980) have made some of the few efforts to determine adsorption capacities for many organic chemicals of toxicological concern. In the future, the isotherm data base should be expanded much more rapidly to include the compounds that are just now being identified as toxic or potentially carcinogenic. There are significant difficulties in determining isotherms for some of these organic compounds. A major difficulty is that many compounds must be analyzed at concentrations that have previously been near the limit of detectability.

Isotherm data for the organic compounds that are listed in Table IV-l have become available only recently, and few attempts have been made to analyze the data to determine whether general patterns exist. Figure IV- I plots selected isotherms for compounds from Table IV- 1 over seven orders of magnitude of equilibrium concentration (McGuire and Suffet, 1980).

Although the isotherms in Figure IV-l were determined by different investigators using different techniques and different carbons, there is surprising agreement between isotherms for the same compound. Clearly, other aspects of the experimental conditions that affect the positions of the isotherms include pH, ionic strength, and temperature.

TABLE W-1 Some Organic Compounds for Range Isotherms Have Been Determined

Which Detailed, Wide-

acetone

acetophenone4

acridine orange4 acridine yellow

adefline4

adipic **acid4**

anethole4

o-anisidine0

benzene

benzidine

benzidine dihydrochioride4 benzoic acid4 benzothiazole4

brornochloromethane:

bromodichloromethane

bromoform

bromophenold

5-bromouracil4

nbutanolb

(di)-n-butylphthalate4 carbon tetrachloride chiorobenzene4

b£s (2-hloroethyl) ethe chiorodibrornethane4

chloroform I hlor2-nitrobenzene4 chlorophenol 5-chlorouracil p-cresol

cydohexanone4 cytosine4 3,3dichlorobenzidineh

dichioromethane:

2,4 dichlorophenolc.e dirnethylphenylcarbinol4 2,4

initrophenolc dimethyl phthalate0 1, 1pheny1 hydrazineh

1,4oxanCb diphenylamine4

EDTA4

ethylbenzene4

ethylene chloride4

5-fluorouracil4

geosmin

guanine4

hexadilorobutadiene4

hydroquinone

p-methoxyphenol

4,4'-methyiene-bis

(2 chloroaniline) *h* methyl ethyl ketone *b* 2-methylisoborneol

naphthalene

-naphthol4

-naphthol4

-naphthy1amine4

nitroaniline4

nitrobenzene4

nitromethaneb

rntrophenolb.c..i

N-nitrooodiphenylamie4 nony1phenol4 parathior}'

pentachlorophenol4

phenol phenyl mercuric acetate4 2-propanoif propionitrile sodium benzene sulfonate styrene4 tetrachloroethylene:

1,2,3,~tetrahydronapththalene4

thymine4 trichloroethylene:

2,4,6~trichlorophenolc

uracil4 urea b p-xylene4

4Dobbseial., 1978. bMCGUIre, 1977.

cZogo, 1975.

d Jam and Snoeyink, 1973. Snoeyink *et,al* 1977.

Radke and Prausnitz, 1972

'Weberezal., 1977.

h Fochtman and Dobbs, 1979. Snoeyink et *al,* 1969.

i Weber and Gould, 1966.

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~-1
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FIGURE IV-1 General and specific adsorption isotherms. From McGuire and Suffet, 1980.

McGuire and Suffet (1978) reviewed the relative importance of these and other *factors* on the adsorption mechanism. In general, the isotherms in Figure IV- 1 were calculated for the neutral forms of the molecules.

Several investigators have shown that there can be significant differences between the adsorption characteristics of different brands of activated carbon (McGuire, 1977; Weber *et al.*, 1977; Zogorski, 1975). Pore size distribution and surface area, base material, chemisorbed oxygen and surface polarity, particle size, and hardness all affect either the capacity, kinetics, or economics of adsorption with activated carbon (McGuire and Suffet, 1978). There are significant differences between bituminous coal base carbons and coconut shell carbons. The capacity will have a significant effect on cost. Thus, the difference in isotherms for different carbons is important. However, the differences among carbons will be reflected primarily in cost, a factor not considered in this report.

The shaded area of Figure IV-1 depicts a general isotherm. At relatively high equilibrium concentrations (depending on how well a compound is adsorbed), the slope of the isotherm is relatively flat. As the equilibrium concentration decreases, the slope increases until it becomes equal to 1.0, indicating compliance with Henry's law of adsorption

(Radke and Prausnitz, 1972a). The more poorly adsorbed compounds (urea, for example) have a slope of 1.0 at high ***Ce*** values. The compounds that are more strongly adsorbed have a slope of 1.0 at much lower *Ce* values. For example, the isotherm for 2,4,&trichlorophenol was determined over five orders of magnitude, and the maximum slope is only *0.592* at 10-8 mol/liter. Figure IV-l also shows that for the isotherms determined on a comparative basis, substituted phenols adsorb much better than low molecular weight alkyl halides.

Our understanding of how specific organic compounds are adsorbed is generally derived from the work on well-adsorbed substituted phenols at mg/liter concentrations. Figure IV-l indicates that the poorly adsorbed and even the moderately well-adsorbed compounds have steep slopes at the 'ug/liter level (1 to 10 x l0 -9 mol/liter). The reduction of compound concentrations two orders of magnitude into the mg/liter range requires a much larger amount of carbon or longer column contact time than a two order of magnitude decrease at the mg/liter level. Thus, reduction to subtrace levels of these specific organics with potential health effects is more difficult than would normally be expected based on the existing level of understanding of organic compound adsorption.

Table IV-2 was compiled from studies describing the adsorption data for individual organic compounds with particular potentials for harmful health effects. The selection of compounds in the table was based on their presence on several recently published lists: Categories of Known or Suspected Organic Chemical Carcinogens Found in Drinking Water National Academy of Sciences, 1977, p. 794), Carcinogens and Suspected Carcinogens in Drinking Water National Cancer Institute, 1978), List of Chemicals Submitted by EPA for Evaluation by the Safe Drinking Water Committee Toxicology Subcommittee National Academy of Sciences, 1979), and the Interagency Regulatory Liaison Group (1978). Pesticides with established maximum contaminant levels (MCL) (U.S. Environmental Protection Agency, 1975) and THM's with proposed composite MCL values (U.S. Environmental Protection Agency, 1978b) are also included in Table IV-2.

Clearly the 58 compounds and classes of compounds listed in these compilations are somewhat repetitive and overlap several types of organic chemicals. The list has been modified and edited for clarity and does not include compounds for which no data on adsorption were available. The committee attempted to provide as much specific information on the ability of a compound to be adsorbed by activated carbon as possible and convenient for a tabular format.

Several guidelines were used to select the references and the adsorp-

TABLE IV-2

Adsorption of Organic Compounds by GAC"

Molecular

Organic

Compounds Weight

Acrylonitrile 53.06

Aidrin 365

78.11

Benzene

Benzo(a). 252.3

pyrene

o-BHC 290.85

y-BHC 290.85

(Lindane)

Bis (2-chloro- 143.01

ethyl) ether

Bromodichloro 163.83

methane

Bromoform 252.75

Carbon tetra 153.82

chloride

Chlordane 764 Chlorobenzene

112.56

Chlorodibromo 208.29 methane

Chloroform 119.38

DDE 318

Equilibrium

Number Adsorption Concentration

of Data Carbon Test Range, Points Type Method mol/liter Comments

2 Unknown Unknown 1.4x t0--9.2 x

6 F300 Isotherm *2.5)(10--7.1)< 10-8*

s oo Isotherm 2.6)< t0--1.3 x

2 NoritNK % reduction Unknown

Unknown Unknown % reduction Unknown

OU-A % reduction 7)< 10-8

II F300 Isotherm 4.2 x 105-I.2x i-

7 F300 Isotherm 7.9 x t0--3.5 >(10-~

15 F400 Isotherm 2 x 10-I.3 x 10-6

II F400 Isotherm 3)(10--2.6 i-

3 F300 Isotherm 1.0 x t0-~-2.3 X 10-8

Isotherm

7 F300

1.2 x i05-t.5 x i0-4

F400 Isotherm 7.2 x 10--l.9 x I0-

7 F400 Isotherm 2.8)(l0-81)(10-6

F300 Isotherm 3.5 x l0--1.1 x

Maximum Surface Concentration, mol/g

9.6 x

3.0 x

3.4)< 10

99.8%

removal

80%

removal I x

1.2 x

1.3 x i0-5

1.0>(to-4

2.6 x I0

5.1)< i0-5

1.5 x 10-2

1.5x i-

I x

1.6 x

References

Procedure Dahm et *al.,*

unknown 1974

Mahon, 1979

Fochtman and Dobbs, 1980

BorneIt, 1979

&Schmidt, 1974

Shevehenko *etal.,* 1974

Dobbs *etal.,* 1978

Dobbs *etal.,* 1978

Weber et *al.,* 1977

Weber et *al.*, 1977

Hansen, 1979b Dobbs *etal.*, 1978

Dobbs *et.al.*, 1978

Weber et *al.*, 1977

Mahon, 1979

Review article

Abstract

Translated abstract

pit 7and9 data pooled

DDT 3545 2 F300 Isotherm 1.0 x I0-85.9 x 10-8

Dichloro 147.01 3 F300 Isotherm 2.7 l05-6.8x l0-

benzene

1,2 Dichloro- 98.96 F300 Isotherm 1.7 x 10--6.6>< i-

ethane

2,4-Dichloro- 221 Unknown Aqua Nu Isotherm 2 I0--2 x 10-6

phenoxyacetic char A

acid (2,4.D)

Dieldrin 381 6 F300 Isotherm 2.1 x 10tQ17 x I0

1,4-Dioxane 88.12 8 F400 Isotherm 2.5 x x

1,1.Diphenyl 184 F400 Isotherm 2.2x 10-6.4.9 x 10

hydfazine

Endrin 381 6 F300 Isotherm 1.8 x 10tQ39 x 10-8

Halogenated 266.4 S F300 Isotherm 1.7 >(l02.9 x 10

phenols

(e.g. pentachloro phenol)

Heptachlor 373.3 2 F300 Isotherm 1.6 I0-8l.5 x 10 Heptachlor 389 Unknown Unknown % reduction Unknown

epoxide

IIexachloro 236.74 I F300 Column Unknown ethane recovery

Methoxychlor 346 Unknown Unknown 0/0 reduction Unknown

Methylene

chloride (dichloro methane)

Nitrosamines

(e.g., N-Nitrosotli phenylamine)

Polychlorinated

biphenyls (1'CB) (e.g., Arochior 1254)

84.9 17 F400 Isotherm 1.7 *x* 10-5.0 *x* i05

2.3 >(I0-

1.4)(l0-

6.9 10-6

4 x 10-0

1.7 x 10

2.6 *x* i04

8.1 >(

6.2 x

2.1 x I0-

3.3 *x*

>80%

removal

Amount of carlson not specified

>80%

removal

5.8 *x* 10

198.07 17 F300 Isotherm 5.0 x 10--3.5 >(10- 2.2)<

Mixture 6 F300 Isotherm 0.5'Lglliter- 6.4mg/g

37,0g/Iiter

Mahon, 1979

I,4-Dichloro- Mahon, 1979

berrene

Dobbs *et.al.,*

1978

Sodium Aly and

salt Fawt, 1965

Mahon, 1979

McGuireet

al., 1978

Fochtman and

Dobbs, 1979

Mahon, 1979

Pentachloro- Dobbs el al.,

phenol,pH3 1978

Mahon, 1979

Abstract Schmidt, 1974

100% Chriswell,

removal et. al., 1977

100 ~g/liter

influent

Abstract Schmidt, 1974

Weber el

a., 1977

Dobbs el al.,

N-Nitroso.

diphenyl - 1978

amine

Arochior Mahon, 1979

1254

Equilibrium Maximum

Number Adsorption Concentration- Surface

Organic Molecular of Data Carbon Test Range, Concentration

Compounds Weight Points Type Method moVllter , mol/g Comments References

Polynuclear Eight - 10 % reduction ppb level Variable 99% Borneif, 1980

aromatic compounds types removal;

hydrocarbons review

article

Simazine 201.69 OU-A %reduction 7)(i- 4 x i- Translated Shevehenko

abstract etal., 1974

Tetrachloro- 165.83 10 F400 Isotherm 6 x 10-IO2.5 x 10-8 6 10- Weberci

ethylene al., 1977

Toluene 92.15 4 F300 Isotherm 1.7 x 10-4.8x i- 95 x i- Mahon, 1979

Toxaphene 412 Unknown F300 Isotherm 5)(10-84)(i- 1 x i04 Hager and

Rizzo1 1974

1,1,1Trichloro- 133.41 - F300 Isotherm 2.7)(10-61.2 x 10- 2.7 x 10- Hansen, 1979b

ethane

Trichloro- 131.39 7 F300 Isotherm 1.1 x 10--4.8 x i- 4.2x i- Dobbs etal.,

ethylene 1978

2,4,5-Trichloro- 269 Unknown Columbia Isotherm Unknown Unknown Follows Weberand

phenoxypropionic LC laangmuir Gould, 1966

acid (2,4,5-TP) isotherm

Xylene 106.2 F300 Isotherm 1.4x i-i.i)< i- 1.2)< 10-Para Dobbs etal.,

isomer 1978

NOTE: All values are for neutral forms of the molecules unless stated otherwise.

a There are no data on adsorption by GAC of the following chemicals with possible health effects: fl-BHC, *bis* (2-chioropropyl) ether, butyl bromide,

dibromochloropropane, I 2-dibromoethane, dichlorofluorornethane, 1,1 -dichloroethene (vinylidene chloride), epichlorohydrin, ethylenethiourea (ETU), ethylene dibromide, ethylene oxide, kepone, methyl iodide, pentachloronitrohenzene (PCNB), polybrominated biphenyls (PBB), 1,1,2-trichioroethane, trichlorofluoromethane, and vinyl chloride.

h Personal communication with K. Ilansen, Calgon Corp., March21, 1979.

data that are cited in the table. Every effort was made to locate each original publication and to transcribe the data from it. In some cases, abstracts were used to obtain adsorption data. Several references contain adsorption data on the same organic compound. Well-documented adsorption isotherms were the first choice. This category was followed by selection of data based on percent reduction. The third choice was data from column tests, which indicate only that the compound is adsorbed but do not indicate sorption capacity.

Table IV-2 indicates that there are adsorption data pertaining to 40 of the *58* specific organics and classes of organic compounds. The data illustrate that a great number of the chemicals of concern are, in fact, adsorbable on activated carbon. Some of these data have been plotted in Figure IV-l; other isotherm data in Table IV-2 can be plotted in a similar fashion for comparison. One investigator claimed that some of the organic compounds being studied were not adsorbable on activated carbon (Dobbs *et al.*, 1978). There is a conflict between the results in Dobbs *et al* (1978) and Dahm *et al.* (1974) regarding the adsorbability of acetone cyanohydrin. Dobbs *et al.* (1978) listed the compound as not adsorbed by activated carbon. Dahm *et al.* (1974) reported percent removal values for the compound that ranged from 30% to 60%.

Equilibrium Models

Equilibrium models have the potential for predicting the adsorption capacities of wide varieties of organics on activated carbon. The information required to use such models includes thermodynamic properties of the solvents, adsorbents, and adsorbates. The following equilibrium models have been proposed to predict adsorption capacity:

ideal adsorbed solution theory, Polanyi theory, solvophobic theory, and the net adsorption energy concept. These models are not equivalent in their data needs, theoretical justifications, and applications. McGuire and Suffet (1978) summarized each of these modeling approaches and listed the references that describe them. Once there is confidence in such predictive techniques, the equilibrium models can hopefully be interfaced with the mass transfer models to predict breakthrough curves of single solutes and multisolute systems.

Summary, Conclusions, and Recommendations

Existing data show that GAC will adsorb many organic compounds from water. Adsorption data for approximately 70% of the specific

organics and classes of organic compounds that are suspected of being harmful to health are given in Table IV-2. Essentially, all of the compounds are adsorbable to some extent, but competitive effects are important in determining the capacity of specific water treatment applications. This is discussed in a later section.

The isotherm data base should be expanded to provide the basic data for the adsorption characteristics of chemicals that are potentially harmful to health. Experimental methods for determining isotherms and reporting of data should be standardized so that the data reported by different researchers can be compared on an equivalent basis.

More data need to be developed on the differences between adsorption kinetics for different classes of organic compounds, since the rate of adsorption is important to process efficiency. The above recommendations on standardizing experimental methods and data-reporting formats also apply to kinetic data.

EFFECTIVENESS OF PRETREATMENT FOR REMOVING SELECTED ORGANIC COMPOUNDS

Processes traditionally used to remove particulates from water also can significantly reduce organic matter. These clarification processes, which include coagulation, sedimentation, and filtration, are used at almost all surface-water treatment plants. Some organics collect on natural particles or particles that are formed during coagulation and, thus, are removed when the particles are removed. Because clarification processes remove adsorbable organic matter and consequently reduce the subsequent rate of saturation of the GAC, these processes should be used to their maximum extent. Lower loading rates will result in a lower GAC regeneration frequency, thereby lowering treatment costs, and should reduce the likelihood of displacement of organics by competitive adsorption because displacement is a function of loading. To the extent that the clarification processes remove nonadsorbable organics, they improve the quality of the water that is produced by the treatment plant and are desirable. Lowering the organic concentration by this procedure will result in a lower demand for disinfectant and lessen the likelihood of reaction of organics with the disinfectant to form undesirable end products.

Two recent reviews describe in detail many characteristics of the coagulation process in conjunction with sedimentation and filtration that are important to the removal of organics (Kavanaugh, 1978; Semmens *et*

al., 1978). The type of coagulant, coagulant dose, nature of the organic matter, and pH are especially important to the removal of organic matter as measured by dissolved organic carbon (DOC), total organic carbon CFOC), fulvic acid concentration, humic acid concentration, or color. The extent of the removals depends greatly upon the type of organic matter present. Removals as high as 95% from synthetic solutions of humic acid have been reported (Semmens *et al.,* 1978); however, typical removals are somewhat lower. TOC removals of 60% were reported for pilot scale studies of Ohio River water treatment, *25%* to 40% removals from surface waters were reported in the Federal Republic of Germany, and removals up to 60% have been reported for fulvic acid, a predominant constituent of organic matter in natural waters (Kavanaugh, 1978; Semmens *et a!.*, 1978).

The best removals of organic matter by coagulation are generally achieved at pH values of S to 6. Snoeyink *et a!.* (1978) have shown that humic substances, the predominant fraction of organic matter in surface waters, are adsorbed better at these low pH values. Consequently, both coagulation and subsequent adsorption may be more effective if conducted at low pH. As reviewed by McCreary and Snoeyink (1977), adsorption isotherms before and after coagulation can be very different.

An alternative means of characterizing the organic content of water is the trilialomethane formation potential THMFP) test, which, under a fixed set of conditions, determines the tendency to form THM's when water is chlorinated (Stevens *et a!.*, 1976). Babcock and Singer (1977) found that over 70% of the THMFP was removed by alum coagulation of a humic acid solution prior to chlorination. Alum coagulation of fulvic acid also showed removal, but not as much. The EPA (U.S. Environmental Protection Agency, 1978c) reported nearly 70% removal from a particular raw water by coagulation, sedimentation, and filtration. Kavanaugh (1978) found that a maximum of about 65% removal of TOC could be achieved from a surface water in California and that the percentage THMFP removal was nearly the same, although the magnitude of the concentration of the haloforms that resulted after chlorination was highly dependent upon pH.

The importance of at least filtration as a pretreatment for GAC is illustrated by the results currently being obtained at the Jefferson Parish water treatment plant in Louisiana, where Mississippi River water is treated by prechlorination with chloramines, coagulation, and sedimentation. After sedimentation, a portion of the flow is passed through a sand filter and then through a GAC adsorber, whereas another portion is passed directly into the GAC adsorber without prior filtration. The GAC

adsorber that receives the prefiltered water removes volatile halogenated organics, TOC, and THMFP much more efficiently than does the GAC adsorber that must also remove the particulates. Interpretation of the data is complicated by the failure to keep the same contact times in both beds.

Removals of specific compounds can also be achieved by the coagulation process. Sridharan and Lee (1972) demonstrated that some phenol, glycine, and citric acid could be removed by coagulation with ferric chloride. Pesticides may be adsorbed to silt (Greve and Wit, 1971) and associated with humic substances (Choi and Chen, 1976), which may also be removed by coagulation. Andelman (1973) has indicated that polynuclear aromatic hydrocarbons (PAH) usually occur in the form of particulates. The same is likely true for other organic compounds. For example, Greve and Wit (1971) observed that nearly all of the 0.24).6 ug/liter of endosulfan in Rhine River water was removed by clarification processes. Robeck *et al.* (1965) reported that nearly all of 10 ppb DDT was removed by coagulation-filtration, but nearly none of the same amount of lindane was eliminated. Thus, by achieving good particulate removal, significant amounts of selected organics may also be removed.

Reactions of chlorine, or other oxidative pretreatment chemicals such as ozone, chlorine dioxide, and permanganate, with organics may increase or decrease adsorbability. To the extent that higher-molecular-weight natural organics are converted to low-molecular-weight THM's, adsorbability is decreased Crable IV-2). Compounds such as phenol may be chlorinated during prechlorination of a water supply. When this occurs, solubility decreases and adsorbability increases when the pH of the solution is below the pK of the chlorinated phenol (Snoeyink *et al.*, 1977). However, as chlorine atoms are substituted onto the phenol ring, the pK is lowered, i.e., the molecule becomes more acidic. It is more likely that the molecule will be ionized at the values found in natural waters; the anionic species is more soluble than the neutral species and is more poorly adsorbed. To minimize THM concentrations in product water, it is better to minimize prechlorination as much as possible and to remove THM precursors by coagulation. Adsorption may also be necessary before final chlorination. Even less is known about the effects of other oxidative pretreatments, e.g., ozone or chlorine dioxide and their influence on subsequent adsorbability.

If proper air pollution control is observed, aeration preceding adsorption may be beneficial if the water contains volatile low-molecular-weight compounds. Such compounds are adsorbed relatively weakly, and removal before adsorption should result in longer intervals between

regenerations. Aeration during full-scale advanced wastewater treatment at Water Factory 21 has resulted in significant removals of volatile compounds. This process should be examined more closely at water treatment plants.

Bank filtration, which is practiced in the Federal Republic of Germany along the Rhine River, may also enhance the adsorption process (see McCreary and Snoeyink, 1977, for a review). As much as *65%* to 75% reductions of DOC are attributed to the biological activity in the bank, dilution effects, and possibly some adsorption. The reduction in DOC reduces the loading on the GAC and probably allows longer intervals between regenerations, although this has not been shown by experimentation. Water quality may be degraded during filtration through the soil by uptake of iron and manganese. It would then be necessary to remove these contaminants prior to adsorption to prevent their interference with that process.

Softening and manganese removal can result in reductions of organics (McCreary and Snoeyink, 1977), as can ozonization (see below).

The subcommittee located no published case histories of the use of PAC to treat the water before GAC. Nonetheless, this possibility should not be overlooked, especially during periodic heavy loads of certain organics, which might result from spills. Carbons can be made with widely different properties. Occasionally, certain compounds in the water supply may not be well removed by the GAC that is in service, but may be removed by specific powdered carbons. The use of PAC in such cases should be investigated.

EFFECTIVENESS OF GAC AS A PRETREATMENT PROCESS FOR DISINFECTANTS

Disinfectants efficiency is increased when GAC or other processes are used to reduce the organic content of water prior to disinfectants. Moreover, during chlorination one can expect fewer side reactions resulting in the production of chlorinated organics. It should be possible to achieve a given level of inactivation of undesirable microorganisms with a lower disinfectant dose in a given period or to use a shorter contact time for the same disinfectant dose to achieve the same level of inactivation. After 25 hazen units of organic color were reduced to S units, Hutchinson and Ridgway (1977) observed a reduction in contact time from 65 to 28 mm at pH 8.5, and from 6 to 2.5 min at pH *6.5* for 99% destruction of *E. coli* with 0.02 mg/liter of chlorine at *50C.* The

reduction in time required for the same concentration of chlorine dioxide to achieve the same kill under the same conditions ranged from 13 to 10 mm at pH *8.5* and from 14 to 10 min at pH *6.5.* For 0.02 mg/liter of ozone concentration at pH *6.5,* the contact time was reduced from 5.5 to 3.5 min, and at pH *8.5* it was reduced from 33 to S min.

The ozone dose that was required to produce a 3 log reduction in the standard plate count in the effluent from a GAC column in use 2 months was less than 20% of that required when no GAC was used. The chlorine dioxide dose that was required for a similar kill was reduced by a factor of 3 when GAC that was in operation for 6 months was used (U.S. Environmental Protection Agency, 1976, Appendix 3).

Nitrification may take place in GAC adsorbers when biological activity is present (see below). When this happens it is easier to use free chlorine for postdisinfection than when ammonia is present. Much more efficient destruction of bacteria and virus then becomes possible, but the likelihood of forming chlorinated organics also increases.

When the GAC adsorber removes biodegradable organic matter, not only is the disinfectant demand reduced, but also the possibilities of regrowth of microorganisms in the distribution system are decreased because the microbial food supply is reduced. Elimination of the biodegradable organic matter also increases the likelihood that residual disinfectants will persist throughout the distribution system, thereby decreasing the chances of biological growth.

Extensive biological growth in shallow beds of GAC may result in sloughing of aggregations of microorganisms into the product water. Disinfectants may be more difficult if such aggregations are present, but this problem can be minimized by more frequent backwashing.

Summary, Conclusions, and Recommendations

Clarification processes (coagulation, sedimentation, filtration) remove significant concentrations of some organics, especially some types of THM precursors and relatively insoluble compounds that may be associated with particulates. In some cases, the removal of THM precursors by clarification may be sufficient to eliminate the need for an adsorption process. There is also some evidence that filtration before GAC adsorption can result in increased life of the carbon or an increase in the time between regeneration.

In some cases, chlorination before adsorption may result in improved adsorption efficiency; in others, it may decrease efficiency. The application of PAC before GAC may be advisable in specific situations.

Disinfectants after GAC adsorption can be achieved with lower doses of disinfectants than if GAC were not used. By decreasing the concentration of biodegradable organic matter, the use of GAC also reduces the possibility that organism regrowth will occur in the distribution system. The subcommittee recommends that:

Adsorption processes should be evaluated together with the clarification processes that will precede them in a water treatment plant.

Research should be conducted on the conjunctive use of PAC and

GAC.

Research should be conducted to evaluate the aeration process for removal of volatile organic compounds during water treatment.

POWDERED ACTIVATED CARBON (PAC)

Several considerations relative to the effectiveness of PAC as the sole adsorbent for removal of organics are the same as those discussed above for GAC. In general, we can expect the same relative selectivity for the removal of organic and inorganic materials. The exceptions are those that depend upon the nature of the carbon surface because PAC usually has different properties than GAC. Lower cost materials are most often used for its manufacture, and the product usually has a much lower density. PAC is generally quite friable, but this is not important because it is usually used on a once-through basis. If friable PAC were to be regenerated, high losses undoubtedly would be observed.

The use of PAC differs from that of GAC in the point of application, the type of reactor used, the relative importance of adsorption kinetics, and the relative nature of competitive adsorption effects.

PAC is generally applied in water treatment plants at the rapid mix unit, which disperses it rapidly. The flocculation and sedimentation units, which usually follow, provide the necessary delay for many organics to adsorb. Other possible points of application include the intake and points after the rapid mix unit. The latter points are usually undesirable because of the reduced time of adsorption. If the carbon is added just ahead of the rapid filter, the contact time is only minutes or a fraction of a minute. PAC may also be applied in solids contact upflow clarifiers. In these units the PAC is suspended and the water being treated is passed through the suspension. High concentrations of PAC can be used in this type of contactor, and recycling of the PAC is possible.

When PAC is applied so that it moves through the treatment units

with the water flow, it tends to equilibrate with the concentration of organics in the water treatment plant effluent. By comparison, GAC at the adsorber inlet tends to equilibrate with the concentration in the water before it comes into contact with the carbon, while GAC at the adsorber outlet tends to equilibrate with the organics in the effluent. The net result is that GAC tends to equilibrate with higher concentrations than does PAC. Because a much lower loading, i.e., mass of organic material adsorbed per mass of carbon, can be achieved at low equilibrium concentration as compared to high equilibrium concentration, more PAC than GAC is generally needed to achieve the desired removal.

To date, PAC has been used extensively in water treatment plants to remove organic compounds that cause offensive taste and odor (AWWA Committee Report, 1977). Very little has been done to evaluate its applicability to the removal of many other compounds of concern, such as THM precursors, TOC, specific chlorinated organics, etc. Some work has been performed using PAC to remove THM's, but only one carbon was used and only one type of water was treated (U.S. Environmental Protection Agency, 1976a). Competitive effects and carbon type can significantly affect results. Therefore, tests should be conducted on other types of waters and with other carbons.

Adsorption on PAC is affected by other processes. For example, when applied in the rapid mix unit the PAC is likely to become enmeshed in floc particles, thereby affecting the adsorption of certain compounds.

When PAC is applied to water containing chlorine, the carbon will act as a reducing agent and destroy the chlorine. This increases the chlorine required to achieve a given level of disinfectants. There is also some evidence that the reaction with chlorine has an adverse effect on the adsorption of organics (McGuire *et al.*, 1978; Snoeyink *et al.*, 1974). The significance of this problem needs further evaluation. It is also not known whether the chlorine that reacts with the carbon or the organic compounds on the carbon surface produces undesirable chlorinated organics that enter the treated water.

Adsorption of molecules that diffuse rapidly should reach equilibrium with the small PAC particles in the water treatment plant. However, large molecules such as humic acid diffuse slowly, and it is very likely that adsorption equilibrium cannot be achieved in the available time.

Adsorbing molecules compete for sites on PAC just as they do on GAC. Most of the same considerations apply to both materials, but one unique difference concerns the displacement of previously adsorbed molecules. In a GAC bed, weakly adsorbed material may be displaced, sometimes resulting in an effluent concentration that is greater than the influent concentration. When PAC is used in a sludge blanket, such as in an upflow solids contact clarifier, it is expected to behave similarly, but when it is applied so that it moves through the treatment plant with the water being treated until it settles out, the effluent concentration will always be less than the influent concentration, although the percent that is removed will not be as high as when there is no competition.

Summary, Conclusions, and Recommendations

Lower loadings can be achieved on PAC than on GAC in a fixed or fluidized bed adsorber. Thus, higher doses of PAC are generally required to achieve equivalent results. PAC is also difficult to regenerate, but, because it costs less, it may be economically justified in certain applications. In general, the same types of compounds are expected to adsorb on PAC as on GAC. When PAC is applied so that it is in contact with water only a short time, it very likely does not support biological activity. Mso, when PAC moves with the water being treated, effluent concentrations greater than the influent will not occur. However, when it is applied in upflow solids contact clarifiers, the time of contact between the carbon particles and the water is longer, and microbial growth may attach to the carbon particles.

More research is recommended to determine the conditions under which PAC is most effective and to ascertain whether the reaction of PAC (as well as for GAC) and its adsorbed compounds with predisinfectants will result in undesirable compounds in the treated water.

COMPETITION ON GAC

Competitive effects are created by adsorption of a wide spectrum of trace organics, which are found in water supplies and generated within the treatment process. These should be considered in order to estimate the overall efficiency of the GAC process. As shown in Figure IV-l, Table IV-2, and by the theoretical calculations of McGuire and Suffet (1980), the adsorbability of the multitude of organics that have been identified in water supplies can vary widely. Therefore, displacement of weakly adsorbed by strongly adsorbed organics is a possibility. Depending upon the relative concentrations of these organics, displacement can also lead to temporarily higher concentrations in the effluent of the GAC bed than in the influent for any given species. Thus, the degree of competition between organic compounds of potential harm to health and their competition with humic substances are considered below.

The bulk of the data illustrating the effects of competitive adsorption derives mostly from controlled laboratory experiments with two component systems. Data from a few pilot plant studies were also examined to determine if competitive effects were significant under actual operating conditions where complex mixtures of various organic contaminants are being treated. In these studies, however, it was difficult to conclude whether or not competition was responsible for earlier-than-expected breakthrough of specific organics and, in some instances, for concentrations of certain organic species in the effluent of the GAC bed being higher than in the influent. This difficulty arises because the composition and concentration of trace organics in the raw water are highly variable. Suffet *et al* (l978a,b) demonstrated influent variability in studies of the effectiveness of GAC beds treating the Philadelphia water supply.

If the influent composition of organic species to the GAC bed is highly variable, then the adsorption equilibrium capacity for each organic must be continually in a state of readjustment, even when competitive adsorption is negligible. Therefore, it is reasonable to expect that desorption of an organic contaminant could occur due to reequilibration with a lower influent concentration. Such desorption thus occurs completely independent of any effect of competitive adsorption and needs to be accounted for separately. This point will be discussed further in the section entitled "Pilot Plant Studies of Competitive Adsorption."

Studies of Competitive Equilibrium Adsorption

Reported laboratory studies of competitive adsorption have been summarized in Table IV-3. In most of these studies two component systems were used. Furthermore, most of the organics tested were not suspected of having potential health effects. In many cases the range of equilibrium concentrations was much higher than the range that would be of practical concern in water treatment (mg/liter concentrations). Although these three factors limit the applicability of results, the data nevertheless provide good insight into the extent and variation of competitive adsorption. Some of the studies in Table IV-3 include mathematical modeling of fixed bed adsorbers (e.g., Crittendon and Weber, 1978a,b,c; Fritz, 1978; Hsieh, 1974; Keinath and Carnahan, 1973; Weber, 1966; Weber and Keinath, 1967; Weber *et al*, 1978b).

In general, the extent of competition depends upon the relative adsorption of each component in a single component system. If two components adsorb equally well, then the competition between them will also be equal and less adsorption of both will occur. On the other hand, should one component be adsorbed much more strongly, then the degree

of competition will be unequal and the weaker component will be displaced to a far greater extent.

Prediction of competitive effects is not always straightforward, even in many of the oversimplified Systems shown in Table IV-3. When competition involves weak organic acids, pH can be very important in determining the competing species and the resulting extent of interactton with other adsorbing organics. (See entries l-4, 7, l-l2, 17-19, and 2- 27 of Table IV-3.) Although models of competitive adsorption assume that all organics will compete for at least some, if not all, of the sites available, studies have already shown exceptions. For example, members of the alkylbenzenesulfonate family exhibit the tendency towards irreversible adsorption which in itself implies restriction of competition (see entries 3, 5, 16, 17, and 41 of Table IV-3). Also, chloroform, in competition with p-nitrophenol, is adsorbed far less than would be predicted from competitive adsorption models based upon the single solute adsorption isotherms, while p-nitrophenol is adsorbed better (see entries 37-39 of Table IV-3). This implies adsorption at different sites.

Table IV-3 shows that nitro-, chloro-, methyl- and bromo-substituted phenols have been studied in some detail in competitive systems. p-Nitrophenol is very strongly adsorbed compared to many organics (entries 1-14). Phenol itself is adsorbed relatively weakly and is displaced most readily in competitive Systems containing substituted phenols (entries l-l9 in Table IV-3). On the other hand, the more highly substituted phenols such as trichlorophenol are strongly adsorbed in neutral form and are less easily displaced (entry *25).*

While most attention has focused upon removal of the trace organics, it may also be necessary to estimate the relative sorptive behavior of humic substances, which are precursors to haloforms. This concern arises if postchlorination is a consideration. In such cases, the displacement of the humic substances by more strongly adsorbed components could control service time of the GAC bed. Entries 29-35 of Table IV-3 indicate that the concentration of humic substances has been much higher than that of the competing component in order to simulate the most likely condition to be encountered in practice. Under such conditions, some displacement of the trace organic was caused by the presence of humic substances.

Snoeyink *et al* (1977) have shown the adsorption behavior of humic substances to vary with the molecular weight fraction. The humic substances can exhibit different degrees of competition with trace organics. Generally, humic substances are relatively weakly adsorbed. However, the much higher concentration of these organics, i.e., mg/liter, as compared with that of the trace organics of concern, i.e., ug/liter, can

TABLE IV-3 Summary of Competitive Equilibrium Studies

Extent of

Decrease

of Each Successof

Equilibrium Component Competitive

Entry Concentration- in the Adsorption

Number Components Range Mixture a Modeling Comments Reference

CD

p-Nitrophenol (PNP) **1O4-lO2M** Mutual Excellent

p-Bromophenol **BP)**

2 PNP(anion) IO5lO2 *M* **PNP> >PBP** Good

PBP (anion)

3 PNP-Benzene *lO5-lO2M* None Moderate

sulfonate (BS)

PNP (anion) **iO5iO2** *M* BSdisplaced; Poor (observed

BS (anion) **PNPuaaf competition**

fected less than

predicted)

5 PNPD-sulto lO3-1O2M DBSirrever NA

nate ([)BS) sibly adsorbed

6 PNP-Benzoic 1O-71O-6 M BA»PNP Good

acid A)

Both components in neutral forms. Strong competition noted.

Electrostatic repulsion caused by anionic charge noted to decrease adsoprtion. Some noncompetitive adsorption of **PBP** suggested.

PNP in neutral form and BS in anionic form. Adsorption on different sites indicated.

Electrostatic repulsion caused by anionic charge noted to decrease adsorption of BS. Some adsorption without competition indicated.

Competition observed only when carbon was preloaded with **PNP.**

Both components in neutral form.

PNP-BA 1O21O-4 *M* BA> **>PNP** Excellent Both components in

1O2M neutral form.

8 PNP-Glucose 1O-21O-7 MI Glucose > >PNP Excellent

O.4-2.7M

lain and Snoeyink, **1973**

lain and Snoeyink, **1973**

Jain and Snoeyink, 1973

lain and Snceyink, 1973

Baldauf, 1978

Baldauf, 1978; **Joasens** *el al.,* **1978; Fritz, 1978**

Rosene and Manes, 1976

Rosene and Manes, 1976

9 **PNP-Urea**

10 PNP(aiiionic)

Aniline (neutral)

II PNP(neutral)

Aniline (cationic)

12 PNP-Chlorn

phenol (PCP)

l02-l07M Urea>>PNB Excellent

l0--3.l0-2 *M* PNP> >Aniline Excellent l03.l02 *M* Aniline > >PNP Excellent

103-10M Mutual Excellent Both components in neutral

form. Strong competition

Rosene and Manes, 1976

Baldauf, 1978

lialdauf 1978 BaIdauf, 1978

13 PNP-PCP IQ *3-l()2M* Mutual Excellent

14 PNP-Phenol

15 PNP-&Phenyl

phenol (OPP)

16 Phenol-DBS

17 Phenol (neutral)

DBS (anionic)

18 Phenol

Toluenesul

fonate)

19 Phenol (neutral).

PBP (neutral)

20 Phenol

Resorcinol

21 Phenol-2,4-

dichloro

phenoxyacetic

acid (2,4 D)

noted.

l0- l02 *M* Phenol> >PNP Excellent

l03.l02 *M* PNP >OPP Excellent

l06-l04M Phenol> >DBS Excellent Some adsorption without

competition suggested. Total

adsorption capacity of mixture

exceeded that of either

maximum, single component

capacity.

l0-104M Phenol>>L)BS Moderate

l05-104M 1S>>Phenol Moderate Phenol in neutral form

and PTS in anionic

form.

Jossenseial., 1978; Fritz, 1978; DiGiano *'gal.,* 1978 DiGianoelal., 1978; Fritz, 1978;Jossens *egal.,* 1978

loosens *el al.,* 1978

Weber and Morris, 1964b

Crittenden and **Weber,** 1978c

Crittenden and Webor, 1978c

l0--10 *M* Phenol> > PBP Excellent Mathews, 1975

l0I.l *M* Phenol> Good Radke and

Resorcinol Praunsnitz, 1972b

I I04M- Phenol >2,4D Excellent llsieh, 1974

4x l04M

""I

'0

Extent of

[)decrease

of Each Successof

Equilibrium Component Competitive

Entry Concentration- in the Adsorption

Number Components Range Mixture a Modeling Comments Reference

22 PCP-p-Cresol l0510l *M* Cresol>PCP Excellent

23 PCP-Phenyl

acetic acid

24 OPP-Dirntro-

sec-butylphenol

([)NOSBP)

25 Dichiorophenol ([)CP)

Trichiorophenol

([CP)

26 DCP (neutral) i09-l0 *M*

TCP (anionic)

27 DCP (anionic) l09-l0M

TCP (anionic)

l03-l02M PAA>>PCP Excellent

l06l0-5 *M* l0-l0- *M*

OPP> > **[)NOSBP** Excellent **[)CP> >TCP** Moderate

TCP> > **DCP Poor (at** higher

concentrations

competition was

reverse ofpre

diction)

TCP»DCP Good

28 DCP-DBS l0310-2 *M* Mutual Excellent

29 llumicsub l06l05 *M* TCP»Humic NA

stances-TCP 10-50 mg/liter substances

Radke and Prausnits, 1972b

Fritz, 1978; Jossens *etal.*, 1978

Keinath and Carnanam, 1973

Both components in neutral Snoeyink *etal.,*

forms. Strong competition 1977

noted, especially at higher

concentrations.

Some adsorption without Snoeyik et al.,

competition indicated; 1977; Murin and

electrostatic interaction also Snceyink, 1979

noted.

Some adsorption without Snceyink *el al.,*

competition indicated. 1977; Murin and

Snoeyink, 1979

Fritz, 1978; Jossens

et. al., 1978

More competition noted at lower Snoeyink egal.,

pH and higher humic 1977; Murin and

substance concentration. Snoeyink, 1979

Humics were weakly

adsorbed.

a.

0

30 Humic substances l0-IOOmg/liter MID> >Humic

Methylisobomeol 0.1-100 ~g/liter substances

(MID)

31 Humic substances 10-40 mg/liter Geosmin»

Geosmin 0.1-100 ~g/liter Humic

substances

32 Humic substances 10-100 mg/liter None

Denranthracene - 10

33 Humic substances S/literal None

Carbon ietrachloride l0~6M

34 Humic substances S/litter Dicidrin>

Dieldrin 10-8~l0~7 M Humic sub

stances

35 Humic substances

PCB (Araclor 1016)

36 Ligninsul

fonic acids

(LSA)-PNP

37 Cloroform

Bromoform

38 Chloroform

PNP

39 Chloroform-

LSA

S

l0-8~l0~~7 *M*

10/literl l0-~-l0~~ *M*

PCD> Humic substances

Mutual

NA

NA

NA

NA NA

NA

Good (simplified system description to two components)

l0~~-I0-~ *M* Chloroform>> Poor (Chloro

Bromoform form displaced

more than predicted)

I0-~-l0 3 *M* Chloroform>PNP Poor (chloroform displaced

more than predicted)

10-50 mg/liter Chloroform>> Poor (chloro

LSA form displaced

more than

predicted)

Even with competition MID adsorption was very effective. More competition noted at lower MID concentrations.

Geosmin displaced to greater extent than MID but was the more strongly adsorbed in single component system.

Limited testing; benranthracene did not associate with humic substances and was well removed by adsorption.

No competitive interaction noted.

Presence of humic substances in much larger concentration than dielcirin produced a significant competitive effect.

Same as above.

Snoeyink e~ *al.* 1977; Herring *et. al.*, 1977

Snoeyink *et al.*, 1977; Herring *et. al.*, 1977

Snoeyink el *al.*, 1977

Weber *et al.* 1978b

Weber et *al.*, 1978b

Weber *et al.* 1978b

Frick *et.al.,* inpreas

Little displacement of Daldauf, 1978

bromoform.

Little displacement of PNP. DaIdauf, 1978

Little displacement of PNP. Baldauf, 1978

TABLE IV-3 (continued)

Extent of

Decrease

of Each Successor

Equilibrium Component Competitive

Entry Concentration- in the Adsorption

Number Components Range Mixture a Modeling Comments Reference

40 10-410t *M* Mutual Excellent Acetone

Propionitrile

41 Nitrochioro

benzene-DBS

42 BA-Glucose

43 BA-Valine

44 BA-Methionine

45 Philathide

Glucose

46 Philathide

Urea

47 Nitromethane M)

Methylethylketone

MEK)-n-Butanol

()-1,4 Dioxane(D)

48 2-Chiorophenol-

&Cresol

2.Methylpyridine

I06-l04M Mutual Excellent

l0-1O *MI* Glucose> >BA Excellent

0.4-2.75 M

IO--1O MI Valine> >BA Excellent

0.6M

i03-i0 MI Methionine> >BA Excellent

0.07 M

102t05 M Glucese>> Excellent

0.2-0.2 M Philathide

lO21O-5 MI Urea> > Philathide Excellent

10-2M

I0--l0 M NMMEK» NA

NB>D

Some adsorption without competition.

Very high concentration of more weakly adsorbed component.

Very high concentration of more weakly adsorbed component.

Very high concentration of more weakly adsorbed component.

Very high concentration of more weakly adsorbed component.

Very high concentration of more weakly adsorbed component.

Radke and Prausritz, 1972

Weber and Morris 1964

Rosene and Manes, 1976

Rosene *el al.*, 1976

Rosene *et al.*, 1976

Rosene and Manes, 1976

Rosene and Manes, 1976

MeGuire, 1977

M Mutual NA Total maximum adsorption Martin and

capacity of mixture **AI-Bahram,**

approximated maximum 1977

adsorption capacity of

strongest adsorber in single

component system.

a.

49 Nitrobenzene

2-Chiorophenol-

Cresol

2-Methylpyridine-

Pyridine

50 PNP-Thourea

Acrylamide

51 Ultrawet (1,ranched

sulfonated alkyl

benzene)-[)Dodecylsulfate

sulfate

52 Sulfonated alkyl-benzene

DNOSBP-Quinine

53 Sulfonated alkyl

benzene

Triethanolamine

2,4-DCP-Nonyl-

phenoxypoly

ethoxyethanol

54 Phenol-Quinine

Dodecylsulfate

Sulfonated alkyl-benzene

2-sec-Butyl-4,6-dinitro-

phenol-2,4-[)-

Nonylphenoxypoly

ethoxyethanol-Phenyl

dimeihyl phosphorodiarnidate

l04-103M Mutual NA Martin and

AI-Bahrani,

1977

Rosene and

i0-2i0-7 MI Mutual Excellent PNP displaced due to very high

I M/0.8M concentrations of other two Manes, 1977

components.

7xI06M NA NA Sorptive capacity of each organic Weber, 1966

Fixed bed was reduced in fixed bed

dynamic operation in comparison with

testing) that obtainable with single

solute at the same

concentration.

3x106M NA NA Same comments as above. Also, Weber and

~xedteed rates of adsorption were Keinath, 1967

dynamic reduced in mixture as

testing) compared with single solute

system.

5>(104M NA NA Same comments Weber and

fixed bed as above. Keinath, 1967

dynamic

testing)

104M NA NA Extent of interaction Weber, 1966

fixed bed unspecified. However,

dynamic significant adsorption capacity

testing) was projected in a fixed bed.

produce competitive displacement of trace organics. These factors suggest that competition between humic substances and trace organics will be difficult to predict unless adsorption experiments are conducted for each water source.

A relative scale of competition is produced by comparing entries in which benzoic acid (BA) adsorption has been studied. Compared to p-nitrophenol (PNP) (entries 6 and 7), BA is weakly adsorbed and, therefore, displaced. However, compared to glucose, valine, and methionine nine (entries 43-45), BA is strongly adsorbed, and only high concentrations of these competing organics can cause displacement. Thus, the competitive effect must always be viewed from knowledge of the other organics in the mixture.

More complex competition among three to eight components has been investigated by McGuire (1977), Martin and Al-Bahrani (1977), and Rosene and Manes (1977). Entries 47-54 summarize their findings (Weber, 1966; Weber and Keinath, 1967). The degree of competition observed by McGuire (1977) in a four-component system (entry 47) was not expected. Single solute isotherms showed that nitromethane and methyl ethyl ketone were much more strongly adsorbed than n-butanol and 1,dioxane at a pH of 8.0. In contrast, the degree of competition observed by Martin and Al-Bahrani (1977) agreed with the relative sorptive behavior of each of the components from single solute isotherms (entries 48 and 49).

The data in Table IV-3 were analyzed by various competitive equilibrium models, e.g., the Langmuir (Weber and Morris, 1964a) and semicompetitive Langmuir (Jam and Snoeyink, 1973) models, the ideal adsorbed solution model (Fritz, 1978; Radke and Prausnitz, 1972a), the empirical three-parameter model (Crittenden, 1976; Fritz, 1978; Mathews, 1975), the modified ideal adsorbed solution model (Baldauf, 1978; DiGiano *et al.*, 1978), and a modified Polanyi model (Rosene and Manes, 1976, 1977; Rosene *et al.*, 1976). None of these is sufficiently acceptable to predict competition among important trace organics without experimental data. However, in principle, the modified Polanyi model could be used to develop predictions based upon knowing only the refractive index, solubility, and bulk solid density of each of the competing species.

Laboratory Studies of Competition in GAC Beds

The objective of several recent studies of competitive adsorption has been to verify proposed dynamic mathematical models that can then be generally applied (Balzli *et al.*, 1978; Crittenden, 1976; Crittenden and Weber, 1978a,b,c; Fritz, 1978; Hsieh *et al*, 1977; Keinath and Carnahan, 1973; Merk, 1978). Model verification has been restricted mainly to two component competition and to a range of concentrations that are considerably higher than those expected in practice for trace organics. There have been no published predictions concerning competition between high concentrations of complex humic substances and very low concentrations of chlorinated organics, which may be encountered in water treatment practice. In fixed bed experiments, Weber *et a'.* (1978b) have shown evidence for displacement of carbon tetrachloride, but not dieldrin, by humic substances.

There are different assumptions regarding the mass transfer controlling step, e.g., external film versus internal pore or surface diffusion and competitive equilibria description. However, the general nature of the breakthrough behavior in studies of mathematical modeling can be predicted to be displacement of the more weakly by the more strongly adsorbed component, i.e., the chromatographic effect. The extent to which the effluent concentration of the weaker adsorbate exceeds that of the influent is determined by both the relative adsorption behavior of the two components and their influent concentrations.

There are complications in the verification of mathematical models to predict GAC bed performance, even for the simplest case of two component mixtures. For example, Crittenden (1976) found it necessary to use the lower value of mass transfer figures for both components to account for hindrance of the flux of the faster diffusing molecule by the slower diffusion. A similar observation regarding the apparent slow rate of desorption was also made by Keinath and Carnahan (1973). Hsieh (1974) used pore diffusion coefficients that were 2 to 10 times greater than determined from independent batch experiments in order to describe the data well, although this correction was not justified by experimental evidence.

Other studies have not included mathematical modeling of competitive adsorption, but they provide interesting qualitative comparisons of competitive effects. Herzing *et al* (1977) showed that competition occurred between a high concentration (10 mg/liter) of humic substances and a low concentration *(50* ug/liter) of methylisoborneol (MIB), which is an odor-producing organic.

The complex equilibrium isotherm picture for a four-component mixture (see entry 47 of Table IV-3) was used by McGuire *et al.* (1978) to describe the breakthrough characteristics for this mixture in small GAC beds. The breakthrough curves showed that I ,4-dioxane was the most poorly adsorbed of all. In fact, halfway through the experiment there was more 1 ,4-dioxane in the effluent than there was in the influent, suggesting that the other three, better adsorbed compounds were competing more efficiently for the same adsorption sites. Because of the complex dynamic and equilibrium capacities of the other three compounds, it was not possible to determine clearly how they were competing on the carbon surface.

Competition in mixtures of three and five components was investigated by Martin and Al-Bahrani (1977). The extent of competition could be predicted qualitatively from the relative adsorptive behavior shown by comparing single-component, equilibrium isotherms. (See entries 49 and *50* of Table IV-3.) Continuous flow, GAC bed experiments further confirmed the same pattern of competition in which the weakest sorbate, pyridine, saturated the bed first and desorbed completely in the five-component system. The breakthrough behavior of the five organics can be ordered in terms of increasing time to reach breakthrough and decreasing magnitude of the desorption effect as follows: pyridine, 2-methylpyridine, o-cresol, 2-chiorophenol, and nitrobenzene. Obviously, the most strongly adsorbed component, nitrobenzene, did not exhibit desorption.

Pilot Plant Studies of Competitive Adsorption

Pilot plant studies have not specifically addressed evaluation of competitive adsorption. Instead, the overall effectiveness of GAC in removing specific organics with possible health effects, including the THM's, has been the focal point. Because these are pilot plant studies, the influent to the GAC bed has not been constant either in composition or in concentration of trace organics. Consequently, the net result of competitive adsorption and simple reequilibration effects is being measured in such studies.

The removal efficiencies for over 18 low-molecular-weight, volatile chlorinated and brominated organics, which are present together in a southern Florida water supply, have been measured by the EPA (U.S. Environmental Protection Agency, 1978c; Wood and DeMarco, 1980). From these measurements, estimates were made of the time for the effluent concentration to reach the influent concentration for 10 of these 18 organics in three different phases of pilot plant study (see Table IV-4). These times are necessarily approximate because the influent concentrations were highly variable and the effluent concentrations did not increase regularly with time. The EPA report did not present sufficient data to determine the importance of variations in influent concentrations.

The average concentrations of *cis*- 1 ,2-dichloroethylene were at least an order of magnitude higher than those for the other components. This

caused rapid initiation of breakthrough with concentrations reaching 1 'Ug/liter in just 3 weeks. However, this component was still relatively strongly adsorbed and effluent concentration did not equal influent concentration until the fourteenth week of operation. In contrast, vinyl chloride and 1, l-dichloroethane, while present in much lower concentrations, appeared much sooner in the effluent.

Only 1, l-dichloroethane and trichloroethylene were displaced to such an extent that effluent concentration was at some time higher than the average influent concentration. In fact, the extent 6f competition among these trace organics cannot be determined by the data provided in Table IV-4. Single component adsorption equilibria data are also needed. Table IV-4 also indicates apparent disparities in competitive effects for both of these two constituents. For example, comparing the average influent concentrations of the first-, second-, and third-listed test periods, it is unexplainable that the time for effluent concentration to reach the influent concentration should be shorter (and very significantly so) in the second and third test periods. Lower influent concentrations during these latter two test periods should have lessened competition if all other factors had remained constant- Such data show how difficult it can be to interpret pilot plant results.

Suffet *et al.* (I 978a) reported the use of gas chromatographic profiles of

- or 3-day composite samples and supplementary gas chromatography-mass spectrometry (GC-MS) to evaluate performance of the GAC columns. Influent and effluent samples were taken over a total of 33 weeks of pilot plant operation at the Torresdale Water Treatment Plant in Philadelphia. The two largest groups of organics that were identified were chlorinated aliphatics and aromatics, of which 19 appear on the EPA list of 129 priority pollutants (U.S. Environmental Protection Agency, 1974). Not all of these 19 compounds appeared continuously. In fact, a major conclusion of this study was that influent water quality varied considerably during the 33-week period, i.e., major GC peaks were highly transient with some periodic shifting to minor peaks while other peaks disappeared completely.

With the exception of chloroform, trichloroacetone, and toluene, GAC removed most organics to a considerable extent during 18 weeks of operation. In general, organics with lower boiling points appeared first in the effluent. However, the effluent concentration seemed to be highly variable. Some components were present in higher concentrations in the first week than in later weeks. This could be due to variations in influent concentrations. Like the EPA pilot plant study at a southern Florida waterworks, the Torresdale study also did not reveal firm evidence of displacement effects caused by competitive adsorption.

The removal of organics, whose concentrations tend to vary widely in

TABLE IV-4 Removal of Trace Organics in Pilot Plant Study of GAC a.b Test Period

January 18-May 20, 1977

August 26-October 18, 1977

November 1. 197.7-January 3, 1978

Time for Time for Time for

E1'11uent Con Effluent Con Effluent Con

Average Concentration to Average Concentration to Average Concentration to

Influent Reach or Ex Influent Reach or Ex Influent Reach or Ex

Concern ceed Influent Concern ceed Influent Concern ceed Influent

, Concentration. , Concentration, , Concentration,

Component ug,liter weeks ug,Iiter weeks $Ug/Iiter weeks

.- 1,2- Dichloro 1.3 17 I.0 7 0.63 8

ethylene

1,1 -Dichloroethane 0.3 13 0.3 3' 0.11 3'

cis- I 2-Dichloro- 29.0 14 19 7 24.5 9

ethylene

Trichioroethylene 0.13 17 0.I 2 0.52 8

Tetrachloroethylene 0.06 N(17)d nil N(7)d nil N(9)d

Chlorobenzene 0.19 N(17) 0.8 N(7) 0.56 N(9)

p-Chlorotoluene 0.11 N(17) 0.2 N(7) nil N(9)

m,p.o-l)ichloro 1.1 N(17) 0.3 N(7) 0.28 N(9)

benzene

Vinyl chloride 0.8 13" 5.4 s 7.4 2

I ,2-1)ichloroethane 0.11 14 5.3 7 7.9 9

a I:ron' U.S. Environmental Protection Agency, 1978c. Only average influent concentrations were reported for the lri()('s indicated. h See text for discussion.

Apparent desorption, i.e., effluent concentration greater than average influent concentration.

N( ). None found after number of days specified in parentheses.

he compound was observed at first sampling after 13 weeks of operation.

the influent, cari be particularly difficult to predict. For example, compounds adsorbed during periods of high concentration later are desorbed due to reequilibration with a lower influent concentration. The extent of adsorption-desorption will depend largely upon the adsorption equilibria. In the extreme case of a strongly adsorbed organic, reequilibration ration within a defined range of fluid phase concentration will not significantly alter the solid phase concentration. Thus, desorption is relatively unimportant. However, even in this case, almost complete disappearance of the organic in the influent will still cause desorption. Laboratory column experiments, in which a low feed concentration of carbon tetrachloride (200 ug/liter) was discontinued, have showed this desorption effect (Weber *el al.*, 1978b). Similar results were obtained with dieldrin.

Love and Symons (1978) showed that a concentration spike of carbon tetrachloride, in which the influent concentration increased from 10 to 55 ug/liter for several weeks and then decreased to less than 1 ug/liter, caused adsorption followed by desorption. However, this produced an increase in effluent concentration that was far less than the maximum influent concentration. The effluent concentration remained at approximately 10 ug/liter for roughly 20 weeks and then dropped below the lower limit of detectability. In this example, the kinetics of adsorption-desorption probably produced a "dampening effect" during reequilibration with the lower carbon tetrachloride concentration in the influent, thereby preventing the sudden appearance of a high concentration in the effluent.

The effect of a varying influent concentration of one component on the adsorption of another component must also be considered. For example, Love and Symons (1978) showed that a "slug" of carbon tetrachloride could cause competitive displacement of chloroform, which was previously adsorbed on the GAC bed; however, the extent to which effluent chloroform concentration increased was not very significant.

In other studies, the order of appearance of various THM species in the effluent of the GAC bed has been measured. At Stuttgart, Federal Republic of Germany, the effluent concentration of chloroform exceeded the influent concentration after 55 days of operation and remained significantly higher for 14 days (Sander *et al,* 1977). However, this occurred for only one of the three GAC types being tested in parallel operation. This suggested that the extent of competition also depends on the type of carbon that is used. Comparisons of GAC types at Duesseldori, Federal Republic of Germany (Poggenburg *et al.,* 1974) and at Cincinnati, Ohio (U.S. Environmental Protection Agency, 1978c) support this argument.

Sander *et al.* (1977) observed that the breakthrough of dichlorobrommethane was much slower than that of chloroform. However, the concentration of dichiorobromethane entering the GAC bed was 60% less than that of chloroform. Therefore, a longer time to breakthrough is not necessarily attributable to better adsorption characteristics. Love *et al.* (1976) also compared the breakthrough behavior of haloforms with results that were similar to those obtained by Sander *et al.* (1977). Competitive adsorption may have been indicated by displacement of chloroform after 6 months of operation. A lesser displacement effect was noted for bromodichloromethane.

The removal of precursors to haloforms by GAC also was reported by Love *et a?.* (1976). In the system that they studied chlorination was not used prior to the GAC. The breakthrough of the precursors that produced bromodichioromethane and dibromochioromethane occurred much sooner than that of the precursors to chloroform formation. Comparison of coal- and lignite-base carbons showed that only the coal-base carbon significantly displaced precursors to all three haloforms. This again indicates that the degree of competition can depend upon carbon type.

Observations of Competitive Effects in Full-Scale Operation

There are limited data for use in interpreting competitive adsorption in full-scale GAC systems. Sorbed phase concentration profiles have been measured for nonpolar chlorine as well as for tetrachloroethylene, hexachiorobutane, and hexachiorocyclohexane at the Duesseldorf Water Works in the Federal Republic of Germany (Poggenburg *et al,* 1974). All of these profiles showed a decrease in concentration with depth, which did not suggest strong competitive effects. However, the adsorbed amounts of each component were considerably different and all of the sorbed phase profiles were very flat, which indicates that the adsorption of these components was relatively weak.

GAC treatment has been evaluated in full-scale testing for a total of 1 yr at the Jefferson Parish Water Treatment Plant on the lower Mississippi River (Brodtmann *et a?.,* 1980). The first phase of study (February-August 1977) was distinguishable from the second phase November-April 1978) by much higher and more variable concentrations of total THM and of precursors to the formation of the various THM species, as measured by the THMFP test.

Brodtmann *et a?.* (1980) observed a strong contrast in effluent concentrations of total THM during these two phases. In the first phase, influent concentration was exceeded after 90 days of operation; after 120 days, effluent concentration was two- to fivefold higher. In the second phase, effluent concentration never exceeded influent concentration during 180 days of operation. Although the influent concentration was much lower in the second phase, the m9st important factor accounting for the lack of a displacement effect was most likely the more consistent nature of the influent concentration. The effluent concentration in the first phase always increased sharply whenever the influent concentration decreased sharply. This indicated that reequilibration was taking place. While Brodtmann *et al.* (1980) also pointed out that the degree of competition afforded by other organics may have been different in these two phases, they provided no evidence.

The Jefferson Parish study also showed that removal of precursors to chloroform and dichlorobromoform was not affected by displacement due to competitive adsorption and/or reequilibration with a changing influent concentration. Instead, a steady-state removal of approximately *50%* was reached after 60 days of operation. Biological activity was suggested as the explanation for this.

Summary, Conclusions, and Recommendations

Dynamic situations in GAC beds can be complicated by a variety of competing species that may all have different concentrations. Table IV-2 shows the variability of adsorption of specific organics that can enter a water treatment process. In general, the relative concentrations of competing species, their degree of competition (i.e., stronger versus weaker adsorbing components), and their relative diffusive properties will influence displacement effects. Even if organics do not compete, shifts in influent concentration will cause the effluent concentration to reequilibrate with it. The extent of the reequilibration will be determined by adsorption equilibria in each case.

Competition can be anticipated between trace organics, which account for only a small fraction of the TOC, and most TOC, which is composed of humic substances originating from normal degradation processes. However, the adsorption properties of humic substances will vary, thereby making competitive interactions more difficult to predict. Table IV-4 shows examples of competitive interaction between humic substances and organics. Because the source of humic substances may be different for each water supply and may vary seasonally, pilot plant studies at specific locations over the seasons of the year will yield the most useful information on the effects of competition.

The wide spectrum of organics that have been identified in water supplies represent an equally wide spectrum of adsorption behavior. This should also lead to competition among organics of differing adsorbabilities for sites on the carbon surface. However, there is little information on the mutual reduction in adsorption capacity for competing organics in the truly multicomponent mixtures that are encountered in drinking water treatment. Data from pilot plant studies show that GAC is still effective, despite effects from competitive adsorption.

The direct information provided by the pilot plant studies seems to be an alternative to the more scientific, but as yet underdeveloped, approach that is provided by mathematical modeling of competitive adsorption. During the limited observation time in pilot plant studies, some empirical interpretation of performance can be obtained if all the major organics of concern are monitored. The results of these studies could then be used to develop a suitable monitoring program that focuses on the least adsorbable organics and/or those in highest concentration. The following conclusions can be made:

1. There are few data on the degree of competition for adsorption sites between trace organics of potential harm to health and the humic substances, which comprise the largest single fraction of organics in water supplies. It is also important to note that different sources of humic substances produced different extents of competition. There are also limited data on the degree of competition among organics of concern.

2. Organics found in water supplies exhibit a wide spectrum of adsorption behavior. Therefore, competition for adsorption sites should be expected. It is conceivable that the effluent concentrations of the more weakly adsorbed components could exceed the concentrations in the influent to the GAC bed if competitive adsorption occurred.

3. Pilot plant studies show that GAC is an effective process for removal of many organic contaminants of health concern despite whatever effects competition may have on adsorbability.

4. Pilot plant studies have shown that effluent concentrations of chloroform and, possibly, 1,1-dichloroethane and trichloroethylene exceeded influent concentrations to the GAC bed; however, from existing data, it is not possible to distinguish a displacement effect due to competitive adsorption from that due to reequilibration with a changing influent concentration.

5. Shifts in concentrations and composition of organics in the influent to the GAC bed, which then cause reequilibration, may be as important as competitive adsorption in determining effluent concentration. Because of the large number of organic components, mathematical predictions of treatment effectiveness for each component

would be impractical, if not impossible.

6. Pilot plant studies over a fairly long term, e.g., conducted throughout the four seasons of the year, would seem to be necessary to evaluate the net effects of competition and reequilibration that could be

expected for organics that are potentially harmful to health under the specific conditions at each treatment facility.

More basic data are needed on the competitive interaction among trace organics of concern to health and between extremely low concentrations of these organics and the relatively high concentrations of humic substances- While it may be impossible to predict competitive effects in complex mixtures, studies of simple, two and three-component systems can generate a relative scale of intensity of competitive interactions. Attempts to find general rules for competitive adsorption and to develop mathematical models should be continued.

Although continued research is recommended, the more immediate and pressing need is to determine whether significant displacement of any organics of health concern occurs in the operation of GAC beds that are intended for treatment of drinking water. Although trace organics of concern in the raw water supply are identified and their concentrations and the variability in their concentrations are measured, pilot plant studies will still be necessary to confirm the relative order of break-through of each contaminant and to assess the importance of any displacement effect. This displacement effect can be caused both by a variable influent composition and by competitive adsorption. Although it is difficult to distinguish between these two factors in pilot plant studies, every effort should be made to determine which is more important.

MICROBIAL ACTIVITY ON GAC

While microbial activity has long been recognized as beneficial in the operation of slow sand filters, it has only recently been given consideration as a controllable, positive feature of treatment with GAC. Electron micrographs provide clear evidence of the presence of microorganisms on the surface of GAC (Weber *et al,* 1978a). The types and number of microorganisms will depend upon the amount and nature of the available substrates. This section evaluates this process in light of the ultimate objective of reducing the concentration of, or eliminating completely, the organic compounds that are potentially harmful to health. Hence, the following questions must be addressed:

1. To what extent does microbial activity interact with adsorption in the process of removing organic contaminants? Does it interfere with or aid removal? Does it extend bed life? How does it remove specific organics of toxicological concern?

2. What is the effect of pretreatment by ozone or chlorine on the extent of microbial activity and overall effectiveness of GAC?

3. What is the impact of microbial colonization of GAC beds on microbiological contamination of the product water? Are the number of microorganisms, including those causing disease, increased?

4. What products of microbiological activity can be expected in the finished water? Are toxicants created by microbial activity on GAC?

Interaction Between Microbial Activity and Adsorption

BIODEGRADABILITY OF ORGANIC COMPOUNDS

For the purposes of discussing the interactions between biological and physicochemical processes occurring on the GAC surface, it is convenient to divide organics into the following four categories:

1. nonadsorbable, nonbiodegradable

2. nonadsorbable, biodegradable

3. adsorbable, nonbiodegradable

4. adsorbable, biodegradable

While simple, this classification scheme is ambiguous because the term nonbiodegradable is not easily defined. Instead, Alexander (1973) has adopted the adjective recalcitrant to describe substances that persist for extended periods under all environmental conditions thus far tested. Recalcitrant Organics include those that are degraded slowly or not at all in nature. Occasionally, some organics that are usually biodegradable are recalcitrant due to specific environmental causes. Alexander outlined the conditions required for biodegradation and listed 15 possible mechanisms to explain recalcitrance. While some of these may be overcome by the environment in a GAC bed, others, such as accessibility of substrate and low concentration of substrate, may not.

Attempts have been made to relate biodegradability to chemical structure (Haller, 1978; Ludz:ack and Ettinger, 1960; Pitter 1976; Pitter *et al.,* 1974; Verschuren 1977). However, general rules are difficult to propose. Of all of the organic chemicals that are potentially harmful to health National Academy of Sciences, 1977), only benzene was included in an extensive review of biodegradability studies made by Ludzack and Ettinger (1960), who concluded that benzene was resistant to biodegradation. Helfgott *et al.* (1977) prepared a relative index for organics that are tested. Included were some Organics with potential health effects, i.e., benzene, chloroform, DDT, and vinyl chloride. They considered all four compounds to be resistant to biodegradation, but benzene has subsequently been shown to be biodegradable (Chambers *et al.,* **l%3;** Verschuren, 1977).

Pitter (1976) evaluated 123 organics in the aliphatic, cycloaliphatic, and aromatic classes. Of these, 21 organics were described as "biologically hard to decompose," and all were in the aromatic class. Included among these organics were dinitrobenzenes and phenols, phenyldiamines, trichlorophenol, nitroanilines, and naphthylamines. In all of the studies that were found in the literature, the experimental conditions were not those to be expected in treatment of drinking water. Most important, the concentrations of organics were in milligrams per liter rather than in micrograms per liter, and the concentrations of biomass were more consistent with biological waste treatment.

The organics that are most likely to be attacked microbially fall in the nonadsorbable, biodegradable category. In treatment with GAC, these organics could be removed by the biofilm surrounding the carbon granules without affecting the adsorption process. The adsorbable, biodegradable category of organics is of more interest because of the strong interaction expected between biological and adsorption processes. This sets GAC apart from sand or other inert media. Various researchers (Benedek, 1977; Tien, 1980; Ying and Weber, 1978) describe the removal mechanism as biodegradation in the biofilm, followed by adsorption of remaining substrate in the internal pore structure. Ying and Weber (1978) have adopted the term biosorption to describe this process. The resulting mathematical model, which has been applied to concentrations of organics as high as those found in wastewater, indicates that adsorption is responsible for removal of biodegradable organics during the initial period of GAC operation. Later, the biofilm develops enough so that biodegradation predominates. This provides for continued, steady-state removals and can explain extended bed life, particularly in wastewater treatment applications of GAC.

In water treatment, the removal of adsorbable, biodegradable organics by microbial activity, rather than by adsorption, enhances the opportunity for the GAC bed to remove the adsorbable, nonbiodegradable organics. This latter category is generally of more concern because it contains many of the synthetic organics that may be suspected carcinogens. Mathematical description of parallel removal processes for these two categories of organics has not yet appeared in the literature, although progress has been indicated. Recalcitrant organics, such as toluene sulfonate and potassium biphthalate, seem to be removed more effectively by GAC than can be explained on the basis of adsorption alone and Weber, 1978). Enhanced biodegradation is implied. Weber (1977) explained that the advantages of GAC over other media in promoting microbial activity are extension of contact time between the substrate and the microorganisms; increased concentration of substrate by adsorption; and enrichment of oxygen concentration on the surface by sorption. With regard to this third explanation, there is evidence that significant amounts of oxygen are adsorbed by GAC (Prober *et al.*, 1975), but the availability of this oxygen to the microbial system is not clear. A further necessary condition for biodegradation is accessibility of the substrate to the microorganism. This becomes critical if the microorganisms are restricted to the outer surfaces by their size while the sorbed organics have penetrated into the macro and micropores. This leads to the question of whether or not GAC can be regenerated biologically. The evidence thus far is incomplete and contradictory.

While the GAC bed is a suitable environment for microbial activity, questions regarding which specific organics are biodegradable and at what rate also remain unanswered by research. In addition to accessibility, the concentration of the substrate is an important factor. Clearly, many organics of concern are present in drinking water in such low concentrations that the opportunities for microbial action may be quite limited unless adsorption occurs first; however, as mentioned above, adsorption may prevent biodegradation if the substrate becomes inaccessible to the microorganism. One factor that could influence substrate availability is reequilibration when feed concentration decreases in a dynamic situation. In this case, sorbed substrate could once again become available to microorganisms. Perhaps the most reasonable picture of microbial action that emerges is that of biodegradation of easily attacked organics in the biofilm surrounding the carbon particles. Ying and Weber (1978) suggested that these are the low-molecular-weight, oxygenated organics. A certain fraction of the humic materials, which are generally known to be precursors of various chlorinated organics, may be easily degraded; however, there is evidence that other fractions are recalcitrant (Mexander, 1973; Helfgott *et al.,* 1977). There has been no evidence to suggest that any of the suspect carcinogens are acted upon by microbial action in the GAC bed.

EVIDENCE OF MICROBIAL ACTION ON GAC BEDS IN WATER TREATMENT

Much of the recent interest on the effect of microbial activity on GAC performance stems from European research and experience. However, in all reports, removal of organics is discussed in terms of nonspecific group measurements such as potassium permanganate demand, UV absorbing substances (at *254* nm), and organic carbon. Hence, there are no specific data on biological degradation of suspect carcinogenic compounds on GAC nor on extended adsorption of such compounds on GAC as a result of biological regeneration of the surface.

A comparison of the reduction in potassium permanganate demand in slow sand filters and GAC beds was made at Bremen, Federal Republic of Germany, from March 1970 to May 1973 (Eberhardt *et a!.,* 1974). As expected, the removal of organics by adsorption on GAC was better initially than removal by slow sand filtration. However, the adsorptive capacity of GAC was exhausted over a 7-month period, and removal of potassium permanganate demand through GAC treatment gradually diminished until both the GAC and slow sand systems gave similar results. Continued microbial action was suggested by the fact that both continued to remove about the same amount of potassium permanganate demand for the next 32 months.

There were seasonal fluctuations in oxygen demand, the maximum occurring in summer (up to 7 mg/liter) and the minimum in winter (down to 1 mg/liter). The investigators concluded that biological activity predominated in summer and adsorption in winter. Part of the oxygen demand in summer was attributed to bioregeneration of the GAC surface. In a closed loop experiment, in which the same batch of water was continuously cycled through a GAC bed, both oxygen consumption and carbon dioxide production continued at a steady level of approximately 5 mg/liter for 2 months. Eberhardt *et a!.* assumed that the production of carbon dioxide resulted from bioregeneration of the GAC surface. Accordingly, this carbon dioxide production is equivalent to IA mg/liter of organic carbon being removed at steady state in a contact time of 30 mm. During actual operation of the GAC beds during the last 9 months of the 3-yr pilot plant study at Bremen, the carbon dioxide production was equivalent to removal of approximately 1.4 mg/liter organic carbon.

Hutchinson and Ridgway (1977) reported that GAC beds have been installed in many waterworks in England in order to reduce residual organics. The fact that the GAC beds were still in service after several years of continuous operation was offered as evidence for the importance of removal of organics by microbial action. However, other than successful reduction of taste and odors, measurements of specific organics and their removal have not been reported. Similar conclusions may be drawn from a summary of the performance of plant installations in the Plains Region of the American Water Works System (Blanck, 1978).

A pilot study at Miami, Florida (Symons, 1980; Wood and DeMarco, 1980) indicated that removal of specific low-molecular-weight, chlorinated organics may have been enhanced by biological activity. This could be due to biodegradation of other adsorbable, biodegradable organics, which decreased the rate at which the sorptive saturation capacity was reached. The contact time before such an effect could be measured was similar to that observed by Eberhardt *et al.* (1974), i.e., approximately 20 mm.

Cairo *et al* (1980) studied contact times of up to 60 min in pilot plant studies at the Torresdale plant in Philadelphia. After 22.5 min of contact time, service time increased greatly beyond that explainable by adsorption. However, service time was measured in terms of satisfying a criterion for removal of TOC. When measured by a criterion for removal of trihalomethanes (THM's), there was no disproportionate increase of service time with contact time. These results do not support the contention that removal of adsorbable, but easily degradable, organics increases adsorption of haloforms.

In studies of long-term operation (180 days) of full-scale GAC beds at the Jefferson Parish Water Treatment Plant, which is located on the lower Mississippi River, Brodtmann *et al.* (1980) observed that a relatively steady-state removal of organic precursors to chloroform production was reached after approximately 60 days of operation. Regardless of the influent concentration of these precursors, which varied by a factor of two, the removal of them approached a steady-state level of approximately *50%,* suggesting that biological activity was responsible.

At Jefferson Parish, the approach to a steady-state removal of organics, which could be interpreted as being produced by microbial activity, was also measured by other group parameters. The approximate steady-state removals of TOC, fluorescent substances, and UV-absorbing mg substances were 30%-50%, 65%, and 60%, respectively. These percentages were reached after periods ranging from 50 to 80 days.

Two other studies of microbial activity on GAC without preozonization provided only limited data on organics removal. Schalekamp (1976) reported on pilot and full-scale operation of GAC beds treating the water of the Lake of Zurich in Switzerland. At the Lenng plant, GAC beds removed approximately I mg/liter chemical oxygen demand (COD) throughout 7 months of operation. However, the continual increase in carbon loading, as measured by dimethylformamide (DMF) extract, suggests that adsorption was continuing during the entire period of operation. A similar situation existed at the Moos water works in Zurich, where carbon loading was still very low after 3 yr of bed operation. Neither the Lenng nor Moos plants can provide meaningful information on the removal of organics before the microorganic contaminants are analyzed further.

Pilot plant evaluation of microbial activity on GAC at Wiesbaden, Federal Republic of Germany, showed a decrease in total carbon of 1.2 mg/liter and a decrease in oxygen of *1.5* mg/liter (Klotz *et al.,* 1976). An attempt was made to determine the contribution of biological activity in removal of organics by operating two GAC beds in parallel, with one bed receiving water that was sterilized by passage through a membrane filtration system. However, firm conclusions cannot be drawn from this experiment because of uncertainties regarding the reliability of the sterilization system.

There has been no evidence to suggest that microbial action removes specific organics that would otherwise escape GAC treatment. On the other hand, it appears that service life of a GAC bed can be extended by microbial action if performance is measured by removal of total organics, e.g., total organic carbon, UV absorbance, or potassium permanganate demand.

Effect of Pretreatment by Ozone and Chlorine on Microbial Action

PREOZONIZATION IN WATER TREATMENT

Whether or not preozonization converts nonbiodegradable to degradable organic compounds, which are then removed by microbial activity on GAC, is open to debate. Rice *et al.* (1978) and Sontheimer *et al.* (1978) have implied that preozonization enhances microbial action on GAC in water treatment, and Guirguis *et al.* (1978) reached a similar conclusion in studies of GAC in wastewater treatment. However, the conclusions of Guirguis *et al* (1978) have been challenged by Randtke (1978) and by Weber (1978), and results at other wastewater treatment facilities (Water Factor 21 and Lake Tahoe) indicated little enhancement of microbial activity by preozonization (Culp and Hansen, 1978).

The evidence for enhanced microbial activity with preozonization is largely indirect because there are few, if any, measurements of ozonization products and their biodegradability in studies of GAC treatment in waterworks. However, the overall positive effects of preozonization on organics removal have been reported at three full-scale waterworks located at Duesseldorf and Muelheim in the Federal Republic of Germany and at Rouen-la-Chapelle in France, as well as at pilot plant plants in Bremen, Federal Republic of Germany, Amsterdam, the Netherlands, and Morsang-sur-Seine in France (Benedek, 1977; Miller *el al.,* 1978). In all these evaluations, the removal of organics has been measured us/mg group characteristics.

Only a few investigators have examined the effectiveness of oxidation and/or coagulation steps preceding GAC. For example, in the study by Eberhardt *et al.* (1974) at the Bremen pilot plant the overall removal of organics by ozonization and GAC was slightly better than by slow sand filtration. (Both systems receiving the same pretreated water.) However, much of the improvement could be traced to the chemical oxidation step rather than the GAC beds. Ozone oxidation accounted for most of the decrease in UV-absorbing substances, as should be expected from the nature of oxidation reactions with ozone.

In pilot plant studies at the Amsterdam waterworks, GAC performance, as measured by removal of UV-absorbing substances, was definitely improved as a result of preozonization (Miller *et al.,* 1978; van Lier *et al.,* 1976). However, the UV absorbance had been reduced 50% by chemical oxidation prior to adsorption. Data reported by Miller *et al.* (1978) for the Muelheim plant indicate that UV extinction was reduced from 6.1 to 1.8 m-1 by preozonization, as compared to a reduction from 6.8 to 4.4 m-1 without preozonization. (Extinction is expressed in terms of a light path length of I m.) These reductions occurred through flocculation and rapid sand filtration.

In agreement with pilot plant results, full-scale testing of preozonization at the Muelheim plant produced significant reductions in dissolved organic carbon (DOC) through ozonization, flocculation, and rapid sand filtration (Sontheimer *et al.,* 1978). The decrease in DOC was 1.2 mg/liter as compared with 0.7 mg/liter when breakpoint chlorination was practiced.

The role of ozone in enhancing microbial activity on GAC is uncertain from the available data. In several studies, depletion of oxygen through the GAC bed was taken as evidence for biodegradation of organics. However, simultaneous nitrification, which consumes oxygen, was a significant factor. In addition, it is conceivable that ozonization, which produces supersaturation with respect to oxygen, could also have caused subsequent deoxygenation due to stripping. These two factors possibly influenced the conclusion reached by Eberhardt *et al.* (1974) that microbial activity on GAC was enhanced by ozone. Admittedly, microbial activity, rather than adsorption, must be considered as the mechanism involved in continued removal of organics by these GAC beds over an extended period of operation. However, from the data of Eberhardt *et al* (1974), who reported GAC treatment with and without preozonization, it is difficult to say that significant improvement in removal of organics occurred within the GAC bed when it was preceded by ozonization.

One of the most significant findings regarding the effect of ozonization on GAC bed performance was reported by Sontheimer *et al.* (1978) from studies at the Muelheim waterworks. A nearly steady-state removal of approximately 80% of the UV-absorbing substances was obtained in pilot plant GAC beds after preozonization. However, in parallel operation of the full-scale plant, in which breakpoint chlorination was followed by preozonization and GAC beds, the removal of the absorbing substances decreased very rapidly. This indicated that the chlorinated organics that were formed in the plant, or their subsequent oxidation products, were less biodegradable and/or less absorbable than in the unchlorinated one. The extension in life of the GAC bed after preozonization can be explained partly by the reduced concentration of UV-absorbing substances reaching the QAC bed, which was caused by more effective coagulation and oxidation processes. Nevertheless, the more or less steady-state removal by the GAC bed after several months of operation still forces the conclusion that biological activity was important. Approximately 1.5 mg/liter DOC was removed during the last 7 months of the pilot plant study after a contact time of 30 min (Jekel, 1977). The extent to which microbial action reduced organics agrees with the findings of Eberhardt *et al.* (1974).

The effect of microbial activity can also be measured indirectly by comparing DOC removal across the GAC bed with the DOC loading on the GAC bed (Sontheimer, 1974). At the Duesseldorf waterworks, a much higher value of DOC loading was anticipated based on the DOC removal than could be measured by extraction of polar and nonpolar organics from the GAC. This suggested that the microbial activity had removed sorbed organics; however. Sontheimer also indicated that loss of volatile DOC and failure to measure nonextractable organics could have been important factors accounting for DOC, which was removed.

Benedek (1977) compared the rates at which organics were removed in pre- and postozonized GAC systems in pilot plant studies at the Morsang-sur-Seine waterworks in France. The GAC beds had a contact time of 16 mm and were in service without regeneration for approximately 1 yr. Both treatment schemes removed a similar amount of organics as measured by group characteristics. Hence, there was no significant beneficial effect of preozonization. However, the ozone concentration was only 0.3-0.4 mg/liter after 10 mm of ozone contact, and the water had been chlorinated prior to treatment. Data from the pilot plant showed a decline in the rate of uptake of organics by GAC over 1 yr in both the pre- and postozonized systems. The attainment of a more or less steady rate of uptake in each system was attributed to biological activity. While this rate was somewhat higher in the preozonized system, Benedek (1977) concluded that the difference in rates was not significant. These rates ;compared quite closely to the range that was measured by Eberhardt *el al.* (1974) at the Bremen pilot plant study. A factor affecting conclusions concerning enhanced biodegradability by ozonization is the possible presence of less degradable chlorinated organics, which were formed as a result of prechlorination.

The effect of preozonization on the removal of precursors to the formation of TH M's can be deduced from studies at the EPA pilot plant study in Cincinnati, Ohio (U.S. Environmentntal Protection Agency, 1978c). Ozonized and unozonized Ohio river waters were fed to GAC beds operating in parallel. The THM formation potential (THMFP) test showed that the ozone-GAC system removed more precursors of THM's (U.S. Environmental Protection Agency, 1978c). This indicates that ozone was able to oxidize the precursors, which were then either adsorbed or biodegraded on GAC. Without ozone, much of the humic material could be recalcitrant. This has also been suggested by microbial studies that were conducted at the Water Research Center in Medmenham, England (Hutchinson and Ridgeway, 1977) and by the studies of Helfgott *et al.* (1977). Addition of ozone could have converted these humic materials to more readily biodegradable forms. With an ozone dose of only 1 mg/liter and a GAC contact time of 9 min, removal of TOC by GAC treatment was consistently and significantly better in the preozonized system over 10 months of operation without regeneration. While effluent concentrations increased rather steadily in both systems, complete saturation was not reached in either. However, the data did not indicate a leveling off of TOC in the preozonized system, which is expected when microbial activity becomes the primary organic removal mechanism.

EFFECT OF OZONE ON ORGANICS

Chapter III, which was prepared by a subcommittee of the Safe Drinking Water Committee, includes published data on the identification of specific end products of ozonization in waterworks treatment. It suffices here to state that more polar organics such as carboxylic acids, catechols, and aldehydes can be expected. Further conclusions regarding the biodegradability of these end products can only be reached indirectly from examination of pilot plant and full-scale operations.

Dosages of ozone of up to *25* mg/liter were not able to reduce THM concentrations (Love *et al.*, 1976). Similar findings were obtained in pilot plant studies of GAC beds in which ozonization of the effluent failed to reduce the THMFP. However, as noted earlier, measurements after GAC contact indicated that the addition of ozone prior to GAC reduced the THMFP (U.S. Environmental Protection Agency, 1978c). This suggests that ozone can oxidize the THM precursors to more absorbable species but cannot alter the original precursors to eliminate chlorination reactions.

Ozonization has been shown to produce less absorbable organics (Benedek, 1977). This can be caused by production of more polar organics such as carboxylic acids, catechols, and aldehydes. Reductions in adsorptive capacity on GAC (as measured by DOC) were also reported by Kuhn *et al.* (1978a,b) in studies of ozonized water from the Lake of Constance in the Federal Republic of Germany, where the applied ozone dosage ranged from *0.45* to 3.5 mg/liter. On the positive side, the combination of ozonization and coagulation seemed to produce very good removals of UV-active organic substances. This process has been successfully implemented at the Muelheim waterworks for DOC reduction (Sontheimer *el al.,* 1978).

EFFECTS OF PRECHLORINATION ON MICROBIAL ACTIVITY IN GAC BEDS

For chlorination to have a detrimental effect on microbial growth within a GAC bed, residual chlorine must be present. The catalytic dechlorination reaction on GAC counteracts this problem (Suidan *et al.,* 1977). A mathematical description of the dechlorination reaction on GAC shows that with a very short contact time (0.6 min), at an application rate of 4 gpm/ft2 and a chlorine dose of S mg/liter, residual chlorine would reach *0.5* mg/liter in approximately 10 days and 1 mg/liter in 40 days. Extrapolating this result to the more usual contact time of 15 mm, which is needed for adsorption and biological activity the rate of advancement of the chlorine residual front would be such that *25* days are required for a value of *0.5* mg/liter to be reached in the first 10% of the bed length. This "breakthrough time" for chlorine residual is proportionally increased with lower feed concentration of free chlorine and longer bed lengths.

The effect of the dechlorination reaction on GAC in a water treatment plant has been reported by Schalekamp (1976). He noted a 50% breakthrough of chlorine, i.e., *0.25* mg/liter, in water from the Lake of Zurich after 25 days of Operation at a contact time of just 0.3 mm. These data suggest that prechlorination may only impede bacterial activity if very long GAC service times are used. Referring to the brewing industry's expenence with dechlorination, Eberhardt (1976) reported that while removal of chlorine was effective, the GAC process was much maligned because of its inability to prevent bacterial growths, which were unacceptable in the product water.

More direct evidence of microbial activity on GAC with prechlorination in waterworks has been given by Schalekamp (1976), Klotz *et al* (1976), and Mueller and Bernhardt (1976). With simultaneous measurements of chlorine residual, bacterial counts, oxygen, carbon dioxide, and TOC, Klotz *et al.* (1976) showed that there was no influence of chlorine on microbial activity below a free residual of 0.1 mg/liter. Values lower than this occurred near the top of the GAC bed. In pilot plant studies at Breman, Eberhardt *et al.* (1974) also noted that oxygen consumption was similar with and without prechlorination. A somewhat opposite view was given in another report by Eberhardt (1976). He stated that chlorination would disturb microbial activity by creating less biodegradable, chlorinated organics. Similar reasoning was given by Miller *et a!.* (197S) when explaining the lack of microbial activity on GAC at the Duesseldorf waterworks. They reasoned that the Rhine River contains chlorinated organics that are not degraded by bank filtration and eventually reach the GAC beds where adsorption, but not microbial activity, occurs. Such a conclusion was supported by measurements of chlorinated organics by Steiglitz *et a!.* (1976).

Sontheimer *et al* (1978) showed that polar chlorinated Organics were produced by breakpoint chlorination at the Muelheim waterworks. In parallel operation of preozonized GAC beds, with and without break-point chlorination, they demonstrated clearly that GAC in the latter system was much more effective in removal of UV-absorbing organics over many months. They concluded that microbial activity on GAC was far more effective if prechlorination was not practiced. Moreover, its enhancement by preozonization depends upon the organics that were present in the treatment process prior to this step.

Therefore, the effects of prechlorination on microbial activity appear to be twofold. The impairment of bacterial growth was relatively minor because the dechlorination reaction in GAC beds greatly reduces free chlorine. However, the more important effect may be the formation of less biodegradable, chlorinated organics prior to treatment with GAC. The extent of formation of chlorinated Organics should depend upon the chlorine dosage and the organic species that are present. An additional consideration would be the relative absorbability of chlorinated organics as compared with their precursors. There are general rules to predict this effect.

Microbial Activity on GAC in Wastewater Treatment

From pilot plant studies at Pomona, California, Parkhurst *et al.* (1967) determined that adsorption capacity could not be completely exhausted even after very long service times. More detailed investigations of microbial degradation on GAC were provided by Weber *et al.* (1970, 1972) in other pilot plant studies that addressed the benefits of microbial activity more directly. Comparison studies of GAC and nonsorptive, bituminous coal clearly showed that more TOC removal and microbial growth occurred on GAC. This suggested that microbial activity was in some way interrelated with the adsorption process. Besik (1973) proposed that the rate of microbial activity in a GAC bed should be even higher than that in a conventional biological treatment process because the substrate adsorbed on the activated carbon is much higher than in the liquid. The interplay between microbial degradation and adsorption was recently confirmed by Maqsood and Benedek (1977).

The denitrification research of Jeris *et al* (1974) also demonstrated the advantage of GAC over sand in promoting microbial activity. In this study, they were unable to achieve significant growth on sand particles. However, using fresh activated carbon, they observed excellent growth and subsequent nitrate removal 2 weeks after start-up.

Because the concentration of biodegradable organics is far greater in wastewater than in water supplies, the extent of microbial activity on GAC beds used in wastewater after either conventional primary or secondary treatment should also be greater. Ying and Weber (1978), Peel and Benedek *(1975),* and Andrews and Tien *(1975)* have all reviewed the evidence for microbial degradation and have reported that from *25%* to 78% of the TOC that was removed in various GAC facilities could be attributed to this mechanism. The estimated rate of biodegradation based upon TOC in wastewater applications of GAC is approximately one order of magnitude greater than in water treatment applications (Benedek, 1977).

The effect of preozonization is unclear. Enrichment of sorbed oxygen, enhancement of biological activity, and increased or decreased absorbability of organics have not been addressed carefully. Guirguis *et al.* (1978) discussed the results from pilot plant operation of a preozonization-GAC system at the Cleveland Westerly physical-chemical waste-water treatment plant. Excellent COD and biochemical oxygen demand (BOD) removals were obtained through 1 yr without regeneration. In addition to oxygen enrichment by ozonization, they proposed that some organics were converted to more absorbable and more biodegradable forms. However, the basis for reaching these conclusions has been challenged by Randtke (1978) and by Weber (1978). An earlier report by Guirguis *et al.* (1976) showed no decrease in BOD after ozonization. Results obtained at the Water Factory 21 Pilot Plant in Orange County, California (Culp and Hansen, 1978) conflicted with those from the Cleveland Westerly plant. Ozonization of unchlorinated trickling filter effluent followed by GAC contact produced no enhancement of COD removal, while ozonization of unchlorinated activated sludge effluent only increased COD removals by 30%. The investigators noted microbial activity on GAC in both ozonized and unozonized systems. In another study (Culp and Hansen, 1978), ozonization (10 mg/liter) of activated sludge effluent at the Lake Tahoe Advanced Waste Treatment Plant almost doubled the bed life of the GAC for COD removal, yet chlorine residuals (1-2 mg/liter) were present in the carbon column effluent. Instead of biological action, the positive effects of ozone were attributed to oxidation reactions.

Microbial Contamination of Product Water

Microorganisms, mainly bacteria, adsorb to GAC and will colonize filter beds. They assimilate nutrients that are adsorbed to the GAC and dissolved nutrients, thereby growing to relatively high densities. Currently, the prevention of this microbial colonization is impractical.

This section will discuss what is known about the adherence and growth of microbes on GAC beds and the effect of bed contamination on the microbial content of effluent water.

ADHERENCE OF MICROBES TO GAC

Marshall (1976) and Daniels (1972) both presented excellent discussions of the factors influencing the attachment of microbes o surfaces. The mechanism of attachment remains unclear; adsorption due to electrochemical double-layer effects, as well as mechanical adhesion, have been proposed. The nature of the microorganisms and the adsorbant are also very important. Adsorption isotherms of mixed bacteria genus and species unspecified) to GAC were reported by Klotz *et al.* (1976). At bacterial concentrations of l0 10 to 108/200 nil of buffer, up to 90% of the bacteria were adsorbed. At bacterial concentrations greater than 1010, the system tended toward saturation. Dead bacteria were adsorbed somewhat more efficiently than live bacteria. No data are available on the adsorption or selective adsorption of individual bacterial species. However, Marshall (1976) has shown that adhesion of bacteria can be dependent upon their ability to produce suitable bridging polymers.

BACTERIAL GROWTH ON GAC BEDS

Standard plate count methods for bacteria from crushed and homogenized GAC have been used for quantitation. The total number of living and dead bacteria has also been determined by microscopy. The temperatures used for growth of the bacteria vary from 220C (Eberhardt *et al.*, 1974) to 270C (Klotz *et al.*, 1976). There are few data on the optimal time of incubation. Eberhardt *et al.* (1974) found colony counts from 2,700-5,200/mi after 72 hr of incubation, depending on the amount of preozonization. Incubation periods of 7 and 10 days have been reported (Klotz *et al,* 1976; Miller *et al.,* 1978), but, generally, 20-day incubations at 220C yield the highest numbers of bacteria.

Van der Kooij (1978) showed that the bacterial counts in GAC beds reached maximal numbers in 20 to 30 days, i.e., approximately l0 8 colony-forming units per gram of GAC at 250C. While fewer colonies formed on sand than on unactivated carbon, the differences were not as great as reported earlier Van der Kooij, 1976). He concluded that these bacteria were not able to utilize sorbed organics on GAC. Only the larger surface area of GAC was used to explain higher colony counts. Both GAC and sand beds showed a decline in bacteria over the l0-month period. He postulated that this was caused by a shift in population to uncountable bacteria Van der Kooij, 1976).

In another study of the microbial growth in GAC beds, Benedek (1977) showed that the total microbial burden varied as a function of filter depth. Microbe levels of 107/cm3 of GAC were found on the surface. This fell to 106 bacteria per cm3 at 40 cm (Benedek, 1977).

Although the water velocity through the GAC bed and the content of organic nutrients in the water would be expected to influence the microbial growth, there are few data available on these potential effects. In studies of velocities ranging from 4 to 20 m/hr, Klotz *et a!.* (1976) observed that the initial growth rate in the bed was slower at higher velocities and that the final counts were lower with lower velocities. By comparing operation of a slow sand filter at 0.3 m/hr and a GAC bed at 3.5 m/hr, Van der Kooij (1978) showed that colony counts were two orders of magnitude lower at the lower filtration rate. Love and Symons (1978) stated that the concentration of bacteria depends on the length of time the GAC sits idle, the concentration of bacteria in the applied water, the amount of TOC, bed depth, temperature, and hydraulic application rate. Unfortunately, they provide none of the data from which these conclusions were made.

Studies on denitrification in fluidized beds may offer insight into factors affecting microbial growth on support media. Jeris *et al.* (1974) showed that even a threefold increase in upflow velocity was insufficient to promote sloughing-off of bacteria in such a way that a steady-state biofilm thickness could be achieved. In later studies, Jeris and Owens (1975) also found that prolonged shutdowns were not detrimental to microbial activity. Oxygen transfer 4imitations may inhibit activity but only when TOC is very high as in the case described by Jeris *et al.* (1977).

There are no compelling data showing that preozonization of water has a significant impact on the microbial growth in GAC beds. Benedek (1977) reported that ozonization increased the growth of aerobic bacteria by 1/2 log. This may or may not be significant. Miller *et al.* (1978) stated that ozonization discourages the growth of anaerobic organisms and destroys slime-forming organisms, but they provided no data.

THE EFFECT OF GAC COLONIZATION ON MICROBIAL CONTENT OF THE EFFLLENT

Studies of the microbial numbers in effluents of operational and pilot GAC filters are not comparable because different culture techniques were used by the investigators. In general, the data indicate that detachment of bacteria from the bed, which results in contamination of the effluent, is a negligible problem. However, there are also notable exceptions. For example, Ford (cited in Love and Symons, 1978) studied a pilot plant in the United Kingdom and found that over a 5-yr period the effluent of GAC contained more bacteria than the effluent of a sand filter. Twenty-five percent of the GAC effluent samples contained more than 500 bacteria/mi.

The experience with GAC in Germany and Switzerland has been interpreted as favorable. During the .3-yr pilot plant study at Bremen (Eberhardt *et al*, 1974), plate counts remained below *50/mi* (assumed as a 2-day, 220C test) with the exception of two brief periods in spring and summer of 1971 when very high plate counts were measured. A 7-day, 270C plate count test was used in pilot plant studies at Wiesbaden (Klotz *et al.*, 1976). Much higher counts, ranging from l0 5 to 10 6/mi, were reported in these studies. This may have been caused by the much longer incubation time used. However, in full-scale operation, counts over a 3-yr period were much lower, i.e., on the order of 100/mi.

High initial plate counts were measured during treatment of reservoir water by ozonization and GAC contact (Mueller and Bernhardt, 1976). Counts remained at 5,000/mi for 12 months, 800-l,000/mi for 6 months, and finally decreased to less than 10/mi for 5 months. Initial counts in the treatment of reservoir water were higher than in groundwater. This was attributed to the higher organic carbon content of the reservoir compared to that of the groundwater (0.8 versus 0.3 mg/liter). The fecal indicators, *Escherichia coli* and *Pseudomonar* sp., were absent as were strains of streptomycetes. The Dohne plant at Muelheim reported effluents containing as many as 3,700 bacteria/mi (Sontheimer *et a!.*, 1978); however, these were reduced to less than 10/mi by ground passage. At the Lenng, Switzerland, waterworks, Schalekamp (1976) reported plate counts of less than 50/mi (3-day, 200C test) in the effluent of GAC beds; however, in pilot plant tests, he found higher counts (from 1,000 to 10,000/mi) throughout 3 months of operation. Backwashing of the full-scale GAC beds twice per week was thought to be responsible for the lower counts. Similar findings were reported by Hansen (cited in Love and Symons, 1978), but conflicting results were obtained by Sylvia *et al.* (cited in Love and Symons, 1978) at the Lawrence, Massachusetts, waterworks, where a transient increase in numbers of bacteria in the effluent was observed following backwash.

In other studies, 15 months of pilot testing at the Amsterdam waterworks showed that GAC beds without preozonization produced bacterial counts of less than 1,000/ml. A 3-day incubation test at 220C was used Van Lier *et al.*, 1976). Also in the Netherlands, Den Blanken (1978) found that the effluents of experimental GAC columns contained l0 2 to 10 4 bacteria/mi. In the United States, GAC effluents from a pilot plant processing Ohio River water contained less than 102 bacteria/mi (Love and Symons, 1978). Similar results were repoted by McElhaney and McKeon (1978) in pilot studies at Philadelphia; however, they observed an initial 5-week period of much higher counts. Finally, at the Rouen waterworks, which consists primarily of preozonization, GAC contact, and postozonization, colony counts in the finished water varied markedly. However, all counts over a 6-month period were less than 600 bacteria/mi, and most were less than 100 (Miller *el a!.*, 1978).

SPECIATION OF BACTERIA ON FILTER BEDS AND IN EFFLUENTS

Few data are available on the species of bacteria colonizing GAC beds and even less are available on relative numbers. Some statements, unaccompanied by data, have been written indicating that "five or six different types of colonies could be recognized" and that "two genera, *Flavobacterium* and *Xanthomonas,* were identified" (U.S. Environmental Protection Agency, 1978c). Maqsood and Benedek (1977) stated that *Pseudomonas* and *Flavobacterium* were the most prevalent genera of bacteria on GAC that was used in wastewater treatment. Den Blanken (1978) found representatives of *A cinetobacte,; Pseudomonas, Caulobacte,; Corynebacterium, Flavobacterium, Alcaligenes, Actinomyces, Bacillus, Planctomyces,* and *Moraxella.*

Some isolated strains of *Pseudomonas* and coryneforms could produce color- and odor-producing substances and antibiotics; however, these were considered absorbable by GAC. For all practical purposes, only *Bacillus, Caulobacier,* and nonpigmented *Pseudomonas* were found in the effluents. Love and Symons (1978) reported the work of Parsons, who classified the bacteria in the effluent of a pilot plant in Miami, Florida. The Organisms identified were strains of *Pseudomonas, Enterobacter agglomerans, Acinetobaczei; Alcaligenesfaecalis, Moraxella,* and *Flavobacterium.* In pilot plant studies at the Philadelphia waterworks, McElhaney and McKeon (1978) identified 10 species of *Pseudomonas.* They pointed out that while none of these were pathogenic, some could become "opportunistic pathogens." This theory demands further research.

Products of Microbiological Activity

In the operation of GAC, microorganisms proliferate actively on the carbon surface for up to several months. The resulting biochemical capabilities of the established microbial cornmunity lead to the mineralization of organic matter with the formation of carbon dioxide and microbial cells. The published research does not indicate which compounds are or are not acted upon by such microbial activity and what compounds may be generated as a consequence of bacterial growth. Attention has been focused on bulk organic materials in water and not on discrete classes of molecules.

Of potential importance also is the recent finding that some normally biodegradable compounds may be destroyed very slowly or not at all at very low concentrations (Boethling and Alexander, 1979). Hence, chemicals at low concentrations may not be destroyed on GAC or, if small amounts are released, may not be destroyed by subsequent biodegradation.

MICROBIOLOGICALLY PRODUCED LOW-MOLECULAR-WEIGHT TOXICANTS

During the last few years, it has become evident that bacteria and other microorganisms form a large number of compounds that are or may be environmental pollutants. The formation of these compounds can be shown readily in microbial cultures that are tested in the laboratory or in model ecosystems, but some have also been found in nature. The production of these toxic chemicals is not restricted to microbial populations developing at low oxygen tensions or under completely anaerobic conditions, and many are produced in maximal quantities when the oxygen supply is high. A few of the products have gained considerable attention because of their potency and the frequency of their production. A few are only now emerging as significant environmental problems.

Microbially produced toxicants have not been identified in the treatment of drinking water by GAC. They are listed here only to illustrate the potential of microbial Systems to create such problems. Methylation of mercury is widely recognized as a serious environmental problem that occurs in many environments in which bacteria develop.

Little organic matter is required for the process, and bacteria are involved. Hydroxylamine, a potent mutagen, can also be formed in culture media by microorganisms. Not only has it been observed in several natural bodies of water, but its formation can be catalyzed in waters by microorganisms Verstraete and Alexander, 1973). Pesticides or molecules related to pesticides are also acted upon microbiologically to give new toxicants. A vast body of literature attests to the ability of bacteria and other heterotrophic microorganisms to convert these chemicals to new inhibitors or to products of great toxicity to humans, animals, and plants than the precursor molecules (Alexander, 1974). In laboratory models of natural water systems, polynuclear aromatic hydrocarbons have been generated both by bacteria (Knorr and Schenk, 1968) and algae (Andelman and Suess, 1970).

No definitive studies have been made to confirm that nitrosarnines can be produced on GAC. However, the precursors to their formation are widespread and have been found in a number of waters. They can also be produced microbiologically in nature. The organic precursors are secondary or tertiary amines, which are natural products that are also found in industrial effluents and in agricultural pesticides. Bacteria also form such amines. The inorganic precursor of nitrosamines is nitrite, only low levels of which are required for the process to occur. Nitrite is formed during nitrification, which occurs on GAC, as well as during denitrification and nitrate reduction. Consequently, the precursors are ubiquitous and are likely to enter or be formed on GAC. Moreover, the process of combining the two precursors into the final toxin is easily accomplished in water, sewage, or soil (Ayanaba and Alexander, 1974; Mills and Alexander, 1976). and the reaction may be affected by microorganisms through their own activities or by organic materials formed microbiologically (Ayanaba and Alexander, 1973; Mills and Alexander, 1976).

Many refractory compounds are subject to cometabolism, although they are not totally biodegraded to yield carbon dioxide. Cometabolism refers to the capacity of microorganisms to degrade compounds that they cannot use as a nutrient source and, thus, cannot totally mineralize. As a result, organic products are generated-products that are usually related structurally to the original chemical; e.g., metabolites formed from DDT, aldrin, heptachior, PCB's, and triazine herbicides. Although there are no studies of cometabolism on the GAC surface, it seems plausible that refractory organic molecules entering water from agricultural, industrial, or domestic operations or generated as a result of chlorination could be acted upon. This would give rise to products that are themselves not suitable substrates and are not attacked readily by microorganisms on

GAC. If these products of cometabolism are not adsorbed and removed from the flowing water, they will appear in the effluent.

HIGH-MOLECULAR-WEIGHT TOXINS-ENDOTOXINS

Since GAC columns are colonized by Gram-negative bacteria, there is concern that lipopolysaccharide endotoxins may be synthesized by these bacteria and may be eluted into the finished water. Complex lipopolysaccharides are found in the outer membrane of all Gram-negative bacteria (Freer and Salton, 1971), and many, but not all, of these lipopolysaccharides possess potent endotoxic activity (Hofstad and Kristoffersen, 1970).

Absorption and Toxicity The dramatic toxicities of endotoxin, such as the production of fever, shock, or Shwartzman's phenomenon (a hemorrhagic reaction), are observed after parenteral administration. Far less is known about the absorption of endotoxin from the intestinal tract or the pathological consequences of absorption. The few data on the intestinal absorption of endotoxin suggest that the amount absorbed is minute. Gans and Matsumoto (1974) assayed endotoxin absorption in lead-sensitized rats. They found that when 5 mg of endotoxin was placed in the Thiry-Vella fistula in rats, only nanogram amounts were absorbed. Even when the rats were subjected to Osmotic shock, the amount absorbed from the fistula, although increased, was so small that "it was unlikely to be of any significance" in normal animals. On the other hand, some investigators consider endotoxin absorption to be very injurious in certain circumstances. Fine and his colleagues (Schweinberg and Fine, 1960) have proposed that the endotoxin that is produced by the resident flora of the gut is absorbed continuously and is detoxified in the liver and in the spleen to render it harmless. However, during shock states detoxification is ineffective, and the absorbed endotoxin is thought to be directly responsible for a state of irreversible shock. This theory has not been accepted universally (Shands, 1975).

Endotoxin has also been proposed as a causal factor in the production of liver injury and cirrhosis. Suppression of the microbial flora of the gut prevents the development of cirrhosis in rats on a choline-deficient diet (Broitman *et al.*, 1964). The addition of endotoxin to the drinking water reverses this protective effect. In addition, animals on a choline-deficient diet become very susceptible to the lethal and hepatotoxic effects of endotoxin (Nolan and Ali, 1968). More recently, Nolan (1975) proposed that endotoxin absorption may contribute to liver diseases in the alcoholic and perhaps to the liver diseases found in obesity bypass patients.

Measurement of Endotoxin Although lipopolysaccharides can be measured chemically, endotoxins can be measured only by biological assay. Most of the tests for activity are time-consuming and expensive, e.g., pyrogenicity and lethality tests. The limulus lysate test developed by Levin and Bang (1964) is without doubt the most sensitive test for endotoxin. It is sensitive in the nanogram to picogram range (Yin *et al.*, 1972). It is a rapid test, and, unlike other biological tests for endotoxin, it is suitable for testing many samples simultaneously. For reasons of economy, efficiency, and sensititvity, it is currently the test of choice.

Measurements of Endotoxin in Drinking Water The amount of endotoxin in drinking water has been measured with the limulus lysate test. DiLuzio and Friedmann (1973) tested tap water that was obtained from a variety of sources. They found endotoxin concentrations ranging from 1 ug to 10 ug/ml in water from Denver, Colorado; Mobile, Alabama; and San Francisco, California. Jorgensen *et al.* (1976) measured endotoxin levels varying from <0.625 ng/ml to 500 ng/ml in drinking water from 10 cities. These authors opined that the high levels found by DiLuzio and Friedman were erroneous. Jorgensen *et a!.* (1976) also suggested that endotoxin levels may be higher in water that had been treated by GAC. On the other hand, Love and Symons (1978), who conducted a 7-month pilot plant study for the EPA, found that the concentration of endotoxin in the effluent of a GAC bed was less than the concentration in the input. The maximal level in the finished water was 11 ng/ml. These data indicate that GAC filtration does not result in excess endotoxin in finished water. Furthermore, the data may be interpreted to suggest that GAC may adsorb lipopolysaccharide endotoxins, but more work is needed to verify this.

Summary, Conclusions, and Recommendations

1. No direct evidence has been given for removal of specific Organics of potential harm to health by microbial activity. Only one study (at the Jefferson Parish Water Works, which was reported by Brodtmann *et al*, 1980), implied that precursors to THM formation were removed by microbial action. An indirect benefit of microbial activity may be the lengthening of GAC service time by removing organics that would otherwise occupy adsorption sites; but this in itself does not imply more effective removal of organics of health concern.

2. While Operation of GAC beds for 6 months to 2 yr without regeneration has shown that microbial activity removes organics, as measured by group parameters such as TOC, potassium permanganate demand, COD, and UV-absorbance, the efficiency of biodegradation is less than that of adsorption, i.e., biodegradation to remove approximately *1.5* mg/liter TOC requires about 30 min of GAC contact (Benedek, 1977; Eberhardt *et al.*, 1974; Jekel, 1977), while adsorption only requires approximately 10 to 15 min.

3. Pilot and full-scale tests of preozonization have shown that Organics are efficiently removed through the total system, including the flocculation and adsorption steps; however, the ability of microbial action to aid in removal of specific organics of potential harm to health has not been reported. Thus far, one study, at the EPA Cincinnati pilot plant (U.S. Environmental Protection Agency, 1 978c), implied that precursors to THM formation were somehow altered by ozonization in such a manner that their removal was made more effective.

4. The role of ozone in promoting microbial activity remains unclear. Conversion of organics to more biodegradable forms and addition of oxygen to the biofilm are two possibilities. On the negative side, evidence shows that ozone may decrease the adsorbability of some organics.

5. While prechlorination does not stop microbial growth on GAC, there is some evidence to suggest that it results in formation of Organics that are much more resistant to biodegradation on the GAC surface.

6. The bacteria that have been reported to grow On GAC beds are considered nonpathogenic. Increases in bacteria in the effluent may be controlled by backwashing.

7. Microorganisms can generate a variety of highly potent, low-molecular-weight toxicants in culture. Studies of models of several environments and some natural systems indicate that toxicants may be, or are indeed, formed. Such products may also be produced on GAC. However, there is a lack of information regarding the identification of organics in the effluent of GAC beds. Thus, while no evidence exists, the possibility that microbial end products of concern enter the finished water cannot be ruled out.

8. The endotoxin content of water that has been filtered through GAC is either not increased or not significantly increased. The measured levels are very low and should pose no risk.

Thus far, evidence of microbial activity in GAC beds has largely been indirect. Of special importance is the identification of organics that are biodegraded. If these are not potentially harmful to health, then more investigation is needed to determine whether microbial action has

actually extended or improved the adsorption of other organics that are potentially harmful to health. This may result if fewer of the internal adsorption sites are occupied because of biodegradation at the surface. Related to this concern about extended removal of organics is the unresolved question of bioregeneration. More careful investigation is needed to determine if adsorbed organics, which are more resistant to biodegradation, can be acted upon by microbes.

The role of ozonization in promoting microbial action needs much further elucidation. This would involve studies to determine the changes in biodegradability and adsorbability that are brought about by ozonization of specific organics that could affect public health. There are similar concerns regarding the practice of prechlorination.

If the use of GAC is to become widespread, research is necessary to identify the factors that are responsible for the initiation of microbial growth on the GAC surface and the microbiological generation of organic compounds on the carbon. Attention should be given not only to the compounds that are present and retained in the bed, but also to those that are released and could appear in the effluent. Research should be directed toward compounds generated from innocuous, natural precursors, as well as toward those that may be formed as a result of microbial action on synthetic industrial waste, agricultural pesticides, household effluents, and compounds that are formed as a result of chlorination of water. The investigations should identify the specific organic molecules thus formed and not simply the quantity of organic carbon that is emitted from GAC. The toxicological significance of such compounds and the possibility of their occurrence in concentrations sufficiently high to be of concern should be assessed.

Although it is unlikely, the possibility that some pathogens may be able to colonize GAC beds should be tested. Of primary importance are enteric pathogens such as *Salmonella, Shigella, Vibrio, Yersinia enterocolitica,* and the enterotoxigenic *Escherichia coli.*

PRODUCTION OF NONBIOLOGICAL SUBSTANCES BY OR WITHIN THE GAC BED

One potential source of chemical breakthrough from a GAC column can be the chemical changes on GAC surfaces. This section evaluates the significance of this potential source of toxic organic chemicals in drinking water. To do this, the subcommittee addressed the following

questions:

1. To what extent does the carbon interact with chemical species on the GAC column and produce chemicals of potential health concern. Does the carbon catalyze reactions or enter into reactions producing new chemicals?

2. What is the impact on reactions at the GAC surfaces that is caused by metals incorporated into GAC?

3. What is the potential for release of chemicals of concern that are formed on GAC?

4. What is the potential health effect of the release of carbon fines during operation of a GAC system?

Carbon as a Catalytic Surface

Few studies have addressed the ability of carbon to catalyze reactions producing new chemical components and their subsequent release to water that is being purified for human consumption. Emphasis has been placed on adsorption and removal. Ishizaki and Cookson (1974) suggested that carbon could mediate chemical changes during water purification, resulting in the release of compounds not originally found in the water. The chemical changes that are mediated by carbon are not only the result of oxidation and reduction reactions, but can stem from catalysis on the carbon surface. The use of carbon as a surface catalyst and catalyst support in industrial processes is well documented.

Catalysis on nonuniform surfaces such as activated carbon is not well understood. Most probably, there are only a few types of catalytically effective adsorption sites on activated carbon. Exceptions would be carbons that have been specially prepared to enhance their catalytic properties. As a result, sites contributing strongly to catalysis may contribute virtually nothing to adsorptive capacity.

While heterogeneous catalytic reactions may be complex,. three individual steps can be identified. These are adsorption, surface reaction, and desorption. Heterogeneous reactions are usually sensitive to methods of preparation. The active sites on the catalytic surface are not necessarily distributed randomly. It appears that the bulk of the reactions that can be catalyzed by activated carbon are caused by the surface oxides and other impurities in the carbon structure. In most carbons, these surface functional groups would represent a small fraction of the available adsorptive sites.

Cookson (1978) has discussed the surface groups on activated carbon and their influence on adsorption and catalysis. Although many investigators have reported the above-mentioned acidic oxides to be likely inhabitants of the carbon surface, there is still no completely documented description. Thus, none of the proposed catalytic mechanisms for carbon have been proven.

A variety of interrelationships can occur between adsorption and catalysis. It appears that a number of catalytic systems have their own peculiarities, making generalization not feasible at this time. Because of the limited amount of data on adsorption to activated carbon from water and catalysis, one is handicapped when attempting to draw specific conclusions. Although data are limited, no toxic chemicals have been reported to be formed by catalysis on GAC. The oxidation reactions catalyzed by GAC yield products that are found in water supplies and would be expected in drinking water processed without the application of GAC.

ORGANIC REACTIONS MEDIATED BY CARBON

Carbon catalyzes the oxidation of sulfide in solution, glucose in the presence of phosphoric acid, oxalic acid, malonic acid, amino acids, phenylthiocarbamide, ascorbic acid, uric acid and its derivatives, and mercaptans (Garten and Weiss, *1959;* Ishizaki and Cookson, 1974; Larsen and Walton, 1940; Rideal and Wright, *1925,* 1926; Weiss, l%2).

Weiss (1962) reported that one of the first studies illustrating the ability of carbon in aqueous solutions to catalyze reactions with Organic materials was conducted by Warburg in 1921. Utilizing aqueous suspensions of charcoal, Warburg outlined the aerial oxidation of amino acids to organic acids and ammonia. Further work illustrated that the adsorption of the amino acid on the carbon surface was an important step in the catalyzed sequence. In 1926 Rideal and Wright showed that an aqueous suspension of sugar charcoal catalyzed the oxidation of oxalic acid. These early investigators also reported that the reaction could be inhibited by a number of compounds, including amyl alcohol, cyanide, thiocyanate, chloroform, aniline, and acetone. These compounds all appeared to act as poisons and probably inhibited the reaction by combining with iron that was contained in the charcoal. Garten and Weiss (1959) proposed a mechanism for the oxidation of these organics by chromenelike structures on the carbon surface. These interpretations need confirmation with modern techniques.

The proposed oxidation of oxalic acid by activated carbon involves the adsorption of oxalate at the site of the carbonium ion on the carbon. An electron can pass from the oxalate into the carbon, resulting in the removal of oxygen as a monovalent peroxide anion. This anion captures the proton that is released simultaneously from the oxalate anion to form hydrogen peroxide. This reaction is possible, since the single electron remaining on carbon has resonance stability. The hydrogen peroxide liberated during the reaction can further oxidize organic components.

Garten and Weiss *(1959)* illustrated the oxidation of malonic acid by activated carbon under acid conditions. The oxidation mechanism of malonic acid appears to differ from that of oxalic acid, but no mechanism has been proposed. The investigators provided the following oxidation equation, which is based on oxygen uptake and carbon dioxide production during the reaction.

2CH2 (COOH)2 + 02 2CH(OH) (COOH)2 (I)

2CH(OH) (COOH)2 + 02 2CHOCO2H + 2C02 + 2H20 (2)

The aerial oxidation of ascorbic acid is also catalyzed by activated carbon. Garten and Weiss (1959) observed that some carbons were unable to catalyze the reactions, and others had considerable effect. Carbons that were prepared at 9000C supported the greatest catalytic activity. This suggests that the basic oxide of the carbon may be involved.

Rideal and Wright (1926) reported that in aqueous solutions substances containing but one polar group, such as alcohol, formic acid, and the higher fatty acids, do not undergo oxidation at the surface of charcoal. Substances containing two adjacent polar groups, such as a-amino acids, phenylthiocarbamide, and oxalic and malonic acids, are readily oxidized by carbon.

The catalytic activity of carbon under more alkaline conditions probably involves the quinone-hydroquinone surface groups. These groups can function as electron acceptor sites that facilitate the chernisorption of electron donors on the surface of the carbon. Under alkaline conditions, the formation of the semiquinones would mediate the transfer of electrons to chemisorbed oxygen. This enables the quinone to play essentially the same role as the carbonium ions of basic carbons and acid solutions.

The catalytic activity of carbons in alkaline solutions has been demonstrated for the oxidation of uric acid, its 1-methyl and 7-methyl derivatives, and mercaptan (Ishizaki and Cookson, 1974; Weiss, l%2).

The oxidation of mercaptans to disulfides by activated carbon in aqueous suspensions has been documented by Ishizaki and Cookion (1974). The adsorption of mercaptan on carbon is a complex phenomenon, because the adsorption of mercaptan and disulfide on the carbon

parallel the conversion of the former, as indicated by the following equation:

2BuSH + y02 (BuS)2 + H20 (3)

where BuSH n-butyl mercaptan and (BuS)2 = butyl disulfide.

The oxidation of mercaptan to disulfide is catalyzed by activated carbon. This catalytic effect is significantly reduced by outgassing at elevated temperatures. Two proposed mechanisms might explain the catalytic nature of activated carbon. One mechanism involves the participation of quinone groups. In this mechanism, the disulfide formation would arise via a redox reaction involving the formation of thiol radicals and semiquinone anions.

The second mechanism is due to metal ions on the surface of the carbon. By outgassing the carbon at elevated temperatures (900%C) and analyzing the metals released, it was determined that the commercial activated carbon contained 0.041 mg of copper per gram of carbon (Ishizaki and Cookson, 1974). The amount of iron was considerably lower, indicating that this commercial carbon was probably impregnated with copper during regeneration. The catalytic activity of carbon in the oxidation of mercaptans can involve both quinone groups and metals on the carbon's surface. One mechanism does not exclude the other, but it is likely that both occur at the same time. Ishizaki and Cookson (1974) proposed a combined mechanism.

Commercial activated charcoal catalyzes the oxidation of potassium urate (Larsen and Walton, 1940). It increased the rate of autoxidation of potassium urate in water solutions of activated carbon. The degree of oxidation that normally occurred in 15 hr was achieved in 10 min in the presence of activated carbon.

Impurities incorporated in activated carbon during regeneration greatly influence its catalytic behavior. Rideal and Wright (1926) studied the influence of nitrogen and iron on carbon's catalytic activity in the oxidation of oxalic acid. When both iron and nitrogen were incorporated into the carbon, the ironcarbon-nitrogen complex produced a carbon with a specific activity that was 800 times that of the original activated carbon. When iron alone was used, the ironcarbon complex produced a carbon with a specific activity that was 50 times that of the original carbon. These studies, along with those of temperature influences, clearly illustrate the effect that activation and regeneration procedures have on carbon's catalytic behavior. Thus, the history of activated carbon prior to regeneration is important. The adsorption to carbon of various metals

and other ions could result in the incorporation of these materials as impurities on the carbon surface, resulting in a carbon with greater catalytic activity than that of the virgin material.

Reactions with Disinfectants

Activated carbon serves as a very effective reducing agent for residual chlorine in aqueous solution. These reactions have been the object of a number of studies. Magee *(1956)*, in particular, indicated that free chlorine would react as follows:

HOCl + C* C*O + HCl **(4)**

If the reaction takes place at high pH, the following reaction is expected:

OCF + C* C*O + Cl (5)

In these reactions, the asterisk (*) indicates the carbon surface. The specific types of surface oxides that form have not been well characterized, but they probably include such groups as phenolic-OH, carbonyl, and carboxyl. These reactions were found to be generally descriptive in that a short time after startup, within the limits of sensitivity of the chloride analysis test, the total chlorine entering the bed was equal to that leaving. As the extent of the carbon oxidation increased, the level of acidic oxides on the surface also increased and the adsorbability for simple phenols decreased (Snoeyink *et al.*, 1974).

Bauer and Snoeyink (1973) proposed the following monochloramine and dichloramine reactions:

NH2Cl + H20 + C*-> C*O + NH3 + HCI **(6)**

2NH2Cl + 2C*O 2C* + N2(gas) + 2H20 + 2CF (7)

2NHCl2 + H20 + C* C*O + N2(gas) + 4HCl **(8)**

Studies with nitrogen trichloride have not been conducted to date, but Atkins *et al.* (1973) presented evidence indicating that it also reacts very rapidly with activated carbon.

However, Reactions *1-5* do not completely describe the oxidation phenomena, because carbon dioxide is observed in the effluent of the

reactor after a certain amount of oxidation (Magee, *1956).* As the reaction increases further (up to l-4 g of free chlorine as C12 per gram of carbon), the oxidation of the carbon has become so extensive that a resulting end product produces a visible dark color in the aqueous solution. This extent of reaction is not expected to occur within 2 to 3 yr under typical operating conditions at a water treatment plant (i.e., chlorine enters the carbon adsorber at a concentration of I to 2 mg/liter or less). The GAC will probably be replaced or regenerated prior to this time, although additional investigation is needed on this subject. Some preliminary identification work on the solution with the dark color has indicated that several purgeable organics, including volatile halogenated organics, are present. Much of the dark color remained after purging the sample. Further work is needed to identify the composition of that material (Snoeyink and McCreary, 1978). Regeneration of the carbon prior to the production of the dark color should result in the volatilization of many of the oxidation products and surface oxides, thereby preventing the formation of undesirable end products.

When activated carbon is used at a water plant, organics collect on its surface. Chlorine residual can now react either with the activated carbon surface or with the adsorbed organics. Whether a significant amount of chlorinated organics is formed by the reaction of chlorine with adsorbed organics and whether such organics, if formed, can be eluted from the bed are questions that must be answered.

There have been *few* studies on the reaction of ozone with activated carbon. The nature of this reaction is of less importance, because, when ozone is used as a predisinfectant, its half-life is such that a relatively small amount, or none, will enter the GAC adsorber. Dietz and Bitner (1972) reported that, when some ozone entered the adsorber, it reacted very readily with the carbon. The reaction consisted of the following three steps taking place, depending upon the amount of ozone that had reacted:

C*XO + 03 **C*XCY+I + 02** (9)

C*XO + 03 C* x-1 O y+1 + C02 **(10)**

C*XO + 03 C* x-2 O + C02 + CO (11)

These reactions show that oxides of unspecified types, 02, CO, and CO2, may form as reaction products. They account for the observed initial weight increase and, after a certain amount of reaction, the weight loss of the carbon. Dietz and Bitner (1972) also found evidence that the ozone converted some of the smaller pores to larger pores, with little change in total surface area, and that surface oxides formed at the entrance to the micropores, which resulted in partial blockage of those pores.

Chlorine dioxide, one of the alternative disinfectants to chlorine, is also a strong oxidizing agent that is probably reduced very readily by GAC. However, there is little information on the reaction of chlorine dioxide with carbon and/or adsorbed Organics and whether any undesirable end products might be formed by such reactions. This subject requires research if chlorine dioxide is to be used as a predisinfectant at a water plant.

Dissolved oxygen also reacts with activated carbon. Prober *et al.* (1975) found uptakes of 10 to 40 mg of oxygen per gram of carbon for commercially available carbons. They noted that equilibrium had not been achieved at these loadings. The uptake resulted in an increase in acidic surface oxides. Only approximately 5% of the amount taken up could be eluted as oxygen. The reaction between oxygen and carbon is important, because it indicates that not all oxygen that is removed during adsorption can be attributed to biological activity and that the nature of the carbon surface may be altered during the adsorption process.

INORGANIC REACTIONS MEDIATED BY CARBON

The catalytic properties of activated carbon can result in the oxidation of inorganic compounds in air contact systems. The acidic oxides on the carbon surface are known to be responsible for many of these catalytic oxidations. Such systems may not be applicable to aqueous solutions because of the possible influence of adsorbed water. For this reason, reactions in the gas are not discussed here.

Studies that consider aqueous systems are few. As is true with organics, the catalytic activity of carbon has not been studied specifically. Most of the available information can be classified as conjecture that is based on extrapolations from observations gathered from adsorption studies with inorganics.

Several investigators have studied the removal of iron from aqueous solutions by treatment with activated carbon (Ford and Boyer, 1973; George and Chaudhuri, 1977; Huang, 1978; Stumm and Lee, l96l). They reported that the oxidation of ferrous ions accelerates in the presence of activated carbon. Their results suggest that carbon can act as a catalyst and that the presence of surface groups can greatly influence the rate of catalytic activity. Puri (1970) reported that the catalytic activity of a carbon that contained oxygen surface groups was more than two orders of magnitude greater than the activity of a carbon that was devoid of these groups.

Huang (1978) reported that the adsorption of Hg2+on activated carbon also involves adsorption accompanied by a reduction of mercury on the surface of the carbon. The activation procedure for activated carbon plays a major role in determining the mechanisms of mercury adsorption and reduction.

This catalytic effect of carbon is greatly influenced by the techniques of its preparation of activation. The effect of activation temperature on a carbon's catalytic potential with inorganics is clearly illustrated by the work of Larsen and Walton (1940). These investigators studied the catalytic activity of activated carbon for oxidizing stannous chloride in solution. The carbons were activated at temperatures ranging from 350C to 8500C. The speed of reaction was greatly influenced by activation temperature, indicating maximum catalytic activity at 5750C. The reaction rates decreased rapidly for carbons that were activated at temperatures above 6500C and below 4500C.

Unfortunately, the undefined nature of the trace metals in water supplies makes it extremely difficult to predict the efficiency of carbon to adsorb metals (Huang and Wu, 1975; Kunin, 1976). For example, many of these metals are bound or complexed with the various organic substances in water, thereby forming complexes that are completely unrelated to the simple ionic states that have been reported for these metals in classical texts on inorganic chemistry.

The problem becomes even more complicated if we consider the thermal regeneration phase of the cyclical process that is associated with the use of carbon. In most systems, carbon is regenerated thermally under controlled conditions by "burning off" the adsorbed organic substances. Under these conditions, the metals, except perhaps mercury, remain in the carbon. These metals accumulate in the carbon. How they affect the adsorptive properties of carbon is not clear.

Chemical Changes Mediated by Adsorbed Compounds

ORGANIC REACTIONS

The subcommittee could find no information concerning a situation in which one adsorbed organic component mediated a reaction with a second. This does not mean that such reactions do not exist or occur on carbon. Investigators simply have not directed research toward this area. Reactions mediated by adsorbed organics are expected to be insignificant.

Various organic chelates will adsorb on carbon and improve the carbon's ability to adsorb various metals such as copper and mercury (Huang, 1978). The presence of these surface metal ions may increase carbon's catalytic activities as discussed in the following section concerning inorganics.

INORGANIC REACFIONS

In the chemical industry, a number of chemical reactions are mediated by adsorbed inorganic compounds on carbon. An example of such a catalyst is palladium on activated carbon. When activated carbon is soaked in a dilute solution of palladium chloride and hydrochloric acid for several hours and then washed, the palladium ions adsorb on the activated carbon and the chloride ions are completely washed from the carbon surface. Catalysts prepared with activated carbon in this manner have demonstrated excellent catalytic activity for liquid-phase hydrogenation of benzene at room temperature (Morikawa *et al.*, 1969). Despite these uses of activated carbon for catalytic reactions, there is a poor understanding of its behavior as a catalyst.

Methods used to prepare activated carbon catalyst include impregnation, precipitation, and adsorption. Impregnation normally involves the heating of the ion to be impregnated on the carbon surface. This may be performed after the ion is first adsorbed on carbon from solutions. The precipitation method involves the precipitation of the specific ion on the carrier. In the adsorption method, ions are deposited on the carbon surface by physical or chemical adsorptive forces. Many of the methods for preparing activated carbon catalysts are similar to processes occurring in water treatment and carbon regeneration. Thus, the importance of the above carbon-metal catalyses in water purification is unknown. Since metals are placed on carbon surfaces during regeneration procedures, this area needs more investigation.

Potential for Release of Catalytic Products

The formation of new Organic or inorganic components as a result of carbon catalytic activity can result in enhanced adsorption or their release to solution. The use of activated carbon as a catalyst for industrial purposes is successful only when high yields of the product are obtained. It follows that a significant release of catalyzed products does occur. While examining adsorption of mercaptan on activated carbon, Ishizaki and Cookson (1974) illustrated that activated carbon catalyzed the oxidation of mercaptan to disullide. They confirmed that the disulfide competes with mercaptan for sorption sites on activated carbon. Adsorption equilibrium constants were established for both the mercaptan and disulfide. In light of this information, it appears that any product that is produced by carbon's catalytic activities would be released to solution in accordance with their adsorption equilibrium and the competitive nature of other solutes in the water phase.

There has been no documentation of organics produced by activated carbon that are potential health hazards. Nitrosarnine formation on activated carbon may be similar to that for ion-exchange resins (Fiddler and Kimoto, 1979). This area has not been investigated.

For inorganic components, the potential for release appears to be less than that of Organic compounds. Most studies have indicated that carbon has a great affinity for inorganic species. The use of activated carbon for treating raw surface waters would not be expected to release significant amounts of inorganic components.

Carbon Fines

Because GAC is friable, fines can be released. The amount of release will depend upon the properties of the activated carbon. Consequently, traces of finely divided particles form constantly and could enter the treated water. McCarty *et al.* (1979) have reported continual bleed-off of carbon fines, primarily of those ranging from *2.5* to *25 um* diameter, from a GAC column utilized in an up-flow, countercurrent, packed bed contractor at Water Factory 21 Advanced Wastewater Treatment facility in Orange County, California. Operation of the column in a gravity downflow mode tended to arrest the process. Total particle counts were 4 times as high in the upflow mode even at 0.2 m/min.

The carbon itself should pose no health problems because of its inertness; however, the carbon particle may have adsorbed and concentrated compounds on its surface which may be released upon ingestion. There are essentially no reliable data on the association and release of adsorbed substances or on fate or the toxicity of the substances after release from carbon fines.

Summary, Conclusions, and Recommendations

Catalysis on the surface of activated carbon most likely involves localized defects that are caused by impurities in the carbon structure or through the adsorption of metals, oxides, and other substances. When adsorption is accompanied by catalytic reactions, kinetic and equilibrium interpretations of the system become extremely complex. A variety of interrelationships can occur between adsorption and catalysis. A number of catalytic systems have their own peculiarities making generalization difficult. Because of the limited amount of data on adsorption on activated carbon from water and catalysis, one is handicapped when attempting to draw specific conclusions. In addition, generalizations are extremely risky, making it difficult to project the possible significance of catalysis in adsorption on activated carbon from water. This subject needs further research.

Activated carbon serves as a catalyst for some reactions in water systems, e.g., oxidization, reduction, and polymerization. These reactions can produce organic and inorganic species that were not originally present. These can be released to the water solution and behave as typical solutes in that they adsorb, desorb, and compete for adsorpton sites.

The studies dealing with adsorption of organics and inorganics have frequently utilized detection procedures that would not provide observation of catalyzed reactions if such were occurring. At this time, we can only conclude that such reactions are possible. However, little can be said concerning the degree of their occurrence during water purification and their possible impacts on public health. There is no doubt that future studies must attempt to clarify the uncertainties that exist.

Carbon may undergo significant changes via its patterns of use and regeneration. The studies that have been reviewed in this chapter point to the effects of adsorbed ions on carbon's catalytic activity for a number of reactions. It would follow that carbons used in the treatment of wastewater may adsorb significant quantities of various metals that become incorporated in the carbon structure during regeneration procedures. Thus, the recycling and regeneration of activated carbon could result in a material that is radically different from the virgin material. This may indicate the need for a control program that is related to carbon monitoring and the use of carbon in the water purification industry.

Industrial secrecy surrounding the manufacture of activated carbon and the varied industrial applications make it difficult to regulate carbon quality for water purification without the implementation of specific quality requirements and the monitoring and control of carbon for water use. Without doubt, this matter demands additional attention. A research evaluation program and controls for carbon use should be adopted until results of future studies indicate that they are unnecessary.

The subcommittee concludes that:

1. The limited amount of data on catalysis by activated carbon makes it impossible to provide specific conclusions on the potential significance of toxic organic production. Nontoxic products have been produced by catalysis on activated carbon during adsorption from water.

2. Chlorine, chlorine dioxide, and ozone react readily with carbon and may react with compounds adsorbed on carbon. There is no evidence to indicate that such reactions, under the conditions that exist in water treatment plants, will or will not produce potentially hazardous compounds.

3. Metals on GAC increase the catalytic potential.

4. Reaction products can be released to the water solution. They behave as typical solutes in that they adsorb, desorb, and compete for GAC sites.

5. Catalytic properties of activated carbon depend upon its method of preparation, surface characteristics as determined by previous uses with particular emphasis on adsorbed metals, and regeneration.

6. Past studies on GAC adsorption have not used techniques that would provide observation of catalyzed reactions if such were occurring.

The subcommittee recommends that:

1. Additional studies should be conducted to assess the potential of GAC-catalyzed reactions for both virgin and regenerated carbons.

2. Studies should be directed toward the need for regulating the quality of carbon that is used in water purification.

3. Techniques should be developed for measuring carbon's catalytic potential and applied as a quality control method.

4. The catalytic potential of producing toxic products by metals that become incorporated onto the carbon surface as a result of use and regeneration must be evaluated.

5. Studies should be conducted to determine levels of carbon fines that pass into drinking water and their biological significance.

6. Research is needed to identify the end products of reactions between activated carbon and disinfectants, especially chlorine and chlorine dioxide. Moreover, the interaction of oxygen with the carbon surface must be evaluated.

REGENERATION OF GAC

In the United States, activated carbon has been used in the treatment of potable water primarily to control taste and odor. The first major GAC installation in this country was built in Hopewell, Virginia, in 196 1. Since then, GAC has been installed in approximately 60 potable water supply Systems to control taste and odor. However, use for this purpose has generally not required GAC regeneration.

The widespread use of GAC will require effective regeneration of spent carbon for economic utilization. This section contains a detailed presentation of the factors that are involved with carbon regeneration technology. Specifically, the character of the original source material, how the GAC source material was utilized, the methods of producing the GAC, and the regeneration of GAC are reviewed. The following questions are addressed:

1. Does the nature of the regeneration process change the adsorption properties of carbon? Are such changes significant to health?

2. Does the spent carbon's past use affect its properties after regeneration? Is this history significant to health?

3. How does GAC change during storage?

4. Does virgin or regenerated carbon contain substances that can be leached into water? Are these substances of significance to health?

5. Does the volatilization of pollutants resulting from the regeneration of spent GAC present risks to health?

The Dependence of Surface Chemistry on Preparation

The adsorptive properties of activated carbon are influenced by the regeneration procedure and contaminating ions. The activated carbon source material has been described in the introduction. Disturbances in the elementary microcrystalline structure, which are caused by such factors as the presence of imperfect (partially burnt-off) graphite layers, changes the arrangement of the electron clouds in the carbon skeleton. As a result, unpaired electrons appear. This condition influences the adsorptive properties of activated carbon, especially for polar or polarizable substances. Another type of disturbance is the presence of hetero atoms in the carbon structure.

Activated carbon contains chemically bonded elements such as oxygen and hydrogen. These elements can be contained in the starting material and remain as a result of imperfect carbonization, or they can become chemically bonded to the surface during activation. In addition, the activated carbon contains ash, which is not an Organic part of the product. The ash content and its composition vary widely with the kind of activated carbon (Anderson and Emmett, 1947; Kipling, *1965).* The adsorption by activated carbon of electrolytes and nonelectrolytes from solution is significantly influenced even by small amounts of ash (Blackburn and Kipling, 1955). The presence of oxygen and hydrogen has a great effect on the properties of activated carbon. These elements combine with atoms of carbon by chemical bonds. They differ from the ash by forming an organic part of the chemical structure of the activated carbon.

Because of the importance of oxygen on carbon's adsorption and catalytic properties, the influence of regeneration on their reaction is discussed below. However, most other chemical groups on carbon have not been well documented. The few studies that were performed did not have the benefit of modern techniques.

When oxygen is adsorbed on a carbon surface, it undergoes a chemical change, even at room temperature. Nitrogen and other gases that are adsorbed on charcoal are easily removed as such. However, oxygen is removed as carbon dioxide only by heating the charcoal at high temperatures. Rhead and Wheeler (1912.1913) pointed out that oxygen combines with the carbon to form a physicochemical complex, Cx Oy of variable composition. This complex decomposes upon heating giving a mixture of carbon monoxide and carbon dioxide.

There are several methods by which oxygen surface complexes can be formed during regeneration. They may be classified into two major groups: methods utilizing oxidizing gases and those involving oxidizing solutions. The most common oxidizing gases are oxygen (Hart *et al.*, 1967), water vapor (Smith, 1959), carbon dioxide (Puri, 1970), and oxides of nitrogen. Some of the oxidizing solutions are acidified potassium permanganate, nitric acid, a mixture of nitric and sulfuric acids (Puri, 1970), chlorine water, and sodium hypochlorite (Behrman and Gustafson, 1935; Donnet *et al.*, 1961, 1963).

Commercial Regeneration Procedures

During the purification of waters and wastes, impurities in the solutions collect in the pores of the carbon. After a while, contaminants begin to break through the GAC bed, and the spent carbon must be reactivated. Various regeneration techniques that have been developed over the years include thermal, chemical, solvent, vacuum, biological, and wet (steam) oxidation methods. Of these methods, thermal regeneration is the most common. These methods of regeneration are reviewed by Lombana and Halaby, 1978; Von Dreusche, 1978; and Inhoffer, 1978.

The compounds adsorbed during water treatment should be removed by thermal regeneration, thereby making GAC a most attractive alternative. While carbons can be regenerated, documentation is needed for changes due to regeneration in hardness, pore size distribution, ash and metal ion buildup, and adsorbability for compounds present in water supplies.

The thermal regeneration of spent carbon is one of the most important factors involved in the economic consideration of activated carbon treatment of water. The adsorbed organic materials are volatilized or oxidized at a high temperature during this process. Ideally, this would be done in such a manner that a maximum amount of adsorbed organics are driven off with a minimum change in the adsorptive properties of the carbon. The success of reactivation depends on a number of factors, including carbon temperature, duration of activation, and the activating gas mixture. Presently available GAC can withstand repeated regeneration and reuse as shown in the field of wastewater treatment.

Two other methods of regeneration that have been successfully used with activated carbon involve chemical solvents and steam. In the first method chemical solvents are added to the carbon bed to desorb the adsorbed material. The solvent is then passed through the carbon bed in the direction Opposite to that of the service cycle until the adsorbate is removed. The bed is then drained of the solvent, and the regenerated carbon is ready to be returned to stream.

If the carbon has been used to remove adsorbates with low boiling temperatures, it can sometimes be regenerated with steam. The steam is passed through the carbon bed Opposite to normal flow. It is then either vented to the atmosphere or condensed and recovered. To avoid air pollution, condensation and recovery are preferable. Approximately 3 to 5 lb of steam are needed to remove each kilogram of adsorbate that is collected by the carbon.

These latter two methods have not enjoyed widespread acceptance. They are not as effective as thermal removal from carbon of the many different compounds that adsorb during water treatment.

Influence of Regeneration on Adsorption

Various regeneration procedures and their influence on the surface structure of carbon have been discussed above. Since regeneration procedures have a major influence on carbon surface chemistry, it follows that adsorption and catalytic potential can be changed greatly by

the regeneration procedure. A number of studies illustrate that nonpolar paraflinic compounds, which are hydrophobic, will adsorb preferentially on carbon that is free from acidic surface oxides (Cookson, 1978). Acidic sites adsorb water, thereby hindering the adsorption of these organics. Acidic functional groups are found on carbon under specific temperature ranges and in the presence of certain reactivation gases. Several studies have suggested that aromatic adsorbates interact with carbonyl type groups on the carbon surface (Cookson, 1978). This interaction is believed to involve the formation of an electron donor-accepter complex of the solute ring structure containing carbonyl groups. The surface density of these chemical groups is also influenced by regeneration procedures.

The presence of metals on the surface of carbon has a significant effect on the adsorption of molecules with localized excess electrons. It appears that the attractive forces that are exerted by the surface metal can increase the rates of adsorption by several orders of magnitude (Cookson, 1978). Regeneration procedures not only affect adsorption properties but also can influence the catalytic behavior of carbon as discussed above. Carbon's potential to catalyze reactions would appear to increase when used carbon is regenerated for reuse. Carbon may adsorb significant quantities of various metals that can become incorporated in the carbon's structure during regeneration procedures. Thus, the recycling and regeneration of carbon can result in a material significantly different from the virgin activated carbon. This catalytic potential should be studied to determine if it is significant.

Sufficient data are not available to determine the difference in adsorption between regenerated and virgin GAC. These data are urgently needed to evaluate the total GAC process since regeneration is an integral part of the process.

CHEMICAL CHANGES DURING STORAGE

During storage, activated carbon undergoes chemical changes as a result of reactions with atmospheric oxygen. The reactions that occur at room temperature bring about an aging process in which the atmospheric oxygen reacts chemically with the carbon surface. This oxygen resides in the chemical structure of carboxyl or lactone type groups (Hart *et al.*, 1967; Smith, 1959). This aging process is expected to reduce the adsorption capacity of carbon for a large number of organic compounds that are found in water (Cookson, 1978). No other chemical changes that are expected to occur during storage would significantly influence any characteristics of the adsorbent.

LEACHING OF CHEMICALS FROM GAC

The extraction and leaching of chemicals from virgin activated carbon have been studied by a few investigators. Again, information is very limited, and few analytical studies have been performed with modern separation and identification techniques such as gas chromatography/mass spectrometry (GC/MS).

A few analytical studies have addressed the leaching of polycyclic aromatic hydrocarbons (PAH) from GAC. The release of PAH from virgin activated carbon has been demonstrated by Borneff (1980). Table IV-5 lists the compounds and concentrations that have been detected. The highest total amount of PAH that has been found on a virgin activated carbon is 250 ug/kg. The largest amount of carcinogenic polycyclics is 37 ug/kg. Fitch and Smith (1979) analyzed two activated carbons and several carbon blacks. They also found insignificant amounts of PAH on the activated carbons, but significant amounts were extracted from some carbon blacks. The procedures used to make carbon blacks differ greatly from those used to make activated carbons. Consequently, the difference in PAH content is not surprising. It is not anticipated that PAH would be released to drinking water in concentrations that are potentially harmful to health, because the total amount is so small and they are strongly adsorbed to activated carbon. Clearly, additional research is needed on virgin activated carbons, as well as regenerated carbons, so that the leaching potential of toxic chemicals can be evaluated completely.

Reference can be made to nitrosamine formation or leaching from resins (Fiddler and Kimoko, 1979). The possibility of nitrosamines leaching from carbon should be investigated.

Activated carbon used for treating raw surface waters would not be expected to release significant inorganic components. Love and Symons (1978) observed insignificant releases of metal ions when they exposed activated carbon to tap water. They also illustrated that the leaching of inorganic ions from activated carbon is unlikely and would probably occur only under stressed conditions.

Pollution Control During Carbon Regeneration

The removal of the adsorbates during regeneration presents another problem-the treatment and disposal of these moieties.

The thermal regeneration of carbon presents the most obvious of problems-the volatization of the adsorbates and the need to restrict their entry into the atmosphere. The disposal of the hot gases leaving a furnace requires an afterburner, wet scrubber, and dust collector.

The afterburner is used to burn gases that are driven off the carbon or formed during oxidation of the impurities. This is a refractory-lined chamber fitted with a burner and excess air injection system. The normal temperature range of operation of the afterburner is 9000C to l,8000C. An ample supply of excess air (50%) must be available to accomplish this burning (Lombana and Halaby, 1978).

A wet scrubber usually follows the afterburner in the treatment scheme for two reasons: to collect the dust, which cannot be combusted in the afterburner, and to cool the gases so that they can be passed through the induced-draft fan. The scrubber is generally made of stainless steel in order to avoid corrosion. Baghouses are also used to remove particulates when air pollution regulations are less stringent and wet scrubbers are not used.

There are some examples of air pollution control systems in operation. As reported by Directo *et al.* (1977), a multihearth furnace used to regenerate carbon that is spent during sewage treatment operations at Pomona, California, discharged flue gases containing both particulate and odorous substances. The air pollution control system at this facility, which consists of a baghouse, was designed to remove 99% of the incoming particulate load. Data indicate that it only removed about *25%;* particulate emissions were quite high, averaging 0.3 kg/hr. Odors were detected during the reactivation operations at the facility. This was confirmed by analytical testing, which detected three odor units per liter.

Studies in a similar vein performed in Kyoto, Japan, examined a number of compounds (Anonymous, 1977). The system was composed of an afterburner and scrubber following the regeneration furnace. Careful analysis of the data shows that, while dust and odor are reduced by the afterburner, the concentrations of sulfurous acid gas and nitrous oxides are increased. The scrubber was ineffective in the removal of nitrous oxides, but did remove sulfurous acid, gas, and dust. In addition, the scrubber increased the odor. However, this was due to the use of secondary effluent for scrubbing. These tests were repeated on carbons that had undergone a second and third reactivation cycle. Following the afterburner, these concentrations were reduced considerably. These studies were also performed with carbons used in wastewater treatment.

In brief, two general categories of exhaust emissions must concern the operators of regeneration facilities. These are particulates and gaseous

TABLE IV-5 Leaching of Polycyclic Aromatic Hydrocarbons from Virgin Activated Carbon

Polycyclic Aromatic Hydrocarbons *Detected, u*g/kga

Activated

Carbon Type I II III IV V VI VII VIII IX X S S++

CarborafTin Powdered 80.0 - - 1.2 - 0.8 - 0.8 **83** 1

Cb

Brillonit

b

Powdered 100 - - - - - - - 100 -

norm,

EPN~A~KohIec Powdered

Gerditd Powdered

Gerditd 0-0.5 mm

Gerditd 1-2.0 mm

Gerdi~ 2-4 mm

Hydraffin Powdered

1I8ff~

28

53.6 - - *5.2* 1.2 2.8 -

110 12.4 -

216 - -

81.6 - -

- 28 -

- 68 8

- 157 37

5.2 2.4 - 257 27

2.0 0.8 - 90 6

4.0 1.2

12.4 9.6 - 10.0 2.4

21.2 3.6 8.4 -

3.2 2.0 - -

1.2 - - - - - - - - - I -

Hydraffin BD6 0.5-2.5 mm 60 3.6 3.6 8.0 1.2 0.8 - 2.4 0.8 20.0 100 16

Hydraflin BDb 0.5-1.5 mm 3.6 - - - - - - - - - 4 -

(extra)

Ilydraflin LWb 0.5-3.0 mm 40 - 8.0 3.2 0.8 0.8 - 1.2 0.8 20.0 75 13 Ilydraflin LWb 0.5-3.0 mm 80 - - 2.4 - 1.6 - 0.8 0.4 - 85 3 (extra)

Ilydraflin TCb Spez. I/Il

KD~A-KohIec Powdered

Norit FND' <5 ~m 25%

S-10~m6%

Norli ~ 10-20 ~m 12%

20-50 ~m 26%

Norit NK' 50-75 ~m 13%

75-90 ~m 3%

>90~m 15%

Rods~ = I.6mm

<0.2 mm

Granul.

<0.2 mm

Norit FNA'

Norit RBWII~

Out normaib

R4-A.KohIec

A-Kohle Nr.

2I8~

80 - - - - - - - - - 80

28 - - - - - - - - - 28

1.6 2

40 -

60 -

60 8.0

2.8

4.0 1.6 0.4 0.8 - 0.8 0.4 - 48 6

- 2.0 - 0.8 - 0.8 - - 64 2

12.0 4.0 1.6 3.2 - 2.8 1.6 - 93 27

- - - - - - 3 -

a I fluoranthene

II benzo (a) anthracene

IlI benzo ~) fluoranthene

IV benzo (b) fluoranthene

V benzo (a) pyrene

VI benzo (glil) perylene

b Produced by Lurgi GmbH1 Frankfurt/Main. Produced by VEB-Cherniefasewerk, F. Engels. ***d*** Produced by A. JWgersberg, IIamburg. Produced by Norit Corp., Amsterdam. 1Produced by E. Merck AG, Darmstadt.

VII perylene

VIII benzo (k) fluoranthene

IX indeno (1,2,3,-dc) pyrene

X pyrene

S sum of polycyclics I-X S + + sum ofcarcinogenic polycyclics

emissions. Particulate emissions are probably most easily controlled via mechanical alterations to the regeneration system. For example, the stirring of carbon within a furnace is a major cause of particulate emission. No stirring of the carbon minimizes entrainment of fines, which results in low particulate emissions.

Gaseous emissions can include sulfur oxides, nitrogen oxides, hydrochloric acid, hydrocarbons, and other organic species. Unfortunately, there have been no studies measuring the gaseous emissions resulting from the regeneration of carbon by modern separation and identification techniques. There is a pressing need for research in this area to confirm the type of chemicals that are discharged, their amounts, and health significance.

Summary, Conclusions, and Recommendations

1. Regeneration procedures influence GAC chemical properties. This in turn will also influence adsorption, catalytic properties, and leachable chemicals. No significant health problems have been documented, but definite conclusions cannot be made because of insufficient data.

2. The previous use of a GAC and the amount of adsorbed contaminants will influence the chemical surface properties that develop during regeneration. There is inadequate information with which to evaluate the effect of these contaminants on adsorption, catalysis, and leaching.

3. The leaching of metals from carbon to water appears to be slight. The amounts leached are not known to produce adverse health effects.

4. The leaching of toxic organics from carbon to water has not been studied sufficiently to draw general conclusions. Although small amounts of PAH's have been detected, they do not appear to leach readily. The analytical studies are few and various regenerated carbon types must be evaluated.

5. Pollutants are discharged during GAC regeneration. Many studies have measured the oxides, hydrocarbons, and

particulate matter present, but few have characterized the discharge sufficiently to evaluate health effects from volatilizing organics.

The subcommittee recommends that:

1. Regeneration procedures must be evaluated to determine their influence on adsorption capacity, catalytic potential, leaching of metals

and toxic organics, and volatilization of toxic discharges during regeneration.

2. The effect of various adsorbed contaminants on the properties of regenerated GAC (both metals and organics) must be evaluated m terms of carbon's adsorption and catalytic properties after regeneration.

3. Studies are needed to evaluate the potential for leaching toxic organics from operating carbon columns. Different carbons should be evaluated from this point of view for PAH's, nitrosarnines, and other organic compounds of potential harm to health.

4. Gases that are discharged during regeneration should be characterized completely with particular attention given to pollutants of potential harm to health.

5. Consideration should be given to testing and regulations for controlling the regeneration process and history of the carbon to be used in drinking water purification if research shows that it is necessary.

ADSORPTION EFFICIENCY OF OTHER ADSORBENTS

This section contains an evaluation of the ability of other adsorbents to adsorb trace Organic compounds during the treatment of drinking water. Two distinctly different processes are considered. One is the use of polymeric adsorbents, which include pyrolyzed polymers such as Ambersorb XE-340 (Rohm and Haas Co.) to remove low-molecular-weight organic compounds of potential harm to health. The other is the use of anion exchange resins to remove humic material.

The following questions are addressed:

1. What is the physical and chemical stability of the resins? What reactions take place between oxidants applied as predisinfectants and resins or compounds adsorbed on resins? Do these reactions result in potentially hazardous compounds that would not be present if resins were not used?

2. How well do polymeric adsorbents adsorb individual trace organic compounds, particularly those that are potentially harmful to health? What is the selectivity of the resin for single Organic compounds?

3. What is the degree of competition on polymeric adsorbents between organic compounds with potential health effects, and how does the interaction with humic substances affect the competition?

4. What is the potential benefit of using ion exchange resins as a treatment method to remove Organic matter before chlorination?

w

CD

TABLE IV-6 Typical Properties of Amberlite Polymeric Adsorbents

Helium Porosity

Volume Surface Average Skeletal Nominal

Resin Chemical Area, Pore Diam., Density, Mesh

Type Nature 0/0 cm3/g m2/g *A* g/cm3 Sizes

Nonpolar0

XAD-l Polystyrene 37 0.69 100 200 1.06 20-50

XAD-2 Polystyrene 42 0.69 330 90 1.08 20-50

XAD-4 Polystyrene Sl 0.99 750 50 1.09 20-50

Intermeduite Polaritya

XAD-7 Acrylicester 55 1.08 450 80 ***1.25*** 20-50

XAD-8 Acrylicester ***52*** 0.82 140 250 1.26 20-50

Synthetic Carbonaceous Adsorbent b

XE-340 Polystyrene 400 6-40 A 18 Vol % 1.34 20-50

(partially 40-100 A 13 Vol 0/o

pyrolyzed) 100-300 A 69 Vol 0/a

a From Kunin, 1976.

bFromRohmand IIaasCo., 1977.

5. What effects on reactions within the bed are caused by the ion exchange resin or anions or cations that are on the surface of the ion exchange resin?

6. How effective are the regeneration processes? Does regeneration cause any health-related problems?

The concerted effort to develop resin adsorbents has been aided by recent advances in polymer chemistry. Efforts have been directed toward the removal of the humic materials from surface and shallow well-water supplies. The humic materials are a problem, particularly in the production of the high-purity water for power utilities and the electronics industries (Applebaum, 1968). Until recently, much of the experience with synthetic resins for potable water concerned the use of cation exchange resins to soften potable water. These water-softening resins remove few of the organics.

Resinous Adsorbents

The available synthetic resins may be classified into the following three major groups:

1. *Ion Exchange Resins.* These are cross-linked polyelectrolytes that are capable of removing ionic species via an ion exchange process; however, they may also function as adsorbents in removing organics or metal chelates. These structures may be formed from cross-linked polymers derived from styrene, acrylates, phenols, and pyridines (Kunin, 1972).

2. *Nonionic Polymeric Adsorbents.* These adsorbents are nonionic, high-surface-area, cross-linked copolymers of styrene, phenol, or acrylate (Table IV-6). Some are hydrophobic; others are hydrophilic. In essence, the macroreticular particle is composed of microspheres that are linked together, creating a continuous network of fine or large pores.

3. Synthetic Carbonaceous Adsorbents. Recently, synthetic carbonaceous adsorbents have been offered commercially. These are the products of the partial pyrolysis of nonionic polymeric adsorbents. They are still in the developmental stage (Slejko and Meigs, 1980).

STABILITY

The stability of the ion exchange resins and polymeric adsorbents is of major importance because their useful life affects the economic evalu ation of processes involving their use. Their useful life may be limited by either physical or chemical degradation Kunin, 1972).

PHYSICAL DEGRADATION

The adsorbents may degrade physically (attrition) into smaller particles either by abrasion or osmotic forces. Although the adsorptive properties of a resin are not affected by attrition (indeed, some of these properties may be improved), attrition is undesirable since it leads to losses of material, excessive pressure drops, and passage of finely divided adsorbent particles into the treated water. The design of the process and equipment are of paramount importance because they can affect the attrition of a resinous adsorbent (Kunin, 1972).

CHEMICAL DEGRADATION

An adsorbent resin can deteriorate chemically in several ways. First, the basic chemistry of the structure may be irreversibly altered due to oxidative reactions resulting from contact with oxygen, chloride, peroxides, Ozone, etc. (Kunin, 1976). Oxidation may destroy the activity of ion exchange resins and alter the nature of the active surfaces of adsorbents.

Second, adsorbent and ion exchange resins may be poisoned due to the irreversible adsorption of some organic and even some inorganic compounds. For example, some anion exchange resins, particularly the strongly basic resins with small pores, can be poisoned after exposure to high levels of humic materials (Abrams, 1975; Kunin, 1976). Apparently, the large molecules enter the pores of the anion exchange resin and are retained because they have a high affinity for the ion exchange sites and low rate of diffusion within the resin.

Third, pores of some adsorbents may become clogged by various colloids that are present in water supplies. These colloids may be siliceous or may contain highly dispersed particles of humic acids. Hydrous oxides of iron, aluminum, and manganese may be precipitated on the surface and in the pores of adsorbents because of only minor changes in pH and oxygen levels.

The effects of chemical deterioration of synthetic resins may be minimized by selection of proper adsorbent, removal of oxygen and chlorine from water to be treated by addition of sulfites, use of optimized or tailored regeneration conditions, use of restorative procedures such as treatment of the adsorbent with chemicals (salt, acid, alkali, etc.), and use of proper pretreatment of the influent. With proper care, the useful life of a resinous adsorbent may be prolonged.

Removal of Humic Substances by Ion Exchange Resins

For approximately 75 yr, ion exchange resins have been used extensively to treat water for a wide range of applications including water softening, water dealkalization, deionization, and removal of color (removal of humic substances), metals, nitrates, ammonia, and cyanides. The use of ion exchange resins for treating potable water has been limited primarily to the softening (removal of calcium and magnesium) of water with cation exchangers both on a municipal scale (Kunin, 1972) and in several million homes (Gulbrandson *et al*, 1972). The cation exchanger does little to remove organic matter. The major disadvantage of the process involves the disposal of the waste salt regenerant. There is sufficient evidence indicating that the spent regenerant may be recycled a number of times without treatment and almost indefinitely by treating the waste brine with ozonization or hydrogen peroxide (Kunin, 1973). However, the reactions of these regenerants and their products have not been examined.

The use of ion exchange resins other than cation exchange resins for treating potable water has been quite limited. In some isolated cases, deionization or demineralization systems (combinations of cation and anion exchange resins) have been used to prepare potable water from brackish water (Clifford and Weber, 1978; Kunin, 1972; Kunin and Downing, 1971). Although the major objective has been the removal of salinity, some TOC was also removed.

There are data on the use of anion exchange resins for the removal of humic matter from water supplies. These data concern long-term studies using systems as large as *1-5* million gallons per day (MGD). Throughout the world, the technique has been used widely in various power utilities (Kunin 1973, 1976). In general, ion exchangers can remove from *50%* to 95% of the humic matter. Some communities have used this technique to remove excess quantities of nitrates contaminating well water supplies (Clifford and Weber, 1978).

In view of the success that has been achieved with ion exchange resins to remove humic substances from water for various industrial purposes (Davis, 1977; Hinrichs and Snoeyink, 1976), it is logical that the technology be given consideration for the processing of drinking water prior to the chlorination process. This step could materially reduce the haloform concentrations in finished water. In essence, the water would be processed by deep beds of strongly basic anion exchange resins that would be regenerated with brine in a manner similar to the way municipal waters are softened with cation exchange resins.

TABLE *W-7* Adsorption of Humic Acids by Anion Exchange Resins

	Humic Acid Removed, %	
Resin	pH2.2	pH7
IRAA10~	97	70
IRA~9l0a	92	52
A~57b	79	22
A~30Bb	71	44
Es-34O~	82	59

Produced by Rohm and Haas Co.

b Produced by Diamond Shamrock Co.

ADSORPTION ISOTHERMS AND COLUMN STUDIES

Davis (1977) studied the adsorption of commercially available humic acids at pH 2.2 and pH 7 by a series of anion exchange resins in batch equilibrium studies. Results are summarized in Table IV-7. Strong base anion exchange resins IRA-410 and IRA-910 removed more than intermediate strength base anion exchange resins *A-57,* A-30B, and ES-340 and weak anion exchange resins Statabed 93 (Rohm and Haas Co.). Cation exchange resins had little or no affinity for humics.

In column tests, IRA-68 (intermediate anion exchange resin) removed 36%-46% of one fraction of the humic acids in a column study at pH 2.2 (Davis, 1977). Only 30% of the exchange capacity could be regenerated with sodium hydroxide. Utilizing a second fraction of the humics, complete removal was accomplished but only 64% was recovered by sodium hydroxide. These data confirm earlier work of Bonsack (1962).

Boening *et al.* (1980) compared the adsorption of commercial humic substances on Diamond Shamrock A-7 and ES-561 weak base anion exchangers with that on Rohm and Haas IR-904 and 1R458 strong base anion exchange resins. They also compared XAD-2, XAD-8, XE-340, and five brands of GAC with the ion exchangers by isotherm and small column studies. The anion exchange resins A-7, IR-904, and 1R458 adsorbed the humic substance better than GAC, whereas the weak base resin ES-561 was comparable to GAC. Column tests on soil fulvic acids and leaf fulvic acids confirmed these data. The investigators observed that the adsorption capacity was a function of the source of organics.

The XAD-2, XAD-8, and XE-340 resins adsorbed only small amounts of humic material. Adsorption on ES-561 was best at pH 8.3 as compared to pH 7.0 and pH 9.5. Clearly, IR-904 was superior to the other resins at all pH's and maintained its capacity between 5.5 and 9.5. Whether the resins can be regenerated with an acceptable loss of capacity remains to be determined. The authors expressed concern about the fouling of strong base resins. Although weak base exchangers have a lower capacity, their use should not be ruled out, since they may regenerate more easily and regeneration is critical for the use of anion exchangers.

PILOT PLANT STUDIES

Kolle (1976) described how the strong base anion exchanger Lewatit, MP-500 A (Bayer, Leverkusen) removed natural color from groundwater at a water treatment plant in Fuhrberg, Federal Republic of Germany. The groundwater contained iron, manganese, sulfate, and humic substances. Traditional water treatment with aeration and permanganate oxidation reduced the dissolved organic carbon from 9 to 6 ppm while removing the metals. During pilot column tests at Fuhrberg, high bacterial growth during lime treatment was an added problem. New or regenerated anion exchange filters removed *58%* of the 6-9 ppm dissolved organic carbon that was present initially. This was reduced to 40% after 5,000 bed volumes at an EBDT of 1.1 min. When the organic carbon was lowered, the bacterial growth decreased. Full-scale testing to develop additional data was recommended to confirm these findings.

Gauntlett (1975) tested MP 500 A resin on treated water from the Thames River in England. His results showed that the resin had a much lower capacity for organic carbon than did a GAC tested in parallel. He also observed that fresh GAC was better than regenerated base anion exchange resins for the removal of total organics as well as dodecyl benzene sulfonate, 2,4-dichlorophenol, and yBHC (0enzene hexachloride) from coagulated and filtered water from the Thames. Lewatit MP 500 A, Amberlite *XE-258,* Permutit TR strong base anion exchange resins, and M P 62 weak anion exchange resins, were used at a quarter of the EBDT of *6.25* mm for GAC. The strong base resins were better than the weak base resins, confirming the laboratory data presented above.

- Jayes and Abrams (1968) applied a weak base anion exchange resin, Durolite A-7 (Diamond Shamrock Co.), for removal of natural color at Lawrence, Massachusetts. The resin was quite effective except when highly colored water was being treated. Under these conditions rapid breakthrough occurred. Regeneration was accomplished with 2% sodium hydroxide. These investigators estimated a resin life in excess of 200

cycles of adsorption-regeneration. Tilsworth (1974) compared strong base anion exchange resins Rohm and Haas IRAAOO, Durolite 5-37, Dowex SA 1273.1, and Dowex ii with GAC for the removal of TOC, COD, and color from lake water and shallow pond water in Alaska. The flow rate through the 3-ft column was 1 gal/min/ft3. Variability of the influent confused the evaluation of breakthrough data. In general, GAC was shown to be superior to the resins for removal of color, TOC, and

COD.

Wood and DeMarco (1980) studied the removal on XE-340, GAC, and IRA-904 anion exchange resins of purgeable organics and THM precursors from raw groundwater, after lime-softening and in finished water. Since TOC analysis did not correlate consistently with THMFP, it was not a good basis for comparison.

The THMFP in the influent to the columns varied in raw water from 600 to 868 ug/liter, in lime-softened water from 394 to 580 ug/liter, and in finished water from 274 to 451 ug/liter. The lime-softening process removed an average of approximately 30% of the THM precursors. Subsequent chlorination and sand filtration removed approximately 24% more. However, this last 24% removal was probably due to conversion of THM precursors to THM's.

Table IV-8 summarizes the pilot plant data. With a 75-cm-deep bed of an adsorbent, IR-904 resin removes more THM precursors (50%) than GAC or XE-340 from raw and lime-softened water, but GAC removes slightly more from finished water. Lime-softening removes approximately as much of the THM precursors as 75 cm of GAC or XE-340 and 60% as much as IR-904 resin. An important fact to consider is that, during raw water application, a I 50cm-deep bed of IR-904 allows 100 ug/liter THM precursors to pass through at startup compared to only 12 ug/liter leakage for 75 cm of GAC. GAC was more effective than other adsorbents in removing precursors from finished water. Dechlorination did not occur on the IR-904 resin used as a postcontactor. The effluent from this process indicates an apparent catalytic effect between chlorine and organcs absorbed on the resln.

In this study IR-904 resin did not remove any of 22 purgeable chlorinated Organic compounds (19 GC peaks) after lime-softening and chlorination. In fact, the level of halogenated Organic compounds increased after finished drinking water entered the resin column. These compounds included chloroform *(1.75* X); bromodichioromethane (1.13 X); trichloroethylene (10 X); 1,1, 1-trichloroethane, 1 ,2-dichloroethane, and carbon tetrachioride (1.5 X); chlorobenzene (1.4 X); and o- and p- dichiorobenzene (2.7 X). The GAC and XE-340 removed volatile organics while removing the THM precursors. GAC is the most

TABLE W-8 Removal of THM Precursors by Pilot Columns of XE-340, IR-904, and GAC after Different Stages of Water Treatment at Hialeah, Florida ab

Average THMFP Removal

Weight

Total THMFP Peroent Vol. Basis, Basis,

Pilot Entering atEnd gloolumnat gilOogat

Columns Column, g of Run 49 days 49 days

Raw water

GAC 7.1 ***29(119)C*** 0.99 0.56

XE-340 7.1 24(119) 0.71 0.33

IR-904 2.6 46(49) 1.21 0.44

IR~904d 2.6 55(49) 1.43 0.26

Lime-softened water

XE-340 ***5.0*** 4(119) 0.09 0.04

IR-904 1.7 32(49) ***0.55*** 0.21

Finished ***water***

XE-340 3.8 0(119) 0.00 0.00

IR-904 1.2 13(49) 0.19 0.07

GAC 1.2 18(49) 0.23 0.13

aWood and DeMarco, 1980.

b Based on breakthrough data for a bed depth of75 cm Number of days in parentheses.

dBed depthOf150CTTI.

successful adsorbent that has been tested for removal of THM precursors from this water. Wood and DeMarco (1980) determined that it appears best to use GAC as an adsorber before final chlorination for combined removal of THM and THM precursors.

Regeneration of Anion Exchange Resins

Regeneration and disposal of spent regenerant solution are major concerns involving resin use. A strong brine and/or alkali regenerant is used for strong base anion exchange resins.

Kolle (1976) accomplished regeneration with two bed volumes of 20 g/liter sodium hydroxide and 100 g4iter sodium chloride. The solution was reused. For every *25,000* volumes of processed water, he estimated

that one volume of spent regenerant would be produced. This is a very small volume.

Gauntlett *(1975)* found the weak base resins to be more readily regenerated, although ammonium hydroxide solution with recovery of ammonia for reuse was not as successful as regeneration with sodium hydroxide.

Kunin (1972) presented evidence indicating that spent regenerant can be recycled a number of times without treatment and almost indefinitely by treating the waste brine with ozone or hydrogen peroxide.

Growth of Microorganisms on Ion Exchange Resins

Daniels (1972) reviewed the adsorption of microorganism onto ion exchange surfaces. He described the attachment of microbes as an ion exchange process between the resin surface and the particular microbial species. The process is a function of the isolectric point of the bacteria, the pH of the media, and the form of the ion exchanger. The specific situation for drinking water application has yet to be studied.

Nitrosamines and Ion Exchange Resins

The following levels of nitrosamines have been found in deionized water:

N-nitrosodimethylamine (NDMA): 0.03-0.34 ug/liter (Fiddler *et al.,*

1977); *<0.25 u*g/liter (Cohen and Bachman, 1978); 0.01 ug/liter (Gough

et al., 1977); N-nitrosodiethylamine, 0.33-0.88 ug/liter (Fiddler *et al.,*

1977).

Gough *et al.* (1977) found 125 ug/kg NDMA in a prewashed batch of anion exchange resin after extraction with solvent. The authors suggested that the nitrosamine was present as a resin impurity. Angeles *et al* (1978) detected NDMA in the effluent from a column containing mixed strong anion and cation resins (previously washed to neutrality with distilled water) after a *1-N* sodium nitrite solution was passed through it. The cationic resin was in its H+ form and the anionic resin was in its OH- form. They postulated that NDMA was formed by cation-acid-catalyzed nitrosation of the amine/ammonium functional group on the strong anion resin during the deionization process. Fiddler and Kimoto (1979) studied the source of nitrosamines and ruled out the acid-catalyzed nitrosation mechanism previously suggested by Angeles *et al.* (1978) since the presence of NDMA occurred only when anion resins were used. They also observered that anion and cation resins did not

accumulate NDMA. In addition, trace levels of metal ions did not significantly enhance the formation of NDMA.

Fiddler and Kimoto (1979) concluded that the source of nitrosamine in municipal drinking water that had been exposed to deionizing resins appeared to be associated with low levels of nitrate and an unknown soluble substance(s) that promoted nitrosarnine formation during the deionization process. The unknown substance(s) could be removed by degassing techniques or by activated carbon treatment. The formation of nitrosamines on activated carbon may also be possible, but this area has not yet been investigated. Nitrosamines can accumulate on GAC by treatment of water containing nitrosamines (Borneff, 1980).

Adsorption Efficiency of Polymeric Adsorbents

Adsorption isotherm data, percent removal data, kinetic data, and small column data are determined to evaluate the adsorbent characteristics. This section reviews available polymeric resin data for low-molecular-weight organic compounds of potential concern to health (Table IV-2).

PERCENT REMOVAL DATA

Chriswell *et al.* (1977) compared the ability of XAD-2 resin and a GAC (Filtrasorb 300) to adsorb 100 representative compounds from water at 100 ug/liter concentrations. They passed 1 liter of the spiked tap water through small-scale columns at a flow rate of 10 ml/min. Their general conclusion was that, under these conditions and under the criterion of percent removal, the XAD-2 was superior for analytical purposes. Only C14 to C20 hydrocarbons and C5 and C7 fatty acids, as well as benzenesulfonic acid, were poorly adsorbed to the extent of showing less than a 50% removal. Also, the resin more readily released its adsorbed organics into an organic solvent so that they could be analyzed.

Van Rossum and Webb (1978) compared the ability of XAD resins 2,4,7,8 and mixtures of two and three resins to adsorb microgram amounts of 13 nonpolar trace organics from distilled and tap water at a flow rate of 1.2 liter/hr. Recovery ranged from 65% to 76%. A mixture of XADA/XAD-8 was the most effective. In a second study of five polar Organics (acids, phthlates, alcohols, and phenols), the effectiveness of the adsorption was XADA > XAD-2 > XAD-7 > XAD-8. Percent breakthrough studies of 50 ug/liter of 24 organics (spiked into tap water) on XAD-2 and

XADA/8 shows phthlates, bis(2-chloroethyl)ether and *n*-hexadecane breakthrough in both columns. XADA/8 was, on the average, 5% better than XAD-2.

Co

TABLE IY-9 Available Data on Adsorption of Selected Organic Compounds on Resin Adsorbents

Equilibrium Maximum

Number Adsorption Concentra- Surface

Organic Molecular of Data Resin Test tion Inange, Concentra

Compounds Weight Points Type Method mg/liter tion, mg/g Comments Reference

Cltloroform 119.4 XE-340 Isotherm <1-3 75 Nodatapoints Neely,inpress

Choloform 119.4 - XA[)-4 Isotherm <1-23 27 Nodatapoints Neely,inpress

Bromortichloro- 147.8 - XE-340 Isotherm <1-5 95 Nodatapoints RobmandHass methane Co., 1977

Deldrin 381 - XE-340 Isotherm 0.6-19 20 Nodatapoints RohmandHaas

Co., 1977

Dieldrin 381 - XAD-4 Isotherm 1.2-10 S Nodatapoints RohmandHaas

Co., 1977

2-Chioroethyl 143 1 XE-349 %reduction 5 33.3 Reportedas Rohmandllaas ether volumetric Co., 1977

capacity

2-Chloroethyl 143 I XE-347 % reduction S 14.3 Reported as Rohm and liass ether volumetric Co., 1977

capacity

2-Chloroethyl 143 XE-348 % reduction S 26.7 Reported as Rohm and Haas ether volumetric Co., 1977

capacity

Chloroform 119.4 9 XE-340 Isotherm 4-200 ""6 Unchangedby Chudyketal.,

10 mg/liter in press of humic substances

ADSORPTION ISOTHERMS

Isotherm data on XAD-l and XAD-2 has been published by Gustafson and Lirio (1968) for many compounds of environmental concern, but are not included on the list of compounds of potential health concern in Table IV-2. The compounds studied included fatty acids, amino acids, sulfonates, tannic acid, and phenols.

Table IV-9 contains the available adsorption isotherm data for a number of organic compounds. It provides specific information on the ability of a compound to be adsorbed by resins. Chudyk *et al* (1979) tested a neutral styrene-divinylbenzene (SDVB) resin, XADA, and the carbonaceous resin XE-340 against several different GAC materials for the adsorption of 2-methylisoborneol (MIB) from water. In terms of adsorption isotherms, the capacity of both resins for MIB was found to be less than that of the carbon with the lowest activity, but the presence of 10 mg/liter of humic acid did not affect the resin capacity in the equilibrium concentration range of 0.1 to 10 ug/liter, whereas it did affect the GAC. They also determined that the isotherms of chloroform on the carbonaceous resin and the lowest capacity carbon were approximately the same and were unchanged by the presence of 10 mg/liter of a commercially available humic acid. On the basis of these isotherms, the authors also reported that they could predict the relative efficiency of removal of MIB by bench scale columns.

Neely (1980) describes a model for the removal of chloroform from water by XE-340 where the resin macropores allow low-molecular-weight organics to diffuse to the micropores, while large molecules or humic substances cannot enter the micropores. Neely presents evidence to suggest that the high adsorptive capacity of XE-340 for chloroform is due at least partially to *absorption.* This capacity is shown to be from 3 to 5 times greater than that shown by five activated carbons that were tested simultaneously. Using the general shape of the isotherms of chloroform on XE-340 and XADA and one or two measurements of capacity, he interpolated the capacity of a series of adsorbents at 2 ppm equilibrium concentration. The chloroform capacities for the polymeric resins followed the trend XAD-1 > XE-225A = XADA > XAD-2 and XE-340> XE-348 > XE-347 for carbonaceous resins.

COLUMN STUDIES-SMALL SCALE

Gustafson and Lirio (1968) studied the breakthrough of phenol and alkyl benzene sulfonate (ABS) in small columns. Phenol breakthrough followed the order XAD-l < XAD-2 < GAC at a flow rate of 2 gal/ft3/min; ABS followed the order XADA GAC < XAD-2. Isotherms showed ABS adsorption. was less on XAD-l < XAD-2 < GAC. This indicates a size effect expressed as column kinetics.

Thurman *et al.* (1978a) determined the chromatographic capacity factor (solute adsorbed/solute void volume) of over 20 compounds of different functionality for analytical method development at a flow rate of 0.12 liter/hr until saturation. XAD-8 favors aromatic over aliphatic compounds and CH3 > COOH > CHO > OH > NH2. The log of the capacity factors was inversely correlated with the log of the solubilities in water. Thurman *et al.* (1978b) reported capacities of 55 umol/g XAD-2 and 80 umol/g for XAD-8 when soil fulvic acid was adsorbed. Capacities of XAD-2 > XAD-8 for acids, but phenols showed XAD-8 with the highest capacity. The fulvics and phenol were eluted with 0 1 *N* sodium hydroxide.

In a series of small column breakthrough studies at pH 8 and empty bed detention time (EBDT) of 2.1 min, McGuire (1977) compared the capacity of XE-340, XAD-2, and XAD-7 resins to that of FiltrasorbA00 for the constituents of a four-mixture solution: nitromethane, n-butanol, methyl ethyl ketone (MEK), and l, 4-dioxane. Extremely small adsorptive capacities were exhibited by the noncarbonaceous resins XAD-2 and XAD-7 in comparison with GAC and XE-340. This is in agreement with results from pilot plant studies (Suffet *et al.*, 1978a,b). While the adsorption capacities were similar, distinct differences were observed in adsorption kinetics in column studies. Breakthrough of each of the four components in the mixture began simultaneously in the XE-340 resin column. The breakthrough curves were also similar in shape. These results are in sharp contrast to those observed in the GAC column. There was evidence of displacement of dioxane by the other compounds, i.e., breakthrough of all components did not occur simultaneously, nor were the shapes of the breakthrough curves similar. The difference in breakthrough behavior between XE-340 and GAC suggests that adsorption on XE-340 may not involve competition to the same extent as on GAC.

Neely (1980) used a l0.2-cm-long, 15-ml bed volume of XE-340 and XADA in columns to follow the breakthrough of I ppm of chloroform in drinking water with 2 ppm TOC. The flow rate was 4 gpm/ft3. On the XADA column, 10% breakthrough was observed at 12 hr, whereas on the XE-340 column, 10% breakthrough did not occur until 180 hr.

To summarize, few studies applying resin for treatment of water supplies have been completed. Present data for chloroform adsorption indicate relative adsorption capacity on XE-340 versus GAC of 3:1 to *5:1* at high chloroform concentrations eely, 1980) and approximately 1:1 at low chloroform concentrations (Chudyk *et al.*, 1979). Data on other low-molecular-weight 6rganics are not available. The degree of competition between organic compounds with potential health effects on polymeric adsorbants has not been studied.

COLUMN STUDIES-PILOT SCALE

Studies on a pilot scale column have been performed to determine the efficiency of carbonaceous and neutral SDVB resins to remove the chemical species found in municipal water supplies. Suffet *et al.* (1978a,b) studied Filtrasorb400, XAD-2, and XE-340 in pilot columns as a post-treatment of chlorinated Philadelphia drinking water from the Delaware River. They used computer-reconstructed gas-chromatographic weekly profiles of 1- and 3-day composite samples and GC/MS to assess 27 identified compounds (BP 600C to 2800C). In one study, XAD2 was found to have a much lower capacity than FiltrasorbA00 for the removal of the species that were present. They observed very early breakthrough for most compounds on XAD-2. A further series of tests involving XE-340 showed that XE-340 possessed adsorptive capacities that were generally much like those of FiltrasorbAO0 for nonpolar low-molecular-weight organic compounds.

Suffet *et al.* (I 978a,b) also observed that GAC removed both high- and low-molecular-weight organics, whereas XE-340 removed the lower-molecular-weight organics. They cautioned that the data are largely qualitative and that interpretation of results are complicated by the highly variable nature of the organic content of the influent to the adsorption column.

Wood and DeMarco (1980) compared the ability of XE-340, IRA-904, an anion exchanger, and Filtrasorb400 GAC to remove purgeable organics, as defined by the technique of Bellar *et al.* (1974), and THMFP as defined by Stevens *et al.* (1976). Determinations were made on raw groundwater, lime-softened water, and finished water from Hialeah, Florida. Breakpoint chlorination was practiced to produce a 3-ppm free chlorine residual. They determined that GAC offered the best promise for the removal of TOC, THMFP, and purgeable halogenated organic compounds in the finished water. The XE-340 did not remove any THMFP whereas GAC removed 20% from finished water.

Table IV- 10 shows that XE-340 always has a greater adsorption capacity than GAC for individual volatile halogenated organics in raw and finished water in 6.4-cm deep beds with 6.2 min EBDT. A value for XE-340 3 times greater than for GAC was generally observed despite a reduction of 30% TOC in finished water. These results were also

TABLE W-l0 Comparative Removal of Volatile Chlorinated Organic

Compounds by XE-340 and GAC in Pilot Columns Mter Different Stages of Water Treatment at Hialeah, Florida

Ratio of average

capacity of

XE-340 to GAG

Average

Stage of Concentration, By By

Compound Treatment ug/liter Volume Weight

Chloroform Finished 67.3 4.9 4

(Range *45~90)b*

Raw 21-29 3.6 3

Dichlor- *(~85%* of Vol. TOX)C

ethane

Lime- 20-25 3.1 2.5

softened

Finished 11-19

(1O~~o of Vol. TOX)C

Brornodi-- Finished 37A7 3.4 2.8

chlor-

methane

Dibromo- Finished 12-34 3 2.5

chlor-

methane

a Wood and DeMarco, 1980.

b High points of 110 and 130 ug/liter at day 14 and 112, respectively, side the range shown.

Vol. TOX = Volatile total organic halogens.

are the only points out-

observed for other purgeable halogenated organics and agree with isotherm data.

A review of specialized studies of the use of XAD resins has been completed by Kennedy (1973). He reported that the *XADA* resin was particularly advantageous for the removal of chlorinated pesticides and phenols from industrial wastewater. He determined that the XAD-8 resin was the best for removal of color from Kraft mill wastes.

Symons (1980) evaluated the efficiency of XE-340 in removing THM's. With an empty bed contact time of 10 min, the column removed all THM compounds for 10 weeks from an influent that had a THM concentration of approximately 125 ug/liter. The effluent concentration rose to 25 ug/liter in the next 20 weeks as the influent concentration dropped steadily to 50 ug/liter.

COMPETIVE ADSORPTION STUDIES

Humic material did not interfere with adsorption of chloroform on XE-340 during isotherm studies (Chudyk *et al.*, 1979). This was confirmed in part in pilot plant studies for adsorption on XE-340. Wood and DeMarco (1980) did not observe the removal of THMFP from finished water. However, XE-340 did remove 24% of the THMFP from raw water. Competition between organics with potential health effects is not known at present.

Regeneration of Polymeric Adsorbents

The removal of adsorbed species from polymeric resins may be accomplished by various means. Kennedy (1973) found that XAD-4, when loaded with chlorinated pesticides, was readily regenerated by either acetone or isopropyl alcohol and that the regenerant could be readily reclaimed for further use. Kennedy also reported that XAD-8, when loaded with Kraff mill color bodies, could be regenerated with a weak base. Crook *et al.* (1975) regenerated XADA with 4% sodium hydroxide when loaded with phenolic wastes.

Gustafson and Lirio (1968) regenerated XAD-l and XAD-2 with 1% sodium hydroxide when columns were saturated with phenol. Ninety-nine percent of the phenol was eluted at a flow rate of 1 gal/ft3/min. Regeneration of XAD- I and XAD-2 by low-polarity solvents or solutions of acid or base for the opposite material was also suggested. They recommended a dilute base for regeneration of Organic color bodies in industrial wastes.

Slejko and Meigs (1980) stated that XE-340 may be regenerated efficiently by steam. XE-340 may be used for shorter periods between regenerations than GAC materials and that after 3 to 4 days in an adsorption mode an *in-situ* regeneration using 37 lb of 1 100C steam per cubic foot of resin is adequate to clean the bed of all steam-purgeable species. Over an extended period of operation, possible buildup of Organics that are not steam-purgeable caused the investigators to suggest a periodic washing with ethyl alcohol.

The Rohm and Haas Co. (1977) reported that carbonaceous resins (XE-340, 347, 348) may be regenerated by water-miscible solvents, such as acetone or methanol, or by water-immiscible solvents, such as toluene and xylene, both followed by a flow of steam to clear the bed of regenerant. For compounds with low boiling points that are not accompanied by heavier adsorbates, or for those compounds that form low-boiling azeotropes with water, steam is an effective primary

regenerant. The investigators also suggested that acid or base regenerants should be effective for the removal of certain ionic organics, but presented no data to support this.

Chudyk *et al.* (1979) investigated the regeneration of an SDVB resin and a XE-340 resin, which had been loaded with MIB or chloroform. Atmospheric steam and/or ethyl alcohol were used as the regenerants. Slejko and Meigs (1980) described how this carbonaceous resin could be purged of chloroform with steam. Steam removed only 5% of the adsorbed MIB while ethanol removed only 20%. However, there were no successive saturation regenerations to determine if MIB applied in subsequent cycles could be recovered.

The SDVB resin proved to be easier to regenerate by these means. The MIB recovery with steam was 23%. This was followed by a further 53% recovery by ethyl alcohol, yielding a total of 76%. A replicate determination yielded recoveries of 34% by steam and a further 34% for the alcohol, for a total of 68%.

Summary, Conclusions, and Recommendations

ANION EXCHANGE RESINS

Much of the limited experience with the use of anion exchange resins to remove humic material has been gained from processing water for electronics and power utilities. In these cases, the anion exchange resins have effectively removed humic material. Resins have been preferred over GAC or PAC by these industries (Kunin 1972, 1976). Laboratory and pilot plant studies have shown that strong base anion exchange resins can remove humic materials as well as or better than GAC. The adsorption capacity is a function of the composition of the aqueous solution.

Present studies indicate that nitrosamines may be generated by passage of water over a strongly basic resin. The exact mechanism has yet to be demonstrated. Since the resins concentrate the potential reactants for forming nitrosamines and also accumulate potential catalysts (iron and copper), the published data on the formation of nitrosamines on anion exchange resins suggest that the use of such resins for potable water should be reconsidered. It may be possible to use anion exchange resins in conjunction with GAC. The resin would remove the bulk of the humic material and the GAC would remove the remainder of the humic material as well as any nitrosamines that had been generated, if any. However, there are no data for such possible systems.

The data on the use of anion exchange resins have been based primarily upon resins that either have been regenerated only a few times or have been in their virgin states. Such data are highly unrealistic for the water treatment industry. For example, the question of acceptable loss of capacity upon regeneration can be addressed only after regenerations are completed. Since regeneration is completed with either brine or caustic, the disposal of waste regenerant can also present serious environmental problems.

POLYMERIC AD5ORBENr5

Experience with synthetic resins and polymeric adsorbents to remove organic compounds from drinking water is limited in comparison with the use of GAC or PAC. Laboratory studies and the few recent pilot plant studies indicate that the synthetic carbonaceous adsorbents of the XE-340 type do not have the broad-spectrum adsorption properties of GAC and that they selectively adsorb lower-molecular-weight organics but apparently do not readily adsorb humic material. However, the data indicate some promise for special situations such as the removal of toxic organics from sources contaminated with low-molecular-weight Organics (Wood and DeMarco, 1980). The synthetic carbonaceous adsorbents are still in their experimental and developmental stages. Some published data show their greater efficiency with chloroform and related low-molecular-weight organics.

There is a lack of information on the effect of chlorine disinfectant before the use of resins under conditions at water treatment plants. Combined chlorine residuals were observed in the effluent during pilot column studies with XE-340 (Suffet *et al.,* 1978b). Since attrition of the resin by chlorine is possible (Kunin, 1976), subsequent studies should consider dechlorination before the adsorption step. Under these conditions, microbial growth should also be monitored.

There is a lack of regeneration information for XE-340. Questions remain concerning the effectiveness of steam for regeneration, the use of solvents for regeneration and their potential health effects, and the number of times resins must be recycled in order to compete economically. These adsorbents may have excellent possibilities for small plants or well waters that are plagued only with haloforms or other lowmolecular-weight compounds, but regeneration studies must be completed to evaluate their utility. The subcommittee recommends that:

1. A survey of several plants using anion exchange resins should be conducted to determine their performance for removal of humic

material. Most of these plants are industrial plants operating in the United States, Great Britain, and the Federal Republic of Germany.

2. The possible formation of nitrosamines on anion exchange resins must be studied.

3. Studies should be made on synthetic carbonaceous adsorbents for systems that use them in conjunction with anion exchange resins or following GAC. Dechlorination before the resin bed treatment should be considered.

4. Studies on the use of the synthetic carbonaceous resins for treating contaminated well waters should be expanded to include regeneration Systems. The effect of chlorine on the adsorption process and resin attrition should also be studied.

5. Pilot column tests on different waters along with appropriate laboratory studies are needed to answer the following crucial questions concerning the regeneration of all resins. What is the rate of loss of capacity due to fouling? What type of regenerant will work best? How will the disposal of regenerant be handled?

ANALYTICAL METHODS TO MONITOR ADSORBENT UNIT PROCESSES IN WATER TREATMENT

This chapter has focused on individual compounds of potential harm to health. Thus, the primary purpose of this section is to evaluate the availability of analytical methods to monitor the operation of adsorbent processes for these compounds at a water treatment plant. The following questions are addressed:

1. Can the monitoring for individual compounds of potential harm to health be completed in other than a research laboratory?

2. Can nonspecific parameters be substituted for monitoring of individual compounds?

The chemical compounds entering an adsorption treatment process are both high- and low-molecular-weight organic compounds with a wide range in polarity. The Committee on Safe Drinking Water National Academy of Sciences, 1977) estimated that 90% by weight of the total organic matter in drinking water is composed of highmolecular-weight organics. This would correspond to natural organic compounds of little-known toxicological importance (Class V; U.S. Environmental Protection Agency, 1978c), but these compounds may

affect the process by competitive adsorption or support of microbial growth. A fraction of these high-molecular-weight organic compounds are precursors that react with disinfectants to produce "disinfectant byproducts" (Class III; U.S. Environmental Protection Agency, 1978c). The remaining 10% of the total organic matter includes, but is not limited to, volatile synthetic organic chemicals that are present in source water and organic chemicals that are disinfection by-products (Classes II and IV; U.S. Environmental Protection Agency, 1978c). A subgroup of the chemicals in the last group are the potentially harmful chemicals (Interagency Regulatory Liaison Group, 1978; National Academy of Sciences, 1977; National Cancer Institute, 1978).

The primary goal of influent analysis is to monitor specific potentially harmful chemicals so that removal efficiencies can be established. The optimum monitoring method is to measure quantitatively the compounds of concern over the entire period of operation. Because concentrations in the influent may vary greatly over time (see section on competition), infrequent grab sampling might not be sufficient for an adequate evaluation of material entering the column. Since minute-to-minute sampling is presently impractical, the variability of these organics in the influent can best be followed by on-line composite sample collection. The variability of the load of humic substances, which include the precursors to compounds that might affect human health, should also be measured. Also, the general load of total organic matter as DOC can be used to follow mass loading of the carbon filter.

Chemical compounds in the effluent may be the same as those that entered the carbon bed, or they may have been changed by chemical or microbial action within the bed. The variability of species type and concentration in the column influent are also reflected in variable effluent concentrations. Competitive effects occur when a strongly adsorbed compound enters the bed and displaces a more weakly adsorbed compound. In this case, the concentration of the displaced compound may be higher in the effluent than in the influent until a new equilibrium is reached. A reequilibration effect is observed when the concentration of a compound in the influent decreases. This compound then desorbs from the carbon. Again, the concentration in the effluent could be higher than in the influent until a new equilibrium is established. This discussion indicates that effluent concentrations are dependent on influent concentrations, in addition to the adsorption dynamics on the column, and would therefore tend to vary.

In addition to monitoring influent and effluent, it may be desirable to monitor the contents of the GAC bed itself to determine when breakthrough will occur. By determining the location in the bed of the

different compounds with potential health effects, one can evaluate column performance as well as the remaining capacity of the column. Indications of pending breakthrough may be easier to evaluate by determining the location of the specific organics.

Monitoring Specific Pollutants of Potential Harm to Health

Since *1975,* a massive effort to identify organic compounds in drinking water by gas chromatography/mass spectrometry (GC/MS) has resulted in an inventory of volatile, relatively nonpolar, soluble organics that are isolated from water by volatilization, solvent extraction, or solid phase adsorption (Keith, 1976). More than 700 compounds have been isolated by these methods and by methods utilizing reverse osmosis as the concentration and isolation tool (U.S. Environmental Protection Agency, 1978b). In the United States, the concentration and frequency of occurrence of THM's are the highest of the volatile organics in drinking water due to the use of chlorination for disinfection (Symons *et al., 1975).*

Two different analytical approaches can be used to determine specific organic compounds of potential harm to health. In one approach individual compounds that have been selected because of health implications are analyzed. In the second, a general "screening" procedure for the isolation of organic compounds is used and the compounds of interest are selectively determined from the same sample matrix.

ANALYSES OF INDIVIDUAL COMPOUNDS WITH A POTENTIAL TO AFFECT HEALTH

Table IV-2 lists specific pollutants of potential harm to health that should be monitored. Specific analytical methods for each of these or groups of these are being developed (Keith and Telliard, 1979). The analysis of THM's is reviewed below to point out general principles of analysis for specific pollutants.

THM's consist of chloroform, dichlorobromomethane, dibromochloromethane, and bromoform. The existing techniques for THM analysis have been reviewed National Academy of Sciences, 1978). Routine monitoring methods are batch analyses, the purge and trap procedure (Bellar *et al.,* 1974), and liquid-liquid extraction (Henderson *et al.,* 1976; Mieure, 1977; Richard and Junk, 1977). Some investigators used other methods such as headspace analysis (Kaiser and Oliver, 1976) and direct water injection Nicholson *et al.,* 1977). The limitations of direct water injection have been documented by Pfaender *et al.* (1978).

THM's are now routinely measured in many laboratories, primarily by

the purge and trap method (Bellar *et a!.,* 1974). Keith (1978) reported

-+20% of the true value for 90% of the individual THM's (> 10 ppb) by this method. He judged that the lowest concentration at which an accurate analysis can be obtained during routine monitoring was no less than *1.5* ug/liter, and he reported background levels of *0.5* ug/liter. Dressman *et al* (1979) and Reding *et al.* (in press) obtained comparable results regarding the overall precision of the purge and trap analysis and the three liquid-liquid extraction methods for routine monitoring of drinking water.

THM monitoring as well as THMFP data for evaluation of GAC columns has been based upon a 1 5-min daily composite (U.S. Environmental Protection Agency, 1978b), but it is not known if this composite accurately represents the load on an adsorbent. Studies are needed to determine if a 15-mm composite is justified. Recently, Westrick and Cummins (1978) have developed THM data for sewage treatment using an outline composite sampler that can collect a sample without headspace. Composite sample collection for evaluation of the control of THM's may give a more representative picture of the THM load on a column.

Appropriate blanks and quality control check samples must be completed to ensure accuracy and reproducibility. Sample transport, pretreatments (e.g., addition of a dechlorination agent), and Storage are of concern because of THM volatility and precursor reactivity (Brass *et a!.*, 1977). Primary calibration standards are needed, as are control samples. Interlaboratory studies to determine the accuracy of analysis are useful as part of the overall quality control program. Thus, quality assurance programs should be instituted to maintain the reliability of monitoring data. Quality assurance, as described by Miller (1979), minimizes errors resulting from sample site selection, sampling frequency, reference materials, and data acquisition Systems, as well as from the analytical method itself.

SCREENING PROCEDURES

The screening procedure consists of a qualitative identification of individual compounds and their subsequent quantitative analysis. A general sequence followed for screening of trace organics is: Sample

Isolation Method Concentration Chromatographic Separation Qualitative Identification Quantification.

One key to the screening procedure is the isolation method that defines the type of compound to be studied and can simultaneously analyze for compounds that are potentially harmful to health. Each method will

TABLE *W*- 11 Methods of Isolation of Organic Chemicals from Aqueous Samples for General Screening Procedures and Specific Analysis a

Sample

State Isolation Techniques Collection Phase

Vapor

Headspace *analysis* Gas

Purge and trap Solid

Solution'

Liquid-liquid extraction (LLE) Liquid

Adsorption by solids Solid

Carbon adsorption method (CAM)

Macroreticular resins (MRR)

Chromatographic liquid phases

Porous polyurethane foam

Freeze Concentration Solid

Reverse osmosis Aqueous-Concentrate

a Update of Suffet and Radzuil, 1976

isolate material selectively. Suffet and Radzuil (1976) have described the methods that can isolate chemicals with health implications (see Table IV- 11). For example, the less-polar-volatile organics of p6tential harm to health are isolated by methods such as the purge and trap volatile organic analysis up. < 1500C) (Grob and Zurcher, 1976), liquid-liquid extraction (Yohe *et al.*, in press), and macroreticular resin accumulators (Chriswell *et al.*, 1977). These methods must be supplemented by specific analyses for compounds that are not isolated by the specific extraction method.

The complex group of trace organics in the extracted sample is chromatographed, and a sample profile or fingerprint is obtained. This constitutes an information pattern in each chromatographic analysis. When the profile is compared to a profile of a set of standards of the known compounds, a tentative identification of the sample components can be made. If standard curves are made for each of the components, an estimate of the amount of the tentatively identified compound can be made. When many profiles of influents and effluents are plotted in the same manner, chromatographic profiles can be compared and differences noted. GC/MS analyses must be used to confirm the identification of the compounds tentatively identified by the isolation method. Examples of the screening of the organic compounds in the influent and effluent of adsorption processes have been reported for purge and trap analyses (Steiglitz *et* al., 1976; Wood and DeMarco,

1980), resin accumulators (Suffet *et al.,* 1978), and liquid-liquid extraction Yohe *et al.,* in press): To monitor an adsorption process for pollutants of potential harm to health concern that are volatile or can be detected by GC techniques, only selected GC/MS analyses may be necessary. GC analysis can be used for monitoring purposes if concentration limits for pollutants are defined.

Nonspecific Organic Analysis

Nonspecific organic analyses lumps together a large number of organic compounds under one collective measurement umbrella. All of the nonspecific analyses should be evaluated on the basis of specific organic compounds identified in Table IV-2.

General organic analyses have been tested extensively by several investigators in an attempt to replace or supplement the complex GC or GC/MS analysis in water treatment monitoring. Correlation among general organic analyses and organic compounds with possible health effects has been attempted in order to develop an economical and rapid monitor for the use of GAC processes.

Stevens and Symons (1973) concluded that no current tests completely measure the total concentration of organic compounds in water. The primary analyses that have been routinely substituted for measurement of the total concentration are elemental, e.g., TOC, DOC, purgeable organic carbon (POC), or nonvolatile TOC (VTOC), and general organic analyses, e.g., COD and the carbon chloroform extracts (CCE). UV absorbance and fluorescence have also been used to follow the efficiency with which organics are removed by GAC. Organic carbon analyses and UV absorbance have been used for process control of GAC plants in the Federal Republic of Germany. The ratio of DOC to UV absorbance was found to change after different water treatment processes.

Symons *el al. (1975)* indicated that NVTOC is a dominant factor influencing the creation of THM's. These workers describe NVTOC as a "reasonable indicator" of THM precursors in drinking water in an 80- city survey. They reported that some correlation existed between NVTOC and CCE data but these data were rather scattered. For drinking water, the NVTOC method did not correlate well with the UV absorbance method of Dobbs *et* a!. (1972), the fluorescence method of Sylvia (1973), or an emission fluorescence scanning (EMFS) method. The two fluorescence methods correlated well with each other.

Sylvia and Donlan (1980) demonstrated a correlation between TOC and fluorescence from numerous water sources. This is comparable with

data of Snoeyink *et a!.* (1977), who reported that fluorescence could be used to monitor adsorption of the lower-molecular-weight fraction of humic material. The EPA (U.S. Environmental Protection Agency, 1978c) has stated that TOC tends to give excessive weight to naturally occurring high-molecular-weight compounds, which are not believed to be hazardous, and that TOC is not a suitable criterion for the design of GAC systems.

Brodtmann *et* a!. (1980) used TOC, LW absorbance, fluorescence, and EMFS during two full-scale water treatment studies with GAC adsorption at the Jefferson Parish Water Plant on the Mississippi River in Louisiana. Samples were collected three times a week from five plant locations during the study. Brodtmann *et* a!. (1980) were unable to correlate any nonspecific organic analyses with each other or with organic compounds having health implications during this study. Wood and DeMarco (1980) and Cairo *et a!.* (1980) also indicated that TOC and THMFP did not correlate well in pilot plant studies in Miami, Florida, and Philadelphia, Pennsylvania, respectively. There have been no successful correlations between breakthrough of specific organic compounds on a GAC column and the breakthrough of those components as measured by general organic parameters.

Table IV-2 shows that the halogenated organics as THM's and low-molecular-weight organics comprise many of the organics that are potentially harmful to health. Higher- molecular-weight organics containing halogens from partially chlorinated humic material are suspected of having implications for health (Sontheimer, 1974). The measurement of total organic halogen (TOX) by the pyrohydrolysis method has been developed in the Federal Republic of Germany by Kuhn and Sontheimer (1973a,b) and evaluated by Dressman *et* a!. (1977). Other methods of TOX analysis exist, e.g., the use of LW oxidation after resin adsorption *(Glaze et a!.*, 1977).

The objective of water treatment in the Federal Republic of Germany is to attain a finished water quality equal in all respects to that of high-quality groundwater (Kuhn *et* a!., 1978a,b). Since chlorinated organics are not naturally found in groundwater, they have been singled out for intensive study.

In the Federal Republic of Germany, TOX has been used to monitor breakthrough behavior of activated carbon filters and to determine the necessity of reactivation in drinking water treatment plants (Kuhn *et a!.*, 1 978a,b). Dissolved organic halogen (DOX) in water and the adsorbed organic chlorine on the GAC have also been studied in that country.

Steiglitz *et* a!. (1977) reported that single substance analysis of Rhine River water by GC and GC/MS and elemental analysis by TOX

indicates that only approximately 10% by weight of the DOX was identified by GC/MS analysis. There was no recognizable correlation between the concentration of DOX and the amounts of specific organics. Kuhn and Fuchs *(1975)*, Sander *et al.* (1 977), and Oliver (1978) showed that DOX increases after chlorination of natural water as do the THM's. The TH M's do not account for all of the increase.

Dressman *el al.* (1977) modified the original pyrohydrolysis method (DOX and TOX) and defined it more properly as a semiquantitative measurement of carbon-absorbable organohalides (CAOX as Cl). They suggested that a reliable lower limit of sensitivity is no less than 10 ug/liter over background values of 10 ug/liter. These authors reported critical problems in accounting for the efficiency of the adsorption step on charcoal for all halogenated organic compounds and the contribution of other halides to the microcoulometric measurement of hydrochloric acid from the burning of charcoal in an oxygen steam environment at l,0000C. An addition to the method to be used for disinfected waters individually analyzes the nonpurgeable CAOX as Cl and purgeable OX by the purge and trap method to determine the approximate CAOX as Cl. In drinking water the purgeable organic halogen can be *25%* of the approximate CAOX as Cl organic halogen.

A differentiation should be made between the TOX measurement of raw water and finished drinking water after chlorination. For example, the raw water measurement may be composed predominantly of low-molecular-weight synthetic organic compounds from industrial origin. The finished water measurement would also include higher-molecular-weight organic compounds that were formed by chlorination during treatment as well as haloforms and possibly others.

The elemental analyses indicate changes of influent concentration, process trends, and general adsorption capabilities. The CAOX as Cl measurement could be a nonspecific analysis of choice, as many organics of potential harm to health are halogenated.

GAC Surface Phase Analysis

The primary purpose of monitoring the adsorbed material is to follow compounds as they move down through the column so that a warning can be provided when harmful compounds are about to break through. While the aqueous phase must be approached by composite sampling, the sampling of the GAC surface phase is somewhat simplified, since the adsorption mechanism stores a composite record on the surface of the absorbent.

Carbon samples can be obtained either by taking samples directly

from the operational bed (Kuhn and Fuchs, 1976) or by sacrificing small columns that are run parallel to the main bed (Fuchs, 1974). If practical, sampling of the main bed is preferable, since it directly samples the process under investigation and avoids problems of scaling down large operations, especially for long composite times when biological growth can occur.

Kolle *et al.* (1975) reported a screening method that avoided the solvent desorption step by vacuum desorption of the volatile compounds from heated samples for analysis by GC and GC/MS. However, there are no experimental details concerning the compounds for which it is useful or its reliability.

Kolle *et al. (1975)* also determined several different profiles of the adsorption pattern for several different chlorinated compounds through-out the GAC bed. Kuhn and Fuchs (1976) have used TOX along the length of a GAC column to monitor breakthrough, but the technique needs further development so TOX can be correlated with specific compounds with health implications.

Summary, Conclusions, and Recommendations

The variability of the complement of organic compounds in the influent to the GAC column affects the efficiency of the adsorptive process for the compounds. On4ine composite sampling augmented by grab sampling of the influent and effluent of the GAC column is necessary because of the variability produced by competitive adsorption, reequilibrium, and desorption.

The analysis of specific organic compounds of health concern on a regular basis will be time-consuming, expensive, and difficult at most water treatment plants. One approach that may be useful is a set of screening protocols, e.g., collection of headspace free samples for purge and trap and resin accumulators using on-line composite samplers. These samples would be compared by chromatographic profiles augmented by GC/MS analyses. This approach would monitor specific organics with health implications at each water treatment plant.

Analytical techniques for monitoring the performance of adsorbent beds need further development. Correlations between nonspecific measurements and compounds of concern should be completed on a site-specific basis, since the specific organic compounds that must be controlled will probably vary among water supplies. The correlation of such measurements as LW absorbance, fluorescence, or analyses of organic carbon (e.g., TOC) with GAC breakthrough of specific organic compounds of concern has not been observed (Brodtmann *et al.*, 1980;

Symons *et al.,* 1975; Wood and Demarco, 1980). However, TOC remains an important measure of the mass loading of an adsorption column.

The correlation of TOX in the aqueous or absorbed phases with organic compounds of concern has not been sufficiently studied. TOX would indicate the mass loading for halogenated compounds and the total amount of chlorination products produced during a water treatment process. This should be developed for routine use, since many compounds with health implications are chlorinated.

THM precursors that participate in the haloform reaction have not been shown to correlate with nonspecific organic analysis. Although fluorescence has been used to monitor humic material (Snoeyink *et al.*, 1977; Sylvia and Donlon, 1980), it has not been shown to correlate with THMFP. TOC and THMFP did not correlate well in pilot column studies (Cairo *et al.,* 1980; Wood and Demarco, 1980). Organic carbon is a collective measure of all organic constitutents, only a few of which are haloform precursors.

On a weight basis, only approximately 10% of all the organic compounds in drinking water have been identified National Academy of Sciences, 1977). The low-molecular-weight polar organics and the nonvolatile high-molecular-weight organics cannot be analyzed by the above-mentioned methods. The screening of these compounds is now becoming possible with the use of high-pressure liquid chromatography (HPLC) analysis. The coupling of HPLC and MS, which is under development, will further expand the analytical possibilities. Research on these techniques is needed to expand our understanding of the more polar organics in water supplies. There is only a minimum of knowledge concerning the health implications of these compounds.

The calibration standards for specific pollutant analysis and reference compounds for the comparison of analytical recovery between methods should be standardized to ensure that analytical methods are accurate and reproducible. Strict quality control and interlaboratory comparisons are integral parts of the validation program.