

DEPARTMENT OF THE ARMY
U.S. Army Corps of Engineers
Washington, DC 20314-1000

DAEN-ECE-G

ETL 1110-3-367

Technical Letter
No. 1110-3-367

20 October 1986

Engineering and Design
TRACE ORGANIC COMPOUNDS IN POTABLE WATER SUPPLIES

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1. Purpose. This letter provides basic information pertaining to the occurrence, detection, and treatment of trace organic compounds that may be found in drinking water and existing and proposed drinking water standards for organic compounds.
2. Applicability. This letter applies to all HQUSACE/OCE elements and field operating activities (FOA) having Army military construction design responsibility.
3. Background. Concern is growing over the discovery of literally hundreds of organic compounds in drinking water. Federal and State surveys to date have identified over 700 organic compounds in potable water supplies; many are toxic and suspected carcinogens, even in minute concentrations. These compounds may be present in finished water as a result of chlorine reacting with naturally occurring organic acids or in surface and groundwater supplies through contamination by pesticides, solvents, or petroleum product constituents. In the latter case, widespread use of a broad array of these organic compounds increases the potential for water supply contamination by runoff, spills, improper disposal practices, or leaks from petroleum storage vessels or pipelines. Some pesticides that are regulated and others being considered for regulation are used at Army installations. As a result, some installations' water supplies contain volatile organic compounds at the alarmingly high level of several thousand micrograms per liter. Trichloroethylene (TCE), a common solvent used both at Army installations and in the civilian sector, is the synthetic organic compound found most often in Federal and State groundwater surveys. (The U. S. Environmental Protection Agency (USEPA) recommended standard for TCE is zero.) Army installations must comply with regulations on levels of organic compounds in drinking water and will be required to install removal equipment if these compounds are detected.
4. Action to be Taken. Information in this letter is intended to supplement TM 5-813-3, Water Supply, Water Treatment, and TM 5-660, Operation of Water Supply and Treatment Facilities at Fixed Army Installations. Enclosure 1 provides design guidance for removing regulated volatile organic compounds from water. More details can be found in Technical Report N-85/11, Strategies for Controlling and Removing Trace Organic Compounds Found in Potable Water Supplies at Fixed Army Installations (U.S. Army Construction Engineering Research Laboratory, 1985).

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5. Implementation. This letter will have routine application, as defined in paragraph 6c, ER 1110-345-100.

FOR THE COMMANDER:

Encl



WILLIAM N. McCORMICK, JR.
Chief, Engineering Division
Directorate of Engineering
and Construction

STRATEGIES FOR CONTROLLING TRACE ORGANIC
COMPOUNDS IN WATER SUPPLIES AT FIXED ARMY INSTALLATIONS

SECTION I. REGULATION AND ANALYSIS OF ORGANIC COMPOUNDS
IN DRINKING WATER SUPPLIES

1. Existing and Proposed Drinking Water Standards for Organic Compounds. The first set of regulations--the National Interim Primary Drinking Water Standards--became effective in 1977 and established enforceable limits on the concentration of trihalomethanes (THMs) and six pesticides in potable water (table 1). Drinking water standards (known as "Recommended Maximum Contaminant Levels" or RMCLs) are proposed for nine volatile synthetic organic compounds (VOCs) (table 2). Other synthetic organic compounds being considered for regulation include several registered pesticides, some polynuclear aromatic hydrocarbons (PAHs), certain esters, and acrylamide (table 3).

2. Analysis of Trace Organics in Water. Many methods have been developed for isolating, resolving, identifying, and quantifying (detecting) the complex mixtures of organic compounds in water. Figure 1 shows some methods involved in these steps. Organic compounds in water typically are detected on the basis of their polarity, volatility, and molecular weight. Table 4 classifies compounds according to these properties.

a. Isolation. Most volatile, polar, and water-soluble organics need not be isolated before analysis. Less polar, volatile organics are isolated by allowing them to partition into the gaseous phase (headspace) above the water; partitioning can be enhanced by using dynamic gas flow or by trapping the organics after they enter the gaseous phase. More highly polar organics, which are difficult to recover with the dynamic headspace-adsorption technique, can sometimes be isolated by applying a concentrating distillation step before headspace removal. Table 5 lists isolation techniques.

b. Resolution. After removing the organic(s) of concern from the water, the isolate typically contains a complex mixture of organic compounds. The most common technique used to resolve this mixture is chromatography, a process of selectively separating a mixture's components into distinct constituents. Table 6 summarizes resolution techniques.

c. Detection. After the organics in water have been isolated and separated, they must be identified and quantified. Table 7 lists methods typically used for observing organics' physical and chemical properties. Although the properties of many organics are well suited to detection using several techniques, the best detectors for both volatile and semivolatile organics are those used in conjunction with gas chromatography. If the nature of the organic compound in the water supply is known, tables 5 through 7 can be used to determine the best way to isolate, resolve, and detect it. After determining what contaminants are present, alternative treatment processes can be considered.

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Table 1. Organic compounds regulated under interim primary drinking water standards

<u>Compound</u>	<u>MCL (mg/L)*</u>
Total THM	0.1
Endrin	0.0002
Lindane	0.004
Toxaphene	0.005
2,4-D	0.1
2,4,4-TP (Silvex)	0.01
Methoxychlor	0.1

*Maximum contaminant level.

Table 2. Proposed standards for volatile synthetic organic compounds

<u>Compound</u>	<u>RMCL (mg/L)*</u>
Trichloroethylene (TCE)	0
Tetrachloroethylene (PCE)	0
Carbon tetrachloride	0
1,1,1-Trichloroethane	0.2
Vinyl chloride	0
1,2-Dichloroethane	0
Benzene	0
1,1-Dichloroethylene	0
Dichlorobenzene	0.75

*Recommended maximum contaminant level.

Table 3. Organic compounds being considered for regulation*

Aldicarb
Chlordane
Dalapon
Diquat
Endothall
Glyphosate
Carbofuran
1,1,2-Trichloroethane
Vydate
Simazine
PAHs
Atrazine
Phthalates
Acrylamide
Dibromochloropropane
1,2-Dichloropropane
Pentachlorophenol
Pichloram
Dinoseb
Alachlor
Ethylene dibromide
Epichlorohydrin
Dibromomethane
Toluene
Xylene
Adipates
Hexachlorocyclopentadiene
2,3,7,8-TCDD (Dioxin)

*Source: USEPA, Federal Register, Vol 48 (5 October 1983).

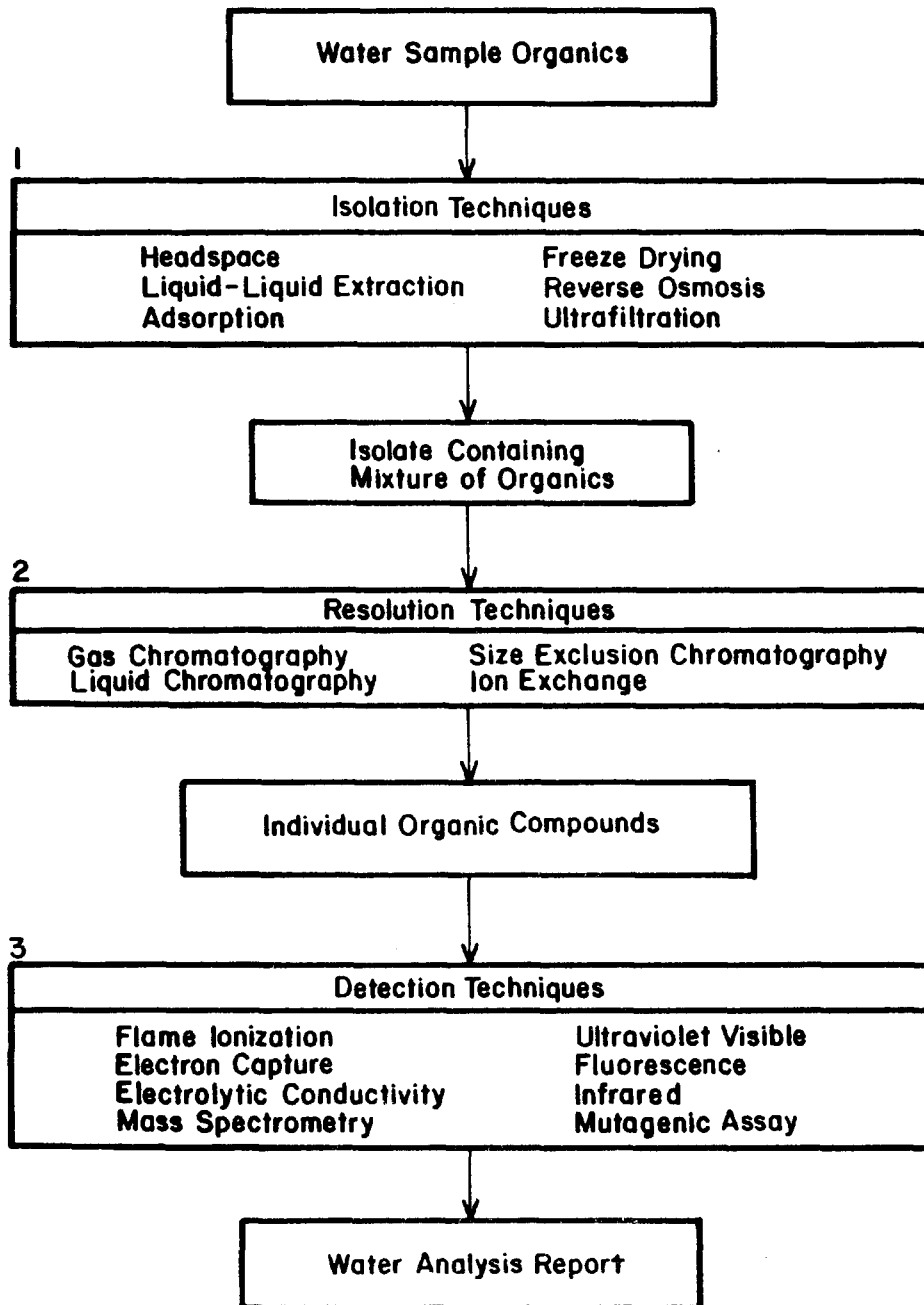


Figure 1. Steps in analyzing organics in water. (Source: R. R. Trussell and A. R. Trussell, "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies," JAWWA, Vol 72, No. 8 [August 1980]. Used with permission.)

Table 4. Schematic classification of organics found in water

Polarity	+				Volatility
	Volatile		Semivolatile		
Polar	Alcohols Ketones Carboxylic acids		Alcohols Ketones Carboxylic acids		Polyelectrolytes Carbohydrates Fulvic acids
Semipolar	Ethers Esters Aldehydes Heterocyclics		Ethers Esters Aldehydes		Proteins Carbohydrates Humic acids
Nonpolar	Aliphatic, aromatic hydrocarbons		Aliphatic, aromatic, alicyclic, arene, hydrocarbons		Lignin
Molecular weight	Low		Medium		High
		+	+	+	+

Table 5. Isolation of organic compounds found in water

Polarity	+				Volatility
	Volatile		Semivolatile		
Polar	None	Liquid-liquid extraction	Derivatization Adsorption Elution pH adjustment	Adsorption Elution	Vacuum distillation Freeze-drying
Semipolar	Headspace	Liquid-liquid extraction Dynamic headspace adsorption	Adsorption Elution		Reverse osmosis
Nonpolar	Headspace adsorption	Headspace	Liquid-liquid extraction		Adsorption Elution Ultrafiltration
Molecular weight	Low		Medium		High
		+	+	+	+

Table 6. Resolution of organic compounds from water:
chromatographic techniques

Polarity	+				Volatility
	Volatile	Semivolatile		Nonvolatile	
Polar	Gas-solid adsorption	Gas-liquid partitioning		Ion exchange	
Semipolar	Liquid-liquid partitioning	Liquid-solid adsorption		Size exclusion	
	Gas-solid partitioning	Gas-liquid partitioning		Filtration	
Nonpolar	Gas-solid adsorption			Size exclusion permeation	
	Gas-liquid partitioning			Liquid-liquid partitioning	
Molecular weight	Low		Medium	High	
	+	+	+	+	

Table 7. Typical detection techniques

Polarity	+				Volatility
	Volatile	Semivolatile		Nonvolatile	
Polar	Flame ionization			Mutagenicity assay	
	Electron capture			Ultraviolet-visible fluorescence	
Semipolar	Thermionic			Infrared	
	Electrolytic conductivity			Nuclear magnetic resonance	
Nonpolar	Microcoulometry			Photoconductivity	
	Mass spectrometry			Pyrolysis	
				Chemical cleavage	
				Oxidation	
Molecular weight	Low		Medium	High	
	+	+	+	+	

SECTION II. TREATMENT PROCESSES

1. Overview. The concentration of particulate and dissolved organic matter in raw water can be reduced by chemical treatment (chemical oxidation, improved coagulation or adsorption, adsorption onto materials such as activated carbon) or by physical treatment (air-stripping, ultrafiltration, or reverse osmosis). Table 8 summarizes these processes. The USEPA has identified methods (table 9) that represent the "best technology treatment techniques or other means generally available" to achieve compliance with the limit for THMs in drinking water--0.1 milligram per liter. These methods are aimed at preventing THM formation and are included in the discussion of chemical treatment processes.

2. Chemical Treatment Processes.

a. Oxidation/Disinfection. These treatment processes are used conventionally at water treatment plants and can be modified to remove some organic contaminants or control THM formation. Possible modifications include relocating the point of disinfection or using an alternative disinfectant and an alternative oxidant for chlorine. Several facilities have moved chlorination to a later step in the treatment process, such as before or after the filters, to reduce the contact time between chlorine and organics. Substituting permanganate, ozone, or chlorine dioxide for chlorine as oxidants improves raw organics removal in the coagulation and subsequent sedimentation and filtration unit processes. The resulting reduction in raw organics reduces the potential for halogenated byproduct formation when chlorine is later applied for final disinfection. A residual disinfectant can be added to the distribution system using chloramines or chlorine dioxide. Use of disinfectants other than conventional chlorine requires approval by The Army Surgeon General. Table 10 compares costs for three sizes of water treatment plants with conventional prechlorination and alternative pretreatment disinfectants.

(1) Potassium permanganate can be applied at the intake or rapid-mix chamber. Enough contact time must be allowed between the potassium permanganate application point and filtration for complete reduction of potassium permanganate to manganese dioxide. If the reaction is not completed, postfiltration deposition of manganese dioxide may result. Solid manganese dioxide produced from permanganate reduction has been shown to be an effective adsorbent of some organic molecules, thereby adding a removal mechanism.

(2) Ozone acts more quickly than chlorine, is effective against some viruses, and does not combine with organic acids to produce THMs. It must be produced onsite by discharging high voltage (5000 to 30,000 volts) between electrodes separated by air, requiring a high initial investment for the equipment. (Capital cost is about two-thirds greater than that for chloramines or chlorine dioxide treatment.) Also, this method cannot provide any residual disinfectant in the distribution system, so another disinfectant also would be required.

Table 8. Treatment processes for organics removal and suitable types and characteristics of compounds removed

Treatment/Separation Processes	Types/characteristics of compounds removed
<u>Chemical</u>	
Chemical coagulation	THM and THM precursors, high-molecular-weight synthetic organics
Oxidation	THM and THM precursors
Clarification	THM and THM precursors
Disinfectant practices	THM
Solvent extraction	Volatile and semivolatile, polar and nonpolar organics of low to medium molecular weight
<u>Adsorption</u>	
Granulated activated carbon (GAC)	THMs, THM precursors, taste- and odor-producing organics, chlorinated hydrocarbon solvents, low-polarity, low-solubility compounds
Powdered activated carbon (PAC)	High-molecular-weight compounds
Synthetic resins	Chlorinated hydrocarbon solvents, low or high molecular weight; depends on compound of interest
<u>Physical</u>	
Evaporation/volatilization	Low-molecular-weight, volatile organics
Distillation	High-molecular-weight, polar volatile organics
Air-stripping	Moderately volatile organics, some aromatics and pesticides, vinyl chloride, THMs, chlorinated benzene, halogenated organic compounds
Steam-stripping	Moderately volatile, medium-molecular-weight organics
Membrane processes (reverse osmosis, ultrafiltration)	Higher molecular weight organics, some priority pollutants

Table 9. USEPA-identified methods to achieve compliance with 0.1 mg/L MCL for THMs

-
- Use chloramines as an alternative or supplemental disinfectant or oxidant.*
 - Use chlorine dioxide as an alternative or supplemental disinfectant or oxidant.*
 - Improve existing clarification for trihalomethane precursor reduction.*
 - Move the point of chlorination to reduce trihalomethane formation and, when necessary, substitute preoxidant chloramines, chlorine dioxide, or potassium permanganate for chlorine.*
 - Use powdered activated carbon for trihalomethane precursor or trihalomethane reduction seasonably or intermittently at dosages not to exceed 10 mg/L on an average annual basis.*
 - Introduce offline water storage for trihalomethane precursor reduction.
 - Provide aeration for trihalomethane reduction when geographically or environmentally appropriate.
 - Introduce clarification where it is not currently practiced.
 - Consider alternative sources of raw water.
 - Use ozone as an alternative or supplemental disinfectant or oxidant.*

*Indicates method is discussed in this ETL. More detailed information about these methods may be found in the USA-CERL Technical Report Strategies for Controlling and Removing Trace Organic Compounds from Potable Water Supplies at Fixed Army Installations, N-85/11 (1985).

Table 10. Cost estimates for alternatives to prechlorination (cents/1000 gal)*

	1 MGD		5 MGD		10 MGD	
	A**	B	A	B	A	B
<u>Chlorination***</u>						
1 ppm dose	2.8	3.7	0.8	1.1	0.5	0.7
3 ppm dose	3.6	5.2	1.2	1.6	0.9	1.2
6 ppm dose	4.3	6.2	1.7	2.3	1.4	1.8
<u>Chloramination***</u>						
0.75 ppm chlorine dose	4.9	5.8	1.5	1.8	0.9	1.1
1.5 ppm chlorine dose	5.9	6.9	1.8	2.2	1.2	1.5
2.2 ppm chlorine dose	7.2	8.4	2.2	2.7	1.5	1.8
<u>Chlorine dioxide***,+</u>						
1 ppm dose	5.6	6.6	2.5	2.8	2.0	2.2
3 ppm dose	9.0	10.3	5.6	6.1	4.9	5.2
<u>Ozonation‡</u>						
(10-min contact time)						
1 ppm dose		6.9		3.5		2.3
3 ppm dose		10.4		5.5		4.0

*All costs shown include capital (when new facilities are indicated), operating and maintenance costs (assuming 70 percent plant capacity), 20-year amortization period, and 8 percent interest. ENR Construction Cost Index = 369.80 (January 1983) and Producer Price Index--Finished Goods = 283.6 (January 1983). Chlorine costs \$300/ton, ammonia costs \$200/ton. The chlorine-to-ammonia ratio is 3:1.

**Case A--Chlorination feed system exists. New feed system for chemicals in question. Case B--New chlorine and other chemical feed system.

***Based on Evaluation of Treatment Effectiveness for Reducing Trihalomethanes in Drinking Water, USEPA Contract 68-01-6292 (July 1983), pp 98-102.

+Sodium chlorite costs \$2000/ton. Contact time is 20 min.

‡Costs projected from 1980 costs given in USEPA publication R32, Treatment Techniques for Controlling Trihalomethanes in Drinking Water (MERL, September 1981).

(3) Chlorine dioxide is an oxidant and a disinfectant. However, it is not a desirable alternative for use at Army installations. The major concern with using chlorine dioxide in potable water treatment has been the formation of chlorite and chlorate, which are inorganic byproducts of reaction. Health effects related to these species are not well understood and, thus, the USEPA has limited the total residual concentrations of chlorine dioxide, chlorite, and chlorate to 0.5 milligrams per liter in potable waters. Chlorine dioxide does not appear to form THMs or other halogenated organics unless free chlorine is present in the chlorine dioxide source. For most water treatment applications, chlorine dioxide is generated under acidic conditions by the reaction of sodium chlorite with hypochlorous acid.

(4) With chloramination, chlorine and ammonia are added during water treatment and enough reaction time is allowed for chloramines to form. The pH and temperature as well as chlorine and ammonia concentrations influence the reaction. If pH is 4.4 or less, nitrogen trichloride, which is malodorous and a poor disinfectant, is formed. Ammonia can be added as ammonium sulfate (25 percent ammonia) with a dry chemical feed system, as anhydrous ammonia (refrigeration gas) fed in solution or diffused in gaseous form, or as aqua ammonia (food-grade) diffused in liquid form. The choice depends on how easily facilities at the treatment plant could be adapted to accommodate ammonia feed. The ammonia dosage is such that the ratio of chlorine to ammonia is 3:1 to 5:1, with a combined chlorine residual of 1 to 2 milligrams per liter required. Chloramines are not recommended for primary disinfection. They may be used to protect the distribution system, although even this may constitute a potential risk. The regulatory agencies should be consulted before using chloramination.

b. Coagulation. Careful control of coagulant type, dosage, and pH has been shown to improve organic acids removal during coagulation and sedimentation. Alum dosage, pH, and the type of organic acids present are the most important factors determining the efficiency of organics removal. Experimentation has shown that the order of chemical addition, and mixing speed and time have no influence when conventional coagulants are used. Jar tests or plant tests determine how to improve clarification for THM control. Table 11 provides suggestions for conducting these tests.

(1) In conducting jar tests, ultraviolet absorbance measurement before and after the test may be used to indicate the level of organics removed. To improve coagulation, once the optimal coagulant dosage is determined, a cationic polymer (approximately 2 milligrams per liter) or clay (approximately 10 milligrams per liter, plus a cationic polymer (0 to 5 milligrams per liter) could be jar-tested. Using a polymer as primary coagulant or as a coagulant aid may widen the pH range in which the coagulant will effectively remove both organics and turbidity. Increasing the lime dosage beyond stoichiometric levels and adding alum or iron to improve organics removal during softening could also be evaluated using jar tests, measuring ultraviolet absorbance before and after treatment. In conducting these tests, it should be remembered that the investigation is concerned with the dosage-response relationship for the organic and not for classical contaminants such as turbidity. Therefore, the best dosage combination for organics removal may not coincide

Table 11. Determining how to improve existing clarification to control THMs

Jar tests
Use ultraviolet absorbance as indicator of organics removal
Vary coagulant or lime dosage
Vary pH
Try cationic polymer or clay plus cationic polymer
If using lime, try adding alum or iron

Plant tests
Measure THM levels in raw and finished water for normal treatment and with modification

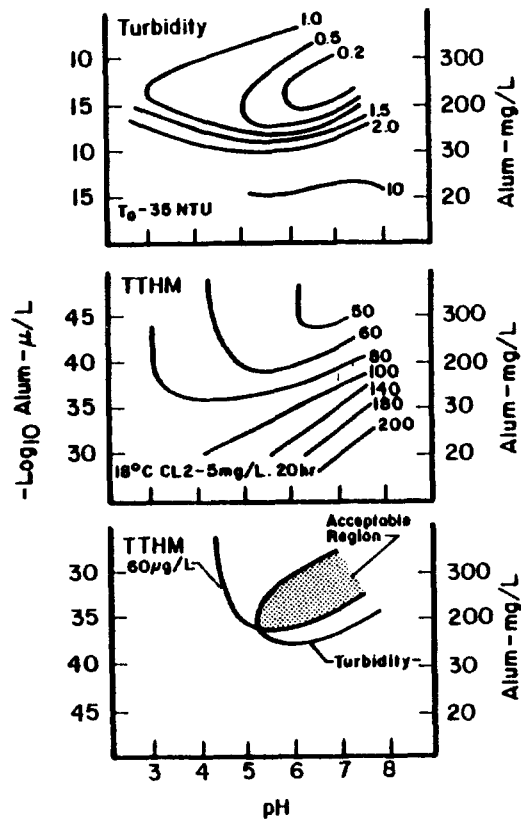


Figure 2. Determining optimal dosage and pH for organics and turbidity removal. (Source: R. R. Trussell and A. R. Trussell, "Evaluation and Treatment of Synthetic Organics in Drinking Water Supplies," JAWWA, Vol 72, No. 8 [August 1980]. Used with permission.)

with the best combination for turbidity or other classic indicators. Figure 2 shows how results of jar tests, using various dosages of alum at a range of pH levels, can be used. THM concentration and turbidity are each plotted on separate graphs for the various coagulant dosages and pH levels tested. The two plots are superimposed to determine the dosage and pH to control both.

(2) After the new coagulant and lime dosage, pH, and effectiveness of coagulant aids have been determined in the lab, these aids could be tested in the plant. For a complete evaluation, the raw and finished water should be sampled during existing operation and during the test. However, if the desired reduction of organic contaminant cannot be obtained in the laboratory, it is strong indication that a more vigorous unit process (e.g., activated carbon, air-stripping) will be required to meet the organic criteria.

(3) Table 12 compares costs for several dosages of alum and polymer needed in treating water to meet the THM regulation. Local costs may vary; still, jar or plant test results can be used similarly to estimate treatment costs based on the required dosage of alternative chemicals.

c. Activated Carbon. Upon contact with water that contains soluble organic materials, activated carbon removes these materials selectively by adsorption. Activated carbon's extremely large surface area per unit weight (approximately 1000 square meters per gram) makes it an efficient adsorptive material. Although many different GAC sizes have been used successfully, typical ranges are mesh sizes 8 X 30, 12 X 40, and 20 X 40. The 20 X 40 size means that the GAC will pass through the U.S. Standard Mesh Size No. 20 (0.03 inch) but be retained on a No. 40 size mesh (0.017 inch). The finer material has a higher rate of adsorption, but also a higher head loss per unit bed depth. Furthermore, since these beds have lower porosity, they have a greater tendency to foul by collecting colloidal materials from the water. Conversely, the 8 X 30 mesh has a lower adsorption rate, lower head loss per unit bed depth, and withstands regeneration with few losses. Both mesh sizes can perform well; the designer must select a size based on characteristics of the water to be treated. Since bed life and suspended solids load are of less concern for GAC applications in potable water treatment (compared with wastewater or industrial waste treatment), adsorption rate may be the consideration in the GAC size selection process. Powdered activated carbon (PAC) typically is smaller than 50 mesh. The adsorption rate for PAC systems is very high. PAC also has an advantage over GAC in that existing mixing, flocculation, and settling basins can be used, whereas GAC would require construction of contacting beds. Both are effective for removing THM precursors; however, unit processes that use PAC have not evolved to the point for which carbon recovery is as straightforward as for GAC systems. For this reason, the design parameters discussed in this ETL emphasize GAC applications.

(1) Adsorption Isotherm. The adsorption isotherm shows the relationship, at a given temperature, between the amount of a substance adsorbed and its concentration in the surrounding solution. Figure 3 shows a typical isotherm for removing a contaminant using four different carbon types. Carbon A is more efficient than carbon B because it adsorbs more compound per unit weight

Table 12. Estimated cost of increased alum and polymer dosages to meet THM maximum contaminant levels*

	<u>Increased dosage, mg/L</u>	<u>Cost, ¢/m³</u> <u>(¢/1000 gal)</u>
Alum**	10	0.16 (0.60)
	20	0.32 (1.20)
	30	0.45 (1.70)
	40	0.61 (2.30)
	50	0.77 (2.90)
Polymer***	0.2	0.11 (0.40)
	0.4	0.21 (0.80)
	0.6	0.34 (1.30)
	0.8	0.45 (1.70)
	1.0	0.55 (2.10)

*Cost includes only that for additional chemicals. No additional capital facilities or O&M requirements are included. Based on Evaluation of Treatment Effectiveness for Reducing Trihalomethanes in Drinking Water, USEPA Contract No. 68-01-6292 (July 1983), p 105.

**Assumed alum cost = \$140/ton.

***Assumed polymer cost = \$2.50/lb.

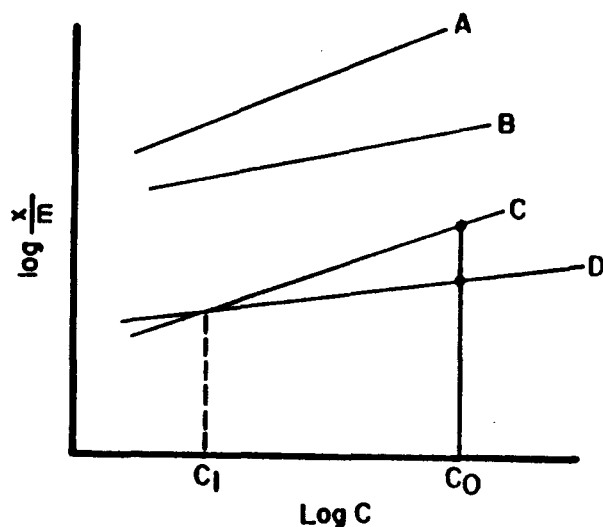


Figure 3. Adsorption isotherms for four carbons. (Source: L. D. Benefield, J. F. Judkins, and B. L. Weand, Process Chemistry for Water and Wastewater Treatment [Prentice-Hall, 1982]. Used with permission.)

of carbon. A carbon with a steeper isotherm usually is preferable to one with a flat isotherm because the adsorptive capacity is higher at higher equilibrium concentrations. Comparing curves C and D, carbon C is preferable if the system will be operated at an equilibrium organic concentration (in the treated water) above C_1 . The slope of the isotherm is used to interpret the removal effectiveness of that carbon for the contaminant measured at that temperature. Figure 4 shows GAC isotherms for several organic compounds, most of which have proposed drinking water standards. The USEPA Treatability Manual contains isotherms for several organic compounds. The potential for removal of both gross organics and specific organic species can be determined from an isotherm test. This procedure will indicate the carbon's approximate capacity and provide a preliminary estimate of the carbon dosage required. An approximation of the amount of carbon consumed per day would be equal to the amount of contaminant to be removed per day, divided by the carbon's adsorptive capacity. For carbon beds, isotherm tests help determine flow rate and bed depth. Isotherm tests also are a convenient way to evaluate the effects of pH and temperature on adsorption. Figure 5 shows a design example using an adsorption isotherm. It should be noted that this isotherm is unique to a particular carbon, water to be treated, temperature, and pH.

(2) Iodine and Molasses Numbers. The iodine and molasses numbers also may give an indication of a carbon's adsorptive capacity. The iodine number represents the milligrams of iodine adsorbed from a 0.02-normal solution at equilibrium under specified conditions. The molasses number is an index of the carbon's adsorptive capacity for color bodies in a standard molasses solution compared to a standard carbon. The iodine number reflects the carbon's efficiency at adsorbing small molecules whereas the molasses number predicts the carbon's affinity for large, organic molecules.

(3) Breakthrough Curve. The breakthrough curve shows the contaminant concentration in the contact bed effluent plotted against the volume of water treated, as figure 6 shows. The breakthrough point is reached when the effluent concentration exceeds a certain level (C_B). The GAC column or bed is exhausted when the effluent contaminant concentration equals or exceeds 95 percent of the influent concentration (C_E).

(4) Design and Operating Parameters. Table 13 shows ranges of design and operating parameters for GAC contactors. This equipment can be built in the form of concrete gravity filters or as steel contactors (figure 7). An existing sand filter can be capped with GAC, but the bed may not be deep enough to allow a contact time adequate for effective removal. Upflow countercurrent columns, in which fresh carbon is added to the top of the column and spent (exhausted) carbon is removed from the bottom, can also be considered. This type system makes more efficient use of the carbon's adsorptive capacity, since all carbon in the system can be completely exhausted before replacement or regeneration. Pilot-scale investigations should be performed to define the most cost-effective flow and bed depth to meet the organic species removal criteria. These variables will be related to (1) the rate of organic species adsorbance, (2) environmental conditions such as pH and temperature, and (3) the presence of other contaminants that may compete for adsorption sites on the carbon. Typical column configurations for pilot testing use flow rates of

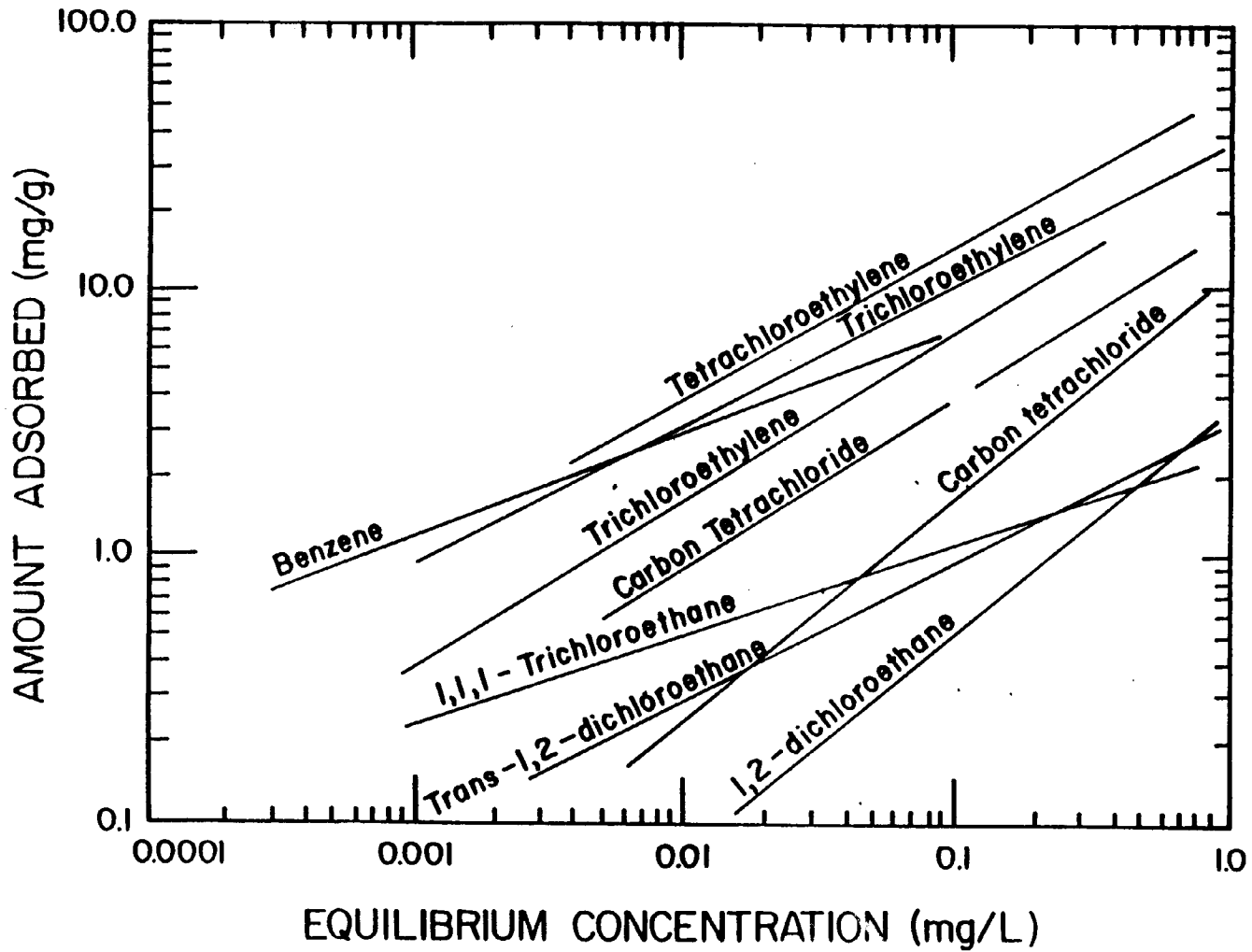


Figure 4. Adsorption isotherms for organic contaminants. (Source: V. Snoeyink, "Control Strategy-Adsorption Techniques," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

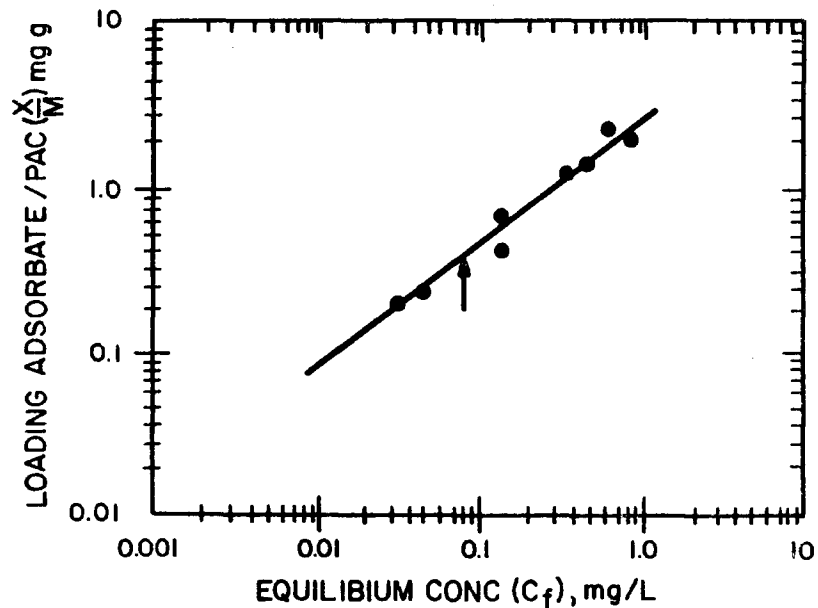


Figure 5. Example adsorption isotherm for determining PAC dosage for chloroform removal from a water using Filtersorb 300. (Source: J.M. Symons, et al., Treatment Techniques for Controlling Trihalomethanes in Drinking Water [USEPA, 1981].) To calculate the PAC dosage for reducing a chloroform concentration from 150 $\mu\text{g/L}$ to 75 $\mu\text{g/L}$, enter the isotherm using the equilibrium concentration of 0.075 mg/L. From the isotherm, $X/M = 0.38$ mg chloroform adsorbed per gram PAC. The required PAC dosage is:

$$\frac{0.075 \text{ mg/L}}{0.38 \text{ mg adsorbed/g PAC}}$$

= 0.197 g/L or 197 mg/L. If the inherent concentration were 200 $\mu\text{g/L}$, the PAC dosage would be:

$$\frac{0.200 - 0.075 \text{ mg/L}}{0.38 \text{ mg/g}}$$

= 0.328 g/L or 328 mg/L.

Table 13. Design and operating considerations for GAC plants

Adsorption isotherm (slope of line)	}	Depend on characteristics of coal and raw water
Shape of breakthrough curve		
Time of exhaustion		
Bed depth (ranges from 2 to 14 ft)		
Empty bed contact time (EBCT) = GAC bed volume/flow (typically 10 min, ranges 9 to 60 min)		
Carbon usage rate (mg/L or lb/1000 gal) = mass of carbon used/volume of water treated at breakthrough point		
Loading rate (bed volumes) = total water volume treated at breakthrough point/GAC bed volume (14,000 to 55,000 bed volumes)		
Linear velocity = flow/bed area (ranges less than 1 to 1.6 ft/min or 2 to 10 gpm/sq ft)		
Backwashing frequency (once per week or less)		
Carbon regeneration--frequency and cost		
Location in treatment plant (after softening, turbidity removal, and filtration; in series or parallel)		

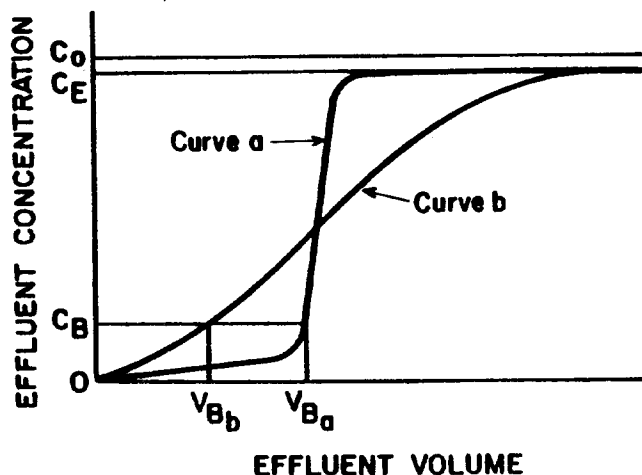
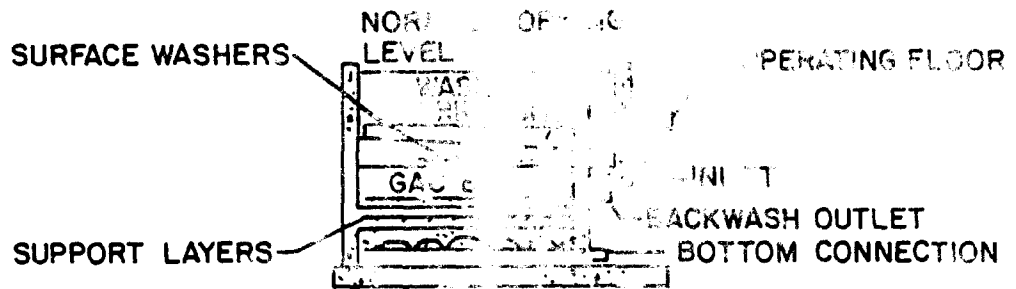
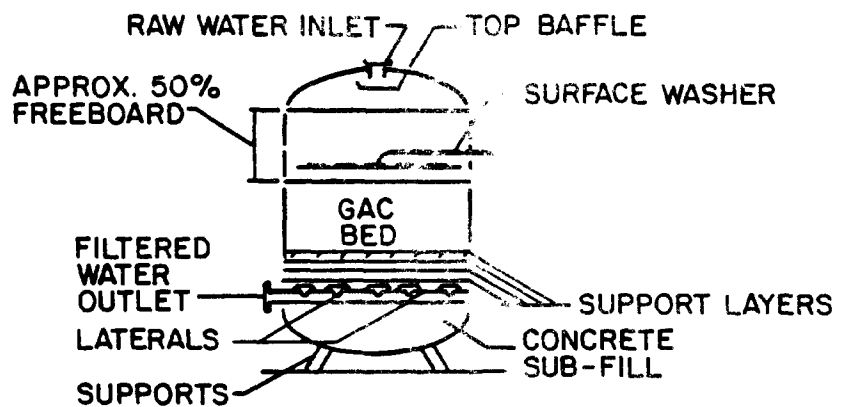


Figure 6. Breakthrough curves. (Source: L. D. Benefield, J. F. Judkins, and B. L. Weand, Process Chemistry for Water and Wastewater Treatment [Prentice-Hall, 1982]. Used with permission.)



GRAVITY CONTACTOR



PRESSURE CONTACTOR

Figure 7. Carbon contactors. (Source: V. Snoeyink, "Control Strategy-- Adsorption Techniques," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

2 to 10 gallons per minute per square foot and carbon bed depths of 10 to 30 feet. Pilot-plant investigations can use column diameters as small as 6 inches without significant error due to wall effects. It is important to perform pilot tests using the water to be treated.

(5) Annual costs for the contactor, carbon, and regeneration process (transportation, storage, and regeneration) can be calculated separately using EPA cost equations. Capital cost for the contactors is figured on a square-foot, volume-per-individual contactor basis, assuming the unit is completely housed. The equations exclude equipment for surface washing and backwashing, the initial carbon charge, and any required carbon-handling facilities outside the pipe gallery or building. If one option is chosen--converting an existing sand filter to a GAC contactor--carbon handling ducts would have to be installed, so a separate equation is included. Table 14 shows design assumptions used in deriving the equations and table 15 shows the actual equations. Other necessary equations are for initial carbon supply and replacement of carbon lost after regeneration:

$$\text{Carbon supply, \$/yr} = (\text{lb GAC})(\text{Cost, \$/lb})(\text{Annual capital recovery factor}) \quad (\text{eq 1})$$

$$\text{Carbon replacement, \$/yr} = (\text{lb GAC replaced})(\text{Cost, \$/lb})(\text{No. replacements/yr}). \quad (\text{eq 2})$$

If a plant uses less than 2000 pounds of carbon per day, it would be more economical to either replace the carbon or regenerate it offsite at a regional multihearth facility. Replacement costs can be estimated using equation 2; estimates for regional multihearth regeneration require two equations: one for transportation and storage and one for regional multihearth regeneration. The area given in the size range column for transportation, storage, and regeneration is in square feet of hearth area. The number of pounds per day of carbon to be regenerated should be divided by the factor 70 pounds per day square foot of hearth area to find the hearth area to use in the equation.

(6) Other GAC costs have been estimated. Table 16 shows capital and operating costs for TCE removal, for three size categories of population, from 500 to 50 micrograms per liter and from 500 to 5 micrograms per liter. Figure 8 compares GAC treatment costs with aeration costs for removing different chlorinated hydrocarbons.

(7) Although PAC technology is less advanced than that for GAC, PAC has been used in water treatment plants to remove organic materials causing taste and odor problems; however, it has not yet been used widely to control THM or to remove other synthetic organics. PAC can be added at several points in the treatment plant to maximize its effectiveness in taste and odor control. Adsorption isotherms should be developed using water from the location at which PAC will be added. New technologies using PAC may make this material more popular for organics removal in the future. Table 17 shows EPA cost estimates of using PAC treatment for four plant sizes.

Table 14. Assumptions for GAC cost equations

<u>Design parameters for postfilter adsorption</u>					
Parameter	Value				
Activated carbon cost	\$0.65/lb (\$1.43/kg)				
Activated carbon loss per reactivation cycle	7%				
Natural gas cost	\$0.0013/scf (\$3.679 x 10 ⁻³ /SM ³)				
Electric power cost	\$0.04/kWh				
Construction cost index	325.0				
Producers price index	243.8				
Direct hourly wage rate	\$11/hr				
Amortization rate	8%				
Amortization period	20 yr				
Loss in adsorptive capacity	0%				
Design capacity	70%				
Empty bed contact time	18 min				
Reactivation frequency	Every 2.4 months				

<u>Assumptions for separate postfiltration systems</u>					
Item	Design capacity, MGD (m ³ /day)				
	1 (4,000)	5 (20,000)	10 (40,000)	100 (400,000)	150 (600,000)
Number of contactors	3	6	12	40	60
Diameter of contactors, in ft (m)	8 (2.4)	12 (3.7)	12 (3.7)	20 (6.1)	20 (6.1)
Depth of contactors, in ft (m)	13 (4.0)	13 (4.0)	13 (4.0)	14 (4.3)	14 (4.3)
Volume of GAC per contactor, in cu ft (m ³)	653.1 (18.5)	1,469.5 (41.6)	1,469.5 (41.6)	4,396.0 (124.4)	4,396.0 (124.4)
Minimum empty bed contact time, in min	18	18	18	18	18

Table 15. GAC capital and O&M operating costs*

Unit	Size range**	Capital costs	Operating costs
Concrete gravity contactor	350-10,600 cu ft (140-28,000 sq ft)	470 USRT ^{0.38} CCI NO	100 USRT ^{0.76} PR ^{.28} PPI ^{0.15} DHR ^{0.48}
Steel gravity contactor	6280-14,100 cu ft (41400-62800 sq ft)	5.6 USRT ^{0.85} CCI NO	6.2 USRT ^{0.9} PR ^{0.4} PPI ^{0.11} DHR ^{0.39}
Pressure carbon contactor	390-2260 cu ft (340-2200 sq ft)	370 USRT ^{0.38} CCI NO	200 USRT ^{0.78} PR ^{0.32} PPI ^{0.2} DHR ^{0.33}
Convert existing filter	370-70,000 sq ft	6.5 USRT ^{0.91} CCI NO	(None)
Regional GAC transporation & storage	1000-20,000 sq ft 30,000-3,000,000 lb/yr	0.88 USRT CCI	0.00018 USRT PPI ^{0.2} DHR ^{0.63}
Regional multihearth regeneration***	27-1510 sq ft	60 USRT ^{0.44} CCI NO	

*Source: R. M. Clark, "Optimizing GAC Systems," Journal of Environmental Engineering Division, ASCE, Vol 109, No. 1 (1983). Used with permission.

**Capital cost USRT is given first, O&M USRT is in parentheses. USRT = use rate, CCI = construction cost index/100, NO = number of units, PR = power cost, \$/kWh, PPI = producer price index/100, DHR = direct hourly wage rate, \$/hr.

***Multiply this cost by percent usage of the facility by your water plant.

Table 16. Preliminary GAC costs for controlling TCE in drinking water (1981 dollars x 1000)*

	Removal of 500 $\mu\text{g/L}$ to 50		
	System size category		
	100-499	1000-2499	10,000-24,999
Population served	100-499	1000-2499	10,000-24,999
Capital expenditures	82.00	344.00	741.00
Cost per 1000 gal	1.53	0.79	0.22

	Removal of 500 $\mu\text{g/L}$ to 5		
	System size category		
	100-499	1000-2499	10,000-24,999
Population served	100-499	1000-2499	10,000-24,999
Capital expenditures	82.00	344.00	741.00
Cost per 1000 gal	1.58	0.82	0.25

*Source: V. Snoeyink, "Control Strategy--Adsorption Techniques," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water (AWWA Research Foundation, 1983). Used with permission.

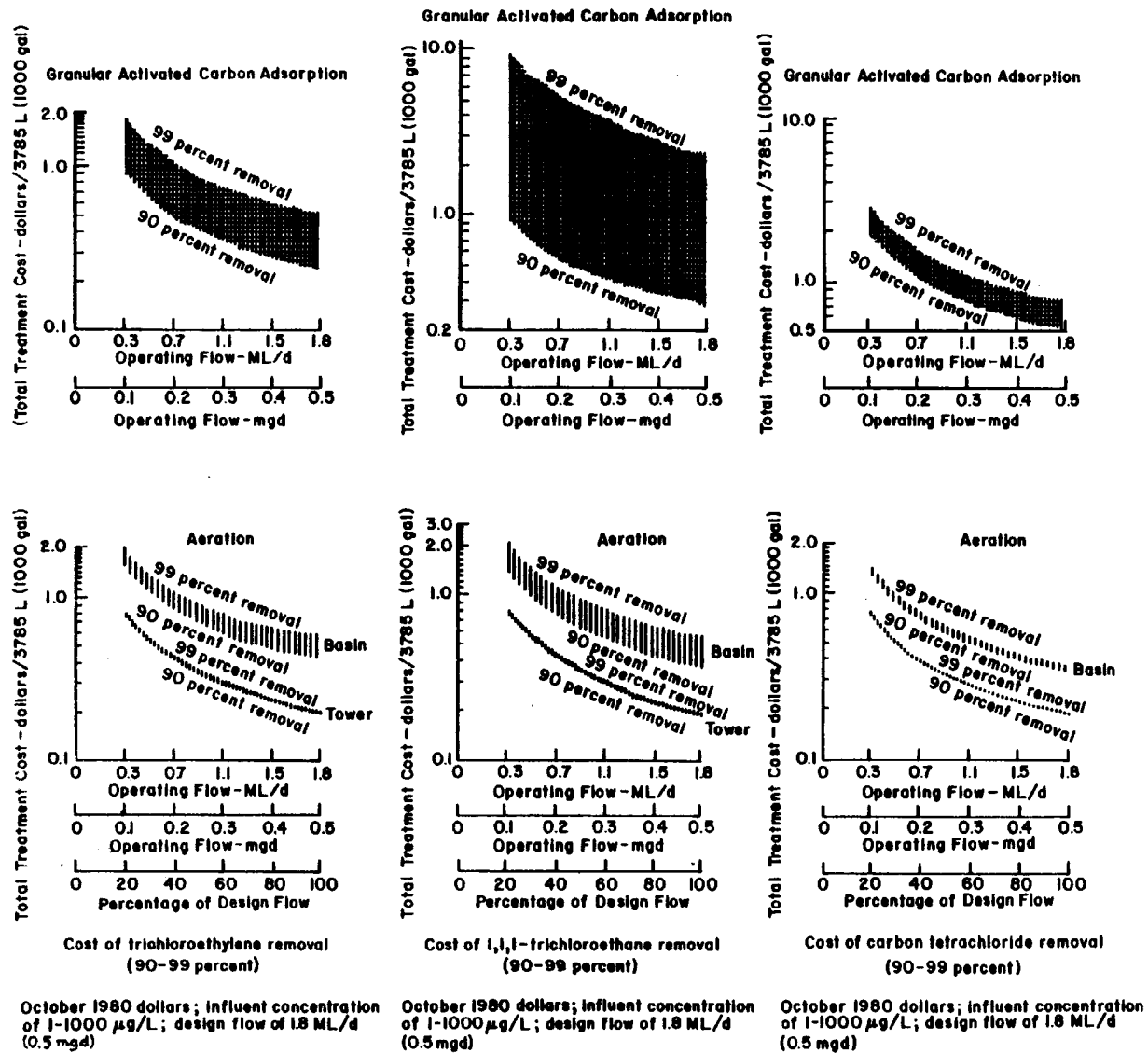


Figure 8. Cost curves for three chlorinated hydrocarbons. (Source: O. T. Love and R. G. Eilers, "Treatment of Drinking Water Containing TCE and Related Industrial Solvents," *JAWWA*, Vol 74, No. 8 [August 1982]. Used with permission.)

Table 17. Cost of treating with powdered activated carbon*

Plant design capacity, m ³ /sec	Powdered activated carbon feed capacity, mg/L**		
	5	15	30
0.438 (1)	2.64 (10.0)	3.09 (11.70)	3.19 (12.10)
0.219 (5)	0.85 (3.20)	1.24 (4.70)	1.29 (4.90)
0.438 (10)	0.61 (2.30)	1.30 (3.90)	1.06 (4.00)
0.657 (15)	0.55 (2.10)	0.95 (3.60)	0.98 (3.70)

*Source: Culp/Wesner/Culp, Evaluation of Treatment Techniques for Reducing Trihalomethanes in Drinking Water, EPA Contract No. 68-01-6292 (July 1983).

**Average annual dosage is 5 mg/L for the 5-mg/L feed capacity, and is 10 mg/L for the 15- and 30-mg/L feed capacities. This is necessary because regulations restrict average annual dosage to an upper limit of 10 mg/L.

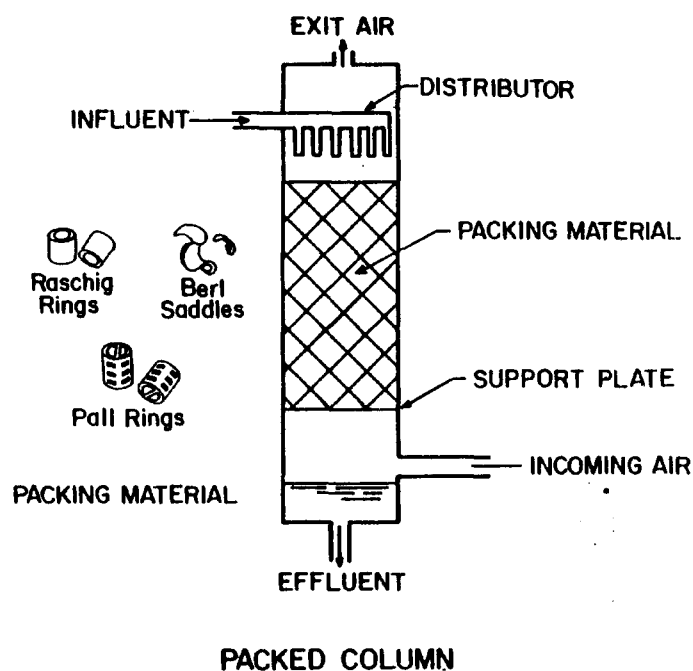


Figure 9. Packed tower aeration unit. (Source: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983. Used with permission.]

d. Ion Exchange Resins. Removal of organic compounds using synthetic resins is an evolving technology with no commercial applications for water treatment as of August 1985. Laboratory tests have shown that resins are not useful as a general organic adsorbent for potable water treatment because they are more selective than activated carbon and thus do not adsorb the broad range of organic species typically desired in treatment systems. In some situations, resins could be superior to activated carbon when a single organic species is of concern; however, in these instances, the information required on the specific resin-organic interactions would necessitate pilot-plant investigations. If a specific organic compound must be removed from the water supply, synthetic ion exchange resin vendors should be contacted to determine if an appropriate resin is available.

3. Physical Treatment Processes.

a. Air-Stripping. Air-stripping is a mass-transfer operation that can reduce the concentration of medium to highly volatile, low- to medium-molecular-weight organics and dissolved gases. Organics and dissolved gases are transferred from liquid to gaseous phase because of the concentration difference in each phase. Compounds that can be removed by air-stripping include THMs, chlorinated benzenes, many simple halogenated organic compounds, some aromatic hydrocarbons, some pesticides, and compounds that are poorly removed by activated carbon adsorption. Thus, air-stripping is a highly complementary process to activated carbon adsorption for waters containing high concentrations of a wide range of organic species.

(1) Aeration Devices. In packed towers (figure 9), water is distributed evenly across the top packing surface and allowed to trickle down around the packing. Air (either by natural draft or blowers) is forced up through the packing material to create a countercurrent flow. The large surface area provided by the packing prolongs contact between the air and water. Diffused aerators (figure 10) and tray aerators (figure 11) also have been used.

(2) Henry's Constant. The amount of compound that can exist in liquid and gaseous phases under given conditions is determined by Henry's constant. Table 18 lists Henry's constants for several compounds; organics with a higher constant are easier to remove. These constants are affected by temperature, increasing by a factor of three for every 10°C rise in temperature.

(3) Desired Removal. The amount of compound to be removed has a bearing on the type of aeration unit to use. Figure 12 shows, for a range of Henry's Constants, the aeration unit that could be expected to achieve various degrees of removal. In general, for 90 percent removal or less, spray towers or diffused aeration units are more economical than other types. If more than 90 percent removal is needed, a packed tower usually will be necessary.

(4) Air-to-Water. A high air-to-water ratio is sometimes needed to achieve the necessary degree of removal. With a 15-foot column filled with 1-inch size packing, 95 percent of TCE can be removed using an air-to-water ratio of 20:1; to remove the same amount of another compound, for example, dichloroethane, an air-to-water ratio of 120:1 is needed.

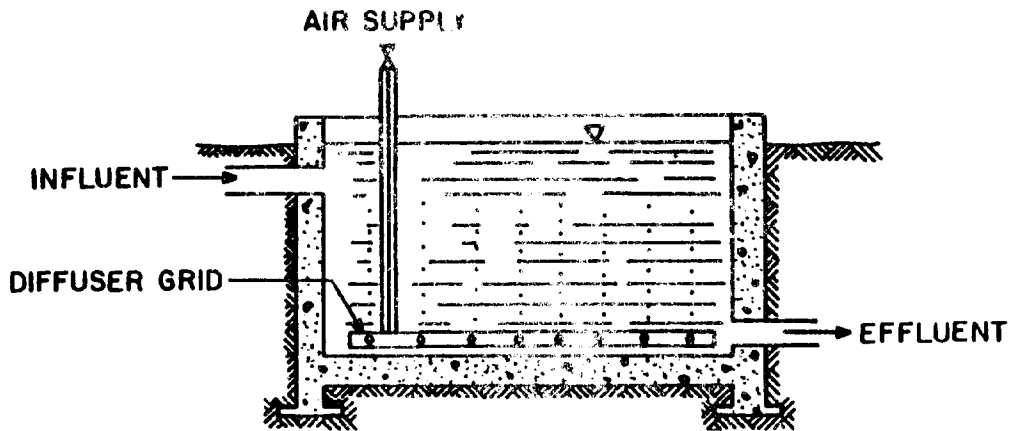


Figure 10. Diffused air basin. (Source: A.F. Hess, J.E. Dyksen, and H.J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

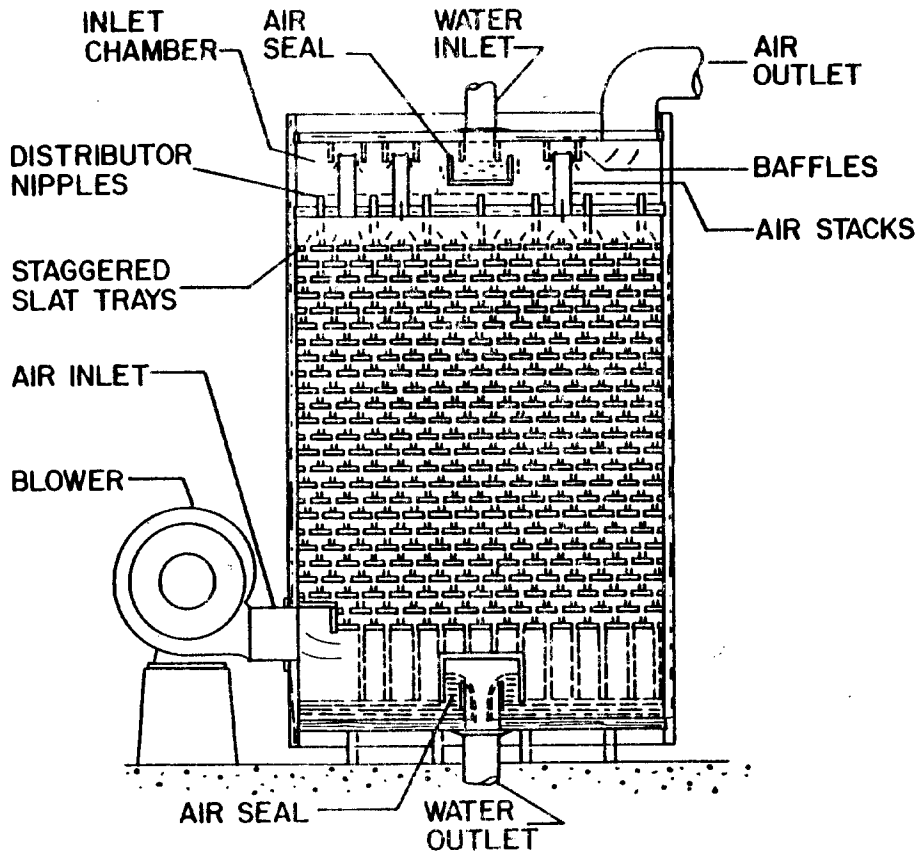


Figure 11. Slat tray aerator. (Source: A.F. Hess, J.E. Dyksen, and H.J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

Table 18. Henry's Law constants for selected compounds*

<u>Compound</u>	<u>Formula</u>	<u>Henry's Constant (atm)**</u>
Vinyl chloride	CH_2CHCl	3.55×10^5
Oxygen	O_2	4.3×10^4
Nitrogen	N_2	8.6×10^4
Methane	CH_4	3.8×10^4
Ozone	O_3	3.9×10^3
Toxaphene***	$\text{C}_{10}\text{H}_{10}\text{Cl}_8^+$	3.5×10^3
Carbon dioxide	CO_2	1.51×10^3
Carbon tetrachloride***	CCl_4	1.29×10^3
Tetrachloroethylene***	C_2Cl_4	1.1×10^3
Trichloroethylene***	CHClCCl_2	5.5×10^2
Hydrogen sulfide	H_2S	5.15×10^2
Chloromethane***	CH_3Cl	4.8×10^2
1,1,1-Trichloroethane***	CCH_3Cl_3	4.0×10^2
1,2,4-Trimethylbenzene***	$\text{C}_6\text{H}_3(\text{CH}_3)_3$	3.53×10^2 (25°C)
Toluene***	$\text{C}_6\text{H}_5\text{CH}_3$	3.4×10^2 (25°C)
Benzene***	C_6H_6	2.4×10^2
1,4-Dichlorobenzene***	$\text{C}_6\text{H}_4\text{Cl}_2$	1.9×10^2
Chloroform***	CHCl_3	1.7×10^2
Bromodichloromethane	CHCl_2Br	1.18×10^2 (EPA, 1980)
1,2-Dichloroethane***	$\text{CH}_2\text{ClCH}_2\text{Cl}$	61
Dibromochloromethane	CHClBr_2	47 (EPA, 1981)
1,1,2-Trichloroethane***	$\text{CHCl}_2\text{CH}_2\text{Cl}$	43
Sulfur dioxide	SO_2	38
Bromoform***	CHBr_3	35
Ammonia	NH_3	0.76
Pentachlorophenol***	$\text{C}_6(\text{OH})\text{Cl}_5$	0.12
Dieldrin***	$\text{C}_{12}\text{H}_{10}\text{OCl}_6$	0.0094

*Source: M. C. Kavanagh and R. R. Trussell, JAWWA, Vol 72, No. 12 (1980).

Used with permission. Bold face indicates compounds discussed in this ETL.

**Temperature 20°C except where noted otherwise.

***Computed from water solubility data and partial pressure of pure liquid at specified temperature.

+Synthetic; approximate chemical formula.

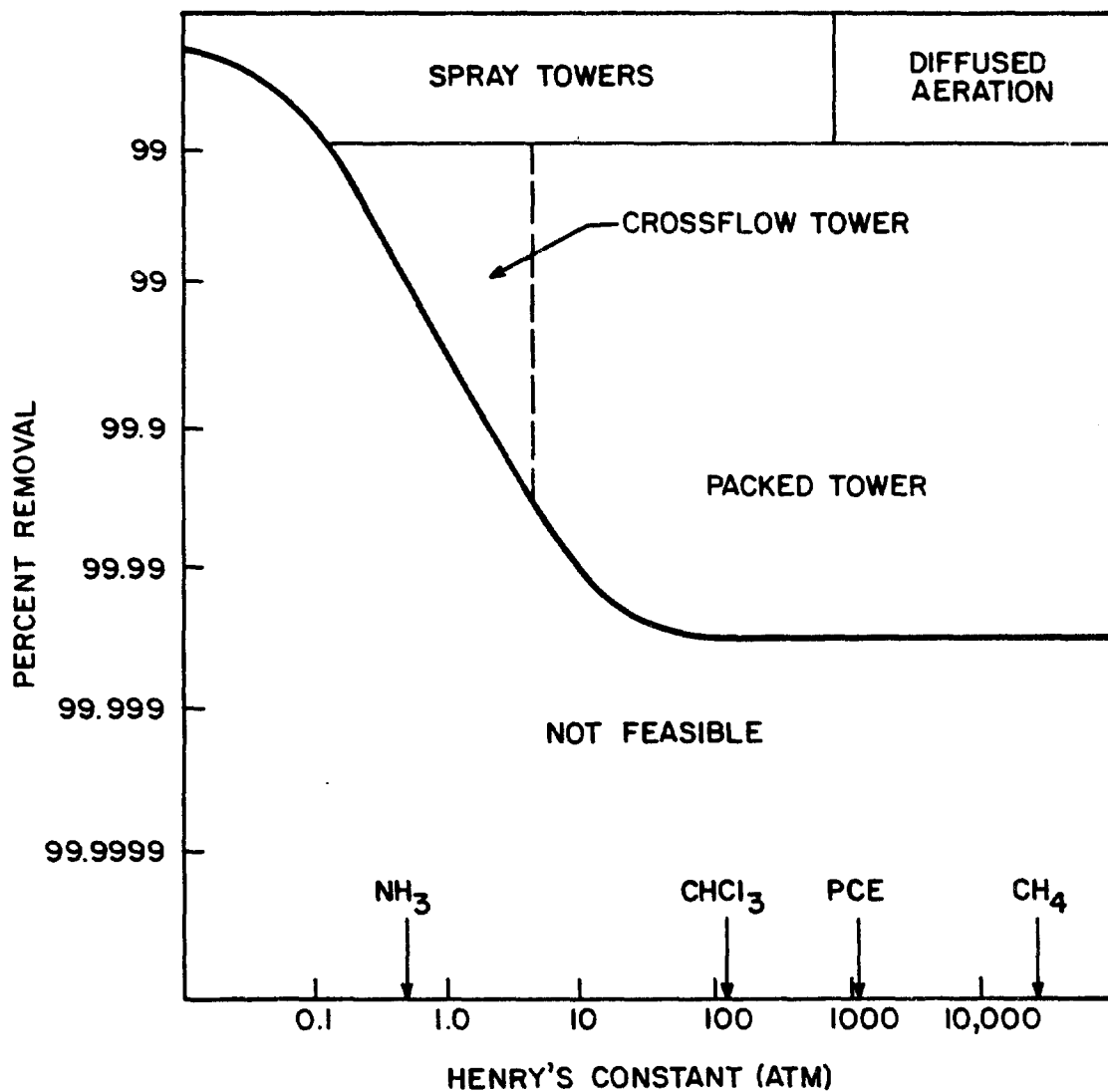


Figure 12. Removal efficiencies of various aeration devices. (Source: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

(5) Column Depth. This influences removal efficiency as well as capital cost. In pilot studies, the column depth can be varied while the air-to-water ratio is held constant. For example, with a 20:1 air-to-water ratio, 80 percent of TCE can be removed using a 6-foot column, whereas 99 percent removal requires a 20-foot column. Figure 13 shows the relationship between packed column depth and air-to-water ratio typically needed to remove 95 percent of three different organic compounds.

(6) Available Surface Area. For a packed tower aeration unit, this is a major consideration in designing the packing material's configuration. In a packed column unit, the packing diameter should be about one-fifteenth of the column diameter.

(7) Temperature. Temperature affects the Henry's Law constant, which in turn determines how much compound will exist in liquid or gaseous phase.

(8) Relative Costs. In many cost studies on aeration units, TCE removal usually is considered representative of average removal costs. Relative costs to remove the same amount of other organic compounds by aeration are ranked below in order of increasing removal costs:

- Vinyl chloride
- PCE
- TCE
- Carbon tetrachloride
- 1,1,1-Trichloroethane
- 1,2-Dichloroethane.

(9) Cost Equations. USEPA has formulated equations that can be used to calculate yearly capital and operating and maintenance (O&M) costs for aeration units (table 19). These air-stripping cost equations consider both diffused aeration basins and aeration towers. Design constraints for diffused aeration basins include a rectangular basin with a length-to-width ratio of 4:1, basin depth of 12 feet, maximum individual basin size of 3800 cubic feet, air supply system sized for a minimum of 5 standard square feet per minute per square foot of basin floor area, minimum air-to-water ratio of 10:1, and continuous operation. For aeration tower design, constraints include a rectangular tower with 16 feet of polyvinyl chloride medium, overall tower height of 22 feet, and continuous operation. The costs are annual, so capital and O&M costs can be added to obtain total treatment costs. The equations include factors for annualizing the capital costs over 20 years at 8 percent interest.

b. Ultrafiltration and Reverse Osmosis (RO).

(1) Ultrafiltration. Ultrafiltration membranes usually filter only substances with molecular weights ranging from 500 to 1 million. The major application is in removing colloidal material and large, organic molecules from solution. THMs and most priority pollutants have molecular weights below 500, so ultrafiltration is not a promising option for removing these regulated contaminants. Capital and operating costs for ultrafiltration units vary

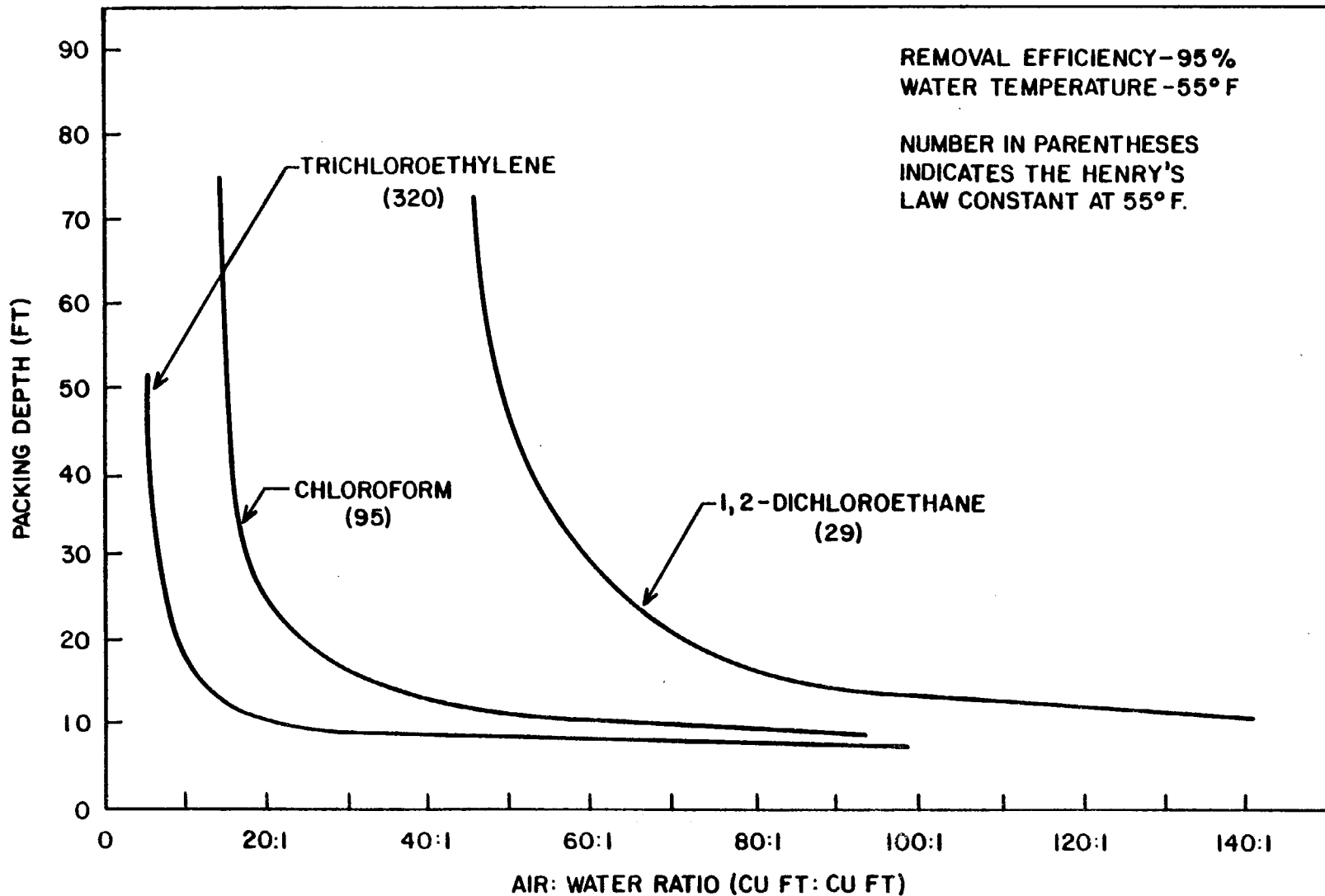


Figure 13. Packing depth versus air-to-water ratio. (Source: A. F. Hess, J. E. Dyksen, and H. J. Dunn, "Control Strategy--Aeration Treatment Technique," Occurrence and Removal of Volatile Organic Chemicals from Drinking Water [AWWA Research Foundation, 1983]. Used with permission.)

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Table 19. Capital and O&M cost equations--aeration units*

	<u>Diffused aeration</u>	<u>Aeration tower</u>
Capital cost		
size range (cu ft)	1900 to 380,000	640 to 256,000
Equation	$15.48 \text{ USRT}^{0.774} \text{ CCI}^{0.993}$	$11.59 \text{ USRT}^{0.7199} \text{ CCI}^{0.9965}$
O&M cost		
size range (cu ft)	1900 to 10,000	680 to 6400
Equation	$472.32 \text{ USRT}^{0.684} \text{ PR}^{0.553}$ $\text{PPI}^{0.0726} \text{ DHR}^{0.298}$	$31.36 \text{ USRT}^{0.625} \text{ PR}^{0.373}$ $\text{PPI}^{0.268} \text{ DHR}^{0.205}$
Size range (cu ft)	10,000 to 380,000	6400 to 256,000
Equation	$112.08 \text{ USRT}^{0.9247} \text{ PR}^{0.720}$ $\text{DHR}^{0.205}$	$6.54 \text{ USRT}^{0.946} \text{ PR}^{0.654}$ $\text{PPI}^{0.176} \text{ DHR}^{0.092}$

*USRT = size of unit--cu ft, CCI = construction cost index/100, PR = power cost--\$/kWh, PPI = producer price index/100, DHR = hourly wage rate--\$/hr.

widely, depending on the application. Capital costs may be as low as \$0.50 per gallon per day of installed capacity (whereas for industrial applications it may be over \$5 per gallon per day) and operating costs are about \$0.22 per 1000 gallons.

(2) Reverse Osmosis. In RO, organic contaminants are separated by adsorption onto the membrane's surface as well as the sieving action through the membrane pores. The polarity of the organic compound and the membrane's porous structure and chemical nature determine how effectively the organics are separated. The molecular weight of the compound should be above 120. Thin film composite and aramid membranes reject organic compounds better than cellulose acetate membranes. Other factors are operating pressure, temperature, and flow conditions. There have been very few applications for organics removal, so cost equations specifically for this purpose are not available.

SECTION III. APPROACH FOR CONTAMINANT CONTROL OR REMOVAL

1. Overview.

A strategy to determine the most cost-effective trace organics treatment or removal processes is summarized below. These steps apply to water supplies with organic contaminants other than THMs.

2. Magnitude and Extent of Contamination.

a. Determine the Source of Contamination. Find out what has caused the contamination (for example, groundwater contamination from landfill, agricultural practices). Site plans, topographic maps, aerial photos and knowledge of the underlying geology are all useful tools. Talking to persons familiar with previous activities (e.g., industry, dumping) in the area will help determine the source of contamination as well as the type of organic compounds that may be present.

b. Sample Several Wells. Sampling should be done by personnel familiar with techniques for groundwater testing and analysis should be done by a US-EPA certified laboratory. Assistance in sampling and analysis techniques can be obtained from the U.S. Army Environmental Hygiene Agency, USA-CERL, or the USEPA. One well in an area may only have one or two contaminants whereas another well in the same area may contain several compounds. The quality of surface water supplies, especially rivers, tends to vary more; it may be that contamination was temporary and no contaminants will be found in the raw water upon further sampling.

3. Determine the Type of Contaminants. Based on water analysis, determine the type(s) of organic compounds present. Are the compounds listed in table 1, 2, or 3? Are the compounds known or suspected to be carcinogenic? Are there several types--for example, some volatile and some nonvolatile? If so, more than one type of treatment may be necessary to remove all the contaminants. Other key items are the concentrations and total flow to be treated.

If a light flow from a single well is involved, perhaps that well could be closed. The concentration of the contaminant will determine what percent removal is necessary (e.g., only a small percentage or over 90 percent removal).

4. Evaluate Treatment Processes. Determine feasible treatment processes for controlling or removing the organics. Consider more than one treatment type if different varieties of compounds are present (e.g., aeration and GAC in series, or ozonation coupled with activated carbon treatment).

5. Estimate Costs. Estimate costs using the equations in tables 10, 12, 15, 17, or 19 to help determine the best alternative treatment(s).

6. Conduct Bench or Pilot-Scale Tests. When seeking to improve coagulation/flocculation, jar tests are appropriate; to evaluate GAC, use bench-scale tests; and for aeration units, conduct pilot tests.

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