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Regulations and Standards
Criteria and Standards Division
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Ambient Water Quality Criteria for Haloethers

AMBIENT WATER QUALITY CRITERIA FOR

HALOETHERS

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U.S. ENVIRONMENTAL PROTECTION AGENCY

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FOREWORD

Section 304 (a)(1) of the Clean Water Act of 1977 (P.L. 95-217), requires the Administrator of the Environmental Protection Agency to publish criteria for water quality accurately reflecting the latest scientific knowledge on the kind and extent of all identifiable effects on health and welfare which may be expected from the presence of pollutants in any body of water, including ground water. Proposed water quality criteria for the 65 toxic pollutants listed under section 307 (a)(1) of the Clean Water Act were developed and a notice of their availability was published for public comment on March 15, 1979 (44 FR 15926), July 25, 1979 (44 FR 43660), and October 1, 1979 (44 FR 56628). This document is a revision of those proposed criteria based upon a consideration of comments received from other Federal Agencies, State agencies, special interest groups, and individual scientists. The criteria contained in this document replace any previously published EPA criteria for the 65 pollutants. This criterion document is also published in satisifaction of paragraph 11 of the Settlement Agreement in Natural Resources Defense Council, et. al. vs. Train, 8 ERC 2120 (D.D.C. 1976), modified, 12 ERC 1833 (D.D.C. 1979).

The term "water quality criteria" is used in two sections of the Clean Water Act, section 304 (a)(1) and section 303 (c)(2). The term has a different program impact in each section. In section 304, the term represents a non-regulatory, scientific assessment of ecological effects. The criteria presented in this publication are such scientific assessments. Such water quality criteria associated with specific stream uses when adopted as State water quality standards under section 303 become enforceable maximum acceptable levels of a pollutant in ambient waters. The water quality criteria adopted in the State water quality standards could have the same numerical limits as the criteria developed under section 304. However, in many situations States may want to adjust water quality criteria developed under section 304 to reflect local environmental conditions and human exposure patterns before incorporation into water quality standards. It is not until their adoption as part of the State water quality standards that the criteria become regulatory.

Guidelines to assist the States in the modification of criteria presented in this document, in the development of water quality standards, and in other water-related programs of this Agency, are being developed by EPA.

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TABLE OF CONTENTS

CRITERIA DOCUMENT

HALOETHERS

CRITERIA

Aquatic Life

The available data for haloethers indicate that acute and chronic toxicity to freshwater aquatic life occur at concentrations as low as 360 and 122 μg/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested.

No saltwater organisms have been tested with any haloether and no statement can be made concerning acute or chronic toxicity.

Human Health

Using the present guidelines, a satisfactory criterion cannot be derived at this time because of the insufficiency in the available data for haloethers.

INTRODUCTION

Haloethers are compounds which contain an ether moiety (R-O-R) and halogen atoms attached to the aryl or alkyl groups. This document covers chlorinated aromatic ethers, namely, chlorophenyl phenyl ethers, bromophenyl phenyl ethers, and polychlorinated diphenyl ethers.

It is not possible to determine the most probable aquatic fate for 4-chlorophenyl phenyl ether from available data. This pollutant is reported to be rapidly degraded by acclimated sewage sludge, but biodegradation data from river-water die-away experiments indicate that this compound has a potential for persistence in natural surface waters. Sorption by organic-rich sediments and bioaccumulation in fish have been demonstrated. Although photolysis may make a minor contribution to the degradation of this pollutant near the air-water surface, oxidation and hydrolysis are probably not important as fate processes. The role of volatilization is uncertain.

A review of the production range (including importation) statistics for 4-chlorophenyl phenyl ether (CAS No. 7005-72-3), which is listed in the initial U.S. Environmental Protection Agency TSCA Inventory (U.S. EPA, 1979), has shown that between 100,000 and 800,000 pounds of this chemical were produced or imported in 1977.*

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* This production range information does not include any production/importation data claimed as confidential by the person(s) reporting for the TSCA Inventory, nor does it include any information which would compromise confidential business information. The data submitted for the TSCA Inventory, including production range information, are subject to the limitations contained in the Inventory Reporting Regulations (40 CFR 710).

The general physical properties of 4-chlorophenyl phenyl ether are as follows.

Molecular weight (calc. from Weast, 1977)	204.66
Melting point (Dow Chemical Company, 1979)	-8°C**
Boiling point at 760 torr (Mailhe and Murat, 1912)	284°C***
Vapor pressure at 25°C (Calc. by Branson, 1977)	0.0027 torr
Solubility in water at 25°C (Branson, 1977)	3.3 mg/l
Log octanol/water partition coefficient (Branson, 1977)	4.08

Among the polychlorinated diphenyl ethers, 4,4'-dichlorophenyl phenyl ether, $C_{12}H_8Cl_2O$, has the following physical properties: molecular weight 239.11, melting point 30°C, boiling point, 312-4°C, density 1.1231, and it is insoluble in water (Weast, 1978-1979).

Very little information pertaining to the environmental transport and fate of 4-bromophenyl phenyl ether was found, and it is, therefore, not possible to determine the most probable aquatic fate at this time. Some inferences can be drawn from experiments performed with this pollutant's chloro analog. 4-Chlorophenyl phenyl ether is reported to be rapidly degraded by acclimated sewage sludge, but biodegradation data from river water die-away

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** Brewster and Stevenson (1940) report a melting point of 46 to 47°C for 2-chlorophenyl phenyl ether. They were apparently unable to prepare a crystalline sample of 4-chlorophenyl phenyl ether.

*** Dow Chemical Company (1979) has determined the boiling point at 760 torr to be 293.03°C.

experiments indicate that this compound has a potential for persistence in natural surface waters. Sorption by organic-rich sediments and bioaccumulation in fish may be important. Although photolysis may make a minor contribution to degradation near the air-water surface, oxidation and hydrolysis are probably not important as fate processes. The role of volatilization in the removal of halogenated aromatic ethers from aquatic systems has not been demonstrated and remains uncertain.

The general physical properties of 4-bromophenyl phenyl ether include:

Molecular weight (Weast, 1977)	249.11
Melting point (Weast, 1977)	18.72°C
Boiling point at 760 torr (Weast, 1977)	310.14°C
Vapor pressure at 20°C (calc. from Dreisbach, 1952)	0.0015 torr
Density	1.4208
Solubility in water	Insoluble
Log octanol/water partition coefficient (calc. by method of Leo, et al. 1971 using the data of Branson, 1977)	4.28

A separate water quality criteria document, entitled "Chloroalkyl Ethers," covers the following compounds:

Bis(chloromethyl) ether
Bis(2-chloroethyl)ether
2-Chloroethyl vinyl ether
Bis(2-chloroisopropyl)ether
Bis(2-chloroethoxy)methane

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Aquatic Life Toxicology*

INTRODUCTION

The only toxicity data for haloethers, other than for those compounds discussed in the criterion document for chloroalkyl ethers, are for 4-bromophenylphenyl ether and freshwater species, the bluegill, fathead minnow, and *Daphnia magna*.

EFFECTS

Acute Toxicity

Daphnia magna has been exposed to 4-bromophenylphenyl ether and is more sensitive than the bluegill with a 48-hour EC_{50} of 360 µg/l (Table 1).

The bluegill 96-hour LC_{50} is 4,940 µg/l.

Chronic Toxicity

A chronic value for 4-bromophenylphenyl ether, 122 µg/l, is derived from an embryo-larval test with the fathead minnow in which adverse effects on survival and growth were observed (Table 2). No acute-chronic ratio can be calculated since no comparable acute value is available for this species.

Summary

Static, acute toxicity tests with freshwater organisms have been conducted with the bluegill and *Daphnia magna* and 4-bromophenylphenyl ether. The cladoceran is more sensitive with a species acute value of 360 µg/l (Table 1). The comparable value for the bluegill is 4,940 µg/l.

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*The reader is referred to the Guidelines for Deriving Water Quality Criteria for the Protection of Aquatic Life and Its Uses in order to better understand the following discussion and recommendation. The following tables contain the appropriate data that were found in the literature, and at the bottom of each table are calculations for deriving various measures of toxicity as described in the Guidelines.

An embryo-larval test has been conducted with the fathead minnow and the same haloether, but no acute-chronic ratio is calculable since no acute value is available for this species.

No saltwater organisms have been tested with any haloether.

CRITERIA

The available data for haloethers indicate that acute and chronic toxicity to freshwater aquatic life occur at concentrations as low as 360 and 122 μg/l, respectively, and would occur at lower concentrations among species that are more sensitive than those tested.

No saltwater organisms have been tested with any haloether and no statement can be made concerning acute or chronic toxicity.

Table 1. Acute values for haloethers (U.S. EPA, 1978)

Species	Method*	Chemical	LC50/EC50 (µg/l)	Species Mean Acute Value (µg/l)
		FRESHWATER SPECIES		
Cladoceran, *Daphnia magna*	S, U	4-bromophenyl-phenyl ether	360	360
Bluegill, *Lepomis macrochirus*	S, U	4-bromophenyl-phenyl ether	4,940	4,940

* S = static, U = unmeasured

Table 2. Chronic values for haloethers (U.S. EPA, 1978)

Species	Test*	Chemical	Limits (µg/l)	Chronic Value (µg/l)
	FRESHWATER SPECIES			
Fathead minnow, *Pimephales promelas*	ELS	4-bromophenyl-phenyl ether	89-167	122

* ELS = early life stage

REFERENCES

U.S. EPA. 1978. In-depth studies on health and environmental impacts of selected water pollutants. U.S. Environ. Prot. Agency, Contract No. 68-01-4646.

Mammalian Toxicology and Human Health Effects

INTRODUCTION

The U.S. EPA is currently charged with establishing water quality criteria for haloethers. This document covers chlorinated aromatic ethers including:

Chlorophenyl phenyl ethers

Bromophenyl phenyl ethers

Polychlorinated diphenyl ethers

A separate document in this series, entitled "Chloroalkyl Ethers," includes the following compounds:

Bis(chloromethyl)ether

Bis(2-chloroethyl)ether

2-Chloroethyl vinyl ether

Bis(2-chloroisopropyl)ether

Bis(2-chloroethoxy)methane

EXPOSURE

Ingestion from Water

Qualitative identifications of several haloethers in raw and finished water have been reported. This information is summarized in Table 1. The nomenclature used in specifying some haloethers creates a certain amount of confusion in evaluating these monitoring data. For instance, in Table 1, pentachlorophenoxy methyl ether is probably the same as pentachlorophenyl methyl ether. The names used in Table 1 are those given in the various cited references.

Shackelford and Keith (1976) have compiled information on the frequency of organic compounds identified in water. This information was taken from both published literature and unpublished results of survey analyses from EPA regional and research laboratories. Although actual levels of the haloethers in waters are not specified, a breakdown is given of the various types of waters found to be contaminated. This information is presented in Table 2.

The study by Ewing and his coworkers (1977) is based on the analysis of 204 water samples collected from 14 heavily industrialized river basins. As indicated in Table 1, pentachlorophenyl methyl ether was found in 12 samples (5.88 percent), with other chlorophenyl ethers found less frequently. As indicated above, the reports of "pentachlorophenoxy methyl ether" probably refer to pentachlorophenyl methyl ether. The studies by Friloux (1971) and the U.S. EPA (1972), both listed in Table 1, were conducted in the New Orleans area.

In the 1975 National Organics Reconnaissance Survey by the U.S. EPA, no haloethers were found in the waters of Miami, Florida; Seattle, Washington; Ottumwa, Iowa; or Cincinnati, Ohio (U.S. EPA, 1975).

TABLE 1

Haloethers Qualitatively Identified in Water
(see text for details)

Haloethers \ Reference	Shackelford and Keith, 1976	Ewing, et al. 1977	Friloux, 1971	U.S. EPA, 1972
Bromophenyl phenyl ether	5*		X	X
Bis(4-chlorophenyl)ether	2*			
Dichlorophenyl chlorophenyl ether	2*			
2,4,4'-Trichloro-2'-hydroxy-diphenyl ether	1*			
Dichlorophenyl methyl ether		1*		
Trichlorophenyl methyl ether		5*		
Tetrachlorophenyl methyl ether		1*		
Pentachlorophenyl methyl ether	10*	12*		
Pentachlorophenoxy methyl ether		2*		

* Frequency of occurrence
X Occurrence reported, but without frequency

TABLE 2

Frequency of Haloethers Identified in Various Types of Water[a]

	Water Type Contaminated[b]					
				Effluent from:		
	FDW	River	Raw Water	CHEM	RS	STP
Bromophenyl phenyl ether	3	2				
Bis(4-chlorophenyl)ether				2		
Dichlorophenyl chlorophenyl ether				2		
2,4,4'-Trichloro-2'-hydroxy-diphenyl ether				1		
Pentachlorophenyl methyl ether	3	3	1		1	2

[a]Source: Shackelford and Keith, 1976
[b]FDW = Finished drinking water
CHEM = Chemical Plant
RS = Raw sewage
STP = Sewage treatment plant

Ingestion from Food

No monitoring data have been found on the levels of haloethers in food.

A bioconcentration factor (BCF) relates the concentration of a chemical in aquatic animals to the concentration in the water in which they live. The steady-state BCFs for a lipid-soluble compound in the tissues of various aquatic animals seem to be proportional to the percent lipid in the tissue. Thus the per capita ingestion of a lipid-soluble chemical can be estimated from the per capita consumption of fish and shellfish, the weighted average percent lipids of consumed fish and shellfish, and a steady-state BCF for the chemical.

Data from a recent survey on fish and shellfish consumption in the United States was analyzed by SRI International (U.S. EPA, 1980). These data were used to estimate that the per capita consumption of freshwater and estuarine fish and shellfish in the United States is 6.5 g/day (Stephan, 1980). In addition, these data were used with data on the fat content of the edible portion of the same species to estimate that the weighted average percent lipids for consumed freshwater and estuarine fish and shellfish is 3.0 percent.

No measured steady-state BCF is available for any of the following compounds (Table 3), but the equation "Log BCF = (0.85 Log P) - 0.70" can be used (Veith, et al. 1979) to estimate the steady-state BCF for aquatic organisms that contain about 7.6 percent lipids (Veith, 1980) from the octanol/water partition coefficient (P). Calculated log P values were obtained using the method described in Hansch and Leo (1979). The adjustment factor of 3.0/7.6 = 0.395 is used to adjust the estimated BCF from the 7.6 percent lipids on which the equation is based, to the 3.0 percent lipids that is the weighted average for consumed fish and shellfish in order to ob-

TABLE 3

Bioconcentration Factors for Haloethers

Chemical	Log P Calc.	Estimated Steady State BCF	Weighted Average BCF
2-Chlorophenyl phenyl ether	4.92	3,030	1,200
3-Chlorophenyl phenyl ether	4.92	3,030	1,200
4-Chlorophenyl phenyl ether	4.92	3,030	1,200
4-Bromophenyl phenyl ether	5.08	4,150	1,640
Bis(4-chlorophenyl) ether	5.63	12,200	4,820
2,4-Dichlorophenyl phenyl ether	5.63	12,200	4,820
2,6-Dichlorophenyl phenyl ether	5.63	12,200	4,820
3,5-Dichlorophenyl phenyl ether	5.63	12,200	4,820

tain the weighted average bioconcentration factor for the edible portions of all freshwater and estuarine aquatic organisms consumed by Americans.

Inhalation

No monitoring information is available on the levels of any haloethers in ambient air.

Dermal

Because of the lack of monitoring data, no evaluation of the importance of dermal exposures can be made for the haloethers.

PHARMACOKINETICS

Pertinent data could not be located in the available literature concerning the pharmacokinetics of haloethers.

EFFECTS

Acute, Subacute, and Chronic Toxicity

The acute and subacute oral toxicity of various chlorinated phenyl ethers is summarized in Tables 4 and 5. Because of the lack of experimental detail presented in this summary of unpublished data by Hake and Rowe (1963), these results are difficult to interpret. However, the reported results on "highly purified" pentachlorophenyl ether compared to the other pentachlorophenyl ether (i.e., "unpurified") suggest that impurities may be major toxic constituents.

Hake and Rowe (1963) report that "small amounts" of hexachlorodiphenyl ether may cause acneform dermatitis in man.

Synergism and/or Antagonism, Teratogenicity, Mutagenicity, and Carcinogenicity

Pertinent data could not be located in the available literature.

TABLE 4

Chlorinated Phenyl Ethers: Summary of Single-dose Oral Feeding Studies on Guinea Pigs*

Total Number of Chlorines	After 4 Days Lethal Dose (mg/kg)	After 4 Days Survival Dose (mg/kg)	After 30 Days Lethal Dose (mg/kg)	After 30 Days Survival Dose (mg/kg)
1 x Cl	700	200	600	100
2 x Cl	1,300	400	1,000	50
3 x Cl	2,200	400	1,200	200
4 x Cl	3,000	400	50	0.5
5 x Cl	3,400	1,800	100	5
6 x Cl	3,600	400	50	5

*Source: Hake and Rowe, 1963

TABLE 5

Chlorinated Phenyl Ethers:
Results of Repeated Oral Feeding of Rabbits[a]

Total Number of Chlorines	Dose (mg/kg)	Number of Doses*	Number of Days	Effect
1	100	19	29	None
2	100	19	29	Mild liver injury
3	100	5	12	Death
	50	20	29	Slight liver injury
	10	20	29	No effect
4	50	4	10	Death
	5	20	29	Severe liver injury
5	50	8	21	Death
	100**	20	29	Moderate liver injury No growth
	10**	20	29	Slight liver injury
	1**	20	29	No effect
6	5	8	10	Death
	1	20	28	Severe liver injury
	0.1	20	28	No effect

*Animals dosed 5 days/week x 4 weeks unless death intervened. Vehicles not specified.

**Highly purified pentachlorophenyl ether

[a]Source: Hake and Rowe, 1963

CRITERIA FORMULATION

Existing Guidelines and Standards

The Occupational Safety and Health Administration (29 CFR 1910.1000) has set a time-weighted average value of 500 µg/m^3 for the following aromatic chloroethers in the air of the working environment: monochlorophenyl phenyl ether, dichlorophenyl phenyl ether, trichlorophenyl phenyl ether, tetrachlorophenyl phenyl ether, and pentachlorophenyl phenyl ether. This value has also been adopted by the American Conference of Governmental and Industrial Hygienists (1974). The standard is designed to prevent chloracne in exposed workers.

Current Levels of Exposure

As detailed in the Exposure section, only limited information is available on the extent of human exposure to haloethers in water, and no information is available on ambient levels of haloethers in air or food. Quantitative estimates of human exposure cannot be made.

Special Groups at Risk

Individuals working with haloethers or living in areas where these haloethers are produced are probably at greater risk than the general population.

Basis and Derivation of Criteria

As indicated, the Threshold Limit Value (TLV) for chlorophenyl phenyl ethers is 500 µg/m^3. By a process analogous to that used by Stokinger and Woodward (1958), this standard could be used to calculate a water criterion. However, since the TLV for these compounds is based on preventing chloracne rather than chronic toxicity, such a calculation would not be appropriate.

Because of the paucity of toxicologic data on the compounds covered in this document, no ambient water quality criteria for the protection of human health can be derived. It should be recognized that many halogenated aromatic compounds display significant toxicologic properties (McConnell and

Moore, 1979). Consequently, the inability to derive criteria for the haloethers is a matter of concern which should be addressed by additional research.

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