

AMBIENT WATER QUALITY ADVISORY

METHYLENE CHLORIDE

OFFICE OF WATER REGULATIONS AND STANDARDS
CRITERIA AND STANDARDS DIVISION
U.S. ENVIRONMENTAL PROTECTION AGENCY
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NOTICES

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FOREWORD

The Criteria and Standards Division of the Office of Water Regulations and Standards has instituted water quality advisories as a vehicle for transmitting the best available scientific information concerning the aquatic life and human health effects of selected chemicals in surface waters. Advisories are prepared for chemicals for which information is needed quickly, but for which sufficient data, resources, or time are not available to allow derivation of national ambient water quality criteria.

Data supporting advisories are usually not as extensive as required for derivation of national ambient water quality criteria, and the strength of an advisory will depend upon the source, type, and reliability of the data available. We feel, however, that it is in the best interest of all concerned to make the enclosed information available to those who need it.

Users of advisories should take into account the basis for their derivation and their intended uses. Anyone who has additional information that will supplement or substantially change an advisory is requested to make the information known to us. An advisory for an individual chemical will be revised if any significant and valid new data make it necessary.

We invite comments to help improve this product.

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ACKNOWLEDGMENTS

AQUATIC LIFE

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SECTION I. Advisories

AQUATIC LIFE

If the estimated or measured ambient concentration of methylene chloride exceeds 770 g/L in fresh or salt water, one or more of the following options must be completed within a reasonable period of time:

1. Obtain more measurements of the concentration.
2. Improve the estimate of the concentration.
3. Reduce the concentration.
4. Obtain additional laboratory and/or field data on the effect of methylene chloride on aquatic life so that a new aquatic life advisory or water quality criterion can be derived.

After a reasonable period of time, unless a consideration of all the available data concerning the ambient concentration and the effects of methylene chloride on aquatic life indicates that the ambient concentration is low enough, it must be reduced.

SECTION II. GENERAL INFORMATION

A. Biological, Chemical, and Physical Properties

The following information on the properties of methylene chloride (dichloromethane) and its persistence in the aquatic environment was obtained from the Handbook of Chemistry and Physics^a or from the QSAR system^b on August 13, 1987. Some of the values were calculated using structure-activity relationships.

<u>Property</u>	<u>Value</u>	<u>Source</u>
Molecular Weight	84.93 g/mole	Calculated
Relative Density (20C)	-	-
Log P	1.25	-
Melting Point	-95.0 °C	Measured
Boiling Point	40.0 °C	Measured
Vapor Pressure	436. mm Hg	Measured
Heat of Vaporization	6,666. cal/mole	Calculated
pKa	(not applicable)	-
Solubility in Water	15.32 g/L	Calculated
BCF	3.86	Calculated
Absorption Coef. [Log (Koc)]	2.02	Calculated

Hydrolysis Half-life = 1000 days

Hydrolysis is not likely to be an important transformation mechanism for this chemical.

Biodegradation Half-life Analysis

This chemical has two halogens and all chemicals in the data base with two halogens have a half-life > 15 days.

Log 10 (Henry's Constant) = -2.50 atm³/mole

It could be concluded that a chemical with these properties will vaporize rapidly from and will not persist in open water.

Neely 100-day Partitioning Pattern

Air	=	56.67%
Water	=	43.15%
Ground	=	0.09%
Hydrosoil	=	0.08%

a Handbook of Chemistry and Physics, 67th Ed., CRC Press, Boca Raton, FL. 1986-1987.

b For information on the QSAR system, see: Hunter, R., L. Faulkner, F. Culver and J. Hill. Draft user manual for the QSAR system. Center for Data Systems and Analysis, Montana State University. November, 1985.

SECTION III. AQUATIC TOXICITY

Introduction

Aquatic life advisory concentrations are conceptually different from national aquatic life water quality criteria. Aquatic life criteria are based on toxicity and bioconcentration data for a sufficiently diverse group of animals and plants to provide reasonable confidence in the appropriateness of the criteria. Advisories are issued for selected chemicals for which sufficient data are not available to allow derivation of national water quality criteria for aquatic life. Because aquatic life advisories are intended to be used to identify situations where there is cause for concern and where appropriate action should be taken, the advisory concentration for a chemical is derived to be equal to or lower than what the Criterion Continuous Concentration (Stephan et al. 1985) would be if a national water quality criterion for aquatic life could be derived for the chemical. If the concentration of a chemical in a variety of surface waters is found to exceed the aquatic life advisory concentration, this may indicate that the U.S. EPA should consider deriving aquatic life water quality criteria for that chemical.

The literature searching and data evaluation procedures used in the derivation of aquatic life advisories are identical to those used in the derivation of water quality criteria for aquatic life (Stephan et al. 1985). However, advisories do not contain a section on "Unused Data" as in a criteria document. This aquatic life advisory concentration for methylene chloride was derived using the procedures described in the "Guidelines for Deriving Ambient Aquatic Life Advisory Concentrations" (Stephan et al. 1986). A knowledge of these guidelines is necessary in order to understand the following text, tables, and calculations. The latest comprehensive literature search for information for this aquatic life advisory was conducted in April, 1987.

The physical and chemical properties of methylene chloride suggest that it is quite volatile and its concentration in static exposures may decline rapidly (Section III A). Based on nominal concentrations, Alexander et al. (1978) reported a 96-hr LC50 of 310,000 $\mu\text{g/L}$ for fathead minnows tested in a static exposure. In a flow-through measured exposure, they calculated a 96-hr LC50 of 193,000 $\mu\text{g/L}$ for the same species. This indicates that data from static, unmeasured exposures are likely to underestimate the toxicity of methylene chloride to aquatic organisms.

According to the advisory guidelines, data from such static exposures should be multiplied by a factor obtained by dividing a flow-through 96-hr LC50 by a comparable 96-hr LC50 derived from a static test that was measured at 0 hr. At the present time, data are not available to allow the calculation of this adjustment factor. Therefore, toxicity data derived from static, unmeasured tests could not be adjusted, and their use in the derivation of an aquatic life advisory concentration may lead to an underestimate of the actual toxicity of methylene chloride.

Effects on Freshwater Organisms

Data on acute toxicity of methylene chloride to freshwater organisms are available for one invertebrate and two species of fish (Table 1). In static, unmeasured exposures, the cladoceran Daphnia magna had a 48-hr LC50 of 220,000 μ g/L while the bluegill (Lepomis macrochirus) and fathead minnow (Pimephales promelas) had 96-hr LC50s of 230,000 and 310,000 μ g/L, respectively. In a flow-through exposure, Alexander et al. (1978) reported an LC50 of 193,000 μ g/L and an EC50 of 99,000 μ g/L for the fathead minnow. Dill et al. (1987) also conducted a flow-through test with fathead minnows and obtained a 96 hr LC50 of 502,000 μ g/L.

In an early life-stage test with fathead minnows (Dill et al. 1987) the wet weight of fish exposed to 142,000 μ g/L was 29% less than the controls (Table 2). Survival was reduced at methylene chloride concentrations greater than 209,000 μ g/L. Due to the absence of any adverse effects at 82,500 μ g/L, a chronic value of 108,000 can be calculated for fathead minnows. Division of the acute value determined by these authors (502,000 μ g/L) by the chronic value results in an acute/chronic ratio of 4.648.

Data are available describing other lethal and sublethal effects of methylene chloride on freshwater organisms (Table 4). Algal population growth, carbon 14 uptake, and chlorophyll a content were affected by concentrations of 550,000 to 2,292,000 μ g/L, while protozoan cell replication was inhibited by levels of 500,000 to > 8,000,000 μ g/L. Birge et al. (1980) and Black et al. (1982) exposed embryos of rainbow trout (Salmo gairdneri), fathead minnows, five species of frogs, and the northwestern salamander (Ambystoma gracile) to methylene chloride in a flow-through measured exposure. They determined EC50s (death and deformity) for each species at hatching and at 4 days post-hatch (Table 4). The EC50s ranged from 13,160 μ g/L for rainbow trout to > 48,000 μ g/L for the leopard frog (Rana pipiens).

Effects on Saltwater Organisms

Data on acute toxicity of methylene chloride to saltwater animals are available for an invertebrate and a fish tested in static, unmeasured exposures (Table 1). The 96-hr LC50s for the mysid, Mysidopsis bahia, and the sheepshead minnow, Cyprinodon variegatus, were 256,000 and 330,000 g/L, respectively.

No data are available on chronic toxicity or other lethal or sublethal effects of methylene chloride on saltwater organisms.

Calculation of Provisional Advisory Concentration

Due to the volatile nature of methylene chloride, data from static, unmeasured tests should not be used in the calculation of the advisory concentration. Although a total of five Species Mean Acute Values (SMAVs) and Genus Mean Acute Values (GMAVs) are available for freshwater and saltwater organisms (Table 3), only data with the fathead minnow were obtained from flow-through tests. Therefore, according to the advisory guidelines, there are not sufficient data available to calculate an advisory concentration for methylene chloride.

However, if data from static unmeasured tests are included, a provisional advisory may be calculated as follows. The lowest GMAV (99,000 g/L) is divided by a factor of 9.0, in accordance with the advisory guidelines, resulting in a provisional Advisory Acute Value (AAV) of 11,000 g/L. The reported acute-chronic ratio (4.648) is combined with two empirical ratios of 25 to derive an Advisory Acute-Chronic Ratio (AACR) of 14.27. Division of the provisional AAV (11,000 g/L) by the AACR (14.27) results in a provisional Advisory Concentration of 770 g/L. Due to the use of static unmeasured data in these calculations, this concentration may underestimate the actual toxicity of methylene chloride to aquatic life and, therefore, should be used with caution.

Table 1. Acute Toxicity of Methylene Chloride to Aquatic Animals

<u>FRESHWATER SPECIES</u>						
<u>Species</u>	<u>Method^a</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>LC50 or EC50 (g/L)</u>	<u>Species Mean Acute Value (g/L)</u>	<u>Reference</u>
Cladoceran (< 24 hr), <u>Daphnia magna</u>	S, U	-	173	220,000	220,000	LeBlanc 1980
Fathead minnow (adult), <u>Pimephales promelas</u>	S, U	-	96	310,000 ^b (LC50)	-	Alexander et al. 1978
Fathead minnow (adult), <u>Pimephales promelas</u>	F, M	-	96	193,000 ^b (LC50)	-	Alexander et al. 1978
Fathead minnow (adult), <u>Pimephales promelas</u>	F, M	-	96	99,000 (EC50 equilibrium)	-	Alexander et al. 1978
Fathead minnow (juvenile), <u>Pimephales promelas</u>	F, M	Reagent (>99.9%)	73-82	502,000 ^b (LC50)	99,000	Dill et al. 1987
Bluegill (Young of year), <u>Lepomis macrochirus</u>	S, U	-	32-48	230,000	230,000	Buccafusso et al. 1981

Table 1. (continued)

<u>Species</u>	<u>Method</u> ^a	<u>Chemical</u>	<u>SALINATER SPECIES</u>			<u>Reference</u>
			<u>Salinity</u> <u>(g/kg)</u>	<u>LC50</u> <u>or EC50</u> <u>(g/L)</u>	<u>Species Mean</u> <u>Acute Value</u> <u>(g/L)</u>	
Mysid, <u>Mysidopsis bahia</u>	S, U	-	-	256,000	256,000	U.S. EPA 1978
Sheepshead minnow (juvenile), <u>Cyprinodon variegatus</u>	S, U	-	10-31	330,000	330,000	Heitmuller et al. 1981

^a S = static; F = flow-through; M = measured; U = unmeasured

^b Data were not used in the calculation of the Species Mean Acute Value due to the presence of results from a more sensitive endpoint.

Table 2. Chronic Toxicity of Methylene Chloride to Aquatic Animals

<u>Species</u>	<u>Test^a</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Chronic Limits^b (µ/L)</u>	<u>Chronic Value (µ/L)</u>	<u>Reference</u>
Fathead minnow <u>Pimephales promelas</u>	ELS	Reagent (> 99.9%)	73-82	82,500-142,000	108,000	Dill et al. 1987

Acute-Chronic Ratios

<u>Species</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Acute Value (µ/L)</u>	<u>Chronic Value (µ/L)</u>	<u>Ratio</u>
Fathead minnow, <u>Pimephales promelas</u>	73-82	502,000	108,000	4.648

^a ELS = early life-stage.

^b Results are based on measured concentrations of Methylene Chloride.

Table 3. Ranked Genus Mean Acute Values with Species Mean Acute-Chronic Ratios

<u>Rank^a</u>	<u>Genus Mean Acute Value (μ/L)</u>	<u>Species</u>	<u>Species Mean Acute Value (μ/L)^b</u>	<u>Species Mean Acute-Chronic Ratio^c</u>
5	330,000	Sheepshead minnow, <u>Cyprinodon variegatus</u>	330,000	-
4	256,000	Mysid, <u>Mysidopsis bahia</u>	256,000	-
3	230,000	Bluegill, <u>Lepomis macrochirus</u>	230,000	-
2	220,000	Cladoceran, <u>Daphnia magna</u>	220,000	-
1	99,000	Fathead minnow, <u>Pimephales promelas</u>	99,000	4.648

^a Ranked from most resistant to most sensitive based on Genus Mean Acute Value.

^b From Table 1.

^c From Table 2.

Provisional Advisory Acute Value = $(99,000 \mu\text{g/L}) / 9.0 = 11,000 \mu\text{g/L}$ (see text).

Advisory Acute-Chronic Ratio = 14.27

Provisional Advisory Concentration = $(11,000 \mu\text{g/L}) / 14.27 = 770 \mu\text{g/L}$

Table 4. Other Data on Effects of Methylene Chloride on Aquatic Organisms

<u>FRESHWATER SPECIES</u>						
<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Duration</u>	<u>Effect</u>	<u>Concentration (µg/L)</u>	<u>Reference</u>
Blue-green alga, <u>Anacystis aeruginosa</u>	-	-	8 days	Incipient inhibition of population growth	550,000	Bringmann and Kuhn 1978a,b
Green alga, <u>Chlorella vulgaris</u>	-	-	3 hr	EC ₅₀ (C ¹⁴ uptake)	2,292,000	Hutchinson et al. 1980
Green alga, <u>Chlamydomonas angulosa</u>	-	-	3 hr	EC ₅₀ (C ¹⁴ uptake)	1,477,000	Hutchinson et al. 1980
Green alga, <u>Scenedesmus quadricauda</u>	-	-	8 days	Incipient inhibition of population growth	1,450,000	Bringmann and Kuhn 1978a,b;1977a
Green alga, <u>Selenastrum capricornutum</u>	-	-	96 hr	EC ₅₀ (chlorophyll <u>a</u>)	> 662,000	U.S. EPA 1978
Protozoan, <u>Chilomonas paramecium</u>	-	-	48 hr	Incipient inhibition of cell replication	> 8,000,000	Bringmann et al. 1980
Protozoan, <u>Pseudomonas putida</u>	-	-	16 hr	Incipient inhibition of cell multiplication	500,000	Bringmann and Kuhn 1977a
Cladoceran (24 hr), <u>Daphnia magna</u>	-	286	24 hr	EC ₅₀ (immobility)	2,270,000	Bringmann and Kuhn 1977b

Table 4. (continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Duration</u>	<u>Effect</u>	<u>Concentration (g/L)</u>	<u>Reference</u>
Rainbow trout (embryo), <u>Salmo gairdneri</u>	Reagent	106	23 days (to hatch)	EC50 (death and and deformity)	13,510	Black et al. 1982
Rainbow trout (embryo-larva), <u>Salmo gairdneri</u>	Reagent	106	27 days (4 days post-hatch)	EC50 (death and deformity)	13,160	Black et al. 1982
Fathead minnow (embryo), <u>Pimephales promelas</u>	Reagent	95.3	5 days (to hatch)	EC50 (death and deformity)	> 34,000	Black et al. 1982
Fathead minnow (embryo-larva), <u>Pimephales promelas</u>	Reagent	95.3	9 days (4 days post-hatch)	EC50 (death and deformity)	34,000	Black et al. 1982
Fathead minnow (juvenile), <u>Pimephales promelas</u>	Reagent (> 99.9%)	73-82	192 hr	LC50	471,000	Dill et al. 1987
Bullfrog (embryo), <u>Rana catesbiana</u>	Analytical	106.8	4 days (to hatch)	EC50 (death and deformity)	30,610	Birge et al. 1980
Bullfrog (embryo-larva), <u>Rana catesbiana</u>	Analytical	106.8	8 days (4 days post-hatch)	EC50 (death and deformity)	17,780	Birge et al. 1980
Pickerel frog (embryo), <u>Rana palustris</u>	Analytical	106.8	4 days (to hatch)	EC50 (death and deformity)	> 32,000	Birge et al. 1980

Table 4. (continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Duration</u>	<u>Effect</u>	<u>Concentration (µg/L)</u>	<u>Reference</u>
Pickereel frog (embryo-larva), <u>Rana palustris</u>	Analytical	106.8	8 days (4 days post-hatch)	EC50 (death and deformity)	> 32,000	Birge et al. 1980
Leopard frog (embryo), <u>Rana pipiens</u>	Reagent	95.8	5 days (to hatch)	EC50 (death and deformity)	> 48,000	Black et al. 1982
Leopard frog (embryo-larva), <u>Rana pipiens</u>	Reagent	95.8	9 days (4 days post-hatch)	EC50 (death and deformity)	> 48,000	Black et al. 1982
Fowler's toad (embryo), <u>Bufo fowleri</u>	Analytical	106.8	3 days (to hatch)	EC50 (death and deformity)	> 32,000	Birge et al. 1980
Fowler's toad (embryo-larva), <u>Bufo fowleri</u>	Analytical	106.8	7 days (4 days post-hatch)	EC50 (death and deformity)	> 32,000	Birge et al. 1980
African clawed frog (embryo), <u>Xenopus laevis</u>	Reagent	97.9	2 days (to hatch)	EC50 (death and deformity)	> 29,000	Black et al. 1982
African clawed frog (embryo-larva), <u>Xenopus laevis</u>	Reagent	97.9	6 days (4 days post-hatch)	EC50 (death and deformity)	> 29,000	Black et al. 1982

Table 4. (continued)

<u>Species</u>	<u>Chemical</u>	<u>Hardness (mg/L as CaCO₃)</u>	<u>Duration</u>	<u>Effect</u>	<u>Concentration (g/L)</u>	<u>Reference</u>
Northwestern salamander (embryo), <u>Ambystoma gracile</u>	Reagent	97.9	5.5 days (to hatch)	EC50 (death and deformity)	23,860	Black et al. 1982
Northwestern salamander (embryo-larva), <u>Ambystoma gracile</u>	Reagent	97.9	9.5 days (4 days post-hatch)	EC50 (death and deformity)	17,820	Black et al. 1982

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SECTION V. EPA CONTACTS

AQUATIC LIFE ADVISORIES

For further information regarding the aquatic life and fish and water exposure advisories contact:

_____ FTS 382-7144 (202)382-7144
_____ FTS 475-7315 (202)475-7315