Canadian Environmental Protection Act

Priority Substances List Supporting Document

Dichloromethane

Eco-Health Branch
Ecosystem Sciences and Evaluation Directorate
Environment Canada
Ottawa, Ontario

UNPUBLISHED FINAL DRAFT-JANUARY 1994

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1.0 Executive Summary

The Canadian Environmental Protection Act (CEPA) requires the Ministers of the Environment and of National Health and Welfare to prepare and publish a Priority Substance List that identifies substances, including chemicals, effluents and wastes that may be harmful to the environment or constitute a danger to human health. The act requires the federal Ministers of the Environment and of National Health and Welfare to assess these substances and determine whether they are "toxic" under the definition of CEPA. This assessment allows for the making of regulations to control any aspect of the substances life cycle. The following supporting document examines the environmental 'toxicity' of dichloromethane (DCM) for the development of the assessment report.

Identity and Physical and Chemical Properties

Dichloromethane (DCM) also commonly known as methylene chloride (CH_2Cl_2) (CAS registry No. 75-09-2), is a clear colourless, highly volatile, nonflammable liquid at room temperature. Dichloromethane has a molecular weight of 84.93, a density of 1.326 $g \cdot mL^{-1}$ @ 20°C, reported vapour pressures of 43 and 46.5 kPa @ 20°C, boiling points between 39.75 and 40.1°C, a log octanol\water partition coefficient (log K_{ow}) of 1.25, a Henry's Law constant of 227.9 $Pa \cdot m^3 \cdot mole^{-1}$ @ 25°C. Dichloromethane has a relatively high water solubility compared to other chlorinated hydrocarbon compounds with reported values between 13 200 and 20 000 $mg \cdot L^{-1}$ @20°C. Dichloromethane absorbs infrared radiation predominantly in the wavelengths between 7 and 13 µm.

Methods of Analysis

Dichloromethane levels in air, water, soil, sediment and tissues are most often determined by gas chromatography (GC) combined with detection with mass spectrometry (MS), electron capture detection (ECD), or flame ionization detection (FID). Reported detection limits are as low as 0.1 $\mu g/m^3$ in air, 30.0 ng/L in water, and 5.0 µg/kg dry wt in soil. Reported detection limits are as low as 0.1 $\mu g \cdot m^{-3}$ in air; 30.0 $ng \cdot L^{-1}$ in water; and 5.0 $\mu g \cdot kg^{-1}$ dry wt in soil.

Uses and Production

Dichloromethane is not produced in Canada but is imported. The quantity of dichloromethane imported and used in Canada annually during the period from 1977 to 1990 ranged from 9 to 13.2 kt. In Canada, dichloromethane is primarily used as a paint remover (56.3 - 69.6%), as a blowing agent for foam production (16 - 29.7 %) and as a component in aerosols (8.7 - 11.8 %). Major global industrial applications of dichloromethane include use in paint removers, as a solvent for degreasing, as a blowing agent in foam production, for photoresist stripping operations, in film processing and as an extraction solvent for spice

oleoresins, hops and for the removal of caffeine from coffee. In the decaffeination process, concern over residual solvent has prompted most decaffeinators to discontinue use of dichloromethane for caffeine extraction.

Sources and Releases

There are no known natural sources of dichloromethane. The dispersive nature of applications of dichloromethane imply that as much as 100% of that used may be released to the environment (Environment Canada 1990). Entry to the environment may occur during production, transportation and storage, as well as from waste disposal sites, industrial effluents, and in effluents of pulp and paper mill operations and water treatment facilities. Quantitative estimates of releases of dichloromethane into the Canadian environment are limited to loadings from industrial effluents. In 1983, in effluents from several industries including automotive painting operations and steel manufacturing, and from sewage treatment plants, dichloromethane was discharged into the Detroit River, Ontario, at rates of 0.03 to 0.31 kg/day. On the Canadian side of the St. Clair river in Ontario, where 18 industrial sources are estimated to release 1.7 billion litres of effluent and cooling water daily, levels of dichloromethane in effluent ranged up to 160 $\mu g/L^{-1}$.

Data on the sources of dichloromethane to the Canadian environment are limited, therefore estimates from other industrialized countries may be of qualitative value. In the United States, the Toxics Release Inventory estimated that in 1989 30.7 million kg of dichloromethane were released into the air, 0.10 million kg into water, 0.75 million kg were injected into underground wells and 0.67 million kg were sent to U.S. landfills and/or other treatment/disposal facilities. The total release of dichloromethane into the United States environment in 1989 was estimated at 45.4 million kg.

Dichloromethane was the most frequently detected organic contaminant in groundwater at waste disposal sites in the U.S. and the 11th most frequently detected in Germany.

Environmental Fate

Volatilization

Dichloromethane has a high vapour pressure and Henry's Law constant; thus the atmosphere plays an important role in its distribution and ultimate fate. A half-life of 25 min. was determined for the evaporation of DCM (1.0 $mg \cdot L^{-1}$) from an aqueous solution stirred at 200 rpm. The troposphere provides and important sink for volatilized DCM. Dichloromethane in the troposphere, has the potential to return to earth, via precipitation, at an estimated, rate of 400 $t \cdot yr^{-1}$ based on the estimated Global emission rate of 500 $kt \cdot yr^{-1}$.

Photolysis, Oxidation and Hydrolysis

Photooxidation and photolysis at sea level is expected to be minimal; however, conditions in the upper troposphere will allow photooxidation to occur as a result of photochemically generated hydroxyl radicals. Lifetimes for DCM in the troposphere are estimated at 109 d to 1.0 yr and half-lives over three Canadian cities (Windsor, Ont.; Edmonton, Alta.; Resolute Bay, N.W.T) ranged from 30 days to several years, values vary with the potential of dichloromethane to photoxidize, which in turn is dependent on the concentration of hydroxyl radical concentration and the light intensity in the region. Migration of dichloromethane from the troposphere to the stratosphere is estimated to take between 5 and 10 years. The relatively long lifetimes in the troposphere allow an estimated 2.0 to 2.5% to enter the stratosphere, where high energy irradiation increase the potential for photolysis and photooxidation. It is estimated that under high altitrude irradiation, as much as 90% of dichloromethane would photoreact with-in 5-20 hours.

Dichloromethane is not expected to undergo hydrolytic cleavage in aqueous media under natural conditions; however, laboratory studies indicate there exists some potential for hydrolysis under conditions of high pH and elevated temperatures. A half-life of 704 years has been estimated for the hydrolysis of dichloromethane in water.

Sorption

Based on its high vapour pressure and water solubility, dichloromethane is expected to be highly mobile in most soils under normal soil conditions. Dichloromethane has been found to adsorb stongly to peat moss, less strongly to bentonite clay, only slightly to dolomitic limestone and not at all to sand. The ability of DCM to absorb to soils is highly dependent on soil type, moisture level and temperature. An estimated soil adsorptive coefficient (Koc) has been found to be relatively low at 18.8.

Biodegradation

Dichloromethane may be rapidly biodegraded in aqueous media by common soil and sludge aerobic and anaerobic bacteria. Degradation proceeds rapidly to completion from hours to weeks depending on microbiota present, depth and type of medium, as well as environmental conditions. In an activated sludge reactor 99.5% of DCM was degraded in 48-h from an initial concentration of 180 $mg \cdot L^{-1}$. Dichloromethane at a concentration of 0.5 $mg \cdot L^{-1}$ was 80% degraded in within three weeks from a sandy loam surface soil. Acclimated microbes were observed to enhance the degradation rate. Byproducts from DCM biodegradation include carbon dioxide and chloride ion.

Bioaccumulation and Biomagnification

Few studies exist that have examined the bioaccumulation potential of DCM; however, calculations based on the octanol/water partition coefficients for DCM provide bioconcentration factors (BCF) of 0.8 and 2.3

for freshwater fish, suggesting a very low potential for bioaccumulation and biomagnification in aquatic life. Similarly, little or no bioaccumulation or biomagnification is expected for terrestrial organisms.

Levels in the Environment

Atmosphere

Mean atmospheric levels of dichloromethane observed at 22 locations across Canada (1991-92) ranged from 0.5 $\mu g/m^3$ in the Longwoods Conservation Area, Ontario to 9.9 $\mu g/m^3$ in Saint John, New Brunswick. The national mean value was approximately 1.7 $\mu g/m^3$, with an isolated maximum value of 311.3 $\mu g/m^3$ reported for Saint John, New Brunswick. Similarly, the overall mean concentration of dichloromethane was 2.6 ug/m^3 (range not reported), in samples of ambient air taken in 1989 from 17 urban sites in Canada. Mean concentrations at 16 sites sampled in additional national surveys conducted between 1988 and 1990 ranged from 1.0 ug/m^3 in Halifax to 6.2 ug/m^3 in Vancouver.

Surface Water

Median levels (and range of reported values) oof dichloromethane in surface water, based upon data at 264 sites across Canada included in a national database and other sources are: Ontario, 0.05 0g/l (non-detectable to 57 µg/L); Quebec, 0.03 µg/L (non-detectable to 2.7 µg/L); New Brunswick, 1.05 µg/L (non-detectable to 6.7 µg/L); Nova Scotia, 0.4 µg/L (non-detectable to 13.9 µg/L); and Newfoundland, 0.71 µg/L (non-detectable to 10.3 µg/L).

Groundwater

In contrast to surface waters where DCM is likely to volatilize, groundwater is likely to transport DCM in a dissolved state. Dichloromethane levels collected from groundwater sites used for drinking water from the provinces of Nova Scotia and Prince Edward Island, ranged between 0.1 and 11.0 $\mu g \cdot L^{-1}$ (n=84) .

The highest reported level of dichloromethane in groundwater in CAnada was 25 g/l in the Weston area of northwest Toronto, measured apporximately 20 years after release of the compound form a ruptured underground storage tank. Groundwater samples taken from a landfill site in Glocester that received organic wastes for many years had initial DCM levels as high as 10 400 $\mu g \cdot L^{-1}$ which were reduced to 4-60 $\mu g \cdot L^{-1}$ after 6 years. Although there was groundwater discharge to surface waters approximately 0.5 km from the site, most of the DCM was suspected not to have migrated to that distance due to anaerobic biodegradation. Dichloromethane levels in leachate from a landfill site in Guelph, were 131 and 1008 $\mu g \cdot L^{-1}$ in 1988 and 1989 respectively, and 577 µg/L at a site in the Muskokas. Under simulated ground water anaerobic reducing conditions the DCM present in the leachate was degraded at a constant rate over a time period of a few months. In Ville Mercier, Quebec, groundwater contamination with dichloromethane and other organics

(extimated to cover and area of 10-15 km^2) threatened local surface water quality. At this site, treated groundwater is discharged to the environment at concentrations reaching approximately 300 $\mu g \cdot L^{-1}$.

With the exception of a few extreme cases of groundwater contamination from landfill leachates, little data exist to accurately define the state of groundwater quality. As previously noted, groundwater down gradient from over 700 waste sites in Germany and the U.S., reported DCM as one of the most frequently detected contaminants, (No. 1 in the U.S. and No. 11 in W. Germany) with a mean concentration in German waters at over 38 $mg \cdot L^{-1}$ and a maximum level close to 500 $mg \cdot L^{-1}$. Comparable Canadian data do not exist; however, it is expected that a similar situation exists in Canada.

Soils

Little information is available on levels of DCM in Canadian soils. Similar to groundwater, data are generally only available for extreme cases of contamination. At the liquid waste disposal site near Ville Mercier, Que., an oil extracted through a groundwater monitoring showed and level of DCM of 2000 $mg \cdot L^{-1}$. This oil sample represents the extreme of soil contamination where the absorptive capacity of the soil has been exceeded. Another study reported levels of DCM at 0.016 $mg \cdot kg^{-1}$ dry wt in a surface soil sample taken beneath the C-I-L warehouse in Vancouver, B.C. All other samples taken in the study were below detection limits (0.005 $mg \cdot kg^{-1}$).

Sediment

No information regarding levels of DCM in sediment was available for Canadian sites. However, since DCM does not appear to have a strong potential for sorption to soils, it is anticipated that concentrations in sediments will closely follow those in the overlying water. One U.S. study reported levels of 1.5 and 3.2 $ng \cdot g^{-1}$. from Lake Pontchartrain, New Orleans, LA., U.S.A..

Biota

No information was available reporting levels of DCM in Canadian biota. Levels in biota are not expected to be high based on the physical and chemical properties of DCM and the low calculated BCF values. One study examining DCM levels in the tissue of oysters and clams reported mean levels between 4.5 and 27 $ng \cdot g^{-1}$ wet weight, Lake Pontchartrain, New Orleans, LA, U.S.A..

Population Exposures

Wildlife

Because of its volatile nature, DCM is likely to be released into the atmosphere, for this reason, inhalation is likely to be the major route of exposure for wild life. It is unlikely that DCM would appear in

wildlife food sources given that DCM precipitates back to earth at a relatively insignificant rate and has a low estimated BCF.

Effects on the Environment

Effects on the Abiotic Environment

A recent computer modelling study predicted the half-lives of dichloromethane over three Canadian cities to vary from a few weeks to several years (Windsor, Ont.; Edmonton, Alta.; Resolute Bay, N.W.T.) (Bunce, 1992). Generally, the study implies that dichloromethane would be unlikely to migrate into and persist in the stratosphere. Thus, DCM has a low potential to contribute to stratospheric ozone depletion.

Dichloromethane and other halocarbons strongly absorb infrared radiation. Thus these compounds have the potential to "trap" the earth's surface radiation and contribute to the greenhouse effect. However, the real significance of dichloromethane's potential to contribute to the greenhouse effect is expected to be minimal when factors including tropospheric half-lives and seasonal changes are considered.

Effects on Aquatic Biota

Fish

An EC_{50} (impairment of swimming ability) of 99.0 $mg \cdot L^{-1}$ for fathead minnows (*Pimephales promelas*). The 96-h LC_{50} in the same study was determined to be 193.0 $mg \cdot L^{-1}$. Other studies involving *P. promelas* the blue gill sunfish (*Lepomis macrohirus*), and the marine fish sheepshead minnow (*Cyprinodon variegatus*), reported 96-h LC_{50}'s within the range of 220-502 $mg \cdot L^{-1}$. A 48-h LC_{50} of 97.0 $mg \cdot L^{-1}$ was reported for the Killifish, *Fundulus heteroclitus* (Burton and Fisher 1990) and a 96-h NOEC for the Sheepshead minnow (*Cyprinodon variegatus*) was reported at 130 $mg \cdot L^{-1}$. A partial life-cycle study with rainbow trout (*Onchorhynchus mykiss)* embryo (23-d) to larval stage (4-d) revealed an LC_{50} of 13.2 $mg \cdot L^{-1}$ and a LOEL of 5.5 $mg \cdot L^{-1}$ for the onset of teratogenic effects.

Amphibians

A chronic study with the frog (*Rana temporaria*) embryo (5-d) to post hatch (4-d) revealed an LC_{50} of 16.9 $mg \cdot L^{-1}$, the lowest mean value of the seven amphibians studied. While other toxicity studies using the frog, toad and salamander species had embryo/larvae LC_{50}'s ranging between 17.8 to >48 $mg \cdot L^{-1}$. Embryo studies with the same amphibians reported 2-5.5 day LC_{50}'s between 23 to >48 $mg \cdot L^{-1}$. Other adverse effects (e.g. teratogenic) reported for amphibian species include LOEC's of 981 $\mu g \cdot L^{-1}$ and 822 $\mu g \cdot L^{-1}$ for *R. catesbeiana* and *R. temporaria*, respectively.

Invertebrates

The lowest concentration correlated with an adverse effect was that for the ubiqutous free-living freshwater nematode, *Panagrellus redivivus*. Dichloromethane levels of 0.9 $\mu g \cdot L^{-1}$ for four days were found to inhibit completion of the fourth larval stage (L4) to adult molt resulting in a considerable reduction in the available adult population. Lethal mutations to the b7 X-linked gene were also exhibited at concentrations as low as 0.849 $\mu g \cdot L^{-1}$. The lowest 48-h LC_{50} reported for aquatic invertebrates was 27 $mg \cdot L^{-1}$ for *Daphnia magna* in its first instar stage. Other studies involving *D. magna*, and the grass shrimp (*Palaemonetes pugio*) reported 48-h LC_{50}'s of 220 and 108.5 $mg \cdot L^{-1}$, respectively.

Plants

All available studies examining aquatic plants were considered not reliable for enviornmetnal assessment.

Effects on Terrestrial Biota

Soil, Sediment and Sludge Biota

A 48-h LC_{50} of 304 $\mu g \cdot cm^{-2}$ was determined for the earthworm (*Eisemia fetida*) in a surface contact study. Unfortunately, the protocol followed for this study does not allow for the extrapolation of this result to field conditions. Dichloromethane has been observed to inhibit enzymatic activity (β-glucosidase, β-acetylglucosaminidase, phosphatase and phosphodiesterase) of soil microbes at 10 $\mu g \cdot g^{-1}$ dry soil, as well as, strongly decreasing the ATP content of the soil by 80-85%. Dichloromethane was also observed to inhibit CO_2 production from freshwater sediment with a reported 7-d EC_{50} of 11.7 $\mu L \cdot g^{-1}$ wet wt.(15.6 $mg \cdot g^{-1}$). Gas production was inhibited in anaerobic sludge reactors at levels as low as 2.5 $mg \cdot L^{-1}$. However, sludge acclimated to DCM for 9-11 d, did not show differences in the rate of glucose metabolism nor the amount of oxygen consumed relative to the control group at DCM concentrations as high as 1000 $mg \cdot L^{-1}$.

Insects

Although DCM is not registered as a pest control product in Canada, it has been used as an effective insect fumigant in other countries. Twenty-four hour LD_{50}'s were determined to be 129.9 and 81.28 $mg \cdot L^{-1}$ for fumigation of *Sitophilus oryzae* and *Trilobium castaneum*, respectively.

Birds and Mammalian Wildlife

Data on DCM toxicity to birds are lacking. However, two studies using chick embryos have, however, been conducted. One study revealed an LD_{50} for an injection of DCM dissolved in ethanol into the yolk of White Leghorn Chidken eggs to be 14.1 $mg \cdot egg^{-1}$. A second study found that the LD_{50} for an injection of DCM

dissolved in olive oil into the air space of White Leghorn chicken eggs was greater than 100 μmol·egg^{-1} (>8.5 mg DCM·egg^{-1}). No apparent teratogenicity was revealed from either of the studies.

To estimate exposure of wildlife to dichloromethane, a worst-case exposure scenario was developed for mink, *Mustela vison*, an opportunistic carnivore, along the St. Clair River. This site was chosen as levels in surface water were the highest recorded across Canada and data on levels in air were available for a nearby rural site (Walpole Island). The main route of exposure is oral. In the absence of toxicological data for wildlife, the results of toxicity studies on laboratory rodents have been used to estimate an effects threshold. The lowest observable effect level (LOEL) reported for hepatic effects following chronic exposure by ingestion of dichloromethane is 50 mg/kg bw/d in rats; the no observed effect level (NOEL) was 5 mg/kg bw/d. Assuming a factor of 10 to account for interspecies variation and extrapolation of results from a laboratory to field situation, the estimated effects threshold is 0.5 mg/kg bw/d. The worst-case exposure scenario is more than 10 times less than this effects threshold. Therefore, dichloromethane is not anticipated to cause effects on mammalian wildlife.

Plants

No information was available addressing the toxicity of DCM to terrestrial plants except for studies on the effects of DCM on seed germination. Immersion of oat and pigweed seeds in DCM for 24-h, inhibited seed germination while soybean seeds were unaffected from 5-h immersion in DCM. Seed germination was enhanced for the light sensitive Grand Rapids lettuce following immersion in DCM for 10 min. to 12 -h.

Waste Management

Removal mechanisms for DCM from contaminated sites may involve air stripping, biodegradation, sorption, chemical oxidation, or any combination of these depending on the site and environmental conditions. Biodegradation, when applicable can be the most effective method. Elimination of DCM from waste water is efficiently carried out through the utilization of biota under certain circumstances. Incineration of DCM at temperatures between 650-850°C can be an efficient means of disposal.

2.0 Introduction

The Canadian Environmental Protection Act (CEPA) requires the Ministers of the Environment and of National Health and Welfare to prepare and publish a Priority Substances List that identifies substances, including chemicals, effluents and wastes which may be harmful to the environment or constitute a danger to human health. The Act also requires the federal Ministers of the Environment and of National Health and Welfare to assess these substances and determine whether they are "toxic" as defined in section 11 of the Act, which states:

> "A substance is toxic if it is entering, or may enter, the environment in a quantity or concentration, or under circumstances:
> a) having or that may have an immediate or long-term harmful effect on the environment;
> b) constituting or that may constitute a danger to the environment of which human life depends;
> c) constituting or that may constitute a danger in Canada to human life or health.

Substances that are assessed as "toxic" according to Section 11 may be placed on Schedule I of the Act, and considered for possible development of regulations, guidelines or codes of practice to control any aspect of their life cycle, from the research and development stage through manufacture, use, storage, transport and ultimate disposal.

The assessment of whether the priority substance, dichloromethane, (referred to as DCM) is "toxic" as defined in CEPA was based on the determination of whether it **enters** or is likely to enter the Canadian environment in a concentration or quantities or under conditions that could lead to **exposure** of humans or other biota at levels that could cause adverse **effects**. This document provides the supporting information for the development of the assessment report for dichloromethane. It provides the background information regarding the physical and chemical properties, environmental levels and releases to the environment, toxicity to freshwater and marine aquatic organisms, toxicity to mammals and birds, kinetics and metabolism, fate and transport processes. Primary sources were reviewed owing to lack of recent, relevant comprehensive reviews.

Data relevant to the assessment of whether DCM is "toxic" to the environment were identified from on-line searches of a number of commercial databases completed in November 1991 by McDonald Environmental Sciences Ltd on behalf of Environment Canada. All data bases were searched without date restrictions except for Chemical Abstracts which was searched from 1987 to present. A list of databases which were searched is provided in Table 1. Manual searches of references cited in journal articles, texts and reports,

and personal contacts with individuals in government agencies were also used. Information obtained after December 1992, was not considered for inclusion in this supporting document.

The information collected was critically evaluated by the following staff of Environment Canada:

R.A. Kent

S. Lesage

M.A. Lewis

E.L. Porter

In addition the environmental portion of the supporting document was reviewed and approved by several peer reviewers including, Dr. Jack Trevors, Department of Environmental Chemistry, University of Guelph; Dr. Nigel Bunce, Department of Chemistry and Biochemistry, University of Guelph; and Dr. Don Mackay, Department of Chemical Engineering and Applied Science, University of Toronto.

Copies of this Supporting Document are available upon request from the:

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Table 1. Data bases searched

AGRICOLA
AQUAREF
AQUIRE
BIOLOGICAL ABSTRACTS
CHEMICAL ABSTRACTS (1987 +)
CAB
CESARS
CHEMICAL EXPOSURE
CHEMICAL NAME
CHEMICAL REGULATIONS
CHEM INTELL
CIS
CODOC
ELIAS
ENVIROLINE
ENVIRONMENTAL BIBILIOGRAPHY
FATE RATE
FEDERAL REGISTER ABSTRACTS
GEOREF (Canole)
GEOREF (Dialog)
IRIS
IRPTC
MEDLINE
MICROLOG
NAQUADAT\ENVIRODAT
NRC PUBS
NRTCR
NTIS
PHYTOTOX (Ottawa)
POLLUTION ABSTRACTS
RTECS
WATER RESOURCES ABSTRACTS
TOXLINE

Note: All data bases were searched in November 1991, without date restrictions, except for Chemical Abstracts which was searched from 1987 to present.

3.0 Identity of Dichloromethane

Dichloromethane (DCM) (CAS Registry No. 75-09-2) is a clear, colourless, highly volatile, non-flammable liquid which is only moderately soluble in water. Its molecular formula is CH_2Cl_2 and is structurally portrayed in Figure 1. The most common synonym for dichloromethane is methylene chloride, other synonyms include methane dichloride, methylene dichloride, methylene bichloride, 1,1-dichloromethane, and chlorure de methylene (French). It is sold commercially under the trade names Aerothene MM, Freon 30, Narkotil, Solaesthin and Solmethine (DPIMR 1988). It is used extensively in industrial, domestic and agricultural applications throughout the world.

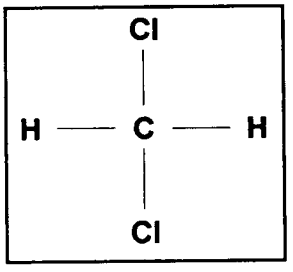


Figure 1. Chemical structure of dichloromethane (DCM).

4.0 Physical and Chemical Properties

Dichloromethane (DCM) is a clear, colourless, relatively stable volatile liquid, with a penetrating ether-like or sweetish odour (Hawley 1977; Verschueren 1983). It has a molecular weight of 84.93 g/ml, a density of 1.326 g/ml @ 20°C (Budavari *et al.* 1989). It has reported water solubilities of 13 200 $mg \cdot L^{-1}$ - 20 000 $mg \cdot L^{-1}$ @ 20°C (Anthony 1979; Verschueren 1983), the highest water solubility of all of the organochlorine compounds (Edwards *et al.* 1982b). It is also readily soluble in most other common organic solvents. Dichloromethane is an excellent solvent for the dissolution of many resins, waxes and fats, and as a result, has many industrial applications. Alone, DCM is essentially non-flammable, yet is highly volatile and exhibits reported vapour pressures of of 43 and 46.5 kPa @ 20°C (Anthony 1979; Verschueren 1983; García-Sánchez *et al.* 1989). Reported boiling point fall within 39.75 and 40.1°C (Budavari *et al.* 1989; Hawley 1977). It has a log octanol\water partition coefficient (log K_{ow}) of 1.25 (WHO 1984) and a Henry's Law constant of 227.9

$Pa \cdot m^3 \cdot mole^{-1}$ @ 25°C (Ashworth *et al.* 1988), indicating a significant tendency for DCM to volatilize from surface waters. Table 2. summarizes these and other physical and chemical properties.

Table 2. Physical and Chemical Properties of Dichloromethane.

Property	Value	Reference
CAS number	75-09-2	Budavari *et al.* (1989)
Chemical Formula	$C \cdot H_2 \cdot Cl_2$	Budavari *et al.* (1989)
Molecular Weight (MW)	84.93	Budavari *et al.* (1989)
Physical State	Volatile liquid @ STP	Hawley (1977)
Colour	Colourless	Hawley (1977)
Odour	Penetrating, ether-like Sweetish	Hawley (1977) Verschueren (1983)
Boiling Point	39.75 °C 39.8 °C 40 °C 40.1 °C	Budavari *et al.* (1989) CCOHS (1987) WHO (1984) Hawley (1977)
Melting Point	-95 °C -96.7 °C	WHO (1984) Anthony (1979)
Density	1.32 $g \cdot mL^{-1}$ @ 20°C 1.33 $g \cdot mL^{-1}$ @ 20°C 1.3255 $g \cdot mL^{-1}$ @ 20°C 1.33479 $g \cdot mL^{-1}$ @ 15°C 1.36174 $g \cdot mL^{-1}$ @ 0°C	CCOHS (1987) WHO (1984) Budavari *et al.* (1989) Budavari *et al.* (1989) Budavari *et al.* (1989)
Diffusivity in Air	9×10^{-5} $m^2 \cdot s^{-1}$	Anthony (1979)
Vapour Pressure	19.6 kPa @ 0 °C 46.5 kPa @ 20 °C 68.1 kPa @ 30 °C 349 mmHg (46.5 kPa) @ 20 °C 500 mmHg (66.6 kPa) @ 30 °C 43 kPa @ 292.5 °K (20°C)	Anthony (1979) Anthony (1979) Anthony (1979) Verschueren (1983) Verschueren (1983) García-Sánchez *et al.* (1989)
Flashpoint	Not flammable as tested by conventional methods	CCOHS (1987)
Surface Tension	28.12 $mN \cdot m^{-1}$ @20 °C	WHO (1984)
Aqueous Solubility	13 200 $mg \cdot L^{-1}$ @ 20°C 20 000 $mg \cdot L^{-1}$ @ 20°C 16 700 $mg \cdot L^{-1}$ @ 25°C 19 400 $mg \cdot L^{-1}$ distilled water @ 23°C 13 600 $mg \cdot L^{-1}$ salt water (30•) @ 20°C	Anthony (1979) Verschueren (1983) Verschueren (1983) Abernethy *et al.* (1986) Abernethy *et al.* (1986)
Octanol/Water Partition Coeff. (log Kow)	1.25	WHO (1984)

Table 2. Physical and chemical properties of methylene chloride (continued).

Property	Value	Reference
Air/Water Partition Coeff.(Henry's Law Constant - $Pa \cdot m^3 \cdot mole^{-1}$)	227.9 @ 25°C	Dilling *et al.* (1977) *
	141.9 @ 10°C	Ashworth *et al.* (1988)
	171.2 @ 15°C	Ashworth *et al.* (1988)
	247.2 @ 20°C	Ashworth *et al.* (1988)
	299.9 @ 25°C	Ashworth *et al.* (1988)
	365.8 @ 30°C	Ashworth *et al.* (1988)
Sorption Coefficient (sludge) ($K = mg\ DCM \cdot g\ dry\ solids^{-1}$)	mixed liquor solids K = 0.06	Dobbs *et al.* (1989)
	primary sludge, K= 0.19	Dobbs *et al.* (1989)
	anaerobically digested sludge, K= 0.08	Dobbs *et al.* (1989)
Odour Threshold	205-307 ppm (713.4-1068.3 $mg \cdot m^{-3}$) in air	CCOHS (1987)
	3.6 ppm ($mg \cdot L^{-1}$) in water	
	5.6 $mg \cdot L^{-1}$ in water	Amoore and Hautala (1983)
		Alexander *et al.* (1982)
Taste Threshold	24 $mg \cdot L^{-1}$ @ 40 °C	Alexander *et al.* (1982)
Conversion Factor for Quantity in Air	1 ppm = 3.47 $mg \cdot m^{-3}$ **	

* Henry's Law constant determined by dividing the reported vapour pressure (Pa) by the water solubility ($moles \cdot m^{-3}$).
** derived from the gas law PV = nRT (101325 $\times 10^{-3}$ x MW/(8.314 x 298))

4.1 Analytical Techniques

The principal methods used for the detection of DCM from any medium involves some form of gas chromatography and spectrophotometry. Table 3. summarizes the techniques and detection limits for analysis of DCM from various matrices.

Table 3. Summary of analytical methods for dichloromethane in varous matrices and their detection limits

Medium	Analytical method	Detection limit	Reference
Air	Gas chromatography (GC) with electron capture detector operated at 250°C	not reported	Cox *et al.* 1976
	Long path infrared absorption using a Fourier transform spectrometer	not reported	Spence *et al.* 1976
	Air samples pumped into cannisters at 15-25 psi. Volatile organics were collected with a cryogenic preconcentration trap and separated with a gas chromatograph, followed by analysis using a flame ionizing detector and electron capture detector, or for specific target compounds, a quadropole mass spectrometer.	≈ 0.1 $\mu g \cdot m^{-3}$	Dann and Wang 1992

Table 3. Summary of analytical methods for dichloromethane in various matrices and their detection limits (continued).

Medium	Analytical method	Detection limit	Reference
Water	DCM from water samples collected into headspace with vacuum distillation with cryogenic trapping of the distillate. Analysis carried out with a GC equipped with a Ni electron capture detector and hydrogen as the carrier gas.	30.0 $ng \cdot L^{-1}$	Comba and Kaiser 1983
	Gas chromatography (GC) using a head space technique. Samples allowed to equilibrate between water and gas phases, samples from head spaces were withdrawn and injected into GC and analysed using a flame ionizing detector at 250°C.	not reported	Chodola *et al.* 1989
	Gas Chromatography using a purge an trap technique with N_2 followed by desorption at 200°C into GC and analysed with a flame ionizing detector at 250°C	0.1 $\mu g \cdot L^{-1}$	Black 1982
	Gas chromatography - isooctane procedure. actived sludge samples purged with helium, DCM trapped and thermally desprbed at 250°C followed by injection directly into GC and analysed with a flame ionizing detector.	not reported	Klečka 1982
	Gas chromatography using a purge and trap technique with an inert gas, traped on a sorbent trap and thermally desorped and analyzed using mass spectrometry.	1.0 $\mu g \cdot L^{-1}$	U.S. EPA 1989a
	High resolution gas chromatography using a purge and trap technique with an inert gas, traped on a sorbent trap and thermally desorped and analyzed using mass spectrometry.	0.03-0.09 $\mu g \cdot L^{-1}$	U.S. EPA 1989b
	Gas chromatography using a purge and trap technique with an inert gas, traped on a sorbent trap and thermally desorped and analysed using a halogen specific detector.	not reported	U.S. EPA 1989c

Table 3. Summary of analytical methods for dichloromethane in various matrices and their detection limits (continued).

Medium	Analytical method	Detection limit	Reference
Wastewater	Gas chromatography using a purge and trap technique with an inert gas, traped on a sorbent trap and thermally desorped and analysed using a halogen specific detector.	0.25 $\mu g \cdot L^{-1}$	U.S. EPA 1982a
	Gas chromatography using a purge and trap techniquewith an inert gas, traped on a sorbent trap and thermally desorped and analysed using mass spectrometry.	2.8 $\mu g \cdot L^{-1}$	U.S. EPA 1982b
Soil	Gas chromatography followed by mass spectrometry	5.0 $\mu g \cdot kg^{-1}$ dry matter	Golder Associates (unpublished) 1989
Soil/Solid Waste	Gas chromatography - purged with an inert gas and trapped on a sorbent trap and desorbed thermally. Analyzed on a halogen specific detector.	5.0 $\mu g \cdot L^{-1}$	U.S. EPA 1986
Sediment	Purged with N^2 and thermally trapped and desorbed at 200°C into a gas chromatograph interfaced with a mass spectrometer.	not reported	Ferrario *et al.* 1985
Tissue	Samples mechanically and ultrasonically disrupted at 4°C , tissue\water homogenate was purged with N_2, volatiles were trapped and thermally desorbed at 200°C into a gas chromatograph interfaced with a mass spectrometer.	not reported	Ferrario *et al.* 1985

5.0 Releases to the Environment

5.1 Uses, Production and Import Levels

Uses

In industry world-wide, DCM is primarily used as a paint remover, as a solvent for degreasing, as a blowing agent in foam production, for photoresist stripping operations, and in film processing (WHO 1984; Edwards *et al.* 1982b; U.S.EPA 1985). It is also used as an extracting solvent for heat sensitive fats, edible fats, cocoa, and butter (WHO 1984) and in the cosmetics industry as a component of the aerosol propellant systems in hair spray formulations (Mary Ann Liebert Inc. 1988). Dichloromethane is also used in the manufacture of pesticides and is a registered insecticidal fumigant for stored grains (Rajendran and Mathu 1981, WHO 1984). The characteristically low flammability make it a solvent of choice for a wide variety of applications including use as a pharmaceutical, as well as a component in the manufacture of synthetic fibres, as a component in fire-extinguishing products, as a coolant and refrigerant , and as a thinning agent in adhesives. In addition, it is used as a laboratory solvent or reagent, as a component of coating systems (eg. paints), in plastics processing and as a component in mould release agents (Anthony 1979, U.S. EPA 1985). It is also used as an effective extraction solvent for spices and beer hops and in the decaffeination of coffee (Anthony 1979).

In paint stripping formulations, as a commercial or household product, DCM is the primary ingredient and acts to penetrate, soften or dissolve the paint film or coating before removal from the painted surface (Pandullo *et al.* 1985). As a foam blowing agent, DCM is used as an auxiliary blowing agent inducing the formation of gaseous foam cells and thereby providing a soft flexible urethane foam product (Pandullo *et al.* 1985). DCM is used in aerosols which are primarily for direct consumer use, i.e. for finishing and coating surfaces, hair sprays, cleaners, room deodorants, and various other household and personal products (Pandullo *et al.* 1985).

In Canada, between 1977 and 1990, the mean net domestic usage, essentially the same as net supply, was 10.99 $kt \cdot yr^{-1}$ (S.D.=1.39) (Environment Canada 1990) compared to the 227 kt being used in the U.S. in both 1985 and 1988 (Chemical Marketing Reporter 1986, 1989). In Canada, industrial surveys between 1977 and 1990 revealed that most of the DCM (56.3-69.6%) is being utilized for the removal of paint and for other solvent applications, with a slight trend for a decrease in use in this area over the 14 year period. Use of DCM as a blowing agent in the manufacture of urethane foams accounted for the next greatest application, involving 16 to 29.7% of the net supply with the most significant increase in this market segment occurring between 1977 and 1984. Aerosol propellants account for the third major market for DCM, explaining 8.7 to 11.8% of the

consumption over the 14 year time period (Environment Canada 1990; CIS 1990). All markets except urethane products experienced growth between 1977 and 1985. In 1994, it is expected that total Canadian supplies from importation will reach 9.7 kt, with 5.8 kt expected to go towards paint removal and solvent applications, 2.9 kt to be used in the manufacture of urethane foams, 0.7 kt to be used for propellants and 0.3 kt to be used for other miscellaneous applications (CIS 1990). Table 4 shows the consumption pattern for dichloromethane in Canada for 1985 to 1990. In the United States, information available on the consumption patterns of DCM indicate that it is mostly used in paint stripping operations (23-30%) and as an aerosol propellants (18-30%) (Chemical Marketing Reporter 1986 & 1989).

Table 4. The annual consumption patterns for dichloromethane in Canada (CIS 1990).

	1985	1986	1987	1988	1989	1990
DOMESTIC CONSUMPTION (kt):						
Paint remover/solvent	7.9	7.8	5.8	5.7	5.5	5.4
Urethane foams	2.9	2.7	2.8	2.9	2.7	2.6
Aerosol propellants	1.5	1.3	1.1	0.9	0.8	0.8
Miscellaneous	0.9	0.6	0.6	0.5	0.2	0.2
Net domestic usage	13.2	12.4	10.3	10.0	9.2	9.0

Production

At present, Canada does not produce or export DCM. The major distributor and importer is Dow Chemical Canada (CIS 1990). Table 5 shows the major Canadian buyers of DCM and its application. In the United States, production levels have been reported to have increased by 11% each year from 1950 to 1978 (NAS 1978); however, between 1979 and 1988 growth in production has decreased on average, 2.7 % each year and is expected to continue to decrease by 3-5% through 1993 (Chemical Marketing Reporter 1989). The recent decline in the production of DCM is attributed to the U.S. government cancer labelling requirement on all consumer goods containing methylene chloride. Present capacity of existing U.S. producers of DCM are shown in Table 6.

Table 5. Major buyers of dichloromethane in Canada (CIS 1990)

Company	End-use	Company	End-use
A&C American Chemical, Montreal	distributor	Halltech, West Hill, Ont.	distributor
A&K Petro-chem Industries, Toronto	distributor	Harcros Chemicals Canada, Toronto, Ont.	distributor
A-Z Sponge & Foam Products, New Westminster, B.C.	urethane foam	Hoechst Canada, Montreal, Que,	distributor

Table 5. Major buyers of dichloromethane in Canada (CIS 1990)

Company	End-use	Company	End-use
Aerosol Laboratories, St-Hubert, Que	aerosols	Hoover Chemical, London, Ont.	urethane foam
Alloycraft, Toronto, Ont.	distributor	Kingsley and Kieth, Etobicoke, Que.	distributor
Amnicon Corp, Downsview, Ont.	urethane foam	Lewrason's Chemicals , London, Ont.	distributor
Apco Industries, Toronto, Ont.	distributor	Lear Seiglar Industries, Ajax, Ont.	urethane foam
Ashland Chemical, Mississauga, Ont.	distributor	MUSAC Decaf Inc., Valleyfield, Que	caffeine exttraction
Axxon, Chemicals, Mississauga, Ont.	distributor	Magna, Concord, Ont.,	urethane foam
Boyle Midway Canada, Toronto, Ont.	aerosols	Reeves Bros, Tononto, Ont.	urethane foam
CCL Industries, Toronto, Ont.	aerosols	Shefford Chemicals, Granby, Que.	distributor
Canada Colors & Chemicals, Toronto, Ont.	distributor	Unilite Industries, Paris, Ont.	urethane foam
C-I-L, Willowdale, Ont.	distributor	Van Waters & Rogers, Vancouver, B.C.	distributor
Coldstream Poducts of Canada, Winnipeg, Man.	urethane foam	Waterville TG, Waterville, Que.	urethane foam
Cromac Chemical, Toronto, Ont.	paint remover	Woodbridge Foam, Woodbridge, Ont.	urethane foam
Curtis-Harris Industries, Coburg, Ont.	urethane foam		
Davidson Rubber, Port Hope, Ont.	blowing agent		
Dow Chemical Canada, Sarnia	distributor		

Table 6. Production of dichloromethane in the U.S.A., 1989 (Chemical Marketing Reporter 1989).

Producer	Annual Capacity (kt)
Dow, Freeport, Tex	49.9
Dow, Plaquermine, La	54.4
LCP, Moundsville, W. Va	23.6
Occidental, Belle, W. Va	40.8
Vulcan, Geismar, La	36.3
Vulcan, Wichita, Kan	59.0

Dichloromethane is made commercially from the chlorination of methyl chloride obtained from the reaction of methanol and hydrogen chloride vapours with a catalyst such as alumina gel, zinc chloride on pumice, cuprous chloride, or activated carbon at 340-350 °C. A less common method of manufacture involves the direct chlorination of methane at high temperatures (485-510°C) producing dichloromethane, chloroform, and carbon tetrachloride as co-products (Anthony 1979, U.S. EPA 1985). Dichloromethane can also be produced in

the liquid phase at 100 to 150°C by refluxing and distilling an aqueous mixture containing methanol, hydrogen chloride, and zinc chloride (Anthony 1979).

5.2 Sources

5.2.1 Natural Releases

There are no known natural sources of DCM (NAS 1978; Singh *et al.* 1981; Edwards *et al.* 1982)

5.2.2 Releases Related to Human Activities

Because of the nature of the applications for DCM (see section 5.1), it may be expected that up to 100% of that produced, i.e. 9.0 kt, could be lost to the environment (Environment Canada 1990). In the United States it has been estimated that approximately 85% (193 kt) of the total DCM consumed enters the environment though dispersive use, largely by evaporation to the atmosphere. Most of the losses during the production of DCM occur through process vents, equipment leaks, equipment openings, relief devices, storage tanks, secondary sources, and truck, rail-car, drum, or barge loading (U.S. EPA 1985). From the information currently available, it is apparent that substantial quantities of DCM are released into the environment; however, accurate estimates of releases of DCM into the Canadian environment are not presently available. Quantitative estimates of dichloromethane releases into the Canadian environment are limited to loadings from industrial effluents. In 1983, effluents from several industries including automotive painting operations and steel manufacturing, and from sewage treatment plants were reported to have discharged dichloromethane into the Detroit River, Ontario, at rates of 0.03 to 0.31 kg/day (Comba and Kaiser, 1985). On the Canadian side of the St. Clair river, Ontario, 18 industrial dischargers are estimated to release 1.7 billion litres of effluent and cooling water on a daily basis, where effluent levels of dichloromethane were measured as high as 160 $\mu g/L^{-1}$ (DOE\MOE 1986).

Data on the sources of dichloromethane to the Canadian environment is limited, therefore estimates from other industrialized countries may be of qualitative value. In the United States, the Toxics Release Inventory estimated that in 1989 30.7 kt of dichloromethane were released into the air, 0.10 kt into water, 0.75 kt were injected into underground wells and 0.67 kt were sent to U.S. landfills and/or other treatment/disposal facilities (TRI 1992). The total release of dichloromethane into the United States environment in 1989 was estimated at 45.4 kt (TRI 1992). The WHO (1984) estimated that world-wide releases of DCM into the

environment accounted for 80% of the world production, which in 1980 was 570 kt. Global emmisions of DCM to the troposphere have been estimated at 500 $kt \cdot yr^{-1}$ (Edwards *et al.* 1982a,b)

Although not as great as atmospheric releases, the releases of DCM to water sources are also significant (WHO 1984). Significant levels of DCM enter the aqueous environment through municipal and industrial activities, including dumping of contaminated solid waste, where DCM is then subject to leaching into groundwater (Patterson *et al.* 1985; Lesage et al. 1990; King and Sherbin 1986; McBride *et al.* 1989; Jackson *et al.* 1985, 1991). Aerial spray applications of contaminated wastewater to the land (i.e. hardwood forests) is also practiced as a remediation procedure (McBride *et al.* 1989). A water effuent sample from a water treatment plant in the vacinity of a chemical waste disposal site near Ville Mercier, Que., was reported to contain DCM at a level of 337 $\mu g \cdot L^{-1}$ (Pakdel *et al.* 1992). Based on recent surveys of the ground water down gradient from over 700 waste sites in Germany and the U.S., DCM was one of the most frequently detected contaminants, (No. 1 in the U.S. and No. 11 in W. Germany) with a mean concentration in German waters at over 38 $mg \cdot L^{-1}$ and a maximum level close to 500 $mg \cdot L^{-1}$ (Kerndorff *et al.* 1992). These surveys indicate the ubiquitous nature of DCM at such sites; and although comparable Canadian data do not exist, it can be expected that a similar scenario would exist in Canada.

Besides groundwater leachate, levels of DCM may enter the environment through waste water effluent, entering directly to a body of water from various industries, such as chemical manufacturing operations (Kaiser and Comba 1986; King and Sherbin 1986) and from by-products of pulp and paper mill operations (Kringstad and Lindstrom 1984; Wallin and Condren 1981; Turoski *et al.* 1983). Methods of removal from water sources can, in many cases, lead to subsequent releases to the atmosphere, particularly through the use of such remediation practices as air stripping. Crume *et al.* (1990) recently examined the risk from aeration of groundwater and determined an expected emission rate of 4.2×10^{-4} g $DCM \cdot s^{-1}$ from an estimated groundwater DCM concentration of 3.3 $\mu g \cdot L^{-1}$.

6.0 Environmental Fate and Levels

When a chemical such as DCM is released to the environment it can enter into and move between the five major environmental compartments of air, water, soil, plants and animals. Once in these compartments, DCM may be enacted upon by many mechanisms by which it can break down, move between compartments or be absorbed or adsorbed to elements within the compartments. In the following section, the environmental fate of DCM is surveyed through an examination of the ability of DCM to volatilize, undergo photolysis, oxidation and hydrolysis; examine its sorptive capacity, its ability to biodegrad, its general mobility and its capacity to bioaccumulate and biomagnify. Measured levels of DCM in the environmental compartments of air or the atmosphere, surface water, groundwater and raw and treated waters, soils, sediments as well as biota are also presented in this section.

6.1 Transport and Transformation

6.1.1 Volatilization

Due to its high vapour pressure and Henry's Law constant dichloromethane is expected to volatilitze rapidly from aqueous media. It is important to note that evaporative removal from water is also dependant on a number of factors including the molecular diameter, molecular weight, the receiving water body characteristics, as well as the properties of the atmosphere above the water (Gowda *et al.* 1985). It can be expected that the rate of transport from surface waters will vary from site to site. Differences in reported rates of evaporization reflect this. For example, Dilling *et al.* (1975 and 1977), determined a half-life of approximately 25 min. for evaporation of DCM at 1.0 ppm ($mg \cdot L^{-1}$) from an aqueous solution, at 25°C, having a solution depth of 6.5 cm, and being continually stirred at 200 rpm. Under conditions of less turbulent waters (stirred for 15 sec every 5 min.) the half-life for evaporation increased by 3.6 fold, to over 90 minutes. These results can be compared to a calculated half-life of 3 h for evaporation of DCM from water one meter deep (Thomas 1982). The influence of the water depth and area of exposed surface is evident from a study done by Chodola *et al.* (1989), where DCM at 0.25, 0.5 and 0.75% of its solubility, volatilized at a rapid rate when dissolved in deionized stagnant water (22°C) under constant air velocity of 2.8 $m \cdot s^{-1}$. The volatilization rates were directly dependant on the surface area to volume ratio of the solution, with a reported correlation coefficient (r^2) of 0.913 and a volatilization rate constant (k') of 0.003 $l \cdot h^{-1}$. The Black River estuary, Maryland, U.S.A.,was found to contain DCM as high as 512 nM (43.5 $\mu g \cdot L^{-1}$) immediately down stream from a sewage treatment plant. Levels were observed to dissipate within 4 km under spring conditions and within 8 km under full ice in the winter. Although the the majority of loss was attributed to volatilization, degenerative processes, involving chemical or

biological mechanisms, were also believed to be important, especially during periods of full ice cover (Helz and Hsu 1978).

The first 10-20 km of the atmosphere, referred to as the tropospheric layer, provides an important sink for volatilized DCM. The annual net domestic use of dichloromethane in Canada (1990) was estimated to be 9.0 kt (Environment Canada, 1990). If it is assumed that 100% of this amount was lost to the troposphere, 203 t could have potentially entered the stratosphere. This amount is based on the estimate that 98% of the dichloromethane which entered the troposphere would undergo photooxidation, thus, approximately 2.0-2.5% would enter the stratosphere (Singh *et al.* 1979; Edwards *et al.* 1982a). Global emission of dichloromethane to the troposphere, estimated at 500 $kt \cdot yr^{-1}$, has the potential to return to earth, via precipitation, at an estimated, relatively low rate of 400 $t \cdot yr^{-1}$ (Edwards *et al.* 1982ab). Precipitation can be an important mechanism by which airborne pollutants are removed from the atmosphere and in order to better test the reliability of the predictions from washout models, an experiment was set up examining the ability of water droplets to scavenge DCM. The ability of water droplets to absorb DCM vapour was clearly established and a direct relationship between the partial pressure of DCM and the measured DCM concentration in the water droplets was found (Lopez *et al.* 1989).

6.1.2 Photolysis, Oxidation and Hydrolysis

Photooxidation and photolysis at sea level is expected to be minimal; howver, in the upper troposphere, photooxidation is expected to be an important degradative process for DCM. Photooxidation occurs as a result of interaction with photochemically generated hydroxyl radicals. The estimated first order 'lifetime' ($\tau_i = 1 \cdot k_i^{-1}$) for DCM under tropospheric conditions is estimated to be 109 d based on 1×10^6 OH molecules $\cdot cm^{-3}$ in the troposphere and from the determined hydroxyl radical oxidation rate for methane (Cox *et al.* 1976). Similarly, the tropospheric 'lifetime' for DCM based on hydroxyl radical reaction rates was calculated to be 1.0 yr, assuming an average tropospheric temperature of 265°K and a global average concentration of hydroxyl radicals of 4×10^5 molecules$\cdot mL^{-1}$ (Edwards *et al.* 1982b). Singh *et al.* (1979) calculated a mean tropospheric residence time of 1.0 yr for dichloromethane subjected to hydroxyl radical attack. It is important to note that the average hydroxyl radical concentration in the troposphere may vary diurnally, seasonally and geographically. The hydroxyl radical (OH) concentration is generally lower during the winter months and therefore the rate loss of DCM would correspondingly be much reduced in a cold winter climate, such as that which occurs in Canada (Singh *et al.* 1981; Bunce 1992). Model calculations were conducted examining the rate of degradation of DCM at three different latitudes in Canada (Bunce 1992). The rate loss of DCM was determined to be proportional to the tropospheric concentration of OH, which is in

turn, dependent on the intensity of the available sunlight. The model estimates the hydroxyl radical concentration for each month of the year over the centers of Windsor, Ont. (lat. 42° N), Edmonton, Alta. (lat. 53° N), and Resolute Bay, N.W.T. (lat. 74° N). Table 7 shows the range in the maximum calculated hydroxyl radical concentrations for four of the months, involving the three locations and their respective estimated half lives. Even in the summer, dichloromethane has a tropospheric half-life of several weeks which is long enough to allow for substantial migration away from the point of emission long before a chemical transformation could occur (Bunce 1992). As such, at these sites, very little is expected to migrate or persist in the stratosphere and DCM is, therefore, not likely to contribute to ozone depletion at these latitudes. Migration of dichloromethane from the troposphere to the stratosphere was estimated to take between 5 ane 10 years (Rowland, 1990)

Table 7. The estimated tropospheric half-life (days) for dichloromethane at three Canadian latitudes (Bunce 1992).

Time of the Year	Windsor, Ont. (lat. 42° N)	Edmonton, Alta. (lat. 53° N)	Resolute Bay, NWT. (lat. 74° N)
March 21	73	140	1100
June 21	31	37	61
September 21	67	120	810
December 21	410	2600	∞ [a]

a No daylight, hence no chemical reactivity.

Most of the DCM entering the troposphere is expected to be destroyed there, with only a small percentage being available for diffusion upward into the stratosphere. An estimated 2.0% (Singh *et al.* 1979) and 2.5 % (Edwards *et al.* 1982a) of original tropospheric DCM levels would be available to enter the stratosphere. The stratosphere is the atmospheric region bounded below by the troposphere and above by the edge of the mesosphere, the latter being approximately 55 km from the earth's surface. At this altitude, high intensity UV radiation dramatically increases the potential for photolysis (NAS 1978). Under simulated high altitude (stratospheric) conditions using light of high energy (~254 nm) and very high intensity (30-120 times that of sunlight ~40 km from the earth's surface), 95% of DCM was observed to photodegrade in 10 minutes in dry air with no NO_2 (reaction products not reported). Based on these rates, it is estimated that under natural, high altitude levels of irradiation, 90% of DCM would photoreact

$$Cl_2 + h\upsilon = 2Cl$$

$$Cl + CH_2Cl_2 = CHCl_2 + HCl$$

$$CHCl_2 + O_2 = CHCl_2O_2$$

$$CHCl_2O_2 = ClO + HCOCl$$

Figure 2. Reactants and products of atmospheric photooxidation of dichloromethane (Spence 1976).

within 5-20 h, suggesting a very low potential for accumulation of DCM in the high atmosphere (Terfertiller and Dilling 1972).

Dilling *et al.* (1976) examined the photooxidation rate of DCM under simulated atmospheric conditions of artificial UV light (290 nm), 35% relative humidity, ultra high purity air (20% O_2, 80% N_2), and in the presence of either nitric oxide or nitrogen dioxide. A half life of >250 h was determined based on the measured DCM photodecomposition rates of <5% in 21 h and <5% in 7 h in atmospheres containing nitric oxide and nitrogen dioxide, respectively. Caution is recommended in using this half-life value as extrapolation from the determined values may involve substantial error. In an attempt to examine the stability of DCM to photooxidation a study was designed to estimate the amount of oxidant generated (e.g. ozone). The study was conducted in the presence of DCM under simulated sea level atmospheric conditions of UV light (>290 nm), nitrogen dioxide, and water vapour in air at 24-25°C for 15 h in a small reactor (Dilling *et al.* 1982). Under these conditions essentially no oxidants were formed and levels of DCM remained relatively constant; however, based on the above estimated half life, little or no change would be expected within the 15 h allowed for the experiment.

An examination of the products of photooxidation of DCM (20 ppm) under an atmosphere of dry air, 5 ppm Cl_2 and high intensity UV irradiation revealed the production of CO_2 (12 ppm) and CO (5 ppm) as the major carbon containing products, but also $COCl_2$ (2 ppm) and HCl (38 ppm) (Spence *et al.* 1976) (see Figure 2.). It is expected that the $COCl_2$ will react further with free radicals or absorb ultraviolet sunlight, with all chlorine atoms ending up as HCl. Production of CO in this process is not expected to significantly increase the natural levels; however, the increase in production of HCl from DCM is expected to be significant considering the large supply of volatile chlorine that DCM supplies (Edwards *et al.* 1982b). Dilling and Terfertiller (1982), reported products from the photolysis of 538 mg $DCM \cdot m^{-3}$ in a continuous flow reactor simulating high atmospheric conditions of 25°C dry air and UV light (λ = 254 nm) to be 8% $HClO_3$, 9% HCl, 16% Cl_2 and ≥30% $HClO_4$.

Methylene chloride in aqueous solutions does not readily undergo photooxidation, photolysis or hydrolysis. Dichloromethane in purified water, at 1 or 10 $mg \cdot L^{-1}$ exposed to UV light (max. emission at 360 nm) for 1, 2, or 5 days at 22 °C, did not undergo significant photolysis relative to the dark controls (Chodola *et al.* 1989). Similarly, Dilling *et al.* (1975) studied the photolysis activity of 1 ppm DCM in an aqueous solution contained in sealed vials, exposed to either sunlight or darkness, over a period of one year, with a range of temperatures over this period approximately falling between -20° to +40°C. No significant difference in reactivities was observed between vials exposed to darkness (0.69 ppm remaining) or light (0.64 ppm remaining). Any degradation which had occurred was assumed to be due to hydrolysis from which a half-life of 18 months was estimated. No products were identified and pH was not measured. Radding *et al.* (1977) and Mabey and

Mill (1978) reported a calculated half-life of 704 years for the hydrolysis of dichloromethane in water at a temperature of 25°C and a pH of 7. The rates of hydrolysis of DCM in aqueous solutions were found to be significantly dependent on the pH. Hydrolysis of DCM in the dark at a temperature of 4°C (control) or 50°C for a period of 7 days was notably, but not statistically elevated when evaluated at pH 9.2 (9 and 11% change). No potential for hydrolysis was observed when analyzed at pH 4.0 (Chodola *et al.* 1989). Although there are some differences in reported rates of hydrolysis, it is clear that under environmentally relevant conditions of temperature and pH, hydrolysis is not expected to contribute significantly to the degradation of DCM in aquatic ecosystems (Chodola *et al.* 1989).

6.1.3 Sorption

Because DCM has a relatively high water solubility and vapour pressure, and a low octanol-water partition coefficient, DCM is expected to be very mobile in soils and sediments and not expected to accumulate, to any great extent under normal conditions.

Studies of the adsorptive properties of DCM have been conducted in a variety of soil media. Dilling *et al.* (1975) reported differences in extent of adsorption between the soil types between granular bentonite clay, dry dolomite limestone, Ottawa silica sand, and peat moss. Ottawa silica sand and dolomitic limestone showed little or no evidence of adsorption of DCM; however, peatmoss, and bentonite clay, examined in a closed system, exhibited notable levels of adsorption (peat moss - 40% adsorption in 10 minutes; 375 ppm clay - 10% adsorbed in 10 minutes; 750 ppm clay - 22% adsorption in 30 minutes. In a study designed to quantify the effects of water content (0.3 to 0.75% by weight for sand and 0.4 to 1.25% for silt-clay) and temperature (4 - 40°C) on equilibrium distribution of organic pollutants in unsaturated Korean soil, Koo *et al.* (1990) showed that as the soil water content increased, the K_{eff} value for DCM decreased (K_{eff}=distribution ratio of pollutants between wet soil as the stationary phase and air as the mobile phase). Similarly, as the temperature increased the K_{eff} values also decreased. Therefore, in wetter and warmer soil, DCM is less likely to be adsorbed. From this, it is apparent that the distribution and transportation of DCM in unsaturated soil is highly dependent on the moisture level and temperature (Koo *et al.* 1990).

Dobbs *et al.* (1989) carried out a study examining the sorption of noxious organic compounds on wastewater solids taken from industrial/domestic wastewater treatment plants from the vicinity of Cincinnati, OH, U.S.A. Dichloromethane adsorbed to mixed liquor solids, primary sludge and anaerobically digested sludge at relatively low levels, reporting sorption coefficients (K) of 0.06, 0.19, and 0.08, respectively, where K equals the concentration of DCM (mg) per gram of dry solids with an equilibrium concentration for DCM equalling 1.0

$mg \cdot L^{-1}$. An estimate of the adsorptive capacity of DCM to soil organic carbon (K_{oc}) is 18.8, a relatively low value determined through the following formula:

$$\log (K_{oc}) = 3.64\text{-}0.55 (\log WS) \quad \text{(Kenaga 1980)}$$

where the water solubility (WS) is taken as 20 000 $mg \cdot L^{-1}$ at 20°C (Verschueren 1983).

6.1.4 Biodegradation

There are numerous studies that report and describe the biological degradation of DCM activated sludge environments. In a bench scale experiment using a continuous flow activated sludge reactor, Stover and Kincannon (1983) reported 99.5% of DCM was degraded by aerobic bateria in 48-h at an initial concentration of 180 $mg \cdot L^{-1}$, and 99.7% removal after 6 days. Rittmann and McCarty (1980) reported 100% degradation of DCM at 1-25 $mg \cdot L^{-1}$ within 20 - 100 h, using sewage effluent bacteria as an inoculant in an aerobic batch suspended fixed film growth experiment. Davis *et al.* (1981) used a microbial population consisting of *Acinetobacter*, *Alcaligenes*, *Flavobacterium*, *Pseudomonas* and a yeast species (*Rhodotorula*) to evaluate the rate of aerobic biodegradation of DCM an aqueous minimal glucose medium at 28°C. Under these conditions DCM disappeared from the minimal aqueous culture media rapidly, with only 4 $mg \cdot L^{-1}$ of the original 50 $mg \cdot L^{-1}$ (92%) remaining after 6 h. No metabolites were detected using GC-MS analysis. Tabak *et al.* (1981) reported 100% aerobic degradation of 5 and 10 $mg \cdot L^{-1}$ of aqueous DCM within 7-d in a static-culture flask in darkness at 25°C, using settled domestic waste water as microbial inoculum. Similarly Klecka (1982) found that DCM-acclimated sludge was able to degrade DCM rapidly to carbon dioxide and chloride, under aerobic conditions. Levels of DCM at 1, 10, and 100 $mg \cdot L^{-1}$ were degraded at 0.14, 2.3 and 7.4 $mg \cdot h^{-1} \cdot g^{-1}$ of mixed liquor suspended solids, respectively. In this same study, the application of a model revealed the rate of biodegradation to be approximately 12 times greater than the rate of volatilization. Therefore, it can be expected that in activated sludge system, which is continuously exposed to DCM, the biodegradative process would be the predominant fate process for this compound.

Biodegradation of synthetic wastewater containing 120 mM DCM (10.2 $g \cdot L^{-1}$) was carried out under aerobic conditions using three DCM degrading bacterial strains. The bioreactor used activated charcoal and sand as the support material within the aqueous minimal medium under controlled environmental conditions. The maximum reported degradation rates were 1.0 and 1.6 $g \cdot L^{-1} \cdot h^{-1}$ for charcoal and sand, respectively. Sand was the better support material because it was stable, indifferent to abrasion and allowed biofilm thickness to be controlled and reached a degradation efficiency of 99.9%, as measured on a per hour basis (Gälli 1987).

At a concentration of 100 µM DCM (8.49 $mg \cdot L^{-1}$), steady-state growth occured in the aerobic, motile bacteria identified as DM1. The highest degradation rate observed for this microorganism, was reported as a release of 0.53 $g \cdot L^{-1} \cdot h^{-1}$ of Cl^- from the closed growth flasks (Brunner *et al.* 1980). A proposed mechanism was suggested for the dehalogenation of DCM by DM1, which could apply to other common strains of bacteria. The process was believed to involve the activity of a halidohydrolase substituting a hydroxyl group for one chlorine atom from DCM. Monochloromethanol, the presumptive intermediate would then spontaneously decompose to formaldehyde (Brunner *et al.* 1980).

Lincoln fine sand collected at 15-23 cm from the soil surface, in the vicinity of Ada, OK, U.S.A., served as the solid portion of the experimental medium and the source of microbiota for the examination of the biodegradation of DCM. The soil was mixed with an aqueous, buffered, minimal salt medium which was exposed to an atmosphere of 4% CH_4 for 6 weeks prior to and during the experiment. Six days after the addition of DCM (~275 $\mu g \cdot L^{-1}$), 98% of it had been degraded; however, soil which did not receive the prior exposure to CH_4 removed only 43% after 6 days. Prior enrichment with CH_4 was able to stimulate the methane-utilizing bacteria and enhance the removal of DCM (Henson *et al.* 1988).

The ability of DCM to biodegrade in soils was recently examined under a variety of conditions and soil types. Davis and Madsen (1991) examined three surface soils (5-35 cm), a sandy soil, a sandy clay loam, and a sandy loam soil as well as a subsurface clay soil (from 1-2 m) under aerobic conditions. In all of the soils, the degradation of 0.5 ppm ($mg \cdot L^{-1}$) DCM could be attributed to biological activity, as little or no loss of the parent compound was observed in the control microcosms which had been previously chemosterilized by the addition of formaldehyde (2% w/w). For sandy loam soil > 80% of DCM degraded within 3 wks, with >75% of the degradation product as CO_2; 80% of DCM was degraded from sandy clay loam after a period of one month with only 14% of the total metabolism of DCM appearing as CO_2; in sandy soil, degradation was slower, as >75% of the DCM was degraded after 139 days with CO_2 production accounting for 17% of the mineralization and occurring only within the first two weeks. For these surface soils, degradation proceeded without a lag period; in contrast, degradation from the subsurface clay soil involved a 50-d lag period followed by rapid and complete degradation of DCM over a period of 2 weeks. In this case, mineralization as CO_2 accounted for only 13% of the total degradation product. The lag period is believed to be due to the reduced initial biomass levels in this soil. Anaerobic biodegradation of DCM (5 $mg \cdot L^{-1}$) in sandy loam soil occurred with a lag period of 70-d with degradation proceeding rapidly to completion over the succeeding 36-d. The time required for the disappearance of 50% of DCM increased directly with the DCM concentration available and was attributable to a noxious effect from DCM at higher doses (5 and 50 $mg \cdot L^{-1}$). Any observed variability in degradation rates between soils was expected to be the result of differences in the number and type of soil microorganisms associating with each soil type. Pre-exposure of the sandy loam soil microorganisms to DCM at 0.5 ppm

($mg \cdot L^{-1}$) for 27 days (time for 100% degradation), followed by re-spiking with 5 ppm ($mg \cdot L^{-1}$) resulted in a substantial increase in the biodegradation rate. In non-adapted soils, 40% of the original 5 ppm ($mg \cdot L^{-1}$) DCM remained in the soil after 219 d and in the adapted soil 100% was degraded in 196 days. This enhancement was accentuated when an second addition of 5 ppm DCM was added after 196 d, and in this case, approximately 90% was degraded after 31 d (Davis and Madsen 1991).

From these studies it is evident that DCM is able to undergo significant levels of biodegradation within a variety of terrestrial and aquatic environments. It is also evident that biodegradation is an important process in the removal of DCM from these environments. However, it should be kept in mind that Canadian climates can be harsh and both soils and water bodies are near, or below, freezing temperatures for much of the year. The low temperatures can slow the biodegradation process dramatically.

The efficient degradation of DCM by anaerobic bacteria has been observed in studies which reflect waste water treatment facilities. Bhattacharya and Parkin (1988) examined the toxic effect of DCM on the anaerobic process in wastewater treatment operations. By using a Chemostat and through continuous additions of DCM, it was shown that, although DCM was observed to inhibit bacterial activity, an estimated 65-70% of the added DCM was biodegraded during this 40-d process. Other available wastewater treatment studies focused on the ability of DCM to inhibit biological activity in sewage sludge, which did not effectively measure the ability of DCM to be biodegraded (Hayes and Bailey 1977; Stuckey *et al.* 1980; Vargas and Ahlert 1987; Bhattacharya and Parkin 1988) (see section 11.2.1).

6.1.5 Mobility

In an investigation of the behaviour of DCM in aqueous environments, the mass flux of DCM from submerged pools into surrounding quiescent deionized water was examined (Chodola *et al.* 1989). In this study the concentrations of DCM which had moved from 600 mL submerged pools into 4 L solutions of water varied over a period of 24 days from 100 to 1250 $mg \cdot L^{-1}$ with little or no consistent pattern. As a result, no conclusions could be drawn from this study. Nonetheless, because the water solubility of DCM is relatively high (13 200 - 20 000 $mg \cdot L^{-1}$), DCM can be expected to be highly mobile in aqueous environments, having the ability to move with soil and water runoff and leach through soils and sediment to groundwater. Reported environmental levels from both surface and groundwater attest to this (see section 6.3.2 and 6.3.3).

6.1.6 Summary of Fate Processes

From the available information, it is clear that DCM can persist in the environment for extended periods, or it may be removed quite rapidly, depending on a variety of circumstances. The processes of hydrolysis, oxidation, photolysis and adsorption under natural systems are not expected to reduce DCM concentrations to any significant degree. The half-lives for these processes are on the order of several months to years. Because DCM has a relatively high water solubility, it is expected that it will have the ability to move with soil and water runoff and leach through soils and sediment. However, volatilization and biodegradation appear to have a much greater effect in reducing DCM concentrations in soil, sediment and water environments.

Table 8. presents a summary of the environmental fate processes that have been described for DCM.

Table 8. Summary of the fate processes for dichloromethane.

Media\Matrix	Process	Dissipation/time	References
Atmosphere	Photolysis	N.I.	
		109 d - lifetime	Cox *et al.* (1976)
		1.0 yr - lifetime	Edwards *et al.* (1982b)
		255 d - $t_{1/2}$	Singh *et al.* (1979)
		Summer $t_{1/2}$:	Bunce (1992)
		Windsor - 31 d	
		Edmonton - 37 d	
		Resolute Bay - 61 d	
		N.Q.	Spence *et al.* (1976)
		N.Q.	Dilliing *et al.* (1975)
		N.Q.	NAS (1978)
		N.Q.	Terferitiller and Dilling (1972)
		N.Q.	Dilliing and Terfertiller (1982)
Water	Photolysis	>250 h - $t_{1/2}$	Dilling *et al.* (1975)
		N.Q.	Chodola *et al.* (1989)
	Photooxidation	N.Q.	Dilling *et al.* (1975)
	Hydrolysis	18 mos. - $t_{1/2}$	Dilling *et al.* (1975)
		704 yrs. - $t_{1/2}$	Mabey and Mill (1978)
		N.Q.	Chodola *et al.* (1989)
	Volatilization	25-90 min. - $t_{1/2}$	Dilling *et al.* (1975, 1977)
		3 h - $t_{1/2}$	Thomas (1982)
		0.003 $l \cdot h^{-1}$ - rate constant (k')	Chodola *et al.* (1989)
	Biodegradation	100% of 5 and 10 $mg \cdot L^{-1}$ (waste water) within 7-d	Tabak *et al* (1981)
		100% of 1-25 $mg \cdot L^{-1}$ in 20-100 h	Rittmann and McCarty (1980)
		92% of 50 $mg \cdot L^{-1}$ in 6-h	Davis *et al.* (1981)

Media\Matrix	Process	Dissipation/time	References
Soils and Sediments and Sludge	Adsorption	Sorption coefficients (K): • mixed liquor solids - 0.06 • primary sludge - 0.19 • anaerobically digested sludge - 0.08	Dobbs *et al.* (1989)
	Aerobic biodegradation	mixed liquor suspended solids degradation rates: 1 $mg \cdot L^{-1} \rightarrow 0.14\ mg \cdot h^{-1} \cdot g^{-1}$ 10 $mg \cdot L^{-1} \rightarrow 2.3\ mg \cdot h^{-1} \cdot g^{-1}$ 100 $mg \cdot L^{-1} \rightarrow 7.4\ mg \cdot h^{-1} \cdot g^{-1}$	Klecka (1982)
		95% of 180 $mg \cdot L^{-1}$ in 48-h (sludge reactor)	Stover and Kincannon (1983)
		43% degradation of ~ 275 $\mu g \cdot L^{-1}$ in 6 d (Lincoln fine sand)	Henson *et al.* (1988)
		Surface soils (0.5 mg $DCM \cdot L^{-1}$): • Sandy loam: >80% degraded in 3 wks • Sandy clay loam: >80% degraded in 1 mo. • Sandy soil: >75% degraded in 139 d.	Davis and Madeson (1991)
		Subsurface soils (0.5 mg $DCM \cdot L^{-1}$): • clay: 50 day lag period; 100% degraded in following 2 wks.	
	Anaerobic biodegradation	Sandy loam soil (5.0 mg $DCM \cdot L^{-1}$): • 70 d lag period; 100% degraded in following 36 d.	Davis and Madeson (1991)
		65-70% biodegraded from 10-80 $mg \cdot L^{-1}$ over 45 d.	Bhattacharya and Parkin (1988)
		N.Q.	Hayes and Bailey (1977)
		N.Q.	Stucky *et al.* (1980)
		N.Q.	Vargus and Ahlert (1987)

N.Q. = Detected but not Quantified
• see also Table 7.

6.2 Bioaccumulation and Biomagnification

Levels of DCM have been reported in the tissue of oysters (*Crassosotrea virginica*) and clams (*Rangia cuneata*) collected from Lake Pontchartrain, New Orleans, Indiana at levels as high as 27 ng·g wet weight^{-1} for *R. cuneata* (result of composite sample) (Ferrario *et al.* 1985; see also Section 6.3.7). Studies directly examining the bioaccumulation ability of DCM to aquatic and terrestrial organisms are lacking; however, calculations based on the octanol/water partition coefficient have been found to provide substantial estimates of the bioaccumulation potential. Neely *et al.* (1974) examined the bioaccumulation potential from muscle of rainbow trout (*Onchorhynchus mykiss*) and the following equation was derived:

$$\log (BCF) = 0.542 \log(K_{ow}) + 0.124$$ (Neely *et al.* 1974)

The log of the octanol/water partition coefficient (K_{ow}) for DCM is 1.25 (WHO 1984) giving a BCF value of 0.8, indicating no bioaccumulation potential. Similarly, an examination of the bioconcentration of thirty chemicals in fathead minnows (*Pimephales promelas*) revealed a linear correlation between the log BCF and the octanol/water partition coefficient (log(P)) expressed by the equation:

$$\log (BCF) = 0.85 \log(P) - 0.70$$ (Veith *et al.* 1979)

Under this equation, again a low BCF of 2.3 is calculated.

From the above data and equations it is evident that although there may be a slight potential for bioaccumulation and biomagnification of DCM, it can be expected to be relatively low in aquatic systems.

Data is lacking which examines directly the ability of DCM to bioaccumulate in terrestrial systems. As in an aquatic ecosystem, DCM exposure in a terrestrial ecosystem via direct plant uptake or animal consumption is expected to be minimal because of its high vapour pressure, relatively high water solubility and low K_{ow}. In the terrestrial environment respiratory exposure would be a likely route of contamination to terrestrial organisms (i.e. wildlife), but given the properties of DCM, bioaccumulation and biomagnification are, again, expected to be minimal.

6.3 Levels in the Environment

6.3.1 Atmosphere

Although it is estimated that nearly 80% of all DCM produced globally is released to the atmosphere (WHO 1984), with the potential for 100% release (Environment Canada 1990), there are few available measurements of atmospheric concentrations. Mean atmospheric levels of dichloromethane observed at 22 locations across Canada (1991-92) ranged from 0.5 $\mu g/m^3$ in the Longwoods Conservation Area, Ontario to 9.9 $\mu g/m^3$ in Saint John, New Brunswick (Dann 1993). The national mean value was approximately 1.7 $\mu g/m^3$, with an isolated maximum value of 311.3 $\mu g/m^3$ reported for Saint John, New Brunswick (Dann 1993). Similarly, the overall mean concentration of dichloromethane was 2.6 ug/m^3 (range not reported), in samples of ambient air taken in 1989 from 17 urban sites in Canada (Environment Canada, 1991a). Mean concentrations at 16 sites sampled in additional national surveys conducted between 1988 and 1990 ranged from 1.0 ug/m^3 in Halifax to 6.2 ug/m^3 in Vancouver (Environment Canada, 1991b).

Pierotti and Rasmussen (1976) report North American continental atmospheric background levels of 36 ppt (125 $\mu g \cdot m^{-3}$), coastal background levels of 35 ppt (122 $\mu g \cdot m^{-3}$), and inland urban levels (St. Louis, MO., U.S.) at 144 ppt (498 $\mu g \cdot m^{-3}$). Dichloromethane levels from the stack of a decaffeination plant in Italy, were measured at an average of 725 ppm (2515 $mg \cdot m^{-3}$) over a period of 90 min. where gas purifiers were in operation (Bertoni *et al.* 1990).

Table 9. Summary of dichloromethane atmospheric concentrations at Canadian sites.

Location	Sampling period (D/M/Y)	No. of samples	Mean $\mu g \cdot m^{-3}$ (S.D.)	Range of values $\mu g \cdot m^{-3}$
New Brunswick - Pt. Lepreau, Main Gate	* 05/07/92 - 20/12/92	37	0.6 (0.6)	0.2-3.5
St. John, Forest Hills	* 24/05/92 - 26/12/92	59	9.9 (47.9)	0.1-311.3
Nova Scotia- Halifax, Bedford Row P.O.	09/06/89 - 06/12/89	27	1.1 (1.0)	0.3-4.4
	05/01/90 - 31/12/90	46	0.6 (0.2)	0.3-1.5
Quebec- Montreal, Pte. aux Trembles,	16/01/89 - 18/12/89	38	3.3 (3.5)	ND-19.4
	11/01/90 - 31/12/90	56	2.2 (5.4)	0.4-40.6

Location	Sampling period (D/M/Y)	No. of samples	Mean $\mu g \cdot m^{-3}$ (S.D.)	Range of values $\mu g \cdot m^{-3}$
Montreal, 1125 Ontario St.	10/05/89 - 18/12/89	32	3.3 (2.0)	1.1-10.8
	11/01/90 - 31/12/90	53	1.2 (0.7)	0.3-4.9
Ontario- Ottawa, 88 Slater St.	05/01/90 - 31/12/90	55	2.7 (1.8)	0.8-9.8
	* 06/01/91 - 21/08/91	41	1.6(0.8)	0.6-4.3
Toronto, 35 Edgar Ave.	04/01/89 - 24/12/89	12	3.4 (2.2)	0.8-8.2
	05/01/90 - 31/12/90	59	1.5 (1.2)	0.2-5.7
	* 06/01/91 - 21/08/91	25	1.5(1.0)	0.4-4.3
Toronto, Perth/Ruskin (Junction Triangle)	04/01/89 - 30/12/89	40	2.9 (1.8)	1.0-10.4
	11/01/90 - 31/12/90	57	1.9 (0.9)	0.6-4.8
	* 18/01/91 - 21/08/91	31	2.1 (1.1)	07-4.7
Toronto, Stouffville	10/01/89 - 24/12/89	34	1.6 (0.9)	0.5-5.5
	05/01/90 - 31/12/90	54	1.3 (0.8)	0.4-4.4
	* 06/01/91 - 04/08/91	24	0.9 (0.5)	0.2-2.5
Hamilton, Elgin/Kelly	28/01/89 - 24/12/89	18	2.6 (2.1)	0.7-8.3
	17/01/90 - 31/12/90	53	5.6 (1.5)	3.2-9.3
	* 06/01/91 - 15/08/91	41	5.3 (3.2)	2.8-22.9
Longwoods Conservation Area	* 12/05/91 - 26/12/91	25	0.5 (0.3)	0.1-1.11
Sarnia, Centennial Park	10/01/89 - 30/12/89	54	1.3 (1.6)	0.3-10.6
	05/01/90 - 25/12/90	56	0.8 (0.5)	0.3-2.5
	* 06/01/91 - 26/12/91	51	1.0 (2.1)	0.2-15.2

Table 9. Summary of dichloromethane atmospheric concentrations at Canadian sites (continued).

Location	Sampling period (D/M/Y)	No. of samples	Mean $\mu g \cdot m^{-3}$ (S.D.)	Range of values $\mu g \cdot m^{-3}$
Windsor, 467 University Ave.	20/07/87 - 30/09/88	39	5.3 (3.4)	1.9-19.7
	04/01/89 - 30/12/89	35	1.9 (2.3)	0.5-12.8
	05/01/90 - 31/12/90	56	1.2 (0.8)	0.5-5.0
	* 06/01/91 - 26/12/91	50	1.7 (1.7)	0.5-9.9
Windsor, College/Prince	29/05/90 - 26/10/90	20	2.2 (1.1)	0.5-4.9
	* 12/01/91 - 26/12/91	39	1.1 (0.5)	0.2-2.5
Walpole Island, St-Clair river	22/01/88 - 12/10/88	28	2.5 (2.7)	0.8-14.8
	05/01/90 - 25/11/90	32	1.3 (0.8)	0.5-3.9
	* 17/02/91 - 20/12/91	32	0.73 (0.8)	0.3-1.6
Manitoba- Winnipeg, 65 Ellen St.	24/12/89 - 30/12/89	2	0.7	0.6-0.7
	05/01/90 - 31/12/90	58	1.2 (1.0)	0.3-4.3
	* 06/01/91 - 26/12/91	47	1.9 (4.7)	0.3-32.2
Alberta- Edmonton, 17 St./105 Ave	27/08/90 - 31/12/90	22	0.5 (0.2)	0.2-0.9
British Columbia- Vancouver, Robson Square	29/11/88 - 29/11/88	1	6.1	6.1
	28/01/89 - 24/11/89	8	4.0 (5.2)	0.9-16.8
	12/03/90 - 25/12/90	10	0.9 (0.6)	0.4-2.2
	* 07/03/91 - 16/08/92	13	1.6 (2.5)	0.3-9.6
Vancouver, 2550 W. 10th. Ave.	07/08/88 - 30/09/88	8	1.8 (0.9)	ND-2.8
Vancouver, Kensington Park	05/12/88 - 05/12/88	1	4.8	4.8

Table 9. Summary of dichloromethane atmospheric concentrations at Canadian sites (continued).

Location	Sampling period (D/M/Y)	No. of samples	Mean $\mu g \cdot m^{-3}$ (S.D.)	Range of values $\mu g \cdot m^{-3}$
	04/01/89 - 06/12/89	6	1.7 (1.2)	0.6-3.7
	17/05/90 - 01/12/90	13	3.7 (3.1)	0.3-10.7
	* 12/01/91 - 11/08/92	19	0.7 (0.5)	0.2-2.5
Vancouver, Rocky Point Park	29/11/88 - 23/12/88	5	6.2 (0.9)	4.7-6.9
	04/01/89 - 24/12/89	41	3.3 (1.7)	1.6-10.0
	05/01/90 - 31/12/90	59	2.0 (4.2)	0.2-32.3
	* 06/01/91 - 02/12/92	126	2.1 (5.6)	0.4-63.5
Surrey, East	11/12/88 - 11/12/88	1	3.4	3.4
	10/01/89 - 18/12/89	9	2.1 (2.1)	0.4-7.3
	29/04/90 - 07/12/90	10	0.5 (0.2)	0.2-0.9
	* 18/01/91 - 10/07/92	14	0.5 (0.3)	0.2-1.5
Richmond, South	17/12/88 - 17/12/88	1	7.7	7.7
	22/01/89 - 30/12/89	11	2.8 (3.1)	0.7-12.0
	05/05/90 - 13/12/90	9	0.6 (0.2)	0.3-1.1
	* 24/01/91 - 03/10/91	7	0.9 (0.5)	0.4-1.7
Burmount - 781S Shellmou	18/03/90 - 19/12/90	17	2.8 (1.7)	0.2-5.2
	* 11/02/91 - 02/12/92	31	2.6 (8.2)	0.4-46.4
Mahon Park	23/05/990 - 25/11/90	6	0.6 (0.5)	0.3-1.6
	* 06/01/91 - 22/08/92	16	0.9 (0.7)	0.2-3.0

Location	Sampling period (D/M/Y)	No. of samples	Mean $\mu g \cdot m^{-3}$ (S.D.)	Range of values $\mu g \cdot m^{-3}$
Burnaby Mtn.	06/03/90 - 10/12/90	8	1.5 (2.6)	0.4-7.9
	* 17/04/91 - 04/08/92	20	1.1 (0.4)	0.4-1.9
Burnaby, 5455 Rumble	13/08/88 - 03/10/88	10	4.0	2.0-8.0
Burnaby, Trans Mountain Pipelines	20/10/88 - 04/11/88	9	1.7 (0.9)	ND-2.7
Burnaby, Piper Street Works Yard	20/10/88 - 04/11/88	8	4.1 (2.8)	1.5-10.2
Burnaby, Forest Hills	07/08/88 - 04/11/88	30	2.5 (1.7)	ND-9.5
Burnaby, Shell Tank Farm	20/10/88 - 04/11/88	9	3.4 (1.9)	1.2-7.9
Burnaby	28/10/88 - 24/12/89	19	2.1 (2.0)	0.3-7.2

(* From Dann, 1993, otherwise from Dann and Wang 1992)
ND = Not Detected (detection limit = 0.1 $\mu g \cdot m^{-3}$)
Method of analysis = Cryogenic preconcentration trap and analysed with a gas chromatography (GC) with a flame ionizing detector and electron capture detector or a quadropole mass spectrometer. For all analyses, approx. 1 L of sample air ws pre-concentrated using liquid oxygen prior to injection and GC separation.

6.3.2 Surface Water

At present, many Canadian provinces conduct special monitoring programs. The National Water Research Institute has undertaken studies to determine DCM levels in selected surface waters. Some of these studies and provincial monitoring programs are described below.

Provincial median levels of dichloromethane(representing 264 sites)from surface waters across Canada, calculated from a national database (NAQUADAT\ENVIRODAT 1991) and other sources (Ayotte 1987; Kaiser and Comba (unpublished) 1992)are: Ontario, 0.05 (non-detectable to 57 µg/L); Quebec,0.03 (non-detectable to 2.7 µg/L); New Brunswick, 1.05 µg/L (non-detectable to 6.7 µg/L); Nova Scotia, 0.4 µg/L (non-detectable to 13.9 µg/L); and Newfoundland, 0.71 µg/L (non-detectable to 10.3 µg/L).

Volatile halocarbons, including DCM, were detected in surface samples from the Niagara river. Dichloromethane, detected using gas chromatography, was found in 6 out of 17 samples (detection limit 20

$ng \cdot L^{-1}$). Values ranged from trace (non-quantifiable) to 45 $ng \cdot L^{-1}$ (Kaiser *et al.* 1983). Following from this study Comba and Kaiser (1984) examined the surface water in Lake Ontario, near the mouth of the Niagara River. Levels of DCM were measured at quantities greater than 3.0 $\mu g \cdot L^{-1}$ using gas chromatographic procedures. The major source apparently was from the Welland Canal outflow at Port Weller and also possibly from the Port Dalhousie area. Investigations of the hypolimnion, or bottom water, in this same body of water, revealed DCM levels falling within the upper range of 1.0-4.0 $\mu g \cdot L^{-1}$ (Comba and Kaiser 1984). A wide range of volatile halocarbons, including DCM, were also identified from the bottom of the upper St. Clair River (between Lake Huron and Lake St. Clair). Samples were taken 25 m off-shore and 0.5 m off the bottom with reported DCM levels ranging from 27.7 to 129.4 $\mu g \cdot L^{-1}$ from 6 samples with one exceptionally high level measured at 5700 $\mu g \cdot L^{-1}$ (Kaiser and Comba 1986; Kaiser and Comba , unpublished 1992). The St. Clair River samples were collected subsequent to a chemical spill. Elevated levels of DCM were detected in the Detroit river (between lake St Clair and Lake Erie), in 94% of all samples, at levels as high as 2.8 $\mu g \cdot L^{-1}$ (Comba and Kaiser 1985). Its presence is primarily attributable to use in automotive painting operations, in steel manufacturing and from sewage treatment plants along the river. In 1983, industries such as Ford Canada, Great es Steel and McLouth Steel were reported to discharge DCM into the river at 0.28, 0.31 and 0.03 $kg \cdot d^{-1}$, respectively (Comba and Kaiser 1985). A joint evaluation of the toxic contaminants of the Niagara River has recently been carried out by the U.S. Environmental Protection Agency, New York State Department of Environmental Conservation, Ontario Ministry of Environment, and Environment Canada. An examination of DCM levels at Fort Erie and Niagara-on-the-Lake reported mean levels of 1322 and 1.27 $\mu g \cdot L^{-1}$ in 1987-88 and 1.63 and 1.48 $\mu g \cdot L^{-1}$ in 1988-89, respectively (DIGRMC 1989 and 1990).

Available measured DCM surface water levels from outside North America include measurements taken in Germany from the confluence of the river Main and the Rhine. Concentrations of DCM reached 100 $\mu g \cdot L^{-1}$ at this location, and with a water flow rate of 90 $m^3 \cdot s^{-1}$, a total DCM burden to the water system was calculated to be 778 $kg \cdot d^{-1}$ (Trapp *et al.* 1990).

In recent years, concern has developed over the effects of chlorination of organic materials and their discharge into natural waters. Significant quantities of chlorine are used by pulp and paper mill operations and water and sewage treatment facilities. In a typical pulp and paper mill operation, the bleaching process involves the use of chlorine and chlorine dioxide in a series of steps. During this process, chlorine radicals form, which are then available to bond with organic carbon to form organochlorine compounds. The formation of DCM from this process is believed to come from the reaction involving a degradation product of lignin and/or impurities in the pulp (Kringstad and Lindström 1984). In an examination of 5 different operations in the paper industry in the U.S. and Canada, DCM was detected, using GC/MS analysis, in both the influent and effluent waters at levels from nondetectable to 7 ppb ($\mu g \cdot L^{-1}$) in 4 of the 5 operations. The differences observed

between influent and effluent waters is questionable since the detection limit was reported to be approximately 10 $\mu g \cdot L^{-1}$. The fifth mill, however, a reported a DCM level of 281 ppb ($\mu g \cdot L^{-1}$) in the influent sample and an effluent sample of 166 ppb ($\mu g \cdot L^{-1}$) (Turoski *et al.* 1983). The importance of DCM from paper industries is not apparent from this study since, in only one mill, was the effluent level higher than the influent level. Examination of DCM from two de-inking operations (Wisconsin, U.S.A.) and one ground wood bleaching operation (Minnesota, U.S.A.) was carried out in cooperation with the U.S. EPA and Gulf South Research Institute (Wallin and Condren 1981). The primary influent and secondary effluent, as well as the air above the aeration tanks, and levels in the primary and secondary sludge were monitored. Dichloromethane was detected in the raw wastewater, but at a level of less than 10 $\mu g \cdot L^{-1}$ and therefore did not qualify for further examination. Nonetheless, DCM effluent levels were reported from four pulp and paper mill operations in the U.S.A. along the Mobile river, Alabama, and were measured at concentrations between 3.8 and 42 $mg \cdot L^{-1}$ (NAS 1978).

Grab water samples from a sewage treatment plant serving a large industrial, as well as a municipal area in Cincinnati, Ohio, U.S.A. were monitored for volatile organics using gas chromatography equipped with a duel flame ionizing detector and a microcoulometric detector, confirmed by GC/MS (Bellar *et al.* 1974). The influent sample was found to contain a level of DCM at 8.2 $\mu g \cdot L^{-1}$ and an effluent level of 2.9 $\mu g \cdot L^{-1}$ was measured before chlorination and a level of 3.4 $\mu g \cdot L^{-1}$ after chlorination. The increase in DCM in the effluent samples is apparently attributable to the chlorination process.

6.3.3 Raw and Treated Water for Drinking

Levels of dichloromethane detected in samples collected from groundwater used as a source for drinking water in the provinces of Nova Scotia and Prince Edward Island ranged between 0.1 and 11.0 $\mu g/L^{-1}$ (NAQUADAT\ENVIRODAT 1991).

Ayotte (1987) examined raw and treated waters for DCM from 18 municipalities within the province of Quebec. Dichloromethane measurements taken in February 1986 revealed that 8 of the municipalities examined, had levels of DCM in raw water from 0.1 $\mu g \cdot L^{-1}$ (Drummondville) to 2.7 $\mu g \cdot L^{-1}$ (Saint-Foy), the remainder being lower than the detection limit (<0.05 $\mu g \cdot L^{-1}$). Measurements of treated and tap water from 7 of the municipalities, over the same time period, ranged from 0.1 $\mu g \cdot L^{-1}$ (Drummondville, Sorel, and Trois-Rivières) to 1.7 $\mu g \cdot L^{-1}$ (Lauzon and Sainte-Foy). In July of the same year, DCM was not detected in raw or treated waters from any of the 18 municipalities.

In nine municipalities around the Great Lakes in southern Ontario, DCM was detected in 78.6-100% of the 14 raw and treated water samples from ten potable water treatment plants with a maximum detected value

of 19 $\mu g \cdot L^{-1}$ in one raw and one treated water sample in the vicinity of Amherstburg. Mean levels of DCM in raw water, for summer, winter and spring samples, were found to be 2.5, 0.7, and 2.6 $\mu g \cdot L^{-1}$ and in treated water were measured at 1.7, 1.5, and 1.4 $\mu g \cdot L^{-1}$, respectively (Otson 1987). Dichloromethane levels from a variety of Canadian water sources are listed in Table 10.

Otson *et al.* (1986) investigated the potential for the formation of DCM from potable water treatment operations during the chlorination procedure. Raw and chlorinated water from ten treatment plants serving populations of greater than 100 000 across Canada were sampled and analysed using a GC\ECD procedure (detection limit (DL) = 50 $\mu g \cdot L^{-1}$). Dichloromethane was not detected in water from any of the water treatment operations; however, it was detected in the chlorine (DL = 0.2 $\mu g \cdot L^{-1}$) in all ten of the treatment operations. Levels of DCM in the chlorine ranged from 0.3 to 4.8 ppm ($\mu g \cdot g^{-1}$), indicating a potential for levels to appear in drinking water.

In the United States, the EPA performed an organics survey in Region V (Illinois, Indiana, Michigan, Minnesota, Ohio, and Wisconsin) which involved an examination of raw water supplies at 83 locations. The levels of DCM at all sites did not exceed 1 $\mu g \cdot L^{-1}$ (U.S. EPA 1975a).

6.3.4 Groundwater

Groundwater accounts for approximately 90% and 3%, respectively, of water sources for livestock watering and irrigation. Groundwater recharge is also believed to account for 30% of Canadian surface waters (Hess 1986). In contrast to surface waters, where DCM is likely to volatilize, groundwater is able to trap and transport DCM. Dichloromethane levels detected in samples collected from ground water sites used for drinking water in the provinces of Nova Scotia and Prince Edward Island ranged between 0.1 and 11.0 $\mu g \cdot L^{-1}$ (NAQUADAT/ENVIRODAT 1991).

There have been numerous cases of groundwater contamination from toxic leachates associated with waste disposal sites and landfills in Canada and throughout the world. The highest reported level of dichloromethane in groundwater in Canada was that of 25 000 000 $\mu g \cdot L^{-1}$ measured in the Weston area of N.W. Toronto. This level was measured apporximately 20 years after its release from a ruptured underground storage tank (Ladanowski *et al.* 1993). The Canadian government disposed of large volumes of organic solvents from its laboratories in Ottawa in a special waste site in Gloucester, Ontario. Disposal involved detonation and partial combustion of bottled solvents in shallow trenches. In 1981, DCM in leachates from this landfill site were found to have contaminated groundwater wells (Jackson *et al.* 1985). A hydro-geochemical survey of the site showed that in addition, leachates were causing serious contamination of an aquifer used as a local drinking

water supply (Patterson *et al.* 1985). Dichloromethane concentrations as high as 10 400 $\mu g \cdot L^{-1}$ were detected in the groundwater from a 1982 survey of the site (Jackson *et al.* 1985). In a following survey of the site in 1988, DCM concentrations had decreased from 4 to a maximum of 60 $\mu g \cdot L^{-1}$ in the outwash aquifer (Lesage *et al.* 1990, Jackson *et al.* 1991). Similarly, DCM contamination of groundwater occurred in the vicinity of a landfill for a chemical manufacturing company located near Sarnia, Ontario. From an examination of leachates from the site, DCM levels were found as high as 160 $\mu g \cdot L^{-1}$ (King and Sherbin 1986). In Guelph, Ontario, a landfill leachate was reported to contain DCM concentrations at levels as high as 131 $\mu g \cdot L^{-1}$ and 1008 $\mu g \cdot L^{-1}$, detected in 1988 and 1989, respectively. The leachate, under simulated groundwater anaerobic reducing conditions, lost DCM to degradation at a constant rate over a time period of a few months (Lesage *et al.* 1989). Lower levels were reported from a study of a Muskoka, Ontario, landfill leachate, where a level of 57 $\mu g \cdot L^{-1}$ was reported in 1989 (Lesage *et al.* 1989). McBride *et al.* (1989) examined DCM levels in leachates from the untreated Muskoka Lakes municipal solid waste landfill near Port Carling, Ontario, and in 1983 reported levels of DCM at 350 $\mu g \cdot L^{-1}$ and 270 $\mu g \cdot L^{-1}$, from a collection trench and leaching trench, respectively. These trenches serve to intercept the leachate flow from a contaminated aquifer emanating from the landfill. As part of the treatment process at this plant the leachate is sprayed into a mixed hardwood forest.

With the exception of a few extreme cases of groundwater contamination from landfill leachates, little data exist to accurately define the state of groundwater quality. Nonetheless, given the high water solubility and low sorptive capacity of DCM, there is significant potential for DCM to leach from contaminated sites and pollute groundwater where it may travel substantial distances unaltered.

Based on recent surveys of over 700 waste sites in Germany and the U.S., DCM was one of the most frequently detected contaminants, (No. 1 in the U.S. and No. 11 in W. Germany) with a mean concentrations from groundwater from the German sites at over 38 $mg \cdot L^{-1}$ (Kerndorff *et al.* 1992). This fact is not surprising considering the extensive domestic and industrial use of DCM..

Table 10. Summary of dichloromethane levels from Canadian waters.

Location	Year, Sampling Period	Number of Sampling sites	Number of Samples (No. detected) †	Mean level $\mu g \cdot L^{-1}$ (SD) ‡	Range of values $\mu g \cdot L^{-1}$
Ontario Niagara R.[1]	1983	17	17 (6)	-	trace - 0.045
St. Clair R. - bottom water [2]	02/11/85 - 04/12/85	21	64 (25)	0.56 (1.27)	0.045 - 5.7
St. Clair R. (5 m from surface)[2]	04/1985	9	9(9)	11.7 (17.6)	15.0 - 57.0

Location	Year, Sampling Period	Number of Sampling sites	Number of Samples (No. detected) †	Mean level $\mu g \cdot L^{-1}$ (SD) ‡	Range of values $\mu g \cdot L^{-1}$
Detroit R. [3]	28/09/82 - 01/10/82 and 30/05/83 - 03/05/83	122	122 (115)	-	max. value 2.8
Niagara R. Fort Erie [4,5]	1987 - 1988	-	76	1.3	90% C.I. min and max: 0.6-2.3
	April 1988 - March 1989	-	100	1.6	90% C.I. min and max: 0.54-3.5
Niagara R. Niagara-on-the-Lake [4,5]	1987 - 1988	-	75	1.3	90% C.I. min and max: 0.66-2.1
	April 1988 - March 1989	-	96	1.5	90% C.I. min and max: 0.63-2.8
Raw and treated water from around the Great Lakes [6]	July - Aug. 1982	10	Raw: 14 (12) Treated: 14 (13)	Raw: 2.5 Treated: 1.7	max. value 19 (Raw and Treated water from the Detroit R.)
	Jan. - Feb. 1983	10	Raw: 14 (11) Treated: 14 (12)	Raw: 0.7 Treated: 1.5	
	Apr.- May 1983	10	Raw: 14 (14) Treated: 14 (14)	Raw: 2.6 Treated: 1.4	
Groundwater Gloucester site [7,8]	1981, 1982, 1988	1	~350	-	N.D. - 10 400
Muskoka Lakes landfill leachate from trenches [9,10]	Apr.1983	1	2	310	350 and 270
	1989	1	1	-	57
Guelph landfill leachate [10]	1988	1	1	-	131
	1989	1	1	-	1008
Groundwater Weston, Toronto [11]	1993	1	-	-	max. value 25 000 000
Quebec Raw and treated water [12]	Feb. 1986	18	Raw: 18 (8) Treated: 18 (7)	Raw: 0.46(0.83) Treated: 0.23(0.45)	Raw: <0.05-2.7 Treated: 0.05-1.7
New Brunswick[b] - lakes and impounded reservoirs	03/06/85 - 06/10/87	10	19 (17)	2.20 (2.40)	0.2-6.2
river water	03/06/85 - 27/10/86	5	12 (11)	2.05 (2.14)	0.2-6.7

Location	Year, Sampling Period	Number of Sampling sites	Number of Samples (No. detected) †	Mean level $\mu g \cdot L^{-1}$ (SD) ‡	Range of values $\mu g \cdot L^{-1}$
well water	10/06/86 - 27/10/86	6	15 (15)	0.71 (0.68)	0.1-2.3
	25/05/87 - 07/10/87	9	20 (20)	0.43 (0.36)	0.1-1.5
	31/05/88 - 21/09/88	10	22 (16)	1.16 (1.02)	0.1-3.8
treated water	03/06/85 - 09/10/85	10	32 (31)	3.76 (10.06)	0.2-72.9
	26/05/86 - 24/10/86	9	16 (10)	0.81 (0.69)	0.1-2.6
	25/05/87 - 07/10/87	9	21 (21)	0.30 (0.15)	0.1-0.7
	30/05/88 - 19/09/88	10	24 (24)	1.62 (2.65)	0.1-11.2
Newfoundland [b] lake water	17/06/85- 07/11/85	5	10 (10)	2.18 (2.36)	0.4-8.2
	10/06/86- 23/10/86	8	17 (12)	0.66 (0.34)	0.1-1.1
	14/06/87- 22/10/87	8	15 (13)	0.85 (0.57)	0.1-0.7
	14/06/88- 25/10/88	6	14 (14)	0.46 (0.33)	0.1-11.2
Municipal treated water	17/06/85- 01/11/85	10	28 (28)	3.79 (3.99)	0.4-13.4
	10/06/86- 23/10/86	9	25 (24)	0.49 (0.55)	0.1-2.6
	14/06/87- 22/10/87	10	21 (20)	1.0 (0.80)	0.1-2.1
	13/06/88- 25/10/88	9	27 (27)	0.73 (0.49)	0.1-1.9
Surface river or channel water	17/06/85- 07/10/85	5	10 (10)	3.43 (3.62)	0.5-10.3
	10/06/86- 22/10/86	2	4 (3)	0.55 (0.34)	0.2-1.0
	16/06/87- 22/10/87	2	4 (4)	0.75 (0.76)	0.1-1.8
Impounded reservoir	15/06/88- 25/10/88	2	5 (5)	0.4 (0.26)	0.3-0.8
Nova Scotia [b] Surface lake water	28/05/85- 24/10/85	6	12 (11)	5.39 (4.84)	1.0-13.9

Location	Year, Sampling Period	Number of Sampling sites	Number of Samples (No. detected) †	Mean level $\mu g \cdot L^{-1}$ (SD) ‡	Range of values $\mu g \cdot L^{-1}$
	05/06/86-25/09/86	3	5 (5)	0.54 (0.44)	0.1-0.9
	15/06/87-27/10/87	4	9 (5)	0.62 (0.44)	0.2-1.3
	14/06/88-19/10/88	6	12 (12)	0.2 (0.04)	0.1-0.3
Surface river water	29/05/85-22/10/85	3	6 (5)	4.73 (5.37)	0.5-13.1
	03/06/86-23/09/86	2	4 (4)	0.38 (0.15)	0.3-0.6
	15/06/87-29/10/87	4	8 (6)	0.51 (0.33)	0.2-1.0
Municipal Treated water	28/05/85-24/10/85	10	26 (25)	7.87 (14.76)	0.4-73.2
	03/06/86-25/09/86	6	18 (16)	1.06 (0.64)	0.4-2.6
	15/06/87-29/10/87	10	23 (19)	0.62 (0.37)	0.1-1.2
	14/06/88-19/10/88	9	28 (27)	0.33 (0.24)	0.1-1.1
Impounded reservoir	28/05/85-24/09/85	1	2 (2)	1.95 (1.34)	1.0-2.9
	04/06/86-23/09/86	1	2 (2)	0.7 (0.43)	0.4-1.0
	17/06/87-28/10/87	2	4 (2)	0.6 (0.46)	0.2-1.0
	16/06/88-18/10/88	2	4 (4)	0.25 (0.06)	0.2-0.3
Groundwater	04/06/86-24/09/86	4	13 (12)	0.62 (0.29)	0.2-1.3
	16/06/88-18/09/88	2	4 (4)	0.28 (0.10)	0.2-0.4
Prince Edward Island [b]	20/05/86-11/09/86	11	27 (27)	0.50 (0.32)	0.2-1.3
Ground well water	19/05/87-15/09/87	10	19 (19)	2.05 (3.05)	0.3-11.0
	17/05/88-22/09/88	8	21 (19)	0.33 (0.20)	0.1-0.7
Municipal treated water	20/05/86-19/05/86	2	5 (5)	0.28 (0.08)	0.2-0.4

Location	Year, Sampling Period	Number of Sampling sites	Number of Samples (No. detected) †	Mean level $\mu g \cdot L^{-1}$(SD) ‡	Range of values $\mu g \cdot L^{-1}$
	19/05/87-15/10/87	8	23 (22)	3.19 (4.58)	0.2-21.7
	19/05/88-22/09/88	9	26 (25)	0.33 (0.15)	0.1-0.7

Source: NAQUADAT\ENVIRODAT 1991 unless other wise indicated:

1. Kaiser *et al.* 1983
2. Kaiser and Comba (unpublished) 1992
3. Comba and Kaiser 1985
4. DIGRMC 1989
5. DIGRMC 1990
6. Otson 1987
7. Jackson *et al.* 1985
8. Lesage *et al.* 1990
9. McBride *et al.* 1989
10. Lesage 1989
11. Ladanowski et al. 1993
12. Ayotte 1987

† Detected samples refer the number of values above the detection limit.

‡ When a value was determined to be less or equal to the detection limit the detection limit was used in the calculation of the mean.

Method of analysis:

a Batch purge and trap/capillary column gas chromatography\mass spectrophotometry (GC\MS). Up to 16 batch samples or surface water (5mL) are spiked with deuterated surrogate standards and internal standards, purged with helium, and volatiles absorbed onto tenax/silica gel/charcoal trap. This is followed by thermal desorption and analysis. Detection limit ranges from 1.0 to 10 $\mu g \cdot L^{-1}$.

b Analysis carried out using a CDS 320 concentrator (purge and trap) coupled to a GC\MS system. The detection limit ranges from 0.1 to 1.0 $\mu g \cdot L^{-1}$.

6.3.5 Soils

Little information is available on soil levels of DCM in Canada. Similar to groundwater, data are only available for extreme cases of contamination. Near Ville Mercier, Quebec, an estimated 40 000 m^3 of heavy liquid organic waste was disposed of at two abandoned sand and gravel pits between 1968 and 1972 (Pakdel et al, 1992). Waste materials dumped at this site included refinery oil residues, a variety of chlorinated hydrocarbons, phenolic compounds, acids, pesticides, insecticides, polymers, paint residues and mercaptans. Oil extracted through a ground water monitoring well and analysed for DCM showed a level of 2000 $mg \cdot L^{-1}$ at this site (Pakdel et al. 1992). This oil sample represents an extreme in soil contamination where the absorptive capacity of the soil was exceeded. Water samples collected from the sand and gravel areas were found to have levels of DCM from 1 to 372 $\mu g \cdot L^{-1}$ at the site. In Vancouver, B.C., a hydrogeological investigation of the shallow soils (0.03 to 2.0 m) beneath the C-I-L Stanchem warehouse, did not reveal levels of DCM which exceeded the detection limit of 0.005 $mg \cdot kg^{-1}$ of dry matter except for one, where a level of 0.016 $mg \cdot kg^{-1}$ was measured in a sample collected from a depth of 0.03 m. Contamination of this soil is thought to be due to paints and water from a 1973 warehouse fire at this site, as well as from possible spillage during routine product handling (Golder Associates (unpublished) 1989).

6.3.6 Sediments

No information was available regarding levels of DCM in sediment from Canadian sites. Sediment from three locations in Lake Pontchartrain, New Orleans, Louisiana, U.S.A. were examined for levels of volatile organic pollutants using a purge and trap technique, followed by GC/MS analysis (detection limits not reported) (Ferrario *et al.* 1985). Levels of DCM in the sediment were undetectable at the Rigolets pass and a mean of 1.5 $ng \cdot g^{-1}$ wet weight (n=5) was reported from the Inner Harbour Navigation Canal and 3.2 $ng \cdot g^{-1}$ wet weight (from a composite sample) from Chef Menteur pass. Characteristics of the sediment were not reported. Since DCM does not appear to have a strong potential for adsorption to soils (see Section 6.1.3 above), it is anticipated that concentrations in sediments would closely follow those in the overlying water.

6.3.7 Biota

No information was available reporting on the levels of DCM in Canadian biota. Levels in biota are not expected to be high based on the physical and chemical properties of DCM and the low calculated BCF values (see Section 6.2). Samples of oysters (*Crassosotrea virginica*) and clams (*Rangia cuneata*) collected from the Inner Harbour Navigation Canal, Chef Menteur pass and the Rigolets pass at the confluent of Lake Pontchartrain, New Orleans, Louisiana, U.S.A. were analyzed for levels of volatile organic pollutants (Ferrario *et*

al. 1985). Organics were removed using a purge and trap procedure and analyzed on a thermal gradient using GC/MS (detection limit not reported). Levels of DCM in oysters were found to have a mean of 7.8 $ng \cdot g^{-1}$ wet weight (n=5) from the Inner Harbour Navigational Canal and composite samples from the Rigolets and the Chef Menteur pass were found to be 4.5 and 27 $ng \cdot g^{-1}$ clam wet weight, respectively.

7.0 Population Exposures

In general, three routes of exposure to environmental contaminants may be of concern for wildlife: oral, inhalation and dermal. Oral exposures might occur via ingestion of contaminated food (i.e. aquatic prey) or water or incidental ingestion of contaminated media (soil, sediment). Inhalation of vapours or particulates might be a significant route of exposure for animals active near point sources. Dermal exposures are likely to be most significant for burrowing mammals (i.e. via contact with contaminated soils) and animals that spend considerable amounts of time partially submerged in contaminated surface waters. Wildlife can also be affected indirectly by removal of their food resources if levels in the environment are sufficiently high to be toxic to plants or invertebrates.

8.0 Effects on Ecosystems

As previously noted in section 6.1.2 , most of the DCM is expected to be destroyed in the troposphere, where an estimated 2.5% (Edwards *et al.* 1982a) and 2.0% (Singh *et al.* 1979) of original tropospheric DCM levels would be available to enter the stratosphere. Given that the net domestic usage of DCM in Canada in 1990 is estimated to be 9.0 kt (Environment Canada 1990), and if it is assumed that 100% of this is lost to the troposphere, 203 t would be available to enter the stratosphere assuming an entry level of 2.25%.

The presence of DCM in the stratosphere could potentially contribute to the destruction of the ozone. Chlorine containing halomethanes absorb UV light at wavelengths found in the stratosphere (185-225 nm), which provide enough energy to dehalogenate DCM giving rise to reactive chlorine atoms. Although many of these chlorine atoms are able to re-enter the troposphere as HCl, each of them has the potential to destroy thousands of ozone molecules, the number depending on the rate of return to the troposphere and the rates of various chemical reactions (NAS 1978). However, because the half-life of DCM in the troposphere is short, and

little migration to the stratosphere should occur there is expected to be an insignificant level of ozone depletion(Bunce 1992). It is expected that at under current release rates for DCM, the rate of 'steady state' ozone reduction is relatively minor, less than 0.05% (NAS 1978).

Dichloromethane and other halocarbons have strong infrared bands which have the potential to absorb radiation from the earth's surface, thereby increasing the average temperatures (Ramanathan 1975). Based on the infrared band absorbance and intensity, Ramanathan (1975) calculated a potential increase in surface temperature of 0.052°K attributable to atmospheric DCM. However, when considering the relatively short half-life of DCM comparerd to other halocarbons (e.g. CFC's), as well as seasonal climatic conditions, the true potential of DCM's contribution to the "greenhouse" effect is expected to be minimal.

8.1 Toxicity to Aquatic Biota

8.1.1a Fish - Acute Effects

Freshwater

An examination of the differences between static and flow-through toxicity of volatile organic chemicals, including DCM were investigated using adult fathead minnows (*Pimephales promelas).* The 96-h LC_{50} values for flow-through and static tests for DCM were 193 (measured) and 310 $mg \cdot L^{-1}$ (nominal), respectively. Further examination under flow-through conditions revealed 24, 48, and 72-h LC_{50}'s of 268.0, 265.0 and 232.4 $mg \cdot L^{-1}$, respectively. Under the same flow-through conditions, the EC_{50} value for loss of equilibrium (impairment of swimming ability) at 24-h was 112.8 $mg \cdot L^{-1}$, and at 48, 72, and 96-h values were 99.0 $mg \cdot L^{-1}$ for each period (Alexander *et al.* 1978).

Static, acute lethality tests were conducted with bluegill sunfish (*Lepomis macrochirus*) according to accepted procedures in U.S. EPA (1975b); however specific details on the proceedure were not provided. The 24, 48, 72, and 96-h LC_{50} concentrations were reported as 229, 224, >220 - <280, and >220 - <280 ppm, respectively. A 96-h no-effect concentration (NOEC) was determined to be 270 ppm (U.S. EPA. 1978).

Young of the year (0.32-1.2 g) bluegill sunfish (*Lepomis macrochirus*) were tested under static conditions. The 24 and 96-h LC_{50}'s were determined to be 230 and 220 $mg \cdot L^{-1}$, respectively (Buccafusco *et al.* 1981).

A 96-h LC_{50} was found to be 330 mg·L^{-1} for 30-d old (mean length 17.6 mm) fathead minnows (*P. promelas*) exposed to DCM in a flow-through system (Geiger *et al.* 1986). Affected fish were observed to swim near the tank bottom and in a comparably equal ratio were observed to exhibit hyper- and hypoactivity. The fish were also observed to respire rapidly, turn dark in colour, and lose equilibrium prior to death. A flow-through acute lethality study exposing groups of 10 fathead minnows (*P. promelas*) for a period of eight days, to six nominal concentrations of DCM ranging from 98 to 1020 mg·L^{-1}, resulted in an estimated 96-h LC_{50} of 502 mg·L^{-1} and a 192-h LC_{50} of 471 mg·L^{-1}. The observed sublethal effect, of a loss of equilibrium, occurred at a concentration above 357 mg·L^{-1}. Time for the onset of this condition was not reported (Dill *et al.* 1987).

Marine

Two studies were available examining the toxic effect of DCM to sheepshead minnows (*Cyprinodon variegatus*). In one of the studies the acute toxicity of a variety of industrial chemicals including DCM were analyzed using 14-28 day old minnows exposed to concentrations of DCM determined from a range finding test. The acute toxicity was measured as 24-h, 48-h, 72-h and 96-h LD_{50}'s giving values based on nominal concentrations of 370, 360, 360 and 330 mg·L^{-1}, respectively. A 96-h no observed effects concentration (NOEC) based on lethality was reported as 130 mg·L^{-1} (Heitmuller *et al.* 1981). Similarly a study was carried out with sheepshead minnows reporting 24, 48, 72, and 96-h LC_{50}'s of 277, 271, 271, and 250 ppm (mg·L^{-1}), respectively and a NOEC of 100 ppm (mg·L^{-1}) (U.S. EPA 1978). Methods used in this test are based on conventions outlined in U.S. EPA (1975b); however exact details of the procedure used were not provided.

Forty-eight hour acute toxicity tests were run on juvenile (<23-d old) killifish (*Fundulus heteroclitus*) exposed to DCM in a marine (10 •) static renewal system. The 48-h LC_{50} was determined to be 97.0 mg·L^{-1} (Burton and Fisher 1990).

8.1.1b **Fish** - Chronic Effects

Between the two fish species represented in a study examining the aquatic toxicity of organic compounds, rainbow trout (*Onchorhynchus mykiss*) embryo and larva exhibited a higher sensitivity than the fathead minnow (*P. promelas*). The reported LD_{50} for rainbow trout embryo (23-d) to 4-d post hatch larvae was determined to be 13.2 mg·L^{-1} and approximately 34 mg·L^{-1} for the fathead minnow (Black *et al.* 1982). The LOEL for the onset of teratogenic effects for *O. mykiss* was determined to be 5.5 mg·L^{-1} (Black *et al.* 1982)

Exposure of <24-h old fathead minnow (*Pimephales promelas*) embryos to measured concentrations of DCM ranging from 29.1 to 321 $mg \cdot L^{-1}$, over 28 days until post-hatch, resulted in a 95% mortality within the first 14 days for all treatment concentrations. Analysis of the degree of hatch impairment of embryos and the presence of deformed larvae at hatch showed no dose related mutagenic or teratogenic effects (Dill *et al.* 1987). A maximum acceptable toxicant concentration (MATC), based on body weight, was found to lie between 82.5 and 142 $mg \cdot L^{-1}$ with a geometric mean for these values of 108 $mg \cdot L^{-1}$

Two to three month old guppies (*Poecilia reticulata*) were subjected to nominal concentrations of DCM under static-renewal conditions. A subsequent 14-d LC_{50} value of 3467 $\mu mol \cdot L^{-1}$ (294 $mg \cdot L^{-1}$) was found and a calculated value, based on Quantitative Structure-Activity Relationships (QSAR), was determined to be 3715 $\mu mol \cdot L^{-1}$ (316 $mg \cdot L^{-1}$) (Könemann 1981). However, this study is not recommended for use in the CEPA assessment of DCM because measured concentrations and survival of the controls were not reported.

8.1.2 **Amphibians** - Chronic Effects

Several species of amphibians are represented in the toxicity data base for DCM, i.e. the frogs *Xenopus laevis, Rana catesbeiana, Rana temporaria, Rana pipiens, Rana palustris* , the toad, *Bufo fowleri*, and the salamander, *Ambystoma gracile*. Of these 7 species, the lowest mean LC_{50} concentration determined was 16.9 $mg \cdot L^{-1}$ in a flow-through test using the embryo and larval stages (5-d embryo and 4-d post hatch) of the frog (*Rana temporaria*). The values for the remaining 6 species fell within the range of 17.78 $mg \cdot L^{-1}$ for *R. catesbeiana* to >48.0 $mg \cdot L^{-1}$ for *R. pipiens* (Birge *et al.* 1980; Black *et al.* 1982). When the toxicity was examined on the embryos, from fertilization to hatch (mean durations of 2-5.5 d), it was found that when definitive LC_{50} values were available, they were slightly higher than embryo to larvae examinations. The range of fertilization to hatch LC_{50} values fell between 23.03 $mg \cdot L^{-1}$ for *R. temporaria* to >48.0 $mg \cdot L^{-1}$ for *R. pipiens*. The LC_{10}'s and LC_{1}'s were determined for two frogs for embryo-larval lethality or teratogenesis, *R. catesbeinana and R. temporaria* had values of 0.981 and 0.092 $mg \cdot L^{-1}$, and 0.822 and 0.070 $mg \cdot L^{-1}$, respectively (Birge *et al.* 1980; Black *et al.* 1982).

8.1.3 **Invertebrates** - Acute Effects

Freshwater

Dichloromethane was evaluated in a static, acute, freshwater toxicity study using first instar *D. magna* which exhibited 24-h and 48-h LC_{50}'s of 33.2 and 27.0 $mg \cdot L^{-1}$, respectively (McCarty 1979). Similarly, the acute toxicity of DCM to *Daphnia magna* revealed 24 and 48-h LC_{50} values of 309 and 224 $mg \cdot L^{-1}$, with a reported no effect concentration (NOEC), based on lethality, to be 68 $mg \cdot L^{-1}$ (U.S. EPA 1978). Specific details of the procedure followed in this study were not provided (U.S. EPA 1975b). A German study examining the toxicity of 173 substances to 24-h *D. magna*, in a static system, revealed 24-h LC_0, LC_{50} and LC_{100} values of 1550, 2270 and 2500 $mg \cdot L^{-1}$, respectively (Bringmann and Kühn 1977). However, this experiment was conducted in beakers covered loosely with filterpaper allowing for substantial volatilization to take place and final concentrations of DCM were not measured, therefore caution is recommended in interpreting these values.

Less than 24-h *D. magna* were used to examine the acute toxicity of several priority pollutants including DCM. The 24-h and 48-h LC_{50}'s were found to be 310 and 220 $mg \cdot L^{-1}$ respectively and a no observed effects concentration (NOEC) was determined to be 68 $mg \cdot L^{-1}$ (LeBlanc 1980). More recently, Abernathy *et al.* (1986) examined the acute toxicity of DCM to 4-6 day old *D. magna* in a closed static freshwater system. The 48-h LC_{50} was determined to be 1599 $mmol \cdot m^{-3}$ (136 $mg \cdot L^{-1}$) and relative to the other 37 hydrocarbons and chlorinated hydrocarbons examined, was strongly correlated with its aqueous solubility.

Several cosmetic ingredients including DCM were evaluated for their developmental toxicity against *Hydra attenuata* (Newman *et al.* 1990). The *Hydra* were monitored for 92 hours. The minimal affective concentration (MAC) of DCM which was observed to interfere with the adult (ie. the degeneration to a "tulip" state - a condition which immediately precedes death of the polyp), was 0.15 $mL \cdot L^{-1}$ (199.5 $mg \cdot L^{-1}$), and that which interfered with the development of hydra artificial "embryos" (cells derived from adult polyps) occurred at 0.45 $mL \cdot L^{-1}$ (598.5 $mg \cdot L^{-1}$) (endpoint identified by the dissolution of the embryo).

Chronic

The developmental and mutagenic effects of DCM were examined in a 96-h static test using the free-swimming, ubiquitous freshwater nematode, *Panagrellus redivivus* (Samoiloff *et al.* 1980; Samoiloff unpublished). Second stage juveniles were exposed to 6 nominal concentrations of DCM from 10^{-8} to 10^{-3} $mol \cdot L^{-1}$ (0.9 to 90 000 $\mu g \cdot L^{-1}$). At the highest concentration, a significant number of larvae were prevented from completing the L3 to L4 molt (frequency of 0.65 relative to controls) and a reduction in the incidence in the L4 to adult molt

occurred at all 6 concentrations tested, with the least inhibition occurring at 10^{-8} mol·L^{-1} (0.9 µg·L^{-1}). The frequency of genetic mutations, after a 120-h exposure to L2 larvae, were found to be 6.0, 10.1 and 9.8 at concentrations of 10^{-8}, 10^{-6} and 10^{-4} mol·L^{-1} (0.9 , 90.0 and 9000 µg·L^{-1}), respectively. Mutation frequency was measured by the number of lethal mutations per 10^5 loci as determined by the X-linked, b7 mutation assay (Samoiloff *et al.* 1980; Samoiloff (unpublished) 1992)

Marine

In the only marine invertebrate study available, forty-eight hour acute toxicity tests were run using juvenile (<20 mm) grass shrimp (*Palaemonetes pugio*) exposed to DCM in a marine (10 •) static renewal system. The 48-h LC_{50} was calculated as 108.5 mg·L^{-1} (Burton and Fisher 1990).

8.1.4 Microorganisms - Chronic Effects

Freshwater

A cell multiplication inhibition test involving the determination of 48-h toxicity threshold concentrations (TGK) for DCM in a static aqueous system was conducted using the bacteria, *Pseudomonas putida* (Bringmann and Kühn 1976) and the saprozoic flagellate protozoa, *Chilomonas paramecium* (Bringmann *et al.* 1980). Toxicity threshold was measured as a drop in cell counts of 5% below the average of controls. The methodology for the two studies is essentially the same. The TGK for *P. putida* was found to be 500 mg·L^{-1} and >8000 mg·L^{-1} for *C. paramecium.* However, in these experiments the test solutions were shaken, there was limited control of volatilization and concentrations of DCM were not measured, therefore caution is recommended in their usefulness for the assessment of DCM.

8.1.5 Plants - Chronic Effects

Freshwater

No studies were available which examined the acute toxicity of DCM to aquatic plants. There are several data sets in Table 11. which describe the chronic toxic effects of DCM to the blue-green algae (*Anacystis aeruginosa*) (Bringmann and Kühn 1978) and the four green algae *Chlorella vulgaris, Chlamydomonas angulosa, Scenedesmus quadricauda,* and *Selenastrum capricornutum* (Bringmann and Kühn 1976, 1978; U.S. EPA 1978; Hutchinson *et al.* 1980). Of the 5 species represented, the green algae (*Scenedesmus quadricauda*) exhibited the

greatest sensitivity to DCM with the toxicity threshold concentration (that which induces a 5% reduction in cell growth relative to the controls) for an 8-d exposure occurring at a concentration of 550 $mg \cdot L^{-1}$ (Bringmann and Kühn 1978). However, the methodology in this, and in the study carried out in 1976 by the same authors, involved some experimental drawbacks including shaking the culture solutions before the onset and during the experiment allowing for substantial volatilization, and did not provide evidence that the concentrations of DCM were measured at any time. Similarly, the experiment by Hutchinson *et al.* (1980), reported a 3-h EC_{50} for photosynthetic inhibition of 17 400 and 27 000 $mol \cdot L^{-1}$ (1477.8 and 2293.1 $mg \cdot L^{-1}$) for *Chlamydomonas angulosa* and *Chlorella vulgaris*, respectively. However, the solutions were stirred for 16-h allowing for substantial volatilization of DCM and no indication that DCM concentrations were analyzed was provided. In an examination of the freshwater green algae (*Selenastrum capricornutum*) the percentage decrease of *in vivo* chlorophyll ***a*** concentrations cultures relative to controls was used as the criterion for toxic effect. The 24, 48, 72 and 96-h EC_{50}'s were determined to all be greater than 560 ppm (560 $mg \cdot L^{-1}$) (U.S. EPA 1978). The methods used in this study followed the recommendations outlined in U.S. EPA (1975b); however, the specific details of the procedure were not provided.

No data were found examining the chronic effect of DCM to marine plants and no data were found in the literature which described the chronic toxic effects of DCM to vascular aquatic plants.

Table 11. The effect of dichloromethane on aquatic biota.

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Fish **Freshwater - Acute**						
Pimephales promelas Fathead minnow	Adult (1.04g, 49.0mm)	Loss of equilibrium:		F,M,GC	12 7.8-8.0 >5.0 —	Alexander *et al.* (1978)
		24-h EC_{50}	112.8 (99.8-150.8)			
		48-h EC_{50}	99.0 (83.2-121.5)			
		72-h EC_{50}	99.0 (83.2-121.5)			
		96-h EC_{50}	99.0 (83.2-121.5)			
		Mortality:				
		24-h LC_{50}	268.0 (213.0-346.6)			
		48-h LC_{50}	265.0 (202.5-369.7)			
		72-h LC_{50}	232.4 (172.4-337.6)			
		96-h LC_{50}	193.0 (140.8-277.8)			
		96-h LC_{50}	310.0 (262-391)	S,N		
Pimephales promelas Fathead minnow	Juveniles (age not specified)	96-h LC_{50}	502.0 (357-855)	F,M,GC	25 7.6-8.1 —	Dill *et al.* (1987)
		192-h LC_{50}	471.0 (428-517)		73-82	
Lepomis macrohirus Bluegill sunfish	0.32-1.2 g	24-h LC_{50}	230.0	S,N	22 7.3 9.7 33	Buccafusco *et al.* (1981)
		96-h LC_{50}	220.0			
Lepomis macrohirus Bluegill sunfish	—	24-h LC_{50}	229 (204-252)	S,M	— — —	U.S. EPA (1978)
		48-h LC_{50}	224 (298-246)		—	
		72-h LC_{50}	>220<280			
		96-h LC_{50}	>220<280			
		96-h NOEC	270			

Table 11. Effects of dichloromethane on aquatic biota (continued)

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Pimephales promelas Fathead minnow	30-d, 17.6 mm	96-h LC_{50}	330.0 (293-372)	F,M	25.4 7.8 7.2 45.1	Geiger *et al.* (1986)
Fish **Marine - Acute**						
Cyprinodon variegatus Sheepshead minnow	—	24-h LC_{50}	277 (246-312)	S,M	— — —	U.S. EPA (1978)
		48-h LC_{50}	271 (234-311)		—	
		72-h LC_{50}	271 (234-311)			
		96-h LC_{50}	250 (211-285)			
		96-h NOEC	100			
Cyprinodon variegatus Sheepshead minnow	14-28 days	24-h LC_{50}	370 (330-410)	S,N	— — —	Heitmuller (1981)
		48-h LC_{50}	630 (310-410)		—	
		72-h LC_{50}	360 (310-410)			
		96-h LC_{50}	330 (280-380)			
		96-h NOEC	130			
Fundulus heteroclitus Killifish	juvenile, <23-d old	48-h LC_{50}	97.0 (89.44-105.14	SR, GC (salinity - 10 ‰)	20 6.1-8.0 >40% sat. —	Burton and Fisher (1990)
Fish **Freshwater - Chronic**	Embryo\Larvae	MATC<24-h embryo to hatch (4-d) + 28-d post hatch	108	F,M,GC	24.8-26.0 6.8-8.6 — —	Dill *et al.* (1987)
Pimephales promelas Fathead minnow						
Pimephales promelas Fathead minnow	Embryo	fertilization to hatch (5-d) LC_{50}	>34	F,M,GLC	20.4 7.8 6.5 95.3	Black *et al.* (1982)
	Embryo\Larvae	5-d embryo + 4-d post hatch LC_{50}	~34.0			

Table 11. Effects of dichloromethane on aquatic biota (continued)

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Onchorhynchus mykiss (Salmo gairdneri) Rainbow trout	Embryo	fertilization to hatch (23-d)		F,M	13.3 7.8 9.4 106.8	Black *et al.* (1982)
		LC_{50}	13.51 (11.32-15.64)			
	Embryo\Larvae	LOEL	5.5			
		23-d embryo + 4-d post hatch LC_{50}	13.16 (10.96-15.32)			
Poecilia reticulata Guppy	2-3 mos.	14-d LC_{50}	294.5 (3467.4 $\mu mol \cdot L^{-1}$)	SR,U	22 — >5 25	Könemann (1981)
Amphibians - chronic						
Rana catesbeiana Bullfrog	Embryo	fertilization to hatch (4-d) LC_{50}	30.61 (21.22-64.66)	F,M,GLC	20.7 7.9 8.8	Birge *et al.* (1980)
	Embryo\Larvae	4-d embryo + 4-d post hatch: LC_{50}	17.78 (11.51-29.83)		106.8	
		LC_{10}	0.98 (0.327-1.908)			
		LC_1	0.092 (0.013-0.225)			
Bufo fowleri Fowlers toad	Embryo	fertilization to hatch (3-d) LC_{50}	>32.0		21.5 7.6 8.8	
	Embryo\Larvae	3-d embryo + 4-d post hatch LC_{50}	>32.0		106.8	
Rana palustris Pickeral frog	Embryo	fertilization to hatch (4-d) LC_{50}	>32.0		21.5 7.6 8.8	
	Embryo\Larvae	4-d embryo + 4-d post hatch LC_{50}	>32.0		106.8	
Xenopus laevis African clawed toad	Embryo	fertilization to hatch (2-d) LC_{50}	>29	F,M,GLC	18.6 7.7 7.4	Black *et al.* (1982)
	Embryo\Larvae	2-d embryo + 4-d post hatch LC_{50}	>29		97.9	

Table 11. Effects of dichloromethane on aquatic biota (continued)

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Rana temporaria Frog	Embryo	fertilization to hatch (5-d) LC_{50}	23.03 (19.04-29.09)		18.6 7.7 7.4 97.9	
	Embryo\Larvae	5-d embryo + 4-d post hatch :				
		LC_{50}	16.93 (10.95-29.04)			
		LC_{10}	0.822 (0.253-1.643)			
		LC_1	0.070 (0.008-0.233)			
Rana pipiens Leopard frog	Embryo	fertilization to hatch (5-d) LC_{50}	>48.0		20.3 7.9 7.5	
	Embryo\Larvae	5-d embryo + 4-d post hatch LC_{50}	>48.0		95.8	
Ambystoma gracils Northwestern salamander	Embryo	fertilization to hatch (5.5-d) LC_{50}	23.86 (19.46-31.89)		18.6 7.7 7.4	
	Embryo\Larvae	5.5-d embryo + 4-d post hatch LC_{50}	17.82 (14.53-21.51)		97.9	
Invertebrates **- Freshwater -** Acute						
Daphnia magna Water flea	<24-h	48-h NOEC 24-h LC_{50} 48-h LC_{50}	68.0 310.0 (280-340) 220.0 (140-330)	S,N	22 7.4-9.4 6.5-9.1 173	LeBlanc (1980)
Daphnia magna Water flea	1st instar	24-h LC_{50} 48-h LC_{50} NOEC	309 (277-341) 224 (140-326) 68	S,M	— — — —	U.S.EPA (1978)
Daphnia magna Water flea	24-h	24-h LC_{50} 24-h LC_0 24-h LC_{100}	2270.0 1550 2500	S,U	20-22 7.6-7.7 saturated —	Bringmann & Kühn (1977)

Table 11. Effects of dichloromethane on aquatic biota (continued)

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Daphnia magna Water flea	4-6d	48-h LC_{50}	136 (1599 $mmol \cdot m^{-3}$)	S,N	23 — — —	Abernethy *et al.* (1986)
Daphnia magna Water Flea	1st instar	24-h LC_{50}	33.2 (25.7-40.8)	S,N	20 7.6 7.7	McCarty (1979)
		48-h LC_{50}	27 (21.4-32.3)		85	
Hydra attenuata	Artificial "embryos" Adult	92-h exposure: Dissolution of embryos: "Tulip" formation in adults:	minimal affective concentrations (MAC): 589.5 (0.45 $mL \cdot L^{-1}$) 199.5 (0.15 $mL \cdot L^{-1}$)	S,— Embryo tests conducted in defined reaggri-gation medium, Adults in defined hydra medium.	— — — —	Newman *et al.* (1990)
Invertebrates **Freshwater -** Chronic						
Panagrellus redivivus Free swimming nematode	L2-adult	96-h molting inhibiiton L3-L4 molt L4-adult molt Genetic mutation frequency (120-h exposure to L2 larvae): 6.0 - 10.1 - 9.8 -	 84.9 (10^{-3} $mol \cdot L^{-1}$) 8.49×10^{-4} - 84.9 (10^{-8} to 10^{-3} $mol \cdot L^{-1}$) 8.49×10^{-4} (10^{-8} $mol \cdot L^{-1}$) 8.49×10^{-2} (10^{-4} $mol \cdot L^{-1}$) 8.49 (10^{-4} $mol \cdot L^{-1}$)	S,N grown in buffered M9-yeast-cholesterol medium Frequency = No. lethal mutations per 10^5 loci as dtermined bv the X-linked b7 assay.	22 — — —	Samoiloff *et al.* (1980)

Table 11. Effects of dichloromethane on aquatic biota (continued)

Species	Life stage	End point	Concentration $mg \cdot L^{-1}$ (95% confidence limits)	Test conditions	Temp °C pH O_2 ($mg \cdot L^{-1}$) $CaCO_3$ ($mg \cdot L^{-1}$)	Reference
Invertebrates **Marine** - Chronic						
Palaemonetes pugio Grass Shrimp	Juvenile, <20 mm	48-h LC_{50}	108.5 (92.37-130.90)	SR, GC (salinity - 10 ‰)	20 6.1-8.0 >40% sat. —	Burton and Fisher (1990)
Micro-organisms						
Chilomonas paramecium Cryptomonad	72-96-h	48-h TGK: threshold toxicity level for 5% inhibition of cell multiplication	>8000.0	S,U	20 6.9 — —	Bringmann *et al.* (1980)
Psuedomonas putida Bacteria		16-h TGK: Threshold toxicity level for 5% inhibition of cell multiplication	500	S,U	25 7.0 — —	Bringmann and Kühn (1977)
Plants **Freshwater** - chronic						
Selenastrum capricornutum Green algae	*in vivo* examination of chlorophyll a	24-h EC_{50} 48-h EC_{50} 72-h EC_{50} 96-h EC_{50}	> 560 > 560 > 560 > 560	S,M	— — — —	U.S. EPA (1978)
Chlamydomonas angulosa Green algae	3-4d exponential phase cells, (5 x 10^4 $cells \cdot mL^{-1}$)	Reduction in photosynthesis 3-h EC_{50}	1477.8 (17 400 $mol \cdot L^{-1}$	S,U	19 6.5 — —	Hutchinson *et al.* (1980)
Chlorella vulgaris Green algae	(20 x 10^4 $cells \cdot mL^{-1}$)		2293.1 (27 000 $mol \cdot L^{-1}$)			
Scenedesmus quadricauda Green algae		8-d TGK: Toxicty threshold for 5% reduction in cell multiplication	1450	S, U	27 7.0 — —	Bringmann and Kühn (1976)
Microcystis aeruginosa Blue-green algae		8-d TT: Toxicty threshold for 5% reduction in cell multiplication	550.0	S,U	27 7.0 — —	Bringmann and Kühn (1978)

MATC = Maximum Acceptable Toxicant Concentration
S = static conditions
SR = static renewal conditons
F = flow through
GC = gas chromatography
GLC = gas liquid chromatography
U = unmeasured concentrations
M = Measured concentration
N = nominal concentrations

8.2 Toxicity to Terrestrial Biota

8.2.1 Effects on Soil, Sediment and Sludge Biota

Kanazawa and Filip (1987) incorporated DCM into arable brown soil (from the locality of west Berlin, Germany) at 10 to 1000 $\mu g \cdot 100\ g^{-1}$ dry weight (0.1 to 10 $\mu g \cdot g^{-1}$) and monitored over a period of 8 weeks. At 10 $\mu g \cdot g^{-1}$, DCM was found to inhibit the enzymatic activity of β-glucosidase, β-acetylglucosaminidase and in part also of proteinase all of which are involved in important soil biochemical reactions. However, after 2 months, it is reported that the activities returned to levels equal to or higher than those of the controls (Kanazawa and Filip 1986). Similarly under the same soil type and conditions, the highest level (10 $\mu g \cdot g^{-1}$) was found to strongly reduce the ATP content (measure of soil biomass) of the soil by 80-85% and inhibited growth of soil fungi by 99.5%, as well as copiotrophic and oligotrophic aerobic bacteria by > 90%. A 99% decrease in cell counts was observed for actinomycetes, again at the highest level. Anaerobic bacteria and aerobic spore-forming bacteria did not appear to be affected by DCM exposure. Except for *Closteridium* species who's numbers increased slightly at all DCM exposure levels. Only the highest concentration provided marked changes.

Earthworms, which are important in maintaining soil fertility, were examined for their responses to 44 different compounds including DCM (Neuhauser *et al.* 1985). To evaluate the toxic effects from DCM exposure, a standardized 48-h contact filter paper test was carried out using the earthworm (*Eisenia fetida*) (Savigny). Because DCM is highly volatile the preparations were carried out as rapidly as possible. From this a 48-h LC_{50} of 304 $\mu g \cdot cm^{-2}$ was determined; however, due to a lack of available soil and contact studies investigating the effects from DCM exposure, it is difficult to extrapolate a toxic level in soil from a given contact value. Through a similar set of experiments *E. foetida* was exposed to concentrations of DCM in paper lined glass vials and a 48-h LC50 of >1000 $\mu g \cdot cm^{-2}$ was determined. This study, however, provided strong indication that substantial time and conditions were available for considerable volatilization of DCM and therefore, caution should be exercised in utilizing this study for assessing the toxicity of DCM.

The top 5 cm of sediment, collected from a freshwater stream at Floradale, Ontario, was exposed to nominal concentrations of DCM from 1.0 to 50 $\mu L \cdot g^{-1}$ wet weight (1.3 to 66.5 $mg \cdot g^{-1}$) in a laboratory study (Trevors 1985). Dichloromethane was observed to effectively inhibit CO_2 evolution having a reported 7-d EC_{50} of 11.7 $\mu L \cdot g^{-1}$ wet weight (15.6 $mg \cdot g^{-1}$). Dichloromethane at all concentrations tested caused highly variable fluctuations between exposure times (1-11 d) and sediment electron transport system (ETS) activity within and between groups . In contrast, oxygen uptake was significantly stimulated by concentrations ranging from 1.0-20 $\mu L \cdot g^{-1}$ wet weight (1.3 to 26.6 $mg \cdot g^{-1}$) (Trevors 1985).

Anaerobic sludge obtained from a Michigan wastewater treatment plant was analyzed for any inhibitory effect from added DCM. A reduction in volume of gas production from sludge biodegradation (gases not identified), was used as an indicator of inhibition, and was evident at all concentrations tested. Levels of DCM at 1, 10, 50, 100, and 300 $mg \cdot L^{-1}$ induced gas reductions as a percent of control at 98, 66, 53, 44, and 22%, respectively (Hayes and Bailey 1977).

Dichloromethane inhibition of anaerobic sludge digestion, as measured by a reduction in gas production, occurred at levels as low as 3.16 $mg \cdot L^{-1}$ in a batch analysis (Stuckey *et al.* 1980). Dichloromethane induced stress in a semi-continuous controlled digester with levels as low as 2.5 $mg \cdot L^{-1}$, significantly increasing the volatile acid levels and reducing gas production by 83% after 21 days. These effects were more pronounced at higher DCM levels (up to 10 $mg \cdot L^{-1}$), although acclimation to DCM did occur after a lag time of 50 days (Stuckey *et al.* 1980). Similarly, in an anaerobic batch experiment, using anaerobic seed from a sewage treatment plant, five different concentrations of DCM between 3.3 and 33.2 $mg \cdot L^{-1}$ were examined for inhibition of daily gas production (CO_2 and CH_4). At these levels, DCM was observed to inhibit gas production at rates directly proportional with the exposed DCM concentrations (Vargas and Ahlert 1987). Bhattacharya and Parkin (1988) similarly examined the toxic effect of DCM on the anaerobic process in waste water treatment, and clearly showed that sudden doses of DCM at 44, 88, 133 $mg \cdot L^{-1}$ immediately stopped bacterial activity in acetate and propionate enrichment systems; however, in contrast, continuous additions of DCM were reported to gradually increase levels of acetate or propionate directly with increasing solid retention times. In addition, an estimated 65-70% of DCM was biodegraded in this process (Bhattacharya and Parkin 1988). These studies are in contrast to results found by Klečka (1982). Sludge acclimated to DCM for 9-11 d and subsequently exposed to DCM at 10, 100 or 1000 $mg \cdot L^{-1}$ for two weeks, did not change the amount of oxygen consumed nor the rate of glucose metabolised relative to the control group.

8.2.2 Effects on Insects

Although not registered as a pest control product in Canada, DCM has been used as an effective insect fumigant in other countries. One available study examined the effect of DCM on the fecundity of the stored grain beetles *Sitophilus oryzae* (L.) and *Trilobium castaneum* (Hbst.). Adults, of the same age, were fumigated with dichloromethane with determined 24-h LD_{50} levels of 129.9 and 81.28 $mg \cdot L^{-1}$ for *S. oryzae* and *T. castaneum*, respectively. Survivors, after 10 days, were collected for productivity studies and left for 14 days to mate and oviposit into grain. No apparent change in the number of progeny produced relative to the controls was observed under these conditions (Rajendran and Mathu 1981).

8.2.3 Effects on Amphibians and Reptiles.

For amphibian toxicity see section 11.1.2 and Table 11. No data examining the toxic effect from DCM to reptiles was found.

8.2.4 Effects on Birds and Mammalian Wildlife

No information on the toxicity of DCM towards avian and mammalian wildlife was found. Therefore for the most part, studies on laboratory mammals willl be used as the basis for discussion of possible toxicity to wildlife. Two studies, which may be used for extrapolation to avian species, involves an examination using chick embryos. Verrett *et al.* (1990) treated 0-h fertile single comb White Leghorn chicken eggs with injections of DCM dissolved in ethanol, into the yolk at concentrations of up to 25.0 $mg \cdot egg^{-1}$. The eggs were injected at time zero and monitored until the final condition of the embryo was apparent. Verrett *et al.* (1990) reported an estimated LD_{50} of 14.13 $mg \cdot egg^{-1}$ with no apparent teratogenic effects. In a similar experiment, Elovaara *et al.* (1979) injected DCM dissolved in olive oil at 5, 25, 50, and 100 $\mu mol \cdot egg^{-1}$ into the air space of fertilized White Leghorn SK 12 strain chicken eggs at 3 and 6 days of incubation. Upon observation on the 14th day of incubation, no apparent dose-response pattern was evident with respect to mortality or the number of malformed survivors.

There are insufficient data on which to base an evaluation of the potential toxicity of DCM to birds.

Due to the lack of data on DCM levels in plants, it is not possible to calculate the potential oral uptake of DCM by herbivorous mammals in the terrestrial environment. Bioconcentration factors have, however, been calculated for fish. It is, therefore, possible to calculate a potential worst-case exposure scenario for a fish-eating mammal such as mink (*Mustela vison*).

To estimate toxicity to wildlife, a worst-case exposure scenario was developed for mink, *Mustela vison*, an opportunistic carnivore, along the St. Clair River. This site was chosen as levels recorded in surface water were the highest from across Canada and levels in air were available for a nearby rural site (Walpole Island). The main route of exposure is oral (Table 12). In the absence of toxicological data for wildlife, the results of toxicity studies on laboratory rodents have been used to estimate an effects threshold. The lowest reported effect level following chronic exposure to by ingestion of dichloromethane is 50 mg/kg bw/d in rats for hepatic changes. The no observed effects level (NOEL) in that study was 5 mg/kg bw/d. Assuming a factor of 10 to account for interspecies variation and extrapolation of results from a laboratory to field situation, the

estimated worst case exposure scenario is more than 10 times less than this effects threshold. Effects on mammalian wildlife are therefore not anticipated under current levels of exposure.

Table 12. Estimated worst-case scenario for total daily exposure of mink in the St. Clair River.

Exposure Route	Environmental Levels	Mink Daily Requirements (per kg-b.w.)[b]	Daily Intake (mg/kg-b.w./d)
Air	1.6 µg/m^3	0.55 m^3/d	0.0009
Surface water	57 µg/L	0.1 L/d	0.0057
Biota (fish)	131.1 µg/kg	155 g/d	0.021
Total	—	—	0.0276

a The level in air is the maximum level measured in a rural environment, Walpole Island, Ontario; the level in surface water is the maximum level measured in the St. Clair River, Ontario; the level in fish is based on a calculated BCF of 2.3 and the above water concentration.

b Inhalation rate from Stahl (1967); drinking rate from Calder and Braun (1983); ingestion rate from Nagy (1987), assuming a diet of 75% fish.

8.3 Toxicity to Terrestrial Plants

No information could be found in the literature which addresses the toxicity of DCM to terrestrial plants except for studies on the effects of DCM on seed germination. Rao *et al.* (1976) found that immersion of Grand Rapid lettuce seeds (*Lactuca sativa* L.) in DCM for 10 min, 1-h or 12-h, was able to induce a significant promotion of dark germination in light sensitive seeds . No inhibitory effect of DCM on seed germination was observed with soy bean seeds (Ellis *et al.* 1976, 1977; Papavizas *et al.* 1979; and Lewis *et al.* 1979); however, in other studies the inhibitory effect of DCM on seed germination is apparent, as in the study by Brewer and Wilson (1975), who found that seed immersion in DCM for 4-5 or 24 h adversely affected propagule germination in both oat and pigweed seeds. The degree of inhibition was directly related to the duration of the DCM treatment and whether or not the propagule was intact. Removing the hulls from the oat grains and seed coats from the pigweed seeds resulted in greater reductions in germination. Coinciding with this was a significant reduction in the evolution of CO_2 from germinating oat grains (66%) and pigweed seeds (30%). A

significant reduction (P=0.05) in germination has also been reported for pea (*Pisum sativum* L.), snap bean (*Phaseolus vulgaris* L.) and cotton (*Gossypium hirsutum*) seeds following a 24-h immersion in DCM (Lewis *et al.* 1979).

Some evidence of antifungal activity attributed to DCM has been reported against fungi commonly associated with soybean seeds (Glycine max 'Wells') (Ellis *et al.* 1976).

Table 13. The effect of dichloromethane on terrestrial biota

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test condiitons	References
Soil						
Unidentified soil micoororganisms	Enzymatic Assays •ß-Glucosidase • ß-acetylglu-cosaminidase • phosphatase • phospho-diesterase	8-wks	10 µg·100 g^{-1} dry soil 100 µg·100 g^{-1} dry soil 1000 µg·100 g^{-1} dry soil	• 1000 µg·100 g^{-1}dry soil was the only concentration which notably inhibited enzymatic activity of all enzymes under test. • After 8 wks, enzymeatic activities had returned to the same or higher levels than the controls.	Ap horizon of arable brown soil from Berlin (west)-Rudow. pH = 6.8 moisture = 50% Closed system	Kanazawa and Filip (1986)
soil microorganisms: Oligotrophic aerobic bacteria Copiotrophic aerobic bacteria Actinomycetes Anaerobic bacteria Clostridium sp. Spore-forming bacteria	ATP content and cell numbers	8-wks	10 µg·100 g^{-1} dry soil 100 µg·100 g^{-1} dry soil 1000 µg·100 g^{-1} dry soil	• Notable decrease in the ATP content at 100 µg·100 g^{-1} dry soil and 80-85% decrease at 1000 µg·100 g^{-1} dry soil. • 99.5% decrease in fungal colonies at 1000 µg·100 g^{-1} dry soil. • >90% decrease in copiotrophic and oligotrophic aerobic bacteria at 1000 µg·100 g^{-1} dry soil • 99% decrease in actinomycetes at 1000 µg·100 g^{-1} dry soil • Total counts of anaerobic bacteria not affected • *Clostridium* sp. increased slightly at all DCM levels • aerobic spore forming bacteria were not affected Note: Organisms were affected only at the dose levels indicated.	Ap horizon of arable brown soil from Berlin (west)-Rudow. pH = 6.8 moisture = 50% Closed system	Kanazawa and Filip (1987)
Eisenia fetida Earthworm (300-500 mg)	LD_{50}	48-h	Initial range of test concentrations varied over 4 logs. Based on these results a narrow, unspecified range of chemical concentrations were then used.	304 µg·cm^{-1} (95% conf. lim.= 258-358) • Amoung the ten least toxic chemicals out of 44 tested • Classified as Moderately toxic	Aqueous DCM added to filterpaper. Temp = 20°C in darkness	Neuhauser *et al.* (1985)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test condiitons	References
Eisenia fetida Earthworm 370-450 mg)	LD_{50}	48-h	Initial range of test concentrations varied over 4 logs. Based on these results a narrow, unspecified range of chemical concentrations were then used.	> 1000 $\mu g \cdot cm^{-2}$ • classified as relatively nontoxic	Note: unclear as to how DCM was applied to paper - may have allowed substancial time for volatilization.	* Roberts and Dorough (1984)
Sediment sediment microbiota	Electron transport system (ETS) activity CO_2 evolution O_2 uptake	1-h , 11-d and 7-d	1-h assay: 0 $\mu L \cdot g^{-1}$ 10.0 20.0 30.0 40.0 50.0 11-d assay: 0 $\mu L \cdot g^{-1}$ 1 5 50 7-d assay: 0 $\mu L \cdot g^{-1}$ 1 5 10 20	ETS activity (μg INT-F^{-1}): 161.6 146.6 148.2 150.3 148.3 190.1 ETS activity fluctuated both within and between concentrations tested. The 7-d EC_{50} for inhibition of CO_2 evolution was 11.7 $\mu L \cdot g^{-1}$ • Stimulation of O_2 uptake was observed at 1.0 to 20 $\mu L \cdot g^{-1}$. No inhibiiton of O_2 uptake was observed.	Surface 5 cm of freshwater stream. Nominal concentrations. Temp = 20°C	Trevors (1985)
Anaerobic sludge microbiota	Gas production	48-h	0 $mg \cdot L^{-1}$ 1 10 50 100 300	Volume of gas 109 mL 107 72 57.5 47.5 24 EC_{50} = 50 $mg \cdot L^{-1}$	Shock addition of DCM to anaerobic sludge. Temp. = 35°C, pH = 7.15-7.4	Hayes and Bailey (1977)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test condiitons	References
Anaerobic sludge microbiota	Gas production	Batch asssay 60-h	0 $mg \cdot L^{-1}$ 3.6 10 32 100	Tot. gas prod. after 60-h (mL): 83 63 48 20 20 EC_{50} = 14 $mg \cdot L^{-1}$	Batch bioassay: nutrient buffer solution, sludge from laboratory digester served as "seed". measured at STP.	Stuckey *et al.* (1980)
		Semi continuous assays 60 days	0 $mg \cdot L^{-1}$ 0.62 2.5 10.0	Tot. gas prod. ($mL \cdot d^{-1}$): 1600 1550 1650 1030 Effluent volatile acids ($mg \cdot L^{-1}$as acetic): 50 60 530 2000	Semi-continuous assays: Temp = 35°C and 1 atm. fate of DCM analysed by GC	
Anaerobic sludge microbiota	Gas production (CO_2 and CH_4)	Batch assay 15-d	0 $mg \cdot L^{-1}$ 3.3 33.2	Approx. max rate ($mL \cdot L^{-1} \cdot d^{-1}$): 312 287 210	Mixed anaerobic culture , Temp = 35°C, gasses analysed using a thermal conductivity detector. Nominal DCM concentrations	Vargas and Ahlert (1987)
Anaerobic acetate and propionate enrichment cultures	Ability to utilize acetate and propionate	Solid Retention Times (SRT): 40 25 15	Slug additon: 44 $mg \cdot L^{-1}$ 88 132 Continuous additon: 20 $mg \cdot L^{-1}$ 40 80	Slug doses at all three concentrations caused failures at all three solid retention times. Systems did not fail; however, effluent concentrations of acetate and propionate were gradually observed to rise directly with increasing DCM levels. • Systems with longer SRTs could tolerate higher DCM levels. • 65-70% reduction in DCM attributed to biodegradation.	Acetate/propionate loading rate was 250 $mg \cdot L^{-1} \cdot d^{-1}$at all three SRTs. Failure = accumulation of 3000 $mg \cdot L^{-1}$ of volatile acids. DCM levels measured after 1,4,and 7 days via GC, FID.	Bhattacharya and Parkin (1988)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test conditons	References
DCM acclimated waste water biota	Biodegradation of DCM	9-11 days for acclim-ation + 50-h for biode-gradation or 24-h for metabolic inhibition studies	1 mg·L^{-1} 10 100	Time for dissappearance of substrate: 3-h 4-h 10-h	Temp = 21°C, pH = 7.2; ^{14}C labelled DCM; GC, FID analysis,	Klečka (1982)
	O_2 consumption and glucose metabolism		10 mg·L^{-1} 100 1000	No significant effect on O_2 consumption and total organic carbon removal at these levels over 24-h		
Insects Stored grain pests: *Sitophilus oryzae* and *Tribolium castaneum*	Number of progeny	24-h	24-h LD_{50}: *S.oryzea*: 2.838 mg·L^{-1} *T. castaneum* 81.28 mg·L^{-1}	Mean no. progeny: control - 2139 fumigated - 2183 control - 4675 fumigated - 4755 • No significant difference between mean number of progeny within species	Temp = 25-30°C, R.H. = 40-90%, Mortality assayed 10 days after fumigation - surviving adults used in productivity study	Rajendran and Mathu (1981)
Birds and Mammals Fertile eggs from Single Comb White Leghorn Chikens	LD_{50}	Injected at time 0-h, moni-tored until final condition was apparent	≥ 0.05 to 25 mg·egg^{-1}.	14.13 mg·egg^{-1} • No teratogenic effects observed	Injected into yolk via absolute ethanol, volume not exceeding 100 µL.	Verrett *et al.* (1980)
Fertile eggs from White Leghorn SK 12 strain	Mortality and teratogenicity	Injected on day 3 or day 6, examined on day 14	5 µmol·egg^{-1} 25 50 100	% Dead: day3 / day6 40 / 40 40 / 30 0 / 20 50 / 22 % Malformed surviors: day3 / day6 0 / 0 0 / 14 13 / 20 25 / 0	DCM dissolved in olive oil and injected into air space at a total volume of 25 µL. • n = 10 at each dose except at 100 µmol·egg^{-1} on day 6, where n = 9.	Elovaara *et al.* (1979)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test condiitons	References
Plants *Lactuca sativa* Grand Rapids lettuce seeds	Germination	Seeds immersed in redistilled DCM for: 10 min, 1-h or 12-h	total immersion in DCM	% germination: control 10 10 min 30 1-h 34 12-h 33	Seeds incubated in the dark at 25°C for 48-h.	Rao *et al.* (1976)
Glycine max Soy bean seeds (cultivars - Hill and Wells)	Germination	Seeds immersed in DCM for 5-h	total immersion in DCM	% germination: Hill: control 60 DCM 63 Wells: control 74 DCM 80 No notable difference from controls.	Seeds incubated in vermiculite or soil at 25°C for 7-d	Ellis *et al.* (1976)
Glycine max Soy bean seeds (cultivars - Amsoy 71 and Wells)	Germination	Seeds immersed in DCM for 2-h	total immersion in DCM	% germination Amsoy 71: control 10 DCM 22 Wells: control 0 DCM 18 Slight increase in the percent of seeds germinating	Seeds stored in darkness for 8 weeks at 40°C following treatment.	Ellis *et al.* (1977)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test conditons	References
Amaranthus retroflexus Pig Weed *Avena sativa* Oats	Germination Respiration	Germination propagules soaked for 4-5 h or for 24-h Respiration Seeds placed in DCM for 7-h	propagules immersed in DCM	% germination relative to controls after 5 d: • 4-5 h exposure stimulated pigweed germination (115%) but inhibited oat germination (72.4%) ; • 24-h exposure inhibited both from germinating (84.3% - Pigweed, 45.8% - Oats). • Removal of hulls of oat grains and seedcoats of pigweed seeds prior to DCM exposure resulted in even greater reductions in germination under same exposure regimes. Scarified propagules: Pig weed: 4-5 h 68.7% 24 h 14.5% Oats: hull-less,before 4-5 h 19.0% hull-less, after 4-5 h 40.7% CO_2 evolution ($mg \cdot h^{-1} \cdot g^{-1}$ dry wt): Oats - day 4: control 0.389 DCM 0.170 Pigweed - day 2: control 3.10 DCM 2.167	Germination propagules placed in petri plates with 3-5 mLs of DCM. •24-h exposure: placed in dark for 24-h and then uncovered to allow for evaporation •4-5 h exposure: plates left for 4-5 h uncovered in germination chamber to allow for evaporation. Respiration Seeds were placed in flasks with 3-5 mLs of DCM and placed in a darkened chamber for 7-h to allow for evaporation. • Germination in water was monitored for 4 days	Brewer and Wilson (1975)

Table 13. Toxicity of dichloromethane to terrestrial biota (continued).

Orgainism	Measured parameter	Total exposure duration	Concentrations	Results	Test conditons	References
Phaseolus vulgaris Snapbean *Pisum sativum* Pea *Beta vulgaris* Sugar beet *Gossypium hirsutum* Cotton	Germination	Seeds soaked for 0.25 - 24 h.	Seeds completely immersed in DCM.	Germination on moist paper towels: • Sugar beet seeds not effected, •Soybean seed germination reduced slightly after 24 h, • Pea seed germination significantly effected after 15 min exposure, • Beans in DCM for 3-h germinated significantly less than non-treated seeds. • Cotton seeds exposed to DCM for 24 h resulted in germination significantly less than non-treated seeds Germination in soil: Soy bean, Pea and Bean seeds were not significantly affected. Note: a significant difference indicates a statistically different value from the controls, P=0.05.	Germination chamber at 25°C for 8-10 d under 24-h light. Soil studies were conducted in sandy loam soil in a green house at 22-25°C and germinability assayed after 2 wks.	Lewis *et al.* (1979))

INT-F = 2-p-iodophenyl-3-p-nitrophenyl-5-phenyl tetrazolium chloride - Formazan

9.0 Waste Management

The removal mechanisms of toxic priority pollutants, including DCM, from a contaminated site may involve air stripping, biodegradation, sorption, chemical oxidation, or any combination of these depending on the environmental site and conditions. Air stripping, which is a very effective method of removing volatile organics from groundwater, was compared in a study to oxidation, using oxidants such as ozone, sodium hypochlorite, chlorine dioxide or hydrogen peroxide. Although the best removal efficiency for all the oxidants tested was found for ozonation, it was believed that the stripping effect, which co-occurred as part of the ozonation procedure, provided the dominant mechanism of removal (Simovic and Jones 1987). One major drawback with the aeration procedure to eliminate DCM is that it will then move directly into the atmosphere. With this in mind, biodegradation may be the ideal method of removal. However, in natural systems there may be several factors which may interfere with the biodegradation of DCM or other xenobiotics, including such factors as environmental conditions, lack of nutrients, and presence of inhibiting substances. Examination of the biological elimination of dichloromethane from contaminated groundwater revealed an inhibitory effect from some co-occurring pollutants (Scholz-Muramatsu *et al.* 1988). In this case, the most significant inhibitors were, 1,2-dichloroethane, ethylbenzene, and xylene. In an examination of the effectiveness between removal mechanisms for a complete-mix continuous flow activated sludge system, biodegradation was the most effective means of removal (93% removed) compared to stripping (7% removed) and sorption (0% removed). This result for DCM was in contrast to the results of other halogenated hydrocarbons in that these others were removed only by stripping. No explanation for this is given (Kincannon *et al.* 1983).

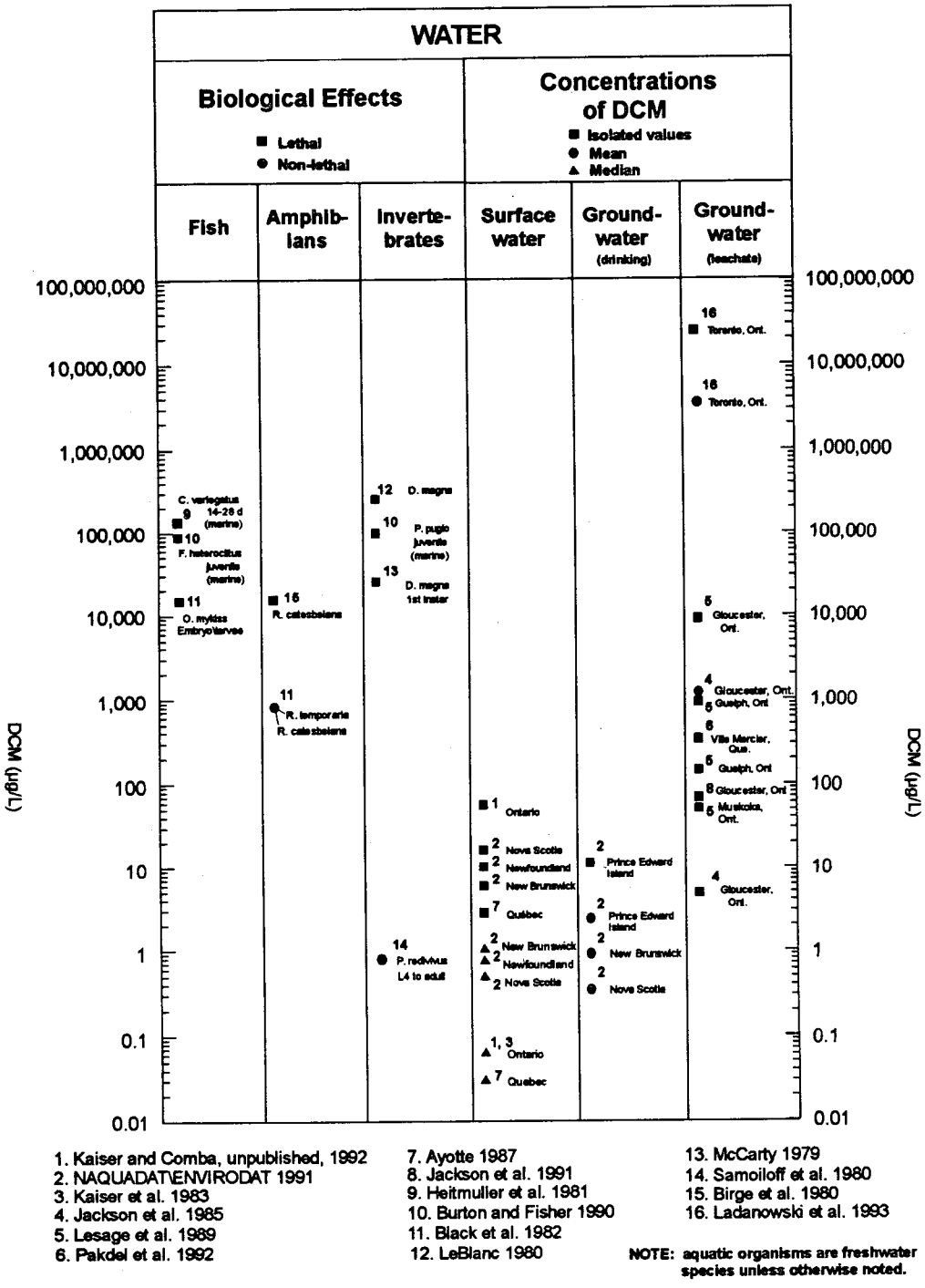
Biological treatment of waste gases is gaining widespread use for effectively removing the pollutant at low cost to the industry and to the environment. For the elimination of DCM from industrial waste gases Gälli (1987) described an efficient sand based fluidized-bed bioreactor using synthetic wastewater. In this system, levels of DCM at 10.2 $g \cdot L^{-1}$ were degraded at 1.6 $g \cdot L^{-1} \cdot h^{-1}$. One disadvantage of this system is in the difficulty in supplying the necessary oxygen levels required for biodegradation. A method designed to overcome this problem involves a modification in the use of a trickle-bed bioreactor where the aqueous phase is kept in circulation and the pollutant is removed from the gas phase flowing through the reactor. Examination of the effectiveness of the trickle-bed bioreactor in removing DCM showed that the system is very stable and not sensitive to fluctuations in DCM concentrations, and that removal of DCM was able to occur at rates as high as 0.2 $g \cdot L^{-1} \cdot h^{-1}$ (Hartmans and Tramper 1991).

In a fluidized-bed bioreactor with an activated carbon base, the ability of the activated carbon to be regenerated was investigated. A problem is that pollutants, which commonly accompany DCM, may effectively kill any microorganisms present and thus render the system useless. For this reason, DCM initially adsorbed to

activated carbon, followed by subsequent biodegradation and regeneration of the activated carbon was investigated (Holst *et al.* 1991). This method was found to be entirely successful under closed conditions, involving pressure impulses of pure oxygen. This procedure was better than aeration alone or oxygenation with low flow rates of pure oxygen.

Incineration of DCM can be an effective means of disposal. For example, incineration of DCM in solvent, where the burn off temperature was 850°C, resulted in complete decomposition of DCM (Oki *et al.* 1990) and incineration in a stabilized thermal combustor at 650°K, was found to be greater than 99.994% efficient (Hung and Pfefferie, 1989). It is therefore believed that incineration of DCM does not provide a pathway into the atmosphere; however, it is important to note that DCM in an aqueous solution did not decompose even at 950 °C (Oki *et al.* 1990).

In an effort to develop an effective method of disposing of DCM it was found that by initially bubbling H_2 or CH_4 into ice-cold DCM followed by subsequent mixing with argon, heating to 500°C and exposing the resulting gas mixture (3.5% DCM, 25% H_2 or CH_4 and 71.5% argon) to incident light (193nm, 180 mwatts) resulted in significant photo-induced dechlorination. The reactions, are believed to involve radical-radical recombination processes involving highly energetic complexes which are either stabilized by collision or fragmented to further reactive radicals. The major products formed include hydrogen chloride, ethylene, acetylene, ethane, propane and vinyl chloride (Poulos *et al.* 1990). This method of removal is not likely as cost effective as other methods and the release of the byproduct of vinyl chloride, being a carcinogen (Sax 1981), is not acceptable and therefore this method is not likely to gain widespread use.



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NOTE: aquatic organisms are freshwater species unless otherwise noted.

Figure 1. Range of dichloromethane (DCM) concentrations in Canadian waters and concentrations causing adverse effects to biota.

10.0 References

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