Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume I: Volatile Organic Compounds
Section 2 - Methylene Chloride

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ABSTRACT

An information base was developed on the physicochemical properties and transport parameters of methylene chloride, which can be used to predict abiotic and biotic transfer of methylene chloride among environmental media (i.e., air, water, soil, and the biosphere) with emphasis on human exposure pathways. Such information should be useful in the multipathway exposure component of health risk assessment for methylene chloride. The environmental literature relevant to methylene chloride was critically reviewed to: (1) determine the intermedia transfer factors relevant to methylene chloride; (2) evaluate measured values; and (3) recommend estimation techniques applicable to methylene chloride (and homologous compounds) for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

1.1 Overview

The assessment of health risk requires the determination of exposure of the human receptor to pollutants from multiple pathways. The movement of chemicals throughout the environment is particularly important to the overall assessment of the exposure to toxic air pollutants since airborne pollutants can be deposited to the soil and water, and can be accumulated in plants and animals. Determination of air toxic contaminant concentrations can be obtained by either pollutant transport modeling or field measurements. Both approaches require an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media.

Risk assessment is often accompanied by uncertainties which arise from the lack of data in various areas leading to reliance on assumptions and default values. For example, the assumptions and default values listed in the CAPCOA guidelines (1992) are designed to err on the side of human health protection to avoid underestimating risk to the public. Major sources of uncertainty in multimedia risk analysis for toxic air pollutants include:

- Extrapolation of toxicity data in animals to humans;
- Air dispersion modeling;
- Estimation of emissions; and
- Analysis of multimedia exposure.

This study addresses the major intermedia transfer factors that are pertinent to multimedia exposure analysis. By identifying the input parameters most critical to multimedia analysis and critically evaluating measured values and estimation techniques, this report should help characterize and minimize the uncertainty associated with estimating risk from multimedia exposure to methylene chloride. A summary of representative values and estimation methods for intermedia transfer parameters for methylene chloride is given in Table 1-1. Although the calculated values presented only apply to specific conditions, representative values have been included for comparison purposes. The details of the reported values and estimation methods are described in the corresponding sections as indicated in Table 1-1.

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Methylene Chloride

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Section in Text
S	0.2355	mol/L	NR	293	NR	IARC, 1979	4.1.1
P_{vp}	57.21	kPa	±4%	298	Measured	Lepori et al., 1991	4.1.2
V_b	0.06450	L/mol	±2%	b.p.$^{(a)}$	Measured	Lepori et al., 1991	4.1.3
MW	84.93309	g/mol	NA	NA	Measured	Cameron and Wichers, 1962	4.1.4
T_{BP}	313.70	K	NR	NA	Measured	Perry, 1927	4.1.5
T_{MP}	176.3	K	NR	NA	Measured	Perry, 1927	4.1.6
T_c	510	K	NR	NA	Measured	Reid et al., 1987	4.1.7
P_c	6355	kPa	NR	NA	Measured	Garcia-Sanchez et al., 1989	4.1.7
ρ	1.3252	g/ml	<1%	293	Measured	Mueller and Ignatowski, 1960	4.1.8
H	0.212	$kPa \cdot m^3/mol$	±10%	293	Measured	Tse et al., 1992	4.2.1
log K_{ow}	1.25	Dimensionless	NR	293	Measured	Hansch and Leo, 1979	4.2.2
log K_{oc}	0.92	Dimensionless	NR	NR	Estimated$^{(b)}$	Valsaraj and Thibodeaux, 1989	4.2.3
BCF	2.34	Dimensionless	±2 orders of magnitude	NR	Estimated$^{(c)}$	Kenaga and Goring, 1980	4.2.4
B_{vd}	7.33	Dimensionless	NR	NR	Estimated$^{(d)}$	Travis and Arms, 1988	4.2.4.1
B_{vw}	NA	Dimensionless	NR	NR	Estimated$^{(e)}$	Briggs et al., 1982	4.2.4.1

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Methylene Chloride

(Continued)

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Section in Text
B_{vaw}	3.56-14.64	Dimensionless	NR	NR	Estimated[f]	See Section 4.2.4.1	4.2.4.1
B_m	1.53×10^{-7}	Dimensionless	NR	NR	Estimated[g]	Travis and Arms, 1988	4.2.4.2
B_b	4.47×10^{-7}	Dimensionless	NR	NR	Estimated[h]	Travis and Arms, 1988	4.2.4.2
D_{air}	0.098	cm^2/s	5-10%	293	Estimated	Reid et al., 1977	4.3.1
D_{water}	1.22×10^{-5}	cm^2/s	5-10%	293	Estimated	Reid et al., 1977	4.3.1
V_d	NA	NA	NA	NA	Estimated[i]	Cohen et al., 1990	4.3.3
Degradation parameters							
k_{air}	14.2×10^{-14}	$cm^3/molec\cdot s$	±25%	298	Recommended value	Atkinson, 1989	4.4.1
$\tau_{1/2\ water}$[j]	25.2	Minutes	±1.7 min.	298	Measured	Dilling et al., 1975	4.4.2
$k_{biodegradation}$	see Table 4-16 for measured values corresponding to specific conditions						

NA = Not Applicable since parameter is strongly dependent on specific environmental conditions.

NR = Not Reported.

(a) Measured at the normal boiling point.

(b) $\log K_{oc} = 0.92 \log K_{ow} - 0.23$

(c) $\log BCF = 2.791 - 0.564 \log S$; S in ppm

(d) $\log B_{vd} = 1.588 - 0.5781 \log K_{ow}$

(e) $B_{vw} = 0.82 + 0.028 K_{ow}^{0.77}/K_d$

(f) Equations 4-23 and 4-24

(g) $\log B_m = -8.056 + 0.992 \log K_{ow}$

(h) $\log B_b = -7.6 + \log K_{ow}$

(i) $V_{d_B} = V_{d_A}\left(\frac{D_B}{D_A}\right)^{2/3}$

(j) Loss from water is primarily by volatilization; therefore, only a half-life is reported.

1.2 Methylene Chloride

Methylene chloride is a chlorinated hydrocarbons and has the chemical formula CH_2Cl_2. It has several chemical synonyms and trade names including: dichloromethane, methylene dichloride, methane dichloride, Aerothene NM, Somethine F30, Freon 30, and F-30. Because of its excellent solvent properties, methylene chloride is widely used in manufacturing, pharmaceutical and food processing industries (CARB, 1989).

It is estimated that about 80% of the methylene chloride used in California is emitted to the atmosphere, with estimated annual statewide emissions averaging 20,000 tons (CARB, 1989). There are no natural sources of methylene chloride and background concentrations measured in the unpolluted troposphere average 35 ppt (USEPA, 1982a; IARC, 1986). Data from monitoring stations indicate statewide population weighted mean concentrations to be between 1.1-2.4 ppb. In 1987, methylene chloride concentrations in the South Coast Air Basin (SoCAB) were the highest in the state, with a population weighted mean concentration of 1.5-3.1 ppb; however, ambient concentrations close to sources have been measured at levels as high as 10.7 ppb.

Use of methylene chloride in consumer products, such as aerosols and paint removers, is expected to increase significantly due to its low toxicity relative to other commonly used solvents and its effectiveness as a CFC replacement (USEPA, 1982a). Evaporative emissions from consumer products may lead to indoor concentrations which far exceed outdoor concentrations. Grupta et al. (1984; cited by CARB, 1989) measured indoor concentrations of 4.2 ppb in areas where outdoor concentrations were in the low ppt range. In a 1991 Los Angeles Total Exposure Assessment Methodology (TEAM) study, Wallace et al. (1991) reported that indoor concentrations of methylene chloride averaged 2-4 times the outdoor concentration. These studies suggest that indoor exposure is a significant pathway which should be considered.

In water, volatilization is the dominant removal mechanism for methylene chloride, with hydrolysis being insignificant (Dilling et al., 1975). In soils, poor sorption to clay may result in buried methylene chloride leaching into groundwater (Howard, 1990). Some studies indicate that biodegradation may be an important removal mechanism for methylene chloride in soils at concentrations up to 400 ppm (Brunner et al., 1980; Davis and Madsen, 1991). Recent studies indicate minimal bioaccumulation of methylene chloride in marine invertebrates, in fish, and in human fat and breast milk (IARC, 1986; McConnell et al., 1975; Antoine et al., 1986; Pellizzari et al., 1982). The dominant mechanism for removal of methylene chloride from the atmosphere is reaction with the radical hydroxyl (OH) (Cox et al., 1976). The amount, if any, of methylene chloride removed via direct photolysis is subject to debate.

Methylene chloride has proven to be mutagenic in bacteria, fungi, plants, nematodes, mice, and rats (IARC, 1979; IARC, 1986). EPA has classified methylene chloride as a Group B2 probable human carcinogen, with inhalation being the dominant route of exposure. Once inhaled, methylene chloride is rapidly absorbed through the lungs and metabolized to carbon monoxide, which then reversibly binds with hemoglobin, forming carboxyhemoglobin (USEPA, 1982a; IARC, 1986; Anderson et al., 1991). Methylene chloride has been shown to readily cross the blood-brain barrier, resulting in narcotic effects. It can also cross the placenta and distribute into the developing fetus, resulting in adverse behavioral effects during postnatal development (USEPA, 1982a; IARC, 1986). In addition, the metabolic pathway leads to reactive intermediates which may be capable of binding to cellular macromolecules, including DNA (CARB 1989). Overall acute toxicity is low, with the main target being the central nervous system. Long term epidemiological studies of workers exposed to mean levels of up to 74 ppm reveal no chronic effects (USEPA, 1982a; U.S. Pharmacopeial Forum, 1989). NIOSH has set the average permissible exposure limit at 75 ppm, with a 15 minute maximum exposure limit of 500 ppm.

2.0 OBJECTIVES

The overall objective of this report is to present information that is pertinent to the prediction of the transfer of methylene chloride between media such as air, water, soil, and biota in order to refine the multipathway exposure component of health risk assessments.

The specific objectives were to: (1) critically review the literature to obtain the parameters necessary to determine environmental intermedia transfer factors for methylene chloride; (2) evaluate and update intermedia transfer factors currently used in multipathway exposure assessments; and (3) provide pollutant-specific estimates where default values are now used, or no value is available.

3.0 METHODOLOGY

In this study, a thorough investigation was conducted of the literature values reported for key factors and parameters which govern the partitioning of methylene chloride in the various important environmental compartments and the food chain, following methylene chloride's release to the atmosphere from stationary and mobile sources. Whenever possible, the reported values for a given parameter were placed on a common basis of units and conditions, and the parameter values were critically evaluated to determine which of these numerical values appear to be of greatest reliability and utility in conducting multipathway exposure assessments. Where no reliable values are found to be available in the literature or default values are currently being used in such discussions, pollutant specific estimates are provided. The details of the methods used, and the properties and parameters investigated, are discussed below.

3.1 Literature Review

A literature search of Dialog (NTIS, Pollution Abstracts, Enviroline, CAS) and UCLA Orion, Melvyl, and EMS library databases was conducted. The UCLA NCITR library was also reviewed for relevant publications. Through this process, the pertinent physicochemical properties, intermedia transport, and biotransformation of methylene chloride were identified, obtained, reviewed, and summarized. The literature evaluation emphasized measured values. Where no measured values were found in the literature, estimation techniques applicable to methylene chloride or homologous compounds were used.

3.2 Selection of Parameters

In order to critically review intermedia transfers, a number of input parameters required in multimedia exposure assessment were considered. The final selection was based on the chemical and physical interpretation of the input parameters, their applicability to different classes of pollutants, and measures of the environmental consequences of intermedia transfers. Specifically, input parameters from the Air Resources Board/Department of Health Services (ARB/DHS) Health Risk Assessment (HRA) software and algorithms (CAPCOA Guidelines, 1990, 1991, 1992) and the South Coast Air Quality Management District Multi-Pathway Health Risk Assessment Input Parameters Guidance Document (SCAQMD, 1988) were considered. Also, the input data required by three alternative multimedia models (SMCM, Fugacity, and GEOTOX) were also evaluated. The following subsections discuss the rationale for selecting input parameters as well as general limitations in their use.

3.2.1 Physicochemical Parameters

The physicochemical properties of methylene chloride are needed for the determination of parameters such as partition coefficients and biotransfer factors, as well as for the analysis of intermedia transport parameters (e.g., mass transfer coefficients). Often the chemical properties that are needed are specific to the correlations that are used to evaluate factors such as partition coefficients and solubility.

A critical literature review was conducted and it was determined that the minimum necessary physicochemical factors for methylene chloride required for conducting a multimedia exposure assessment of methylene chloride as described by CAPCOA, 1992 and other models (e.g., SMCM, Fugacity, and GEOTOX) are as follows:

- Water Solubility;
- Vapor Pressure (as a function of temperature);
- Molar Volume (at the boiling point);

- Boiling Point; and
- Molecular Weight.

The definition of these parameters and the results of the literature review are presented in Section 4.0.

3.2.2 Partition Coefficients

Methylene chloride released to the environment is distributed to various environmental compartments as a result of transport processes. The net transport of methylene chloride from one compartment to another is limited by equilibrium constraints and quantified by partition coefficients. Thus, the partition coefficient, H_{ij} is generally defined as

$$H_{ij} = C_i/C_j \tag{3-1}$$

where C_i is the equilibrium concentration in compartment i and C_j is the equilibrium concentration in compartment j. The following types of partition coefficients for methylene chloride were considered in this study:

- Henry's Law Constant;
- Octanol-Water Partition Coefficient;
- Soil/Water-Organic Carbon Partition Coefficient; and
- Bioconcentration Factors.

Values for some partition coefficients for methylene chloride reported in the literature have been determined experimentally in simulated ecosystems and estimated for others. These partition coefficients are discussed individually in Section 4.2.

3.2.3 Intermedia Transport Parameters

In order to estimate the rate of methylene chloride transport across environmental phase boundaries, one must first be able to describe the transport mechanisms and consequently estimate the associated transport parameters as a function of the appropriate environmental conditions. Intermedia transport processes occur by either convective transport (not addressed in this report) or interfacial transport from one environmental compartment to another.

The relevant intermedia transfer parameters for methyl chloride are as follows:

- Diffusion Coefficients in Air and Water;
- Intermedia Mass Transfer Coefficients;
- Dry Deposition Velocity;
- Washout Ratios; and
- Biotransfer Factors.

These intermedia transport parameters are defined and discussed in Section 4.3. In addition, bioavailability and pharmacokinetics should also be considered in evaluating methylene chloride accumulation in biological receptors as briefly discussed in Section 4.2.6.

3.2.4 Degradation Processes

Reaction rates for individual abiotic and biotic degradation processes are often expressed as the first order or "pseudo" first order reaction rate. These first order reaction rate constants can be used to estimate overall environmental degradation half-lives. Degradation rates are determined for an individual chemical or biochemical transformation processes within specific media. Since degradation processes involve chemical changes as opposed to intermedia transport processes which involve the flux of the unchanged chemical through the environment, degradation half-lives for soil, water, and air do not account for intermedia transport of a chemical and are, therefore, not necessarily representative of a chemical's actual persistence within a particular environmental medium (Howard et al., 1991). Degradation processes considered significant to assessing the transformation of methylene chloride in the environment (Howard, et al., 1991) are as follows:

Hydroxyl radical (OH) reaction in air: The most significant degradation process for methylene chloride in the atmosphere is its reaction with atmospheric OH radicals during daylight hours with the reaction rate constant (k_{OH}) being 1.42×10^{-13} $cm^3/molec\cdot s$ at 298K (Atkinson, 1989). Other potential degradation reactions include nighttime reaction with the gaseous nitrate (NO_3) radical and reaction of methylene chloride with ozone. However, only the reaction with OH radicals is fast enough to be an important atmospheric loss process for methylene chloride (see Section 4.4.1).

Biodegradation in water and soil: Biodegradation is one of the most important environmental processes that cause the breakdown of environmental compounds. It is a significant loss mechanism in soil and aquatic systems and plays an important role in wastewater treatment. The biodegradation half-lives reported by Davis and Madsen (1991) for aerobic conditions range from 1.3-54.8 days depending on the soil type and initial concentration. These half-lives can be significantly shorter if the soil is preexposed to methylene chloride for 50 days. Brunner et al. (1980) found biodegradation rates to decrease by about 40% under anaerobic conditions. In general, biodegradation rates in water and soil under aerobic conditions are higher than anaerobic biodegradation.

Photolysis in air and water: Half-lives for direct photolysis are based on irradiation of a chemical in solution at environmentally important wavelengths (>290 nm). Photolysis rates in air are assumed to equal those in solution. The typical frequencies of maximum absorption, λ_{max}, and whether or not absorption occurs at wavelengths >290 nm may indicate whether a chemical has the potential to undergo photolysis in the environment. Hubrich and Stuhl (1980) determined that methylene chloride does not absorb wavelengths greater than 255 nm; therefore, no tropospheric photolysis is expected to occur. The results of studies performed by Dilling et al. (1976) on methylene chloride in an aqueous solution indicate that photolysis is negligible.

Photooxidation reactions with alkylperoxy ($RO_2\cdot$) radicals, hydroxyl ($OH^{\cdot}$) radicals or singlet oxygen ($^1O_2$) in water: For some chemical classes, reactions with photooxidants in sunlit waters can be important. As with photooxidation in air by OH radicals, the range of half-lives is calculated from reaction rate constants and monitored concentrations of oxidants in relatively oligotrophic and eutrophic natural waters (Howard et al., 1991). This degradation process is not considered significant compared to evaporation.

Hydrolysis in water and soil: Hydrolysis only applies to a limited number of chemicals that have hydrolyzable functional groups such as esters, aliphatic halogens, amides, carbamates, and phosphate esters. Dilling et al. (1975) measured a methylene chloride half-life due to hydrolysis of 18 months. Therefore, hydrolysis is not a significant removal process compared to volatilization.

In summary, the following abiotic and biotic degradation processes were evaluated for methylene chloride:

- Photooxidation Rate/Half-Life in Air;
- Biodegradation Rate/Half-Life in Water;
- Evaporation Rate/Half Life in Water;
- Biodegradation Rate/Half-Life in Soil; and
- Overall Half-Life in Environmental Media.

These processes are discussed further in Section 4.4.

4.0 PRESENTATION OF RESULTS

The following subsections define, discuss, and summarize the findings of the literature search for each of the parameters reviewed for this study. Equations defining input parameters and estimation techniques are presented, where appropriate.

Values found in the literature for the input parameters are summarized in Tables 1-1 through 4-16. Data in the tables are arranged by decreasing order of reliability. Measured values of known uncertainty are listed first. Measured values reported without estimates of uncertainty are listed next, followed by calculated values reported with the corresponding prediction equations and uncertainty estimates. Calculated values reported without their associated estimation equations were reported last.

Values from references for which the derivation of the results could not be ascertained and multiple references to the same measured value are listed below the dotted line in the summary tables. The scientific confidence in these results is clearly limited; they have been included only to reflect the range of values commonly reported in the current environmental literature. Values for input parameters have been converted to consistent SI units to facilitate comparison of results. The converted values have been reported with same number of significant figures as the values reported in the corresponding reference. Specific conversion equations are shown in the tables. It should be noted that commonly used forms of estimation equations often require input parameters in non-SI units. These cases have been identified in the text following presentation of the appropriate equations.

4.1 Physicochemical Parameters for Methylene Chloride

Section 3.2.1 describes the general need for using physicochemical parameters in multipathway assessment. This section defines the specific physicochemical parameters that should be used for multimedia analysis of pollutants and discusses the results of the literature survey.

4.1.1 Solubility in Water

The water solubility (S) of a chemical is defined as the maximum amount of the chemical that will dissolve in pure water at a specific pressure, temperature and pH. The units of aqueous solubility are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, μg/L, mol/L etc.). Less common units are mole fraction and molal concentration (moles per kg of solvent). In this report solubility is given in mol/L to be consistent with SI units. Values for the water solubility of methylene chloride found in the literature are summarized in Table 4-1. Most solubility data were reported at 25° C. Reported solubilities vary between 0.2284 mol/L at 283 K (Dilling, 1977) and 0.2565 mol/L at 310 K (Paterson and Mackay, 1989). Since solubility of organics typically increases with temperature (Lyman et al., 1990), assessment of the consistency of the above results is difficult. The solubility value of 0.1530 mol/L reported by Riddick and Bunger (1970) and later referenced by Howard (1990) appears to be low in comparison to other reported values.

Abraham et al. (1985) used the Ostwald coefficient as a surrogate for solubility. This empirically derived coefficient represents the volume of a gas which can be dissolved in a unit volume of solvent (in this case water) at a specific temperature and pressure (Reid et al., 1987). Ostwald coefficients are often used for heterogenous solvents whose molecular weight is difficult to characterize, thereby prohibiting the expression of solubility in terms of mole fraction. Conversion of Abraham's reported Ostwald coefficients to units of mol/l yields solubility values which are uniformly higher than other reported values. Examination of other values which Abraham et al. (1985) derived from Ostwald coefficients and expressed in conventional units shows that Ostwald coefficients appear to overestimate physicochemical parameters (for example, vapor pressure calculated using Ostwald coefficients was 91.80 kPa versus other reported values of 56-58 kPa). Therefore, use of the Ostwald coefficients reported by Abraham may be unreliable.

Table 4-1. Solubility of Methylene Chloride in Water*

Solubility mol·l^{-1}	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
0.1530	1.30(c)	weight %	NR	298	Measured(i)	Riddick and Bunger, 1970	Kiss, 1949
0.2830	0.8573(g)	log L(f)	±20%	310	Calculated(e)	Abraham et al., 1985	
0.3839	0.9726(g)	log L(f)	±20%	298	Calculated(e)	Abraham et al., 1985	
0.2565	256.5(d)	mol·m^{-3}	NR	310	Calculated(e)	Paterson and Mackay, 1989	Abraham et al., 1985
0.2355	20(a)	g·l^{-1}	NR	293	NR	CARB, 1989	USEPA, 1982a
0.2355	20(a)	g·l^{-1}	NR	293	NR	Merlin et al., 1992	USEPA, 1982a
0.1625	1.38(h)	g/100 ml H_2O	NR	293	NR	IARC, 1986	
0.2331	19,800(b)	ppm	NR	298	NR	Dilling et al., 1975	Kirk-Othmer, 1964
0.2884	19,400(b)	ppm	NR	283	NR	Dilling, 1977	McConnell et al., 1975
0.1554	13,200(a)	g/m^3	NR	293	NR	Mackay and Shiu, 1981	Neely, 1976
0.1530	13,000(a)	mg·l^{-1}	NR	298	NR	Howard, 1990	Riddick, 1986
0.1554	13.2(h)	g/kg	NR	293	NR	Kirk-Othmer, 1979	NR
0.2355	2.0(h)	g/100 ml H_2O	NR	293	NR	USEPA, 1982a	Weast and Astle, 1969
0.1554	13,200(b)	ppm	NR	293	NR	McConnell et al., 1975	NR
0.2355	20,000(b)	ppm	NR	293	NR	U.S. EPA, 1982b	Callahan et al., 1979
0.2355	2(h)	g/100 g H_2O	NR	293	NR	IARC, 1979	Hardie, 1964

Table 4-1. Solubility of Methylene Chloride in Water
(Continued)

Solubility $mol \cdot l^{-1}$	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
0.1966	16,600$^{(a)}$	mg/l	NR	298	NR	Verschueren, 1983	
0.2355	20,000$^{(a)}$	mg/l	NR	293	NR	Verschueren, 1983	

NR = Not reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) $20\ g \cdot l^{-1} \times 1\ mol/84.94\ g = 0.2335\ mol \cdot l^{-1}$

(b) $19{,}800\ ppm = 19{,}800\ \mu g \cdot ml^{-1} \times 1\ g/10^6\ \mu g \times 1000\ ml \cdot l^{-1} \times 1\ mol/84.94\ g = 0.2331\ mol \cdot l^{-1}$

(c) $1.30\% = 1.30\ g$ methylene chloride/g water$\times 1\ mol/84.94\ g \times 1000\ g/l\ water \times 1/100\% = 0.1530\ mol \cdot l^{-1}$

(d) $256.5\ mol \cdot m^{-3} \times 1\ m^3/1000\ l = 0.2565\ mol \cdot l^{-1}$

(e) Calculated from Ostwald coefficients (Abraham et al., 1985).

(f) L = Ostwald coefficient. An empirically derived representation of the volume of a gas which can be dissolved in a unit volume of solvent in (in this case, water) (see (e)).

(g) $$10^{.9726} = 9.3\ l = \left[\frac{(9.3\ l)\ (1\ atm)}{\left(0.08206\ \frac{l\ atm}{mole\ K}\right)(298\ K)} = 0.3839\ \frac{moles}{l} \right]$$

(h) $$13.2\ g/kg * \frac{1\ kg}{1\ H_2O} = 13.2\ g/l * \frac{1\ mole}{84.94\ g} = .1554\ \frac{mole}{l}$$

(i) Riddick and Bunger provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

4.1.2 Vapor Pressure

The saturation vapor pressure, P_{VP}, is a measure of the volatility of a chemical in its pure state and is an important determinant of the rate of vaporization. Estimating P_{VP} requires information on the following properties: (1) critical temperature; (2) critical pressure; and (3) heat of vaporization, and/or the vapor pressure at some reference temperature. The units of P_{VP} can be stated in atm, torr, mm Hg, or Pa. In this report P_{VP} is given in kPa.

The vapor pressure of methylene chloride is dependent on temperature and it can be calculated from the following Antoine equation applicable for a temperature range of 264 K to 312 K (Reid et al., 1987):

$$\log_{10} P_{VP} = A - B/(C + T) \qquad (4\text{-}1)$$

$$(\text{where } P_{VP} \text{ in kPa; } T \text{ in K})$$

The constants in the Antoine Equation for methylene chloride were empirically derived by Dykyj (1984) and reported by Stephenson et al. (1987):

$A = 6.1849$

$B = 1126.53$

$C = - 43.46$

Values of vapor pressure measured at 298 K range from 53.16 kPa (Stull, 1947) to 58.40 (IARC, 1986). Many of the values cited in the literature descend from the measurements of Perry (1927), who reported a vapor pressure value at 297.6 K of 56.37 kPa. More recent measurements by Dykyj (1987) and Lepori et al. (1991) place the vapor pressure at a slightly higher value of 57.21-57.41 kPa. Perry's experiments were done with purified methylene chloride and represent reliable values. The discrepancy may result from the 0.4 K temperature difference at which these measurements were made or from instrumental and experimental differences.

Table 4-2. Vapor Pressure of Methylene Chloride as Cited in the Environmental Literature*

Vapor Pressure (kPa)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
43	43	kPa	±10 kPa	292.5	Measured$^{(a)}$	Garcia-Sanchez et al., 1989	
47.38	47.38	kPa	±3.4 kPa	293	Measured$^{(b)}$	Jancso et al., 1990	
55	55	kPa	±10 kPa	297.6	Measured$^{(a)}$	Garcia-Sanchez et al., 1989	
57.21	57.21	kPa	±4%	298	Measured$^{(c)}$	Lepori et al., 199	
70.30	529.02$^{(d)}$	mm Hg	±.02 mm Hg	303	Measured$^{(e)}$	Mueller and Ignatowski, 1960	
57.92	435.8$^{(d)}$	mm Hg	NR	298	Measured$^{(f)}$	Riddick and Bunger, 1970	Stull, 1947
47.19	355.1$^{(d)}$	mm Hg	NR	293.3	Measured$^{(g)}$	Perry, 1927	
56.37	424.2$^{(d)}$	mm Hg	NR	297.6	Measured$^{(g)}$	Perry, 1927	
57.43	57.43	kPa	NR	298	Calculated$^{(h)}$	Stephenson et al., 1987	Dykyj, 1987$^{(i)}$
91.80	9.18×10^4	Pa	NR	310	Calculated$^{(j)}$	Paterson and Mackay, 1989	Abraham et al., 1985
48.18	0.4770$^{(k)}$	bar	±25%	293	NR	Tse et al., 1992	DIPPR, 1985$^{(l)}$
46.38	349$^{(d)}$	mm Hg	NR	293	NR	CARB, 1989	USEPA, 1982a
46.53	46.53	kPa	NR	293	NR	Mackay and Shiu, 1981	
57.80	434.9$^{(d)}$	mm Hg	NR	298	NR	Howard et al., 1991	Boublik, 1984
53.16	400$^{(d)}$	mm Hg	NR	297.1	NR	IARC, 1986	Weast and Astle, 1985
53.16	400$^{(d)}$	mm Hg	NR	297.1	NR	Jordan, 1954	Stull, 1947

Table 4-2. Vapor Pressure of Methylene Chloride as Cited in the Environmental Literature
(Continued)

Vapor Pressure (kPa)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
48.16	362.4(d)	torr	NR	293	NR	U.S. EPA, 1982b	Callahan et al., 1979
53.16	400(d)	mm Hg	NR	297.1	NR	Stull, 1947	Perry, 1927
58.40	58.40	kPa	NR	298	NR	Mackay and Shiu, 1981	Dilling, 1977
58.21	438(d)	mm Hg	NR	298	NR	Dilling, 1977	Hayduk and Laudie, 1974
56.61	426(d)	mm Hg	NR	298	NR	Dilling et al., 1975	Kirk-Othmer, 1964
46.38	349(d)	mm Hg	NR	293	NR	U.S. Pharmacopeial Forum, 1989	NR
46.5	46.5	kPa	NR	293	NR	Kirk-Othmer, 1979	NR
48.16	362.4(d)	mm Hg	NR	298	NR	McConnell et al., 1975	NR
57.94	436(d)	mm Hg	NR	298	NR	USEPA, 1982a	Weast and Astle, 1969
53.16	400(d)	mm Hg	NR	297.1	NR	IARC, 1979	Perry, 1973
68.1	68.1	kPa	NR	303	NR	Kirk-Othmer, 1979	NR
46.38	349(d)	mm Hg	NR	293	NR	Verschueren, 1983	
66.45	500(d)	mm Hg	NR	303	NR	Verschueren, 1983	

NR = Not reported.

* For a given temperature, the listed order is by decreasing confidence in reported values (see Section 3.0).

Table 4-2. Vapor Pressure of Methylene Chloride as Cited in the Environmental Literature
(Continued)

(a) Measured using the "open-tubed" technique.

(b) Measured using differential capacitance manometer apparatus.

(c) Measured using head-space gas chromatograph.

(d) 349 mm Hg×1 atm/760 mm Hg×101 kPa·atm^{-1} = 46.38 kPa

(e) Measured using a Scathard equilibrium still plus a manometer/cathometer system.

(f) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

(g) Vapor Pressure of purified methylene chloride measured using a Gaertner cathotometer.

(h) Calculated from the Antoine equation; values for A, B, and C empirically derived by Dykyj, 1984 (see text).

(i) Document published in Czech.

(j) Calculated from Ostwald coefficients.

(k) 0.4770 bar = 0.4770 atm×101 kPa·atm^{-1} = 48.18 kPa

(l) DIPPR = Design Institute for Physical Property Data

As is the case with solubility measurements, vapor pressure of 91.80 kPa calculated by Paterson and Mackay (1989) from Ostwald coefficients correlations is significantly higher than other reported values, and therefore, may be unreliable.

4.1.3 Molar Volume

The molar volume (V_b) of methylene chloride, expressed in units of cm^3/mol, is the volume of a mole of liquid methylene chloride at the normal boiling temperature. The molar volume of an organic liquid is a useful parameter because it has been correlated with the normal boiling point and it is used in techniques for estimating diffusion coefficients in air and water.

The molar volume of methylene chloride is presented in Table 4-3. The value of 64.5 cm^3/mol measured by Lepori et al. (1991) is considered more accurate than the value reported by Stephenson et al. (1987). Stephenson et al. (1987) calculated molar volume by dividing the molecular weight of methylene chloride (84.9 g/mol) by the density (1330 g/L) to obtain a value of 63.9 cm^3/mol; however, the density value used was measured at 288.15 K, not at the normal boiling temperature (313 K), yielding a lower molar volume than the measured value of Lepori et al. (1991).

4.1.4 Molecular Weight

The molecular weight is used for converting from mass to concentration and in various correlations of transport properties (e.g., diffusion coefficients). Cameron and Wichers, in their 1962 report to the International Commission on Atomic Weights, rigorously defined all the atomic weights, accounting for the isotopic distribution of each. The molecular weight of methylene chloride based on their report is 84.93309 g/mol. The reported literature values vary from 84.92 to 85.0. The variation among reported values is due to the number of significant figures reported or rounding to significant figures.

Table 4-3. Molar Volume of Methylene Chloride*

Molar Volume (cm^3/mol)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
64.5	64.50[(a)]	cm^3/mol	±2%	b.p.[(b)]	Measured[(c)]	Lepori et al., 1991	
63.9	63.9	m^3/mol	NR	288.15	Calculated[(d)]	Stephenson et al., 1987	Kirk-Othmer, 1979

NR = Not reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) $64.50\ cm^3/mol \times 1\ L/1000\ cm^3 = 0.06450\ L/mol$

(b) Measured at the normal boiling point.

(c) Measured using head-space gas chromatograph.

(d) Calculated as $\frac{\text{molecular weight}}{\text{density}}$.

4.1.5 Boiling Point Temperature

The boiling point temperature, T_{BP}, is defined as the temperature at which the vapor pressure of a liquid is equal to the total pressure above the liquid. For pure compounds, the normal T_{BP} is defined as the T_{BP} at one atmosphere of pressure. T_{BP} provides an indication of the physical state and volatility of a chemical. T_{BP} is also an important parameter used in the prediction of other physical properties.

Examples of boiling points reported in the literature for methylene chloride are listed in Table 4-4. Reported values range from 312.75 K (Riddick and Bunger, 1970) to 313.7 K (Perry, 1927). The 0.3% difference between the highest and lowest reported values probably results from variation in experimental methods and from difference in rounding to significant figures. If one applies the standard pressure of 101 kPa to Eq. 4-2, then the boiling point temperature for methylene chloride can be obtained from:

$$T_{BP} = B/(A - \log_{10}P) - C \qquad (4\text{-}2)$$

$$T_{BP} = 312.93 \text{ K}$$

which agrees with the values reported in Table 4-4.

4.1.6 Melting Point Temperature

The melting point of a pure substance is defined as the temperature at which its crystals are in equilibrium with the liquid phase at atmospheric pressure. T_{mp} provides an indication of the physical state of a chemical, at the temperature of interest, and can also be used in the prediction of other physicochemical properties, such as vapor pressure and K_{ow}. At well defined temperatures, the melting point is identical to the freezing point.

Examples of melting points reported in the literature for methylene chloride are listed in Table 4-5. The 0.9% difference between the highest and lowest reported values [176.2K (Buckingham, 1982) to 177.9K (Weast and Astle, 1981)] is probably the result of subtle variations in experimental procedures and from differences in rounding to significant figures.

Table 4-4. Boiling Point of Methylene Chloride*

Boiling Point (K)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	References	Source Cited
312.75	39.75(a)	°C	NR	1 atm	Measured(b)	Riddick and Bunger, 1970	Maryott, 1941
313.70	313.70	K	NR	NR	Measured(c)	Perry, 1927	
313.0	313.0	K	NR	NR	Measured(d)	Reid et al., 1987	NR
313	40(a)	°C	NR	1 atm	NR	CARB, 1989	USEPA, 1982a
312.75	39.75(a)	°C	NR	1 atm	NR	Howard, 1990	NR
312.8	39.8(a)	°C	NR	1 atm	NR	Kirk-Othmer, 1979	NR
313	40(a)	°C	NR	1 atm	NR	USEPA, 1982a	Weast and Astle, 1969
314	41(a)	°C	±1°C	NR	NR	Verschueren, 1983	
313	104(e)	°F	NR	NR	NR	U.S. Pharmacopeial Forum, 1989	NR
312.7	39.7(a)	°C	NR	NR	NR	Mackay and Shiu, 1981	
313	40 (a)	°C	NR	NR	NR	Weast and Astle, 1981	
312.95	312.95	K	NR	NR	NR	Stephenson et al., 1987	DIPPR(f), 1985
313	40(a)	°C	NR	NR	NR	IARC, 1986	Weast and Astle, 1985
313.7	40.7(a)	°C	NR	NR	NR	Jordan, 1954	Stull, 1947
313.7	40.7(a)	°C	NR	NR	NR	Stull, 1947	Perry, 1927

Table 4-4. Boiling Point of Methylene Chloride*
(Continued)

Boiling Point (K)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	References	Source Cited
313.1	40.1[a]	°C	NR	NR	NR	Buckingham, 1982	NR
312.75	39.75[a]	°C	NR	NR	NR	U.S. EPA, 1982b	Callahan et al., 1979
313.1	40.1[a]	°C	NR	NR	NR	IARC, 1979	NR
313.1	40.1[a]	°C	NR	NR	NR	McConnell et al., 1975	NR

NR = Not reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) 39.75 °C + 273 = 312.75 K

(b) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

(c) Measured in a boiling ethyl bromide bath.

(d) Reid et al. (1987) provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for boiling point measurements.

(e) (104 °F -32) × 0.5556 + 273 = 313 K

(f) Design Institute for Physical Property Data

Table 4-5. Melting Point of Methylene Chloride*

Melting Point (K)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	References	Source Cited
176.3	-96.7[a]	°C	NR	f.p.[b]	Measured[c]	Perry, 1927	
178.1	178.1	K	NR	f.p.[b]	Measured[d]	Reid et al., 1987	NR
177.86	-95.14[a]	°C	NR	NR	Measured[e]	Riddick and Bunger, 1970	Dreisbach, 1961
177	-96[a]	°C	±1°C	NR	NR	CARB, 1989	USEPA, 1982a
177	-96[a]	°C	±1°C	NR	NR	USEPA, 1982a	Weast and Astle, 1969
176.45	176.45	K	NR	f.p.[b]	NR	Stephenson et al., 1987	DIPPR[f], 1985
176.2	-96.8	°C	NR	f.p[b]	NR	Buckingham, 1982	NR
176.3	-96.7	°C	NR	f.p.[b]	NR	Kirk-Othmer, 1979	NR
176	-97[a]	°C	NR	f.p.[b]	NR	IARC, 1979	NR
178	-95	°C	NR	NR	NR	U.S. EPA, 1982b	Callahan et al., 1979
176	-97[a]	°C	NR	NR	NR	Verschueren, 1983	
177.9	-95.1[a]	°C	NR	NR	NR	Mackay and Shiu, 1981	
176.3	-96.7[a]	°C	NR	NR	NR	Stull, 1947	Perry, 1927
177.9	-95.1[a]	°C	NR	NR	NR	Howard, 1990	NR
177.9	-95.1[a]	°C	NR	NR	NR	Weast and Astle, 1981	
177.9	-95.1[a]	°C	NR	NR	NR	IARC, 1986	Weast and Astle, 1985

Table 4-5. Melting Point of Methylene Chloride*
(Continued)

NR = Not reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) 273 - 95.14° C = 177.86 K

(b) Reported as freezing point temperature

(c) Measured in an ice bath.

(d) Reid et al. (1987) provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for melting point measurements.

(e) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

(f) Design Institute for Physical Property Data

4.1.7 Critical Temperature and Pressure

The critical temperature of a pure substance is defined as the temperature above which a gas cannot be liquified. The critical pressure of a pure substance is defined as the minimum pressure required to liquify a gas at its critical temperature. T_c and P_c are parameters often used in estimation of physicochemical parameters such as boiling point, liquid density, vapor pressure, and heat of vaporization.

Examples of critical temperatures reported in the literature for methylene chloride are listed in Table 4-6. Garcia-Sanchez et al. (1989) notes that the values he measured are slightly low due to unforeseen experimental artifacts. The most reliable value is between the measured values of 510 K (Riddick and Bunger, 1970; Reid et al., 1987) and 518 K (Perry, 1927; Stephenson et al., 1987).

Examples of critical pressures reported in the literature for methylene chloride are listed in Table 4-7. Variations among the reported valued are probably due to differences in the critical temperature values at which the experiments were performed. Because details of the experiments were not provided, it is difficult to identify the most reliable critical pressure value but it appears that the value reported by Reid et al. (1987) is the commonly used critical pressure for methylene chloride.

4.1.8 Liquid Density

The liquid density (ρ) of a substance is the ratio of its mass to its volume, with units of g/cm^3. The density varies with molecular weight, molecular interactions, and temperature. Density can be used to estimate the molar volume and is a useful parameter in correlations used to estimate diffusion coefficients in air and water.

Examples of densities reported in the literature for methylene chloride are listed in Table 4-8. Small differences in the values stem either from the number of significant figures

Table 4-6. Critical Temperature of Methylene Chloride*

Critical Temperature (K)	Reported Value	Reported Units	Reported Uncertainty	Technique	References	Source Cited
518.1	245.1(a)	°C	NR	Measured	Perry, 1927	
510	237(a)	°C	NR	Measured(b)	Riddick and Bunger, 1970	Dzung, 1946
510	510	K	NR	Measured(c)	Reid et al., 1987	NR
508.0	508.0	K	NR	Measured(d)	Garcia-Sanchez et al., 1989	
518.5	518.5	K	NR	NR	Stephenson et al., 1987	DIPPR(e), 1985
518	245(a)	°C	NR	NR	Kirk-Othmer, 1979	NR

NR = Not reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) converted to degrees K by adding 273 to the indicated temperature (in degrees C).

(b) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

(c) Reid et al. (1987) provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for critical temperature measurements.

(d) Samples were confined by Hg in an inverted tube. Critical temperature was determined by the observation of the disappearance of the gas-to-liquid meniscus.

(e) AIChE, Design Institute for Physical Property Data

Table 4-7. Critical Pressure of Methylene Chloride*

Critical Pressure (kPa)	Reported Value	Reported Units	Reported Uncertainty	Technique	References	Source Cited
6355	6355	kPa	NR	Measured[a]	Garcia-Sanchez et al., 1989	
6363	63[b]	bar	NR	Measured[c]	Reid et al., 1987	NR
6150.9	60.9[b]	atm	NR	Measured[d]	Riddick and Bunger, 1970	Kirk-Othmer, 1979
6170.99	61.099[b]	atm	NR	NR	Kirk-Othmer, 1979	NR
6171	6171	kPa	NR	NR	Stephenson et al., 1987	DIPPR[e], 1985

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Samples were confined by Hg in an inverted tube. Critical pressure was determined by the observation of the disappearance of the gas-to-liquid meniscus.

(b) 63 bar = 63 atm×101 kPa/atm = 6363 kPa

(c) Reid et al. (1987) provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for critical pressure measurements.

(d) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data

(e) AIChE, Design Institute for Physical Property Data

Table 4-8. Liquid Density of Methylene Chloride*

Liquid Density (g/cm^3)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
1.3252	1.3252	g/ml	NR	293	Measured(a)	Mueller and Ignatowski, 1960	
1.3168	1.3168(b)	g/cm^3	NR	298	Measured(c)	Riddick and Bunger, 1970	Timmermans, 1933
1.3078	1.3078(b)	g/cm^3	NR	303	Measured(c)	Riddick and Bunger, 1970	Timmermans, 1933
1.317	1.317(b)	g/cm^3	NR	298	Measured(d)	Reid et al., 1987	NR
1.3266	1.3266	g/ml	NR	293	NR	Weast and Astle, 1981	
1.3266	1.3266	g/ml	NR	293	NR	IARC, 1986	Weast and Astle, 1985
1.326	1.326(b)	g/cm^3	NR	293	NR	Kneller and Geiger, 1989	Dreisbach, 1959
1.3157	1315.7(e)	kg/m^3	NR	293	NR	Kirk-Othmer, 1979	NR
1.33	1.33	g/ml	NR	293	NR	CARB, 1989	WHO, 1984
1.326	1.326	g/ml	NR	293	NR	USEPA, 1982a	Weast and Astle, 1969
1.33	1.33	g/ml	NR	288	NR	Buckingham, 1982	NR
1.335	1.335	g/ml	NR	288	NR	IARC, 1979	NR

NR = Not reported.

* For a given temperature, the listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Measured using a bicapillary pycometer in vacuo.

(b) 1.3168 g/cm^3 = 1.3168 g/ml

(c) Riddick and Bunger (1970) provide a collection of experimentally derived physical properties of organic solvents. Values presented represent their interpretation of the most reliable data.

(d) Reid et al. (1987) provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for liquid density measurements.

(e) $1315.7\ kg/m^3 \times 1000\ g/kg \times 1\ m^3/10^6\ cm^3 \times 1\ cm^3/ml = 1.3157\ g/ml$

reported or from the different temperatures at which the density was measured. The measured values for the temperature range of 293K - 303K range from 1.3078 g/cm^3 to 1.3252 g/cm^3.

4.2 Partition Coefficients for Methylene Chloride

Section 3.2.2 provides general equations for the various partition coefficients. The definition and reported values for the individual partition coefficients are presented in the following subsections.

4.2.1 Henry's Law Constant

The Henry's Law constant is a particularly important parameter for evaluating chemical partitioning between air and water and is required as an input parameter in most multimedia models. The Henry's Law constant of a chemical (H_i) is defined as:

$$H_i = P_i/C_i \tag{4-3}$$

where P_i is the partial pressure of the compound (e.g., kPa), at the system temperature, and C_i is the concentration (e.g., mol/m^3) of the chemical in the aqueous phase in equilibrium with the air phase.

The Henry's Law constant may be determined experimentally or estimated, although it is preferable to use an experimentally determined value. An estimated value of H_i can be obtained from the following equation (Lyman et al., 1990; Reid et al., 1987):

$$H_i = P_{vp}/S \tag{4-4}$$

where S is the solubility in water (e.g., mol/m^3) and P_{vp} is the saturation vapor pressure (e.g., kPa). This expression is valid only for solutes for which the activity coefficient is constant at concentrations ranging from the solubility limit and below.

The following empirical correlations for the Henry's Law for methylene chloride as a function of temperature was proposed by Leighton and Calo (1981).

$$H' = [0.21935 \exp(17.42-(3645/T))/T] \qquad \text{(Leighton and Calo, 1981)} \qquad (4\text{-}5)$$

where $H' = H/RT$, is the dimensionless Henry's Law constant, T is the temperature in K, and R is the gas constant ($R = 8.314\ \text{Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$). This correlation is valid between the temperatures of 273 and 298 K. An alternate correlation was proposed in a later study by Gossett (1987)

$$H = \exp[6.653-(3817/T)] \qquad \text{(Gossett, 1987)} \qquad (4\text{-}6)$$

where H is the Henry's Law constant ($\text{atm}\cdot\text{m}^3/\text{mol}$) and T is the temperature (K). This correlation is valid between the temperatures of 283 and 308 K.

Figure 4.1 illustrates that the values derived from these two correlations can differ by up to 50%, with most other values reported in the literature between those derived from the two correlations. Mackay and Shiu (1981) asserted that ±10% error can be expected in the measurement of Henry's Law constants. However, the 50% difference between the values reported by Leighton and Calo (1981) and Gossett (1987) is too large to be explained by such experimental anomalies.

Leighton and Calo's (1981) measurements were based on air stripping of dissolved methylene chloride. However, Leighton and Calo (1981) failed to demonstrate that the aqueous methylene chloride concentration was measured under equilibrium conditions, and their technique suggests that aqueous concentrations may have been artificially low, resulting in higher values for the Henry's Law constant.

Gossett (1987) calculated Henry's Law constants based on a ratio of head space concentrations from sealed bottles with different water volumes. According to Gossett (1987), the use of relative, rather than absolute, concentration measurements accounts in

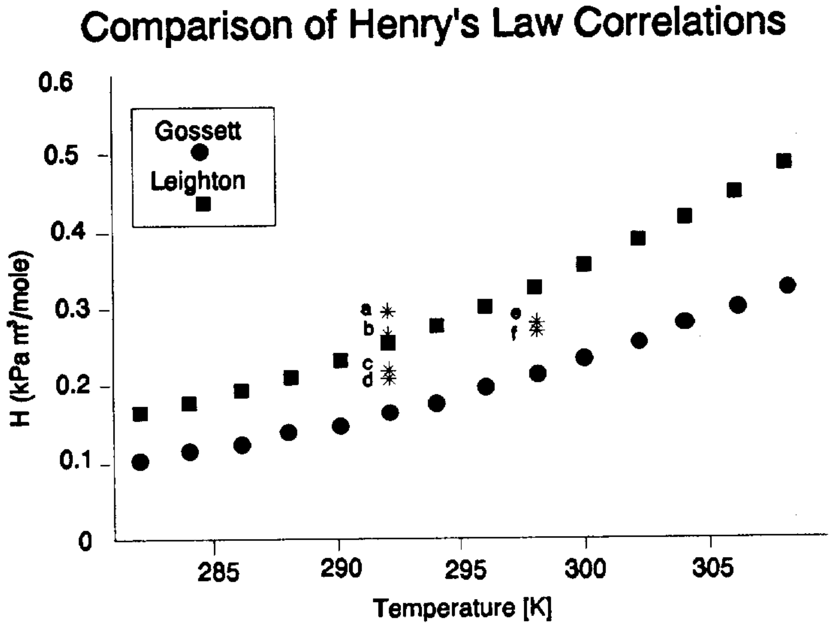

Figure 4.1. **Comparison of Henry's Law constants reported in the literature. The correlations derived by Gossett (1987) (solid circles) and Leighton and Calo (1981) (solid squares) are shown in the valid temperature range. Asterisks indicate other values reported by: a. McConnell, 1975; b. Lopez et al., 1989; c. Tse et al., 1992; d. CARB, 1989; e. Dilling, 1975; and f. Mackay and Shiu, 1981.**

part for potential non-equilibrium conditions. Gossett acknowledged that the measured Henry's Law values for methylene chloride are lower than other reported values, and attributes this to his better purification of methylene chloride. Because of methylene chloride's low solubility, most investigators usually dissolve methylene chloride in methanol in an attempt to create a homogenous liquid phase. Gossett claimed that his use of a closed system, without air stripping, avoids the use of a cosolvent such as methanol, therefore, resulting in an uncontaminated methylene chloride solution, resulting in lower Henry's Law constants. Nevertheless, Gossett's measured Henry's Law constants for compounds besides methylene chloride are comparable to those of Leighton and other investigators, refuting his claim of increased purity resulting in uniformly lower values.

Based on the above analysis, the true Henry's Law constant probably lies between the values reported by Leighton and Calo (1981) and Gossett (1987). In an earlier study, Mackay and Shiu (1981) critically evaluated reported Henry's Law constants and recommended a value of 0.260 $kPa \cdot m^3/mol$ at 298 K, while more recently Tse et al. (1992) measured a value of 0.212 $kPa \cdot m^3/mol$ which is probably most reliable measurement at 293 K. Both these values (0.26 and 0.212 $kPa \cdot m^3/mol$) fall between those of Leighton and Calo and Gossett. Table 4-9 presents Henry's Law constants reported in the literature which range from 0.20 to 0.30 $kPa \cdot m^3/mol$.

It should be noted that ideally, accurate prediction of the Henry's Law constant should account for conditions found in the environment. For example, Mackay et al. (1979) demonstrated that the presence of dissolved organic compounds, such as humic and fulvic acids could result in sorption which reduces the volatilization rate of a compound, resulting in a field Henry's Law constant which is lower than the laboratory Henry's Law constant by a factor of $1+F$, where F is the ratio of sorbed concentration over dissolved concentration. Similar conclusions were also reported in a later study by Estes and Vilker (1989), who found that halocarbons bind to dissolved silica and montmorillonite.

4.2.2 Octanol-Water Partition Coefficient

The octanol-water partition coefficient, K_{ow}, is defined as the equilibrium ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system by the following equation:

$$K_{ow} = C_o/C_w \tag{4-7}$$

Table 4-9. Henry's Law Constant of Methylene Chloride*

Henry's Law Constant ($kPa \cdot m^3/mol$)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
0.212	0.0021(a)	$atm \cdot m^3/mol$	±10%	293	Measured(b)	Tse et al., 1992	
0.221	0.00219(a)	$atm \cdot m^3/mol$	±17%	297.8	Measured(c)	Gossett, 1987	
0.295	0.1192(d)	dimensionless	±3%	297.9	Measured(e)	Leighton and Calo, 1981	
0.260	0.260	$kPa \cdot m^3/mol$	±0.02	298	Measured(f)	Mackay and Shiu, 1981	Dilling, 1977
0.265	0.1089(d)	dimensionless	NR	293	Calculated(g)	Lopez et al., 1989	Leighton and Calo, 1981
0.20	0.20	$kPa \cdot m^3/mol$	NR	293	Calculated(h)	CARB, 1989	U.S. EPA, 1982a
0.205	0.00203(a)	$atm \cdot m^3/mol$		293	Calculated(h)	U.S. EPA, 1982b	
0.273	0.11(d)	dimensionless	NR	298	NR	Dilling et al., 1975	Brown, 1975
0.273	0.11(d)	dimensionless	NR	298	NR	Dilling, 1977	Pearson and McConnell, 1975
0.27	0.00268(a)	$atm \cdot m^3/mol$	NR	NR	NR	Howard, 1990	Dilling, 1977
0.300	0.1234(i)	$K_{air/water}$	NR	293	NR	McConnell et al., 1975	NR

NR = Not reported.

* For a given temperature, the listed order is by decreasing confidence in reported values (see Section 3.0).

(a) $0.00219\ atm \cdot m^3/mol \times 101\ kPa/atm = 0.221\ kPa \cdot m^3/mol$

(b) Gas chromatography was used to measure the infinite dilution activity coefficient (γ^{∞}). Henry's Law constant calculated as $H(T) = \gamma^{\infty} \times P_{vap}(T)$, where H(T) is in $atm \cdot m^3/mol$ and P_{vap} is the vapor pressure in atm.

Table 4-9. Henry's Law Constant of Methylene Chloride*
(Continued)

(c) Measured by adding equal amounts of methylene chloride to two sealed bottles containing different volumes of water. Henry's Law constant calculated from the ratio of headspace concentrations between the two bottles.

(d) 0.1192 × RT × 1 kPa/1000 Pa = 0.295 kPa·m^3/mol, where R is the gas constant (R = 8.314 Pa·m^3/mol·K), and T is the temperature in K.

(e) Measured by bubbling air through a homogeneous aqueous methylene chloride solution to strip the methylene chloride from solution. Henry's law constant calculated as the ratio of the concentration in the air over the concentration in the water, as detected by dual flame ionizing gas chromatography.

(f) Mackay reviewed the literature through 1979 and recommended a specific value for the Henry's law constant.

(g) Calculated from the correlation derived by Leighton and Calo (1981), see Eq. 4-5.

(h) Calculated by dividing the saturation vapor pressure by the aqueous solubility.

(i) $K_{air/water}$ = 0.1234 = dimensionless Henry's law constant, see footnote (d).

where C_o is the concentration in octanol phase and C_w is the concentration in aqueous phase. Kow is dimensionless when the concentrations of C_o and C_w are in the same units (e.g., mol/cm^3). K_{ow} is an important parameter used in the assessment of environmental fate and transport for organic chemicals because the octanol phase is a surrogate for the lipid phase or organic carbon content of environmental compartments. K_{ow} for hydrophobic compounds such as methylene chloride is considered as one of the most important physicochemical characteristics related to sorption on soil and sediments and bioaccumulation. Since K_{ow} has been correlated to water solubility, soil/sediment adsorption coefficients, and bioconcentration factors for aquatic life (Lyman et al., 1990), it is a key variable used in the estimation of these properties. Although K_{ow} is expected to vary with temperature and pH, its temperature dependence is rarely reported. Table 4-10 presents log K_{ow} values for methylene chloride. The measured value of 1.25 for log K_{ow} reported by Hansch and Leo (1979) is considered the most reliable.

The value measured by Sato and Nakajima (1979) is high due to the difference in solubility of methylene chloride in olive oil, used by Sato, and in n-octanol, used by Hansch and Leo. In addition, Sato's use of gas chromatography may result in high K_{ow} values due to its difficulty in determining low concentrations of methylene chloride in water (Kenaga and Goring, 1980). Values for log Kow estimated from correlations to water solubility range from 0.734 (Kenaga and Goring, 1980) to 2.11 (Isnard and Lambert, 1989). This variation stems from the different collections of compounds with which these correlation equations were derived. The most reliable correlation for short chain chlorinated hydrocarbons, such as methylene chloride, has been proposed by Isnard and Lambert (1989):

$$\log K_{ow} = 4.81 - 0.77 (\log S + 0.0032 (T_{mp} - 25)) \tag{4-8}$$

where S is the aqueous solubility in g/m^3 and T_{mp} is the melting point in K.

Table 4-10. Octanol-Water Partition Coefficient (K_{ow}) for Methylene Chloride*

log K_{ow} (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
1.32	NR	310	Measured[a]	Sato and Nakajima, 1979	
1.25	NR	NR	Measured[b]	Hansch and Leo, 1979	
1.26	NR	NR	Calculated[c]	U.S. EPA, 1982b	U.S. EPA, 1982b
1.29	NR	NR	Estimated[d]	Isnard and Lambert, 1989	
1.55	NR	NR	Estimated[e]	Isnard and Lambert, 1989	
1.41	NR	NR	Estimated[f]	Chiou et al., 1979	Chiou et al., 1977
1.55	NR	NR	Estimated[g]	Banerjee et al., 1980	
0.734	± 1.96 orders of magnitude	NR	Estimated[h]	Kenaga and Goring, 1980	
1.25	NR	293	NR	CARB, 1989	WHO, 1984
1.25	NR	310	NR	Paterson and Mackay, 1989	NR
1.25	NR	NR	NR	Howard, 1990	Hansch and Leo, 1985
1.25	NR	NR	NR	IARC, 1986	Hansch and Leo, 1979
1.25	NR	NR	NR	U.S. EPA, 1982a	DeForest, 1979

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

Table 4-10. Octanol-Water Partition Coefficient (K_{ow}) for Methylene Chloride*
(Continued)

(a) Gas chromatography was used to measure the methylene chloride concentration present in the gas and olive oil phases of vials, at equilibrium.

(b) Hansch and Leo provide a collection of experimentally derived partition coefficients for organic chemicals. Values presented represent their interpretation of the most reliable data.

(c) Calculated from the FRAGMENT computer simulated models, which bases K_{ow} on the Structure-Activity relationships.

(d) $\log K_{ow} = 4.81 - 0.77 (\log S + 0.0032 (T_{mp} - 25))$; S in g/m^3, T_{mp} is the melting point temperature in K.

(e) $\log K_{ow} = 3.15 - 0.72 \log S - 0.018 (\log S)^2$; S in mol/m^3.

(f) $\log K_{ow} = 5.00 - 0.670 \log S$; S in µmol/L.

(g) $\log K_{ow} = 5.2 - 0.68 \log S$; S in µmol/L.

(h) $\log K_{ow} = 4.158 - 0.80 \log S$; S in ppm.

4.2.3 Soil/Water-Organic Carbon Coefficient

The organic carbon partition coefficient (K_{oc}) is a measure of the tendency for organics to adsorb onto the soil (or sediment) and is defined as the ratio of the amount (mass) of a chemical adsorbed per unit mass of organic carbon in the soil or sediment to the concentration of the chemical in the soil (or sediment) solution at equilibrium,

$$K_{oc} = \frac{\text{(mg chemical adsorbed/kg organic carbon)}}{\text{(mg chemical dissolved/liter of solution)}} \tag{4-9}$$

The available methods for estimating K_{oc} involve empirical relationships with other properties of a chemical such as solubility, octanol-water partition coefficient, or bioconcentration factor for aquatic life. Lyman et al. (1990) recommends the following estimation correlations for chlorinated hydrocarbons; however, methylene chloride was not included as a study chemical in the development of either of these correlations.

$$\log K_{oc} = 1.377 + 0.544 \log K_{ow} \qquad \text{(Kenaga and Goring, 1980)} \tag{4-10}$$

$$\log K_{oc} = -0.557 \log S + 4.277 \qquad \text{(Chiou et al., 1979)} \tag{4-11}$$

where S is the solubility in μmol/L.

Valsaraj and Thibodeaux (1989) report the following correlation, developed by Curtis et al. (1986), in which methylene chloride was used as a study chemical.

$$\log K_{oc} = 0.92 \log K_{ow} - 0.23 \tag{4-12}$$

The results in Table 4-11 show that values for log K_{oc} reported in the literature range from 0.597 - 2.06. Differences in measured values are attributed to the dependence of K_{oc} on soil characteristics such as organic carbon content, pore size distribution, moisture content, ionic strength, pH, and temperature. The specific chemical composition of the soil

Table 4-11. Soil/Organic Carbon Coefficient (K_{oc}) for Methylene Chloride*

log K_{oc} (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	References	Sources Cited
0.92	NR	NR	Estimated[a]	Valsaraj and Thibodeaux, 1989	Curtis et al., 1986
1.11	NR	NR	Estimated[b]	Jury et al., 1990	Jury et al., 1984
2.06	± 1.37 orders of magnitude	NR	Estimated[c]	Kenaga and Goring, 1980	
2.05	NR	NR	Estimated[c]	Lyman et al., 1990	Kenaga and Goring, 1980
1.29	NR	NR	Estimated[d]	Lyman et al., 1990	Chiou et al., 1979
1.05	NR	NR	Estimated[e]	Grathwohl, 1990	Chiou et al., 1979
1.04	NR	NR	Estimated[f]	Lyman et al., 1990	Karickhoff et al., 1979
0.944	NR	NR	Estimated[g]	U.S. EPA, 1982b	
0.597	NR	NR	Estimated[h]	Chiou et al., 1983	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) log $K_{oc} = 0.92 \log K_{ow} - 0.23$

(b) K_{oc} was calculated using a mathematical model which accounts for the physicochemical properties of methylene chloride and the physical and chemical properties of a sandy soil.

(c) log $K_{oc} = 1.377 + 0.544 \log S$; S in µmol/L

(d) log $K_{oc} = 4.277 - 0.557 \log S$; S in µmol/L

(e) log $K_{oc} = 4.04 - 0.557 \log S$; S in mole fraction

(f) log $K_{oc} = 0.44 - 0.54 \log S$; S in mole fraction

(g) log $K_{oc} = \log K_{ow} - 0.317$

(h) log K_{om} (soil-organic matter coefficient) $= 0.904 \log K_{ow} - 0.779$; $K_{oc} = 1.70 K_{om}$ (soil with 1.9% organic matter).

organic carbon (i.e., humic acid, fulvic acid, humin) can also affect sorption of methylene chloride to soils. Grathwohl (1990) has shown that soil organic matter which contains functional groups which are low in oxygen have lower polarity, and thus, greater sorption affinity for organic compounds. Based on these findings, he has proposed adding a correction factor to K_{oc}-K_{ow} correlation equations:

$$\log K_{oc} = a \log K_{ow} + b + 1.52 \log ([H]/[O]) - 0.73 \qquad (4\text{-}13)$$

where [H]/[O] is the ratio the number of hydrogen to oxygen atom present in the functional groups of the specific soil organic matter of interest. The variability of the calculated values is attributed to the use of different estimation equations as previously described.

4.2.4 Bioconcentration Factors and Bioaccumulation

4.2.4.1 Bioconcentration in Aquatic Organisms

The traditional measure of a chemical's potential to accumulate in an organism is the bioconcentration factor (BCF), which is defined as a chemical's wet-weight concentration in an organism or tissue divided by its concentration in the medium through which exposure occurs by direct contact (e.g., water for aquatic organisms, or air for terrestrial organisms). The concept of BCF addresses partitioning of a chemical into an organism by non-food routes. Specifically, BCF is defined as:

$$BCF = \frac{\text{(equilibrium concentration of chemical in receptor)}}{\begin{array}{c}\text{(concentration of chemical in the medium}\\ \text{through which exposure occurs by direct contact)}\end{array}} \qquad (4\text{-}14)$$

It is convenient to use the same units for both the numerator and denominator which results in a dimensionless BCF. The term BCF is used with the assumption that uptake across external membranes from the media with which the receptor is in direct contact is the chief pathway for chemical uptake by the organism. For compounds with low log K_{ow}

values (less than 3), such as methylene chloride, transfer across membranes is controlled by aqueous diffusion processes and limited by lipid solubility resistance (Thomann, 1989). It is important to note that BCF values are compound-specific, medium-specific, and species-specific, and experimental data should be used whenever possible. In the absence of measured data, various correlations may be utilized to estimate BCF values. BCF is frequently correlated with the Kow or solubility (S) (Lyman et al., 1990)

$$\log(\mathrm{BCF}) = A + B\log(K_{ow}) \tag{4-15}$$

or

$$\log(\mathrm{BCF}) = C + D\log(S) \tag{4-16}$$

where A, B, C, and D are empirical constants. For example, the following correlations have been suggested for chlorinated hydrocarbons.

$$\log(\mathrm{BCF}) = 0.76\log K_{ow} - 0.23 \quad \text{(Veith et al., 1980)} \tag{4-17}$$

$$\log(\mathrm{BCF}) = 5.00 - 0.670\log S \quad \text{(Chiou et al., 1977)} \tag{4-18}$$

where S is the solubility in μmol/L. It is noted, however, that methylene chloride was not included as a study chemical in the development of Eqs. 4-17 and 4-18.

Table 4-12 presents methylene chloride BCF values for different aquatic organisms. It can be seen that reported values for BCFs can vary significantly. Interspecies variations in BCF can result from differences in an organism's life stage, lipid content, size, uptake mechanisms, and ability to degrade methylene chloride. The highest reported BCF for methylene chloride was in algae (BCF = 7.50; Geyer et al., 1991). This value is probably influenced by the high surface area to volume ratio of algae, which increases its contact with the water and subsequent uptake of methylene chloride. Additional differences among measured values are due to different experimental conditions such as exposure time, organic content of the water, experimental system design, experimental deviation and range of exposure concentrations of methylene chloride in water. Since many of the experiments were short term studies, BCFs may have been determined in systems that did not reach equilibrium.

Table 4-12. Bioconcentration Factor (BCF)(a) for Methylene Chloride in Aquatic Organisms*

BCF(a) (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
6.33	±0.342 log units	NR	Estimated(b)	Kenaga and Goring, 1980	
2.34	±1.99 orders of magnitude	NR	Estimated(c)	Kenaga and Goring, 1980	
5.25	NR	NR	Estimated(d)	Veith et al., 1980	
6.31	NR	NR	Estimated(e)	Veith et al., 1980	Neely et al., 1974
4.86	NR	NR	Estimated(f)	Kenaga and Goring, 1980	Goring, 1972
6.0	NR	NR	Estimated(g)	U.S. EPA, 1982b	
2.29	NR	NR	Estimated(h)	Veith et al., 1980	
4.90	NR	NR	Estimated(i)	Neely, 1979	Smith et al., 1986
4.90	NR	NR	Estimated(j)	Chiou et al., 1977	
4.47	NR	NR	Estimated(k)	Kenaga, 1980	
7.50(l)	NR	NR	Estimated(m)	Geyer et al., 1991	
1.43(n)	NR	NR	Estimated(o)	Geyer et al., 1991	
0.68(p)	NR	NR	Estimated(q)	Geyer et al., 1991	
0.47(p)	NR	NR	Estimated(r)	Geyer et al., 1991	Eastmond et al., 1984
2.44	NR	NR	Estimated(s)	Markwell et al., 1989	

NR = Not Reported.

Table 4-12. Bioconcentration Factor (BCF)(a) for Methylene Chloride in Aquatic Organisms*
(Continued)

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) BCF in fish unless otherwise indicated.

(b) log BCF = 0.124 + 0.542 log K_{ow}

(c) log BCF = 2.791 - 0.564 log S; S in ppm

(d) log BCF = 0.76 log K_{ow} - 0.23

(e) log BCF = 0.542 log K_{ow} + 0.124

(f) log BCF = 3.41 - 0.508 log S; S in µmol/L

(g) log BCF = 0.907 log K_{ow} - 0.21

(h) log BCF = 0.84 log K_{ow} - 0.70

(i) log BCF = 3.41 - 0.508 log S; S in µmol/L

(j) log BCF = 5.00 - 0.670 log S; S in µmol/L

(k) log BCF = 0.495 log S - 1.476; S in ppm

(l) BCF in algae (Chlorella fusca)

(m) log BCF = 0.740 log K_{ow} - 0.050

(n) BCF in mussels (Mytilus edulis)

(o) log BCF = 0.899 log K_{ow} - 0.970

(p) BCF in water flea (Daphnia magma)

(q) log BCF = 0.899 log K_{ow} - 0.970

(r) log BCF = 0.961 log K_{ow} - 1.53

(s) log BCF = 1.11 log K_{ow} - 1.0

Another important factor to be considered with respect to bioconcentration studies is the sorption of methylene chloride to suspended particles and sediments (see Section 4.2.3), For example, Geyer et al. (1991) showed that mussels (BCF = 1.43), which are in high contact with bottom sediments, had 110% higher BCF values than water fleas (BCF = 0.68), which live and feed near the top of the water column. Thus, the feeding mode and specific habitat of aquatic organisms should be considered when assessing bioconcentration of methylene chloride. For benthic organisms, Markwell et al. (1989) suggested a three-phase partition model between the interstitial water, the sediment, and the organism, with the sediment organism partitioning correlated to K_{ow}.

In contrast to BCF, the bioaccumulation factor (BAF) is a BCF which accounts for partitioning of a chemical into an organism by both food and non-food routes. BAFs account for uptake, excretion, intestine to blood assimilation efficiency, and organism growth. A BAF/BCF ratio significantly greater that 1 indicates the tendency for a chemical to reach increasingly higher concentrations in organisms which are higher up the food chain. Relatively low uptake and high excretion rates, which will prevent food chain buildup, are expected for compounds with low $\log K_{ow}$ values (less than 5), such as methylene chloride (see Table 4-10). It is also interesting to note that McConnell et al. (1975) studied C1 and C2 chlorinated hydrocarbons in the marine environment and found no bioaccumulation of methylene chloride, with concentrations in primary consumers reaching an asymptotic level. Moreover, upon return to unpolluted waters, methylene chloride concentrations in primary consumers returned to background levels.

4.2.4.2 Bioconcentration of Methylene Chloride in Vegetation

The concept of BCFs can also be applied to accumulation of methylene chloride in vegetation. Plant accumulation of methylene chloride can involve several different mechanisms, including: (1) root adsorption, (2) root uptake followed by transpirational translocation of methylene chloride from roots to shoots, (3) volatility of methylene chloride from soils and hydroponic solutions followed by foliar adsorption, (4) contamination of plant foliage by methylene chloride laden soil, and (5) atmospheric deposition and leaf-uptake of methylene chloride vapor. Trapp et al. (1990) suggested that root uptake and translocation of chemicals with low K_{ow}, such as methylene chloride, in the transpiration stream is a significant plant contamination mechanism. Above ground portions of vegetation are thought to be principally impacted by vapor phase transfers (Bacci et al., 1990a; McCrady et al., 1990). Only a negligible fraction of volatile organics such as methylene chloride is expected to sorb to particles in the atmosphere (Bidleman, 1988) as its primary states are gaseous and dissolved forms. Thus, it can be assumed that contamination of plants by direct deposition of particles onto which methylene chloride is adsorbed is a negligible exposure pathway. However, volatilization of methylene chloride from contaminated soil could be an important transport mechanism that can result in significant quantities of airborne methylene chloride being adsorbed by plant shoots.

Root Bioconcentration Factor

The concentration of methylene chloride in vegetation due to root uptake (C_{vr}) can be estimated by

$$C_{vr} = C_s B_{vd} \tag{4-19}$$

where C_s is the concentration of methylene chloride in soil (e.g., ng/kg soil) and B_{vd} is a methylene chloride-specific bioconcentration factor determined on a dry-weight basis

$$B_{vd} = \frac{\text{(concentration of methylenechloride in plant)}}{\text{(concentration of methylenechloride in soil)}} \tag{4-20}$$

where the concentration in the plant, C_{vr}, is based on dry mass (e.g., ng chemical/kg dry plant). Travis and Arms (1988) suggested that, for the above-ground portion of plants, the following correlation for B_{vd} can be used:

$$\log B_{vd} = 1.588 - 0.5781 \log K_{ow} \quad r^2 = 0.525 \tag{4-21}$$

For root crops, Briggs et al. (1982) proposed the following definition for the root bioconcentration factors based on plant wet mass:

$$B_{vw} = \frac{C_{veg}}{C_{soil}} \tag{4-22}$$

in which C_{veg} is the chemical concentration in the wet root plant (i.e., ng chemical/kg soil). Thus, B_{vw} is related to B_{vd}, the root bioconcentration on a dry basis, by

$$B_{vw} = B_{vd} \times f_{dw} \tag{4-23}$$

where f_{dw} is the fraction of dry plant matter in the wet root plant. Briggs et al. (1982) proposed the following correlation for B_{vw} applicable to hydrophobic organic compounds:

$$B_{vw} = \frac{0.82 + 0.028\, K_{ow}^{0.77}}{K_d} \tag{4-24}$$

in which $K_d = K_{oc}\, \chi$ where χ represents the mass fraction of the soil natural organic carbon. It is emphasized that methylene chloride was not included in the development of the above correlation.

Air-to-Leaf Bioconcentration Factor

The basis for a vapor-phase bioconcentration factor for various airborne contaminants, including methylene chloride, from the atmosphere to vegetation was developed by Bacci et al. (1990a). These authors suggested that the air-to-leaf route should be regarded as the main mode of contamination for higher plant leaves, mosses and lichens for non-polar, volatile chemicals. Accordingly, the chemical concentration in the plant can be obtained from

$$B_{vaw} = \frac{C_{va}^{(v)}}{C_a^{(g)}} \tag{4-25}$$

where $C_a^{(g)}$ is the chemical vapor concentration in the air phase (e.g., ng/m^3) and $C_{va}^{(v)}$ is the concentration of the chemical in the plant on a wet plant basis (e.g., ng/m^3 fresh plant). Alternatively, B_{vaw} can be expressed as

$$B_{vaw} = \frac{C_{va}\rho_p}{C_a^{(g)}F_v} \tag{4-26}$$

where C_{va} is the chemical concentration in the plant on a dry plant mass basis (e.g., ng/kg fresh plant), $C_a^{(g)}$ is the concentration of a chemical in the air (e.g., ng/m^3), and F_v represents the fraction of the chemical in the vapor phase. If methylene chloride is assumed to exist in air entirely as a vapor, then F_v equals 1. B_{vaw} represents the air-to-leaf bioconcentration factor on a fresh plant mass basis. It has been suggested that B_{vaw} can be correlated with the chemical's water-air and octanol-water partition coefficient and the leaf properties (Bacci et al., 1990b).

No measured or estimated values of bioconcentration factors were found for root uptake air-to-leaf, and deposition routes for methylene-chloride. Although B_{vaw} has not been measured for methylene chloride, air-to-leaf correlations have been proposed in the literature

$B_{vaw} = 0.19 + 0.7/H' + 0.05\ K_{ow}/H'$ (Paterson and Mackay, 1991) (4-27)

$B_{vaw} = 0.022\ K_{ow}\ /\ H'$ (Bacci et al., 1990) (4-28)

where B_{vaw} is the air-to-leaf bioconcentration based on wet mass, K_{ow} is octanol/water partition coefficient as previously defined, and H' is the dimensionless Henry's Law constant defined as H' = H/RT (T is the temperature in K and R is the gas constant). It is noted that the bioconcentration factor on a dry plant basis, B_{va}, is related to B_{vaw}.

$$B_{vw} = B_{va} \times f_{dw} \tag{4-29}$$

Using, for example, K_{ow} value of 17.78 and H' value of 0.11, a range of 3.56 - 14.64 was obtained for B_{vaw} from Eqs. 4-27 and 4-28. These values indicate that, for the portion of methylene chloride present in the vapor phase, air-to-leaf transfer can be a major pathway for bioconcentration in vegetation. However, it must be noted that methylene chloride was not used as a study chemical in the development of the above correlations. Thus, the above estimates of B_{vaw} values for methylene chloride should only be regarded as indicative of the order of magnitude of B_{vaw} for methylene chloride.

4.2.4.3 Biotransfer Factors in Milk, Beef, and Eggs

The biotransfer factor (B_{TF}) concept addresses chemical accumulation in the receptor through food uptake. It has been suggested in the literature that the biotransfer factor (B_{TF}) may be more useful than BCFs in addressing exposure via food uptake since chemical exposure to feedstock animals may occur through both food and water pathways (Travis and Arms, 1988).

At steady state, the pathway specific biotransfer factor, B_{TFi}, for pathway i, can be expressed as

$$B_{TF} = C_j \bigg/ \left(\sum_{i=1}^{N} L_i \, C_{in} \right) = \left[\sum_{k=1}^{N} (Ex_k H_{kj}) + K_j V_j \right]^{-1} \tag{4-31}$$

V_j is the volume of the receptor and C_j and C_{in} are the concentrations of the contaminant in the receptor (or target organ) and the media associated with the receptor route. L_i represents the intake rate and Ex_k is the elimination stream associated with the particular pathway. H_{kj} is the partition coefficient between receptor j and elimination stream k. The overall biochemical transformation of a given contaminant via first order reaction kinetics is given by the rate constant K_j. For example, one can define a B_{TF} for the concentration of a contaminant in cow's milk where $\Sigma L_i C_{in}$ is the total contaminant intake during grazing, water drinking, and inhalation. In general, the B_{TF} is not constant since V_j, the volume of the receptor, may vary with time, and the partition coefficient, H_{kj}, and the reaction rate constant, K_j, are likely to be a function of the activity of the receptor. Thus, one is led to conclude that B_{TF} and B_{TFi} are likely to be time variant parameters. Despite this concern, the concept of biotransfer factors is rooted in environmental exposure assessment.

As previously noted, feedstock animals may be exposed to methylene chloride through ingestion of contaminated feed crops and drinking water, as well as direct inhalation. Human exposure can subsequently result from ingestion of contaminated animal products. Therefore, assessing the magnitude of human exposure to a contaminant such as methylene chloride from ingestion of animal products depends largely on the ability to predict the extent of its bioaccumulation in aquatic and terrestrial food chains. Biotransfer factors for organics in beef and milk have been correlated with the equilibrium octanol/water partition coefficient (Travis and Arms, 1988); even though B_{TF} should be regarded as a transport parameter rather than simply a physicochemical property (Cohen, 1989). It is important to note that B_{TF} correlations determined by Travis and Arms (1988) are subject to uncertainties in the input data from which B_{TF} values were derived. For instance, McKone and Ryan (1989) noted that the uncertainty in the Travis and Arms (1988) correlations for 95% confidence interval for both the feed to milk biotransfer factor, B_m, and the feed to meat biotransfer factor, B_b, is approximately 2 orders of magnitude.

The biotransfer factors for milk (B_m) and meat (beef; B_b) have been defined by Travis and Arms (1988) as follows:

$$B_m = \frac{\text{(concentration in milk (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \tag{4-32}$$

$$B_b = \frac{\text{(concentration in meat (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \tag{4-33}$$

Measured concentration of organics in milk or meat fat are converted on a whole milk or fresh meat basis, assuming meat contains 25% fat and whole milk contains 3.68% fat.

Travis and Arms (1988) derived a log K_{ow} vs. log B_m correlation based on data for 28 organic chemicals in milk (methylene chloride was not included) which yielded the following equation:

$$\log B_m = -8.056 + 0.992 \log K_{ow} \tag{4-34}$$

In the above equation, B_m was based on data for ingestion only and did not include contaminant uptake via inhalation or dermal absorption. Using Eq. 4-34 and a log (K_{ow}) value of 1.25 (Hansch and Leo, 1979), one obtains log (B_m) equals -6.82 (or $B_m = 1.53 \times 10^{-7}$), which implies very little transfer of methylene chloride to milk due to ingestion. Also, one should note that methylene chloride was not one of the chemicals used in developing Eq. 4-34 and its log K_{ow} value of 1.25 is below the range of log K_{ow} from which the correlation was derived. One is also cautioned that in applying K_{ow} correlations derived from regression analysis, it is important to verify that the value of K_{ow} is within the range of applicability of the correlation. Also, methylene chloride is likely to be metabolized in the receptor (USEPA, 1982a) and thus, more detailed pharmacokinetic studies may be required to precisely determine the level of methylene chloride accumulated in bioreceptors (e.g., cattle).

Feed-to-beef transfer factors (B_b) can be estimated using the following correlation (Travis and Arms, 1988):

$$\log B_b = -7.6 + \log K_{ow} \quad n = 36, r = 0.81 \tag{4-35}$$

Using the value of log K_{ow} for methylene chloride, log B_b equals -6.35. The concerns and limitations mentioned above for B_m are also applicable for B_b. Kenaga (1980) reported the following correlations for bioconcentration factors in beef:

$$\log B_b = -0.495 (\log S) - 1.476 \quad n = 23, r = 0.817 \tag{4-36}$$

$$\log B_b = 0.5 (\log K_{ow}) - 3.457 \quad n = 23, r = 0.790 \tag{4-37}$$

$$\log B_b = 0.701 (\log K_{oc}) - 3.825 \quad n = 23, r = 0.732 \tag{4-38}$$

where B_b, S (in ppm), K_{ow}, and K_{oc} are defined previously.

Experimentally determined or calculated biotransfer factor values for feed to egg were not found in the literature. The CAPCOA guidelines assume that the transfer for eggs is the same as that of meat and this approximation appears to be a reasonable assumption in the absence of data to the contrary.

The measurement-specific definition of BCF and B_{TF} above must be distinguished from other terms used to describe increasing chemical concentration in an organism via the food chain. Such terms include biomagnification and bioaccumulation (Lyman et al., 1990). Biomagnification refers to a further increase in concentration attributable to uptake from food. Bioaccumulation is a broader term that indicates uptake from all sources and thus includes effects of both biomagnification and bioconcentration (Clark et al., 1988). These terms are associated with increasing concentrations along a food chain, which could result in higher concentrations in top-order consumers.

The overall bioaccumulation factor K_b can be shown to be related to the biotransfer factors by the following relation (Cohen, 1989)

$$K_b = C_j/C_i = B_{TF}(\sum_{i=1}^{N} L_i C_{in})/C_i \tag{4-39}$$

where C_j is the concentration of the contaminant in the receptor, C_i is the concentration in the media most directly associated with the exposure route, B_{TF} is the biotransfer factor, L_i is the intake rate via grazing, water drinking, and inhalation, and C_{in} is the concentration in either the feed, drinking water, inhaled air.

Bioaccumulation and bioconcentration factors are a function of the receptor type, the chemical type and temperature. The bioaccumulation factor is equivalent to the bioconcentration factor when the exposure takes place primarily via contact with a single medium (e.g., inhalation of a volatile chemical such as methylene chloride). The above approach assumes implicitly that K_b is time invariant. For biota, K_b (or BCF) is often correlated with K_{ow} (Kenaga and Goring, 1980; Mackay, 1982; Veith and Rosian, 1983).

4.2.5 Bioavailability

The bioavailability of a chemical is defined as the fraction of a compound in a matrix that is released from that matrix, absorbed by an organism, and hence, is available to elicit a biological effect. The release and uptake of a chemical constitute facets of bioavailability, although its biological effect is often used as a measure of bioavailability. Since risk is considered to be a function of both exposure and toxicity, bioavailability is an important consideration in determining potential risk from airborne contaminants (SCAQMD, 1988). Bioavailability is often considered when assessing dose from inhalation and ingestion pathways. For ingestion routes, CAPCOA (1991) allows for using compound-specific bioavailability factors where evidence warrants but does not provide any values for methylene chloride. The CAPCOA (1991) guidelines assume 100% absorption for inhaled compounds. Since methylene chloride is likely to be present primarily in the gaseous phase, the assumption of 100% bioavailability via inhalation is considered reasonable.

Once absorbed through the lung, methylene chloride is metabolized by either mixed function oxidases (MFO) or by glutathione S-transferase (GST) to carbon monoxide (Anderson et al., 1987). Carbon monoxide in the blood reversibly binds to hemoglobin forming carboxyhemoglobin (COHb) which impairs respiratory, cardiovascular, and neurological function (USEPA, 1982a; IARC, 1986). Residual methylene chloride and carbon monoxide are eliminated by exhalation over period of 10-15 hours after the cessation of exposure (Shusterman et al., 1990; Anderson et al., 1991).

In determining the uptake of methylene chloride by the human receptor, tissue/gas and blood/gas partition coefficients are required when estimating the dose or dose rate. Table 4-13 lists tissue and tissue/gas partition coefficients for methylene chloride in various human organs. Different measurement techniques and organs tested make comparisons difficult. However, tissue partition coefficients for methylene chloride are generally lower than the K_{ow}, reflecting the heterogenous makeup of human organs. Because all these values represent either modeled data or in-vitro measurements at a single time point, conclusions about accumulation of methylene chloride in human tissues are difficult to draw. As with solubility and vapor pressure, Abraham et al.'s (1985) use of Ostwald coefficient to calculate blood/gas partition coefficients may be unreliable (see Sections 4.1.1 and 4.1.2).

4.3 Intermedia Transport Parameters of Methylene Chloride

The following subsections define the specific intermedia transport factors considered in this study and review the reported and estimated parameter values.

4.3.1 Diffusion Coefficients in Air and Water

Molecular diffusion is the net transport of a molecule within a single phase (e.g., liquid or gas) that results from intermolecular collisions rather than turbulence or bulk transport. Diffusion can result from pressure, temperature, and concentration gradients but under environmental conditions, only diffusion due to concentration gradient is considered. The diffusive flux due to concentration gradients is defined by Fick's Law as:

$$J_A = -D_{AB}\, dC_A/dx \qquad (4\text{-}40)$$

Table 4-13. Tissue/Blood and Tissue/Gas Partition Coefficients for Methylene Chloride*

Partition Coefficient[a] (dimensionless)	Media Tested	Technique	References	Source Cited
8.94	Blood/air	Measured[b]	Anderson et al., 1991	
9.7	Blood/air	Measured[c]	Sato and Nakajima, 1979	
9.7	Blood/air	Calculated[d]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
19.4	Blood/air	Modelled[e]	Zwart et al., 1992	
1.46	Liver/blood	Measured[b]	Anderson et al., 1991	
0.92	Liver/blood	Calculated[f]	Abraham et al., 1985	
7.2	Liver/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
12.40	Fat/blood	Measured[b]	Anderson et al., 1991	
5.8	Kidney/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
0.75	Kidney/blood	Calculated[f]	Abraham et al., 1985	
6.0	Brain/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
1.02	Brain/blood	Calculated[f]	Abraham et al., 1985	
85	Fat/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
4.8	Muscle/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
0.98	Muscle/blood	Calculated[f]	Abraham et al., 1985	
5.8	Lung/air	Calculated[c]	Paterson and Mackay, 1989	Fiserova-Bergerova and Diaz, 1986
0.69	Lung/blood	Calculated[f]	Abraham et al., 1985	

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) All partition coefficients reported are for humans and defined as the ratio of concentrations corresponding to the ratio indicated in the second column.

(b) Methylene chloride concentrations in samples of various organs and air were analyzed using gas chromatography. The ratio of these concentrations was taken to be the partition coefficient.

(c) Gas chromatography was used to measure the methylene chloride concentration from equilibrated blood and air phases.

(d) Partition coefficients were calculated by taking a ratio of the solubility of methylene chloride in a specific organ to the solubility of methylene chloride in air.

(e) A multi-compartmental model was used to predict blood/air partitioning.

(f) Partition coefficients were calculated by taking a ratio of Ostwald coefficients for each pair of organs.

in which J_A is the diffusion flux for compound A (e.g., mg/m^2·s), dC_A/dx is the concentration gradient along the x direction and D_{AB} is the diffusion coefficient of A in medium B (e.g., units of cm^2/s). For example, for air/water exchange processes, molecular diffusion dominates chemical transport near the air/water interphase (in both the air and water phases). In general, the mass flux, N (e.g., mg/m^2·s) across an interface (between two phases) is expressed by an equation of the form

$$N = K\Delta C \tag{4-41}$$

in which ΔC is an appropriate concentration driving force and K is an appropriate mass transfer coefficient. Correlations of mass transfer coefficients include a dependence on the molecular diffusivity, which can be estimated as described below.

To calculate the flux in air and water, the diffusion coefficient must be known. Although various theories and correlations exist to predict the value of diffusion coefficients in water, experimental measurements are preferred whenever possible. Unfortunately, the experimental measurements of diffusion coefficients require considerable effort. Since molecules in liquids are densely packed and strongly affected by force fields of neighboring molecules, diffusion coefficients for liquids are much smaller than those for low-pressure gases. Diffusion coefficients in gases at one atmosphere and near room temperature typically range from 0.1 to about 1 cm^2/s (Cussler, 1984).

Table 4-14 presents values for diffusion coefficients of methylene chloride in air and water. No experimental values were found in the literature; however, diffusion coefficients in air can be calculated by using the Fuller et al. (1966) correlation

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2} \;,\; \mathrm{cm}^2/\mathrm{s} \;,\; \text{where } M_r = \frac{M_A + M_B}{M_A\, M_B} \tag{4-42}$$

Table 4-14. Diffusion Coefficient of Methylene Chloride*

Media	Diffusion Coefficient (cm^2/s)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
Air	0.098	0.098	cm^2/s	NR	293	Calculated(a)	Lyman et al., 1990	Fuller et al., 1966
Air	0.104	0.104	cm^2/s	NR	NR	NR(b)	Lopez et al., 1989	Reid et al., 1977
Air	0.09(c)	9×10^{-6}	m^2/s	NR	NR	NR	Kirk-Othmer, 1979	NR
Water	1.22×10^{-5}	1.22×10^{-5}	cm^2/s	NR	293	Calculated(d)	Lyman et al., 1990	Wilke and Chang, 1955
Water	1.13×10^{-5}	1.13×10^{-5}	cm^2/s	NR	NR	Calculated(e)	Lyman et al., 1990	Hayduk and Laudie, 1974
Water	1.08×10^{-5}	1.08×10^{-5}	cm^2/s	NR	NR	NR[b]	Lopez et al., 1989	Reid et al., 1977

NR = Not Reported

* For a given phase, the listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Calculated from the correlation derived by Fuller et al. (1966) and reported by Lyman et al. (1990), see Eq. 4-42.

(b) Reid et al. provide summaries and assessments of the physical properties of gases and liquids. They note that all values are from experimental studies; however, they do not cite specific references for diffusion coefficient measurements.

(c) $9 \times 10^{-6}\ m^2/s \times 100^2\ cm^2/s/m^2/s = 0.09\ cm^2/s$

(d) Calculated from the correlation derived by Wilke and Chang (1955) and reported by Lyman et al. (1990), see Eq. 4-44.

(e) Calculated from the correlation derived by Hayduk and Laudie (1974) and reported by Lyman et al. (1990), see Eq. 4-45.

in which the subscripts B and A denote the solute (e.g., methylene chloride) and air, respectively, T is the temperature (K), M is the molecular weight, P is the pressure (atm), and V_A and V_B are the molar volumes (cm^3/mol) for air and the solute gas, respectively.

Diffusion coefficients in air can also be calculated using the Wilke and Lee (1955) method reported by Lyman et al. (1990).

$$D_{BA} = \frac{B' T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2 \, \Omega} \quad , \ \mathrm{cm^2/s} \qquad (4\text{-}43)$$

where $$B' = 0.00217 - 0.00050 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

$$M_r = (M_A + M_B)/M_A M_B$$

σ_{AB} = characteristic length of molecule A interacting with B, Å

M = molecular weight

T = temperature (K)

P = pressure (atm)

Ω = collision integral (see Lyman, 1990; Reid et al., 1987)

Correlations commonly used to calculate diffusion coefficients in water are given below.

Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \times 10^{-8} \, (\phi_W \, M_W)^{1/2} \, T}{\eta_W \, V_B^{0.6}} \quad , \ \mathrm{cm^2/s} \qquad (4\text{-}44)$$

where M_W is molecular weight of water (g/mol), T is temperature (K), η_W is viscosity of water (cP), V_B is molar volume of solute B at its normal boiling temperature (cm³/mol), and $\emptyset_W$ is the solvent association factor which equals 2.6 for water (Wilke and Chang, 1955). Using Eq. 4-44 to calculate the diffusion coefficient of methylene chloride in water, a value of 1.22×10^{-5} cm²/s was obtained.

Hayduk and Laudie (1974)

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} V_B^{0.589}} \text{ , cm}^2\text{/s} \tag{4-45}$$

where η_w is viscosity of water (cP), V_B is molar volume (cm³/mol).

Hayduk et al. (1982)

$$D_{BW} = 1.25 \times 10^{-8} \left(V_B^{-0.19} - 0.292\right) T^{1.52} \eta_W^{\epsilon^*} \text{ , cm}^2\text{/s} \tag{4-46}$$

where V_B is molar volume (cm³/mol), η_W is viscosity of water (cP), and $\epsilon^* = (9.59/V_B) - 1.12$.

4.3.2 Gaseous Mass Transfer Across the Air-Water Interface

The traditional approach to calculating the flux of a compound between air and water phases is to use the two-film theory in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's Law constant (Lewis and Whitman, 1924). The flux, N, can be expressed as:

$$N = K_G (C_g - H'C_l) = K_L (C_l - C_g/H') \tag{4-47}$$

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H' is the unitless Henry Law's constant, and C_g and C_l are concentrations in gas and liquid phase, respectively. The overall mass transfer coefficients for the gas and liquid phase can be defined as:

$$1/K_G = 1/k_g + H'/k_l \tag{4-48}$$

$$1/K_L = 1/k_l + 1/H'k_g \tag{4-49}$$

where k_g is a gas-phase mass transfer exchange coefficient and k_l is a liquid-phase mass transfer coefficient. The important parameters that are needed in order to predict N are H' (see Section 4.2.1) and the mass transfer coefficients k_g and k_l. The mass coefficients depend on the prevailing turbulence level (as determined by water currents or wind), on temperature, on properties of the solute such as diffusivity, or molecular size (Mackay and Yeun, 1983), and on the depth of the water body (Cohen, 1986). Thus, one must ensure that k_g and k_l are determined for the appropriate environmental conditions. Predictive equations, appropriate for screening-level analysis, that can be used to estimate k_g and k_l are given in Sections 4.3.2.1 and 4.3.2.2.

Experimental studies of volatilization in laboratory wind-wave tanks have demonstrated that for most non-reactive and sparingly water soluble organics $H'k_g > k_l$; thus, for such chemicals, the liquid-side resistance to mass transfer is greater than the gas-side resistance. In general, for chemicals for which k_l is of the same order of magnitude as $H'k_g$, both k_l and k_g should be considered as given in Eqs. 4-47 - 4-49. However, for methylene chloride in an aqueous solution, k_l (Section 4.3.2.2) is the more important transport coefficient controlling methylene chloride exchange between air and water.

4.3.2.1 Air/Water-Air Side - Mass Transfer Coefficient (k_g) for Methylene Chloride

Numerous theories and empirical equations have been proposed to predict k_g. The theoretical expressions for k_g as proposed by Brutsaert (1975) are particularly useful for predicting k_g. For a rough surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^+\left(C_D^{-1/2} - 5\right) + 7.3\ Re_o^{0.25}\ Sc_a^{1/2}\right]^{-1},\quad Re_o > 2 \tag{4-50}$$

and for a smooth surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^+\left(C_D^{-1/2} - 13.5\right) + 13.6\ Sc_a^{2/3}\right]^{-1},\quad Re_o < 0.13 \tag{4-51}$$

in which the Schmidt number, Sc_a, is given by the ratio ν_a/D_a, where D_a is molecular diffusivity in air (Section 4.3.1), U_{10} is the wind speed at a reference height (usually 10 meters), C_D is the wind drag (or stress) coefficient, ϵ_D^+ is the ratio of the eddy momentum diffusivity (ϵ_m) to the eddy mass diffusivity (ϵ_D), often approximated to be near unity, and Re_o is the roughness Reynolds number. Eqs. 4-50 and 4-51 are strictly applicable to a neutral atmospheric condition. However, as suggested by Brutsaert (1975), Eqs. 4-50 and 4-51 are probably still satisfactory even under very unstable, but apparently not under stable conditions. For non-neutral conditions, the mass flux equations Eq. 4-47 must be used with caution since the bulk gas phase concentration as used in Eq. 4-47 may lie outside the dynamic sublayer (Brutsaert, 1975). Under such conditions, a detailed air quality model which considers the concentration profile at the air-side must be considered. Thus, one should regard the use of the estimation methods for k_g as given in this section as suitable for neutral conditions and for screening-level analysis for non-neutral conditions. The prediction of k_g for non-neutral conditions can be accomplished using the approach as presented by Brutsaert (1975). However, it should be noted that within the context of screening-level analysis, as is the case in the CAPCOA model, the application of Eqs. 4-50 and 4-51 is sufficient especially for sparingly soluble hydrophobic organic compounds.

The use of Eqs. 4-50 and 4-51 requires the wind drag coefficient velocity as input. The wind-drag coefficient, C_D, is defined as (Wu, 1980)

$$C_D = \left(\frac{U_W^*}{U_{10}}\right)^2 \left(\frac{\rho_w}{\rho_a}\right) = \left(\frac{U_a^*}{U_{10}}\right)^2 \tag{4-52}$$

in which U_W^* is the surface shear velocity given by:

$$U_W^* = \sqrt{\frac{\tau_s}{\rho_w}} \tag{4-53}$$

where τ_s is the shear stress imparted by the wind on the water surface, ρ_w is the water density, ρ_a is the air density, and U_{10} is the wind speed measured at a reference height (usually 10m) above the water surface. It is noted that the water-side friction velocity U_w^* and U_a^* are related through the simple relation $\rho_a(U_a^*)^2 = \rho_w(U_w^*)^2$ which arises from the condition of stress equality at the air/water interface. Given wind speed profile data, one can estimate U^*_a using the following equation:

$$U_a^* = U_{10}\, k \left[\ln\left(\frac{z_{10}}{z_o}\right) - \psi_M\left(\frac{z}{L}\right) + \psi_M\left(\frac{z_o}{L}\right) \right]^{-1} \tag{4-54}$$

where k is the von Karman constant (k = 0.4), U_{10} is the velocity at the reference height, z_{10}, ψ_M is a stability function, and L is the Obukhov stability parameter (Holtslag and Van Ulden, 1983; and reference therein). It is noted that for neutral conditions the function ψ_M is set to zero. The roughness Reynolds number, Re_o, is defined by:

$$Re_o = U_a^*\, z_o/\nu_a \tag{4-55}$$

where z_o is the effective surface roughness height and ν_a is the kinematic viscosity of air. The effective surface roughness height can be estimated for smooth water surfaces as (Brutsaert, 1975)

$$z_o \approx 0.135(\nu_a/U^*_a) \quad , \quad \text{cm} \tag{4-56a}$$

and for a rough surface,

$$z_o = a(U^*_a)^b \quad , \quad \text{cm} \tag{4-56b}$$

in which U^*_a is the air-side friction velocity (cm/s) and ν_a is the kinematic viscosity (cm/s^2). The parameters a and b are given by $a = 1.69 \times 10^{-2}$ and $b = -1$ for $U^*_a \leq 6.89$ cm/s, and $a = 1.65 \times 10^{-4}$, $b = 1.4$ for $U^*_a > 6.89$ cm/s (Jirka and Brutsaert, 1984). An alternative correlation for z_o was proposed by Wu (1980) for a large water fetch in which z_o was expressed by:

$$z_o = 0.0144(U^*_a)^2/g \quad , \quad (g = 981,\ \text{cm/s}^2) \tag{4-56c}$$

For a large water fetch, the wind-stress coefficient near neutral conditions can be estimated from (Cohen, 1983)

$$C_D = 8.5 \times 10^{-4} \quad , \qquad U_{10} < 5 \text{ m/s} \tag{4-57a}$$

$$C_D = [0.85 + 0.11\ (U_{10} - 5)] \times 10^{-3} \quad , \qquad 5 \text{ m/s} \leq U_{10} \leq 20 \text{ m/s} \tag{4-57b}$$

$$C_D = 2.5 \times 10^{-3} \quad , \qquad U_{10} > 20 \text{ m/s} \tag{4-57c}$$

or (Wu, 1980)

$$C_D = (0.8 + 0.065U_{10}) \times 10^{-3} \quad , \qquad U_{10} \geq 1 \text{ m/s} \tag{4-58}$$

As an illustration of the above approach, the gas-side mass transfer coefficient as obtained from Eqs. 4-50, 4-51 (with linear interpolation in the region $0.13 \leq Re_o \leq 2$), and Eqs. 4-56b and 4-58 for z_o and C_D, respectively, for methylene chloride at 20°C is given in Figure 4.2.

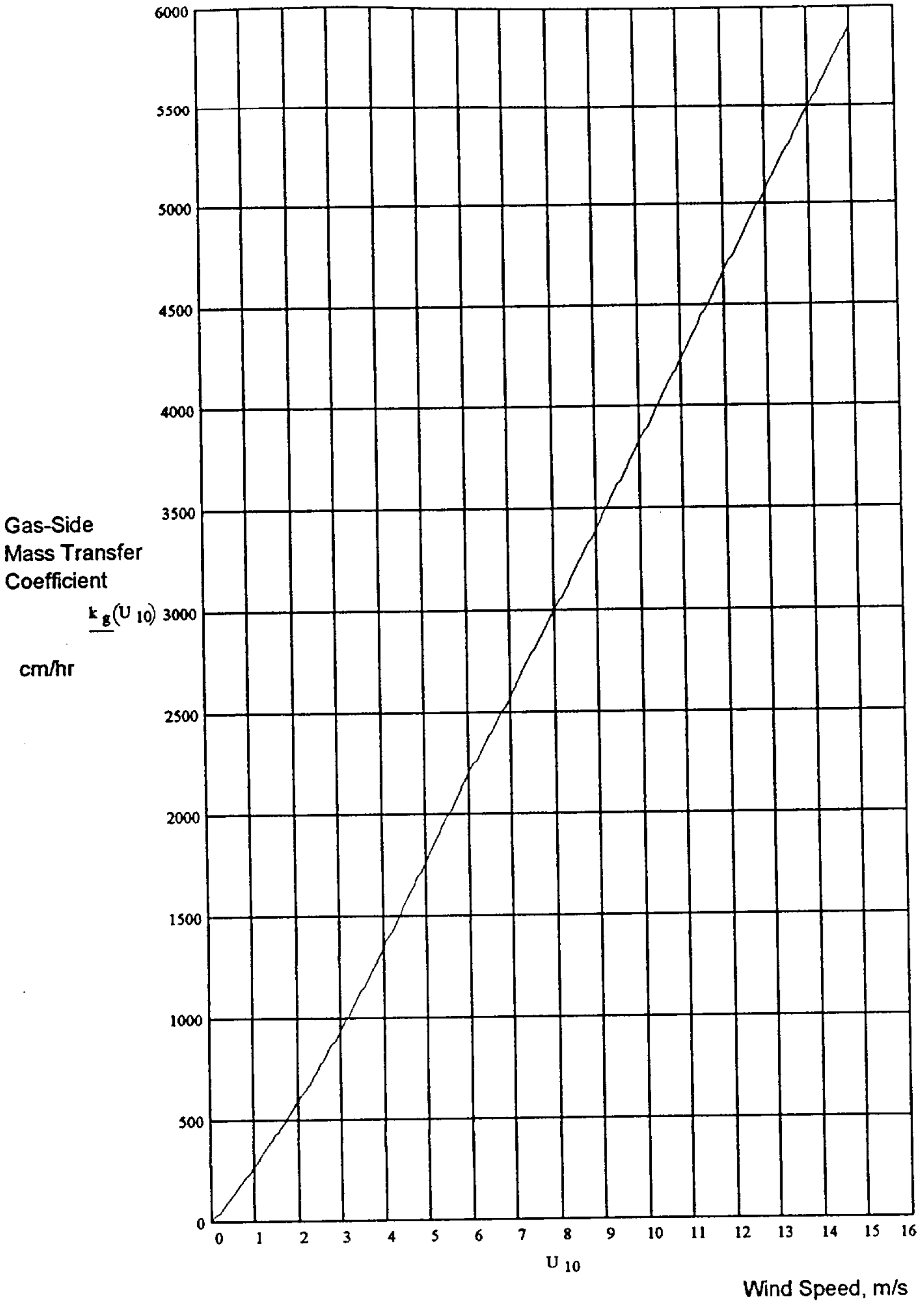

Figure 4.2. Gas-Side Mass Transfer Coefficient for Methylene Chloride at 20°C for Water/Air Mass Transfer at Large Fetch. (Based on the Correlation of Brustsaert, 1975).

Other alternate expressions for k_g under neutral (or near-neutral) conditions have been proposed in the literature. For example, Lyman et al. (1990) recommends the correlation of Southworth (1979) for k_g

$$k_g = 1137.5 \; (V_{wind}+V_{curr}) \sqrt{\frac{18}{MW}} \quad , \qquad cm/hr \tag{4-59}$$

where V_{wind} and V_{curr} are the velocities of the wind and water current, respectively (m/s), and MW is the molecular weight of the contaminant of interest. As an example, using V_{wind} = 3 m/s and V_{curr} = 1 m/s, k_g for methylene chloride is estimated as 2094 cm/hr. It is important to note that the atmospheric stability condition for which Eq. 4-59 applies was not reported. Moreover, the theoretical basis of the Southworth (1979) equation is questionable because of the linear additivity of the wind and air currents in Eq. 4-59. The hydrodynamic effects of the wind relative to the water current on the roughness and velocity of the water surface are likely to be very different, as supported by later researchers (cited by Cohen, 1986) who have found that the effect of wind velocity and current velocity on k_g vary by different powers. Finally, a convenient correlation for k_g, determined based on laboratory measurements in a small wind-wave tank (fetch < 3m) under near neutral conditions, was proposed by Mackay and Yeun (1983).

$$\frac{k_g}{U_a^*} = 46.2 \times 10^{-3} \; Sc_a^{-.067} \tag{4-60}$$

Eq. 4-60 results in k_g values which are about 20%-40% higher than predicted by Eqs. 4-50 and 4-51. The higher prediction by the Mackay and Yeun (1983) correlation may be, in part, due to the difference in surface roughness condition in their short fetch wind-wave tank, for a given U_a^*, relative to the condition that would exist at long fetch.

4.3.2.2 Air/Water - Liquid Side - Mass Transfer Coefficient (k_l) for Methylene Chloride

The water-side mass transfer coefficient, k_l, for large water bodies (i.e., reservoirs, lakes, oceans) can be estimated using the theoretical correlation of Cohen and Ryan (1985), which was found to be in excellent agreement with available data for a water-side friction velocity in the range of 0.5-6 cm/s,

$$k_l/U_w^* = a\ Sc_w^{-n} \tag{4-61a}$$

in which Sc_w is the Schmidt number given by the ratio ν_w/D_w where ν_w is the water kinematic viscosity and D_w is the chemical molecular mass diffusivity in water. The constants a and n are weak functions of the dimensionless water surface velocity U_s^+ ($U_s^+ = U_s/U_w^*$, in which U_s is the wind-induced surface water velocity), given by:

$$a = a_0 - a_1 \ln U_s^+ \tag{4-61b}$$
$$n = n_0 - n_1 \ln U_s^+$$

where

$$a_0 = 0.09691;\ a_1 = 0.01053;$$
$$n_0 = 0.5778;\ n_1 = 0.01771 \tag{4-61c}$$

For a long fetch (say ≥ 30m), the surface velocity is equal to about 3.5% of the wind speed (i.e., $U_s = 0.035\ U_{10}$), while for short fetch (say less than about 10m), $U_s \approx 0.020\ U_{10}$ (Wu, 1975; Plate and Friedreich, 1984). Eq. 4-61a was found to be in excellent agreement with laboratory data from wind-wave facilities with an average error of about 16 percent. As an illustration, the dependence of k_l on wind speed for methylene chloride at 20°C is shown in Figure 4.3 where Eqs. 4-53 and 4-58 were used to determine U_w^*.

The prediction of k_l in flowing water bodies (e.g., rivers) requires consideration of the river current and the river depth (Cohen, 1986). There are numerous studies on the reaeration coefficient in flowing streams (O'Connor, 1983), and the water-side mass transfer coefficient k_l can be estimated from the reaeration coefficient, k_v (e.g., hr^{-1}), by using the following relation:

$$k_l = \left(\frac{D}{D_o}\right)^{1/2} h\ k_v \tag{4-62}$$

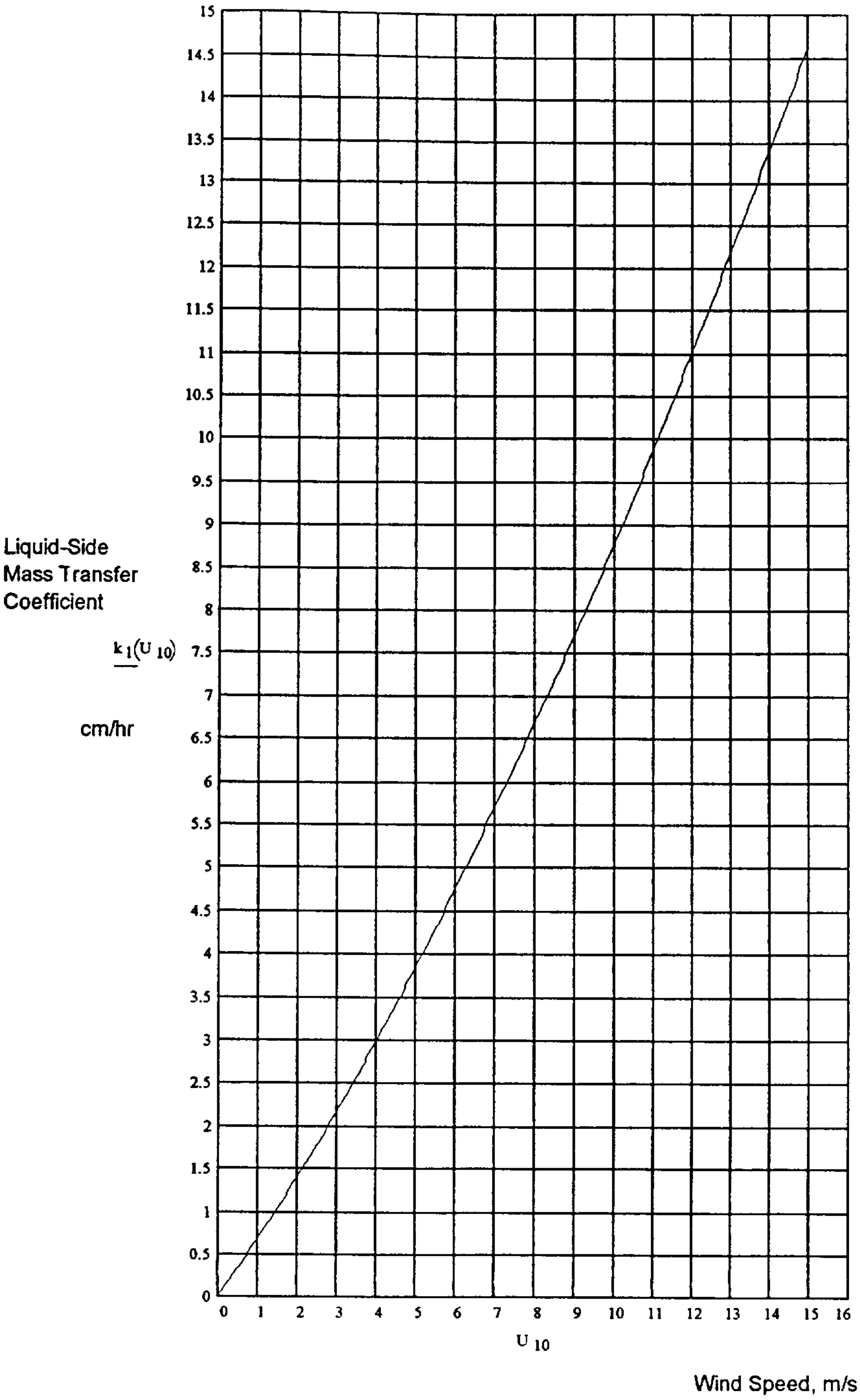

Figure 4.3 Liquid-Side Mass Transfer Coefficient for Methylene Chloride for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlation of Cohen and Ryan, 1985).

in which h is the depth of the water body (e.g., m), D is the mass diffusivity of the compound of interest (e.g., methylene chloride), D_o is the mass diffusivity of oxygen in water at 20°C, and h is the river depth (Cohen, 1986). Lyman et al. (1982) recommended the following empirical correlations, which are based on field data, for predicting k_v:

$$k_v = 1.08\,(1 + 0.17\,F^2)\,(V_{curr}\,S)^{0.375}, \;\; hr^{-1} \tag{4-63a}$$

$$k_v = 0.00102\,V_{curr}^{2.695}\,h^{-3.085}\,S^{-0.823}, \;\; hr^{-1} \tag{4-63b}$$

$$k_v = 638\,V_{curr}\,S, \; hr^{-1} \tag{4-63c}$$

in which S is the river bed slope (m drop/ m run), F is the Froude number ($F = V_{curr}/gh$), and h is the river depth (m). The use of an average value of k_v determined from the above three equations was recommended by Lyman et al. (1982). Other relations for k_v that are suitable when bed slope information is not available were recommended by Shen (1982), Lyman et al. (1990), and Shen et al. (1993). For example, the empirical correlation which was recommended by Shen (1982) and Shen et al. (1993) can be written as

$$k_v = 22.05\,(1.024)^{T-20}\,U_s^{0.67}\,h^{-1.85} \quad , \quad hr^{-1} \tag{4-63d}$$

in which T is the temperature (°C), U_s is the water current (m/s), and h is the water depth (m). As an illustration, the liquid-side mass transfer coefficient, k_l, obtained from Eqs. 4-62 and 4-63d for methylene chloride at 20°C is shown in Figure 4.4.

Example:

In order to estimate K_L for methylene chloride for a neutral atmospheric condition, proceed along the following steps:

1) Select temperature, wind speed, and the correlation appropriate for the water body of interest.
2) Select a value of the Henry's Law constant from Table 4-9 and convert to dimensionless Henry's Law constant as per footnote (h) in Table 4-9.

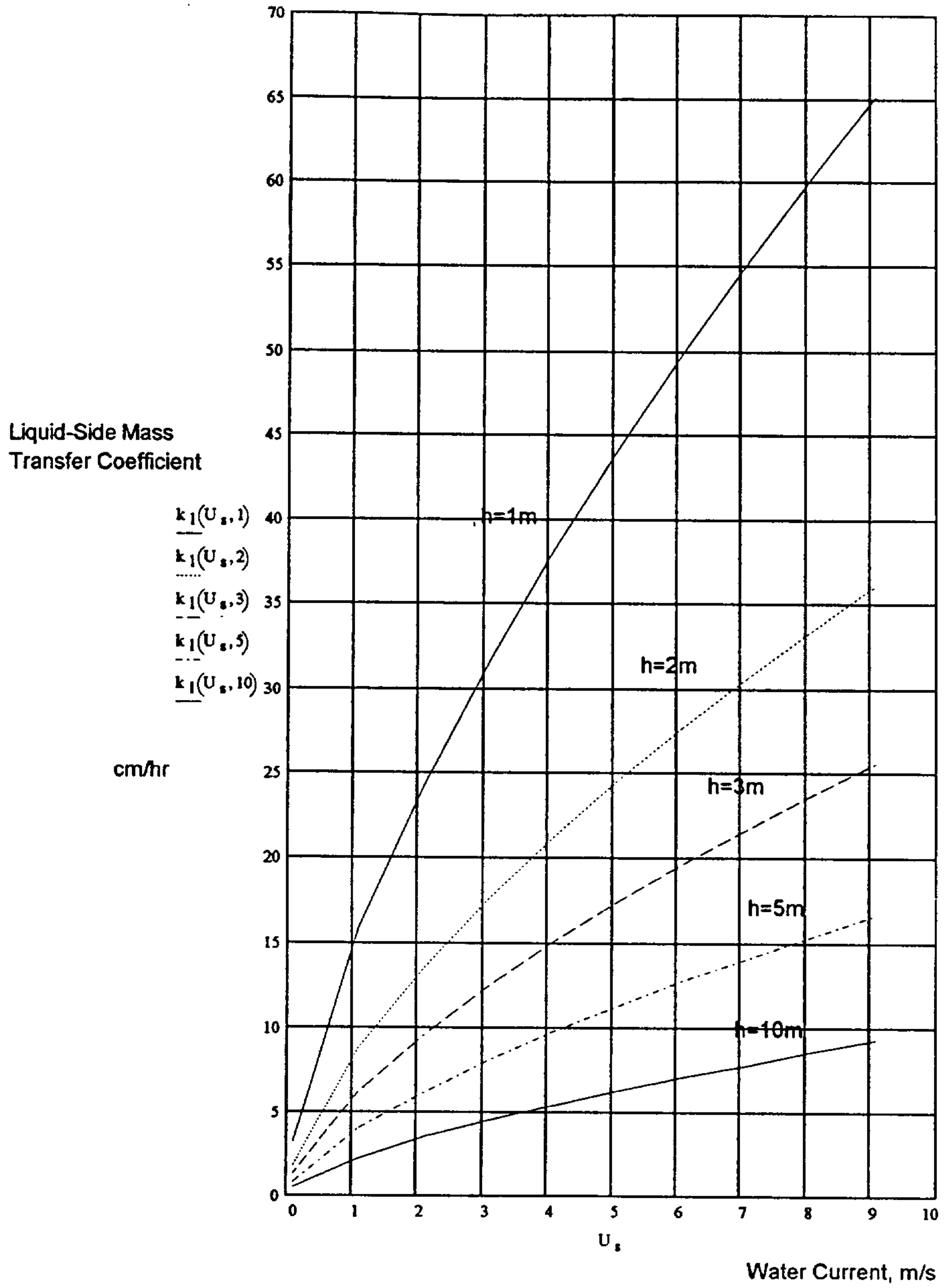

Figure 4.4. Liquid-Side Mass Transfer Coefficient for Methylene Chloride at 20°C for a Flowing River BAsed on Eqs. 4-62 and 4-63d (h=river depth).

3) Determine the value of k_l from a suitable correlation selected from Section 4.2.2 once a wind speed and type of water body are selected.

4) Determine k_g from either Eq. 4-50 or 4-51 depending on the resulting value for Re_o. Note that a value for U^*_a is required and this can be estimated from Eqs. 4-53, 4-57a - 4-57c, and 4-58 or from wind speed profile data.

5) Use Eq. 4-49 to determine K_L.

As an illustration, consider the volatilization of methylene chloride from a large water body (i.e., large reservoir or lake) at 20°C. The kinematic viscosities for the air and water phases were calculated to be 0.15 cm^2/s and 0.01 cm^2/s, respectively (Reid et al., 1987). The diffusion coefficients in air and water were estimated to be 0.098 cm^2/s and 1.13×10^{-5} cm^2/s using Eqs. 4-42 and 4-45, respectively. The gas-side mass transfer coefficient k_g at 20°C, obtained from Eqs. 4-50 and 4-51 (with linear interpolation of k_g in the region $0.13 \le Re_o \le 2$), and Eqs. 4-56b and 4-58 for z_o and C_D, respectively, is given, as a function of wind speed, in Figure 4.2. The liquid-side mass transfer coefficient, k_l, obtained from Eq. 4-60, at 20°C, is given in Figure 4.3. As an example, at U_{10} = 5 m/s, k_g = 1772 cm/hr (Figure 4.2) and k_l = 3.74 cm/hr (Figure 4.3). Thus, using, for example, a value of 0.088 for the dimensionless Henry's Law constant (Table 4-9) leads to

$$K_L = \left[\frac{1}{3.74} + \frac{1}{0.088 \times 1772}\right]^{-1} = 3.74 \qquad , \qquad cm/hr \tag{4-63e}$$

Alternatively, one can directly determine K_L for methylene chloride for the selected wind speed, using Figure 4.5. As can be seen from this example, the first term on the right hand side of Eq. 4-63e dominates. Thus, the liquid-side resistance $(1/k_l)$ to methylene chloride mass transfer across the water/air interface makes up about 97.6% of the total resistance $(1\backslash K_L)$ to mass transfer. Therefore, for methylene chloride $K_L \approx k_l$, and since $Hk_g >> k_l$ for all wind speeds, the approximation that $K_L = k_l$ is appropriate for methylene chloride.

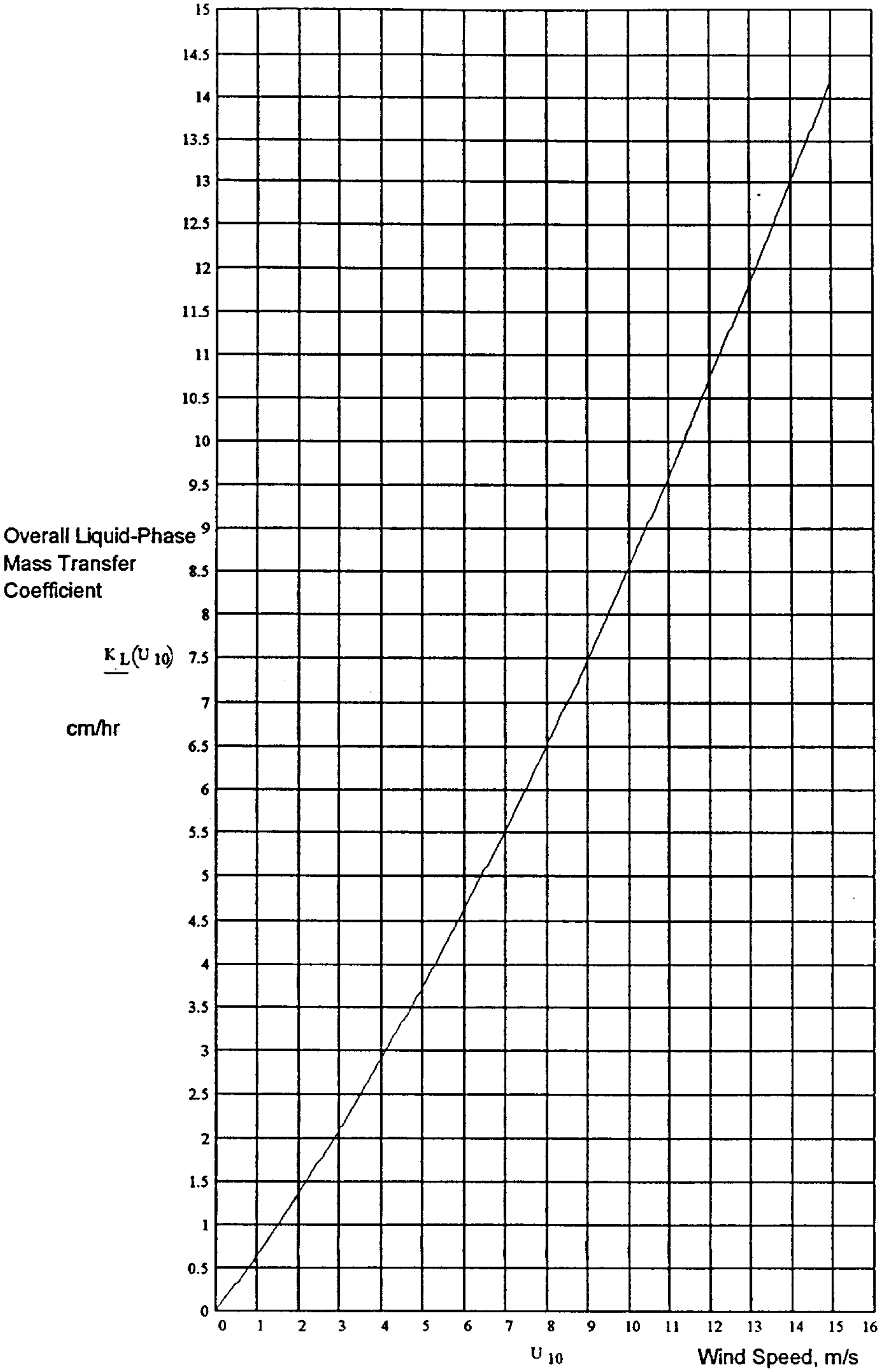

Figure 4.5 Overall Liquid-Side Mass Transfer Coefficient for Methylene Chloride for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlations of Cohen and Ryan, 1985 and Brutsaert, 1975).

4.3.3 Dry Deposition

Dry deposition may be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989). Dry deposition is affected by a multiplicity of factors that often interact in complex ways. The most important factors are the characteristics of the atmosphere, the nature of the surface, and properties of the depositing species. Transport of gases through the atmosphere depends on their eddy and Brownian diffusivities. In addition, solubility and chemical reactivity also factors affect the capture of gases by surfaces.

The dry deposition flux of a gaseous chemical can be expressed by

$$N_A = V_d\, C_a \tag{4-64}$$

where N_A is the flux in mass per unit area, per unit time, C_a is the mass of the pollutant in the particle phase per unit volume of air, and V_d is the overall chemical dry deposition velocity.

Dry deposition velocities can vary by several orders of magnitude depending on the surface characteristic (e.g., type of vegetative cover), the chemical type, and meteorological conditions. It is interesting to note that Sehmel (1980), in his critical review of particle and dry gas deposition velocity as it relates to its use in atmospheric transport modes, observed that a deposition velocity of 1 cm s^{-1} is generally assumed, often due to the lack of any better estimate. The CAPCOA model currently uses deposition velocities of 2 cm s^{-1} and 5 cm s^{-1} for controlled and uncontrolled sources, respectively.

Dry deposition of methylene chloride is expected to be of minor importance as an atmospheric loss process compared to reaction with hydroxyl (OH) radicals (CARB, 1989). Since no experimentally determined values for dry deposition velocity of methylene chloride were found in the literature, the method used by Cohen et al. (1990b) is described here as a possible approach to estimate the dry deposition velocity. According to this method, the dry deposition velocity is proportional to $D^{2/3}$ (where D is the molecular diffusivity in air). Thus, if the dry deposition velocity for a given chemical is known, the value for methylene chloride (for the same deposition surface and meteorological conditions) can be calculated using the equation

$$V_{d_B} = V_{d_A}\left(\frac{D_B}{D_A}\right)^{2/3} \tag{4-65}$$

where V_{dB} is the dry deposition velocity of methylene chloride, V_{dA} is dry deposition velocity of a reference chemical for which deposition velocity is known (was measured), D_B is a diffusion coefficient of methylene chloride, and D_A is a diffusion coefficient of the reference chemical. The reference chemical should be chosen to approximate the surface reactivity of the chemical of interest.

Calculation of dry deposition velocity for methylene chloride: [The deposition velocity for SO_2 and CO_2 was given by Sehmel (1980; 1984)].

Air: M_A = 28.97 g/mol (Lyman et al., 1990)
V_A = 20.1 cm^3/mol (Lyman et al., 1990)

<u>**Calculation of V_d based on CO_2**</u>

CO_2: $V_{d_{CO_2}}$ = 0.3 cm/s

D_{CO_2} = 0.155 cm^2/s at 298 K (Fuller et al., 1966)

(1) - Methylene chloride
(2) - CO_2

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-66}$$

$$V_{d_1} = 0.3\left(\frac{0.101}{0.155}\right)^{2/3} \tag{4-67}$$

$$V_{d_1} = 0.22 \text{ cm/s} \tag{4-68}$$

Calculation of V_d based on SO_2

SO_2: $M_{SO_2} = 64$ g/mol

$V_{SO_2} = 41.1$ cm³/mol (Fuller et al., 1966)

(1) - Methylene chloride

(2) - SO_2

$D_{\text{methylene chloride}} = 0.10$ cm²/s, at K

$V_{d_{SO_2}} = 0.04\text{-}2.7$ cm/s for different deposition surfaces (e.g., 0.04 cm/s was measured for asphalt and 2.7 cm/s was measured for an alfalfa surface)

From Eq. 4-42, at 25°C, the diffusion coefficient for SO_2 in air can be estimated as

$$D_{SO_2} = \frac{10^{-3}\,(298)^{1.75}\,\sqrt{0.05}}{1\,\left[(20.1)^{1/3} + (41.1)^{1/3}\right]^2} = 0.125 \text{ cm}^2\text{/s} \tag{4-69}$$

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-70}$$

Lower Limit:

$$V_{d_1} = 0.04\left(\frac{0.101}{0.125}\right)^{2/3} = 0.034 \text{ cm/s} \tag{4-71}$$

Upper Limit:

$$V_{d_1} = 2.7\left(\frac{0.101}{0.125}\right)^{2/3} = 2.34 \text{ cm/s} \tag{4-72}$$

It is noted that since SO_2 is more reactive than methylene chloride in the aqueous phase, the dry deposition velocity obtained using SO_2 as the reference chemical will be high if the deposition surface for the SO_2 data was moist. Thus, based on the above example, the deposition velocity for methylene chloride is expected to be in the range of about 0.03 cm/s to 2.3 cm/s. The actual value will depend on the prevailing meteorological and surface conditions in the area of interest (Sehmel, 1980; 1984; Davidson and Wu, 1989). Also, in computing the deposition velocity for methylene chloride, the appropriate environmental conditions should be selected for the reference deposition velocity.

4.3.4 Wet Deposition

Wet deposition (scavenging) can increase the overall deposition rate of methylene chloride and thus, increase methylene chloride concentration in the soil, water and vegetation due to direct deposition. Both rain and snow can remove methylene chloride from air, however snowfall is not considered a significant removal process in most of the heavily populated regions in California. In addition, wet deposition is episodic; therefore, the climatological conditions of the location in question must be considered when evaluating the relative importance of wet deposition as a removal process.

The degree of wet deposition is usually estimated from knowledge of the washout ratio, W, defined as

$$W = C_{rainwater}/C_{air} \tag{4-73}$$

in which $C_{rainwater}$ and C_{air} are the concentrations (e.g., ng/m^3) of methylene chloride in rainwater (at ground level) and in the gaseous phase (i.e., in the atmosphere), respectively. Thus, the wet deposition flux (e.g., ng/m^2·hr), $\dot{M}_w$, is given by

$$\dot{M}_w = W \cdot R \cdot C_{air} \tag{4-74}$$

where R is the precipitation rate (e.g., m/hr). When compared with the washout ratios for highly water soluble (e.g., methanol), and hence efficiently removed, organic compounds of $W = 10^4$-10^5 (Eisenreich et al., 1981; Leuenberger et al., 1985; Atkinson, 1988), it appears that wet deposition of gaseous methylene chloride will be of relatively minor importance as an atmospheric removal process for this compound.

Rain scavenging of methylene chloride can be predicted using the detailed approach described by Lopez et al. (1989), Tsai et al. (1991), and Clay (1992). However, a simple upper-limit estimate can be obtained by assuming that the raindrops are in equilibrium with the air phase when they reach ground level. This assumption is supported by the analysis of Slinn et al. (1978) and Cohen (1986) who assert that raindrops that have fallen through 10 meters of polluted atmosphere will be nearly at equilibrium with gaseous phase. Thus, the maximum concentration of the dissolved chemical in rain, $C_w^{(d)}$ (ng/m^3 water), is given by

$$C_w^{(d)} \approx \frac{C_a^{(g)}}{H_{aw}} \tag{4-75}$$

in which $C_a^{(g)}$ is the concentration of the chemical in the atmosphere in the vapor phase (e.g., ng/m^3 air), and H_{aw} is the dimensionless Henry's Law constant (i.e., $H_{aw} = C_a^{(g)}/C_w^{(d)}$).

4.4 Degradation

Understanding degradation processes is important for determining atmospheric lifetimes, which in turn, can be used to estimate spatial dispersion and distribution of a compound. Section 3.2.4 describes the general degradation procedures that were considered for methylene chloride. The following subsections define the specific degradation processes that were considered most applicable to methylene chloride and the findings of the literature survey are also presented.

4.4.1 Atmospheric Degradation

Potentially important atmospheric degradation processes for volatile organic compounds include direct photolysis and oxidation via the hydroxyl (OH) radical, nitrate (NO_3) radical, and ozone (O_3). The most significant of these degradation processes for methylene chloride is its reaction with atmospheric OH radicals (Perry et al., 1976; Atkinson, 1989; CARB, 1989; Howard, 1990).

Because methylene chloride has been shown to be one of the most reactive chlorinated hydrocarbon measured to date, it will degrade before reaching the stratosphere (Cox et al., 1976; Perry et al., 1976; Jeong and Kaufman, 1982). Therefore, one need only consider tropospheric processes and concentrations when calculating reaction rates, lifetimes and half-lives.

The reaction of methylene chloride with OH can be described by the following reactions (Howard and Evenson, 1976; Davis et al., 1976; CARB, 1989):

$$CH_2Cl_2 + OH \text{ ----> } CHCl_2 + H_2O \tag{4-76}$$

$$CHCl_2 + O_2 \text{ ----> } OOCHCl_2 \tag{4-77}$$

The peroxy radical ($OOCHCl_2$) will then undergo one of the following three reactions:

$$OOCHCl_2 + NO \text{ ----> } OCHCl_2 + NO_2 \tag{4-78}$$

$$OOCHCl_2 + RO_2 \text{ ----> } OCHCl_2 + \text{other products} \tag{4-79}$$

$$OOCHCl_2 + HO_2 \text{ ----> } HOOCHCl_2 + O_2 \tag{4-80}$$

$OCHCl_2$ is known to eliminate a chlorine which will then react with hydrocarbons in the atmosphere to yield HCl (CARB, 1989).

The reaction rate constant for the reaction of methylene chloride with OH can be described as a function of temperature by the Arrhenius expression:

$$k_{OH} = A \cdot e^{(-Ea/RT)}\ \mathrm{cm^3/molec \cdot s} \tag{4-81}$$

where:

A = a pre-exponential factor
Ea = activation energy in kcal/mol
R = universal gas constant = 1.987 cal/deg·mol
T = the temperature in K

Numerous investigators have used flash photolysis-resonance fluorescence techniques to measure reaction rates and develop Arrhenius expressions for the reaction of methylene chloride with OH. The results of these studies are summarized in Table 4-15. Atkinson (1989) critically evaluated the existing literature and based on a unit-weighted least squares analysis recommended the following Arrhenius expression, which is valid over the temperature range 245-455 K and the pressure range 107-1300 Pa:

$$k_{OH} = 8.54 \times 10^{-18}\ T^2\ e^{(-500 \pm 212/T)}\ \mathrm{cm^3/molec \cdot s} \tag{4-82}$$

where the range of calculated uncertainty in the constant of 8.54 was +8.2 and -4.2. Based on this expression, Atkinson (1989) recommends a rate constant for reaction of methylene chloride with OH of 1.42×10^{-13} ±25% cm³/molec·s at 298 K. This reaction rate constant can be used in combination with estimates of tropospheric OH concentrations to calculate atmospheric lifetimes and half-lives using the following equations:

$$\text{lifetime} = \tau = 1/k_{OH} \cdot [OH] \tag{4-83}$$

$$\text{half-life} = \tau_{1/2} = \ln 2\ /k_{OH} \cdot [OH] \tag{4-84}$$

Using the rate constant recommended by Atkinson (1989) and a 24 hour integrated global average tropospheric OH concentration of 1×10^6 molec/cm³ (Singh et al., 1982; Atkinson, 1989; CARB, 1989; Howard, 1990, Prinn et al., 1992), the atmospheric lifetime of methylene chloride due to reaction with OH approximately 80 days and the corresponding atmospheric half-life is approximately 60 days. Lifetimes of this length mean that methylene

Table 4-15. Rate Constants and Half-Lives for Reaction of Methylene Chloride with OH*

Half-life[a] (days)	Rate Constant	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
57	14.2×10^{-14}	cm^3/molec·s	±25%	298	Recommended(b)	Atkinson, 1989	
61	13.2×10^{-14}	cm^3/molec·s	$\pm2.75\times10^{-14}$	298	Recommended(b)	CARB, 1989	
55	14.5×10^{-14}	cm^3/molec·s	$\pm2.0\times10^{-14}$	298	Measured(c)	Perry et al., 1976	
52	15.5×10^{-14}	cm^3/molec·s	$\pm3.4\times10^{-14}$	296±2	Measured(c)	Howard and Evenson, 1976	
55	14.6×10^{-14}	cm^3/molec·s	$\pm2.2\times10^{-14}$	298	Measured(c)	Jeong and Kaufman, 1982	
69	11.6×10^{-14}	cm^3/molec·s	$\pm5.0\times10^{-14}$	298	Measured(c)	Davis et al., 1976	
52	15.5×10^{-14}	cm^3/molec·s	$\pm3.4\times10^{-14}$	296	Measured(c)	Perry et al., 1976	Howard and Evenson, 1976
77	10.4×10^{-14}	cm^3/molec·s	NR	298	Measured(d)	Cox et al., 1976	
73	11.0×10^{-14}	cm^3/molec·s	NR	298	Calculated(e)	Altshuller, 1980	Davis et al., 1976
116	6.9×10^{-14}	cm^3/molec·s	NR	265	Calculated(e)	Altshuller, 1980	Davis et al., 1976

NR = Not Reported

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Half-life calculated as $\tau_{1/2} = \frac{\ln(2)}{k_{OH}[OH]}$; where k_{OH} = reaction rate constant and [OH] = tropospheric concentration of OH radicals. For all cases, the concentration of tropospheric OH was assumed to be 1×10^6 molec/cm^3

(b) Recommended by the author(s) based on measured values

(c) Reaction rate of OH + CH_2Cl_2 was measured using a flash photolysis resonance fluorescence technique

(d) Reaction rate of OH + CH_2Cl_2 was calculated by comparing the formation rate of NO to the disappearance rate of HONO

(e) Altshuller (1980) used the Arrhenius expression developed by Davis et al., 1976 ($k = 4.27\times10^{-12}\cdot e^{(-1095/T)}$) to calculate reaction rates at different temperatures chloride can be transported out of local basins in which it was emitted and impact downwind locations throughout the hemisphere (CARB, 1989). Although with a lifetime of approximately 80 days, methylene chloride will be well mixed in the troposphere, it is unlikely to reach the stratosphere in significant concentrations.

While reaction of methylene chloride with the OH radical is the dominant removal process during daylight hours, at night reaction with the gaseous nitrate (NO_3) radical must be considered. Although NO_3 is expected to react with methylene chloride in an analogous manner to OH, no studies have been found which report measured rate constants for reaction of methylene chloride with the nitrate radical or the corresponding atmospheric lifetimes. Similarly, no studies have been identified which report measured reactions of methylene chloride with ozone. However, several studies state that reaction of methylene chloride with compounds other than OH are insignificant (Perry et al., 1976; CARB, 1989; Howard, 1990).

Several studies have measured direct photolysis of methylene chloride and found it to be negligible (Cox et al., 1976; Howard, 1990). Additionally, photolysis in the presence of NO_x has been found to be negligible (Dilling et al., 1976; CARB, 1989). Hubrich and Stuhl (1980) used the Lambert-Beer law to determine the absorption cross-section (σ) of methylene chloride and found no absorption at wavelengths above 255 nm. Since the troposphere only experiences electromagnetic radiation at wavelengths greater than 290 nm, no tropospheric photolysis of methylene chloride is expected to occur.

Reaction rate constants for methylene chloride against the OH radical, and their corresponding half-lives are summarized in Table 4-15.

4.4.2 Loss from Water

The primary removal process of methylene chloride from water is volatilization, with photolysis and hydrolysis being of secondary importance (CARB, 1989; Howard, 1990). For example, Dilling et al. (1975) measured the hydrolysis half-life of methylene chloride at

298 K to be 18 months, and Halmann et al. (1992) noted that in the absence of metal catalysts, photolysis of methylene chloride in water is negligible.

4.4.3 Biodegradation in Soil, Water and Sludge

Microbial degradation of methylene chloride occurs in water, sludge, and soil. Several strains of gram-negative motile bacilli have been identified which use methylene chloride as a sole carbon source completely mineralizing it in the process (Rittmann and McCarty, 1980; Brunner et al., 1980). Degradation occurs via a two step process in which methylene chloride is dehalogenated and then metabolized by Glutathione (Klecka, 1982; Davis and Madsen, 1991). If initial bacterial levels are low, as in clay soils, a lag time may be necessary before the onset of biodegradation. This period allows for induction of dehalogenase enzymes and subsequent population growth. Davis and Madsen (1991) reported the need for a 50 day lag time before the onset of biodegradation in clay soils, and Klecka (1982) reported the need for an 11 day lag time before enzyme induction in low organic carbon sludge. Earlier studies which assert that methylene chloride is not subject to biodegradation may have not been carried out long enough to overcome this lag period.

Optimum degradation occurs at temperatures between 28°C and 33°C and under basic conditions (Brunner et al., 1980; Klecka, 1982). Freedman and Gossett (1991) showed degradation to be significantly inhibited at pH less than 6. Biodegradation can occur under both aerobic and anaerobic conditions, but is significantly higher under the former (Brunner et al., 1980; Davis and Madsen, 1991). High organic carbon levels increase biodegradation rates due to better nutrient availability; however, if organic carbon content is too high bacterial blooms may lead to anaerobic conditions, which will decrease biodegradation rates (Klecka, 1982; Jury et al., 1990; Davis and Madsen, 1991). High substrate (methylene chloride) concentrations may be toxic to bacteria, thereby decreasing biodegradation rates (Brunner et al., 1980; Klecka, 1982; Davis and Madsen, 1991).

Table 4-16 presents biodegradation half-lives and rate constants for methylene chloride in different media. In many cases, biodegradation constants are not directly reported in the literature. Thus, where biodegradation rate constants for methylene chloride were not reported in research papers reviewed for this study, they were calculated, whenever feasible, based on data available in the literature. Biodegradation rate constants (k) were determined assuming first-order kinetics for biodegradation processes. The assumption of the first order kinetics is reasonable at low methylene chloride concentrations, in homogenous media, or as a first order approximation. The first-order rate law states that the rate is the product of the rate constant and the chemical concentration.

$$\frac{dc}{dt} = -kC \tag{4-85a}$$

which can be integrated to yield:

$$\ln \frac{C}{C_o} = -kt \tag{4-85b}$$

where C_o is initial methylene chloride concentration, C is methylene chloride concentration at time t, k is a rate constant (obtained from the slope of a plot of $\ln C/C_o$ vs. time), and t is a time interval. The rate constants determined using Eq. 4-85b can be used to calculate the biodegradation half-life ($\tau_{1/2}$) of methylene chloride using the following equation:

$$\tau_{1/2} = \frac{\ln 2}{k} \tag{4-86}$$

From the results in Table 4-16, it can be seen that the fastest biodegradation rates for methylene chloride were measured under aerobic conditions in high organic carbon soils (sandy loam). Conversely, media with low initial bacteria levels (clay and sludge) required significant lag times before the onset of biodegradation. It can also be seen that there is wide range of values for biodegradation rate constants and corresponding biodegradation

Table 4-16. Biodegradation Rate Constants and Half-Lives for Methylene Chloride*

Half-life[a] (days)	Rate Constant (day $^{-1}$)	Reported Uncertainty	Experimental Medium	Temperature (K)	Conditions[b]	References
54.8	0.013	NR	Sand	298	Aerobic	Davis and Madsen, 1991
12.7	0.055	NR	Sandy clay loam	298	Aerobic	Davis and Madsen, 1991
9.4	0.074	NR	Sandy loam	298	Aerobic	Davis and Madsen, 1991
7.2 (+50 day lag)	0.096	NR	Clay	298	Aerobic	Davis and Madsen, 1991
31.4	0.022	NR	Water	301-306	Aerobic/pH = 9	Brunner et al., 1980
2.1 (+11 day lag)	0.330	NR	Activated sludge	294	pH = 7.2	Klecka, 1982
69.3	0.010	NR	Water	293	NR	Rittmann and McCarty, 1980
100	.00693	NR	Soil surface zone	NR	Dry soil	Jury et al., 1990

NR = Not Reported

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Half-life calculated as $\tau_{1/2} = \frac{\ln(2)}{k\,[OH]}$; where k = reaction rate constant.

(b) All values from experimental measurements.

half-lives for methylene chloride which can be attributed to different experimental conditions such as microbial population, dissolved oxygen, the availability of nutrients, other sources of carbon, inhibitors, temperature, and pH. Additionally, methylene chloride may volatilize from soil. The rate of volatilization depends on soil water content, organic carbon content, porosity, depth, and ambient temperature. Because experimental methods for measuring biodegradation rates are not standardized, the results reported in the literature are often not comparable and apply only to a particular set of experimental conditions. Thus, it is not feasible to derive a single value for the biodegradation rate constant and the corresponding half-life for methylene chloride.

5.0 Multimedia Distribution of Methylene Chloride

Multimedia distribution of a chemical can be estimated using the Spatial-Multimedia-Compartmental (SMCM) model (Cohen et al., 1990b). Using the SMCM model and equations and parameters described in this report and by Cohen (1986, 1990), the general pattern of multimedia flux and partitioning of methylene chloride was determined for the South Coast Air Basin (SoCAB) as a representative area. The SoCAB was used because approximately 80% of methylene chloride emissions in California occur in the SoCAB (CARB, 1989; TRI, 1990; Bode, 1993). The input parameters used for predictions are listed in Table 4-17 (physicochemical and thermodynamic properties of methylene chloride) and Table 5-1 (geographic properties for the SoCAB).

The multimedia distribution of methylene chloride as shown in Figure 5.1 reveals that the highest concentrations of methylene chloride occur in the water and biota. In this example, methylene chloride in the water compartment originates from the air phase through air/water mass transfer. Direct contact between the biota and water leads to the accumulation of methylene chloride in biota concentrations. The relatively low concentration in biota is not surprising given the low BCF for methylene chloride. Concentration in the soil and sediment are low due to high soil biodegradation and volatilization rates. It is not surprising, given the relatively high Henry's law constant for methylene chloride, that about 98% of the total mass of methylene chloride present in the environment is found in the atmosphere.

Table 5-1. Geographic Properties of the SoCAB

Parameter	Reported Value	Reference
source strength	2,810 mol/hr	Bode, 1993
wind speed	4.0 m/s	Smith et al, 1984
air compartment mixing height	540 m	Smith et al, 1984
air pressure	1 atm	Smith et al, 1984
avg. water depth	15 m	Jones, 1971
avg. water temp.	14°C (winter) 20°C (summer)	Jones, 1971
water flow rate	45,500 m^3/hr	Jones, 1971
air/water and sediment/water interfacial area	527 m^2	Cohen et al, 1990
density of soil	1.5×10^6 g/m^3	Cohen et al, 1990
fraction organic carbon for soil, sediment, and suspended solids	0.04	Cohen et al, 1990
soil slope	5%	USDOA, 1980
main soil composition	loam	USDOA, 1980
air/soil interfacial area	10,619 km^2	SCAQMD, 1991
avg. suspended solid particle diameter	0.001 cm	Cohen et al, 1990
percent volume of water for suspended solids	5×10^{-4}%	Cohen et al, 1990
water/suspended solids interfacial area	7.75 km^2	Cohen et al, 1990
percent volume of water for biota	5×10^{-5}%	Cohen et al, 1990
avg. yearly rainfall	410 mm	USDOA, 1980
avg. yearly temperature	16.7°C	USDOA, 1980

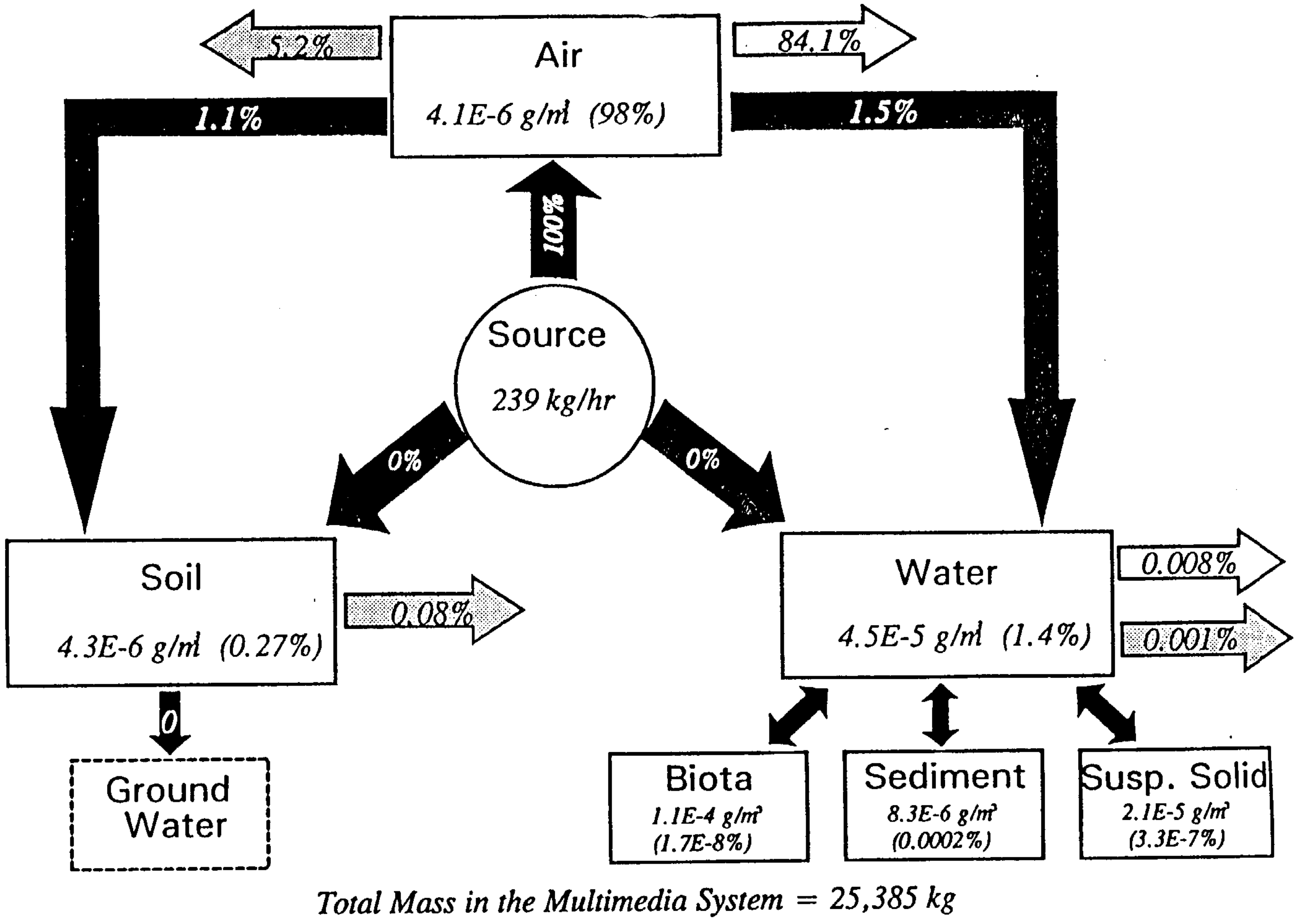

Figure 5.1. **Multimedia Flux and Partitioning of Methylene Chloride**. Solid arrows represent intermedia transfer and input into the system. Double ended arrows represent equilibrium between two compartments. Open arrows represent losses due to advection, gray arrows represent losses due to degradation.

Approximately 85% of the loss of methylene chloride from the system is via advection out of the air compartment. It is important to keep in mind that because of methylene chloride's atmospheric lifetime of 80 days (Atkinson, 1989), much of the amount transported out of the system may impact downwind areas.

Predicted air concentrations compare well to measured concentrations: For the SoCAB, 1.2 ppb was predicted vs 1.9 ppb measured (CARB, 1989). This illustrates that when used with reasonable input parameters, the SMCM box model for the atmosphere provides a reasonable estimation of average air concentrations. Finally, the concentrations in other compartments should be regarded as screening-level estimates given the uncertainty in site-specific parameters.

6.0 SUMMARY AND CONCLUSIONS

The summary of intermedia transfer factors is given in Section 1.1 with the key findings and conclusions regarding multimedia exposure to methylene chloride given below:

- Methylene chloride partitions mainly into the air where it has a lifetime of approximately 80 days. This results in a long-distance transport of methylene chloride.

- Reaction with the hydroxyl (OH) radical is the main removal mechanism from the air, while volatilization is the main removal mechanism from the water.

- Measured bioconcentration factors and biotransfer factors which address partitioning through food uptake were not found in the literature. Thus, this report only presents (except where noted) estimated values based on empirical correlations.

- No experimentally measured values of soil sorption or bioconcentration have been found. Thus, the reported values are based on correlations derived from other chlorinated hydrocarbons. Given the extensive industrial and commercial use of methylene chloride, there is merit in an experimental determination of these parameters.

- There are conflicting studies regarding whether or not methylene chloride bioaccumulates. The most recent studies indicate little bioaccumulation; however, this area needs further study.

- Reported Henry's Law constants for methylene chloride differ by 50%. Since this is the main parameter used to predict air/water partitioning it is critical that experimental measurements be revisited.

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Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume I: Volatile Organic Compounds
Section 3 - Formaldehyde

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ABSTRACT

An information base was developed on the physicochemical properties and transport parameters of formaldehyde, which can be used to predict abiotic and biotic transfer of formaldehyde among environmental media (i.e., air, water, soil, and the biosphere) with emphasis on human exposure pathways. This information is useful in the multipathway exposure component of health risk assessment for formaldehyde. The environmental literature relevant to formaldehyde was critically reviewed to: (1) determine the intermedia transfer factors relevant to formaldehyde; (2) evaluate measured values; and (3) recommend estimation techniques applicable to formaldehyde (and homologous compounds) for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

1.1 Overview

The assessment of health risk requires the determination of exposure of the human receptor to pollutants from multiple pathways. The movement of chemicals throughout the environment is particularly important to the overall assessment of the exposure to toxic air pollutants since airborne pollutants can be deposited to the soil and water, and can be accumulated in plants and animals. Determination of air toxic contaminant concentrations can be obtained by either pollutant transport modeling or field measurements. Both approaches require an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media.

Risk assessment is often accompanied by uncertainties which arise from the lack of data and reliance on assumptions and default parameter values. For example, the assumptions and default values listed in the CAPCOA guidelines (1992) are designed to err on the side of human health protection to avoid underestimating risk to the public. Major sources of uncertainty which may either overestimate or underestimate risk include:

- Extrapolation of toxicity data in animals to humans;
- Air dispersion modeling;
- Estimation of emissions; and
- Analysis of multimedia exposure.

This study addresses the final major source of uncertainty listed above, analysis of multimedia exposure. By identifying the input parameters most critical to multimedia analysis and critically evaluating measured values and estimation techniques, this report should help characterize the uncertainty associated with estimating risk from multimedia exposure to formaldehyde. A summary of representative values and estimation methods for intermedia transfer factors for formaldehyde is given in Table 1-1. The listed parameter values typically apply to specific conditions; however, they are included in the Table for comparison purposes and the appropriate sections in the report that discuss these values or estimation methods are indicated in Table 1-1.

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Formaldehyde

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (°C)	Technique	References	Section in Text
S	13.32	mol/L	NR	NR	NR	U.S. EPA, 1986	4.1.1.
P_{vp}	5.160×10^2	kPa	NR	25	NR	Howard, 1989	4.1.2
V_b	29.6	cm^3/mol	NR	NR	Calculated	Reid et al., 1987	4.1.3
MW	30.03	g/mol	NR	NR	NR	IUPAC, 1987	4.1.4
T_{BP}	-19	°C	NR	NA	NR	U.S. EPA, 1984	4.1.5
T_{MP}	(-118)-(-92)	°C	NR	NA	NR	Verschueren, 1992	4.1.6
T_C	137.2-141.2	°C	NR	NA	NR	U.S. EPA, 1984	4.1.7
P_C	6.637-6.784	MPa	NR	NR	NR	U.S. EPA, 1984	4.1.7
ρ	0.8153-0.9151	g/ml	NR	-20/-80	NR	U.S. EPA, 1984	4.1.8
H	3.401×10^{-2}	$Pa\cdot m^3/mol$	±0.146	25	Experimental	Betterton and Hoffmann, 1988	4.2.1
$\log K_{ow}$	0.35	unitless	NR	NR	Calculated	U.S. EPA, 1987	4.2.2
$\log K_{oc}$	0.7-1.57	unitless	NR	NR	Calculated	see Table 4-8	4.2.3
BCF				see Table 4-9 for specific estimation correlations			4.2.4
$\log B_{vd}$	1.39	unitless	NR	NR	Calculated	Travis and Arms, 1988	4.2.4.1
B_{vaw}	3,581-58,997	unitless	NR	NR	Calculated	see Section 4.2.4.1.	4.2.4.1

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Formaldehyde
(Continued)

Parameter	Reported Value	Reported Units	Reported Uncertainty	Temperature (°C)	Technique	References	Section in Text
$\log B_m$	-7.71	unitless	NR	NR	Calculated	Travis and Arms, 1988	4.2.4.2
$\log B_b$	-7.25	unitless	NR	NR	Calculated	Travis and Arms, 1988	4.2.4.2
D_{air}	1.65×10^{-1}	cm^2/s	7.6%	25 (Absolute average error)	Calculated	Lyman et al., 1990	4.3.1
D_{water}	2.22×10^{-5}	cm^2/s	±8.8%	25 (Absolute average error)	Calculated	Lyman et al., 1990	4.3.1
V_d		NA	NA	NA	see Section 4.3.3.1		4.3.3.3
K_L, K_G			see Section 4.3.2 for recommended estimation methods				
Wet deposition					see Section 4.3.4		
Degradation Parameters							
$\tau_{½\ air}$	0.51-2.1	day	see Tables 4-11 and 4-12 and Section 4.4.3 for values corresponding to specific conditions				4.4.1
$\tau_{½\ soil}$	1-7	day			see Section 4.4.3		
$\tau_{½\ water}$	1-7	day			see Section 4.4.3		

NR = Not Reported.

NA = Not Applicable.

1.2 Formaldehyde

At room temperature, formaldehyde is a colorless, flammable gas with a pungent, suffocating odor. It irritates mucous membranes intensely. Formaldehyde is a probable human carcinogen (IARC, 1987). In humans, formaldehyde is known to cause a wide range of health effects such as ocular, nasal, and dermal irritation through inhalation and direct contact and nausea and headaches through inhalation. Formaldehyde occurs both naturally and anthropogenically. Natural sources include forest fire, animal wastes, and seawater (from photochemical reactions). Anthropogenic sources include exhaust from diesel, gasoline and especially methanol powered motor vehicles as primary sources, photooxidation of emitted hydrocarbons as secondary sources, formaldehyde related production plants, wood stoves, cigarette smoke, fumigant, soil disinfectant, embalming fluid, leather tanning, and emissions from plywood, and resin-treated fabrics and paper.

Formaldehyde is a polar organic which is highly soluble in water (55%; Howard, 1989). Formaldehyde is likely to partition into the water compartment given its high aqueous solubility and a low Henry's Law Constant (3.27×10^{-7} atm·m^3/mol; Howard, 1989). Given the above, it is likely that rain scavenging could be an efficient mechanism for removing formaldehyde from the atmosphere to the terrestrial and aquatic environments during rainy seasons. It is noted that the contribution of formaldehyde to acid rain is a concern since it forms formic acid in rain droplets. Its atmospheric lifetime is approximately 4 hours due to both photolysis and reaction with OH radicals (Howard, 1989; Winer and Busby, 1993). The low log K_{ow} (0.35; Howard, 1989) of formaldehyde suggests that it will not bioconcentrate in aquatic organisms. Also, the adsorption of formaldehyde to sediments is minimal (Howard, 1989). It is noted that the major exposure pathway of formaldehyde is believed to be through inhalation from both indoor and outdoor sources (Howard, 1989).

2.0 OBJECTIVES

The overall objective of this report is to present information that is pertinent to the prediction of the transfer of formaldehyde between media such as air, water, soil, and biota in order to refine the multipathway exposure component of health risk assessments. The specific objectives of the study were to: (1) critically review the literature to obtain the parameters necessary to determine environmental intermedia transfer factors for formaldehyde; (2) evaluate and update intermedia transfer factors currently used in multipathway exposure assessments; and (3) provide pollutant-specific estimates where default values are now used, or no value is available.

3.0 METHODOLOGY

In this study, a thorough investigation was conducted of the literature values reported for key factors and parameters which govern the partitioning of formaldehyde in the various important environmental compartments and the food chain, following formaldehyde's release to the atmosphere from stationary and mobile sources. Whenever possible, the reported values for a given parameter were placed on a common basis of units and conditions, and the parameter values were critically evaluated to determine which of these numerical values appear to be of greatest reliability and utility in conducting multipathway exposure assessments. Where no reliable values are found to be available in the literature or default values are currently being used in such discussions, pollutant specific estimates are provided. The details of the methods used, and the properties and parameters investigated, are discussed below.

3.1 Literature Review

A literature search of Dialog (NTIS, Pollution Abstracts, Enviroline, CAS) and UCLA Orion, Melvyl, and EMS library databases was conducted. The UCLA NCITR library was also reviewed for relevant publications. Through this process, references pertaining to the physicochemical properties, intermedia transport, and biotransformation of formaldehyde were identified, obtained, reviewed, and summarized. Thorough reviews of input parameters such as solubility, Henry's Law constant, dry deposition, and reaction rate constants in air have been published, and are cited throughout this report. The literature evaluation emphasized measured values. Where no measured values were found in the literature, estimation techniques applicable to formaldehyde or homologous compounds were used. These findings underscore the need for reliable estimation techniques.

3.2 Selection of Parameters

In order to provide a state-of-the-art assessment of intermedia transfer parameters, a number of input parameters were considered. The final selection was based on the chemical and physical interpretation of the input parameters, their applicability to different classes of pollutants, and measures of the environmental consequences of intermedia transfers. Specifically, input parameters from the Air Resources Board/Department of Health Services (ARB/DHS) Health Risk Assessment (HRA) software and algorithms (CAPCOA Guidelines, March 1990, January 1991 and January 1992) and the South Coast Air Quality Management District Multi-Pathway Health Risk Assessment Input Parameters Guidance Document (SCAQMD, 1988) were considered. Also, the input data required by three alternative multimedia models (SMCM, Fugacity, and GEOTOX; see Cohen, 1986) were also evaluated. The following subsections discuss the rationale for selecting input parameters as well as general limitations in their use.

3.2.1 Physicochemical Parameters

The physicochemical properties of formaldehyde are needed for the determination of parameters such as partition coefficients and biotransfer factors, as well as for the analysis of intermedia transport parameters (e.g., mass transfer coefficients). Often the chemical properties that are needed are specific to the correlations that are used to evaluate factors such as partition coefficients and solubility.

A critical literature review was conducted and it was determined that the minimum necessary physicochemical factors for formaldehyde required for conducting a multimedia exposure assessment of formaldehyde as described by CAPCOA, 1992, and other models (i.e., SMCM, Fugacity, and GEOTOX) are as follows:

- Water Solubility;
- Vapor Pressure (as a function of temperature);
- Molar Volume (at the boiling point);
- Boiling Point; and
- Molecular Weight.

The definition of these parameters and the results of the literature review are presented in Section 4.0.

3.2.2 Partition Coefficients

Formaldehyde released to the environment is distributed to various environmental compartments as a result of transport processes. The net transport of formaldehyde from one compartment to another is limited by equilibrium constraints and quantified by partition coefficients. Thus, the partition coefficient, H_{ij} is generally defined as

$$H_{ij} = C_i/C_j \tag{3-1}$$

where C_i is the equilibrium concentration in compartment i and C_j is the equilibrium concentration in compartment j. The following types of partition coefficients for formaldehyde were considered in this study:

- Henry's Law Constant;
- Octanol-Water Partition Coefficient;
- Soil/Water-Organic Carbon Partition Coefficient; and
- Bioconcentration Factors.

Values for some partition coefficients for formaldehyde reported in the literature have been determined experimentally in simulated ecosystems and estimated for others. These partition coefficients are discussed individually in Section 4.2.

3.2.3 Intermedia Transport Parameters

In order to estimate the rate of formaldehyde transport across environmental phase boundaries, we must first be able to describe the transport mechanisms and consequently estimate the associated transport parameters as a function of the appropriate environmental conditions. Intermedia transport processes occur by either convective transport (not addressed in this report) or interfacial transport from one environmental compartment to another.

Interfacial mass transfer coefficients are required to predict the mass flux of formaldehyde across the various interfaces and thus, its accumulation in the environmental medium of interest. The relevant intermedia transfer parameters for formaldehyde are as follows:

- Diffusion Coefficients in Air and Water;
- Intermedia Mass Transfer Coefficients;
- Dry Deposition Velocity;
- Washout Ratios; and
- Biotransfer Factors.

These intermedia transport parameters are defined and discussed in Section 4.3. In addition, bioavailability and pharmacokinetics should also be considered in evaluating formaldehyde accumulation in biological receptors as briefly discussed in Section 4.2.6.

3.2.4 Degradation Processes

Reaction rates for individual abiotic and biotic degradation processes are often expressed as the first order or "pseudo" first order reaction rate. These first order reaction rate constants can be used to estimate overall environmental degradation half-lives. Degradation rates are determined for an individual chemical or biochemical transformation processes within specific media. Since degradation processes involve chemical changes as opposed to intermedia transport processes which involve the flux of the unchanged chemical through the environment, degradation half-lives for soil, water, and air do not account for intermedia transport of a chemical and are, therefore, not necessarily representative of a chemical's actual persistence within a particular environmental medium (Howard et al., 1991). Degradation processes considered significant to assessing the transformation of formaldehyde in the environment are as follows:

Hydroxyl (OH) radical reaction in air: The most significant degradation processes for formaldehyde in the atmosphere are its reaction with atmospheric OH radicals during daylight hours, with reported reaction rate constants (k_{OH}) ranging from 5.5×10^{-12} to 1.58×10^{-11} cm^3 $molec^{-1}s^{-1}$ at 298 K (Atkinson, 1989), and its photolysis at wavelengths between ~290 and 370 nm. Other potential degradation reactions include nighttime reaction with the gaseous nitrate (NO_3) radical and reaction of formaldehyde with ozone. However, only the reaction with OH radicals and photolysis are fast enough to be important atmospheric loss processes for formaldehyde (see Section 4.4.1). Reported atmospheric lifetimes of formaldehyde due to reaction with OH radicals range from 6.2 hours to 3 days (Finlayson-Pitts and Pitts, 1986; Watson et al., 1988; Atkinson, 1989; Winer and Busby, 1993).

Biodegradation in water and soil: Biodegradation is one of the most important environmental processes that cause the breakdown of environmental compounds. It is a significant loss mechanism in soil and aquatic systems and plays an important role in wastewater treatment. Bacteria are the most significant group of microorganisms involved in biodegradation. Soil, water and wastewater treatment systems provide the most important habitats for the biodegradation of pollutants. In all three habitats both aerobic and anaerobic conditions exist. The half-lives reported by Howard (1989) were 30 hours for aerobic conditions and 48 hours for anaerobic conditions.

Photolysis in air and water: Half-lives for direct photolysis are based on irradiation of a chemical in air or in solution at environmentally important wavelengths (>290 nm). Photolysis rates in air are assumed to equal those in solution unless they are measured directly in air, as in the case of formaldehyde. The typical frequencies of maximum absorption, λ_{max}, and whether or not absorption occurs at wavelengths >290 nm may indicate whether a chemical has the potential to undergo photolysis in the environment. Finlayson-Pitts and Pitts (1986) summarized the photochemistry of formaldehyde and reported that formaldehyde absorbs wavelengths up to approximately 370 nm; therefore, formaldehyde will photolyze in the troposphere, with a reported atmospheric lifetime due to photolysis of 4 hours (Winer and Busby, 1993) and a reported half-life due to photolysis of 6 hours (Howard, 1989).

Photooxidation reactions with alkylperoxy (RO_2) radicals, hydroxyl ($OH^{\cdot}$) radicals or singlet oxygen ($^1O_2$) in water: For some chemical classes, reactions with photooxidants in sunlit waters can be important. As with photooxidation in air by OH radicals, the range of half-lives is calculated from reaction rate constants and monitored concentrations of oxidants in relatively oligotrophic and eutrophic natural waters (Howard et al., 1991). This degradation process is not considered significant compared to evaporation.

Hydrolysis in water and soil: Hydrolysis only applies to a limited number of chemicals that have hydrolyzable functional groups such as esters, aliphatic halogens, amides, carbamates, and phosphate esters. Half-life of formaldehyde as a result of hydrolysis is not available.

In summary, the following abiotic and biotic degradation processes were evaluated for formaldehyde:

- Photooxidation Rate/Half-Life in Air;
- Biodegradation Rate/Half-Life in Water;
- Evaporation Rate/Half Life in Water;
- Biodegradation Rate/Half-Life in Soil; and
- Overall Reaction Half-Life in Environmental Media.

These processes are discussed further in Section 4.4.

4.0 PRESENTATION OF RESULTS

The following subsections define, discuss, and summarize the findings of the literature search for each of the parameters reviewed for this study. Equations defining input parameters and estimation techniques are presented, where appropriate.

Values found in the literature for the input parameters are summarized in Tables 4-1 through 4-12. Data in the tables are arranged by decreasing order of reliability. Measured values of known uncertainty are considered the most reliable and are thus listed first. Measured values reported without estimates of uncertainty are listed next, followed by calculated values reported with the corresponding prediction equations and uncertainty estimates. Calculated values reported without their associated estimation equations were reported last.

Values from references for which the derivation of the results could not be ascertained and multiple references to the same measured value are listed below the dotted line in the summary tables. Although the scientific confidence in these results is limited, they have been included only to reflect the range of values commonly reported in the current environmental literature. Values for input parameters have been converted to consistent SI units to facilitate comparison of results. The converted values have been reported with same number of significant figures as the values reported in the corresponding reference. Specific conversion equations are shown in the tables. It should be noted that commonly used forms of estimation equations often require input parameters in non-SI units. These cases have been identified in the text following presentation of the appropriate equations.

4.1 Physicochemical Parameters for Formaldehyde

Section 3.2.1 describes the general need for using physicochemical parameters in multipathway assessment. This section defines the specific physicochemical parameters that should be used for multimedia analysis of pollutants and discusses the results of the literature survey.

4.1.1 Solubility in Water

The water solubility (S) of a chemical is defined as the maximum amount of the chemical that will dissolve in pure water at a specific pressure, temperature and pH. The units of aqueous solubility are usually stated in terms of weight per weight (ppm, ppb, g/kg, etc.) or weight per volume (mg/L, μg/L, mol/L etc.). Less common units are mole fraction and molal concentration (moles per kg of solvent). In this report solubility is given in mol/L to be consistent with SI units. Values for the water solubility of formaldehyde reported in the literature are summarized in Table 4-1.

4.1.2 Vapor Pressure

The saturation vapor pressure, P_{VP}, is a measure of the volatility of a chemical in its pure state and is an important determinant of the rate of vaporization. Estimating P_{VP} requires information on the following properties: (1) critical temperature; (2) critical pressure; and (3) heat of vaporization, and/or the vapor pressure at some reference temperature. The units of P_{VP} can be stated in atm, torr, mm Hg, or Pa. In this report P_{VP} is given in kPa.

The vapor pressure of formaldehyde is dependent on temperature and it can be calculated from the following Antoine equation (Reid et al., 1987):

$$\log_{10} P_{vp} = A - (B/(C + T)) \qquad (4\text{-}1)$$

(where P_{vp} in Pa; T in °C)

Table 4-1. Solubility(1) of Formaldehyde in Water*

Solubility (mol/L)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
13.32(a)	4×10^5	mg/L	NR	NR	NR	U.S. EPA, 1986	Merck Index, 1976
18.32(b)	55	%	NR	NR	NR	Howard, 1989	Merck Index, 1983

NR = Not Reported.

(1) The water solubility of a chemical is defined as the maximum amount of the chemical that will dissolve in water at a specific temperature, pressure, and pH.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value: $\text{mg/L} \times \frac{1\ \text{mol formaldehyde}}{30.03\ \text{g formaldehyde}} \times \frac{1\ \text{g}}{1000\ \text{mg}} = \text{mol/L}$

(b) Conversion from reported value: $\%\left(\frac{\text{g}}{\text{g}}\right) \times \frac{1\ \text{mol formaldehyde}}{30.03\ \text{g formaldehyde}} \times \frac{1\ \text{g water}}{1\ \text{ml}} \times \frac{1000\ \text{ml}}{\text{L}} = \frac{\text{mol}}{\text{L}}$

Constants of the Antoine Equation for formaldehyde were empirically derived by Dykyj (1984) and reported by the U.S. EPA (1984):

A = 9.28176
B = 959.43
C = 243.392

Reported values for vapor pressure of formaldehyde over a range of temperatures are listed in Table 4-2.

4.1.3 Molar Volume

The molar volume (V_b) of formaldehyde, expressed in units of cm^3/mol, is the volume of a mole of liquid formaldehyde at the normal boiling temperature. The molar volume of an organic liquid is a useful parameter because it has been correlated with the normal boiling point and it is used in techniques for estimating diffusion coefficients in air and water.

The molar volume of formaldehyde is estimated to be 29.6 cm^3/mol as calculated by the Le Bas method (Reid et al., 1987) and a higher value of 37.41 cm^3/mol is calculated by the critical volume correlation, $V_b = 0.285\ V_c^{1.048}$, where V_c is the critical volume in units of cm^3/mol, as described by Reid et al. (1987).

4.1.4 Molecular Weight

The molecular weight is used for converting from mass to concentration and in various correlations of transport properties (e.g., diffusion coefficients).

The reported value of molecular weight of formaldehyde is 30.03 g/mol (IUPAC, 1987).

Table 4-2. Vapor Pressure of Formaldehyde as Cited in the Literature*

Vapor Pressure (kPa)	Reported Value	Reported Units	Reported Uncertainty	Temperature (°C)	Technique	References	Source Cited
$5.160\times10^{2(a)}$	3883	mm Hg	NR	25	NR	Howard, 1989	Daubert and Danner, 1985
$1.329^{(a)}$	1×10	mm Hg	NR	-88	NR	U.S. EPA, 1986; U.S. EPA, 1988; U.S. EPA, 1984	Verschueren, 1977 Kirk-Othmer, 1980
$1.329^{(a)}$	10	mm Hg	NR	-88	NR	Perry and Green, 1984	
$2.658^{(a)}$	20	mm Hg	NR	-79.6	NR	Perry and Green, 1984	
$5.316^{(a)}$	40	mm Hg	NR	-70.6	NR	Perry and Green, 1984	
$7.974^{(a)}$	60	mm Hg	NR	-65	NR	Perry and Green, 1984	
$1.329\times10^{(a)}$	100	mm Hg	NR	-57.3	NR	Perry and Green, 1984	
$2.658\times10^{(a)}$	200	mm Hg	NR	-46	NR	Perry and Green, 1984	
$5.316\times10^{(a)}$	400	mm Hg	NR	-33	NR	Perry and Green, 1984	
$1.010\times10^{(a)}$	760	mm Hg	NR	-19.5	NR	Perry and Green, 1984	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value = $\mathbf{mmHg} \times \dfrac{\mathbf{101000\ Pa}}{\mathbf{760\ mmHg}} \times \dfrac{\mathbf{1\ kPa}}{\mathbf{1000\ Pa}} = \mathbf{kPa}$

4.1.5 Boiling Point Temperature

The boiling point temperature, T_{BP}, is defined as the temperature at which the vapor pressure of a liquid is equal to the total pressure above the liquid. For pure compounds, the normal T_{BP} is defined as the T_{BP} at one standard atmosphere of pressure on the liquid. T_{BP} provides an indication of the physical state and volatility of a chemical. T_{BP} is also an important parameter used in the prediction of other physical properties.

Examples of boiling points reported in the literature for formaldehyde are listed in Table 4-3. Reported values range from -21 to -19 °C.

4.1.6 Melting Point Temperature

The melting point of a pure substance is defined as the temperature at which its crystals are in equilibrium with the liquid phase at atmospheric pressure. T_{mp} provides an indication of the physical state of a chemical, at the temperature of interest, and can also be used in the prediction of other physicochemical properties, such as vapor pressure and K_{ow}. At well defined temperatures, the melting point is identical to the freezing point.

Examples of melting points reported in the literature for formaldehyde are listed in Table 4-4. Reported values range from -118 to -92 °C.

4.1.7 Critical Temperature and Pressure

The critical temperature of a pure substance is defined as the temperature above which a gas cannot be liquefied (i.e., where there is no distinction between the gas and liquid phases). The critical pressure of a pure substance is defined as the minimum pressure required to liquify a gas at its critical temperature. T_c and P_c are parameters often used in estimation of physicochemical parameters such as boiling point, liquid density, vapor pressure, and heat of vaporization.

Table 4-3 Boiling Point Temperature (T_{BP}) of Formaldehyde*

Boiling Point (°C)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	References	Source Cited
-19	-19	°C	NR	101.3 kPa	NR	U.S. EPA, 1984	Kirk-Othmer, 1980
-19.4	-19.4	°C	NR	NR	NR	U.S. EPA, 1988	U.S. EPA, 1983
-19.5	-19.5	°C	NR	NR	NR	Howard, 1989	
-21/-19	-21/-19	°C	NR	NR	NR	Verschueren, 1992	
-21	-21	°C	NR	NR	NR	Perry and Green, 1984	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

Table 4-4 Melting Point of Formaldehyde*

Melting Point (°C)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	References	Source Cited
-118/-92	-92	°C	NR	NR	NR	Verschueren, 1992	
-92	-92	°C	NR	NR	NR	Perry and Green, 1984	
-92	-92	°C	NR	NR	NR	Howard, 1989	
-118	-118	°C	NR	NR	NR	Verschueren, 1977, 1992	
-118	-118	°C	NR	NR	NR	U.S. EPA, 1984	Kirk-Othmer, 1980

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

Critical temperatures reported in the literature for formaldehyde range from 137.2 to 141.2° C (U.S. EPA, 1984) with the more commonly-accepted value of 135.15° C reported by Reid et al. (1977). Critical pressures reported in the literature for formaldehyde range from 6.637 to 6.784 M Pa (U.S. EPA, 1984) with a value of 6.565 M Pa reported by Reid et al. (1977).

4.1.8 Liquid Density

The liquid density (ρ) of a substance is the ratio of its mass to its volume, with units of g/cm^3. The density varies with molecular weight, molecular interactions, and temperature. Density can be used to estimate the molar volume, with units of l/mol, and is a useful parameter in correlations used to estimate diffusion coefficients in air and water.

Examples of densities reported in the literature for formaldehyde are listed in Table 4-5.

4.2 Partition Coefficients for Formaldehyde

Section 3.2.2 provides general equations for the various partition coefficients. The definition and findings of the literature search for the individual partition coefficients are presented in the following subsections.

4.2.1 Henry's Law Constant

The Henry's Law constant is a particularly important parameter for evaluating chemical partitioning between air and water and is required as an input parameter in most multimedia models. In most environmental situations, the aqueous concentrations of dissolved formaldehyde is small, and thus, Henry's Law applies. The Henry's Law constant of a chemical (H_i) is defined as:

$$H_i = P_i/C_i \qquad (4\text{-}2)$$

Table 4-5 Liquid Density of Formaldehyde*

Liquid Density (g/cm^3)	Reported Value	Reported Units	Reported Uncertainty	Temperature (°C)	Technique	References	Source Cited
0.815	0.815	g/ml	NR	-19.5	Estimated	Reid et al. 1977	
0.8153	0.8153	g/ml	NR	-20	NR	U.S. EPA, 1984	Kirk-Othmer, 1980
0.9151	0.9191	g/ml	NR	-80	NR	U.S. EPA, 1984	Kirk-Othmer, 1980

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

where P_i is the partial pressure of the compound (e.g., Pa), at the system temperature, and C_i is the concentration (e.g., mol/m^3) of the chemical in the aqueous phase in equilibrium with the air phase.

The Henry's Law constant may be determined experimentally or estimated, although it is preferable to use an experimentally determined value. H_i can be estimated by using the saturation vapor pressure and solubility data in the following equation (Reid et al., 1987; Lyman et al., 1990):

$$H_i = P_{vp}/S \tag{4-3}$$

where S is the solubility (e.g., mol/m^3) and P_{vp} is the saturation vapor pressure of the compound (e.g., Pa). This expression is valid only for solutes for which the activity coefficient is constant at concentrations ranging from the solubility limit and below.

Betterton and Hoffmann (1988) utilized Nash's fluorescence method to measure the Henry's Law constant of formaldehyde. The reported value is $(2.97 \pm 0.69) \times 10^3$ M atm^{-1} ($3.401 \times 10^{-2} \pm 0.146$ Pa·m^3/mol). Zhou and Mopper (1990) measured the Henry's Law constant of formaldehyde at temperatures ranging from 10 to 45 °C with both freshwater and seawater. The reported values for freshwater range from 1.020×10^{-2} to 1.247×10^{-1} Pa·m^3/mol [$(0.81$ to $9.9) \times 10^3$ M atm^{-1}]. The reported values for seawater range from 7.372×10^{-3} to 1.148×10^{-1} Pa·m^3/mol [$(1.9$ to $13.7) \times 10^3$ M atm^{-1}]. Based on these measurements, Zhou and Mopper (1990) reported that the Henry's Law constant of formaldehyde is highly dependent on temperature as described by the following correlations:

$$\text{For freshwater:} \quad \log H_i = -6.0 + 2{,}844/T \quad , \quad \text{M/atm} \tag{4-4}$$

$$\text{For seawater:} \quad \log H_i = -6.7 + 3{,}069/T \quad , \quad \text{M/atm} \tag{4-5}$$

where T is the temperature in K. They also concluded that salinity did not have an apparent effect on the Henry's Law constant for formaldehyde. Reported values of Henry's Law constant for formaldehyde are listed in Table 4-6. The values range from 7.372×10^{-3} to 1.247×10^{-1} Pa·m^3/mol.

Table 4-6. Henry's Law Constant of Formaldehyde*

Henry's Law Constant (Pa·m^3/mol)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
3.401×10^{-2} (a)	2.97×10^{3} (c)	M/atm	$\pm 6.9 \times 10^{2}$ M/atm	298	Experimental	Betterton and Hoffmann, 1988	
2.722×10^{-2} (a)	3.71×10^{3} (c)	M/atm	$\pm 4.0 \times 10^{2}$ M/atm	298	Experimental/ Seawater	Zhou and Mopper, 1990	
7.372×10^{-3} (a)	1.37×10^{4} (c)	M/atm	$\pm 1.0 \times 10^{3}$ M/atm	283	Experimental/ Seawater	Zhou and Mopper, 1990	
1.279×10^{-2} (a)	7.9×10^{3} (c)	M/atm	$\pm 4.0 \times 10^{2}$ M/atm	290	Experimental/ Seawater	Zhou and Mopper, 1990	
4.040×10^{-2} (a)	2.5×10^{3} (c)	M/atm	$\pm 2.0 \times 10^{2}$ M/atm	303	Experimental/ Seawater	Zhou and Mopper, 1990	
5.316×10^{-2} (a)	1.9×10^{3} (c)	M/atm	$\pm 1.0 \times 10^{2}$ M/atm	308	Experimental/ Seawater	Zhou and Mopper, 1990	
1.148×10^{-1} (a)	8.8×10^{2} (c)	M/atm	$\pm 6.0 \times 10^{1}$ M/atm	318	Experimental/ Seawater	Zhou and Mopper, 1990	
1.020×10^{-2} (a)	9.9×10^{3} (c)	M/atm	$\pm 1.1 \times 10^{3}$ M/atm	283	Experimental/ Freshwater	Zhou and Mopper, 1990	
2.971×10^{-2} (a)	3.4×10^{3} (c)	M/atm	$\pm 3.0 \times 10^{2}$ M/atm	298	Experimental/ Freshwater	Zhou and Mopper, 1990	
5.050×10^{-2} (a)	2.0×10^{3} (c)	M/atm	$\pm 1.0 \times 10^{2}$ M/atm	303	Experimental/ Freshwater	Zhou and Mopper, 1990	

Table 4-6. Henry's Law Constant of Formaldehyde*
(Continued)

Henry's Law Constant ($Pa \cdot m^3/mol$)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
6.733×10^{-2} (a)	1.5×10^{3} (c)	M/atm	$\pm 1.0 \times 10^{2}$ M/atm	308	Experimental/ Freshwater	Zhou and Mopper, 1990	
9.182×10^{-2} (a)	1.1×10^{3} (c)	M/atm	±0.0 M/atm	313	Experimental/ Freshwater	Zhou and Mopper, 1990	
1.247×10^{-1} (a)	8.1×10^{2} (c)	M/atm	$\pm 4.0 \times 10^{1}$ M/atm	318	Experimental/ Freshwater	Zhou and Mopper, 1990	
1.188×10^{-2} (a)	8.5×10^{3}	M/atm	NR	293	Calculated◆	Betterton and Hoffmann, 1988	Blair and Ledbury, 1925
3.303×10^{-2} (b)	3.27×10^{-7}	$atm \cdot m^3/mol$	NR	293.2	NR	Howard, 1989	Dong and Dasgupta, 1986
9.969×10^{-2} (b)	9.87×10^{-7}	$atm \cdot m^3/mol$	NR	NR	NR	U.S EPA, 1986	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value: $\frac{1}{M\ atm^{-1}} \times \frac{101000\ Pa}{atm} \times \frac{m^3}{1000\ L} = \frac{Pa \cdot m^3}{mol}$

(b) Conversion from reported value: $\frac{atm \cdot m^3}{mol} \times \frac{101000\ Pa}{1\ atm} = \frac{Pa \cdot m^3}{mol}$

(c) The reported Henry's Law constant is defined by the authors as: $H_i = C_{aq}/P_i$ where C_{aq} is the concentration of formaldehyde in the aqueous phase and P_i is the partial pressure of formaldehyde in the gas phase.

◆ Calculated using vapor pressure data of Blair and Ledbury (1925).

4.2.2 Octanol-Water Partition Coefficient

The octanol-water partition coefficient, K_{ow}, is defined as the equilibrium ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system by the following equation:

$$K_{ow} = C_o/C_w \tag{4-6}$$

where C_o is the concentration in octanol phase and C_w is the concentration in aqueous phase. When the concentrations of C_o and C_w are in the same units (e.g., mol/cm^3), values for K_{ow} are unitless. K_{ow} is an important parameter used in the assessment of environmental fate and transport for organic chemicals because the octanol phase is a surrogate for the lipid phase or organic carbon content of environmental compartments. K_{ow} for hydrophobic compounds such as formaldehyde is an important physico-chemical parameter that is used to correlate sorption onto soil and sediments and bioaccumulation. Although K_{ow} is expected to vary with temperature and pH, its temperature dependence is rarely reported. Reported K_{ow} values for formaldehyde are listed in Table 4-7.

Lyman et al. (1990) recommends the following correlation for estimating log K_{ow}:

$$\log K_{ow} = \frac{\log S - 4.184}{-0.922} \tag{4-7}$$

where S is the aqueous solubility in mg/L. The above correlation was derived from testing 90 compounds of mixed classes. Using S values of 4×10^5 mg/L (U.S. EPA, 1986) and 5.5×10^5 (Howard, 1989), the resulting log K_{ow} values calculated from the correlation are -1.538 and -1.688, respectively. The low K_{ow} value for formaldehyde is outside the range of K_{ow} for which the correlations were derived; thus, the values of K_{ow} for formaldehyde reported in Table 4-7 should be regarded as highly approximate, but indicative of the high aqueous solubility of formaldehyde and its low degree of sorption by soils and sediments and low level of bioaccumulation in the environment.

Table 4-7. Octanol-Water Partition Coefficient (K_{ow})[1] for Formaldehyde*

log K_{ow} (dimensionless)	Reported Uncertainty	Temperature (°C)	Technique	Reference	Source Cited
0.35	NR	NR	Calculated◆	Howard, 1989	U.S. EPA, 1987
-0.87	NR	NR	Calculated†	Lyman et al., 1990	Hansch and Leo, 1979
-1.538	NR	NR	Calculated‡	Lyman et al., 1990	Kenaga and Goring, 1980
-1.688	NR	NR	Calculated▲	Lyman et al., 1990	Kenaga and Goring, 1980
0	NR	NR	NR	U.S. EPA, 1986	

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

[1] Octanol-Water partition coefficient (K_{ow}) is defined as the ratio of the concentration of a chemical in the octanol phase to its concentration in the aqueous phase in a two-phase octanol/water system. Values for K_{ow} are thus dimensionless.

◆ Graphical Exposure Modeling System (GEMS), U.S. EPA (1987).

† Calculated using Leo's Fragment Constant Method (Hansch and Leo, 1979)

‡ Calculated from $\log K_{ow} = \frac{\log S - 4.184}{-0.922}$ (Lyman et al., 1990); $S = 4 \times 10^5$ mg/L (U.S. EPA, 1986)

▲ Calculated from $\log K_{ow} = \frac{\log S - 4.184}{-0.922}$ (Lyman et al., 1990); $S = 5.5 \times 10^5$ mg/L (Howard, 1989)

4.2.3 Soil/Water-Organic Carbon Coefficient

The organic carbon partition coefficient (K_{oc}) is a measure of the tendency for organics to adsorb onto the soil (or sediment) and is defined as the ratio of the amount (mass) of a chemical adsorbed per unit mass of organic carbon in the soil or sediment to the concentration of the chemical in the soil (or sediment) solution at equilibrium,

$$K_{oc} = \frac{\text{(mg chemical adsorbed/kg organic carbon)}}{\text{(mg chemical dissolved/liter of solution)}} \qquad (4\text{-}8)$$

The available methods for estimating K_{oc} involve empirical relationships with other properties of a chemical such as solubility, octanol-water partition coefficient, or bioconcentration factor for aquatic life. Lyman et al. (1990) recommends the following estimation correlations for estimating K_{oc} (Karickhoff et al., 1979) for mostly aromatic or polynuclear aromatics:

$$\log K_{oc} = -0.54 \log S + 0.44 \qquad (4\text{-}9)$$

where S is the aqueous solubility in mole fraction. Using S values of 0.24 (U.S. EPA, 1986) and 0.33 (Howard, 1989) mole fraction, the calculated log K_{oc} values are 0.77 and 0.70, respectively.

Another correlation proposed by Kenaga and Goring (1980) for a wide variety of chemicals is given below.

$$\log K_{oc} = 0.544 \log K_{ow} + 1.377 \qquad (4\text{-}10)$$

Using log K_{ow} of 0.35 (U.S. EPA, 1987), the calculated log K_{oc} value is 1.57. The log K_{oc} values for formaldehyde obtained from literature correlations are given in Table 4-8.

Table 4-8. Soil/Organic Carbon Coefficient (K_{oc}) for Formaldehyde*

log K_{oc} (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	References	Sources Cited
0.77	NR	NR	Calculated[◆]	Lyman et al., 1990	Karickhoff et al., 1979
0.70	NR	NR	Calculated[†]	Lyman et al., 1990	Karickhoff et al., 1979
1.57	NR	NR	Calculated[‡]	Lyman et al., 1990	Kenaga and Goring, 1980

NR = Not Reported.

[*] Listed order is by decreasing confidence in reported values (see Section 3.0).

[◆] Calculated from $\log K_{oc} = -0.54 \log S + 0.44$, $S = 0.24$ mole fraction (U.S. EPA, 1986)

[†] Calculated from $\log K_{oc} = -0.54 \log S + 0.44$, $S = 0.33$ mole fraction (Howard, 1989)

[‡] Calculated from $\log K_{oc} = 0.544 \log K_{ow} + 1.377$, $\log K_{ow} = 0.35$ (U.S. EPA, 1987)

4.2.4 Bioconcentration Factors and Bioaccumulation

4.2.4.1 Bioconcentration and Bioaccumulation for Aquatic Organisms

The traditional measure of a chemical's potential to accumulate in an organism is the bioconcentration factor (BCF), which is defined as a chemical's wet-weight concentration in an organism or tissue divided by its concentration in the medium through which exposure occurs by direct contact (e.g., water for aquatic organisms, or air for terrestrial organisms). The concept of BCF addresses partitioning of a chemical into an organism by non-food routes. Specifically, BCF is defined as:

$$\text{BCF} = \frac{\text{(equilibrium concentration of chemical in receptor)}}{\begin{array}{c}\text{(concentration of chemical in the medium}\\ \text{through which exposure occurs by direct contact)}\end{array}} \qquad (4\text{-}11)$$

It is convenient to use the same units for both the numerator and denominator which results in a dimensionless BCF. The term BCF is used with the assumption that uptake across external membranes from the media with which the receptor is in direct contact is the chief pathway for chemical uptake by the organism. For compounds with low log K_{ow} values (less than 3), such as formaldehyde, transfer across membranes is controlled by aqueous diffusion processes and limited by lipid solubility resistance (Thomann, 1989). It is important to note that BCF values are compound-specific, medium-specific, and species-specific, and experimental data should be used whenever possible. In the absence of measured data, various correlations may be utilized to estimate BCF values. BCF is frequently correlated with the K_{ow} or solubility (S) through the following correlations (Lyman et al., 1990):

$$\log(\text{BCF}) = A + B \log(S) \qquad (4\text{-}12)$$

or

$$\log(\text{BCF}) = C + D \log(K_{ow}) \qquad (4\text{-}13)$$

where A, B, C, and D are empirical constants. For example, Kenaga and Goring (1980) proposed the following general correlation for fish BCF

$$\log BCF = 2.791 - 0.564 \log S \qquad (4\text{-}14)$$

where S is the aqueous solubility in ppm. Using S values of 4×10^5 (U.S. EPA, 1986) and 5.5×10^5 ppm (Howard, 1989), the BCF is calculated from Eq. 4-14 to be 0.43 and 0.36, respectively. Veith et al. (1980) proposed a fish BCF correlation of the form of Eq. 4-13 with C = -0.23 and D = 0.76 for a wide range of chemical classes. Another general correlation was suggested for estimating log BCF for chemicals of eight mixed classes by Kenaga and Goring (1980):

$$\log BCF = 1.119 \log K_{oc} - 1.579 \qquad (4\text{-}15)$$

Using log K_{oc} values of 0.77, 0.70, and 1.57 (Table 4-8), BCF values are calculated from Eq. 4-15 to be 0.19, 0.16, and 1.51, respectively.

Table 4-9 presents formaldehyde BCF values calculated from these correlations. Since formaldehyde is water soluble (13.32 to 18.32 mol/L) and has a low K_{ow} value (-1.688 to 0.35), it is not expected to bioconcentrate to any significant degree in organisms. The calculated BCF values (0.16 to 1.51) in Table 4-9 seem to support this assertion.

In contrast to BCF, the bioaccumulation factor (BAF) for biota is a BCF which accounts for partitioning of a chemical into an organism by both food and non-food routes. BAFs should account for uptake, excretion, intestine to blood assimilation efficiency, and growth dilution (dilution of the concentration of a chemical as a result of an increase in the lipid weight of an organism). Compounds with low log K_{ow} values (less than 5), such as formaldehyde, are expected to have relatively low uptake and high excretion rates, which will prevent food chain buildup. In these cases, the BAF will equal the lipid normalized BCF, which will be comparable in value to K_{ow} (Thomann, 1989).

Table 4-9. Bioconcentration Factor (BCF)(a) for Formaldehyde in Aquatic Organisms[*]

BCF(a) (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	References	Source Cited
0.19	NR	NR	Calculated[◆]	Lyman et al., 1990	Kenaga and Goring, 1980
0.16	NR	NR	Calculated[†]	Lyman et al., 1990	Kenaga and Goring, 1980
1.51	NR	NR	Calculated[‡]	Lyman et al., 1990	Kenaga and Goring, 1980
0.43	NR	NR	Calculated[◊]	Lyman et al., 1990	Kenaga and Goring, 1980
0.36	NR	NR	Calculated[▲]	Lyman et al., 1990	Kenaga and Goring, 1980

NR = Not Reported.

[*] Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Bioconcentration factor is defined as a chemical's wet-weight concentration in an organism or tissue divided by its concentration in the medium through which exposure occurs by direct contact.

[◆] Calculated from $\log BCF = 1.119 \log K_{oc} - 1.579$; $\log K_{oc} = 0.77$ (Lyman et al, 1990)

[†] Calculated from $\log BCF = 1.119 \log K_{oc} - 1.579$; $\log K_{oc} = 0.70$ (Lyman et al, 1990)

[‡] Calculated from $\log BCF = 1.119 \log K_{oc} - 1.579$; $\log K_{oc} = 1.57$ (Lyman et al, 1990)

[◊] Calculated from $\log BCF = 2.791 - 0.564 \log S$; $S = 4 \times 10^5$ ppm (U.S. EPA, 1987)

[▲] Calculated from $\log BCF = 2.791 - 0.564 \log S$; $S = 5.5 \times 10^5$ ppm (Howard, 1989)

4.2.4.2 Bioconcentration of Formaldehyde in Vegetation

The concept of BCFs has also been applied to accumulation of formaldehyde in vegetation. Plant accumulation of formaldehyde can involve several different mechanisms, including: (1) root adsorption, (2) root uptake followed by transpirational translocation of formaldehyde from roots to shoots, (3) volatility of formaldehyde from soils and hydroponic solutions followed by foliar adsorption, (4) contamination of plant foliage by formaldehyde laden soil, and (5) atmospheric deposition of formaldehyde vapor. Trapp et al. (1990) suggested that root uptake and translocation of chemicals with low K_{ow}, such as formaldehyde, in the transpiration stream is a significant plant contamination mechanism. Above ground portions of vegetation are thought to be principally impacted by vapor phase transfers (Bacci et al., 1990; McCrady et al., 1990). Only a negligible fraction of formaldehyde is expected to sorb to particles in the atmosphere (Bidleman, 1988) as its primary states are gaseous and dissolved forms. Thus, it can be assumed that contamination of plants by direct deposition of particles onto which formaldehyde is adsorbed is a negligible exposure pathway. However, volatility of formaldehyde from soil is an important transport mechanism that can result in significant quantities of airborne formaldehyde being adsorbed by plant shoots (McCrady et al., 1990).

Root Bioconcentration Factor

The concentration of formaldehyde in vegetation due to root uptake (C_{vr}) can be estimated from (Topp et al., 1989)

$$C_{vr} = C_s \, B_{vd} \tag{4-16}$$

where C_s is the concentration of formaldehyde in soil (e.g., ng/kg soil) and B_{vd} is a formaldehyde-specific bioconcentration factor determined on a wet-weight basis (i.e., fresh plant).

$$B_{vw} = \frac{\text{(concentration of formadehyde in plant)}}{\text{(concentration of formaldehyde in soil)}} \tag{4-17}$$

where the concentration in the plant, C_{vr}, is based on wet mass (e.g., ng chemical/kg fresh plant). Travis and Arms (1988) proposed the following correlation for the above-ground portion of plants bioconcentration factor, B_{vw}:

$$\log B_{vw} = 1.588 - 0.5781 \log K_{ow} \tag{4-18}$$

Using $\log K_{ow} = 0.35$ (U.S. EPA, 1987), $\log B_{vd}$ is calculated to be 1.386.

For root crops, Briggs et al. (1982) proposed the following definition for the root bioconcentration factors based on plant wet mass:

$$B_{vw} = \frac{C_{veg}}{C_{soil}} \tag{4-19}$$

in which C_{veg} is the chemical concentration in the wet plant (i.e., ng chemical/kg soil). Thus, B_{vw} is related to B_{vd}, the root bioconcentration on a dry basis, by

$$B_{vw} = B_{vd} \times f_{dw} \tag{4-20}$$

where f_{dw} is the fraction of dry plant matter in the wet plant. Briggs et al. (1982) proposed the following correlation for B_{vw} applicable to hydrophobic organic compounds:

$$B_{vw} = \frac{0.82 + 0.028\, K_{ow}^{0.77}}{K_d} \tag{4-21}$$

in which $K_d = K_{oc} \cdot \chi$ where χ represents the mass fraction of the soil natural organic carbon. It is emphasized that formaldehyde was not included in the development of the above correlation and thus Eq. 4-21 only provides an estimate of B_{vw} for formaldehyde given values of K_{oc} and χ for the specific soil under consideration.

Air-to-Leaf Bioconcentration Factor

The vapor-phase bioconcentration factor for various airborne contaminants, including formaldehyde, from the atmosphere to vegetation can be estimated following the approach of Bacci et al. (1990). These authors suggested that the air-to-leaf route should be regarded as the main mode of contamination for higher plant leaves, mosses and lichens for non-polar, volatile chemicals. The dimensionless air-to-leaf bioconcentration factor can be expressed as

$$B_{vaw} = \frac{C_{va}\rho_p}{C_a F_v} \qquad (4\text{-}22)$$

where C_{va} is the chemical concentration in the plant on a fresh (i.e., wet) plant mass basis (e.g., μg/kg fresh plant), C_a is the concentration of a chemical in the air (e.g., $\mu g/m^3$), F_v represents the fraction of the chemical in the vapor phase, and ρ_p is the fresh plant density (e.g., kg/m^3). If formaldehyde is assumed to exist in air entirely as a vapor, then F_v equals 1. B_{va} represents the air-to-leaf bioconcentration factor on a dry plant mass basis. It has been suggested that B_{vaw} can be correlated with the chemical's water-air and octanol-water partition coefficient and the leaf properties (Bacci et al., 1990).

No measured or estimated values of bioconcentration factors were found for root uptake air-to-leaf, and deposition routes for formaldehyde. Although B_{va} has not been measured for formaldehyde, there are air-to-leaf correlations that have been proposed in the literature and these can be used to estimate B_{vaw}.

$$B_{vaw} = 0.19 + 0.7/H_i' + 0.05\,K_{ow}/H_i' \qquad \text{(Paterson et al., 1991)} \qquad (4\text{-}23)$$

$$B_{vaw} = 0.022\,K_{ow}\,/\,H_i' \qquad \text{(Bacci et al., 1990)} \qquad (4\text{-}24)$$

where B_{vaw} is the air-to-leaf bioconcentration based on wet mass, K_{ow} is octanol/water partition coefficient as previously defined, and H_i' is the dimensionless Henry's Law constant defined as $H_i' = H_i/RT$ (T is the temperature in K and R is the gas constant). It is noted that B_{va} is related to B_{vaw}.

$$B_{vaw} = B_{va} \times f_{dw} \tag{4-25}$$

Using, for example, K_{ow} value of 2.24 ($\log K_{ow} = 0.35$) and H_i' value of 1.38×10^{-5} ($H_i = 3.4 \times 10^{-2}$ Pa·m³/mol at 298 K and $R = 8.291$ Pa·m³/mol·K), a range of 3,581 to 58,997 was obtained for B_{vaw} from Eqs. 4-23 and 4-24. These values indicate that, for the portion of formaldehyde present in the vapor phase, air-to-leaf transfer can be a major pathway for bioconcentration in vegetation. However, it must be noted that formaldehyde was not used as a study chemical in the development of the above correlations. Thus, the above estimates of B_{vaw} values for formaldehyde should only be regarded as indicative of the order of magnitude of B_{vaw} for formaldehyde.

4.2.4.3 Biotransfer Factors in Milk, Beef, and Eggs

The biotransfer factor (B_{TF}) concept addresses chemical accumulation in the receptor through food uptake. It has been suggested in the literature that the biotransfer factor (B_{TF}) may be more useful than BCFs in addressing exposure via food uptake since chemical exposure to feedstock animals may occur through both food and water pathways (Travis and Arms, 1988).

At steady state, the pathway specific biotransfer factor, B_{TFi}, for pathway i, can be expressed as

$$B_{TFi} = C_j / L_i C_{in} \tag{4-26}$$

and the overall biotransfer factor can be expressed as (Cohen, 1989)

$$B_{TF} = C_j \Big/ \left(\sum_{i=1}^{N} L_i\, C_{in} \right) = \left[\sum_{k=1}^{N} \left(Ex_k H_{kj} \right) + K_j V_j \right]^{-1} \tag{4-27}$$

V_j is the volume of the receptor and C_j and C_{in} are the concentrations of the contaminant in the receptor (or target organ) and the media associated with the receptor route. L_i represents the intake rate and Ex_k is the outflow stream associated with the particular pathway. H_{kj} is the partition coefficient between receptor j and elimination stream k. The overall biochemical transformation of a given contaminant via first order reaction kinetics is given by the rate constant K_j. For example, one can define a B_{TF} for the concentration of a contaminant in cow's milk where $\Sigma L_i C_{in}$ is the total contaminant intake during grazing, water drinking, and inhalation. In general, the B_{TF} is not constant since V_j, the volume of the receptor, varies with time, and the partition coefficient, H_{kj}, and the reaction rate constant, K_j, are probably a function of the activity of the receptor. Thus, one is led to conclude that B_{TF} and B_{TFi} are likely to be time variant parameters. Despite this concern, the concept of biotransfer factors is rooted in environmental exposure assessment.

As previously noted, feedstock animals are exposed to formaldehyde through ingestion of contaminated feed crops and drinking water, as well as direct inhalation. Human exposure can subsequently result from ingestion of contaminated animal products. Assessing the magnitude of human exposure to a contaminant such as formaldehyde from ingestion of animal products depends largely on the ability to predict the extent of its bioaccumulation in aquatic and terrestrial food chains. Biotransfer factors for organics in beef and milk have been correlated with the equilibrium octanol/water partition coefficient (Travis and Arms, 1988); nevertheless, the concept of B_{TF} should be regarded as a transport parameter rather than simply a physicochemical property (Cohen, 1989). It is important to note that B_{TF} correlations determined by Travis and Arms (1988) are subject to uncertainties in the input data from which B_{TF} values were derived. For instance, McKone and Ryan (1989) noted that the uncertainty in the Travis and Arms (1988) correlations for 95% confidence interval for both the feed to milk biotransfer factor, B_m, and the feed to meat biotransfer factor, B_b, is approximately 2 orders of magnitude.

The biotransfer factors for milk (B_m) and meat (beef; B_b) have been defined by Travis and Arms (1988) as follows:

$$B_m = \frac{(\text{concentration in milk (mg/kg)})}{(\text{daily intake of organic (mg/d)})} \qquad (4\text{-}28)$$

$$B_b = \frac{\text{(concentration in meat (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \tag{4-29}$$

Measured concentration of organics in milk or meat fat are converted on a whole milk or fresh meat basis, assuming meat contains 25% fat and whole milk contains 3.68% fat.

Travis and Arms (1988) derived a log K_{ow} vs. log B_m correlation based on data for 28 organic chemicals in milk (formaldehyde was not included) which yielded the following equation:

$$\log B_m = -8.056 + 0.992 \log K_{ow} \tag{4-30}$$

In the above equation, B_m was based on data for ingestion only and did not include contaminant uptake via inhalation or dermal absorption. Using Eq. 4-30 and a log (K_{ow}) value of 0.35, one obtains log (B_m) = -7.709, which implies very little transfer of formaldehyde to milk due to ingestion. The validity of applying the regression equation of Travis and Arms (1988) may be questionable since formaldehyde was not one of the 28 chemicals used for the regression analysis and its log K_{ow} value of 0.35 is below the range of log K_{ow} from which the correlation was derived. One is cautioned that in applying K_{ow} correlations derived from regression analysis, it is important to verify that the value of K_{ow} is within the range of applicability of the correlation. Also, formaldehyde is likely to be metabolized in the receptor (U.S. EPA, 1982) and thus, more detailed pharmacokinetic studies may be required to precisely determine the level of formaldehyde accumulated in bioreceptors (e.g., cattle).

Feed-to-beef transfer factors (B_b) can be estimated using the following correlation:

$$\log B_b = -7.6 + \log K_{ow} \quad n = 36, r = 0.81 \quad \text{(Travis and Arms, 1988)} \tag{4-31}$$

Using the value of log K_{ow} of 0.35 for formaldehyde, log B_b equals -7.25. The concerns and limitations mentioned above for B_m are also applicable for B_b. Kenaga (1980) reported the following correlations for bioconcentration factors in beef:

$$\log B_b = -0.495 (\log S) - 1.476 \qquad n = 23, r = 0.817 \qquad (4\text{-}32)$$

$$\log B_b = 0.5 (\log K_{ow}) - 3.457 \qquad n = 23, r = 0.790 \qquad (4\text{-}33)$$

$$\log B_b = 0.701 (\log K_{oc}) - 3.825 \qquad n = 23, r = 0.732 \qquad (4\text{-}34)$$

where B_b, S (in ppm), K_{ow}, and K_{oc} are defined previously.

Experimentally determined or calculated biotransfer factor values for feed to egg were not found in the literature. At present, the assumption stated in the CAPCOA guidelines that the transfer for eggs is the same as that of meat appears to be a reasonable assumption in the absence of data to the contrary.

The measurement-specific definition of BCF and B_{TF} above must be distinguished from other terms used to describe increasing chemical concentration in an organism via the food chain. Such terms include biomagnification and bioaccumulation. Biomagnification refers to a further increase in concentration attributable to uptake from food. Bioaccumulation is a broader term that indicates uptake from all sources and thus includes effects of both biomagnification and bioconcentration (Clark et al., 1988). These terms are associated with increasing concentrations along a food chain, which could result in higher concentrations factors in top-order consumers.

The overall bioaccumulation factor K_b can be shown to be related to the biotransfer factors by the following relation (Cohen, 1989)

$$K_b = C_j / C_i = B_{TF} \left(\sum_{N}^{i=1} L_i C_{in}\right) / C_i \qquad (4\text{-}35)$$

where C_j is the concentration of the contaminant in the receptor, C_i is the concentration in the media most directly associated with the exposure route, B_{TF} is the biotransfer factor, L_i

is the intake rate via food intake, water drinking, and inhalation, and C_{in} is the concentration in either the food intake (e.g., pasture grass or feed), drinking water, or inhaled air.

Bioaccumulation factors are a function of the receptor type, the chemical type and temperature. The bioaccumulation factor is equivalent to the bioconcentration factor when the exposure takes place primarily via contact with a single medium (e.g., inhalation of a volatile chemical such as formaldehyde). The above approach assumes implicitly that K_b is time invariant. For biota, K_b (or BCF) is often correlated with K_{ow} (Kenaga and Goring, 1980; Mackay, 1982; Veith and Rosian, 1983).

4.2.5 Bioavailability and Relation to Toxicology

The bioavailability of a chemical is defined as the fraction of a compound in a matrix that is released from that matrix, absorbed by an organism, and hence, is available to elicit a biological effect. The release and uptake of a chemical constitute facets of bioavailability, although its biological effect is often used as a measure of bioavailability. Since risk is considered to be a function of both exposure and toxicity, bioavailability is an important consideration in determining potential risk from airborne contaminants (SCAQMD, 1988). Bioavailability is often considered when assessing dose from inhalation and ingestion pathways. For ingestion routes, CAPCOA (1991) allows for using compound-specific bioavailability factors where evidence warrants but does not provide any values for formaldehyde. The CAPCOA (1991) guidelines assume 100% absorption for inhaled compounds. Since formaldehyde is likely to be present primarily in the gaseous phase, the assumption of 100% bioavailability is considered reasonable.

With the exception of occupational exposure, the majority of the population is exposed to formaldehyde through inhalation and to a lesser extent, through ingestion. It has been reported that when formaldehyde is ingested it is converted to harmless metabolites (Scheuplein, 1985). The reason is that formaldehyde is a product of normal cellular metabolism and there are detoxification pathways developed within the body. Systemic absorption of formaldehyde, however, produces dermal sensitization in approximately 4%

of persons patch-tested, which makes formaldehyde the tenth most common cause of dermatitis (Williams and Burson, 1985).

In vivo experiments conducted by Ma and Harris (1988) seem to indicate that formaldehyde reacts with the first site of contact and may not penetrate into cells to interact with DNA. Genetic damage in test systems in vivo is also evident (IARC, 1987). Observed genotoxic effects include DNA-protein crosslinks, sister chromatid exchanges, gene mutations, single strand breaks, and chromosomal aberrations (IARC, 1987). In animal tests, formaldehyde produces squamous cell carcinomas in the nasal passages of male and female rats and male mice, but no significant teratogenic or reproductive effects even when the dose was high enough to cause death in the parent due to cytotoxicity (CARB, 1991). One possible explanation is that due to the short half-life of formaldehyde, its available residence time is insufficient to cross the placenta and damage the embryo. Based on these tests, it is generally accepted that formaldehyde is mutagenic and potentially carcinogenic in animals.

The actual mechanism by which formaldehyde exerts its toxicity in the body is still unknown. There seems to be a threshold in the human body because formaldehyde is important in normal mammalian metabolism. Catalyzed by formaldehyde dehydrogenase and glutathione, formaldehyde is metabolized to formic acid which is then oxidized to carbon dioxide in detoxifying pathways (CARB, 1991). It has also been reported that clearance from the plasma of animals and humans is rapid (CARB, 1991).

Formaldehyde appears to exert its toxicity when detoxification pathways become saturated (when the organism is exposed to high concentrations of formaldehyde) (Casanova-Schmitz et al., 1984; Casanova and Heck, 1987; Casanova et al., 1989). When detoxification pathways are not saturated, genotoxic damages are recognized and repaired by DNA repair enzymes; however, when saturation occurs, excess formaldehyde interacts with DNA and other cellular molecules and the site of damage is close to the site of entry.

4.3 Intermedia Transport Parameters of Formaldehyde

The following subsections define and review the pertinent literature information for the specific intermedia transport factors considered in this study.

4.3.1 Diffusion Coefficients in Air and Water

Molecular diffusion is the net transport of a molecule within a single phase (e.g., liquid or gas) that results from intermolecular collisions rather than turbulence or bulk transport. Diffusion can result from pressure, temperature, and concentration gradients but under environmental conditions, only diffusion due to concentration gradient is considered. The diffusive flux due to concentration gradients is defined by Fick's Law as:

$$J_A = -D_{AB}\, dC_A/dx \tag{4-36}$$

in which J_A is the diffusion flux for compound A (e.g., mg/m^2·s), dC_A/dx is the concentration gradient along the x direction and D_{AB} is the diffusion coefficient of A in medium B (e.g., units of cm^2/s). For example, for air/water exchange processes, molecular diffusion dominates chemical transport near the air/water interphase (in both the air and water phases). In general, the mass flux, (e.g., ng/m^2·s), N, across an interface between two phases is expressed by an equation of the form

$$N = K\Delta C \tag{4-37}$$

in which ΔC is an appropriate concentration driving force and K is an appropriate mass transfer coefficient. Correlations of mass transfer coefficients include a dependence on the molecular diffusivity which can be estimated as described below.

Table 4-10 presents values for diffusion coefficients of formaldehyde in air and water. No experimental values were found in the literature; however, diffusion coefficients in air can be calculated by using the Fuller et al. (1966) correlation

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2} \;,\quad \mathrm{cm}^2/\mathrm{s}, \quad \text{where } M_r = \frac{M_A + M_B}{M_A\, M_B} \qquad (4\text{-}38)$$

in which the subscripts B and A refer to the solute gas (e.g., formaldehyde) and air, respectively, T is the temperature (K), M is the molecular weight, P is the pressure (atm), and V_A and V_B are the molar volumes (cm^3/mol) for air and the solute gas, respectively. The calculated diffusion coefficient, D_{BA}, is 1.65×10^{-1} cm^2/s.

Diffusion coefficients in air can also be calculated using the Wilke and Lee (1955) method.

$$D_{BA} = \frac{B' T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2\, \Omega} \;,\quad \mathrm{cm}^2/\mathrm{s} \qquad (4\text{-}39)$$

where $$B' = 0.00217 - 0.00050 \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}$$

$$M_r = (M_A + M_B)/M_A M_B$$

σ_{AB} = characteristic length of molecule A interacting with B, Å

M = molecular weight

T = temperature (K)

P = pressure (atm)

Ω = collision integral (see Lyman et al., 1990)

Table 4-10. Diffusion Coefficient of Formaldehyde*

Media	Diffusion Coefficient (cm^2/s)	Reported Absolute Average Error	Temperature (K)	Technique	References	Source Cited
Air	1.65×10^{-1}	7.6%	298	Calculated[a]	Lyman et al., 1990	Fuller et al., 1966
Air	1.87×10^{-1}	4.3%	298	Calculated[b]	Lyman et al., 1990	Wilke and Lee, 1955
Water	2.22×10^{-5}	8.8%	298	Calculated[c]	Lyman et al., 1990	Wilke and Chang, 1955
Water	2.06×10^{-5}	5.8%	298	Calculated[d]	Lyman et al., 1990	Hayduk and Laudie, 1974
Water	1.84×10^{-5}	NR	298	Calculated[e]	Reid et al., 1987	Hayduk et al., 1982

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a)
$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P\,(V_A^{1/3} + V_B^{1/3})^2}\ ,\quad cm^2/s\ ,\quad \text{where } M_r = \frac{M_A + M_B}{M_A\, M_B}$$

where $T = 298$ K
$M_r = 0.0678$
$M_A = 28.97$ g/mol
$M_B = 30.03$ g/mol
$P = 1$ atm
$V_A = 20.1\ cm^3/mol$
$V_B = 29.6\ cm^3/mol$

(b)
$$D_{BA} = \frac{B' T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2\, \Omega}\ ,\quad cm^2/s$$

where

$B' = 2.04\times10^{-3}$
$T = 298$ K
$M_r = 0.0678$
$P = 1$ atm
$\sigma_{AB} = 3.681$ Å
$\Omega = 1.081$

Table 4-10. Diffusion Coefficient of Formaldehyde
(Continued)

(c)

$$D_{BW} = \frac{7.4 \times 10^{-8} (\varnothing_W M_W)^{1/2}\, T}{\eta_W\, V_B^{0.6}} \quad , \quad \mathrm{cm^2/s}$$

where
$\varnothing_W = 2.6$
$M_W = 18$ g/mol
$T = 298$ K
$\eta_W = 0.8904$ cP
$V_B = 29.6$ cm^3/mol

(d)

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14}\, V_B^{0.589}}$$

where
$\eta_W = 0.8904$ cP
$V'_B = 29.6$ cm^3/mol

(e)

$$D_{BW} = 1.25 \times 10^{-8} \left(V_B^{-0.19} - 0.292\right) T^{1.52} \eta_W^{\epsilon^*} \; , \quad \mathrm{cm^2/s}$$

where $\varepsilon^* = -0.796$

$\eta_W = 0.8904$ cP
$T = 298$ K
$V_B = 29.6$ cm^3/mol

Correlations commonly used to calculate diffusion coefficients in water are given below.

Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \times 10^{-8}(\phi_W\, M_W)^{1/2}\, T}{\eta_W\, V_B^{0.6}} \quad , \quad cm^2/s \qquad (4\text{-}40)$$

where M_W is molecular weight of water (g/mol), T is temperature (K), η_W is viscosity of water (cP), V_B is molar volume of solute B at its normal boiling temperature (cm^3/mol), and ϕ_W is the solvent association factor which equals 2.6 for water (Wilke and Chang, 1955). Using Eq. 4-40 to calculate the diffusion coefficient of formaldehyde in water, a value of 2.22×10^{-5} cm^2/s was obtained.

Hayduk and Laudie (1974) proposed an alternative correlation for D_{BW} given as,

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14}\, V_B^{0.589}} \quad , \quad cm^2/s \qquad (4\text{-}41)$$

where η_w is viscosity of water (cP), V_B is molar volume (cm^3/mol). Based on Eq. 4-41, D_{BW} is calculated to be 2.06×10^{-5} cm^2/s.

A modified form of Eq. 4-41 was later proposed by Hayduk et al. (1982)

$$D_{BW} = 1.25 \times 10^{-8} \left(V_B^{-0.19} - 0.292\right) T^{1.52} \eta_W^{\epsilon^*} \quad , \quad cm^2/s \qquad (4\text{-}42)$$

where V_B is molar volume (cm^3/mol), η_W is viscosity of water (cP), and $\epsilon^* = (9.58/V_B)-1.12$. The resulting D_{BW} based on Eq. 4-42 is 1.84×10^{-5} cm^2/s.

4.3.2 Gaseous Mass Transfer Across the Air-Water Interface

The traditional approach to calculating the flux of a compound between air and water phases is to use the two-film theory in which it is assumed that the concentrations immediately on either side of the interface are in equilibrium as can be expressed by a Henry's Law constant (Lewis and Whitman, 1924). The flux, N, can be expressed as:

$$N = K_G\,(C_g - H'C_l) = K_L\,(C_l - C_g/H') \qquad (4\text{-}43)$$

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H' is a unitless Henry Law's constant, and C_g and C_l are concentrations in gas and liquid phases, respectively. The overall mass transfer coefficients for the gas and liquid phase can be defined as:

$$1/K_G = 1/k_g + H'/k_l \qquad (4\text{-}44)$$

$$1/K_L = 1/k_l + 1/H'k_g \qquad (4\text{-}45)$$

where k_g is a gas-phase mass transfer exchange coefficient (cm/s) and k_l is a liquid-phase mass transfer coefficient. The important parameters that are needed in order to predict N are H' (see Section 4.2.1) and the mass transfer coefficients k_g and k_l. The mass coefficients depend on the prevailing turbulence level (as determined by water currents or wind), on temperature, on properties of the solute such as diffusivity, or molecular size (Mackay and Yeun, 1983), and on the depth of the water body (Cohen, 1986). Thus, one must ensure that k_g and k_l are determined for the appropriate environmental conditions. Predictive equations, appropriate for screening-level analysis, that can be used to estimate k_g and k_l are given in Sections 4.3.2.1 and 4.3.2.2. It must be noted that Eqs. 4-43 through 4-45 are for physical mass transfer and for the case of formaldehyde a detailed treatment that includes the effect of chemical reactions (in the aqueous phase) may have to be considered.

4.3.2.1 Air/Water - Air Side - Mass Transfer Coefficient (k_g) for Formaldehyde

Numerous theories and empirical equations have been proposed to predict k_g. The theoretical expressions for k_g as proposed by Brutsaert (1975) are particularly useful for predicting k_g. For a rough surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2} \left[\epsilon_D^{+} \left(C_D^{-1/2} - 5 \right) + 7.3 \, Re_o^{0.25} \, Sc_a^{1/2} \right]^{-1}, \quad Re_o > 2 \tag{4-46}$$

and for a smooth surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2} \left[\epsilon_D^{+} \left(C_D^{-1/2} - 13.5 \right) + 13.6 \, Sc_a^{2/3} \right]^{-1}, \quad Re_o < 0.13 \tag{4-47}$$

in which the Schmidt number, Sc_a, is given by the ratio ν_a/D_a, where D_a is molecular diffusivity in air (Section 4.3.1), U_{10} is the wind speed at a reference height (usually 10 meters), C_D is the wind drag (or stress) coefficient, ϵ_D^{+} is the ratio of the eddy momentum diffusivity (ϵ_m) to the eddy mass diffusivity (ϵ_D), often approximated to be near unity, and Re_o is the roughness Reynolds number. Eqs. 4-46 and 4-47 are strictly applicable to a neutral atmospheric condition. However, as suggested by Brutsaert (1975), Eqs. 4-46 and 4-47 are probably still satisfactory even under very unstable, but apparently not under stable conditions. For non-neutral conditions, the mass flux equations Eq. 4-43 must be used with caution since the bulk gas phase concentration as used in Eq. 4-43 may lie outside the dynamic sublayer (Brutsaert, 1975). Under such conditions, a detailed air quality model which considers the concentration profile at the air-side must be considered. Thus, one should regard the use of the estimation methods for k_g as given in this section as suitable for neutral conditions and for screening-level analysis for non-neutral conditions. The prediction of k_g for non-neutral conditions can be accomplished using the approach as presented by Brutsaert (1975). However, it should be noted that within the context of screening-level analysis, the application of Eqs. 4-46 and 4-47 is sufficient especially for sparingly soluble hydrophobic organic compounds.

The use of Eqs. 4-46 and 4-47 requires the wind drag coefficient velocity as input. The wind-drag coefficient, C_D, is defined as (Wu, 1980)

$$C_D = \left(\frac{U_W^*}{U_{10}}\right)^2 \left(\frac{\rho_w}{\rho_a}\right) = \left(\frac{U_a^*}{U_{10}}\right)^2 \tag{4-48}$$

in which U_W^* is the surface shear velocity given by:

$$U_W^* = \sqrt{\frac{\tau_s}{\rho_w}} \tag{4-49}$$

where τ_s is the shear stress imparted by the wind on the water surface, ρ_w is the water density, ρ_a is the air density, and U_{10} is the wind speed measured at a reference height (usually 10m) above the water surface. It is noted that the water-side friction velocity U_w^* and U_a^* are related through the simple relation $\rho_a(U_a^*)^2 = \rho_w(U_w^*)^2$ which arises from the condition of stress equality at the air/water interface. Given wind speed profile data, one can estimate U^*_a using the following equation:

$$U_a^* = U_{10}\, k \left[\ln\left(\frac{z_{10}}{z_o}\right) - \psi_M\left(\frac{z}{L}\right) + \psi_M\left(\frac{z_o}{L}\right) \right]^{-1} \tag{4-50}$$

where k is the von Karman constant ($k = 0.4$), U_{10} is the velocity at the reference height, z_{10}, ψ_M is a stability function, and L is the Obukhov stability parameter (Holtslag and Van

Ulden, 1983; and reference therein). It is noted that for neutral conditions the function ψ_M is set to zero. The roughness Reynolds number, Re_o, is defined by:

$$Re_o = U_a^* z_o/\nu_a \tag{4-51}$$

where z_o is the effective surface roughness height and ν_a is the kinematic viscosity of air. The effective surface roughness height can be estimated for smooth water surfaces as (Brutsaert, 1975)

$$z_o \approx 0.135(\nu_a/U^*_a) \quad , \quad \text{cm} \tag{4-52}$$

and for a rough surface,

$$z_o = a(U^*_a)^b \quad , \quad \text{cm} \tag{4-53}$$

in which U^*_a is the air-side friction velocity (cm/s) and ν_a is the kinematic viscosity (cm/s^2). The parameters a and b are given by $a = 1.69\times10^{-2}$ and $b = -1$ for $U^*_a \leq 6.89$ cm/s, and $a = 1.65\times10^{-4}$, $b = 1.4$ for $U^*_a > 6.89$ cm/s (Jirka and Brutsaert, 1984). An alternative correlation for z_o was proposed by Wu (1980) for a large water fetch in which z_o was expressed by:

$$z_o = 0.0144(U^*_a)^2/g \quad , \quad (g=981, \text{ cm/s}^2) \tag{4-54}$$

For a large water fetch, the wind-stress coefficient near neutral conditions can be estimated from (Cohen, 1983)

$$C_D = 8.5\times10^{-4} \quad , \quad U_{10} < 5 \text{ m/s} \tag{4-55}$$

$$C_D = [0.85 + 0.11\,(U_{10} - 5)]\times10^{-3} \quad , \quad 5 \text{ m/s} \leq U_{10} \leq 20 \text{ m/s} \tag{4-56}$$

$$C_D = 2.5\times10^{-3} \quad , \quad U_{10} > 20 \text{ m/s} \tag{4-57}$$

or (Wu, 1980)

$$C_D = (0.8 + 0.065U_{10}) \times 10^{-3} \quad , \qquad U_{10} \geq 1 \text{ m/s} \tag{4-58}$$

As an illustration of the above approach, the gas-side mass transfer coefficient as obtained from Eqs. 4-46, 4-47 (with linear interpolation in the region $0.13 \leq Re_o \leq 2$), and Eqs. 4-53 and 4-58 for z_o and C_D, respectively, for formaldehyde at 20°C is given in Figure 4.1.

Other alternate expressions for k_g under neutral (or near-neutral) conditions have been proposed in the literature. For example, Lyman (1990) recommends the correlation of Southworth (1979) for k_g

$$k_g = 1137.5 \left(V_{wind} + V_{curr}\right) \sqrt{\frac{18}{MW}} \quad , \qquad \text{cm/hr} \tag{4-59}$$

where V_{wind} and V_{curr} are the velocities of the wind and water current, respectively (m/s), and MW is the molecular weight of the contaminant of interest. As an example, using V_{wind} = 3 m/s and V_{curr} = 1 m/s, k_g for formaldehyde is estimated as 3523 cm/hr. It is important to note that the atmospheric stability condition for which Eq. 4-59 applies was not reported. Moreover, the theoretical basis of the Southworth (1979) equation is questionable because of the linear additivity of the wind and air currents in Eq. 4-59. The hydrodynamic effects of the wind relative to the water current on the roughness and velocity of the water surface are likely to be very different, as supported by later researchers (cited by Cohen, 1986) who have found that the effect of wind velocity and current velocity on k_g vary by different powers. Finally, a convenient correlation for k_g, determined based on laboratory measurements in a small wind-wave tank (fetch < 3m) under near neutral conditions, was proposed by Mackay and Yeun (1983).

$$\frac{k_g}{U_a^*} = 46.2 \times 10^{-3} \, Sc_a^{-0.67} \tag{4-60}$$

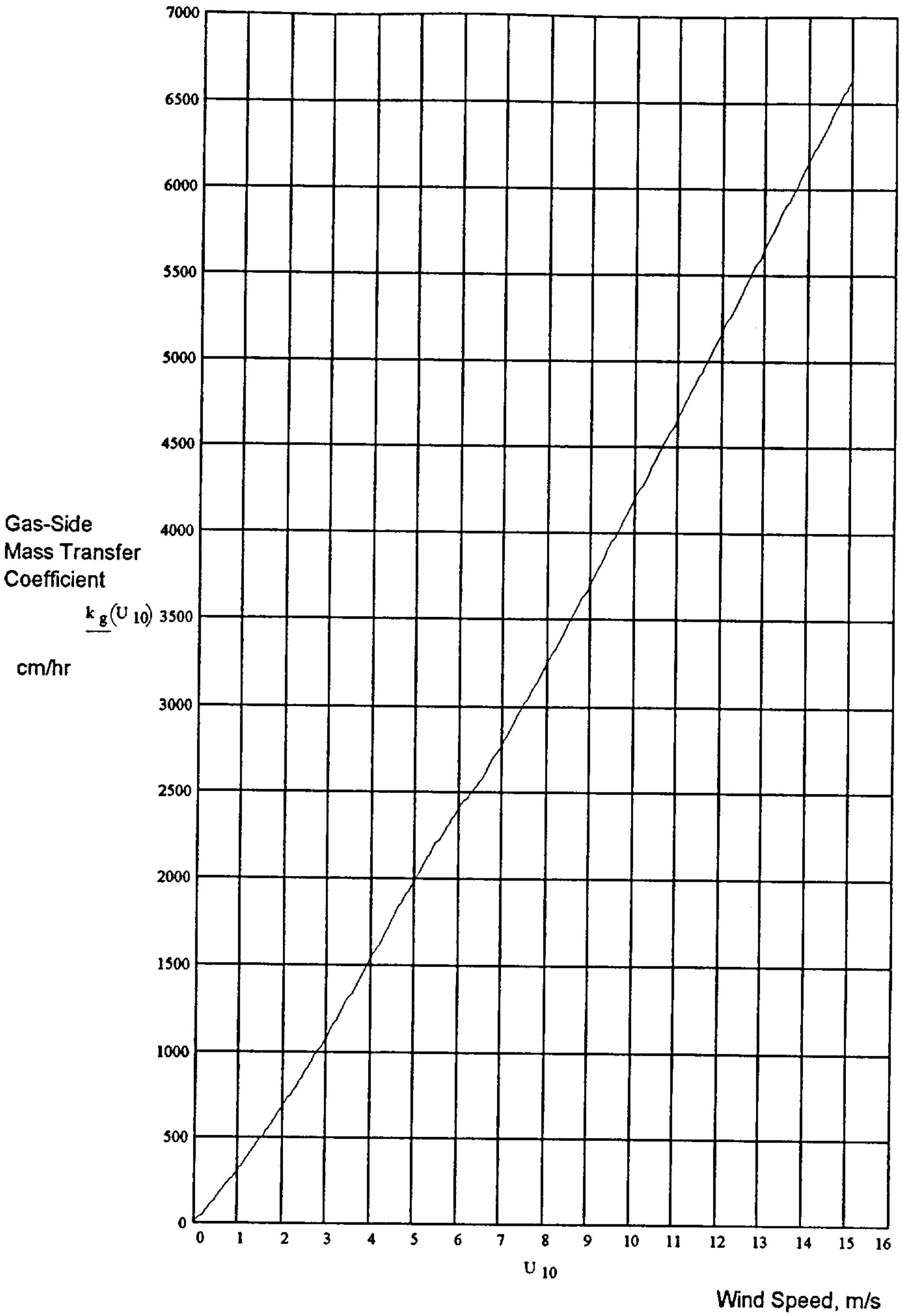

Figure 4.1 Gas-Side Mass Transfer Coefficient for Formaldehyde at 20°C for Water/Air Mass Transfer at Large Fetch. (Based on the Correlation of Brustsaert, 1975).

Eq. 4-60 results in k_g values which are about 20%-40% higher than predicted by Eqs. 4-46 and 4-47. The higher prediction by the Mackay and Yeun (1983) correlation may be, in part, due to the difference in surface roughness condition in their short fetch wind-wave tank, for a given U_a^*, relative to the condition that would exist at long fetch.

4.3.2.2 Air/Water - Liquid Side - Mass Transfer Coefficient (k_l) for Formaldehyde

The water-side mass transfer coefficient, k_l, for large water bodies (i.e., reservoirs, lakes, oceans) can be estimated using the theoretical correlation of Cohen and Ryan (1985), which was found to be in excellent agreement with available data for a water-side friction velocity in the range of 0.5-6 cm/s,

$$k_l/U_w^* = a\, Sc_w^{-n} \qquad (4\text{-}61)$$

in which Sc_w is the Schmidt number given by the ratio ν_w/D_w where ν_w is the water kinematic viscosity and D_w is the chemical molecular mass diffusivity in water. The constants a and n are weak functions of the dimensionless water surface velocity U_s^+ ($U_s^+ = U_s/U_w^*$, in which U_s is the wind-induced surface water velocity), given by:

$$a = a_0 - a_1 \ln U_s^+ \qquad (4\text{-}62)$$

$$n = n_0 - n_1 \ln U_s^+ \qquad (4\text{-}63)$$

where

$$a_0 = 0.09691;\ a_1 = 0.01053; \qquad (4\text{-}64)$$

$$n_0 = 0.5778;\ n_1 = 0.01771$$

For a long fetch (say ≥ 30m), the surface velocity is equal to about 3.5% of the wind speed (i.e., $U_s = 0.035\ U_{10}$), while for short fetch (say less than about 10m), $U_s \approx 0.020\ U_{10}$ (Wu, 1975; Plate and Friedrich, 1984). Eq. 4-61 was found to be in excellent agreement with laboratory data from wind-wave facilities with an average error of about 16 percent. As an illustration, the dependence of k_l on wind speed for formaldehyde at 20°C is shown in Figure 4.2 where Eqs. 4-49 and 4-58 were used to determine U_w^*.

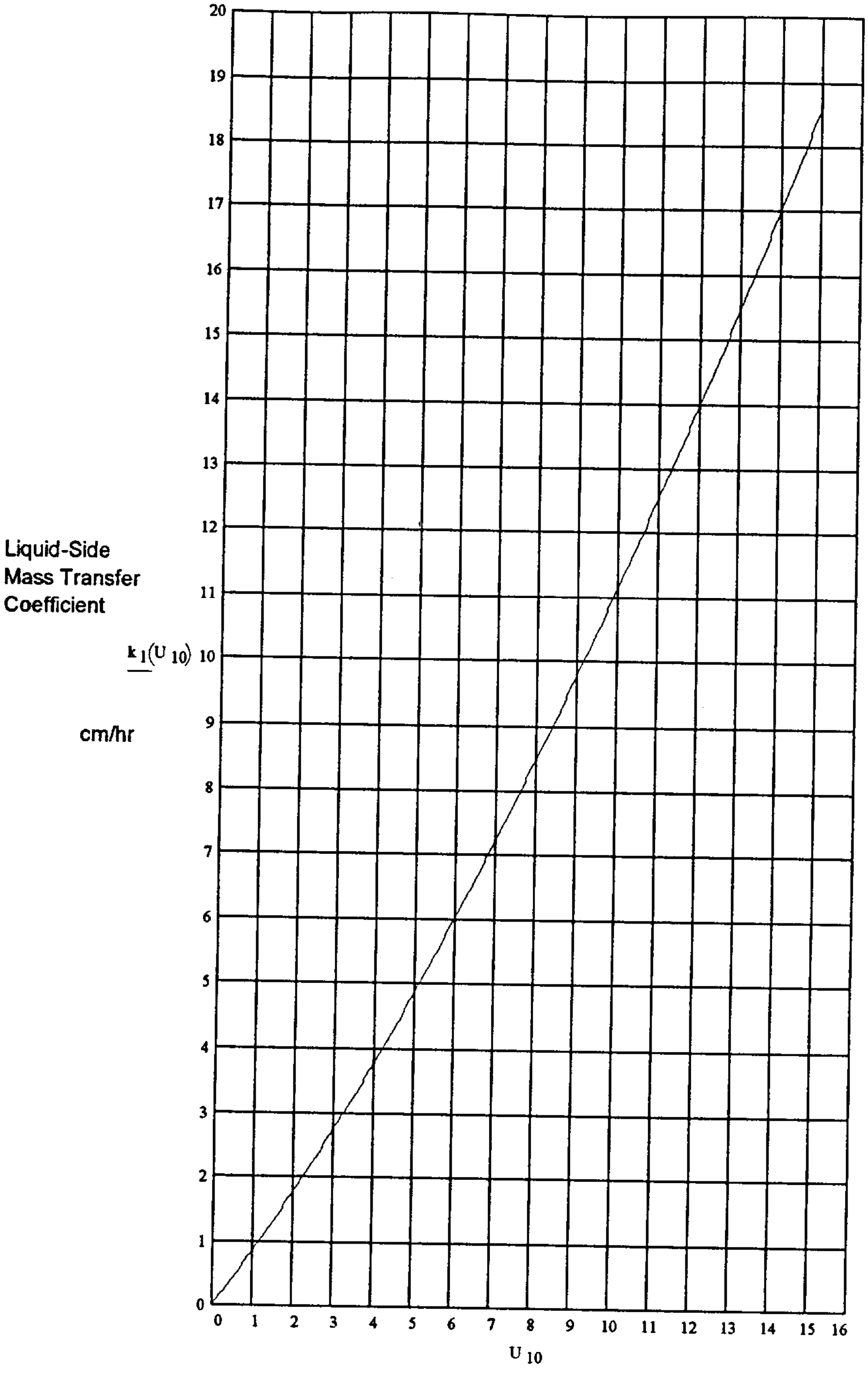

Figure 4.2 Liquid-Side Mass Transfer Coefficient for Formaldehyde for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlation of Cohen and Ryan, 1985).

The prediction of k_l in flowing water bodies (e.g., rivers) requires consideration of the river current and the river depth (Cohen, 1986). There are numerous studies on the reaeration coefficient in flowing streams (O'Connor, 1983), and the water-side mass transfer coefficient k_l can be estimated from the reaeration coefficient, k_v (e.g., hr^{-1}), by using the following relation:

$$k_l = \left(\frac{D}{D_o}\right)^{1/2} h\, k_v \tag{4-65}$$

in which h is the depth of the water body (e.g., m), D is the mass diffusivity of the compound of interest (e.g., formaldehyde), D_o is the mass diffusivity of oxygen in water at 20°C, and h is the river depth (Cohen, 1986). Lyman et al. (1982) recommended the following empirical correlations, which are based on field data, for predicting k_v:

$$k_v = 1.08\,(1 + 0.17\,F^2)\,(V_{curr}\,S)^{0.375},\ \ hr^{-1} \tag{4-66}$$

$$k_v = 0.00102\,V_{curr}^{2.695}\,h^{-3.085}\,S^{-0.823},\ \ hr^{-1} \tag{4-67}$$

$$k_v = 638\,V_{curr}\,S,\ hr^{-1} \tag{4-68}$$

in which S is the river bed slope (m drop/ m run), F is the Froude number ($F = V_{curr}/gh$), and h is the river depth (m). The use of an average value of k_v determined from the above three equations was recommended by Lyman et al. (1982). Other relations for k_v that are suitable when bed slope information is not available were recommended by Lyman et al. (1990), Shen (1982), and Shen et al. (1993). For example, the empirical correlation which was recommended by Shen (1982) and Shen et al. (1993) can be written as

$$k_v = 22.05\,(1.024)^{T-20}\,U_s^{0.67}\,h^{-1.85} \quad , \quad hr^{-1} \tag{4-69}$$

in which T is the temperature (°C), U_s is the water current (m/s), and h is the water depth (m). As an illustration, the liquid-side mass transfer coefficient, k_l, obtained from Eqs. 4-65 and 4-69 for formaldehyde at 20°C is shown in Figure 4.3.

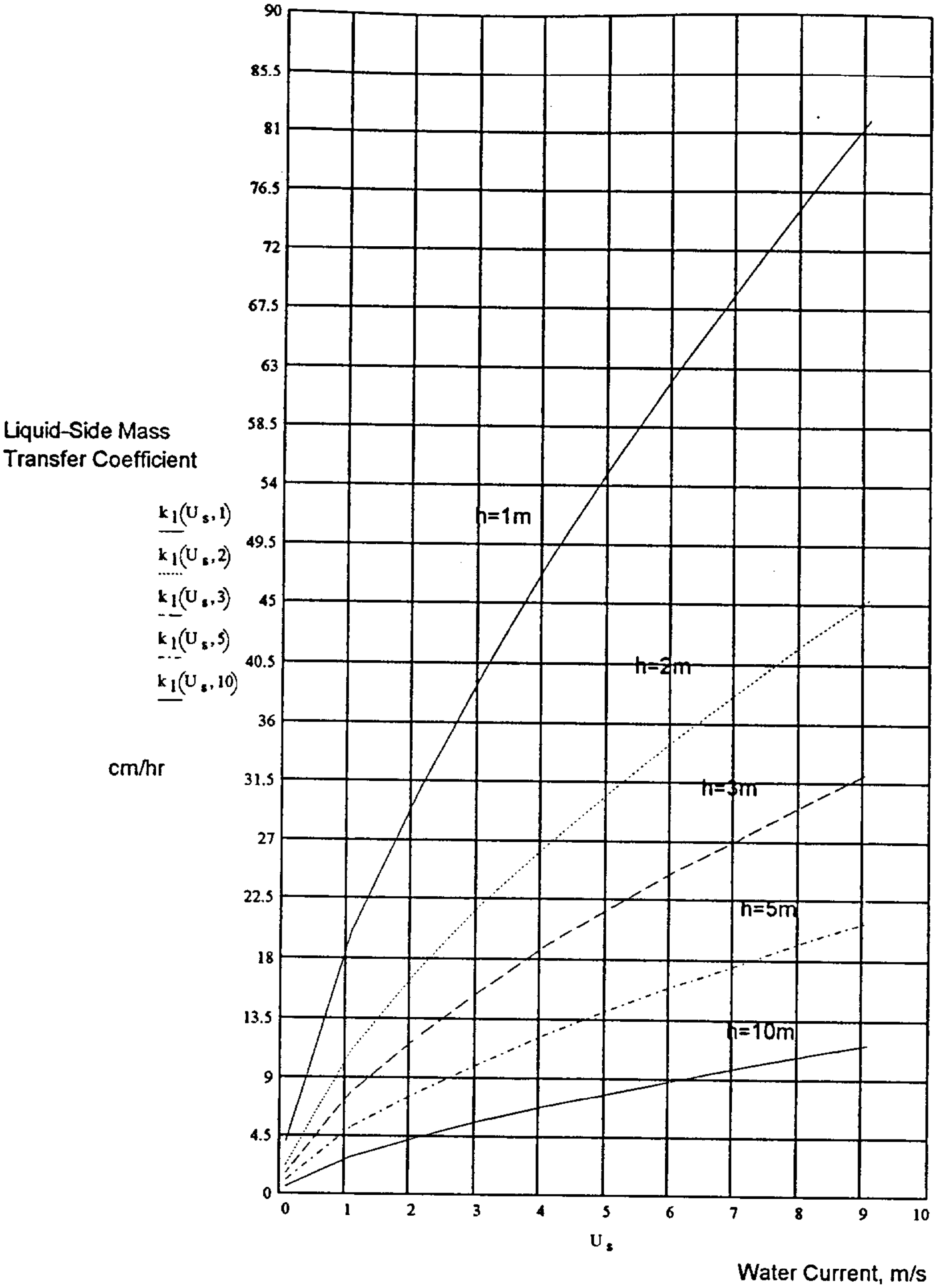

Figure 4.3 Liquid-Side Mass Transfer Coefficient for Formaldehyde at 20°C for a Flowing River Based on Eqs. 4-65 and 4-69 (h=river depth).

Example:

In order to estimate k_l and k_g for formaldehyde for a neutral atmospheric condition, proceed along the following steps:

1) Select temperature, wind speed, and the correlation appropriate for the water body of interest.
2) Determine the value of k_l from a suitable correlation selected from Section 4.2.2 once a wind speed and type of water body are selected.
3) Determine k_g from either Eq. 4-46 or 4-47 depending on the resulting value for Re_o. Note that a value for U^*_a is required and this can be estimated from Eqs. 4-48, 4-55 to 4-57, and 4-58 or from wind speed profile data.

As an illustration, consider the volatilization of formaldehyde from a large water body (i.e., large reservoir or lake) at 20°C. The air and water kinematic viscosities at 20°C are calculated as 0.15 cm^2/s and 0.01 cm^2/s, respectively (Reid et al., 1987). The diffusion coefficients of formaldehyde in air and water were estimated as 0.16 cm^2/s and 1.8×10^{-5} cm^2/s, respectively, from Eqs. 4-38 and 4-41. The gas-side mass transfer coefficient k_g at 20°C, obtained from Eqs. 4-46 and 4-47 (with linear interpolation of k_g in the region $0.13 \leq Re_o \leq 2$), and Eqs. 4-53 and 4-58 for z_o and C_D, respectively, is given, as a function of wind speed, in Figure 4.1. The liquid-side mass transfer coefficient, k_l, obtained from Eq. 4-60, at 20°C, is given in Figure 4.2. As an example, at $U_{10} = 5$ m/s, $k_g = 1987$ cm/hr (Figure 4.1) and $k_l = 4.7$ cm/hr (Figure 4.2).

4.3.3 Dry Deposition

Dry deposition may be broadly defined as the transport of particulate and gaseous contaminants from the atmosphere onto surfaces in the absence of precipitation (Davidson and Wu, 1989). Dry deposition is affected by a multiplicity of factors that often interact in complex ways. The most important factors are the characteristics of the atmosphere (e.g., wind speed and atmospheric stability), the nature of the surface, and properties of the depositing species. Transport of gases through the atmosphere depends on their eddy and Brownian diffusivities. Solubility and chemical reactivity may be dominant factors affecting capture of gases by surfaces.

The dry deposition flux of a gaseous chemical can be expressed by

$$N_A = V_d C_a \tag{4-70}$$

where N_A is the flux in mass per unit area, per unit time, C_a is the mass of the pollutant in the particle phase per unit volume of air, and V_d is the overall chemical dry deposition velocity. The CAPCOA model currently uses deposition velocities of 2 cm s^{-1} and 5 cm s^{-1} for controlled and uncontrolled sources, respectively.

Dry deposition of formaldehyde is expected to be of minor importance as an atmospheric loss process compared to the most rapid photolysis and reaction with hydroxyl (OH) radical pathways (Finlayson-Pitts and Pitts, 1986; Winer and Busby, 1993). Since no experimentally determined values for dry deposition velocity of formaldehyde were found in the literature, the estimation method used was the approach adapted by Cohen et al. (1990). According to this method, the dry deposition velocity is proportional to $D^{2/3}$ (where D is the molecular diffusivity in air). Thus, if the dry deposition velocity for a given chemical is known, the value for formaldehyde can be calculated using the equation

$$V_{d_B} = V_{d_A} \left(\frac{D_B}{D_A} \right)^{2/3} \tag{4-71}$$

where V_{dB} is the dry deposition velocity of formaldehyde, V_{dA} is dry deposition velocity of a reference chemical for which deposition velocity is known (was measured), D_B is a diffusion coefficient of formaldehyde, and D_A is a diffusion coefficient of the reference chemical.

Example: *Calculation of dry deposition velocity for formaldehyde: [The deposition velocity for SO_2 and CO_2 was given by Sehmel (1980; 1984)].*

Calculation of V_d based on CO_2

CO_2: $V_{d_{CO_2}} = 0.3$ cm/s

$D_{CO_2} = 0.155\ \text{cm}^2/\text{s}$ (Fuller et al., 1966)

(1) - Formaldehyde

(2) - CO_2

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-72}$$

$$V_{d_1} = 0.3\left(\frac{0.165}{0.155}\right)^{2/3} \tag{4-73}$$

$$V_{d_1} = 0.31\ \text{cm/s} \tag{4-74}$$

Calculation of V_d based on SO_2

Air: $M_A = 28.97$ g/mol (Lyman et al., 1990)

$V_A = 20.1\ \text{cm}^3/\text{mol}$ (Lyman et al., 1990)

SO_2: $M_{SO_2} = 64$ g/mol

$V_{SO_2} = 41.1\ \text{cm}^3/\text{mol}$ (Fuller et al., 1966)

From Eq. 4-38, at 25° C, the diffusion coefficient for SO_2 in air can be estimated as

$$D_{SO_2} = \frac{10^{-3}\ (298)^{1.75}\ \sqrt{0.05}}{1\ [(20.1)^{1/3} + (41.1)^{1/3}]^2} = 0.121\ \text{cm}^2/\text{s} \tag{4-75}$$

(1) - Formaldehyde
(2) - SO_2

$D_{\text{formaldehyde}} = 0.165\ cm^2/s$ at 298 K

$V_{d_{SO_2}} = 0.04\text{-}2.7$ cm/s for different deposition surfaces (0.04 cm/s was measured for asphalt and 2.7 cm/s was measured for an alfalfa surface)

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \tag{4-76}$$

Lower Limit:

$$V_{d_1} = 0.04\left(\frac{0.165}{0.125}\right)^{2/3} = 0.048\ \text{cm/s} \tag{4-77}$$

Upper Limit:

$$V_{d_1} = 2.7\left(\frac{0.165}{0.125}\right)^{2/3} = 3.24\ \text{cm/s} \tag{4-78}$$

Thus, based on the above example, the deposition velocity for formaldehyde is expected to be in the range of about 0.05 cm/s to 3.2 cm/s. Since formaldehyde is reactive in the aqueous phase (see Section 4.4.2), its dry deposition velocity is likely to be bound by the values obtained using SO_2 and CO_2 (which have different aqueous phase reactivities) as the reference chemicals. The actual dry deposition will depend on the prevailing meteorological and surface conditions in the area of interest (Sehmel, 1980; 1984; Davidson and Wu, 1989). Therefore, in computing the deposition velocity for formaldehyde, the appropriate environmental and surface conditions should be selected for the reference deposition velocity.

4.3.4 Wet Deposition

Wet deposition (scavenging) can increase the overall deposition rate of formaldehyde and thus, increase formaldehyde concentration in the soil, water and vegetation due to direct deposition. Both rain and snow can remove formaldehyde from air, however snowfall is not considered a significant removal process in most of the heavily populated regions in California. In addition, wet deposition is episodic; therefore, the climatological conditions of the location in question must be considered when evaluating the relative importance of wet deposition as a removal process.

The degree of wet deposition is usually estimated from knowledge of the washout ratio, W, defined as

$$W = C_{rainwater}/C_{air} \tag{4-79}$$

in which $C_{rainwater}$ and C_{air} are the concentrations (i.e, ng/m^3) of formaldehyde in rainwater (at ground level) and in the gaseous phase (i.e., in the atmosphere), respectively. Thus, the wet deposition flux (e.g., ng/m^2·hr), $\dot{M}_w$, is given by

$$\dot{M}_w = W \cdot R \cdot C_{air} \tag{4-80}$$

where R is the precipitation rate (m/hr). Estimating from formaldehyde concentrations in rain water and in air (Kippel and Warneck, 1978; Grosjean and Wright, 1983), the washout ratio for formaldehyde is on the order of 10^3-10^4. When compared with the washout ratios for other highly water soluble (e.g., methanol), and hence efficiently removed, organic compounds of $W = 10^4$-10^5 (Eisenreich, 1981; Leuenberger et al., 1985; Atkinson, 1988), it appears that wet deposition of gaseous formaldehyde will be of importance as a loss process for this compound.

An approximate estimate of the raindrop concentration of formaldehyde can be obtained by assuming that the raindrops are in equilibrium with the air phase when they reach ground level. This assumption is supported by the analysis of Cohen (1986) that suggests that raindrops falling through 10 meters of polluted atmosphere are nearly at equilibrium with gaseous chemical. Thus, the concentration of the dissolved chemical in rain, $C_w^{(d)}$ (ng/m^3 water), is given by

$$C_w^{(d)} = \frac{C_a^{(g)}}{H_{aw}} \qquad (4\text{-}81)$$

in which $C_a^{(g)}$ is the concentration of the chemical in the atmosphere in the vapor phase (e.g., ng/m^3 air), and H_{aw} is the dimensionless Henry's Law constant (i.e., $H_{aw} = C_a^{(g)}/C_w^{(d)}$). It must be noted, however, that since formaldehyde can react in the aqueous phase, such transformation may be required for a detailed treatment of formaldehyde rain scavenging.

4.4 Degradation

Understanding degradation processes is important for determining atmospheric lifetimes, which in turn, can be used to estimate spatial dispersion and distribution of a compound. Section 3.2.4 describes the general degradation procedures that were considered for formaldehyde. The following subsections define the specific degradation processes that were considered most applicable to formaldehyde and the findings of the literature survey are also presented.

4.4.1 Atmospheric Degradation

Potentially important atmospheric degradation processes for volatile organic compounds include direct photolysis and oxidation via the hydroxyl (OH) radical, nitrate (NO_3) radical, and ozone (O_3). The most significant of these degradation processes for formaldehyde are its reaction with atmospheric OH radicals and photolysis (Finlayson-Pitts and Pitts, 1986; Atkinson, 1989; Howard, 1989; Winer and Busby, 1993).

Because formaldehyde has been shown to have a short atmospheric lifetime, it will degrade before reaching the stratosphere (Finlayson-Pitts and Pitts, 1986; Atkinson, 1989; Howard, 1989; Winer and Busby, 1993). Therefore, we need only consider tropospheric processes and concentrations when calculating reaction rates, lifetimes and half-lives.

The UV-visible adsorption spectrum of formaldehyde extends from ~290 to ~370 nm in the actinic region (Finlayson-Pitts and Pitts, 1986) and photolysis is the most rapid degradation pathway for formaldehyde. The reported atmospheric lifetime is four hours (Winer and Busby, 1993), with two dissociation processes resulting from photolysis (Finlayson-Pitts and Pitts, 1986):

$$HCHO + h\nu \xrightarrow{(\lambda\ <\ 370\ nm)} HCO + H \qquad (4\text{-}82)$$

$$HCHO + h\nu \xrightarrow{(\lambda\ <\ 370\ nm)} H_2 + CO \qquad (4\text{-}83)$$

The dissociation process shown in Eq. 4-82 is a significant process because it provides a source of HO_2 radicals and ultimately OH radicals, which are important in tropospheric chemistry.

Reported atmospheric lifetimes and half-lives for formaldehyde due to photolysis are listed in Table 4-11.

The reaction of formaldehyde with OH radicals proceeds predominantly by H-atom abstraction and can be described by the following reactions (Finlayson-Pitts and Pitts, 1986; Platt et al., 1979; Atkinson, 1989):

$$HCHO + OH \text{ ----> } \cdot CHO + H_2O \qquad (4\text{-}84)$$

$$\cdot CHO + O_2 \text{ ----> } CO + HO_2 \qquad (4\text{-}85)$$

The reaction rate constant for the reaction of formaldehyde with OH can be described as a function of temperature by the Arrhenius expression:

$$k_{OH} = A \cdot e^{(-Ea/RT)}\ cm^3/molec \cdot s \qquad (4\text{-}86)$$

where: A = a pre-exponential factor

Ea = the activation energy in kcal/mol

R = the universal gas constant = 1.987 cal/deg·mol

T = the temperature in K

Table 4-11. Atmospheric Lifetimes and Half-Lives for Photolysis of Formaldehyde*

Half-life	Lifetime	Reported Uncertainty	Temperature (K)	Technique	References
2.77 hours	4.0 hours[a]	NR	NR	Calculated	Winer and Busby, 1993
1.25 hours	1.8 hours	NR	NR	Calculated	Calvert et al., 1972
6.0 hours	8.66 hours	NR	NR	Measured◆	Howard, 1989
2.77 hours	4.0 hours[a]	NR	NR	NR	Atkinson, 1988

NR = Not Reported.

* Listed order is by decreasing confidence in reported values (see Section 3.0).

◆ Measured in simulated sunlight.

[a] For solar zenith angle of 0.

Numerous investigators have used flash photolysis-resonance fluorescence techniques to measure reaction rates and develop Arrhenius expressions for the reaction of formaldehyde with OH radicals. The results of these studies for measurements made at 298 K are summarized in Table 4-12. Atkinson (1989) critically evaluated the existing literature and based on a unit-weighted least squares analysis recommended the following Arrhenius expression, which is valid over the temperature range 228-426 K:

$$k_{OH} = (1.25^{+0.20}_{-0.18}) \times 10^{-17}\ T^2\ e^{(648 \pm 45)/T}\ \mathrm{cm^3/molec \cdot s} \tag{4-87}$$

Based on this expression, Atkinson (1989) recommends a rate constant for reaction of formaldehyde with OH of $(9.77 \pm 2.93) \times 10^{-12}$ cm³/molec·s at 298 K.

This reaction rate constant can be used in combination with estimates of tropospheric OH concentrations to calculated atmospheric lifetimes and half-lives using the following equations:

$$\text{lifetime} = \tau = 1/k_{OH} \cdot [OH] \tag{4-88a}$$

$$\text{half-life} = \tau_{1/2} = \ln 2\ /k_{OH} \cdot [OH] \tag{4-88b}$$

For example, using the rate constant recommended by Atkinson (1989) and a 24 hour integrated global average tropospheric OH concentration 1×10^6 molec/cm³ (Singh et al., 1982; Atkinson, 1989; CARB, 1989; Howard, 1990, Prinn et al., 1992), the atmospheric lifetime of formaldehyde due to reaction with OH is approximately 1.2 days and the corresponding atmospheric half-life is approximately 0.8 days. Using a 12-hour average OH concentration of 1.6×10^6 molec/cm³, Winer and Busby (1993) reported the atmospheric lifetime of formaldehyde to be 1.9 days. Finlayson-Pitts and Pitts (1986) reported the atmospheric lifetime of formaldehyde in relatively clean (OH concentration = 5.0×10^5 molec/cm³) and moderately polluted (OH concentration = 5.0×10^6 molec/cm³) conditions to be 2.6 days and 6.2 hours, respectively.

While photolysis and reaction of formaldehyde with the OH radical are dominant removal processes during daylight hours, at night reaction with the gaseous nitrate (NO_3)

Table 4-12. Rate Constants, Lifetime, and Half-Lives for Reaction of Formaldehyde with OH■

Lifetime(+) (day)	Half-life (day)	Rate Constant (cm^3/molec·s)	Reported Uncertainty in Rate Constant	Temperature (K)	Technique	References	Source Cited
NR	0.57(+)	14×10^{-12}	$\pm 3.5 \times 10^{-12}$	298	Measured	Atkinson, 1989	Morris and Niki, 1971a
NR	0.53(+)	15.3×10^{-12}	NR	298	Measured	Atkinson, 1989	Morris and Niki, 1971b
NR	0.51(+)	15.8×10^{-12}	$\pm 9.0 \times 10^{-13}$	298±2	Measured	Atkinson, 1989	Niki et al., 1978
NR	1.45(+)	5.5×10^{-12}	$\pm 7.0 \times 10^{-13}$	298	Measured	Atkinson, 1989	Smith, 1978
NR	0.81(+)	9.86×10^{-12}	$\pm 1.13 \times 10^{-12}$	298	Measured	Atkinson, 1989	Stief et al., 1980
NR	0.61(+)	13.2×10^{-12}	$\pm 4.0 \times 10^{-13}$	298	Measured	Atkinson, 1989	Zabarnick et al., 1988
NR	0.61(+)	13.1×10^{-12}	$\pm 4.0 \times 10^{-13}$	298	Measured	Atkinson, 1989	Zabarnick et al., 1988
1.9(a)	1.3	NR	NR	NR	Calculated*	Winer and Busby, 1993	
2.6(b)	1.8	NR	NR	NR	Calculated*	Finlayson-Pitts and Pitts, 1986	
0.26(c)	0.18	NR	NR	NR	Calculated*	Finlayson-Pitts and Pitts, 1986	
NR	NR	9.77×10^{-12}	$\pm 2.93 \times 10^{-12}$	298	Calculated*	Atkinson, 1989	
3(d)	2.1	NR	NR	NR	Calculated*	Atkinson, 1988	
NR	NR	9.0×10^{-12}	NR	NR	NR	Atkinson, 1988	
1.1	0.79(e)	NR	NR	NR	NR	Howard, 1989	
NR	0.396(f)	NR	NR	NR	NR	Howard, 1989	

NR = Not Reported.

Table 4-12. Rate Constants, Lifetime, and Half-Lives for Reaction of Formaldehyde with OH☒
(Continued)

☒ Listed order is by decreasing confidence in reported values (see Section 3.0).

* Calculated from: $\text{lifetime} = \tau = \frac{1}{k_{OH}[OH]}$ $\quad$ $\textit{half-life} = \tau_{\frac{1}{2}} = \frac{\ln 2}{k_{OH}[OH]}$

(+) Conversion from reported rate constant is from the equation specified in footnote *, where k_{OH} is the OH radical rate constant and [OH] is assumed to be 1×10^6 molec/cm^3 (Atkinson, 1988).

(a) $[OH] = 1.6\times10^6$ molec/cm^3, 12-hour average

(b) $[OH] = 5.0\times10^5$ molec/cm^3, relatively clean conditions

(c) $[OH] = 5.0\times10^6$ molec/cm^3, moderately polluted conditions

(d) $[OH] = 1.0\times10^6$ molec/cm^3, 12-hour average

(e) in clean air

(f) in polluted air

radical must be considered. Although NO_3 is expected to react with formaldehyde in an analogous manner to OH, the reported atmospheric lifetime is 84 days (Winer and Busby, 1993). The reported atmospheric lifetime of formaldehyde due to reaction with ozone is $>2\times10^4$ years (Winer and Busby, 1993). Therefore, in addition to photolysis, reaction of formaldehyde with compounds other than OH are insignificant.

Reaction rate constants for formaldehyde against the OH radical, and their corresponding half-lives are summarized in Table 4-12.

4.4.2 Transformation in Water

Formaldehyde, in an aqueous solution is hydrated to form methylene glycol (Moller, 1966; Howard, 1989)

$$HCHO + H_2O \rightarrow CH_2(OH)_2 \qquad (4\text{-}89a)$$

as well as polymeric formaldehyde addition products $HO(CH_2O)_xH$, where x has an average value of 3 (Moller, 1966). Since formaldehyde is present as two distinct dissolved species in the aqueous phase, the air/water partition coefficient (i.e., the dimensionless Henry's Law constant) is generally defined as:

$$H' = \frac{C_a}{C_w} = \frac{[HCHO]_g}{[HCHO]_{aq} + [CH_2(OH)_2]_{aq}} \qquad (4\text{-}89b)$$

where $[HCHO]_g$ is the concentration of formaldehyde in the gas phase and $[HCHO]_{aq}$ and $[CH_2(OH)_2]_{aq}$ are the aqueous phase concentrations of formaldehyde and its products, respectively.

4.4.3 Biodegradation in Soil, Water, and Sludge

Formaldehyde can be biodegraded under both aerobic and anaerobic systems. Adroer et al. (1990) studied the biodegradation of formaldehyde by *Pseudomonas putida.* Results indicate that the degradation process is initiated by a dismutation reaction yielding formic acid and methanol as products. Biodegradation pathways of formaldehyde result in the formation of HCOOH and CH_3OH as intermediates and subsequently CO_2 and H_2O (Verschueren, 1992).

Howard et al. (1991) suggest that the degradation half-life in both soil and surface water (aerobic conditions) range from about 1 day to 7 days. Degradation of formaldehyde under anaerobic conditions is slower with a half-life reported to range from 4 days to about 28 days.

5.0 SUMMARY AND CONCLUSIONS

5.1 General Recommendations

When using intermedia transfer parameters to predict multimedia partitioning of formaldehyde in the environment, the following general recommendations should be considered:

Physicochemical Properties

Among the physicochemical parameters recommended in this reported for multimedia analysis of formaldehyde (i.e. solubility, vapor pressure, molar volume, boiling point, and molecular weight), the experimentally derived aqueous solubility is particularly important because it can be used to predict chemical-specific K_{oc}, K_{ow}, and BCF values. Although solubility is site specific (that is, it depends on pH, temperature, and pressure), under common environmental conditions, the site-specific variability of the aqueous solubility is expected to be minor.

Partition Coefficients

Experimentally determined and calculated partition coefficients for formaldehyde are presented in this report for Henry's Law constant, K_{ow}, K_{oc}, BCFs for various aquatic organism and root uptake. It is noted that measured values for the air-to-leaf partition coefficient and other biotransfer factors which address partitioning through food uptake were not found in the literature.

The concept of B_{TF}s for milk, beef, eggs and vegetable should be revisited since it is based implicitly on the assumption of steady state conditions. For instance, Travis and Arms (1988) derived their correlation by pooling data from a number of independent studies. In addition, the original studies from which Travis and Arms (1988) derived their correlations for B_{TF}s did not include formaldehyde as a study compounds, and did not consider inhalation as a pathway for bioaccumulation in meat.

Intermedia Transport Parameters

Although a measured value for dry deposition velocity for formaldehyde was not found in the literature, it can be estimated as shown in Section 4.3.4. Sehmel (1980) and Davidson and Wu (1989) critically reviewed experimentally measured deposition velocities for other gaseous compounds (such as criteria air pollutants) and reported variability over two orders of magnitude, depending on the deposition surface and other factors. Thus, when estimating the dry deposition velocity, the approprate reference chemical, the meteorological conditions, and surface characteristics must be carefully considered.

5.2 Key Findings and Recommendations for Formaldehyde

The following are the key findings regarding intermedia transfer factors for formaldehyde:

- Photolysis and reaction with the hydroxyl (OH) radical are the main removal mechanisms from the air, while biodegradation is the main removal mechanism from water.

- Since the K_{ow} of formaldehyde is low (see Table 4-7), it is not expected to bioconcentrate or bioaccumulate.

- Formaldehyde is not expected to adsorb strongly onto the soil and thus, it may easily leach into the groundwater.

- Experimental measurements of the solubility and vapor pressure of formaldehyde for the range of temperatures commonly encountered in the environment would enhance the ability to describe the behavior of formaldehyde in the environment.

- The octanol/water partition coefficient for formaldehyde is known only approximately and further studies may be needed.

- Little is known regarding the reaction kinetics of formaldehyde in aqueous systems. Such information is needed to better describe the transport and fate of formaldehyde in aqueous systems as well as water/air and soil/air transfer processes for formaldehyde.

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13. ABSTRACT *(Maximum 200 Words)*

The objective of this project was to develop information on the transfer of toxic air pollutants between environmental media. this information is needed to support the refinement of the multipathway exposure component of health risk assessments. Information was reviewed for seven pollutants: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), hexavalent chromium [Cr(VI)], benzo[a]pyrene, methylene chloride, benzene, mercury, and formaldehyde. Volume I discusses the volatile organic compounds: benzene, methylene chloride and formaldehyde. The literature was reviewed to obtain estimates of intermedia transfer factors, and pollutant-specific estimates where data were deficient. Calculations for chemical concentration in the various media are reviewed, as are several approaches to calculate partitioning into the non-biological compartments. The report contains references for all data, and includes justifications where choices were made for the most accurate value. The use of estimated quantities is so indicated, and the basis for each estimate is provided, along with any associated uncertainties.

14. SUBJECT TERMS

multipathway exposure assessment, hazardous air pollutants, health risk assessment, health risk assessment, environmental cancer effects, intermedia transfer factors, dioxin, PAH, BaP, benzo[a]pyrene, mercury, chromium, formaldehyde, benzene, methylene chloride.

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