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Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume II: Metals and Non-Volatile Organic Compounds

CALIFORNIA ENVIRONMENTAL PROTECTION AGENCY

AIR RESOURCES BOARD
Research Division

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Final Report

Contract No. A032-170

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DISCLAIMER

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ABSTRACT

California's regulations for air toxics require the application of multimedia assessment of human health risk. This approach requires knowledge of intermedia transfer factors (ITFs) for specific toxic air pollutants. In order to meet the above need, a critically evaluated information base on ITFs was developed for a selected number of air toxics. The specific chemicals were selected in order to allow the assessment of ITFs for the following chemical classes: (1) volatile organics (benzene); (2) hydrophilic/reactive volatile organic compounds (formaldehyde); (3) volatile chlorinated low molecular weight hydrocarbons (methylene chloride); (4) particle-bound organics (benzo(a)pyrene and 2,3,7,8-TCDD); (5) reactive metals (chromium VI); and (6) metals that are mobilized through formation of organo-metallic compounds (mercury). Experimental data and estimates of ITFs for the above chemicals were critically evaluated. Detailed reports for seven compounds were prepared and are available as separate chemical-specific volumes of ITF information. The complete set of chemical-specific ITF volumes prepared in this project should provide a useful resource for future development of ITF estimation methods for specific chemical classes.

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EXECUTIVE SUMMARY

Toxic air pollutants which are released to the atmosphere as the result of a variety of human-related activities (air emissions and/or direct discharge to surface water, etc.) move across environmental boundaries and are therefore found in most media (Figure 1.1). Therefore, it is logical to employ a multimedia approach for a comprehensive and integrated approach to evaluating the risks associated with toxic air pollutants.

Indeed California's air pollution regulations for air toxics are deeply rooted in the process of multimedia assessment of human health risk. The assessment of human health risks requires the determination of exposure of the human receptor to pollutants from multiple pathways. The approach requires an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media. For example, in one of the approaches recommended by the State of California Environmental Protection Agency (CALEPA), given monitored or modeled atmospheric concentrations of air toxics, one can resort to appropriate empirical or theoretical algorithms to estimate the transfer, and thus, the accumulation of the pollutants of interest in both non-biological media (e.g., atmosphere, surface water, soil) and biological media (e.g., fish, cattle, vegetation). The resultant media concentrations can then be used to estimate the total dose (or average daily dose) of the given air toxic contaminants and subsequently the associated human health risks (Figure 1.2). The above multipathway exposure analysis involves a variety of chemical-specific intermedia transfer factors (ITFs). These ITFs are needed to estimate the rate of movement of chemicals from one medium to another as well as their level of accumulation in various environmental compartments (e.g., water, soil, vegetation).

Although the multimedia approach to exposure analysis and risk assessment is attractive, its implementation is often accompanied with uncertainties. These uncertainties arise from the lack of data in some areas (e.g., dose-response data, population activity patterns, environmental chemical concentrations), which leads to reliance on models where certain assumptions and default parameter values are introduced. Generally, the

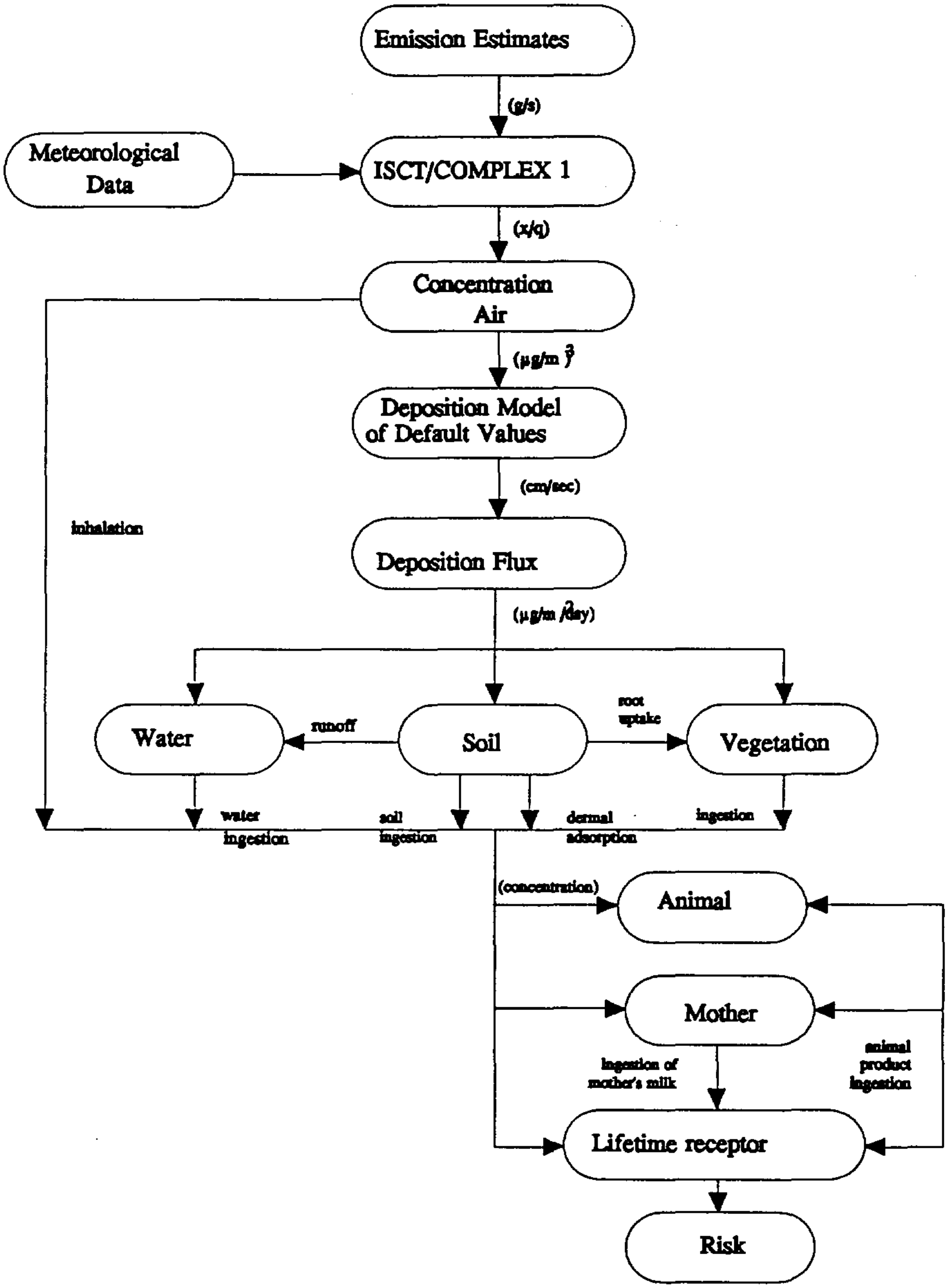

Figure 1.1 Exposure Flowchart

(Source: "Health Risk Assessment Guidelines for Non-Hazardous Incinerators", ARB/DHS, August 1990)

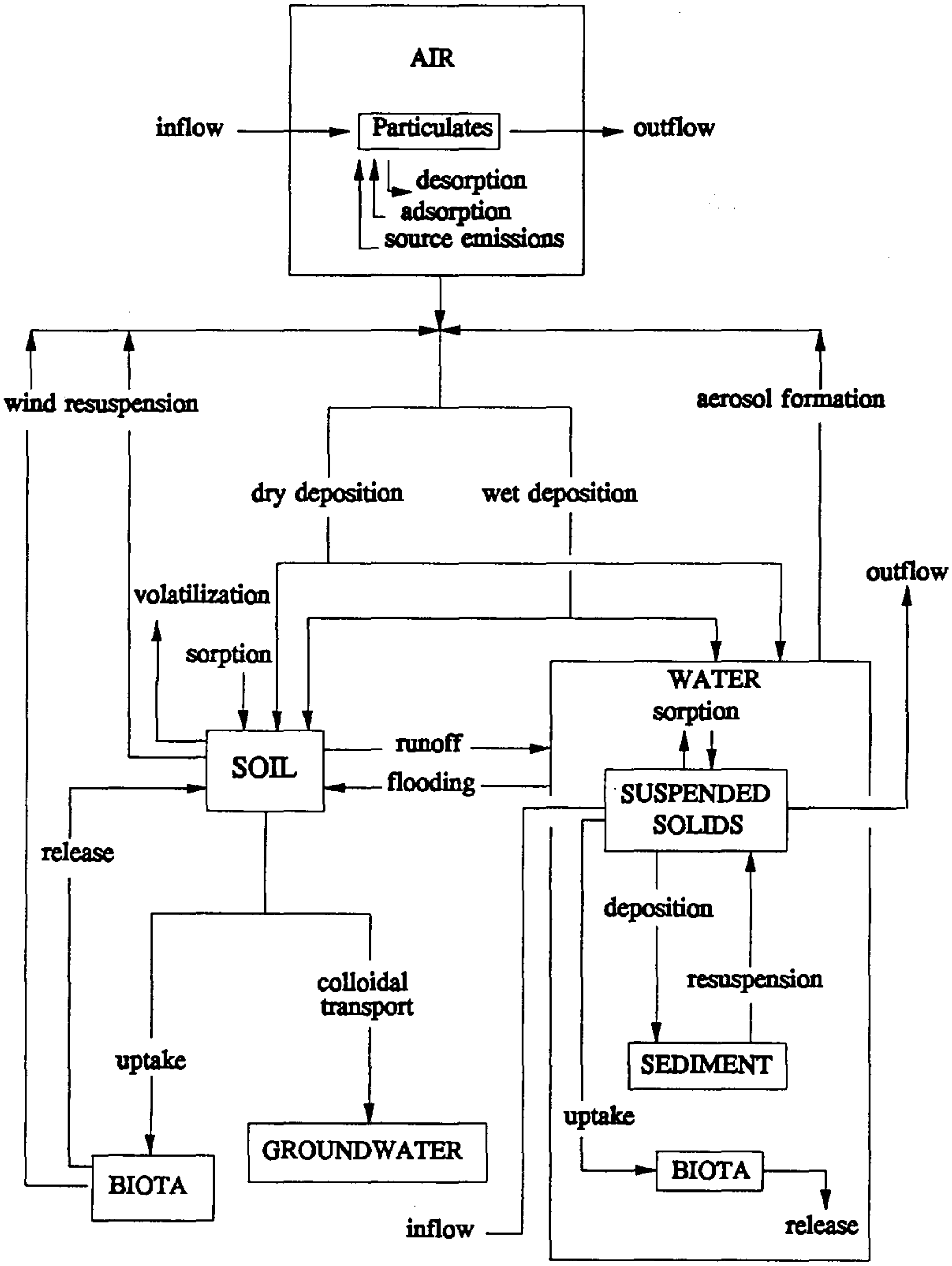

Figure 1.2 Schematic of Multimedia Transport Processes of Particle-Bound Pollutants

assumptions employed and the use of default parameter values 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 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 focused on the last category of multimedia exposure analysis which requires knowledge of intermedia transport processes. Uncertainties in the predictions of multimedia exposure analysis is the consequence of both the lack of understanding of some intermedia transport processes and the frequent use of approximate treatments of intermedia transport processes and estimated intermedia transport factors. Such uncertainties can be reduced by using the most accurately available intermedia transfer factors such as pollutant physicochemical, partitioning, mass transfer and degradation parameters.

This study provides information on some of the major intermedia transfer factors (ITFs) used in a number of different multimedia models including the CAPCOA (1992) guidelines. These guidelines provide procedures for preparation of health risk assessments required under AB 2588. Under some circumstances, the CAPCOA (1992) guidelines allow for submission of an uncertainty analysis associated with the risk assessment. Thus, chemical-specific ITF information should be valuable for assessing uncertainty analyses submitted to the California Air Resources Board (CARB).

In order to meet the above needs, a critically evaluated information base on ITFs was developed for a selected number of air toxics. The specific chemicals were selected in order to allow the assessment of ITFs for the following chemical classes: (1) volatile organics (benzene); (2) hydrophilic/reactive volatile organic compounds (formaldehyde); (3) volatile chlorinated low molecular weight hydrocarbons (methylene chloride); (4) particle-bound organics (benzo(a)pyrene and 2,3,7,8-TCDD); (5) reactive metals (chromium VI); and (6) metals that are mobilized through formation of organo-metallic compounds (e.g., mercury). Experimental data and estimates of ITFs were critically evaluated and detailed specific reports were prepared and are part of this final report. The complete set of ITF reports (see Table 1) prepared in this project should provide a useful resource for future development of ITF estimation methods for specific chemical classes.

The overall objective of the individual ITF reports is to present information on chemical-specific intermedia transfer factors which is pertinent for multimedia exposure pathways estimation and for health risk assessments. The purpose of the chemical-specific ITF reports is to: (1) critically review existing literature to determine pertinent intermedia transfer parameters for the study chemicals; (2) evaluate and update intermedia transfer factors currently used in multimedia exposure estimations; and (3) provide pollutant-specific estimates where no data are available or where default values are used.

Since the results of this study may be used to support efforts in multipathway analysis of exposure to the study chemicals, a number of multimedia contaminant transport models were reviewed in terms of algorithms, default values, underlying assumptions, and the influence of the overall logic on the estimates of risk. Based on this review, selected physicochemical properties, partition coefficients, and intermedia transport coefficients were critically evaluated.

TABLE 1

INTERMEDIA TRANSFER FACTORS FOR MULTIPATHWAY EXPOSURE ANALYSIS: COMPOUND CLASSES AND CHEMICALS STUDIED

Chemical Class	Specific Chemical Reviewed	Volume Number
Volatile Organics Hydrocarbons	Benzene	I
Reactive Metals	Chromium VI	II
Particle-Bound Organics	2,3,7,8-TCDD	III
Volatile Chlorinated Low Molecular Weight Hydrocarbons	Methylene Chloride	IV
Particle-Bound Organics (PAH Group)	Benzo(a)pyrene	V
Metals Mobilized through Formation of Organo-Metallic Compounds	Mercury	VI
Hydrophilic/Reactive Volatile Organic Compounds	Formaldehyde	VII

Physicochemical Properties

Physicochemical properties are important for the analysis of intermedia transport parameters such as mass transfer coefficients and for the determination of parameters such as partition coefficients, biotransfer factors, and mass transfer coefficients. The specific physicochemical parameters considered in this study are given below.

- Water Solubility;
- Vapor Pressure;
- Density;
- Molar Volume;
- Boiling Point;
- Molecular Weight;
- Melting Point; and
- Heat of Vaporization.

Partition Coefficients

Once released to the environment, toxic air pollutants will be distributed to various compartments due to various transport processes. The net chemical transport from one compartment to another may be limited by equilibrium constraints which are quantified by appropriate partition coefficients. The partition coefficient, H_{ij} is generally defined as

$$H_{ij} = C_i/C_j$$

where C_i and C_j are the concentration in compartment i and j, respectively, at equilibrium. In this study, the following partition coefficients were considered:

- Henry's Law Constant;
- Octanol-Water Partition Coefficient;
- Gas Phase/Particle Partitioning Coefficient;
- Soil/Water-Organic Carbon Partition Coefficient;
- Bioaccumulation Factors; and
- Bioconcentration Factors.

It is noted that bioaccumulation factors and bioconcentration factors often represent steady-state concentrations rather than an equilibrium state. These factors are also at times based on the total chemical concentration which includes particle-bound and dissolved forms of the chemical under consideration; thus, in such cases, the reported bioconcentration factors do not represent thermodynamic constraints and simply represent the partitioning obtained for the particular set of experimental conditions for which these factors were obtained.

Transport Parameters

The transport of toxic air pollutants in the environment is governed by either convective transport in a given medium (not addressed in this report) or intermedia transport from one environmental compartment to another. It is important to note that some chemicals (e.g., semi-volatile organics) can be present in both the gaseous and particle-bound forms. Thus, the exchange of such chemicals between the atmosphere and the terrestrial and aquatic environments depends on both the dry and wet deposition of their gaseous and particle-bound forms, as well as on wind resuspension. The relevant intermedia transfer and transformation parameters considered in this study include:

- Diffusion Coefficients in Air and Water;
- Mass Transfer Coefficients for Air/Water Exchange;
- Dry Deposition Velocity;
- Precipitation Scavenging;
- Colloidal Transport in Soils and Sediment/Water;
- Biotransfer Factors; and
- Chemical and Biotransformations.

These intermedia transport parameters are defined and discussed in detail in each of the chemical-specific ITF reports. In addition, a brief discussion is provided of the available information on bioavailability and the implication for its accumulation in biological receptors. Finally, the chemical and biotransformations of the study chemicals in each of the major environmental media (i.e., air, water, soil and sediment) are reviewed and the range of relevant reaction half-lives are summarized and discussed.

The evaluation of the above ITFs was carried out for seven chemicals (see Table 1) that are relevant for the determination of the behavior of the study chemicals in various media and the food chain after their release into the atmosphere from stationary and mobile sources. Reported values for the selected parameters were compiled and evaluated. In cases where a wide range of values were reported from different studies, the reported experimental and estimated ITFs were reviewed to assess the reliability of the reported parameter values. Data in the ITF 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 reported uncertainty estimates. Calculated values reported without their associated estimation equations were reported last.

Each one of the chemical-specific ITF reports (see Table 1) is a self-contained volume that provides an overview of the nature of the chemical considered, its entry route to the environment, environmental chemical and bio-transformations, definitions of the various intermedia transfer factors considered in the study, a critical evaluation of ITF data and estimation methods, a summary of recommended ranges of ITF values, chemical-specific ITF estimation methods, and recommendations for future improvements in estimating ITFs for the study chemicals.

Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume II: Metals and Non-Volatile Organic Compounds
Section 1 - Hexavalent Chromium

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ABSTRACT

An information base was developed on the biotic and abiotic transfer of hexavalent chromium within and between environmental media (i.e., air, water, soil, and the biosphere), with emphasis on human exposure pathways from emissions to the ambient atmosphere. The environmental literature relevant to hexavalent chromium was critically reviewed to: (1) determine the intermedia transfer factors relevant to hexavalent chromium; (2) evaluate measured values; and (3) recommend estimation strategies applicable to hexavalent chromium (and analogous transition metals) for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

The assessment of health risk requires the determination of exposure of the human receptor to pollutants from multiple pathways. The movement of chemicals through the environment is particularly important to the overall assessment of human exposure to toxic air pollutants since airborne pollutants can be deposited to 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 by field measurements. Both approaches require an understanding of the complex physical, chemical, and biological processes that govern the movement of pollutants through environmental media. Although the multimedia approach is attractive, its implementation is hampered by many obstacles. In particular, there are significant deficiencies in our understanding of various intermedia transport and transformation processes (Allen et al., 1989). Additional uncertainties arise from the lack of experimental data in some areas, leading to reliance on assumptions and default values.

One air toxic compound that has received significant attention in recent years is hexavalent chromium. The problems of assessing exposures to hexavalent chromium are unusually complex because of the differential carcinogenicity and toxicity of trivalent and hexavalent chromium compounds (Bianchi and Levis, 1985; cited by Gochfeld, 1991). Paradoxically, hexavalent chromium [Cr(VI)] is a potent carcinogen while trivalent chromium [Cr(III)] is an essential trace element (Bianchi and Levis, 1985). Because the toxicity is a function of the oxidation state of chromium and its aqueous concentration, it is imperative that the reactions that control the oxidation state and aqueous concentration be understood (Rai et al., 1989).

Conventional questions regarding the environmental fate and transport of chromium are complicated by the need to understand speciation of chromium, not only between the trivalent and hexavalent states, but among different hexavalent salts, including the insoluble, soluble, and partially soluble salts (Gochfeld, 1991). It appears that among hexavalent salts, the partially water soluble salts (e.g., strontium chromate; Wiegand et al., 1988) are more carcinogenic than either the insoluble salts (e.g., lead chromate) or the soluble ones (e.g., sodium or potassium chromates and dichromates) (Mancuso, 1975; cited by Gochfeld, 1991; Levy and Martin, 1983; IARC, 1980; Lyon et al., 1969; Hayes, 1982; Sunderman, 1984; cited by Wiegand et al., 1988). The slow dissolution of sparingly soluble Cr(VI) salts from inhaled particles may provide a chronic source of chromate (CrO_4^{2-}) anions to adjacent lung cells, as compared to soluble Cr(VI) salts which might dissolve rapidly, enter the bloodstream and become sequestered in red blood cells (Wiegand, et al., 1988), or to insoluble Cr(VI) salts which might not contribute any significant source of chromate anions.

In environmental settings Cr(VI) exists only in compounds in the solid or dissolved phase (Nieboer and Jusys, 1988). It is the concentration of Cr(VI) compounds in the dissolved phase that is relevant to the possible chemical transformation and toxic effects of Cr(VI). The major exposure pathway for Cr(VI) is believed to be inhalation. Therefore, intermedia transfer factors associated with exposure via inhalation of aerosols (either solid or liquid particles suspended in a gas) are emphasized in this report. The particle size distributions of dusts and soils to which Cr(VI) compounds are bound, as well as the size distribution of the pure compounds as emitted by industrial processes, require thorough consideration because the particle size distribution is a significant factor influencing the inhalation pathway. Also, the behavior of chromium species in different soils under different conditions varies in a complex fashion that cannot be adequately predicted without site-specific measurements (Bartlett, 1991). In order to evaluate risks from exposure to chromium, it has been suggested that consideration should be given to (Gochfeld, 1991):

- Establishing the form and quantity of chromium in the environment and assess its bioavailability;

- Establishing the routes of exposure and how these might affect the chromium species to which individuals are exposed;

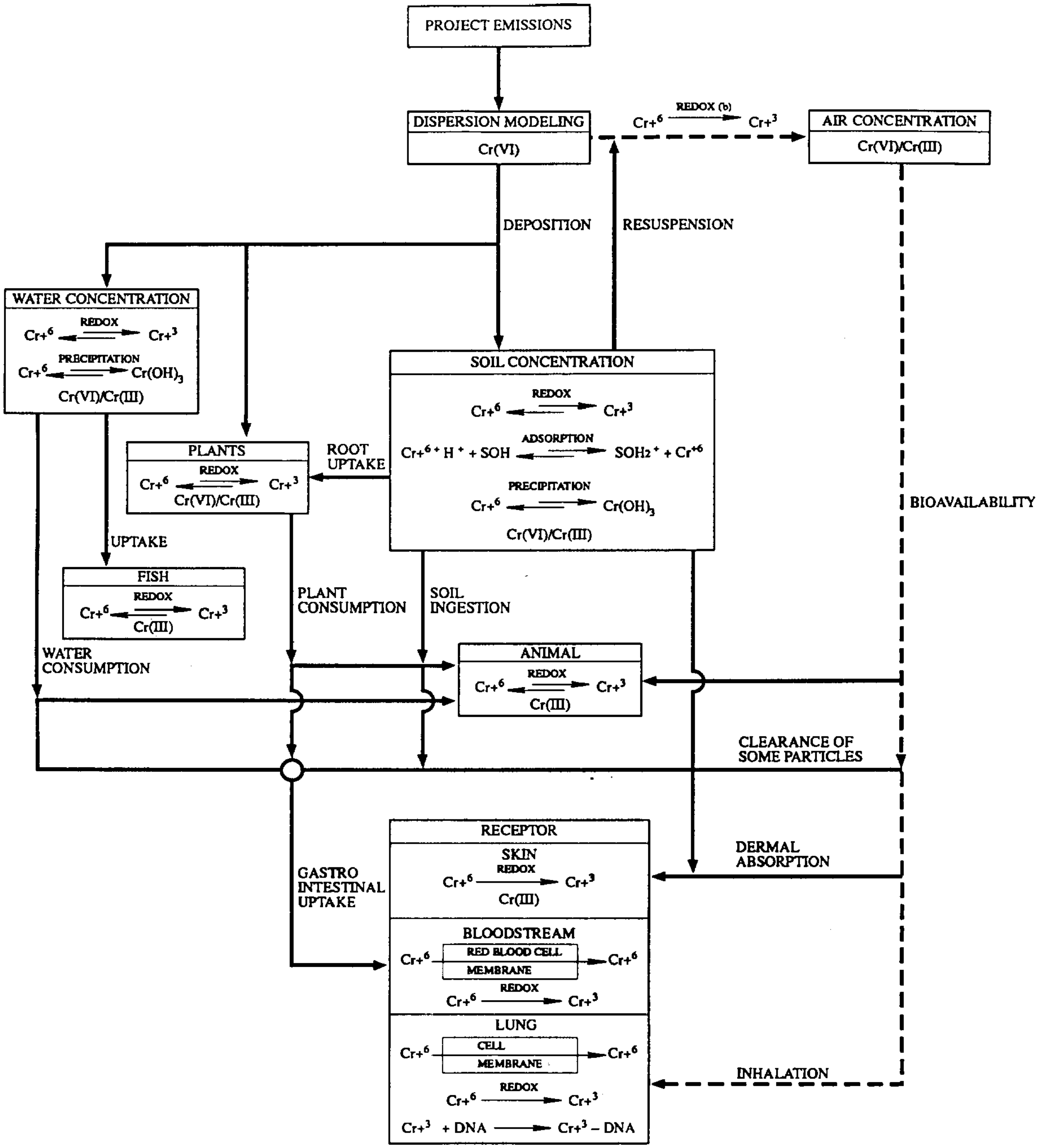
- Distinguishing each of the exposure sites (i.e., skin, lungs, and intestinal track) as target organs on one hand or routes of exposure on the other; and

- Developing an understanding of the mechanisms by which different chromium species exert toxic effects and the conditions under which these effects are manifest.

Identifying the appropriate intermedia transfer factors to facilitate the evaluation of hexavalent chromium exposure according to the above principles is the focus of this report.

Figure 1.1 presents significant exposure routes for ambient concentrations of Cr(VI) compounds released to the atmosphere. As Figure 1.1 illustrates, the major transformation processes, especially electron transfer or "redox" reactions, are critical to the exposure assessment process. The transformation processes that affect the oxidation state of chromium are strongly dependent on environmental conditions such as pH, soil type, concentration of reactive species, and organic matter. With the exception of the organic matter fraction, these site-specific conditions are seldom considered in multimedia models, which are typically designed to predict the fate and transport of organic compounds. Organic compounds can be transformed via chemical and bio- transformations to form other compounds. By contrast, the element chromium is conserved but it can be transformed between different oxidation states. For reasons discussed in detail in Section 5.0, Cr(VI) can be readily transformed to Cr(III) in biological systems with the possible exception of plants, and bioaccumulation of chromium as Cr(VI) does not occur in animals or animal products.

Hexavalent chromium compounds have characteristically low vapor pressures. Thus, the transport of Cr(VI) is dominated by particle transport and solubilization. Multimedia models such as MINTEQ (Felmy et al., 1983) and EXAMS (Burns et al., 1981) are available to assess certain aspects of Cr(VI) exposure but there is no single model available to treat all of the exposure pathways shown in Figure 1.1 according to the current understanding of its environmental behavior. A detailed discussion of the various variables that affect the distribution of Cr(VI) in the environment is provided in Sections 4 - 8. A summary of representative values and estimation techniques for intermedia transfer factors is provided in Table 1-1.



(a) REACTIONS SHOWN ARE FOR ILLUSTRATIVE PURPOSES ONLY AND ARE NOT STOCHIOMETRICALLY BALANCED

(b) FRACTION OF Cr^{+6} REDUCED DEPENDS ON ENVIRONMENTAL CONDITIONS; THE OXIDATION REACTION, $Cr^{+3} \longrightarrow Cr^{+6}$, IS NOT EXPECTED TO OCCUR

– – – MAJOR ROUTES

—— MINOR ROUTES

Figure 1.1. Exposure Routes for Hexavalent Chromium (a)

Table 1-1. Summary of Intermedia Transport and Transformation Factors for Cr(VI)

Parameter	Representative Value or Comment	Estimation Technique	Report Section or Eq. No.	Reference
Deposition Velocity, V_d	0.075(a)-1.0(b) cm/s	$V_d = \int_0^\infty V_d(a)F(a)da$	5.1.1.2 (5-2)	Schroeder et al., 1987; Nriagu et al., 1988
Atmospheric Lifetime	7-10 days(c)	(d)	5.1.1.2	U.S. EPA (1980b; cited by CARB, 1988); ATSDR, 1992
Wet Deposition Concentration, $\overline{C}_{wf}^{(p)}$	(e)	(e)	5.1.1.3	Tsai et al., 1991
Atmospheric Reaction Half-life, $\tau_{1/2}$	13-16 hours	(f)	5.1.2	Grohse et al., 1988
Water-Phase Reaction: Half-life, $\tau_{1/2}$				
Aerobic	No measurable reduction	$\tau_{1/2} = \ln 2/K$	5.2.1	Saleh et al., 1989
Aerobic plus S^{2-}	Air interferes with reduction			
Anaerobic plus S^{2-}	Instantaneous			
Water-Solid-Phase Reaction $\tau_{1/2}$	(g)	(g)	5.3.1	Amacher and Baker, 1982 (cited by Bartlett and James, 1988); Saleh et al., 1988
Resuspension	(h)	(h)	5.3.3	Clay, 1992

Table 1-1. Summary of Intermedia Transport and Transformation Factors for Cr(VI)
(Continued)

Parameter	Representative Value or Comment	Estimation Technique	Report Section or Eq. No.	Reference
Biological Reaction $\tau_{1/2}$	Minutes to hours	(f)	5.4.4	Connet and Wetterhahn, 1983 (cited by Nieboer and Jusys, 1988)
Inhalation Bioavailability	0.3%(i)	(d)	6.1	Fraser and Lum, 1983 (cited by Clement, 1988)
Gastrointestinal Absorption Factor	<5% of intake	(d)	6.2	Donaldson and Barreras, 1966
Dermal Absorption Factor	4% of intake	(d)	6.3	Walhberg, 1968 (cited by Clement, 1988)
Dermal Uptake Rate	1.1 µg Cr(VI)/cm^2/hr	(d)	6.3	Baranowska-Dutkiewicz, 1981 (cited by ATSDR, 1992)

(a) Estimated for urban environments; Nriagu et al., 1988.

(b) Based on particle size of 1 µm; Schroeder et al., 1987.

(c) Assumed particle size not cited.

(d) Not cited.

(e) Calculated dependent on site-specific measurements of Cr(VI) in the aerosol phase. "Washout coefficient" is given as the ratio $\overline{C}_{wf}^{(p)} / C_a^{(p)}$.

(f) Reaction $\tau_{1/2}$ presumably calculated according to Eq. 4-7.

(g) Reaction $\tau_{1/2}$ for soils highly dependent of site-specific conditions; see Table 5-2 and Section 5.3.1 for experimental conditions.

(h) See Cowherd et al. (1988) for specific procedures.

(i) Applies to fly ash matrix; a bioavailability factor of 1 is recommended for mists of soluble chromates and dichromates.

2.0 OBJECTIVES

The overall objective of this report is to present information pertinent to the prediction of the transfer of hexavalent chromium between environmental 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 hexavalent chromium; (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.

A thorough investigation was conducted of literature values reported for key factors and parameters which determine the fate and transport of hexavalent chromium, following its release as an air pollutant from stationary and mobile sources. These data were critically evaluated to obtain recommendations for numerical values which appear to be of the greatest reliability and utility in conducting multipathway exposure assessments. Where no reliable values were found in the literature or default values are currently being used, this report offers pollutant-specific estimation techniques. The details of the methods used, and the properties and parameters investigated, are discussed below.

3.0 METHODOLOGY

The method of approach for this project consisted of several phases in which input parameters were selected, published values for these parameters were collected and evaluated for those parameters for which measured values could not be found in the literature. Since the results of this study may be used to support the CAPCOA (1992) guidelines, the logic behind the current CAPCOA (1992) model algorithms, default values, and underlying assumptions, as well as the influence of the overall logic on estimates of risk, were reviewed. In addition, the Multi-Pathway Health Risk Assessment Input Parameters Guidance Document (SCAQMD, 1988) which provides information in connection with the CAPCOA (1992) model was reviewed in detail to determine the exposure pathways considered by the model. Although this report considers the general issues pertaining to multipathway exposure to Cr(VI), the report also presents, where appropriate, procedures for analyzing intermedia transport relevant to the CAPCOA (1992) model.

3.1 Literature Review

A literature search of Dialog (NTIS, Pollution Abstracts, Enviroline), Science Citation Index and UCLA Orion, Melvyl, and EMS library databases was conducted. Sources referenced in these publications were also obtained. Through this process, references pertaining to the physicochemical properties, intermedia transport, and bioavailability of hexavalent chromium were identified, obtained, reviewed, and summarized.

3.2 Selection of Parameters

In order to provide a state-of-the-art assessment of intermedia transfers, a number of input parameters were considered. The final selection was based on considerations of the environmental consequences of intermedia transfers. Specifically, input parameters from the ARB/DHS Health Risk Assessment (HRA) software and algorithms (CAPCOA, 1992) and the SCAQMD guidance document (SCAQMD, 1988) were considered.

A review of the literature revealed that the processes that chiefly determine the speciation, transformation and thus, also the transport of hexavalent chromium in the environment are as follows:

(1) Oxidation-Reduction (Redox) reactions;
(2) Solubility and precipitation equilibria;
(3) Sorption on soils;
(4) Uptake by biota;
(5) Microbial transformations; and
(6) Atmospheric dry and wet deposition.

These processes, which strongly depend on the physicochemical properties of the study environment, will be introduced in Section 4.0, Environmental Chemistry of Hexavalent Chromium. The above processes and their importance in affecting the fate and intermedia transfers of Cr(VI) are discussed in Section 5.0, Fate and Transport of Hexavalent Chromium. The implications of these processes to exposure pathways are presented in Section 6.0. Values found in the literature for quantifying the above processes are summarized in Section 7.0. Finally, recommendations for incorporating the current understanding of these processes with respect to multimedia modeling of Cr(VI) are provided in Section 8.0.

3.3 Selection of Representative Hexavalent Chromium Compounds

Hexavalent chromium does not exist in pure cationic form but as an oxyanion in various compounds (e.g., CrO_4^{2-}, $HCrO_4^-$, $Cr_2O_7^{2-}$). Since the toxic manifestations of chromium exposure appear to be determined by the bioavailability and biochemical interactions of specific chromium compounds rather than by elemental chromium, it is necessary to selectively determine the amounts of Cr(VI) compounds rather than the total chromium content in a wide variety of matrices (Katz, 1991). Over 30 inorganic compounds containing Cr(VI) are used industrially (Nriagu, 1988), however, only the compounds presenting the greatest known health risks as determined by the U.S. Department of Health and Human Services (ATSDR, 1992) are emphasized in this report. According to the National Institute for Occupational Safety and Health (NIOSH) criteria documents (NIOSH, 1975, cited by Katz, 1991), noncarcinogenic Cr(VI) is the chromium in the mono- and dichromates (CrO_4^{-2} and $Cr_2O_7^{-2}$) of hydrogen, lithium, sodium, potassium, rubidium, cesium, and ammonium, and in chromium trioxide. The chromium in all other hexavalent chromium compounds was identified by NIOSH (1975) as carcinogenic. For the purposes of this report, the Cr(VI) compounds identified by ATSDR (1992) will be considered major Cr(VI) compounds emitted to the atmosphere. These Cr(VI) compounds are listed in Table 3-1, along with their corresponding formulas, molecular weights, aqueous solubilities, and uses.

Table 3-1. Aqueous Solubility and Uses of Major Hexavalent Chromium Compounds

Cr(VI) Compound(a)	Formula	Molecular Weight(b) (g/mol)	Aqueous Solubility(b)	Uses(c)
Ammonium dichromate(d)	$(NH_4)_2Cr_2O_7$ and variable composition	252.06	Soluble; 30.8 g/100 mL	Ceramics
Calcium chromate	$CaCrO_4 \cdot 2H_2O$	192.09	Partially soluble; 16.3 g/100/mL	Metal primers, corrosion inhibitor, high temperature batteries
Chromium (VI) trioxide(d) (colloquially called chromic acid)	CrO_3 (H_2CrO_4 in water)	99.99	Soluble in water; 61.7 g/100 mL	Corrosion inhibitor in cooling towers, photoengraving, and offsite printing
Lead chromate	$PbCrO_4$ $PbO \cdot PbCrO_4$ $Pb_2(OH)_2CrO_4$	323.18 546.37 564.39	Insoluble in cold water(e)	Color pigment
Potassium chromate(d)	K_2CrO_4	194.20	Soluble; 62.9 g/100 mL	Reagent textile mordant pigments
Potassium dichromate(d)	$K_2Cr_2O_7$	294.19	Soluble; 4.9 g/100 mL	Oxidizing agent reagent electroplating
Sodium chromate(d)	Na_2CrO_4	161.97	Soluble; 87.3 g/100 mL	Inks, tanning, dyeing
Sodium dichromate(d)	$Na_2Cr_2O_7 \cdot 2H_2O$	298.00	Soluble; 238 g/100 mL	Production of chromium pigments, CrO_3 and Cr salts
Strontium chromate	$SrCrO_4$	203.61	Partially soluble; 0.12 g/100 mL	Corrosion inhibiting pigment, plating additive
Zinc chromate	$ZnCrO_4$(f)	181.37	Insoluble in cold water	Corrosion-inhibiting pigment

(a) Source: ATSDR, 1992.
(b) Source: Weast, 1975.
(c) Source: Nieboer and Jusys, 1988
(d) Considered noncarcinogenic by NIOSH (1975).
(e) Aqueous solubility of $PbCrO_4$ is 0.0000058 mg/100 mL.
(f) Also $ZnO \cdot ZnCrO_4 \cdot xH_2O$, $3ZnCrO_4 \cdot K_2CrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$, zinc yellow.

4.0 SOURCES AND CHEMISTRY OF HEXAVALENT CHROMIUM

Chromium is a naturally occurring element that combines with other elements to form predominantly inorganic compounds found in rocks, soil, water, and volcanic dusts, and organic complexes in plants and animals. Chromium is present in the environment in several different oxidation states, the most common of which are chromium (III), and chromium (VI) (ATSDR, 1992). Metallic chromium (0) is not found in nature but is produced principally from the naturally occurring mineral chromite ($FeO \cdot Cr_2O_3$). Chromium metal is used mainly in making steel and other alloys. Chromite contains chromium in the trivalent form and is used as brick lining for high temperature industrial furnaces.

Hundreds of Cr(III) compounds are known (WHO, 1988). Most Cr(VI) compounds are produced industrially by heating Cr(III) compounds in the presence of mineral bases (e.g., soda ash) and atmospheric oxygen (CARB, 1988b). Chromium (VI) compounds are used in chrome plating, the manufacture of dyes and pigments, leather tanning, wood preservative, and treatment of cooling water. Smaller amounts are used in drilling muds, textiles, and toner for copying machines (ATSDR, 1992). Trivalent chromium may be oxidized to hexavalent chromium during the combustion process (WHO, 1988). The type of compound in which Cr(VI) is present and the particle size distribution depends initially on the emission source. The major sources of Cr(VI) in California (CARB, 1988b) and corresponding particle sizes are shown in Table 4-1.

Cary (1982) summarized the general chemistry of chromium. Chromium, atomic number 24, is found in group VIA of the periodic table and is a member of the first transition series. Its configuration is (Ar) $3d^5 4s^1$. The characteristic oxidation states are positive II, III, and VI. In acid solution Cr^{+2} (chromous), Cr^{+3} (chromic), and $Cr_2O_7^{-2}$ (dichromate) are representative and in basic solution $Cr(OH)_2$ CrO_2^- (chromite), and CrO_4^{-2} (chromate) are representative. In its highest oxidation state (VI), chromium forms exclusively oxy compounds and all are potent oxidizing agents.

Table 4-1. Hexavalent Chromium Containing Compounds Emitted from Major Sources in California(a)

Emission Source	**Cr(VI) Compound**	**Formula**	**Particle Size**
Chrome Platers	Chromic Acid	H_2CrO_4	Small Particles to 100μm(b)
Cooling Towers	Chromates(c)	CrO_4^{2-}	Larger droplets(d)
Refractory Production	Chromates(a)	CrO_4^{2-}	0.22-0.28 μm(f)
Chromate Production	Chromates	CrO_4^{2-}	0.32-0.37μm(f)
Pigment Users	Chromium oxide	CrO_3	0.32-0.37μm(f)
	Zinc chromate	$ZnCrO_4^{2-}$(g)	0.32-0.37μm(f)
	Strontium chromate	$SrCrO_4$	0.32-0.37μm(f)
	Calcium chromate	$CaCrO_4$	0.32-0.37μm(f)
	Lead chromate	$PbCrO_4$(h)	0.32-0.37μm(f)
Fuel Combustion(e)	Chromates(e)	CrO_4^{2-}	Small Particles
Windblown Dust(i)	Chromates(i)	Various(i)	>8μm(i)

(a) Table adapted from CARB (1988b), unless otherwise referenced.

(b) Stern, 1982.

(c) Added as sodium dichromate ($Na_2Cr_2O_7$).

(d) The droplet size depends on cooling tower design and meteorological conditions; there are currently no reliable techniques for the respirable drop size (<10 μm) (CARB, 1988b).

(e) Presumes oxidation of Cr(III) to Cr(VI) during combustion process (WHO, 1988).

(f) Geometric mean (Gafafer, 1953; cited by Pacyna and Nriagu, 1988).

(g) Also $ZnO \cdot ZnCrO_4 \cdot xH_2O$, $3ZnCrO_4 \cdot K_2CrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$; zinc yellow.

(h) Also $PbO \cdot PbCrO_4$, $Pb_2(OH)_2CrO_4$.

(i) Cited by Pacyna and Nriagu, 1988.

The most stable ion state of chromium is Cr(III) which leads to the chemical inertness of Cr(III) complexes (Cary, 1982). Trivalent chromium bonds with oxygen, nitrogen, and sulfur; many organic complexes are known (Cary, 1982). The formation of metal hydroxides plays an important role in the chemistry of chromium in soils and water systems. Chromium (VI) can be coprecipitated with aluminum hydroxide over the pH range of about pH 7 to pH 9.4 (Cary, 1982). The presence of Cr(VI) in the environment is of particular importance because in this oxidation state, chromium is most toxic and is often water soluble (NIOSH, 1975).

The three important reactions or processes controlling the distribution of hexavalent chromium in environmental systems are redox, precipitation-dissolution and sorption-desorption (Saleh et al., 1989). The relationship between these processes is depicted in Figure 4.1. Although these processes are complex and interrelated, each must be considered in order to predict the aqueous concentrations, mobility, and toxicity of chromium in the environment (Rai et al., 1989). The general chemistry of these reactions is discussed in the following subsections whereas the implications of these reactions in environmental media are discussed in Section 5.

4.1 Redox Reactions

To understand the propensity for chromium to change oxidation states, both in environmental media and in living cells, requires a thorough understanding of redox reactions and poses major challenges to the analytical laboratory (Gochfeld, 1991). A redox reaction consists of two parts or half-reactions. These are the oxidation reaction in which a substance donates electrons and the simultaneous reduction reaction in which a substance accepts electrons.

An analogy can be drawn between redox reactions in the hydrosphere and acid-base reactions. The activity of the hydrogen ion, H^+, is used to express the degree to which water is acidic or basic. By analogy, *electron activity* expresses the degree to which water is reducing or oxidizing. Water with high electron activity is said to be reducing while water

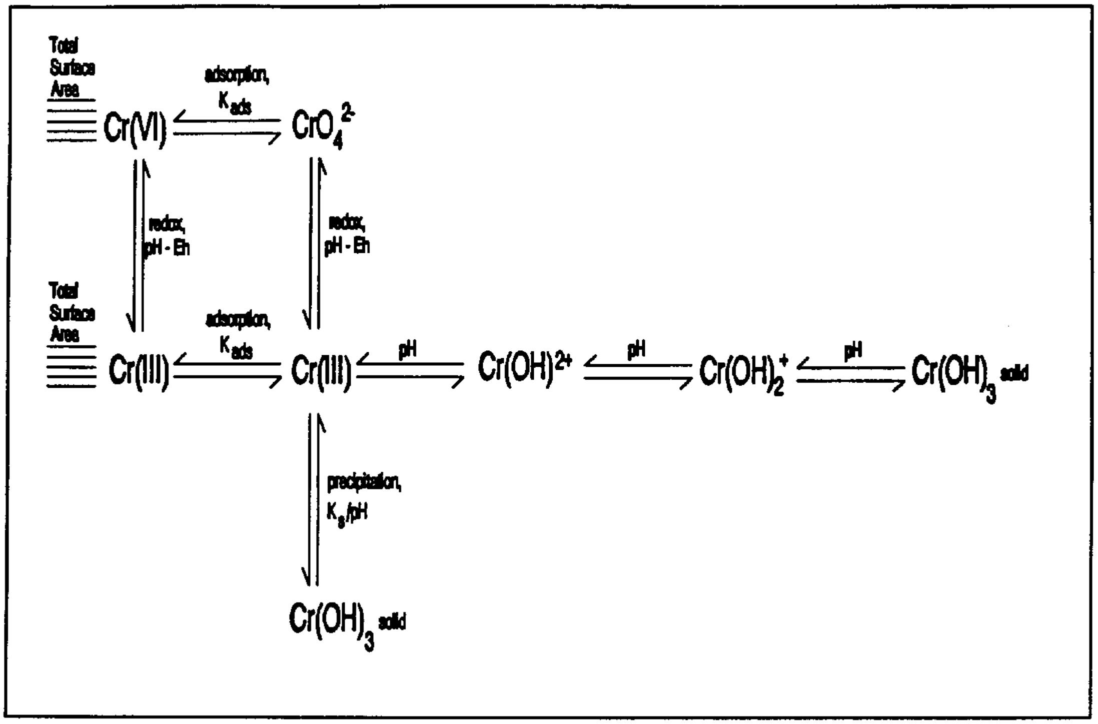


Figure 4.1 Major Processes Influencing the Speciation of Cr(VI) in Environmental Media

with low electron activity is said to be oxidizing (Manahan, 1991). Just as pH can be defined as

$$\text{pH} = -\log(a_{\text{H+}}) \tag{4-1}$$

where $a_{\text{H+}}$ is the activity of the hydrogen ion in aqueous solution, the redox intensity factor, pE, is defined as

$$\text{pE} = -\log(a_{\text{e-}}) \tag{4-2}$$

where $a_{\text{e-}}$ is the activity of the electron in aqueous solution. pE reflects the ratio of electron acceptors (oxidants) to donors (reductants) in a redox couple. High values of pE correspond to strongly oxidizing systems, usually characterized by aerobic environments, whereas low values of pE reflect reducing conditions characteristic of anaerobic environments. Although the concept of pE is meaningful only under equilibrium conditions, the range of the individual values of pE does give an indication of the relative degree of equilibrium. Systems near equilibrium should have a small range of pE values while systems far from equilibrium should have a broad range (Scott and Morgan, 1990).

The redox potential (Eh) of the system is an alternative to pE that is equivalent at any specified temperature and equivalent intensity factor (Scott and Morgan, 1990)

$$E_h = E^\circ \text{ (redoxcouple)} + \frac{2.3\ RT}{nF} \log \frac{[\text{oxid}]}{[\text{red}]} \tag{4-3}$$

where E° is the standard electrode potential, R is the universal gas constant, T is the Kelvin temperature, F is the Faraday constant, and n is the number of electrons stated in the half-reaction. The activity of the oxidant and reductant are represented by [oxid] and [red], respectively.

Values of Eh are more often used when experimental data for the electrode potential (E°) for the redox couple are available, whereas pE is convenient to use when equilibrium constant data are available. The range of Eh values in aqueous systems is approximately from -0.8 to +1.2V (Bodek et al., 1988). Figure 4.2 shows theoretical Eh-pH relationships between dissolved chromium species at equilibrium (Baes and Messmer, 1977; Hem, 1977, cited by Nriagu, 1988). At total chromium concentrations below 500 mg L^{-1}, the dominant Cr(VI) species are the oxyanions $HCrO_4^{2-}$ and CrO_4^{2-} with the equilibrium concentrations being between pH dependent (Nriagu, 1988 and Calder, 1988).

$$HCrO_4^- \rightarrow CrO_4^{2-} + H^+ \tag{4-4}$$

In basic solutions above pH 6 (e.g., physiological pH), CrO_4^{2-} is the dominant species. Therefore, the biochemistry of Cr(VI) presented in this report assumes that Cr(VI) is present as the chromate anion, even in cases where the initial exposure was to the dichromate anion.

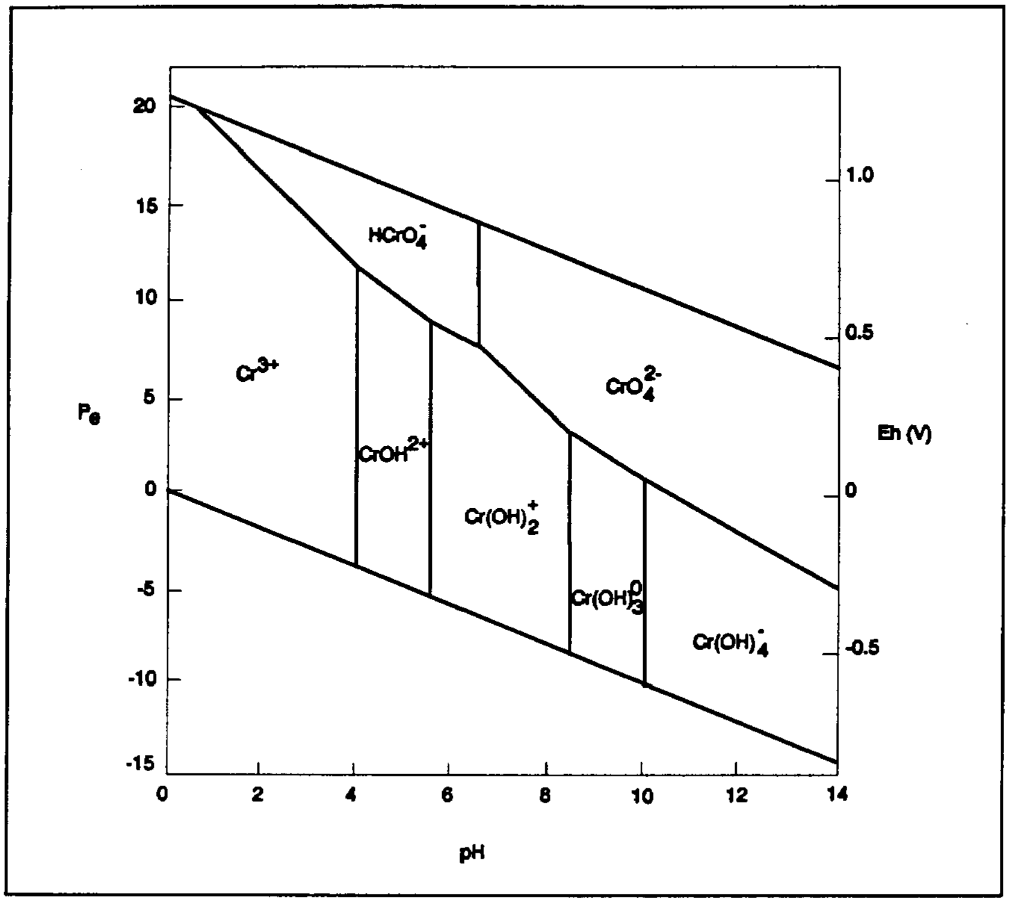


Figure 4.2 **Areas of dominance of dissolved chromium species at equilibrium in the system Cr + H_2O + O_2 at 25°C and 1 atm. (Data from Baes and Messmer; Hem, 1977)**

Whether reduction of Cr(VI) added to, or formed in, soil or water occurs depends primarily upon Cr(VI) being in a more favorable position than the usual oxygen, nitrogen, or manganese electron sinks to accept electrons from a reactive organic (or iron or sulfur) electron source (Bartlett and James, 1988). An Eh - pH balance favoring reduction of Cr(VI) means the activities of the usual electron acceptors will be low and those of the available electron donors will be high (Bartlett and James, 1988).

The rate of electron transfer between oxidizing and reducing species is important in assessing speciation of inorganic materials in the environment. However, determining redox reaction rates is complicated, requiring specific knowledge of the chemistry of the oxidant and reductant, and the reaction mechanism, as well as consideration of all possible effects of the physical and chemical properties of the reaction medium (Bodek et al., 1988).

Saleh et al. (1989) studied the kinetics of chromium transformations in the environment. This group used the environmental fate modeling concepts advanced by Burns et al. (1981) to evaluate the relative importance of different transformation and transport processes and to evaluate their experimental kinetics data. The rate constants and half-lives (presented in Sections 5.2 and 5.3) were calculated assuming first-order kinetics with respect to Cr(VI) reduction or Cr(III) oxidation. For example, in the reaction (Saleh et al., 1989):

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (4\text{-}5)$$

$$-dC/dt = KC \qquad (4\text{-}6a)$$

where C is the concentration of Cr(VI) at time t, the first-order rate constant was given by:

$$k = 2.303/t \log (C_o/C_t) \qquad (4\text{-}6b)$$

and the half-life by:

$$\tau_{1/2} = \ln 2/k \qquad (4\text{-}7)$$

The relevant half-reactions used by Saleh et al. (1989) to evaluate their experimental results are listed below:

$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$	+1.33 E°(v)	(4-8)
$C_6H_4O_2$ (quinone) $+ 2H^+ + 2e^- \leftrightarrow C_6H_4(OH)_2$	+0.669 E°(v)	(4-9)
$S + 2e^- \leftrightarrow S^{2-}$	-0.51 E°(v)	(4-10)
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.77 E°(v)	(4-11)

Where E° for a redox couple is small, the potential of the system to reduce Cr(VI) is dominated by the relative concentrations of dissolved Cr(VI) compounds and the reducing species as represented by Eq. 4-3. The major reduction processes studied by Saleh et al., (1989) are listed below.

Reduction of Cr(VI) by dihydroxyphenols

Dihydroxyphenols were used to represent organic compound such as humic or fulvic acids. Combining half reaction 4-8 as a reduction and half reaction 4-9 as an oxidation gives the following reaction:

$$Cr_2O_7^{2-} + 8H^+ + 3C_6H_4(OH)_2 \leftrightarrow 2Cr^{3+} + 3C_6H_4O_2 + 7H_2O \qquad (4\text{-}12)$$
$$\mathrm{Log}\ K_{eq} = 64$$

Reduction of Cr(VI) by sulfides

Discharge of industrial wastes, decomposition of organic matter and sulfate reduction provide dissolved sulfides (Richard and Bourg, 1991). Combining half reaction 4-8 and half reaction 4-10 as an oxidation gives the following reaction:

$$Cr_2O_7^{2-} + 3S^{2-} + 14H^+ \leftrightarrow 3S + 2Cr^{3+} + 7H_2O \qquad (4\text{-}13)$$
$$\mathrm{Log}\ K_{eq} = 187$$

Reduction of Cr(VI) by ferrous iron

Weathering of Fe(II)-containing minerals (biotite, hematite, some clays, etc.) and some industrial wastes generate dissolved Fe(II) ions (Richard and Bourg, 1991). Chromate reduction occurs in solution rather than at mineral surfaces by reaction with ferrous ions (Eary and Rai, 1989). Combining half reaction 4-8 as a reduction and half reaction 4-14 as an oxidation gives the following:

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \leftrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O \qquad (4\text{-}14)$$
$$\mathrm{Log}\ K_{eq} = 57$$

Saleh et al. (1989) achieved good agreement between the Cr(VI) transformations predicted by Eqs. 4-12 - 4-14 and the experimental values. However, Bodek et al. (1988) concluded that the best (but most tedious) approach to understanding redox properties of the aqueous environment and their possible impact on added pollutants is to consider the reaction of the pollutant (i.e., hexavalent chromium) with each of the major species present in the environment (e.g., dissolved oxygen, organics, sulfide species, and iron(II) and iron(III), in the dissolved phase, and iron(II) and iron(III), manganese(II) and manganese(IV), in the solid phase). Thus, measured concentrations of Cr(VI) and major species expected to participate in redox reactions may be needed to adequately predict the transformations of Cr(VI) for exposure assessment purposes.

4.2 Precipitation - Dissolution Reactions

In studies of environmental water quality, it is often necessary to know the solubility of a given solid and whether a solid phase can precipitate from water of a given composition. Such questions can often be resolved through consideration of the chemical equilibria between solids and aqueous solutions. The state of chemical thermodynamic equilibrium reflects two important quantities (Bodek et al., 1988):

(1) The current state of the water, with respect to its ability to dissolve or precipitate certain solids, and
(2) The expected change in concentrations of dissolved substances, if certain solid phases were to dissolve in, or precipitate from, the water.

Figure 4.3 shows a summary of the aqueous solubilities of $Cr(OH)_3$ as a function of pH as (Rai et al., 1989). There are no significant constraints on the solubility of chromate anions in water. However, solubility can significantly reduce the concentration of Cr(III) in water above pH 4 or 5 (Calder, 1988). The dominant Cr(III) species occurring in waters also depend on pH with the major reactions being (Calder, 1988):

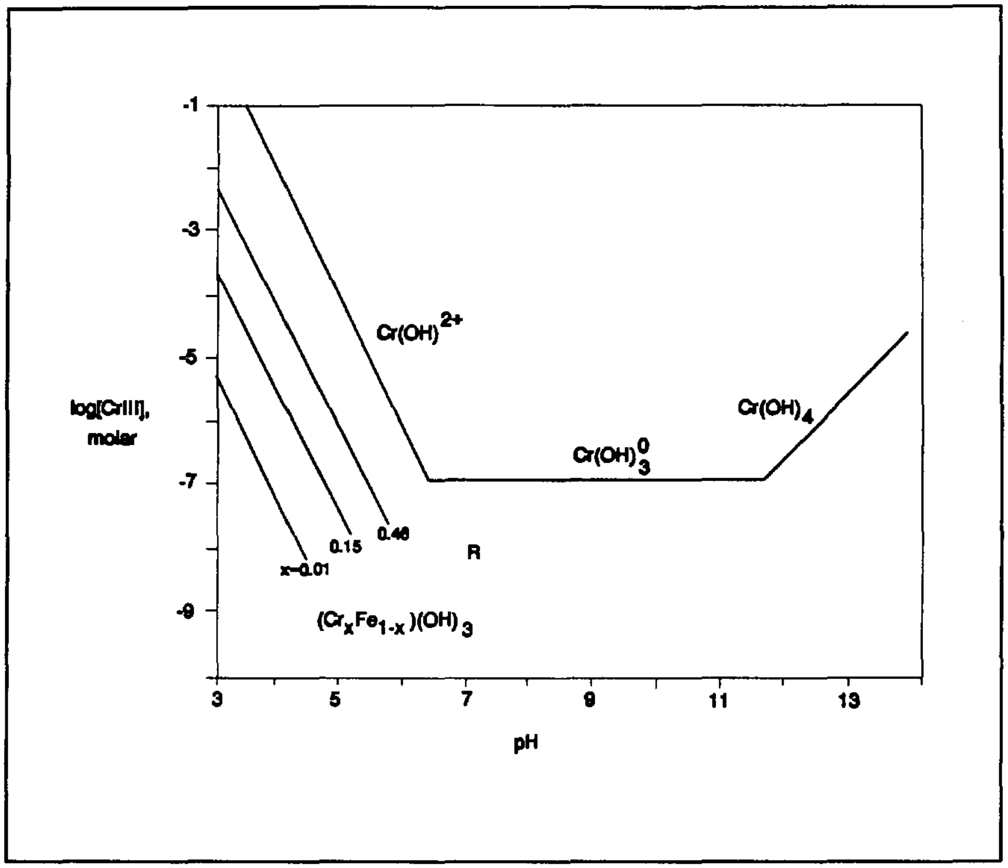


Figure 4.3 **Solubility-controlling solids of Cr(III). Solid line represents $Cr(OH)_3$. Dashed lines represent $(Cr,Fe)(OH)_3$ at different values of $Cr(OH)_3$ mole fractions (x).**

$$Cr^{3+} + H_2O \leftrightarrow CrOH^{2+} + H^+ \qquad (4\text{-}15)$$

$$CrOH^{2+} + H_2O \leftrightarrow Cr(OH)_2^+ + H^+ \qquad (4\text{-}16)$$

$$Cr(OH)_2^+ + H_2O \leftrightarrow Cr(OH)_3^\circ + H^+ \qquad (4\text{-}17)$$

$$Cr(OH)_3^\circ + H_2O \leftrightarrow Cr(OH)_4^- + H^+ \qquad (4\text{-}18)$$

The dominant species in waters between pH 6 and 8 is $Cr(OH)_2^+$. In acidic waters, $CrOH^{2+}$ and Cr^{3+} predominate and in more alkaline waters, $Cr(OH)_3^\circ$ and $Cr(OH)_4^-$ predominate (Baes and Messmer, 1977; cited by Calder, 1988). It has recently been shown that $(Cr,Fe)(OH)_3$ has an even lower solubility that $Cr(OH)_3$ and has the rapid precipitation/dissolution kinetics necessary to be an important solubility-controlling compound (Sass and Rai, 1987; cited by Rai et al., 1989). In the absence of solubility-controlling solids [e.g., $Cr(OH)_3$ and $(Cr,Fe)(OH)_3$], aqueous concentrations of Cr(VI) under acidic to slightly alkaline conditions will be primarily controlled by sorption/desorption reactions (Rai, et al., 1989).

4.3 Sorption - Desorption

An understanding of sorption and attenuation is necessary to assess the fate of inorganic compounds in the environment. Sorption refers to the removal of solute from the aqueous phase of an environmental system at the surface of the solid phase. The bioavailabilities of dissolved versus sorbed and insoluble species also differ: dissolved species are much more available to both plants and animals (Bodek et al., 1988).

Sorption of Cr(VI) onto mineral surfaces can affect its rate of reduction and also prevent its reduction altogether. Sorption of Cr(VI) occurs because dissolved anionic species (e.g., CrO_4^{2-}) are attracted to mineral surfaces that have a net electrical charge due to imperfections or substitutions in the crystal lattice or chemical dissociation reactions at the particle surface (Freeze and Cherry, 1979; cited by Calder, 1988). Chromium (VI) sorbed by mineral solids that have exposed inorganic hydroxyl groups on their surfaces can be represented by (Rai, et al., 1989):

$$\equiv OH + H^+ + CrO_4^{2-} \overset{K_{CrO4}^{2-}}{\leftrightarrow} \equiv OH_2^+\text{-}CrO_4^{2-} \tag{4-19}$$

Where $\equiv OH$ is an inorganic hydroxyl site, and $\equiv OH_2^+\text{-}CrO_4^{2-}$ is the sorbed surface complex. The equilibrium distribution is given by K_{CrO4}^{2-}. The degree of CrO_4^{2-} sorption is determined by the concentration of surface sites (i.e., mole of $\equiv OH$ sites/gram of material), the magnitude of the individual equilibrium constants, and the solution pH (Rai, et al., 1989). Sorption of Cr(VI) by the reducing surface itself may occur on organic aluminum or iron sites (Bartlett and James, 1988). The sorption of chromate on hydrous ferrous hydroxide (Dzombak and Morel, 1990) provides one example.

$$\equiv FeOH + CrO_4^{2-} + H^+ = \equiv FeCrO_4^- + H_2O \qquad (4\text{-}20)$$

As a general rule, any environmental factor affecting sorption/desorption of phosphate in soils can be considered to affect the availability of Cr(VI) in soils (Bartlett and James, 1988).

Similar to redox and precipitation reactions, the sorption of inorganic species such as Cr(VI) is highly influenced by the environmental conditions of the specific system, thus, no species-unique sorption constants can be applied to a broad range of soils. In contrast to most organic chemicals, a particular inorganic species may be highly mobile in one environment and essentially immobile in another, depending on such factors as soil chemistry, pH, redox potential, solute, and ligand concentrations in the water (Bodek et. al, 1988). Table 4-2 qualitatively summarizes the major physical and chemical properties of soils, soil water, and solutes that affect sorption and precipitation. A result of this complexity is that the extent of sorption of an inorganic pollutant cannot be initially estimated with the degree of reliability usually desired for transport modeling (Bodek, et al., 1988).

4.4 Analysis of Hexavalent Chromium in Environmental Media

It would be desirable for all analyses related to the environmental role of chromium should differentiate between Cr(VI) and Cr(III) (WHO, 1988). Current methods allow this determination in most matrices at environmental concentrations; however, identification of particular Cr(VI) species will require much research (WHO, 1988). Many of the determinations of chromium in plant and soil matrices have been analyzed by semiquantitative methods and major problems exist in the accurate measurement of low ambient chromium concentrations (i.e., nanogram/gram or ppb levels) (Cary, 1982). A further complication is the need to distinguish Cr(VI) from total chromium, and perhaps, to identify individual chromate compounds.

Table 4-2. Parameters That Affect the Sorption and Precipitation of Cr(VI)(a) in the Soil Matrix

Soil Matrix	Soil Solution
Soil Solids	
Composition	pH
Hydrous oxides (Fe, Mn, Al)	Eh
Silicates - clay content,	Ionic Strength
type of clay	Ionic Composition
Organic Material	Competing Ions
Carbonate minerals	
Specific Area	
Cation Exchange Capacity	
pH (content of basic species)	
Eh [content of redox active species, e.g., Fe(II), Mn(IV)]	
Aeration Status (saturated, unsaturated)	
Microbial Type and Population	
Temperature	

(a) From Bodek et al.(1988); does not include engineering properties.

5.0 FATE AND TRANSPORT OF HEXAVALENT CHROMIUM IN ENVIRONMENTAL MEDIA

The chemistry of Cr(VI) which is of environmental significance is often that of the chromate ion (CrO_4^{2-}) contributed from chromate compounds which may be soluble in aqueous solutions. Soluble ionic forms of Cr(VI) in soils or natural waters will persist indefinitely unless chromium is removed by (Bartlett, 1991):

- Reduction to the trivalent form;
- Sorption;
- Precipitation/Dissolution; or
- Uptake by living cells.

Thus, Cr(VI) deposited to a soil from the atmospheric may dissolve in soil water and become mobile. Some of the mobilized Cr(VI) will be sorbed, some will be reduced by both biotic and abiotic processes, and some may be leached into groundwater and runoff water (Cary, 1982). The distribution of Cr(VI) among these reservoirs is related to soil pH, organic matter, and reducing agents (Bloomfield and Pruden, 1980), as well biota such as microbes and earthworms (Coleman, 1988; Arillo and Melodia, 1991). Determining the fate of Cr(VI) is complicated by the formation of organic Cr(III) compounds which may be soluble or insoluble in soil solution (Cary, 1982). Such organic compounds are probably formed by reduction of Cr(VI) by organic matter rather than by interaction of Cr(III) with organic matter (Cary, 1982). These transformation and distribution processes are briefly discussed with respect to environmental media (air, water, soil, and biota) in the following subsections.

5.1 Air

Chromium in the atmosphere originates from a wide variety of natural and anthropogenic sources and exists in the atmosphere as an aerosol. Anthropogenic sources of chromium include not only chromium industries, but also most combustion processes

(WHO, 1988). The oxidation state of chromium emissions is not well defined quantitatively, although it can be assumed that the heat of combustion may oxidize an unknown proportion of chromium to the hexavalent state (WHO, 1988). At any particular time and location, the amount of chromium in the atmosphere depends on (Nriagu et al., 1988): (1) the intensity of the entrainment processes; (2) the proximity to the source; (3) the amount of chromium released; (4) the degree of mixing determined by meteorological factors; (5) the aging history (e.g., redox transformations); and (6) the rate of removal of the suspended particulate matter. The spatial distribution is particularly influenced by land use patterns, with urban centers generally being mild hot spots of chromium pollution (Nriagu, et al., 1988). The California Air Resources Board (1988b) suggests that two major factors must be considered in assessing the behavior of chromium in the atmosphere: (1) the fate of the chromium-bearing particulate matter; and (2) the chemical behavior of the chromium in the airborne particles (i.e., is chromium emitted in the hexavalent state converted to trivalent or vice-versa?). The fate of particles containing Cr(VI) is primarily determined by deposition processes which greatly determine the extent of the exposed population. The chemical behavior of the Cr(VI) within the particle (i.e., redox reactions) influences the concentration of Cr(VI) at the receptor. Thus, the major processes affecting the fate and transport of hexavalent chromium in the atmosphere are deposition and redox reactions.

5.1.1 Atmospheric Deposition

The mechanisms by which particles are removed from the atmosphere are by gravitational fallout (dry deposition) and by washout and rainout (wet deposition), and these processes are sensitive functions of particle size. In air, chromium compounds are present mostly in fine dust or mist particles which eventually settle over land and water via dry and wet deposition. No naturally occurring gaseous forms of chromium have been reported although they have been formed under laboratory conditions (Cary, 1982). Since hexavalent chromium compounds have characteristically low vapor pressures (except chromyl chloride which is not considered a study compound by ATSDR, 1992) and are associated with particles (Cary, 1982; Nriagu et al., 1988), the transport of hexavalent chromium in the atmosphere is dominated by the movement and deposition of chromium in the particle-bound form. Therefore, the dispersion and deposition of gaseous species need not be considered as a transport process. The transport of particulate matter in the atmosphere depends largely on particle size and density, as well as on factors such as frequency of rainfall.

5.1.1.1 Particle Size Distribution

The way in which airborne particles interact with the environment is greatly affected by particle size. For example, deposition from the atmosphere onto soil, vegetation, and other surfaces is a function of particle size and surface characteristics. The extent to which airborne particles penetrate the human respiratory system and cause visibility reduction is also determined mainly by particle size (Nriagu et al., 1988). Little information exists on the distribution of chromium as a function of size for the atmospheric aerosol (WHO, 1988). The mass median diameter of the ambient atmospheric particles containing hexavalent chromium has been estimated as approximately 1 μm (Milford and Davidson, 1985; Ondov et al., 1989). However, chromium emissions from various sources have quite different particle size distributions as indicated in Table 4-1. Particles less than 5-10 μm are typically emitted from combustion sources of chromium, or from chrome plating operations which use standard air pollution control equipment that effectively remove larger particles (CARB, 1988b). Stern (1982) gives the particle size of droplets from chromeplating industries (presumably without pollution controls) at 100 μm. Cooling towers generally emit larger particles which settle out near the source (CARB, 1988b). The particle size distribution is especially important in assessing the exposure to chromium of the general population living near these sources since the relatively small stack height in this industry may limit the long-range transport of emitted particles (Pacyna and Nriagu, 1988). The size distribution of Cr(VI)-containing particles emitted from various sources is shown in Figure 5.1 (Gafafer, 1953; Davison et al., 1974; Lee et al., 1975; Smith et al., 1979; cited by Nriagu, 1988).

Cox et al. (1985) studied the speciation of chromium in ferrochrome smelter dust emitted from an electric arc furnace and found 55% of the Cr(VI) detected in all particles concentrated in particles <0.7 μm in diameter, which was only 12% of the total particle

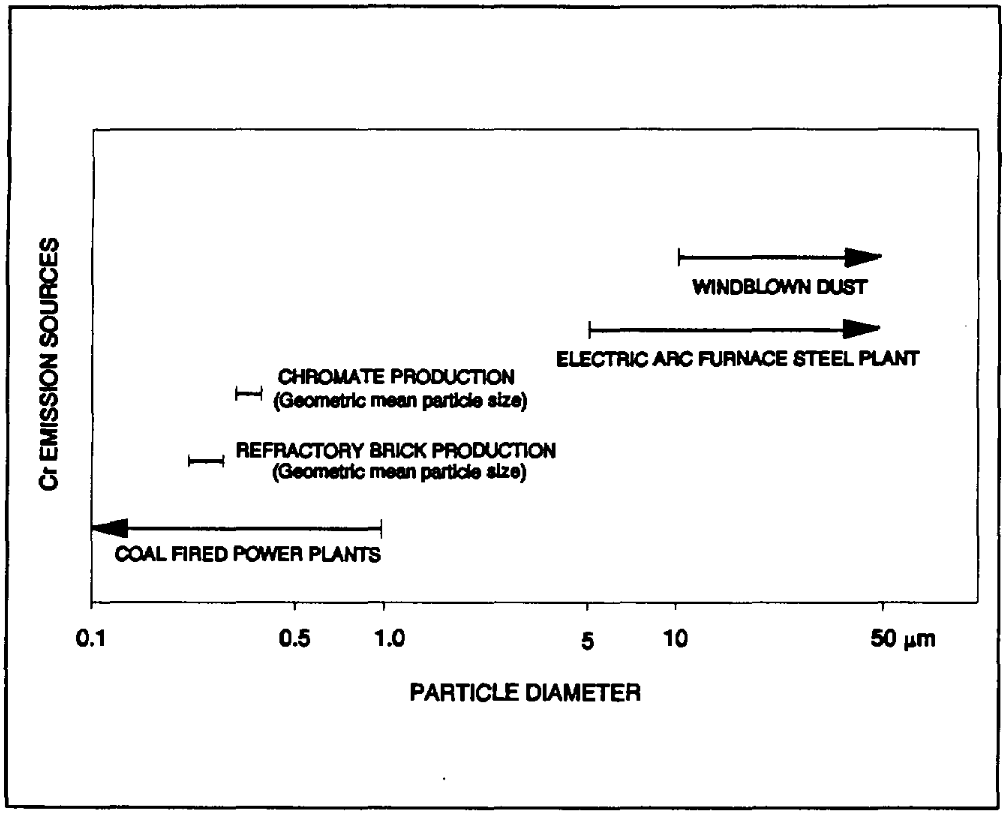


Figure 5.1 **Size distribution of Cr-containing particles emitted from various sources. (After Gafafer, 1953; Davison et al., 1974; Lee et al., 1975; Smith et al., 1979)**

mass. Thus, the extent of dry and wet deposition of Cr(VI) are sensitive functions of the source-specific particle size distribution and the concentration distribution of Cr(VI) within the particle phase for wet deposition.

5.1.1.2 Dry Deposition

Dry deposition of particles is an intermedia transport process responsible for removing pollutants from the atmosphere. The dry deposition is governed by the turbulent transfer of particulate species from the atmosphere to the earth's surface. This includes gravitational settling but excludes deposition of particles sorbed in precipitation, which is considered wet deposition. The flux of particle-bound pollutants from the atmosphere can be represented by the following equation:

$$N_a = V_d C_a^{(p)} \tag{5-1}$$

where $C_a^{(p)}$ is the mass of the pollutant in the particle phase per unit volume of air, and V_d is the overall chemical deposition velocity for particle-bound species (Cohen, 1986). The overall chemical deposition velocity is defined as:

$$V_d = \int_0^{\infty} V_d(a) F(a) da \tag{5-2}$$

where $V_d(a)$ is the deposition velocity for particle diameter *a*, and *F*(*a*) is the normalized chemical distribution such that *F(a)da* is the mass fraction of the particle-bound chemical present in particle fraction in the size range *a* to *a+da*. While for organic chemicals appropriate relations for *F*(*a*) can be derived based on vapor phase/particle partitioning (e.g., Tsai et al., 1991), such an approach is not feasible for non-volatile inorganic species. Thus, for chromium compounds, experimental data for *F*(*a*) are essential.

The dry deposition velocity can be estimated using a variety of prediction methods. For example, for dry deposition of particles onto a vegetation canopy, the model of Slinn (1982) can be utilized to estimate the dry deposition velocity as a function of particle size. Also, the simple correlations proposed by Whicker and Kirchner (1987), Baes et al. (1984) and Strenge and Napier (1989) can be used to estimate the dry deposition velocity as a function of the type and density (i.e., kg/m^2) of the vegetative cover. Dry deposition onto a water surface can be estimated using the model of Williams (1982). The application of the above models in screening-level multimedia transport and fate models is discussed by Cohen (1986), Cohen and Clay (1993) and Clay (1992) and Chetty (1991).

It has been suggested (U.S. EPA, 1980b; cited by CARB, 1988b; ATSDR, 1992) that chromium-containing particles can typically remain airborne for up to 7-10 days. Thus, chromium-containing particles may remain airborne long enough to allow long distance transport by wind (Hana et al., 1982; CARB, 1988b). Therefore, the question of possible atmospheric transformation of Cr(VI) is important as discussed in Section 5.1.2.

5.1.1.3 Wet Deposition

Both rain and snow can remove chromium from air, however snowfall is not considered a significant removal process in most California urban environments. In order to describe the mass balance of chromium in the environment, the transport parameters associated with rain scavenging of atmospheric particles must be obtained. The effects of rain scavenging of particles can be considered from two different perspectives. One perspective is that rain scavenging provides a natural method of removing contaminants from the atmosphere. The other perspective is that rain containing the scavenged particle may also be considered a source of contamination for other environmental media (e.g., water, soil, vegetation).

The removal of particle-bound pollutants by rain scavenging can be determined from a chemical mass balance on the spectrum of raindrops as they travel to the ground. The chemical mass balance on a single rain drop is given by (Tsai et al., 1991)

$$\frac{d\left(C_w^{(p)}\,\frac{\pi D_d^3}{6}\right)}{d\tau} = \int_0^\infty E(a,D_d)\left(\frac{\pi D_d^2 L_c}{4L_c/V_t}\right) C_a^{(p)} F(a)\,da \tag{5-3}$$

where

$C_w^{(p)}$ = chemical concentration in rain water (ng/m^3 of water)

$C_a^{(p)}$ = total chemical concentration in the particle phase in the atmosphere (ng/m^3 of air)

$E(a,D_d)$ = collection efficiency of a particle of diameter a by a raindrop D_d

$F(a)$ = the mass fraction distribution of the chemical in the particle phase, defined such that $F(a)da$ is the mass fraction of the chemical within the size fraction a to $a+da$

L_c = height of cloud base (m)

τ = travel time of a raindrop from the cloud base (hr.), given as $\tau = L_c/V_t$

V_t = the raindrop terminal velocity m/hr defined in Eq. 5-4

$$V_t(D_d) = \begin{cases} 40.55\ D_d, & D_d \leq 0.001 \text{ m} \\ 130(D_d)^{1/2}, & D_d > 0.001 \text{ m} \end{cases} \tag{5-4}$$

where D_d is the diameter of a raindrop (centimeters).

Assuming a constant radius of the raindrop during travel from the cloud base to the ground, Eq. 5-4 can be integrated between $\tau = 0$ and $\tau = L_c/V_t$ (i.e., time to reach the ground level) over the range of particle and raindrop sizes. The resulting expression for the average concentration of the chemical in rainwater (e.g., ng/m^3 water), $\overline{C}_{wf}^{(p)}$, is given as:

$$\overline{C}_{wf}^{(p)} = \overline{C}_{wo}^{(p)} + \frac{1}{V_r} \int_0^\infty \left[\frac{3}{2} C_a^{(p)} \left(\frac{L_c}{D} \right) \int_0^\infty E(a,D_d) F(a) da \right] \frac{\pi D_d^3}{6} N_d dD_d \tag{5-5}$$

in which V_r is the volume of rain per unit volume of air at ground level given by

$$V_r = \int_0^\infty \frac{\pi D_d^3}{6} N_d dD_d \tag{5-6}$$

in which N_d is the raindrop size distribution such that $N_d dD_d$ is the number of raindrops per unit volume of air in the size range between D_d and $D_d + dD_d$. Finally, $\overline{C}_{wo}^{(p)}$ denotes the average concentration of the particle-bound chemical in rainwater at the cloud height (i.e., the initial rainwater concentrations, e.g., ng/m^3). The collision efficiency $E(a,D_d)$ and raindrop size distribution can be evaluated as described by Tsai et al. (1991). Theoretical or empirical methods to determine *F(a)* for Cr(VI) are not available. Therefore, for Cr(VI), the mass fraction of the chemical in the aerosol phase must be obtained from site-specific measurements. It is important to note that Eq. 5-5 assumes the particle phase component of the chemical is non-reactive in the raindrop. However, given the slight acidity of rainwater and the likely presence of oxidizable species, this assumption may be too restrictive for hexavalent chromium which could be reduced under these conditions. Thus, Eq. 5-5 provides an upper-limit estimate of the concentration of Cr(VI) in rainwater. The corresponding "washout coefficient" can be obtained by dividing Eq. 5-5 by the concentration of Cr(VI) in the air phase, i.e., $C_a^{(p)}$.

5.1.2 Atmospheric Chemistry of Hexavalent Chromium

The extent to which hexavalent chromium may be reduced in the atmosphere is of a significant concern. Grohse et al. (1988) studied the fate of hexavalent chromium in the atmosphere using reaction chamber and field studies. The general conditions under which Cr(VI) may undergo atmospheric conversion are as follows (Grohse et al., 1988):

(1) In the presence of "acidic" species, e.g., HNO_3, Cr(VI) will react with "oxidizable" species such as aldehydes, unsaturated hydrocarbons, substituted aromatic compounds, and inorganic species such as V^+, V^{2+}, and Fe^{2+}.

(2) Measurements of ambient levels of Cr(VI) demonstrated an average half life [50% conversion to Cr(III)] of 13 hours when exposed to simulated atmospheric reactants. Assuming wind speeds greater than one mile per hour, one might expect the vast majority of Cr(VI) collected within a few miles of a Cr(VI) source to remain in the hexavalent state.

(3) Based on the series of chamber tests, no conclusion was reached regarding the effect of humidity on the reduction of Cr(VI). For most of the tests, the relative humidity was fixed between 20 to 30 percent.

(4) Chamber tests were not run to isolate photochemical influence in the conversion of Cr(VI) species. However, field reaction studies conducted in a manner similar to chamber tests showed that conversion rates at night were indistinguishable from those found in the daylight hours.

(5) The reaction chamber tests tend to be consistent with Cr(VI) behavior in solution. One possible explanation may be the formation of fine aerosols (droplets) that simulate solution chemistry.

In the field studies (Grohse et al., 1988), samples obtained from a chrome plating facility contained measurable amounts of Cr(VI) at a distance of at least 0.5 km from the source. Reduction of Cr(VI) at distances >0.5 km could not be measured due to lower levels of Cr(VI). Based on this study, the average reaction half-life for Cr(VI) is 16 hours from field studies and 13 hours from laboratory studies (Grohse et al., 1988). The reaction half-lives determined by Grohse et al. (1988) are considered more reliable than the atmospheric half-life of 4.8 days cited by U.S. EPA, 1987 (U.S. EPA, 1984a) because the U.S. EPA (1987) reference did not specify whether the half-life pertained to reaction or transport, or to a combination of both processes.

Limited tests in conjunction with a literature review indicate that conversion of Cr(III) to Cr(VI) is not a likely chemical pathway (Grohse et al., 1988). Oxidation of Cr(III) to Cr(VI) could occur in the atmosphere if sufficient concentration of MnO_2 was present. However, MnO_2 also acts as an oxidizing agent with NO_2, SO_2 and other reducing agents likely to be present in the atmosphere in much higher concentrations than Cr(III) compounds. Therefore, the above findings suggest that oxidation of Cr(III) to Cr(VI) is not likely to occur to any significant degree.

5.2 Water

Bartlett (1991) described the major processes in the chromium cycle in natural waters and soil as occurring between Cr(III) and Cr(VI) conversions, with lesser processes involving oxidation and mobilization of chromium (III). The uncertainties are mainly in the understanding of the factors that control these processes (Bartlett, 1991). Naturally occurring chromium in water originates from mineral weathering processes, soluble organic chromium (III), sediment load, and precipitation (Cary, 1982). Chromium (VI) from atmospheric deposition of anthropogenic emissions may also be present. Most of the particulate chromium in water settles to the bottom, however, a small amount may dissolve and remain soluble for years before settling out. The fraction of chromium present in the hexavalent state forms a number of oxyacids or anions. As presented in Section 4.2, the two primary dissolved species of Cr(VI) are the hydrochromate ($HCrO_4^-$) and chromate (CrO_4^{2-}) (Saleh et al., 1989; Baes and Messmer, 1977). These anionic species are quite soluble and thus the distribution of Cr(VI) in waters is controlled by the solubility of the specific Cr(VI) compound and subsequent redox reactions (Richard and Bourg, 1991), rather than precipitation or sorption processes. Although exposure to hexavalent chromium via ocean water is not considered in the CAPCOA model (1992), it is interesting to note that chromium concentrations in seawater are dominated by the hexavalent form, probably due to the generally oxidizing conditions of the ocean and low suspended particulate concentration (except in estuaries) (Mayer, 1988).

To evaluate the fate of hexavalent chromium in water, the following factors must be considered (Shupack, 1991):

- The thermodynamic stability of each oxidation state as a function of pH.

- The kinds of species, i.e., anions, cations, and polymeric ions that can form for each oxidation state as a function of environmental conditions such as pH, temperature, and the presence of other reductants and oxidants.

Reduction of Cr(VI) can occur under a variety of conditions, even in the presence of oxygen, if a suitable electron donor is available (Anderson, et al., 1992). The most important naturally occurring reducing agents in waters (in order of decreasing reducing strength) are organic substances, hydrogen sulfide, sulfur, iron sulfide, ammonium and nitrite (excluding kinetic considerations) (Bodek et al., 1988). Other potential reducing agents include aqueous Fe(II) and Fe(II)-containing minerals (e.g., glaucinite, biotite, chlorite, and magnetite) (Eary and Rai, 1989; cited by Anderson et al., 1992). These species may favor reactions with trace-level pollutants rather than major species. Due to kinetic limitations, local inhomogeneity, and local catalytic effects of organisms, redox equilibrium conditions may not be attained in many environmental systems, and several of the above species may coexist (Bodek et al., 1988).

5.2.1 Surface Water

Redox reactions are highly significant in the environmental chemistry of natural waters and wastewater. Saleh et al. (1989) conducted experiments to study reduction of Cr(VI) in experimental waters, representing a broad range of characteristics, in the presence of typical reducing agents (i.e., S^{2-}, Fe^{2+}, and the organic matrix represented by dihydroxyphenol). The results indicated thermodynamic stability of dissolved Cr(VI) under aerobic conditions. Natural and reference waters. Oxidation and reduction rates were evaluated in single phase water systems and two-phase water-solid systems. The major findings of Saleh et al. (1989) for water-phase systems are listed in Table 5-1 with the results for the water-solid systems presented in Section 5.3. Some of the investigated reactions, such as the reduction of Cr(VI) to Cr(III) by S^{2-} or Fe^{2+} ions under anaerobic conditions, were instantaneous.

Earlier researchers (Schroeder and Lee, 1975; cited by Richard and Bourg, 1989) reported complete reduction of Cr(VI) within one day, in the presence of dissolved sulfides. No reduction of Cr(VI) was measured in several experimental waters without the presence of added reducing agents (Saleh et al., 1989). Although the aqueous chemistry of chromium is complicated, Saleh et al., (1989) were successful in predicting the overall transport and

Table 5-1. Water-phase Reduction of Cr(VI) [a]

Experiment	**Important Findings**
Cr(VI) spiked to five waters under aerobic conditions for 41 days	No measurable reduction
Cr(VI) plus 6.4 mg L^{-1} S^{2-} in rainwater and hard water under aerobic and anaerobic conditions for 21 and 78 days, respectively	Air interferes with reduction of Cr(VI) by S^{2-}; anaerobic reduction was instantaneous and irreversible
Cr(VI) plus 16 mg L^{-1} Fe^{2+} in rainwater and hard water under aerobic and anaerobic conditions for 13 and 23 days, respectively	Reduction was instantaneous but reversible; oxidation $\tau_{1/2}$ was 99 to 173 days with coefficient of variation of 5.7 - 5.9%
Cr(VI) spiked to secondary municipal effluent under aerobic conditions for 41 days	No measurable reduction

(a) Source: Saleh et al. (1989); reaction $\tau_{1/2}$ calculated assuming first-order kinetics with respect to Cr(VI) reduction or Cr(III) oxidation.

transformation of Cr(VI) in microcosm and column experiments using kinetics data derived from a simplified laboratory experiment, the Eh-pH data, and the aquatic system characteristics. However, the most reliable characterization of the redox status of a natural water is still considered to be a complete chemical analysis of all redox-active species (Scott and Morgan, 1990; Bodek et al., 1988).

In many waters, there is a possibility of oxidation of Cr(III) to Cr(VI). The typical oxidizing agents in water (in order of decreasing oxidizing strength) are oxygen, nitrate, nitrite, ferric hydroxide, ferric phosphate, sulfate, sulfur, carbon dioxide and bicarbonate. Reactions, such as the oxidation of Cr(III) by MnO_2, are much slower and exhibit kinetic controls. Dissolved oxygen by itself did not induce measurable oxidation of Cr(III), spiked into experimental waters, even after 128 days (Saleh et al., 1989). Slow oxidation of Cr(III) to Cr(VI) was only noted in one of the natural waters and sediments with half-lives ranging from 2 to 9 years. In all cases, the extent of oxidation of Cr(III) did not exceed 15% of the initial Cr(III) present. Schroeder and Lee (1975) have also shown in simulated natural water systems that Cr(III) can be oxidized by manganese dioxide and slowly by oxygen. However, the oxidation of Cr(III) can be inhibited by competing substances in natural water (Cary, 1992).

5.2.2 Groundwater

Groundwater contamination by Cr(VI) is a problem in industrial areas where Cr(VI) containing wastes have leaked from surface impoundments or lagoons (Calder, 1988), and could conceivably pose an exposure pathway near facilities with high emissions that are located on sandy soils with low organic content. Leaching processes have not been well characterized, but identification of Cr(VI) in shallow sand and gravel aquifers is evidence that leaching occurs (Bartlett and James, 1988; Calder, 1988). The concentration and mobility of chromium in groundwater are strongly dependent on its speciation which, in turn, is determined by pE and pH conditions. Cr(VI) predominates under oxidizing conditions generally found within shallow aquifers within a few meters of the atmosphere via the unsaturated zone (Calder, 1988). In deeper aquifers, no replenishment of oxygen consumed by hydrochemical and biochemical reactions occurs and reducing conditions develop (Calder, 1988).

Evidence from natural-gradient tracer tests (Anderson, et al., 1992) indicates that significant reduction of Cr(VI) occurred under the mildly reducing conditions (elevated manganese but low iron concentrations) of a sewage contaminated sandy aquifer. Reduction of Cr(VI) by organics was dependent on both the type and amount of organic material. When Cr(VI) is transported by groundwater, it may be precipitated as Cr(III) if the groundwater enters a low redox zone caused by organics, Fe(II), or dissolved sulfides (Anderson et al., 1992; Calder, 1988). In field and laboratory studies, Cr(VI) movement has been found to be unretarded or only slightly retarded by adsorption to aquifer materials (Calder, 1988). No reaction half-life for Cr(VI) in groundwater was found in the literature.

5.3 Soil and Sediment

The composition of soil is influenced by the composition of the parent rock from which it is formed. Thus, the background concentrations of chromium varies greatly (Cary 1982). Elemental chromium is not found in nature. The most important naturally occurring chromium mineral is chromite ($FeO \cdot Cr_2O_3$). Most of the chromium in soil is water-insoluble or bound to the soil (Bartlett, 1991). As chromium is weathered from minerals, most will initially be present in the trivalent state which may be adsorbed on other metal hydroxides and is not very available to plants (Cary et al., 1977b).

Chromium may exist naturally in the plus VI oxidation state, but its presence in the environment is almost always the result of human activities (WHO, 1988). Hexavalent chromium is relatively stable and mobile in soils that are sandy or have low organic content (Bloomfield and Pruden, 1980; Frissel et al., 1975; cited by Cary, 1982). Naturally occurring chromates are rare and found only in highly oxidizing environments (Richard and Bourg, 1991). They include the minerals (Nriagu, 1988): tarapacaite - $K_2[CrO_4]$; lopezite - $K_2[Cr_2O_7]$; chromatite - $Ca[CrO_4]$; crocoite - $Pb[CrO_4]$; phoenicochroite - $Pb_2[CrO_4]O$; santanaite - $Pb_{11}[CrO_4]O_{12}$; iranite - $Pb[CrO_4] \cdot H_2O$; vauquelinite - $Pb_2Cu[CrO_4][PO_4](OH)$; beresovite - $Pb_6[CrO_4]_3CO_3]O_2$; dietzeite - $Ca_2[IO_3]_2[CrO_4]$; fornacite - $(Pb,Cu)_3[(Cr,As)O_4]_2(OH)$; hemihedrite - $ZnF_2Pb_{10}[CrO_4]_6[SiO_4]_2$; and embreyite $Pb_5[CrO_4]_2[PO_4]_2 \cdot H_2O$.

The major processes controlling the fate and transport of Cr(VI) in soil are redox reactions, sorption, and resuspension of particles (precipitation reactions were considered as primarily water phase reactions in Section 5.2).

5.3.1 Redox Reactions in Soil and Sediment

The reduction of Cr(VI) to Cr(III) by soil carbon compounds and the oxidation of Cr(III) to Cr(VI) by manganese oxides and are both thermodynamically spontaneous reactions (Bartlett, 1991). Some of the Cr(VI) added to an aerobic soil from atmospheric deposition will be reduced, and some of the Cr(III) added to the same soil will oxidize (Bartlett, 1991). High concentrations of Cr(VI) may quickly exhaust the readily available reducing power of the matrix and excess Cr(VI), the thermodynamically stable form in air, may persist for years in soils. The marvel of the chromium cycle in soil is that oxidation and reduction can take place at the same time; soils that are good oxidizers are also good reducers (Bartlett, 1991). While these observations appear contradictory, they reflect the complexity of predicting the fate of Cr(VI) in soils.

Bloomfield and Pruden (1980) re-investigated earlier claims that Cr(VI) is readily reduced to Cr(III) under normal soil conditions and found that the analytical methods used in previous investigations (Bartlett and Kimble, 1976) were unreliable because the soil extracts would have contained organic matter capable of reducing Cr(VI). Bloomfield and Pruden (1980) found the reduction of Cr(VI) in soil of normal pH was not particularly rapid under aerobic conditions. Amacher and Baker (1982; cited by Bartlett and James, 1988) found the kinetics of Cr(VI) to be straight forward and simple first order reaction. They measured a reduction half-life of 55 days from addition of Cr(VI) to Haegerstown loam at 26° C and pH 5.0. Reduction of Cr(VI) by fulvic acids was slow but increased when the temperature was raised (Amacher and Baker, 1982; cited by Bartlett and James, 1988). Adding Cr(VI) to a soil kept moist and aerated until the organic matter has reached a steady state of slow oxidation (Bartlett, 1986) will result in extremely slow reduction of Cr(VI), even if the soil is quite acid. Light may bring about photooxidation of soil organic matter accompanied by reduction of Cr(VI) (Bartlett, unpublished data; cited by Bartlett, 1991).

Under anaerobic conditions, the reducing effect was quite large when the soil contained undecomposed plant material (Bloomfield and Pruden, 1980). The same study found that the efficiency of soils in reducing Cr(VI) increased with decreasing pH. Subsoil did not fit the same sequence as the topsoils, tending to reduce less and sorb more Cr(VI) than topsoil of the same pH. Under anaerobic conditions, Cr(VI) was extensively reduced at pH 6.65 in the presence of 0.5% dried plant matter, but the soil alone was only slightly more effective than under aerobic conditions.

Table 5-2 summarizes the kinetics of redox transformations characteristic of sediment systems as studied by Saleh et al. (1989). This group found the reduction of Cr(VI) by S^{2-} or Fe^{2+} ions instantaneous under anaerobic conditions. The reduction of Cr(VI) by organics in sediments was much slower and depended on both the type and amount of organic material (Saleh et al., 1989).

Under extreme conditions weathering may be accelerated by oxidation of Cr(III) to Cr(VI). Because the redox potential of the Cr(VI)/Cr(III) couple is so high (Eq. 4-8), only a few oxidants present in natural systems (i.e., dissolved oxygen, MnO_2, and reduced carbon) are capable of oxidizing Cr(III) to Cr(VI). Oxidation of Cr(III) by dissolved oxygen has been found to be very slow (Rai, et al., 1989) which leaves MnO_2 as the most likely oxidant of Cr(III) in the environment. Thus, if soluble Cr(III) is added to an "average" soil, a portion of the soluble Cr(III) will become immediately oxidized by manganese oxides to Cr(VI) (Cary, 1982). The rest of the Cr(III) may remain reduced for long periods of time, even in the presence of electron accepting manganese oxides. However, this less available Cr(III) can be mobilized by low molecular weight organic complexers and then oxidized where redox conditions are optimal. Addition of organic residues to soils containing high levels of oxidized manganese will result in formation of unstable Mn(III) organic complexes that not only temporarily prevent Cr(III) oxidation but also catalyze the reduction of Cr(VI). (Bartlett and James, 1988).

Table 5-2. Water-Solid-Phases Reduction of Cr(VI)(a)

Experiment (Type)	Important Findings
(Batch)	
Cr(VI) in 10% montmorillinite clay or natural soil with lake water, rainwater, and hard water under aerobic and anaerobic conditions for 14 days	No measurable reduction and/or sorption
Cr(VI) in lake water plus 10% sediment(b) under aerobic and anaerobic conditions for 7 days	Aerobic reduction, $\tau_{1/2}$ was 15 min; Anaerobic reduction, $\tau_{1/2}$ was instantaneous
Cr(VI) in lake water plus 1% sediment(b) under aerobic and anaerobic conditions for 71 days	Aerobic reduction appeared to be a two-step process: reduction $\tau_{1/2}(1)$ was 35 days, reduction $\tau_{1/2}(2)$ was 231 days; Anaerobic reduction $\tau_{1/2}$ instantaneous. Aerobic oxidation $\tau_{1/2}$ was 2.63 years
Cr(VI) in lake water plus 1% natural soil(c) under aerobic and anaerobic conditions for 24 days	No measurable reduction and/or sorption
Cr(VI) in lake water plus 1% potting soil(d) under aerobic and anaerobic conditions for 10 days	Aerobic reduction $\tau_{1/2}$ was 11.2 days; Anaerobic reduction $\tau_{1/2}$ was 21.5 days
Cr(VI) in lake water plus 1% garden soil(e) or Trinity River sediment(f) or Mississippi River sediment(g) under aerobic and anaerobic conditions for 10 days	No measurable aerobic reduction; Anaerobic reduction was: Garden soil(e) $\tau_{1/2}$ = 4 days, Trinity River sediment(f) $\tau_{1/2}$ = 6 days, Miss. River sediment(g) $\tau_{1/2}$ = 53 days
Cr(VI) in rainwater plus 1% garden soil(e) or natural soil(c) under anaerobic conditions for 14 days	Garden soil(e), $\tau_{1/2}$ was 2.2 days Natural soil(c), $\tau_{1/2}$ was 2.2 days

Table 5-2. Water-Solid-Phases Reduction of Cr(VI)[a] *(Continued)*

Experiment (Type)	Important Findings
(Microcosm)	
Lake water with 1% sediment[b] under aerobic conditions for 47 days, uncovered	Apparent equilibrium in 20 days, reduction, $\tau_{1/2}$ was 33 days
Lake water with 1.2% sediment[b] under anaerobic conditions for 95 days, covered	Apparent equilibrium in 52 days, reduction, $\tau_{1/2}$ was 31.5 days
Hardwater with 2% Mississippi River sediment[g] under aerobic conditions for 81 days, covered	Apparent equilibrium in 55 days, reduction, $\tau_{1/2}$ was 34.7 days
Hardwater with 3% Trinity River sediment[f] under aerobic conditions for 81 days, covered	Apparent equilibrium in 45 days, reduction, $\tau_{1/2}$ was 140 days

(a) Source: Saleh et al. (1989); reaction $\tau_{1/2}$ calculated assuming first-order kinetics with respect to Cr(VI) reduction or Cr(III) oxidation.
(b) Cross Lake sediment: 0.99 - 1.01% organic carbon in sediment determined on dry weight basis.
(c) Natural soil: 0.72% organic carbon in sediment determined on dry weight basis.
(d) Potting soil: 12.35 - 13.67% organic carbon in sediment determined on dry weight basis.
(e) Garden soil: 2.71 - 2.99% organic carbon in sediment determined on dry weight basis.
(f) Trinity River: 0.23 - 0.25% organic carbon in sediment determined on dry weight basis.
(g) Mississippi River: 0.77 - 0.78% organic carbon in sediment determined on dry weight basis.

Since it is not possible to predict how chromium compounds will behave in soil until the soil environment has been adequately characterized (Gochfeld and Whitmer, 1991), Bartlett and James (1988) suggest the following three tests for determining the reducing capacities of soils and the fate of Cr(VI) in these soils:

(1) **Total Cr(VI) Reducing Capacity.** Use the Walkley-Black (1934) soil organic matter determination in which carbon oxidizable by $K_2Cr_2O_7$ is measured by titrating the Cr(VI) not reduced by a soil sample (in suspension with concentrated H_2SO_4) with $Fe(NH_4)_2(SO_4)_2$.

(2) **Available Reducing Capacity.** Shake 2.5 cm^3 of moist soil 18 hours with 25 mL of 0.1 to 10mM chromium as $K_2Cr_2O_7$ in 10mM H_3PO_4, filter or centrifuge, and determine Cr(VI) not reduced in the extract by the s-diphenylcarbazide method.

(3) **Reducing Intensity.** The procedure is the same as that used in (2) above except that 10mM KH_2PO_4 should be used in the matrix solution in place of H_3PO_4.

The results from these simple analytical tests could be useful in determining the redox properties of soil within the risk assessment zone of impact and refining exposure assessment estimates resulting from dermal, soil ingestion, plant ingestion, and resuspension pathways.

5.3.2 Sorption/Desorption

Soil pH will determine both the speciation of Cr(VI) and the charge characteristic of the colloidal surface with which it reacts. Above pH 6.4, $HCrO_4^-$ dissociates to CrO_4^{2-} as the dominant form of Cr(VI) in dilute aqueous systems (Deltombe et al., 1966; cited by Bartlett and James, 1988) which may be sorbed in a similar fashion as SO_4^{2-} and HPO_4^{2-}. Soil pH also affects the quantities of positive and negative charges on soil colloids (MacKenzie, 1977; Parfitt, 1978; cited by Bartlett and James, 1988). Thus, binding of Cr(VI) species in soils depends on soil mineralogy and soil pH (Bartlett and James, 1988).

James and Bartlett (1983) found indications that Cr(VI) was protected from reduction by sorption to amorphous aluminum, iron oxides, and organic complexes present in A and B horizons of several northern acid soils. However, more highly weathered southern soils adsorbed more Cr(VI) than the less weathered northern soil, but the southern soils did not bind Cr(VI) in such a way to prevent its reduction (James and Bartlett, 1983). Since both reduction and sorption can occur simultaneously in many soils, it is not always possible to assign the cause of Cr(VI) disappearance as being caused by reduction or sorption (Bartlett, 1991).

5.3.3 Resuspension

Particle induction to the atmosphere from the soil environment due to wind and mechanical erosion could present a significant exposure via the inhalation pathway. For particles <50 μm, the resuspension process is induced by both mechanical and wind disturbances which provide sufficient energy to overcome gravitational forces and allow particles to be dispersed by the wind (Clay, 1992). Since resuspended dusts contain particles less than 10μm (i.e., PM10), such particles are respirable and may reach the lower respiratory tract.

The rate of resuspension of particles due to the wind action can be estimated by the approach described by Cowherd et al. (1988). The procedure is based on characterizing the surfaces from which particles may be resuspended into two categories: (1) "limited reservoirs' characterized by a non-homogeneous surface (e.g., a mixture of gravel, sporadic vegetative cover) with a threshold friction velocity; and (2) "unlimited reservoirs" characterized by a uniform surface (e.g., agricultural soil) with a low threshold friction velocity. Specific procedures for incorporating the estimates of resuspension rates of particle-bound pollutants into multimedia models, based on the U.S. EPA approach (Cowherd et al., 1988) can be developed as discussed by Clay (1992).

5.4 Uptake By Biota

Determining the biological uptake and subsequent bioconcentration of hexavalent chromium is complicated by the various forms of chromium compounds initially administered and ultimately determined in the organism. There is much evidence to show that Cr(VI) can be taken up by biota. Unfortunately, total chromium rather than Cr(VI) concentrations were overwhelmingly determined in biota. Thus, bioconcentration factors and transfer coefficients for Cr(VI) are largely unavailable. A typical example is the widely cited bioconcentration studies performed by Calamari et al. (1982; cited in the SCAQMD guidance document, 1988) in which rainbow trout were exposed to Cr(VI) as $K_2Cr_2O_7$ but total chromium concentrations were measured in the fish. Given the propensity of Cr(VI) to be reduced by biological systems (Arillo and Melodia, 1991), the conservative assumption that all chromium present in the fish is present in the hexavalent form and may be bioaccumulated as such is not valid. Thus, human exposure to Cr(VI) by ingesting biota is not considered a significant exposure pathway, except possibly in the case of direct consumption of plants. The biological uptake of Cr(VI) and subsequent reduction processes are discussed in the following sections.

5.4.1 Accumulation in Aquatic Organisms

No bioconcentration factors for chromium as Cr(VI) in fish were found in the literature. The studies described below pertain to uptake of Cr(VI) or total chromium from the environment but the form of chromium within the organism was not established. Thus, the use of total chromium bioconcentration factors for Cr(VI) may be inappropriate. Fish do not accumulate chromium from water into their bodies to any great extent. Fish muscle has been found to have very little capacity for accumulating chromium. A large number of accumulation studies have been done on rainbow trout (*Salmo gairdneri*) (Holdway, 1988). Bioconcentration factors near unity were calculated after 10 days of exposure to chromium (Fromm and Stokes, 1962; cited by Holdway, 1988). The highest BCF found for rainbow trout was about 3 (Calamari et al., 1982). Bioconcentration factors approaching 10 have been found in other organs (Holdway, 1988). The only exceptions to very low bioconcentration factors appear to be direct chromium uptake in bottom dwelling fish via the diet or gills from contaminated sediments (Holdway, 1988). In the most extreme example, brown bullhead (*Ictalurus nebulosus*) concentrated chromium in liver and muscle tissue 1,822 to 2,622 times the river-water concentration, but below the sediment concentration (Reisinger, 1979; cited by Holdway, 1988). In bottom-feeder bivalves, such as the oyster (*Crassostrea virginica*), blue mussel (*Mytilus edulis*), and soft shell clam (*Mya arenaria*), the BCFs values for Cr(III) and Cr(VI) may range from 86 to 192 (U.S. EPA, 1980a; U.S. EPA, 1984b; Fishbein, 1981; Schmidt and Andren, 1984; cited by ATSDR, 1992). Table 5-3 summarizes bioconcentration factors for total chromium in aquatic organisms. Bioconcentration factors determined for total chromium has been applied to Cr(VI) in some multimedia models although it is unlikely that Cr(VI) may bioaccumulate.

The assertion that chromium is ingested by fish with food was proposed by Elwood et al., (1980; cited by Loutit et al., 1988) who stated "it is possible that food is probably a more significant source of chromium than water." However, for chromium in the hexavalent form, several researchers have found that for fish, dissolved Cr(VI) passes readily through the gill membrane (Knoll and Fromm, 1960; Buhler et al., 1977; cited by Holdway, 1988) and rapidly accumulates in other organs (Buhler et al.,. 1977; cited by Holdway, 1988). Other researchers (Arillo and Melodia, 1990, cited by Arillo and Melodia, 1991) have shown that fish skin mucus contains molecules (probably protein-bound sulfhydryl groups) capable of reducing Cr(VI) nonenzymatically.

The literature on chromium bioconcentration suggests that Cr(VI) is not expected to biomagnify in the aquatic food chain. Whittle et al., (1977; cited by Holdway, 1988) stated that higher tropic levels contain reduced levels of chromium. This statement has been supported by several studies which also found decreasing concentrations of chromium along the food chain (Holdway, 1988). When Cr(VI) is intracellularly sequestered and converted to Cr(III), the metal is less easily absorbed by predators, and thus can hardly move through the food chain (Arillo and Melodia, 1991) as either Cr(III) or Cr(VI).

Table 5-3. Bioconcentration Factors for Total Chromium

Organism	BCF	Reference	Source Cited
Rainbow Trout:			
Muscle	~1 3[(a)]	Holdway, 1988; Calamari et al., 1982	Fromm and Stokes, 1962; Calamari et al., 1982
Organs	<10	Holdway, 1988	Fromm and Stokes, 1962
Bottom Dwellers:			
Brown Bullhead	1822-2622	Holdway, 1988	Reisinger, 1979
Oyster, Blue Mussell, Softshell Clam	86-192[(a)]	ATSDR, 1992	U.S. EPA, 1980a; U.S. EPA, 1984; Fishbein, 1981; Schmidt and Andren, 1984

(a) Initial exposure was to Cr(VI) but only total chromium was determined in the organism.

5.4.2 Accumulation in Plants

As chromium is weathered from minerals, most of the chromium will be present in the trivalent state which may be adsorbed on other metal hydroxides and thus it is not very available to plants (Cary et al., 1977a,b). Although higher concentrations of chromium have been reported in plants growing in high chromium-containing soils (e.g., soil near ore deposits or chromium-emitting industries and soil fertilized by sewage sludge) compared with plants growing in normal soils, most of the increased uptake in plants is retained in roots, and only a small fraction of the total chromium is translocated in the above-ground part of edible plants (Cary, 1982; WHO, 1988). Leaves usually contain higher chromium concentrations than grains (Smith et al., 1989). In an attempt to design crop practices that might increase the chromium in food and feed crops, Cary et al., (1977a,b) also found that plants accumulated chromium from nutrient solutions but retained most of this chromium in the roots.

Shewry and Peterson (1974) found that plant tissues that tend to accumulate iron also accumulate chromium. Chromium uptake was found to increase with increasing chromate concentration and most of the chromium accumulated by the roots was present in a soluble, non-particulate form in the plant vacuoles. Although chromium is largely retained in the roots of plants, the oxidation state of chromium, pH, presence of humic substances and plant species, affect plant uptake and transport (Smith et al., 1989). Chromium will be more available to plants growing in a neutral to basic soil than in an acidic soil probably due to the mobility of Cr(VI) under these conditions. Probably the trace amounts of chromium in plants enter by root uptake of the chromate anion. It seems likely that the hexavalent form is the most important species of chromium available to plants and microorganisms (Bartlett, 1991). However, as Smith et al. (1989) stressed, there is a notable dearth of information pertaining to the speciation of chromium in plants. For instance, Kwan (1988; cited by Smith et al., 1989) reports a bioconcentration factor of 1000 for an aquatic plant (*Lemna minor*) exposed to Cr(VI), but there is insufficient information presented to determine the form in which chromium was present in the plant.

There are conflicting views on the uptake and translocation of Cr(VI) in plants. Ramachandran et al. (1980) suggest that CrO_4^{2-} is reduced to Cr(III) at the surface of root cells although one study found chromate in plants, which indicates that dissolved Cr(VI) may be taken up by plants without immediate reduction. For instance, chromate was found in the xylem sap of *L. scoparium* but not in the soluble plant fraction (Lyon et al., 1969; cited by Cary et al., 1977a). It has been shown that Cr(VI) enters the plant through the root by active transport in barley (*Hordeum vulgare L.*) (Skeffington et al., 1976, cited by Cary, 1982). Uptake of CrO_4^{2-} by intact barley seedlings was stimulated by Ca^{2+} but inhibited by SO_4^{2-} and other Group VI anions (Shewry and Peterson, 1974). Later authors (Smith et al., 1989) have interpreted the findings Skeffington (1976) and Shewry and Peterson (1974) to deduce that Cr(VI) uptake is a metabolically mediated process via the sulfate pathway and thus, is readily transported around the plant. However, Cary (1982) reports there is no evidence that Cr(VI) is translocated in the plant. Hexavalent chromium appears to be reduced during passage from culture solutions to plant leaves but the site of this reduction is unknown (Cary et al., 1977a).

It appears that most of the Cr(VI) entering a plant leaf from deposition is rapidly immobilized although some Cr(VI) may be slowly translocated (Cary, 1982). Immobilization can be due to absorption or to reduction to Cr(III) followed by adsorption or chelation (Cary, 1982). If Cr(VI) deposition of leaf surfaces is high, leaf damage will result (Cary, 1982).

The reason for the restricted chromate transport in plants has not been established (Shewry and Peterson, 1974) but may be related to the role of chromium in plant metabolism. Whether chromium is an essential element in plants has been debated (Smith et al., 1989; Shewry and Peterson, 1974) and thus, suitable transport mechanisms for chromium may not have evolved in plants. The World Health Organization (WHO, 1988) reports that it is unknown whether chromium is an essential nutrient for plants, yet all plants contain the element. In more recent work, Richard and Bourg (1991) suggested that Cr(III) is an essential nutrient in plant metabolism (amino- and nucleic acid synthesis).

5.4.3 Accumulation in Animals

Chromium is an element of which trace levels are required but which, when accumulated to excess becomes quite toxic. There is also no indication of biomagnification of chromium along the terrestrial food chain (soil-plant-animal) (Cary, 1992; cited by ATSDR, 1992). Because it is an essential metal in animals, metabolic pathways for chromium must have evolved (Nieboer and Jusys, 1988). There is solid evidence that Cr(III) binds to the Fe(III) transport protein, transferrin (Nieboer and Jusys, 1988). Petrilli and De Flora (1978) reported that hexavalent chromium is selectively concentrated in erythrocytes (red blood cells) where it undergoes metabolic deactivation to the trivalent form.

Chromate is chemically unstable at physiologic pH but does not decompose as easily as expected on the basis of the highly positive standard reduction potential so frequently reported in health risk assessment documents (E° = 1.33v) (Nieboer and Jusys, 1988). At pH 7.4, chromate is capable of oxidizing both low-molecular weight reductants (e.g., cysteine, ascorbate, glutathione, lipoic acid) and proteins. These reactions proceed by second order kinetics and thus are dependent on the concentration of both the chromate and reductant. Using the published rate constants and concentrations of reductants in biologic fluids ranging from 10^{-1} to 10^{-5} M, and assuming similar chromate concentrations, Connet and Wetterhahn (1983) calculated reduction half-lives ranging from minutes to hours (cited by Nieboer and Jusys, 1988). Consequently, a biologic half-life of the order of hours is not considered unrealistic (Nieboer and Jusys, 1988) for humans.

The metabolism studies performed by Van Brunwaene et al. (1984) showed that radioactively labeled Cr(VI) can be absorbed orally lactating dairy cows. A transfer coefficient into milk of 1×10^{-5} days/L was reported. However, the chromium in the milk was determined by radioactivity measurements of ^{51}Cr. Since radioactivity measurements cannot distinguish Cr(VI) from other forms of chromium and any Cr(VI) absorbed orally by the cow was probably quickly reduced to Cr(III), it may be inappropriate to apply the transfer coefficient of Van Bruwaene et al. (1984) to the secretion of Cr(VI) into milk. By analogy, one would not expect secretion of Cr(VI) into mother's milk.

5.4.4 Microbial Accumulation and Transformation

Microorganisms have the potential to accumulate chromium (Coleman, 1988) and reduce Cr(VI) to Cr(III). Although high levels of Cr(VI) are toxic to microorganisms (Bartlett, 1991) chromium is important to yeast metabolism (Anderson et al., 1977; cited by Coleman, 1988). The redox status and the microbial ecology of an aquatic system are interrelated. Many of the most important redox reactions in natural waters and waste waters are effected by microorganisms. Microbial populations are distinctly different in oxic and anoxic environments; depending on the redox status, they may consist of aerobes, denitrifiers, fermenters, or methanogens (Stumm and Morgan, 1981; cited by Scott and

Morgan, 1990). In addition, the fate of aqueous contaminants and the rate of transformation is highly dependent on the redox status.

Chromium accumulation has been shown to occur in the natural environment, in bacteria periphytic to a crab (*Helice crassa*) carapace and in sewage fungus (Johnson et al., 1981; Gray and Clarke, 1984; cited by Coleman, 1988), and may contribute to chromium in the food chain. In this regard, it is noted that Coleman (1988) did not report the oxidation state of the chromium either to which the organisms were exposed or found in the organisms. Coleman (1988) also summarizes additional laboratory studies which reflect accumulation of chromium in bacterium exposed to Cr(VI) but the analytical techniques used in these studies indicate that total chromium rather than Cr(VI) was measured in the bacteria. The active uptake of chromate by the sulfate transport system has been shown in microorganism *Neurospora crassa* (Roberts and Marzluf, 1971; cited by WHO, 1988), analogous to the mechanism demonstrated in plants (Shewry and Peterson, 1974), but there is no evidence to support bioaccumulation of chromium as Cr(VI) in bacteria.

Reduction of Cr(VI) under anaerobic conditions was achieved using an *Enterobacteria cloacae* strain isolated from activated sludge (Wang et al., 1989). The rate of chromate reduction depended on cell density and chromate concentration (Wang et al., 1989). Indirect reduction of Cr(VI) may result from microbially produced hydrogen sulfide in a seawater/sediment system (Smillie et al., 1981 cited by Coleman, 1988).

6.0 BIOAVAILABILITY

The bioavailability of a chemical is a complex phenomenon generally considered to be influenced by the desorption of the contaminant from its matrix and the transport of the desorbed substance across a biological membrane (Clement, 1988). An important consideration in assessing the bioavailability of Cr(VI) is the aqueous solubility of both the particular chromate salt released to the atmosphere and the particle matrix in which Cr(VI) enters the body (Gochfeld and Whitmer, 1991). All chromate anions have the same bioavailability irrespective of source but the chromate concentration within biological systems is largely a function of solubility. Because of the complexity of both biological systems and the environmental chemistry of chromium, there is no single bioassay technique available to evaluate the bioavailability of Cr(VI) to humans (Fraser and Lum, 1983). The following subsections discuss the bioavailability of Cr(VI) by inhalation, ingestion, and dermal exposure pathways.

6.1 Bioavailability by Inhalation

The absorption of inhaled chromium compounds depends on a number of factors, including physical and chemical properties of the particles (oxidation state, size, solubility) and the activity of alveoloar macrophages (ATSDR, 1992). Soluble chromates are rapidly absorbed through the epithelium of the alveoli and bronchi and cleared into circulation, where part is preferentially accumulated by the red blood cells and part is excreted by the kidneys (WHO, 1988; Wiegand et al., 1988).

For chemicals present on or in a fly ash matrix, (the expected form from fuel combustion), bioavailability is affected by primarily two factors (1) the fraction of fly ash that is deposited in the respiratory tract and (2) the fraction of pollutant that is released from the fly ash matrix (Clement, 1988). Regarding the first factor, the Clement (1988) report sites a study where the particle size distribution of fly ash was determined to range from between 0.4 μm to 13 μm (Pirney, 1987). Based on this distribution and other human deposition studies, the Clement (1988) report estimated that roughly 60% of inhaled particles were deposited in the respiratory tract and 40% exhaled. The distribution of chromium in fly ash favors the particle surface, thus the surface areas exposed to possible reaction is maximized (Natusch and Wallace, 1974; cited by Cary, 1982). Regarding the second factor, fly ash leaching studies have shown that only 0.3% percent of chromium can be leached from fly ash under harsh conditions (Fraser and Lum, 1983 cited by Clement, 1988). SCAQMD (1988) cautions that the 0.3% leaching factor is based on Cr (III) and should not be used if the Cr is known to exist as Cr(VI), e.g., dichromate mists from cooling towers. For chemicals known to be pulmonary carcinogens, such Cr(VI), the fraction conservatively assumed to be bioavailable is 1.0 (SCAQMD, 1988).

In an experiment to determine the bioavailability of chromium from Whetlerite dust (a granular, activated carbon material impregnated with 2.02% total chromium as 0.98% insoluble hexavalent chromium, 0.30% soluble hexavalent chromium, and 0.74% insoluble trivalent chromium, and other metals used to adsorb toxic gases) administered intratracheally to rats, Salem and Katz (1989) failed to detect any Cr(VI) in the lungs or kidneys of rats and concluded that chromium is present in biological matter in the trivalent form.

6.2 Bioavailability by Ingestion

Ingestion of Cr(VI) could occur from ingestion of water, soil, and clearance of large particles from the respiratory tract to the esophagus. It is widely accepted that Cr(VI) is reduced intracellularly to Cr(III) so human exposure to hexavalent chromium from ingestion of animals or animal products (including mother's milk) is considered unlikely.

Small amount of chromium are present in food and feed plants but the form is not well characterized (Cary, 1982). The likely form is soluble Cr(III) organic compounds such as Cr(III) oxalate in plants (Lyon et al., 1969; cited by Smith et al., 1989) and Cr(III) amino acid complexes in food (Nieboer and Jusys, 1988). The absorption of Cr(VI) orally administrated has been reported not to exceed 5% of the dose (Donaldson and Barreras, 1966; cited by WHO, 1988). The absorption efficiency of chromium is reported to be inversely proportional to the dose (Anderson, 1986; cited by ATSDR, 1992). The study of Donaldson and Barreras (1966; cited by WHO, 1988) also suggested reduction of Cr(VI) by the acidic gastric juice.

In many exposure assessments, particularly where children are involved, soil ingestion may be involved raising the question of the cancer risk associated with ingestion of hexavalent compounds (Gochfeld, 1991). There is a dearth of literature dealing with mobility and bioavailability of Cr(VI) in soils due, in part, to the high instability of Cr(VI) in soils. Ready leaching, plant uptake, and reduction make Cr(VI) difficult to follow (Bartlett and James, 1988).

6.3 Bioavailability by Dermal Absorption

Dermal absorption of Cr(VI) deposited to soil and water is influenced by the nature of the vehicle (transport fluid) and the structure of the strateum corneum (Clement, 1988). The overall bioavailability is taken as the product of these two components. Percutaneous absorption of chromium appears to be related to valence state, the particular salt employed, and the concentration applied (Nieboer and Jusys, 1988). The major findings of a comprehensive literature review (Petersen 1982, and Polak, 1983; cited by Nieboer and Jusys, 1988) are as follows:

(1) Cr(VI) compounds penetrate the skin more readily than do Cr(III) compounds.

(2) The penetration by chromate increases with increasing pH.

(3) The penetration by Cr(III) salts depends on the nature of the anion.

(4) The difference in penetration by Cr(VI) and Cr(III) compounds appears to be governed by the epidermal layer, which forms the main barrier to uptake.

(5) Skin and skin components reduce chromate.

(6) Cr(VI) binds strongly to skin and skin proteins.

Walhberg (1968) reported that the maximum absorption was 4% for a 0.261 M solution of sodium dichromate; however, this study did not mimic soil exposure conditions (Clement, 1988). An absorption rate of 1.1 μg Cr(VI)/cm^2/hour was measured by Baranowska-Dutkiewicz (1981; cited by ATSDR, 1992) for 0.1 m solution.

Allergic contact dermatitis is the most prominent reaction from the interaction of chromium with skin (Nieboer and Jusys, 1988). Chromium is generally accepted as being the second most common skin allergen in the general population, after nickel (Polak, 1983; cited by Haines and Nieboer, 1988); in men, it is the most frequent sensitizer (Cronin, 1980; cited by Haines and Nieboer, 1988).

7.0 AREAS OF POSSIBLE IMPROVEMENT

The assessment of multipathway exposure to hexavalent chromium would benefit by considering the following:

(1) The likely transformation of hexavalent chromium to trivalent chromium by redox reactions in environmental media such as air, soil, and animals.

(2) The current uses of bioconcentration factors generally assume that measured chromium is present in the hexavalent form, although the trivalent state would be favored. Given the intracellular reduction of Cr(VI), there is no reason to expect that ingestion of animal or animal products would result in exposure to hexavalent chromium.

(3) The bioavailability of hexavalent chromium from various matrices should be considered, especially from matrices such as fly ash and paint spray.

(4) Resuspension of particles which may be a significant exposure pathway that is currently not considered in most multipathway exposure models.

(5) Redox reactions in which trivalent chromium may be oxidized to hexavalent chromium such as in moist soils.

(6) Where exposure to hexavalent chromium is considered critical to the outcome of a refined risk assessment, intermedia modeling of exposure to Cr(VI) could be supplemented with measurements of impacted soils (and possibly waters) to determine applicable redox conditions.

(7) The use of the default values for particle deposition velocity, depending on whether the emission source is controlled or uncontrolled, without considering Cr(VI) distribution within the particle phase. The dry deposition velocities of chromium-containing particles will depend on the mass distribution of Cr(VI) as a function of particle size.

Finally, despite the extensive body of literature that exists for chromium, the following major questions need to be addressed in the general conduct of the exposure assessment and in site-specific evaluations of exposure to chromium:

- What is the form of chromium when it is released to the atmosphere?

- What is the form of chromium when it reaches the exposure boundary?

- What factors govern the movement of chromium from the environment to the body?

- What influences the bioavailability of chromium for the different routes of exposure and in what form is chromium present in the human and ecological receptors?

8.0 REFERENCES

Agency for Toxic Substances and Disease Registry (ATSDR), U.S. Department of Health & Human Services, Draft Toxicological Profile for Chromium, 1992.

Allen, D.T., Cohen, Y., and Kaplan, I.R. (Eds.), Intermedia Pollutant Transport, Plenum Press, New York, 1989.

Amacher, M.C. and Baker, D.E., Redox Reactions Involving Chromium, Plutonium, and Manganese in Soils, DOE/DP/04515-1. Institute for Research on Land & Water Resources, Pennsylvania State University and U.S. Dept. of Energy, Las Vegas, Nevada, 166 pp., 1982.

Anderson, R.A., Polansky, M.M., Brantner, J.H., and Roginski, E.E., Chemical and Biological Properties of Biologically Active Chromium, In International Symposium on Trace Element Metabolism in Man and Animals, Freising, pp. 269-271, 1977.

Anderson, R.A., Chromium Metabolism and its Role in Disease Processes in Man, Clinical Physiology and Biochemistry, 4, 31-41, 1986.

Anderson, L.D., Kent, D.B., and Davis, J.A., Batch Experiments Characterizing the Reduction of Cr(VI) Using Suboxic Material from a Mildly Reducing Sand and Gravel Aquifer, American Chemical Society 203rd National Meeting, San Francisco, CA, April 5-10, 1992.

Arillo, A. and Melodia, F., Protective Effects of Fish Mucus Against Cr(VI) Pollution, Chemosphere, 20, 397-402, 1990.

Arillo, A. and Melodia, F., Reduction of Hexavalent Chromium by the Earthworm *Eisenia foetida* (Savigny), Ecotoxicity and Environmental Safety, 21, 92-100, 1991.

Baes, C.F. and Messmer, R.F., The Hydrolysis of Cations, John Wiley and Sons, New York, 211, 1976.

Baes, C.F., III. Sharp, R.D., Sjoreen, A.L., and Shore, R.W., A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides Through Agriculture, Prepared for the U.S. Department of Energy, ORNL-5786, 1984.

Baranowska-Dutkiewicz, B., Absorption of Hexavalent Chromium by Skin in Man, Archives of Toxicology, 47, 47-50, 1981.

Bartlett, R.J., Chromium Cycling in Soils and Water: Links, Gaps, and Methods, Environmental Health Perspectives, 92, 17-24, 1991.

Bartlett, R.J. and James, B. R., Mobility and Bioavailability of Chromium in Soils, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, 267-383, 1988.

Bartlett, R.J. and Kimble, J.M., Behavior of Chromium in Soils. I. Trivalent Forms, II. Hexavalent Forms, Journal of Environmental Quality, 5, 379-386, 1976.

Bianchi, V. and Levis, A.G., Mechanisms of Chromium Genotoxicity, In Carcinogenic and Mutagenic Metal Compounds: Environmental and Analytical Chemistry and Biological Effects (E. Marian, R.W. Fre, W. Hardi, and E. Schalatter, Eds.), Gordon and Breach Science Publishers, London, 269-294, 1985.

Bloomfield, C. and Pruden, G., The Behavior of Cr(VI) in Soil Under Aerobic and Anaerobic Conditions, Environmental Pollution Series, 23, 103-114, 1980.

Bodek, I., Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H., Environmental Inorganic Chemistry Properties, Processes, and Estimation Methods, Pergamon Press, New York, 1988.

Buhler, D.R., Stokes, R.M., and Caldwell, R.S., Tissue Accumulation and Enzymatic Effects of Hexavalent Chromium in Rainbow Trout (*Salmo gairdneri*), Journal of the Fisheries Research Board of Canada, 34, 9-18, 1977.

Burns, L.A., Cline, D.M., and Lassiter, R.R., Exposure Analysis and Modeling Systems (EXAMS) User Manual and Systems Documentation, U.S. EPA, Athens Georgia, 1981.

Calamari, D., Vighi, M., and Bacchi, E., Toxicokinetics of Low Levels of Cd, Cr, Ni, and Their Mixtures in Long-term Treatment on *Salmo giardneri*, Chemosphere, 11, 59-70, 1982.

Calder, L. M., Chromium Contamination of Groundwater, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), Wiley, New York, 215-29, 1988.

California Air Resources Board, Proposed Airborne Toxic Control Measure for Emissions of Hexavalent Chromium from Chrome Plating and Chromic Acid Anodizing Operations, 1988a.

California Air Resources Board, Proposed Hexavalent Chromium Control Plan, 1988b.

CAPCOA, "Air Toxics 'Hot Spots' Program Risk Assessment Guidelines," 1992.

Cary, E.E., Chromium in Air, Soil and Natural Waters, Biological and Environmental Aspects of Chromium, Langard, Ed., Elsevier Biomedical Press, 1982, and Topics in Environmental Health. Biological and Environmental Aspects of Chromium, 5, 49-64, 1982.

Cary, E.E., Allaway, W.H., and Olson, O.E., Control of Chromium Concentrations in Food Plants, Journal Agricultural and Food Chemistry, 25(2), 305-309, 1977b.

Cary, E.E., Allaway, W.H., and Olson, O.E., Control of Chromium Concentrations in Food Plants. 1. Absorption and Translocation of Chromium by Plants, Journal of Agricultural and Food Chemistry, 25(2), 300-304, 1977a.

Chetty, S., Multimedia Total Dose Analysis, Master's Thesis, UCLA, 1991.

Clay, R.E., Multimedia Environmental Distribution of Gaseous, Dissolved, and Particle-Bound Pollutants, Master of Science Thesis, Chemical Engineering Department, UCLA, 1992.

Clement Associates, Inc., South Coast Air Quality Management District, Multi-Pathway Health Risk Assessment Input Guidance Document, 1988.

Cohen, Y., Intermedia Transport Modeling in a Multimedia Environment, In Pollutants in a Multimedia Environment, Y. Cohen (ed.), Plenum Press, New York, 1986.

Cohen, Y. and Clay, R.E., Multimedia Transport and Fate of Particle-Bound Chemicals, Paper 93-WA-73.04, Air and Waste Management Association, 86th Annual Meeting, Denver, Colorado, June 13-18, 1993.

Coleman, R.N., Chromium Toxicity: Effects on Microorganisms with Special Reference to the Soil Matrix, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 335-368, 1988.

Connet, P.H. and Wetterhahn, K.E., Metabolism of the Carcinogen Chromate by Cellular Constituents, In Structures and Bonding. Inorganic Elements in Biochemistry, Springer-Verlag, Berlin, 54, 93-124, 1983.

Cowherd, C., Muleski, G.E., and Linsey, J.S., Control of Open Fugitive Dust Sources, NTIS Report Number PB89-103691, 1988.

Cox, III, X.B., Linton, R.W., and Butler, F.E., Determination of Chromium Speciation in Environmental Particles. Multitechnique Study of Ferrochrome Smelter Dust, Environmental Science and Technology, 19(4), 345-52, 1985.

Cronin, E., Contact Dermatitis, Churchill Livingstone, New York, 1980.

Davison, R.L., Natusch, D.F.S., Wallace, J.R., and Evans, Jr., C.A., Trace Elements in Fly Ash. Dependence of Concentration on Particle Size, Environmental Science and Technology, 13, 1107-1113, 1974.

Deltombe, E., deZoubov, N., and Pourbaix, M., Chromium, In Atlas of Electrochemical Equilibrium in Aqueous Solutions, (M. Pourbaix, Ed.; J.A. Franklin, Eng. transl.), Pergamon Press, Oxford, pp. 256-271, 1966.

Donaldson, Jr., R.M. and Barreras, R.F., Intestinal Absorbtion of Trace Quantities of Chromium, Journal of Laboratory and Clinical Medicine, 68, 484-493, 1966.

Dzombak, D.A. and Morel, F.M.M., Surface Complexation Modeling Hydrous Ferric Oxide, John Wiley and Sons, New York, 1990.

Eary, L.E. and Rai, D., Kinetics of Chromate Reduction by Ferrous Ions Derived from Hematite and Biotite at 25 °C, American Journal of Science, 289, 180-213, 1989.

Elwood, J.W., Beauchamp, J.J., and Allen, C.P., Chromium Levels in Fish from a Lake Chronically Contaminated with Chromates from Cooling Towers, International Journal of Environmental Studies, 14, 289-298, 1980.

Felmy, A.R., Girvin, D.C., and Jenne, E.A., Minteq - A Computer Program for Calculating Aqueous Geochemical Equilibrium, Battelle Pacific Northwest Laboratories, Richland, WA, 1983.

Fishbein, L., Sources, Transport and Alterations of Metal Compounds: An Overview. I. Arsenic, Beryllium, Cadmium, Chromium and Nickel, Environmental Health Perspectives, 40, 43-64, 1981.

Fraser, J.L. and Lum, K.L., Availability of Elements of Environmental Importance in Incinerated Sludge Ash, Environmental Science and Technology, 17(1), 52-4, 1983.

Freeze, R.A. and Cherry, J.A., Groundwater, Prentice-Hall, Englewood Cliffs, New Jersey, 1979.

Frissel, M.J., Poelstra, P., and Reisinger, P., The Behavior of Chromium in Aquatic and Terrestrial Food Chains, EUR 5375e, Boite postale 1003, Luxembourg, pp. 27-42, 1975.

Fromm, P.O. and Stokes, R.M., Assimilation and Metabolism of Chromium by Trout, Research Journal of the Water Pollution Control Federation, 34, 1151-1155, 1962.

Gafafer, W.M., Health of Workers in the Chromate Producing Industry, U.S. Fed. Public Health Service Pub. 192, 1953.

Gochfeld, M., Setting the Research Agenda for Chromium Risk Assessment, Environmental Health Perspectives, 92, 3-5, 1991.

Gochfeld, M. and Whitmer, C., A Research Agenda for Environmental Health Aspects of Chromium, Environmental Health Perspectives, 92, 141-144, 1991.

Gray, N.F. and Clarke, J., Heavy Metals in Heterophobic Slimes in Irish Rivers, Environmental Technology Letters, 5, 201-206, 1984.

Grohse, P.M., Gutnecht, W.F., Hodson, L., and Wilson, B.M., The Fate of Hexavalent Chromium in the Environment, California Air Resources Board Report No. ARB/R-89/379, 1988.

Haines, A.T. and Nieboer, E., Chromium Hypersensitivity, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 497-532, 1988.

Hana, S.R., Briggs, G.A., and Hosker, R.P., Handbook on Atmospheric Diffusion, Office of Energy Research, U.S. Department of Energy, 1982.

Hayes, R.B., Carcinogenic Effects of Chromium, In Biological and Environmental Aspects of Chromium, Elsevier Biomedical Press, Amsterdam, pp. 221-247, 1982.

Hem, J.D. Reactions of Metal Ions at Surfaces of Hydrous Iron Oxides, Geochimica et Cosmochimica Acta, 41, 527-538, 1977.

Holdway, D.A., The Toxicity of Chromium to Fish, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds), John Wiley and Sons, New York, 20, 360-397, 1988.

IARC, Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, 23, 205-323, 1980.

James, B.R. and Bartlett, R.J., Behavior of Chromium in Soils: VII. Adsorption and Reduction of Hexavalent Forms, Journal of Environmental Quality, 12(2), 177-81, 1983.

Johnson, J., Flower, N., and Loutit, M.W., Contribution of Periphytic Bacteria to the Contribution of Chromium in the Crab *Helice crassa*, Microbial Ecology, 7, 245-252, 1981.

Katz, S.A., The Analytical Biochemistry of Chromium, Environmental Health Perspectives, 92, 13-16, 1991.

Knoll, J. and Fromm, P.O., Accumulation and Elimination of Hexavalent Chromium in Rainbow Trout, Physiological Zoology, 33, 1-8, 1960.

Kwan, K.H.M., Ph.D. Thesis, University of London, pp. 402, 1988.

Lee, Jr., R.E., Crist, H.L., Riley, A.E., and MacLeod, K.E., Concentration and Size of Trace Metal Emissions from a Power Plant, a Steel Plant, and a Cotton Gin, Environmental Science and Technology, 7, 643-647, 1975.

Levy, L.S. and Martin, P.A., The Effects of a Range of Chromium-Containing Materials on Rat Lung, Department of Environmental and Occupational Health, University of Aston in Birmingham, UK, July, 1983.

Loutit, M., Bremer, P., and Aislabie, J., The Significance of the Interaction of Chromium and Bacteria in Aquatic Habitats, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 317-334, 1988.

Lyon, G.L., Peterson, P.J., and Brooks, R.R., New Zealand Journal of Science, 12, 541, 1969.

MacKenzie, R.M., Manganese Oxides and Hydroxides, In J.B. Dixon and S.B. Weed, Eds. Minerals in Soil Environments, (J.B. Dixon and S.B. Weed, Eds.), Soil Science Society of America, Madison, WI, pp. 181-193, 1977.

Manahan, S., Environmental Chemistry, Fourth Edition, Lewis Publishers, Chelsea, Michigan, 1991.

Mancuso, T.F., Considerations of Chromium as an Industrial Carcinogen, In Proceedings of the International Conference on Heavy Metals in the Environment (T.C. Hutchinson, Ed.), Institute for Environmental Studies, Toronto, pp. 343-356, 1975.

Mayer, L.M., Geochemistry of Chromium in the Oceans, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 173-84, 1988.

Milford, J.B. and Davidson, C.I., The Sizes of Particulate Trace Elements in the Atmosphere - A Review, Journal Air Pollution Control Association, 35, 1249-1260, 1985.

National Institute for Occupational Safety and Health (NIOSH), Criteria for a Recommended Standard: Occupational Exposure to Chromium (VI), United States Department of Health, Education and Welfare, Washington, D.C., 1975.

Natusch, D.F.S. and Wallace, J.R., Urban Aerosol Toxicity: The Influence of Particle Size, Science, 186, 695-699, 1974.

Nieboer, E. and Jusys, A.A., Biologic Chemistry of Chromium, Chromium in the Natural and Human Environments, (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 21-79, 1988.

Nriagu, J.O., Pacyna, J.M., Milford, J.B., and Davidson, C.I., Distribution and Characteristic Features of Chromium in the Atmosphere, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, 1988.

Nriagu, J.O., Production and Uses of Chromium, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 81-103, 1988.

Ondov, J.M., Choquette, C.E., Zoller, W.H., Gordon, B.E., Bierman, A.H., and Heft, R.E., Atmospheric Behavior of Trace Elements on Particles Emitted from a Coal-Fired Power Plant, Atmospheric Environment, 23, 2193-3104, 1989.

Pacyna, J.M. and Nriagu, J.O., Atmospheric Emissions of Chromium from Natural and Anthropogenic Sources, In Chromium in the Natural and Human Environments (J.O. Nriagu and E. Nierboor, Eds.), John Wiley and Sons, New York, pp. 105-123, 1988.

Parfitt, R.L., Anion Adsorption by Soils and Soil Materials, Advances in Agronomy, 20, 1-50, 1978.

Petersen, N.B., The Effects of Chromium on the Skin, In Biological and Environmental Aspects of Chromium (S. Langård, Ed.), Elsevier Biomedical Press, Amsterdam, 5, 249-275, 1982.

Petrilli, F.L. and De Flora, S. Metabolic Deactivation of Hexavalent Chromium Mutagenicity, Mutation Research, 54, 139-147, 1978a.

Pirney, M., Multiple Pathway Health Risk Assessment: York County, Pennsylvania Resource Recovery Project, Prepared for New York County Solid Waste Management Authority, York County, Pennsylvania, 1987.

Polak, L., Immunology of Chromium, In Chromium: Metabolism and Toxicity (D.Burrows, Ed.), CRC Press, Boca Raton, Florida, pp. 51-136, 1983.

Rai, D., Eary, L.E., and Zachara, J.M., Environmental Chemistry of Chromium, The Science of the Total Environment, 86, 15-23, 1989.

Ramachandran, V., D'Souza, T.J., and Mistry, K.B., Uptake and Transport of Chromium in Plants, Journal of Nuclear Agriculture and Biology, 9, 4, 126, 1980.

Reisinger, H.J., II, Heavy Metals in a Small Schuykill River, Pennsylvania Impoundment, Master's thesis, Millersville State College, Pennsylvania, 1979.

Richard, F.C. and Bourg, A.C.M., Aqueous Geochemistry of Chromium: A Review, Water Research, 25, 7, 807-816, 1991.

Roberts, K.R. and Marzluf, G.A., The Specific Interaction of Chromate with the Dual Sulfate Permease System of Neurospora crassa, Archives of Biochemistry and Biophysics, 142, 651-659, 1971.

Saleh, F.Y., Parkerton, T.F., Lewis, R.V., Huang, J.H., and Dickson, K.L., Kinetics of Chromium Transformations in the Environment, Science of the Total Environment 86, 1-2, 25-41, 1989.

Salem, H. and Katz, S.A., Speciation, Bioavailability and Systemic Distribution of Chromium from Whetlerite Dust, Science of the Total Environment, 86, 59-64, 1989.

Sass, B.M. and Rai, D., Solubility of Amorphous Chromium (III)-Iron(III) Solid Solution, Inorganic Chemistry, 26, 2228-2232, 1987.

Schmidt, J.A. and Andren, A.W., Deposition of Airborne Metals into the Great Lakes: An Evaluation of Past and Present Estimates, Advances in Environmental Science Technology, 14, 81-103, 1984.

Schroeder, R.L. and Lee, G.F., Potential Transformation of Chromium in Natural Waters, Water, Air, and Soil Pollution, 4, 355-365, 1975.

Schroeder, W.H., Dobson, M., Kane, D.M., and Johnson, N.D., Toxic Trace Elements Associated with Airborne Particulate Matter: A Review, Journal Air Pollution Control Association, 37, 1267-1285, 1987.

Scott, M.J. and Morgan, J.J., Energetics and Conservative Properties of Redox Systems, In Chemical Modeling of Aqueous Systems II (D.C. Melchior and R.L. Bassett Eds.), pp. 368-378, 1990.

Shewry, P.R. and Peterson, P.J., The Uptake of Chromium by Barley Seedlings (*Hordeum vulgare L*), Journal of Experimental Botany, 25(87), 785-97, 1974.

Shupack, S.I., The Chemistry of Chromium and Some Resulting Analytical Problems, Environmental Health Perspectives, 92, 7-11, 1991.

Skeffington, R.A., Shewry, P.R., and Petersen, P.J., Chromium Uptake and Transport in Barley Seedlings *Hordeum-Vulgare*, Planta (Berl.), 132, 209-214, 1976.

Slinn, W.G.N., Prediction for Particle Deposition to Vegetative Canopies, Atmospheric Environment, 16(7), 1785-1792, 1982.

Smillie, R.H., Hunter, K., and Loutit, M., Reduction of Chromium (VI) by Bacterially Produced Hydrogen Sulphide in a Marine Environment, Water Research, 15, 1351-1354, 1981.

Smith, S., Petersen, P.J., and Kwan, K.H.M., Chromium Accumulation, Transport and Toxicity in Plants, Toxicological and Environmental Chemistry, 24, 241-251, 1989.

Smith, R.D., Campbell, J.A., and Nielson, K.K., Characterization and Formation of Submicron Particles in Coal-fired Plants, Atmospheric Environment, 13, 607-617, 1979.

South Coast Air Quality Management District (SCAQMD), Multi-pathway Health Risk Assessment Input Parameters Guidance Document, prepared by Clement Associates, Inc., June, 1988.

Stern, R.M., Chromium Compounds: Production and Occupational Exposure, In Topics in Environmental Health, Biological and Environmental Aspects of Chromium (S. Langard, Ed.), Amsterdam, 5, 16-47, 1982.

Strenge, D.L. and T. Napier, Radiological Assessment, Engineering Geology, 26(4), 405-410, 1989.

Stumm, W. and Morgan, J.J., Aquatic Chemistry, 2nd ed., Wilely-Interscience, New York, 1981.

Sunderman, F.W., Recent Advances in Metal Carcinogenesis, Annals of Clinical Laboratory Science, 14, 93-122, 1984.

Tsai, W., Cohen, Y., Sakugawa, H., and Kaplan, I., Dynamic Partitioning of Semivolatile Organics in Gas/Particle/Rain Phases During Rain Scavenging, Environmental Science and Technology, 25(12), 2012-2023, 1991.

U.S. EPA, Ambient Water Quality Criteria for Chromium, Office of Water Regulations and Standards, Criteria and Standards, Washington, D.C.,, U.S. Environmental Protection Agency, EPA-440/5-80-035, 1980a.

U.S. EPA, Health Assessment Document for Chromium, Environmental Assessment and Criteria Office, Research Triangle Park, N.C., U.S. Environmental Protection Agency, EPA-600/8-83-014F, 1984b.

U.S. EPA, Fate of Toxic and Hazardous Materials in the Environment, Environmental Sciences Research Laboratory, RTP, NC, EPA-60013-80-84, NTIS PB80-221984, 1980b.

U.S. EPA, Superfund Public Health Evaluation Manual, 1987.

U.S. Department of Health and Human Services (USDHHS), Chromium, Environmental Health Perspectives, 92, 1992.

U.S. EPA, Health Effects Assessment for Hexavalent Chromium, U.S. Environmental Protection Agency, Cincinnati, OH, EPA/540/1-86/019, NTIS PB86-134301, 1984a.

U.S. Environmental Protection Agency, Exposure Profiles for RCRA Risk-Cost Analysis Model, Office of Solid Waste, Prepared by Environ Corporation, 1984a.

Van Bruwaene, R., Gerber, G.B., Kerchmann, R., Colard, J., and Van Kerkom, J., Metabolism of ^{51}Cr, ^{54}Mn, ^{59}Fe and ^{60}Co in Lactating Cows, Health Physics, 46(5), 1069-1082, 1984.

Walhberg, J.E., Percutaneous Absorption of Radioactive Strontium Chloride Sr89 ($SrCl_2$), Archives of Dermatology 97, 336-339, 1968.

Walkley, A. and Black, I.A., An Examination of the Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method, Soil Science, 37, 29-38, 1934.

Wang, P., Tsukasa, M., Komori, K., Sasatsu, M., Toda, K., and Ontake, H., Isolation and Characterization of an *Enterobacter cloacae* strain that Reduces Hexavalent Chromium under Anaerobic Conditions, Applied and Environmental Microbiology, pp. 1665-1669, July, 1989.

Weast, R.C., Handbook of Chemistry and Physics, CRC Press, Cleveland, 1975.

Whicker, F.W. and T. Kirchner, Pathway: A Dynamic Food-Chain Model to Predict Radionuclide Ingestion after Fallout Deposition, Health Physics, 52(6), 717-727, 1987.

Whittle, K.J., Hardy, R., Holden, A.V., Johnson, R., and Pentreath, R.J., Occurrence and Fate of Organic and Inorganic Contaminants in Marine Animals, In Aquatic Pollutants and Biological Effects with Emphasis on Neoplasia, (N.F. Kraybell et al., Eds.) Ann. N.Y. Academy of Science, 298, 47-79, 1977.

WHO, Environmental Health Criteria 61: Chromium, World Health Organization, 197, 1988.

Wiegand, H.J., Ottenwalder, H., and Bolt, H.M., Recent Advances in Biological Monitoring of Hexavalent Chromium Compounds, The Science of the Total Environment, 71, 309-315, 1988.

Williams, R. M., A Model of the Dry Deposition of Particles to Water Surfaces, Atmospheric Environment, 16(8), 1933-1938, 1982.

Development of Intermedia Transfer Factors for Toxic Air Pollutants

Volume II: Metals and Non-Volatile Organic Compounds
Section 2 - 2,3,7,8,-Tetrachlorodibenzo-p-doxin (2,3,7,8-TCDD)

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ABSTRACT

An information base was developed on the abiotic and biotic transfer of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) among environmental media (i.e., air, water, soil, and the biosphere) with emphasis on human exposure pathways. The environmental literature was critically reviewed to: (1) determine the intermedia transfer factors relevant to 2,3,7,8-TCDD; (2) evaluate measured values; and (3) recommend estimation techniques applicable to 2,3,7,8-TCDD (and homologous compounds) for use in the absence of measured values.

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1.0 INTRODUCTION AND BACKGROUND

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.

Although the multimedia approach to analyzing risk is attractive, its implementation is hampered by major obstacles. In particular, there are deficiencies in our understanding of various intermedia transport processes (Allen et al., 1989). Consequently, there are uncertainties in the predictions of the multimedia approaches that employ approximate treatment of intermedia transport processes. Such uncertainties can be reduced by using the most accurately available pollutant physicochemical and partitioning data, and a reasonable description of mass transfer and degradation processes.

Risk assessment is often accompanied with uncertainties which arise from the lack of data in various areas which lead to reliance on model assumptions and default values. Generally, the assumptions employed and the use of default values are designed to err on the side of human health protection to avoid underestimating risk to the public (CAPCOA Guidelines, 1992). Major sources of uncertainty include:

1. Extrapolation of toxicity data in animals to humans;
2. Air dispersion modeling;
3. Estimation of emissions; and
4. Analysis of multimedia exposure.

In this report, the fourth major source of uncertainty listed above, analysis of multimedia exposure, is addressed. By identifying the input intermedia transfer factors most critical to multimedia analysis and critically evaluating the measured values and estimation techniques, this report should help characterize and minimize the uncertainty associated with estimating risk from multimedia exposure to 2,3,7,8-TCDD. A summary of representative values and estimation methods for intermedia transfer parameters for 2,3,7,8-TCDD is given in Table 1-1. The values listed correspond to either the first value listed in the tables or to the estimation technique emphasized in the supporting text. Although the presented parameter values only apply to specific conditions, these representative values have been included for comparison purposes. A discussion of the pertinent major intermedia transfer parameters and estimation methods relevant to 2,3,7,8-TCDD is provided in Sections 1.1 - 5.

1.1 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)

2,3,7,8-TCDD belongs to a class of compounds that are referred to as polychlorinated dibenzo-p-dioxins (PCDDs) or just dioxins. Dioxins are chemically classified as halogenated aromatic hydrocarbons. There are 75 different dioxins. 2,3,7,8-TCDD is among the most intensely studied of all compounds because of its high toxicity and potential carcinogenicity. It has chlorine atoms located at the 2,3,7, and 8 positions on the dibenzo-p-dioxin nucleus as shown in the chemical structure below (CARB, 1986).

2,3,7,8-TCDD is a white crystalline solid at a room temperature. It lacks reactive functional groups and is stable toward heat, acids, and bases. 2,3,7,8-TCDD is a lipophilic compound with a very low water solubility and vapor pressure.

In air, 2,3,7,8-TCDD is likely to be present partly in the gas phase and partly sorbed to particles. Distribution of 2,3,7,8-TCDD in vapor and particulate phase determines which transport and intermedia transfer processes are dominant and how fast they occur. The important processes that are responsible for the removal of 2,3,7,8-TCDD from the atmosphere are photochemical degradation, hydroxyl (OH) radical attack and dry and wet

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of 2,3,7,8-TCDD

Parameter	Representative Measured (or Calculated) Values	Units	Temperature (K)	Estimation Equation	Sources Cited	Corresponding Section in Text
S	6×10^{-11}	mol/L	295	(a)	Marple et al., 1986	4.1.1
P_{vp}	0.98×10^{-7}	Pa	298	(a)	Podoll et al., 1986	4.1.2
ρ	1.827	g/cm^3	298	Section 4.1.3	Boer et al., 1972	4.1.3
T_{MP}	575-580	K	NA	(a)	Section 4.1.6	4.1.6
MW	321.984	g/mol	NA	(a)	IUPAC, 1979	4.1.5
ΔH_v	85	kJ/gmol	Melting point	(a)	Schroy et al., 1985	4.1.6
H	1.6	Pa m^3/mol	NR	$H=P_{vp}/S$	Podoll et al., 1986	4.2.1
log K_{ow}	6.64	Dimensionless	294-298	(a)	Marple et al., 1986	4.2.2
log K_{oc}	6.6-7.39	Dimensionless	NR	(a)	Section 4.2.3	4.2.3
BCF (aquatic organisms)	See Table 4-8 for measured values corresponding to specific experimental conditions.					
B_v	See Table 4-9 for measured values corresponding to specific experimental conditions.					
B_{vsw}	(9.6×10^7-2.2×10^8)	Dimensionless	NR	Eqs. 4-14 and 4-15	Section 4.2.4	4.2.4
B_m	0.035	Day/kg	NR	$\log B_m = -8.056 + 0.992 \log K_{ow}$	Travis and Arms, 1988	4.2.5

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of 2,3,7,8-TCDD

(Continued)

Parameter	**Representative Measured (or Calculated) Values**	**Units**	**Temperature (K)**	**Estimation Equation**	**Sources Cited**	**Corresponding Section in Text**
B_b	0.1	Day/kg	NR	$\log B_b = 7.6 + \log K_{ow}$	Travis and Arms, 1988	4.2.5
BCF (terrestrial organisms)	See Table 4-12 for estimated values corresponding to specific conditions.					
D_{air}	0.047	cm^2/s	298	Eq. 4-27	Wilke and Lee, 1955	4.3.1
D_{water}	5.1×10^{-6}	cm^2/s	298	Eq. 4-30	Hayduk and Laudie, 1974	4.3.1
K_G	NA	NA	NA	$1/K_G = 1/k_g + H/k_l$	Section 4.3.2	4.3.2
K_L	NA	NA	NA	$1/K_L = 1/k_l + 1/Hk_g$	Section 4.3.2	4.3.2
k_g	NA	NA	NA	Eqs. 4-35, 4-36	Brutsaert, 1975	4.3.2.1
k_l	NA	NA	NR	$k_l V_w^* = a\ Sc^{-n}$	Cohen and Ryan, 1985	4.3.2.2
V_d (particle-bound)	(1.8-4.8)	cm/s	NR	Eq. 4-57		4.3.3.1
V_d (vapor-phase)	NA	NA	NR	Eq. 4-59	Cohen et al., 1990	4.3.3.1
Λ_p^*	NA	Dimensionless	NA	Eq. 4-68	Tsai et al., 1991	4.3.3.2
W	$(\sim 10^3)$	Dimensionless	298	$W = C_{rainwater}/C_{air}$	Shiu et al., 1988	4.3.3.2

Table 1-1. Summary of Representative Values or Estimation Equations for Intermedia Transfer Parameters for Multimedia Assessment of 2,3,7,8-TCDD

(Continued)

Parameter	Representative Measured (or Calculated) Values	Units	Temperature (K)	Estimation Equation	Sources Cited	Corresponding Section in Text
$\tau_{1/2\ (OH)}$	(1.4)	Days	NR	Section 4.4.1	Atkinson, 1991	4.4.1
$\tau_{1/2}$ (photolysis)	See Table 4-16 for values corresponding to specific conditions.					4.4.1
$\tau_{1/2}$ (biodegradation)	See Table 4-17 for values corresponding to specific conditions.					4.4.3
$\tau_{1/2}$ (overall)	See Table 4-18 for values corresponding to specific conditions.					4.4.4

NR = Not reported.

NA = Not applicable or see text for details of the estimation method. (The designation NA in the "Units" column indicates that any set of consistent units can be used.)

(a) Measured value available.

deposition. 2,3,7,8-TCDD deposited onto surfaces can photodegrade or it can volatilize. Once 2,3,7,8-TCDD moves into soils or sediments, however, it is apparently strongly sorbed (U.S.EPA, 1990). It is also noted that 2,3,7,8-TCDD in soils and sediments is considered to be essentially nonbiodegradable. Erosion and aquatic transport of sediment appear to be dominant transport mechanism for sorbed 2,3,7,8-TCDD in aquatic systems. Observations on bioaccumulation indicate that 2,3,7,8-TCDD is readily bioconcentrated in organisms.

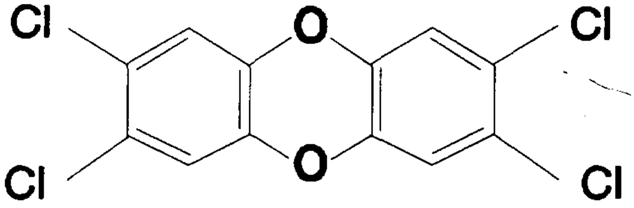

Figure 1.1 Chemical Structure of 2,3,7,8-TCDD

2.0 OBJECTIVES

The overall objective of this report is to present information pertinent to the prediction of the transfer of 2,3,7,8-TCDD between media such as air, water, soil, and biota in order to refine the multipathway exposure component of health risk assessment for this compound. The specific objectives were to: (1) critically review the literature to obtain the parameters necessary to determine environmental intermedia transfer factors for 2,3,7,8-TCDD; (2) evaluate and update intermedia transfer factors currently used in multipathway exposure assessments; and (3) provide pollutant-specific estimates of intermedia transfer factors where default values are now used, or no values are available.

A thorough investigation was conducted of literature values reported for key factors and parameters which determine the partitioning of 2,3,7,8-TCDD in the various compartments and the food chain, following 2,3,7,8-TCDD's release to the atmosphere from stationary and mobile sources. Whenever possible, differing reported values for a given parameter were placed on a common basis of units and conditions. These data were critically evaluated to arrive at recommendations for these numerical values which appear to be of greatest reliability and utility in conducting multipathway exposure assessments. Where no reliable values were found in the literature or default values are currently being used, this report provides pollutant-specific estimates. The details of the methods used, and the properties and parameters investigated, are discussed below.

3.0 METHODOLOGY

The method of approach for this study consisted of several phases in which key parameters for intermedia transfer analysis were selected, published values for these parameters were collected and evaluated, and estimation techniques were evaluated for those parameters for which measured values could not be found in the literature. Since the results of this study may be used to support the CAPCOA (1992) guidelines, parameters and exposure pathways which are relevant to the CAPCOA model were specifically considered.

3.1 Literature Review

Through an extensive literature search, references pertaining to the physicochemical properties, intermedia transport, and biotransformation of 2,3,7,8-TCDD were identified, obtained, reviewed, and summarized. The literature evaluation emphasized measured values. Estimation techniques applicable to 2,3,7,8-TCDD or homologous compounds are emphasized throughout this report where measured values are unavailable for selected parameters.

3.2 Selection of Parameters

In order to provide a critical assessment of intermedia transfers, a number of parameters were considered. The final selection was based on the chemical and physical interpretation of the intermedia transfer parameters, their applicability to different classes of pollutants, and measures of the environmental consequences of intermedia transfers. Specifically, input parameters from the ARB/DHS Health Risk Assessment (HRA) software and algorithms (CAPCOA Guidelines, January 1992) and the South Coast Air Quality Management District Multi-Pathway Health Risk Assessment Input Parameters Guidance Document (SCAQMD, 1988) were reviewed. Three alternative multimedia models (COSMCM, Fugacity, and GEOTOX) were also evaluated (see Cohen, 1986; Allen et al., 1989). The following subsections discuss the rationale for selecting intermedia transfer parameters as well as general limitations in their use.

3.2.1 Physicochemical Parameters

A critical literature review was conducted and it was determined that the minimum necessary physicochemical factors for 2,3,7,8-TCDD required for conducting a multimedia exposure assessment of 2,3,7,8-TCDD as described by CAPCOA, 1992, and other models (i.e., COSMCM, Fugacity, and GEOTOX) are as follows:

- Water Solubility;
- Vapor Pressure;
- Density;
- Melting Point;
- Molecular Weight; and
- Heat of Vaporization.

The definition of these parameters and the results of the literature review are presented in Section 4.1

3.2.2 Partition Coefficients

2,3,7,8-TCDD released to the environment is distributed among various environmental compartments as a result of various intermedia transport processes. The net transport of 2,3,7,8-TCDD, in the dissolved or vapor phase, 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

$$H_{ij} = C_i/C_j \qquad (3\text{-}1)$$

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 2,3,7,8-TCDD were considered in this study:

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

It should be noted, however, that bioaccumulation factors and often bioconcentration factors represent steady-state conditions. These factors are also sometimes based on total concentrations which include particle-bound 2,3,7,8-TCDD and thus, in such cases, the reported coefficients are not thermodynamically constrained and simply represent the partitioning obtained for the particular experimental conditions. Values for some partition coefficients for 2,3,7,8-TCDD 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 2,3,7,8-TCDD 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 flux of 2,3,7,8-TCDD across the various interfaces and thus, its accumulation in the environmental medium of interest. The CAPCOA (1992) approach and other methodologies were reviewed and it was determined that the relevant intermedia transfer parameters for 2,3,7,8-TCDD are as follows:

- Diffusion Coefficients in Air and Water;
- Intermedia Mass Transfer Coefficients;
- Dry Deposition Velocity;
- Washout (Scavenging) Ratio; and
- Biotransfer Factors.

These intermedia transport parameters are defined and discussed in Section 4.3. Intermedia transport of 2,3,7,8-TCDD depends on whether it is present in the vapor or particulate phase as discussed in Section 4.3.3 In addition, available information on bioavailability and pharmacokinetics of 2,3,7,8-TCDD and the implication for its accumulation in biological receptors is briefly in Section 4.2.7.

3.2.4 Degradation Processes

Reaction rates for individual abiotic and biotic degradation processes involve chemical transformations within specific media. Environmental reactions are often expressed as the first or "pseudo-first" order reaction rates. The first order reaction rate constants are often reported as degradation half-lives for soil, water, and air. It is important to note that these half-lives do not account for intermedia transport of a chemical and are, therefore, not representative of a chemical's actual persistence within a particular environmental medium. The degradation processes considered for assessing the transformation of 2,3,7,8-TCDD in the environment are listed below.

- Photooxidation Rate/Half-life in Air;
- Photolysis Rate/Half-Life in Air;
- Photolysis Rate/Half-life in Water;
- Biodegradation Rate/Half-Life in Water;
- Biodegradation Rate/Half-Life in Soil; and
- Overall Half-Life in a Given Environmental Media.

A brief overview of the above degradation processes is given below with an extended discussion and presentation of the reported half-lives given in Section 4.4

Photooxidation in air: It is known that the chemical loss processes for organic compounds present in the atmosphere in the gas phase primarily involve photolysis and chemical reaction with OH and NO_3 radicals and with O_3, with the OH radical reaction being the most important of these loss processes for the majority of organic compounds. The reaction rates of OH and NO_3 radicals and O_3 with 2,3,7,8-TCDD have not been experimentally measured. However, estimates of rate constants for OH radical reaction with 2,3,7,8-TCDD have been reported. For example, Atkinson (1991) estimated an atmospheric lifetime of 1.4 days for the reaction of 2,3,7,8-TCDD with OH radicals.

Biodegradation in water and soil: Biodegradation is an important environmental process responsible for 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. The half-lives reported in Howard et al. (1991) for aerobic conditions are considerably shorter than those for anaerobic conditions (ranging from 1.2 - 1.6 years to 4.6 - 6.1 years, respectively). These values for biodegradation half-lives indicate that microbial degradation of 2,3,7,8-TCDD is very slow.

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). For 2,3,7,8-TCDD photolysis rates in air are generally assumed to equal to 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. The reported photolysis half-life of 2,3,7,8-TCDD in water and air ranges from 1.1 to 3.6 days (cited by Howard et al., 1991).

Photooxidation reactions with alkylperoxy ($RO_2.$), hydroxyl radicals ($OH^{\cdot}$) 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). No data for the photooxidation half-life of 2,3,7,8-TCDD have been reported (Howard et al., 1991) and this degradation process is not considered in this report.

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. Since 2,3,7,8-TCDD does not contain hydrolyzable functional groups, hydrolysis is not a relevant degradation process.

Studies on degradation of 2,3,7,8-TCDD in different environmental media often report values for half-lives without determining specific loss mechanisms involved. Thus, in this report, when loss mechanisms are not apparently reported half-lives are assumed to be overall half-lives that account for both reaction and transport half-lives.

4.0 PRESENTATION OF RESULTS

Intermedia transfer parameters are summarized in Tables 1-1 through 4-18 and these data are tabulated by a 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 or estimated values reported with the corresponding prediction equations and uncertainty estimates. Values reported without their associated estimation equations are 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 but they have been included 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 the 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

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

4.1.1 Solubility of 2,3,7,8-TCDD 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.

Values for the water solubility of 2,3,7,8-TCDD found in the literature are summarized in Table 4-1. Adams and Blaine (1986) and Marple et al. (1986) reported the measured values of water solubility of 2,3,7,8-TCDD as 7.91 ng/L (2.4×10^{-11} mol/L) at 293-295 K and 19.3 ppt (6×10^{-11} mol/L) at 295 K, respectively, with corresponding reported uncertainties of ± 2.7 ng/L and 3.7 ng/L, respectively. Other values for water solubility of 2,3,7,8-TCDD reported in the literature range from 6×10^{-10} to 6×10^{-11} mol/L. In a recent assessment of risks from exposure to dioxins (U.S. EPA, 1990), a value of 19.3 ng/L was adopted.

4.1.2 Vapor Pressure of 2,3,7,8-TCDD

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 units of Pascal (Pa).

Table 4-2 summarizes values for vapor pressure of 2,3,7,8-TCDD found in the literature. Podoll et al. (1986), Rordorf (1985), and Jaber and Podoll (1983; cited by Mill, 1985) reported experimental vapor pressures at 298 K with known uncertainties. The vapor pressures of 0.98×10^{-7} Pa reported by Podoll et al. (1986) and 1.01×10^{-7} Pa reported by Jaber and Podoll (1983) are in a very good agreement. The vapor pressure at 298 as reported by Podoll et al. (1986) cited selected by the U.S. EPA (1990). Vapor pressures can also be calculated from the Antoine equation as reported by Schroy et al. (1984) based on experimental vapor pressure data for 2,3,7,8-TCDD:

Table 4-1. Solubility(a) of 2,3,7,8-TCDD in Water*

Solubility (mol/L)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
6×10^{-11}(b)	19.3	ppt	±3.7 ppt	295	Measured	Podoll et al., 1986;	Marple et al., 1986 Travis and Hattemer-Frey, 1989; ATSDR, 1989; U.S. EPA, 1990; U.S. EPA, 1992
2.4×10^{-11}(c)	7.91	ng/L	±2.7 ng/L	293-295	Measured	ATSDR, 1989;	Adams and Blaine, 1986 U.S. EPA, 1990
9.8×10^{-10}(d)	3.17×10^{-7}	g/L	NR	298	Measured	Freeman and Schroy, 1984;	Webster et al., 1983 Schroy et al., 1984
6.2×10^{-10}(e)	0.2	ppb	NR	298	Measured	Crummett and Stehl, 1973;	Skelly et al. - personal communication Dullin et al., 1986; Adams and Blaine, 1986; Mill, 1985; U.S. EPA, 1985; NRCC, 1981; U.S. EPA, 1990
5.02×10^{-7}	5.02×10^{-7}	mol/L	NR	NR	Estimated(f)	NRCC, 1981	NRCC, 1981
6.2×10^{-10}(g)	0.0002	mg/L	NR	NR	--	Schroy et al., 1984	Esposito et al., 1980
6.2×10^{-10}	6.2×10^{-10}	mol/L	NR	NR	--	McKone, 1985	Mabey et al., 1981
6.2×10^{-10}	6.2×10^{-10}	mol/L	NR	NR	--	McKone, 1985	Schaum, 1984

Table 4-1. Solubility of 2,3,7,8-TCDD in Water*
(Continued)

Solubility (mol/L)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
7×10^{-9} - 6×10^{-10}	7×10^{-9} - 6×10^{-10}	mol/L	NR	NR	NR	Marple et al., 1986	Plimmer et al., 1973; Kearney et al., 1973; Mill, 1985; Crummett and Stehl, 1973
$6\times10^{-10(a)}$	0.0002	ppm	NR	NR	NR	Kenaga, 1980	NR
$6.2\times10^{-10(g)}$	0.0002	mg/L	NR	NR	NR	Crosby, 1985	NR

NR = Not Reported.

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

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

(b) Conversion from reported value: $\text{ppt } (= \text{ng/L}) \times \frac{1 \text{ mol TCDD}}{322 \text{ g TCDD}} \times \frac{1 \text{ g}}{1\text{x}10^9 \text{ ng}} = \text{mol/L}$

(c) Conversion from reported value: $\text{ng/L} \times \frac{1 \text{ mol TCDD}}{322 \text{ g TCDD}} \times \frac{1 \text{ g}}{1\text{x}10^9\text{ng}} = \text{mol/L}$

(d) Conversion from reported value: $\text{g/L} \times \frac{1 \text{ mol TCDD}}{322 \text{ g TCDD}} = \text{mol/L}$

(e) Conversion from reported value: $\text{ppb} = \mu\text{g/L} \times \frac{1 \text{ mol TCDD}}{322 \text{ g TCDD}} \times \frac{1 \text{ g}}{1\text{x}10^6\mu\text{g}} = \text{mol/L}$

(f) The melting point correction of measured value for water solubility (6.2×10^{-10} mol/L by Crummett and Stehl, 1973) resulted in a liquid solubility of 5.02×10^{-7} mol/L.

(g) Conversion from reported value: $\text{mg/L} = \frac{1 \text{ mol TCDD}}{322 \text{ g TCDD}} \times \frac{1\text{g}}{1000 \text{ mg}} = \text{mol/L}$

Table 4-2. Vapor Pressure of 2,3,7,8-TCDD*

Vapor Pressure (Pa)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
$0.98\times10^{-7(a)}$	7.4×10^{-10}	torr	$\pm0.4\times10^{-10}$ torr	298	Measured	Podoll et al., 1986; U.S. EPA, 1990; U.S. EPA, 1992	Podoll et al., 1986
4.50×10^{-6}	4.5×10^{-6}	Pa	$\pm2\times10^{-6}$ Pa	298	Measured	Travis and Hattemer-Frey, 1989	Rordorf, 1985
4.6×10^{-7}	3.49×10^{-9}	mm Hg	$\pm0.05\times10^{-9}$ mm Hg	303	Measured	U.S. EPA, 1990	Schroy et al., 1984
$1.01\times10^{-7(a)}$	7.6×10^{-10}	torr	$\pm0.4\times10^{-10}$ torr	298	Measured	Mill, 1985	Jaber and Podoll, 1983
$1.99\times10^{-7(b)}$	$1.5\times10^{-9(c)}$	mm Hg	NR	298	Extrapolated	Freeman and Schroy, 1984; ATSDR, 1989; Schroy et al., 1985; U.S. EPA, 1990	Schroy et al., 1984
$2.26\times10^{-4(b)}$	$1.7\times10^{-6(d)}$	mm Hg	NR	298	Estimated	U.S. EPA, 1985; NRCC, 1981	Firestone, 1977
$1.33\times10^{-4(b)}$	1×10^{-6}	mm Hg	NR	298	--	U.S. EPA, 1985	Mabey et al., 1981
$1.33\times10^{-3(a)}$	10^{-6}	torr	NR	NR	--	McKone, 1985	Schaum, 1984
$0.93\times10^{-7(a)}$	7×10^{-10}	torr	NR	NR	NR	Crosby, 1985	NR
$1.86\times10^{-7(b)}$	1.4×10^{-9}	mm Hg	NR	298	NR	ATSDR, 1989	NR

NR = Not reported.
* Listed order is by decreasing confidence in reported values (see Section 3.0).

(a) Conversion from reported value: $\mathbf{torr \times \frac{101x10^3\ Pa}{760\ torr} = Pa}$

(b) Conversion from reported value: $\mathbf{mm\ Hg \times \frac{101x10^3\ Pa}{760\ mm\ Hg} = Pa}$

(c) Reported value determined from the following equation: logP=12.89784-(6477.132/T), mm Hg (T in K)

(d) Reported value was estimated from gas chromatography.

$$\log_{10} P_{vp} = 12.89784 - (6477.132/T) \qquad (4\text{-}1)$$

(where P is in mm Hg; T in K)

The above equation is applicable for the temperature range of 298 K to 578 K. Based on this equation, Schroy et al. (1984) estimated a vapor pressure of 1.99×10^{-7} Pa at a temperature of 298 K which is about a factor of two greater than the measured values at the same temperature.

4.1.3 Density and Molar Volume of 2,3,7,8-TCDD

The density (ρ) of a substance is the ratio of its mass to its volume with units of g/cm^3. The density varies not only with molecular weight but also with molecular interaction and structure. The density of 2,3,7,8-TCDD at different temperatures is presented in Table 4-3.

The molar volume is a useful parameter in correlations used to estimate diffusion coefficients in air and water. The molar volume, V_b, of 2,3,7,8-TCDD, expressed in units of cm^3/mol is the volume of a mole of liquid 2,3,7,8-TCDD at its normal boiling temperature. The molar volume is a parameter which is used in correlating various physicochemical properties including the molecular diffusion coefficients in air and water. The molar volume of 2,3,7,8-TCDD is estimated to be 254.5 cm^3/mol following the method presented in Lyman et al. (1990) using the parameter values in Table 17-4 of that reference.

4.1.4 Melting Point Temperature of 2,3,7,8-TCDD

The melting point, T_{MP}, 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 be also used in the prediction of other physicochemical properties such as vapor pressure and parameters such as K_{ow}. Examples of melting points reported in the literature for 2,3,7,8-TCDD are listed in Table 4-4.

Table 4-3. Density[(a)] of 2,3,7,8-TCDD*

Density (g/cm^3)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
1.827	NR	298	Estimated	Schroy et al., 1984	Boer et al., 1972
1.720	NR	MP[(b)]	Estimated	Schroy et al., 1984	Reid et al., 1977
1.021	NR	NBP[(c)]	Estimated	Schroy et al., 1984	Reid et al., 1977

NR = Not Reported

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

(a) Density of a substance is the ratio of its mass to its volume with units of g/ml.

(b) Melting point.

(c) Normal boiling point.

Table 4-4. Examples of Melting Point Temperature (T_{MP}) Reported in the Literature for 2,3,7,8-TCDD*

Melting Point (K)	Reported Value	Reported Units	Reported Uncertainty	Conditions	Technique	Reference	Source Cited
575-578	302-305	°C	NR	NR	NR	U.S. EPA, 1990	U.S. EPA, 1987b
578	305	°C	NR	NR	NR	ATSDR, 1989	Schroy et al., 1985
578-579	305-306	°C	NR	NR	NR	U.S. EPA, 1985	Pohland and Young, 1972
578	305	°C	NR	NR	NR	Schroy et al., 1984	Esposito et al., 1980
576-580	303-307	°C	NR	NR	NR	Crosby, 1985	NR
576-580	303-307	°C	NR	NR	NR	Crummett and Stehl, 1973; Mill, 1985	Skelly et al. - personal communication
579	306	°C	NR	NR	NR	NRCC, 1981	Firestone, 1977

NR = Not Reported.

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

4.1.5 Molecular Weight of 2,3,7,8-TCDD

The molecular weight is used for converting from mass to concentration and in various correlations of transport properties (e.g., diffusion coefficients). The molecular weight of 2,3,7,8-TCDD is 321.974 g/mol, as accepted by IUPAC (IUPAC, 1979; cited by Schroy et al., 1984).

4.1.6 Heat of Vaporization

The heat of vaporization, ΔH_v, is defined as the quantity of heat required to convert a unit mass of liquid into a vapor without a rise in temperature, at constant pressure. Its most important use in multimedia analysis is in estimating other physicochemical properties and partitioning of a chemical between gas and particle phase. Schroy et al. (1985) reported a measured value for ΔH_v for 2,3,7,8-TCDD of 85 kJ/gmol at melting point and an estimated value of 71.81 kJ/gmol at normal boiling point.

4.2 Partition Coefficients

The specific definitions for the various partition coefficients and the findings of the literature search for the individual partition coefficients are presented in the following sections.

4.2.1 Henry's Law Constant for 2,3,7,8-TCDD

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 situations, the aqueous concentration of dissolved 2,3,7,8-TCDD is very small and Henry's Law is applicable. Henry's Law constant of a chemical (H_i) is defined as:

$$H_i = P_i / C_i \tag{4-2}$$

where P_i is the partial pressure of the contaminant in (e.g., Pa) at the system temperature and total pressure, 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 by using the saturation vapor pressure and solubility data in the following equation (Lyman et al., 1990 and Reid et al., 1987):

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

P_{vp} is the saturation vapor pressure (e.g., Pa) and S is the aqueous phase solubility (e.g., mol/m^3). Eq. 4-3 is valid only for solutes for which the activity coefficient is constant at concentrations ranging from the solubility limit and below.

The values for Henry's Law constant are obtained from various literature sources summarized in Table 4-5. No measured value for Henry's Law constant of 2,3,7,8-TCDD was found in the literature. All values reported were either calculated by the vapor pressure/water solubility ratio technique or they were calculated based on estimation of the activity coefficients for 2,3,7,8-TCDD. A Henry's Law value of 1.6 Pa m^3/mol (Podoll et al., 1986) was adopted in a recent study by the U.S. EPA (1990). The low Henry's Law constants reported for 2,3,7,8-TCDD indicate that it is not a volatile compound as confirmed for example in the early experimental work of Crosby et al. (1971). Nonetheless, Nash and Beall (1980) and other researchers (e.g., Young, 1983; Cerlesi et al., 1989) demonstrated in field and environmental chamber studies that 2,3,7,8-TCDD can indeed volatilization should be considered when assessing the environmental transport and fate of this chemical.

Table 4-5. Henry's Law (H) Constant for 2,3,7,8-TCDD*

Henry's Law Constant (Pa m^3/mol)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
1.6(a)	12.3	torr L/mol	NR	NR	Calculated(c)	Podoll et al., 1986; U.S. EPA, 1990	
1.6(a)	12.2	torr L/mol	NR	NR	Calculated(d)	Mill, 1985	
0.212(b)	2.1×10^{-6}	atm m^3/mol	NR	NR	Calculated(e)	Schroy et al., 1984	
8.2(b)	8.1×10^{-5}	atm m^3/mol	NR	298	Calculated(f)	ATSDR, 1989	Palausky et al., 1986
212.1(b)	2.1×10^{-3}	atm m^3/mol	NR	NR	---	U.S. EPA, 1984	Mabey et al., 1981
0.15(b)	1.5×10^{-6}	atm m^3/mol	NR	NR	NR	Crosby, 1985	NR
64.6(b)	6.4×10^{-4}(g)	atm m^3/mol	NR	NR	NR	ATSDR, 1989	Podoll et al., 1986

NR = Not Reported

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

(a) Conversion from reported value: $\text{torr L/mol} \times \dfrac{101000 \text{ Pa}}{760 \text{ torr}} \times \dfrac{10^{-3}\text{m}^3}{1 \text{ L}} = \text{Pa m}^3\text{/mol}$

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

(c) $H = P_{VP}/S$; $P_{VP} = 7.4\times10^{-10}$ torr; $S = 6\times10^{-11}$ M

(d) $H = P_{VP}/S$; $P_{VP} = 7.6\times10^{-10}$ torr; $S = 6.2\times10^{-11}$ M

(e) Calculated based on activity coefficient.

(f) Estimated from water solubility and vapor pressure.

(g) Reported value is an error. The actual value is in the original reference (See first value in Table).

4.2.2 Octanol-Water Partition Coefficient for 2,3,7,8-TCDD

The 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 of a two-phase octanol/water system which is at equilibrium:

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

where C_o is the concentration in octanol phase and C_w is the concentration in aqueous phase. K_{ow} is usually reported as a dimensionless partition coefficient (i.e., C_o and C_w have the same units).

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 2,3,7,8-TCDD is considered as one of the important physicochemical parameters related to sorption on soils and sediments and bioaccumulation. Since K_{ow} has been correlated with 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, its temperature dependence is rarely reported.

Table 4-6 presents log K_{ow} values for 2,3,7,8-TCDD. Marple et al. (1986) reported experimentally determined K_{ow} of $4.24\ (\pm\ 2.73) \times 10^6$ for the temperature range of 294-296 K, yielding a log K_{ow} of 6.64 and this value was adopted in a recent U.S. EPA (1990) study. The other measured value for log K_{ow} found in the literature was 7.02 ± 0.5 (Burkhard and Kuehl, 1986). The available log K_{ow} data reported in the literature ranged from 6.15 to 8.93. The high K_{ow} for 2,3,7,8-TCDD indicates that this chemical tends to sorb strongly to organic components in the soil and sediment and it has high bioconcentration potential for organisms exposed to 2,3,7,8-TCDD.

Table 4-6. Octanol-Water Partition Coefficient (K_{ow})[a] for 2,3,7,8-TCDD*

log K_{ow} (dimensionless)	Reported Uncertainty (log K_{ow})	Temperature (K)	Technique	Reference	Source Cited
6.64	6.18-6.84	294-296	Measured	Marple et al., 1986; U.S. EPA, 1990; U.S. EPA, 1992	Marple et al., 1986
7.02	±0.5	NR	Measured	U.S. EPA, 1990; U.S. EPA, 1992	Burkhard and Kuehl, 1986
7.16	NR	NR	Estimated[b]	Marple et al., 1986	Perkaw et al., 1980
7.16	NR	NR	Estimated[c]	Jackson et al., 1987	Dragun, 1986
6.84	NR	NR	Estimated[b]	Marple et al., 1986; Mill, 1985	Johnson, 1982
8.93	NR	NR	Estimated[d]	Marple et al., 1986	Webster et al., 1983
7.11	NR	NR	Estimated[e]	Mill, 1985	
6.15	NR	NR	Estimated	Schroy et al., 1984; SCAQMD, 1988	Monsanto Research Corp., 1983
6.15-7.28	NR	NR	Estimated	U.S. EPA, 1990; ATSDR, 1989; U.S. EPA, 1985a	U.S. EPA, 1984
8.84	NR	NR	NR	McKone, 1985	Mabey et al., 1981
6.84	NR	NR	NR	McKone, 1985	Schaum, 1984
6.19	NR	NR	NR	Neely, 1979	Branson et al., 1979

Table 4-6. Octanol-Water Partition Coefficient (K_{ow})(a) for 2,3,7,8-TCDD
(Continued)

log K_{ow} (dimensionless)	Reported Uncertainty (log K_{ow})	Temperature (K)	Technique	Reference	Source Cited
8.5	NR	NR	NR	U.S. EPA, 1990; Podoll et al., 1986	Sarna et al., 1984
6.84	NR	298	NR	U.S. EPA, 1985	Mabey et al., 1981
6.15	NR	NR	NR	Marple et al., 1986; U.S. EPA, 1985; NRCC, 1981	Kenaga, 1980
6.15	NR	NR	NR	Kenaga, 1980	NR
6.85	NR	NR	NR	Crosby, 1985	NR
6.6(f)	NR	NR	NR	SCAQMD, 1988	Podoll et al., 1986
6.6(f)	NR	NR	NR	Thomann, 1989	Neely, 1979

NR = Not Reported.

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

(a) 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 in a two-phase octanol/water system. Values for K_{ow} are thus dimensionless.

(b) Fragment additivity.

(c) Estimated using methods from Leo and Hansch-Leo.

(d) HPLC - fragment additivity.

(e) $\log K_{ow} = -\log S(M) - 0.01\ MP + 0.7$ (Yalkowsky, 1983); S = water solubility (mol/L), MP = melting point (°C).

(f) This value was not found in the source cited.

4.2.3 Soil/Water-Organic Carbon Coefficient for 2,3,7,8-TCDD

The organic carbon partition coefficient (K_{oc}) is a measure of the tendency for organics to sorb 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,

$$K_{oc} = \frac{(\text{mg chemical adsorbed/kg organic carbon})}{(\text{mg chemical dissolved/liter of solution})} \tag{4-5}$$

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. Earlier studies (e.g., Jackson et al., 1987; McKone, 1985; Mill, 1985) utilized the K_{oc} - K_{ow} correlation proposed by Karickhoff et al. (1979) and the K_{oc} - solubility correlations proposed by Chiou et al. (1979) and Means et al. (1980). It is important to note that these correlations were derived for polycyclic aromatics and chlorinated hydrocarbons; however, 2,3,7,8-TCDD or other chlorinated dibenzodioxins were not included as study chemicals.

The results in Table 4-7 show values for log K_{oc} reported in the literature in a range of 5.67 - 7.39. Differences in measured values are attributed to the dependence of K_{oc} on soil characteristics such as organic carbon and moisture content, pore size distribution, ionic strength, pH, and temperature. Also, presence of other organic chemicals (co-contaminants) in the soil matrix can greatly influence the partitioning of 2,3,7,8-TCDD between the soil solid-phase and soil water (Jackson et al., 1987).

The variability of the estimated K_{oc} values is attributed to the use of different estimation equations as previously described. Even when the same equation (Karickhoff et al., 1979) was used to estimate K_{oc} different results were reported in the literature (Jackson et al., 1987; McKone, 1985; Mill, 1985) because different values for K_{ow} were used in the correlation.

Table 4-7. Soil/Water - Organic Carbon Coefficient (K_{oc})(a) for 2,3,7,8-TCDD*

log K_{oc}(b)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
6.66	NR	NR	Measured	Walters et al., 1989	
7.39	NR	NR	Measured	Jackson et al., 1987	
6.6	±0.7 (log K_{oc})	NR	Estimated(c)	Walters et al., 1989; U.S. EPA, 1990	Walters and Giuseppi-Elie, 1988
6.63	NR	NR	Estimated(d)	McKone, 1985	
6.95	NR	NR	Estimated(e)	Jackson et al., 1987; Howard et al., 1991	
6.04	NR	NR	Estimated(f)	Mill, 1985	
6.9	NR	NR	Estimated(g)	Mill, 1985	
6.52	NR	NR	--	U.S. EPA, 1985	Mabey et al., 1981
5.67	NR	NR	Estimated	Schroy et al., 1984; Jensen et al., 1981	Kenaga, 1980
6.0-7.39	NR	NR	Estimated	ATSDR, 1989	Schroy et al., 1985; Jackson et al., 1987; Marple et al., 1986
6.3-7.3	NR	NR	NR	U.S. EPA, 1992	U.S. EPA, 1990
5.99(h)	NR	NR	NR	U.S. EPA, 1985	NRCC, 1981

Table 4-7. Soil/Water - Organic Carbon Coefficient (K_{oc})[a] for 2,3,7,8-TCDD*
(Continued)

NR = Not Reported.

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

(a) K_{oc} is estimated as the ratio of the mass of chemical adsorbed per unit mass of organic carbon in the soil or sediment to the concentration of the chemical in the solution at equilibrium.

(b) Units for K_{oc} are as follows:

$$K_{oc} = \frac{\mu\text{g adsorbed/g organic carbon}}{\mu\text{g/ml solution}} = \frac{\text{ml solution}}{\text{g organic carbon}}$$

(c) The value estimated by log-linear extrapolation of sorption isotherm data generated by using water/methanol mixtures, in accord with the cosolvent theory.

(d) $\log K_{oc} = \log K_{ow} - 0.21$ (Karickhoff et al., 1979); $\log K_{ow} = 8.84$ (Mabey et al., 1981).

(e) $\log K_{oc} = \log K_{ow} - 0.21$ (Karickhoff et al., 1979); $\log K_{ow} = 7.16$ (Dragun, 1986).

(f) $\log K_{oc} = -0.557 \log S + 4.277$ (Chiou et al., 1979); S = solubility in ppb.

(g) $\log K_{oc} = 1.00 \log K_{ow} - 0.21$ (Karickhoff et al., 1979); $\log K_{ow} = 7.11$.

(h) This value was not found in the source cited.

4.2.4 Bioconcentration Factors for 2,3,7,8-TCDD

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:

$$\mathrm{BCF} = \frac{\text{(equilibrium concentration of chemical in receptor)}}{\begin{array}{c}\text{(concentration of chemical in the medium}\\ \text{through which exposure occurs by direct contact)}\end{array}} \quad (4\text{-}6)$$

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. 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 empirical correlations may be utilized to estimate BCF values. BCF is frequently correlated with the K_{ow} or solubility (S) through (Lyman et al., 1990)

$$\log(\mathrm{BCF}) = A + B \log(K_{ow}) \quad (4\text{-}7)$$

or

$$\log(\mathrm{BCF}) = C + D \log(S) \quad (4\text{-}8)$$

where A, B, C, and D are empirical constants. For example, Veith et al. (1980) derived the following parameter values: $A = -0.23$, $B = 0.76$, for Eq. 4-7 based on a wide range of chemical classes and applicable for fish BCF. Kenaga and Goring (1980) derived the values of $C = 2.791$ and $D = -0.564$, for use in Eq. 4-8 for fish BCF, also based on a wide range of chemical classes.

Recently, Banerjee and Baughman (1991) suggested the following fish BCF correlation for high MW organics which is applicable for compounds with high K_{ow} values

$$\log(\mathrm{BCF}) = -1.13 + 1.02 \log(K_{ow}) + 0.84 \log(S_{octanol}) + 0.0004\,(T_{mp} - 25); \quad (r = 0.95) \tag{4-9}$$

where $S_{octanol}$ is molar solubility of the chemical in octanol and T_{mp} is melting point in °C. It is interesting to note that for 2,3,7,8-TCDD, Eq. 4-9 leads to a BCF value of 350 using $\log(K_{ow}) = 6.64$ (Marple et al., 1986), $\log(S_{octanol}) = -3.82$ (Crummett and Stehl, 1973), and $T_{MP} = 306°C$.

Table 4-8 presents 2,3,7,8-TCDD BCF values for different aquatic organisms. It can be seen that reported values for BCFs can vary significantly. Differences among measured values are due to different experimental conditions such as exposure time, organisms tested, experimental system design, and range of exposure concentrations of 2,3,7,8-TCDD in water. Since many of those experiments were short term studies, the reported BCFs may reflect systems that did not reach equilibrium.

Another important factor to be considered with respect to bioconcentration studies is the low solubility of 2,3,7,8-TCDD and its strong sorption to suspended particles and sediments. For example, Matsumura and Benezet (1973) showed that mosquito larvae, which are bottom feeders, had much higher BCF than brine shrimp and fish when 2,3,7,8-TCDD was introduced into the system in the form of residues on sand. Thus, the feeding mode of aquatic organisms should be considered when assessing bioconcentration of 2,3,7,8-TCDD.

Differences among estimated values of BCF are attributed, in part, to the different organisms used in the development of the BCF correlations and the variability in the solubility and K_{ow} values used in those developing correlations.

Table 4-8. Bioconcentration Factor (BCF)[a] for 2,3,7,8-TCDD in Aquatic Organisms*

Bioconcentration Factor (dimensionless)	Organism	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
49[f]	Daphnia (algae)	NR	NR	Measured[b]	Matsumura and Benezet, 1973	
2,198[f]	Daphnia (algae)	NR	NR	Measured[c]	Matsumura and Benezet, 1973	
218[f]	Ostracod (algae)	NR	NR	Measured[b]	Matsumura and Benezet, 1973	
107[f]	Ostracod (algae)	NR	NR	Measured[c]	Matsumura and Benezet, 1973	
121[f]	Brine shrimp	NR	NR	Measured[b]	Matsumura and Benezet, 1973	
1,570[f]	Brine shrimp	NR	NR	Measured[d]	Matsumura and Benezet, 1973	
9,222[f]	Mosquito larvae	NR	NR	Measured[d]	Matsumura and Benezet, 1973	
2,846[f]	Mosquito larvae	NR	NR	Measured[e]	Matsumura and Benezet, 1973	
-	Fish - northern brook silverside	NR	NR	Measured[d]	Matsumura and Benezet, 1973	
54	Fish - northern brook silverside	NR	NR	Measured[e]	Matsumura and Benezet, 1973	
2,000-18,600[g]	Algae	NR	NR	Measured[h]	Isensee and Jones, 1975	
1,200-5,000[g]	Duckweed	NR	NR	Measured[h]	Isensee and Jones, 1975	
1,400-47,100[g]	Snails	NR	NR	Measured[h]	Isensee and Jones, 1975	
7,800-68,000[g]	Daphnids	NR	NR	Measured[h]	Isensee and Jones, 1975	

Table 4-8. Bioconcentration Factor (BCF)[a] for 2,3,7,8-TCDD in Aquatic Organisms

(Continued)

Bioconcentration Factor (dimensionless)	Organisms	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
1,000-63,300[g]	Gambusia	NR	NR	Measured[h]	Isensee and Jones, 1975	
2,000-27,900[g]	Catfish	NR	NR	Measured[h]	Isensee and Jones, 1975	
8,558-28,664	Rainbow trout	NR	NR	Measured[i]	Mehrle et al., 1988	
37,000-86,000	Rainbow trout	NR	NR	Estimated[j]	Mehrle et al., 1988	
467,000	Rainbow trout	NR	NR	Estimated[k]	Mehrle et al., 1988	Kenaga and Goring, 1980
1,000,000	Fish	NR	NR	Estimated[l]	Mehrle et al., 1988	Chiou et al., 1977
79,433	Fish	NR	NR	Estimated[m]	Mill, 1985	Lyman et al., 1982
3,000-9,000	NR	NR	NR	Estimated[n]	U.S. EPA, 1984	
7,000-9,270	Rainbow trout	NR	NR	NR	Mehrle et al., 1988	Branson et al., 1985; Isensee, 1978; Adams et al., 1986
7,900-9,300	Fathead minnows	NR	NR	NR	ATSDR, 1989	Adams et al., 1986; EPA, 1985b
20,000[o]	All fresh water fish	NR	NR	NR	U.S. EPA, 1990	
24,100[p]	Cold water species	NR	NR	NR	U.S. EPA, 1990	
7,900[q]	Warm water species	NR	NR	NR	U.S. EPA, 1990	

Table 4-8. Bioconcentration Factor (BCF)(a) for 2,3,7,8-TCDD in Aquatic Organisms*
(Continued)

Bioconcentration Factor (dimensionless)	Organisms	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
39,000	Rainbow trout Salmo gaidneri	NR	NR	NR	ATSDR, 1989	Mehrle et al., 1988
2,000	Freshwater fish	NR	NR	NR	SCAQMD, 1988	Thomas, 1983
5,000	Freshwater fish	NR	NR	NR	SCAQMD, 1988	Matsumura, 1977
9,270	Freshwater fish	NR	NR	NR	SCAQMD, 1988	Branson et al., 1983
86,000	Freshwater fish	NR	NR	NR	SCAQMD, 1988	Petty et al., 1986
390-13,000	Alga, snail, daphnid	NR	NR	NR	SCAQMD, 1988	Isensee and Jones, 1975; Isensee, 1978
660-7070	Alga, snail, daphnid	NR	NR	NR	SCAQMD, 1988	
35,500	Fish	NR	NR	NR	Schroy et al., 1985	Kenaga, 1980
10	Fish	NR	NR	NR	McKone, 1985	Kenaga and Morris, 1983
49,000	Fish	NR	NR	NR	Travis and Hattemer-Frey, 1989	Mehrle et al., 1988
5,400	Fish - flowing water	NR	NR	NR	Kenaga, 1980	Branson et al., 1978
35,500	Fish - static water	NR	NR	NR	Kenaga, 1980	Isensee and Jones, 1975

NR = Not Reported.

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

(a) BCF is the concentration of a chemical in an organism divided by the concentration of a chemical in water at "equilibrium".

Table 4-8. Bioconcentration Factor (BCF)[a] for 2,3,7,8-TCDD in Aquatic Organisms*
(Continued)

(b) 2,3,7,8-TCDD was introduced directly into ambient water with the primary food organisms.

(c) Primary food organisms allowed to pick up 2,3,7,8-TCDD from glass surface and then given to the test organisms.

(d) 2,3,7,8,-TCDD introduced into system in the form of residues on sand.

(e) Two-step bioconcentration of 2,3,7,8-TCDD by mosquito larvae and northern brook silverside.

(f) BCF values determined on fresh water weight basis.

(g) BCF values determined on dry weight basis.

(h) 2,3,7,8-TCDD was sorbed to soils (Lakeland sandy loam soil and Matapeake silt loam soil) and then placed in the bottom of glass aquaria.

(i) Measured for 28 days - the system did not reach steady-state.

(j) Estimated with computer program 90% steady-state.

(k) Estimated by using equation $\log BCF = 2{,}791 - 0.564 \log S$; S = water solubility in ng/L.

(l) Estimated by using equation $\log BCF = 3.41 - 0.508 \log S$; S = water solubility in ng/L.

(m) Estimated by using the equation $\log BCF = 0.564 \log S + 2.791$; S = solubility in ppm.

(n) Estimated by using the following equations:

$\log BCF = 0.542 \log K_{ow} + 0.124$ (Kenaga and Goring, 1980; Veith et al., 1980)
$\log BCF = 0.76 \log K_{ow} - 0.23$ (Veith et al., 1980)
$\log BCF = 0.79 \log K_{ow} - 0.40$ (Veith and Rosian, 1983)
$\log BCF = 0.635 \log K_{ow} + 0.7285$ (Kenaga and Goring, 1980)
$\log BCF = 0.85 \log K_{ow} - 0.70$ (Veith et al., 1980; Veith and Rosian, 1983)
$BCF = 0.048 K_{ow}$ (Veith and Rosian, 1983)
$\log K_{ow} = 6.15$ (Branson, 1983)
$\log K_{ow} = 6.84$ (Mabey et al., 1982)
$\log K_{ow} = 7.14$ (Neely, 1979)
$\log K_{ow} = 7.28$ (Leo, 1979)

(o) Geometric mean for all fresh water fish. Most reliable in concentration range of 0.038 to 107 ppt.

(p) Geometric mean for cold water species. Most reliable in concentration range of 0.038 to 107 ppt.

(q) Warm water species concentration was 0.87 ppt.

4.2.4.1 Bioconcentration of 2,3,7,8- TCDD in Vegetation

The concept of BCFs has also been applied to accumulation of 2,3,7,8-TCDD in vegetation. Plant accumulation of 2,3,7,8-TCDD can involve several different mechanisms, including: (1) root adsorption, (2) root uptake followed by transpirational translocation of 2,3,7,8-TCDD from roots to shoots, (3) volatility of 2,3,7,8-TCDD from soils and hydroponic solutions followed by foliar adsorption, (4) contamination of plant foliage by 2,3,7,8-TCDD laden soil, and (5) atmospheric deposition of airborne particle-bound 2,3,7,8-TCDD and vapor phase absorption (McCrady et al., 1990). Some authors suggested that root uptake and translocation of 2,3,7,8-TCDD in the transpiration stream is a significant plant contamination mechanism (Sacchi et al., 1986; Cocucci et al., 1979). However, transpiration stream transport of 2,3,7,8-TCDD, an extremely hydrophobic compound with reported log K_{ow} values of 6.64 (Marple et al., 1986), is not likely to be significant due to strong adsorption of 2,3,7,8-TCDD to the organic components of plant xylem tissue (McCrady et al., 1987; Briggs et al., 1982). Current thought on highly hydrophobic organic contaminants such as 2,3,7,8-TCDD is that sorption to outer portions of below ground vegetation is the principal cause of transfer from soil to plant roots and that the translocation of a contaminant from polluted soil to plant leaves, via root uptake, is negligible (Briggs et al., 1982; Ryan et al., 1988; Bacci et al., 1990). Above ground portions of vegetation are thought to be principally impacted by vapor phase transfers (Bacci et al., 1990; McCrady et al., 1990). Also, volatility of 2,3,7,8-TCDD from soil is an important transport mechanism that can result in significant quantities of airborne 2,3,7,8-TCDD being adsorbed by plant shoots (McCrady et al., 1990).

<u>*Root Bioconcentration Factor*</u>

Briggs et al. (1982) proposed the following definition for the root bioconcentration factors for root crops:

$$B_{vw} = \frac{C_{veg}}{C_{soil}} \qquad (4\text{-}10)$$

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

$$B_{vw} = B_{vd} \times f_{dw} \tag{4-11}$$

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:

$$B_{vw} = \frac{0.82 + 0.028\, K_{ow}^{0.77}}{K_d} \tag{4-12}$$

in which $K_d = K_{oc} \cdot \chi$ where χ represents the mass fraction of the soil natural organic carbon. It is emphasized that 2,3,7,8-TCDD was not included in the development of the above correlation and thus Eq. 4-12 only provides an estimate of B_{vw} for 2,3,7,8-TCDD given values of K_{oc} and χ for the specific soil under consideration.

Air-to-Leaf Bioconcentration Factor

The basis for a vapor-phase vegetation bioconcentration factor for various airborne contaminants, including 1,2,3,4-TCDD (2,3,7,8-TCDD not included), was developed by Bacci et al. (1990, 1992). These authors suggested that the air-to-leaf route should be regarded as the main mode of contamination via the air pathway for higher plant leaves, mosses, and lichens for non-polar, low-volatility chemicals. The dimensionless air-to-leaf bioconcentration factor on a wet plant basis, B_{vaw}, can be expressed as

$$B_{vaw} = \frac{C_{va} \rho_p}{C_a F_v} \tag{4-13}$$

where C_{va} is the chemical concentration in the plant on a wet (i.e., fresh) plant mass basis (e.g., mg/kg fresh plant), C_a is the concentration of a chemical in the air (e.g., mg/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). 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, 1992).

Table 4-9 presents plant uptake transfer factors for 2,3,7,8-TCDD found in the literature. Reported values were mostly obtained as ratios of measured concentrations of 2,3,7,8-TCDD in plants and soils. It is important to note that the literature is often unclear as to the mechanism of plant contamination. Outer portions of below ground vegetation contained concentrations probably due to sorption. Translocation with transpiring water has been hypothesized as the cause for contamination of above ground portions in two studies (Cocucci et al., 1979; Sacchi et al., 1986), while contamination by soil particles has been hypothesized as the cause for contamination of above ground vegetation in two other studies (Young, 1983; Wipf et al., 1982). Also, the literature is not consistent in its reporting of fresh weight vs. dry weight of studied plants and in some papers such information was not provided. The values reported in the literature indicate a low potential for 2,3,7,8-TCDD bioconcentration in plants via root uptake.

Kew et al. (1989) reviewed inconsistencies in the results and conclusions from investigations reported in the literature on plant uptake of 2,3,7,8-TCDD. These authors noted the wide variation in reported values for plant uptake bioconcentration factors, and suggested several explanations, including variable bioavailability for 2,3,7,8-TCDD uptake from different soil types, different experimental and analytical approaches, and attributing root uptake and translocation of 2,3,7,8-TCDD to plant shoots without excluding plant accumulation of 2,3,7,8-TCDD from air.

No measured or estimated values of bioconcentration factors were found for air-to-leaf and deposition routes for 2,3,7,8-TCDD. Although B_{vaw} has not been measured for 2,3,7,8-TCDD, there are the air-to-leaf correlations that have been proposed in the literature

$$B_{vaw} = 0.19 + 0.7/H_i' + 0.05\ K_{ow}/H_i' \quad \text{(Paterson and Mackay, 1991)} \qquad (4\text{-}14)$$

$$B_{vaw} = 0.022\ K_{ow} / H_i' \quad \text{(Bacci et al., 1990)} \qquad (4\text{-}15)$$

Table 4-9. Plant Uptake Bioconcentration Factors(a) for 2,3,7,8-TCDD*

Value (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
0.0006-0.113(b)	≤3.8% SE	298	Measured(c)	Sacchi et al., 1986	
0.0012-0.135(b)	≤3.8% SE	298	Measured(d)	Sacchi et al., 1986	
0.0027-0.048(e)	≤3.8% SE	298	Measured(f)	Sacchi et al., 1986	
0.0073- 0.35(e)	≤3.8% SE	298	Measured(g)	Sacchi et al., 1986	
0.01-0.272(h)	≤4.3% SE	298	Measured(f)	Sacchi et al., 1986	
0.012-0.86(i)	≤4.3% SE	298	Measured(g)	Sacchi et al., 1986	
0.4(j)	NR	NR	Measured	Cocucci et al., 1979	
0.84(k)	NR	NR	Measured	Cocucci et al., 1979	
1.8(l)	NR	NR	Measured	Cocucci et al., 1979	
0.25(m)	NR	NR	Measured	Cocucci et al., 1979	
0.43(n)	NR	NR	Measured	Cocucci et al., 1979	
0.23(o)	NR	NR	Measured	Cocucci et al., 1979	
0.31(p)	NR	NR	Measured	Cocucci et al., 1979	
0.67(q)	NR	NR	Measured	Cocucci et al., 1979	
0.66(r)	NR	NR	Measured	Cocucci et al., 1979	

Table 4-9. Plant Uptake Bioconcentration Factors(a) for 2,3,7,8-TCDD*
(Continued)

Value (dimensionless)	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
0.38(s)	NR	NR	Measured	Cocucci et al., 1979	
0.51(t)	NR	NR	Measured	Cocucci et al., 1979	
0.59(u)	NR	NR	Measured	Cocucci et al., 1979	
0.0009-0.0042(v)	NR	NR	Measured	Wipf et al., 1982	
0.01-0.17(w)	NR	NR	Measured	Wipf et al., 1982	
< 0.017(x)	NR	NR	Measured	Isensee and Jones, 1971	
0.02-1.81(y)	NR	NR	Measured	Young, 1983	
0.011	NR	NR	Estimated(z)	Travis and Arms, 1988	
0.003(aa)	NR	NR	NR	Travis and Hattemer-Frey, 1989	Travis and Arms, 1988
0.013(bb)	NR	NR	NR	Travis and Arms, 1988	Helling et al., 1973
3×10^{-5}	NR	NR	NR	McKone, 1985	NR

NR = Not Reported.

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

(a) Plant uptake bioconcentration factor defined as (Travis and Arms, 1988): $B_V = \frac{\text{mg of compound/kg of dry plant}}{\text{mg of compound/kg of dry soil}}$

(b) This range was calculated based on reported measured concentrations of 2,3,7,8-TCDD in the plants and soil on fresh weight basis by dividing concentration in plant by concentration in the soil. Concentrations were measured on 7th, 34th and 57th day.

(c) 2,3,7,8-TCDD incorporation in aerials parts of been plants grown on soil with added peat. Mechanism of 2,3,7,8-TCDD incorporation in aerials parts of the plant reported by authors was translocation by the transpiration.

Table 4-9. Plant Uptake Bioconcentration Factors(a) for 2,3,7,8-TCDD*
(Continued)

(d) Same as (c) for maize plants.

(e) Same as (b) except concentrations were measured on 8th and 77th day.

(f) Same as (c) but without added peat.

(g) Same as (f) for maize plants.

(h) This range was calculated by dividing concentration of 2,3,7,8-TCDD in 2nd leaf of bean plants by concentration in soil.

(i) This range was calculated by dividing concentration of 2,3,7,8-TCDD in 3rd lead of maize plants by concentration in soil.

(j) This value was calculated by dividing measured concentration of 2,3,7,8-TCDD in aerial parts of carrot plants by concentration in soil (fresh weight basis).

(k) This value was calculated by dividing measured concentration of 2,3,7,8-TCDD in underground inner parts of carrot plants by concentration in soil (fresh weight basis).

(l) This value was calculated by dividing measured concentration of 2,3,7,8-TCDD in underground outer parts of carrot plants by concentration in soil (fresh weight basis).

(m) Same as (j) for potato plants.

(n) Same as (k) for potato plants.

(o) Same as (l) for potato plants.

(p) Same as (j) for potato plants.

(q) Same as (k) for potato plants.

(r) Same as (l) for potato plants.

(s) Same as (j) for potato plants.

(t) Same as (k) for narcissus plants.

(u) Same as (l) for narcissus plants.

(v) This range was calculated by dividing measured concentrations of 2,3,7,8-TCDD in apples, pears, plums, figs, peaches and apricots by concentration in contaminated soil in Seveso, Italy. > 95% of whole fruit concentrations (apples, pears, peaches) was in the peels. Reference was unclear as to whether reported concentrations in fruit was based on fresh or dry weight.

(w) This range was calculated by dividing measured concentrations of 2,3,7,8-TCDD in carrots by concentration of 2,3,7,8-TCDD in contaminated soil in Seveso.

(x) No residues of 2,3,7,8-TCDD were found in mature oat and soybean plants grown on soil treated with [^{24}C} TCDD to achieve a concentration of 60 ppb.

(y) This range was obtained for grasses and broadleaf plants grown on soils which has received 9 years of 2,4,5-T herbicide applications contaminated with 2,3,7,8-TCDD. It was not clear whether concentrations are on a fresh or dry weight basis.

(z) The value was estimated using the estimation equation derived by Travis and Arms (1988): $\log B_{vsw} = 1.588 - 0.578 \log K_{ow}$; $\log K_{ow} = 6.15$

(aa) The value can not be reproduced from the cited source.

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 universal gas constant). It is noted that B_{va} is related to B_{vaw}.

$$B_{vaw} = B_{va} \times f_{dw} \qquad (4\text{-}16)$$

Using, for example, K_{ow} value of 4.4×10^6 and H_i' value of 0.001, a range of 9.6×10^7 - 2.2×10^8 was obtained for B_{vaw} from Eqs. 4-14 and 4-15. These values indicate that, for the portion of 2,3,7,8-TCDD present in the vapor phase, air-to-leaf transfer is a major pathway for bioconcentration in vegetation. However, it must be noted that 1,2,3,4-TCDD (not 2,3,7,8-TCDD) was used as the study chemical in the development of the above correlations. Thus, the above estimates of B_{vaw} values for 2,3,7,8-TCDD should only be regarded as indicative of the order of magnitude of B_{vaw} for 2,3,7,8-TCDD.

Accumulation Due to Dry Deposition of Particle-Bound 2,3,7,8-TCDD

Another process that can contribute to the above ground vegetation concentration is the dry deposition of particle-bound 2,3,7,8-TCDD onto plants. Only a portion of the chemical deposited is captured by the plant canopy and in general, as the particle size increases, there is less likelihood of initial retention (Witherspoon and Taylor, 1970; Markin, 1981). The fraction of the particles initially deposited and retained on the plants is dented by the interception factor. The dry deposition velocity and the interception factor are needed for the estimation of the accumulation of 2,3,7,8-TCDD in vegetation due to deposition. The interception factor is related to leaf area and roughness, plant biomass, plant density, and other factors (Baes et al., 1984; Markin, 1981). Interception fractions related to dry matter yield of pasture and hay crops have been established for the major classes of feed crops and vegetables (Baes et al., 1984; Stevens and Gerbec, 1988). Using the interception factor, the deposition flux intercepted by the plant canopy, N_p (e.g., $\mu g/m^2 \cdot day$), is given by

$$N_p = V_d \left(1 - e^{\beta M_p}\right) C_a \tag{4-17a}$$

in which V_d is the particle deposition velocity (e.g., m/day) discussed in Section 4.3.3.1, β is foliar interception constant (m^2/kg of dry vegetation) and M_p is the plant dry mass inventory (kg/m^2), and C_a is the concentration of the particle-bound chemical in the atmosphere (e.g., μg/m^3). A simple mass balance on a plant, assuming constant plant mass and chemical input due to dry deposition and chemical loss due to weathering results in the following equation for the chemical concentration in the plant, C_p (e.g., μg/kg dry plant matter)

$$C_p = \frac{N_p}{M_p k_p} \left(1 - e^{-k_p t}\right) \tag{4-17b}$$

in which k_p is a first-order weathering constant (e.g., 1/day), and t is the time during which dry deposition is being considered. A 14-day half-life (i.e., $\tau_{1/2} = \ln 2/k_p$) is commonly used for particulate loss by weathering processes. It is interesting to note that half-lives measured in field studies range from about 2 to 34 days with a median of 10 days (Baes et al., 1984). Finally, values for the foliar interception constant can be obtained from a number of literature sources (Baes et al., 1984; Stevens and Gerbec, 1988; see also Fries and Paustenbach, 1990).

Accumulation Due to Wet Deposition

Wet deposition as described in Section 4.3.3.2 could also be an important process that contributes to accumulation of 2,3,7,8-TCDD in the above ground vegetation. However, no measured data on 2,3,7,8-TCDD accumulation in plants due to wet deposition were found in the literature. In order to predict the concentration of 2,3,7,8-TCDD in plants due to intermittent wet deposition, one must first perform a mass balance for 2,3,7,8-TCDD transported to the surface in rainwater, and secondly, one must be able to reasonably determine the fraction of 2,3,7,8-TCDD in precipitation that is captured by the plant canopy. Given the variability in the types of plants, their physiology and their complex interaction with the surrounding environment, it is apparent that the determination of 2,3,7,8-TCDD accumulation in vegetation due to wet deposition is difficult. However, it may be feasible to develop a simple model to determine an upper-bound estimate of the contribution of wet deposition to the accumulation of dioxin by plants. For example, by using the "washout" ratio (Section 4.3.3.2), one can estimate the concentration of dioxin in precipitation. Thus, a simple mass balance on a plant during a given rain event, assuming no degradation of dioxin during rain, leads to an upper-limit estimate of the contribution of rain to the chemical concentration in the plant, $C_p^{(w)}$ (e.g., μg/kg plant matter)

$$C_p^{(w)} = \Lambda_p^{*} C_a^{(p)} V_w / M_p \tag{4-17c}$$

in which Λ_p^{*} is the washout ratio described in Section 4.3.3.2, $C_a^{(p)}$ is the atmospheric concentration of the particle-bound chemical (e.g., $\mu g/m^3$), and V_w is the volume of rainwater intercepted by the plant canopy (e.g., m^3/m^2), over a unit soil surface area and M_p is the plant mass inventory (e.g., kg plant matter/m^2 soil surface).

4.2.5 Biotransfer Factors for 2,3,7,8-TCDD 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

$$B_{TFi} = C_j / L_i C_{in} \tag{4-18}$$

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

$$B_{TF} = C_j \,/\, \left(\sum_{i=1}^{N} L_i C_{in}\right) = \left[\sum_{k=1}^{N} Ex_k H_{kj} + K_j V_j\right]^{-1} \tag{4-19}$$

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 (or elimination) stream associated with the particular pathway. H_{kj} is the partition coefficient between receptor j and outflow stream k. The overall biochemical transformation of a given contaminant via first order reaction kinetics is given by the rate constant K_j while the subscript k represents a specific elimination pathway. 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 feeding, 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 dependent on 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 2,3,7,8-TCDD 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 2,3,7,8-TCDD 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), although 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:

$$B_m = \frac{\text{(concentration in milk (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \tag{4-20}$$

$$B_b = \frac{\text{(concentration in meat (mg/kg))}}{\text{(daily intake of organic (mg/d))}} \tag{4-21}$$

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.

As shown in Table 4-10, Travis and Arms (1988) derived a log K_{ow} vs. log B_m correlation based on data for 28 organic chemicals in milk (2,3,7,8-TCDD was included) which yielded the following equation:

$$\log B_m = -8.056 + 0.992 \log K_{ow} \quad r=0.74 \quad 2.81 < \log K_{ow} < 6.89 \tag{4-22}$$

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. 4-22 and a log (K_{ow}) value of 6.64 (Marple et al., 1986), one obtains log (B_m) of -1.46 (or B_m = 0.035).

Table 4-11 summarizes values for feed-to-meat transfer (B_b) factors for 2,3,7,8-TCDD ranging from 0.1 to 0.4 day/kg. The values of 0.4 and 0.22 were estimated based on the study of Jensen et al. (1981) and the value of 0.1 was calculated from the following correlation (2,3,7,8-TCDD was included as a study chemical):

$$\log B_b = -7.6 + \log K_{ow} \qquad n = 36,\ r = 0.81 \qquad \text{(Travis and Arms, 1988)} \tag{4-23}$$

Although other correlations for B_b are available (e.g., Kenaga, 1980), these did not include 2,3,7,8-TCDD as one of the study chemicals.

Table 4-10. Feed-to-Milk Transfer Factor (B_m)(a) for 2,3,7,8-TCDD*

Feed-to-Milk Transfer Factor	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
0.035(b)	Day/kg	NR	NR	Estimated	Section 4.2.5	
0.04(c)	Day/kg	NR	NR	Calculated	SCAQMD, 1988	SCAQMD, 1988
0.008(d)	NR	NR	NR	Estimated	SCAQMD, 1988	Jensen and Hummel, 1982
0.09(d)	NR	NR	NR	Estimated	SCAQMD, 1988	Jensen et al., 1981
0.058(d)	Day/kg	NR	NR	NR	Travis and Hattemer-Frey, 1989	Travis and Arms, 1988

NR = Not Reported.

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

(a) The feed-to-milk conversion factor (B_m) is a biotransfer factor (BTF) that is defined as (Travis and Arms, 1988):

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

(b) This value was calculated based on the correlation of Travis and Arms (1988):
$\log B_m = -8.056 + 0.992 \log K_{ow}$; $\log K_{ow} = 6.6$ (Marple et al., 1986)

(c) This value is an average of three values:
0.09 (Jensen et al., 1981)
0.008 (Jensen and Hummel, 1982)
0.035 (Travis and Arms, 1988)

(d) This value was not found in the source cited and it was not clear how it was derived.

Table 4-11. Feed-to-Meat Transfer (B_b)[a] Factor for 2,3,7,8-TCDD*

Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
0.4	Day/kg	NR	NR	Estimated[b]	SCAQMD, 1988	Jensen et al., 1981
0.1	Day/kg	NR	NR	Estimated[c]	Travis and Arms, 1988	
0.22	Day/kg	NR	NR	Estimated[d]	Travis and Hattemer-Frey, 1989	Jensen et al., 1981

NR = Not Reported.

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

(a) The feed to meat (beef) conversion factor (B_b) is a biotransfer factor defined as (Travis and Arms, 1988): $B_b = \frac{\text{concentration in meat (mg/lg)}}{\text{daily intake of organic (mg/d)}}$

(b) Estimated from a pharmacokinetic extrapolation of 2,3,7,8-TCDD concentration in beef fat at steady state.

(c) Calculated using the estimation equation: $\log B_b = -7.6 + \log K_{ow}$; $\log K_{ow} = 6.15$

(d) Estimated by dividing 2,3,7,8-TCDD concentration in meat by daily intake of 2,3,7,8-TCDD.

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} as discussed above must be distinguished from other terms used to describe the accumulation of a 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 factors in top-order consumers.

The overall bioaccumulation factor K_b can be shown to be related to the biotransfer factors, when exposure occurs in a single medium, by the following relation (Cohen, 1989):

$$K_b = C_j/C_i = B_{TF}(\sum_{i=1}^{N} L_i C_{in})/C_i \tag{4-24}$$

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 and C_{in} is the concentration in either the feed, drinking water, inhaled air. It is important to note that bioaccumulation factors are a function of the receptor characteristics, 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. 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).

Bioconcentration Factors for 2,3,7,8-TCDD in Terrestrial Organisms Including Humans

The concept of BCFs has also been used to quantify the accumulation potential of 2,3,7,8-TCDD in terrestrial animals including humans. BCF in terrestrial animals is defined as the 2,3,7,8-TCDD concentration in the test organisms or tissues divided by the concentration in food when a steady state is reached (Geyer et al., 1986). Since the above type of bioconcentration factor (BAF) addresses partitioning of a chemical into organisms via non-dietary routes as previously stated, it seems to be inappropriate to use the same term in this case and instead in this report the term bioaccumulation factor is used as discussed in the previous section.

Table 4-12 summarizes BAFs for 2,3,7,8-TCDD in different terrestrial organisms and humans. It is interesting to note that BAF values for terrestrial animals are much lower than BCFs for aquatic organisms.

4.2.6 Bioavailability and Exposure Routes for 2,3,7,8-TCDD

The bioavailability of a chemical is defined as the fraction of a compound in a matrix that can be released from that matrix and consequently absorbed by an organism, and hence, is available to elicit a biological effect (SCAQMD, 1988). 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. Experimental studies of the bioavailability of PCDDs from soil and fly ash after ingestion suggest that about 15% - 50% of this chemical mixture may be bioavailable (Poiger and Schlater, 1980; McConnell et al., 1984; Lucier et al., 1986; van den Berg et al., 1985; U.S. EPA, 1987a). The CAPCOA (1992) guidelines recommend a bioavailability factor of 0.43 for dioxins.

Table 4-12. Bioaccumulation Factor (BAF)[a] for 2,3,7,8-TCDD in Terrestrial Animals Including Humans*

BCF (dimensionless)	**Organism (tissue)**	**Reported Uncertainty**	**Temperature (K)**	**Technique**	**Reference**	**Source Cited**
10.9-24.5[b]	Rat (liver)	NR	NR	Measured	Geyer et al., 1986	Kociba et al., 1978
3.7-24.5[b]	Rat (fat)	NR	NR	Measured	Geyer et al., 1986	Kociba et al., 1978
0.7[c]	Beef cattle (liver)	NR	NR	Measured	Geyer et al., 1986	Jensen et al., 1981
3.5[c]	Beef cattle (fat)	NR	NR	Measured	Geyer et al., 1986	Jensen et al., 1981
24.8[d]	Beef cattle (fat)	NR	NR	Measured	Geyer et al., 1986	Jensen et al., 1981
0.01	Cattle (milk)	NR	NR	Measured	Travis and Arms, 1988; U.S. EPA, 1990	Jensen and Hummel, 1982
24-40[e]	Rhesus monkey (fat)	NR	NR	Measured	Geyer et al., 1986	Bowman et al., 1985
0.92[f]	Cattle (fat)	NR	NR	Estimated	McKone, 1985	Kenaga, 1980
104-206[g]	Human adipose tissue	NR	NR	Estimated	Geyer et al., 1986	
153[h]	Human adipose tissue	NR	NR	Estimated	Geyer et al., 1986	
0.05	Beef	NR	NR	Estimated	Travis and Arms, 1988; U.S. EPA, 1990	Kenaga, 1980

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

(a) BCF in terrestrial animals is defined as the 2,3,7,8-TCDD concentration in the test organisms or tissues divided by the concentration in food when a steady state is reached.

(b) Determined at the end of 2-year study.

(c) Determined after 28 days.

(d) Determined after 499 days using a linear one compartment pharmacokinetic model; it was calculated that a steady state in cattle would be reached in 499 days.

(e) Determined after 4 years.

(f) Estimated from the following equation: log BCF = -3.457 + 0.5 (log K_{ow}).

(g) Determined from daily intake of 2,3,7,8-TCDD in food (fish, meat, dairy products).

(h) Estimated from a pharmacokinetic model using experimentally determined 2,3,7,8-TCDD half-life of 5 years in a man.

Exposure Routes

Occupational exposure to 2,3,7,8-TCDD due to manufacture of the herbicides ceased to exist with the ending of production of pesticides containing the contaminant 2,3,7,8-TCDD. Presently, the major sources of 2,3,7,8-TCDD loading to exposure include contaminated soil, dumpsites, and municipal incinerators. Because of the high lipophilicity and long half-life of 2,3,7,8-TCDD, the highest exposure is attributed to the food chain, i.e., from ingestion of contaminated fish, beef, dairy products, and other foods. Ingestion of contaminated soil and dermal contact with contaminated soil, dust, and sediment, and inhalation of contaminated dust and vapor further contribute to human exposure. Dermal and oral exposure from soil depend on the bioavailability of 2,3,7,8-TCDD which is affected by factors such as soil type and contact time. Although inhalation exposure can occur, there are no studies on the inhalation toxicity of 2,3,7,8-TCDD (ATSDR, 1989).

4.2.7 Gas/Particle Partitioning of 2,3,7,8-TCDD

Vapor/particle partitioning of 2,3,7,8-TCDD in the atmosphere is controlled by its vapor pressure and the total suspended particle (TSP) concentration. Semivolatile organic compounds (SOC), such as 2,3,7,8-TCDD, bound to atmospheric particles appear to consist of both a nonexchangeable fraction, which is strongly adsorbed to active sites or embedded within the particle matrix and is not in equilibrium with its vapor phase, and an exchangeable fraction, which is more loosely attached and is controlled by the concentration of SOC vapors in air (Bidleman, 1988). Junge (1977) presented a model of exchangeable SOC adsorption to aerosols. The adsorbed fraction (ϕ), solute saturation vapor pressure (p°, mm Hg) and total surface area of aerosols (S_T, cm^2/cm^3 air) were related through:

$$\phi = cS_T/(p^\circ + cS_T) \qquad (4\text{-}25)$$

Junge assumed that $c = 1.7 \times 10^{-4}$ atm-cm and did not vary among compounds. This equation and other treatments of adsorption to aerosols have been reviewed by Pankow (1987). It is important to note that the Junge correlation only quantifies the exchangeable fraction of SOC between the particle and gas phase; however, the effect of nonexchangeable material can be significant for some organics including 2,3,7,8-TCDD (Pankow, 1988). Therefore, if the chemical of interest has significant nonexchangeable effects, experimental values for partitioning should be utilized. At present, however, the available experimental data are insufficient to ascertain if there is a nonexchangeable fraction of particle-bound 2,3,7,8-TCDD.

4.3 Intermedia Transport Parameters

The following subsections define the specific intermedia transport factors considered in this study as well as the results of the literature review.

4.3.1 Diffusion Coefficients of 2,3,7,8-TCDD 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:

$$J_A = -D_{AB}\, dC_A/dx \qquad (4\text{-}26a)$$

in which J_A is the diffusion flux for compound A (e.g., $mg/m^2 \cdot s$), 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., $mg/m^2 \cdot s$), across an interface between two phases is expressed by an equation of the form

$$N = K\Delta C \qquad (4\text{-}26b)$$

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

Diffusion coefficients in air can be calculated by using the Fuller et al. (1966) and Wilke and Lee (1955) correlations

Fuller et al. (1966)

$$D_{BA} = \frac{10^{-3} T^{1.75} \sqrt{M_r}}{P \, (V_A^{1/3} + V_B^{1/3})^2} \;, \quad cm^2/s \;, \quad \text{where } M_r = \frac{M_A + M_B}{M_A M_B} \qquad (4\text{-}27)$$

in which the subscript B and A denote the solute (e.g., 2,3,7,8-TCDD) and air, respectively, T is temperature (K), M is molecular weight, P is the pressure (atm), and V_A and V_B are the molar volumes for air and the solute in question, respectively.

Wilke and Lee (1955)

$$D_{BA} = \frac{B' T^{3/2} \sqrt{M_r}}{P \sigma_{AB}^2 \, \Omega} \;, \quad cm^2/s \qquad (4\text{-}28)$$

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} is characteristic length of molecule A interacting with B, Å, M is molecular weight, T is temperature (K), P is pressure (atm), and Ω is collision integral (see Lyman et al., 1990, pp. 17-13, 17-14; Reid et al., 1987).

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

Wilke and Chang (1955)

$$D_{BW} = \frac{7.4 \times 10^{-8}(\phi_W M_W)^{1/2} T}{\eta_W \, V_B^{0.6}} \quad , \quad cm^2/s \tag{4-29}$$

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).

Hayduk and Laudie (1974)

$$D_{BW} = \frac{13.26 \times 10^{-5}}{\eta_W^{1.14} \, V_B^{0.589}} \quad , \quad cm^2/s \tag{4-30}$$

where η_W is viscosity of water (cP) (1 cP = 1 poise = 1 g/cm.s) and V_B is molar volume (cm^3/mol).

Hayduk et al. (1982)

$$D_{BW} = 1.25 \times 10^{-8}(V_B^{-0.19} - 0.292) T^{1.52} \eta_W^{\epsilon^*} \tag{4-31}$$

where V_B is molar volume (cm^3/mol), η_W is viscosity of water (cP), and $\epsilon^* = (9.59/V_B) - 1.12$.

Table 4-13 presents values for diffusion coefficients of 2,3,7,8-TCDD in air and water. No experimental values were found in the literature. Podoll et al. (1986) calculated diffusion coefficients in air and water by using Wilke and Lee (Wilke and Lee, 1955) and Hayduk and Laudie (Hayduk and Laudie, 1974) correlations respectively. The methods of Fuller et al. (1966) and Hayduk et al. (1982) were used to calculate diffusion coefficients in air and water respectively, in this report.

Table 4-13. Diffusion Coefficient in Air and Water for 2,3,7,8-TCDD*

Media	Diffusion Coefficient (cm^2/s)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	Reference	Source Cited
Air	0.047	0.047	cm^2/sec	4.3% Absolute average error	298	Estimated$^{(a)}$	Podoll et al., 1986	
Water	5.1×10^{-6}	5.1×10^{-6}	cm^2/sec	5.8% Absolute average error	298	Estimated$^{(b)}$	Podoll et al., 1986	
Air	0.045	0.045	cm^2/s	NR	298	Estimated	Freeman and Schroy, 1984	Schroy et al., 1984
Water	5.6×10^{-6}	5.6×10^{-6}	cm^2/s	NR	298	Estimated	Freeman and Schroy, 1984; Schroy et al., 1984	Reid et al., 1977
Air	0.052	0.052	cm^2/s	7.6% Absolute average error	298	Estimated$^{(c)}$	Section 4.3.1	
Water	4.7×10^{-6}	4.7×10^{-6}	cm^2/s	NR	298	Estimated$^{(d)}$	Section 4.3.1	

NR = Not Reported.

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

Table 4-13. Diffusion Coefficient in Air and Water for 2,3,7,8-TCDD*
(Continued)

(a) Wilke and Lee method, 1955.

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

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

M = molecular weight

T = temperature (K)

P = pressure (atm)

Ω = collision integral

(b) Hayduk and Laudie method, 1974.

$$D_{BW} = \frac{13.26 x 10^{-5}}{\eta_W^{1.14} \, V_B^{0.589}} \quad , \quad cm^2/s$$

where η_w is viscosity of water (cP), V'_B is molar volume (cm^3/mol)

Table 4-13. Diffusion Coefficient in Air and Water for 2,3,7,8-TCDD*
(Continued)

(c) Fuller et al. method, 1966.

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

(all variables are defined in Section 4.3.1)

P = 1 atm

T = 298 K

M_A = 28.97 g/mol (Lyman et al., 1990)

M_B = 322 g/mol (Section 4.1.5)

V_A = 20.1 cm^3/mol (Table 17-3, in Lyman et al., 1990)

V_B = 254.5 cm^3/mol (estimated from Table 17-4 in Lyman et al., 1990)

(d) Hayduk et al. method, 1982.

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

(all variables are defined in Section 4.3.1)

V_B = 254.5 cm^3/mol [footnote (c)]

T = 298 K

η = 0.8906 cP at 25°C (Lyman et al., 1990)

ϵ^* = $(9.59/V_B) - 1.12$

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:

$$N = K_G (C_g - H'C_l) = K_L (C_l - C_g/H') \tag{4-32}$$

where K_G and K_L are the overall mass transfer coefficients (cm/s) for the gas and liquid phase, respectively, H' is 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:

$$1/K_G = 1/k_g + H'/k_l \tag{4-33}$$

$$1/K_L = 1/k_l + 1/H'k_g \tag{4-34}$$

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 and 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.

4.3.2.1 Air/Water - Air/Side - Mass Transfer Coefficient (k_g) for 2,3,7,8-TCDD

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:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2} - 5\right) + 7.3\ Re_o^{0.25}\ Sc_a^{1/2}\right]^{-1}, \quad Re_o > 2 \qquad (4\text{-}35)$$

and for a smooth surface, k_g is given by:

$$\frac{k_g}{U_{10}} = C_D^{1/2}\left[\epsilon_D^{+}\left(C_D^{-1/2} - 13.5\right) + 13.6\ Sc_a^{2/3}\right]^{-1}, \quad Re_o < 0.13 \qquad (4\text{-}36)$$

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. 4-35 and 4-36 are strictly applicable to a neutral atmospheric condition. However, as suggested by Brutsaert (1975), Eqs. 4-35 and 4-36 are probably still satisfactory even under very unstable, but apparently not under stable conditions. For non-neutral conditions, the mass flux equations Eq. 4-32 must be used with caution since the bulk gas phase concentration as used in Eq. 4-32 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. 4-35 and 4-36 is sufficient especially for sparingly soluble hydrophobic organic compounds.

The use of Eqs. 4-35 and 4-36 requires the wind drag coefficient velocity as input. The wind-drag coefficient, C_D, is defined as (Wu, 1980)

$$C_D = \left(\frac{U_W^*}{U_{10}}\right)^2 \left(\frac{\rho_w}{\rho_a}\right) = \left(\frac{U_a^*}{U_{10}}\right)^2 \tag{4-37}$$

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

$$U_W^* = \sqrt{\frac{\tau_s}{\rho_w}} \tag{4-38}$$

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:

$$U_a^* = U_{10}\ k \left[\ln\left(\frac{z_{10}}{z_o}\right) - \psi_M \left(\frac{z}{L}\right) + \psi_M\left(\frac{z_o}{L}\right) \right]^{-1} \tag{4-39}$$

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

$$Re_o = U_a^*\ z_o/\nu_a \tag{4-40}$$

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)

$$z_o \approx 0.135(\nu_a/U^*_a) \quad , \quad \text{cm} \tag{4-41}$$

and for a rough surface,

$$z_o = a(U^*_a)^b \quad , \quad \text{cm} \tag{4-42}$$

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 $U^*_a \le 6.89$ 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

$$z_o = 0.0144(U^*_a)^2/g \quad , \quad (g=981, \text{cm/s}^2) \tag{4-43}$$

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

$$C_D = 8.5\times10^{-4} \quad , \quad U_{10} < 5 \text{ m/s} \tag{4-44}$$

$$C_D = [0.85 + 0.11\,(U_{10} - 5)]\times10^{-3} \quad , \quad 5 \text{ m/s} \le U_{10} \le 20 \text{ m/s} \tag{4-45}$$

$$C_D = 2.5\times10^{-3} \quad , \quad U_{10} > 20 \text{ m/s} \tag{4-46}$$

or (Wu, 1980)

$$C_D = (0.8 + 0.065U_{10})\times10^{-3} \quad , \quad U_{10} \ge 1 \text{ m/s} \tag{4-47}$$

As an illustration of the above approach, the gas-side mass transfer coefficient as obtained from Eqs. 4-35, 4-36 (with linear interpolation in the region $0.13 \le Re_o \le 2$) and Eqs. 4-42 and 4-47 for z_o and C_D, respectively, for 2,3,7,8-TCDD at 20°C is given in Figure 4.1.

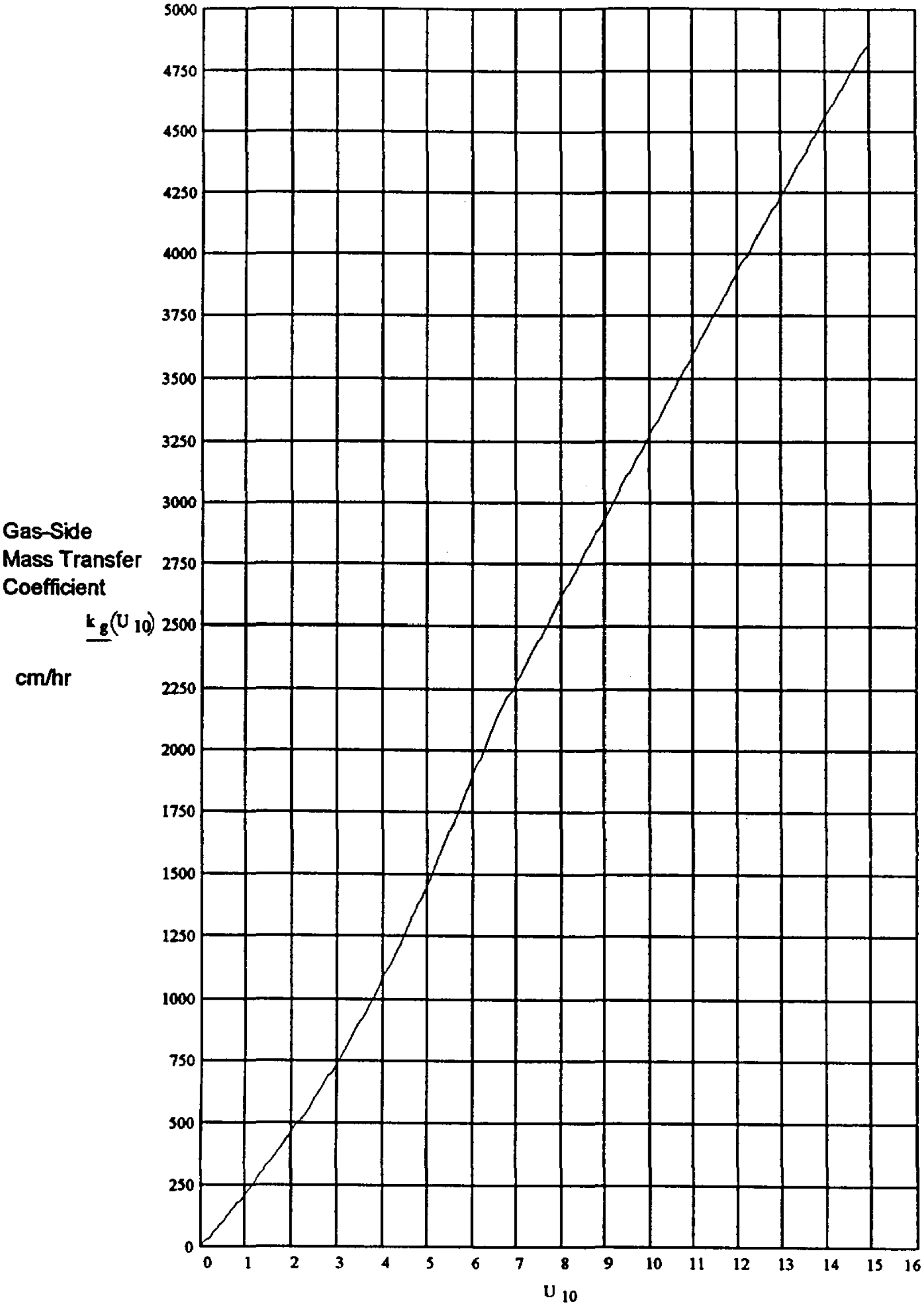

Figure 4.1. Gas-Side Mass Transfer Coefficient for 2,3,7,8-TCDD at 20°C for Water/Air Mass Transfer at Large Fetch. (Based on the Correlation of Brustsaert, 1975).

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

$$k_g = 1137.5\,(V_{wind}+V_{curr})\sqrt{\frac{18}{MW}} \quad , \qquad cm/hr \tag{4-48}$$

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 2,3,7,8-TCDD is estimated as 1076 cm/hr. It is important to note that the atmospheric stability condition for which Eq. 4-48 applies was not reported. Moreover, the theoretical basis of Southworth (1979) equation is questionable because of the linear additivity of the wind and air currents in Eq. 4-48. 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).

$$\frac{k_g}{U_a^*} = 46.2 \times 10^{-3}\ Sc_a^{-0.67} \tag{4-49}$$

Eq. 4-49 results in k_g values which are about 20%-40% higher than predicted by Eqs. 4-35 and 4-436 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 2,3,7,8-TCDD

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,

$$k_l/U_w^* = a\ Sc_w^{-n} \tag{4-50}$$

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:

$$a = a_0 - a_1 \ln U_s^+ \tag{4-51}$$
$$n = n_0 - n_1 \ln U_s^+$$

where

$$a_0 = 0.09691;\ a_1 = 0.01053;$$
$$n_0 = 0.5778;\ n_1 = 0.01771 \tag{4-52}$$

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. 4-52 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 2,3,7,8-TCDD at 20°C is shown in Figure 4.2 where Eqs. 4-38 and 4-47 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

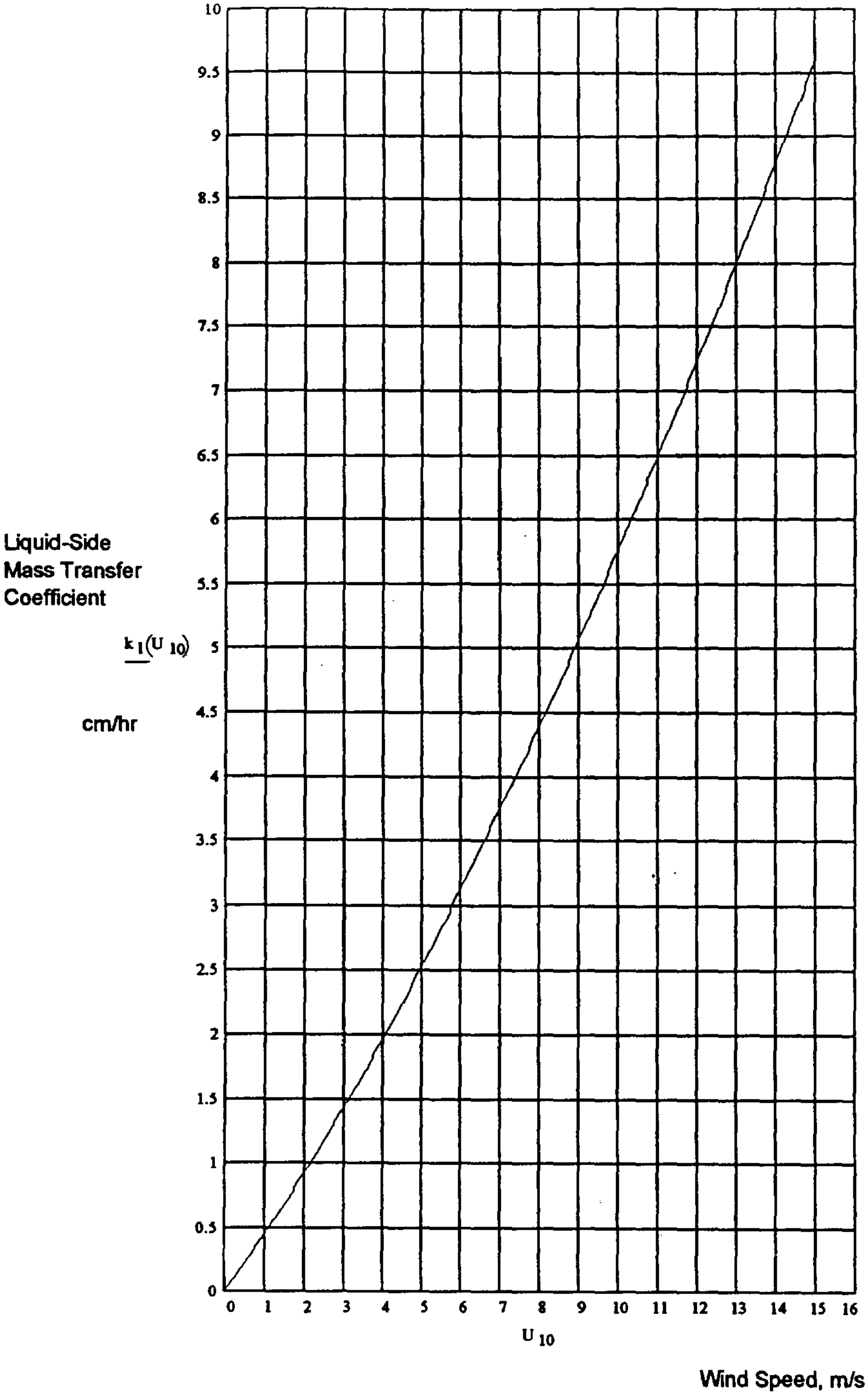

Figure 4.2 Liquid-Side Mass Transfer Coefficient for 2,3,7,8-TCDD for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlation of Cohen and Ryan, 1985).

coefficient k_l can be estimated from the reaeration coefficient, k_v (e.g., hr^{-1}), by using the following relation:

$$k_l = \left(\frac{D}{D_o}\right)^{1/2} h\ k_v \qquad (4\text{-}53)$$

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., 2,3,7,8-TCDD), 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:

$$k_v = 1.08\ (1 + 0.17\ F^2)\ (V_{curr}\ S)^{0.375},\ hr^{-1} \qquad (4\text{-}54a)$$

$$k_v = 0.00102\ V_{curr}^{2.695}\ h^{-3.085}\ S^{-0.823},\ hr^{-1} \qquad (4\text{-}54b)$$

$$k_v = 638\ V_{curr}\ S,\ hr^{-1} \qquad (4\text{-}54c)$$

in which S is the river bed slope (m drop/ m run), and F is the dimensionless 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

$$k_v = 22.05\ (1.024)^{T-20}\ U_s^{0.67}\ h^{-1.85} \quad , \quad hr^{-1} \qquad (4\text{-}55a)$$

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. 4-53 and 4-55a for 2,3,7,8-TCDD at 20°C is shown in Figure 4.3.

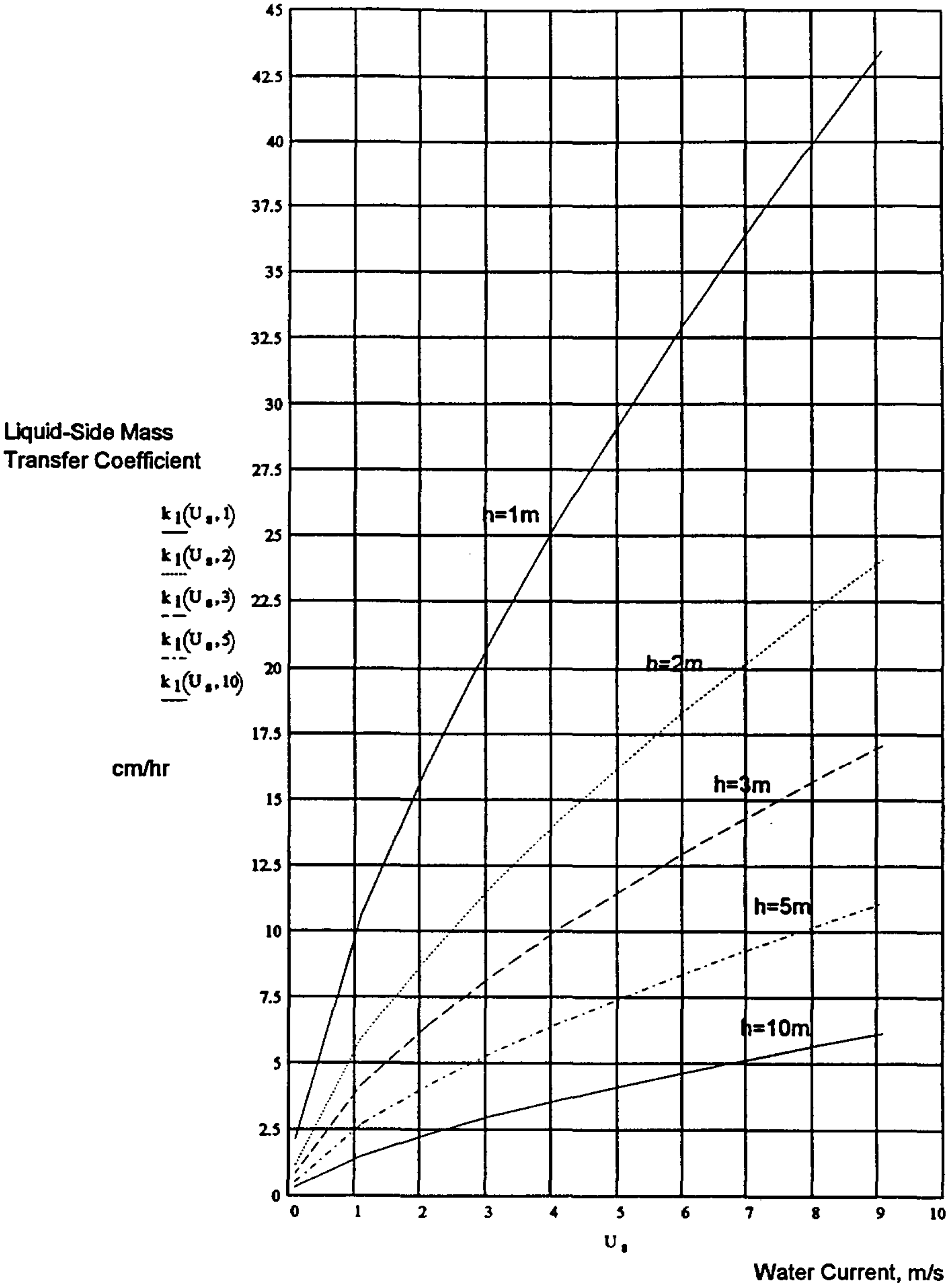

Figure 4.3. Liquid-Side Mass Transfer Coefficient for 2,3,7,8-TCDD at 20°C for a Flowing River Based on Eqs 4-53 and 4-55a (h=river depth).

Example:

In order to estimate K_L for 2,3,7,8-TCDD 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 4-5 and convert to dimensionless Henry's Law constant as per footnote (h) in Table 4-5.
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. 4-35 or 4-36 depending on the resulting value for Re_o. Note that a value for U^*_a is required and this can be estimated from Eqs. 4-38, 4-44 - 4-46, and 4-47 or from wind speed profile data.
5) Use Eq. 4-34 to determine K_L.

As an illustration, consider the volatilization of 2,3,7,8-TCDD 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 0.049 cm^2/s and 5.05×10^{-5} cm^2/s, using Eqs. 4-27 and 4-30, respectively. The gas-side mass transfer coefficient k_g at 20°C, obtained from Eqs. 4-35 and 4-36 (with linear interpolation of k_g in the region $0.13 \leq Re_o \leq 2$), and Eqs. 4-42 and 4-47 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. 4-49, at 20°C, is given in Figure 4.2. As an example, at $U_{10}=5$ m/s, $k_g=1461$ cm/hr (Figure 4.1) and $k_l=2.52$ cm/hr (Figure 4.2). Thus, if a value of 0.00065 for the dimensionless Henry's Law constant is selected from Table 4-5 (after conversion to a non-dimensionless Henry's law), then

$$K_L = \left[\frac{1}{2.52} + \frac{1}{0.00065 \times 1617}\right]^{-1} = 0.69 \qquad , \qquad \text{cm/hr} \qquad (4\text{-}55b)$$

Alternatively, one can directly determine K_L for 2,3,7,8-TCDD for the selected wind speed, using Figure 4.4. As can be seen from this example, the two terms on the right hand side of Eq. 4-55b are of the same order of magnitude. The liquid-side resistance ($1/k_l$) to 2,3,7,8-TCDD mass transfer across the water/air interface makes up about 27.2% of the total resistance ($1\backslash K_L$) to mass transfer. Therefore, for 2,3,7,8-TCDD both k_l and k_g must be considered when determining the overall mass transfer coefficients.

4.3.3 Atmospheric Deposition of 2,3,7,8-TCDD

Atmospheric deposition is an intermedia transport process responsible for removing 2,3,7,8-TCDD from the atmosphere. Total atmospheric deposition is attributed to both dry and wet deposition. It is important to distinguish between deposition of 2,3,7,8-TCDD in vapor and particle-bound phases since different transport mechanisms are involved. Also, since different chemicals will reside in different portions of the particle size distribution, it is important to take into account both the particle-size distribution and the chemical distribution within the particle phase.

Particle/Vapor Distribution of 2,3,7,8-TCDD

Although a few studies have suggested that 2,3,7,8-TCDD is found mainly in the particle-bound phase (Hunt and Maisel, 1990; Goldfarb and Harrad, 1991), the ambient air measurements of Eitzer and Hites (1987; 1989a; 1989b) showed that a significant portion of tetrachloroisomers (including 2,3,7,8-TCDD) were present in the gas phase. Bidleman (1988) has estimated that 20-60% of TCDDs should exist in the gas phase in urban and background air. Hagenmaier et al. (1986) and Scheidl et al. (1985) reported that 63% of the total 2,3,7,8-TCDD emissions from a municipal waste incinerator was in the vapor phase and 37% in the particulate phase. Nielsen et al. (1986) stated that the reported distribution of PCDDs between particulate and vapor phase varies widely, but suggested that an average of 20-30% resides in the particulate phase, while 70-80% resides in the gas phase.

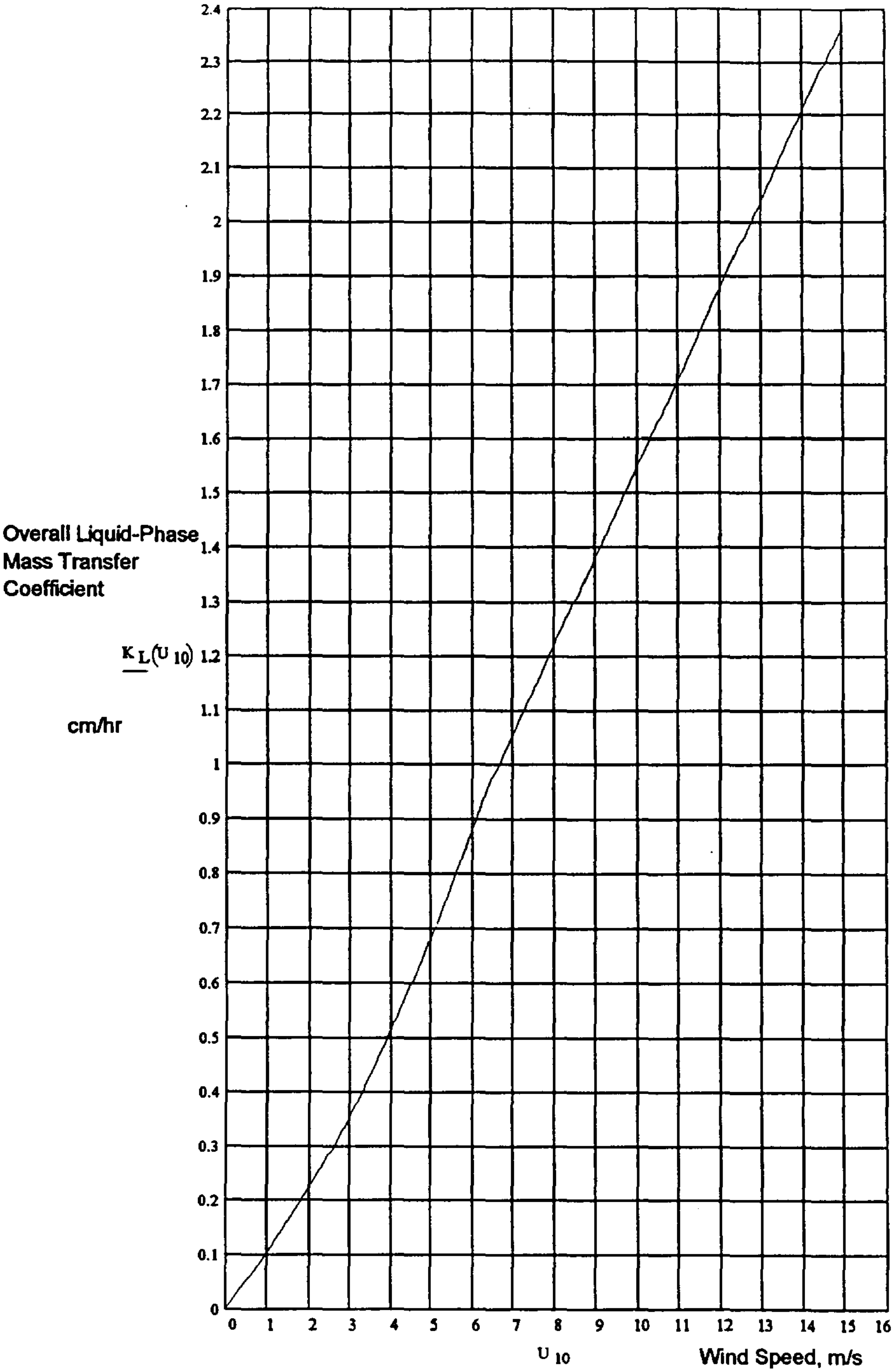

Figure 4.4 Overall Liquid-Side Mass Transfer Coefficient for 2,3,7,8-TCDD for Water/Air Mass Transfer at Large Fetch. (Based on the Theoretical Correlations of Cohen and Ryan, 1985 and Brutsaert, 1975).

Particle Size Distribution for 2,3,7,8-TCDD-Containing Particles

The way in which airborne particles interact with the environment is greatly affected by particle size. For example, dry and wet deposition from the atmosphere onto soil, vegetation, and other surfaces is a function of particle size. The extent to which airborne particles penetrate the human respiratory system is also effected mainly by particle size.

Nessel et al. (1991) presented fly ash particles size distribution from a resource recovery facility and these distribution data were used to determine 2,3,7,8-TCDD deposition rate. Clement and Karasek (1982) measured distribution of tetrachlorodibenzodioxins (TCDD) adsorbed on size-fractionated municipal incinerator fly ash particles. Particle size ranges (microns) were < 63, 63-106, 106-150, 150-250, 250-850, light ash (> 850) and agglomerate particles (> 850). The highest concentrations of TCDD occurred on 250-850 micron particles. Conversely, a much lower TCDD concentration was found on the smallest (< 63 microns) size fraction. There was an almost uniform decrease in TCDD level with respect to particle size. Also, the TCDD concentrations were greater in the light ash particles than the agglomerate particles. The 250-850-micron particles contained a much larger proportion of TCDD than did the < 63-micron particles.

4.3.3.1 Dry Deposition Velocity of 2,3,7,8-TCDD

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. Transport of particles through the atmosphere depends on these diffusivities and on the rate of sedimentation. Sedimentation is significant only for particles with diameters greater than about 1 micrometer (Davidson and Wu, 1989). For particles, the shape, size, and density may determine whether capture by surface roughness elements occurs. Particles may be deposited and subsequently resuspended or they may adhere to the surface or may react chemically, producing irreversible changes in the deposited material. For gases, solubility and chemical reactivity may be dominant factors affecting particle capture by the surface.

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 a better estimate.

2,3,7,8-TCDD in Particle-Bound Phase

The flux of particle-bound pollutants from the atmosphere N_a (e.g., $\mu g/m^2 \cdot s$) can be represented by the following equation:

$$N_a = V_d C_a^{(p)} \qquad (4\text{-}56)$$

where $C_a^{(p)}$ is the mass of the pollutant in the particle phase per unit volume of air (e.g. $\mu g/m^3$), and V_d is the overall particle deposition velocity (m/s). The overall deposition velocity for the particle-bound chemical relates the rate of dry deposition to the ambient concentration and is defined as:

$$V_d = \int_0^\infty V_d(a) F(a) da \qquad (4\text{-}57)$$

where $V_d(a)$ is the deposition velocity for particle diameter a, $F(a)$ is the chemical distribution defined such that

$$\int_0^\infty F(a) da = 1 \qquad (4\text{-}58)$$

where *F(a)da* is the mass fraction of the chemical present in the particle phase in size range *a* to *a+da*. The distribution *F(a)* can be determined either from an appropriate correlation (e.g., Junge correlation as defined in Section 4.2.6) assuming all particles absorb with equal tendency, or from an appropriate experimental measurement. Given the distribution *F(a)*, the dry deposition of particle-bound 2,3,7,8-TCDD can be calculated given data or appropriate models for dry deposition of atmospheric particles as a function of particle size.

Table 4-14 presents values for deposition velocities of 2,3,7,8-TCDD in particle-bound phase. Presented values, based on the study of Hwang (1990), were calculated based on estimated deposition rates and the ambient air concentration for particulate-form 2,3,7,8-TCDD from the air dispersion modeling by Hwang (1990) at 200 m and 800 m from the stack. The estimated deposition velocities ranged from 9.8×10^{-5} to 4.8 cm/s. The value of 9.8×10^{-5} cm/s seems to be very low and there could be an error in the reported data by Hwang (1990) that were used to calculate this value.

The dry deposition velocity can be estimated using a variety of prediction methods. For example, for dry deposition of particles onto a vegetation canopy, the model of Slinn (1982) can be utilized to estimate the dry deposition velocity as a function of particle size. Also, the simple correlations proposed by Whicker and Kirchner (1987), Baes et al. (1984) and Strenge and Napier (1989) can be used to estimate the dry deposition flux as a function of the type and density (i.e., kg/m^2) of the vegetative cover. Dry deposition onto a water surface can be estimated using model of Williams (1982). The application of the above models in screening-level multimedia transport and fate models is discussed in the studies of Cohen (1986), Cohen et al. (1991), and in the studies of Clay (1992) and Chetty (1991).

2,3,7,8-TCDD in Vapor Phase

Dry deposition of gaseous 2,3,7,8-TCDD is expected to be of minor importance as an atmospheric loss process by analogy with the polychlorobiphenyls (Atkinson, 1991; Eisenreich et al., 1981). Since no experimentally determined values for the dry deposition

Table 4-14. Dry Deposition Velocity(a) for 2,3,7,8-TCDD*

Deposition Velocity (cm/s)	Phase	Reported Uncertainty	Temperature (K)	Wind Velocity	Technique	Reference	Source Cited
3(b)	Particle-bound	NR	NR	NR	Estimated(c)	Hwang, 1990	
4.8(d)	Particle-bound	NR	NR	NR	Estimated(c)	Hwang, 1990	
1.8(e)	Particle-bound	NR	NR	NR	Estimated(c)	Hwang, 1990	
0.02	Vapor				Estimated(f)	Section 4.3.3	
3.4	Vapor				Estimated(g)	Section 4.3.3	
0.14	Vapor				Estimated(h)	Section 4.3.3	
0.000098(i)	Particle-bound	NR	NR	NR	Estimated(c)	Hwang, 1990	
0.0023(j)	Particle-bound	NR	NR		Estimated	Travis and Hattemer-Frey, 1989	Radian, 1987

NR = Not Reported.

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

(a) Dry deposition velocity is known to be a function of meteorological conditions, the nature of the surface, and properties of the depositing species (Davidson and Wu, 1989).

(b) Calculated as follows:

$$\frac{6.3\times10^{-4}\ \text{(deposition rate at 0.8 km } (\mu\text{g/m}^2\text{.yr}))}{6.5\times10^{-10}\ \text{(conc. at 0.8 km } (\mu\text{g/m}^3))} = 9.69\times10^{5}\ \text{m/yr} = 3\ \text{cm/s}$$

(emissions from 3000 TPD incinerator)

Table 4-14. Dry Deposition Velocity for 2,3,7,8-TCDD*

(Continued)

(c) Estimated based on dispersion modeling for 2,3,7,8-TCDD in particle-bound phase.

(d) Calculated as follows:

$$\frac{\textbf{0.168 (max. deposition rate } (\mu g/m^2.yr))}{\textbf{1.1x10}^{-7}\textbf{ (max. conc. at 200 m } (\mu g/m^3))} = \textbf{15.3x10}^{5}\textbf{ m/yr = 4.8 cm/s}$$

(emissions from 120 TPD incinerator)

(e) Calculated as follows:

$$\frac{\textbf{0.28 (deposition rate at 0.8 km } (\mu g/m^2.yr))}{\textbf{4.9x10}^{-8}\textbf{ (conc. at 0.8 km } (\mu g/m^3))} = \textbf{71428 m/yr = 1.8 cm/s}$$

(emissions from 120 TPD incinerator)

(f) Eqs. 4-53a and 4-53c in Section 4.3.3.1 in this report.

(g) Eqs. 4-53a and 4-53d in Section 4.3.3.1 in this report.

(h) Eq. 4-53f in Section 4.3.3.1 in this report.

(i) Calculated as follows:

$$\frac{\textbf{3.7x10}^{-8}\textbf{ (max. deposition rate } (\mu g/m^2.yr))}{\textbf{1.2x10}^{-9}\textbf{ (max. conc. at 200 m } (\mu g/m^3)} = \textbf{30.8 m/yr = 0.000098 cm/s}$$

(particulate emissions from 3000 tons per day (TPD) incinerator) This value appears to be unusually low compared with other estimates.

(j) This value was not found in the source cited.

velocity of 2,3,7,8-TCDD in vapor phase were found in the literature, the estimation method adopted by Cohen et al. (1990) can be used. 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 2,3,7,8-TCDD can be calculated using the following equation

$$V_{d_B} = V_{d_A}\left(\frac{D_B}{D_A}\right)^{2/3} \qquad (4\text{-}59)$$

where V_{dB} is the dry deposition velocity of 2,3,7,8-TCDD, V_{dA} is the dry deposition velocity of an appropriate reference chemical (which has a similar chemical surface reactivity to the chemical of interest) for which the deposition velocity is known (was measured) at the meteorological and surface conditions of interest, D_B is a diffusion coefficient of 2,3,7,8-TCDD, and D_A is a diffusion coefficient of the reference chemical.

Example: *Calculation of deposition velocity for 2,3,7,8-TCDD: [The deposition velocity for SO_2 and CO_2 was given by Sehmel (1980; 1984)].*

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

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

$D_{CO_2} = 0.155\ \mathrm{cm^2/s}$ at 298 K (Reid et al., 1987)

(1) - 2,3,7,8-TCDD

(2) - CO_2

$$V_{d_1} = V_{d_2}\left(\frac{D_1}{D_2}\right)^{2/3} \qquad (4\text{-}60a)$$

$$V_{d_1} = 0.3\left(\frac{0.047}{0.155}\right)^{2/3} \qquad (4\text{-}60b)$$

$$V_{d_1} = 0.135\ \mathrm{cm/s} \qquad (4\text{-}60c)$$

Calculation of V_d based on SO_2

(1) - 2,3,7,8-TCDD

(2) - SO_2

air: M_A = 28.97 g/mol (Lyman et al., 1990) SO_2: M_{SO2} = 64 g/mol

V_A = 20.1 cm³/mol (Lyman et al., 1990) V_{SO2} = 41.1 cm³/mol (Fuller et al., 1966)

Using Eq. 4-27, the diffusivity of SO_2 in air can be estimated as shown below

$$D_{SO_2} = \frac{10^{-3}\ (298)^{1.75}\ \sqrt{0.05}}{1\ [(20.1)^{1/3} + (41.1)^{1/3}]^2} = 0.125\ m^2/s\ ,\quad cm^2/s \qquad (4\text{-}60d)$$

$D_{2,3,7,8\text{-}TCDD}$ = 0.047 cm²/s (see Table 4-13) at 298 K and 1 atm

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

$$V_{d_1} = V_{d_2} \left(\frac{D_1}{D_2}\right)^{2/3} \qquad (4\text{-}60e)$$

Lower Limit:

$$V_{d_1} = 0.04 \left(\frac{0.047}{0.125}\right)^{2/3} = 0.02\ cm/s \qquad (4\text{-}60f)$$

Upper Limit:

Therefore, when estimating the deposition velocity for 2,3,7,8-TCDD, the appropriate environmental conditions (e.g., wind speed, temperature) and surface characteristics should be selected for the reference chemical deposition velocity. Since SO_2 is reactive in the aqueous phase, a higher estimate of the deposition velocity would result for moist deposition surfaces when SO_2 is used as the reference chemical. In the above example, CO_2 is a more appropriate reference chemical relative to SO_2.

4.3.3.2 Wet Deposition of 2,3,7,8-TCDD

2,3,7,8-TCDD in Particle-Bound Phase

Wet deposition (scavenging) can increase the overall deposition rate of particle-bound 2,3,7,8-TCDD and thus increase 2,3,7,8-TCDD concentration in the soil, water, and vegetation due to direct deposition. Both rain and snow can remove 2,3,7,9-TCDD from air, however, snowfall is not considered a significant removal process in most of the heavily populated regions in California.

In order to adequately describe the mass balance of a chemical in the environment, the transport parameters associated with rain scavenging must be obtained. The effects of rain scavenging of particles can be considered from two different perspectives. One perspective is that rain scavenging provides a natural method of removing contaminants from the atmosphere. The other perspective is that rain containing the scavenged particles may also be considered a source of contamination for other environmental media (e.g., water, soil, vegetation).

The removal of particle-bound pollutants by rain scavenging can be determined from a chemical mass balance on the spectrum of raindrops as they travel to the ground. The chemical mass balance on a single rain drop is given by (Tsai et al., 1991)

$$\frac{d\left(C_w^{(p)}\,\dfrac{\pi D_d^3}{6}\right)}{d\tau} = \int_0^{\infty} E(a,D_d)\left(\frac{\pi D_d^2 L_c}{4L_c/V_t}\right) C_a^{(p)} F(a)\,da \qquad (4\text{-}61)$$

where

$C^{(p)w}$ = chemical concentration in rain water (ng/m^3 of water)

$C^{(p)}_a$ = chemical air phase concentration in the particle phase (ng/m^3 of air)

$E(a,D_d)$ = collection efficiency of a particle of diameter a by a raindrop of diameter D_d

$F(a)$ = the mass fraction distribution of the chemical in the particle phase, defined such that $F(a)da$ is the mass fraction of the chemical within the size fraction a to $a+da$

τ = travel time of a raindrop from the cloud base (hr.)

V_t = raindrop terminal velocity can be estimated from Easter and Hales (1984)

$$V_t(D_d) = 40.55\,D_d, \quad D_d \le 0.001 \text{ m} \qquad (4\text{-}62)$$
$$= 130(D_d)^{1/2}, \quad D_d > 0.001 \text{ m}$$

where D_d is the diameter of a raindrop (meters).

The collection efficiency can be approximated by the empirical correlation of Ryan and Cohen (1986), which is based on the field data of Radke et al. (1980). Recently, Tsai et al. (1990) demonstrated that the Ryan and Cohen (1986) correlation was of sufficient accuracy to describe field rain scavenging for PAHs. The collection efficiency is given by the following equation

$$E(a) = \left[\frac{S - \dfrac{1}{12}}{S + \dfrac{7}{12}}\right]^{1.5}, \quad a > 1.35\ \mu\text{m} \qquad (4\text{-}63)$$

$$
\begin{array}{ll}
= 0.0005 & , \quad 0.09\,\mu m \le a \le 1.35\,\mu m \\
= 0.125 & , \quad a < 0.9\,\mu m
\end{array}
$$

where $S = 0.1038a^2$ and a is the particle diameter (cm).

Given experimental data for *F(a)*, the average concentration of 2,3,7,8-TCDD in the particle-bound form can be obtained by integrating Eq. 4-54 over spectra of raindrop sizes and particle sizes, between $\tau = 0$ (i.e., cloud base) and $\tau = L_c/V_t$ (i.e., the time to reach ground level). Accordingly, the following expression for the average 2,3,7,8-TCDD concentration in rainwater, at ground level, $\overline{Cw_f}$, is obtained

$$\overline{Cw_f} = \overline{Cw_o} + \frac{C_a}{V_r}\int_0^\infty \frac{3}{2}\frac{L_c}{D_d}\left[\int_0^\infty E(a)F(a)d(a)\right]\frac{\pi D_d^3}{6} N_{D_d} dD_d \tag{4-64}$$

in which C_a is the atmospheric mass concentration of the chemical in the particle-bound form (e.g., ng/m^3), $\overline{Cw_0}$ is the average initial concentration at the cloud base, and V_r is the volume of rain per volume of air given by

$$V_r = \int_0^\infty \frac{\pi D_d^3}{6} N_{D_d} dD_d \tag{4-65}$$

where N_D is the raindrop size distribution expressed such that $N_D dD_d$ is the number of raindrops, per unit volume of air, between diameters D_d and $D_d + dD_d$. The raindrop size distribution, N_{D_d}, can be approximated by the Marshall-Palmer (1948) distribution.

$$N_{D_d} = N_o\, e^{-cD_d} \tag{4-66}$$

in which

$N_o = 0.08\ cm^{-4}$

$c = 41 R_{Rain}^{-0.21}$

where the rate of rainfall, R_{Rain}, is expressed in units of cm/hr.

In the absence of field data for *F(a)*, the correlation of Junge et al. (1977), along with the particle size distribution can be utilized using the rain scavenging model of Tsai et al. (1991).

An upper limit estimate of the "washout" ratio, defined as

$$\Lambda_p^* = \frac{\overline{C_w^{(p)}}}{C_a^{(p)}} \tag{4-67}$$

can be obtained by considering the washout ratio at the beginning of the rain event. Following the analysis of Tsai et al., (1991), one obtains

$$\Lambda_p^* = \frac{\int_0^\infty \left\{ \overline{C_{wo}^{(p)}} + \frac{3}{2} \frac{C_s^{(p)} Lc}{2D_d} \int_0^\infty E(a,D_d) \frac{\pi D_d^2}{4} n(a) da \right\} \frac{\pi D_d^3}{6} N_{D_d} dD_d}{C_a^{(p)} \int_0^\infty \frac{\pi D_d^3}{6} N_{D_d} dD_d} \tag{4-68}$$

$\overline{C_w^{(p)}}$ and $\overline{C_{wo}^{(p)}}$ are the concentrations of the particle-bound chemical in the rainwater at the cloud-base and at ground level, respectively, n(a) is the particle size distribution, $C_s^{(p)}$ is the concentration of the surface-bound chemical expressed on a surface-area basis (e.g., ng/m^2 of particle; i.e., $C_s^{(p)} = C_a^{(p)}/S_t$ where S_t is the surface area of particles per unit volume of air).

<u>2,3,7,8-TCDD in Vapor Phase</u>

Limited data are available concerning the importance of wet deposition for gaseous 2,3,7,8-TCDD. Shiu et al. (1988) estimated a washout ratio, W, defined as

$$W = C_{rainwater}/C_{air} \tag{4-69}$$

for 2,3,7,8-TCDD to be ~10^3 at 298 K assuming that the raindrop reaching ground level are saturated with dissolved 2,3,7,8-TCDD. Bidleman (1988) derived a similar washout ratio (~10^3) for gaseous tetrachlorodibenzo-p-dioxin from the ambient air data of Eitzer and Hites (1987). When compared with the washout ratios for highly water soluble, and hence efficiently removed, organic compounds of $W = 10^5$-10^6 (Bidleman, 1988; Eisenreich et al., 1981; Atkinson, 1988; Leuenberger et al., 1985), it appears that wet deposition of gaseous 2,3,7,8-TCDD will be of relatively minor importance as a loss process for this compound.

Rain scavenging of the vapor component of 2,3,7,8-TCDD which is present in the atmosphere can be predicted using the approach described by Tsai et al. (1991) and Clay (1992). An upper-limit estimate can be obtained by assuming that the raindrops are in equilibrium with the air phase when they reach ground level. Thus, the maximum concentration of the dissolved chemical in rain, $C_w^{(d)}$ (ng/m^3 water), is given by

$$C_w^{(d)} \approx \frac{C_a^{(g)}}{H_{aw}} \tag{4-70}$$

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., $H_{aw} = C_a^{(g)}/C_w^{(d)}$).

4.3.4 Resuspension

Particle induction to the atmosphere from the soil environment due to wind and mechanical erosion could present a significant exposure via the inhalation pathway. For particles <50 microns, the resuspension process is induced by both mechanical and wind disturbances which provide sufficient energy to overcome gravitational forces and allow particles to be dispersed by the wind (Clay, 1992). Since resuspended dusts may be small enough (i.e., $<10\mu m$) to reach the lower respiratory tract, it is necessary to consider the impact of wind resuspension of contaminated soil on exposure to 2,3,7,8-TCDD.

Cowherd et al. (1988) provided an assessment methodology that can be used to model the wind erosion of soil particles. The procedure is based on characterizing the surfaces from which particles may be resuspended into two categories: (1) "limited reservoirs" characterized by a non-homogeneous surface (e.g., a mixture of gravel, sticks, sporadic vegetative life) and where wind erosion is retarded by various features of the terrain; and (2) "unlimited reservoirs" characterized by a uniform surface (e.g., agricultural soil) with a low threshold friction velocity. The above approaches can be conveniently incorporated into multimedia transport and fate models as described by Clay (1992).

4.4 Degradation

The following subsections discuss the specific degradation processes that were considered most applicable to 2,3,7,8-TCDD and the findings of the literature survey are presented.

4.4.1 Atmospheric Degradation of 2,3,7,8-TCDD

Potentially important tropospheric degradation processes for 2,3,7,8-TCDD which need to be considered are photolysis and chemical reaction with OH and NO_3 radicals and with O_3. The rates of these processes depend on whether 2,3,7,8-TCDD is present in the gas or particle phase (2,3,7,8-TCDD distribution between gas and particle phase is discussed in Sections 4.3.3 and 4.2.6). The experimental and theoretical data available concerning the gas- and particle-phase reactions of 2,3,7,8-TCDD lead to the expectation that the dominant tropospheric loss processes of 2,3,7,8-TCDD in the vapor phase will be photolysis and reaction with the OH radical (Atkinson, 1991). For particle-bound 2,3,7,8-TCDD, dry and wet deposition is expected to dominate photolysis or chemical reaction as a removal process. In the following subsections, the tropospheric degradation processes of gas- and particle-phase 2,3,7,8-TCDD are discussed.

OH Radical Reaction Half-life for 2,3,7,8-TCDD in Gas Phase

Although OH radical reaction is expected to play an important role in the atmospheric degradation of 2,3,7,8-TCDD, no experimental data exist concerning this reaction, in part due to its low vapor pressure and the difficulty of working with a toxic compound of this kind. However, methods are available for the reliable estimation of the OH radical rate constant for 2,3,7,8-TCDD (Atkinson, 1991). Using this reaction rate constant and a literature value for the mean tropospheric concentration of OH radicals, an atmospheric lifetime or half-life can be calculated based on the following equations:

$$\text{lifetime} \qquad T = 1 / (k_{OH} \times [OH]) \tag{4-71}$$

$$\text{half-life} \qquad \tau_{1/2} = \ln 2 / (k_{OH} \times [OH]) \tag{4-72}$$

Table 4-15 summarizes estimated values for OH radical photooxidation half-lives of 2,3,7,8-TCDD. Reported half-lives range from 1.4 to 13.3 days. The value of 1.4 days reported by Atkinson (1991) should be considered most reliable since his estimation methods were well documented in comparison to other reported estimated values. For example, Podoll et al. (1986) calculated an OH half-life using an estimated value of the reaction rate constant from unpublished work.

OH Radical Reaction Half-Life for 2,3,7,8-TCDD in Particle-Bound Phase

At the present time, no experimental data are available for particle- or aerosol-phase reactions of PCDDs with OH radical and no estimated values were found in the literature. Although no data exist, that chemical reactions of particle-associated PCDDs are likely to be slow (Atkinson, 1991).

Atmospheric Photolysis of 2,3,7,8-TCDD in Gas Phase

2,3,7,8-TCDD absorbs electromagnetic radiation above 290 nm, and can be expected, therefore, to be subject to photolysis by sunlight. However, to date, no experimental data

Table 4-15. OH Radical Photo-oxidation Reaction Half-Lives for 2,3,7,8-TCDD in Air*

Reaction Half-life (days)	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Technique	References
1.4(c)	2(b)	Days	NR	NR	Estimated(a)	Atkinson, 1991
2(c)	3(d)	Days	NR	Room temperature	Estimated(a)	Atkinson, 1987
13.3	320(e)	Hours	NR	NR	Estimated(a)	Mill, 1985
9.3	9.3	Days	NR	NR	Estimated(f)	Howard et al., 1991
8.3	200(g)	Hours	NR	NR	Estimated(a)	Podoll et al., 1986

NR = Not Reported.

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

(a) Applies only to TCDD in vapor phase - gas phase reaction.

(b) Atmospheric lifetime calculated with OH radical reaction rate constant k_{OH} of 19×10^{-12} $cm^3 \cdot molecule^{-1}$ s^{-1} and $[OH] = 1.5 \times 10^6$ molecule cm^{-3} (Prinn et al., 1987).

(c) Half-life $\tau_{1/2}$ was calculated from the reported lifetime as follows: $\tau_{1/2} = \tau \times \ln 2$; τ = atmospheric lifetime.

(d) Atmospheric lifetime calculated with OH radical reaction rate constant k_{OH} of 9×10^{-12} $cm^3/molec \cdot s$.

(e) Calculated with OH radical reaction rate constant k_{OH} of 2×10^8 $M^{-1}s^{-1}$; $[OH] = 3 \times 10^{-15}$ M [Singh, 1977].

(f) Scientific judgement based upon estimated value constant for reaction with OH radical [Atkinson, 1987].

(g) Calculated with OH radical reaction rate constant k_{OH} of 3×10^8 $M^{-1}s^{-1}$; $[OH] = 3 \times 10^{-15}$ M [Singh, 1977].

exist concerning the adsorption cross-sections or photolysis quantum yields of 2,3,7,8-TCDD in the gas phase (Atkinson, 1991). In the absence of gas-phase photolytic data, the aqueous-phase photolysis lifetime data can be used assuming that the spectral properties and quantum yield for photolysis of 2,3,7,8-TCDD vapor are the same as those in dilute aqueous solutions (Mill, 1985).

Table 4-16 presents estimated values for atmospheric photolytic half-lives of 2,3,7,8-TCDD in air, water, and on glass surfaces. Reported half-lives for water range from 0.8 to 6 days, while half-lives in air range from 0.04 to 3.4 days. It is important to note that all half-lives were estimated based on the spectral properties and quantum yields derived from hexane or acetonitrile solutions and thus these values represent a lower limit because of much faster photolysis rates in organic solvents than in water due to higher solubility of 2,3,7,8-TCDD in organic solvents than in water. An accurate measurement of the vapor-phase quantum yield for 2,3,7,8-TCDD is needed in order to evaluate reliably the relative importance of photolysis and OH radical photooxidation as loss processes for 2,3,7,8-TCDD in the atmosphere.

Atmospheric Photolysis of 2,3,7,8-TCDD in Particle-Bound Phase

At the present time, no experimental data are available for particle- or aerosol-phase photolysis of PCDDs in general and 2,3,7,8-TCDD in particular, although it may be expected that the photolysis rates of these compounds in rainwater, fog, and cloudwater will be similar to those calculated for surface waters (Atkinson, 1991).

4.4.2 Photolysis of 2,3,7,8-TCDD in Water

As noted above, 2,3,7,8-TCDD absorbs electromagnetic radiation above 290 nm, and can be expected, therefore, to be subject to photolysis by sunlight. The rate of photolysis in water is given by Eq. 4-59 in Section 4.4.1.

Table 4-16. Photolysis Rate Constants/Half-Lives for 2,3,7,8-TCDD*

Half-life (days)	Reaction Rate Constant day^{-1}	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Medium	Technique	References	Sources Cited
3.4-1.1		3.4-1.1	Days	NR	NR	Air/water	Estimated(a)	Howard et al., 1991	Dullin et al., 1986; Jackson et al., 1986; Lyman et al., 1982
0.04(h)	17.3	1.2×10^{-2}(b)	Min^{-1}	NR	NR	Air	Calculated(f)	Mill, 1985	
0.04(h)	17.3	0.012(b)	Min^{-1}	NR	NR	Air	Calculated(f)	Podoll et al., 1986	Mill et al., 1982; Petersen, 1976
5(h)	0.14	0.14(c)	Day^{-1}	NR	NR	Water	Calculated(d)	Podoll et al., 1986; SCAQMD, 1988	Podoll et al., 1986
1.11(h)	0.61	0.61(c)	Day^{-1}	NR	NR	Water	Calculated(e)	Podoll et al., 1986	
0.8(h)	0.78	0.78(c)	Day^{-1}	NR	NR	Water	Calculated(f)	Podoll et al., 1986	
2.1(h)	0.32	0.32(c)	Day^{-1}	NR	NR	Water	Calculated(g)	Podoll et al., 1986	
6(h)	0.15	0.15(c)	Day^{-1}	NR	298	Surface water	Calculated(f)	Dullin et al., 1986	
5.4(h)	0.13	0.13(c)	Day^{-1}	NR	NR	Surface water	Calculated(d)	Mill, 1985	
1.2(h)	0.58	0.58(c)	Day^{-1}	NR	NR	Surface water	Calculated(e)	Mill, 1985	

Table 4-16. Photolysis Rate Constants/Half-Lives for 2,3,7,8-TCDD *(Continued)*

Half-life (days)	Reaction Rate Constant day^{-1}	Reported Value	Reported Units	Reported Uncertainty	Temperature (K)	Medium	Technique	References	Sources Cited
0.08$^{(h)}$	0.81	0.81$^{(c)}$	Day^{-1}	NR	NR	Surface water	Calculated$^{(a)}$	Mill, 1985	
2.2$^{(h)}$	0.32	0.32$^{(c)}$	Day^{-1}	NR	NR	Surface water	Calculated$^{(a)}$	Mill, 1985	
5.8$^{(h)}$	0.037	2.61×10^{-5}	Min^{-1}	±20%	298	Glass surface	Measured	Nestrick et al., 1980	
1.6		40	Hours	NR	NR	Air	NR	Travis and Hattemer-Frey, 1989	Mill, 1985; Dullin et al., 1986; Podoll et al., 1986
4.9		118	Hours	NR	NR	Water (winter)	NR	ATSDR, 1989	NR
0.9		21	Hours	NR	NR	Water (near surface, clear sky)	NR	ATSDR, 1989	NR

NR = Not Reported.

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

(a) Scientific judgement based upon measured rate constant for photolysis in an 90:10 mixture of distilled water and acetonitrile under summer sunlight (low $\tau_{1/2}$) [Dullin et al., 1986] and adjusted for relative winter sunlight intensity (high $\tau_{1/2}$) [Lyman et al., 1982].

Table 4-16. Photolysis Rate Constants/Half-Lives for 2,3,7,8-TCDD*
(Continued)

(b) Calculated using the following equation:

$k_{pE} = (0.04)\Sigma\varepsilon_{\lambda}J_{\lambda}$

assuming that the light intensity J_{λ} and photolysis quantum yield ε_{λ} of 2,3,7,8-TCDD vapor are similar to those of 2,3,7,8-TCDD in hexane for summer sunlight at 40°L.

(c) Calculated by using the following equation:

$kpE = \phi\Sigma L_{\lambda}\varepsilon_{\lambda}$

where k_{pE} is the photolysis rate constant in sunlight, ϕ is the quantum yield, L_{λ} is the solar flux over a wavelength interval λ, and ε_{λ} is the average extinction coefficient over the same wavelength interval.

(d) Calculated for winter sunlight at 40°L.

(e) Calculated for spring sunlight at 40°L.

(f) Calculated for summer sunlight at 40°L.

(g) Calculated for fall sunlight at 40°L.

(h) Half-life calculated as $\tau_{1/2} = \ln 2/k$; k = rate constant.

Based on presently available data, it is difficult to predict the fate of 2,3,7,8-TCDD in aquatic media under actual environmental photolytic conditions, as opposed to laboratory conditions, for the following reasons: (1) unlike in experimental solutions, sorption of 2,3,7,8-TCDD to sediments and suspended solids is significant in natural aquatic media and thus the apparent photolysis rates are reduced with an increase in the magnitude of the sorption equilibrium coefficient and the mass/volume ratio of available sediment (Podoll et al., 1986); (2) 2,3,7,8-TCDD is expected to photolyze in the presence of organic hydrogen atom donating substrate(s) (Crosby et al., 1973; Crosby, 1978) which may or may not be available in natural surface waters. Because of the low 2,3,7,8-TCDD solubility in water, organic solvent aquatic solutions are used in laboratory experiments to measure spectral properties and quantum yields. The presence of these organic solvents can increase photolysis rates since they are facile hydrogen donors.

Table 4-16, which is discussed in Section 4.4.1.3, presents values of aquatic photolysis rate constants and half-lives for 2,3,7,8-TCDD.

4.4.3 Biodegradation of 2,3,7,8-TCDD in Water and Soil

Investigations on the biodegradability of 2,3,7,8-TCDD have focused on microbial degradation. Arthur and Frea (1989) provided a comprehensive review of studies conducted during the 1970s and 1980s and they concluded that 2,3,7,8-TCDD is recalcitrant to microbial degradation. Matsumura and Benezet (1973) tested approximately 100 strains of microorganisms and only 5 strains showed any ability to degrade 2,3,7,8-TCDD, but mineralization was not observed. Hutter and Philippi (1982) also screened pure and mixed cultures of microorganisms for their ability to metabolize 2,3,7,8-TCDD and reported that microbial action on 2,3,7,8-TCDD is very slow even under optimum conditions. Bumpus et al. (1985) tested the white rot fungus, Phanerochaete chrysosporium, and concluded that the strain was able to degrade halogenated aromatic rings. Other studies have confirmed the relatively limited ability of microorganisms both in aquatic and soil environments to metabolize 2,3,7,8-TCDD (Quensen and Matsumura, 1983; Matsumura et al., 1983; Camoni et al., 1982; Ward and Matsumura, 1978; Kearney, 1972). The following factors have been proposed in the literature to explain the resistance of 2,3,7,8-TCDD to microbial metabolism: (1) Organisms previously unexposed to 2,3,7,8-TCDD may lack the enzymatic or biological potential to degrade the compound; (2) Low cell membrane penetration due to negligible lipid solubility; (3) Potential 2,3,7,8-TCDD toxicity to environmental microorganism and consequent inhibition of biodegradation; and (4) The binding of 2,3,7,8-TCDD to soil and sediment which limits the bioavailability of 2,3,7,8-TCDD in the environment. Matsumura et al. (1983) and Quensen and Matsumura (1983) found that the nature of the solvent was the most important factor affecting 2,3,7,8-TCDD metabolism. These authors concluded that the implication of the above finding for environmental biodegradation is that 2,3,7,8-TCDD needs to be solubilized and made bioavailable to induce degradative enzymes.

Table 4-17 presents biodegradation half-lives and rate constants for 2,3,7,8-TCDD in different media. In most cases, biodegradation constants are not directly reported in the literature. Thus, where biodegradation rate constants for 2,3,7,8-TCDD 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 first-order rate law states that the rate is the product of the rate constant and the chemical (substrate) concentration (i.e., $dC/dt = -k\,C$). The following form of the first-order rate law equation was used to calculate biodegradation rate constants presented in Table 4-17.

$$\ln \frac{C}{C_o} = -kt \tag{4-73}$$

where C_o is initial 2,3,7,8-TCDD concentration, C is 2,3,7,8-TCDD 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 assumption of first-order kinetics is reasonable at low 2,3,7,8-TCDD concentrations, in homogeneous media, or as a first-order approximation. The rate constants were subsequently used to calculate the biodegradation half-life ($\tau_{1/2}$) of 2,3,7,8-TCDD.

Table 4-17. Biodegradation Rate Constants/Half-Lives for 2,3,7,8-TCDD*

Half-life (day)	Rate Constant (day^{-1})	Reported Uncertainty	Experimental Medium	Technique (Conditions)	References
590-418	NR	NR	Surface water	(Aerobic)(a)	Howard et al., 1991
2360-1672	NR	NR	Surface water	(Anaerobic)(b)	Howard et al., 1991
11809-836	NR	NR	Ground water	(Aerobic)(b)	Howard et al., 1991
1035(c)	0.00067(d)	NR	White rot fungus	Measured	Bumpus et al., 1985
365(c)	0.019(e)	NR	Outdoor pond	Measured	Matsumura et al., 1983
433(c)	0.0016(f)	NR	Outdoor pond	Measured	Matsumura et al., 1983
578(c)	0.0012(h)	NR	Aquatic ecosystem(g)	Measured	Matsumura et al., 1983
154(c)	0.0045(j)	NR	Aquatic ecosystem(i)	Measured	Matsumura et al., 1983
53(c)	0.013(l)	NR	Aquatic ecosystem(k)	Measured	Matsumura et al., 1983
139(c)	0.005(n)	NR	Aquatic ecosystem(m)	Measured	Matsumura et al., 1983
347(c)	0.002(p)	NR	Aquatic ecosystem(o)	Measured	Matsumura et al., 1983
4621(c)	0.00015(r)	NR	Aquatic ecosystem(q)	Measured	Matsumura et al., 1983
866(c)	0.0008(t)	NR	Aquatic ecosystem(s)	Measured	Matsumura et al., 1983
9902(c)	0.00007(v)	NR	Aquatic ecosystem(u)	Measured	Matsumura et al., 1983
198(c)	0.0035(w)	NR	Soil	Measured	Matsumura et al., 1983

Table 4-17. Biodegradation Rate Constants/Half-Lives for 2,3,7,8-TCDD*

(Continued)

Half-life (day)	Rate Constant (day^{-1})	Reported Uncertainty	Experimental Medium	Technique (Conditions)	References
18(c)	0.039(x)	NR	Soil + nutrients	Measured	Matsumura et al., 1983
10(c)	0.067(y)	NR	Soil + nutrients	Measured	Matsumura et al., 1983
115(c)	0.006(z)	NR	UV irradiation + fungus	Measured	Katayama and Matsumura, 1991
9242(c)	7.5×10^{-5}(aa)	NR	Fungus	Measured	Katayama and Matsumura, 1991
8.6(c)	0.08(bb)	NR	UV irradiation + fungus + other pollutants	Measured	Katayama and Matsumura, 1991

NR = Not Reported.

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

(a) Based upon soil die-away test data (low $\tau_{1/2}$) [Kearney et al., 1971] and lake water and sediment die-away data [Ward and Matsumura, 1978].

(b) Scientific judgement based upon estimated unacclimated aqueous aerobic biodegradation half-life.

(c) This value was calculated as follows: $\tau_{1/2} = \ln 2/k$; k = rate constant.

(d) Calculated as follows: $\ln \frac{C}{C_o} = -kt$ where C = 1222 pmol; C_o = 1250 p mol; t = 30 days.

(e) Calculated as follows: $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 49.7%; t = 365 days.

Table 4-17. Biodegradation Rate Constants/Half-Lives for 2,3,7,8-TCDD
(Continued)

(f) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 29.4\%$; $t = 760$ days.

(g) Lake water and lake sediments, no nutrients.

(h) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 70\%$; $t = 300$ days.

(i) Lake water and sediment; glucose added as a nutrient; metabolites measured in the aqueous phase.

(j) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 47.4\%$; $t = 167$ days.

(k) Lake water and sediment; bactopeptone added as a nutrient; metabolites measured in the aqueous phase.

(l) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 11.08\%$; $t = 167$ days.

(m) Lake water with sediment; glucose + bactopeptone added as nutrients; metabolites measured in aqueous phase.

(n) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 43\%$; $t = 167$ days.

(o) As (m) but metabolites measured in the sediment.

(p) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 92\%$; $t = 39$ days.

(q) As (i) but metabolites measured in the sediment.

(r) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 97.5\%$; $t = 167$ days.

(s) As (g) but metabolites measured in the sediment.

(t) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 77\%$; $t = 333$ days.

(u) As (k) but metabolites measured in the sediments.

(v) Calculated as $\ln \frac{C}{C_o} = -kt$ where $C_o = 100\%$; $C = 96\%$; $t = 588$ days.

Table 4-17. Biodegradation Rate Constants/Half-Lives for 2,3,7,8-TCDD*

(Continued)

(w) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 66%; t = 4 months.

(x) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 58%; t = 14 days.

(y) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 39%; t = 14 days.

(z) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 80%; t = 40 days.

(aa) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 99.7%; t = 40 days.

(bb) Calculated as $\ln \frac{C}{C_o} = -kt$ where C_o = 100%; C = 3%; t = 28 days.

(cc) Pollutants added were DDT, TCB, heptachlor; experiments were carried out in Petri dish.

$$\tau_{1/2} = 0.693/k \qquad (4\text{-}74)$$

From the results in Table 4-17, it can be seen that the fastest biodegradation rates for 2,3,7,8-TCDD were measured under aerobic conditions with nutritional enrichment and added solvents. As expected, 2,3,7,8-TCDD biodegradation under anaerobic conditions is much slower than under aerobic conditions. It can also be seen that there is a wide range of values for biodegradation rate constants and corresponding biodegradation half-lives for 2,3,7,8-TCDD which can be attributed to different experimental conditions such as microbial population, chemical concentration, dissolved oxygen, the availability of nutrients, other sources of carbon, inhibitors, temperature, and pH. 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 2,3,7,8-TCDD.

4.4.4 Overall Half-Life for 2,3,7,8-TCDD in Environmental Media

The overall half-life generally indicates the persistence of a chemical in a particular environmental medium. The overall half-life includes both transport and reaction half-lives. The transport half-life quantifies the residence time of the unchanged chemical in an environmental medium in the absence of transformation while reaction half-life is based on the degradation rates of the chemical and biological transformation processes. Although transport and reaction half-lives should be distinguished as two different terms, many researchers characterize the persistence of 2,3,7,8-TCDD in different environmental media by a single value since it is difficult to reliably quantify the specific loss mechanisms involved. The mechanisms most likely responsible for TCDD disappearance include photodegradation, wind and water movement of contaminated particles, volatilization, microbial degradation, and biomass removal (Young, 1983).

Table 4-18 presents examples of the overall half-lives reported in the literature for 2,3,7,8-TCDD in different environmental media. Reported values were mostly obtained either from measured or estimated initial concentration of 2,3,7,8-TCDD in an environmental medium and remaining concentration of 2,3,7,8-TCDD after certain time period. In some cases, attempts were made to identify the major loss mechanisms.

Table 4-18. Examples of Overall Half-Lives for 2,3,7,8-TCDD in Environmental Media as Reported in the Literature*

Half-life Value	Rate Constant	Reported Uncertainty	Media	Loss Mechanism	Technique	References	Sources Cited
Few hours	NR	NR	Leaves of plants	Photolysis	NR	ATSDR, 1989	Choudhry and Hutzinger, 1982; Sacchi et al., 1986
5.6 days	NR	NR	Grass	Volatilization, wind resuspension, degradation fall-out, washout	Measured	Jensen et al., 1983	
3.9-7.1 days	NR	NR	Grass	Volatilization + photochemical dechlorination	Measured	Nash and Beall, 1980; Jensen et al., 1983	Nash and Beall, 1980
> 1 year	NR	NR	Lake water alone	NR	NR	ATSDR, 1989	NR
> 1.5 year	NR	NR	Sediment-containing lake water	NR	NR	ATSDR, 1989	NR
65 days	NR	NR	Leachate water	NR	Measured	Nash and Beall, 1980	
57 days	NR	NR	Leachate water	NR	Measured	Nash and Beall, 1980	
7-24 days	NR	NR	Soil	Volatilization	Measured	Nash and Beall, 1980	
16 days	NR	NR	Soil	Volatilization	Measured	Nash and Beall, 1980	
425 days	NR	NR	Lake land and sandy loam	NR	Measured	Nash and Beall, 1980	Kearney et al., 1972

Table 4-18. Examples of Overall Half-Lives for 2,3,7,8-TCDD in Environmental Media as Reported in the Literature*
(Continued)

Half-life Value	Rate Constant	Reported Uncertainty	Media	Loss Mechanism	Technique	References	Sources Cited
535 days	NR	NR	Hagerston silty clay loam	NR	Measured	Nash and Beall, 1980	Kearney et al., 1972
450-650 days	NR	NR	Soil	NR	Measured	Nash and Beall, 1980	Kearney et al., 1972
9.1 yrs.	0.076/yr.(a)	6.2-17 yr (95% CLs)	Soil	Volatilization + chemo- and photo-transformation surface + in-soil movement	Measured	Cerlesi et al., 1989	Cerlesi et al., 1989
12-0.9 days(c)	1.8-24/month(b)	NR	Soil	Photodecomposition + volatilization	Measured	di Domenico et al., 1982	diDomenico et al., 1982
3 days	6.9/month(d)	27-18/month	Soil	Photodecomposition + volatilization	Measured	di Domenico et al., 1982	
10-14 months(e)	NR	NR	Soil	Photodegradation + volatilization	Measured	di Domenico et al., 1980	
> 10 years(f)	NR	NR	Soil	Photodegradation + volatilization	Measured	di Domenico et al., 1980	
12 years	0.0578/year	NR	Soil	Photodegradation	Measured	Clements, 1989	Young, 1983
1-3 years	NR	NR	Soil surface	NR	NR	ATSDR, 1989	Bumpus et al., 1985; U.S. EPA, 1985b

Table 4-18. Examples of Overall Half-Lives for 2,3,7,8-TCDD in Environmental Media as Reported in the Literature*
(Continued)

Half-life Value	Rate Constant	Reported Uncertainty	Media	Loss Mechanism	Technique	References	Sources Cited
10-12 years	NR	NR	Interior of soil	NR	NR	ATSDR, 1989	Freeman and Schroy, 1986 HSDB, 1987; Miller et al., 1987
29 years	0.0239/year	NR	Soil	NR	NR	SCAQMD, 1988	Bumpus et al., 1985
12 years	NR	NR	Soil	NR	NR	McKone, 1985	Kimbrough et al., 1984
12 years	NR	NR	Soil	NR	--	McKone, 1985	Schaum, 1984

NR = Not Reported.

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

(a) Estimated from regression analysis.

(b) Obtained by reiterative fitting of the steady-state function to 11 independent sets of data groups.

(c) Half-life calculated as: $\tau_{1/2} = \ln 2/k$; k = rate constant.

(d) Estimated by employing the logarithmic forms of the original functions.

(e) Estimated from regression function after 1 month.

(f) Estimated from regression function after 17 months.

5.0 AREAS FOR POSSIBLE IMPROVEMENT

The assessment of multipathway exposure to 2,3,7,8-TCDD could benefit from considering the following issues:

- Data on 2,3,7,8-TCDD distribution in the particle and gas phase would help to improve the estimation of dry and wet deposition of 2,3,7,8-TCDD, which would subsequently improve the estimation of 2,3,7,8-TCDD concentration in vegetation, water and soil.

- Resuspension of particles which may be a significant exposure pathway that is currently not considered in most multipathway exposure models.

- The dry deposition velocities of 2,3,7,8-TCDD-containing particles as a function of the mass distribution of 2,3,7,8-TCDD in the particle size.

- Bioavailability of 2,3,7,8-TCDD from various matrices may need to be considered given the strong binding properties of 2,3,7,8-TCDD.

Finally, despite the extensive body of literature that exists for 2,3,7,8-TCDD, the following major questions need to be addressed in the general conduct of the exposure assessment and in site-specific evaluation of exposure to 2,3,7,8-TCDD.

- What is the fraction of 2,3,7,8-TCDD in particle-bound and vapor phase when it is released to the atmosphere?

- What is the fraction of 2,3,7,8-TCDD in particle-bound and vapor phase when it reaches the exposure boundaries?

- What influences the bioavailability of 2,3,7,8-TCDD for the different routes of exposure?

6.0 REFERENCES

Adams, W.J. and Blaine, K.M., A Water Solubility Determination of 2,3,7,8-TCDD, Chemosphere, 15, 1397-1400, 1986.

Adams, W.J., DeGraeve, G.M., Sabourin, T.D., Cooney, J.D., and Mosher, G.M., Toxicity and Bioconcentration of 2,3,7,8-TCDD to Fathead Minnows (*Pimephales promelas*). Chemosphere, 15, 1503-1511, 1986.

Agency for Toxic Substance and Disease Registry (ATSDR), U.S. PHS Toxicological Profile for 2,3,7,8-Tetrachloro-dibenzo-p-dioxin, 1989.

Allen, D.T., Cohen, Y., and Kaplan, I.R. (Eds.), Intermedia Pollutant Transport: Modeling and Field Measurements, Plenum Press, N.Y., 1989.

Arthur, M.F. and Frea, J.I., 2,3,7,8-Tetrachlorodibenzon-p-dioxin: Aspects of its Important Properties and its Potential Biodegradation. Journal of Environmental Quality, 18, 1-11, 1989.

Atkinson, R., Atmospheric Lifetimes of Dibenzo-p-dioxins and Dibenzofurans. The Science of Total Environment, 104, 17-33, 1991.

Atkinson, R., Atmospheric Transformation of Automotive Emissions, in Air Pollution, the Automobile, and Public Health, A.Y. Watson et al. (Eds.), NAP, W-PC, 1988.

Atkinson, R., Estimation of OH Radical Reaction Rate Constants and Atmospheric Lifetimes for Polychlorobiphenyls, Dibenzo-p-dioxins, and Dibenzofurans. Environmental Science and Technology, 21, 305-307, 1987.

Bacci, E., Cerejeira, M.J., Gaggi, C., Chemello, G., Calamari, D., and Vighi, M., Bioconcentration of Organic Chemical Vapours in Plant Leaves: The Azalea Model. Chemosphere, 21, 525-535, 1990.

Bacci, E., Cerejeira, M.J., Gaggi, C., Chemello, G., Calamari, D., and Vighi, M., Chlorinated Dioxins: Volatilization from Soils and Bioconcentration in Plant Leaves. Bulletin of Environmental Contamination and Toxicology, 48(3), 401-408, 1992

Baes, C.F., Sharp, R.D., Sjoreen, A.L., and Shor, R.W., A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture. ORNL-5786, Oak Ridge National Laboratory, Oak Ridge, Tenn. 1984.

Banerjee, S. and Baughman, G., Bioconcentration Factors and Lipid Solubility. Environmental Science and Technology, 25, 536-539, 1991.

Bidleman, T.F., Atmospheric Processes: Wet and Dry Deposition of Organic Compounds are Controlled by Their Vapor-Particle Partitioning. Environmental Science and Technology, 22, 361-367, 1988.

Boer, F.P., van Remoortere, F.P., and Muelder, W.W., The Preparation and Structure of 2,3,7,8-Tetrachloro-p-dioxin and 2,7-Dichloro-p-dioxin. Journal of the American Chemical Society, 96(3), February, 1972.

Bowman, R.E. et al., Unpublished results cited in Weerasinghe, N.C. and Gross, M.L., Origins of Polychlorodibenzo-p-dioxins (PCDD) and Polychlorodibenzofurans (PCDF) in the Environment, in Dioxins in the Environment, M.A. Kamrin and P.W. Rodgers (Eds.), Hemisphere Publishing Corp., Washington, DC, 133-151 (1985).

Branson, D.R., Takahashi, I.T., Parker, W.M., and Blau, G.E., Bioconcentration Kinetics of 2,3,7,8-tetrachlorodibenzo-p-dioxin in Rainbow Trout. Environ. Tox. Chem., 4, 779-788, 1985.

Branson, D.R., Takahashi, I.T., Parker, W.M., and Blau, G.E., Bioconcentration Kinetics of 2,3,7,8-TCDD in Rainbow Trout. Dow Chemical Co., Midland, MI, September 28, 1983.

Branson, D.R., Takahashi, I.T., and Parker, W.M., Unpublished Report, Environmental Sciences Research, The Dow Chemical Co., Midland, Mich., Nov 15, 1985.

Branson, D.R., Takahashi, I.T., and Parker, W.M., Unpublished Report, Environmental Sciences Research, The Dow Chemical Co., Midland, Michigan, Nov. 15, 1978.

Branson, D.R., Takahashi, I.T., and Parker, W.M., Unpublished Data, The Dow Chemical Co., Midland, Mich., 1979.

Briggs, G.G., Bronislau, R.H., and Evans, A., Relationship between Lipophilicity and Root Uptake and Translocation of Non-ionized Chemicals by Barley. Pesticide Science, 495-504, 1982.

Brutsaert, W., A Theory for Local Evaporation (or Heat Transfer) from Rough and Smooth Surfaces at Ground Level, Water Resources Research, 11(4), 543-550, 1975.

Bumpus, J.A., Tien, M., Wright, D., and Aust, S.D., Oxidation of Persistent Environmental Pollutants by a White Rot Fungus. Science, 228, 1434-1436, 1985.

Burkhard, C.P. and Kuehl, D.W., N-octanol/Water Partition Coefficients by Reverse Phase Liquid Chromatography/Mass Spectrometry for Eight Tetrachlorinated Planar Molecules. Chemosphere, 15, 163-167, 1986.

California Air Resources Board (CARB) Public Hearing to Consider the Adoption of a Regulatory Amendment Identifying Chlorinated Dioxins and Dibenzofurans as Toxic Air Contaminants, 1986.

Camoni, I., Dimuccio, A., Pontecorvo, D., Taggi, F., and Vergori, I., Laboratory Investigation for the Microbial Degradation of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Soil by Addition of Organic Compost. Pergamon Ser. Environ. Sci., 5, 95-103, 1982.

CAPCOA, Air Toxics "Hot Spots" Program Risk Assessment Guidelines, Prepared by AB 2588 Risk Assessment Committee of the California Air Pollution Control Officers Association (CAPCOA), January, 1992.

Cerlesi, S., Domenico, A., and Ratti, S., 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) Persistence in the Seveso (Milan, Italy) Soil. Ecotoxicology and Environmental Safety, 18, 149-164, 1989.

Chetty, S.L., Multimedia Total Dos Analysis, Masters of Science Thesis, Chemical Engineering Department, UCLA, 1991.

Chiou, C.T., Freed, V.H., Schmedding, D.H., and Kohnert, R.L., Partition Coefficients and Bioaccumulation of Selected Organic Chemicals. Environmental Science and Technology, 11, 475-478, 1977.

Chiou, C.T., Peters, C.K., and Freed, V.H., Physical Concept of Soil-Water Equilibrium for Non-ionic Organic Compounds. Science, 206, 831-832, 1979.

Choudhry, G.G. and Hutzinger, O., Photochemical Formation and Degradation of Polychlorinated Dibenzofurans and Dibenzo-p-dioxins, Residue Rev., 84, 115-161, 1982.

Clark, T., Clark, K., Paterson, S., and Mackay, D., Wildlife Monitoring, Modeling and Fugacity. Environmental Science and Technology, 22(2), 1988.

Clay, R.E., Multimedia Environmental Distribution of Gaseous, Dissolved, and Particle-Bound Pollutants, Master of Science Thesis, Chemical Engineering Department, UCLA, 1992.

Clement, R.E. and Karasek, F.W., Distribution of Organic Compounds Adsorbed on Size-fractionated Municipal Incinerator Fly-ash Particles, Journal of Chromatography, 234, 395-405, 1982.

Cocucci, S., DiGerolano, F., Verdenio, A., Cavallaro, A., Colli, G., Invernizzi, G., and Luciani, L., Absorption and Translocation of Tetrachlorodibenzo-p-dioxine by Plants from Polluted Soil, Experientia, 35/4, 482-484, 1979.

Cohen, Y., Allen, D.T., Clay, R.E., Rosselot, K., Tsai, W., Klee, H., and Blewitt, D., Multimedia Assessment of Emissions (MAB) from the AMOCO Corporation Yorktown Refinery (AMOCO/EPA Pollution Prevention Project) A&WMA 84th Annual Meeting and Exhibition, Paper #91-84.6, 1991.

Cohen, Y., Intermedia Transport Modeling in Multimedia Systems, in Pollutants in a Multimedia Environment, Plenum Press, N.Y., 1986.

Cohen, Y., Intermedia and Multimedia Concepts in Environmental Monitoring, in Intermedia Pollutant Transport: Modeling and Field Measurements, Allen, D.T., Cohen, Y. and Kaplan, I.R., (Eds.), Plenum Press, 1989.

Cohen, Y., Mass Transfer Across a Sheared, Wavy Air-Water Interface, International Journal of Heat and Mass Transfer, 26, 1289-1297, 1983.

Cohen, Y. and Ryan, P.A., Multimedia Modeling of Environmental Transport: Trichloroethylene Test Case, Environmental Science and Technology, 19(5), 412-417, 1985.

Cohen, Y., Tsai, W., Chetty, S.L., and Meyer, G.J., Dynamic Partitioning of Organic Chemicals in Regional Environment: A Multimedia Screening-Level Modeling Approach. Environmental Science and Technology, 24(10), 1549-1558, 1990.

Cowherd, C., Muleski, G.E., and Linsey, J.S., Control of Open Fugitive Dust Source, NTIS Report No. PB 89-103691, 1988.

Crosby, D.G., Moilaner, K.K., and Wong, A.S., Environmental Generation and Degradation of Dibenzodioxins and Dibenzofurans, Environmental Health Prespectives, Exp. Issue, 5, 259-266, 1973.

Crosby, D.G., Wong, A.S., Plimmer, J.R., and Woolson, B.A., Photodecomposition of Chlorinated Dibenzo-p-dioxins. Science, 173, 748-749, 1971.

Crosby, D.G., The Degradation and Disposal of Chlorinated Dioxins, in Dioxins in the Environment, Kamrin & Rodgers (eds.), Hemisphere Press Corp., Washington DC, 195-204, 1985.

Crummett, W.B. and Stehl, R.H., Determination of Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Various Materials. Environmental Health Perspectives, 5, 15-25, 1973.

Davidson, C.I. and Wu, Y.C., Dry Deposition of Particles and Vapors, in Acid Precipitation, D.C. Adriano (ed.), Advances in Environmental Science Series, Spring-Verlag, N.Y., 1989.

di Domenico, A., Silano, V., Viviano, G., and Zapponi, G., Accidental Release of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) at Seveso, Italy. Ecotoxicology and Environmental Safety, 4, 339-345, 1980.

di Domenico, A., Viviano, G., and Zapponi, G., Environmental Persistence of 2,3,7,8-TCDD at Seveso, in Chlorinated Dioxins and Related Compounds: Impact on the Environment, pp. 105-114, 1982.

Dragun, S., Personal Communication, E.C. Jordan Co., Southfield, MI, 1986.

Dullin, D., Drossman, H., and Mill, T., Products and Quantum Yields for Photolysis of Chloroaromatics in Water. Environmental Science and Technology, 20, 72-77, 1986.

Easter, R.C. and Hales, J.M., in PLUVIUS: A Generalized One-Dimensional Model of Reactive Pollutant Behavior Including Dry Deposition, Precipitation Formation, and Wet Removal, Report PNL-4046 BD2, Batelle Pacific Northwest Lab, Richland, WA, 1984.

Eisenreich, S.J., Looney, B.B., and Thornton, J.D., Airborne Organic Contaminants in the Great Lakes Ecosystem, Environmental Science and Technology, 15, 30-38, 1981.

Eitzer, B.D. and Hites, R.A., Atmospheric Transport and Deposition of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, Environmental Science and Technology, 23, 1396-1401, 1989a.

Eitzer, B.D. and Hites, R.A., Concentrations of Dioxins and Dibenzofurans in the Atmosphere. International Journal of Environmental Analytic Chemistry, 27, 215-230, 1987.

Eitzer, B.D. and Hites, R.A., Polychlorinated Dibenzo-p-dioxins and Dibenzofurans in the Ambient Atmosphere of Bloomington, Indiana, Environmental Science and Technology, 23, 1389-1395, 1989b.

Esposito, M.P., Teirnan, T.O., and Dryden, F.B., Dioxins, U.S. EPA, IBRL, Office of Research and Development, Cincinnati, Ohio, EPA-600/2-80-197, Nov. 1980.

Firestone, D., Determination of Polychlorodibenzo-p-dioxins and Polychlorodibenzofurens in Commercial Gelatins by Gas-liquid Chromatography. J. Agric. Food. Chem., 25, 1274-1280, 1977.

Freeman, R.A. and Schroy, J.M., Environmental Mobility of Dioxins, for presentation at the 8th ASTM Aquatic Toxicology Symposium to be held on April 15, 16, and 17, 1984 at the Draw Bridge Inn, Fort Mitchell, Kentucky.

Freeman, R.A. and Schroy, J.M., Modeling the Transport of 2,3,7,8-TCDD and Other Low Volatility Chemicals in Soils, paper for presentation at the AIChE National Meeting held on August 19-22, 1984, Philadelphia, Pennsylvania.

Fries, G.F. and Paustenbach, D.J., Evaluation of Potential Transmission of 2,3,7,8-Tetrachlorodibenzo-p-dioxin-Contaminated Incinerator Emissions to Humans via Foods. Journal of Toxicology and Environmental Health, 29, 1-43, 1990.

Fuller, B.N., Schettler, P.D., and Giddings, J.C., A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients, Industrial and Engineering Chemistry, 58, 19-57, 1966.

Geyer, H.J., Scheunert, I., Filser, J.G., and Korte, F., Bioconcentration Potential (BCP) of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) in Terrestrial Organisms Including Humans. Chemosphere, 15, 1495-1502, 1986.

Goldfarb, T.D. and Harrad, S.J., Consideration of the environmental impact of the volatilization of PCDDs and PCDFs. Chemosphere, 23, 1669-1674, 1991.

Hagenmaier, H., Kraft, M., Jager, W., Mayer, V., Lutzke, K., and Siegel, D., Comparison of Various Sampling Methods for PCDDs and PCDFs in Stack Gas, Chemosphere, 15, 1187-1192, 1986.

Hayduk, W. and Laudie, H., Prediction of Diffusion Coefficients for Non-electrolytes in Dilute Aqueous Solutions, AIChE Journal, 20, 611, 1974.

Hayduk, W., Minhas, B.S., and Lan, J., Correlations for Prediction of Molecular Diffusivities in Liquid, The Canadian Journal of Chemical Engineering, 60, 295, 1982.

Helling, C.S., Isensee, A.R., Woolson, E.A, Ensor, P.D.J., Jones, G.B., Plimner, J.R., and Kearney, P.C., Chlorodioxins in Pesticides, Soil, and Plants, Journal of Environmental Quality, 2, 171-178, 1973.

Holtslag, A.A.M. and Van Ulden, A.P., A Simple Scheme for Daytime Estimates of the Surface Fluxes from Routine Weather Data, Journal of Climate Applied Meteorology, 22, 517-529, 1983.

Howard, P.H., Boethling, R.S., Jarvis, W.F., Meyan, W.M., and Michalenko, E.M., (Eds.), Handbook of Environmental Degradation Rates, Lewis Publishers, Inc., Chelsea, MI, 1991.

Hunt, G.T. and Maisel, B.E., Atmospheric PCDDs/PCDFs in Wintertime in a Northeastern U.S. Urban Coastal Environment. Chemosphere, 20, 1455-1462, 1990.

Hutter, R. and Philippi, M., Studies in Microbial Metabolism of TCDD under Laboratory Conditions. In Chlorinated Dioxins and Related Compounds Impact on the Environment, O. Hutzinger et al. (Eds.), Pergamon Press, N.Y., 87-93, 1982.

Hwang, S.T., Estimation of Multimedia Environmental Contamination of 2,3,7,8-TCDD Emissions from Municipal Waste Incinerators. Environmental Progress, 9, 93-97, 1990.

International Union of Pure and Applied Chemistry (IUPAC), Atomic Weights of the Elements, 1977. Pure and Applied Chemistry, 51, 405-533, 1979.

Isensee, A.R., Bioaccumulation of 2,3,7,8-Tetrachlorodibenzo-para-dioxin, Ecol. Bull., 27, 255-262, 1978.

Isensee, A.R. and Jones, G.E., Absorption and Translocation of Root and Foliage Applied 2,4-Dichlorophenol, 2,7-Dichlorodibenzo-p-dioxin, and 2,3,7,8-Tetrachlorodibenzo-p-dioxin. J. Agr. Food Chem., 19, 1210-1214, 1971.

Isensee, A.R. and Jones, G.E., Distribution of 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) in Aquatic Model Ecosystem. Environmental Science and Technology, 9, 668-672, 1975.

Jaber, H. and Podoll, T., 1983 SRI, Unpublished Results, as cited by Mill (1985).

Jackson, D.R., Roulier, M.H., Grotta, H.M., Rust, S.W., and Warner, J.S., Solubility of 2,3,7,8-TCDD in Contaminated Soils, in Chlorinated Dioxins and Dibenzofurans in Perspective, Rappe, Choudry, Keith (Eds.), Lewis Publishers, Inc., 1987.

Jensen, D.J., Getzendaner, M.E., Hummel, R.A., and Turley, J., Residue Studies for (2,4,5-Trichlorophenoxy)acetic Acid and 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Grass and Rice. J. Agric. Food Chem., 31, 118-122, 1983.

Jensen, D.J., Hummel, R.A., Mahle, N.H., Kocher, C.W., and Higgins, H.S., A Residue Study on Beef Cattle Consuming 2,3,7,8-Tetrachlorodibenzo-p-dioxin. J. Agric. Food Chem., 29, 265-268, 1981.

Jensen, D.J. and Hummel, R.A., Secretion of TCDD in Milk and Cream Following the Feeding of TCDD to Lactating Dairy Cows. Bull. Environm. Contam. Toxicol., 29, 440-446, 1982.

Jirka, G.H. and Brutsaert, W., Measurements of Wind Effects on Water-Side Controlled Gas Exchange in Riverine Systems, Gas Transfer at Water Surfaces, Brutsaert, W. and G.H. Jirka (Eds.) D. Reidel Publishing Company, Dordecht, Holland, 1984

Johnson, H., Aquatic Fate Process Data for Organic Priority Pollutants, Mabey, W.R., Ed., U.S. EPA Final Report, Contract 68-01-3867, 1982.

Junge, C.B., in Fate of Pollutants in the Air and Water Environments, Part I, Suffet, I.H. (Ed.), Wiley, N.Y., 7-26, 1977.

Karickhoff, S.W., Brown, D.S., and Scott, T.A., Sorption of Hydrophobic Pollutants on Natural Sediments. Water Research, 13, 241-248, 1979.

Katayama, A. and Matsumura, F., Photochemically Enhanced Microbial Degradation of Environmental Pollutants. Environmental Science and Technology, 25, 1329-1333, 1991.

Kearney, P.C., Woolson, E.A., and Ellington, C.P., Persistence and Metabolism of Chlorodioxins in Soils. Environmental Science and Technology, 6, 1017-1019, 1972.

Kearney, P.C., Woolson, E.A., Isensee, A.R., and Helling, C.S., Tetrachlorodibenzodioxin in the Environment: Sources, Fate, and Decontamination. Environmental Health Perspectives, 273-277, Sept. 1973.

Kenaga, E.E., Correlation of Bioconcentration Factors of Chemicals in Aquatic and Terrestrial Organisms with Their Physical and Chemical Properties. Environmental Science Technology, 14(5), 553-556, 1980.

Kenaga, E.E. and Goring, C.A.I., Relationship Between Water Solubility, Soil Sorption, Octanol-Water Partitioning, and Concentration of Chemicals in Biota. Aquatic Toxicology, 13, 78-109, 1980.

Kenaga, E.E. and Morris, L.A., Environmental Toxicity of TCDD, in Human and Environmental Risks of Chlorinated Dioxins and Related Compounds, Tucker, Young, Gray (eds.), Plenum Press, New York, 1983.

Kew, G.A., Schaum, J.L., White, P., and Evans, T.T., Review of Plant Uptake of 2,3,7,8-TCDD from Soil and Potential Influences of Bioavailability. Chemosphere, 18, 1313-1318, 1989.

Kimbrough, R.D., Falk, H., Stehr, P., and Fries, G., Health Implications of 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) Contamination of Residential Soil, from Public Health Risks of the Dioxins, proceedings of a symposium held on October 19-20, 1983 at the Rockefeller University, NY City, publisher Kaufmann, CA, 1984.

Kimbrough, R.D., Falk, H., and Stehr, P., Health Implications of 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) Contamination of Residential Soil. J. Toxicol. Environ. Health, 14, 47-93, 1984.

Kociba, R.J., Keyes, D.G., Beyer, J.E., Carreon, R.M., Wade, C.E., Dittenber, A.D., Kalnins, R.P., Frauson, L.E., Park, C.N., Barnard, S.D., Hummel, R.A., and Humiston, C.G., Results of a Two-year Chronic Toxicity and Oncogenicity Study of 2,3,7,8-Tetrachlorodibenzo-p-dioxin in Rats. Toxicology and Applied Pharmacology, 46(2), 279-303, 1978.

Leuenberger, C., Ligocki, M.P., and Pankow, J.F., Trace Organic Compounds in Rain - 4. Identities, Concentrations, and Scavenging Mechanisms for Phenols in Urban Air and Rain, Environmental Science and Technology, 19, 1053-1058, 1985.

Lewis, W.K. and Whitman, W.G., Principles of Gas Absorption, Industrial and Engineering Chemistry, 16(12), 1215-1220, 1924.

Lucier, G.W., Rumbaugh, R.C., McCoy, Z., Hass, R., Harvan, P., and Albro, P., Ingestion of Soil Contaminated with 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) Alters Hepatic Enzyme Activities in Rats. Fundamental and Applied Toxicology, 6, 364-371, 1986.

Lyman, W.J., Reel, W.F., and Rosenblatt, D.H., Handbook of Chemical Property Estimation Methods, McGraw-Hill, New York, 1982, 1990.

Mabey, W.R., Smith, J.H., Podoll, R.T., Johnson, H.L., Mill, T., Chou, T., Gates, J., Partridge, I.W., and Vandenberg, D., Aquatic Fate Process Data for Organic Priority Pollutants. U.S. EPA, EPA 440/4-81-014, 1981.

Mackay, D., Correlation of Bioconcentration Factors, Environmental Science and Technology, 16(5), 274-278, 1982.

Mackay, D. and Yeun, A.T.K., Mass Transfer Coefficient Correlations of Volatilization of Organic Solutes from Water, Environmental Science and Technology, 17(4), 1983.

Markin, G.P., Translocation and fate of the insecticide Mirex within a Bahia Grass Pasture Ecosystem, Environ. Pollut. Ser. A, 26, 227-241, 1981.

Marple, L., Berridge, B., and Throop, L., Measurement of the Water-Octanol Partition Coefficient of 2,3,7,8-Tetrachlorodibenzo-p-dioxin, Environmental Science and Technology, 20, 397-399, 1986.

Marple, L., Brunck, R., and Throop, L., Water Solubility of 2,3,7,8-Tetrachlorodibenzo-p-dioxin. Environmental Science and Technology, 20, 180-182, 1986.

Marshall, J. and Palmer, W., The Distribution of Raindrops with Size, J. Meteorology, 5, 165-166, 1948.

Matsumura, F., Absorption, Accumulation and Elimination of Pesticides by Aquatic Organisms. Environ. Sci. Res., 10, 77-105, 1977.

Matsumura, F. and Benezet, H.J., Studies on the Bioaccumulation and Microbial Degradation of 2,3,7,8-Tetrachlorodibenzo-p-dioxin. Environmental Health Perspectives, 253-258, Sept. 1973.

Matsumura, F., Quensen, J., and Tsushimoto, G., Microbial Degradation of TCDD in a Model Ecosystem, in Human and Environmental Risks of Chlorinated Dioxins and Related Compounds, Tucker et al. (Eds.), Plenum Press, NY, pp. 191-219, 1983.

McConnell, E.E., Lucier, G.W., Rumbaugh, R.C., Albro, P.W., Harvan, D.J., Hass, J.R., and Harris, M.W., Dioxin in Soil: Bioavailability after Ingestion by Rats and Guinea Pigs. Science, 223, 1077-1079, 1984.

McCrady, J.K., McFarlane, C., and Gander, L.K., The Transport and Fate of 2,3,7,8-TCDD in Soybean and Corn. Chemosphere, 21, 359-376, 1990.

McCrady, J.K., McFarlane, C., and Lindstrom, F.T., The Transport and Affinity of Substituted Benzenes in Soybean Stems. J. Exp. Bot., 38, 1875-90, 1987.

McKone, T.E., Dioxin Risk Management at Times Beach, Missouri: An Evaluation, Lawrence Livermore National Laboratory, May 1985.

McKone, T.E., The Use of Environmental Health-Risk Analysis for Managing Toxic Substances, paper prepared for the Proceedings of 78th Annual Meeting of the Air Pollution Control Association, Detroit, Michigan, June 16-21, 1985.

McKone, T.E. and Ryan, P.B., Human Exposures to Chemicals through Food Chains: An Uncertainty Analysis. Environmental Science and Technology, 23(9), 1989.

Means, J.C., Wood, S.G., Hassett, J.J., and Banwart, W.L., Sorption of Polynuclear Aromatic Hydrocarbons and by Sediments and Soils. Environmental Science and Technology, 14, 1524-1528, 1980.

Mehrle, P.M., Buckler, D.R., Little, B.B., Smith, L.M., Petty, J.D., Peterman, P.H., Stalling, D.L., DeGraeve, G.M., Coyle, J.J., and Adams, W.J., Toxicity and Bioconcentration of 2,3,7,8-Tetrachlorodibenzodioxin and 2,3,7,8-Tetrachlorodibenzofuran in Rainbow Trout. Environ. Toxicol. Chem., 7, 47-62, 1988.

Mill, T., Mabey, W.R., Bomberger, D.C., Chou, T.-W., Hendry, D.G., and Smith, J.H., Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water, EPA 600/3-82-027, 1982.

Mill, T., Prediction of the Environmental Fate of Tetrachlorodibenzodioxin, in Dioxins in the Environment, Kamrin & Rodgers (eds.), Hemisphere Press Corp., Washington DC, pp. 195-204, 1985.

Mill, T., Tetrachlorodibenzodioxins: Rates of Photolysis Volatilization in the Environment, prepublication manuscript, SRI: Menlo Park, California.

Miller, G.C., Herbert, V.R., and Zepp, R.G., Chemistry and Photochemistry of Low-Volatility Organic Chemicals on Environmental Surfaces, Environmental Science and Technology, 21, 1164-1167, 1987.

Monsanto Company, Physical Property Research, Cheng, S.C., Hileman, F.E., Schroy, J.M., Dayton, Ohio and St. Louis, Missouri, Nov 1983 to March 1984. (Measurement of vapor pressure at four temperature levels, and development of the heat of sublimation from the correlation of the vapor pressure data using the Clausius-Clapeyron equation. Estimates of the heat of vaporization were made using the measured heat of sublimation and the heat of fusion.)

Nash, R.G. and Beall, M.L., Distribution of Silver 2,4-D and TCDD Applied to Turf in Chambers and Field Plots. J.Agric. Food Chemistry, 28, 614-623, 1980.

National Research Council of Canada (NRCC), Associate Committee on Scientific Criteria for Environmental Quality, Polychlorinated Dibenzo-p-dioxins: Criteria for their effects on man and his environment, Publication NRCC No.18574 of the Environmental Secretariat, 1981.

Neely, W.B., Estimating Rate Constants for the Uptake and Clearance of Chemicals by Fish. Environmental Science and Technology, 13, 1506-1510, 1979.

Nessel, C.S., Butler, J.P., Post, G.B., Held, J.C., Gochfeld, M., and Gallow, M.A., Evaluation of the Relative Contribution of Exposure Routes in a Health Risk Assessment of Dioxin

Emissions from a Municipal Waste Incinerator. Journal of Exposure Analysis and Environmental Epidemiology, 1, 283-307, 1991.

Nestrick, T.J., Lamparski, L.L., and Townsend, D.I., Identification of Tetrachlorodibenzo-p-dioxin Isomers at the 1-ng Level by Photolytic Degradation and Pattern Recognition Techniques. Analytic Chemistry, 52, 1865-1874, 1980.

Nielsen, K.K., Moeller, J.T., and Rasmussen, S., Reduction of Dioxins and Furans by Spray Dryer Absorption from Incinerator Flue Gas. Chemosphere, 15, 1267-1254, 1986.

O'Connor, D., Wind Effects of Gas-Liquid Transfer Coefficients, Journal of Environmental Engineering, 109(3), 731-752, 1983.

Palausky, J., Kapila, S.T., Manahan, J.B., Yanders, A.F., Malhotra, R.K., and Clevenger, T.E., Studies on Vapor Phase Transport and Role of Dispersing Medium on Mobility of 2,3,7,8 TCDD in Soil. Chemosphere, 15, 1389-1396, 1986.

Pankow, J.F., Review and Comparative Analysis of the Theories on Partitioning Between the Gas and Aerosol Phases in the Atmosphere, Atmospheric Environment, 21, 2275-84, 1987.

Pankow, J.F., Review and Comparative Analysis of the Theories on Partitioning Between the Gas and Aerosol Particulate Phases in the Atmosphere, Atmospheric Environment, 22, 1405-1409, 1988.

Paterson, S. and Mackay, D., Correlation of the Equilibrium and Kinetics of Leaf-Air Exchange of Hydrophobic Organic Chemicals, Environmental Science and Technology, 25, 866-871, 1991.

Perkaw, J., Eschenroeder, A., Goyer, M., Stevens, J., and Wechsler, A., An Exposure and Risk Assessment for 2,3,7,8-Tetrachlorodibenzo-p-dioxin, Office of Water Regulations and Standards, U.S. EPA: Washington, D.C., 1980.

Petersen, J.T., Calculated Actinic Fluxes (290-700mm) for Air Pollution Photochemistry Applications, EPA 600/6-76-025, 1976.

Petty, J.D., Smith, L.M., Peterman, P.H., Mehrle, P.M., Buckler, D.R., and Stalling, D.L., Bioconcentration of TCDD and TCDF by Rainbow Trout in a Flow-through Exposure. Presented at Society of Environmental Toxicology and Chemistry (SETAC) Seventh Annual Meeting, November 2-5, 1986, Alexandria, Virginia.

Plate, E.J. and Freidrich, R., Reaeration of Open Channel Flow, Gas Transfer at Water Surfaces, W. Brutsaert and G.H. Jirka (Eds.), Dordecht, Holland, 1984.

Plimmer, J.R, Klingbiel, V.I., Crosby, D.G., and Wong, A.S., Chlorodioxinx - Origins and Fate, Blair, E.H. (Ed.), Advances in Chemistry Series 120, American Chemical Society, Washington, D.C., pg. 46, 1973.

Podoll, R.T., Jaber, H.M., and Mill, T., Tetrachlorodibenzodioxin: Rates of Volatilization and Photolysis in the Environment, Environmental Science and Technology, 20, 490-492, 1986.

Pohland, A.B. and Young, G.C., Preparation and Characterization of Chlorinated Dibenzo-p-dioxins, Journal of Agric. Food Chem., 20, 1093-1099, 1972.

Poiger, H. and Schlater, C., Influence of Solvents and Adsorbents on Dermal and Intestinal Absorption of TCDD, Fd Cosmet. Toxicology, 18, 477-481, 1980.

Prinn, R., Cunnold, D. Rasmussen, R., Simmonds, P., Alyea, F., Crawford, A., Fraser, P., and Rosen, R., Atmospheric Trends in Methyl Chloroform and the Global Average for the Hydroxyl Radical, Science, 238, 945-950, 1987.

Quensen, J.F. and Matsumura, F., Oxidative Degradation of 2,3,7,8-Tetrachlorodibenzo-p-dioxin by Microorganisms. Environmental Toxicology and Chemistry, 2, 261-268, 1983.

Radke, C., Hobbs, P., and Blutgroth, M., Scavenging of Aerosol Particles by Precipitation, Journal of Applied Meteorology, 19, 715-722, 1980.

Reid, R.C., Prausnitz, J.M., and Sherwood, T.K., The Properties of Gases and Liquids, 3rd Edition, McGraw-Hill Book Company, New York, 1977.

Reid, R.C., Prausnitz, J.M., and Poling, B.E., The Properties of Gases and Liquids, 4th Edition, McGraw-Hill Book Company, New York, 1987.

Rordorf, B.F., Thermodynamic and Thermal Properties of Polychlorinated Compounds: The Vapor Pressures and Flow Tube of Ten Dibenzo-Para-Dioxines, Chemosphere, 14, 885-892, 1985.

Ryan, J.A., Bell, R.M., Davidson, J.M., and O'Connor, G.A. Plant Uptake of Non-Ionic Organic Chemicals from Soils, Chemosphere, 17, 229-2323, 1988.

Ryan, P.A. and Cohen, Y., Multimedia Transport of Particle-Bound Organics: Benzo(a)pyrene Test Case, Chemosphere, 15, 31-47, 1986.

Sacchi, G.A., Vigaro, P., Fortunati, G., and Cocucci, S.M., Accumulation of 2,3,7,8-tetrachlorodibenzo-p-dioxin from soil and nutrient solution by bean and maize plants, Experientia, 42, 586-588, 1986.

Sarna, L.P., Hodge, P.E., and Webster, G.R.B., Octanol Water Partition Coefficients of Chlorinated Dioxins and Dibenzofurans by Reversed Phase HPLC Using Several C_{18} Columns, Chemosphere, 13, 975, 1984.

Schaum, J., Risk Analysis of TCDD Contaminated Soil, Technical report, EPA-600/8-84-031, U.S. EPA, 1984.

Scheidl, K., Kuna, R.P., and Wurst, F., Chlorinated Dioxins and Furans Emissions from Municipal Incineration, Chemosphere, 14, 913-917, 1985.

Schroy, J.M., Hileman, F.D., and Cheng, S.C., Physical/Chemical Properties of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin, in Aquatic Toxicology and Hazard Assessment, Bahner & Hansen (eds.), PA: ASTM, pp. 409-421, 1985.

Schroy, J.M., Hileman, F.D., and Cheng, S.C., Physical/Chemical Properties of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin, Chemosphere, 14, 877-880, 1985.

Schroy, J.M., Hileman, F.D., and Cheng, S.C., The Uniqueness of Dioxins? Physical/Chemical Characteristics, for presentation at the 8th ASTM Aquatic Toxicology Symposium to be held on April 15, 16, and 17, 1984 at the Draw Bridge Inn, Fort Mitchell, Kentucky.

Sehmel, G.A., Particle and Gas Deposition: A Review, Atmospheric Environment, 14, 983-1011, 1980.

Sehmel, G.A., Deposition and Resuspension in Atmosphere Science and Power Production, Randerson, D. (Ed.), Published by U.S. Department of Energy, DOE/TIC-27601, 1984.

Shen, T., Estimation of Organic Compound Emissions from Waste Lagoons, Journal of the Air Pollution Control Association, 32, 79-82, 1982.

Shen, T., Schmidt, C.E., and Card, T., Assessment and Control of VOC Emissions from Waste Treatment and Disposal Facilities, Van Nostrand Reinhold Publishing, New York, New York, 1993.

Shiu, W.Y., Doucette, W., Gobas, F.A.P.C., Andrew, A., and Mackay, D., Physico-Chemical Properties of Chlorinated Dibenzo-p-dioxins, Environmental Science and Technology, 22, 651-658, 1988.

Singh, H.B., Ludwig, F.L., and Johnson, W.B., Tropospheric Ozone: Concentrations and Variabilities in Clean Remote Atmospheres. Atmospheric Environment, 12, 2185-2196, 1978.

Skelly, N.E, Kallos, G., and Shadoff, L., Dow Chemical Company, personal communication.

Slinn, W.G.N., Prediction for Particle Deposition to Vegetative Canopies, Atmospheric Environment, 16, 1785-1792, 1982.

South Coast Air Quality Management District (SCAQMD), Multipathway Health Risk Assessment Input Parameters Guidance Document, 1988.

Southworth, G.R., The Role of Volatilization in Removing Polycyclic Aromatic Hydrocarbons from Aquatic Environments, Bulletin of Environmental Contamination and Toxicology, 21, 507-514, 1979.

Stevens, J.B. and Gerbec, B.N., Dioxin in the Agricultural Food Chain, Risk Analysis, Vol. 8, 379-335, 1988.

Strenge, D.L. and Napier, T., Radiological Assessment, Engineering Geology, 26(4), 405-410, 1989.

Thomann, R.V., Bioaccumulation Model of Organic Chemical Distribution in Aquatic Food Chains, Environmental Science and Technology, 23(6), 699-707, 1989.

Thomas, N.A., Memorandum to C.B. Stephen, U.S. EPA, Duluth, MN, July 22, 1983.

Travis, C.C. and Arms, A.D., Bioconcentration of Organics in Beef, Milk, and Vegetation, Environmental Science and Technology, 22, 271-274, 1988.

Travis, C.C. and Hattemer-Frey, A., Multimedia Partitioning of Dioxin, in Intermedia Pollutant Transport, Allen, Cohen, Kaplan (Eds.), 1989.

Tsai, W., Cohen, Y., Sakugawa, H., and Kaplan, I.R., Dynamic Partitioning of Semi-Volatile Organics in Gas/Particle/Rain Phases During Rain Scavenging. Environmental Science and Technology, 25(12), 2012-2022, 1991.

U.S. EPA, Ambient Water Quality Criteria for 2,3,7,8-Tetrachlorodibenzo-p-dioxin, Office of Water Regulations and Standards, W. DC, Report 440/5-84-007, 1984.

U.S. EPA, Background Document to the Integrated Risk Assessment for Dioxins and Furans from Chlorine Bleaching in Pulp and Paper Mills, Washington, D.C., EPA 56015-90-014, 1990.

U.S. EPA, Estimating Exposure to Dioxin-like Compounds, EPA/600/6-88/005B, Review Draft, August, 1992.

U.S. EPA, Health Assessment Document for Polychlorinated Dibenzo-p-Dioxins, EPA/600/8-84/014F, 1985.

U.S. EPA, Office of Solid Waste and Emergency Response. National Dioxin Study. Report to Congress, Washington, D.C., EPA 530/SW-87-025, 1987b.

U.S. EPA, Review and Development of Methodologies for Estimating Exposure to Dioxin. Washington, D.C., 1987a.

van den Berg, M., de Vroom, B., van Greevenbroek, M., and Olie, K., Bioavailability of PCDDs and PCDFs Adsorbed on Fly Ash in Rat, Guinea Pig and Syrian Golden Hamster, Chemosphere, 14, 865-869, 1985.

Veith, G.D., Macek, K.J., Petrocelli, S.R., and Caroll, J., An Evaluation Using Partition Coefficients and Water Solubility to Estimate Bioconcentration Factors for Organic Chemicals in Fish, Aquatic Toxicology, ASTM STP 707, Baton, Parrish, Hendricks (eds.), 1980.

Veith, G.D. and Rosian, P., Estimating Bioconcentration Potential from Octanol/Water Partition Coefficient. In Physical Behavior of PCBs in the Great Lakes, Simmons (ed.), Ann Arbor Science, Michigan, 269-282, 1983.

Walters, R.W. and Guiseppi-Elie, A., Sorption of 2,3,7,8-Tetrachlorodibenzo-p-dioxin to Soils from Water/Methanol, Environmental Science and Technology, 22, 819-825, 1988.

Walters, R.W., Ostazeski, S.A., and Guiseppi-Elie, A., Sorption of 2,3,7,8-Tetrachlorodibenzo-p-dioxin from Water by Surface Soils, Environmental Science and Technology, 23:4, 480-484, 1989.

Ward, C.T. and Matsumura, F., Fate of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) in a Model Aquatic Environment, Arch. Environm. Contam. Toxicol., 7, 349-357, 1978.

Webster, G., Sarna, L., and Muir, D., K_{ow} of 1,3,6,8-TCDD and OCDD by Reverse Phase HPLC, University of Manitoba: Winnipeg, Manitoba, Canada R3T 2N2, publication preprint, 1983.

Whicker, F.W. and Kirchner, T., Pathway: A Dynamic Food-Chain Model to Predict Radionuclide Ingestion after Fallout Deposition, Health Physics, 52, 717-727, 1987.

Williams, R.M., A Model of the Dry Deposition of Particles to Water Surfaces, Atmospheric Environment, 16, 1933-1938, 1982.

Wilke, C.R. and Chang P., Correlation of Diffusion Coefficients in Dilute Solutions, AIChE Journal, 1, 264-70, 1955.

Wilke, C.R. and Lee, C.Y., Estimation of Diffusion Coefficients for Gases and Vapors, Industrial and Engineering Chemistry, 47, 1253, 1955.

Wipf, H.K., Homberger, E., Neuser, N., Ranalden, V.B., Vetter, W., and Vuillernier, J.P., TCDD Levels in Soil and Plant Samples from the Seveso Area. In Chlorinated Dioxins and Related Compounds: Impact on the Environment, Hutzinger, O., et al. (Eds.), Pergamon Press, N.Y., 1982.

Witherspoon, J.P. and Taylor, F.G., Interception and Retention of Simulated Fallout by Agricultural Plants, Health Physics 19, 493-499, 1970.

Wu, J., The Wind-Stress Coefficient over Sea Surface near Neutral Conditions - A Revisit. Journal of Physical Oceanography, 10, 727-740, 1980.

Wu, J., Wind-Induced Drift Current, Journal of Fluid Mechanics, 68, 49-70, 1975.

Young, A.L., Long-Term Studies on the Persistence and Movement of TCDD in a Natural Ecosystem, in Human and Environmental Risks of Chlorinated Dioxins and Related Compounds, in Tucker et al. (Eds.), Plenum Publishing Corp., New York, 1983.