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Environmental Protection
Agency

Office of Research and
Development
Washington DC 20460

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June 1994
External Review Draft

EPA

Estimating Exposure to Dioxin-Like Compounds

Review Draft (Do Not Cite or Quote)

Volume III: Site-Specific Assessment Procedures

Notice

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.

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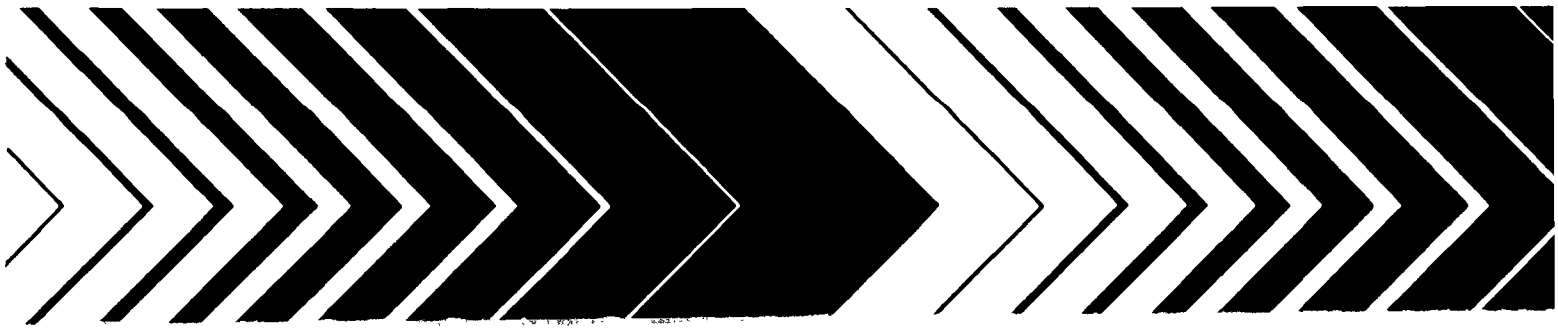

Next Stages in the Reassessment Process

As described previously, public briefings will be held during the first week of the public comment period to be followed by formal public hearings in December 1994. After the close of the public comment period, the Agency's Science Advisory Board (SAB) will review the draft documents in public session (early 1995). Following SAB review, the draft documents will be revised, comments and revisions will be incorporated, and final documents will be issued.

8/30/94
Date

Acting Carl R. Gerber
Assistant Administrator
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Billing Code: 6560-50-P

ecosystems from exposure to dioxins. Research efforts are focused on the study of organisms in aquatic food webs to identify the effects of dioxin exposure that are likely to result in significant population impacts. A report titled, *Interim Report on Data and Methods for the Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) Risks to Aquatic Organisms and Associated Wildlife* (EPA/600/R-93/055), was published in April 1993. This report will serve as a background document for assessing dioxin-related ecological risks. Ultimately, these data will support the development of aquatic life criteria which will aid in the implementation of the Clean Water Act.

As mentioned previously, completion of the health assessment and exposure documents involves three phases: Phase 1 involved drafting state-of-the-science chapters and a dose-response model for the health assessment document, expanding the exposure document to address dioxin related compounds, and conducting peer-review workshops by panels of experts. This phase has been completed.

Phase 2, preparation of the risk characterization, began during the September 1992 workshops with discussions by the peer-review panels and formulation of points to be carried forward into the risk characterization. Following the September 1993 workshop, this work was completed and was incorporated as Chapter 9 (Volume III) of the draft health assessment document. This phase has been completed.

Phase 3 is currently underway. It includes making External Review Drafts of both the health assessment document and the exposure document available for public review and comment.

scientific experts from outside the Agency reviewed the draft documents and provided valuable comments. It also should be noted that outside scientists have been heavily involved throughout the developmental process of writing and reviewing these draft documents. With this notice, the External Review Drafts of both draft documents are being released for a 120-day public review and comment period.

Current Stage of the Scientific Reassessment of Dioxin

The scientific reassessment of dioxin consists of five activities:

1. Update and revision of the health assessment document for dioxin.
2. Laboratory research in support of the dose-response model.
3. Development of a biologically based dose-response model for dioxin.
4. Update and revision of the dioxin exposure assessment document.
5. Research to characterize ecological risks in aquatic ecosystems.

The first four activities have resulted in two draft documents (the health assessment document and exposure document) for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds. These companion documents, which form the basis for the Agency's reassessment of dioxin, have been used in the development of the risk characterization chapter that follows the health assessment (Chapter 9, Volume III). The process for developing these documents consisted of three phases which are outlined in later paragraphs.

The fifth activity, which is in progress at EPA's Environmental Research Laboratory in Duluth, Minnesota, involves characterizing ecological risks in aquatic

to hear and receive public comments and reviews of the proposed plans, and to receive any current, scientifically relevant information.

In the Fall of 1992, the Agency convened two peer-review workshops to review draft documents related to EPA's scientific reassessment of the health effects of dioxin. The first workshop was held September 10 and 11, 1992, to review a draft exposure assessment titled, *Estimating Exposures to Dioxin-Like Compounds*. The second workshop was held September 22-25, 1992, to review eight chapters of a future draft *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds*. Peer-reviewers were also asked to identify issues to be incorporated into the risk characterization, which was under development.

In the Fall of 1993, a third peer-review workshop was held on September 7 and 8, to review a draft of the revised and expanded Epidemiology and Human Data Chapter, which also would be part of the future health assessment document. The revised chapter provided an evaluation of the scientific quality and strength of the epidemiology data in the evaluation of toxic health effects, both cancer and noncancer, from exposure to dioxin, with an emphasis on the specific congener, 2,3,7,8-TCDD.

Prior to each workshop, the draft documents or chapters were made available in keeping with the Agency's continuing commitment to conduct the reassessment of dioxin in an open and participatory manner, to keep the public informed of its progress, and to encourage public participation in the document development process. The public also was invited to attend the workshops, to present oral comments, and/or to submit written comments. At each workshop, a panel of

adverse health effects of dioxin in people, of the pathways to human exposure, and of the toxic effects of dioxin to the environment. The reassessment is part of the Agency's goals to improve the research and science base and to incorporate improved research and science into EPA decisions.

History

In 1985 and 1988, the Agency prepared assessments of the human health risks from environmental exposures to dioxin. Also, in 1988, a draft exposure document was prepared that presented procedures for conducting site-specific exposure assessments to dioxin-like compounds. These assessments were reviewed by the Agency's Science Advisory Board (SAB). At the time of the 1988 assessments, there was general agreement within the scientific community that there could be a substantial improvement over the existing approach to analyzing dose response, but there was no consensus as to a more biologically defensible methodology. The Agency was asked to explore the development of such a method. The Agency's reassessment activities are in response to this request.

Stages in the Reassessment Process That Have Been Completed

The EPA had endeavored to make each phase of the reassessment of dioxin an open and participatory effort. On November 15, 1991, and April 28, 1992, public meetings were held to discuss the Agency's plans and activities for the reassessment,

For the exposure assessment document, send comments to: Dioxin Exposure Assessment Comments, Technical Information Staff (8601), Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, 401 M Street, S.W., Washington, DC 20460.

FOR FURTHER INFORMATION, CONTACT:

For questions on the overall reassessment of dioxin or technical questions on the health assessment document: William Farland, Office of Health and Environmental Assessment (8601), Office of Research and Development, U.S. Environmental Protection Agency, 401 M Street, S.W., Washington, DC 20460; telephone (202) 260-7315; fax (202) 260-0393.

For technical questions on the exposure assessment: John Schaum, Exposure Assessment Group (8603), Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, 401 M Street, S.W., Washington, DC 20460; telephone (202) 260-8909; fax (202) 260-1722.

SUPPLEMENTARY INFORMATION:

The Scientific Reassessment of Dioxin

In April 1991, EPA announced that it would conduct a scientific reassessment of the health risks of exposure to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and chemically similar compounds collectively known as dioxin. The EPA has undertaken this task in response to emerging scientific knowledge of the biological, human health, and environmental effects of dioxin. Significant advances have occurred in the scientific understanding of mechanisms of dioxin toxicity, of the carcinogenic and other

Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268; telephone (513) 569-7562; fax (513) 569-7566. Please provide your name, mailing address, document title, and EPA number.

Please note that the two summary volumes also will be made available as WordPerfect 5.1 files on 3½" PC-DOS formatted disks. Please request by document title and EPA number:

Risk Characterization Chapter (Vol. III-Health), EPA/600/BP-92/001ca (disk)

Executive Summary Chapter (Vol. I-Exposure), EPA/600/6-88/005Caa (disk)

The draft documents will be provided for inspection at the ORD Public Information Shelf, EPA Headquarters Library, 401 M Street, S.W., Washington, DC 20460, between the hours of 10:00 a.m. and 2:00 p.m., Monday through Friday, except for Federal holidays, and at all of the EPA Regional and Laboratory libraries.

Submitting Comments

All comments must be in writing. Commenters should submit three copies of each comment, and if commenting on both documents—the health assessment document and the exposure assessment—submit separate comments rather than combined submissions.

For the health assessment document, send comments to: Dioxin Health Assessment Comments, Technical Information Staff (8601), Office of Health and Environmental Assessment, U.S. Environmental Protection Agency, 401 M Street, S.W., Washington, DC 20460.

ADDRESSES:

Requesting Documents

Due to the large size of both draft documents (each is over 1,000 pages in length), the documents will be available as follows:

Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds, EPA/600/BP-92/001a, 001b, 001c. (Note: The full document is 3 volumes and approx. 1,100 pages.)

OR

Risk Characterization Chapter, EPA/600/BP-92/001c. (Note: This third volume of the 3-volume set integrates health and exposure information on dioxin and related compounds; approx. 100 pages.)

AND/OR

Estimating Exposure to Dioxin-Like Compounds, EPA/600/6-88/005Ca, Cb, Cc. (Note: The full document is 3 volumes and approx. 1,300 pages.)

OR

Executive Summary Chapter of the Exposure Document, EPA/600/6-88/005Ca. (Note: This first volume of the 3-volume set summarizes the exposure information; approx. 100 pages.)

To obtain a paper copy of these draft documents, interested parties should contact the ORD Publications Center, CERI-FRN, U.S. Environmental Protection

Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, dioxin)

AGENCY: U.S. Environmental Protection Agency (EPA)

ACTION: As part of the Agency's reassessment of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD; hereinafter referred to as simply dioxin), two External Review Draft documents are being made available for a 120-day public review and comment period.

SUMMARY: This notice announces the availability of two External Review Draft documents for public review and comment:

1. *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds* (EPA/600/BP-92/001a-c)
2. *Estimating Exposure to Dioxin-Like Compounds* (EPA/600/6-88/005Ca-c)

During the public comment period, public comment meetings will be convened to take formal comments on the draft documents. These meetings are being planned for the first two weeks of December at five locations: Washington, DC; New York, NY/New Jersey; Chicago, IL; Dallas, TX; and San Francisco, CA. Detailed information will be provided in a future *Federal Register* notice.

The draft documents also will be reviewed at a Science Advisory Board meeting to be held after the public comment period has ended, early next year. Information about this meeting will be published in a future *Federal Register* notice.

DATES: The draft documents will be made available on September 13, 1994. Comments must be postmarked by January 13, 1994.

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EPA/600/6-88/005Cc
June 1994
External Review Draft

ESTIMATING EXPOSURE TO DIOXIN-LIKE COMPOUNDS

VOLUME III: Site-Specific Assessment Procedures

NOTICE

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Exposure Assessment Group
Office of Health and Environmental Assessment
U.S. Environmental Protection Agency
Washington, D.C.

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FOREWORD

The Exposure Assessment Group (EAG) within the Office of Health and Environmental Assessment of EPA's Office of Research and Development has three main functions: (1) to conduct exposure assessments, (2) to review assessments and related documents, and (3) to develop guidelines for exposure assessments. The activities under each of these functions are supported by and respond to the needs of the various EPA program offices. In relation to the third function, EAG sponsors projects aimed at developing or refining techniques used in exposure assessments.

The purpose of this document is to present and evaluate methods for conducting site-specific assessments of exposure to dioxin-like compounds. It is the third in a three volume set addressing these compounds. The first volume provides an overall executive summary and the second volume describes the properties, sources, environmental levels, and background exposures to dioxin-like compounds. The document is intended to be used as a companion to the health reassessment of dioxin-like compounds that the Agency is publishing concurrently. It is hoped that these documents will improve the accuracy and validity of risk assessments involving this important family of compounds.

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PREFACE

In April 1991, the U.S. Environmental Protection Agency (EPA) announced that it would conduct a scientific reassessment of the health risks of exposure to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) and chemically similar compounds collectively known as dioxin. The EPA has undertaken this task in response to emerging scientific knowledge of the biological, human health, and environmental effects of dioxin. Significant advances have occurred in the scientific understanding of mechanisms of dioxin toxicity, of the carcinogenic and other adverse health effects of dioxin in people, of the pathways to human exposure, and of the toxic effects of dioxin to the environment.

In 1985 and 1988, the Agency prepared assessments of the human health risks from environmental exposures to dioxin. Also, in 1988, a draft exposure document was prepared that presented procedures for conducting site-specific exposure assessments to dioxin-like compounds. These assessments were reviewed by the Agency's Science Advisory Board (SAB). At the time of the 1988 assessments, there was general agreement within the scientific community that there could be a substantial improvement over the existing approach to analyzing dose response, but there was no consensus as to a more biologically defensible methodology. The Agency was asked to explore the development of such a method. The current reassessment activities are in response to this request.

The scientific reassessment of dioxin consists of five activities:

1. Update and revision of the health assessment document for dioxin.
2. Laboratory research in support of the dose-response model.
3. Development of a biologically based dose-response model for dioxin.
4. Update and revision of the dioxin exposure assessment document.
5. Research to characterize ecological risks in aquatic ecosystems.

The first four activities have resulted in two draft documents (the health assessment document and exposure document) for 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and related compounds. These companion documents, which form the basis for the Agency's reassessment of dioxin, have been used in the development of the risk characterization chapter that follows the health assessment. The process for developing these documents consisted of three phases which are outlined in later paragraphs.

The fifth activity, which is in progress at EPA's Environmental Research Laboratory in Duluth, Minnesota, involves characterizing ecological risks in aquatic ecosystems from exposure to dioxins. Research efforts are focused on the study of organisms in aquatic food webs to identify the effects of dioxin exposure that are likely to result in significant population impacts. A report titled, *Interim Report on Data and Methods for the Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) Risks to Aquatic Organisms and Associated Wildlife* (EPA/600/R-93/055), was published in April 1993. This report will serve as a background document for assessing dioxin-related ecological risks. Ultimately, these data will support the development of aquatic life criteria which will aid in the implementation of the Clean Water Act.

The EPA had endeavored to make each phase of the current reassessment of dioxin an open and participatory effort. On November 15, 1991, and April 28, 1992, public meetings were held to inform the public of the Agency's plans and activities for the reassessment, to hear and receive public comments and reviews of the proposed plans, and to receive any current, scientifically relevant information.

In the Fall of 1992, the Agency convened two peer-review workshops to review draft documents related to EPA's scientific reassessment of the health effects of dioxin. The first workshop was held September 10 and 11, 1992, to review a draft exposure assessment titled, *Estimating Exposures to Dioxin-Like Compounds*. The second workshop was held September 22-25, 1992, to review eight chapters of a future draft *Health Assessment Document for 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD) and Related Compounds.* Peer-reviewers were also asked to identify issues to be incorporated into the risk characterization, which was under development.

In the Fall of 1993, a third peer-review workshop was held on September 7 and 8, 1993, to review a draft of the revised and expanded Epidemiology and Human Data Chapter, which also would be part of the future health assessment document. The revised chapter provided an evaluation of the scientific quality and strength of the epidemiology data in the evaluation of toxic health effects, both cancer and noncancer, from exposure to dioxin, with an emphasis on the specific congener, 2,3,7,8-TCDD.

As mentioned previously, completion of the health assessment and exposure documents involves three phases: Phase 1 involved drafting state-of-the-science chapters and a dose-response model for the health assessment document, expanding the exposure

document to address dioxin related compounds, and conducting peer review workshops by panels of experts. This phase has been completed.

Phase 2, preparation of the risk characterization, began during the September 1992 workshops with discussions by the peer-review panels and formulation of points to be carried forward into the risk characterization. Following the September 1993 workshop, this work was completed and was incorporated as Chapter 9 of the draft health assessment document. This phase has been completed.

Phase 3 is currently underway. It includes making External Review Drafts of both the health assessment document and the exposure document available for public review and comment.

Following the public comment period, the Agency's Science Advisory Board (SAB) will review the draft documents in public session. Assuming that public and SAB comments are positive, the draft documents will be revised, and final documents will be issued.

Estimating Exposures to Dioxin-Like Compounds has been prepared by the Exposure Assessment Group of the Office of Health and Environmental Assessment, Office of Research and Development, which is responsible for the report's scientific accuracy and conclusions. A comprehensive search of the scientific literature for this document varies somewhat by chapter but is, in general, complete through January 1994.

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The Exposure Assessment Group (EAG) within EPA's Office of Health and Environmental Assessment was responsible for the preparation of this document. General support was provided by Versar Inc. under EPA Contract Number 68-D0-0101. Dr. William Farland, as overall Director of the Dioxin Reassessment, provided policy guidance and technical comments. Matthew Lorber of EAG served as EPA task manager (as well as contributing author) providing overall direction and coordination of the production effort.

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1. INTRODUCTION

1.1. BACKGROUND

In May of 1991, the Environmental Protection Agency (EPA) announced a scientific reassessment of the human health and exposure issues concerning dioxin and dioxin-like compounds (56 FR 50903). This reassessment has resulted in two reports: a health reassessment document (EPA, 1994), and *Estimating Exposure to Dioxin-Like Compounds* [this three-volume report], which expands upon a 1988 draft exposure report titled, *Estimating Exposure to 2,3,7,8-TCDD* (EPA, 1988). The health and exposure reassessment documents can be used together to assess potential health risks from exposure to dioxin-like compounds. In a related area, EPA has also discussed the data and methods for evaluating risks to aquatic life from 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) (EPA, 1993).

The purpose of the exposure portion of the dioxin reassessment is to describe the causes and magnitude of background exposures, and provide site-specific procedures for evaluating the incremental exposures due to specific sources of dioxin-like compounds.

In September of 1992, EPA convened workshops to review the first public drafts of the health (EPA, 1992a) and the exposure documents (EPA, 1992b). The current draft of the exposure document incorporates changes as a result of that workshop as well as other review comments.

The exposure document is presented in three volumes. Following is a summary of the material contained in each of the three volumes:

Volume I - Executive Summary

This volume includes summaries of findings from Volumes II and III. It also includes a unique section on research needs and recommendations for dioxin-like compounds.

Volume II - Properties, Sources, Environmental Levels, and Background Exposures

This volume presents and evaluates information on the physical-chemical properties, environmental fate, sources, environmental levels, and background human exposures to dioxin-like compounds. It summarizes and evaluates relevant information obtained from published literature searches, EPA program offices and

other Federal agencies, and published literature provided by peer reviewers of previous versions of this document. The data contained in this volume is current through 1993 with some new information published in early 1994.

Volume III - Site-Specific Assessment Procedures

This volume presents procedures for evaluating the incremental impact from sources of dioxin release into the environment. The sources covered include contaminated soils, stack emissions, and point discharges into surface water. This volume includes sections on: exposure parameters and exposure scenario development; stack emissions and atmospheric transport modeling; aquatic and terrestrial soil, sediment, and food chain modeling; demonstration of methodologies; and uncertainty evaluations including exercises on sensitivity analysis and model validation, review of Monte Carlo assessments conducted for dioxin-like compounds, and other discussions. The data contained in this volume is current through 1993 with some new information published in early 1994.

1.2. TOXICITY EQUIVALENCY FACTORS

Dioxin-like compounds are defined to include those compounds with nonzero Toxicity Equivalency Factor (TEF) values as defined in a 1989 international scheme, I-TEFs/89. This procedure was developed under the auspices of the North Atlantic Treaty Organization's Committee on Challenges of Modern Society (NATO-CCMS, 1988a; 1988b) to promote international consistency in addressing contamination involving CDDs and CDFs. EPA has adopted the I-TEFs/89 as an interim procedure for assessing the risks associated with exposures to complex mixtures of CDDs and CDFs (EPA, 1989). As shown in Table 1-1, this TEF scheme assigns nonzero values to all chlorinated dibenzo-p-dioxins (CDDs) and chlorinated dibenzofurans (CDFs) with chlorines substituted in the 2,3,7,8 positions. Additionally, the analogous brominated compounds (BDDs and BDFs) and certain polychlorinated biphenyls (PCBs, see Table 1-2) have recently been identified as having dioxin-like toxicity (EPA, 1994) and thus are also included in the definition of dioxin-like compounds. However, EPA has not assigned TEF values for BDDs, BDFs, and PCBs. In the case of PCBs, research on the applicability of the TEF approach is ongoing but there is not yet any formal EPA policy. The nomenclature adopted here for purposes of describing these compounds is summarized in Table 1-3.

Table 1-1. Toxicity Equivalency Factors (TEF) for CDDs and CDFs.

Compound	TEF
Mono-, Di-, and Tri-CDDs	0
2,3,7,8-TCDD	1
Other TCDDs	0
2,3,7,8-PeCDD	0.5
Other PeCDDs	0
2,3,7,8-HxCDD	0.1
Other HxCDDs	0
2,3,7,8-HpCDD	0.01
Other HpCDDs	0
OCDD	0.001
Mono-, Di-, and Tri-CDFs	0
2,3,7,8-TCDF	0.1
Other TCDFs	0
1,2,3,7,8-PeCDF	0.05
2,3,4,7,8-PeCDF	0.5
Other PeCDFs	0
2,3,7,8-HxCDF	0.1
Other HxCDFs	0
2,3,7,8-HpCDF	0.01
Other HpCDFs	0
OCDF	0.001

Source: EPA, 1989.

Table 1-2. Dioxin-Like PCBs.

IUPAC No.	Congener
77	3,3',4,4'-tetra PCB
81	3,4,4',5-tetra PCB
105	2,3,3',4,4'-penta PCB
114	2,3,4,4',5-penta PCB
118	2,3',4,4',5-penta PCB
126	3,3',4,4',5-penta PCB
156	2,3,3',4,4',5-hexa PCB
157	2,3,3',4,4',5'-hexa PCB
167	2,3',4,4',5,5'-hexa PCB
169	3,3',4,4',5,5'-hexa PCB
189	2,3,3',4,4',5,5'-hepta PCB

Source: EPA, 1992a.

Table 1-3. Nomenclature for dioxin-like compounds.

Term/Symbol	Definition
Congener	Any one particular member of the same chemical family; e.g., there are 75 congeners of chlorinated dibenzo-p-dioxins.
Homologue	Group of structurally related chemicals that have the same degree of chlorination. For example, there are eight homologues of CDDs, monochlorinated through octochlorinated.
Isomer	Substances that belong to the same homologous class. For example, there are 22 isomers that constitute the homologues of TCDDs.
Specific congener	Denoted by unique chemical notation. For example, 2,4,8,9-tetrachlorodibenzofuran is referred to as 2,4,8,9-TCDF.
D	Symbol for homologous class: dibenzo-p-dioxin
F	Symbol for homologous class: dibenzofuran
M	Symbol for mono, i.e., one halogen substitution
D	Symbol for di, i.e., two halogen substitution
Tr	Symbol for tri, i.e., three halogen substitution
T	Symbol for tetra, i.e., four halogen substitution
Pe	Symbol for penta, i.e., five halogen substitution
Hx	Symbol for hexa, i.e., six halogen substitution
Hp	Symbol for hepta, i.e., seven halogen substitution
O	Symbol for octa, i.e., eight halogen substitution
CDD	Chlorinated dibenzo-p-dioxins, halogens substituted in any position
CDF	Chlorinated dibenzofurans, halogens substituted in any position
PCB	Polychlorinated biphenyls
2378	Halogen substitutions in the 2,3,7,8 positions

Source: EPA, 1989.

The procedure relates the toxicity of 210 structurally related individual CDD and CDF congeners and is based on a limited data base of in vivo and in vitro toxicity testing. By relating the toxicity of the 209 CDDs and CDFs to the highly-studied 2,3,7,8-TCDD, the approach simplifies the assessment of risks involving exposures to mixtures of CDDs and CDFs (EPA, 1989).

In general, the assessment of the human health risk to a mixture of CDDs and CDFs, using the TEF procedure, involves the following steps (EPA, 1989):

1. Analytical determination of the CDDs and CDFs in the sample.
2. Multiplication of congener concentrations in the sample by the TEFs in Table 1-1 to express the concentration in terms of 2,3,7,8-TCDD equivalents (TEQs).
3. Summation of the products in Step 2 to obtain the total TEQs in the sample.
4. Determination of human exposure to the mixture in question, expressed in terms of TEQs.
5. Combination of exposure from step 4 with toxicity information on 2,3,7,8-TCDD to estimate risks associated with the mixture.

Samples of this calculation for several environmental mixtures are provided in EPA (1989). Also, this procedure is demonstrated in Volume III of this assessment in the context of the demonstration of the stack emission source category. The seventeen dioxin-like congeners are individually modeled from stack to exposure site. TEQ concentrations are estimated given predictions of individual congener concentrations using Steps 2 and 3 above.

1.3. OVERALL COMMENTS ON THE USE OF THE DIOXIN EXPOSURE DOCUMENT

Users of the dioxin exposure document should recognize the following:

1. This document does not present detailed procedures for evaluating multiple sources of release. However, it can be used in two ways to address this issue. Incremental impacts estimated with procedures in Volume III can be compared to background exposure estimates which are presented in Volume II. This would be a way of comparing the incremental impact of a specific source to an individual's total exposure. If the releases

from multiple sources behave independently, it is possible to model them individually and then add the impacts. For example, if several stack emission sources are identified and their emissions quantified, and it is desired to evaluate the impact of all sources simultaneously, then it may be possible to model each stack emission source individually and then sum the concentrations and depositions at points of interest in the surrounding area.

2. The procedures and estimates presented in this three-volume exposure document best serve as general examples for evaluating exposures to dioxin-like compounds, rather than specific assessments. This document was not generated for purposes of supporting any specific regulation. Rather, it is intended to be a general information source which Agency programs can adopt or modify as needed for their individual purposes. For example, the demonstration scenarios of Volume III were not crafted as Agency policy on "high end" or "central tendency" scenarios for evaluating land contamination, stack emissions, or effluent discharges. Rather, they were designed to illustrate the site-specific methodologies in Volume III.

3. The understanding of the exposure to dioxin-like compounds continues to expand. Despite being one of the most studied groups of organic enivronmental contaminants, new information is generated almost daily about dioxin-like compounds. This document is considered to be current through 1993, with some information published early in 1994 included as well. Section IV of Volume I, Executive Summary, discusses research needs for dioxin exposure evaluation.

1.4. NOTES ON THE USE OF PROCEDURES IN VOLUME III

Numerous parameter values are used in this document and it is important to understand their degree of "endorsement" by EPA. The parameters can be divided into the following four classes for purposes of addressing this issue:

1) **First Order Defaults:** As defaults, these parameters are independent of site specific characteristics and can be used for any assessment. Also, as first order defaults, it is felt that the values selected for the demonstration scenarios carry a sufficient weight of evidence from current literature such that these values are recommended for other assessments. Several of the chemical specific parameters, such as the Henry's Constant, H, and the organic carbon partition coefficient, Koc, fall into this category. The qualifier

above, "current literature", indicates that new information could lead to changes in these values.

2) **Second Order Defaults:** Like the above category, these parameters are judged to be independent of site specific characteristics. However, unlike the above category, the current scientific weight of evidence is judged insufficient to describe values selected for demonstration purposes as first order defaults. Parameters of principal note in this category are the bioconcentration parameters specific to the chemicals, such the Biota Sediment Accumulation Factor, or BSAF. This parameter translates a bottom sediment concentration to a fish tissue concentration. The science is evolving for this parameter, including thought on the extent to which BSAFs generated for one species at one site can be generalized to other sites and/or species, the differences in BSAF between column and bottom feeders, the differences between past and ongoing contamination, and so on. Users should carefully review the justification for the SOD values selected for the demonstration scenarios before using the same values.

3) **Site Specific:** These parameters should or can be assigned values based on site-specific information. The information provided on their assignment for the demonstration of methodologies in this document can be useful where site specific information is unavailable. A key class of site specific are the source strength terms - the soil concentrations, effluent discharge rates, and stack emission rates. Others include physical properties (organic carbon contents of soil and sediment, climate variables, areas, distances, and volumes) and parameters for bioconcentration algorithms (yields of vegetations, cattle raising practices, fish lipid contents).

4) **Exposure Parameters:** The exposure parameters have not been categorized as have the contaminant fate and transport/transfer parameters. Assignment of these values are critical as Lifetime Average Daily Dose (LADD) estimates are linearly related to parameter assignments - doubling exposure duration assumptions double LADDs, and so on. Some exposure parameters are appropriately described as first order defaults. These include: lifetime, body weights, water ingestion rates, inhalation rates, and an exposure duration for a childhood pattern of soil ingestion. All of the other exposure parameters are better described as either second order defaults or site specific parameters. All exposure parameters were developed based on information and recommendations in EPA's *Exposure*

Factors Handbook (EPA, 1989b) and *Dermal Exposure Assessment: Principles and Applications* (EPA, 1992c).

The end products of the exposure assessment procedures presented in this document are estimates of potential dose expressed in mg of dioxin-like compound/kg-day. The procedures for converting these dose estimates to risk estimates are provided in a companion document on health assessment which EPA is publishing concurrently and which addresses the same compounds. It is also noted that EPA has recently focused on the indirect impacts from combustor emissions (EPA, 1993b). Much of the information in that document, such as procedures for estimating stack emissions, dispersion/deposition modeling, and fate, transport, and food chain impact modeling, coincides with information in this document.

The scope of each chapter in Volume III is summarized below.

Chapter 2, Estimating Exposure and Risks, presents overall framework for conducting exposure assessments. It provides procedures for identifying exposure pathways, estimating contact rates and resulting exposure levels. Approaches for defining exposure scenarios are presented. Procedures for using the Toxicity Equivalency Factors in exposure assessments are discussed here.

Chapter 3, Evaluating Atmospheric Releases of Dioxin-Like Compounds from Combustion Sources, provides procedures to estimate the emission rates of dioxin-like compounds from combustion processes and further atmospheric transport modeling procedures from the stack to the surrounding land surface. This chapter describes and demonstrates the use of the COMPDEP model on a hypothetical incinerator and lists the associated atmospheric dispersion and deposition estimates from that model exercise.

Chapter 4, Estimating Exposure Media Concentrations, provides procedures for estimating concentrations of the dioxin-like compounds in exposure media (soil, air, water, biota) resulting from soil contamination, effluent discharges, and stack emissions.

Chapter 5, Demonstration of Methodology, develops hypothetical scenarios and generates exposure estimates to demonstrate the methodologies of this document.

Chapter 6, User Considerations, discusses key issues for users of the methodologies. All model parameters are listed and categorized according to the scheme noted above. Sensitivity analysis is conducted on the algorithms estimating exposure

media concentrations. An exercise on estimating the releases from a bounded area of soil contamination is presented. The purpose of this exercise is to determine whether a reservoir of soil contamination would be depleted prior to an assumed duration of exposure.

Chapter 7, Uncertainty, discusses the sources and possible magnitude of uncertainty in the exposure assessment procedures. Uncertainty and variability of fate and transport, and exposure parameters, are discussed. Modeled exposure media concentrations are compared with concentrations that have been found in the literature, and alternate modeling approaches are demonstrated and compared with modeling approaches discussed in Chapter 5 and demonstrated in Chapter 6.

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2. ESTIMATING EXPOSURES AND RISKS

2.1. INTRODUCTION

In this chapter, the framework for assessing exposure and risk to 2,3,7,8-TCDD and related dioxin-like compounds will be described. Section 2.2 introduces the exposure equation and its key terms. Section 2.3 describes how risk is estimated given estimates of exposure. It also discusses the use of toxicity equivalency factors. Section 2.4 provides the overview of the procedures used in this document, and provides a roadmap for finding pertinent information in other chapters of the document. Section 2.5 describes the development of exposure scenarios for this assessment. Section 2.6 describes the exposure parameters chosen for the exposure pathways of this assessment.

The development of exposure assessment methods, scenarios and associated parameter values raises many issues which are generic to all chemicals. In order to keep the scope of this document reasonable, the decision was made to focus on issues specific to dioxin-like compounds and to avoid evaluating generic issues. Thus, priority is given to addressing issues such as fish bioconcentration, dermal absorption, degradation, and other chemical/physical properties of these compounds. The approach used to address generic issues such as soil ingestion rates, inhalation rates and other behavior parameters is based on previously published Agency documents, primarily the Exposure Factors Handbook (EPA, 1989a). Another generic issue which has been raised in connection with this document is the use of Monte Carlo procedures to define exposure scenarios. These procedures require distributions for the input parameters used in the assessment. Such distributions have not been established by the Agency. Decisions on the use and definition of such distributions affect assessments of all chemicals and cut across all Agency programs. Thus, it is not appropriate to establish such polices in this document. However, individuals outside of the Agency have published assessments which applied Monte Carlo procedures to problems involving dioxin-like compounds. In recognition of the high interest in this area, a general description of this technique and summaries of assessments which applied it to dioxin-like compounds are included in Chapter 7 of this Volume.

The Agency does have efforts underway to evaluate these generic issues. For example, the Office of Health and Environmental Assessment (OHEA) is in the process of

revising the Exposure Factors Handbook and plans to hold public review meetings in 1993. In addition, OHEA is developing a guidance document on generating exposure scenarios which will be issued for review in 1993. Several offices have projects specific to Monte Carlo:

- Office of Health and Environmental Assessment - A Workshop on approaches to evaluating uncertainty (including the use of Monte Carlo) was held in 1992.
- Office of Policy, Planning and Evaluation - A workshop on using Monte Carlo methods is scheduled for 1993.
- Office of Pollution Prevention and Toxics - A handbook on the use of Monte Carlo is being developed and is scheduled for publication in 1993.

Readers interested in generic Monte Carlo procedures are best served in these forums.

2.2. EXPOSURE EQUATION

This document describes procedures for conducting exposure assessments to estimate either potential or internal dose. A potential dose is defined as a daily amount of contaminant inhaled, ingested, or otherwise coming in contact with outer surfaces of the body, averaged over an individual's body weight and lifetime. An internal dose is defined as the amount of the potential dose which is absorbed into the body (EPA, 1991). Section 2.3 below discusses the relevancy of this distinction for dioxin-like compounds.

The general equation used to estimate potential dose normalized over bodyweight and lifetime is as follows:

$$\text{Lifetime Average Daily Dose (LADD)} = \frac{\text{(exposure media concentration x contact rate x contact fraction x exposure duration)}}{\text{(body weight x lifetime)}} \quad (2\text{-}1)$$

This procedure is used to estimate dose in the form needed to assess cancer risks. Each of the terms in this exposure equation is discussed briefly below:

- **Exposure media concentrations:** These include the concentrations in soil for dermal contact and soil ingestion exposure pathways, in vapor and particulate phase in air for inhalation exposure pathways, in water for a

water ingestion pathway, and in food products such as fish, fruits and vegetables, and beef and milk, for food ingestion pathways. The concentrations used should represent a temporal average over the time of exposure. Chapter 4 provides procedures for estimating exposure media concentrations.

- **Contact rate:** These include the ingestion rates, inhalation rates, and soil contact rates for the exposure pathways. These quantities are generally the total amount of food ingested, air inhaled, etc. Only a portion of this material may be contaminated. The next term, the contact fraction, which is 1.0 or less, reduces the total contact rate to the rate specific to the contaminated media.
- **Contact fraction:** As noted, this term describes the distribution of total contact between contaminated and uncontaminated media. For example, a contact fraction of 0.8 for inhalation means that 80% of the air inhaled over the exposure period contains dioxin-like compounds in vapor form or sorbed to air-borne particulates. The contact fractions for the exposure pathways of air inhalation and water ingestion are related to the time individuals spend at home. Other pathways such as fish ingestion or ingestion of home grown foods are not related to time at home. Similarly, contact fractions for individuals exposed at work places relate largely to time spent at the work place. EPA (1989a) discusses several time use studies which can be used to make assumptions about time spent at home (and outdoors at the home environment) versus time spent away from home. Generally, these time use studies asked participants to keep 24 hour diaries of all activities. Studies summarized were national in scope, involved large numbers of individuals, cross-sections of populations in terms of age and other factors, and up to 87 categories of activities. Results from different studies consistently indicate that the average adult spends between 68 to 73% of time at the home environment.
- **Exposure duration:** This is the overall time period of exposure. Values of 9 years and 20 years are used in the example scenarios described in Chapter 5. The value of 9 years corresponds to the average time spent at one

residence (EPA, 1989a), and was used as an exposure duration for a non-farming family living in a rural setting. Twenty years was used as the exposure duration for farming families in a rural setting. Another exposure duration demonstrated in Chapter 5 is one associated with a childhood pattern of soil ingestion. The exposure duration in this case is 5 years.

- **Body weight:** For all the pathways, the human adult body weight of 70 kg is assumed. This value represents the United States population average. The body weight for child soil ingestion is 17 kg (EPA, 1989a).
- **Lifetime:** Following traditional assumptions, the average adult lifetime assumed throughout this document is 70 years. Even though actuarial data indicate that the United States average lifetime now exceeds 70 years, this convention is used to be consistent with other Agency assessments of exposure and risk.

2.3. RISK EQUATION

Although estimation of risk is technically beyond the scope of an exposure assessment, the exposure assessor needs some background understanding in this area. The primary source of information on the health risks of the dioxin-related compounds is the Health Reassessment that EPA is publishing concurrently with this document (EPA, 1993). However some general considerations for using exposure estimates in support of cancer risk assessments are summarized here. The usual procedure used to calculate an upper-limit incremental cancer risk is as follows:

$$R = 1 - e^{-q_1^* d} \approx q_1^* d \qquad (2\text{-}2)$$

when $q_1^* d < 10^{-3}$ and where q_1^* is the 95% upper confidence limit of the linearized cancer slope factor of the dose-response function (expressed in inverse units of the dose quantity, typically kg-day/mg) and d is the dose (typically in mg/kg-day). The dose is generally equal to the potential dose given above in Equation (2-1). The slope factor, q_1^*, for 2,3,7,8-TCDD has been previously estimated by EPA as 0.156 kg-d/ng. The derivation

of this factor is described in EPA (1984a) and further background is provided in EPA (1981). The Agency is currently reevaluating this slope factor and the reader should consult the companion Health Reassessment (EPA, 1994) for the current policy.

EPA derived the 1984 slope factor for 2,3,7,8-TCDD from animal feeding studies on the basis of potential (i.e., administered) dose. Thus, for purposes of consistency, when using this slope factor to estimate risk to humans, the exposure assessor should provide the dose estimate as a potential dose. This point raises issues specific to the various pathways.

The absorption which occurred during the animal experiments EPA used to derive the 1984 slope factor for 2,3,7,8-TCDD was estimated to be 55% (Farland, 1987). The review of literature on bioavailability in Appendix C of Volume 2 of this assessment indicates that the gut absorption of 2,3,7,8-TCDD in humans when the vehicle is soil is 20-40% of potential dose. Fries and Marrow (1975) found that 50-60% of the 2,3,7,8-TCDD was absorbed by rats from feed. Rose, et al. (1976) estimated that 86% of 2,3,7,8-TCDD in a mixture of acetone and corn oil fed by gavage to rats was absorbed. EPA (1984), using animal data and information on fate of particles in the respiratory system, estimated that the fraction of 2,3,7,8-TCDD absorbed into the body ranges from 0.25 to 0.29. What this discussion indicates is that the absorption for human ingestion and inhalation pathways might range from 20-80% of potential dose, which compares to 55% found in the laboratory experiments. If no adjustment were made to potential dose estimates, then human risk estimates might be overestimated (when absorption is in the 20% range) or underestimated (in the 80% range). This discrepancy is not felt to be large enough or certain enough to warrant an absorption correction factor.

The rate of absorption of vapor-phase 2,3,7,8-TCDD into the lungs has not been studied, but it seems reasonable to assume that the absorption in the vapor phase should exceed that of absorption from bound 2,3,7,8-TCDD on particulates, probably above 50%. There is also an unknown uncertainty introduced when assuming that the q_1^* developed from a feeding study can be used for an inhalation pathway. Thus, it is unclear what adjustment is needed to account for differences between the feeding study and a vapor-phase inhalation exposure. Accordingly, it is recommended that assessors not attempt any such adjustments at this point, but fully acknowledge the uncertainty.

Estimating risks associated with dermal exposure introduces several issues to

consider. First, use of an oral dose-response function may not be applicable to the dermal route. Second, dermal absorption of dioxin-like compounds from soil appears to be much lower than that which occurred in the dose-response feeding studies. EPA (1992a) indicates that 0.1 - 3% of 2,3,7,8-TCDD may be dermally absorbed from soil, which is significantly less than the 55% absorption found in the laboratory feeding experiments. It is assumed for this assessment that an absorption fraction of 0.03 (3%) applies to 2,3,7,8-TCDD as well as the other dioxin-like compounds. Specifically, this assessment estimates the total amount of compounds applied to skin and then reduces it by 97% to estimate the absorbed dose. This is the only pathway in which an absorption fraction is used to adjust a dose. Because of this adjustment, an additional adjustment to the risk equation, Equation (2-2) above, is needed when estimating risk from dermal exposure in a manner consistent with other exposure pathways: the slope factor should be multiplied by (100%) / (55%), or about 2, to convert it to an absorbed basis. Finally, the assessor should acknowledge that considerable uncertainty is introduced by applying an oral based dose-response function to dermal exposure.

Another set of issues facing the exposure/risk assessor is how to estimate exposure to mixtures of dioxin-like compounds with differing slope factors. EPA (1989b) has proposed a procedure to address this issue, which is to adjust the risk estimate using a "toxicity equivalency factor", commonly referred to as TEF. The TEF for a congener of interest is the cancer potency of that congener divided by the cancer potency of 2,3,7,8-TCDD. As shown in Table 1-1 in Chapter 1, the TEF for 2,3,7,8-TCDD is 1 and all other dioxin-like compounds have TEFs less than 1. The combined risk resulting from exposure to a mixture of dioxin-like compounds can be computed using the TEFs and assuming that the risks are additive:

$$Risk = 1 - e^{-q_1^* \sum (TEF_i \, d_i)} \qquad (2\text{-}3)$$

where q_1^* is the cancer slope factor for 2,3,7,8-TCDD (kg-day/mg), TEF_i is the toxicity equivalency factor for dioxin-like compound i, d_i is the potential dose for dioxin-like compound i (mg/kg-day), and n is the total number of dioxin-like compounds to which an individual is exposed.

2.4. PROCEDURE FOR ESTIMATING EXPOSURE

Section 2.2 described the exposure equation as it applies to dioxin and dioxin-like compounds. Before making exposure estimates, the assessor needs to gain a more complete understanding of the exposure setting and be prepared to estimate exposure media concentrations. The purpose of this section is to provide guidance for the procedures followed in this assessment to define such settings and estimate exposure media concentrations. The approach used here is termed the exposure scenario approach. Brief descriptions of the steps and associated document chapters are presented below and summarized in Figure 2-1.

Step 1. Identify Source

Three principal sources are addressed in this document. The first, identified as "soil", is called a source in that the starting point of the assessment is soil contamination. Of course, the ultimate source for soil contamination is some unidentified cause for the soil to become contaminated. For exposure and risk assessment purposes, the cause for contamination is not relevant except to assume that the cause is not ongoing and that the impact of the "initial" levels is what is being evaluated. The soil source is further characterized as off-site or on-site. Off-site implies that the soil contamination is located some distance from the site of exposure. The site of exposure could be a residence or farm, and the site of contamination could be a landfill, for example. On-site implies that the soil contamination is on the site of exposure. The second principal source is called "stack emissions." Unlike the soil source, the contamination is assumed to be on-going. Stack emissions in particulate form are assumed to deposit onto the soils and vegetations of the site of exposure, and emissions in vapor form result in air-borne concentrations which transfer into vegetations at sites of exposure. It is noted that individuals working at the site where stack emissions occur are also exposed. The procedures in this document only apply to residents who are not associated with the site where stack emissions occur. The third principal source is called "effluent discharges". Such discharges represent point source inputs to surface water bodies. Like the stack emission source, impacts to surface water bodies are assumed to be ongoing during the period of exposure. Unlike either of the above two sources, only the impacts to water and fish are considered for this source category.

STEPS		DOCUMENT CHAPTERS
Step 1.	Identify Sources	
	A. Soil, on and off-site	Chapter 4, Volume II
	B. Stack emissions	Chapter 3, Volume III Chapter 3, Volume II
	C. Effluent Discharges	Chapter 3, Volume II
Step 2.	Estimate Release Rates	
	A. Volatilization, erosion, etc.	Chapter 4, Volume III
	B. Stack emissions	Chapter 3, Volume III Chapter 3, Volume II
	C. Effluent discharges	Chapter 4, Volume III Chapter 3, Volume II
Step 3.	Estimate Exposure Point Concentrations	
	A. Transport, bioaccumulation, etc.	Chapter 4, Volume III
	B. Atmospheric dispersion, deposition, etc.	Chapter 3, Volume III
Step 4.	Characterize Exposed Individuals and Exposure Patterns	
	A. Contact rates, exposure durations	This Chapter
Step 5.	Put It Together in Terms of Exposure Scenarios	
	A. Scenario concept expanded	This Chapter
	B. Demonstration with scenarios	Chapter 5, Volume III
Step 6.	Estimate Exposure and Risk	
	A. Equations and background	This Chapter
	B. Results for example scenarios	Chapter 5, Volume III
Step 7.	Assess Uncertainty	
	A. Parameter uncertainty/variability, validity of media concentrations, other models	Chapter 7, Volume III
	B. Sensitivity analysis, parameter discussions	Chapter 6, Volume III

Figure 2-1. Roadmap for assessing exposure and risk to dioxin and dioxin-like compounds.

Step 2. Estimate Release Rates

Estimating the release of contaminants from the initial source is the first step towards estimating the concentration in the exposure media. Releases from soil contamination include volatilization, and wind and soil erosion. Chapter 4 on estimating exposure media concentrations describes fate and transport modeling procedures for estimating soil releases. Stack emissions and effluent discharges are point source releases into the environment. Background on stack emissions including details on modeling from the stack to a site of exposure are provided in Chapter 3.

Step 3. Estimate Exposure Point Concentrations

Contaminants released from soils, emitted from stacks, or discharged into surface waters move through the environment to points where human exposure may occur. Contaminated soil that is near but not at the site of exposure is assumed to slowly erode and contaminate the exposure site soil, but to a level lower than the level at the contaminated site. The only time when the source concentrations equal the exposure concentrations is for the soil pathways, soil ingestion and dermal contact, when the soil contamination is on-site. Chapter 3 describes the use of the COMPDEP Model used to estimate dispersion of stack plumes to arrive at air-borne concentrations at the site of exposure as well as deposition rates of stack emitted particulates. Chapter 4 describes how soil and vegetation concentrations are estimated given particulate deposition rates, and also how release rates from soil initially contaminated translate to exposure point concentrations. Chapter 4 also describes a simple dilution model which translates effluent discharges into surface water and fish tissue concentrations.

Step 4. Characterize Exposed Individuals and Exposure Patterns

The patterns of exposure are described in Sections 2.5 and 2.6 of this Chapter. Exposed individuals in the scenarios of this assessment are individuals who are exposed in their home environments. They are adult residents who also recreationally fish, have a home garden, farm, and are children ages 2-6 for the soil ingestion pathway. Each of these pathways are evaluated separately. Since it is unlikely that single individuals would experience all of these pathways, the exposures across pathways are not added. Exposure pathways evaluated, which have generally been alluded to in discussions above,

include inhalation, ingestion, and soil dermal contact. Each pathway has the set of parameters including contact rates, contact fractions, body weights, and lifetime. These parameters were defined earlier in Section 2.2.

Step 5. Put It Together in Terms of Exposure Scenarios

A common framework for assessing exposure is with the use of "settings" and "scenarios." Settings are the physical aspects of an exposure area and the scenario characterizes the behavior of the population in the setting and determines the severity of the exposure. A wide range of exposures are possible depending on behavior pattern assumptions. An exposure scenario framework offers the opportunity to vary any number of assumptions and parameters to demonstrate the impact of changes to exposure and risk estimates. Exposure estimates for six example scenarios are demonstrated in Chapter 5.

Step 6. Estimate Exposure and Risk

Section 2.2 described the basic equation that estimates exposure for every assumed pathway in an exposure scenario. Chapter 5 demonstrates the methodology on six example scenarios, which includes the generation of exposure estimates for ten different exposure pathways and three different dioxin-like compounds.

Step 7. Assess Uncertainty

Chapter 7 provides a discussion on the validity of exposure media concentration estimation, and possible sources of uncertainty associated with this methodology. These uncertainties should be considered when applying this procedures to a particular site. Chapter 6 on User Considerations includes discussions on other pertinent topics such as sensitivity of model results to parameter selection, and judgements on use of the parameters selected for the demonstration scenarios for other applications.

2.5. STRATEGY FOR DEVISING EXPOSURE SCENARIOS

EPA (1992b) states, "In exposure scenario evaluation, the assessor attempts to determine the concentrations of chemicals in a medium or location and link this information with the time that individuals or populations contact the chemical. The set of assumptions about how this contact takes place is an exposure scenario." These assumptions can be

made many different ways producing a wide variety of scenarios and associated exposure levels. The number of people exposed at different levels form a distribution of exposures. Ideally assessors would develop this entire distribution to fully describe the exposed population. Such distributions could be defined using Monte Carlo techniques if sufficient input data are available. However, as discussed in Section 2.1 above, generic issues surrounding use of Monte Carlo are not evaluated here. Discussions of how other assessors have applied Monte Carlo to problems involving dioxin-like compounds are presented in Chapter 7. Since the necessary information for developing a population distribution is rarely available, EPA (1992b) recommends developing a central and high end scenario to provide some idea of the possible range of exposure levels. This section will illustrate this procedure as applied to the dioxin-like compounds. In addition, this section identifies the exposure pathways which are relevant to these compounds, and provides background and justification for the exposure parameters which were selected for the demonstrations in Chapter 5.

For any physical setting, a wide variety of exposure scenarios are possible. The range of exposure levels results from a number of different factors including individual behavior patterns, proximity of individuals to the source of contamination, the fate characteristics of the contaminant, and others. In order to illustrate the possible range, the assessor should try to characterize a central and high end scenario. The general strategy recommended here for defining these scenarios is to first identify and quantify the source of contamination. Next, the assessor should determine the geographic area that is impacted by this source. The contaminant levels are likely to vary widely over this area. Select locations of interest within this area such as the location of the nearest exposed individual or most heavily populated area. For each of these locations, identify behavior patterns which characterize central and high end exposure patterns. Central scenarios correspond to average or median levels and high end scenarios are defined as levels above the 90th percentile but within the actual range of exposure levels (EPA, 1992b).

Statistical data are rarely available to precisely define such scenarios. Instead judgement is usually required to identify behavior patterns meeting these criteria. For example, most rural areas probably include both farming and nonfarming residents. Farmers who grow or raise much of their own food could be selected to represent the high end scenario and those living in typical residential areas could represent the central

scenario. Alternatively, if more detail is desired, central and high end scenarios could be defined for both segments of the population, i.e., farmers and residents. For each scenario, determine relevant exposure pathways and assign values for exposure parameters such as contact rate, exposure duration, and so on, which represent a central and/or high end pattern for the type of receptor. Finally, compute the associated exposure level. The resulting range of exposure levels for each location can be used to illustrate the possible range of exposures.

Reference has been made in this chapter to the example scenarios found in Chapter 5, Demonstration of Methodology. Four "source categories", categories of contamination sources described in Chapter 4, are demonstrated in Chapter 5. The on-site soil and stack emission sources are assumed to expose a relatively large population in a rural area containing residences and farms. For these sources, both central and high end scenarios are defined in the manner outlined above. Specifically, a central scenario is based on typical behavior at a residence and the high end is based on a farm family that raises a portion of its own food. For the other two sources, off-site soil and effluent discharges, only one scenario each will be defined and demonstrated. The off-site soil source category will be demonstrated with a high end scenario - a farm is located near the site of contamination. Soil on the farm becomes impacted through the process of soil erosion. Other individuals within a community can also be impacted by a site of high soil contamination. Such individuals would include those visiting or trespassing on the site, volatilized residues can reach their residences, they may obtain water and fish from a nearby impacted water body, and so on. As such, alternate scenarios demonstrating the impact of a site of soil contamination could be developed. For the sake of brevity, and also considering that those residing nearest the contaminated are most impacted, only a high end scenario is developed for the off-site soil source category. The effluent discharge source category is unique in that only the pathways of water ingestion and fish ingestion are considered. For this category, fish and water ingestion patterns will be those adopted for the central scenarios. Again, other patterns of fish and water ingestion could be evaluated for this source category. As a matter of brevity again, only central patterns of behavior with regard to fish and water ingestion are demonstrated.

The methodologies used to estimate exposure media concentrations are described in Chapter 4 as screening level in their technical sophistication, but site specific in their

application. Defining populations that are typical of central and/or high end exposures is clearly a site specific exercises. Assessors need to make the kinds of assumptions discussed here for their own source and populations of concern. Many acceptable ways could be used to define central and high end scenarios. The approach used here was done for demonstration purposes only. On the other hand, the example scenarios in Chapter 5 were carefully crafted to be plausible and meaningful, considering key factors such as source strength, fate and transport parameterization, exposure parameters, and selection of exposure pathways. For example, a beef and milk exposure pathway is demonstrated only for the high end scenarios. Farmers raise cattle for beef and dairy products and are assumed to obtain a portion of their intake of these products from their own farm, whereas non-farming residents are assumed not to be exposed to contaminated farm products.

Key source strength terms were carefully developed and defined. Key source strength terms include soil concentrations, effluent discharge rates, and stack emission rates. For the demonstration of methodologies of this assessment, concentrations of dioxin-like compounds in contaminated soils for the off-site soil source category were set at 1 ppb, which was a typical concentration of 2,3,7,8-TCDD found in Superfund-like sites studied in the National Dioxin Study (EPA, 1987). Concentrations in soil used for the on-site source category were characterized as typical of background levels and assigned a value of 1 ppt, three orders of magnitude lower than the 1 ppb for off-site soil contamination. Researchers investigating concentrations of 2,3,7,8-TCDD in "background" or "rural" settings have typically found it in the ppt range or not detected it (with a detection limit generally less than 1 ppt). Introductory sections of Chapter 5 provide a more complete description of the example scenarios.

2.6. EXPOSURE PATHWAYS AND PARAMETERS

The dioxin-like compounds have been found primarily in air, soil, sediment and biota and to a lesser extent in water. Thus, the most likely exposure pathways are:

- Ingestion of soil, water, beef, dairy products, fish, fruit, and vegetables
- Dermal contact with soil
- Inhalation of particulates and vapors.

The following sections describe the selection of central and high end exposure parameters

for these pathways. Table 2-1 summarizes all the exposure parameters selected to represent the central and high end demonstration scenarios of Chapter 5.

2.6.1. Soil Ingestion

Soil ingestion occurs commonly among children during activities such as mouthing of toys and other objects, nonsanitary eating habits, and inadvertent hand-to-mouth transfers. In addition to normal soil ingestion activities, some individuals exhibit behavior known as pica which involves intentional soil ingestion. Soil ingestion rates associated with pica are probably much higher. No measured values for pica patterns have been reported in the literature, though EPA (1989a) reports that other assessments have assumed values such as 5 and 10 g/day. This document considers only normal soil ingestion among children.

To a lesser extent, soil ingestion also occurs among adults from activities such as hand-to-mouth transfer when eating sandwiches or smoking. However, the data to estimate the adult rate of soil ingestion is essentially unavailable, so adult soil ingestion is not demonstrated in this assessment. Paustenbach (1987) and Sheenan et al. (1991) have suggested calculating exposures for this pathway (as well as dermal contact and inhalation) separately over three to four age periods to reflect major changes in body weight, surface area and inhalation rates. In general, exposure assessments can be refined by estimating exposures separately over each year of age that is of interest and summing to get the total. Age specific data for body weight, surface area and inhalation rate are presented in EPA (1989a and 1992b). These procedures are not presented here, but readers interested in refining exposure estimates are encouraged to check the above references for further guidance.

Based on the review of literature, particularly the studies of Binder et al. (1986) and Clausing et al. (1986), the following values for soil ingestion were suggested in EPA (1989a): average soil ingestion in the population of young normal children (under the age of 7) is estimated at approximately 0.1 to 0.2 g/d. An upper-range ingestion estimate among children with a higher tendency to ingest soil materials, although not a pica pattern, could be as high as 1 g/d. However, a value of 0.8 g/day is recommended for high end exposure estimates. The values of 0.2 g/d and 0.8 g/d were the values adopted for the central and high end exposure scenarios in Chapter 5.

Table 2-1. Summary of exposure pathway parameters selected for the demonstration scenarios of Chapter 5.

Pathway description	Contact rates	Contact fractions	Comments
Soil Ingestion			
Central	200 mg/d	1.0	Only pathway specific to an age-range; 2- to 6-year-old children
High End	800 mg/d	1.0	
Soil Dermal Contact			
Central	0.2 mg/cm^2-event 5000 cm^2 40 events/yr	1.0	Unlike other pathways, daily contact is not assumed; approach instead estimates contact in terms of contact/ event * events/yr; both soil pathways distinguish typical and high end contact by contact rate rather than contact fraction; high end based on behavior of farmers; typical pattern based on non-farming adults; a "dermal absorption fraction" reduces the amount contacting the body to an amount absorbed by the body.
High End	1.0 mg/cm^2-event 1000 cm^2 350 events/yr	1.0	
Dermal absorption fraction: 0.03			
Vapor/Dust Inhalation			
Central	20 m^3/day	0.75	Indoor/outdoor air quality assumed equal; contact fraction can be used to reflect a different assumption; central contact fraction is an average time-at-home based on time use surveys
High End	20 m^3/day	0.90	
Water Ingestion			
Central	1.4 L/day	0.75	2.0 L/day evaluated as 90th percentile value in EPA (1989a), who instead recommend 1.4 L/day as an average consumption rate; like inhalation pathways, 0.75 contact fraction is an average time-at-home estimate
High End	2.0 L/day	0.90	

(continued on the following page)

Table 2-1. (continued)

Pathway description	Contact rates	Contact fractions	Comments
Beef Fat Ingestion			
Central	NA	NA	Central scenario includes adults who do not home produce their beef supply; 22 g/day beef fat assumes 100 g/day average beef consumption and 22% fat
High End	22 g/day	0.44	
Milk Fat Ingestion			
Central	NA	NA	Like beef ingestion, central scenarios do not include home milk production; 10.5 g/day milk fat assumes 300 g/day whole milk and 3.5% fat
High End	10.5 g/day	0.40	
Fish Ingestion			
Central	1.2 g/day	1.00	Unlike other exposure pathways, contact rate is rate of contaminated fish - hence contact fraction is 1.00; 1.2 g/day based on 3 recreationally caught fish meals/yr; 4.1 g/day based on 10 recreationally caught fish meals/yr
High End	4.1 g/day	1.00	
Fruit Ingestion			
Central		0.20	200 g/day is average total fruit consumption rate; 44% assumed above ground and unprotected - no below ground unprotected fruit; contact fraction of 0.20 based on a range of rates of 0.09 to 0.33 for wide variety of fruits (EPA, 1989a)
Above ground unprotected	88 g/day		
Below ground unprotected	0 g/day		
High End		0.30	
Above ground unprotected	88 g/day		
Below ground unprotected	0 g/day		

(continued on the following page)

Table 2-1. (continued)

Pathway description	Contact rates	Contact fractions	Comments
Vegetable Ingestion			
Typical		0.25	140 g/day is average total vegetable consumption rate; 54% assumed above ground and unprotected, 20% assumed below ground and unprotected; central contact fraction of 0.25 based on a range of rates of 0.04 to 0.75 rates for wide variety of vegetables (EPA, 1989a)
Above ground unprotected	76 g/day		
Below ground unprotected	28 g/day		
High End		0.40	
Above ground unprotected	76 g/day		
Below ground unprotected	28 g/day		

Exposure Duration: A duration of 9 years was assumed for the "residence" setting based on mobility data showing the average time in one residence was 9 years (EPA, 1989a). A duration of 20 years was evaluated as the 90th percentile of time in one residence, and was selected for the "farm" settings, which assumes that farming families live in a given residence longer than a non-farming family. These values apply to all pathways with no variation, except for soil ingestion, which was demonstrated only for children and was at 5 years.

Body Weight/Lifetime: The standard assumptions of a 70 kg adult and 70 years lifetime were assumed for all pathways, except that of soil ingestion. In that case, a body weight of 17 kg was used.

A number of investigators have suggested that lower values are more appropriate for soil ingestion rates. These suggestions are being evaluated by the Office of Health and Environmental Assessment in connection with the revisions to the *Exposure Factors Handbook* (EPA, 1989a). To date, a final position has not yet been reached. As discussed in Section 2.1, it was decided to not independently evaluate such generic issues in this document. Thus, the soil ingestion rates adopted here reflect those previously accepted by the Agency, but should be updated if and when the Agency adopts new values. Note that the general need to update values for exposure factors as new information becomes available applies to all factors. It has been emphasized in this discussion on soil ingestion just because it appears that changes are most imminent here.

For the soil ingestion pathway, contact fraction refers to the portion of ingestion soil

which is contaminated. For the residential setting, the assumption is made here that all soil ingestion by children occurs in and around the home, and that all the soil at the home is contaminated. Thus, a value of 1 has been adopted in the example scenarios presented in Chapter 5. If the soil contact occurs primarily outdoors, climatic factors such as snow cover, frozen soil, rain, etc. can substantially limit contact and ingestion of soil. In situations where the contaminated area is located remote from where children live, and children have some access to these areas (if the areas are parks or playgrounds, e.g.), lower fractions would be appropriate.

2.6.2. Soil Dermal Contact

The total annual dermal contact, expressed in mg/yr, is the product of three terms: the contact rate per soil contact event, the surface area of contact, and the number of dermal contact events per year. EPA (1992a) recommends the following ranges for these terms:

- Contact rate: 0.2 to 1.0 mg/cm^2-event
- Adult surface area: 5000 to 5800 cm^2
- Event frequency: 40 to 350 events/year.

An event frequency and contact rate near the upper end of these ranges may be appropriate for an high end exposure activity pattern such as farming, where the individual more often comes in contact with soil and may be exposed to fugitive dust emissions while they work. An event frequency of 40 and 350, and a contact rate of 0.2 and 1.0 mg/cm^2-event, are assumed for the central and high end exposure scenarios in Chapter 5. However, the exposed surface area of 5000 cm^2 may be reduced for farmers. This area corresponds to 25% of the total body area and apparel such as short sleeves, shoes, socks and short pants. Farmers working in the field are likely to wear long pants at least, if not also long sleeves. Although EPA (1992a) indicates that clothing is not always effective in preventing dermal contact, it seems reasonable that a value of 1000 cm^2 (5% of total body area) representing hands, neck, and face might be more appropriate in a farming scenario. Values of 5000 and 1000 cm^2 were selected for the central and high end scenarios in Chapter 5.

The considerations for contact fraction are similar to those for soil ingestion; i.e., that all contact occurs with contaminated soil at the residence or farm site. Accordingly a

value of 1 was selected for the example scenarios presented in Chapter 5.

One further adjustment was made for this exposure pathway. The contact as estimated above is the amount of soil which contacts the body. EPA (1992a) indicates that only a small percent of strongly hydrophobic organic compounds such as 2,3,7,8-TCDD are absorbed into the body from soil dermal contact. The "dermal absorption fraction" recommended for 2,3,7,8-TCDD in EPA (1992a) was 0.001 (0.1%) to 0.03 (3%). EPA (1992a) recommends using the upper end of this range for application to other dioxin-like compounds as a conservative assumption until these compounds have been tested. An absorption fraction of 0.03 was used for the three compounds demonstrated in Chapter 5. The dermal contact exposure pathway was the only one in which such an absorption fraction was used.

2.6.3. Vapor and Dust Inhalation

EPA (1989a) describes derivation of the commonly used ventilation rates of 20 and 23 m^3/day. As noted in that reference, these values assume 16 hours of light activity and 8 hours of resting. Other recommendations in that reference are a rate of 30 m^3/day for high end exposures, and to derive specific ventilation rates (EPA (1989a) gives information to do so) for specific activity patterns. The example scenarios of this assessment all use 20 m^3/day.

An additional assumption needs to be made for the vapor and dust inhalation pathways. This pertains to an assumption concerning the differences in air quality between indoor and outdoor conditions. Algorithms for both particulate and vapor-phase air-borne concentrations of contaminants are specific to outdoor air. Hawley (1985) assumed, based on several other studies in which measurements were made, that the concentration of suspended particulate matter in indoor air is equal to 75% of that outside. Also, his report stated that most household dust is outdoor dust that is transported into the house, and that only a small percentage is developed from sources within. He then concluded that 80% of the indoor dust is identical in contaminant content to outdoor soil. Refinements to the concentration of contaminants on indoor versus outdoor dust should have a minor effect on exposure estimates. A similar trend is assumed for air-borne vapor phase concentrations. For this reason, differences between indoor and outdoor concentrations are not specifically considered, or equivalently, no distinctions are made for

outdoor and indoor air quality.

The contact fraction for this pathway is equal to the fraction of total inhaled air which is contaminated. Thus it relates largely to percent of time spent in the contaminated area. For the example exposure scenarios presented in Chapter 5, the contact fraction corresponds to percent time at home. EPA (1989a) suggests a range of 0.75 to 1.0; the lower value will be adopted as the central value used in the residence setting. The value selected for high end scenarios will be 0.90 instead of 1.00, recognizing that 1.00 is more likely a bounding rather than a high end estimate.

2.6.4. Water Ingestion

The water ingestion rate of 2 L/day is traditionally assumed for exposure through drinking water. However, EPA (1989a), after review of several literature sources, concludes that 2.0 L/day may be more appropriately described as a 90% value, or a value for high end exposure estimates. For this reason, a water ingestion rate of 2 L/day is assumed only for the high end exposure estimates. Since the high end scenario includes a farm and the farming family, it is also argued that farm labor requirements justify the higher rate of water ingestion. EPA (19899a) recommends a rate of 1.4 L/day as representative of average adult drinking water consumption. This is the rate used for central scenarios in Chapter 5. The difference in central and high end tendencies is also modeled using the contact fraction. Again, this fraction is based on the time spent at home. The value of 0.75 is used to model the central estimate, for the residence setting, and the value of 0.90 is used to model the high end estimate, for the farm setting.

2.6.5. Beef and Dairy Product Ingestion

If contaminated beef or dairy products from one source are marketed along with uncontaminated products from many sources, only a small percent of the product consumed by an individual may be contaminated. The potential effects of such "market dilution" of beef and dairy products on human exposure are discussed briefly in EPA (1984a), at more length by Fries (1986), and at much greater length in EPA (1985) for the particular case of cattle production in Missouri. Aspects of the beef industry in this region specifically noted in EPA (1985) as important to estimating exposure were type of activity within the industry (e.g. cow-calf production, "backgrounding" - preparing calves for

feedlots, feeding for slaughter), replacement rates as a function of activity, fractions of cattle fed to maturity outside contaminated areas before slaughter, and slaughter categories and rates relative to national figures. EPA (1984a and 1985) concluded that dilution will vary widely between different marketing areas. EPA (1984a and 1985) and Fries (1986) noted that the subpopulations most likely to receive high exposures are beef producers, dairy farmers, and their direct consumers. The residents in the central exposure scenario in Chapter 5 are not assumed to be producers or direct consumers of farm products, and for this reason, the central estimate scenarios do not include a beef and milk pathway. The high end farming scenarios do have these pathways, meaning that the farmers home slaughter for beef and also obtain a portion of their milk from their lactating cattle.

Average consumption rates and fat content data for beef and dairy products are described in EPA (1989a). Summary information presented in that reference comes principally from a U.S. Department of Agriculture Nationwide Food Consumption Survey (NFCS) conducted in 1977-1978 (described in EPA, 1984b), with additional information added by Fries (1986). The NFCS covered intake of 3,735 possible food items by 30,770 individuals characterized by age, sex, geographic location, and season of the year. The average beef fat consumption rates listed in EPA (1989a) ranges from 14.9 to 26.0 g per 70-kg person/day, with a single high consumption estimate of 30.6 g per 70-kg person/day. Based on this information, EPA (1989a) recommends using a beef fat consumption rate of 22 g/day (based on an arithmetic mean from studies summarized in EPA (1989a) of 100 g/day whole beef and 22% fat content). This may underestimate the amounts eaten by households who home slaughter; i.e., the availability of beef by farming families raising beef for slaughter might lead to consumption habits for beef that exceed those of the general population. Milk fat consumption from all dairy products ranges from 18.8 to 43 g per 70-kg person/day. Considering fresh milk only, the milk fat consumption is reported as 8.9 to 10.7 g per 70-kg person/day in various studies summarized in EPA (1989a), with a single high consumption estimate of 35 g per 70-kg person/day. An arithmetic mean milk fat consumption rate of 10.5 g/day is derived in EPA (1989a) (this assumes 300 g/day whole milk and 3.5% fat). This may also underestimate the consumption rate of farming families who consume milk supplied by their own cattle. The rate of beef and milk fat consumption assumed for the high end farming scenarios in

Chapter 5 are 22 and 10.5 g/day, respectively.

Consumption rates of beef and milk are expressed in terms of fat ingested per day because dioxin-like compounds tend to partition strongly toward lipids. It is assumed that virtually all of such compounds will be found in the fat portion of milk or beef. Further, the algorithms to estimate concentrations in these food products estimated fat concentrations and not whole product concentrations.

EPA (1989a) also reports on another survey of 900 rural farm households (USDA, 1966), including some where the farm's beef and dairy cattle supply a portion of the household's beef and milk. In these situations, the average percent of homegrown beef and milk (dairy products) is 44% and 40%, respectively. Contact fractions of 0.44 and 0.40 were used in this assessment for the high end farming scenarios. Lacking better information, EPA (1989a) recommends a contact fraction for beef and dairy of 75% if the intent is to estimate high end estimates for a farmer who uses a portion of his farm's products.

2.6.6. Fish Ingestion

EPA (1989a) concludes that consumption rate data from two studies, that of Puffer (1981) and Pierce, et al. (1981) are most appropriate for estimating consumption rates for recreational fishing from large water bodies. The recommended 50th percentile consumption rate, or typical rate, for this subpopulation is 30 g/day, and the 90th percentile rate is 140 g/day. Table 2-2 contains ingestion rates for freshwater and estuarine fish and shellfish. These are based on an analysis of the results of the USDA 1977-78 National Food Consumption Survey. If using these data, the assessor should consider the following points:

1) The survey was conducted over a three day period. Thus, it does not represent long term behavior patterns which is the interest of exposure assessments used to support analysis of chronic health effects. This problem introduces uncertainty into the estimates of medians (50th percentile) and other percentiles. It can provide appropriate estimates of the average.

2) Because most of the persons surveyed did not eat fish or shellfish during the survey period, the 50th percentile values are zero. The mean values are more appropriate to use as central tendency estimates of fish and shellfish consumption over a lifetime.

Table 2-2. Fish consumption estimates from the USDA 1977-78 National Food Consumption Survey (consumptions were recorded for three day periods; N = 36249; units are grams/day/person; SF = Shellfish.).

Estimate	Fresh No SF	Fresh With SF	Estuarine No SF	Estuarine With SF	Marine No SF	Marine With SF	Total No SF	Total With SF
Mean	1.64	1.64	2.50	4.27	7.72	8.23	11.85	14.15
50th %	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
90th %	0.00	0.00	4.73	9.80	28.33	30.00	42.07	51.04
95th %	5.29	5.29	14.50	28.35	48.37	51.17	66.15	75.60
99th %	38.00	38.00	56.00	80.00	93.33	97.07	128.00	146.17

Source: USDA (1983).

However, these averages are on a per capita basis, ie. averaged across all survey participants (including fish eaters and nonfish eaters). The average fish consumed by fish eaters is probably a more relevant estimate of central exposures. This value would be higher than the per capita average.

3) These data represent total ingestion rates of store-bought fish. Obviously, what is of interest for a site specific survey is the amount of fish consumed from waters within the study area. Assuming local surveys are not available EPA (1989b) recommends approaching this problem by using judgement to estimate the number of fish meals (100 to 200 g) per year that a person may reasonably consume from the water body of concern. By comparing these judgement based values to the national survey data the assessor can make some evaluation of their reasonableness. If evidence exists that subsistence fishing occurs in the area of interest, then even higher levels than those given in Table 2-1 may be warranted. Wolfe and Walker (1987) found subsistence fish ingestion rates up to 300 g/d in a study conducted in Alaska.

For smaller water bodies, EPA (1989a) recommends that site-specific information be obtained via surveys of local fisherman to obtain the most appropriate fish consumption information for site-specific assessments. Alternately, EPA (1989a) recommends using judgement regarding how many fish meals per year an individual could obtain from the contaminated waters and assuming meal sizes of 100 to 200 g. Consumption of commercial fish (at restaurants or from markets) raises market dilution issues analogous to those described earlier for beef and milk. For this reason, exposed individuals in both the central and high end scenarios in Chapter 5 are assumed to obtain their contaminated fish intake from a nearby contaminated stream or pond; other fish they may consume is not considered in this assessment.

The examples used in this assessment assume that the contaminated waters are small lakes or streams which are occasionally fished on a recreational basis. Further it is assumed that an individual could eat 3 to 10 meals per year from the contaminated waters. Assuming an average meal size of 150 g, this translates to 450 to 1500 g/year or an average of 1.2 to 4.1 g/day. The central estimate for the example scenarios in Chapter 5 will therefore be 1.2 g/day, and the high end will be 4.1 g/day. Since these fish ingestion rates are rates of ingestion of contaminated fish, the contact fraction would be 1.

2.6.7. Fruits and Vegetables

EPA (1989a) estimated ingestion rates for individuals who have home gardens and hence grow a portion of their fruit and vegetable intake. Their approach was to review the literature and derive average intake rates for all individuals, whether or not they have a home garden, and considering a variety of different fruits and vegetables. A typical and high end exposed individual had the same total ingestion rates. Their exposure was distinguished by the contact fractions; high end exposed individuals grew a larger proportion of their intake in their home gardens.

The average amounts of fruit and vegetable consumption are 200 and 140 g/day, respectively. These total ingestion rates are further refined considering two factors pertinent to estimation of concentration of dioxin-like compounds: whether the vegetation is grown below (carrots, e.g.) or above ground (tomatoes), and whether the edible portion is protected (citrus) or unprotected (apples). Chapter 4 discusses distinct procedures for estimating vegetative concentrations for below and above ground vegetation. Also, both algorithms assume that inner portions of vegetation are largely unimpacted, whereas outer portions of both above and below ground vegetation are impacted (see Chapter 4 for further detail on these algorithms and assumptions). Therefore, for fruits or vegetables which are protected, it can be assumed that there will be no exposure since the outer portions are not eaten. Results from a food consumption survey, such as that from Pao, et al. (1982), can be used to determine percent of total fruit/vegetable intake which is below/above ground and which is protected/unprotected. Such an exercise was undertaken using data from Pao, et al. (1982) summarized in EPA (1989a) to arrive at the following percentages:

	I. Fruits		II. Vegetables	
	Above	Below	Above	Below
Protected	56%	0	25%	1%
Unprotected	44%	0	54%	20%

As seen, it was found that there are no fruit grown underground, and there was a fairly similar proportion of protected and unprotected fruit. Fruits considered protected for this exercise included oranges, grapefruits, and cantaloupe; unprotected fruits included apples, peaches, pears, and strawberries. It is noted that this is clearly not a complete inventory,

but only those fruits from the survey of Pao as summarized in EPA (1989a). Similarly, these percentages are not being recommended as general values for other site-specific assessments. For this assessment, it will be assumed that a total ingestion rate of unprotected above ground fruit is 88 g/day (0.44*200 g/day), and that there is no ingestion of unprotected under ground fruit. Vegetables above ground and unprotected include: cabbage, cucumbers (including cucumbers as pickles), lettuce, tomatoes, broccoli, spinach, string beans, and squash. Above ground protected vegetables include: corn, lima beans, and peas (several kinds). Below ground unprotected vegetables included potatoes and carrots; mature onions were considered below ground and protected. Assumed for this assessment are ingestion rates of unprotected above ground vegetables of 76 g/day (0.54*140 g/day) and unprotected below ground vegetables of 28 g/day (0.20*140 g/day).

These ingestion rates are defined as total ingestion rates of unprotected above/below ground fruits/vegetables. Only a portion of these are homegrown. Data summarized in EPA (1989a) shows that the fraction of vegetables consumed that are homegrown ranges from 0.04 to 0.75, depending on type. The overall average of the data is 0.25, which is recommended as a contact fraction for the average home gardener. The recommendation for the high end exposure was 0.40. These contact fractions were adopted as the central and high fractions for the example scenarios in Chapter 5. Similar data for fruits show a homegrown range of 0.09 to 0.33, with an average of 0.20, which is the central estimate used in Chapter 5. EPA (1989a) recommends a high end value of 0.30, which is the value used for the high end exposure scenarios.

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3. EVALUATING ATMOSPHERIC RELEASES OF DIOXIN-LIKE COMPOUNDS FROM COMBUSTION SOURCES

3.1. INTRODUCTION

Since the late 1970's, it has become well established that the combustion of certain fuels containing both organic material and chlorides can form polychlorinated dibenzo-p-dioxins (CDDs) and poylchlorinated dibenzofurans (CDFs). This discovery has prompted world-wide research to identify combustion sources, to characterize the conditions favoring the formation of CDDs and CDFs within the combustion process, and to characterize the emission of dioxin-like compounds to the air from the stack of the process.

The purpose of this chapter is to provide site-specific procedures for evaluating the emission of dioxin-like compounds from stationary combustion sources. The first step is to characterize stack emissions in terms of mass of TCDD/F congener released, and then to partition that release into a vapor and a particle phase. Using atmospheric transport modeling, these releases are translated to ambient air vapor and particle phase concentrations, and wet and dry particulate deposition amounts, in the vicinity of the release. This chapter demonstrates these procedures on a hypothetical incinerator using an air dispersion model called COMPDEP. A second purpose of this chapter, therefore, is to provide the background and justification for the model inputs and key parameters for COMPDEP. The final results for this model simulation are vapor and particle phase concentrations, and particulate deposition amounts of the specific dioxin-like congeners, which are then used for the demonstration of the stack emission source category in Chapter 5 of this Volume.

This chapter is structured as follows:

- Section 3.2 describes the generation of congener specific emission factors. These factors are defined as the mass of congener emitted per mass of feed material combusted. Subsections within Section 3.2 discuss: 1) a heirachy of preferred options for generating such emission factors, starting with site-specific stack testing for specific congeners and ending with engineering evaluations when no other data is available, 2) an approach to estimating congener-specific emission factors if homologue group emission

factors are all that is available, including a presentation of source category homologue group profiles generated with limited data, 3) the emission factors for the example incinerator demonstrated in Chapter 5, and assuming a feed rate into the example incinerator, emissions expressed on a mass per time basis (which is required for transport modeling), 4) partitioning of emissions into a vapor and a particle phase for atmospheric transport modeling, and 5) a procedure to estimate the mass released and concentrations for a related emission of a combustor, that of ash. It is noted that a similar discussion on emission factors is presented in Chapter 3 on Sources in Volume II of this assessment. However, the Volume II discussion derives national average emission factors for various combustor types as a basis for estimating total annual releases to the air in the United States from each combustion source category in comparative units of grams of Toxic Equivalent (TEQs) emissions per year.

- Section 3.3 describes a general air modelling procedure for evaluating the fate and transport of dioxin-like compounds emitted from stacks. The discussion presents a general review of dispersion theory, a general review of dry particle deposition, and a general review of the wet deposition algorithm employed in this analysis. EPA's COMPDEP air dispersion and deposition model is reviewed. Wherever pertinent, Section 3.3 describes the assumptions and parameter values that were used in the demonstration of methodologies in Chapter 5 of this Volume.

- Sections 3.2. and 3.3. summarized input data and assumptions (emission rates, vapor/particle partitioning assumptions, etc.) that were made for the demonstration of the methodologies for evaluating stack emissions in Chapter 5 of this Volume. Section 3.4 supplies all other key assumptions for the stack emission demonstration, such as stack height and exit temperatures, meteorological data, and others. This Section also provides the final results from the COMPDEP modeling, including vapor phase air concentrations at various distances in the predominant wind direction, and dry and wet deposition fluxes, also at various distances in the predominant wind direction.

- Section 3.5 closes out the chapter by summarizing critical aspects for making site specific evaluations of stack emission sources.

3.2. ESTIMATING THE EMISSIONS OF DIOXIN-LIKE COMPOUNDS FROM ANTHROPOGENIC COMBUSTION SOURCES

Estimating the emission factor is the first step in assessing a specific stack emission source of dioxin-like compound release. For this assessment, an "emission factor" is defined as the total mass (in vapor and particulate forms) of dioxin-like compound emitted per mass of feed material combusted.

This assessment recommends the generation of emission factors for individual dioxin-like congeners for a site-specific assessment. Chapter 3 on Sources in Volume II of this assessment also derives emission factors. However, the Volume II discussion derives national average emission factors for TEQ emissions for various combustor types as a basis for estimating total annual releases to the air in the United States in comparative units of grams TEQ per year.

In the past, EPA converted the concentrations of TCDD/F mixtures into an equivalent concentration of 2,3,7,8-TCDD (Cleverly, et al., 1989, 1991; EPA, 1987a; Mukerjee and Cleverly, 1987) when deriving an emission factor. The fate, transport, and transfer parameters of 2,3,7,8-TCDD were applied to model the environmental fate of this TEQ mixture. This perspective has been changed in the following procedure. In order to increase the level of accuracy, the air dispersion modeling was done separately for each of the toxic congeners. Only at the interface to human exposure, e.g., ingestion, inhalation, dermal absorption, etc., are the individual congeners recombined and converted into the toxic equivalence of 2,3,7,8-TCDD to be factored into the quantitative risk assessment. It is recommended that a site-specific assessment, or even an assessment of a source category, be based on congener-specific emissions rather than TEQ emissions.

Section 3.2.1 presents a strategy for development of emission factors for conducting a site-specific assessment. Section 3.2.2 describes an approach to estimating congener-specific emission factors when all that is available are homologue group emission factors. Section 3.2.3 summarizes the emission factors for the hypothetical incinerator demonstrated in Chapter 5. Section 3.2.4 presents an in-depth evaluation of the partitioning of emissions between a vapor and a particle phase for further atmospheric transport modeling. This discussion includes subsections on measurements of partitioning at the stack, measurements of partitioning in ambient air, and the theoretical approach used in this assessment for vapor/particle partitioning. Section 3.3.5 closes this section

on emission factors by describing procedures to estimate the mass of ash (fly and bottom) produced and the concentration of dioxin-like compounds on ash.

3.2.1. A Strategy for Generating Emission Factors

The following is a heirarchal listing of data collection options for emission factors:

A. *For facilities that are built and operational*, it is preferred that direct stack measurements be used, using EPA recommended congener-specific stack monitoring and analytical protocols. Stack monitoring provides concentrations and mass release rates of the pollutant, actual volume of stack gas and temperature. Care should be taken to ensure that the emissions characterization reflects a wide range of operating conditions and also accounts for deterioration in emissions output of the facility over its useful life. Procedures to convert data expressed in concentrations or mass release rates to an emission factor are as follows:

1. Test data of emissions are first placed into common units of measurement. English units are converted into metric, and the concentration term (mass of pollutant per unit volume of combustion gas emitted from the stack) should be corrected to the standard temperature and pressure on a dry gas basis, and standard percent carbon dioxide or oxygen within the combustion gas (e.g.,12% CO_2). These adjustments may be necessary if more than one test occurred for stack emissions.
2. The next step involves converting the mass emission concentration of the specific dioxin-like congener in units of nanograms per normal cubic meter (at standard temperature and pressure) of combustion gas corrected to 12% carbon dioxide into an equivalent emission factor in units of grams of pollutant emitted from the stack per kilogram of combustable material or feed (g CDD and CDF/kg feed) that was incinerated at the facility during the duration of stack sampling. This is done as follows:

$$E_f = \frac{C_{fg}\ V_{fg}\ 0.001}{M_w} \qquad (3\text{-}1)$$

where:

E_f = emission factor, μg/kg
C_{fg} = concentration in flue gas, ng/dscm
V_{fg} = volume of combustion gas/unit of time, dscm/hr
M_w = mass of waste incinerated/unit of time, kg/hr
0.001 = units conversion factor

3. As a final step, the average emission factor of each congener is derived by summing the emission factors and dividing by the number of data points used. The average should represent an approximation of long-term emissions. Many air dispersion models require emission factors in units of amount of the pollutant emitted per second of time. Therefore the average emission factor must be adjusted accordingly by adjusting the units in Equation (3-1) to a time-scale of one second.

B. *For facilities that have been constructed, but not yet operational, or are in the planning stages of development,* the following procedure is recommended:

1. Collect and review stack test reports which have measured the emissions of specific dioxin-like congeners from facilities that are most similar in technology, design, operation, capacity, fuel, waste feed composition, and pollution control as the facility under consideration.
2. Determine if the stack test reports used EPA recommended stack monitoring and analytical protocols specific to dioxin-like compounds and discard those data not in conformance.
3. When combining data from a test results of a number of facilities, care should be taken to convert emissions, process feed rates and stack gas parameters to consistent units of measurement.
4. Ranges and average values should be developed for purposes of exposure

analysis.

C. *If no congener-specific data exists for a specific facility or similar facilities*, then use homologue profile emissions from similar facilities. Steps 1-4 in B above pertain here as well. Estimating congener-specific emission factors given homologue emission factors is described in Section 3.2.2 below.

D. *If no data exist relevant to a specific facility*, then the *Compilation of Air Pollution Emission Factors* (EPA, 1985; and subsequent updates), should be used. This compilation was put together and is periodically updated by EPA's Office of Air Quality Planning and Standards (OAQPS), and is commonly referred to as AP-42. Care should be taken to select emission factors which were developed for technologies that best match the facility under consideration. The basic limitation of these of these data is the fact that emission factors are not usually reflective of specific emission control equipment.

OAQPS's AP-42 document provides TCDD/F emission factors for municipal waste combustors, sewage sludge incinerators, and medical waste incinerators. At this time, emissions from hazardous waste incinerators are not addressed in AP-42. Emission factors presented in AP-42 are designed for estimating emissions from a large number of sources over a wide area. They are averages of values determined at one or more individual facilities. The individual values which are used to develop the average may vary considerably. The use of AP-42 emission factors to estimate emissions from any one facility should be done with great care.

E. *In the absence of suitable AP-42 emission factors*, clearly documented engineering evaluations may be used. Documentation should include copies of emission test reports used to derive the emission estimates, any assumptions made and the rationale for the conclusions that were made.

3.2.2. Use of Homologue Profiles for Estimating Congener Specific Emission Factors

This section describes emission factors for homologue groups of dioxin-like compounds from various stack emission sources. These emission factors are described in units of μg homologue emitted/kg feed material combusted. These are presented for

comparative purposes only, and should not be interpreted as representative of the sources described. Most of the profiles are based on very limited data generated under limited emission controls.

When only homologue emission factors are available, then rough estimates of congener specific factors can be made. First, an equal probability of occurrence of the specific congener is assumed based on relative proportionality. For example, 2,3,7,8-TCDD is one congener out of 22 possible congeners in the TCDD homologue. Therefore, the probability of occurrence is assumed to be the ratio of 1/22 or 0.045. Multiplication of a total TCDD emission factor by 0.045 gives an approximation of the emission factor for 2,3,7,8-TCDD. Table 3-1 lists the number of dioxin-like congeners within a homologue group and the total number of congeners within that homologue group.

The use of this procedure may be the only way to evaluate source or site-specific emissions of dioxin-like polychlorinated biphenyls (PCBs), known as the coplanar PCBs. No congener specific test data of coplanar PCBs from incinerators or combustion sources could be found for this assessment. The data that are available usually have reported PCBs as the sum total of all PCBs present in the sample without further speciation of toxic congeners or congener groups (EPA, 1987b). The greatest level of detail in any test report is a further breakdown of total PCBs into homologue groups, e.g., mono - deca-chlorobiphenyl.

Figure 3-1 displays the homologue profiles for 11 specific source categories. Following now are brief summaries of the reference materials for these homologue profiles. ***Again, it is emphasized that these homologue profiles are not offered as source generalities; they are mostly generated on a small number of different facilities not including a range of emission controls. It is not known whether tested facilities represent the average, or are higher or lower than typical facilities in each source category.***

1. Municipal Solid Waste Incineration (MSWI): Municipal incinerators can be classified into four general design categories: mass burn, modular, refuse-derive fuel (RDF), and fluidized-bed combustors (EPA, 1991). Figure 3-1 depicts the homologue profile of TCDD/Fs from MSWIs. It was constructed by merging emissions data from ten modern mass burn technologies (EPA, 1983; EPA, 1988a; Knisley, et al., 1986; Seelinger, et al., 1986; EPA, 1988b; Marklund, et al., 1985; Siebert, et al., 1991; Entropy, 1987).

Table 3-1. The number of dioxin-like and total congeners within dioxin, furan, and coplanar PCB homologue groups.

Homologue Group	n: number of dioxin-like congeners	N: number of total congeners	1/N
1. Dioxins			
Tetra-CDD	1	22	0.022
Penta-CDD	1	14	0.071
Hexa-CDD	3	10	0.100
Hepta-CDD	1	2	0.500
Octa-CDD	1	1	1.000
2. Furans			
Tetra-CDF	1	38	0.026
Penta-CDF	2	28	0.036
Hexa-CDF	4	16	0.063
Hepta-CDF	2	4	0.250
Octa-CDF	1	1	1.000
3. Coplanar PCBs			
Tetra-Chloro PCBs	2	42	0.024
Penta-Chloro PCBs	4	46	0.022
Hexa-Chloro PCBs	4	42	0.024
Hepta-Chloro PCBs	1	24	0.042

2. Hazardous Waste Incineration: Hazardous waste incinerators have not been extensively evaluated for stack emissions of dioxin-like compounds. Only a few reports appear in the published literature from which homologue emission factors can be developed (NATO, 1988; EPA, 1992), and these do not give complete inventories of emissions. Therefore, homologue emission factors were estimated based on a series of emission tests at a rotary kiln waste incinerator in Biebesheim, German (EPA, 1992). Figure 3-1 depicts the homologue profile for this single hazardous waste incinerator.

3. Drum and Barrel Reclamation Furnace: Dioxin-like compounds were measured by EPA in the stack gas emissions of a drum and barrel reclamation furnace as part of the

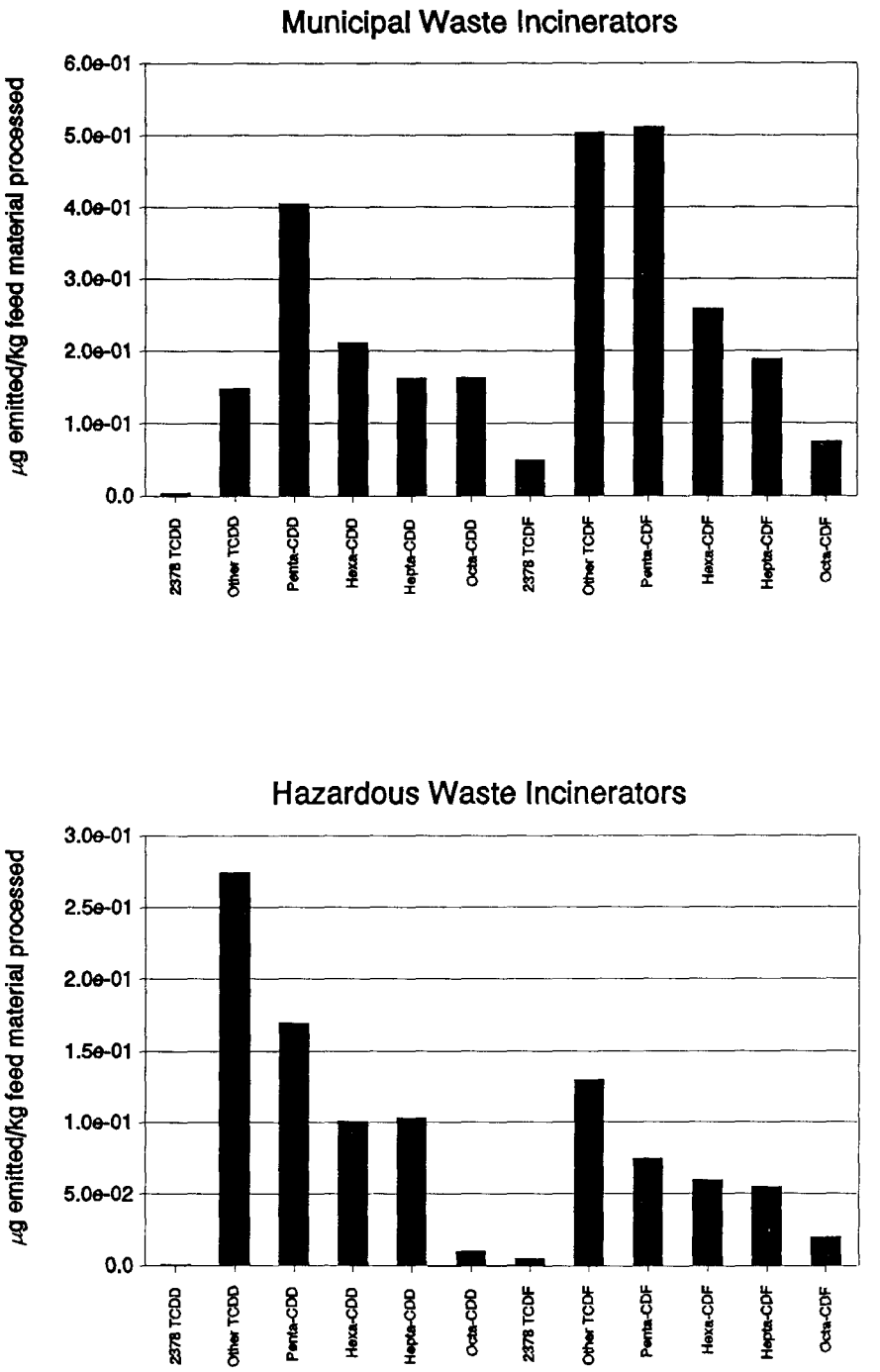
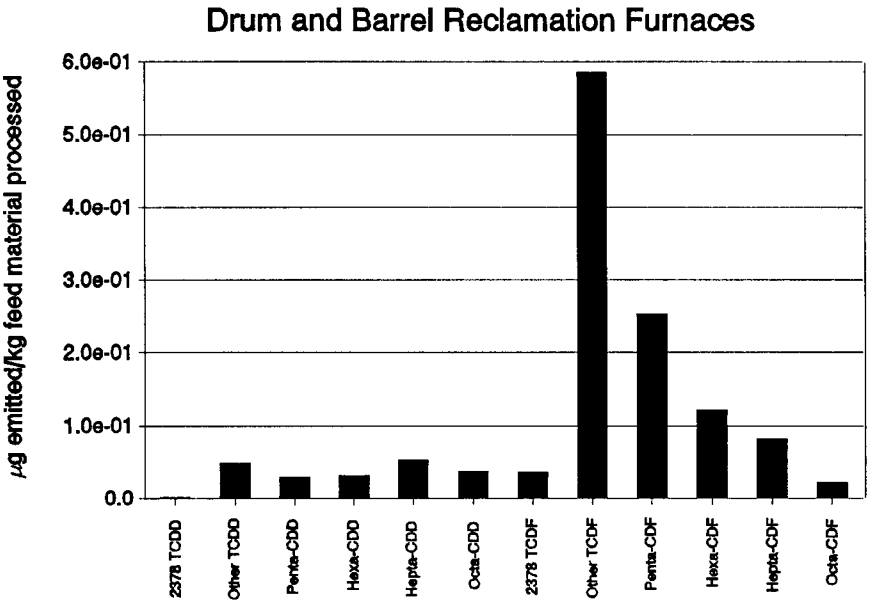


Figure 3-1. Homologue emission factors for source categories of dioxin-like compound release.



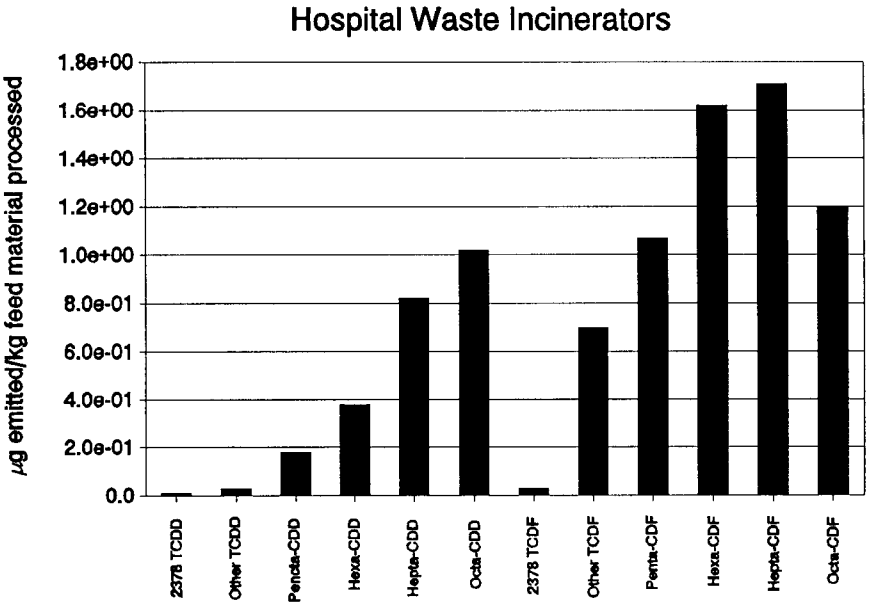
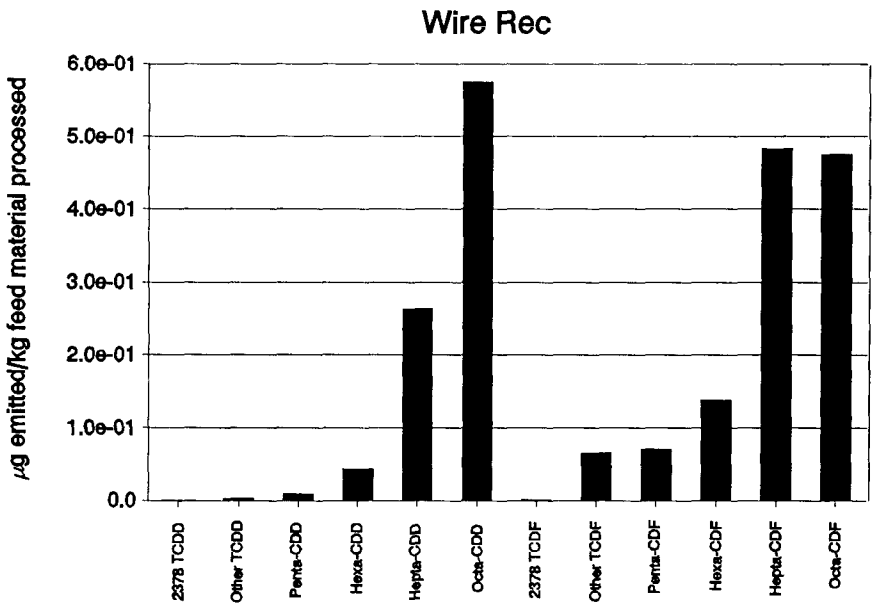


Figure 3-1. (cont'd)



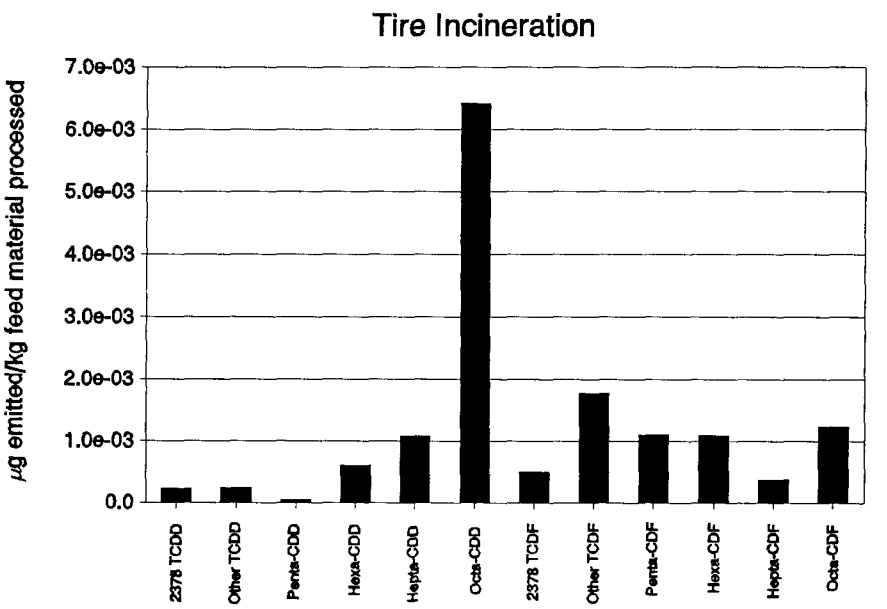
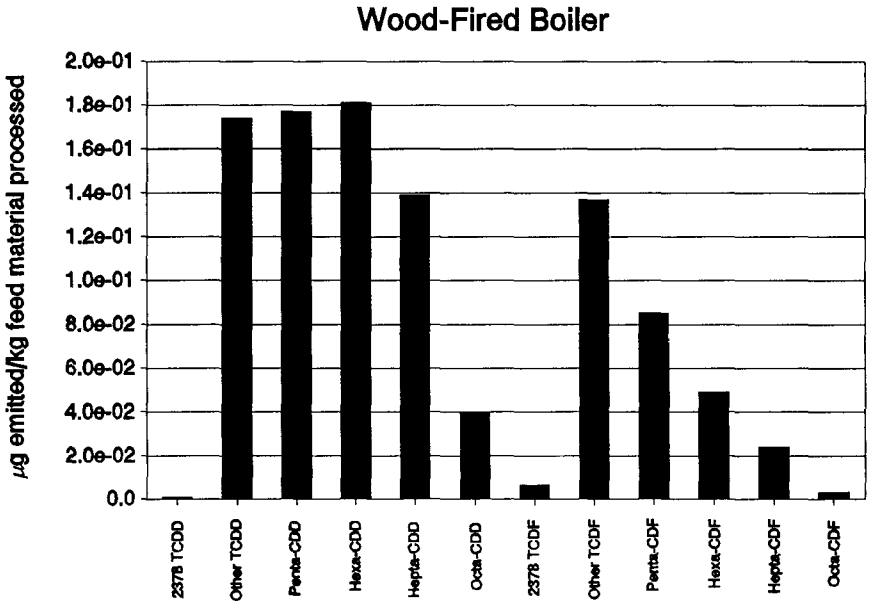


Figure 3-1. (cont')



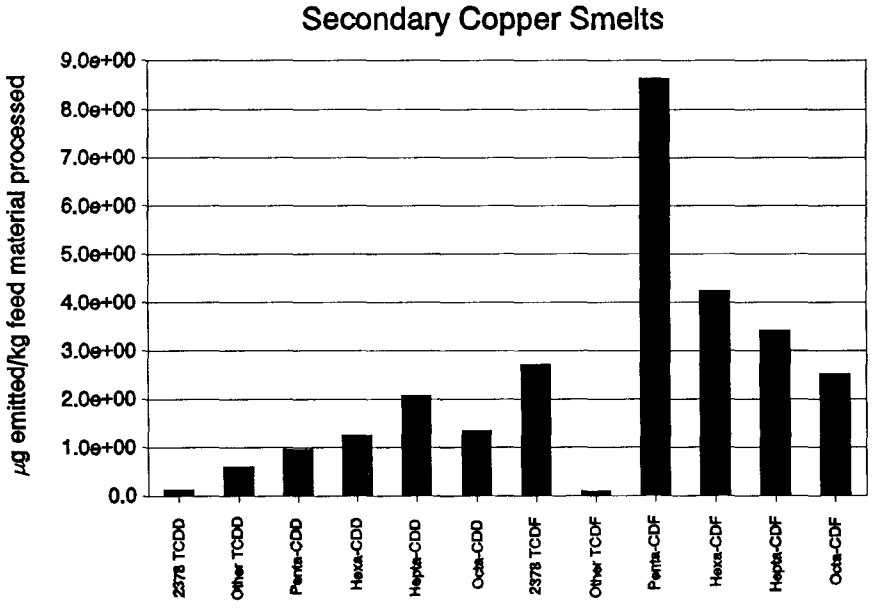
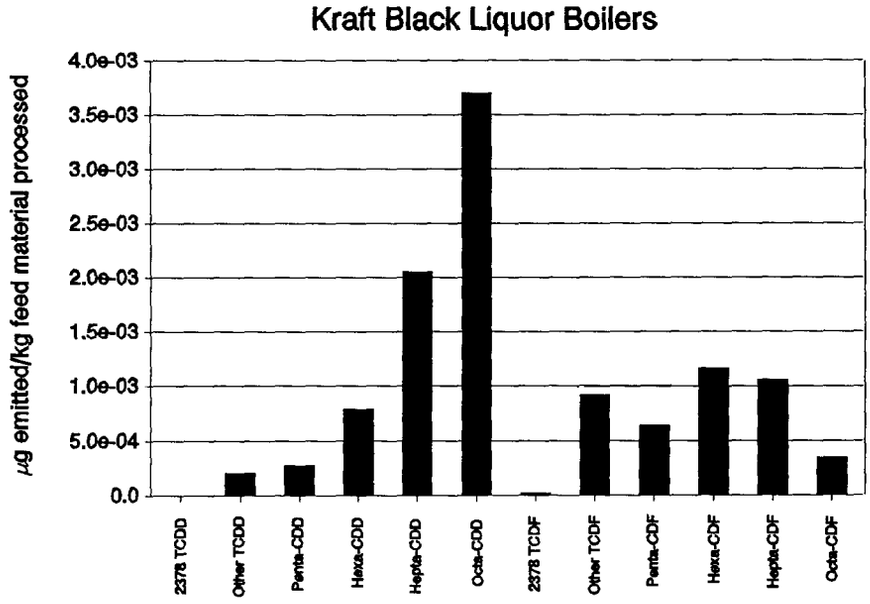


Figure 3-1. (cont'd)



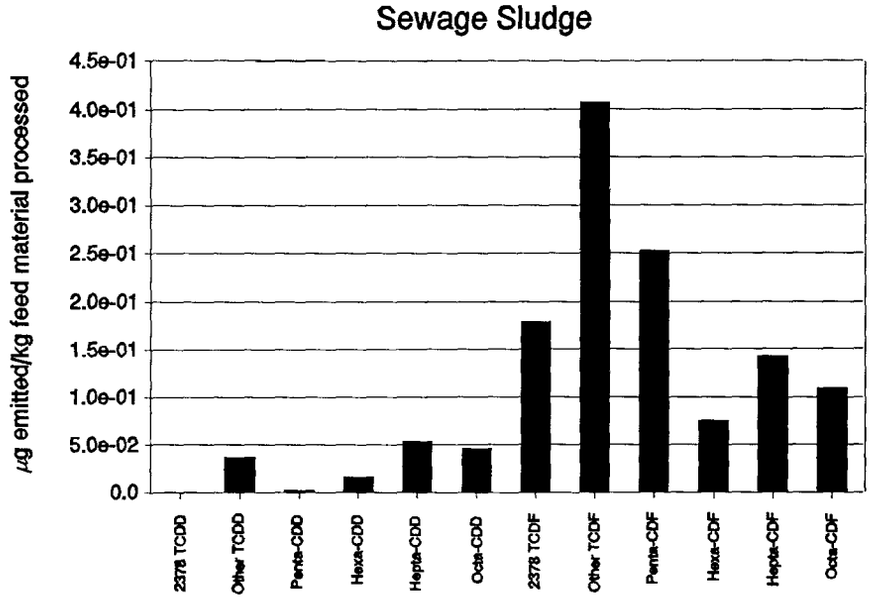


Figure 3-1. (cont'd)

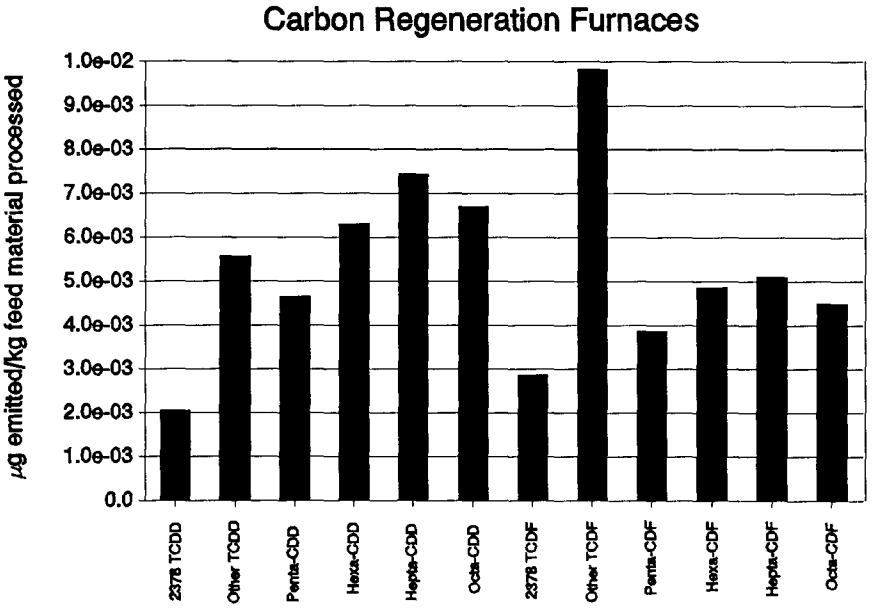


Figure 3-1. (cont'd)

National Dioxin Study of Combustion Sources conducted in 1986 (EPA, 1987d). The tested facility was judged by EPA to be typical of the industry. These plants operate a furnace to prepare used steel 55-gallon drums for cleaning to base metal. The cleaned drums are repaired, repainted, relined and sold for reuse. The used drums processed at the tested facility were from the petroleum and chemical industry. The drum burning process subjected the used drums to an elevated temperature in a tunnel furnace for a sufficient time so that the paint, interior linings, and previous contents were burned or disintegrated. The furnace was fired by auxiliary fuel. Used drums were loaded onto a conveyor that moved at a fixed feed rate. As the drums passed through the preheat and ignition zone of the furnace, additional contents of the drums drained into the furnace ash trough. A drag conveyor moved these sludges and ashes to a collection pit. The drums were air cooled as they exited the furnace. Exhaust gases from the burning furnace were drawn through a breaching fan to a high-temperature afterburner. The homologue profile for drum and

barrel reclamation furnaces, shown in Figure 3-1, was developed from EPA stack tests of this operation (EPA, 1987d).

4. Medical Waste Incinerators: The State of California Air Resources Board (CARB) has stack tested a number of hospital waste incinerators in southern California (CARB, 1990). Congener-specific emissions of PCDD/Fs were measured in the stack gas emissions of 7 facilities. Figure 3-1 displays the homologue profile constructed from the average emission of three facilities tested by CARB identified as facilities A - C in their summary overview of emissions (CARB, 1990).

5. Scrap Electric Wire Incineration: Dioxin-like compounds emitted to the air from scrap electric wire incineration were measured from a facility during EPA's National Dioxin Study of combustion sources (EPA, 1987d). The objective of wire incineration is to remove the insulating material and reclaim the metal (e.g., copper, silver, and gold) comprising the electric wire, hence these facilities are sometimes referred to as wire reclamation incinerators. The reclaimed metal is then sold to a secondary metal smelter. The tested facility was judged by EPA to be typical of this industry. Insulated wire and other metal-bearing scrap material were fed to a combustion unit where incineration of the material was assisted by the combustion of natural gas. The estimated temperature during combustion was 650° C, and combustion transpired in both a primary and secondary chamber. The tested facility was equipped with a high temperature afterburner to further destroy organic compounds entrained in the combustion gases prior to discharge to the air from the stack. Figure 3-1 displays the homologue distribution developed from this single facility.

6. Automobile Tire Incineration: Homologue emissions factors shown in Figure 3-1 were developed from an automobile tire incinerator stack tested by the State of California Air Resources Board (CARB, 1991). The facility consists of two excess air furnaces equipped with steam boilers to recovery the energy from the heat of combustion. Discarded whole tires are fed to the incineration units at a rate of 3000 kg/hr. The furnaces are equipped to burn natural gas as auxiliary fuel. The steam produced from the boilers is used to drive electrical turbine generators to produce 14.4 megawatts of electricity. The facility is equipped with a dry acid gas scrubber and fabric filter for the control of emissions prior to exiting the stack. These devices are capable of greater than 95% reduction and control of dioxin-like compounds prior to discharge from the stack.

7. Industrial Wood-Burning Facilities: The homologue profile shown in Figure 3-1 for this source category was developed from measurements of stack emissions from an industrial wood-burning furnace (EPA, 1987d). The tested facility was judged by EPA as being typical of these combustion technologies. The facility was located at a lumber products plant that manufactures overlay panels and other lumber wood products. The wood-fired boiler tested was a three-cell dutch oven equipped with a waste heat boiler. During normal operation, the furnace is 100% fired with scrap wood from the lumber plant. The feed wood is typically a mixture of bar, hogged wood, and green and dry planar shavings. For the stack test from which the homologue profile was developed, the feed was mostly wood from fir and hemlock. Nearly all the wood fed to the lumber plant had been stored in sea water adjacent to the facility, and therefore had a significant concentration of inorganic chloride. The scrap wood fed to the boiler had not been treated with chemical preservatives, such as pentachlorophenol. The wood was fed to the boiler by a screw conveyor that dumps the feed into a pile in the primary combustion chamber. The furnace was operated at air in 50% excess of stoichiometric requirements. Boilers captured the heat of combustion and transfered the heat into steam for co-generation of energy at the plant. The exhaust gases from the boiler passed through a cyclone and fabric filter prior to discharge from the stack. The facility was equipped with a cyclone and fabric filter to control emissions. Emissions testing at this facility demonstrated that the fabric filter was reducing dioxin emissions by about 90% (EPA, 1987d).

8. Metal Reclamation Plants: Metal reclamation plants are secondary metal smelting facilities which include secondary copper smelters, secondary aluminum smelters, secondary magnesium smelters, and secondary ferrous smelters. The only complete information with regard to the potential stack emission of dioxin-like compounds is from a secondary copper smelter tested by EPA during the National Dioxin Study (EPA, 1987d). The homologue profile shown in Figure 3-1 was developed from this facility. The tested facility was a secondary copper smelter that recovers copper and precious metals from copper and iron-bearing scrap. The copper and iron-bearing scrap was fed to a blast furnace, which produced a mixture of slag and black copper. The blast furnace was a batch-fed cupola furnace. Four to five tons of metal-bearing scrap were fed to the furnace per charge, with materials typically being charged 10 to 12 times per hour. Coke was used to fuel the furnace, which represented 14% (by wt) of the total feed. During the

dioxin stack tests, the feed consisted of electronic telephone scrap and other plastic scrap, brass and copper shot, iron-bearing copper scrap, precious metals, copper bearing residues, refinery by-products, converter furnace slag, anode furnace slag, and metallic floor cleaning material. Oxygen enriched combustion air for combustion of the coke was blown up through the bottom of the furnace. At the top of the blast furnace were four natural gas-fired afterburners to aid in completing combustion of the exhaust gases. Particulate emissions were controlled by fabric filters, and the flue gas then was discharged into a common stack.

9. Kraft Black Liquor Recovery Boilers: EPA stack tested three kraft black liquor recovery boilers for the emission of dioxin in conjunction with the National Dioxin Study (EPA, 1987d). The three sites were judged by EPA to be typical of Kraft black liquor recovery boilers, and the homologue profile shown in Figure 3-1 was derived from these three sites. These sources are associated with the production of pulp in the making of paper using the Kraft process. In this process, wood chips are cooked in large vertical vessels called digesters at elevated temperatures and pressures in an aqueous solution of sodium hydroxide and sodium sulfide (Someshwar and Pinkerton, 1992). Wood is broken down into two phases: a soluble phase containing primarily lignin, and an insoluble phase containing the pulp. The spent liquor (called black liquor) from the digester contains sodium sulfate and sodium sulfide that the industry finds beneficial in recovering for reuse in the Kraft process. In the recovery of black liquor chemicals, weak black liquor is first concentrated in multiple-effect evaporators to about 65% solids. The concentrated black liquor also contains 0.5% - 4% weight chlorides (EPA, 1987d). Recovery of beneficial chemicals is accomplished through combustion in a Kraft black liquor recovery furnace. The concentrated black liquor derived from the pulping process is sprayed into a furnace equipped with a heat recovery boiler. The bulk of the inorganic molten smelt that forms in the bottom of the furnace contains sodium carbonate and sodium sulfide in a ratio of about 3:1 (Someshwar and Pinkerton, 1992). The combustion gas is usually passed through an electrostatic precipitator that collects particulate matter prior to being vented out the stack. The particulate matter can be processed to further recover and recycle sodium sulfate.

10. Sewage Sludge Incineration: EPA has conducted stack emission testing for dioxin from sewage sludge incineration at three multiple-hearth sewage sludge incinerators

(EPA, 1987d). The homologue profile shown in Figure 3-1 was developed from tests on these three incinerators. Multiple hearth incinerators are the dominant technology in use in the United States today for the incineration of sewage sludge.

11. Granular activated carbon regeneration furnaces: Granular activated carbon (GAC) is an adsorbent that is widely used in the control of pollutants in wastewater discharged from chemical and pharmaceutical industries, and in the treatment of finished drinking water at water treatment plants. Industrial manufacture of activated carbon is mostly obtained from the heat treatment of nut shells and coal under pyrolytic conditions (Buonicore, 1992). The properties of GAC make it ideal for adsorbing and controlling vaporous organic and inorganic chemicals entrained in combustion plasmas, as well as soluble organic contaminants in industrial effluents and drinking water. The high ratio of surface area to particle weight (e.g, 600 - 1600 m^2/g), combined with the extremely small pore diameter of the particles (e.g., 15-25 Å) increases the adsorption characteristics (Buonicore, 1992). GAC will eventually become saturated and the adsorption properties will significantly degrade. When this occurs, the GAC usually must be replaced and discarded, which significantly increases the costs of pollution control. The introduction of carbon reactivation furnace technology in the mid 1980's created a method involving the thermal treatment of used GAC to thermolytically desorb the synthetic compounds and restore the adsorption properties for reuse (Lykins, et al., 1987).

The used GAC can contain compounds that are precursors to the formation of PCDD/Fs during the thermal treatment process. EPA measured precursor compounds in spent GAC used as a feed material to a carbon reactivation furnace tested during the National Dioxin Study (EPA, 1987d). The total chlorobenzene content of the GAC ranged from 150 ppb to 6,630 ppb. Trichlorobenzene was the most prevalent species present, with smaller quantities of di- and tetra-chorobenzenes detected. Total halogenated organics were measured to be about 150 ppm.

EPA has stack tested two GAC reactivation furnaces for the emission of dioxin (EPA, 1987d; Lykins, et al., 1987). The homologue profile shown in Figure 3-1 was developed from the tests at these two facilities. One facility was an industrial carbon reactivation plant, and the second facility was used to restore GAC at a municipal drinking water plant. The industrial carbon regeneration plant processed 36,000 kg/day of spent GAC used in the treatment of industrial wastewater effluents. Spent carbon was

reactivated in a multiple-hearth furnace, cooled in a water quench, and stored and shipped back to primary chemical manufacturing facilities for reuse. The furnace fired natural gas, and consisted of seven hearths arranged vertically in series. The hearth temperatures ranged from 480° C to 1000° C. The spent GAC contained about 40% weight moisture. The used GAC was fed to the top hearth. In the furnace, the spent carbon was dried and the organics adsorbed onto the carbon particles were volatilized and burned in the heated combustion atmosphere. The regenerated carbon dropped from the bottom hearth of the furnace to a quench tank to reduce the temperature. Air pollutant emissions were controlled by an afterburner, a sodium spray cooler, and a fabric filter. Temperatures in the afterburner were about 930° C.

The second GAC reactivation facility tested by EPA consisted of a fluidized-bed furnace located at a municipal drinking water treatment plant (Lykins, et al., 1987). The furnace was divided into three sections: a combustion chamber, a reactivation section and a dryer section. The combustion section was fired by natural gas, and consisted of a stoichiometrically balanced stream of fuel and oxygen. These expanding gases of combustion provided heat, and suspended and fluidized the carbon. Temperatures of combustion were about 1,000° C. The reactivation section outside the combustion chamber allowed for the complete volatilization of the heated GAC. Off-gasses from the reactivation/combustion section were directed through an acid gas scrubber and high-temperature afterburner prior to discharge from a stack.

Another combustion process for which emissions data were sought was coal combustion in electric power generating facilities (utility boilers). Currently there is conflicting and extremely limited data on emission of dioxin-like compounds from coal-fired utility boilers (NATO,1988). The few published results of stack testing and monitoring of emissions from facilities in the United States have shown that dioxin has not been detected in stack gas emissions (NATO, 1988). Therefore, a homologue profile for this source category was not developed. The federal Clean Air Act requires an assessment of stack emissions of toxic air contaminants, including CDDs and CDFs, from coal-fired utility boilers. The EPA is currently collaborating with the U.S. Department of Energy in stack sampling seven facilities for CDD and CDF emissions. These results will be included in the final version of this document.

A homologue profile also could not be developed for a industrial category of potential concern, portland cement kilns. The database on stack emissions of dioxin from these units is just now becoming available. Volume 2, Chapter 3 of this assessment reviews current emissions inventories for cement kilns burning and not burning hazardous waste as auxiliary fuel in the production of cement clinker. In evaluating the TEQ of the mixture of CDDs and CDFs discharged from the stack of individual facilities, it became apparent that there was no consistent pattern to the relationship of total CDDs and CDFs to the estimated dioxin TEQ. For example, the ratio of total PCDD/Fs to the TEQ ranged from about a factor of 5:1 to a factor of 1000:1. A lower ratio reflects a skewing towards penta and tetra-chlorinated congeners in the distribution, and a higher ratio reflects a greater proportion of hexa, hepta, and octa chlorinated congeners in the emissions. Until more information becomes available from stack testing additional sources, a homologue profile of this industry will not be derived from the existing data.

3.2.3. Estimation of Emissions of Dioxin-Like Compounds from the Hypothetical Incinerator

The emission factors for the dioxin-like compounds from the stack of the hypothetical waste incinerator were derived from actual stack monitoring and emissions testing of an incinerator burning a complex mixture of organic waste. The concentrations of the specific PCDD/F congeners in units of nanograms per dry standard cubic meter (at 20° C; 1 atm.; 7% O_2) were available, as were the volume of gas escaping from the stack and feed rates for the material being combusted during the stack tests. Using procedures described in Section 3.2.1, this data was converted to emission factors. Such factors for three test runs are shown in Table 3-2. The fourth column is the average of these emission factors converted to g/sec units, which are the appropriate units for the application of the COMPDEP model. The conversion assumed a constant feed rate of 200 metric tons of feed material per day (further details on the hypothetical incinerator are found in Section 3.5). Human exposures to the coplanar PCBs emitted from a combustion source is not demonstrated in Chapter 5. Therefore, an estimation of congener-specific emission factors of coplanar PCBs for the hypothetical incinerator are not provided.

In order to put the emissions from the hypothetical waste incinerator into perspective, they can be compared with emissions from other incineration sources that are

similarly controlled, e.g., equipped with scrubbers and/or fabric filters. Such air pollution control devices can reduce the amount of dioxin that is formed within the system by >99% prior to the release from the stack. In this comparison, emissions from the following types of incineration processes were used (CARB, 1990; EPA, 1993): medical waste incineration; hazardous waste incineration; sewage sludge incineration; and municipal solid waste incineration. For comparisons, all emissions factors are expressed in units of nanograms TCDD-TEQ (Toxic Equivalent) emitted from the stack per kg of waste combusted, and are presented as ranges in measurements (minimum to maximum). This should not be confused as typical of the incineration source category, but specific only to sources having scrubbers and/or fabric filters. Volume 2, Chapter 3 of this assessment gives an overview of dioxin emissions from incineration technologies equipped with a variety of pollution control systems. The emissions from the hypothetical incinerator is ranked with the other types of waste incinerators that are well controlled with some combination of a scrubber device and/or a fabric filter, as follows:

1. Medical waste incineration: 25 - 200 ng TEQ/kg waste combusted.
2. Hazardous waste incineration: 0.18 - 119 ng TEQ/kg waste combusted.
3. **Hypothetical waste incinerator: 4.5 ng TEQ/kg waste combusted.**
4. Municipal solid waste incineration: 0.05 - 3 ng TEQ/kg waste combusted.
5. Sewage sludge incineration: 0.002 - 0.03 ng TEQ/kg sludge combusted.

From these comparisons it appears that the TCDD-TEQ emission factor derived for the hypothetical incinerator lies well within the range of emission factors developed from measured incineration sources burning a diversity of waste material, but employing similar air pollution control technology. The hypothetical incinerator was arbitrarily assigned a waste combustion rate of 200,000 kg waste/day. This charging rate conforms to a large medical waste incinerator, an average hazardous waste facility, and moderate sewage sludge and municipal waste incinerators.

3.2.4. Estimation of the Vapor Phase/Particle Phase Partitioning of Emissions of Dioxin-Like Compounds

The first step in the air modeling is the partitioning of total emissions into a vapor and a particle state. This section will review data on partitioning at the point of stack emission, in ambient air, and a theoretical approach to estimating the partitioning of dioxin-

Table 3-2. Emission factors and average emissions used for the hypothetical incinerator.

Congener	Emission Factors Test 1	Test 2	Test 3	Emissions
	---------- ng/kg ----------			- g/sec -
2378-TCDD	0.052	0.031	0.037	9.3E-11
Other TCDD	0.826	0.870	0.913	2.0E-9
12378-PeCDD	0.148	0.056	0.048	1.9E-10
Other PeCDD	1.390	0.322	0.783	1.9E-9
123478-HxCDD	0.104	0.165	0.056	2.5E-10
123678-HxCDD	0.157	0.187	0.130	3.6E-10
123789-HxCDD	0.148	0.165	0.117	3.3E-9
Other HxCDD	2.440	0.670	1.040	3.2E-9
1234678-HpCDD	2.350	0.957	0.957	3.3E-9
Other HpCDD	4.040	1.650	2.170	6.0E-9
OCDD	4.260	1.390	3.130	6.7E-9
2378-TCDF	3.300	2.390	2.170	6.0E-9
Other TCDF	20.00	15.70	14.30	3.8E-8
12378-PeCDF	0.435	0.165	0.226	6.3E-10
23478-PeCDF	0.243	0.139	0.122	3.9E-10
Other PeCDF	6.280	4.480	3.480	1.1E-8
123478-HxCDF	0.478	0.365	0.357	9.2E-10
123678-HxCDF	0.478	0.343	0.313	8.7E-10
123789-HxCDF	0.357	0.165	0.226	5.7E-10
234678-HxCDF	0.243	0.117	0.074	3.3E-10
Other HxCDF	1.490	0.313	0.943	2.1E-9
1234678-HpCDF	0.243	0.565	0.696	1.2E-9
1234789-HpCDF	0.391	0.096	0.165	5.0E-10
Other HpCDF	241.0	2.380	2.180	5.4E-9
OCDF	1.570	0.478	0.971	2.2E-9

like compounds in ambient air. The true vapor/particle partitioning of dioxin under different conditions has not been directly measured, and therefore, is usually implied from these limited data or by theoretical means.

3.2.4.1. *Vapor phase/particulate phase inferences from stack measurements*

While the available literature is weak in this area, various investigators have made inferences on the vapor phase/particulate phase (V/P) partitioning from in-the-stack sampling of PCDD/F emissions from combustion sources. Sampling systems which have been used basically consist of a particulate filter followed by a section designed to condense vapors in impinger glassware surrounded by an ice bath, and a resinous material suitable for absorbing vapor phase compounds. Depending on where the congener is distributed within the component parts of the sampling apparatus, the investigator reports the fraction associated with particulate, and the fraction found in the vapor absorbing material. In order to collect sufficient mass of particulate for accurate analytical determination of the concentration of the recovered congener at sub-part per trillion levels of detection, it is often necessary to sample in stack for periods of four hours or longer. This introduces the possibility of movement of the collected dioxin sample from one part of the sampling train to another through adsorption, desorption, particulate blow-off, or other such phenomena as the sampling train continues to be exposed to the hot combustion gases. No real-time sampling method currently exists to instantaneously measure the concentration and physical state of the various PCDD/F congeners in the fluid turbulence of the hot combustion plasma characteristic of gases from combustion traveling up a cylindrical stack. For these reasons, V/P partitioning based on stack test data is highly uncertain. Additional laboratory research is needed that is specifically directed at identifying the physical state partitioning of individual PCDD/F congeners at the exit to the stack under varying temperature profiles and conditions of particulate loading and acid gas concentration. Table 3-3 is a summary of the percent distribution of PCDD/Fs between the vapor-phase (V) and the particulate phase (P) as interpreted by various stack sampling techniques employed in the measurement of the compounds during incinerator operations.

Cavallaro, et al. (1982) performed a series of stack tests on six municipal solid waste (MSW) incinerators in Italy. He was one of the first investigators to interpret the V/P ratio from where the PCDD/F segregated with the sampling train, e.g., the particulate filter and resinous trap. From these data, the percent distribution of congener groups were estimated. Cavallaro observed that the PCDD/F emissions from the stack of the tested incinerators seemed to predominate in vapor phase. He attributed this to the possibility that the relatively high temperatures of the combustion gases during sampling (700 to

Table 3-3. Percent distribution of dioxins and furans between vapor-phase (V) and particulate-phase (P) as interpreted by various stack sampling methods.

		4-CDD	5-CDD	6-CDD	7-CDD	8-CDD	4-CDF	5-CDF	6-CDF	7-CDF	8-CDF
Cavallaro, et al.	V	95	91	94	99	89	NR	NR	NR	NR	96
1982	P	5	9	6	1	11	NR	NR	NR	NR	4
Cavallaro, et al.	V	9	38	69	57	14	59	NR	NR	NR	60
1982	P	91	62	31	43	86	41	NR	NR	NR	40
Cavallaro, et al.	V	99	99	99	99	99	99	NR	NR	NR	99
1982	P	1	1	1	1	1	1	NR	NR	NR	1
Cavallaro, et al.	V	85	92	99	98	99	99	NR	NR	NR	99
1982	P	15	8	1	2	1	1	NR	NR	NR	1
Cavallaro, et al.	V	97	90	63	82	59	80	NR	NR	NR	97
1982	P	3	10	37	18	42	20	NR	NR	NR	3
Cavallaro, et al.	V	100	99	99	100	99	100	NR	NR	NR	100
1982	P	0	1	1	0	1	0	NR	NR	NR	0
Benfenati, et al.	V	94	NR	NR	NR	NR	NR	NR	NR	NR	NR
1986	P	6	NR	NR	NR	NR	NR	NR	NR	NR	NR
Tiernan, et al.	V	75	68	67	55	64	75	70	64	69	86
1984	P	25	32	33	45	36	25	30	36	31	14
Tiernan, et al.	V	95	90	88	85	98	86	98	89	88	98
1984	P	5	10	12	15	2	14	2	11	12	2
Tiernan, et al.	V	91	91	89	77	56	92	89	91	72	65
1982	P	9	9	11	23	44	8	11	9	28	35
Tiernan, et al.	V	17	22	45	84	85	7	10	22	63	77
1982	P	83	78	55	16	15	93	90	78	37	23
Clement, et al.	V	98	92	96	93	73	97	96	98	98	94
1985	P	2	8	4	7	27	3	4	2	2	6
Clement, et al.	V	84	55	54	72	20	95	73	70	52	68
1985	P	16	45	46	28	80	5	27	30	48	32
Clement, et al.	V	100	99	98	93	95	100	100	99	99	98
1985	P	0	1	2	7	5	0	0	1	1	2
Hagenmaier, et al.	V	62	42	25	20	20	68	55	40	25	0
1986	P	38	58	75	80	80	32	45	60	75	100
Battelle 1988	V	90	NR	NR	NR	NR	NR	NR	NR	NR	NR
	P	10	NR	NR	NR	NR	NR	NR	NR	NR	NR
EPA 1990a	V	56	42	30	26	18	62	56	45	37	21
	P	44	58	70	74	82	38	44	55	63	79
Radian 1986	V	16	16	16	20	16	16	14	17	16	17
	P	84	84	84	80	84	84	84	83	84	83
Average	**V**	**76**	**70**	**71**	**73**	**63**	**76**	**66**	**64**	**62**	**73**
V/P	**P**	**24**	**30**	**29**	**27**	**37**	**24**	**34**	**36**	**38**	**27**

NR = not reported; NRs not counted in average estimations

900° C) may have promoted desorption of PCDD/Fs from particulate, although the sampling probe was kept at a constant 150° C.

Benfenati, et al. (1986) describes the stack testing of a modular MSW incinerator in Italy having a combustion capacity of 1500 kg/hour. The purposes of the study were to analyze the concentration of TCDD and TCDF at various points of the incineration process, to estimate the vapor phase versus the particulate phase partitioning at various sampling points corresponding to changes in temperatures, and to estimate the TCDD/TCDF control efficiency of the pollution control device (an electrostatic precipitator). Comparisons were made between the distribution of TCDD/TCDF after the secondary furnace in a region where combustion gas temperature was about 330° C, and the distribution at the stack where combustion gas temperature was 230° C. Benfenati observed that approximately 85% of the TCDD was in the vapor phase at the exit to the furnace, and approximately 95% of the TCDD was in the vapor phase at the stack. It was concluded that most of the TCDD predominated in vapor phase at the point of release from the stack at the reported temperature of 230° C. However, Benfenati could not exclude the possibility that the TCDD was adsorbed onto ultra fine, submicron aerosol particles.

Tiernan, et al. (1984) reported on the distribution of PCDD/Fs recovered in the stack sampling apparatus (EPA Modified Method 5) following the stack testing of a mass burn MSW incinerator operating in Japan. In the Modified Method 5 procedure, the sampling probe is maintained at a temperature of 120°C while the stack gases are isokinetically sampled. The facility was equipped with a dry scrubber combined with a fabric filter as the primary pollution control device. Tiernan observed congener-specific variability in the V/P partitioning inferred from the sampling method. However, greater than 55% of the PCDD/Fs were estimated to be in vapor phase at the point of release to the stack. In an earlier stack test (Tiernan, et al., 1982) of an MSW incinerator equipped with an electrostatic precipitator, Tiernan found that 45% to 89% of the PCDD/Fs were associated with particulate.

Clement, et al. (1985) stack tested a mass burn MSW incinerator operational in Canada for the emission of PCDD/Fs. Three 24-hour stack samples were taken using the EPA Modified Method 5 train with a stack temperature of 230 - 250° C. The components of the sampling train were analyzed separately. Clement observed that more than 95% of the total PCDD/Fs detected in the sampling train samples was found in the impingers used

to condense vapor phase organic pollutants. Interpretation of this is difficult. However, it is implied from these data that most of the PCDD/Fs prevailed in vapor phase.

Hagenmaier, et. al (1986) conducted field tests of two different stack test methods for the accuracy, precision, and comparability of PCDD/F measurements. Both instruments were similarly constructed with a glass fiber filter for the capture of particulate-bound contaminants, a series of water or ice-cooled impingers to promote condensation of vapor phase contaminants, followed by an absorbing material to trap vapor phase pollutants. Eight parallel stack sampling experiments were carried out over a three week period using the sampling trains known as the German simple dilution method and the EPA Modified Method 5. Although the two methods reported quite similar total concentrations of PCDD/Fs, the distribution of PCDD/Fs between the heated glass filter, and ice-cooled impingers and the sorbent trap were remarkably different. In one train, referred to as Train A by Hagenmaier, the temperature in the filter housing was 140° C, and in the second train, Train B, the temperature was 90° C. The stack gas temperature in both cases was 230° C. Hagenmaier found that the percentage of PCDD/Fs in the glass fiber filter was markedly greater in Train B than in Train A. Up to 93% of the PCDDs and 90% of the PCDFs were detected in the particulate filter in Train B. By comparison, 73% and 58% of PCDDs and PCDFs, respectively, were detected in the particulate filter in Train A. Although Hagenmaier's data is used in Table 3-3, Hagenmaier theorized that this difference in the distribution of PCDD/Fs in the two sampling trains was due to the differences in the temperature of the glass fiber filter housing.

EPA (1990a) conducted a field validation study for the EPA stack testing Method 23 (the Modified Method 5) for the collection and retention efficiency of PCDD/Fs. A carbon-13 labelled congener was metered into the sampling probe just preceding the glass fiber filter using a dynamic spiking system. The validation procedure involved the isokinetic sampling in the stack of a large mass burn MSW incinerator. Sampling *in situ* in the stack while using a dynamic spiking system demonstrated that most of the isotope was recovered in the filter trap and front half of the sampling train designed to capture particulate, and a lower amount was recovered in the XAD resin designed to capture vapor phase organic compounds. In the particular tests in which the overall percent recovery of the dynamic spike were found to be acceptable, the XAD resin and condensor contained about 49% of the isotope, and 51% was associated with carbonaceous particulate.

3.2.4.2. *Discussion of vapor/particle ratios derived from stack testing methods*

It is apparent that the stack sampling method gives inconclusive and contradictory evidence of the V/P partitioning of PCDD/Fs at the stack of incinerators. Although most of the researchers report finding the greatest quantity of PCDD/Fs captured within the resinous material having the physical/chemical properties of absorbing vapor phase organic compounds, a few studies have reported the opposite. What is unusual about the V/P distributions in Table 3-3 is the lack of complete consistency despite the similarity of sampling method. Although the stack gas temperatures may vary, the probe and housing to the sampling instrument is usually kept at a standard temperature while traversing the hot flue gas. A more consistent pattern of V/P should have emerged.

Hagenmaier, et al. (1986) has postulated that, depending on the temperature of the glass fiber particulate filter housing, the PCDD/Fs might desorb (volatilize) from particulate matter trapped in the filter during the 4 hours of sampling time required of the stack sampling method. Therefore, Hagenmaier does not believe that the distribution of PCDD/Fs between the particulate filter, the condensing impingers, and the vapor absorber gives a true indication of the V/P partitioning of these compounds at the stack.

Tests also have been devised by the EPA (1990a) to study the effect a change in temperature of the glass fiber filter housing might have on the distribution of PCDD/Fs in the sampling train. During the sampling period, two sampling trains were used: one inlet to the electrostatic precipitator (ESP), and the other placed near the outlet to the ESP. Temperatures of the filter housing were raised from the standard 120° C to 215° C in both sampling trains. In agreement with the observations of Hagenmaier, et al. (1986), an increase in temperature generally resulted in a change in the distribution of the recovered 13-C labelled PCDD/F congeners. However, the temperature effect was most apparent within the sampling train inlet to the ESP. In the inlet sampling train, the higher filter box temperature increased the relative percentage of PCDD/Fs trapped in the impingers and XAD-2 resin. An amount estimated to be in the vapor phase, based on the segregation of the compounds within the component parts of inlet sampling train, is as follows (with a range listed from low to high temperature): TCDD = 20 - 55% vapor; HxCDD = 10 - 30% vapor; OCDD = 5 - 18% vapor; HxCDF = 18 - 58% vapor; OCDF = 5 - 18% vapor. In the outlet sampling train (characteristic of stack emissions), this dramatic shifting of the congeners from the filter to the XAD-2 did not occur with an increase in

temperature. Interpretation of the vapor phase partitioning in the outlet sampling train from low to high temperatures was as follows: TCDD = 90 - 95% vapor; HxCDD = 85 - 90% vapor; HxCDF = 90 - 95% vapor; OCDD = 75 - 90% vapor; OCDF = 78 - 90% vapor. Both these interpretations were developed using a 500 ng PCDD/F spiked congener. Notice that the vapor phase to particle phase ratio is significantly different between the inlet and outlet sampling trains: in the inlet train most of the PCDD/F congeners seemed to predominate in the particle phase at the standard temperature of the filter housing, whereas in the outlet train most of the PCDD/F congeners seemed to predominate in the vapor phase, as interpreted by the distribution within the apparatus.

The temperature-dependent partitioning has recently been observed by Janssens, et al. (1992) during field validation studies involving the sampling of operating incinerators in Belgium. Janssens observed that the fraction of PCDD/Fs collected in the heated portion of the particulate glass filter (temperatures in the range of 250 to 300° C) showed an expected partitioning according to the vapor pressures of the compounds. It was found that a very low proportion of the PCDD/Fs were found in the particle phase; nearly all the compounds were detected in the vapor phase. Moreover, Janssens observed that higher temperatures seemed to favor the vaporous state of the lower chlorinated congeners (compounds having one to five chlorines on the aromatic ring), and the particulate phase for higher chlorinated congeners (five to eight chlorines). This agrees well with the decrease in vapor pressures that occurs with an increase in chlorination, and an increase in vapor pressure that occurs with a decrease in chlorination of PCDD/Fs. Adding to the theory of Hagenmaier, et al. (1986), Janssens believed that either the sampling apparatus was giving a true distribution of the V/P ratio of individual congeners, or that a significant portion of the congeners were reversibly sorbed onto particulate surfaces and could be eluded to vapor phase by the passage of the volume of sampled combustion gas over a lengthy time interval, neither of which could be proven by his study.

Benfenati, et al. (1986) has suggested that what may be reported as vapor phase may actually consist of nucleated aerosol particles having diameters less than 0.1 micrometers. The impingers in the sampling method are located a few centimeters behind the heated particulate glass fiber filter, and are bathed in an ice bath. The dramatic reduction in temperature within the impinger glassware may cause sublimation from vapor phase to nucleation of aerosol particles. Downstream of the impingers is the vapor

absorbing material, usually XAD-2 resin. Although this has been shown to be an excellent trap for semi-volatile organic compounds, the retention of submicron size particles with PCDD/Fs adsorbed onto the surfaces, or absorbed into the interior spaces, cannot be ruled out or excluded as a possible explanation for investigators reporting a preponderance of concentration both in the impingers and the vapor trap.

Complicating any meaningful interpretation of the data is the long duration of sampling time required in the stack measurement method. In order to reach a sub-ppt level of detection of PCDD/Fs for reliable quantification of specific congeners, sampling proceeds until approximately a five gram mass of particulate is gathered in the particulate filter. This may require *in situ* placement of the sampling apparatus such that samples are taken isokinetically, and the stack interior diameter is traversed for four or more hours. Thus the sampling instrument is continuously exposed to the hot gas plasma over a long sampling moment. In addition the hot gases also contain precursor compounds, chlorides, oxides of sulfur and HCl which may have an effect on the success of accurately sampling PCDD/Fs. Although Janssens, et al. (1992), Hagenmaier, et al. (1986), and EPA (1990a) have all but excluded the possibility that sampling under these conditions creates results by producing PCDD/Fs or destroying PCDD/Fs somewhere within the sampling train, the possibility that the method creates an illusion of the true V/P ratio cannot be excluded.

The above discussions have indicated the variability in the data and the uncertainty with the stack results of vapor/particle partitioning. For these reasons, these data will not be used to infer the V/P distribution of PCDD/Fs at the point of release from the stack.

3.2.4.3. *Vapor/particle partitioning of PCDD/Fs from ambient air sampling*

The measurement of PCDD/Fs in air under ambient conditions has only been achieved since the late 1980's. Although there may be some variations, the ambient air sampler usually consists of a glass fiber filter followed by a polyurethane foam (PUF) plug some distance downstream in the direction of air flow. Typically, these are active samplers utilizing electric pumps to regulate the flow of sampling air to some predetermined rate, usually in the range of 300 - 400 cubic meters of air over a 24-hour sampling period. Unlike the stack sampling method, the particulate filter is not artificially heated, nor is there a condensing component where the sampled air is quickly cooled in order to force condensation of vapor phase semi-volatile organics. Hence this sampling

scheme should be more useful to the interpretation of the vapor phase/particle phase partitioning of PCDDs/Fs under ambient conditions. Such observations are made on the basis of the segregation of the dioxin congener in the filter versus the PUF plug. The PUF plug has been verified to efficiently trap vapor phase semi-volatile pesticides and organic species (Wagel, et al., 1989), and the glass fiber filter uses filter paper with porosities to 0.1 microns to collect particulate matter. Because sampling of PCDD/Fs is not instantaneous (i.e. real time measurement), but requires 24-hour air sampling to assure a level of detection of about 0.03 pg/m^3, the interpretation of the V/P ratio should be construed as operationally defined rather than a direct empirical observation. Under this assumption, the V/P ratio is relative and not absolute. The following is a review of ambient air sampling providing sufficient information of the relative V/P partitioning of PCDD/F congeners at ambient conditions. Table 3-4 provides a summary of the V/P ratio inferred from these reports.

Oehme, et al. (1986) first described a method sensitive enough for the congener-specific measurement of PCDD/Fs at 0.1 pg/m^3 levels of detection in ambient air. Such low levels of detection introduced the possibility of taking ambient air samples in the vicinity of known combustion sources of PCDD/Fs to reliably establish an association with sack emissions. Oehme tested the performance and reliability of an ambient air sampler consisting of a glass fiber filter followed by a polyurethane foam plug. Ambient air was sampled over a predetermined period after first spiking the filter with a known concentration of $^{13}C_{12}$ labelled PCDD/F standards. This experiment was designed to determine the percent of the initial spiked labelled standard that could be recovered from the sampler after sampling 1000 m^3 of ambient air. The percent recovery of the standard was a measure of the collection and retention efficiency of the sampler. After collecting a sample, the particulate filter and the PUF plugs were extracted and analyzed separately. This was done in order to establish the particle phase and vapor phase partitioning of the PCDD/F congeners. Oehme demonstrated that the sampling method was capable of a high degree of reliability in sampling sub-part per trillion concentrations of PCDD/Fs as indicated by highly satisfactory recovery of the isotopically labelled standards in the apparatus, e.g., 88 - 102% recoveries. From the results of separately analyzing the filter and the PUF, Oehme postulated on the typical distribution of PCDD/Fs between vapor and particles in ambient air. They suggested that TCDF and PeCDF were mainly present in the vapor

Table 3-4. Percent distribution of dioxins and furans between vapor phase (V) and particulate phase (P) in ambient air as observed in ambient air sampling studies.

Source		4-CDD	5-CDD	6-CDD	7-CDD	8-CDD	4-CDF	5-CDF	6-CDF	7-CDF	8-ODF
Harless & Lewis 1992[1]	V	79	80	76	30	15	77	74	71	41	6
	P	21	20	24	70	85	23	26	29	59	94
Harless & Lewis 1992[1]	V	97	95	88	36	10	93	88	85	57	9
	P	3	5	12	64	90	7	12	15	43	91
Eitzer & Hites 1989	V	87	67	22	3	NR	91	63	27	8	NR
	P	13	33	78	97	NR	9	37	73	92	NR
Eitzer & Hites 1989	V	ND	67	17	0	0	98	73	45	20	0
	P	ND	33	83	100	100	2	27	55	80	100
Eitzer & Hites 1989	V	ND	80	33	4	0	88	67	23	5	0
	P	ND	20	67	96	100	12	33	77	95	100
Eitzer & Hites 1989	V	ND	67	20	0	0	88	57	30	0	0
	P	ND	33	80	100	100	12	43	70	100	100
Eitzer & Hites 1989	V	100	33	40	4	2	100	70	33	0	0
	P	0	67	60	96	98	0	30	67	100	100
Hunt & Maisel 1990	V	NR	NR	8	0	22	86	58	27	0	0
	P	NR	NR	92	100	78	14	42	73	100	100
Hunt & Maisel 1990; T=18°C	V	NR	NR	0	0	0	95	57	0	0	NR
	P	NR	NR	100	100	100	5	43	100	100	NR
Bobet, et al. 1990	V	ND	100	35	18	0	80	29	0	0	0
	P	ND	0	65	82	100	20	71	100	100	100
Bobet, et al. 1990	V	ND	ND	0	0	0	ND	ND	ND	ND	ND
	P	ND	ND	100	100	100	ND	ND	ND	ND	ND
Hites 1991 T=3°C	V	60	13	0	0	0	0	40	12	0	2
	P	40	87	100	100	100	100	60	88	100	98
Hites 1991 T=18°C	V	92	72	55	12	0	ND	72	70	7	0
	P	8	28	45	88	100	ND	28	30	93	100
Hites 1991 T=28°C	V	95	87	55	40	0	ND	100	62	22	2
	P	5	13	45	60	100	ND	0	38	78	98
Hunt & Maisel 1992	V	ND	ND	0	0	0	96	56	0	0	ND
	P	ND	ND	100	100	100	4	44	100	100	ND
Average	**V**	**87**	**69**	**30**	**10**	**4**	**83**	**65**	**35**	**11**	**2**
V/P	**P**	**13**	**31**	**70**	**90**	**96**	**17**	**35**	**65**	**89**	**98**

[1] V/P based on percent recoveries of isotopically labeled PCDD/F in filter or PUF and corrected to 100% with author's permission.
NR = not reported; ND = not detected; NR and NDs not included in average estimations

phase, and HxCDD, HxCDF as well as the less volatile isomers of HpCDF, HpCDD, OCDF, and OCDD, were mainly present in the particle phase. Oehme took over 60 ambient air samples with this device in rural, suburban, and urban areas of Europe.

Eitzer and Hites (1989) reported on the measurement of PCDD/Fs in the ambient

atmosphere of Bloomington, Indiana while using a similarly configured ambient air sampling method, the General Metals Works PS-1 sampler. Ambient air is drawn through a glass fiber filter followed by a polyurethane foam plug (PUF). This was a long-term study designed to investigate the daily and seasonal variability of the compounds in the ambient air as measured at a single location, and to examine the vapor-phase, particulate-phase partitioning of the chlorinated congeners under ambient conditions. Samples were taken at four different sites over a 2-3 day sampling period until 1500 to 2400 m^3 of ambient air volume had passed through the apparatus. Sampling was conducted monthly from August, 1985 through July, 1986. The quantitative method produced a limit of detection of the individual chlorinated congeners in the range of ~1 femtogram/m^3. Eitzer and Hites (1989) operationally defined the vapor-phase/particle-bound phase of the chlorinated congeners as any compounds found in the PUF plug and the glass fiber filter, respectively. The V/P ratio was subject to certain restrictions of the sampling method, which the authors identified as: 1. Particles smaller than 0.1 microns would pass through the filter paper of the glass fiber particulate filter and be absorbed into the polyurothane foam; 2. Diurnal temperature variation could cause particle-bound PCDD/Fs collected and retained in the filter to vaporize and be "blown-off" to the PUF plug by the passage of the sampled air stream; 3. At these relatively large sampling volumes of ambient air, it is possible that some breakthrough on the PUF plug occurs, and a portion of the PCDD/F sample is lost. The investigators were able to rule-out the latter condition through the addition of a XAD-2 resin trap after the PUF. This was one of the first reports on the congener-specific V/P partitioning in the ambient air under variable average ambient temperatures. Although they could find no seasonal effect on the total concentrations of PCDD/Fs, seasonal change in temperature did affect the V/P ratio. It was noted that during the warm summer months the V/P ratio was as great as 2:1, and during the cold winter months the V/P ratio could be <0.5. Thus, at warm temperatures most of the lower chlorinated congeners, e.g., mono through penta-chlorinated PCDD/Fs, were mostly found in the vapor phase and the hexa - octachlorinated congeners were mostly particulate-bound. The colder winter temperatures produced the effect of more eventually splitting the V/P distribution of the lower chlorinated species. The higher chlorinated congeners, e.g., hexa-, hepta-, and octa-PCDD/Fs, mostly were found to be particle-bound at both the warm and cold temperatures. These quantitative results of the V/P ratio of individual congeners at three

ambient air temperatures (3° C, 16 - 20° C, and >28° C) was again reported by Hites (1991), as shown in Table 3-8. Through these analyses, Eitzer and Hites (1989) and Hites (1991) found two dependant variables controlled the V/P ratio in ambient air: 1. the ambient air temperature; and 2. the vapor pressures of the PCDD/F congeners. The authors concluded that because the lower chlorinated compounds have higher vapor pressures, they will be found mostly in the vapor phase, and because the higher chlorinated congeners have lower vapor pressures, they will prevail in the ambient air bound to particulate matter.

Wagel, et al. (1989) reported on the performance of the General Metals Works PS-1 sampler for the collection and retention of PCDD/Fs while sampling ambient air. This sampler configuration consists of a quartz glass fiber filter followed by a polyurethane foam (PUF) plug, and the investigators added an XAD-2 resin cartridge after the PUF. The addition of the XAD was a check on whether breakthrough of any PCDD/F congeners occurred from the PUF during sampling. The PS-1 is the sampler most often used in the U.S. to quantify PCDD/Fs in air under ambient conditions. The protocol of this research was to use two samplers co-located. The particulate filter of one sampler was spiked with $^{13}C_{12}$-labelled PCDD/F congeners while the second sampler was used to provide background measurements of native (non-labelled) PCDD/Fs. Both units were operated to sample ambient air for 24-hours. The average ambient temperature during the sampling period was 24° C. Following the sampling the filter and PUF were removed and extracted according to published procedures (Wagel, et al., 1989). Performance of the PS-1 sampler was reported as percent recovery of the labelled standards initially spiked onto the particulate filter. The percent recovery was calculated by subtracting the background contributions from the total detected spike concentration and dividing by the concentration of the labelled standard initially added to the filter. The percent recoveries were reported in a range of from 85% to 124%, with an average recovery of 102%. This indicated a high degree of reliability in collecting and retaining PCDD/Fs in the sampler during the 24-hr sampling period.

A second series of experiments were conducted to investigate the distribution of PCDD/Fs within the sampling apparatus, e.g., the particulate filter versus the PUF plug, by extracting and analyzing the filter and PUF separately. Subject to the caveats previously discussed, the investigators made observations regarding the V/P ratio of PCDD/F

congeners. It was observed that PCDD/Fs having 7-8 chlorines were mostly detected in the particulate filter, and lower chlorinated species were mostly detected in the PUF. Wagel, et al. (1989) suggested that it was possible that the lower chlorinated congeners volatilized from the particulate filter (somewhat affected by the rate of flow of the sampled air volume), and then were retained by the PUF. Furthermore, Wagel, et al. (1989) warned that if results of separately analyzing the filter and PUF are used to derive a vapor phase and particle phase partitioning of the PCDD/Fs under ambient conditions, then this may give erroneously high estimates of the amount present in vapor phase.

Harless and Lewis (1992) have quantitatively evaluated the performance of the General Metals Works PS-1 sampler for the trace-level measurement of PCDD/Fs in ambient air, adding to the growing evidence that results are actual measurements and not an artifact of the sampling method. In this study, three samplers were used in the same general vicinity, and were operated for a 24-hour period until an air volume of 350 - 400 m^3 had passed through the system. The quartz glass fiber particulate filters of two of the samplers were then spiked with $^{13}C_{12}$ labeled PCDD/F congener with a known concentration after the 24-hour sampling period. The three samplers were then operated another 24-hours. The samplers were then shut down, and the filters and PUF plugs were removed and extracted and analyzed for PCDD/Fs separately according to prescribed procedures. A separate series of experiments involved precleaning the glass fiber particulate filters, and adding the isotopically labelled PCDD/F spike to the filter prior to sampling for seven days until about 2660 m^3 of ambient air had been sampled. Results of this study confirmed the accuracy and reliability of the PS-1 sampler for collecting and retaining PCDD/Fs at sub-ppt concentrations in ambient air. Performance was defined as the percent of the initial concentration of the labelled isotope recovered in the sampling apparatus following the operation over the predetermined sampling period. The average efficiency of recovery of the 0.8 ng $^{13}C_{12}$-1,2,3,4,-TCDD isotope that was spiked onto the filter prior to sampling was 91%, and similar efficiencies were observed for the recovery of the other labeled PCDD/Fs. Additionally, Harless and Lewis (1992) used the spiking system to observe the distribution of PCDD/Fs in the filter and the PUF after sampling 400 m^3 of ambient air. It was observed that most of the hepta-, and octa-CDD/Fs were retained by the glass fiber filter, indicating that these compounds were primarily particulate-bound, and most of the tetra-, penta-, and hexa-CDD/Fs volatilized and were

collected by the PUF plug. When partitioning was observed on a congener-specific basis, significant differences were observed in the V/P ratio, as shown in Table 3-4.

Hunt and Maisel (1990) reported on the ambient air measurement of PCDD/Fs in a northeastern U.S. urban coastal environment during the fall and winter seasons. Isomer-specific sampling was conducted with the General Metal Works PS-1 sampler in and around Bridgeport, Connecticut from November, 1987 through January, 1988. Nine sampling sessions consisting of a total of 43 ambient air samples were taken in this study. Each sampling session was conducted either over a 24-hour or 72-hour period until about 350 m^3 and 600 m^3 of air volume had passed through the sampler. Hunt and Maisel (1990) reported on the typical vapor phase/particle bound partitioning of individual congeners during cold ambient air temperatures. The V/P ratio was based on the results of separately analyzing the PUF plugs and the glass fiber particulate filters for the presence of PCDD/Fs. From these data, the investigators concluded that greater than 92% of all the congeners of PCDD/Fs were particulate bound (operationally defined as detected in the particulate filter). The 2,3,7,8-TCDD isomer was not detected in any of the 43 collected samples (reported limit of detection was 5-20 fg/m^3). The particulate bound distribution (reported as a percent of the detected concentration) for some of the other congeners were as follows: 2,3,7,8-TCDF = 93%; 1,2,3,7,8-PeCDF = 94%; 2,3,4,7,8-PeCDF = 99%; 1,2,3,4,7,8-HxCDF = 97%; 1,2,3,4,6,7,8-HpCDF = 100%; 1,2,3,6,7,8-HxCDD = 96%; and the 1,2,3,4,6,7,8-HpCDD = 92%. The vapor phase/ particle bound distribution observed in this study is probably controlled by the cold January temperatures from which these observations were derived (average temperature = -5° C).

At a later date, Hunt and Maisel (1992) conducted ambient air monitoring of PCDD/Fs in multiple locations in the warm climate of southern California for the State of California Air Resources Board (CARB). Ambient air samplers, e.g., the General Metal Works PS-1 sampler, were primarily placed in areas of high population density that contained known combustion sources of PCDD/Fs, but sites were also sampled that were considered removed from the influences of any local sources. The purpose of the study was to evaluate the congener-specific spacial distribution of PCDD/Fs in ambient air near environmental sources of the compounds, and in remote locations, in order to provide a baseline to evaluate population exposures within the region. Monitoring sites were established at eight locations in the South Coast Air Basin in and around the city of Los

Angeles. Nine discrete sample sets were collected from December, 1987 through March, 1989. The authors defined a sample set as consisting of five to seven stations at which one or two co-located samplers were operated. Microscale meteorological data was collected during sampling to include wind speed, wind direction, barometric pressure, and temperature. One sampling site was chosen to investigate the distribution of PCDD/Fs in ambient air where average ambient temperatures ranged from 16-20°C. This was done by the usual procedure of separately analyzing the filter and the PUF and making the assumption that what is detected in the glass fiber filter is particulate bound, and what is trapped in the PUF is in vapor phase. The authors noted that under these conditions, the V/P partitioning is operationally defined by the ambient air sampling system, and therefore may not be a true indication of the partitioning in the atmosphere. The majority of the hexa through octa CDD/F congeners were detected in the filter, and the authors observed that they were mainly associated with particulate matter. The authors found these observations were consistent with the V/P ratio observed by Eitzer and Hites (1989) in warm climate conditions. In addition, the authors noted that these observations give further evidence that vapor pressures of the specific PCDD/F compounds and ambient air temperatures strongly influence the V/P partitioning. Therefore the tetra- and penta-CDD/Fs are expected to predominate in vapor phase during warm seasons. However, during the cold temperatures of the winter season these congeners are expected to be primarily associated with particulate matter in the ambient air.

Bobet, et. al. (1990) reported the results of an ambient air monitoring network operated by Environment Canada to temporally measure PCDD/Fs in the ambient air in southwestern Ontario, Canada. The intent of the study was to monitor possible environmental impacts of a large refuse-derived fuel municipal waste combustor operational in the City of Detroit, Michigan. The ambient air monitoring network consisted on two stations, one in Windsor, Ontario, and the other located in the Walpol Island Indian Reservation 18 km to the northeast of Windsor. The former site was considered in an urban area near the expected point of maximum impact from the stack emissions from the MWC, and the other site was considered rural, and away from the influence of any stationary combustion source. PCDD/F samples were collected once every 24 days using an high-volume ambient air sampler consisting of a Teflon-coated glass fiber particulate filter and a PUF adsorbent trap. Ambient air was sampled over a 24-hour period from July,

1987 to August, 1988 with a total sample volume of 800 - 1000 m^3 of air. From August on, the samplers were operated over a 48-hour period, and 1600 - 2000 m^3 of air passed through the sampler. Mean total concentrations of PCDD/Fs were compared between the urban and rural sites, and Bobet observed that concentrations measured at the urban site were 4 -20 times greater than at the rural site. Additionally, the V/P partitioning of PCDD/Fs (as operationally defined by detection in the PUF verses detection in the filter) was investigated at both sampling stations. Bobet stated that the V/P may be influenced by "blow-off" of particulate from the filter to the PUF, and/or the passage of particulate matter <0.1 microns from the filter to the PUF, and if this is the case, then the vapor phase partitioning may be too great as interpreted by the method. Under these circumstances the authors suggested that the V/P partitioning should be considered as roughly representative of the vapor/particulate phases in the ambient air. On a total concentration basis, and on a total of 12 separate ambient air samples, the investigators found the following average percent vapor phase versus percent particle phase partitioning of the PCDD/F homologues at the Windsor, Ontario station: TCDD = not detected; PeCDD = 100% V/ 0% P; HxCDD = 35% V/ 65% P; HpCDD = 18% V/ 82% P; OCDD = 0% V/100% P; TCDF = 80% V/20% P; PeCDF = 29% V/ 71% P; HxCDF = 0% V/100% P; HpCDF = 0% V/ 100% P; OCDF = 0% V/ 100% P. At the rural Walpole Island station, no TCDD, PeCDD or TCDF - OCDF were detected in any of the 5 separate ambient air samples. All of the detected HxCDD, HpCDD and OCDD was found in the particulate filter indicating a V/P distribution of 0% V/ 100% P for these compounds. The authors did not report the average ambient air temperature at the two stations.

3.2.4.4. *Discussion of the vapor/particle partitioning in ambient air sampling studies*

The studies that have been reviewed here indicate the following:

- The high-volume ambient air sampler consisting of a glass fiber particulate filter and polyurethane foam absorbent trap is a reliable method for the collection and retention of PCDDs/Fs in ambient air.
- Current analytical methods assure detection limits, on a congener specific basis, of about 0.03 pg/m^3.
- Experiments involving the recovery of isotopically labelled PCDD/Fs within the

sampler after 24-hours operation indicate that the sampler does not create artifacts representative of either sample losses or the synthesis of dioxin.

- Because the sampler is not artificially heated or cooled, but is allowed to operate at existing ambient air temperatures during sampling sessions, the method can be used to imply the vapor phase and particle bound partitioning of PCDD/Fs in ambient air. This is accomplished by separately extracting and analyzing the glass fiber filter and the polyurethane foam for the presence of PCDD/F congeners.

- However, the V/P ratio interpreted from these results is operationally defined. This will only give an approximate indication of the V/P ratio since mass transfer between the particulate filter and the vapor trap cannot be ruled out. The particulate filter paper porosity is $\geq$ 0.1 microns, and therefore it is possible that aerosol particles with diameters $<$ 0.1 microns will pass through the filter and be trapped in the polyurethane foam plug. If this is the case, then the percent observed in vapor phase will be overestimated. The method involves ambient air sampling at a relatively high sample volume, around 300-400 m^3 of air, over a 24-hour period. It is possible that PCDD/Fs that are not sorbed to particulate matter captured in the filter may be volatilized by subtle changes in ambient temperature, and that PCDD/F in the vapor phase may be carried with the sampling air flow to the PUF sorbent trap. If this were to occur, then the interpretation of the percent of the PCDD/Fs partitioned to the vapor phase would be an over estimate. Unfortunately there are no empirical data that have demonstrated that any of these effects may actually occur.

3.2.4.5. *Theoretical prediction of vapor/particle partitioning of PCDD/Fs under ambient conditions*

Bidleman (1988) offers a theoretical construct for estimating the vapor phase/particle bound partitioning of PCDD/Fs in ambient air. Bidleman presents the theory that a portion of the semivolatile compounds found in ambient air are freely exchangeable between the vapor and particle phases. Bidleman defines a second portion, the nonexchangeable fraction, as the quantity that is strongly and irreversibly adsorbed to particulate matter, and is not at equilibrium with a corresponding vapor phase. Bidleman cites an earlier model by Junge (1977), a theoretical model based on adsorption theory, which mathematically described the exchangeable fraction of the semivolatile organic

compound adsorbed to aerosol particles as a function of solute saturation vapor pressure and total surface area of atmospheric aerosol particles available for adsorption. This is given by:

$$\phi = \frac{c\,S_T}{p + c\,S_T} \qquad (3\text{-}2)$$

where:

ϕ = adsorbed fraction, unitless

c = constant developed by Junge, atm-cm

S_T = total surface area of atmospheric aerosols in relation to total volume of air, cm^2/cm^3

p = solute saturation vapor pressure, atm^{-1}

Although Junge treated the term 'c' in Equation (3-2) as a constant, e.g., c = 1.7 E-4 atm-cm, Bidleman notes that it actually is variable and quite dependent on the chemical's sorbate molecular weight, the surface concentration of the chemical on aerosol particles (assuming monolayer coverage), and the difference between the heat of desorption from the surface of a particle and the heat of vaporization of the liquid-phase sorbate.

Bidleman (1988) poses the question as to whether it is the chemical's sub-cooled liquid vapor pressure (P_l) or the chemical's crystalline solid vapor pressure (P_s) that ultimately controls the rate of adsorption to aerosol particles. P_l and P_s are related according to Equation (3-3) developed by Bidleman (1988). The sub-cooled liquid vapor pressure is estimated by extrapolating below the melting point of the compound.

$$\ln\left(\frac{P_l}{P_s}\right) = \frac{\Delta S_f\,(\,T_m - T\,)}{R\,T} \qquad (3\text{-}3)$$

where:

P_s = crystalline solid vapor pressure, atm^{-1}

P_l = liquid sub-cooled vapor pressure, atm^{-1}

ΔS_f = entropy of fusion, atm-m^3/mole-deg K

R = universal gas constant, atm-m^3/mole-deg K

T_m = melting point, K

T = ambient air temperature, K

Bidleman notes that a satisfactory estimate of $\Delta S_f/R$ observed in other treatments of this subject is 6.79. This can be substituted for $\Delta S_f/R$ in Equation (3-3), and used as a constant. Bidleman argues that the use of P_l in Junge's equation, the sub-cooled liquid vapor pressure, makes the most accurate estimation of the vapor phase/particle bound partitioning of semi-volatile organic compounds in ambient air. To support his argument, Bidleman gives the example of the comparison of the application of the crystalline solid (P_s) versus the sub-cooled liquid (P_l) vapor pressure of TCDD in Junge's equation to estimate the V/P partitioning at an ambient air temperature of 20°C in an urban air shed. The P_s predicts a V/P partitioning of 0%/100%, whereas the P_l predicts a V/P of 20%/80%. Bidleman then compares these predictions against the V/P partitioning of TCDD as observed by Eitzer and Hites (1986) from the sampling of ambient air for PCDD/Fs in Bloomington, Indiana. His conclusions are that the prediction of the V/P ratio using the sub-cooled liquid vapor pressure of TCDD best fits the observed partitioning interpreted from directly measuring PCDD/Fs in ambient air, e.g., most tetra-, and penta-CDD congeners are prevalent in the vapor phase, and the higher chlorinated congeners are mainly particle bound (as operationally defined by the sampling method).

Calculations of ϕ (the fraction that is bound to particulate) from Equation (3-2) can be made on a congener-specific basis for the PCDD/Fs. The estimate of 1.7 E-4 atm-cm for the value c can be assumed from the work of Junge (1977) as cited by Bidleman (1988). The sub-cooled vapor pressures can be converted from the crystalline solid vapor pressures of the specific congeners found in Volume 2, Chapter 2, of this assessment, by applying Equation (3-3). The melting points of the specific congeners are also referenced in Chapter 2, Volume 2. Bidleman (1988) provides estimates of average total surface areas of aerosol particles relative to average total volume of air (cm^2/cm^3), the term S_T in Equation (3-2), citing a study by Whitby (1978). In addition, Whitby estimated the average total volume of aerosol particles per volume of air (V_t = cm^3 particles/cm^3 of air). Whitby's (1978) calculations varied according to the density of aerosol particles in the ambient air in different air sheds. These were as follows (units of S_T of cm^2/cm^3, V_T of cm^3/cm^3):

- Clean continental background

  S_T = 4.2 E-7
  V_T = 6.5 E-12

- Average background

  S_T = 1.5 E-6
  V_T = 3.0 E-11

- Background plus local sources

  S_T = 3.5 E-6
  V_T = 4.3 E-11

- Urban

  S_T = 1.1 E-5
  V_T = 7.0 E-11

Bidleman noted that if the average particle density of aerosol particles suspended in urban air is assumed to be 1.4 grams/cm^3, then the surface area of the average urban aerosol particles is 11 m^2/g, and the average total suspended particulate is 98 μg/m^3, following the calculations of Whitby. This was regarded as being in close agreement to the average monitored total suspended particulate of 79 μg/m^3 for 46 cities surveyed in the United States in 1976. Therefore, Whitby's values for S_T were judged by Bidleman to be adequate for purposes of calculating and estimating ϕ. If these assumptions are applied to the variables in Equation (3-2), the value for ϕ, the fraction of the PCDD/F congener reversibly adsorbed to particles in ambient air, can be calculated. Table 3-5 shows the calculated fraction of the congener that is bound to particles suspended in ambient air over a range of air shed classifications.

The values of the fraction of PCDD/Fs adsorbed to particulate in the ambient air can be compared against measurements of partitioning of the PCDD/Fs in ambient air as a simple means of validating these calculations. Bidleman (1988) compared theoretical predictions of the fraction of TCDD partitioning to suspended particulate in urban air to the measurements taken by Eitzer and Hites (1986) in an urban setting as a way of qualitatively addressing the "reasonableness" of his calculations. He found that the model's estimation of the fraction of PCDD/Fs bound to particles (based primarily on adsorption theory and using the sub-cooled liquid vapor pressure of 2,3,7,8-TCDD) did agree with the ambient measurements of Eitzer and Hites (1986) at 20°C. Therefore the model was judged to be reasonable in it's estimation of the physical state partitioning of PCDD/Fs in ambient air.

Table 3-5. Fraction of dioxins and furans calculated to partition to particles in various classifications of ambient air using the method of Bidleman (1988), Junge (1977), and Whitby (1978).

	Ambient Air Classification:			
	Clean Continental	Background	Background + Local Sources	Urban
2378-TCDD	0.09	0.26	0.45	0.72
12378-PeCDD	0.26	0.55	0.74	0.90
123478-HxCDD	0.60	0.84	0.93	0.98
123678-HxCDD	0.76	0.92	0.96	0.99
123789-HxCDD	0.86	0.96	0.98	0.99
1234678-HpCDD	0.85	0.95	0.98	0.99
OCDD	0.98	0.99	1.00	1.00
2378-CDF	0.05	0.15	0.29	0.57
12378-PeCDF	0.14	0.38	0.58	0.82
23478-PeCDF	0.22	0.50	0.70	0.88
123478-HxCDF	0.66	0.87	0.94	0.98
123678-HxCDF	0.64	0.86	0.94	0.98
123789-HxCDF	0.50	0.78	0.89	0.96
234678-HxCDF	0.63	0.86	0.93	0.98
1234678-HpCDF	0.73	0.91	0.96	0.99
1234789-HpCDF	0.83	0.94	0.98	0.99
OCDF	0.98	0.99	1.00	1.00

3.2.4.6. *Discussion of vapor/particle partitioning*

This subsection has reviewed stack testing data, ambient air sampling data, and theory rooted in basic physical chemistry that either imply, directly deduce or theoretically calculate the V/P partitioning in the ambient air. From this review it is generally concluded that:

1. The stack test methods in use today to monitor and measure the concentration of PCDD/Fs emitted to the air from combustion sources do not provide a credible basis for assuming the vapor phase and particle bound partitioning at the point of release. There is no consistent pattern to the interpretation of V/P based on where the PCDD/F segregates in the instrument, e.g., the glass fiber filter or the XAD resin. Factors that may contribute

to this are: the relatively long residence time spent traversing the stack interior; the probe to the instrument is inserted into a relatively hostile environment of the hot combustion gas; the static temperature of the particulate filter caused by heating the particulate filter housing; the fact that located between the particulate trap and the vapor trap is a condensing section consisting of glass tubing surrounded by an ice bath.

2. On the other hand, the ambient air sampling methods do give an approximate indication of the V/P ratio that seems to be responsive to changes in temperature, and degree of chlorination of the PCDD/Fs. This is in accordance with what would be expected from their individual vapor pressures. There is no artificial heating or cooling of any component of the sampler. The sampler is exposed to actual temperature, pressure, and humidity of the ambient air. This removes the possibility that the vapor phase-particle bound partitioning, operationally defined as the compound segregating to the particulate trap and vapor trap, is actually an artifact induced by artificial heating and cooling within the system. Therefore the methods present a realistic picture of partitioning under variable ambient conditions. However, the method has certain limitations that currently prevent deriving a true measurement of V/P partitioning in the ambient air. Among these limitations are:

a. The glass fiber filter designed to capture and retain particulate matter has filter pours down to 0.1 μm diameter. Particles less than this diameter will pass through the filter and be retained in the polyurethane foam vapor trap downstream. If this is the case, the amount of PCDD/Fs observed to be particle bound would be underestimated, and the amount observed to be in vapor phase would be overestimated.

b. The relatively high sampling volume passed through the system (200 to 400 m^3 of air per 24 hours) may redistribute the more volatile congeners from the filter to the absorbent trap by a process known as 'blow-off'.

3. Until sampling methods are improved and modified such that they give results that indicate the true V/P ratio of PCDD/Fs in ambient air, the theoretical construct described by Bidleman (1988; and detailed above) is used to calculate the V/P ratio for purposes of air dispersion and deposition modeling of emissions from the hypothetical case demonstrated in Chapter 5. Key advantages to the theoretical approach are that the theoretical construct relies on current adsorption theory, considers the molecular weight and the degree of halogenation of the congeners, uses the boiling points and vapor

pressures of the congeners, and uses the availability of surface area for adsorption of atmospheric particles that correspond to a variety of ambient air shed classifications having variable particulate matter densities.

3.2.5. Estimation of the Concentration of Dioxin-Like Compounds in Incineration Ash

The ash that is collected by the particulate matter control device preceding the stack is known conventionally as fly ash. Fly ash is the airborne combustion residue from burning the fuel. Bottom ash is the ash residue that results from the combustion of the organic solids within the combustion chamber, and usually is collected below a grate system used to convey combustible fuels into the fire zone, or is collected at the bottom of the combustion chamber. In general, there are many factors that may influence the formation of particulate matter known as fly ash from the incineration of organic wastes. Among these factors are: the heating value of the incinerated material (BTU/kg), the percent moisture in the fuel, the furnace temperature and combustion efficiency, and the efficiency of particulate matter capture by the air pollution control device (Brunner, 1984; OTA, 1989). Fly ash, and not the bottom ash, contains most, if not all, the dioxin-like congeners. This can be explained by the synthesis of dioxin that occurs on the reactive surface of fly ash. Therefore, the following estimation of the ash generation rate, and the concentration of dioxin-like compounds in the ash particles, will focus solely on fly ash to the exclusion of bottom ash. Because bottom ash is mostly free of these contaminants, and is about 10 to 100 times the mass of fly ash, the mixing of fly ash with bottom ash will dilute the concentration of dioxin by about a factor of 10 - 100.

Estimation of the mass of fly ash generated, and concentration of dioxin-like compounds can be determined by the following (if no actual data exists):

1. Determine the mass of fly ash generated per day at the facility. This can be estimated from the percent control of particulate matter (PM) of the air pollution control device (APCD) installed at the facility. For example, if a combustor emits 0.5 kg of particulate matter per hour of operation, then 12 kg of PM is released from the stack in one day. If PM is controlled by 99%, then this rate of emission represents one percent of the fly ash generated by the combustion process. The amount of fly ash that is collected by the APCD would be 100 times the amount emitted, or 1200 kg/day.

2. Estimate the congener-specific concentration of PCDD/Fs contained in the

collected fly ash. This is done by assuming that what is prevented from exiting the stack is contained in the fly ash collected by the pollution control device. If, for example, 10 picograms PCDD/F is emitted per gram of PM from the facility per day, and the APCD reduces emissions by 99%, then 100 times more PCDD/F concentration, or 1000 picograms PCDD/F per gram fly ash, would be in the collected fly ash. If the concentration of dioxin in emitted fly ash and the percent control of dioxin are known, then the concentration of dioxin in the mass of collected fly ash can be estimated. It is important to make such estimations in order to evaluate the potential environmental impact of ash management practices before the operation of the facility, and to select appropriate disposal practices to preclude future adverse conditions from arising.

3. Now estimate total mass, including fly and bottom ash, and final concentrations. If bottom ash mass is estimated at ten times fly ash, than the total ash generated in this example would be 1200 + 1200*10 = 13,200 kg/day. If fly and bottom ash were mixed for disposal, which is common, than the average concentration of the total ash would be one-tenth that estimated for fly ash.

The hypothetical example in Chapter 5 does not assess impacts associated with ash disposal. Section 4.4.3.1 of Chapter 4 describes procedures for estimating impacts from ash disposal given ash concentrations and mass generated.

3.3. AIR DISPERSION/DEPOSITION MODELING OF THE STACK GAS EMISSIONS OF DIOXIN-LIKE COMPOUNDS

It has been customary for EPA to use air dispersion/deposition models to estimate the atmospheric transport, the deposition flux, and the ambient air concentrations of specific pollutants attributable to smokestack emissions from an industrial combustion source. Air dispersion models are mathematical constructs that approximate the physical and chemical processes occurring in the atmosphere that directly influence the dispersion of gaseous and particulate emissions from smokestacks of stationary combustion sources. These models are computer programs encompassing a series of partial differential and algebraic equations to calculate the dispersion and deposition of the emissions. Concentration and deposition isopleths of the pollutants discharged from the stack are computed at specified distances from the smokestack. These quantities are used to estimate the magnitude of potential exposures to the human receptor.

Numerous dispersion/deposition models have been developed. This document focuses on the COMPDEP model. COMPDEP was first described in EPA (1990b). Recent revisions to the computer code were made, and this newer version was used to generate the results for the hypothetical incinerator of this assessment. A principal change that was made allows the user to define 10 particle size categories. Earlier versions allowed only 3 size categories. Use of COMPDEP is this assessment is not intended to imply that COMPDEP is the only acceptable model to use in the analysis of ambient air concentrations, and wet and dry deposition.

Subsection 3.3.1 below presents an overview of the dispersion and deposition algorithms in the COMPDEP model. Subsection 3.3.2 discusses dry deposition fluxes, including pertinent assumptions made in the application of the COMPDEP model for the hypothetical combustor demonstrated in Chapter 5. Subsection 3.3.3 discusses particle size distributions for emitted particles. Subsection 3.3.4 discusses wet deposition, again noting key assumptions for the hypothetical combustor. Subsection 3.3.5. closes the section with guidance indicating that the COMPDEP model should be run twice for assessments - once to model particle fate and transport, and once for the vapor phase.

3.3.1. Basic Physical Principles Used to Estimate Atmospheric Dispersion/Deposition of Stack Emissions

Air dispersion/deposition models use the basic physical processes of advection, turbulent diffusion, and removal to estimate the atmospheric transport, resulting ambient air concentration, and settling of particles. Advection describes the physical movement of the air pollutants by the horizontal movement of wind. Turbulent diffusion is the "spreading" of the emissions plume with distance from the stack due to multi-directional fluctuations in air movement. Removal refers to mechanisms which remove emissions from the atmosphere. This can be caused by the force of gravity exerted on the particle mass, Brownian movement of aerosol particles, and scavenging of particles. Scavenging is the removal of particles or vapors by precipitation.

COMPDEP contains modifications of the Industrial Source Complex model (Short-Term version), and COMPLEX I to incorporate algorithms to estimate dispersion, and resulting ambient air concentrations and wet and dry deposition flux. COMPLEX I is a second level screening model applicable to stationary combustion sources located in

complex and rolling topography (EPA, 1986a). The COMPDEP model was developed by EPA to provide estimates of air concentrations and deposition rates of the stack emissions of contaminants from industrial sources located in varied terrain (e.g., from simple to complex terrain). Simple and complex terrain are defined as topogragraphy that is either below or above the effective stack height of the source (Turner, 1986). To account for pollutant deposition, the concentration algorithms in COMPLEX 1 were replaced with those from the Multiple Point Source Algorithm with Terrain Adjustments Including Deposition and Sedimentation (MPTER-DS) model (Rao and Sutterfield, 1982). The MPTER-DS algorithms incorporate the gradient transfer theory described by Rao (1981), and are extensions of the traditional Gaussian plume algorithms. The dispersion algorithms contained in the Industrial Source Complex, Short-term version (ISCST), have been incorporated in COMPDEP to analyze ground-level receptors located below the height of the emission plume (EPA, 1986b). COMPDEP uses the generalized Briggs (1975, 1979) equation to estimate plume-rise and downwind dispersion as a function of wind speed and atmospheric stability. A wind-profile exponent law is used to adjust the observed mean wind speed from the measurement height to the emission height for the plume rise and pollutant concentration calculations. The Pasquill-Gifford curves are used to calculate lateral and vertical plume spread (EPA, 1986a). These curves are based on Pasquill's definitions of atmospheric stability classes, e.g., extremely unstable, moderately unstable, slightly unstable, neutral, slightly stable, and moderately stable, that correspond to various intensities of solar radiation and wind speeds (Seinfeld, 1986). The incorporation of these two basic models into COMPDEP permits analysis of a source located in all types of terrain.

3.3.2. Estimation of Dry Surface Deposition Flux

Dry deposition is one removal process that is simulated by the COMPDEP model. Dry deposition refers to the transfer of airborne particulate matter to the earth's surface (including water, soil, and vegetation) whereby it is removed from the atmosphere. The deposition of vapor-phase contaminants is not considered in the COMPDEP model. The general processes controlling the transfer of particulate from some height above the surface through the surface layer down to the immediate vicinity of the surface are the forces of gravity and turbulent diffusion (Seinfeld, 1986), followed by diffusion through

the laminar sub-layer (defined as a thickness of 10^{-1} to 10^{-2} cm) to the surface. The rate at which contaminants sorbed to atmospheric particulates are removed by the physical forces of gravity, atmospheric turbulence, and diffusion is termed the "deposition flux" (Kapahi, 1991), and is mathematically represented by F_d. The deposition flux, F_d, is a function of the concentration of the chemical contaminant on particulate, C_o, and the settling velocity of the contaminated particles can be defined by:

$$F_d = V_d C_o \qquad (3-4)$$

where:

F_d = dry deposition flux of contaminants sorbed to particles, $\mu g/m^2$-sec

V_d = the particulate settling velocity, m/sec

C_o = concentration of pollutant on settling particles, $\mu g/m^3$

In general, Chamberlain and Chadwick (1953) first defined the settling velocity, V_d, as the quotient of the deposition flux, F_d, divided by the airborne concentration, Co:

$$V_d = - \frac{F_d}{C_o} \qquad (3-5)$$

Sehmel (1980) noted that the value for F_d in Equation (3-5) has a minus sign because the downward flux is negative, whereas the deposition velocity is positive. By this relationship, Chamberlain and Chadwick (1953) first introduced the concept of plume depletion: as the plume emission is dispersed with downwind distance from the stack, the deposition flux decreases with distance from the source.

The basic dynamics in the physics of modeling dry deposition have not changed significantly since Sehmel's (1980) comprehensive scientific review. The factors that most influence the predicted deposition flux can be divided as being either meteorological influences, or the influences of the properties of the pollutant under analysis. Meteorological influences include the friction velocity, represented as μ_*, and the aerodynamic surface roughness, represented as z_o. These terms are used to describe the

wind speed profile above the Earth's surface. In most cases, the analyst uses a graphical procedure to determine values for μ_* and z_o. If the logarithm of wind speed is plotted for near neutral atmospheric stability as a function of height from the surface, then the values for the constant z_o is fitted to a straight line on a semi-logarithmic scale. This can be described mathematically by Equation (3-6). In most cases, the friction velocity is a percentage of the wind speed.

$$\mu = \left(\frac{\mu^*}{\lambda}\right) \ln \left(\frac{z + z_o}{z_o}\right) \qquad (3\text{-}6)$$

where:

μ = the measured wind speed, cm/sec

μ_* = the friction velocity, cm/sec

z = the measured height above the surface, cm

z_o = surface roughness length, cm

λ = von Karman's constant, approx. = 0.4

As a general rule, particles greater than 30 micrometers (μm) in diameter will be removed from the atmosphere primarily by the force of gravity, whereas particles less than 30 μm will be removed primarily by atmospheric turbulence. The deposition flux for the smaller particles is influenced by many factors, including: the distribution of particles by diameter and density; assumptions of atmospheric turbulence; the friction of the ground surface and the height of the stack release of emissions. Deposition flux is also affected by the partitioning properties of the pollutant. These properties will determine how much of the pollutant is sorbed to the particle and how much is in the vapor phase. A detailed list of the many factors that can affect dry deposition is shown in Table 3-6.

The COMPDEP estimates dry deposition flux based on empirical associations developed by Sehmel (1980) and Sehmel and Hodgson (1978) relating the deposition flux to the deposition velocity of particles. The downward motion represented by deposition velocity is controlled by the gravitational settling velocity, atmospheric resistance, surface resistance and the atmospheric surface friction layer. This model assumes that a fraction of the particulate comes into contact with the ground surface by the combined processes

Table 3-6. Factors that influence the dry deposition removal rate in the atmosphere.

Micrometeorological Variables	Characteristics of Particles	Characteristics of Gases	Surface Variables
Aerodynamic roughness	Agglomeration	Chemical Activity	Accommodation:
Mass transfer of	Diameter	Diffusion effects	Exudates
Particles	Diffusion effects	Brownian	Trichomes
Gases	Brownian	Eddy	Pubescence
Heat transfer	Eddy	Partial pressure in equilibrium with the surface	Wax
Momentum transfer	Particle	Solubility	Biotic surface
Atmospheric stability	Momentum		Canopy growth
Diffusion	Heat		Dormant
Friction velocity	Electrostatic effects		Expanding
Inversion layer	Attraction		Senescent
Pollutant concentration	Repulsion		Canopy structure
Relative humidity	Gravity settling		Areal density
Seasonal variation	Hygroscopicity		Bark
Solar radiation	Impaction		Bole
Surface heating	Interception		Leaves
Temperature	Momentum		Porosity
Terrain effects	Physical properties		Soils
Turbulence	Resuspension		Stem
Wind velocity	Solubility		Type
Zero plane displacement effect	Thermophoresis		Electrostatic properties
Mass transfer of			Water
Particles			Pollutant penetration of canopy
Gases			
Heat transfer			
Momentum transfer			

Source: Adapted from Sehmel (1980).

of gravitational settling, atmospheric turbulence, and Brownian diffusion. The COMPDEP model contains enhancements to calculate dry deposition flux using a computerized routine developed by the State of California Air Resources Board (CARB, 1986). The CARB algorithms represent Sehmel's (1980) empirical relationships for transfer resistances as a function of particle size, density, surface roughness, and friction velocity. In the CARB model, integrated resistances to mass transfer are computed within two layers. In the first layer, which extends from one centimeter to one meter above the surface, atmospheric turbulence dominates mass transfer. In the second layer, which lies within one centimeter of the surface, the resistance to mass transfer is derived from particle deposition

measurements that were taken in a wind tunnel over various surfaces using mono-dispersed particles (Sehmel, 1980; Sehmel and Hodgson (1978).

Despite what is currently known about the physical and chemical processes that influence the final deposition flux of particles released from a stationary combustion source, a more thorough understanding of the influence of particle size on deposition velocity is needed. In Sehmel's (1980) review of settling velocities corresponding to particle diameter it was noted that the range of values spanned several orders of magnitude. This complicates efforts to make generalizations of V_d by particle diameter for air modelling purposes. Although dry particle deposition velocities have been estimated from both field studies and laboratory experiments, derived velocities are limited and highly uncertain. This is due largely to the complex and variable array of factors that can influence the rate of deposition (as depicted in Table 3-6).

In the general classification of particles, particles < 2.5 micrometers (μm) in diameter are referred to a "fine particles", and those > 2.5 μm are "coarse particles". Sehmel (1980) offers the most current review of dry deposition settling velocities for a variety of depositing materials having a broad range of particle diameters. This summary appears in Table 3-7.

For the example application of the COMPDEP model in Chapter 5, particles less than 2 μm were represented by a 1 μm size and were calculated by COMPDEP to deposit at a velocity of about 0.007 cm/sec. Particles between 2 and 10 μm were represented by a 6.78 μm size and were calculated to deposit at a velocity of about 0.3 cm/sec. Finally, particles greater than 10 μm were represented by a 20 μm size and were calculated to deposit at a velocity of 2.5 cm/sec, although the variable ambient air temperature resulted in more variable calculations. The derivation of these particle size representations is given in the next section.

3.3.3. Estimation of the Particle Size Distribution in the Stack Emissions

Certain inferences must be made concerning the distribution of particulate differentiated on the basis of particle diameter before the COMPDEP program can predict deposition flux of the dioxin-like congeners. The diameters of small particles comprising particulate matter in stack emissions are usually measured in units of one millionth of a meter (micrometer, commonly called micron, abbreviated by the letters μm. Unfortunately,

Table 3-7. A summary of dry deposition velocities for particles.

Depositing Material	Particle D Diameter (μm)	Deposition Surface	Deposition Velocity (cm/s)
Particles	0.03-30	Grassland	10^{-3}-40
Pollen	20	Grassland	4.5
	32-35	Grassland	9.9
	90-100	Grassland	20
Natural aerosol	1-10	Grass shard	0.8
Pb Auto exhaust			

Source: Sehmel (1980).

few studies describe the distribution of particulate matter entrained in the emissions from various combustion technologies broken down and fractionated by particle diameter. The distribution of particulate matter by particle diameter will differ from one combustion process to another, and is greatly dependent on such factors as: 1) the efficiency of various air pollution control devices, 2) the composition of the feed/fuel, 3) the design of the combustion chamber, 4) the amount of air used to sustain combustion, and 5) the temperature of combustion. Table 3-8 gives an example of a particle diameter distribution as measured at a stack on an incinerator. This example distribution will be assumed for the hypothetical incinerator.

Although the COMPDEP model can simulate up to 10 particle size categories, only three particle sizes are assumed for the model runs of the demonstration in this assessment. These three sizes are generalized from the data in Table 3-8:

• **Category 1:** $\leq 2\ \mu$m • **Category 2:** > 2 to $\leq 10\ \mu$m • **Category 3:** $> 10\ \mu$m

After selecting the particle size distribution, it is necessary to calculate the mass emission rate of the particulate-bound congeners of PCDDs/Fs by particle size category. This is accomplished by calculating the proportion of surface area (available for adsorption of PCDD/Fs) for a given particle diameter. The ratio of the surface area to volume is

Table 3-8. Generalized particle size distribution (μm), and proportion of available surface area, in particulate emissions from incineration.

Particle Diameter (μm)[a]	Particle Radius (μm)	Surface Area/ Volume	Fraction of Total Weight	Proportion Available Surface Area	Fraction of Total Surface Area
>15.0	7.50	0.400	0.128	0.0512	0.0149
12.5	6.25	0.480	0.105	0.0504	0.0146
8.1	4.05	0.741	0.104	0.0771	0.0224
5.5	2.75	1.091	0.073	0.0796	0.0231
3.6	1.80	1.667	0.103	0.1717	0.0499
2.0	1.00	3.000	0.105	0.3150	0.0915
1.1	0.55	5.455	0.082	0.4473	0.1290
0.7	0.40	7.500	0.076	0.5700	0.1656
<0.7	0.40	7.500	0.224	1.6800	0.4880

Total surface area: 3.4423 μm^2

Notes: a. Geometric mean diameter in a distribution. Distribution from EPA (1980).

proportional to the ratio of the surface area to weight for a particle with a given radius. Multiplying this proportion times the weight fraction of particles of a specific diameter (μm) gives a value that approximates the amount of surface area available for chemical adsorption. The surface area to volume ratio can be described as follows:

(a) Assume aerodynamic spherical particles.

(b) Specific surface area of a spherical particle with radius,r:

$$S = 4 \pi r^2$$

(c) Volume of spherical particle with radius, r:

$$V = 4/3 \pi r^3$$

(d) The ratio of surface area to volume is:

$$S/V = 4 \pi r^2 / (4/3 \pi r^3)$$

$$S/V = 3/r$$

Dividing the surface area for each particle category by the total available surface area for all particles gives an estimation of the fraction of total area on any size particle. Multiplication of the emission rate of the dioxin-like congener times the fraction of available surface area will estimate the emission rate of the pollutant per particle size. The fraction of total surface area was computed for the three particle size categories. The fraction of total surface areas for the ranges of particle diameters are summed with each particle size category to represent a single fraction of total surface area for the given particle size category, as follows:

- Particulate category 1: fraction of total surface area = 0.875
- Particulate category 2: fraction of total surface area = 0.095
- Particulate category 3: fraction of total surface area = 0.030

Thus by these assumptions, 87.5% of the emission rate of the dioxin-like congener is calculated to be associated with particles less than $\leq$ 2 μm in diameter, 9.5% of the emission is associated with the particle size of > 2 to $\leq$ 10 μm, and only 3% of the emission is associated with particles greater than 10 μm. To assist in deposition modeling of the emissions from the hypothetical incinerator, the particle size distribution is further simplified by assuming a median particle diameter to represent each broad particle size category, as follows:

- Particulate category 1 = 1 μm particle diameter
- Particulate category 2 = 6.78 μm particle diameter
- Particulate category 3 = 20 μm particle diameter

3.3.4. Estimation of Wet Deposition Flux

Wet deposition occurs by precipitation (rain, hail, snow) physically washing out the chemically contaminated particulate and vapors from the atmosphere. Vapor scavenging is not yet well understood and is not addressed in the COMPDEP model. The remainder of this discussion refers only to the wet deposition of particles.

Wet deposition flux depends primarily on the fraction of the time precipitation occurs and the fraction of material removed by precipitation per unit of time by particle size. Based on these relationships, scavenging coefficients were developed by Cramer (1986) for varying types and intensities of precipitation relative to different particle

diameters by incorporating the observations of Radke, et al. (1980) in a study of scavenging of aerosol particles by precipitation. The principal assumptions made in computing wet deposition flux are: (1) The intensity of precipitation is constant over the entire path between the source and the receptor; (2) The precipitation originates at a level above the top of the emission plume so that the precipitation passes vertically through the entire plume; (3) The flux is computed on the bases of fraction of the hour precipitation occurs as determined by hourly precipitation measurements compiled by the National Weather Service. The remaining fraction (1-f) is subject only to dry deposition processes. Thus no dry deposition occurs during hours of steady precipitation, and dry deposition occurs between the periods of precipitation. Wet deposition flux is estimated using Equation (3-7), in which case the total weight of material in settling category n results from the washout by rain at a distance x downwind from the stack release:

$$WDep(n) = f \frac{\Lambda(n,j)\ \phi_n\ K\ Q}{\sqrt{2\pi}\ \sigma_y\ u(h)} \exp\{-\Lambda(n,j)\ (\frac{x}{u(h)})\} \exp\{-1/2\ (\frac{y}{\sigma_y})^2\}$$

(3-7)

where:

WDep(n)	=	wet deposition flux, g/m^2-sec
f	=	fraction of time precipitation occurs (fraction of hour)
Λ(n,j)	=	fraction of material removed per unit time in the nth particle size category and jth precipitation intensity category, also known as the scavenging coefficient, sec^{-1}
ϕ_n	=	fraction of total source material in the nth particle size category
K	=	units conversion factor
Q	=	emission rate, g/sec
σ_y	=	standard deviation of crosswind deposition distribution, m
u(h)	=	wind speed at stack height, m/sec
x	=	downwind distance from source to receptor, m
y	=	crosswind distance from source to receptor, m

The relationship between the scavenging coefficient, $\Lambda(n,j)$, and the particle size and precipitation intensity was derived from the review of wet deposition studies of aerosol particles by Cramer (1986). Table 3-9 displays the scavenging coefficients assigned to the generalized particle size categories and precipitation events used for computing estimates of wet deposition in the application of the COMPDEP for the demonstration scenarios in Chapter 5. The value of f in Equation (3-7) is applied to each hour of reported precipitation as determined from the National Weather Service meteorological observations. In computing the dry deposition which occurs between the periods of precipitation, a factor of (1-f) was used to estimate the fraction of the material that is subject to dry deposition. The same scavenging coefficient was used for both rainfall and snowfall.

3.3.5. The Requirement to Run the COMPDEP Model Twice

In order to provide estimates of ambient air concentrations of vapor-phase and particle-phase dioxins, combined with estimates of wet/dry particle deposition flux, it is necessary to run the COMPDEP model twice. Both model runs should assume a "unit emissions release rate", e.g., 1 g/s. Results from these unit runs can easily be transformed to final outputs given assumptions on emissions in vapor and particle forms. Two assumptions are required, as outlined above. One is the total emission rate of the compound, in units of mass/time (g/sec), and the second is the vapor/particle partitioning of this total emission. The two runs are:

- **Run 1: To estimate vapor-phase concentration of the contaminant in ambient air.**

COMPDEP should be run with the wet/dry deposition switches turned to the "off" position. This is to isolate the ambient air concentration of the contaminant in vapor-phase from the calculation of wet and dry particle deposition flux. This inactivates a plume depletion equation that subtracts out losses in ambient air concentration due to particle deposition. What is left are the Gaussian dispersion algorithms.

With the "unitized" emission rate, one can reconstruct the actual predicted ambient air concentration ($\mu g/m^3$) of vapors by multiplying the "actual" vapor-phase emission rate (g/s) by the "unitized" modeling result. For example, let the actual stack gas emission rate of total (vapor plus particle components) contaminant be $1x10^{-5}$ g/s, and the V/P ratio (expected under ambient conditions) be 60%V/40%P. Then the "actual" emission rate of the vapor-phase portion of the contaminant is calculated to be $6x10^{-6}$ g/s ($1x10^{-5}$ g/s *

Table 3-9. Wet deposition scavenging coefficients per particle diameter category (micrometers), expressed per second of time.

Precipitation Intensity	Particle Diameter Category (μm)		
	≤ 2	> 2 and ≤ 10	> 10
Heavy	1.46 E-3	4.64 E-3	9.69 E-3
Moderate	5.60 E-3	8.93 E-4	9.69 E-3
Light	2.20 E-4	1.80 E-4	9.69 E-3

Notes: Light = trace to 0.10 in/hr; Moderate = 0.11 to 0.30 in/hr; Heavy = > 0.30 in/hr

0.6). If the "unitized" ambient air concentration at the ground-level receptor is estimated by the COMPDEP model to be $1x10^{-8}$ $\mu g/m^3$ (i.e., this concentration is predicted with a unit emission rate of 1 g/s), then the "actual" predicted air concentration at that receptor can be estimated as:

$$(6x10^{-6}\ g/s \div 1\ g/s) * 1x10^{-8}\ \mu g/m^3 = 6x10^{-14} \mu g/m^3$$

- **Run 2: To estimate wet and dry particle deposition flux, and the ambient air concentration of the contaminant that is particle-bound.**

COMPDEP should be run with the wet/dry particle deposition switches turned to the "on" position, and using a "unit emission rate" of 1 g/s. This second run is considered a simulation of particle-bound contaminant only. Outputs of this run include unitized deposition rate and unitized ambient air concentrations of particles.

Like the vapor-phase run, the "actual" deposition flux (g/m^{-2} -yr) and "actual" particle-phase airborne concentrations can then be determined by multiplying the "actual" emission rate (g/s) of the particle-bound portion of the total contaminant emissions by the "unitized" modeling result at the ground receptor. For example, let the "actual" emission rate of the particle-bound portion of the contaminant be $4x10^{-6}$ g/s, and the "unitized" dry deposition flux at the ground receptor be $1x10^{-5}$ g/m^2-yr. Then the "actual" predicted dry

deposition flux is $4x10^{-11}$ g/m^2 ($4x10^{-6}$ g/s ÷ 1 g/s * $1x10^{-5}$ g/m^2-yr). Using this same procedure, this second run provides the airborne concentration of contaminants bound to particles (μg/m^3).

Inhalation exposures are estimated as the sum of vapor and particle phase concentrations. Air-to-plant transfers require the vapor phase concentrations for vapor transfers and the particle-phase depositions. The air-to-soil algorithm requires particle phase depositions.

3.4. RESULTS OF THE AIR DISPERSION MODELING OF CONGENER-SPECIFIC EMISSIONS FROM THE HYPOTHETICAL ORGANIC WASTE INCINERATOR

The preceding subsections have presented general procedures for conducting air modeling of the emissions of dioxin-like compounds from the stack to the ground, starting with estimation of emission factors, vapor/particle partitioning at the stack, and proceeding to atmospheric dispersion and deposition using EPA's COMPDEP model. Where appropriate, previous subsections have also included discussion on the assumptions and the selection of parameters for the hypothetical incinerator which is demonstrated in Chapter 5. For example, Section 3.2.3 provided the emission factors that were used in this demonstration. This section will provide all other details of the hypothetical incinerator and provide the final results of the COMPDEP model simulations.

To reiterate, the purpose of the hypothetical construct is to help readers understand how to apply these principles to the air dispersion modeling and analysis of dioxin emissions from the source. Therefore, generalizations should not be made on the basis of this example regarding the magnitude of the emissions release and associated environmental impact.

A completely hypothetical incinerator was devised to serve as the example. Accordingly, a hypothetical, but realistic, incineration technology, facility size, stack height, and geographical location was selected. The hypothetical incineration facility has an assumed total daily capacity of 200 metric tons of organic waste materials. The emission rates of specific congeners of PCDD/Fs were derived from the stack testing and monitoring of emissions from a modern incinerator of this size. These emissions are expressed in units of g/sec, and are shown for the hypothetical incinerator in Table 3-10.

In constructing the hypothetical case, the following was defined: stack height;

Table 3-10. Emission of PCDD/Fs (g/sec) from the hypothetical incinerator.

Congener	Emissions grams/sec	Vapor grams/sec	Particulate grams/sec	V/P Ratio
2378-TCDD	9.23E-11	5.08E-11	4.15E-11	.55/.45
Other TCDD	2.00E-09	1.10E-09	9.00E-10	.55/.45
12378-PeCDD	1.93E-10	5.02E-11	1.43E-10	.26/.74
Other PeCDD	1.91E-09	4.97E-10	1.41E-09	.26/.74
123478-HxCDD	2.50E-10	1.75E-11	2.33E-10	.07/.93
123789-HxCDD	3.63E-10	7.26E-12	3.56E-10	.02/.98
123678-HxCDD	3.30E-10	1.32E-11	3.17E-10	.04/.96
Other HxCDD	3.19E-09	1.28E-10	3.06E-09	.04/.96
1234678-HpCDD	3.27E-09	6.54E-11	3.20E-09	.02/.98
Other HpCDF	6.03E-09	1.21E-10	5.91E-09	.02/.98
OCDD	6.73E-09	6.73E-11	6.66E-09	.01/.99
2378-TCDF	6.03E-09	4.28E-09	1.75E-09	.71/.29
Other TCDF	3.83E-08	2.72E-08	1.11E-08	.71/.29
12378-PeCDF	3.87E-10	1.63E-10	2.24E-10	.42/.58
23478-PeCDF	6.33E-10	1.90E-10	4.43E-10	.30/.70
Other PeCDF	1.09E-08	3.92E-09	6.98E-09	.36/.64
123478-HxCDF	9.20E-10	5.52E-11	8.65E-10	.06/.94
123678-HxCDF	8.70E-10	5.22E-11	8.18E-10	.06/.94
123789-HxCDF	5.73E-10	6.30E-11	5.10E-10	.11/.89
234678-HxCDF	3.33E-10	2.33E-11	3.10E-10	.07/.93
Other HxCDF	2.10E-09	1.47E-10	1.95E-09	.07/.93
1234678-HpCDF	1.15E-09	4.60E-11	1.10E-09	.04/.96
1234789-HpCDF	5.00E-10	1.00E-11	4.90E-10	.02/.98
Other HpCDF	5.35E-09	1.61E-10	5.19E-09	.03/.97
OCDF	2.23E-09	2.23E-11	2.21E-09	.01/.99

stack diameter; exit velocity of the gaseous emissions from the stack; and temperature of the exhaust gases characteristic of incineration facilities of this size. In order to access historical meteorological data for air modeling purposes, the hypothetical facility was located in a specific geographical area having specific meteorological conditions. To

simplify the ambient air modeling and deposition, the hypothetical organic waste incinerator was assumed to exist in a simple terrain setting (e.g., flat terrain). By definition, simple terrain refers to an area where the terrain features are all lower in elevation than the top of the stack of the stationary source under analysis.

The dispersion and deposition computations performed by the COMPDEP model require data on wind speed, wind direction, wind profile above the surface, and hourly precipitation data. When performing a regulatory analysis, e.g., to set air quality permit conditions, EPA's *Guideline on Air Quality Models* (EPA, 1986a) recommends the use of five consecutive years of representative meteorological data. However, in this example analysis only one year of meteorological data was used as compiled at the Denver-Stapleton International Airport by the National Weather Service (NWS), because this was not intended as a regulatory analysis. Hourly measurements of wind speed, wind direction, temperature, and precipitation were used as a basis of computing annual average ground-level concentrations of dioxin in ambient air, and as a basis for the estimation of the dry and wet deposition flux. The Pasquill-Gifford (P-G) stability categories, were used as defined in the Modeling Guidelines. The specifications of stability categories depending on wind speed, cloud cover and mixing heights were established by Pasquill (1961), and later modified by Turner (1964). Reference is made here to Tables 9-3 and 9-4 on pages 9-21,22 of the Modeling Guidelines which gives a method for estimating P-G Stability Categories for daytime and nighttime conditions based on surface roughness and the wind speed profiles distributed in the United States.

To summarize, inputs for the COMPDEP model included hourly meteorological data, source characteristics and receptor features. Hourly meteorological data requirements are the mean wind speed, the direction from which the wind is blowing, the wind-profile exponent, the ambient air temperature, the Pasquill stability category, the vertical potential temperature gradient with height, the mixing layer height, and the frequency distribution of hourly precipitation. Source input data requirements included the congener-specific mass emission rate partitioned by vapor and particulate; the physical stack measurements, e.g., diameter, base elevation of the stack, and exit velocity and temperature of the stack gas, and settling parameters for particulate matter for both dry and wet deposition. Table 3-10 is a review of the congener-specific emissions data, and Table 3-11 is a review of the modeling parameters used in the air quality modeling of the hypothetical incinerator

Table 3-11. Modeling parameters used in the COMPDEP modeling of PCDD/F emissions from the hypothetical incinerator.

Technology:	Modeled after an actual organic waste incinerator		
Rate of organic waste combustion:	200 metric tons per day		
Air Pollution Control System:	Assumed to consist of dry scrubber combined with a baghouse (fabric filters) resulting in 99% reduction and control of CDDs/CDFs.		
Stack Height:	30.48 m	Stack Temp.:	400° Kelvin
Stack Diameter:	1.52 m	Stack Exit V:	8.9 m s^{-1}
Anemometer Height:	10 m	Source elevation:	0 m
Terrain:	Assumed simple	Z min.	10 m

Modeled Options:		
	Terrain adjustments	Yes
	Stack downwash	No
	Gradual plume rise	Yes
	Buoyancy induced dispersion	Yes
	Gravitational settling/deposition	Yes
	Wet Deposition	Yes
	Calm winds processing option	Yes
	Building wake effects	No

Exponents for power law wind increase with height:

0.07
0.07
0.10
0.15
0.35
0.55

Particle size categories for dry/wet deposition analysis:

Category 1: ≤2 μm represented by 1.0 μm diameter
Category 2: >2-≤10 μm represented by 6.78 μm
Category 3: >10 μm represented by 20.0 μm
Particle density: 1.4 g cm^{-3}

Fraction of CDD/CDF particle bound emission by particle size category:

Category 1: 0.88
Category 2: 0.09
Category 3: 0.03

Example of dry deposition settling velocities predicted by the CARB algorithm:

1.0 μm:	7.11 E-3 cm s^{-1}
6.78 μm:	2.87 E-1 cm s^{-1}
20 μm:	2.47 cm s^{-1}

Wet deposition scavenging coefficients:	Table 3-9
National Weather Service data:	Denver-Stapleton Airport; 1989
Grid system:	Polar every 22.5°

The output of the COMPDEP model for both surface deposition and ambient air impacts is a concentration array for 160 ground-level receptors around the incinerator, e.g., 10 receptor points along each of the 16 wind directions every 22.5° on the polar azimuth. Vapor and particle phase concentrations are in units of grams per cubic meter of air (g/m^3), and particle-bound depositions are in units of grams per square meter of surface area per year (g/m^2-yr). Results for both ambient air and surface deposition were estimated at concentric radial distances from the incinerator of 0.2, 0.5, 0.8, 0.9, 1.0, 2.0, 5.0, 10, 20, 30, 40, and 50 kilometers. The maximum annual average ground-level vapor and particle-phase air concentrations of all modeled congeners is estimated to occur 900 meters from the center of the stack. Tables 3-12, 3-13, and 3-14 display the annual average vapor-phase, particle-phase, and total (vapor + particle) air concentrations of dioxin-like congeners at various distances in the direction of the maximum impact. Tables 3-15, 3-16, and 3-17 display the dry, wet, and total (dry + wet) deposition fluxes of dioxin-like compounds at various distances in the direction of maximum impact. The maximum annual average dry deposition flux occurs 800 meters from the center of the stack, although there is no significant difference from the 900 m distance where the maximum annual average ambient air concentration occurs. The maximum annual average wet deposition occurs 200 meters from the center of the stack, which is what is expected from the algorithm (refer to subsection 3.3.4. Estimation of Wet Deposition Flux).

3.5. REVIEW OF PROCEDURES FOR ESTIMATING SITE-SPECIFIC IMPACTS FROM A STACK EMISSION SOURCE

This chapter has detailed a procedure for evaluating site-specific impacts from stack emission sources. For purposes of demonstration, a hypothetical incinerator was defined, and using the COMPDEP model, estimates of vapor-phase concentrations and particle phase depositions at points around the stack were made. Three major points for estimating impacts of dioxin-like compounds using the COMPDEP or other models are as follows:

1. Characterize the emissions on a congener-specific basis: Although much of the information available on stack emission sources in on a TEQ or a homologue group basis, and not a congener-specific basis, the approach in this assessment, and the recommendation made here, is to conduct site-specific assessments using specific

Table 3-12. Predicted annual average vapor-phase concentrations of PCDD/Fs (g/m^3).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	4.68E-19	7.57E-18	9.85E-18	9.91E-18	9.81E-18	6.53E-18	2.69E-18	1.18E-18	4.93E-19	2.94E-19	2.05E-19	1.56E-19
Other TCDD	1.01E-17	1.64E-16	2.13E-16	2.15E-16	2.13E-16	1.42E-16	5.82E-17	2.56E-17	1.07E-17	8.74E-18	4.45E-18	3.38E-18
12378-PeCDD	4.63E-19	7.48E-18	9.73E-18	9.80E-18	9.69E-18	6.46E-18	2.66E-18	1.17E-18	4.87E-19	1.39E-18	2.03E-19	1.54E-19
Other PeCDD	4.58E-18	7.40E-17	9.63E-17	9.69E-17	9.59E-17	6.39E-17	2.63E-17	1.16E-17	4.82E-18	1.37E-17	2.01E-18	1.53E-18
123478-HxCDD	1.61E-19	2.61E-18	3.40E-18	3.42E-18	3.38E-18	2.25E-18	9.27E-19	4.07E-19	1.70E-19	2.26E-18	7.08E-20	5.38E-20
123789-HxCDD	6.69E-20	1.08E-18	1.41E-18	1.42E-18	1.40E-18	9.34E-19	3.84E-19	1.69E-19	7.05E-20	3.46E-18	2.94E-20	2.23E-20
123678-HxCDD	1.22E-19	1.97E-18	2.56E-18	2.58E-18	2.55E-18	1.70E-18	6.99E-19	3.07E-19	1.28E-19	3.08E-18	5.34E-20	4.06E-20
Other HxCDD	1.18E-18	1.90E-17	2.48E-17	2.49E-17	2.47E-17	1.64E-17	6.76E-18	2.97E-18	1.24E-18	2.97E-17	5.16E-19	3.92E-19
1234678-HpCDD	6.03E-19	9.75E-18	1.27E-17	1.28E-17	1.26E-17	8.42E-18	3.46E-18	1.52E-18	6.35E-19	3.11E-17	2.65E-19	2.01E-19
Other HpCDF	1.11E-18	1.80E-17	2.34E-17	2.35E-17	2.33E-17	1.55E-17	6.39E-18	2.81E-18	1.17E-18	5.74E-17	4.88E-19	3.71E-19
OCDD	6.20E-19	1.00E-17	1.31E-17	1.31E-17	1.30E-17	8.66E-18	3.56E-18	1.57E-18	6.54E-19	6.47E-17	2.72E-19	2.07E-19
2378-TCDF	3.95E-17	6.38E-16	8.31E-16	8.36E-16	8.27E-16	5.51E-16	2.27E-16	9.96E-17	4.16E-17	1.70E-17	1.73E-17	1.32E-17
Other TCDF	2.51E-16	4.05E-15	5.28E-15	5.31E-15	5.25E-15	3.50E-15	1.44E-15	6.33E-16	2.64E-16	1.08E-16	1.10E-16	8.36E-17
12378-PeCDF	1.50E-18	2.42E-17	3.15E-17	3.17E-17	3.14E-17	2.09E-17	8.61E-18	3.78E-18	1.58E-18	2.18E-18	6.58E-19	5.00E-19
23478-PeCDF	1.75E-18	2.83E-17	3.68E-17	3.71E-17	3.67E-17	2.44E-17	1.01E-17	4.42E-18	1.84E-18	4.30E-18	7.69E-19	5.84E-19
Other PeCDF	3.62E-17	5.85E-16	7.61E-16	7.66E-16	7.58E-16	5.05E-16	2.08E-16	9.13E-17	3.81E-17	6.78E-17	1.59E-17	1.21E-17
123478-HxCDF	5.09E-19	8.23E-18	1.07E-17	1.08E-17	1.07E-17	7.10E-18	2.92E-18	1.28E-18	5.36E-19	8.40E-18	2.23E-19	1.70E-19
123678-HxCDF	4.81E-19	7.78E-18	1.01E-17	1.02E-17	1.01E-17	6.72E-18	2.76E-18	1.21E-18	5.07E-19	7.94E-18	2.11E-19	1.61E-19
123789-HxCDF	5.81E-19	9.40E-18	1.22E-17	1.23E-17	1.22E-17	8.11E-18	3.34E-18	1.47E-18	6.12E-19	4.95E-18	2.55E-19	1.94E-19
234678-HxCDF	2.15E-19	3.48E-18	4.52E-18	4.55E-18	4.50E-18	3.00E-18	1.23E-18	5.42E-19	2.26E-19	3.01E-18	9.43E-20	7.17E-20
Other HxCDF	1.36E-18	2.19E-17	2.85E-17	2.87E-17	2.84E-17	1.89E-17	7.78E-18	3.42E-18	1.43E-18	1.90E-17	5.95E-19	4.52E-19
1234678-HpCDF	4.24E-19	6.86E-18	8.92E-18	8.98E-18	8.89E-18	5.92E-18	2.44E-18	1.07E-18	4.47E-19	1.07E-17	1.86E-19	1.41E-19
1234789-HpCDF	9.22E-20	1.49E-18	1.94E-18	1.95E-18	1.93E-18	1.29E-18	5.30E-19	2.33E-19	9.71E-20	4.76E-18	4.05E-20	3.08E-20
Other HpCDF	1.48E-18	2.39E-17	3.11E-17	3.13E-17	3.10E-17	2.07E-17	8.50E-18	3.73E-18	1.56E-18	5.04E-17	6.50E-19	4.94E-19
OCDF	2.06E-19	3.32E-18	4.33E-18	4.35E-18	4.31E-18	2.87E-18	1.18E-18	5.19E-19	2.17E-19	2.14E-17	9.02E-20	6.86E-20

Table 3-13. Predicted annual average particle-phase air concentrations of PCDD/Fs (g/m^3).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	2.27E-22	6.18E-18	8.03E-18	8.08E-18	8.00E-18	5.31E-18	2.16E-18	9.32E-19	3.78E-19	2.21E-19	1.52E-19	1.14E-19
Other TCDD	4.92E-21	1.34E-16	1.74E-16	1.75E-16	1.73E-16	1.15E-16	4.68E-17	2.02E-17	8.20E-18	4.79E-18	3.30E-18	2.47E-18
12378-PeCDD	7.81E-22	2.13E-17	2.76E-17	2.78E-17	2.75E-17	1.83E-17	7.43E-18	3.20E-18	1.30E-18	7.60E-19	5.23E-19	3.92E-19
Other PeCDD	7.73E-21	2.10E-16	2.73E-16	2.75E-16	2.72E-16	1.81E-16	7.35E-17	3.17E-17	1.29E-17	7.52E-18	5.18E-18	3.88E-18
123478-HxCDD	1.27E-21	3.46E-17	4.50E-17	4.52E-17	4.48E-17	2.97E-17	1.21E-17	5.22E-18	2.12E-18	1.24E-18	8.52E-19	6.38E-19
123789-HxCDD	1.94E-21	5.30E-17	6.88E-17	6.92E-17	6.85E-17	4.55E-17	1.85E-17	7.98E-18	3.24E-18	1.89E-18	1.30E-18	9.77E-19
123678-HxCDD	1.73E-21	4.72E-17	6.13E-17	6.16E-17	6.10E-17	4.05E-17	1.65E-17	7.11E-18	2.89E-18	1.69E-18	1.16E-18	8.70E-19
Other HxCDD	1.67E-20	4.56E-16	5.92E-16	5.96E-16	5.90E-16	3.91E-16	1.59E-16	6.87E-17	2.79E-17	1.63E-17	1.12E-17	8.41E-18
1234678-HpCDD	1.75E-20	4.77E-16	6.20E-16	6.23E-16	6.17E-16	4.10E-16	1.67E-16	7.19E-17	2.92E-17	1.71E-17	1.17E-17	8.80E-18
Other HpCDF	3.23E-20	8.80E-16	1.14E-15	1.15E-15	1.14E-15	7.55E-16	3.07E-16	1.33E-16	5.38E-17	3.15E-17	2.17E-17	1.62E-17
OCDD	3.64E-20	9.92E-16	1.29E-15	1.30E-15	1.28E-15	8.51E-16	3.46E-16	1.50E-16	6.07E-17	3.55E-17	2.44E-17	1.83E-17
2378-TCDF	9.56E-21	2.60E-16	3.38E-16	3.40E-16	3.37E-16	2.23E-16	9.09E-17	3.92E-17	1.59E-17	9.31E-18	6.41E-18	4.80E-18
Other TCDF	6.07E-20	1.65E-15	2.15E-15	2.16E-15	2.14E-15	1.42E-15	5.77E-16	2.49E-16	1.01E-16	5.91E-17	4.07E-17	3.05E-17
12378-PeCDF	1.23E-21	3.34E-17	4.34E-17	4.37E-17	4.32E-17	2.87E-17	1.17E-17	5.04E-18	2.04E-18	1.20E-18	8.22E-19	6.16E-19
23478-PeCDF	2.42E-21	6.60E-17	8.57E-17	8.62E-17	8.53E-17	5.66E-17	2.30E-17	9.94E-18	4.04E-18	2.36E-18	1.62E-18	1.22E-18
Other PeCDF	3.81E-20	1.04E-15	1.35E-15	1.36E-15	1.34E-15	8.92E-16	3.63E-16	1.57E-16	6.35E-17	3.71E-17	2.56E-17	1.92E-17
123478-HxCDF	4.73E-21	1.29E-16	1.67E-16	1.68E-16	1.66E-16	1.11E-16	4.50E-17	1.94E-17	7.88E-18	4.60E-18	3.17E-18	2.37E-18
123678-HxCDF	4.47E-21	1.22E-16	1.58E-16	1.59E-16	1.57E-16	1.05E-16	4.25E-17	1.84E-17	7.45E-18	4.35E-18	3.00E-18	2.25E-18
123789-HxCDF	2.79E-21	7.59E-17	9.86E-17	9.92E-17	9.82E-17	6.52E-17	2.65E-17	1.14E-17	4.64E-18	2.72E-18	1.87E-18	1.40E-18
234678-HxCDF	1.69E-21	4.61E-17	5.99E-17	6.02E-17	5.96E-17	3.96E-17	1.61E-17	6.95E-18	2.82E-18	1.65E-18	1.13E-18	8.50E-19
Other HxCDF	1.07E-20	2.91E-16	3.78E-16	3.80E-16	3.76E-16	2.50E-16	1.02E-16	4.38E-17	1.78E-17	1.04E-17	7.16E-18	5.36E-18
1234678-HpCDF	6.04E-21	1.64E-16	2.14E-16	2.15E-16	2.13E-16	1.41E-16	5.74E-17	2.48E-17	1.01E-17	5.88E-18	4.05E-18	3.03E-18
1234789-HpCDF	2.68E-21	7.30E-17	9.48E-17	9.53E-17	9.43E-17	6.26E-17	2.55E-17	1.10E-17	4.46E-18	2.61E-18	1.80E-18	1.35E-18
Other HpCDF	2.84E-20	7.73E-16	1.00E-15	1.01E-15	9.99E-16	6.63E-16	2.70E-16	1.16E-16	4.73E-17	2.76E-17	1.90E-17	1.43E-17
OCDF	1.21E-20	3.29E-16	4.27E-16	4.29E-16	4.25E-16	2.82E-16	1.15E-16	4.95E-17	2.01E-17	1.18E-17	8.09E-18	6.06E-18

Table 3-14. Predicted total (vapor + particle) ambient air concentrations of PCDD/s (g/m^3).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	4.68E-19	1.38E-17	1.79E-17	1.80E-17	1.78E-17	1.18E-17	4.85E-18	2.11E-18	8.71E-19	5.15E-19	3.58E-19	2.70E-19
Other TCDD	1.01E-17	2.98E-16	3.87E-16	3.90E-16	3.86E-16	2.57E-16	1.05E-16	4.58E-17	1.89E-17	1.35E-17	7.75E-18	5.85E-18
12378-PeCDD	4.63E-19	2.87E-17	3.74E-17	3.76E-17	3.72E-17	2.47E-17	1.01E-17	4.37E-18	1.79E-18	2.15E-18	7.26E-19	5.46E-19
Other PeCDD	4.59E-18	2.84E-16	3.70E-16	3.72E-16	3.68E-16	2.45E-16	9.98E-17	4.33E-17	1.77E-17	2.13E-17	7.19E-18	5.41E-18
123478-HxCDD	1.63E-19	3.72E-17	4.84E-17	4.86E-17	4.81E-17	3.20E-17	1.30E-17	5.62E-18	2.29E-18	3.50E-18	9.23E-19	6.92E-19
123789-HxCDD	6.89E-20	5.41E-17	7.02E-17	7.06E-17	6.99E-17	4.64E-17	1.89E-17	8.15E-18	3.31E-18	5.35E-18	1.33E-18	9.99E-19
123678-HxCDD	1.23E-19	4.91E-17	6.38E-17	6.42E-17	6.35E-17	4.22E-17	1.72E-17	7.42E-18	3.01E-18	4.76E-18	1.21E-18	9.11E-19
Other HxCDD	1.19E-18	4.75E-16	6.17E-16	6.21E-16	6.14E-16	4.08E-16	1.66E-16	7.17E-17	2.91E-17	4.60E-17	1.17E-17	8.80E-18
1234678-HpCDD	6.20E-19	4.87E-16	6.32E-16	6.36E-16	6.30E-16	4.18E-16	1.70E-16	7.34E-17	2.98E-17	4.82E-17	1.20E-17	9.00E-18
Other HpCDF	1.14E-18	8.98E-16	1.17E-15	1.17E-15	1.16E-15	7.71E-16	3.14E-16	1.35E-16	5.50E-17	8.89E-17	2.21E-17	1.66E-17
OCDD	6.57E-19	1.00E-15	1.30E-15	1.31E-15	1.30E-15	8.60E-16	3.50E-16	1.51E-16	6.13E-17	1.00E-16	2.47E-17	1.85E-17
2378-TCDF	3.95E-17	8.99E-16	1.17E-15	1.18E-15	1.16E-15	7.74E-16	3.18E-16	1.39E-16	5.75E-17	2.63E-17	2.37E-17	1.80E-17
Other TCDF	2.51E-16	5.71E-15	7.42E-15	7.47E-15	7.39E-15	4.92E-15	2.02E-15	8.82E-16	3.65E-16	1.67E-16	1.51E-16	1.14E-16
12378-PeCDF	1.50E-18	5.77E-17	7.49E-17	7.54E-17	7.46E-17	4.96E-17	2.03E-17	8.82E-18	3.62E-18	3.38E-18	1.48E-18	1.12E-18
23478-PeCDF	1.75E-18	9.43E-17	1.23E-16	1.23E-16	1.22E-16	8.11E-17	3.31E-17	1.44E-17	5.88E-18	6.66E-18	2.39E-18	1.80E-18
Other PeCDF	3.62E-17	1.62E-15	2.11E-15	2.12E-15	2.10E-15	1.40E-15	5.70E-16	2.48E-16	1.02E-16	1.05E-16	4.14E-17	3.12E-17
123478-HxCDF	5.14E-19	1.37E-16	1.78E-16	1.79E-16	1.77E-16	1.18E-16	4.79E-17	2.07E-17	8.41E-18	1.30E-17	3.39E-18	2.54E-18
123678-HxCDF	4.86E-19	1.30E-16	1.68E-16	1.69E-16	1.68E-16	1.11E-16	4.53E-17	1.96E-17	7.96E-18	1.23E-17	3.21E-18	2.41E-18
123789-HxCDF	5.84E-19	8.53E-17	1.11E-16	1.11E-16	1.10E-16	7.33E-17	2.99E-17	1.29E-17	5.26E-18	7.67E-18	2.12E-18	1.59E-18
234678-HxCDF	2.17E-19	4.96E-17	6.44E-17	6.48E-17	6.41E-17	4.26E-17	1.73E-17	7.49E-18	3.05E-18	4.66E-18	1.23E-18	9.22E-19
Other HxCDF	1.37E-18	3.13E-16	4.06E-16	4.09E-16	4.04E-16	2.69E-16	1.09E-16	4.72E-17	1.92E-17	2.94E-17	7.75E-18	5.81E-18
1234678-HpCDF	4.30E-19	1.71E-16	2.22E-16	2.24E-16	2.21E-16	1.47E-16	5.98E-17	2.58E-17	1.05E-17	1.66E-17	4.23E-18	3.17E-18
1234789-HpCDF	9.49E-20	7.45E-17	9.67E-17	9.73E-17	9.63E-17	6.39E-17	2.60E-17	1.12E-17	4.56E-18	7.37E-18	1.84E-18	1.38E-18
Other HpCDF	1.51E-18	7.97E-16	1.03E-15	1.04E-15	1.03E-15	6.84E-16	2.78E-16	1.20E-16	4.88E-17	7.80E-17	1.97E-17	1.47E-17
OCDF	2.18E-19	3.32E-16	4.31E-16	4.34E-16	4.29E-16	2.85E-16	1.16E-16	5.01E-17	2.03E-17	3.32E-17	8.18E-18	6.13E-18

Table 3-15. Predicted annual dry deposition fluxes of particle-bound PCDD/Fs (g/m^2-yr).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	3.20E-14	4.38E-13	5.30E-13	5.23E-13	5.08E-13	3.04E-13	1.10E-13	4.29E-14	1.53E-14	8.18E-15	5.28E-15	3.79E-15
Other TCDD	6.93E-13	9.49E-12	1.15E-11	1.13E-11	1.10E-11	6.59E-12	2.38E-12	9.31E-13	3.31E-13	1.77E-13	1.14E-13	8.21E-14
12378-PeCDD	1.10E-13	1.51E-12	1.82E-12	1.80E-12	1.75E-12	1.05E-12	3.78E-13	1.48E-13	5.25E-14	2.81E-14	1.82E-14	1.30E-14
Other PeCDD	1.09E-12	1.49E-11	1.80E-11	1.78E-11	1.73E-11	1.04E-11	3.74E-12	1.46E-12	5.19E-13	2.78E-13	1.80E-13	1.29E-13
123478-HxCDD	1.79E-13	2.45E-12	2.97E-12	2.93E-12	2.84E-12	1.70E-12	6.15E-13	2.40E-13	8.54E-14	4.58E-14	2.96E-14	2.12E-14
123789-HxCDD	2.74E-13	3.75E-12	4.54E-12	4.48E-12	4.35E-12	2.61E-12	9.41E-13	3.68E-13	1.31E-13	7.01E-14	4.52E-14	3.25E-14
123678-HxCDD	2.44E-13	3.34E-12	4.05E-12	3.99E-12	3.87E-12	2.32E-12	8.38E-13	3.28E-13	1.16E-13	6.24E-14	4.03E-14	2.89E-14
Other HxCDD	2.36E-12	3.23E-11	3.91E-11	3.86E-11	3.75E-11	2.24E-11	8.10E-12	3.17E-12	1.13E-12	6.03E-13	3.89E-13	2.80E-13
1234678-HpCDD	2.47E-12	3.38E-11	4.09E-11	4.03E-11	3.92E-11	2.35E-11	8.47E-12	3.31E-12	1.18E-12	6.31E-13	4.07E-13	2.92E-13
Other HpCDF	4.55E-12	6.23E-11	7.55E-11	7.44E-11	7.23E-11	4.33E-11	1.56E-11	6.11E-12	2.17E-12	1.16E-12	7.51E-13	5.39E-13
OCDD	5.13E-12	7.02E-11	8.51E-11	8.39E-11	8.15E-11	4.88E-11	1.76E-11	6.89E-12	2.45E-12	1.31E-12	8.47E-13	6.08E-13
2378-TCDF	1.35E-12	1.84E-11	2.23E-11	2.20E-11	2.14E-11	1.28E-11	4.62E-12	1.81E-12	6.42E-13	3.44E-13	2.22E-13	1.60E-13
Other TCDF	8.55E-12	1.17E-10	1.42E-10	1.40E-10	1.36E-10	8.14E-11	2.94E-11	1.15E-11	4.08E-12	2.19E-12	1.41E-12	1.01E-12
12378-PeCDF	1.73E-13	2.37E-12	2.87E-12	2.83E-12	2.75E-12	1.64E-12	5.93E-13	2.32E-13	8.25E-14	4.42E-14	2.85E-14	2.05E-14
23478-PeCDF	3.41E-13	4.67E-12	5.66E-12	5.58E-12	5.42E-12	3.25E-12	1.17E-12	4.58E-13	1.63E-13	8.73E-14	5.63E-14	4.04E-14
Other PeCDF	5.37E-12	7.35E-11	8.91E-11	8.78E-11	8.53E-11	5.11E-11	1.84E-11	7.21E-12	2.56E-12	1.37E-12	8.87E-13	6.37E-13
123478-HxCDF	6.66E-13	9.11E-12	1.10E-11	1.09E-11	1.06E-11	6.33E-12	2.29E-12	8.94E-13	3.18E-13	1.70E-13	1.10E-13	7.89E-14
123678-HxCDF	6.30E-13	8.62E-12	1.04E-11	1.03E-11	1.00E-11	5.99E-12	2.16E-12	8.46E-13	3.00E-13	1.61E-13	1.04E-13	7.46E-14
123789-HxCDF	3.93E-13	5.38E-12	6.51E-12	6.42E-12	6.24E-12	3.74E-12	1.35E-12	5.27E-13	1.87E-13	1.00E-13	6.48E-14	4.65E-14
234678-HxCDF	2.38E-13	3.26E-12	3.95E-12	3.90E-12	3.79E-12	2.27E-12	8.19E-13	3.20E-13	1.14E-13	6.10E-14	3.94E-14	2.83E-14
Other HxCDF	1.50E-12	2.06E-11	2.49E-11	2.46E-11	2.39E-11	1.43E-11	5.16E-12	2.02E-12	7.18E-13	3.85E-13	2.48E-13	1.78E-13
1234678-HpCDF	8.50E-13	1.16E-11	1.41E-11	1.39E-11	1.35E-11	8.09E-12	2.92E-12	1.14E-12	4.06E-13	2.17E-13	1.40E-13	1.01E-13
1234789-HpCDF	3.77E-13	5.16E-12	6.26E-12	6.17E-12	5.99E-12	3.59E-12	1.30E-12	5.07E-13	1.80E-13	9.65E-14	6.23E-14	4.47E-14
Other HpCDF	3.99E-12	5.47E-11	6.63E-11	6.53E-11	6.35E-11	3.80E-11	1.37E-11	5.37E-12	1.91E-12	1.02E-12	6.60E-13	4.74E-13
OCDF	1.70E-12	2.33E-11	2.82E-11	2.78E-11	2.70E-11	1.62E-11	5.84E-12	2.28E-12	8.11E-13	4.35E-13	2.81E-13	2.01E-13

Table 3-16. Predicted annual wet deposition fluxes of particle-bound PCDDs/Fs (g/m^2-yr).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	4.33E-12	6.85E-13	3.78E-13	3.26E-13	2.85E-13	1.18E-13	3.42E-14	1.14E-14	3.01E-15	1.22E-15	6.02E-16	3.37E-16
Other TCDD	9.38E-11	1.48E-11	8.20E-12	7.06E-12	6.18E-12	2.57E-12	7.42E-13	2.47E-13	6.52E-14	2.63E-14	1.31E-14	7.30E-15
12378-PeCDD	1.49E-11	2.36E-12	1.30E-12	1.12E-12	9.81E-13	4.07E-13	1.18E-13	3.92E-14	1.03E-14	4.18E-15	2.07E-15	1.16E-15
Other PeCDD	1.47E-10	2.33E-11	1.29E-11	1.11E-11	9.71E-12	4.03E-12	1.16E-12	3.88E-13	1.02E-13	4.14E-14	2.05E-14	1.15E-14
123478-HxCDD	2.42E-11	3.83E-12	2.12E-12	1.82E-12	1.60E-12	6.63E-13	1.92E-13	6.38E-14	1.68E-14	6.80E-15	3.37E-15	1.89E-15
123789-HxCDD	3.71E-11	5.87E-12	3.24E-12	2.79E-12	2.44E-12	1.01E-12	2.93E-13	9.77E-14	2.58E-14	1.04E-14	5.16E-15	2.89E-15
123678-HxCDD	3.30E-11	5.22E-12	2.89E-12	2.49E-12	2.18E-12	9.04E-13	2.61E-13	8.70E-14	2.30E-14	9.27E-15	4.59E-15	2.57E-15
Other HxCDD	3.19E-10	5.05E-11	2.79E-11	2.40E-11	2.10E-11	8.73E-12	2.52E-12	8.41E-13	2.22E-13	8.96E-14	4.44E-14	2.48E-14
1234678-HpCDD	3.34E-10	5.28E-11	2.92E-11	2.51E-11	2.20E-11	9.14E-12	2.64E-12	8.80E-13	2.32E-13	9.38E-14	4.65E-14	2.60E-14
Other HpCDF	6.16E-10	9.74E-11	5.38E-11	4.64E-11	4.06E-11	1.69E-11	4.87E-12	1.62E-12	4.28E-13	1.73E-13	8.57E-14	4.79E-14
OCDD	6.94E-10	1.10E-10	6.07E-11	5.23E-11	4.58E-11	1.90E-11	5.49E-12	1.83E-12	4.83E-13	1.95E-13	9.66E-14	5.40E-14
2378-TCDF	1.82E-10	2.88E-11	1.59E-11	1.37E-11	1.20E-11	4.99E-12	1.44E-12	4.80E-13	1.27E-13	5.12E-14	2.54E-14	1.42E-14
Other TCDF	1.16E-09	1.83E-10	1.01E-10	8.72E-11	7.63E-11	3.17E-11	9.15E-12	3.05E-12	8.05E-13	3.25E-13	1.61E-13	9.01E-14
12378-PeCDF	2.34E-11	3.70E-12	2.04E-12	1.76E-12	1.54E-12	6.40E-13	1.85E-13	6.16E-14	1.63E-14	6.57E-15	3.25E-15	1.82E-15
23478-PeCDF	4.62E-11	7.31E-12	4.04E-12	3.48E-12	3.04E-12	1.26E-12	3.65E-13	1.22E-13	3.21E-14	1.30E-14	6.42E-15	3.59E-15
Other PeCDF	7.27E-10	1.15E-10	6.35E-11	5.47E-11	4.79E-11	1.99E-11	5.75E-12	1.92E-12	5.05E-13	2.04E-13	1.01E-13	5.66E-14
123478-HxCDF	9.01E-11	1.43E-11	7.88E-12	6.79E-12	5.94E-12	2.47E-12	7.13E-13	2.37E-13	6.27E-14	2.53E-14	1.25E-14	7.01E-15
123678-HxCDF	8.52E-11	1.35E-11	7.45E-12	6.42E-12	5.62E-12	2.33E-12	6.74E-13	2.25E-13	5.93E-14	2.39E-14	1.19E-14	6.63E-15
123789-HxCDF	5.31E-11	8.41E-12	4.64E-12	4.00E-12	3.50E-12	1.45E-12	4.20E-13	1.40E-13	3.70E-14	1.49E-14	7.39E-15	4.14E-15
234678-HxCDF	3.23E-11	5.11E-12	2.82E-12	2.43E-12	2.13E-12	8.83E-13	2.55E-13	8.50E-14	2.24E-14	9.06E-15	4.49E-15	2.51E-15
Other HxCDF	2.04E-10	3.22E-11	1.78E-11	1.53E-11	1.34E-11	5.57E-12	1.61E-12	5.36E-13	1.42E-13	5.71E-14	2.83E-14	1.58E-14
1234678-HpCDF	1.15E-10	1.82E-11	1.01E-11	8.66E-12	7.59E-12	3.15E-12	9.10E-13	3.03E-13	8.00E-14	3.23E-14	1.60E-14	8.95E-15
1234789-HpCDF	5.11E-11	8.08E-12	4.46E-12	3.85E-12	3.37E-12	1.40E-12	4.04E-13	1.35E-13	3.55E-14	1.43E-14	7.11E-15	3.97E-15
Other HpCDF	5.41E-10	8.56E-11	4.73E-11	4.07E-11	3.57E-11	1.48E-11	4.28E-12	1.43E-12	3.76E-13	1.52E-13	7.52E-14	4.21E-14
OCDF	2.30E-10	3.64E-11	2.01E-11	1.73E-11	1.52E-11	6.30E-12	1.82E-12	6.06E-13	1.60E-13	6.46E-14	3.20E-14	1.79E-14

Table 3-17. Predicted total (dry + wet) deposition fluxes of particle-bound PCDD/Fs (g/m^2-yr).

Downwind distance, km	0.2	0.5	0.8	0.9	1	2	5	10	20	30	40	50
2378-TCDD	4.33E-12	1.12E-12	9.08E-13	8.49E-13	7.93E-13	4.23E-13	1.44E-13	5.43E-14	1.83E-14	9.40E-15	5.88E-15	4.13E-15
Other TCDD	9.38E-11	2.43E-11	1.97E-11	1.84E-11	1.72E-11	9.16E-12	3.12E-12	1.18E-12	3.96E-13	2.04E-13	1.27E-13	8.94E-14
12378-PeCDD	1.49E-11	3.86E-12	3.12E-12	2.92E-12	2.73E-12	1.45E-12	4.95E-13	1.87E-13	6.28E-14	3.23E-14	2.02E-14	1.42E-14
Other PeCDD	1.47E-10	3.82E-11	3.09E-11	2.89E-11	2.70E-11	1.44E-11	4.90E-12	1.85E-12	6.22E-13	3.20E-13	2.00E-13	1.40E-13
123478-HxCDD	2.42E-11	6.28E-12	5.08E-12	4.75E-12	4.44E-12	2.37E-12	8.06E-13	3.04E-13	1.02E-13	5.26E-14	3.29E-14	2.31E-14
123789-HxCDD	3.71E-11	9.62E-12	7.78E-12	7.27E-12	6.79E-12	3.62E-12	1.23E-12	4.65E-13	1.56E-13	8.05E-14	5.04E-14	3.54E-14
123678-HxCDD	3.30E-11	8.56E-12	6.93E-12	6.48E-12	6.05E-12	3.23E-12	1.10E-12	4.14E-13	1.39E-13	7.17E-14	4.49E-14	3.15E-14
Other HxCDD	3.19E-10	8.28E-11	6.70E-11	6.26E-11	5.85E-11	3.12E-11	1.06E-11	4.01E-12	1.35E-12	6.93E-13	4.34E-13	3.04E-13
1234678-HpCDD	3.34E-10	8.66E-11	7.01E-11	6.55E-11	6.12E-11	3.26E-11	1.11E-11	4.19E-12	1.41E-12	7.25E-13	4.54E-13	3.18E-13
Other HpCDF	6.16E-10	1.60E-10	1.29E-10	1.21E-10	1.13E-10	6.02E-11	2.05E-11	7.73E-12	2.60E-12	1.34E-12	8.37E-13	5.87E-13
OCDD	6.94E-10	1.80E-10	1.46E-10	1.36E-10	1.27E-10	6.78E-11	2.31E-11	8.71E-12	2.93E-12	1.51E-12	9.43E-13	6.62E-13
2378-TCDF	1.82E-10	4.73E-11	3.82E-11	3.57E-11	3.34E-11	1.78E-11	6.06E-12	2.29E-12	7.69E-13	3.96E-13	2.48E-13	1.74E-13
Other TCDF	1.16E-09	3.00E-10	2.43E-10	2.27E-10	2.12E-10	1.13E-10	3.85E-11	1.45E-11	4.89E-12	2.51E-12	1.57E-12	1.10E-12
12378-PeCDF	2.34E-11	6.07E-12	4.91E-12	4.59E-12	4.29E-12	2.29E-12	7.78E-13	2.94E-13	9.87E-14	5.08E-14	3.18E-14	2.23E-14
23478-PeCDF	4.62E-11	1.20E-11	9.69E-12	9.06E-12	8.46E-12	4.51E-12	1.54E-12	5.80E-13	1.95E-13	1.00E-13	6.27E-14	4.40E-14
Other PeCDF	7.27E-10	1.89E-10	1.53E-10	1.43E-10	1.33E-10	7.10E-11	2.42E-11	9.12E-12	3.07E-12	1.58E-12	9.88E-13	6.93E-13
123478-HxCDF	9.01E-11	2.34E-11	1.89E-11	1.77E-11	1.65E-11	8.80E-12	3.00E-12	1.13E-12	3.80E-13	1.96E-13	1.22E-13	8.59E-14
123678-HxCDF	8.52E-11	2.21E-11	1.79E-11	1.67E-11	1.56E-11	8.33E-12	2.84E-12	1.07E-12	3.60E-13	1.85E-13	1.16E-13	8.13E-14
123789-HxCDF	5.31E-11	1.38E-11	1.12E-11	1.04E-11	9.74E-12	5.19E-12	1.77E-12	6.67E-13	2.24E-13	1.15E-13	7.22E-14	5.07E-14
234678-HxCDF	3.23E-11	8.37E-12	6.77E-12	6.33E-12	5.92E-12	3.15E-12	1.07E-12	4.05E-13	1.36E-13	7.01E-14	4.39E-14	3.08E-14
Other HxCDF	2.04E-10	5.28E-11	4.27E-11	3.99E-11	3.73E-11	1.99E-11	6.77E-12	2.55E-12	8.59E-13	4.42E-13	2.77E-13	1.94E-13
1234678-HpCDF	1.15E-10	2.98E-11	2.41E-11	2.26E-11	2.11E-11	1.12E-11	3.83E-12	1.44E-12	4.86E-13	2.50E-13	1.56E-13	1.10E-13
1234789-HpCDF	5.11E-11	1.32E-11	1.07E-11	1.00E-11	9.36E-12	4.99E-12	1.70E-12	6.41E-13	2.16E-13	1.11E-13	6.94E-14	4.87E-14
Other HpCDF	5.41E-10	1.40E-10	1.13E-10	1.06E-10	9.91E-11	5.28E-11	1.80E-11	6.79E-12	2.28E-12	1.17E-12	7.35E-13	5.16E-13
OCDF	2.30E-10	5.97E-11	4.83E-11	4.51E-11	4.22E-11	2.25E-11	7.66E-12	2.89E-12	9.71E-13	4.99E-13	3.13E-13	2.19E-13

congener emissions. This is because fate and transport parameters, and bioconcentration/biotransfer parameters, are different for the various congeners. Assuming one set of such parameters for TEQ emissions can lead to a different estimated exposure media TEQ concentration than assuming congener-specific parameters and then, given estimated congener-specific concentrations, calculating TEQ exposure media concentrations with the TEF scheme. Emission factors were used in this assessment todescribe source and site-specific emissions. These are defined as the mass of contaminant emitted per mass of feed material combusted. Procedures to convert other emission data, such as mass per time emitted or concentration emitted, are presented.

2. Estimate the vapor/particle partitioning for atmospheric transport and deposition modeling: Vapors are dispersed assuming Gaussian plume dispersion algorithms, and particles are transported and deposited via wet and dry deposition. The principal output of the atmospheric transport model, COMPDEP, used for further exposure analysis are the vapor and particle phase concentrations, and the wet and dry deposition totals at sites of exposure. There is some thought that the partitioning between the vapor and particle phases at the stack differs from the partitioning in ambient air. Such a difference might be due to the difference in temperature at the stack versus temperature of ambient air. If so, then deposition and dispersion trends in the close vicinity of the stack may differ from such trends further from the stack. Currently the data to support such a hypothesis is lacking; the earlier review of stack vapor/particle partitioning was inconclusive. Also, modeling approaches for such differences are unavailable. Instead, the approach in this chapter is to assume one partitioning scheme (separate V/P partitioning for individual congeners) for atmospheric transport and dispersion modeling. The scheme adopted in this assessment is based on a theoretical approach described by Bidleman (1988).

3. Conduct atmospheric dispersion and deposition modeling: The COMPDEP model is used in this assessment to estimate vapor and particle-phase concentrations, and wet and dry deposition totals for points around the stack emission source. Key inputs are vapor phase and particulate phase emission rates (rather than emission factor units, atmospheric transport models require emission rates in units of mass/time, or g/sec), stack descriptors (stack height, exit temperature, etc.), atmospheric transport parameters (particle size distributions, dry deposition velocity), meteorological data (hourly rainfall, windspeeds, etc.), and terrain descriptions. Procedures to translate the final model

outputs of concentrations and deposition fluxes into exposure media concentrations is given in Chapter 4, Section 4.5.

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4. ESTIMATING EXPOSURE MEDIA CONCENTRATIONS

4.1. INTRODUCTION

The purpose of this chapter is twofold. First, it describes the algorithms used to determine exposure media concentrations of the dioxin-like compounds. Discussion of the algorithms are structured around four "source categories." These categories roughly translate to beginning points, or origins, of contamination. The source categories are also the basis for the example scenarios described in Chapter 5. Second, it provides information about all the model parameters and justification for the values selected for the demonstration of methodologies in Chapter 5. Parameter discussions appear immediately following descriptions of modeling methodologies.

Section 4.2 provides an introduction to the type of modeling used in this assessment. Section 4.3 describes the algorithms used for the first source category, on-site soil, where the contaminants occur in surface soils, and this contamination source and subsequent exposure occur at the same site. The second source category, described in Section 4.4, is termed off-site soil. The contaminated soil is remote from the exposure, such as in a landfill impacting a nearby residence. Section 4.5 describes algorithms to determine exposure media concentrations resulting from stack emissions, the third source category. Chapter 3 laid the groundwork for this section by describing the use of air dispersion/deposition models as applied to a point source to generate two key quantities: air-borne contaminant vapor phase concentrations at a site of exposure, and particulate phase deposition rates. Section 4.5 describes how modeled concentrations and depositions translate to soil, vegetative, and water concentrations. Section 4.6 concludes the chapter with a discussion of algorithms specific to the fourth source category, point-source effluent discharges into surface water bodies.

Algorithms are presented which estimate exposure media concentrations for: 1) surface soils, 2) surface water impacts: suspended and bottom sediment and dissolved phase concentrations, 3) air including the vapor phase and in particulate form, and 4) biota including beef, milk, fruit and vegetables, and fish.

4.2. BACKGROUND FOR SOLUTION ALGORITHMS

Literally hundreds of fate and transport models have been published which differ widely in their technical sophistication, level of spatial or temporal resolution, need for site specific parameterization, and so on. This makes selection of the most appropriate one for any particular situation very difficult. EPA has published model selection criteria documents (EPA, 1987b; EPA, 1988d) and a software system (Integrated Model Evaluation System, IMES, Version 2.01, 1992, Office of Health and Environmental Assessment, Office of Research and Development, U.S EPA) to help assessors with model selection.

Relatively simple, screening level models are used to model fate, transport, and transfer of dioxin-like compounds from the source to the exposure media in this assessment. Simple assumptions are often made in order to arrive at the desired result, which is long-term average exposure media concentrations. Perhaps the most critical of the assumptions made is the assumption that the source strength remains constant throughout the period of exposure: the initial soil concentration of dioxin-like compound remains the same for that exposure period, and stack emissions and effluent discharges remain steady throughout this period. It is important to understand that EPA is not endorsing the algorithms of this assessment as the best ones for use in all dioxin assessments. They are suggested as reasonable starting points for site-specific or general assessments, and as will be discussed shortly, most multi-media exposure modeling has included similar screening level approaches. The assumptions behind models are described carefully throughout this chapter. If these assumptions do not apply to a particular situation, or where assessors require more spatial or temporal resolution, more complex models should be selected. References to other models are made in this and other sections throughout the chapter.

Finally, it cannot be overemphasized that measured concentrations are generally more reliable than modeled ones. Assessors should use measured concentrations if available and if such measurements can be considered spatially and temporally representative for the exposed populations.

The first examples of similar multimedia compartment modeling were probably the "fugacity" models proposed by Mackay (1979) and Mackay and Paterson (1981, 1982). Fugacity in this context is defined as the tendency for a chemical to escape from one

environmental media compartment into another. The fugacity of a chemical present in an environmental media compartment is modeled using common fate and transport parameters such as octanol water partition coefficients, Henry's Constants, water solubilities, and so on. The fugacity concept is based on the fact that at equilibrium, equal fugacities are established in all compartments of a system. Examples of fugacity modeling include the transfer of nonionic organic chemicals between the atmosphere and surface water (Mackay, et al., 1986), between the atmosphere and plants (Riederer, 1990), and for food chain modeling (Travis and Hattemer-Frey, 1987). A definitive text on multimedia compartment modeling using the fugacity approach has recently been published (Mackay, 1991). One possible drawback for the fugacity approach applied to the types of source categories discussed in this assessment is that it does not consider spatial variability of concentrations within a compartment. For example, air concentrations vary depending on the distance from a source of air emissions, such as a stack or a site of soil contamination. The fugacity approach would typically treat air as a single compartment with a uniform concentration.

The transfer of contaminants between compartments and multimedia modeling approaches have been extensively studied at the National Center for Intermedia Transport at the University of California, Los Angeles. Their multimedia compartment model, MCM (Cohen and Ryan, 1985), provides several useful algorithms for intermedia transfer factors that would have application for dioxin-like compounds. More recently, this group has introduced the spatial multimedia compartment model (Cohen, et al., 1990), which allows for non-uniformity in some compartments. Such a model would be more suitable for the types of source categories of this assessment, since there is non-uniformity within a compartment as noted above in the air compartment example.

An early approach which merged simplistic multimedia modeling with human exposure was termed the exposure commitment method, developed by Bennett (1981). An exposure commitment is defined as a contaminant concentration in human tissue. Exposure commitments are calculated from transfer factors that are estimated as the ratios of the steady-state concentrations of a contaminant in adjoining compartments of an exposure pathway. An example of adjoining compartments is air to plants to livestock to diet. This method has been applied to both PCBs (Bennett, 1983) and 2,3,7,8-TCDD (Jones and Bennett, 1989). These applications have required measured concentrations of

the contaminants in different compartments in order to estimate the transfer factors. The retrospective nature of this approach limits its usefulness for general applications.

One of the early multimedia models which also had human exposure as the endpoint, but did not require retrospective data, was the GEOTOX model (McKone and Layton, 1986). This model had air (vapor and particle phases), water (surface and ground water, including bottom sediments of surface water bodies), soil (soil gas, water, and solid subcompartments), and biomass (eggs, milk, meat, fish, and vegetation including food crops) compartments. The most recent evolution of this model can be found in McKone and Daniels (1991).

Multimedia modeling approaches have been extensively used to evaluate the exposure to dioxins. Paustenbach, et al. (1992) evaluated the exposure and risk to humans from residential and industrial soil contamination by 2,3,7,8-TCDD. Simple models were used to estimate the concentrations of 2,3,7,8-TCDD in air-borne suspended particulates and fish that reside in nearby streams impacted by the contaminated soil. Together with concentrations in contaminated soil, Paustenbach evaluated human exposures via soil ingestion, dermal contact, particulate inhalation, and fish consumption. They also used Monte Carlo techniques on exposure parameters (in contrast to fate and transport parameters) to determine a range of residential and industrial soil concentrations that would result in a specified risk level. The risk level chosen for their demonstration was 10^{-5}, which was determined by multiplication of the Lifetime Average Daily Doses (LADDs in mg/kg-day) and the cancer slope factor for 2,3,7,8-TCDD of 9700 $(mg/kg\text{-}day)^{-1}$ derived by Keenan, et al. (1991). Residential soil concentrations less than 20 ppb did not pose a lifetime cancer risk greater than 10^{-5}. For industrial sites, concentrations in soil that could pose a 10^{-5} risk ranged between 131 and 582 ppb, depending on the amount of time the industrial worker spend outdoors under typical exposure conditions.

Travis and Hattemer-Frey (1991) evaluated human exposure to 2,3,7,8-TCDD from a broader perspective. The principal assumption of the Fugacity Food Chain model used for Travis' human exposure assessment is that atmospheric concentrations of 2,3,7,8-TCDD can be empirically linked to water, soil, and vegetative concentrations, which in turn are linked to agricultural produce, meat, milk, eggs, and fish concentrations. Simple models for atmospheric depositions onto plants, air-to-leaf transfers of vapor phase

2,3,7,8-TCDD onto plants, transfers to cattle beef and milk, and other models, are presented. They also compared their model predictions of exposure media concentrations to literature values, and concluded that their approaches resulted in concentrations comparable to those found in the literature. This effort by Travis and Hattemer-Frey is examined in more detail in Section 5.6 of Chapter 5.

Exposure to 2,3,7,8-TCDD using simplistic multimedia models has also been assessed for specific sources. Goeden and Smith (1989) evaluated the impact to fish and subsequent human exposure by consumption of fish to dioxins and furans emitted by a resource-recovery facility. Surface water sediment concentrations in a lake were estimated as a simple weighted average of concentrations on three kinds of particles entering the lake: soil via erosion whose concentration was estimated given contaminated particle depositions onto soil (and considering mixing and soil half-lives), deposition of background uncontaminated suspended particulates directly onto the lake, and direct deposition of contaminated particles onto the lake. Fries and Paustenbach (1990) also evaluated the impact of incinerator emissions of 2,3,7,8-TCDD, but they evaluated human exposure via consumption of food crops, meat, and milk. EPA (1990d) used a simple dilution model to evaluate the impact of pulp and paper mill effluent discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF into surface water bodies.

This is only a cursory summary of the wealth of multimedia modeling approaches that are available, and the application of such modeling approaches for evaluating human exposure to 2,3,7,8-TCDD. While there are many similarities and differences among the approaches, they all share one characteristic in common - they have all been described as "screening level models". Without attempting a definition of the qualifier, "screening level", such a qualifier for these models seems to imply the following types of common features: assumptions of equilibrium and/or steady state conditions between compartments, lack of substantial (if any) spatial or temporal resolution, the use of biotransfer or bioconcentration concepts which simply relate an environmental concentration (air or water concentration, e.g.) to a biomass concentration (plant or fish concentrations), and so on. A counterpoint to screening level models might be what are termed "site-specific" or "mechanistic" models. Such models are more theoretically sophisticated, contain more spatial and temporal resolution, attempt to simulate actual mechanisms of fate and transport rather than depend on empirical relationships developed

from data, could involve complex food chain approaches to model biomass concentrations (to counter the simple biotransfer or bioconcentration approaches), and generally are highly parameterized requiring site-specific data that is often not readily available.

Because of the complexity of the multimedia environment, modeling of contaminant fate in such an environment has tended to remain simple. However, there are complex models which can be applied to smaller subsets of the multimedia environment, and which have been applied to assessments of dioxin-like compounds. One example is the COMPDEP model, which was used in this assessment to evaluate the impact of stack emissions of dioxin-like compounds. That model allows for complexities of terrain, varying weather patterns, vapor/particle partitioning, etc., to be considered. That model is further described in Chapter 3. Another example of more complex modeling was the use of the WASP4 model in a comprehensive evaluation of bioaccumulation of 2,3,7,8-TCDD in Lake Ontario (EPA, 1990b). That application required a substantial amount of site-specific parameterization.

With the exception of the COMPDEP model, the models used for this assessment are better described as screening level rather than mechanistic or site-specific. Many of the algorithms used are the same or very similar to the ones found in references above. Except for the effluent discharge source category, which uses a non-spatially resolved dilution model for surface water impacts, the algorithms do consider spatial differences between the source and site of impact or site of exposure. For example, the algorithm estimating surface water impacts from a site of soil contamination, while simple in its framework, does incorporate the following: the area of the site that is contaminated, the area of the watershed which drains into the water body, the erosion rates of the site of contamination as well as the rest of the watershed, the proximity of the site to the water body, the concentration of the contaminant at the site of contamination as well within the watershed other than the contaminated site, the lipid content of the fish, and the organic carbon fractions of the suspended and bottom sediments of the water body. Assignments for all these parameters impact water and fish concentrations, and it is certainly arguable that they are all site-specific parameters. From this perspective, it could be argued that most of the algorithms of this assessment are generally screening level in their theoretical sophistication, but site specific in their application.

Sections in other chapters of this volume address key issues relating to the use and

credibility of the algorithms described in this chapter. Chapter 5, which demonstrates the methodology, makes observations concerning exposure media concentrations in Section 5.6.1. Chapter 6, on User Considerations for use of the models and algorithms of this assessment, discusses categorization of model parameters and conducts sensitivity analysis exercises on key fate, transport, and transfer algorithms. Chapter 7 on Uncertainty also has critical discussions including: when possible, comparison of exposure media concentration estimations of 2,3,7,8-TCDD made in the demonstration scenarios with literature values, comparison with alternate modeling approaches, and general discussions of parameter assignment uncertainty and algorithm uncertainties.

Figures 4-1 through 4-4 are flow diagrams showing interim compartment concentrations modeled, and principal processes modeled and assumptions made in the intermedia transfer. Sections 4.3. through 4.7 describe the algorithms for the four source categories considered in this assessment, and background and assignment of parameters for the demonstration scenarios of Chapter 5.

4.3. ALGORITHMS FOR THE "ON-SITE SOIL" SOURCE CATEGORY

As earlier noted, the contamination and exposure occur at the same site for this source category. The contamination is assumed to originate at the soil surface. As such, the soil itself is the exposure media for the dermal contact and soil ingestion pathways. Sections 4.3.1 through 4.3.4 describe the algorithms for estimating concentrations of the dioxin-like compounds in: bottom sediment, suspended solids, and in the dissolved phase in the water column of surface water bodies (4.3.1), in the air in the vapor phase (4.3.2) and particulate phase (4.3.3), and in biota including fish (4.3.4.1), home-grown vegetables and fruit (4.3.4.2), and beef and milk (4.3.4.3).

4.3.1. Surface Water and Sediment Contamination

The principal assumption in the algorithm estimating the impact to surface water and surface water sediments (suspended and bottom sediments) from an area of contaminated soil is that such an impact is correlated to surface soil concentrations at that site as well as surface soil concentrations within a larger area draining into the water body. This drainage area is commonly referred to as a watershed. Further, the impact to the water body is assumed to be uniform. This tends to be more realistic for smaller water

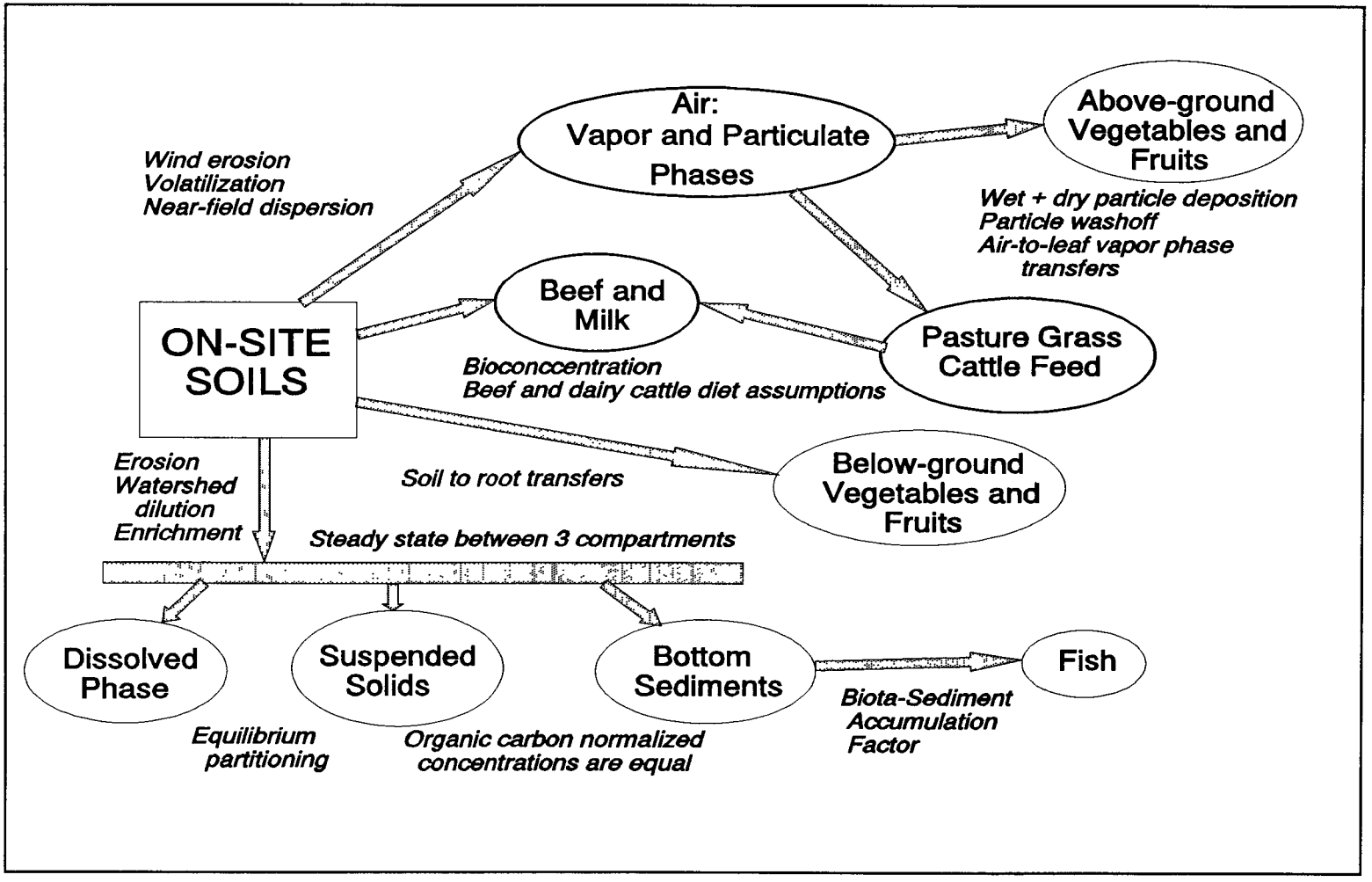


Figure 4-1. Diagram of the fate, transport, and transfer relationships for the on-site source category.

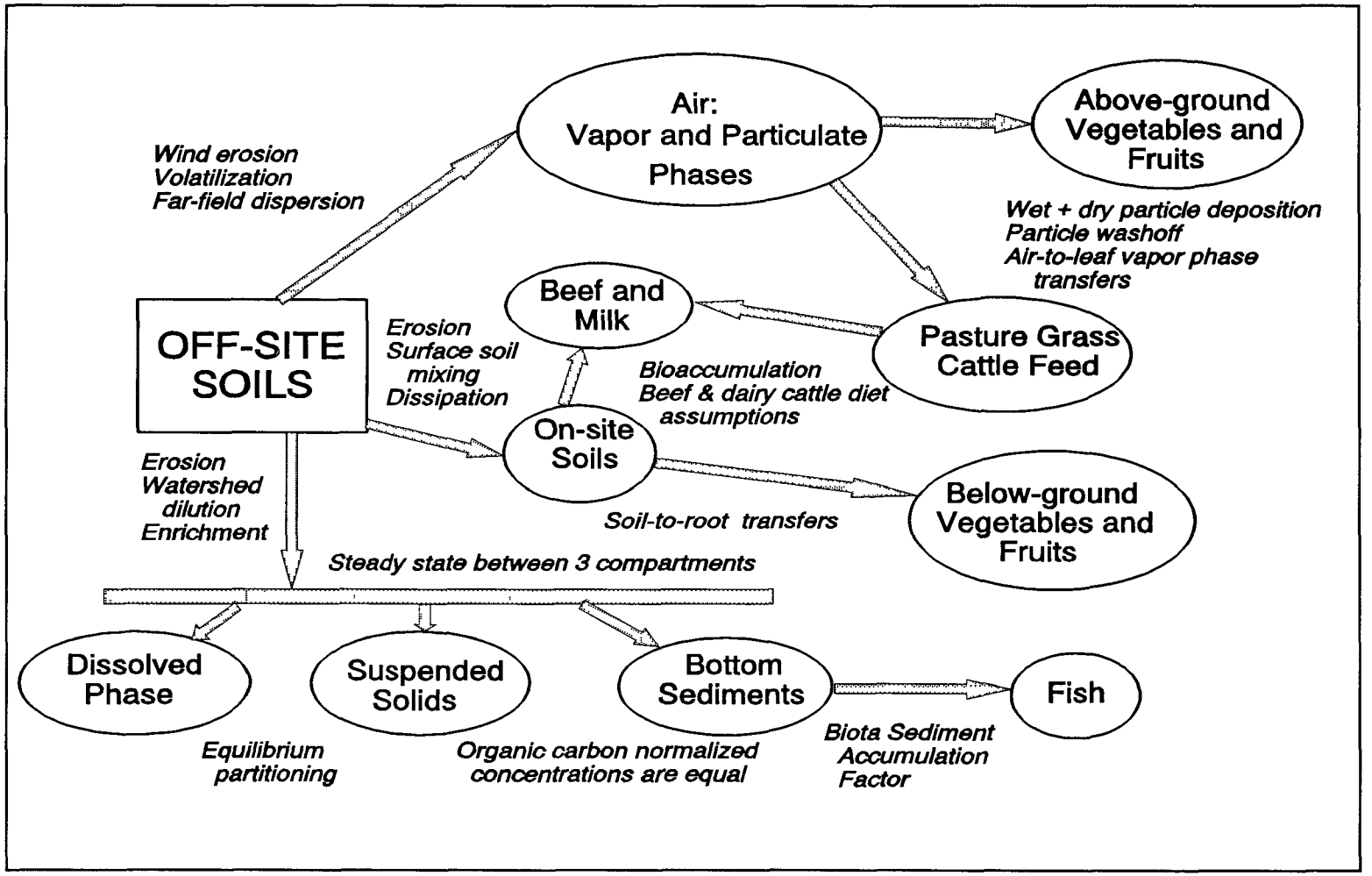


Figure 4-2. Diagram of the fate, transport, and transfer relationships for the off-site source category.

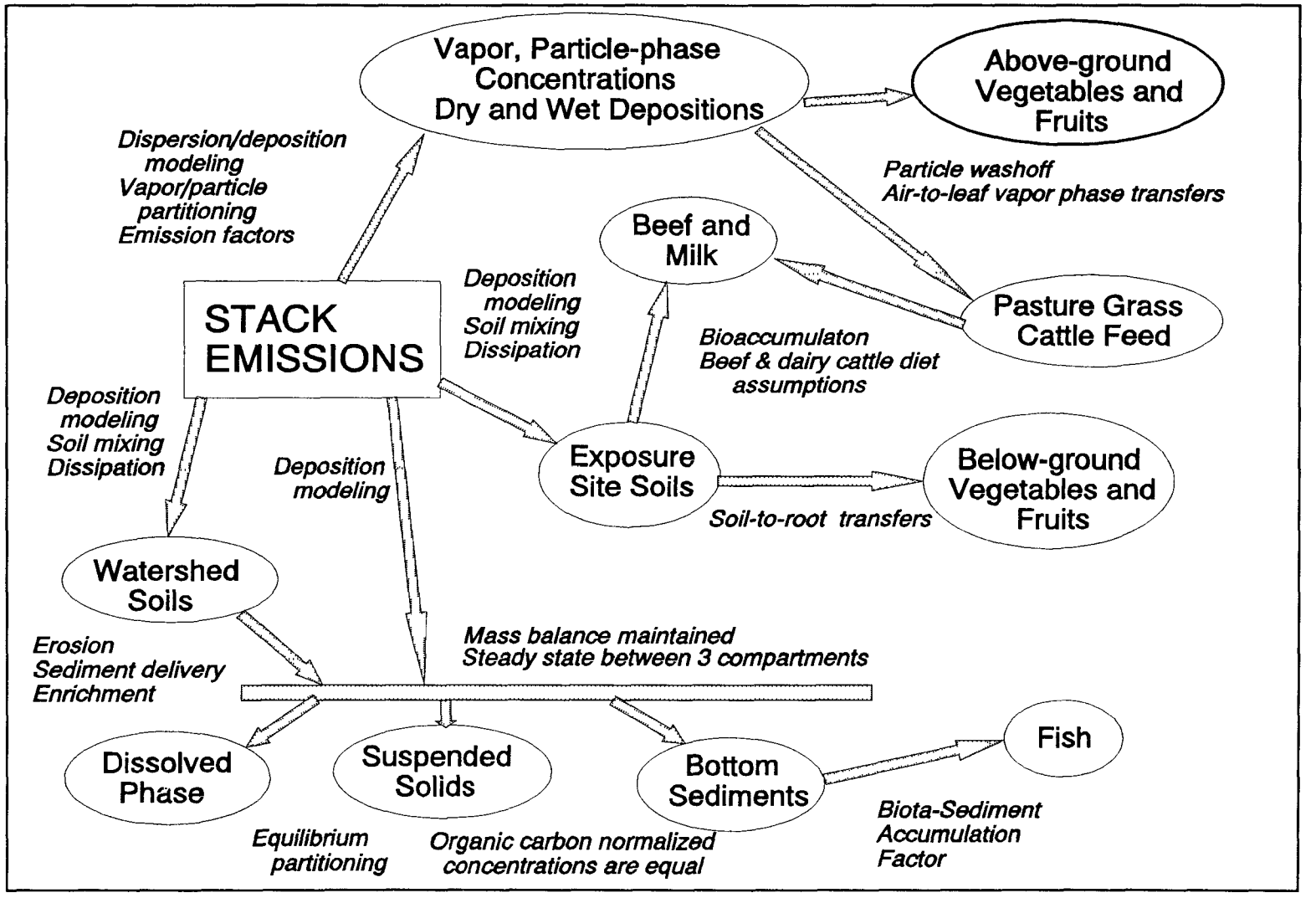


Figure 4-3. Diagram of the fate, transport, and transfer relationships for the stack emission source category.

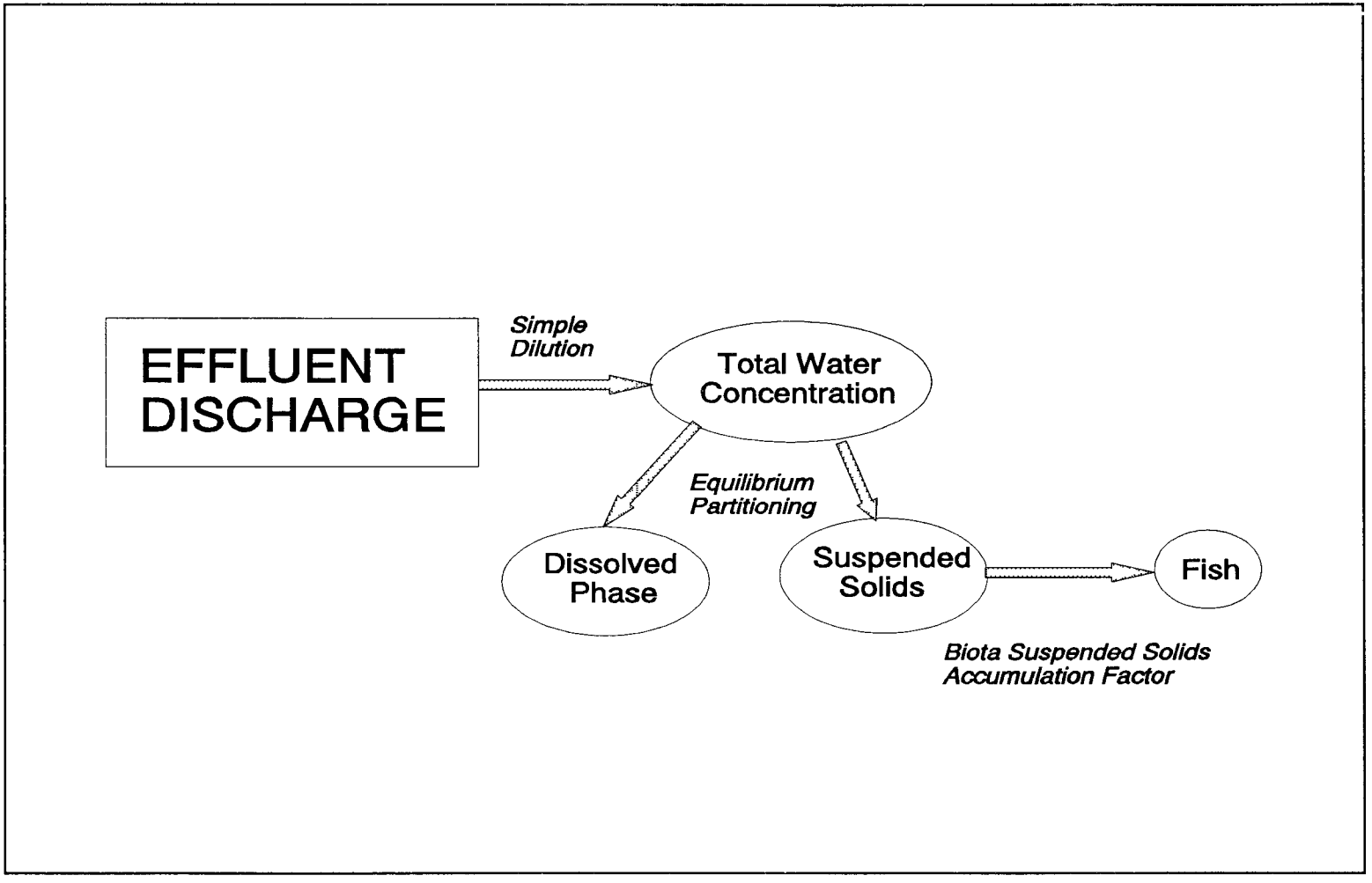


Figure 4-4. Diagram of the fate, transport, and transfer relationships for the effluent discharge source category.

bodies as compared to large river systems. Other key assumptions in the surface water impact algorithm are:

- Soil erosion estimates, coupled with sediment delivery ratios, can be used to describe the impact of a contaminated site relative to other soils in the watershed which contribute sediments to the water body;
- The sorption of dioxin-like compounds onto surface soil, suspended solids and bottom sediments is principally a function of the contaminant's organic carbon partition coefficient, Koc, and the organic carbon content of soils and sediments;
- The concentration of contaminants in soil eroding from a site are initially higher than the concentrations at the site itself - it is "enriched" with contaminants. This enrichment occurs because some processes of transport, such as wind erosion or soil erosion, favor lighter soils (silts and clays) which have higher surface area to volume ratios (more binding sites) as well as higher organic matter contents on the average (which also favors more binding of organic chemicals). Other processes such as volatilization or degradation may counteract the enrichment noted at the edge of a site - concentrations on soil entering a water body may be less than those leaving the site;
- The concentration of contaminants in sediment suspended in the water column exceeds the concentration in bottom sediments. Similar reasoning as the above enrichment argument applies: particulates which remain in suspension tend to be lighter and more enriched with organic matter as compared to particulates which settle to the bottom of water bodies. It should be noted that suspended solids, in this algorithm, are simply a reservoir into which dioxin-like compounds sorb; more complex models consider sorption onto more than one reservoir of suspended materials including suspended particulates and dissolved organic matter;
- Suspended and bottom sediments originate principally as soil erosion; a mass balance is maintained such that a part of the soil reaching the water body through erosion remains as suspended particulates, and a part settles to bottom sediments.
- A steady state is achieved between concentrations in the dissolved phase in the water column, concentrations in the sorbed phase in the water column, and concentrations in bottom sediments;
- Volatilization out of the water body or degradation of residues in the water body are not modeled. Neglecting these dissipation processes has the net effect of

overestimating water body impact. On the other hand, bottom sediment resuspension is not modeled. Not modeling resuspension would have a net effect of underestimating water column impacts; and

- Estimating the average impact to the water body, rather than a localized impact which may be the case if the contaminated soil is very near the water body, is suitable for purposes of this assessment procedure.

Concentrations in bottom sediment are desired because fish concentrations are estimated as a function of bottom sediment concentrations (see Section 4.3.4.1). Concentrations in suspended solids are desired because they are used to estimate bottom sediment concentrations, and dissolved phase concentrations are needed for estimating drinking water exposures.

The solution begins with the mass balance statement:

The mass of contaminant entering the water body	=	An amount which remains as dissolved in the water column + An amount which remains sorbed to suspended materials + An amount which remains sorbed to particles settling to the bottom

This can be described mathematically as:

$$C_{swb}\, ER_w = C_{wat}\, V_{wat} + C_{ssed}\, M_{ssed} + C_{sed}\, M_{sed} \qquad (4\text{-}1)$$

where:

C_{swb}	=	concentration on soil entering water body, mg/kg
ER_w	=	total watershed annual soil erosion, kg/yr
C_{wat}	=	dissolved-phase concentration in water column, mg/L
V_{wat}	=	water body annual volume, L/yr
C_{ssed}	=	concentration on suspended sediment, mg/kg
M_{ssed}	=	mass of suspended sediment introduced per year, kg/yr
C_{sed}	=	concentration on sediment settling to bottom, mg/kg
M_{sed}	=	mass of bottom sediment introduced per year, kg/yr

Other equations based on assumptions stated above and needed for this solution are:

1) mass balance of soil is maintained:

$$ER_w = M_{ssed} + M_{sed} \quad (4\text{-}2)$$

$$M_{ssed} = f_s \, ER_w \quad (4\text{-}3)$$

$$M_{sed} = (1 - f_s) \, ER_w \quad (4\text{-}4)$$

where:

f_s = fraction of annual erosion remaining as suspended materials, unitless

2) equilibrium between sorbed and dissolved phases is maintained; suspended sediments are enriched in comparison to bottom sediments:

$$C_{wat} = \frac{C_{ssed}}{Kd_{ssed}} \quad (4\text{-}5)$$

$$C_{sed} = C_{ssed} \frac{OC_{sed}}{OC_{ssed}} \quad (4\text{-}6)$$

where:

Kd_{ssed} = soil-water partition coefficient for contaminant in suspended sediment, L/kg

OC_{ssed} = fraction organic carbon in suspended sediment, unitless

OC_{sed} = fraction organic carbon in bottom sediment, unitless

Now, Equations (4-2) through (4-6) can be substituted into the right hand side of Equation (4-1) so that this side can be function a one concentration, C_{ssed}, and one erosion amount, ER_w. Factoring out C_{ssed} then gives:

$$C_{swb}\ ER_w = C_{ssed}\ \{\ \frac{V_{wat}}{Kd_{ssed}} + f_s\ ER_w + \frac{OC_{sed}}{OC_{ssed}}\ (\ 1 - f_s\ )\ ER_w\ \} \qquad (4\text{-}7)$$

The bracketed quantity in the right hand side of Equation (4-7) can be termed ϕ, so that C_{ssed} can be solved as $(C_{swb}\ ER_w)/\phi$. Now, the numerator in this term can be expanded to describe contaminant contributions by a site of contamination and contaminant contributions by the rest of the watershed. Included in this solution is the assumption made above that soils eroding into water bodies are "enriched":

$$C_{swb}\ ER_w = C_s\ SL_s\ A_s\ E\ SD_s + C_w\ SL_w\ (\ A_w - A_s\ )\ E\ SD_w \qquad (4\text{-}8)$$

where:

C_{swb}	=	concentration on soil entering water body, mg/kg
ER_w	=	total watershed erosion, kg/yr
C_s	=	contaminated site soil concentration of dioxin-like compound, mg/kg
E	=	enrichment ratio, unitless
SL_s	=	unit soil loss from contaminated site area, kg/ha-yr
A_s	=	area of contaminated site, ha
SD_s	=	sediment delivery ratio for soil eroding from contaminated site to water body, unitless
C_w	=	average concentration of dioxin-like compound in effective area of watershed not including contaminated site, mg/kg
SL_w	=	average unit soil loss for land area within watershed not including contaminated site, kg/ha-yr
A_w	=	effective drainage area of watershed; the area contributing sediment which mixes with the sediment originating from A_s, ha
SD_w	=	sediment delivery ratio for watershed, unitless

Finally, the right hand side of Equation (4-8) can be termed, ρ, and the concentration in suspended sediment, C_{ssed}, is equal to ρ/ϕ. All the terms in ρ/ϕ are input parameters or can be solved as a function of input parameters. Other water body concentration terms, C_{wat} and C_{sed}, can now be solved using Equations (4-5) and (4-6). Note that this solution

is most applicable to small water bodies to ponds and streams. The differences in the two water systems can be expressed in the parameters, effective watershed area, A_w, water body volume, V_{wat}, and organic carbon contents of suspended solids and bottom sediments, OC_{ssed} and OC_{sed}. Guidance on these terms and assignment of values for the demonstration scenarios in Chapter 5 is now given.

- **C_s and C_w:** These are concentrations of dioxin-like compounds in the contaminated site soil, C_s, and the average within the effective area of the watershed, C_w. The contaminated site concentrations drive the concentrations assumed for most exposures, and is a principal user input (for the on-site source category, the contaminated site is also the site of exposure). The simplest assumption for C_w is that it is 0.0. However, examination of soil data from around the world shows that, where researchers have measured concentration in what they described as "background" or "rural" settings, soil concentrations of PCDDs and PCDFs are in the non-detect to low ng/kg (ppt) range. Example Scenarios 1 and 2 in Chapter 5 demonstrate the on-site source category. For these example scenarios, C_w and C_s are both initialized at 10^{-6} mg/kg (1 ppt) for all example compounds representing low concentrations that might be possible for basin-wide areas.

- **E:** Enrichment refers to the fact that erosion favors the lighter soil particles, which have higher surface area to volume ratios and are higher in organic matter content. Therefore, concentrations of organic contaminants, which are a function of organic carbon content of sorbing media, would be expected to be higher in eroded soil as compared to in-situ soil. While enrichment is best ascertained with sampling or site-specific expertise, generally it has been assigned values in the range of 1 to 5 for organic matter, phosphorous, and other soil-bound constituents of concern (EPA, 1977). The enrichment ratio would be expected to be higher in sandy soils as compared to silty or loamy soils because the finer silt particles which erode from a soil generally characterized as sandy are more a deviation from the norm compared to silt particles which erode from a soil generally characterized as silty or loamy. The example scenarios in Chapter 5 modeled mid-range agricultural loam soils (as modeled with organic carbon fractions, soil loss parameters as discussed below, etc.). The enrichment ratio will therefore be assigned a

value of 3.0 in all circumstances.

- **SL_s and SL_w:** These are the unit soil loss, in kg/ha, from the exposure site and the average from the effective land area draining into the surface water body. In the simplest case, the unit losses can be considered equal. In the most complicated solution, the effective drainage area can be broken up into "source areas", where each source area can be unique in terms of the erosion potential, concentration of contaminant, and so on. The total contribution equals the sum of contributions from each source area, as: $\Sigma C_j * SL_j * A_j * E_j * SD_j$ for the right hand side of Equation (4-8) for j number of source areas not including the exposure site. For direct input into Equation (4-8), the terms C_j, SL_j, A_j, E_j, and SD_j, should be determined and C_w, SL_w, E_w, and SD_w should be estimated as weighted averages over all source areas, A_j. The effective drainage area, A_w, would be the sum of all source areas, A_j.

For the example scenarios in Chapter 5 demonstrating the on-site source categories, SL_s and SL_w are assumed equal. This generally assumes that erosion parameters for the site of exposure mirror the averages for the drainage area. Also, the enrichment ratio, E, is assumed to be constant for all watershed soils. For the off-site soil source category, the site of contamination is assumed to have different erosion characteristics. The following is offered as general guidance and background for estimation of unit soil losses in this assessment.

The unit soil loss is commonly estimated using the Universal Soil Loss Equation. This empirical equation estimates the amount of soil eroding from the edge of a field (Wischmeier and Smith, 1965):

$$SL = R\ K\ LS\ C\ P \qquad (4\text{-}9)$$

where:

SL	=	average annual soil loss, Eng. tons/acre-year
R	=	rainfall/runoff erosivity index, t-ft/ac-yr
K	=	soil erodibility factor, t/ac-(unit of RF)
LS	=	topographical factor, unitless
C	=	cover and management practice, unitless

P = supporting practices factor, unitless.

Several references are available to evaluate USLE factors for agricultural and non-agricultural settings (EPA, 1977; USDA, 1974; Wischmeier, 1972; Novotny and Chesters, 1981). For this assessment, values for these terms will based on assumptions about contaminated sites and rural soils. Justification and assumptions are given below. It should be noted that more sophisticated models are available for estimating erosion rates (i.e., CREAMS as described in Knisel, 1980), and should be considered in actual site-specific assessments.

- **Rainfall/erosivity index, R:** The R term represents the influence of precipitation on erosion, and is derived from data on the frequency and intensity of storms. This value is typically derived on a storm-by-storm basis, but it has been compiled regionally for the development of average annual values (EPA, 1977). Annual values range from < 50 for the arid western United States to > 300 for the Southeast. The value used in this assessment will be 160, which is typical of rainfall patterns seen in much of the midwestern United States.

- **Soil erodibility, K:** The soil erodibility factor reflects the influence of soil properties on erosion, with values ranging from <0.05 for non-erodible sandy soils to >0.50 for highly erodible silty soils. The value used in this assessment will be 0.30, which is typical of, for example, sandy or silty loam soils with 2% - 4% organic matter contents.

- **Length-slope factor, LS:** The topographic factor reflects the influence of slope steepness and length of the field in the direction of the erosion. Steeper slopes and longer lengths lead to higher LS values, with a range of 0.1 for slopes <1.0% and lengths <100 ft to >2.0 for slopes generally >10%. The two key considerations for its assignment, therefore, are the size of the field for which erosion estimates are being made, and the slope of that field. The example scenarios in Chapter 5 had field sizes of 0.4 ha (1 ac) for a rural residence, 4 ha (10 ac) for a small rural farm, and 10 ha (25 ac) for an off-site contamination site. Guidance for use of the Universal Soil Loss Equation stops short

of defining appropriate sizes of field for which unit estimates are to be derived, except that the USLE was developed for agricultural "fields" where cover, slope, soil type, etc. are assumed to be uniform. For purposes of estimating erosion losses in this assessment, a field of 4 ha for estimating the LS factor will be used. In a rural watershed with agricultural and non-agricultural settings, this would be a reasonable average area of uniformity. If square shaped, a 4 ha area translates to a side length of 200 m. For purposes of assignment of the LS factor, it will be assumed that the contaminated site has a 2% slope. EPA (1977) (and other references as noted above) show nomagraphs giving the LS factor as a function of slope length and slope. With a 200 meter slope length and a 2% slope, the LS factor is approximately 0.20. This factor will be used for all soil loss estimates required in this estimates.

- **Support practice factor, P:** The support practice factor reflects the use of surface conditioning, dikes, or other methods to control runoff/erosion. P can be no greater than 1.0. However, values less than 1.0 should only be assigned when specific practices are employed which are designed to reduce erosion. For the example scenarios in Chapter 5, it will be assumed that no such practices are in place at the site of concern or throughout the watershed to control erosion. Therefore, a value of 1.0 will be assumed.

- **Management practice factor, C:** The final term in the USLE is the cover and management practice factor, C, which primarily reflects how vegetative cover and cropping practices, such as planting across slope rather than up and down slope, influences erosion. C values can be no greater than 1.0, with this value appropriate for bare soils. A C value of 1.0 is an appropriate choice for active landfills or sites of high soil contamination (like Superfund sites) mostly devoid of vegetation. For an inactive landfill with grass cover or any area with dense vegetative cover such as grass, a value of 0.1 or less is appropriate. Values greater than 0.1 but less than 0.7 are appropriate for agricultural row crops, which offer more protection than bare soil, but not as much protection as dense vegetation. Three erosion estimates are required for scenarios demonstrated in Chapter 5. One is for areas of high soil contamination, or the scenario demonstrating the "off-site" source category. It will be assumed that the off-site

contaminated site is largely devoid of vegetation in this case, and a value of 1.0 will be assumed. A second erosion estimate is needed to characterize average unit soil loss throughout a watershed draining into a surface water body. The example scenarios are based on a rural setting which has agricultural and non-agricultural (i.e., rural residences) areas. The C value in this circumstance will be assumed to be 0.3. Finally, an soil erosion estimate is needed in the algorithm transporting contaminated soil from an area of high soil contamination to a nearby site of contamination, as part of the algorithms developed for the "off-site" source category. In this case, the land between a site of soil contamination and the nearby site of exposure will be assumed to be covered with dense vegetation, such as grass. In this case, the C value will be 0.1.

As just described, three unit soil loss estimates are required for this estimates and the difference between the three will be expressed in the C term. Multiplication of the five USLE terms gives unit soil loss estimates of 9.60 (with C = 1.0), 0.96 (with C = 0.1), and 2.88 (with C = 0.3) t/ac-yr. The value of SL_s and SL_w for the demonstration of the on-site scenario in Chapter 5 is 2.88 t/ac-yr. Since Equation (4-8) and other uses of unit soil loss estimates are needed in kg/ha-yr, these unit losses are easily converted to 21515, 2152, and 6455 kg/ha-yr.

- **A_s and A_w:** These are the area terms, including the area of the contaminated site, and the effective drainage area of the watershed, both in ha. The scenarios demonstrated in Chapter 5 have assumed 0.4 ha (1 acre roughly) for exposure sites described as rural residences, 4 ha (10 acres) for farms, and 10 ha (25 acres) for an off-site area of soil contamination. If the area of contamination is at the site of exposure, as in the "on-site" source category, then A_s should be assigned an area equalling the site of exposure (and the concentration term, C_s, should equal the average soil concentration over this site of exposure). If the area of contamination is away from the site of exposure, as in the "off-site" source category, A_s should equal the total area of contamination (and again C_s should equal the average soil concentration over this area).

The total area impacting a river system has been termed a watershed. For purposes of this assessment, an "effective" drainage area will almost always be less than the total area of a watershed. A "watershed" includes all the land area which contributes

water to a river system. For large river systems, this area is in the order of thousands of square miles and includes several tributaries and smaller streams feeding into the main branch of the river. Each stream and tributary has its own sub-basin, whose sediment originates from a land area much smaller than thousands of square miles. If the contaminated site lies within that sub-basin, that it would be appropriate to include only the area within that sub-basin as the effective drainage area. This is one circumstance where an "effective drainage area" would be less than a total watershed area. Another consideration for determining the effective drainage area is the positioning of the contaminated site with respect to the point where water is extracted for drinking and fish are caught for consumption. If these points are significantly upstream in the river system in relation to the contaminated site, there is no reason to conclude that sediments or water near where the water is extracted are impacted by the contaminated site. If these withdrawal points are downgradient of the contaminated site, then there is reason to believe that sediments and water are impacted. However, if they are downgradient from the contaminated site but not at the bottom of the watershed, then sediment and water quality further downgradient from the withdrawal points is not of concern and land draining into these downgradient portions would not be part of the "effective drainage area". One further possible consideration is how far upgradient in the watershed one should go when determining the size of the effective drainage area. While sediments introduced at the furthest points may eventually work their way down to the mouth of the watershed, this may take geologic time and not recent historic time. Therefore, sediment quality near a site of contamination need not consider these far reaches.

For a standing water body such as a lake or a pond substantially fed by ground water recharge, an assumption that probably should be made using the simple framework of this assessment is that all sediments within the lake/pond are completely mixed. Therefore, the effective area should equals all area around the lake/pond contributing sediment, and, as in the above discussion on river systems, a part of the land area contributing sediments to streams or rivers which may feed the standing water body.

From this discussion, it is clear that determination of an effective drainage area depends on site specific considerations, but it will likely be less than the total watershed area. For purposes of demonstration, the effective drainage area, A_w, will be assumed to be 4,000 hectares (10,000 acres, 15.6 mi^2). Furthermore, it will be assumed that the

water body in question is part of a river system, which mainly impacts the assignment of the total suspended solids parameter, TSS (as discussed below). This assignment is not based on any specific sites that have been studied. It is only justified as being a reasonable size for dilution of contaminated soils which originate from contaminated site. Given the other area terms discussed above, 0.4, 4, and 10 ha, then the assignment of 4000 ha would appear to add a substantial amount of clean soil for mixing considerations.

A useful data source for this term and the suspended sediment term below, for specific sites in the United States, is Appendix F in Mills, et al. (1985). This appendix includes a compilation of data from river and reservoir sediment deposition surveys, including total drainage area, water body volumes, and rates of sediment deposition (mass/area-time). A caution in using this and similar data bases when evaluating specific sites is that, again, these total drainage areas are just that, total areas. Water bodies in this data base are located in the 48 conterminous states. An estimate of suspended sediment concentrations can be made using the water volume and the sediment deposition rates from this data, and an assumption on sediment deposition velocity. The specific weight of sediments in the water body, also supplied in this appendix, can be used to estimate sediment deposition velocity.

- **SD_s and SD_w:** These are the sediment delivery ratios applied to the exposure site and the watershed as a whole. Such a ratio is required because not all the soil which erodes from an area deposits into the receiving water body. The following delivery ratio was proposed for construction sites (EPA, 1977):

$$SD_s = (3.28 \ DL)^{-0.22} \qquad (4\text{-}10)$$

where:

SD_s = sediment delivery ratio from site of interest, unitless
DL = distance from site to receiving water body, m
3.28 = converts m to ft (empirical equation was developed for units of ft).

Note that the sediment delivery empirical equation simplifies all land features pertinent to erosion to a function only of length. The equation was developed to estimate

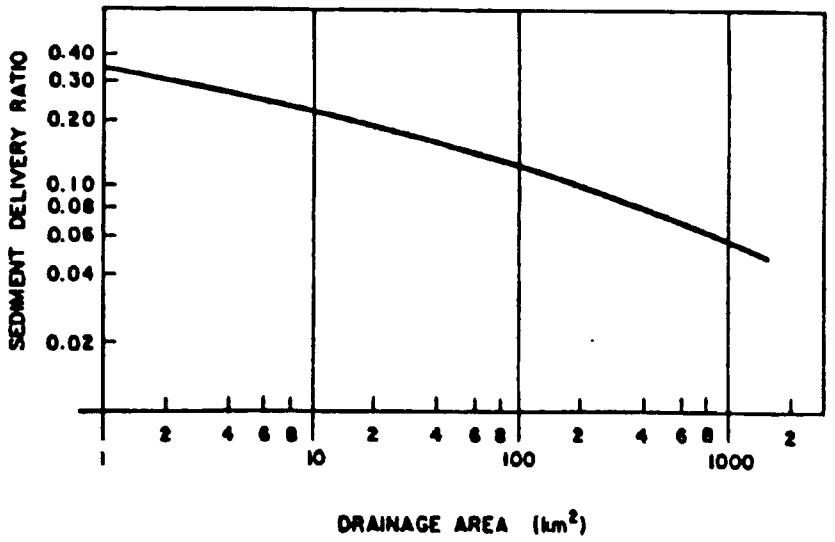
sediment loads from construction sites to nearby surface water bodies, and from distances up to 250 m (800 ft, roughly). Without specific information on the sites from which it was developed, it is assumed that the land area between the construction sites and the receiving water body is "average" and this relationship can be used for applications other than construction sites.

As noted in previous bullets, the example scenarios demonstrating the on-site source category assumed $C_s = C_w$, and $SL_s = SL_w$. The impacted water body was assumed to be 150 meters away from the site of contamination, also the site of exposure for the on-site source category. This distance translates to a delivery ratio of 0.26. Site-specific conditions could result in a larger (steeper slope, e.g.) or smaller proportion of the eroded soil being delivered to the water body than would be estimated with this equation.

Figure 4-5 shows a watershed delivery ratio as a function of watershed size (figure from Vanoni, 1975). As seen, the ratio decreases as land area increases. The total watershed size assumed for the example scenarios in Chapter 5 was 4,000 hectares, or 40 km^2. From Figure 4-5, this translates to a watershed delivery ratio, SD_w, of 0.15.

- **f_s:** As soil erodes into the water body, it will settle onto the bottom to become bottom sediment. Part of the settled material will become resuspended because of turbulent flow. The finest materials in eroded soil may not settle for a long time, and essentially always be in suspension. One way to arrive at the fraction of annually eroding material which remains in suspension ("remains in suspension" for purposes of discussion - in reality, little, if any, will remain in suspension, but will rather deposit and resuspend) involves complex modeling. A wealth of such models exist, such as those described in Wang (1989). The approach used here is more simple than those in Wang (1989).

If an average level of suspended material in the water were specified, in units of mg/L, what would be known with otherwise required parameters is the total amount of erosion reaching the water body (as discussed above) as well as the annual water volume (discussed below). A required parameter for this assessment will therefore be the level of suspended solids in the water body, TSS. With this parameter and the annual water flow volume, V_{wat}, the total suspended load equals, TSS (mg/L) * V_{wat} (L/yr). The assignment of these two terms are 10 mg/L and $1.524*10^{10}$ L/yr, leading to a total suspended load of



Source: Vanoni, 1975

Figure 4-5. Watershed delivery ratio, SD_W, as a function of watershed size.

$1.524 * 10^{11}$ mg/yr, or $1.524*10^5$ kg/yr. Total erosion into the water body, in similar units, equals, $A_s * SL_s * SD_s + (A_W - A_s) * SL_W * SD_W$. With parameter assignments as discussed above, the total annual erosion equals 3.87×10^6 kg/yr. Therefore, the fraction of total load that is suspended is 0.04 ($1.524*10^4/3.87*10^6$).

Given this formulation, the f_s term is not a model input value, but is solved on the basis of the other parameters noted.

- **TSS:** This is the total suspended sediment in the water body. This value will be lower for standing water bodies such as ponds or lakes as compared to streams or rivers. The more turbulent flow in rivers will suspend sediments to a greater degree than a relatively calm lake. A complex modeling exercise evaluating the impact of 2,3,7,8-TCDD to Lake Ontario assumed a suspended sediment concentration of 1.2 mg/L (EPA, 1990b). For use in pond or lake settings, an assumption of a suspended sediment concentration of 1-2 mg/L is reasonable. All example scenarios in Chapter 5 assume that the 4,000 ha watershed drains into a river suitable for supporting fish for consumption and water for

drinking purposes. General guidance offered for the potential for pollution problems in rivers and streams as a function of average suspended sediment concentration are: 10 mg/L or less - no problem, 100 mg/L or less - potential problem, and greater than 100 mg/L - probable problem. A cutoff concentration for protection of aquatic life is 80 mg/L (Mills, et al., 1985). The value assumed for TSS for all example scenarios in Chapter 9 is 10 mg/L, indicating no turbidity problems and a river supportive of fish for consumption.

- **V_{wat}**: The stream in the example scenarios will be assumed to derive its annual flow only from the effective drainage area, A_w. This would imply that the scenarios are best described as sub-basins (see the discussion on effective drainage area, A_w, above). Given the area of drainage, one way to estimate annual flow volume is to multiply total drainage area (in length squared units) times a unit surface water contribution (in length per time). The *Water Atlas of the United States* (Geraghty et al., 1973) provides maps with isolines of annual average surface-water runoff, which they define as all flow contributions to surface water bodies, including direct runoff, shallow interflow, and ground-water recharge. The range of values shown include 5-15 in/yr throughout the Midwest cornbelt, 15-30 in/yr in the South and Northeast, 1-5 in/yr in the desert Southwest, and a wide range of 10-40 in/yr in the far West. For this assessment, an assumed 15 in/yr is used to estimate the annual flow volume. Over a 4,000 hectare drainage area, total flow volume equals 1.524×10^{10} L/yr (15 in/yr * 0.0254 m/in * 4,000 ha * 10,000 m^2/ha * 1000 L/m^3).

- **Kd_{ssed}**: This adsorption partition coefficient describes the partitioning between suspended sediment and the water column. For numerous applications for organic contaminants, particularly for estimating the partitioning between soil and soil water, this partition coefficient has been estimated as a function of the organic carbon partition coefficient and the fraction organic carbon in the partitioning media:

$$Kd_{ssed} = Koc \quad OC_{ssed} \qquad (4\text{-}11)$$

where:

Kd_{ssed} = partition coefficient between suspended sediment and water, L/kg

Koc = organic carbon partition coefficient for contaminants, L/kg or cm^3/gm

OC_{ssed} = fraction organic carbon content of suspended sediment, unitless.

The organic carbon partition coefficient, Koc, can be a measured value or it can be estimated. Schroy, et al. (1985) listed an organic solids/water partition coefficient of 468,000 for 2,3,7,8-TCDD. Information in Jackson, et al. (1986), imply that this is a very low partition coefficient for 2,3,7,8-TCDD. They obtained soil samples contaminated with 2,3,7,8-TCDD from 8 sites in the Times Beach area of Missouri, and 2 from industrial sites in New Jersey. These contaminated soils had 2,3,7,8-TCDD concentrations ranging from 8 to 26,000 μg/kg (ppb), and organic carbon contents ranging from 0.015 to 0.08. They determined soil water partition coefficients, Kd_s, for these soil samples, and using the organic carbon fraction data, estimated Kocs for 2,3,7,8-TCDD. The mean Koc from these ten samples was roughly 24,500,000. EPA (1990b) evaluated the Koc for sorption of 2,3,7,8-TCDD onto Lake Ontario sediments. They concluded that log Koc was greater than 6.3 (Koc = 2,000,000), but less than 7.3 (Koc = 20,000,000).

In the absence of measured values, the Koc can be estimated from a chemical's octanol water partition coefficient, Kow. Empirical equations relating Kow to Koc are listed in Lyman, et al. (1982). Of six different equations listed in that reference, the following derived by Karickhoff, et al. (1979) is used to estimate the Koc for the example compounds in Chapter 5:

$$\log Koc = \log (Kow) - 0.21 \qquad (4\text{-}12)$$

where:

Koc = organic carbon partition coefficient, L/kg

Kow = octanol water partition coefficient, unitless

This equation was empirically developed from a limited number of hydrophobic contaminants (n = 10, R^2 = 1.00). It implies that Koc is very similar to Kow for strongly sorbed compounds such as the dioxin-like compounds. Using the log Kow of 6.64 given in this assessment for 2,3,7,8-TCDD in Karickhoff's relationship estimates a Koc of roughly 2,700,000.

- **OC_{sed}, OC_{ssed}:** The organic carbon content of solids and sediments of water bodies are generally higher than organic carbon contents of the surrounding lands. Furthermore, organic carbon contents of suspended organic materials and solids are typically greater than those of bottom sediments. A significant sink for strongly hydrophobic contaminants such as the dioxin-like compounds is thought to be suspended, or non-settling, organic material. In modeling 2,3,7,8-TCDD in Lake Ontario (EPA, 1990b) using the WASP4 model, a compartment separate from suspended solids termed "non-settling organic matter" served as a permanent sink. For purposes of this assessment, a single reservoir of suspended materials onto which incoming dioxin-like compounds sorb is principaily characterized by OC_{ssed}, and the values selected for OC_{sed} and OC_{ssed} should reflect the relative partitioning behavior of suspended and bottom materials. As noted above, these water body carbon contents are also related to the organic carbon contents of surrounding soils. The model parameter, OC_{sl}, is the soil organic carbon fraction and is required for modeling of soil contamination by dioxin-like compounds. Foth (1978) lists the organic nitrogen content of several soil types ranging from sand and sandy loam to clay. The range from that list is 0.0002 - 0.0024 on a fractional basis. Assuming a carbon to nitrogen ratio of 10 (Brady, 1984; who notes that C:N ratios vary from 8 to 15, with the typical range of 10 to 12), organic carbon ranges from 0.002 to 0.024. A soil organic carbon fraction, OC_{sl}, is assumed to be 0.01 for all example settings in Chapter 9, which is in the middle of this range. The organic carbon content of bottom sediments, OC_{sed} will be higher at 0.03. Bottom sediments originate as erosion from surrounding land, but also include decay of organic materials within water bodies. The organic carbon content of suspended materials can approach 0.20, but OC_{ssed} will be assumed to be 0.05 for the example settings in Chapter 5.

4.3.2. Vapor-Phase Air Concentrations

The algorithms for estimating vapor-phase concentrations of contaminants were presented and derived in Hwang, et al. (1986). These procedures were developed for soil surface and subsurface contamination with polychlorinated biphenyls, PCBs. The models are based on the assumptions that: 1) PCBs move through the soil primarily by vapor phase diffusion, i.e., leaching is not considered, 2) PCB vapor in the soil matrix reaches a local equilibrium with pore air, 3) degradation processes for PCBs were not considered ,

and 4) the PCB contamination occurs at the surface and extends down infinitely. These assumptions are similar to the general types of assumptions that have been made for all the algorithms estimating exposure media concentrations in this assessment. The procedures in that PCB assessment were also used for this assessment. Details of the derivation are presented in Hwang, et al. (1986).

The average flux rate over an exposure duration of ED can be estimated as:

$$FLUX = \frac{(2)\ (E_{slp})\ (D_{ea})\ (C_s)\ (H)\ (41)\ (10^{-6})}{Kd_s\ [\ (\pi)\ (I)\ (ED)\ ]^{0.5}} \qquad (4\text{-}13)$$

where:

FLUX	=	average volatilization flux rate of contaminant from soil, g/cm^2-s
E_{slp}	=	soil pore porosity, unitless
D_{ea}	=	effective diffusivity of contaminant in air, cm^2/s
C_s	=	contaminant concentration in soil, ppm or mg/kg
H	=	Henry's Constant of contaminant, atm m^3/mol
Kd_s	=	soil/water partition coefficient, cm^3/g
ED	=	exposure duration, s
I	=	interim undefined term for calculation, cm^2/s
	=	$\dfrac{D_{ea}\ E_{slp}}{E_{slp} + P_{soil}\ (1\text{-}E_{slp})\ [Kd_s/(41\ H)]}$
P_{soil}	=	particle bulk density of soil, g/cm^3.

The effective diffusivity, D_{ea}, is solved as a function of contaminant diffusivity in air, and soil pore porosity:

$$D_{ea} = D_c\ E_{slp}^{0.33} \qquad (4\text{-}14)$$

where:

D_{ea}	=	effective diffusivity of contaminant in air, cm^2/s
D_c	=	molecular diffusivity of contaminant in air, cm^2/s
E_{slp}	=	soil pore porosity, unitless.

The soil adsorption partition coefficient, Kd_s, is given as:

$$Kd_s = Koc \quad OC_{sl} \tag{4-15}$$

where:

Koc = contaminant organic partition coefficient, L/kg

OC_{sl} = fraction organic carbon in soil, unitless.

It is noted in Hwang, et al. (1986) that this procedure would tend to overestimate emissions and resulting exposures in situations involving small spills which would not involve deep contamination. It is also noted that the average flux rate is inversely proportional to the square root of the duration of exposure - the longer the duration of exposure, the lower will be the average flux rate. Whereas this solution assumes an unlimited reservoir of contaminant, it is an unsteady state solution (unlike other solution strategies) and is essentially an average flux rate over an amount of time defined by the exposure duration. Inherent in the solution was the consideration that residues dissipate by volatilization at the surface layers, resulting in contaminants diffusing upwards from deeper soil layers over time. With this longer path of diffusion, volatilized amounts decrease, and hence the average flux over time also decreases.

Vapor-phase concentrations along the center (y=0.0) of an area source can be estimated from (Hwang, 1987):

$$C_{va} = \frac{(2/\pi)^{0.5} \quad FLUX \quad a \quad 10^{10} \quad erf(e)}{u_m \; S_z} \quad (e^{-0.5\,(Z/S_z)^2}) \tag{4-16}$$

where:

C_{va} = vapor-phase concentration of contaminant in air, $\mu g/m^3$

FLUX = Average volatilization flux rate of contaminant from soil, g/cm^2-s

a = side length parallel to the wind direction, m

U_m = mean annual wind speed, m/s

S_z = vertical dispersion coefficient in air, m

z = height of the exposed individual, m

erf	=	error function
e	=	error function term, unitless
	=	$b/(2*(2*S_y)^{.5})$
b	=	side length perpendicular to the wind direction, m
S_y	=	horizontal dispersion coefficient in air, m
10^{10}	=	converts g/cm^2-m to $\mu g/m^3$.

This was the model used to estimate on-site vapor-phase concentrations. The dispersion terms, S_z and S_y can be estimated using site-specific wind rose data. In the absence of data, these terms can be estimated assuming the most common stability class, D, as:

$$S_y = 0.1414\ X^{0.894} \quad \text{(4-17a)}$$

$$S_z = 0.222\ X^{0.725} \quad \text{(4-17b)}$$

where:

$S_{y,z}$	=	horizontal and vertical dispersion coefficient, m
X	=	distance upwind of the contaminated site, m.

Background on Koc and OC_{sl} were given in Section 4.3.1. above. Guidance for other terms in this algorithm now follow.

- **E_{slp}:** Porosity is defined as the pore space in soils occupied by air and water, and for sandy surface soils show a range of 0.35-0.50. Medium to fine-textured soils (loams, clays, etc.) show a higher range of 0.40-0.60 (Brady, 1984). Soil porosities in the example settings were 0.50.

- **H:** Henry's Constants were discussed in Volume 2, Chapter 2. The values of H used for the three example compounds were: for 2,3,7,8-TCDD - $1.65*10^{-5}$ atm m^3/mole; for 2,3,4,7,8-TCDF - $4.99*10^{-6}$ atm m^3/mole; and for 2,3,3',4,4',5,5'-HPCB - $1.00*10^{3}$ atm m^3/mole.

- **P_{soil}:** Particle bulk density is defined as the mass of a volume of soil solids. This contrasts the more common parameter, bulk density, which is the mass of a unit of dry soil, which includes both pores and solids. Particle bulk density, P_{soil}, has a narrow range of 2.60 to 2.75, and for general calculation purposes, Brady (1984) recommends a value of 2.65 for average mineral surface soils, the value used for the example settings.

- **ED:** The exposure duration is simply the amount of time individuals are exposed. Two exposure durations were used in the demonstration scenarios, 9 years for "central" and 20 years for "high end" exposures. Used in this algorithm, and as discussed earlier, longer exposure durations translate to lower average volatilization fluxes. This presumes a soil concentration assumed to be uniform over depth starting at time zero, and to become depleted over time. The selected exposure durations of 9 ($2.83*10^8$ sec) and 20 years ($6.31*10^8$ sec) was used.

- **D_c:** Molecular diffusivities in air of the example compounds could not be found in the literature. However, diffusivities of one compound can be estimated from another with the following (Thibodeaux, 1979):

$$\frac{D_a}{D_b} = \left(\frac{MW_b}{MW_a}\right)^{0.5} \qquad (4\text{-}18)$$

where:

$D_{a,b}$ = Molecular diffusivities of compounds a and b, cm^2/s

$MW_{a,b}$ = Molecular weights of compounds a and b, g/mole

Thibodeaux (1979) lists the molecular diffusivity of diphenyl at 25 C at 0.068. Given the molecular weight of diphenyl of 154 g/mole, the diffusivities of the example compounds are: 2,3,7,8-TCDD (MW = 322) = 0.047; 2,3,4,7,8-TCDF (MW = 340) = 0.046; and 2,3,3',4,4',5,5'-HPCB (MW = 396) = 0.043.

- **U_m:** Mean annual windspeeds vary from between 2.8 and 6.3 m/s (EPA,

1985b). An assumption of 4.0 m/s in the absence of site-specific average wind speeds was made for the example scenarios of this assessment.

- **a, b, z, and x:** Simple assumptions can be made to assign values to the length terms above: a, b, z, and x. Assuming a square-shaped contaminated site, a equals b which equals the square root of the area of the site. A common assumption for z, the height of the exposed individual, is 2 m. The x term can be assumed equal to a side length (a or b), or can equal the side length plus the distance to the exposed individual if the contamination is not on-site and dispersion is modeled as "near field." For the residence and farm setting examples in Chapter 5, where the contamination was on-site, the x term was equal to a side length.

4.3.3. Particulate-Phase Air Concentrations

The method for determining the flux of soil particles due to wind erosion for on-site conditions was developed in EPA (1985b) based on Gillette's (1981) field measurements of highly erodible soils. A key assumption for this solution is that the soil surface is assumed to be exposed to the wind, uncrusted, and to consist of finely divided particles. This creates a condition defined by EPA (1985b) as an "unlimited reservoir" and results in maximum dust emissions due to wind only. This wind erosion flux is given as (EPA, 1985b):

$$E_e = 0.036 \quad (1-V) \quad (U_m/U_t)^3 \quad F(x) \qquad (4\text{-}19)$$

where:

E_e = total dust flux of $< 10\ \mu$m particle due to wind erosion, g/m^2-hr
V = fraction of vegetation cover, unitless
U_m = mean annual wind speed, m/s
U_t = threshold wind speed, m/s
$F(x)$ = a function specific to this model.

EPA (1985b) provides details allowing for the application of this equation under a variety of circumstances. The following is offered as guidance specific to on-site

conditions:

- **V:** For a "residence" or "farm", grass or crops are likely to substantially cover the soil, and the fraction of vegetative cover can range from 0.5 (minimal coverage) to 0.9 (more lush coverage). For the residence example settings, V was set at 0.9 which assumes a continual grass cover over the contaminated soil. The V for the farm settings was instead 0.5. The area of contamination for the example farm settings was larger than the residence setting, 10 acres to 1 acre. The land where crops were grown was also contaminated; the 0.5 value for V assumes that the cropland is totally or partially bare at some times - perhaps during spring land preparation and fall harvest.

- **U_m, U_t:** As given above in Section 4.3.2. on vapor phase air concentrations, the mean annual wind speed, U_m, assumed in the example scenarios was 4.0 m/s. The threshold wind velocity, U_t, is the wind velocity at a height of 7 m above the ground needed to initiate soil erosion. It depends on nature of surface crust, moisture content, size distribution of particles, and presence of non-erodible elements. It can be estimated on the basis of the following procedure (EPA, 1985b):

Step 1. Determine the Threshold Friction Velocity

This is the wind speed measured at the surface needed to initiate soil erosion. EPA (1985b) shows how it can be determined as a function of soil aggregate size distribution. However, for the "unlimited reservoir" approach for which Equation (4-19) was developed, soil particles are assumed to be fine at 1.5 mm or less as an average. This translates to a threshold friction velocity of 75 cm/s and less. A value of 50 cm/s might be reasonably assumed to be representative of these types of surfaces, and was assumed for this assessment.

Step 2. Estimate the "Roughness Height"

EPA (1985b) graphically shows the roughness height for a range of possible conditions. Included in this range are a roughness height of 0.1 cm for natural snow, 1.0 cm for a plowed field, 2.0-4.0 cm for grassland, 4.0 cm for a wheat field or for suburban residential dwellings, and up to 1000 cm for high rise buildings. The assumption made for

the residence and farm example settings was 4.0 cm, following the information given for a wheat field or a suburban residence.

Step 3. Estimate Ratio of Threshold Wind Speed at 7 m to Friction Velocity

A chart provided by EPA (1985b) shows this ratio as a function of roughness height. For a roughness height of 4.0 cm, this ratio is seen to be 13.

Step 4. Estimate Threshold Wind Speed

This is simply the product of the ratio given in step 3 above and the friction velocity. Using values given above, 50 cm/sec * 13 = 6.5 m/sec.

- **F(x):** The model-specific function, F(x), is determined by first calculating the dimensionless ratio x, where $x = 0.886\ U_t/U_m$, and finding F(x) from a chart of F(x) versus x, as provided in EPA (1985b). For $U_t = 6.5$ and $U_m = 4.0$, $x = 1.44$ and $F(x) = 1.05$.

The unit dust flux is easily converted to a total contaminant flux by multiplying by soil concentration and area:

$$WE = (2.8 \times 10^{-13})\ C_s\ E_e\ A_s \qquad (4\text{-}20)$$

where:

WE	=	contaminant wind erosion emission rate, g/s
E_e	=	total dust flux of $<10\ \mu$m particle due to wind erosion, g/m^2-hr
C_s	=	contaminant concentration in soil, ppb or ng/g
A_{sc}	=	area of contaminated site, m^2
$2.8*10^{-13}$	=	converts ng/hr to g/sec.

The next step in estimate particulate-phase contaminant concentration is to estimate the dispersion term. The model that is used is the same as the one used to estimate on-site vapor phase dispersion given in Equation (4-16) above. The following two changes obtain the correct "FLUX" term for use in Equation (4-16):

1) Instead of WE, a total flux term presented here in units (g/sec) consistent with

other particulate flux terms discussed in this chapter, an appropriate "FLUX" for Equation (4-16) is a unit flux term: $C_s * E_e$ (ng/m^2-hr). Since the algorithm for E_e was developed for 10 μm size particles, the multiplication of E_e by C_s assumes that the concentration of contaminant on 10 μm size particulates is the same as that for the soil overall.

2) $C_s * E_e$ is still not in the right units for Equation (4-16). The conversion term of Equation (4-16), 10^{10}, should instead be, .00028.

Substituting $C_s * E_e$ for FLUX, and .00028 for 10^{10} in Equation (4-16) will allow for the estimate of C_{pa}, the particulate phase concentration of contaminant in air, in units of $\mu g/m^3$.

4.3.4. Biota Concentrations

This section summarizes the algorithms to estimate contaminant concentrations in fish, vegetation (including vegetables for human consumption and pasture grass or fodder grown on contaminated soil for beef cattle consumption), beef, and milk. As will be shown, all algorithms are simple empirical equations which relate an environmental media concentration to a biota concentration, using a "biotransfer" or "bioaccumulation" factor.

4.3.4.1. *Fish concentrations*

The procedure and supportive data for the algorithm to estimate fish tissue concentrations can be found in Cook, et al. (1991), and more recently in an assessment of risk of 2,3,7,8-TCDD to aquatic life and associated wildlife (EPA, 1993) which EPA is conducting as part of its reassessment of dioxin-like compounds. The information in those reference focuses on 2,3,7,8-TCDD, although there is discussion on the related compounds covered in this assessment including other PCDDs, PCDFs, and PCBs. These compounds share a high degree of hydrophobicity that increases as the degree of chlorination increases. Cook, et al. (1991) note that this corresponds in general to an increase in lipophilicity and an increase in ability to bind to organic carbon in sediments and to dissolved organic matter in water. However, these tendencies are not paralleled by an increase in bioaccumulation. Only the 2,3,7,8-chlorine-substituted congeners are substantially bioaccumulated by fish, although large quantities of other PCDD and PCDF congeners are found in sediments. This pattern of bioaccumulation results because of higher rates of metabolism of PCDDs and PCDFs in fish as compared to the

2,3,7,8-chlorine-substituted congeners (EPA, 1992; Cook, et al., 1991, with references to Muir et al., 1986; Gobas, 1990). While the highly chlorinated 2,3,7,8-substituted congeners are very slowly accumulated, they have very slow elimination rates.

2,3,7,8-TCDD and other planar polyhalogenated aromatic hydrocarbons often have not been detected in water from aquatic ecosystems even when biota are highly contaminated. Because surface layers of bottom sediments are a good indicator of the relative amount of chemical in the system over the time scale involved for bioaccumulation of super-hydrophobic chemicals, a term known as the Biota to Sediment Accumulation Factor, or BSAF, has been offered as a measure of site-specific bioaccumulation potential. This term was recently proposed to replace equivalent terms which were known as the Bioavailability Index, or BI (Kuehl, et al., 1987; Cook, et al., 1991; EPA, 1990b), the Accumulation Factor, AF (Lake, et al., 1990) and the Biota to Sediment Factor, or BSF (Parkerton, et al., 1993; Parkerton, 1991; Thomann, et al., 1992). BSAF is defined as:

$$BSAF = \frac{C_{lipid}}{C_{oc}} \qquad (4\text{-}21)$$

where:

BSAF = biota to sediment accumulation factor, unitless

C_{lipid} = concentration of contaminant in lipid of fish, mg/kg,

C_{oc} = concentration of contaminant in bottom sediment organic carbon, mg/kg

The surface water algorithms estimate concentration of contaminant in bottom sediments (see Section 4.3.1 above). This concentration, C_{sed}, can be converted to an organic carbon basis as a function of OC_{sed}:

$$C_{oc} = \frac{C_{sed}}{OC_{sed}} \qquad (4\text{-}22)$$

where:

C_{oc} = concentration of contaminant in bottom sediment organic carbon, mg/kg;

C_{sed} = concentration of contaminant in bottom sediment, mg/kg;
OC_{sed} = fraction organic carbon in bottom sediment, unitless

The organic carbon content of bottom sediments was assumed to 0.03; see Section 4.3.1. for the derivation of C_{sed}.

Since the accumulation of contaminant is assumed to occur only in fish lipid, a correction term to estimate the whole fish tissue concentrations is needed since fish consumption in g/day refers to whole fish consumption. The correction term is simply f_{lipid}, and so whole fish concentrations are simply $C_{lipid} * f_{lipid}$.

The BSAF was developed as a measure of bioaccumulation potential rather than as a predictor, as it is being used here. It is uncertain as to whether measured BSAFs are generally applicable to other water bodies. Efforts are underway to evaluate the general applicability of BSAFs (P. Cook, Duluth Environmental Research Laboratory, US EPA, 6201 Congdon Boulevard, Duluth, MN 55804, personal communication). Using the BSAF approach as a predictive tool greatly underplays the complexity of the processes transferring contaminants from aquatic ecosystems to aquatic organisms. EPA (1993) provides a comprehensive discussion on aquatic impacts and processes for 2,3,7,8-TCDD and related compounds. Following are some of the key issues to consider:

1) **Resident vs. Migratory Species:** Parkerton (1991) applied a bioenergetics-based bioaccumulation model in an attempt to duplicate BSAFs for 2,3,7,8-TCDD found for carp and blue crabs in the Passaic River, New Jersey. He showed nearly a ten-fold difference in 2,3,7,8-TCDD BSAF calculated from data for resident species as compared to migratory species in the Passaic River. This would be expected for fish which also reside part of the time in relatively clean water bodies; migration would enable depuration of residues from fish. The possibility that migration patterns might explain some of the results for fish concentrations of 2,3,7,8-TCDD in the Lake Ontario bioaccumulation study was also raised (EPA, 1990b). That assessment also discussed a related issue of concern - to consider lakewide average sediment concentrations or concentrations near where sampled fish were captured in calculating the BSAF. Even within a large lake, more sedentary populations of fish may be impacted by localized contamination.

2) **Past history of contamination:** If contamination of surface water bodies with hydrophobic compounds like the dioxin-like compounds has occurred principally in the past, then it can be expected that most of the contamination occurs in or near the bottom sediment layer and not within the water column. Furthermore, if inputs to water bodies are declining or low in comparison to past loadings, then sediments would be undergoing depuration - residue levels would be declining, and the system may not be equilibrium. EPA (1990b) noted that very low BAF*s (defined as a fish to sediment ratio not including the sediment organic carbon and fish lipid considerations of BSAFs) and BSAFs for 2,3,7,8-TCDD in Lake Ontario contrasts higher BAF*s for other hydrophobic compounds such as DDE or PCBs. An explanation offered is that loadings to the Lake may be declining, such that there is a substantial disequilibrium between sediments, water, fish, and their prey. One parameter required in the bioenergetics model Parkerton (1991) used (referred to in the above bullet) was a ratio of contaminant concentration in bottom sediment to that in suspended sediment, rs/rw. In modeling exercises on the Passaic River, he found closer agreement between measured and predicted BSAFs with this ratio equal to 10 in contrast to 1, the only two values tested; a ratio of ten means that the concentration of contaminant in bottom sediment is ten times higher than it is in the suspended sediment. BSAFs predicted by the model were developed as the ratios in modeled fish lipid concentrations divided by modeled bottom sediment organic carbon normalized concentrations. Measured BSAFs used actual Passaic River fish lipid and bottom sediment concentrations of 2,3,7,8-TCDD. BSAFs predicted with this ratio equal to 1 were roughly 4 times as high as measured BSAFs, and BSAFs found with rs/rw equal to 10 were twice as high as measured. A related result of his modeling exercise was that, at best fit between modeled and measured BSAFs where the rs/rw was 10, dietary exposures explained over 50% of the BSAFs for carp and 85% in blue crabs, in contrast to water column exposures. He speculates that prey organisms consist of benthic animals which ingest contaminated bottom sediment. If the food chain begins near bottom sediments, and if food chain exposures are a principal explanation for fish tissue dioxin concentrations, than it follows that a model would perform better when bottom sediment concentrations drive fish tissue concentrations rather than water column concentrations, or equivalently, when rs/rw = 10. Finally, he notes that 2,3,7,8-TCDD contamination in Passaic river largely occurred as a result of historical loadings. The picture that emerges

from Parkerton's modeling is as follows: sediments are serving as an internal source of contaminants due to past historical loadings, and the water column is in disequilibrium with bottom sediments and driven only by depuration of bottom sediment concentrations. The bioaccumulation of these compounds in carp and blue crabs appears to be mediated by trophic transfer via the benthic foodweb. In both the Lake Ontario and Passaic River studies, concentrations of 2,3,7,8-TCDD were higher in deeper bottom sediments as compared to surficial bottom sediments - this implies historical loadings and possibly depuration of surficial residues.

This issue is non-trivial for the methodology of this assessment, since an assumption for deriving suspended and bottom sediment concentrations is that the contamination is ongoing, and that the hypothetical water body may be closer to a state of equilibrium as compared to situations where contamination was principally in the past. The BSAF assumed for 2,3,7,8-TCDD in the demonstration scenarios of 0.09 is more in line with data from EPA (1990b) on Lake Ontario and from Parkerton (1991) from data in Passaic River, then with other data (presented later) where historical loadings are not as clear a principal source of bottom sediment contamination. The issue of ongoing versus historical contamination should be considered when assigning site-specific BSAFs.

3) **Variations among fish species:** Feeding habits, age, migratory patterns, and lipid contents (including lipid content of edible vs. inedible fish tissues) are just a few of the interacting factors which determine a site-specific BSAF as a function of fish species. The demonstration of this approach in Chapter 5 assigns a single BSAF to each of the three example contaminants. Although not unlike other simplifications of this assessment, such approaches are recognized as oversimplifications.

4) **Study designs to obtain BSAFs:** Although there is some evidence that BSAFs specific to a contaminant may be applicable to other aquatic settings, data to evaluate such a hypothesis is still sparse. Even data sets that do exist need to be carefully evaluated before deriving BSAFs. Such an evaluation should consider sediment as well as fish species data. Critical factors for sediment sampling include location, number, depth of sampling, variability, availability of organic carbon fraction information, and so on. Similar issues are pertinent for fish sampling and analysis.

Following now are guidance for the terms required for estimating fish tissue

concentrations.

- **BSAF:** Table 4-1 summarizes literature from which biota sediment accumulation factors for dioxin and furan congeners could be developed. Only five sets of data were found in the literature. The data from the Wisconsin River (Kuehl, et al. 1987) and that from 1 lake in Sweden (Kjeller, et al. 1990) both show decreasing BSAF with increasing chlorination. The BSAF of 2.94 for 2,3,7,8-TCDD determined from a lake in Sweden should be questioned since it is more than an order of magnitude different than any of the other data. Causes for this discrepancy could be manifold. Some observations from Kjeller, et al. (1990) might shed some light on this result. Although sediment data was from three water bodies, 8 of the 9 Pike samples (pike samples were composites of 2-5 fish from one location in the water body) were from one of the water bodies. This is why only data from the one water body was summarized in Table 4-1. This water body, Lake Vanern, was clearly the most contaminated of the three water bodies studied. A paper mill was located at the northern part of this lake and the authors concluded that discharges from this mill impacted the lake. The average of 2,3,7,8-TCDD and 2,3,7,8-TCDF organic carbon normalized concentrations for five sediment samples from this lake was 297 pg/g; the analogous average concentration for 10 samples taken from another lake, Lake Vattern (6 samples), and a river, Dala (4 samples), was 65 pg/g. A similar disparity between Lake Vanern and the other water bodies is found with the penta-CDD/CDF concentrations: 205 pg/g vs. 108 pg/g, with similar comparisons for the hexa-, hepta, and octa-CDD/CDF. The sediment and corresponding pike sample nearest this mill had the highest concentrations reported - pike samples were given as 3000 and 833 pg/g lipid normalized 2,3,7,8-TCDF and 2,3,7,8-TCDF (a composite from 5 pike taken at this sampling station), respectively, and sediment was 1800 and 244 pg/g organic carbon normalized for 2,3,7,8-TCDF and 2,3,7,8-TCDD. Note the BSAF for 2,3,7,8-TCDD implied from this data point is 3.41. Another consideration for high BSAFs might be the source of contamination. Speculation from the Lake Ontario and Passaic River field data was that contamination principally occurred in the past, whereas in the Swedish data, contamination appears to have been ongoing at the time of sampling. This might be one indication that BSAFs for aquatic systems where contamination is ongoing might be greater than from systems where the contamination is primarily historical.

Table 4-1. Available Biota to Sediment Accumulation Factors, BSAF, for dioxin-like compounds.

Reference/Congener	Fish Species	Water Body	# Sed. samples / # Fish samples	BSAF	Comments
Kuehl, et al., 1987	Carp	Wisconsin River	1/1		Laboratory flow through experiment using Wisconsin River sediment and Lake Superior water; BSAFs determined from one "representative" sediment sample and one "composited" fish sample; sediment organic carbon and fish lipid contents given in article; no other details provided.
2,3,7,8-TCDD				0.27	
2,3,7,8-TCDF				0.06	
1,2,3,7,8-PeCDD				0.06	
1,2,3,6,7,8- & 1,2,3,4,7,8-HxCdd				0.035	
1,2,3,6,7,8-HxCDF				0.037	
1,2,3,4,6,7,8-HpCDD				0.0048	
1,2,3,4,6,7,8-HpCDF				0.0033	
US EPA, 1990b		Lake Ontario			Comprehensive field study on bioaccumulation of 2,3,7,8-TCDD in Lake Ontario; BSAFs are estimated given 55 sediment samples and specific number of fish samples as noted; report evaluates matching fish with with sediment data from sites where fish were caught.
2,3,7,8-TCDD	Brown Trout		55/81	0.03	
	Lake Trout		55/81	0.07	
	Smallmouth Bass		55/14	0.05	
	White Perch		55/38	0.20	
	Yellow Perch		55/77	0.03	
Kjeller, et al., 1990	Pike	Lake Vanern in Sweden	4/6		Results presented at right derived from data in Kjeller, et. al (1990); data includes sediment samples from four sites in Lake Vanern and 6 composited (2-5 fish in composite) pike associated with the four sites; pike concentrations reported in article on a lipid basis; Lake Vanern is near a paper mill.
2,3,7,8-TCDD				2.94	
1,2,3,7,8-PeCDD				1.03	
1,2,3,4,7,8-HxCDD				0.17	
1,2,3,6,7,8-HxCDD				0.086	
1,2,3,7,8,9-HxCDD				0.018	
OCDD				0.002	
2,3,7,8-TCDF				1.40	
12348/12378-PeCDF				0.25	
2,3,4,7,8-HxCDF				0.71	

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Table 4-1. (cont'd)

Reference/Congener	Fish Species	Water Body	# Sed. samples # Fish samples	BSAF	Comments
Kjeller, et al. (1990) (cont'd)					
123479/123478-HxCDF				0.036	
1,2,3,6,7,8-HxCDF				0.065	
1,2,3,7,8,9-HxCDF				0.27	
2,3,4,6,7,8-HxCDF				0.047	
1,2,3,4,6,7,8-HpCDF				0.0009	
1,2,3,4,7,8,9-HpCDF				0.023	
1,2,3,4,6,7,8-HpCDF				0.006	
OCDD				0.0001	
Parkerton, T.F. 1991		Passaic River			7 "resident" fish species were best represented by carp; "migratory" species were eel and striped bass; BSAFs at left are for 2,3,7,8-TCDD, given 61 bottom sediment samples and specific number of fish samples as noted; TCDD contamination attributed to historical industrial input, particularly a 2,4,5-T plant operation 1940s to 60s.
2,3,7,8-TCDD	Resident fish		61/11	0.081	
	Migratory fish		61/15	0.009	
	Blue Crab		61/14	0.055	
Connecticut Department of Environmental Protection (CDEP, 1992)		21 different water bodies			Data supplied by CDEP (1992); complete data description, study design, and interpretation in Chapter 7, Section 7.2.3.2. CDEP established a monitoring program to evaluate the impact of newly operating resource recovery facilities to soil, sediment, and fish. BSAFs at left are for the four congeners; they are derived from the average of 346 sediment samples and 521 total fish samples covering the six species noted at left.
2,3,7,8-TCDD	Carp		346/521	0.86	
2,3,7,8-TCDF	Channel catfish		346/521	0.25	
2,3,4,7,8-PCDF	White catfish		346/521	0.47	
Total TEQ	White sucker		346/521	0.24	
	Brown bullhead				
	Yellow perch				

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Table 4-1. (cont'd)

Reference/Congener	Fish Species	Water Body	# Sed. samples # Fish samples	BSAF	Comments
US EPA, 1993		different water bodies			Results compiled by EPA (1993) for 2,3,7,8-TCDD; details can be found in each study:
2,3,7,8-TCDD	Smelt			0.04	Batterman, et al. (1989)
	Sculpin			0.12	same
	Herring Gull			0.43	EPA (1990b) and Braune and Norstrom (1989)
	Bullhead			0.05	Cook (unpublished) as listed in EPA (1993)
	Sandworm			0.48	Rubinstein, et al. (1983)
	Clam			0.93	same
	Shrimp			0.73	same

The Swedish data also illustrates some of the complexities of interpreting literature data. First, the sediment data was expressed concentrations normalized to "sediment contents of organic material" (sic). This was interpreted as organic matter normalized, not organic carbon normalized. Parkerton (1991) assumed that organic carbon was 45% of organic matter to derive BSAFs when organic carbon data was unavailable; following this lead, organic matter normalized concentrations in Kjeller, et al. (1990) were divided by 0.45 to arrive at organic carbon normalized concentrations. Also, there was not an exact match in "sites" between sediment samples and fish samples; these sites were physical locations within the large lake where samples were taken. There were five sites where sediment samples were taken, and five sites where composited pike samples were taken in Lake Vanern. However, one of the sediment and one of the pike samples were from unique sites; only four sites had both sediment and pike samples. The results in Table 4-1 were derived using average sediment and pike concentrations from only these four sites. Another way to have derived BSAFs would be to average all lake sediment and pike concentrations; since there may be some relationship between sediment and pike concentrations based on lake location, it was decided to include only the four sites with both fish and sediment samples. Finally, there were two sets of results listed for 1,2,3,4,6,7,8-HpCDF as though there were two unique sets of analyses for the same congener; this is why there are two entries for this congener in Table 4-1.

A complete discussion of the data generated by the Connecticut Department of Environmental Protection (CDEP, 1992) is included in Chapter 7, Section 7.2.3.2. Generally, water bodies tested were mostly in rural/suburban settings rather than urban settings. Concentrations of 2,3,7,8-TCDD in surface soils and bottom sediments were in the low ppt level, indicating background impacts. BSAFs generated with that data were 0.24 to 0.85 for TEQs, 2,3,7,8-TCDD, 2,3,7,8-TCDF, and 2,3,4,7,8-PCDF.

Excluding the Swedish data, there are 26 reported BSAFs for dioxin-like congeners in Table 4-1. These range from 0.009 to 0.93, with lower BSAFs associated with higher chlorinated congeners. A BSAF of 0.09 will be assumed for 2,3,7,8-TCDD in the demonstration scenarios in Chapter 5. Although there is indications of declining BSAFs with increasing chlorination, there is probably not sufficient grounds to assign a BSAF for the second example compound, 2,3,4,7,8-PCDF, significantly different from that of 2,3,7,8-TCDD. The BSAF for this example furan will also be 0.09. In demonstrating the

suite of dioxin-like congeners for the stack emission scenario, a profile of BSAF values is crafted generally reflecting the trend of lower BSAF for higher chlorinated congeners, but this profile cannot be rigorously defended, for obvious reasons.

It should be noted that all bioconcentration or biotransfer parameters, such as the BSAF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

EPA (1990b) estimates BSAFs for PCBs and other selected chemicals (DDE, HCB, etc.) for Lake Ontario from several data sets. Parkerton, et al. (1993) summarizes BSAFs for PCBs and other compounds from other water bodies using other data sets. A selected summary by water body taken from these two sources for PCBs is given in Table 4-2.

Two trends are apparent. First, the BSAFs for PCBs appear to exceed those of the dioxin and furan congeners by an order of magnitude and more. Second, and from limited data, it would appear that BSAFs increase from dichloro- through hexa- or perhaps hepta-chloro PCBs, and then decrease thereafter. An assignment of a BSAF for 2,3,3',4,4',5,5'-HPCB is not apparent from the data summary below. The data point from Siskiwit for the single heptachloro-PCB, which was 2,2',3,4',5,5',6-HPCB, was estimated by Parkerton (1991) as 12.5. The BSAF for flounder from New Bedford Harbor estimated by Parkerton (1991) was 0.84, with BSAFs for lobster and crab as 1.29 and 2.74, respectively. A value of 2.00 is assigned to 2,3,3',4,4',5,5'-HPCB for the example scenarios in Chapter 5.

Finally, it should be noted that these assignments are based on data on vertebrate rather than invertebrate aquatic species. It is generally recognized that invertebrates do not possess the enzymatic capability to metabolize hydrophobic compounds as effectively as higher chordates. As a result, invertebrate species such as mussels, clams, oysters, shrimp, crabs and lobsters may have BSAF values much higher than those observed for fish. Parkerton (1991) and Parkerton, et al. (1993) reviewed the literature to estimate BSAFs of 1 to 5 for species including grass shrimp, sandworms, deposit feeding clams, and blue mussel for PCDD/PCDFs and PCBs.

Table 4-2. Available Biota to Sediment Accumulation Factors, BSAF, for PCBs.

Congener	Fish Species	Water Body	BSAF	Comments
PCB	trout, salmon, perch, bass	Lake Ontario	1.40, 0.77 0.52, 0.86, 3.35, 1.42,	Compiled in EPA (1990b) from several data sources, years of study, and fish species. Summary in this table includes all uniquely derived BSAFs for PCBs for species noted. PCBs not further identified except BSAF value of 0.58 specific to Aroclor 1254.
trichloro-PCB tetrachloro-PCB pentachloro-PCB hexachloro-PCB heptachloro-PCB octachloro-PCB	lake trout, whitefish	Siskiwit Lake	0.45-2.6 0.71-1.3 3.4-9.4 2.9-20.8 12.5 2.2-12.7	Compiled by Parkerton, et al. (1993) from data in Swackhammer, et al. (1988) and Swackhammer and Hites (1988); Parkerton presents data for individual congeners - summary at left aggregates by chlorination and includes both fish species; only one data point presented for heptachloro-PCB.
Total PCB	Three species of marine fish	Rio de La Plata Argentina	4.40	Determined by Parkerton et al. (1993) from Columbo, et al. (1990) on total PCBs; Columbo reference also has data on PCB IUPAC congeners 5-8, 14, 19, 28-31, 52, 101, 110, 138, 153, 180.
dichloro-PCB trichloro-PCB tetrachloro-PCB pentachloro-PCB hexachloro-PCB heptachloro-PCB octachloro-PCB nonachloro-PCB	New Bedford Harbor flounder, lobster, crab		0.11-0.59 0.26-0.65 0.65-1.02 1.05-2.08 1.29-4.00 0.84-2.74 0.23-1.17 0.02-0.38	Compiled by Parkerton, et al. (1993) from data in BOS (1990); summary at left is the range of values specific to the PCB congener grouping, and averaged across noted species.

- **f_{lipid}:** Lipid contents of edible fish species have not been compiled, although such a compilation would clearly be useful if applying a BSAF in an assessment mode such as is done here. BSAFs are typically developed on the basis of whole fish lipid content, so estimates of whole fish concentrations should be made with a whole fish lipid content. Parkerton, et al. (1993) cautions, however, that lipid contents of edible portions of fish may be lower than lipid contents of some of the fish portions that were sampled and used to develop BSAFs. Non-edible high lipid content portions include, for example, liver and hepatopancreas. Parkerton, et al. (1993) develops the parameter, β, which is defined as the ratio of the lipid content of the edible portion and the sampled tissue. To demonstrate the impact of this ratio, Parkerton used data from Niimi and Oliver (1989) which included PCB and other halocarbon compound concentration in whole fish and fillets of fish taken from the Great Lakes. The β (defined here as the ratio of lipid in fillet to lipid of whole fish) for these fish, which included brown trout, lake trout, rainbow trout, and coho salmon, ranged from 0.22 to 0.51. The ratio of fillet to contaminant concentrations ranged from 0.20 to 0.54.

In the context of the current model, concentrations in fish for estimating exposure are estimated as the product of: organic carbon normalized bottom sediment concentrations * BSAF * f_{lipid}. BSAFs (in theory) are independent of fish tissue being sampled - they are ratios of the organic carbon normalized concentration and fish lipid concentration. Users should be aware, however, that the f_{lipid} value assigned should correspond to the fish concentration of interest - that could be whole fish if the model is used in validation exercises or edible fish if the model is used for exposure assessment. Cook, et al. (1990) and EPA (1993) assumed a lipid content of 0.07 for fish in discussions of BSAF and related methodologies for estimating bioaccumulation of 2,3,7,8-TCDD in aquatic ecosystems. This assessment will also assume a f_{lipid} of 0.07, and since its use in this context is in exposure assessment, this value could be thought of as a edible portion lipid fraction.

Different lipid contents have been reported for the same fish, so generalizations are difficult to make at this point. EPA (1990b) lists percent lipid contents for Lake Ontario fish including brown trout: 14.3%, lake trout: 21.1%, coho salmon: 6.45%, yellow perch: 5.2%, and white perch: 17.1%. Kuehl, et al. (1987) lists a range of percent lipid for carp taken at different days during a study of between 13.0 and 18.7%.

4.3.4.2. *Vegetation concentrations*

Vegetation concentrations are required for the estimation of exposure to homegrown fruits and vegetables, and also for the beef and dairy food chain algorithms. Three principal assumptions are made to estimate vegetative concentrations:

- Outer surfaces of bulky below ground vegetation are impacted by soils which contain dioxin-like compounds. Inner portions are largely unimpacted.
- Translocation of dioxin-like compounds from roots to above ground portions of plants are negligible compared to other mechanisms which impact above ground portions of plants. As such, translocation into above ground portions will be assumed to be zero.
- Similar to the assumption concerning transport of contaminants from outer to inner portions of below ground vegetation, it will be assumed that outer and not inner portions of above ground bulky vegetation are impacted.

Concentration of contaminants in below ground vegetation is only required for vegetables (carrots, potatoes, e.g.) grown underground. The basis for the below ground algorithm is the experiments of Briggs, et al. (1982) on uptake of contaminants into barley roots from growth solution, and their elaboration of a Root Concentration Factor. The below ground concentration is given by:

$$C_{bgv} = \frac{C_s \ RCF \ VG_{bg}}{Kd_s} \qquad (4\text{-}23)$$

where:

C_{bgv} = fresh weight concentration of below ground vegetables, mg/kg

C_s = contaminant concentration in soil, ppm or mg/kg

Kd_s = soil-water partition coefficient, L/kg

= $Koc * OC_{sl}$

Koc = contaminant organic partition coefficient, L/kg

OC_{sl} = fraction organic carbon in soil, unitless.

RCF = root concentration factor equaling the ratio of the contaminant concentration in roots (fresh weight basis) and the concentration in soil water, unitless

VG_{bg} = empirical correction factor for below ground vegetation which accounts for the differences in the barley roots for which the RCF was derived and bulky below ground vegetables, unitless

Two processes, air-borne vapor phase absorption and air-borne particle deposition, are assumed to contribute to above ground vegetation concentrations:

$$C_{abv} = C_{vpa} + C_{ppa} \quad (4-24)$$

where:

C_{abv} = concentration in above-ground vegetation, expressed on a dry weight basis, mg/kg or ppm

C_{vpa} = contribution of concentration due to vapor-phase absorption or airborne contaminants, mg/kg or ppm

C_{ppa} = contribution of concentration due to wet plus dry deposition of contaminated particulates onto plant matter, mg/kg or ppm.

The basis for a vapor-phase bioconcentration factor for various airborne contaminants, including 1,2,3,4-TCDD, from the atmosphere to vegetation was developed by Bacci, et al. (1990, 1992), with amendments suggested by McCrady and Maggard (1993), and McCrady (1994). Bacci and coworkers conducted laboratory growth chamber experiments on the vapor-phase transfer of 14 organic compounds from air to azalea leaves, and developed a generalized model to predict the vapor-phase bioconcentration factor based on a contaminant Henry's Constant, H, and octanol water partition coefficient, Kow. A similar experiment by McCrady and Maggard (1993) conducted for 2,3,7,8-TCDD vapor transfer to grass leaves suggested that the Bacci empirical algorithm to estimate the transfer factor would greatly overestimate it. Further details on these experiments are in the section below on this critical bioconcentration parameter, termed B_{vpa} in this assessment. The algorithm estimating plant concentrations as a function of vapor-phase air concentrations is:

$$C_{vpa} = \frac{B_{vpa} \; C_{va} \; VG_{ag}}{1000 \; d_a} \qquad (4\text{-}25)$$

where:

C_{vpa} = contribution concentration due to vapor-phase absorption or airborne contaminants, mg/kg or ppm

B_{vpa} = mass-based air-to-leaf biotransfer factor, unitless [(μg contaminant/kg plant dry)/(μg contaminant/kg air)]

C_{va} = vapor-phase concentration of contaminant in air, $\mu g/m^3$

VG_{ag} = empirical correction factor which reduces vegetative concentrations considering that B_{vpa} was developed for transfer of air-borne contaminants into leaves rather than into bulky above ground vegetation

d_a = density of air, kg/m^3, 1.19

1/1000 = converts resulting concentration from μg/kg to mg/kg.

Several exposure efforts for 2,3,7,8-TCDD (Fries and Paustenbach, 1990; Stevens and Gerbec, 1988; Connett and Webster, 1987; Travis and Hattemer-Frey, 1991), have modeled the accumulation of residues in vegetative matter (grass, feed, vegetables) resulting from deposition of contaminated particulates. Key components of their approach, as well as the one for this assessment, include:

- Vegetative concentrations result from particulate deposition onto plant surfaces.
- Vegetative dry matter yield is the reservoir for depositing contaminants; this reservoir varies according to crop.
- Not all particulate deposition reaches the plant, some goes directly to the ground surface; the "interception fraction", less than 1.0, reduces the total deposition rate. This fraction can be related to the percent ground that is covered by the vegetation.
- Weathering processes, such as wind or rainfall, remove residues that have deposited onto plant surfaces via particle deposition, and this process is reasonably modeled as a first-order exponential loss with an associated weathering dissipation rate.

All the above references have justified a dissipation rate derived from a half-life of 14 days (based principally on field measurements described in Baes, et al. (1984)); this is the value used for all dioxin-like compounds in this assessment as well. As well, a portion of particles depositing as wet deposition are not retained on the vegetation after the rainfall. A retention factor reduces total wet deposition considering this.

- Vegetative concentrations may not reach steady state because of harvesting or grazing, but a steady state algorithm is used.

The steady state solution for plant concentrations attributed to wet plus dry particle deposition is:

$$C_{ppa} = \frac{F}{1000\ k_w\ Y_j} \qquad (4\text{-}26)$$

where:

C_{ppa} = Vegetative concentration due to settling of contaminated particulates onto plant matter, mg/kg or ppm

F = unit contaminant wet plus dry deposition rate onto plant surfaces, $\mu g/m^2$-yr

k_w = first-order weathering dissipation constant, 1/yr

Y_j = dry matter yield of crop j, kg/m^2

1/1000 = converts $\mu g/kg$ to mg/kg

The unit contaminant wet plus dry deposition rate, F, is given as:

$$F = C_{pa}\ (V_d\ I_j + RN\ R_w\ W_p\ I_j) \qquad (4\text{-}27)$$

where:

F = unit contaminant wet plus dry deposition rate onto plant surfaces, $\mu g/m^2$-yr

C_{pa} = air-borne particulate phase contaminant concentration, $\mu g/m^3$

V_d = deposition velocity, m/yr

I_j = fraction of particulates intercepted by crop j during deposition, unitless

RN = annual rainfall, m/yr

R_w = fraction of particles retained on vegetation after rainfall, unitless

W_p = volumetric washout factor for particulates, unitless

Following is brief guidance on assignment of values to the terms in Equations (4-23) to (4-27).

- **C_s and Kd_s:** This is the soil concentration and soil/water partition coefficient, respectively. The soil concentration is specified for the on-site source category. For the two source categories where soil contamination is distinct from the site of exposure, the soil concentration at the site of exposure is estimated. As discussed in Section 4.4.1 below, two soil concentrations including one for a no-till and one for a tilled situation, are estimated. For estimating below ground vegetable concentration, the tilled concentration is required. The soil partition coefficient is a function of the contaminant organic carbon partition coefficient, Koc, and the soil organic carbon fraction, OC_{sl}, as discussed above in Section 4.3.1. Division of C_s by Kd_s results in the equilibrium soluble phase concentration of the contaminant, in mg/L.

- **RCF:** Briggs, et al. (1982) conducted experiments measuring the uptake of several compounds into barley roots from growth solution. He developed the following relationship for lipophilic compounds tested (lipophilic compounds were identified as those tested that had log Kow 2.0 and higher (n = 7, r = 0.981):

$$\log RCF = 0.77 \log (Kow) - 1.52 \qquad (4\text{-}28)$$

where:

RCF = root concentration factor equaling the ratio of the contaminant concentration in roots (fresh weight basis) and the concentration in soil water, unitless

Kow = contaminant octanol water partition coefficient, unitless

Since his experiments were conducted in growth solution, the RCF is most appropriately applied to soil water in field settings. This is why the C_s was divided by Kd_s in Equation (4-23).

- **VG_{bg}:** This correction factor and the one used to correct for air-to-leaf transfer of contaminants, VG_{ag}, are based on a similar hypothesis. That hypothesis for VG_{bg} is that the uptake of lipophilic compounds into the roots of this experiments is due to sorption onto root solids. High root concentrations were not due to translocation to within portions of the root hairs. Direct use of the RCF for estimating concentrations in bulky below ground vegetation would greatly overestimate concentrations since an assumption (stated above) is that there is insignificant translocation to inner parts of below ground bulky vegetation for the dioxin-like compounds. Concentrations in outer portions of edible below ground vegetation would mirror concentrations found in barley roots, by this hypothesis.

VG_{bg} can be estimated by assuming that the outer portion, or skin, of below ground vegetables would contain concentrations that can be predicted directly using the RCF, but that the inner portions would effectively be free of residue. The correction factor can be estimated as the ratio of the mass of the outer portion to mass of the entire vegetable:

$$VG_{bg} = \frac{MASS_{skin}}{MASS_{vegetable}} \qquad (4\text{-}29)$$

where:

VG_{bg} = below ground vegetation correction factor, unitless
$MASS_{skin}$ = mass of a thin (skin) layer of below ground vegetables
$MASS_{vegetable}$ = mass of the entire vegetable

Simplifying assumptions are now made to demonstrate this ratio for a carrot and a potato. First, it will be assumed that the density of the skin and of the vegetable as a whole are the same, so the above can become a skin to whole vegetable volume ratio. The thickness of the skin will be assumed to be same as the thickness of the barley root for which the RCF was developed. Without the barley root thickness in Briggs, et al. (1982),

what will instead be assumed is that the skin thickness is equal to 0.03 cm. This was the thickness of a leaf from broad-leaved trees assumed by Riederer (1990) in modeling the atmospheric transfer of contaminants to trees. The shape of a carrot can be assumed to be a cone. The volume of a cone is given as $(\pi/3)r^2l$, where r is a radius of the base and l is length. Assuming a carrot base radius of 1 cm and a length of 15 cm, the volume is 16 cm^3. The curved surface area of a cone is given as: $\pi(r^2 + l^2)^{1/2}$, which equals 47 cm^2, given the r and l assumptions. The volume of the cone surface area is 47 cm^2 * 0.03 cm, or 1.41 cm^3. The skin to whole plant ratio for this carrot is 0.09 (1.41/16). A similar exercise is done for a potato, assuming a spherical shape with a radius of 3 cm. The volume is given as $4/3\pi^3$, or 113 cm^3. The surface area of a sphere is $4\pi^2$, or 113 cm^2, and the volume of this surface area is 3.39 cm^3. The skin to whole plant ratio for the potato is 0.03.

This exercise indicates upper bounds for such an empirical parameter. For exposure assessments, other factors which reduce vegetative concentrations should also be considered and will be considered in this empirical correction factor in this assessment. Additional reductions in concentration result from peeling, cooking, or cleaning, for example. Wipf, et al. (1982) found that 67% of unwashed carrot residues of 2,3,7,8-TCDD came out in wash water, and 29% was in the peels. A peeled, washed carrot correction factor might instead be, 0.09*0.04, or 0.004 (0.09 from above; 0.04 = 100% - 67% - 29%). A 96% reduction in the estimated VG_{bg} for the potato (the potato is cleaned and the skin is not eaten; additional reductions possibly when cooking the potato) would equal 0.001. In a site-specific application, the type of vegetation, preparation, and so on, should be considered. The VG_{bg} for underground vegetables for this assessment is assumed to be 0.01. This is less than the estimates of 0.09 and 0.03 for the carrot and potato above, but greater than it might be if based on this discussion on cleaning, washing, peeling, and so on.

- **C_{va}, C_{pa}:** The vapor-phase concentration of contaminant in air, C_{va}, used in this algorithm is estimated using procedures described in Section 4.3.2 above. The particle-phase concentration of contaminant in air, C_{pa}, is estimated using procedures described in Section 4.3.3.

- **B_{vpa}:** Bacci, et al. (1990, 1992) conducted laboratory experiments on the air-to-leaf transfer of vapor-phase concentrations of 14 organic contaminants to azalea leaves. With their results, they developed an empirical relationship for a vapor-phase bioconcentration factor from air to azalea leaves, termed in this assessment the B_{vpa}, but which was termed BCF by Bacci and coworkers. They related the B_{vpa} to the chemical octanol-water and air-water partition coefficients, Kow and Kaw. The air-water partition coefficient, Kaw, is a dimensionless form of Henry's Law constant, H, derived by dividing H by the product of the ideal gas constant, R, and the temperature, T. The most general form of the air-to-leaf transfer factor is on a unitless volumetric basis: [ng contaminant/L or leaf]/[ng contaminant/L of air], and is given as:

$$\log B_{vol} = 1.065 \log Kow - \log \left(\frac{H}{R\,T} \right) - 1.654 \qquad (4\text{-}30)$$

where:

B_{vol} = Bacci volumetric air-to-leaf biotransfer factor, unitless [(μg contaminant/L of wet leaf)/(μg contaminant/L air)]

Kow = contaminant octanol water partition coefficient, unitless

H = contaminant Henry's Constant, atm-m^3/mol.

R = ideal gas constant, 8.205 x 10^{-5} atm-m^3/mol-deg K

T = temperature, 298.1 K

-1.654 = empirical constant

Bacci, et al. (1990) showed that the volumetric transfer factor can be transformed to a mass-based transfer factor by assuming that 70% of the wet leaf is water, the leaf density is 890 g/L, and the air density is 1.19 g/L:

$$B_{vpa} = \frac{1.19\ g/L\ \ B_{vol}}{0.3\ \ 890\ g/L} \qquad (4\text{-}31)$$

where:

B_{vpa} = mass-based air-to-leaf biotransfer factor, unitless [(μg contaminant/kg plant dry)/(μg contaminant/kg air)]

B_{vol} = Bacci volumetric air-to-leaf biotransfer factor, unitless [(μg contaminant/L of wet leaf)/(μg contaminant/L air)]

Bacci's experiments were conducted under conditions which would not account for photodegradation of his test chemicals from the leaf surfaces. A recent study by McCrady and Maggard (1993) which investigated the uptake and photodegradation of 2,3,7,8-TCDD sorbed to grass foliage suggests a significant difference in experimental B_{vol} for grass plants. The authors note that the log B_{vol} for 2,3,7,8-TCDD and azalea plants, using Bacci's empirical relationship, was estimated as 8.5. The experimental log B_{vol} for 2,3,7,8-TCDD and grass plants reported by McCrady was 6.9 when photodegradation was accounted for, and 7.5 in the absence of photodegradation. Since the photodegradation experiments by McCrady best represent outdoor conditions, their work suggests that the air-to-leaf transfer factor estimated by Bacci's algorithm may be 40 times too high for vapor-phase transfer of 2,3,7,8-TCDD onto grass leaves.

While McCrady's experiments included consideration of photodegradation of 2,3,7,8-TCDD, it is uncertain as to how their results can be generalized to other dioxin-like compounds and vegetations other than grass. There is very little information in the literature on the photodegradation of dioxins and furans on plant surfaces. McCrady and Maggard (1993) cite Crosby and Wong (1977) as the only other work measuring photodegradation of 2,3,7,8-TCDD from leaf surfaces. In that work, 2,3,7,8-TCDD was applied as a 15 ppm concentration in Agent Orange, and McCrady speculated that the rapid photodegradation measured in those experiments occurred because the herbicide formulation contained carriers and organic solvents that may have promoted photodegradation. Some experiments conducted in organic solvents (Crosby, et al., 1971; Buser, 1976) and in water (Friessen, et al., 1990) noted reductive dechlorination resulting in dioxin compounds of lower chlorination. Other experiments did not find such reductive dechlorination (Dulin, et al., 1986; Friessen, et al., 1990 who found reductive dechlorination in one experiment, but not in another). An important issue to consider, at least, for the process of photodegradation of dioxins and furans on leaf surfaces is the possible formation of lower chlorinated congeners of non-zero toxic equivalency.

Another issue discussed by McCrady is that the theoretical time for the grass tissue to reach a steady state in his experiments is much shorter than that indicated in the Bacci

experiments. Using Bacci's results, McCrady noted that the azalea leaves theoretically take greater than 400 days to reach equilibrium, in comparison to less than 20 days to reach equilibrium for the grass plants in his experiments. This difference is not entirely due to photodegradation. McCrady (personal communication, J. McCrady, Corvallis Environmental Research Laboratory, EPA) suggests that the 50-day exposure time used in Bacci's experiments may allow for considerable diffusion into the newly formed plant surface wax. The sorbed TCDD residues may be trapped and unable to volatilize. Thus, for estimating contaminant concentrations in animal feeds such as relatively short-lived grass plants, the equilibrium B_{vol} from the Bacci azalea model may overestimate the contaminant concentration in grass. On the other hand, McCrady's experiments may have been conducted in too short a time frame, with the sum of uptake and elimination phases being less than 10 days in the various experimental designs. The volatilization and photodegradation rates reported by McCrady may be higher than what might occur for the longer exposure times expected in real world situations, where growth and residue trapping may occur.

These arguments are being presented to demonstrate the uncertainty in choosing either of the two reported B_{vol} values for estimating plant contaminant concentrations. McCrady's results pertaining to 2,3,7,8-TCDD cannot be generalized to other dioxin-like compounds or other contaminants in terms of commonly available contaminant parameters such as H or Kow. Therefore, a McCrady framework similar to Bacci's for estimating congener-specific B_{vpa} cannot be offered at this time. On the other hand, their work strongly suggests that the Bacci model may be inappropriate for terrestrial vegetations of this assessment, including vegetables/fruits and vegetations of the beef/milk food chain model, and Bacci's experiments, because of their length of time, the use of an azalea leaf of high wax content, and lack of an artificial light source simulating photodegradation, are likely to have overestimated the air to leaf transfers.

What will be done for this assessment is to first estimate a congener-specific B_{vol} using the Bacci algorithm of Equation (4-30) above. Then, it will be transformed into a mass-based B_{vpa} as in Equation (4-31), except that the assumptions McCrady and Maggard used for fraction of grass plant that is wet weight, 85%, and the grass leaf density, 770 g/L, will instead be used as more representative of vegetations of this assessment. Most importantly, the B_{vpa} calculated this way will be empirically reduced by

a factor of 40 for all dioxin-like congeners as suggested by the difference in McCrady's experiments as compared to Bacci's.

It should be noted that all bioconcentration or biotransfer parameters, such as the B_{vpa}, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

- **VG_{ag}:** The same discussion for this correction factor for below ground vegetation applies here. Fruits such as apples, pears, plums, figs, peaches, and so on, can be approximated by spheres, and upper bound estimates of correction factors would be less than 0.05. Peeling, cooking, and cleaning further reduces residues. The VG_{ag} for unspecified above ground fruits and vegetables in this assessment is assumed to be 0.01. Like VG_{bg}, this value is assigned considering that it should be less than estimated just based on surface volume to whole fruit volume ratios.

Two other VG_{ag} values are required for this assessment. One is for pasture grass and the other for other vegetations consumed by cattle. Both are required to estimate concentrations in these vegetations consumed by cattle in order to estimate beef and milk concentrations. A VG_{ag} value of 1.0 was used to estimate pasture grass concentrations since there appears to be a direct analogy to exposed azalea and grass leaves. However, VG should be less than the other general category of cattle vegetations defined in this assessment, "hay/silage/grain". Recognizing that pasture grass is important in terms of amount consumed in the lifetime of a beef cow, and the fact that it is a leafy vegetation, it is considered seperately, whereas other cattle vegetations are lumped together in this second category. As described below in Section 4.3.4.3, this second general category of non-grass cattle vegetations include some thin leafy (hay) as well as bulky (corn silage and other grains) vegetations to consider. A volume ratio of outer surface to whole surface area to volume vegetation could be used to assign a value to VG, if specific assumptions concerning proportions of each type of vegetative cattle intake were made. An appropriate assumption for a fully protected vegetation such as grain would be zero.

Silage can be considered part protected and part leafy. Since specific assumptions concerning hay/silage/grain intake are not being made for this exercise, a simple assumption that VG equals 0.50 for hay/silage/grain is instead made, without rigorous justification.

The only experimental evidence that a VG_{ag} for vapor transfers of dioxin-like compounds is justified came in a recent study by McCrady (1994). McCrady experimentally determined uptake rate constants, termed k_1, for vapor phase 2,3,7,8-TCDD uptake into several vegetations including kale, grass, pepper, spruce needles, apple, tomato, and azalea leaves. Recall that the similar experimental design of both McCrady and Maggard (1993), and Bacci, et al. (1990; 1992), included an initial phase where vegetations in experimental chambers were exposed to the vapor-phase organic chemicals. The uptake which occurs during this initial phase is described with the rate constant, k_1. A second "elimination" phase then occurs where organic vapors are removed from the chambers and the chemicals allowed to volatilize or otherwise dissipate from the vegetation. The rate constant for this phase is termed k_2. A steady state bioconcentration factor, or B_{vpa} in this assessment, is then estimated as k_1/k_2. The uptake rate constants from air to the whole vegetations estimated in the recent experiments by McCrady (1994) demonstrate the concept behind the VG parameter. The uptake rate for an apple divided by the uptake rate for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry weight basis). For the tomato and pepper, the same ratios were 0.03 and 0.08. The VG_{ag} was 0.01 for fruits and vegetables in this assessment, but note above that the simple exercise with a conical carrot and spherical potato estimated a surface volume to whole fruit volume ratio of 0.09 (carrot) to 0.03 (potato); a value of 0.01 for fruits and vegetable empirically considers factors such as washing or peeling which would reduce exposures. McCrady (1994) then went on to normalize his uptake rates on a surface area basis instead of a mass basis; i.e., air to vegetative surface area instead of air to vegetative mass. Then, the uptake rates were substantially more similar, with the ratio of the apple uptake rate to the grass being 1.6 instead of 0.02; i.e., the apple uptake rate was 1.6 times higher than that of grass, instead of 1/50 as much when estimated on an air to dry weight mass basis. The ratios for tomato and pepper were 1.2 and 2.2, respectively. In his article, McCrady (1994) concludes, "The results of our experiments have demonstrated that the exposed surface

area of plant tissue is an important consideration when estimating the uptake of 2,3,7,8-TCDD from airborne sources of vapor-phase 2,3,7,8-TCDD. The surface area to volume ratio (or surface area to fresh weight ratio) of different plant species can be used to normalize uptake rate constants for different plant species." McCrady does caution, however, that uptake rates are only part of the bioconcentration factor estimation, and is unsure of the impact of surface area and volume differences on the elimination phase constant, k_2 (personnal communication, J. McCrady, US EPA, ERL-Corvallis, Corvallis, OR 97333). Still, his recent experiments do appear to justify the use of a VG parameter since the B_{vpa} were developed on an air to whole plant mass basis, and his results are consistent with the assignment of 0.01 for fruits and vegetables.

- **kw:** Fries and Paustenbach (1990) note that this approach may overestimate concentrations because crops can be harvested or pastures grazed before the plant concentrations reach steady state, and that a kw based on a weathering half-life of 14 days may be too long given experimental results of Baes, et al. (1984) which showed a range of 2-34 days, and a median value of 10 days. Stevens and Gerbec (1987) considered harvest intervals by including the exponential term, $(1-e^{-kt})$, and assigning values of t based on harvest intervals of different crops. This assessment uses a kw of 18.02 yr^{-1}, which is equivalent to a half-life of 14 days.

- **I_j and Y_j:** Interception values and crop yields were determined in the afore-mentioned assessments based on geographic-specific crop yield data provided in Baes, et al., (1984) and the following types of crop-specific relationships estimating interception fraction based on yield (Y), also presented in Baes, et al., (1984):

corn silage: $I = 1 - e^{-0.768Y}$

hay/grasses: $I = 1 - e^{-2.88Y}$

lettuce: $I = 1 - e^{-0.068Y}$

Judgments by Fries and Paustenbach (1990) on high, medium, and low yields of silage, hay, and pasture grass, and the use of the first two interception equations above (the first for silage, and the second for hay and grass), can give some guidance on interception

fractions and yields for these crops:

	Yield (kg/m^2)	Intercept Fraction
corn silage	0.30 (low)	0.20
	0.90 (med)	0.50
	1.35 (high)	0.64
hay	0.25 (low)	0.51
	0.45 (med)	0.73
	1.30 (high)	0.98
grass	0.05 (low)	0.13
	0.15 (med)	0.35
	0.35 (high)	0.64

This information can be used for cattle intake of vegetation, and the resulting beef and milk concentrations. The medium values for grass, 0.15 kg/m^2 yield and 0.35 interception, were used for the example setting in Chapter 5. An average of the medium values for hay and silage, 0.63 kg/m^3 yield and 0.62 interception, were used for the second category of cattle vegetations for Chapter 5, the hay/silage/grain category.

Stevens and Gerbec (1988), using yields obtained from the Minnesota State Agricultural Office, derived the following yield and interception estimates, respectively, for vegetables for human consumption in their assessment: lettuce - 8.6,0.72; tomatoes - 12.0,0.55; and beans - 2.7,0.18. Average yields and interception fractions from their exercise: 7.8 kg/m^2 and 0.48, were used in the example setting in Chapter 5. These vegetable yields are fresh weight, so they need to be converted to a dry weight basis in order to estimate a C_{ppa} appropriate for use in Equation (4-23). Since vegetables are generally 80 ->90% water, a fresh to dry weight conversion factor of 0.15 was used, resulting in an average vegetable dry matter yield of 1.17 (7.8 * 0.15). This was used in the example settings in Chapter 5.

- V_d: Particles settle to the ground surface and plant surfaces due to the forces of gravity. Gravitational settling velocity is a function of particle size, with more rapid settling occurring with larger particles. The algorithm used to estimate the concentration of contaminated particulates in air estimates the suspension of particles less than and equal to 10 μm, which is commonly referred to inhalable size particles. Seinfeld

(1986) listed a gravitational deposition velocity of 1 cm/sec for 10 μm size particles. This deposition velocity will be used in this assessment, and in units of m/yr, this equals 315,360 m/y.

- **RN:** Geraghty, et al. (1973) provides a map showing isolines average annual rainfall throughout the United States. This map shows low rates of 5 to 20 inches/year in the desert Southwest, moderate rates of 25 to 40 in/yr in the Midwest cornbelt, 40 to 60 in/yr in the South, and so on. The example scenarios of Chapter 5 were described as rural, with land in agricultural and non-agricultural settings. A rate of 1 m/yr (39 in/yr) will be used in the example scenarios.

- **R_w:** It is assumed that dry depositions fully adhere to plant surfaces; the weathering constant, k_w, models the loss of the vegetative reservoir of particle bound contaminants due to wind, rain, or other weathering process. However, it is not clear that wet deposition should also be assumed to fully adhere during a wet deposition event. Hence, the R_w parameter, or fraction of wet deposition adhering, was introduced. Prior modeling efforts of the impact of depositions of dioxin-like compounds to vegetations are unclear with regard to wet deposition. Stevens and Gerbec (1988), Fries and Paustenbach (1990), Webster and Connett (1990), and Travis and Hattemer-Frey (1991) all model particle deposition impacts of 2,3,7,8-TCDD to vegetations in air-to-beef/milk modeling. None of them discuss the distinction in wet and dry deposition, and model "total deposition" impacts, describing total as wet and dry deposition, total deposition, or simply as deposition. On the other hand, McKone and Ryan (1989) reduce the wet deposition portion of total deposition. They promote use of a "b", which they define as the fraction of material retained on vegetation from wet deposition. They recommend a value between 0.1 and 0.3.

The clearest indication of the fate of wet deposition of particles can be found in Hoffman, et al. (1992). In that field study, simulated rain containing soluble radionuclides and insoluble particles labeled with radionuclides was applied to pasture-type vegetation under conditions similar to those found during convective storms. The fraction of the labeled particles found to remain on the vegetation after the rainfall varied from 0.24 to 0.37. Nine values comprised this range, including particle sizes of 3, 9, and 25 μm, and

cover described as clover, fescue, and mixed (a site with old field vegetations including fescue, grasses, weeds, and wild flowers). Based on this work, the R_w will be assumed to be 0.30 for all vegetations and dioxin congeners of this assessment.

- **W_p:** Washout ratios are generally defined as the concentration of contaminant in rain to the concentration of contaminant in air. Concentrations of contaminants in air and rain water can be derived as a mass of contaminant divided by a mass of air/water or a volume of air/water. Mackay, et al. (1986) shows that volume-based washout ratios (mass of contaminant mixing in m^3 air or water, e.g.) exceed mass-based washout ratios (mass of contaminant mixing in kg of air or water) by a factor of 815, which is the ratio of water and air densities. The washout ratio used in this assessment is a volumetric ratio based on methodologies described by Bidleman (1988). Using a volumetric ratio then allows for direct use of contaminant concentrations estimated in this methodology since they are already on a $\mu g/m^3$ volume basis.

Bidleman (1988) defines the overall washout ratio as: (mass contaminant/volume rain) ÷ (mass contaminant)/(volume air). Bidleman (1988) also discusses that fact that overall washout includes both wet deposition of particulates and scouring of contaminants in the vapor phase. He includes methodologies for estimating the vapor/particulate ratios for semi-volatile organic compounds (abbreviated SOCs) and also for estimating the washout ratios for vapors. However, he claims that if H is sufficiently high, vapor dissolution in droplets is negligible and only the particulate fraction is removed by wet deposition. He claims this to be the situation for n-alkanes, PCBs, chlordane, DDT, and 2,3,7,8-TCDD. Developing overall washout ratios for these and several other SOCs, he estimates that vapor scouring accounts for 1% of the overall washout ratio for 2,3,7,8-TCDD. For PCBs, he estimates similar percentages of 2, 4, and 28% for Aroclors 1260, 1254, and 1248, respectively. Based on this work, it will be assumed that vapor scouring of the dioxin-like compounds is small in comparison to wet deposition and the washout ratio for this assessment will only be applied to the air-borne particulate concentration of dioxin-like compounds.

Bidleman (1988) does not provide a chemical or site-specific equation which estimates the particle-phase washout ratio (which he does for the vapor-phase washout ratio). Rather, he summarizes available data and concludes that there is a wide range of

the particle-phase washout ratio, W_p, for SOC: between $2x10^3$ and $1x10^6$. He claims that a typical range is 10^5 to 10^6, and uses a W_p of 2×10^5 in his exercises to estimate the overall washout ratio for several SOCs.

Koester and Hites (1992) list vapor and particle scavenging ratios for congener groups of dioxin-like compounds. To derive these ratios, they used air concentrations for congener groups that were taken at one time period in Bloomington and Indianapolis, Indiana, and rainfall depositions of these compounds at these sites measured during a second period of time. Using the Bidleman vapor/particle partitioning model used in this assessment, they estimate the vapor/split for the air concentrations. With these observations and models, they conclude that the overall washout ratio (sum of vapor and particle ratios) ranges from 10^4 to 10^5, which contrasts the typical range of 10^5 to 10^6 noted above from Bidleman (1988). Also, their calculations indicate that vapor scavenging of dioxin-like compounds is comparable to particle scavenging, also in contrast to the Bidleman analysis summarized above. However, they did not state whether their washout ratios were volume or mass-based. If they were mass-based, then a conversion to volume based would put them in the 10^7 to 10^8 range, which seems improbable given the Bidleman summary above. Therefore, it will be assumed that are volume-based, and they are appropriate to use for this assessment. Since no clear trend for particle washout ratios with regard to the degree of chlorination increased appears in Koester and Hites' data, the midpoint of their calculated range, $5 * 10^4$, will be used for all example compounds in this assessment.

As a final note, the multiplication of the above terms, $W_p * C_{pa} * RN * R_w$, does result in wet deposition in appropriate units of $\mu g/m^2$-yr, although that is not immediately obvious. First, multiplication of W_p, in (μg contaminant/m^3 rain) ÷ ($\mu g/m^3$ air), and C_{pa}, in μg contaminant/m^3 air, leaves a partial term in units of μg contaminant/m^3 rain. Then, multiplication of this partial term times annual rainfall rate, thought of as m^3/m^2-yr instead of m/yr, gives the final quantity in the appropriate units.

When calculating concentrations in below ground fruit and vegetables using Equation (4-23), C_{bgv} is on a fresh weight basis since the RCF developed by Briggs, et al. (1982) is on a fresh weight basis, and no correction for estimating exposures is necessary. However, C_{abv} as estimated in Equation (4-24) is on a dry weight basis, and should be

multiplied by a dry weight to fresh weight conversion factor when applied to above ground fruits and vegetables. A reasonable estimate for this parameter for fruits and vegetables is 0.15 (which assumes 85% water), which was used in this assessment. When using Equation (4-24) to estimate C_{abv} for the beef and milk food chain algorithm, a conversion to fresh weight is not required, however, since the algorithms were developed assuming dry weight concentrations.

4.3.4.3. *Beef and milk concentrations*

The algorithm to estimate the concentration of contaminant in beef and/or milk was based on methods developed by Fries and Paustenbach (1990). They developed the beef bioconcentration factor for 2,3,7,8-TCDD, which is defined as the ratio of the concentration of the contaminant in beef fat to the concentration in the dry matter dietary intake of the beef cattle. They discussed bioavailability, which, as they define it, is the fraction of ingested contaminant which is absorbed into the body. It depends on the vehicle of ingestion - dioxin in corn oil has a bioavailability in the range of 0.7 to 0.8, in rodent feed it has an estimate of 0.5, while in soil it has a range of 0.3 to 0.4. They emphasized the importance of the differences in diet between cattle raised for beef and those which are lactating in explaining different food product concentrations. Although there is likely to be some difference in the bioconcentration tendencies for lactating cattle and beef cattle, Fries and Paustenbach in fact used the same bioconcentration for beef fat and milk fat, and the same will be done here.

The concentration in the fat of cattle products is given as:

$$C_{fat} = (BCF\ DF_s\ B_s\ AC_s) + (BCF\ DF_g\ AC_g) + (BCF\ DF_f\ AC_f) \quad (4\text{-}32)$$

where:

C_{fat} = concentration in beef fat or milk fat, mg/kg

BCF = bioconcentration ratio of contaminant as determined from cattle vegetative intake (pasture grass or feed), unitless

DF_s = fraction of cattle diet that is soil, unitless

B_s = bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless

AC_s = average contaminant soil concentration, mg/kg
DF_g = fraction of cattle diet that is pasture grass, unitless
AC_g = average concentration of contaminant on pasture grass, mg/kg
DF_f = fraction of cattle diet that is feed, unitless
AC_f = average concentration of contaminant in feed, mg/kg.

The following is offered as brief guidance to these terms and also the justification for the values selected in the example Scenarios in Chapter 5.

- **BCF:** Fries and Paustenbach (1990) developed the concept of a beef/milk bioconcentration ratio and applied it to 2,3,7,8-TCDD. BCF is defined as the concentration of contaminant in fat of cattle products (i.e., dairy and beef) divided by the concentration in dry matter intake. The key difference in the dietary intake of cattle raised for beef versus cattle raised for dairy is that cattle raised for beef tend to be pastured more than dairy cattle and be more exposed to contaminated soil, whereas lactating cattle are more often fed high quality feed, including grains which are expected to be substantially residue free since they are a protected vegetation. Based on literature studies of cattle consuming feed contaminated with dioxin-like compounds, Fries and Paustenbach (1990) calculated a BCF of between 4 and 6, and assumed a value of 5.0 for 2,3,7,8-TCDD. Being developed directly from data of cattle ingesting contaminated feed, this BCF value of 5.0 already considers the bioavailability of the experimental contaminated feed. It will be assumed that the bioavailability of the cattle vegetations in this assessment equal that of the experimental feed. Therefore, a value of 5.0 can go directly into Equation (4-32) when applied to concentrations in grass and pasture. However, this value should not be applied to soil, since it has been shown that TCDD on soil is less bioavailable than TCDD on other vehicles. This is why a B_s appears in Equation (4-32) - it adjusts BCF when applied to a soil concentration. The value of B_s is described below. The Fries and Paustenbach (1990) literature review is reproduced in Table 4-3, which additionally shows results generated based on information in McLachlan, et al. (1990).

Although the BCF of 5 determined by Fries and Paustenbach (1990) for 2,3,7,8-TCDD appears high based on the literature for this compound, Fries and Paustenbach (1990) discuss how short duration feeding trials (the 21 days of Jensen and Hummel

Table 4-3. Ratios of dioxins and furans in milk fat (MF) and body fat (BF) to concentrations in diets of farm animals.

Animal	Days	Compound	BF:diet	MF:diet	Reference
Goats	56	2,3,7,8-TCDD	-	2.8	Arstilla et al. (1981)
Cows	21	2378-TCDD	-	4.4	Jensen &Hummel (1982)
Cows	70	123678-HxCDD	3.9	5.7	Firestone, et al. (1979)
		1234678-HpCDD	0.4	0.6	
		OCDD	0.1	0.1	
Steers	28	2378-TCDD	3.5	-	Jensen, et al. (1981)
Heifers	160	123689-HxCDD	2.1	-	Parker, et al. (1980)
		1234678-HpCDD	0.2	-	
		OCDD	0.05	-	
		1234678-HpCDD	0.3	-	
		OCDF	0.1	-	
Cow	92[1]	2378-TCDD	-	4.32	McLachlan, et al. (1990)
		12378-PCDD	-	4.16	
		123478-HxCDD	-	2.02	
		123678-HxCDD	-	1.74	
		123789-HxCDD	-	2.24	
		1234679-HpCDD	-	0.20	
		1234678-HpCDD	-	0.36	
		12346789-OCDD	-	0.52	
		234/78-TCDF	-	0.94	
		1234/78-PCDF	-	0.73	
		23478-PCDF	-	3.10	
		123478/9-HxCDF	-	2.34	
		123678-HxCDF	-	2.00	
		234678-HxCDF	-	1.78	
		1234678-HpCDF	-	0.41	
		1234789-HpCDF	-	0.99	
		12346789-OCDF	-	0.20	
		TEQ	-	2.50	

[1] McLachlan, et al. (1990) was not a dosed feeding study; the single cow studied was given normal rationing. The first sample was taken Feb 16, 1989, two months after the last calving on Dec. 22, to maximize the possibility that steady state had been reached. The 92 days listed was from Dec. 22 until the last sample on Mar. 24.
Source: Fries and Paustenbach (1990), and McLachlan, et al. (1990).

(1982) and the 28 days of Jensen, et al. (1981)) do not result in steady state bioconcentration ratios. Extrapolating the data to a point where steady state is speculated to be reached, Fries and Paustenbach (1990) developed the arguments for the range of 4 to 6 for 2,3,7,8-TCDD. The second example compound in Chapter 5 was 2,3,4,7,8-PCDF. Fries and Paustenbach (1990) observed that bioconcentration ratios for PCDDs and PCDFs decreased significantly as chlorination increased, although their literature seems to imply that this effect is most pronounced for hepta- and octa- PCDDs and PCDFs. They could not locate data in the literature for penta-PCDDs or PCDFs.

McLachlan, et al. (1990) was the only source found where BCFs for cow milk could be generated for furan congeners. They conducted a mass balance of dioxin and furan congeners in a lactating cow. They carefully accounted for 16 of the 17 dioxin and furan congeners of toxicity equivalency to 2,3,7,8-TCDD in the intake of a lactating cow in food, air, and water, and measured amounts in feces, urine, and milk, while attributing the rest of the intake to a compartment they termed, storage/degradation/experimental error. They obtained data well into steady state, and provided information necessary to estimate milk BCFs including: average daily wet weight food ingestion intake by the cattle (dry weight assumed to be 30% of wet weight for cattle feed); ng/day congeners in feed, water, and air; L/day milk production (density assumed to be 0.9 g/cm^3); and percent fat in milk. The BCFs generated are shown in Table 4-3, and the one noted for 2,3,4,7,8-PCDF is 3.10. It is clear that the data in Table 4-3 is not definitive in establishing BCFs for specific congeners. Only the McLachlan data is complete, and it includes one cow and one lactating period. The data of Firestone, et al. (1979), as interpreted by Fries and Paustenbach, shows a BCF for milk fat of 5.7 for 1,2,3,6,7,8-HxCDD, compared to the milk fat BCF of 1.74 developed from McLachlan data.

In Chapter 5, the McLachlan data will be used for purposes of demonstration. The BCF value for 2,3,7,8-TCDD value is 4.3 and the BCF for 2,3,4,7,8-PCDF is 3.1, in the demonstration scenarios which include a dioxin, a furan, and a PCB. For the demonstation of the incinerator, the suite of dioxin-like compounds are demonstrated, and the full BCF set developed by McLachlan and coworkers will be used.

A review of the literature for PCBs is given in Table 4-4. Although PCBs, dioxins, and furans are related compounds in terms of environmental fate characteristics, a difference in bioaccumulation potential is noted with higher degrees of chlorination, based

Table 4-4. Ratios of PCBs in milk fat (MF) and body fat (BF) to concentrations in diets of lactating cows[a].

Animal	Days	Compound	Concentration in Diet, ppm	BF:diet	MF:diet	Reference & Comments
Lactating Cows	20	Aroclor 1254	12.1	-	3.1	Fries, et al. (1973)
	40	Aroclor 1254	12.1	-	4.4	
	60	Aroclor 1254	12.1	3.4	4.8	
						Tuinstra, et al. (1981), data is:
Lactating Cows	56	dichloro-PCBs	0.05	-	0.4	average of 2 congeners
		tetrachloro-PCBs	0.001	-	5.9	one congener
		pentachloro-PCBs	0.003	-	1.2	average of 2 congeners
		hexachloro-PCBs	0.009	-	2.2	average of 7 congeners
		heptachloro-PCBs	0.010	-	2.3	average of 8 congeners
		octachloro-PCBs	0.005	-	3.8	average of 5 congeners
		nanochloro-PCBs	0.001	-	4.0	one congener
Lactating Cows	60	Aroclor 1254	0.51	2.8	3.7	Willett, et al. (1987);
	120	Aroclor 1254	2.82	2.4	3.9	values at left reflect different
	180	Aroclor 1254	18.97	3.7	4.8	average intake over three periods noted.
Lactating Cows	20	Aroclor 1254	2.56	-	1.2	Willett and Liu (1982)
Lactating Cows	32	Aroclor 1254	10.25	-	4.2	Perry, et al. (1981)

[a] see text for full details of noted studies.

on the study of Tuinstra, et al. (1981). Their work implies increasing bioaccumulation potential as the degree of chlorination increases. They developed BCF values (defined in the same manner as in this assessment) for a suite of congeners identified to occur in Aroclor 1260 administered to lactating cows. Therefore, their data allowed for a partial examination on congener bioaccumulation patterns. The results given in Table 4-4 are interpreted from the data supplied in Tuinstra, et al. (1981). Tuinstra determined the identity and percentage of specific congeners which comprise Aroclor 1260. He was able to identify 36 congeners, but could only quantify 27 of them (because of the unavailability of standards for 9 congeners). These 27 comprised 81%, by mass, of the Aroclor 1260. Tuinstra was able to estimate BCF values for most, but not all, of the identified congeners - for 23 of the 27 congeners they identified (which equaled 77% of the congeners, by mass, of Aroclor 1260). As seen in Table 4-4, the average congener-group BCF value increases from about 2 to 4 going from hexa- to nanochloro-PCBs. However, there was a wide range of measured BCF values for specific congeners. In the heptagroup, for example, Tuinstra estimated BCF values between 0.4 and 5.2. Fries, et al. (1973) showed increasing BCF values in milk fat at 20, 40, and 60 days for Aroclor 1254 up to a value of 4.8 at day 60. The body fat BCF value at 60 days, the only time such a measurement was taken, was 3.4. The trend of having a higher BCF value for milk fat as compared to body fat for lactating cows was also noted by Willett, et al. (1987). They fed lactating cattle Aroclor 1254 sorbed to ground corn. In three sequential periods of 60 days, they fed the cattle 10, 100, and then 1000 mg/day of Aroclor 1254. Given their average daily dry matter intake of 19.5 kg during the experiment, the concentration during each of those 3 periods was 0.51, 5.13, and 51.28 mg/kg (ppm). However, milk and body fat concentrations of PCBs were given after 60, 120, and 180 days, so that for estimation of the BCF value, what is needed is average concentration of Aroclor intake after these periods. These averages are 0.51, 2.82, and 18.97 mg/kg. Given the reported concentrations of PCBs in milk and body fat after these experimental periods, BCF values were estimated and given in Table 4-4. Two studies, that of Willett and Liu (1982) and Perry, et al. (1981), contained data from which estimates of BCF could be made, except that these studies did not report daily dry matter intake. An estimate of 19.5 kg/day was assumed for lactating cattle for these studies, which was the experimental dry matter intake noted by Willett, et al. (1987). Willett and Liu (1982) dosed cattle for only 20

days, and arrived at the lowest noted BCF value for Aroclor 1254, 1.2. The trend of increasing BCF value over time of dosing was noted by Fries, et al. (1973). Willett, et al. (1990) conclude that steady state is reached after about 60 days, so that estimates of BCF made from experiments less than 60 days may not reflect steady state conditions. Perry, et al. (1984) had a high BCF value, 4.2, despite the dosing period being only 32 days. This would appear to be the result of having a high concentration in the diet. Similarly high BCF values with corresponding high concentration in dosed intake were noted in Fries, et al. (1973) and Willett, et al. (1987). It should be noted that the concentrations in body fat in the studies of Willett and Liu (1982) and Perry, et al. (1981) were corrected as recommended by Willett, et al. (1990) in estimating BCF values.

Five trends for PCBs were discussed above: 1) that steady state is reached after approximately 60 days, 2) that higher BCF values appear to result with higher concentrations in feed, 3) that BCF values for milk fat may exceed those of body fat for lactating cows (this also seems true for dioxins/furans; see Table 4-3), 4) that the BCF values tend to increase with increasing chlorination of PCB congener groups, and 5) that this fourth trend is based on a limited set of data and much variability exists within specific congener groups.

Generally there is a sparsity and inconsistency in the data which would allow for definitive estimation of BCF values for the example heptachloro-PCB example compound in Chapter 5, 2,3,3',4,4',5,5'-PCB. Most of the data noted is for Aroclor 1254, and this data implies BCF values between 1.2 and 4.8. Based on the results from Tuinstra, et al. (1981) for the average of eight heptachloro-PCBs, a BCF value of 2.3 will be assigned to 2,3,3',4,4',5,5'-PCB.

It should be noted that all bioconcentration or biotransfer parameters, such as the BCF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

- **Soil bioavailability, B_s**: This parameter reduces the bioconcentration ratio, F,

considering that soil is a less efficient vehicle of transfer compared to feed. Remember that the values of BCF appropriate for Equation (4-32) already consider bioavailability and were developed from experimental data placing the BCF of 2,3,7,8-TCDD in the 4 to 6 range. Fries and Paustenbach (1990) reviewed several studies on the oral bioavailability of TCDD in soil in the diet of rats, and concluded that soil is a less efficient vehicle of transfer as compared to rat feed. If the same is true for cattle - that soil is less efficient than their feed - than the BCF value must be reduced when applied to soil ingestion. Most studies reviewed by Fries and Paustenbach used corn oil as the positive control, since there is a high absorption of TCDD in rats when corn oil is used as the vehicle, with 70-83% of the administered TCDD dose absorbed. Their literature review on rat data showed that the bioavailability of TCDD in soil was between 0.4 and 0.5 that in corn oil, or 0.3 to 0.4 overall. The literature implied a range of 0.5 to 0.6 of TCDD in standard rat feed is absorbed, and although few studies were available, a similar 50% absorption rate of TCDD in cattle feed was noted. They concluded, therefore, that the rat data was a reasonable surrogate for cattle. The B_s can be thought of as the ratio of BCF values between soil and feed, or, $(BCF_{soil})/(BCF_{feed})$. If the difference in BCF_{soil} and BCF_{feed} is explained solely by bioavailability differences, than the ratio of overall bioavailability of soil to feed should equal this ratio. As described above for rat data, the overall bioavailability of soil was 0.3-0.4, and the overall bioavailability of feed was 0.5-0.6. The ratio of overall bioavailabilities is, therefore, (0.3-0.4)/(0.5-0.6). If the argument that this ratio equals the ratio of BCFs is valid, than this would lead to a B_s of 0.5 to 0.8. This implies that absorption of TCDD when soil is the vehicle is 50 to 80% of what it would be if feed were the vehicle. These assumptions and implications are made for this assessment, and the soil bioavailability term, B_s, used for all example compounds in Chapter 5 is 0.65.

- **Soil diet fraction, DF_s:** Fries and Paustenbach (1990) report that soil intake by cattle feeding on pasture varies between 2 and 18% of total dry matter intake, depending on whether the grazing area is lush or not. The soil diet fraction would be lower for cattle which are barn-fed with minimal opportunity for contaminated soil intake. Cattle raised for milk are rarely pastured, so one possible assumption for estimating milk fat concentrations would be a DF_s of 0.0. Fries and Paustenbach (1990) assumed between 0 and 2% of the dry matter intake by lactating cattle was soil in various

sensitivity tests. Since cattle raised for beef are commonly pastured, a conservative assumption would be a high DF_s of 0.15 (15%), although a more reasonable assumption which would consider grazing in lush conditions and/or a portion of diet in feed or supplemental feed leads to DF_s less than 0.10. Fries and Paustenbach (1990) assumed DF_s of between 0 and 0.08 for beef cattle in various sensitivity tests. The example settings in Chapter 5 assume 0.02 (2%) for lactating cattle, and 0.04 (4%) for beef cattle.

- **Feed and grass diet fractions, DF_f and DF_g:** The sum of the three diet fractions, $DF_s + DF_f + DF_g$ must equal 1.0. Setting DF_s equal to 0.02 (2%) for lactating cattle assumed that they are pastured to some extent or could be taking in residues of soil sticking to home grown feed. Assuming lactating cattle graze a small amount of time, the DF_g for lactating cattle will be 0.08 (8%). This assessment simplifies the definitions of dairy and beef cattle diets by defining non-pasture grass vegetation simply as "feed". Feeds include hay, silage, grain, or other supplements. While dairy cattle are lactating, 90% of their dietary intake is assumed to be in this general category. Beef cattle spend a significant amount of time pasturing. However, their diet is supplemented with hays, silages, and grains, and particularly so in colder climates where they need to be housed during the winter. In this assessment, the simple assumption that they ingest equal proportions of pasture grass and feeds is made. Therefore, with 4% soil ingestion, DF_f and DF_g are both 48% for beef cattle.

Fries and Paustenbach (1990) summarize pertinent literature to conclude that cattle raised for beef are not slaughtered without an intervening period of high-level grain feeding. Agricultural statistics (USDA, 1992) show that 32.9 million cattle were slaughtered in 1991. Of this number, 6.1 million were cows and bulls that likely did not go through a feedlot prior to slaughter. Quarterly statistics from 1991 show that at any time, cattle and calves on feed for slaughter range from 10 to 12 million. Fries uses these statistics to conclude that 75 to 80% of the total beef supply is from animals that went through a feedlot finishing process, and that the portion of beef that did not go through a feedlot process are (generally speaking) those 6.1 million cows and bulls (personal communication, G. Fries, USDA Agricultural Research Service, Beltsville, Maryland, 20705). He suggests that a representative feedlot finishing process would include a length of 120 days and diet consisting of 20% corn silage and 80% grain. The grains can

be assumed to be residue-free, since grains are protected and, as discussed above, little within plant translocation of outer contamination can be assumed. Also, the ears of the corn silage are in the same category, leaving only the stalks and leaves of the corn silage impacted by atmospheric transfers of dioxin-like compounds.

A feedlot finishing process is important to consider if assessing beef impacts in a site-specific assessment. However, data could not be found in the literature which measured the impact of this process to beef concentrations. Such impacts could occur as the result of increased weight gain from substantially residue-free feeds. Fries and Paustenbach (1990) and Stevens and Gerbec (1988) modeled the impact of a residue-free grain-only diet for four months prior to slaughter. Based on within-cow dilution and depuration considerations, both efforts estimated that the feedlot process would reduce beef concentrations by about one-half. This was the assumption used in the beef food chain validation exercise described in Chapter 7, Section 7.2.3.9.

The demonstration scenarios of Chapter 5 assume that farming families slaughter a portion of their cattle for home consumption. A dilution/depuration reduction is not assumed for these demonstrations.

- **Average contaminant soil concentration, AC_s:** The simplest assumption for AC_s would be that it equals the initial level of contamination, C_s. However, this would be too high if the cattle also graze in uncontaminated areas. Where cattle have random access to all portions of a grazing area with contaminated and uncontaminated portions, a ratio of the spatial average of the contaminated area to the total area should be multiplied by C_s to estimate AC_s. If cattle spend more time in certain areas, these areas should be weighted proportionally higher. Different assumptions for determining AC_s might also be in order when using Equation (4-32) to estimate milk fat as compared to beef fat concentrations. Lactating cattle, if pastured, might graze on different areas than beef cattle. After determining a spatial average based on current conditions, a second consideration might be given to temporal changes. If soil levels are expected to change over time (due to changes in source strength or other factors) then the concentrations should be averaged over the exposure duration as well. The example scenarios in Chapter 5 where beef and milk exposures were estimated were termed "farms". The methodologies in this chapter were used to estimate the average soil concentration over

the entire farm property. Assuming the cattle are raised on the farm property, than 100% of their intake of soil comes from the farm. This means that the average soil concentration, AC_s in Equation (4-32), is equal to the level of contamination given as the initial level, or determined as average for the farm based on fate and transport algorithms.

- **Average feed and pasture grass concentration, AC_f and AC_g:** The concentration of contaminant in pasture grass or feed is equal to C_{abv} as calculated in Equation (4-24). As detailed in Section 4.3.4.2. above, pasture grass or feed grown on-site can be impacted by air-to-plant vapor phase transfer and particulate deposition. Refinements noted above include the empirical parameter VG_{ag} equals 1.00 when applying the air-to-leaf transfer algorithm to pasture grass and 0.50 when applied to cattle feed. A refinement noted here, and like AC_s above, is that an assumption needs to be made about the fraction of feed or fraction of pasture grass that is impacted by contamination. Part of the feed diet could come from outside sources and not be contaminated, and part of the grazing area could be far from a localized area of soil contamination, making it less impacted by contaminated particulates or vapors. The simplest assumption is that the entire vegetative diet of the cattle includes pasture grass and feed impacted by the contaminated soil, in which case AC_f and AC_g would equal C_{abv}. For the sake of simplicity and consistency, the assumption made for AC_s was also made for AC_f and AC_g in the example Scenarios in Chapter 5. That is, the grass and feed intakes of beef and dairy cattle originate within the farm property and concentrations in grass and feed are a function of the soil concentrations within the farm property; AC_f and AC_g are equal to C_{abv} as calculated in Equation (4-24). For site-specific situations, AC_f and AC_g should be estimated as C_{abv} reduced according to assumptions on quality of cattle feed, and impacts of air-borne contaminants on grazing land and cattle feed grown at the site where cattle are raised.

There is one final but critical note on solving for beef and milk concentrations given a solution for C_{fat} as in Equation (4-32). Human daily ingestion amounts are typically expressed in whole product rather than the fat portion of product. Whole milk is 4% fat, meaning that the C_{fat} needs to be multiplied by 0.04 to get whole milk concentration. Similarly, beef is generally 18-22% fat, meaning that the C_{fat} needs to be multiplied by

0.18-0.22 to get whole beef concentration. However, the ingestion rates in this assessment for beef and milk were developed on a fat basis, so no adjustment is necessary.

4.4. ALGORITHMS FOR THE "OFF-SITE" SOURCE CATEGORY

As noted in Section 4.1, the contaminated soil is remote from the site of exposure for the "off-site" source category. A common example is an industrial site with soil contamination or a landfill with contaminated soil. Section 4.4.3. below discusses some considerations for specific types of off-site soil contamination, including the disposal of ash from incinerators, the disposal of sludge from paper and pulp mills, and sites of industrial contamination such as those on the NPL. The example setting in Chapter 5 is 10 hectares in size, has sparse vegetation, and has contamination levels of the example compounds that are in the same range as those found on NPL sites. Since many of the parameters in the algorithms discussed below are specific to particular off-site soil contamination sites, guidance in this section will be specific to the example setting in Chapter 5.

Several of the algorithms estimating exposure media concentrations for the off-site source category are the same or very nearly the same as in the on-site source category. Following now are bullet summaries for similarities and small refinements to these algorithms. Sections below describe algorithms that are unique for the off-site source category.

- **Surface water impacts:** Methodologies and assumptions for estimating surface water impacts for the on-site source category (described in Section 4.3.1.) are also used for this source category. In applying this algorithm for the example scenario demonstrating the off-site source category in Chapter 5, Example Scenario 3, the important assumption was made that the average concentration of contaminants in the watershed was very low compared to the concentration on the contaminated soil - hence, C_w (average concentrations on watershed soils other than the contaminated site) was set to 0.0. Setting C_w to 0.0 could also be justified by saying that the demonstration scenario only demonstrated the incremental impact of the

contaminated site. The unit erosion rate from the contaminated site, SL_s, is assumed to be 9.6 t/ac-yr (English units). The unit erosion rate from other areas of the watershed, SL_w, is assumed to be 2.9 t/ac-yr. Derivation of these terms is given above in Section 4.3.1. The contaminated site is assumed to be 150 meters away from the water body, and SD_s is estimated therefore as 0.26. The effective drainage area, A_w, is 4000 ha. From Figure 4-5, it is seen the sediment delivery ratio associated with this drainage area is approximately 0.15, which is assumed for the example scenario in Chapter 5. The contaminated site for the example scenario is 10 ha.

- **Vapor-phase air concentrations:** The volatilization of contaminants from soil can be estimated similarly to the way described in Section 4.3.2 for the on-site source category. Section 4.4.2 describes a dispersion model which transports contaminants through the air to the exposure site. The far-field dispersion model described in Section 4.4.2 differs from the near-field dispersion model presented in Section 4.3.2.
- **Particulate-phase air concentrations:** The same model for particulate flux due to wind erosion is used for the off-site source category as described in Section 4.3.3. However, two parameters might be different than described above (Equation (4-18)) if the model is applied to off-site soil contamination when the soil is bare. One is the vegetative cover, V, which might be more appropriately assigned a 0.0 implying no ground cover for an active landfill or an industrial site. The other is the threshold wind speed, U_t. The different assumption would be in roughness height, assumed 4 cm for a residence or farm setting, but perhaps more appropriately assumed to be 1.0 cm for bare soil. This value is appropriate for a tilled field (EPA, 1985b). With this change, a U_t is calculated as 8.25 m/sec, and F(t) is calculated as 0.5. Note that V and U_t might be the same as a residential or farm setting if the off-site soil contamination had a grass cover. Once a flux has been calculated, the far-field dispersion model described in Section 4.4.2. below is used for estimating air-borne particulate-phase contaminant concentrations at the exposure site.

- **Biota concentrations:** The basic strategy for estimating biota concentrations - as a linear function of environmental media concentrations (bottom sediment concentrations, soil, air) and based on bioaccumulation or biotransfer factors (along with diet fractions, etc.) - remains the same. Section 4.4.1. describes how exposure site soil concentrations are estimated from concentrations at the off-site source. Exposure site soil then becomes a "source" for plant, beef, and milk contaminant concentrations. Similarly, air-borne particle and vapor-phase contaminants originating from the off-site become sources for pasture grass and feed concentrations, which are above ground vegetations. As described below, exposure site soil concentrations are a function both of the amount of soil estimated to erode from the off-site contamination, and of a mixing depth which is different for "tilled" vs. "untilled" situations. The soil concentration used for cattle ingestion of soil is assumed to be untilled. The soil concentration used to estimate concentrations in underground vegetables is assumed to be tilled. The algorithm to estimate fish tissue concentrations as a function of bottom sediment concentrations remains the same for this source category.

The soil ingestion and dermal exposure pathways are still a function of exposure site soil concentrations; i.e., no assumption of direct contact with the off-site contamination is made. Also, both of these direct soil exposure pathways used the untilled soil concentrations.

Section 4.4.1. discusses how exposure site soil concentrations are calculated from off-site concentrations. Section 4.4.2. describes adjustments to the volatilization flux algorithm and the far-field dispersion model which transports vapor and particulate-phase residues to the nearby exposure site. Section 4.4.3. discusses considerations for specific types of off-site soil contamination.

4.4.1. Exposure Site Soil Concentrations

The key assumptions for the solution strategy estimating exposure site soil concentrations resulting from an off-site soil contamination source are: 1) the exposure site soil becomes contaminated due to erosion of contaminated soil from the source to the

exposure site, 2) the soil eroding off the site of contamination is "enriched" in comparison to the soil at the site - eroded soil has higher contaminant concentrations than in-situ soil, 3) the amount of soil at the exposure site does not increase, which means that soil delivered to the site via erosion is matched by an equal amount which leaves the site, and 4) not only does soil erode off the contaminated site en route to the exposure site, but soil between the contaminated site and the exposure site also erodes to the exposure site.

The third and fourth assumption translate to:

$$D_1 + D_2 = R \qquad (4\text{-}33)$$

where:

D_1 = mass of soil delivered from off-site contaminated source, kg

D_2 = mass of soil delivered from land area between contaminated source and exposure site, kg

R = mass of soil removed from exposure site, kg.

The mass balance equation for exposure site soil concentrations can now be qualitatively stated as (with "ΔC" used as shorthand for change in exposure site soil concentration over time):

ΔC = (the incremental addition to C resulting from the change in erosion of contaminated soil) - (the incremental substraction of C resulting from removal of now contaminated soil from the exposure site) - (the incremental substraction of C resulting from dissipation of residues at the exposure site)

This can be expressed mathematically as:

$$\frac{dC}{dt} = \frac{D_1 C_o E}{M} - \frac{RC}{M} - kC \qquad (4\text{-}34)$$

where:

C	=	the exposure site soil concentration, mg/kg
D_1	=	mass of soil delivered from off-site contaminated source, kg/yr
C_o	=	concentration of contaminant at contaminated site, mg/kg
E	=	enrichment ratio, unitless
M	=	mass of soil at exposure site into which contaminant mixes, kg
R	=	mass of soil removed from exposure site, kg/yr
k	=	first order dissipation rate constant, 1/yr.

Assuming that the contaminant concentration at the exposure site, C, is initially 0, Equation (4-34) can be solved to yield:

$$C = \frac{D_1 C_o E}{R + kM} \left[1 - e^{-\left(\frac{R}{M} + k\right) t} \right] \qquad (4\text{-}35)$$

which computes C as a function of time, t (in years since k is in years). This can be solved for various increments of time starting from a time when the exposure or contaminated site initially became contaminated, or it can be simplistically assumed that the contamination has existed at the contaminated site for a reasonably large amount of time such that the exponential term approaches zero. This can be alternately stated that the assumption is made that the system has reached steady state over a long period of time. Either way, the exponential term drops out, and C is estimated as:

$$C = \frac{D_1 C_o ER}{R + kM} \qquad (4\text{-}36)$$

Equation (4-36) was used to estimate exposure site concentrations resulting from off-site contamination for the example scenario in Chapter 5. Guidance for estimation of these terms including justification for their values as selected in the example settings are:

- **E:** A discussion of the enrichment ratio was given in Section 4.3.1. Its use in that application was to estimate the enrichment of soil delivered to a surface water body and the resulting impacts to suspended and bottom sediments. It's value was placed in the 1 to 5 range, and the value of 3 was chosen for all contaminants. The same value will be used for estimating concentrations in soil that result from erosion of contaminated soils to nearby sites of exposure.

- **k:** For the on-site source category, and for contaminated soil at the off-site contaminated location, the assumption is made that residues do not degrade or dissipate to the point of reducing the concentration of the "initial" soil levels. This was partly based on information indicating generally low rates of biological or chemical degradation for the dioxin-like compounds of this assessment, coupled with the assumption that on-site and off-site contamination was sufficiently deep implying a reservoir of contaminant that would remain available during a period of exposure. These assumptions are less likely to be valid for residues which have migrated over the surface to deposit on the exposure site. The deposition is likely to result in only a thin layer of contaminated soil. Though very small, surface-related dissipation mechanisms such as photolysis, volatilization, or degradation, might reduce surface soil contaminant concentrations. For these reasons, a "dissipation" rate constant is assumed to apply to delivered contaminant, where the precise mechanisms of dissipation are not specified, but could include transport (volatilization, erosion) and degradation (photolysis, biodegradation) mechanisms. The studies on 2,3,7,8-TCDD described in Young (1983) imply a dissipation half-life of 10 years. Fries and Paustenbach (1990) suggested the use of a half-life of at least 10 years, and used a 15 year half-life in their example scenarios on the impact of air-borne deposition of 2,3,7,8-TCDD originating from stack emissions. This assessment uses a dissipation half-life of 10 years for all of the three example compounds in Chapter 5. This half-life translates to a first-order dissipation rate constant of 0.0693 yr^{-1}.

- **M:** The delivered contaminant mixes to a shallow depth at the exposure site. The mixing depth depends on activities which disturb the surface, such as construction, plowing, vehicle traffic, movement of cattle or other animals, burrowing action of animals, other biological activity, normal leaching, and raindrop splash. Mixing depths for fallout plutonium have been found to be 20 cm on cultivated land and 5 cm on uncultivated forest and rangeland (Foster and Hakonson, 1987). Fries and Paustenbach (1990) suggested a depth of 15 cm for agricultural tillage, but assumed values of 1 and 2 cm for various sensitivity tests. However, they did not need to make a distinction between tilled and untilled situation because vegetation (pasture grass and forage for estimating beef and milk fat concentration; above ground fruits and vegetables for human consumption) was assumed to be impacted only by particulate deposition and not root uptake. In another assessment on indirect impacts from incinerator emissions, EPA (1990a) estimated vegetation concentrations as a function of particulate depositions, root uptake, and air-to-leaf transfer from the vapor phase. Different mixing depths for untilled and tilled concentration estimation was required. For root uptake estimation for vegetable and other crops, the estimated soil concentrations assuming a tillage mixing depth of 20 cm. For soil concentrations in untilled situations, they assumed a mixing depth of 1 cm. The methodology of this assessment uses 5 cm for the untilled and 20 cm for the tilled conditions for the off-site soil source category. Soil concentrations for calculation of concentrations of underground vegetables will be a function of a 20-cm depth. This assumption is made because tilling gardens is assumed to distribute surface residues to the 20-cm depth. Soil concentrations for dermal contact, soil ingestion, and pasture grass and soil intake for cattle grazing will assume a depth of 5 cm. These activities are assumed to occur on soil which has not been tilled. As will be described in Section 4.5, tilled and untilled depths of mixing are also required for the stack emission source category. For that source category, the tilled mixing depth is also assumed to be 20 cm, but the untilled mixing depth will instead be assumed to be 1 cm. The difference is made because of the assumed differences in the processes of erosion and air deposition. Erosion is a turbulent process, mixing soils from the contaminated site with soils between the contaminated and exposure site, while air deposition of particles happens uniformly over a landscape in a less turbulent manner.

Given the area of the exposure site, the mass of soil into which the eroded

contaminant is mixed can be calculated as:

$$M = A_{es}\ B_{soil}\ d \qquad (4\text{-}37)$$

where:

M	=	mass of soil for contaminant mixing per unit depth, kg/m
A_{es}	=	area of exposure site, m^2
B_{soil}	=	soil bulk density, kg/m^3
d	=	depth of mixing, m

- **D_1 and D_2:** The first step in deriving both these amounts of soil is to use the Universal Soil Loss Equation (USLE). This approach was described above. Justification was given for an assumption of unit soil loss from the contaminated site of 9.6 t/ac-yr (see Section 4.3.1). D_1 equals this unit loss times the area of contamination times a sediment delivery ratio. The example scenario in Chapter 5 assumed that the exposure site was 150 meters from the contaminated site, and using Equation (4-10), the sediment delivery ratio is 0.26. The unit loss assumed for the area between the contaminated site and the exposure site is 0.96 t/ac-yr. Since this area is adjacent to the exposure site, there is no sediment delivery, and D_2 equals this unit loss times the area between the contaminated and exposure sites.

D_2 and D_2 can now be expressed as:

$$D_1 = 0.224\ SL_1\ SD_1\ A_{LS} \qquad (4\text{-}38a)$$

$$D_2 = 0.224\ SL_2\ SD_2\ A_{BLE} \qquad (4\text{-}38b)$$

where:

$D_{1,2}$	=	mass of soil delivered from off-site contaminated source, D_1, and from the land area between contaminated source and exposure site, D_2, kg/yr,
$SL_{1,2}$	=	average annual unit soil loss, Eng. tons/acre-year, equal to 9.6 t/ac-yr for SL_1 and 0.96 t/ac-yr for SL_2

$SD_{1,2}$ = sediment delivery ratio, unitless, 0.26 for SD_1 (with distance = 150 meters) and 1.00 for SD_2,

A_{LS}/A_{BLE} = land area of contaminated site, A_{LS}, and of area between contaminated site and exposure site, A_{BLE}, m^2

.224 = converts t/ac-yr to kg/m^2-yr.

An adjustment is made to the sediment delivery ratio, SD_1, considering the size discrepancies between the contaminated site and the exposure site. For example, if the contaminated site is larger than the exposure site, then the amount of eroded soil delivered 150 meters downgradient would not all mix with soil at the exposure site. On the other hand, if the contaminated site were smaller than the exposure site, than the full amount of eroded soil delivered 150 meters downgradient would be contained within the exposure site. A simple correction factor, equaling the ratio of a side length of the exposure site (assumed square-shaped) and a side length of the contaminated site size (also assumed square shaped), is used to adjust the sediment delivery ratio:

$$SD_{1a} = SD_1 \ CF \qquad (4\text{-}39)$$

where:

SD_{1a} = adjusted sediment delivery ratio corresponding to SD_1, unitless

SD_1 = sediment delivery ratio reducing the amount eroding from the contaminated site to be delivered to the exposure site, unitless

CF = $A_{ES}^{0.5}/A_{LS}^{0.5}$ if $A_{ES} < A_{LS}$

= 1 if $A_{ES} > A_{LS}$

A_{ES} = area of exposure site, m^2

A_{LS} = area of contaminated site, m^2

Similar considerations are pertinent to the land area between the contaminated and exposure site. Remember that the algorithm assumed that some "clean" (D_2) and some "contaminated" soil (D_1) erodes onto the exposure site, and that a similar amount of soil entering the exposure site (R, which equals $D_1 + D_2$) leaves the exposure site so as to maintain a mass balance. The amount of clean soil eroding from upgradient sources

mixing with exposure site soil can be larger than the amount of contaminated soil if the exposure site is larger than the contaminated site. If the exposure site is smaller than the contaminated, and similar to the solution for SD_{1a} above, then only the small corridor defined by the size of the exposure site contributes clean soil. Either way (i.e., the exposure site is larger or smaller than the contaminated site), the size of the land area contributing clean soil is defined by the size of the exposure site. A_{BLE} can be estimated as the product of the distance between the exposure and contaminated site, and the side length of the exposure site:

$$A_{BLE} = DL \; SL \qquad (4\text{-}40)$$

where:

A_{BLE} = land area between contaminated and exposure site, m^2
DL = distance from landfill to exposure site, m
SL = side length of exposure site, m
= $(A_{ES})^{0.5}$
A_{ES} = area of exposure site, m^2.

4.4.2. Off-Site Transport of Air-borne Contaminants

Estimating the dispersion and resulting exposure site concentrations of air-borne contaminants, originating at the site of contamination in a vapor or a particle phase, requires a different solution for the off-site as compared to the on-site situation. A simplified solution, given as a virtual point source model, can be found in Turner (1970). This model approximates the dispersion that occurs from an area source by using an imaginary point source. This point is located upwind of the actual source at a distance calculated to create a lateral dispersion at the site equal to its width:

$$C_{air} = \frac{2.03 \; FLUX \; A_{sc} \; FREQ \; 10^{10}}{VD \; S_z \; U_m} \qquad (4\text{-}41)$$

where:

C_{air} = concentration of contaminant in air, $\mu g/m^3$

FLUX = average contaminant flux rate, g/cm^2-s

A_s = area of contaminated site, m^2

FREQ = frequency wind blows from source to receptor, unitless

VD = virtual distance, source center to receptor, m

S_z = vertical dispersion coefficient, m

U_m = average wind speed, m/s

10^{10} = converts g/cm^2 to $\mu g/m^2$.

The term, FREQ, has been added to this equation to appropriately account for changing wind directions, and hence, obtain a more accurate annual average air concentration. The vertical dispersion, S_z, is estimated as an empirical function of the distance from the source center to receptor:

$$S_z = 0.222\ x^{0.725} - 1.7\ ,\ x < 1000\ m \qquad (4\text{-}42a)$$

$$S_z = 1.260\ x^{0.516} - 13.0\ ,\ x > 1000\ m \qquad (4\text{-}42b)$$

where:

S_z = vertical dispersion coefficient, m

X = actual distance from source center to receptor, m.

The virtual distance, VD, is an empirical function of the width of the contaminated area and the actual distance from source center to receptor:

$$VD = 2.514\ a + x \qquad (4\text{-}43)$$

where:

VD = virtual distance, source center to receptor, m

a = width of contaminated area perpendicular to wind direction - defined previously as side length for assumed square-shaped contaminated area, m

X = actual distance from source center to receptor, m.

Prior guidance on windspeed (Section 4.3.2) indicated windspeeds ranged from 2.8 to 6.3 m/sec, and suggested a mid-range of 4.0 m/sec in the absence of better information. Where the wind blows from all directions equally, then it will blow from one compass sector about 15% of the time. On these bases, a windspeed of 4.0 m/sec and a FREQ of 0.15 were used in the example scenarios in Chapter 5. In most places, however, wind direction is much less variable, and the appropriate value is best determined with site specific information.

4.4.3. Specific Cases of Off-Site Soil Contamination

This section provides background information on specific sites of soil contamination which have been studied for the presence and impact of dioxin-like compounds. These include landfills used for disposal of ash from municipal waste combustion facilities, the disposal of sludge from pulp and paper mills, and sites of soil contamination typified by the sites monitored in the National Dioxin Study (in many cases, Superfund sites or sites that were in some stage of being considered for inclusion on the NPL list at the time of the study; EPA, 1987). Discussion of these particular sites does not imply that they represent the bulk of such sites nationally, or that they are discussed here based on any critical environmental or exposure rational. They are discussed because they present unique issues for emissions and fate and transport of dioxin-like compounds from sites of soil contamination, and because they have been studied. Issues discussed below are pertinent for other types of off-site soil contamination sites.

4.4.3.1. *Landfills receiving ash from municipal waste incinerators*

Particular issues regarding landfills receiving ash include: the impact of soil cover on releases, the ash concentrations, the size of such landfills, the quantity of ash generated by incinerators, and the fugitive emissions that result from ash management. Key sources providing information for this section include a methodology document describing approaches to estimating environmental releases and exposures to ash (EPA, 1991), and a contractor report applying these types of methodologies using site-specific data from several ash landfills (MRI, 1990). Each of the identified topics will be discussed in turn.

- **Landfill Cover:** Whether or not ash is covered once it is disposed of at the landfill is critical in determining releases and subsequent exposures. Currently, practices at operating landfills vary from no coverage after disposal on active portions of the landfill to daily coverage of disposed ash. MRI (1990) visited six facilities disposing ash, including ash monofills and municipal solid waste landfills. In one of the facilities, an ash monofill located at the site of the combustor, the disposal area encompassed 15 acres and did not use daily cover until final elevation was reached. At that time, a clean cover of 2 feet of soil would be applied. At a second facility, located at the site of the combustor but landfilling municipal solid waste as well as ash, ash was used for different purposes, including a subbase roadbed material, as soil substitute for earth work, and as a daily cover for MSW receipts. An assumption of bare surfaces (i.e., no vegetation) during the period of landfilling activity, with concentrations of dioxin-like compounds equal to concentrations in the ash would appear to be appropriate assumptions for practices at these two landfills.

Where daily cover is employed, however, appropriate assumptions are not straightforward. Of the remaining four sites studied by MRI, two employed daily covers ("clean cover material" in one case and a "HDPE liner" in the other, sic), and daily coverage practices were not discussed for two sites. Approaches described for airborne emissions and erosion losses would have to be modified when daily cover is applied. First, losses of contaminants via overland soil or wind erosion could not be expected to occur when cover (soil cover or otherwise) is in place, although the active part of the landfill would be subject to erosion during an operating day. Even in that case, however, site-specific practices might include little or no ash disposal during periods of soil-erosion-producing storms. Depending on site-specific practices, one might estimate annual erosion losses using methodologies described in this assessment, and then empirically reduce erosions losses based on these practices and scientific judgement.

Air emissions from active portions of the landfill, as in wind erosion and volatilization, also are obviously impacted by cover practices. These emissions would occur during the actual disposal. Wind erosion and volatilization fluxes could be estimated as given in earlier sections, and then reduced by two-thirds, which might correspond to an assumption of disposal during 1/3 of a day or a year, etc. When covered by soil or a synthetic cover, wind erosion losses would not occur. However, buried residues may

diffuse through layers of clean soil and be released via volatilization.

Estimates of volatilization release via diffusion through clean cover have been made. A rigorous approach for such estimates is detailed in Hwang, et al. (1986). Use of this approach requires a computer to iteratively solve a partial differential equation, expressed in terms of a Fourier series. It can be shown, with these equations, that the vapor emission rate through such a cover will not reach steady state for hundreds of years. Hwang's approach was applied to an earlier assessment for 2,3,7,8-TCDD (EPA, 1988b). Calculations were performed for 2,3,7,8-TCDD contamination with a thickness of contamination of 8 ft, and clean caps ranging from 10 to 25 cm. The results of this exercise suggest that the average emission rate of a 70-year period are 1/4 to 1/5 of what they would be without the cap. Based on this exercise, a simple assumption might be made that a clean cap will reduce the average emission rate calculated without a clean cap by 80%. However, these results are not consistent with those described in Jury, et al. (1990). The analytical solution developed by Jury was demonstrated on 35 organic compounds. One exercise conducted by Jury was to estimate the cover thickness required to restrict volatilization to less than 0.7% of the mass incorporated in soil. For 2,3,7,8-TCDD, the thickness was estimated at 0.7 cm for a sandy soil and 0.2 cm for a clayey soil. This appears to contradict the work of Hwang since it shows an essentially insignificant loss for a cap much less thick than the 10-25 cm cap in the exercises using Hwang's approach. However, Jury's approach allows for assumptions on degradation of the buried compound. For that exercise, Jury assumed that the half-life for 2,3,7,8-TCDD was 1 year. This is a very rapid degradation rate, given information that the dioxin-like compounds resist degradation, particularly when not exposed to sunlight. On the other hand, the Hwang model assumes no degradation loss, and as such, the generalization from his exercise might be an overestimate. Hwang's exercise might also have overestimated since it assumed a rather thick 8-ft layer of subsoil contamination. From these arguments, it would appear that neither exercise appropriately evaluated the difference in volatilization in a no cover versus a cover situation.

The above discussions concerned flux calculations when cover practices are used. One set of adjustments discussed reduced a total potential flux of volatilized or wind eroded losses based on a portion of the time that the ash would be uncovered. A second discussion indicated that some loss via volatilization might be modeled with a clean cap.

In any case, it is clear that cover practices will reduce losses. Cover practices must be considered when evaluating the exposure to ash disposed of in landfills.

- **Ash Concentrations:** A key consideration, of course, in modeling transport of dioxin-like compounds from an ash landfill is the concentration on the ash. Ash concentrations of dioxin-like compounds have been found to vary widely, from non-detect (generally less than 0.1 ppb) to the hundreds and thousands of part per billion. Table 4-5 appears in EPA (1991) and summarizes concentrations of dioxin-like compounds and PCBs found in fly, bottom, and combined ash. These data are a summary of 19 references, ranging in publication date from 1974 to 1990. It should be noted that, except for 2,3,7,8-TCDD and 2,3,7,8-TCDF, results listed are for congener groupings defined by degree chlorination.

- **Size of Landfill and Amount of Ash Landfilled:** The size of the landfill and the amount of ash applied daily or over time are both required for estimating exposures nearby. These can both be obtained from site-specific observations. Amounts of daily disposed ash are required to estimate fugitive particulate emissions, as will be discussed shortly. Amounts of daily or ultimate disposal are also tied to landfill size, or the portion of a landfill that is active on a daily basis. One common practice is to fill cells of a landfill one at a time, and once filled, to cover with a 2-ft (or so) layer of clean soil. The appropriate size in this case is the average size of a landfill cell. If daily coverage is applied, than the size for modeling purposes corresponds to the area over which daily coverage occurs. This can also vary depending on the depth of disposal during a day. A six-inch daily coverage, for example, would take twice as much space as a 1-ft depth of daily disposal. If the intent of a day's disposal is to cover over the entire area of an active cell, then depth of coverage need not be considered in determining landfill size.

Determination of landfill size (or the size of the active portion of the landfill) may be required in the absence of site-specific information, such as in the planning stages for a new incinerator. This is where details on landfill management need to be determined. One important detail, as already noted, is the amount of ash generated for daily disposal. Cook (1991) assumes that bottom and fly ash combined comprise about 11% of total receipts on a volume basis. However, a relationship between ash generated and solid waste

Table 4-5. Ranges of concentrations of PCDDs, PCDFs, and PCBs in municipal waste combustor ash (results in ng/g or ppb).

Constituent	Fly Ash (ref)	Combined Ash	Bottom Ash
MCDD	2.0	ND	NR
DCDD	0.4-200	ND-120	NR
T_3CDD	1.1-82	ND-33	NR
T_4CDD	ND-250	0.14-14	<0.04-410
PCDD	ND-722	0.07-50	ND-800
H_6CDD	ND-5,565	0.07-78	ND-1,000
H_7CDD	ND-3,030	0.07-120	ND-290
OCDD	ND-3,152	0.07-89	ND-55
2,3,7,8-TCDD	ND-330	0.02-0.78	<0.04-6.7
Total PCDD	**5-10,883**	**6.2-350**	**ND-2,800**
MCDF	41	1.1	NR
DCDF	ND-90	ND-42	NR
T_3CDF	0.7-550	ND-14	NR
T_4CDF	ND-410	2.3-9	10.1-350
PCDF	ND-1800	1.6-37	0.07-430
H_6CDF	Tr-2,353	1.2-35	ND-920
H_7CDF	Tr-887	0.62-36	ND-210
OCDF	ND-398	0.18-8.4	ND-11
2,3,7,8-TCDF	0.05-5.4	0.41-12	ND-13
Total PCDF	**3.73-2,396**	**6.14-153.9**	**ND-1,600**
Mono CB	0.29-9.5	ND	ND-1.3
Di CB	0.13-9.9	0.126-1.35	ND-5.5
Tri CB	ND-110	0.35-14.3	ND-80
Tetra CB	0.5-140	16.5	ND-47
Penta CB	0.87-225	ND	ND-48
Hexa CB	0.45-65	ND-39	NR
Hepta CB	ND-0.1	ND	NR
Octa CB	ND-1.2	ND	NR
Nona CB	ND	ND	NR
Deca CB	ND	ND	NR
Total PCB	**ND-360**	**ND-32.15**	**ND-180**

ND = not detected at the detection limit Tr: 0.01<Tr<0.1 ng/g NR = Not reported

Source: EPA (1991).

received by an incinerator on a mass basis is more useful for estimating daily disposal amounts. In a recent EPA (1990f) report on ash characterization, ash mass was estimated as an average of 29.5% of municipal solid waste received in five facilities studies, with a narrow range of 25-35%. This mass was estimated on a wet weight basis. Ash is wetted when exiting the incinerator, and water comprises 20-30% of the total weight at that point. If the ash is immediately trucked for landfill disposal, its total weight includes the weight of this quench water. Often ash is stored at the incinerator site in piles prior to disposal, that storage ranging from hours to days. In this circumstance, much of the quench water would have drained off or evaporated, and then the total weight hauled would be closer to a dry weight estimate. In summary, the amount of ash generated to be disposed of a daily basis can be estimated as: the daily receipt of municipal solid waste (tons) * a wet weight ash fraction (0.25-0.35) * a wet to dry weight conversion if appropriate (wet weight * 0.80, e.g.).

- **Fugitive Particulate Emissions:** Fugitive emissions can occur from the time ash exits the incinerator for temporary storage at the facility site (or immediate loading onto trucks for disposal) until ultimate disposal. Approaches to estimate fugitive releases from incinerator ash management are described in EPA (1991), and will be summarized here.

As noted, ash can be wet when exiting the quench tank. If stored at the facility site prior to disposal in a landfill, leaching from piles can occur. Because dioxin-like compounds are strongly hydrophobic, however, the impact of leaching is unlikely to occur much beyond the soil beneath and near the storage piles. If loaded onto trucks when very wet, leaking onto roadways may also occur. If these storage piles are left uncovered, they would of course be subject to erosion losses, which might move residues further from the piles than just leaching of water from the piles.

Of more concern than water-borne losses due to ash management are fugitive emissions of dry ash. Wind erosion, which can occur from open storage piles or uncovered portions of the landfill, is a fugitive emission that has been discussed for soil contamination. Specific practices in the management of ash can also result in fugitive emissions. Such practices include: 1) loading onto and dumping out of trucks, 2) truck transport from the incinerator facility to the landfill site, 3) truck or other traffic over paved

or unpaved roadways at the incinerator site, at the landfill site, or other roadways containing contaminated dust, and 4) spreading and compacting of ash at the landfill site. A set of empirical emission factor equations for estimating fugitive particulate emissions, called "AP-42" equations, have been developed by EPA's Office of Air Quality Planning and Standards (EPA, 1985a; EPA, 1988a). Specifics on applying these equations for ash management are described in EPA (1991). An example of their application using site-specific information for ash management is detailed in MRI (1991). An abbreviated listing of emission factor equations that have been used in these two publications are:

- Vehicular traffic over unpaved roadways. Dust on the surfaces of roads, both unpaved and paved, can become suspended due to vehicular traffic. When these roadways are near ash storage piles or within the landfill, that dust can become contaminated. The emission factor equation for emissions from unpaved roadways is:

$$E_{up} = 1.7\ k_{unp} \left(\frac{s}{12}\right) \left(\frac{Vs}{48}\right) \left(\frac{W}{2.7}\right)^{0.7} \left(\frac{nw}{4}\right)^{0.5} \left(\frac{365-P}{365}\right) \qquad (4\text{-}44)$$

where:

E_{up} = emission flux for unpaved surfaces, kg/VKt (VKt equals vehicle kilometer traveled)

k_{unp} = particle size multiplier specific to the unpaved road emission flux equation, unitless

s = silt content of unpaved roadway, %

Vs = vehicle speed, km/hr

W = vehicle weight, kg

nw = number of wheels per vehicle, unitless

P = number of days with at least 0.254 mm (0.01 inch) precipitation per year, unitless.

- Emissions off trucks in transit. Although no emission factor equations have specifically been developed for trucks while in transit from the incinerator facility to the landfill, such emissions can occur if the ash is dry, and partially or completely uncovered.

The following equation for estimating emissions from open storage piles has been suggested for use in estimating fugitive emissions from trucks in transit (EPA, 1991; the emission factor equation from EPA, 1985a). Note that use of this equation will require specific management assumptions in order to estimate the number of uncovered hectares per day: the number of trucks in use per day, the surface area of trucks, the percent of uncovered area if a tarpaulin is used, the moisture content of ash, and so on.

$$E_t = 1.9 \left(\frac{s}{1.5}\right) \left(\frac{f}{15}\right) \left(\frac{365-P}{365}\right) \qquad (4\text{-}45)$$

where:

E_t = particulates emitted from trucks in transit, kg/day/hectare

s = silt content material of ash, %

P = number of days with >0.25 mm precipitation per year

f = percentage of time that the unobstructed wind speed exceeds 5.4 m/s.

- Loading and unloading. The unloading operations at the disposal site may result in the release of fugitive dust. The following emission factor equation provides emission factors for kilograms of particulate emitted per megagram (metric ton, or 1000 kg) of soil loaded and unloaded:

$$E_{lu} = 0.0016\ k_{unl} \left(\frac{U_m}{2.2}\right)^{1.3} \left(\frac{M}{2}\right)^{-1.4} \qquad (4\text{-}46)$$

where:

E_{lu} = emission factor for loading and unloading, kg fugitive dust/MT ash

k_{unl} = particle size multiplier, dimensionless

U_m = wind speed, m/s

M = material moisture content, %.

- Spreading and compacting of ash at the landfill. An emission factor specifically for ash spreading and compacting has not been developed. However, emission factor equations for similar applications have been applied for estimating fugitive emissions due

to spreading and compacting. MRI (1990) used an AP-42 emission factor developed for dozer moving of overburden in western surface coal mines. Kellermeyer and Ziemer (1989) assumed that the spreading and compaction of ash was analogous to vehicular transport on unpaved surfaces, and used the emission factor for that process. A third possible assumption is that the processes of spreading and compacting are analogous to agricultural tillage. That emission factor equation for agricultural tillage is:

$$E_{at} = 5.38 \; k_{at} \; s^{0.6} \qquad (4-47)$$

where:

E_{at} = emission factor for agricultural tillage, kg/ha
k_{at} = particle size multiplier, dimensionless
s = silt content, %.

When applying such equations, there are further key issues to consider. These include:

- Concentrations on fugitive ash emissions: When such an emission occurs from ash surfaces, such as from storage piles, off trucks in transit, in spreading and compacting, and so on, than there is a good argument to assume that such concentrations on such emissions are "enriched" in comparison to an ash average. The argument here is similar to the argument for enrichment assumed for eroded soils: processes resulting in fugitive air emissions favor lighter particles with more surface area and hence more sites for binding. No data could be found to assign a value to an ash enrichment ratio. MRI (1990) did, however, take data on municipal waste combustor facility roadway dust, and based on that data and statistical evaluations, speculated that fly ash constituted the principal source of lead and cadmium found on paved surfaces. Since fly ash is finer than bottom or combined ash, one hypothesis for this finding is that fugitive emissions from ash management at the combustor site transported these finer particles to roadway surfaces. This is not to imply, however, that concentrations in dust suspended from roadways due to traffic should be higher in concentration than concentrations in ash - this enrichment concept only applies to ash surfaces themselves. Rather, the concentration on roadway suspended dust should be lower than on the ash. This is because contaminated dust on

roadways mixes with clean dust from other sources. As noted, MRI (1990) did take roadway dust samples, and their data appears to place such a dilution factor (concentration on roadway dust divided by concentration on ash) in the range of 0.1 to 0.3. Specifically, they took particulate samples from landfill haul routes while at the same time taking samples of incinerator ash being delivered for disposal the same day. Each paired sample (roadway particulate and ash), were measured for four metals: As, Cd, Cr, and Pb. Several paired samples were taken on both paved and unpaved haul routes. Ratios were then generated for roadway particulate metal concentrations over ash metal concentrations. Results were: As - paved and unpaved ratios were similar and consistently near 0.1 (roadside particulate concentrations of As were 10% of ash concentrations of As), Cd - paved and unpaved ratios were similar and ranged between 0.0 and 0.4, Cr - paved ratios ranged from 0.3 to 0.6, while unpaved had a wide range of 0.3 to 2.0, Pb - paved and unpaved ratios were similar between 0.0 and 0.2. For analogous situations - daily deliveries of contaminated ash - one might assume a dilution factor in the 0.1-0.2 range.

- Selection of values for emission factor equations: As noted, all these equations are empirical equations. They were developed from data on sites where such emissions occur, such as strip mining sites. EPA (1988a) describes the range of conditions over which such equations were developed. What is meant by "conditions" are such factors as the range of vehicle weights in the data set, the range in number of wheels on such vehicles, and so on. Application of these equations for situations not included within these ranges should be done cautiously. Very critical also is the selection of the particle size multiplier variable, k. These values range from about 0.10 to no higher than 1.0. Lower k values are used to estimate emissions of the smallest sized particles; generally particles less than 5 μm in diameter. Higher k values are used to estimate emissions of all sized particles less than a higher diameter, usually either 15 or 30 μm. If these equations are used to only estimate particulate inhalation exposures, than the k value corresponding to 10 μm sized particles, or inhalable sized particles, should be used. When used to estimate total emissions, than the highest k value listed should be used. Such estimations are appropriate when also evaluating impacts to off-site soils or vegetation.

- Controls for fugitive emissions: All these equations were developed when no fugitive emission controls were in place. Common controls for roadway dust suppression

include wetting or use of a chemical dust suppressant. Ash transported in trucks is commonly wetted and/or a tarpaulin is used to control emissions off trucks. There is no guidance or data on the effectiveness of such controls, but they must be considered. In demonstrating these procedures, EPA (1991) assumed that controls on emissions resulted in 90% reductions in potential emissions. If a control is known to be in place and used on a regular basis, than this percent reduction is probably a reasonable starting assumption.

4.4.3.2. *Land application of sludge from pulp and paper mills*

This discussion focuses on an assessment on the land application of sludge from bleached kraft and sulfite pulp and paper mills (EPA, 1990e). Focusing on this source of sludge does not imply that pulp and paper mills produce more sludge than other industries, or that sludge from pulp and paper mills contains more dioxin-like compounds than other sludges. However, it is known that dioxin-like compounds are found in pulp and paper mill sludges. Also, because of the 104-mill study in 1988, much information is available on the content and disposal of this sludge (further information on the 104-mill study can be found in EPA (1990c) and EPA (1990d)). Some of the issues briefly discussed below for pulp and paper mill sludges would also pertain to sludges containing dioxin-like compounds from other sources.

EPA (1990e) described frequency distributions of concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF for 79 mills reporting this information and also broke out the data based on disposal option. Although EPA (1990e) used the disposal option breakout of concentrations in their assessment of the impacts of the various options, it is not felt that the disposal option of choice is based on concentration. Over all options, the median (50% percentile as given in EPA (1990e)) and maximum 2,3,7,8-TCDD concentrations found in sludges were 51 and 3800 ng/kg (ppt), respectively. The median and maximum 2,3,7,8-TCDF concentrations found were 158 and 17100 ppt.

Fate and transport for contaminants is sludge is dependent on disposal means. Of the approximate 2.5 million metric tons of pulp and paper mill sludge generated annually (as estimated in the 1988 104-mill study), five principal options for disposal were noted: landfilling (44% of all sludge disposed), surface impoundments (24%), land application (12%), incineration (12%), and distribution and marketing (8%). Impacts by incineration were not discussed in EPA (1990e) and are not discussed in this section. Key issues

pertaining to each disposal issue are now discussed.

- **Landfilling:** The issue of coverage as discussed above for ash landfills is relevant for any landfill. However, fugitive particulate emissions during sludge handling and disposal is not an issue as it was for disposal of ash from incinerators due to the differences in moisture content. Sludge is much higher in moisture at the time it is disposed of in comparison to ash - with moisture contents as high as 90%.

- **Surface Impoundments:** It was assumed in EPA (1990e) that sludge disposed of in surface impoundments have a higher moisture content as compared to sludge disposed of in landfills. Surface impoundments were located at the mill site, explaining the assumption for a higher moisture content. A surface impoundment in the EPA (1990e) assessment was defined as a facility in which the sludges are stored or disposed on land without a cover layer of soil. For this type of management, soil cover would not be an issue. Concentrations would be those measured in the sludge. Also, vegetative cover would be expected to be minimal, which would influence parameters associated with soil erosion.

- **Land Application:** Twelve percent of all sludge produced annually was land applied. Four of the 104 mills applied the sludge to forest land, two mills land applied the sludge to agricultural land, and two mills used the sludge for abandoned mine reclamation. The high organic matter content (EPA (1990e) assumed a 25% organic carbon fraction in sludge) and high fraction of clay-sized particles make sludge an attractive soil amender. Sludge is either applied to the land surface with or without incorporation. When not incorporated, sludge can be assumed to replace surface soils and concentrations would be those in the sludge. When incorporated, soil concentrations can be estimated simply as (in mg/kg): (mass of contaminant added, mg)/(mass of sludge added, kg + mass of soil in mixing zone, kg). One key issue when incorporated is the number of years of such treatments. Most of the land application uses of paper and pulp mill sludges reported in EPA (1990e) made applications in only one year. As easily seen in the above suggested equation, higher concentrations result with more years of incorporation. The other key issue with incorporation, of course, is the depth of incorporation. For agricultural

applications, the depth of incorporation assumed in EPA (1990e) was 15 cm, similar to the 20 cm incorporation assumed for home vegetable gardening in this assessment. For silvicultural uses, the assumption in EPA (1990e) was 2.5 cm, which corresponds to some but minimal mixing. For abandoned mine reclamation, the assumption was 0 cm incorporation. Routes of exposure might also vary from focuses in this document depending on land application choice. When applied to agricultural land, impacts to food crops would demand particular attention (the procedures in this assessment were demonstrated with home grown vegetables, although of course impacts to food crops are critical when agricultural field soils are impacted by dioxin-like compounds). When applied to forest land, ecological impacts might warrant particular attention, as was discussed and demonstrated in EPA (1990e). A final issue to consider when land applying sludge to land is a rate of dissipation/degradation of dioxin-like compounds. Landfills and surface impoundments have ongoing surface applications and over time, the total depth of applications in the range of meters, so an assumption of a constant source strength over a period of exposure, as was assumed in this assessment for soil contamination sources, is reasonable. However, if only a few centimeters of surface soil are impacted, which might be the case for single applications to land and/or surface applications with no incorporation, an assumption of dissipation may be warranted. EPA (1990e) assumed no degradation of 2,3,7,8-TCDD in their assessment of impacts from land applications.

- **Distribution and Marketing Uses:** The volume of sludge distributed and marketed was approximately 8% of the total amount of sludge generated for the 104-mill study. For this use, sludge was composted and then sold as a soil amendment in residential, agricultural, and commercial settings. More attention to the dermal contact pathway appears appropriate for this usage. Site-specific factors, and the values for these factors used in EPA (1990e), include: 1) depth of incorporation - 0, 15 and 25 cm in assumptions characterized as high, best, and low estimates, 2) garden size - 0.016 and 0.022 hectares characterized as low/best estimate and high, and referencing a national gardening survey, 3) rate of application - between 5 and 20 dry metric tons per hectare references a USDA publication on use of sewage sludge compost for soil improvement and plant growth, and 4) years of using such compost - 20 without specific reference. The years of application is needed for estimating soil concentrations during and after the period

of exposure, using a simple ratio as discussed above in land application.

4.4.3.3. *Sites studied in the National Dioxin Study*

The National Dioxin Study (EPA, 1987a) focused on sites of known or suspected contamination of soil by 2,3,7,8-TCDD. There were 7 "Tiers" of investigation, with roughly decreasing expectations of finding 2,3,7,8-TCDD. Tiers 1 and 2 included 2,4,5-TCP production and associated disposal sites (Tier 1) and sites where 2,4,5-TCP was used as a precursor in the manufacture of pesticidal products and associated disposal sites (Tier 2). These tiers had the highest expectation for finding 2,3,7,8-TCDD. There were originally thought to be 450 sites that would fall in Tiers 1 and 2, but after investigation, only 100 sites were included for study. Some were downgraded into Tier 3. Of the 100 sites studied, 20 were on or were proposed for inclusion in the Superfund National Priorities List. Tiers 3 and 5 were associated with 2,4,5-TCP formulation (Tier 3) and use (Tier 5). Tier 6 were organic chemical or pesticide manufacturing facilities were 2,3,7,8-TCDD was suspected of being present. Tier 4 included combustion sources and are not discussed further in this section. Tier 7, basically an examination of background areas, are also not discussed here.

Issues that are identified as important in fate and transport modeling for this subcategory of off-site sources include concentrations, the possibility of ground water contamination, and site-specific characterization. These are discussed in turn.

- **Concentrations:** Only 11 of the 100 Tier 1 and Tier 2 sites were eventually classified as requiring "no further action" because 2,3,7,8-TCDD soil concentrations were very low, < 1 ppb, or not detected (with detection limits generally at 1.00 ppb). Where it was detected, a general trend was to find very high concentrations where 2,4,5-TCP production wastes were stored or disposed of, with much lower concentrations at soils near these particular areas. At hot spots, concentrations were as high as 2,000 parts per million, but generally soil concentrations were in the parts per billion. It was this parts per billion generalization that led to the assignment of a 1 ppb soil concentration for the demonstration of the off-site source category in Chapter 5. There were findings in the low ppb range for Tiers 3, 5, and 6, but at much lower frequency and no findings higher than the tens of ppb range. For exposure assessments, the characterization of soil

concentrations in a site containing hot spots has to be carefully considered. For site evaluations and proposed options for remediation, an areally weighted average might be considered, although this could dilute loss estimates depending on the area chosen - choosing a large area corresponding to property lines might, for example, lead to an "average" concentration orders of magnitude lower than concentrations found in hot spots. One approach which should be considered is a "hot spot" impact compared to an areally averaged impact. It should also be remembered that removal of highly contaminated soils is a common practice and another option for evaluation would be a concentration assuming hot spots are removed.

- **Potential for Ground Water Contamination:** PCBs have been found in ground water in sites associated with dielectric fluids of transformers. Oils can migrate through soils as a separate immiscible phase and reach ground water, which has been the common explanation for PCB impacts to ground water. Ground water contamination by 2,3,7,8-TCDD has very rarely been found in ground water, although it has been released to the environment in an oil matrix. The Times Beach area of Missouri is the principal example of this release, where waste oils containing 2,3,7,8-TCDD were used for dust control. Ground water sampling did occur in many of the Tier 1 and 2 National Dioxin Study sites, but the results were mostly non-detects. One occurrence at 0.18 ppt was noted for the Hyde Park site of Hooker Chemical in Niagara, NY, and a high of 1.8 ppb was found in an on-site monitoring well at National Industrial Environmental Services in Furley, KS. There were, however, numerous high occurrences in sub-soil samples in hot spot areas, in bottom sediments of evaporation lagoons, and so on, in the hundreds of ppb range.

There have been some limited experimentation showing different patterns of 2,3,7,8-TCDD migration in soils in the presence of solvents or in an oily matrix. Palusky, et al (1986) studied the mobility of 2,3,7,8-TCDD in soils associated with each of 6 solvents. Migration was found to be higher with aromatic solvents and chloroform in comparison to saturated hydrocarbons and methanol. They speculated that the extent of migration related to the solubility of 2,3,7,8-TCDD in the solvent. Puri, et al. (1989) studied the migration potential of 2,3,7,8-TCDD in soil, water, and waste oil mixtures. Over time, they observed a reversible sorption pattern of TCDD, and concluded that a carrier medium with a significant amount of waste oil would play a dominant role in the

movement of TCDD through soils.

- **Site-specific Characterization:** In the case of landfills or sludge land application sites, the assignment of a soil concentration and an area can be made with some reasonableness. Such is not the case with the industrial contamination sites such as those studied in the National Dioxin Study, as briefly discussed above in the concentration bullet. Most of the sites studied in the National Dioxin Study were in the order of tens of hectares to below ten hectares. On the other hand, the Dow Chemical site in Midland, Michigan is described as a site 607 ha in size (Nestrick, et al, 1986). That area corresponds to the size of the property, and the many soil sampling sites within that area were described as "background". Several of the pesticide formulator sites studied in Tier 3 were 2 hectares or less in size. Many of the them were extensively or partially paved with buildings, which complicate fate and transport modeling. Some of the Tier 5 sites of 2,4,5-TCP use were agricultural fields, which are less complicated to describe. However, two sites were described as 2500 acres in size, which again is very large and makes assignment of an average soil concentration non-trivial. Other use sites were described as railyards and railroad rights of way. While estimates of loss into air could be made in complicated sites such as these, use of soil erosion modeling becomes very complicated if not undoable with paved areas, buildings, drainage ditches, roads, and the like.

4.5. ALGORITHMS FOR THE STACK EMISSION SOURCE CATEGORY

Contaminants emitted from incinerator stacks are transported in air and deposit on the exposure site, water bodies that may be used for drinking or fishing purposes, and on surrounding land. Chapter 3 describes the application of the COMPDEP (reference) model to obtain vapor-phase air concentrations and deposition rates of particles at a specified distance from an example stack emission source. These quantities are assumed to be given for purposes of discussion in this section; further discussion of the air transport modeling is given in Chapter 3.

Estimating soil concentrations based on particulate depositions follows a similar approach as estimating exposure site soil concentrations resulting from erosion of contaminated soil from off-site areas of contamination. Section 4.5.1. describes how soil concentrations are estimated given total (wet plus dry) deposition rates. Surface water

impacts are assumed to result from direct deposition onto surface water bodies as well as erosion from the impacted effective drainage area. This solution is an extension of the solution given in Section 4.3.1. for the on-site source category, and is given in Section 4.5.2. Following now are bullet summaries for similarities and small refinements to algorithms previously discussed:

- **Air impacts:** The atmospheric transport modeling described in Chapter 3 was comprised of two computer simulations: one which considered that emissions were in a vapor form and were transported as such, and one which considered that emissions were in particle form and likewise were transported as such. The result of the vapor-phase runs was a unitized ambient air concentration at various distances up to 50 km in all directions from the stack. Only the results in the predominant wind direction were used in this demonstration. The result of the particle-phase runs were an ambient reservoir of air-borne contaminants sorbed to particulates (used only for inhalation exposures), and wet and dry deposition unit rates also at various distances up to 50 km. By "unitized", what is meant is that emissions for the vapor or particle runs can be thought of as "1" mass/time (g/sec) emissions. Results for all distances are linear with respect to this emission rate; that is, if the rate of vapor contaminant determined to be emitted is "5", than ambient air concentrations at any location are 5 times what they are when "1" is assumed to be emitted. The same holds true for emissions in the particle phase. Chapter 3 developed a framework for assigning a vapor and a particle fraction for specific dioxin congeners. For example, 2,3,7,8-TCDD was assumed to have a vapor fraction of 0.55 (55% was in vapor form) and a particle fraction of 0.45. The final model results for air concentrations, and dry and wet deposition rates for all congeners, starting from these unit model runs and then incorporating congener-specific emission rates and vapor/particle splits, are given in Tables 3-12 to 3-17. The vapor-phase air concentrations were used to model vapor phase transfers in the vegetative bioconcentration algorithms. They were also used, summed with the simulated reservoir of particle-bound

contaminants, to estimate the total reservoir of contaminant available for inhalation exposures.

- **Vegetative impacts:** The rates of wet and dry deposition modeled by COMPDEL were used to determine vegetative impacts. The model for particle deposition impacts to vegetations is described in Section 4.3.4.2 above. Of course, this above section solves for dry deposition as a reservoir times a dry deposition velocity (for dry deposition), and as a reservoir times rainfall and a washout factor (for wet deposition); such a solution is not required for the stack emission source category since the deposition totals are estimated by the COMPDEP model. Other parameters for the vegetative model - the B_{vpa} (air-to-leaf vapor transfer factor), the R_w (fraction of wet deposition retained on vegetation surfaces), crop yields and interceptions, and the vegetative washout factor, k_w, are used for the stack emission source category.
- **Biota concentrations:** The algorithm estimating concentration in fish tissue based on bottom sediment concentrations is the same as in previous source categories. Modeled rates of contaminant deposition on particles onto the exposure site are used to estimate a "tilled" and an "untilled" soil concentration, as described below in Section 4.5.1. Underground vegetable concentrations are a function of tilled soil concentrations. The soil concentration used for cattle soil ingestion is untilled. Beef and milk concentrations are again a function of vegetative and soil concentrations, diet fractions, and bioconcentration and bioavailability factors as described in Section 4.3.4.3.

4.5.1. Steady-State Soil Concentrations

Chapter 3 describes the use of the COMPDEP Model to estimate the particulate phase deposition rates at the exposure site. This total deposition rate, F, includes both dry and wet deposition, and is used to estimate the steady state soil concentrations. The deposition of contaminated particulates from the air is assumed to be somewhat analogous to the process of eroding contaminated soil from an off-site source depositing on an exposure site. Specifically, the following assumptions are also made: 1) only a thin layer

of soil becomes contaminated, 2) this layer is either "untilled" or "tilled", depending on surface activities, and 3) surface residues are assumed to dissipate with a half-life of 10 years corresponding to a first order decay rate of 0.0693 yr^{-1}. Considerations of upgradient erosion and exposure site soil removal are not made. Depositions occur over the exposure site and surrounding land area on an on-going basis. It might be said that upgradient soil concentrations are similar to exposure site concentrations at all times. Like the soil source categories, a tilled mixing depth of 20 cm is assumed. However, an untilled mixing depth of 1 cm is assumed for this source category, in contrast to the 5 cm assumed for the off-site soil source category. It is felt that the process of erosion assumed to transport contaminated soil in the off-site soil source category to a site of exposure is a more turbulent process. It assumes that contaminated soils mix with "clean" soils that are between the site of contamination and the site of exposure. In contrast, ongoing airborne deposition of particles is felt to be a less turbulent process impacting all watershed soils simultaneously; hence the assumption of a 1-cm mixing depth. The qualitative mass balance statement (similar to the one made above in Section 4.4.1, with ΔC equalling change in exposure site soil concentrations over time) can now be made as:

ΔC = (the incremental addition to C resulting from the change in deposition of stack emitted particulates) - (the incremental substraction of C resulting from degradation of residues at the exposure site)

This is mathematically stated as:

$$\frac{dC}{dt} = \frac{F}{M} - kC \qquad (4-48)$$

where:

C = the exposure site soil concentration, mg/kg

F = deposition rate of contaminant on particles, mg/yr

M = mass of soil at exposure site into which contaminant mixes, kg

k = first order dissipation rate constant, 1/yr.

The solution to this equation is:

$$C = \frac{F}{kM} \left(1 - e^{-kt} \right) \qquad (4\text{-}49)$$

which computes C as function of time, t. Similar to the assumption made above in Section 4.4.1., the steady state solution for C is simply F/kM. The deposition rates supplied by the COMPDEP model are in units of g/m^2-yr, so a conversion to mg/yr requires a multiplication by the land area of the exposure site and a multiplication of 1000 mg/g. Procedures to estimate M are given above in Section 4.4.1.

4.5.2 Surface Water Impacts

The solution for stack emission impacts to surface water bodies is an extension of the solution for soil contamination described in Section 4.3.1. Stack emissions deposit onto soils within the effective drainage area to result in an average basin-wide soil concentration. Soil erosion then delivers contaminants to surface waters as in Section 4.3.1. Stack emissions also directly deposit onto and impact the surface water body as well. All the assumptions laid out at the beginning of Section 4.3.1 apply here as well. New quantities needed for this solution include: a rate of contaminant deposition onto soils of the effective drainage area used to estimate average soil concentrations (such concentrations are estimated using the approach given in Section 4.5.1. above), a rate of contaminant deposition onto the water body, and a rate of particulate matter deposition onto the water body.

Equations (4-1) through (4-8) are now displayed again with these additions.

$$C_{swb}\, ER_w + DEP_c = C_{wat}\, V_{wat} + C_{ssed}\, M_{ssed} + C_{sed}\, M_{sed} \qquad (4\text{-}50)$$

where:

C_{swb} = concentration on soil entering water body, mg/kg

ER_w = total watershed annual soil erosion, kg/yr

DEP_c = total annual direct deposition of contaminant, mg/yr

C_{wat} = dissolved-phase concentration in water column, mg/L
V_{wat} = water body annual volume, L/yr
C_{ssed} = concentration on suspended sediment, mg/kg
M_{ssed} = mass of suspended sediment introduced per year, kg/yr
C_{sed} = concentration on sediment settling to bottom, mg/kg
M_{sed} = mass of bottom sediment introduced per year, kg/yr

Mass balance and equilibrium equations continue:

$$ER_w + DEP_p = M_{ssed} + M_{sed} \quad (4\text{-}51)$$

$$M_{ssed} = f_s\, ER_w + f_{sd}\, DEP_p \quad (4\text{-}52)$$

$$M_{sed} = (1 - f_s)\, ER_w + (1 - f_{sd})\, DEP_p \quad (4\text{-}53)$$

$$C_{wat} = \frac{C_{ssed}}{KD_{ssed}} \quad (4\text{-}54)$$

$$C_{sed} = C_{ssed}\, \frac{OC_{sed}}{OC_{ssed}} \quad (4\text{-}55)$$

where:

DEP_p = total annual direct deposition of particulate matter, kg/yr
f_s = fraction of annual erosion remaining as suspended materials, unitless
f_{sd} = fraction of annual deposition remaining as suspended material, unitless
Kd_{ssed} = soil-water partition coefficient for contaminant in suspended sediment, L/kg
OC_{ssed} = fraction organic carbon in suspended sediment, unitless
OC_{sed} = fraction organic carbon in bottom sediment, unitless

Substituting again as in Equation (4-7):

$$C_{swb}\ ER_w + DEP_c = C_{ssed}\ \{\ \frac{V_{wat}}{Kd_{ssed}} + f_s\ ER_w + f_{sd}\ DEP_p + \frac{OC_{sed}}{OC_{ssed}}$$

$$[\ (\ 1 - f_s\ )\ ER_w + (\ 1 - f_{sd}\ )\ DEP_p\ ]\ \} \qquad (4\text{-}56)$$

As before, the bracketed quantity in the right hand side of Equation (4-56) can be termed ϕ, so that C_{ssed} can be solved as $(C_{swb}\ ER_w + DEP_c)/\phi$. The numerator in this term can be expanded to describe contaminant contributions by the effective drainage area which has received depositions, the first quantity in the numerator, and to describe direct depositions, the second quantity:

$$C_{swb}\ ER_w + DEP_c = C_w\ SL_w\ A_w\ E\ SD_w + RDEP_c\ A_{wat}\ 1000 \qquad (4\text{-}57)$$

where:

C_{swb} = concentration on soil entering water body, mg/kg

ER_w = total watershed erosion, kg/yr

DEP_c = annual deposition of contaminant on water body, mg/yr

E = enrichment ratio, unitless

C_w = average soil concentration of dioxin-like compound in effective area of watershed, mg/kg

SL_w = average unit soil loss for land area within watershed, kg/ha-yr

A_w = effective drainage area of watershed, ha

SD_w = sediment delivery ratio for watershed, unitless

$RDEP_c$ = rate of contaminant deposition, g/m^2-yr

A_{wat} = area of water body, m^2

1000 = converts g to mg

Again as before, the right hand side of Equation (4-57) can be termed, ρ, and the concentration in suspended sediment, C_{ssed}, is equal to ρ/ϕ. Other water body concentration terms, C_{wat} and C_{sed}, can now be solved using Equations (4-54) and (4-55).

Guidance on these terms and assignment of values for the demonstration scenarios in Chapter 5 is now given.

- **C_{swb} and ER_w:** Equation (4-57) shows all the terms necessary to arrive at an estimate of the annual contaminant entry into the water body via erosion, the C_{swb} * ER_w term. Section 4.5.1 describes the algorithm to estimate soil concentrations given a deposition rate of contaminant. One deposition rate will be chosen to represent average deposition rates over the effective drainage area of the watershed (the effective drainage area is termed A_w). This rate will be the rate given in COMPDEP modeling at 0.5 kilometers, which implies that the water body and the effective drainage area into the water body are near the stack. Tables 3-15 and 3-16 (Chapter 3) display wet and dry deposition rates for this distance. These rates are added to arrive at total deposition, shown in Table 3-17. Second, a representative mixing depth to characterize average watershed soil concentrations needs to be selected. Previous algorithms used a mixing depth of 20 cm for tillage activities, specifically home gardening, and 1 and 5 cm for non-tilled soil concentrations (1 cm for the stack emission and 5 cm for the off-site soil source category). For the sake of demonstration, it will be assumed that a representative watershed depth will equal 10 cm, which might be interpreted as an average of tilled and untilled lands within the effective drainage area. The values for SL_w (6455 kg/ha-yr), A_w (4000 ha), ER (3), and SD_w (0.15) were all given and discussed in Section 4.3.1. and will not be repeated here.

- **DEP_c:** The second quantity of Equation (4-57) describes the annual input to the surface water body that comes from direct deposition. This term is $RDEP_c$ * A_{wat} * 1000, where $RDEP_c$ is the rate of contaminant deposition onto the water body, A_{wat} is the area of the water body, and 1000 converts g to mg. The rate of contaminant deposition at 0.5 km will also be used to describe direct deposition impact to the surface water body, since for demonstration purposes, there is no justification for saying this distance is further or nearer the point of stack emission. The area of the water body has not been required for any other reason, and one will now be given. First, the effective drainage area of 4000 ha is relatively small and will result in a relatively small stream, at 1.524×10^7 m^3/yr flow volume. This volume is also equal to the average cross sectional area of the stream (m^2)

times stream velocity (m/yr). Assuming a stream velocity of 4.73 * 10^6 m/yr (15 cm/sec; 1/2 ft/sec), which is reasonable for a small stream, the cross sectional area is solved as 3.22 m^2. An average 1 meter depth and 3.22 meter width appear reasonable. This width times the stream length would give stream surface area, A_{wat}. Assuming a rectangular shaped watershed, dimensions of 40 ha wide by 100 ha long (to arrive at the 4000 ha effective drainage) seem reasonable. This length of 100 ha translates to 10000 meters, and the full surface area of the stream is 32200 m^2. This will be the value assumed for A_{wat}.

- **DEP_p:** The rate of particulate deposition onto the lake is required to achieve a mass balance of all annual soil erosion + particle deposition contributions to water body solids. The rate of particulate matter emitting from the stack and arriving at downwind locations was not supplied in Chapter 3. Instead, a literature value of 0.03 g/m^2-yr developed by Goeden and Smith (1989) will be used. This value was based on modeling emissions from a resource recovery facility. Total particulate emissions from the stack were projected to be 4.63 g/s, and the deposition rate onto a nearby lake was modeled to be 0.03 g/m^2-yr. No further information was supplied. Now, with the surface area as solved for above at 32200 m^2, the total particle deposition, DEP_p in kg/yr, is 966 g/yr.

- **f_s and f_{sd}:** These are the fractions of total erosion and depositing particles remaining as suspended materials within a year. As discussed in the solution for the "on-site source category" in Section 4.3.1, f_s was solved for as: a value for total suspended solid, TSS of 10 mg/L, multiplied by a total flow volume V_{wat} of 1.524 x 10^{10} L/yr, divided by the total erosion into the water body, 3.87 x 10^{12} mg/yr. This resulted in an f_s of 0.039. Note that this implies a total suspended load of 152,400 kg/yr. It could be assumed that the minuscule 1 kg/yr of particles directly depositing onto the stream remain in suspension during the year, on the basis of being smaller in size than eroded soil. This assumption will, in fact, be made, but it will be supported as follows.

In a quiescent water body, settling occurs through gravity and can be expressed in terms of Stokes Law:

$$V_s = (g / 18\mu) (\rho_s - \rho) d^2 \quad (4\text{-}58)$$

where:

V_s	=	Stokes settling velocity, cm/sec
g	=	acceleration of gravity, 980 cm/sec^2
μ	=	absolute viscosity of water, g/cm-sec (poise)
	=	0.089 g/cm-sec @ 25 C
ρ_s	=	particle density, g/cm^3
ρ	=	density of water, 1 g/cm^3
d	=	particle diameter, cm

For purposes of this discussion, a reasonable assignment of particle density of is 2.5 g/cm^3 for depositing particles or eroding soil. Therefore, making substitutions, the right hand side of Equation (4-58) reduces to 918 d^2.

Now, assumptions for the particle sizes of eroding soil and depositing particles can be made to arrive at a ratio of settling velocities, V_{ssoil}/V_{spart}. The basis for assigning an enrichment ratio for delivery of contaminants via soil erosion was that fine-sized particles were the ones eventually reaching the water body via erosion. Lick (1982) states that a major fraction of the sediments (suspended and bottom) in the Great Lakes are fine grained, silts and clays, and that data from Lake Erie indicates that 90% of the sediments are of this category. Brady (1984) shows USDA's classification of soils according to particle size, and gives a range of 0.0002 to 0.005 cm for silt sized particles and less than 0.0002 for clay size particles. The following assumptions are made to arrive at a representative diameter for particles in eroded soil: eroded soil is comprised of a 50/50 split of these two sized particles, silt-sized particles are, on the average 0.0026 cm in diameter, and clay size particles are 0.0001 cm in diameter. With these assumptions, the average particle size for eroding soil is 0.0014 cm. The settling velocity for a 0.0014 cm particle is 1.8 x 10^{-3} cm/sec. In Section 3.4.3, Chapter 3, the argument was developed that 87.5% of the total emission rate of dioxin-like congeners would be associated with particles less than 2 μm. The basis of this argument was a surface area to volume ratio, with smaller particle sizes having significantly larger ratios. This does not mean that 87.5% of the 1 kg/yr depositing particles are of this size. However, for this discussion,

the size of depositing particles will be assumed to be 2 μm (2 x 10^{-4} cm), since these size particles deliver most of the dioxin-like compounds to the water body (and the ultimate purpose of this exercise is to determine a value for the fraction of depositing particles which remain suspended and impact suspended sediment concentrations). The settling velocity, V_{spart}, is estimated as 3.7 x 10^{-5} cm/sec.

The ratio V_{ssoil}/V_{spart} is about 50. Said another way and with all the assumptions and simplifications made above, depositing particles will remain in suspension 50 times longer than eroding soil in a quiescent water body.

Given this high a difference in settling velocities, it seems reasonable to assume f_{sb} equals 1.0. The fraction of soil erosion remaining in suspension, f_s, will be estimated given TSS, V_{wat}, etc., as before (see Section 4.3.1), only DEP_p (the total amount of depositing particles, in kg/yr) will comprise a given increment of suspended materials when solving for f_s.

- **V_{wat}, OC_{ssed}, OC_{sed}, and Kd_{ssed}:** These have all been discussed in Section 4.3.1. The values for these parameters in the demonstration scenarios in Chapter 5 are: V_{wat} = 1.524 x 10^{10} L/yr, OC_{ssed} = 0.05, OC_{sed} = 0.03, and Kd_{ssed} = OC_{sed} * Koc, where Koc is the organic partition coefficient of the contaminant.

4.6. ALGORITHMS FOR THE EFFLUENT DISCHARGE SOURCE CATEGORY

As discussed in Volume II, Chapter 3, dioxin-like compounds can be released to waterways via various types of effluent discharges such as discharges from municipal waste water treatment facilities and pulp and paper mills using chlorine bleaching. Also discussed is the fact that these emissions have declined substantially in recent years, especially from pulp and paper mills. Since the procedures for considering point source discharges to waterways are somewhat different than those associated with the nonpoint source procedures for soil contamination and stack emissions, they are covered separately in this section. This source category is also different from others in that effluent discharges into surface water bodies are assumed only to impact fish and water.

The approach used in this report is an extension of the "simple dilution" model described in the Superfund Exposure Assessment Manual (EPA, 1988c). Other models are available which offer more spatial and temporal resolution than the model described here.

One such model is the EXposure Analysis Modeling System, or EXAMS (Burns, et al., 1982, and Burns and Cline, 1985). The EXAMS and a simple dilution model were both applied in an assessment of effluent discharges from pulp and paper mills (EPA, 1990d). In this assessment, 98 of the 104 pulp and paper mills were modeled with both models using site-specific information (water body flow rates from STORET for all but 6 of the mills, effluent flow rates and contaminant discharges, etc.). Three key quantities - one model result and two model parameters - led to a range of exposure conditions for humans consuming fish impacted by discharges from these pulp and paper mills: a water column concentration, a bioconcentration factor (BCF) applied to the water column concentration to get fish tissue concentration, and a fish ingestion rate. The simple dilution model was used to estimate total water concentrations - i.e., mg TCDD total/L water. The EXAMS model was used to estimate dissolved phase water column concentration - i.e., mg TCDD dissolved in water column/L water. Then, with each set of water concentrations, two sets of exposure estimates (a low and a high estimate, in one sense) were generated - one with a BCF of 5,000 and a fish ingestion rate of 6.5 g/day, and one with a BCF of 50,000 and a fish ingestion rate of 30 g/day. Note that in deriving the range of results in that exercise, the BCF was applied to both a total and a dissolved phase water concentrations. EPA (1993) discusses several bioconcentration/bioaccumulation empirical parameters for 2,3,7,8-TCDD, and makes the clear distinction for those which are to be applied to a total water concentration versus those applied to a concentration in the dissolved phase. The dilution and EXAMS model study indicated that the simple dilution model generally estimated higher water column contaminant concentrations compared to the EXAMS model, although this trend was not consistent among all water bodies modeled. The results from both models were comparable when the receiving water body had relatively low suspended solids concentration.

One key limitation of the EXAMS and the simple dilution model for use with dioxin-like compounds in aquatic systems is that they do not account for sediment transport processes. The EXAMS model was designed to determine the fate of transport of contaminants in the dissolved phase. Another spatially and temporally resolved model for this source category is the Water Analysis Simulation Package, the most up-to-date version termed WASP4 (Ambrose, et al., 1988). This model does include sediment processes and has been applied in a comprehensive evaluation of 2,3,7,8-TCDD

bioaccumulation in Lake Ontario (EPA, 1990b). It requires extensive site-specific parameterization, but should be considered for more detailed site-specific evaluations of strongly hydrophobic and bioaccumulating contaminants such as the dioxin-like compounds.

The dilution model described below will be demonstrated in Chapter 5 with a set of data developed using site-specific data from the 104 pulp and paper mills of the 104-mill study. As will be discussed below, a hypothetical effluent discharge will have characteristics developed as the average of key characteristics from the 104 mill study. These key data include: flow rates of the receiving water bodies, suspended solids concentration in these receiving water bodies, effluent discharge flow rates, suspended solids in the effluent discharges, organic carbon content of solids in the effluent stream, and discharges of 2,3,7,8-TCDD.

4.6.1. The Simple Dilution Model

The principal assumption for the simple dilution model is that contaminants released into a water body uniformly mix and equilibrate with the surrounding water in an area near the effluent discharge point. This area is commonly referred to as a "mixing zone". For application of this model with dioxin-like compounds, what is desired is a concentration on the suspended solids in this mixing zone. Multiplication of the organic carbon normalized concentration on suspended solids and a Biota Suspended Solids Accumulation Factor, or BSSAF, will result in a concentration of contaminant in fish lipids. This is defined similarly to the BSAF used for other source categories of this assessment, except that the organic carbon normalized concentration is that of suspended solids rather than of bottom sediments.

The BSSAF is one of several empirical factors discussed for estimating the impact to fish in water bodies impacted by 2,3,7,8-TCDD (EPA, 1993). Others include the BSAF, total and dissolved phase bioconcentration factors (BCFs), and total and dissolved phase bioaccumulation factors (BAFs). BAFs and similar to BSAFs and BSSAFs in that all three reflect total exposure of fish to contaminant, including water column, sediment, and food chain exposures. The BCFs reflect water column exposures only. EPA (1993) states that there is currently no data available on organic carbon normalized concentrations of dioxin-like compounds on suspended solids, hence no basis to compare BSAF and BSSAF. This

assessment assumes a similar numerical assignment of BSSAFs and BSAFs.

The total water concentration in a simple dilution model is:

$$C_{tot} = \frac{MASS_c}{Q_e + Q_u} \quad (4\text{-}59)$$

where:

C_{tot} = total water concentration, mg/L
$MASS_c$ = mass of contaminant in discharge, mg/hr
Q_u = flow at a point just upstream of effluent discharge, L/hr
Q_e = effluent flow, L/hr

Dissolved phase and suspended sediment concentrations are then estimated using an approach developed by Mills, et al. (1985) and others:

$$C_{wat} = \frac{C_{tot}}{1 + (Kd_{mix} \; TSS_{mix} \; 10^{-6})} \quad (4\text{-}60)$$

$$C_{ssed} = Kd_{mix} \; C_{wat} \quad (4\text{-}61)$$

where:

C_{wat} = dissolved-phase water concentration of contaminant, mg/L
C_{tot} = total water column concentration, sorbed + dissolved, mg/kg (note: mg/kg is essentially equal to mg/L since 1 L ≈ 1 kg)
Kd_{mix} = suspended sediment-water partition coefficient for contaminant in mixing zone, L/kg
TSS_{mix} = total suspended solids in water column in mixing zone, mg/L
C_{ssed} = concentration of dioxin-like compounds on suspended sediments, mg/kg
10^{-6} = converts mg/L to kg/L

The total suspended solids concentration in the mixing zone is a function of the suspended

solids just upstream of the discharge point and the suspended solids introduced in the effluent stream:

$$TSS_{mix} = \frac{TSS_u\ Q_u + TSS_e\ Q_e}{Q_u + Q_e} \quad (4\text{-}62)$$

where:

TSS_{mix} = adjusted total suspended solids concentration, mg/L
TSS_u = total suspended solids concentration at a point just upstream of effluent discharge, mg/L
TSS_e = total suspended solids concentration in effluent discharge, mg/L
Q_u,Q_e = upstream and effluent discharge flow rates, L/hr

The suspended solids partition coefficient in the mixing zone is a function of the organic carbon partition coefficient of the contaminant and the organic carbon fraction of suspended solids:

$$Kd_{mix} = Koc\ OC_{mix} \quad (4\text{-}63)$$

where:

Kd_{mix} = suspended sediment-water partition coefficient in the mixing zone, L/kg
Koc = compound specific organic carbon partition coefficient, L/kg
OC_{mix} = organic carbon content of suspended sediments in the mixing zone, unitless

This organic carbon content can be solved as the weighted average concentrations of the organic carbon contents of the suspended solids in the effluent discharge and the suspended solids of the receiving water body:

$$OC_{mix} = \frac{TSS_u\ Q_u\ OC_u + TSS_e\ Q_e\ OC_e}{TSS_u\ Q_u + TSS_e\ Q_e} \quad (4\text{-}64)$$

where:

OC_{mix} = organic carbon content of suspended solids in mixing zone, unitless

TSS_u = total suspended solids concentration at a point just upstream of effluent discharge, mg/L

TSS_e = total suspended solids concentration in effluent discharge, mg/L

Q_u, Q_e = upstream and effluent discharge flow rates, L/hr

OC_u, OC_e = organic carbon contents of suspended solids upstream of the discharge point and within effluent discharge stream

Fish lipid concentrations for this solution are then given as:

$$C_{lipid} = BSSAF \frac{C_{ssed}}{OC_{mix}} \quad (4\text{-}65)$$

where:

C_{lipid} = fish lipid concentration, mg/kg

BSSAF = biota suspended solids accumulation factor, unitless

C_{ssed} = concentration of dioxin-like compounds on suspended sediments, mg/kg

OC_{mix} = organic carbon content of suspended sediments, unitless

Finally, whole fish concentrations are simply this lipid concentrations times a fraction of fish lipid, or $C_{lipid} * f_{lipid}$.

The key model parameter is the BSSAF. A value of 0.09 for 2,3,7,8-TCDD was assumed for BSAF based on data from Lake Ontario. One important difference between the Lake Ontario ecosystem and the effluent discharge source category is that the impact to Lake Ontario is thought to be principally historical (EPA, 1990b), while for the effluent source category, the impact is, by definition, ongoing. This difference may translate to differences in assignment of BSSAF as compared to BSAF. Consider two aquatic settings where bottom sediments are found to have equal concentrations of dioxin-like compounds - one in which contamination is ongoing and one in which contamination is

primarily in the past. For the aquatic setting where contamination occurred in the past, water column and suspended sediment concentrations would be lower as compared to the aquatic setting where contamination is ongoing, because water column impacts are only a function of depuration of bottom sediments for the historically impacted water body. It is certainly arguable that exposure of aquatic organisms is greater in the ecosystem where impacts are ongoing, as compared to a system where impacts are historical, when bottom sediment concentrations are equal in the two systems. Now recall the assumption made for the soil contamination and stack emission source categories (in both cases the water body impact is ongoing) concerning the relationship between suspended and bottom sediments - that the organic carbon normalized concentrations are equal. If this is a valid assumption for a system with ongoing impacts, and if in fact fish are relatively more exposed when impacts are ongoing rather than historical, then this argues that a BSSAF for an ongoing contamination setting should be greater in numerical value than a BSAF for a setting where contamination was historical.

However, no data could be found to support such a hypothesis, and there would be no numerical basis for an assumed difference between BSAF and BSSAF. For this reason, the values assumed for BSSAF and BSAF are equal for this assessment. It should be noted that all bioconcentration or biotransfer parameters, such as the BSSAF, are qualified as second order defaults for purposes of general use. Section 6.2. of Chapter 6 discusses the use of parameter values selected for the demonstration scenarios, including a categorization of parameters. Second order defaults are defined there as parameters which are theoretical and not site specific, but whose values are uncertain in the published literature. The parameter values in this category should be considered carefully by users of the methodology.

The effluent discharge solution algorithm was evaluated using data and information from the 104 pulp and paper mill study (EPA, 1990c), which measured discharges of 2,3,7,8-TCDD from 104 mills in 1988, and from the National Study of Chemical Residues in Fish (NSCRF; EPA, 1992a), which measured fish tissue concentrations of 2,3,7,8-TCDD at points downstream from several of these mils. A third modeling study (EPA, 1990d) collected critical data for this modeling evaluation, such as harmonic mean flows downstream of the mills. Finally, the National Council for Air and Stream Improvement (NCASI) provided details on their assessment of this data, which was used here.

Importantly, this information included linking specific fish samples to specific mills. A full description of this modeling evaluation is in Chapter 7, Section 7.2.3.6.

There was a dichotomy of model performance as a function of the size of the receiving water body. For most of the mills, the receiving water bodies had harmonic mean flows around 10^8 L/hr, with a range of 10^7 to 10^9 L/hr. A small number of mills, however, discharged into more substantial receiving water bodies which had an average flow of 5×10^{10} L/hr. Comparing model predictions of fish tissue concentrations for mills discharging into the smaller water bodies, it was found that the model tended to underpredict fish tissue concentrations - the average predicted whole fish concentration was near 7 ppt, whereas the average observed whole fish concentration was near 15 ppt. The same was not true for the large receiving water bodies. In that case, the average whole fish tissue concentration observed was an order of magnitude or more higher than predicted whole fish concentration. No precise explanation could be given for this result. The most likely explanation is that, for these large water bodies, there were other sources of dioxin releases. This comparative exercise did assume inherently that the effluent discharge was the sole source of fish tissue concentrations of 2,3,7,8-TCDD.

It was noted that, for the smaller receiving water bodies, an increase in the assumed BSSAF of 0.09 (which was the value of BSAF assumed otherwise in this assessment) to 0.20 resulted in an average model prediction of fish tissue concentration of near 15 ppt, essentially the same as the observed fish concentration. This could be some empirical evidence for the argument developed above - that the BSSAF for a system with ongoing impacts should be greater in numerical value than a BSAF developed from data on an ecosystem where impacts were primarily historical.

In any case, parameters for the demonstration scenario in Chapter 5 for this source category were derived from 104-mill data. Data from only 77 of the mills was used for the following parameter developments. Mills not included are: 1) the ten mills discharging into the largest water bodies, 2) 9 mills for which EPA (1990d) was unable to derive harmonic mean flows from STORET data, and 3) 8 mills for which data on total suspended solids content in the effluent stream was unavailable from EPA (1990c; actually 11 mills did not suspended solids data, but three were in other categories deleted).

Values of model parameters for the demonstration are now summarized:

- **TSS_u, TSS_e:** The average upstream total suspended solids term from the 77

mills, TSS_u, was 9.5 mg/L. The average suspended solids concentration within the effluent streams from the 77 mills was 70 mg/L.

- **OC_u, OC_e:** No information was available on the organic carbon content of the suspended solids upstream of the effluent discharge point. A value of 0.05 was assigned, which was the value assigned for other source categories. No data as well could be found for the organic carbon content of the effluent solids. However, such solids are essentially biosolids from biological treatments of mill sludges. The organic carbon content of such solids is expected to be much higher than 0.05. The value recommended for OC_e was 0.36 (Steven Hinton, PhD., P.E., National Council of the Paper Industry for Air and Stream Improvement, Inc.; Department of Civil Engineering, Tufts University, Medford, MA 02155). This was based on an average proportion of carbon in algal biomass of 0.36 given in Morel (1983).

- **Q_u, Q_e:** Flow values for the receiving water and effluent stream were summarized in EPA (1990d). The average effluent flow rate, Q_e, for the 77 mills was $4.10 * 10^6$ L/hr, and for the receiving water body, Q_u, was $4.65 * 10^8$ L/hr.

- **Koc, BSSAF, f_{lipid}:** Values of Koc and f_{lipid} are the same ones which have been used for the other source categories. As discussed in the introduction to this section, the Biota Suspended Solids Accumulation Factor, BSSAF, will be assumed to be the same as the Biota Sediment Accumulation, BSAF. This value is 0.09 for 2,3,7,8-TCDD.

- **$MASS_c$:** The mass of 2,3,7,8-TCDD exiting from the 77 mills averaged 0.197 mg/hr. However, this data was pertinent for 1988. Since then, pulp and paper mills have reduced the discharge of dioxin-like compounds in their effluents by altering the pulp bleaching processes. Gillespie (1992) reports that data on effluent quality from all 104 mills demonstrate reductions in discharges of 2,3,7,8-TCDD of 84%. On this basis, the value of $MASS_c$ for all three example compounds will be 0.0315 mg/hr (16% of 0.197 mg/hr).

Using these parameters in the simple dilution model for 2,3,7,8-TCDD results in the following:

1) If the mass loadings of 2,3,7,8-TCDD are assumed to be fully sorbed to solids in the effluent discharge, and not to exist in the soluble phase in the discharge, than the concentration of 2,3,7,8-TCDD on discharging effluent solids is $1.1 * 10^{-4}$ mg/kg, or 110

ppt.

2) The total suspended solids concentration in the mixing zone, TSS_{mix}, equals 10.0 mg/L. The organic carbon content of suspended solids in the mixing zone, OC_{mix}, is estimated as 0.069. It is seen how the effluent discharge influences these two key quantities: the unadjusted TSS_u was given as 9.5 mg/L, and the unadjusted OC_u was 0.05.

3) The overall suspended solids concentration of 2,3,7,8-TCDD in the mixing zone after mixing and equilibrating with surrounding water, C_{ssed}, was 4.5 ppt. This compares to the concentration that might be on the effluent solids of 110 ppt, indicating more than an order of magnitude reduction in concentration by mixing with solids of the receiving water body, and partitioning into the water column.

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5. DEMONSTRATION OF METHODOLOGY

5.1. INTRODUCTION

This document has provided methodologies and background information for conducting site-specific exposure assessments to the dioxin-like compounds. Volume II contains key information pertinent to the methodologies described in this Volume. Chapter 2 of Volume II described physical and chemical properties of these compounds, Chapter 3 described sources of dioxin-like compound release, and Chapter 4 described their occurrence in environmental and exposure media. This Volume lays out the methodologies demonstrated in this chapter. Chapter 2 summarized an overall exposure assessment framework, Chapter 3 described mechanisms of formation of dioxin-like compounds in stack emissions and the fate and transport modeling of releases from the stack to a site of exposure, and Chapter 4 provided methodologies to estimate exposure media concentrations for four sources of contamination, which were termed source categories.

The purpose of this chapter is to put all this information together and demonstrate the methodologies that have been developed. For this demonstration, exposure scenarios are developed which are associated with the four source categories. These categories were defined in Chapter 4, and are:

- **On-site soil**: The source of contamination is soil and both the source and exposure site are on the same tract of land.
- **Off-site soil**: The source of contamination is soil and this source is located distant and upgradient/upwind from the site of exposure.
- **Stack emissions**: Exposed individuals reside downwind of the site where stack emissions occur and are exposed to resulting air-borne contaminants, and soil and vegetation on their property is impacted by deposition of contaminated particulates.
- **Effluent discharge**: A discharge of dioxin-like compounds in effluents impacts surface water and fish. Exposure occurs through consumption of the impacted fish and water.

The demonstration in this chapter is structured around what are termed exposure scenarios. As defined in Chapter 2, an exposure scenario includes a description of the physical setting of the source of contamination and the site of exposure, behavior of

exposed individuals, and exposure pathways. Chapter 2 also described the objective of exposure assessors to determine "central" and "high end" exposure scenarios. This objective was an important one for this demonstration, and the strategy to design such scenarios is detailed in Section 5.2 below. For the two soil source categories and the effluent discharge source category, three dioxin-like compounds are demonstrated for each of the exposure scenarios, including 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, and 2,3,3',4,4',5,5'-HPCB. For the stack emission source, a different approach is taken with regard to compounds demonstrated. One compound is 2,3,7,8-TCDD, as in the other source categories. An addition demonstration estimates TEQ exposures given emission rates of dioxin-like compounds with non-zero Toxicity Equivalency Factors (TEFs) from a stack. Individual congeners emitted by the stack are transported to a site of exposure using the dispersion/deposition model, COMPDEP. Further modeling then takes the key quantities for each congener, the air concentrations (vapor and particulate phases), in $\mu g/m^3$, and the total deposition (dry and wet deposition summed), in $\mu g/m^2$-yr, and determines congener specific exposure media concentrations. The toxic equivalent concentration for each congener is estimated by multiplying the individual congener concentration estimated by the individual congener's TEF. Finally, the individual TEQ concentrations are summed to arrive at an exposure media concentration equalling total TEQ for that media.

Section 5.2 describes the strategy for development of the demonstration exposure scenarios. Section 5.3 gives a complete summary of the demonstration scenarios. Section 5.4 provides some detail on the example compounds demonstrated. Section 5.5 describes the source strength terms for the scenarios. Section 5.6 summarizes the results for all scenarios, which are exposure media concentrations for all exposure pathways, and exposure estimates which are Lifetime Average Daily Doses (LADDs) for all pathways and for all example compounds.

5.2. STRATEGY FOR DEVISING EXPOSURE SCENARIOS FOR DEMONSTRATION PURPOSES

Chapter 2 of this document contained Figure 2-1, a roadmap for assessing exposure to dioxin-like compounds. These procedures assess individual exposures to known sources of contamination. Central and high end exposure patterns, and exposure parameters consistent with these definitions were proposed in that chapter. The

demonstration in this chapter attempts to merge procedures for estimating individual exposures to known sources of contamination and current thoughts on devising central and high end exposure scenarios.

An exposure assessor's first task in determining patterns of exposure is to fully characterize the exposed population in relation to the source of contamination. If the extent of contamination can be characterized, then the exposed population would be limited to those within the geographically bounded area. An example of this situation might be an area impacted by stack emissions. Chapter 3 demonstrated the use of COMPDEP atmospheric dispersion model to predict ambient air concentrations and depositions rates for all points surrounding the stack. Results listed in Tables 3-12 through 3-17 were only for the prevailing wind direction. As can be seen on these tables, the points of maximum impact were within 1 km of the stack. By overlaying the concentration isopleths onto a population density map, the exposed population can be identified. If the extent of contamination is not as clearly defined, such as extent of impact of nonpoint source pollution (impacts from use of agricultural pesticides, e.g.) or the compound is found ubiquitously without a clearly defined source, then the emphasis shifts from geographical bounding to understanding ambient concentrations, exposure pathways and patterns of behavior in general populations.

After identifying the exposed population, the next task is to develop an understanding of the continuum of exposures. The exposures faced by the 10 percent of the population most exposed has been defined as high end exposures. Those faced by the middle of the continuum are called central exposures. Another important estimate of exposure level is a bounding exposure, which is defined as a level above that of the most exposed individual in a population. Arriving at such an understanding can be more of an art than a science. One consideration is the proximity of individuals within an exposed population to the source of contamination. For the incinerator example discussed above, one might begin an analysis by assuming that bounding or high end exposures occur within a kilometer from the stack, in the prevailing wind direction. Another important consideration is the relative contribution of different exposure pathways to an individual's total exposure. While individuals residing at this distance from the incinerator might experience the highest inhalation exposures, they may not experience other exposure pathways associated with contaminated soil on their property - such as consumption of

home grown vegetables, dermal contact, or soil ingestion. Families with home gardens and individuals who regularly work in those gardens may reside over a kilometer from the incinerator and possibly be more exposed because of their behavior patterns. Screening tools, such as the spreadsheets developed for this assessment, can be used in an iterative mode to evaluate the interplay of such complex factors. When applied to a real world situation, information should be sought as to the makeup and behavior patterns of an exposed population.

The demonstration in this chapter attempts to be consistent with the goal of quantifying central and high end exposures. However, it is not exhaustive in its analysis, nor should it be construed as a case study with generalizable results. All the scenario definitions, parameter values, and so on, were construed to be plausible and reasonable, and to demonstrate the application of a site-specific methodology, not to set any regulatory precedent.

Following are bullet summaries of key features of the structure and intent of the demonstrations.

- **Exposed populations:** Exposed individuals are assumed to reside in a rural setting. Exposures occur in the home environment, in contrast to the work environment or other environments away from home (parks, etc.). The presumption is made that the sources of contamination of this assessment can occur in rural settings in the United States. Sources demonstrated include basin-wide soils with concentrations characteristic of background levels, much smaller areas of soils with concentrations that have been found in industrial sites, stack emissions, and effluent discharges where characteristics of the effluent stream including contaminant discharges were developed from recent data from pulp and paper mills. (see Section 5.5. below for more details on source strength terms). It is further assumed that the behavior patterns associated with the exposure pathways can exist in rural settings. Several of these behaviors characterized as high end relate to individuals on farms as compared to behaviors characterized as central for individuals not on farms. The exposed population for this demonstration, therefore, consists of rural individuals in farming and non-farming residences.

For each of the four source categories demonstrated, the exposed populations can be further defined:

-- On-site soils: The on-site source category is demonstrated with soil concentrations that have been found and characterized in the literature as "background" and "rural", or not associated with an identified source. For this source, the exposed population includes all individuals within a rural area for which the background concentration can be considered representative.

-- Off-site soil: Demonstration of this source category entails a finite area of soil contamination, in contrast to the demonstration of the on-site source category, where soils containing low levels of dioxin-like compounds exist throughout a large region. The site of contamination is a 10-acre site having elevated soil concentrations that have been found in the United States in industrial sites. A working hypothesis is made that the population most exposed are those residing very near the site. Their soil is assumed to become contaminated over time due to the process of erosion; these processes normally do not carry contaminants long distances across land, particularly land developed with residences or where erosion is interrupted with ditches or surface water bodies. People from the surrounding community can be impacted by visiting or trespassing on the contaminated land, volatilized residues may reach their home environments, they may obtain water and fish from impacted water bodies, and so on. It seems reasonable to assume that those residing near these sites comprise the principally exposed individuals, or equivalently, the individuals experiencing the high end or bounding exposures associated with these areas of soil contamination.

-- Stack emissions: As indicated earlier, the populations exposed to stack emissions can be identified by overlaying results of an atmospheric dispersion modeling exercise over a map containing population density information. Such an exercise was not done for this demonstration. Instead, simulated ambient air concentrations

and deposition rates were taken from tables in Chapter 3 for two locations, one for use in a central scenario and another for a high end scenario.

-- Effluent discharges: This source category is unique from the others in that soils or air are not impacted by the source. Only the surface water body into which the effluent is discharged is impacted. The only exposure pathways considered for this source category are drinking water and fish ingestion. The exposure parameters used to demonstrate this source category were those developed for the central scenario. Those that could be recreationally fishing in the impacted water body or using it as a source of drinking water could be characterized as central, high end, or bounding. There is no particular rationale for selecting central exposure behavior in demonstrating this source category.

- **Proximity to sources of contamination:** As noted above, the on-site soil contamination source category was demonstrated using soil concentrations typical of background levels that have been found in rural settings. In this case, proximity to the source of contamination was not an issue. Proximity to a stack emitting dioxin-like compounds was identified as an important determinant for identifying the continuum of exposures. Assuming there is a uniform distribution of exposure-related behaviors among exposed populations, i.e., their behavior patterns are not a function of where they live in relation to the stack, the most exposed individuals will be those exhibiting high end exposure behavior nearest the stack. This was the assumption made for purposes of this demonstration. A set of high end exposure behaviors and pathways were demonstrated for individuals residing 500 meters east of the stack, and a set of central exposure pathways were demonstrated for individuals residing 5000 meters east of the stack. The highest ambient air concentrations, and dry and wet deposition rates were simulated to occur at 200 to 1000 meters downwind, justifying 500 meters as an appropriate point for assuming high end impacts. Tables 3-12 through 3-17 listing concentrations and depositions rates as a function show that air

concentrations and dry depositions rates at 5000 meters are only about half of what they are at 500 meters, although wet deposition rates are about 20 times higher at 500 meters as compared to 5000 meters. Without rigorous justification, the model output (concentrations and deposition rates) at 500 and 5000 meters was felt to appropriately characterize high end and central exposures. The above bullet justifies a definition of principally exposed individuals as those nearest the site of high soil contamination in the demonstration of the off-site source category, while recognizing that lesser exposures can occur for other individuals in the community. These lesser exposures will not be demonstrated. Instead, the off-site soil source categories will only be demonstrated with a single, high end scenario. Individuals exposed will be assumed to reside 150 meters downgradient from the site of soil contamination. The above bullet also discussed how a surface water body impacted by effluent discharges could be used (for drinking and recreationally fishing) by individuals exhibiting central, high end, or bounding exposure behavior patterns. Intuitively, proximity should be an issue because impacts to fish and water are likely to be higher nearer to the point of discharge. However, the simplistic model estimating impacts from effluent discharges uses a simple dilution approach to obtain water and suspended sediment concentrations. The suspended sediment concentrations are used to estimate fish impacts. For this approach, therefore, proximity cannot be rigorously evaluated. Exposure parameters for water and fish ingestion corresponding to central behavior patterns were used in the demonstration of the effluent discharge source category.

- **Central and high end exposure patterns:** Chapter 2 described the exposure pathways that are considered in this methodology, and justified assignment of key exposure parameters (contact rates and contact fractions, exposure durations, and so on) as central or high end estimates. That chapter notes that the exposure pathways identified were those that were consistent with the sources of contamination, and consistent with literature which identified predominant media where these compounds were found. The bullet above discussing exposed population indicated that several of the behavior

assumptions were specific to individuals on farm, and that these behavior patterns were evaluated as high end. High end behaviors assumed to be different for individuals on farms versus central behaviors for individuals not on farms include: residing on larger tracts of land (10 acres assumed for farmers; 1 acre assumed for non-farmers), ingestion of home produced and impacted beef and milk, tendencies to reside in a single location longer (20 years versus 9 years), tendencies to be present in the home environment longer (90% of the time versus 75% of the time), and patterns of soil dermal contact designed to be plausible for farmers working with soil versus those incidentally contacting soil. Other patterns of behavior modeled as central and high end are not specifically associated with farming and not farming, but are assumed to be plausible for individuals in rural settings. These include home gardening for fruit and vegetables, inhalation exposures, children that ingest soil, and the use of impacted surface water bodies for drinking and fish to be ingested.

- **Plausibility of source strength terms:** The objective to determine plausible levels of source strength contamination was an important one for this demonstration. The source terms are soil concentrations, effluent discharge rates, and stack emission rates. Section 5.5 describes the source terms in detail.
- **Appropriate estimation of exposure media concentrations**: The realism of estimated exposure media concentrations is dependent on the appropriateness of the models used for such estimations and the assignment of parameter values for those models. One way to arrive at a judgement as to the realism of estimated concentrations is to compare predictions with observations. To the extent possible (i.e., given the availability of appropriate data), model predictions of exposure media concentrations are compared with occurrence data in Chapter 7 on Uncertainty. As is shown, predictions fell within the realm of observed data. Chapter 4 describes the justification of all model parameter values. Many of the parameters are specific to the contaminants. Some contaminant properties were estimated as empirical functions of contaminant-specific parameters, such as the

octanol water partition coefficient, Kow, and others were measured values. For non-contaminant parameters such as soil and sediment properties, patterns of cattle ingestion of soil (and other bioaccumulation/biotransfer parameters), and many others, selected values were carefully described and crafted to be plausible.

5.3. EXAMPLE EXPOSURE SCENARIOS

As noted above, all exposures occur in a rural setting. Exposure pathways were those which could be associated with places of residence in contrast to the work place or other places of exposure. The example scenarios are structured so that all the behaviors associated with high end exposures are included in the "high end" scenarios and all the central behaviors are in the scenarios characterized as "central". To summarize, the components which distinguished the high end exposure scenarios in contrast to the central scenarios include:

- Individuals in the central scenarios lived in their homes and were exposed to the source of contamination for only 9 years, in contrast to individuals in the high end scenarios, who were exposed for 20 years (except for the exposure pathway of soil ingestion, where the individuals are assumed to be children ages 2-6, and in both the central and high end scenarios, the exposure duration is 5 years).
- Individuals in the central scenarios lived on properties 1 acre in size, whereas individuals in the high end scenarios lived on properties 10 acres in size.
- Individuals in the high end scenario associated with the stack emission source category lived 500 meters from the incinerator, whereas individuals in central scenario lived 5000 meters from the incinerator.
- High end individuals obtained a portion of their beef and milk using home produced beef and milk - such individuals are obviously farmers. Beef and milk ingestion pathways were not assessed for non-farming rural individuals, representing the central scenarios.
- Ninety percent of the inhaled air and ingested water by the high end individuals were assumed to be contaminated, whereas only 75% of these exposures were with impacted media for the central individuals. This is

based on time at home versus time away from home assumptions for central versus high end individuals. Also, individuals in high end scenarios were assumed to consume 2.0 L/day of water as compared to 1.4 L/day consumed by individuals in central scenarios.

- Although their total intake of fruit and vegetables was assumed to be the same, a larger proportion of the intake of those food products in the high end household was home grown and impacted as compared to the central household.
- The rates of ingestion of soil by children and of recreationally caught and impacted fish were higher for the high end individuals than the central individuals.

These are the distinguishing features for the central and high end exposure scenarios. For the sake of convenience mainly, all the scenarios defined below as high end are called "farms", and all central scenarios are called "residences". The assertion is not being made that all behaviors are likely to occur simultaneously (or in some cases, simply to occur) on a farm or a non-farm residence, although several of the high behavior patterns are specific to farms. In an exhaustive site-specific analysis, one might begin by evaluating all possible pathways, further evaluating pathways of most exposure, and then determining what pathways occur simultaneously for identified individuals in the exposed population. Only then can be the assessor begin to define a continuum of exposures.

The following bullets describe six exposure scenarios that are demonstrated. The numbering scheme and titles will be referenced for the remainder of this chapter:

Exposure Scenarios 1 and 2: On-site Soil Contamination, Residence and Farm

Surface soils on a 4,000 m^2 (1-acre roughly) rural residence (Scenario 1) and on a 40,000 m^2 (10-acre roughly) small rural farm (Scenario 2) are contaminated with the three example contaminants. The concentrations of the contaminants are uniformly set at 1 part per trillion, which was evaluated as reasonable background levels (see Section 5.5 below). Bottom sediment in a nearby stream becomes contaminated. Water and fish in that stream are subsequently impacted. Fish are recreationally caught and eaten, and the water is extracted for drinking purposes, perhaps at a downstream water system intake. However, water concentration predictions are only those which are estimated to occur in

the drainage area impacting the generally smaller size stream. For background soil concentrations, river system impact should be similar to local stream impact justifying the drinking water pathway for these scenarios.

Exposure Scenario 3: Off-site Soil Contamination, Farm

A 40,000 m^2 rural farm is located 150 m (500 ft roughly) from a 40,000 m^2 area of bare soil contamination; an area that might be typical of contaminated industrial property. The surface soil at this property is contaminated with the three example compounds to the same concentration of 1 part per billion. This is evaluated as reasonable for industrial sites of contamination of dioxin-like compounds, and three orders of magnitude higher than concentrations for Scenarios 1 and 2. As in the above and all scenarios, bottom sediment in a nearby stream is impacted, which impacts the drinking water supply and fish which are recreationally caught and consumed by members of this farming household. A similarly sized stream is impacted for this source category as in the on-site source category. It is less likely that water concentrations for this stream would be similar to concentrations at a point where water is withdrawn for drinking purposes. Nonetheless, to be consistent with the demonstration of the on-site source category and the stack emission source category, drainage area sizes and stream sizes were the same. It can be said that the stream size is plausible for recreational fishing, so impacts to fish are appropriately estimated and compared among the source categories.

Exposure Scenarios 4 and 5: Stack Emissions, Residence and Farm

A 4,000 m^2 rural residence (Scenario 4) is located 5000 meters from an incinerator, and a 40,000 m^2 (Scenario 5) rural farm is located 500 meters downwind from an incinerator. Emission data of the suite of dioxins and furans with non-zero TEFs is available. This allows for estimation of impacts from 2,3,7,8-TCDD alone, and estimation of TEQ impacts. The modeling of the transport of these contaminants from the stack to the site of exposure and other points in the watershed used the COMPDEP model. Details on the stack emission source and the COMPDEP model application are found in Chapter 3. A nearby impacted stream feeds into a drinking water system and supports fish for recreational fishing.

Exposure Scenario 6: Effluent discharge into a river

As has been discussed, this source category is different from others in that the air, soil, and vegetation at a site are not impacted. Rather, only surface water impacts are considered. Therefore, central and high end behaviors associated with places of residence are less pertinent for this source category. Exposure parameters associated with central behaviors for the water and fish ingestion pathways were chosen to demonstrate this source category. The source strength was developed from data on pulp and paper mill discharges of 2,3,7,8-TCDD; more detail on this source strength term development is provided in Section 5.5 below. The discharges of the other two example compounds are assumed to be the same for purposes of demonstration. Obviously, however, there is less of a tie to real data for the discharge rate for these other two example compounds. Also noteworthy for this source category as compared to the others is the size of the surface water body into which discharges occur. The other source categories all were demonstrated on water bodies with annual flow rates of $1.5 * 10^{10}$ L/yr. The river size into which the example effluent was discharged was developed from data from the 104 pulp and paper mill study (as discussed in Section 5.5 below). This river size was $4 * 10^{12}$ L/yr, two orders of magnitude larger than the other streams. In this demonstration, therefore, use of impacted water in a drinking water system would appear to be more plausible.

5.4. EXAMPLE COMPOUNDS

Three compounds were demonstrated for the two soil source categories, on- and off-site soil contamination, and for the effluent discharge source category. For purposes of illustration, one compound was arbitrarily selected from each of the major classes of dioxin-like compounds. They are: 2,3,7,8-tetrachlorodibenzo-p-dioxin, 2,3,4,7,8-pentachlorodibenzofuran, and 2,3,3',4,4',5,5'-heptachloro-PCB. For the remainder of this chapter, these compounds will be abbreviated as 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, and 2,3,3',4,4',5,5'-HPCB.

These compounds demonstrate a range of expected results because of the variability of their key fate and transport parameters. The log octanol water partition coefficients (log Kow) for 2,3,7,8-TCDD, 2,3,4,7,8-PCDF, and 2,3,3',4,4',5,5'-HPCB were 6.64, 6.92, and 7.71, respectively. Whereas the span of reported log Kow ranged from

less than 6.00 to greater than 8.00, only a few reported values were at these extremes. Increasing log Kow translates to the following trends: tighter sorption to soils and sediments and less releases into air and water, less accumulation in plants and in cattle products (beef, milk), and more accumulation in fish. The Henry's Constants for the three compounds span the range of reported values, with the value of the PCB compound the highest of all reported at $3.0 * 10^{-3}$. There were few values less than the $4.99 * 10^{-6}$ reported for 2,3,4,7,8-PCDF. Higher Henry's Constants translate to greater amounts of volatilization flux. A summary of the chemical specific parameters for these three compounds is given in Table 5-1.

For the stack emission demonstration, Scenarios 4 and 5, a different approach was taken. Like the above source category demonstrations, exposures to 2,3,7,8-TCDD alone are determined. Given that the stack emission data included emission rates for all dioxins and furans with non-zero toxicity equivalency factors (abbreviated TEFs), and the atmospheric transport modeling led to estimates of ambient air concentrations, and wet and dry deposition rates at various distances for these compounds, an opportunity presented itself for demonstrating an approach to estimating TEQ impacts. This approach takes the individual deposition rates and concentrations for the dioxins and furans with non-zero TEFs and models the exposure media concentrations individually with unique fate and bioaccumulation parameters, and then determines a final TEQ exposure media concentration using TEFs. Results for this approach are hereafter termed "TEQ" results. The deposition rates, air concentrations, TEFs, and chemical specific parameters for 2,3,7,8-TCDD and the individual congeners are provided in Table 5-2.

5.5. SOURCE TERMS

This section describes the source terms for the example scenarios. Source terms for the soil contamination sources, the on- and off-site soil sources, include the areas of contamination and soil concentrations. This section also summarizes the exposure site soil concentrations that result from erosion of contaminated soil from the nearby soil contamination site in the example scenario demonstrating the off-site soil source category, Scenario 3. The source terms for the stack emission scenarios, 4 and 5, are the emission rates of contaminants from the stacks. Discussions of these rates are provided in Chapter 3. As noted in that Chapter, emission rates were determined from actual test data. This

Table 5-1. Environmental fate parameters for the three example compounds demonstrated for the soil contamination source categories and the effluent discharge source category.

Description	2,3,7,8-TCDD	2,3,4,7,8-TCDF	2,3,3',4,4,' 5,5- HPCB
Kow: log octanol water part coef*	6.64	6.92	7.71
Koc: organic carbon part coef., L/kg	$2.7*10^{6}$	$5.1*10^{6}$	$3.2*10^{7}$
H: Henry's Constant, atm-m^3/mole	$1.7*10^{-5}$	$5.0*10^{-6}$	$1.0*10^{-3}$
Da: molecular diffusivity in air, cm^2/s	0.05	0.05	0.05
k: dissipation rate for eroding contaminants, yr^{-1}	0.0693	0.0693	0.0693
kw: first-order plant wash-off rate, yr^{-1}	18.02	18.02	18.02
B_{vpa}: air-to-leaf transfer factor, unitless	$1.0*10^{5}$	$5.3*10^{5}$	$2.3*10^{4}$
BCF: beef/milk biotransfer factor, unitless	4.3	3.1	2.3
BSAF/BSSAF: bottom sediment (BSAF) or suspended sediment (BSSAF) biota sediment accumulation factor, unitless	0.09	0.09	2.0
RCF: root concentration factor, unitless	$3.9*10^{3}$	$6.4*10^{3}$	$2.6*10^{4}$

* Kow is not strictly required for the fate and transport algorithms, but it was used in the estimation of other parameters, and is otherwise a commonly known and important environmental fate parameter

section does list TEQ emissions in grams per second, and the exposure site soil concentrations that result from stack emission depositions. The source term for the effluent discharge example scenario is the rate of discharge of dioxin-like compounds. This is briefly discussed in this section, with reference to a more detailed discussion in Chapter 7, Section 7.2.3.6.

Key source terms are summarized in Table 5-3. Following now are discussions on these terms for all scenarios.

Scenarios 1 and 2

The residence in Scenario 1 is 4,000 m^2 and in Scenario 2 is 40,000 m^2 in size.

Table 5-2. Key source terms and fate parameters for 2,3,7,8-TCDD and for individual dioxin and furan congeners with non-zero TEFs for the demonstration of the stack emission source category[1].

Compound	TEF	deposition $\mu g/m^2$-yr	air concen. $\mu g/m^3$	H	log Kow	RCF	B_{vpa}	Koc	BSAF	BCF
2378-TCDD	1.0	$1.1*10^{-6}$	$1.4*10^{-11}$	$1.6*10^{-5}$	6.64	$3.9*10^{3}$	$1.0*10^{5}$	$2.7*10^{6}$	0.09	4.32
12378-PeCDD	0.5	$3.9*10^{-6}$	$2.9*10^{-11}$	$2.6*10^{-6}$	6.64	$3.9*10^{3}$	$6.3*10^{5}$	$2.7*10^{6}$	0.09	4.16
123478-HxCDD	0.1	$6.3*10^{-6}$	$3.7*10^{-11}$	$1.2*10^{-5}$	7.79	$3.0*10^{4}$	$2.3*10^{6}$	$3.8*10^{7}$	0.04	2.02
123789-HxCDD	0.1	$9.6*10^{-6}$	$5.4*10^{-11}$	$1.2*10^{-5}$	7.79	$1.3*10^{4}$	$6.9*10^{5}$	$1.2*10^{7}$	0.04	2.24
123678-HxCDD	0.1	$8.6*10^{-6}$	$4.9*10^{-11}$	$1.2*10^{-5}$	7.30	$1.3*10^{4}$	$6.9*10^{5}$	$1.2*10^{7}$	0.04	1.74
1234678-HpCDD	0.01	$8.6*10^{-5}$	$4.9*10^{-10}$	$7.5*10^{-6}$	8.20	$6.2*10^{4}$	$1.0*10^{7}$	$9.8*10^{7}$	0.005	0.36
OctaCDD	0.001	$1.8*10^{-4}$	$1.0*10^{-9}$	$7.0*10^{-9}$	7.59	$2.1*10^{4}$	$2.4*10^{9}$	$2.4*10^{7}$	0.0001	0.52
2378-TCDF	0.1	$4.7*10^{-5}$	$9.0*10^{-10}$	$8.6*10^{-6}$	6.53	$3.2*10^{3}$	$1.5*10^{5}$	$2.1*10^{6}$	0.09	0.94
23478-PeCDF	0.5	$1.2*10^{-5}$	$9.4*10^{-11}$	$6.2*10^{-6}$	6.92	$6.4*10^{3}$	$5.3*10^{5}$	$5.1*10^{6}$	0.09	3.10
12378-PeCDF	0.05	$6.1*10^{-6}$	$5.8*10^{-11}$	$6.2*10^{-6}$	6.79	$5.1*10^{3}$	$3.8*10^{5}$	$3.8*10^{6}$	0.09	0.73
123478-HxCDF	0.1	$2.3*10^{-5}$	$1.4*10^{-10}$	$1.4*10^{-5}$	7.30	$1.3*10^{4}$	$5.9*10^{5}$	$1.2*10^{7}$	0.04	2.34
123678-HxCDF	0.1	$2.2*10^{-5}$	$1.3*10^{-10}$	$6.1*10^{-6}$	7.30	$1.3*10^{4}$	$1.4*10^{6}$	$1.2*10^{7}$	0.04	2.00
123789-HxCDF	0.1	$1.4*10^{-5}$	$8.5*10^{-11}$	$1.0*10^{-5}$	7.30	$1.3*10^{4}$	$8.3*10^{5}$	$1.2*10^{7}$	0.04	2.00
234678-HxCDF	0.1	$8.4*10^{-6}$	$5.0*10^{-11}$	$1.0*10^{-5}$	7.30	$1.3*10^{4}$	$8.3*10^{5}$	$1.2*10^{7}$	0.04	1.78
1234678-HpCDF	0.01	$3.0*10^{-5}$	$1.7*10^{-10}$	$5.3*10^{-5}$	7.90	$3.7*10^{4}$	$6.8*10^{5}$	$4.9*10^{7}$	0.005	0.41
1234789-HpCDF	0.01	$1.3*10^{-5}$	$7.5*10^{-11}$	$5.3*10^{-5}$	7.90	$3.7*10^{4}$	$6.8*10^{5}$	$4.9*10^{7}$	0.005	0.99
OctaCDF	0.001	$6.0*10^{-5}$	$3.3*10^{-10}$	$1.9*10^{-6}$	8.80	$1.8*10^{5}$	$1.7*10^{8}$	$3.9*10^{8}$	0.0001	0.20

[1] Column headings are:

TEF:	Toxic Equivalency Factor	Deposition:	wet + dry deposition at 500 m, $\mu g/m^2$-yr
H:	Henry's Constant, atm-m^3-mole	air concentration:	vapor + particle phase air at 500 m, $\mu g/m^3$
log Kow:	log octanol water partition coefficient	RCF:	root concentration factor, unitless
B_{vpa}:	air-to-leaf transfer factor, unitless	Koc:	organic carbon partition coeff., L/kg
BSAF:	Biota sediment accumulation factor, unitless	BCF:	beef/milk biotransfer factor, unitless

note: k, dissipation rate for eroding contaminants (.0693 yr^{-1}), and kw, first-order plant washoff rate (18.01 yr^{-1}) assumed to be equal for all congeners

Table 5-3. Summary of key source terms for the six exposure scenarios and the three example compounds.

	2,3,7,8-TCDD	2,3,4,7,8-PCDF	2,3,3',4,4,5,5'-HPCB
I. Soil Concentrations, μg/kg (ppb)			
Source Category 1: On-Site Soil			
Scenario 1. Central	0.001	0.001	0.001
Scenario 2. High End	0.001	0.001	0.001
Source Category 2: Off-Site Soil			
Off-site soil concentration	1.000	1.000	1.000
Scenario 3. High End No-till	0.279	0.279	0.279
Tilled	0.077	0.077	0.077
	2,3,7,8-TCDD	TEQ	
Source Category 3: Stack Emissions			
Scenario 4. Central No-till	$1*10^{-7}$	$3*10^{-6}$	
Tilled	$5*10^{-9}$	$2*10^{-7}$	
Scenario 5. High End No-till	$1*10^{-6}$	$2*10^{-5}$	
Tilled	$5*10^{-8}$	$1*10^{-6}$	
Watershed soils	$1*10^{-7}$	$2*10^{-6}$	
II. Emission Rates for Stack Emissions (g/sec) and Effluent Discharges (mg/hr)			
Source Category 3: Stack Emissions Scenarios 4 & 5:	2,3,7,8-TCDD $9.2*10^{-11}$	TEQ $1.5*10^{-9}$	
Source Category 4: Effluent Discharges Scenario 6:	0.0315	0.0315	0.0315

III. Land Areas, m^2

Source Category 1: On-site Soil		Source Category 2: Off-site Soils	
Scenario 1. Central	4,000	Contamination Site:	40,000
Scenario 2. High End	40,000	Scenario 3. High End	40,000
Source Category 3: Stack Emissions			
Scenario 4. Central	4,000		
Scenario 5. High End	40,000		

Chapter 4 in Volume II discussed soil concentrations of the dioxin-like compounds found in the literature. As noted in that chapter, concentrations of the coplanar PCBs were not found in the literature; soil concentrations assigned for 2,3,3',4,4',5,5'-HPCB will be the same as the other two compounds. Scenarios 1 and 2 were designed to demonstrate exposures to low concentrations which might be considered "background" soil concentrations. Soil concentrations of 2,3,7,8-TCDD and 2,3,4,7,8-PCDF described as "background" or "rural" by researchers were found in the non-detect to low ng/kg (ppt) in Illinois, Ohio, and Minnesota in the United States (EPA, 1985; Reed, et al., 1990), and in Sweden (Broman, et al. 1990) and England (Creaser, et al., 1989; Stenhouse and Badsha, 1990). Tier 7 of EPA's National Dioxin Study (EPA, 1987) consisted of "background" sites, or sites that did not have previously known sources of 2,3,7,8-TCDD contamination. The purpose of this tier was to provide a basis for comparison for the other 6 tiers of study, which did include sites of known or suspected 2,3,7,8-TCDD contamination. The results were that 17 of 221 urban sites and only 1 of 138 rural sites had detectable levels of 2,3,7,8-TCDD, with a range of positives of 0.2 to 11.2 ng/kg (ppt). While the value of 1 ng/kg selected for these scenarios may not be a true "background" concentration, the intent in designing Scenarios 1 and 2 was to select a concentration that might be typical of areas where no known identifiable source impacts the soil.

Scenario 3

This scenario was designed to be plausible for properties located near inactive industrial sites with contaminated soil. The selection of 1 μg/kg (ppb) for the three compounds was based on 2,3,7,8-TCDD findings associated with the Dow Chemical site in Midland, MI (EPA, 1985; Nestrick, et al. 1986) as well as the 100 industrial sites evaluated in the National Dioxin Study (which included the Dow Chemical site; EPA, 1987). In that study, most of the sites studied had soil concentrations in the parts per billion range. The farm size was 40,000 m^2, as in all high end scenarios. Table 5-3 shows these concentrations for the example compounds at the site of contamination, and also for the tilled and untilled condition at the sites of exposure. Exposure site soil is assumed to become contaminated over time due to erosion of soil from the contaminated site. The "tilled" condition distributes the eroded contaminants to a depth of 20 cm and impacts the estimated concentrations on underground vegetables grown at home.

The"untilled" condition distributes the eroded contaminants only to a depth of 5 cm, and results in a soil concentration for which soil exposure pathways, ingestion and dermal contact, are estimated. Note that there are no differences in concentrations at the exposure site among the three example contaminants. Three key factors influence the concentrations estimated to occur at sites near a site of soil contamination. First are the source strength terms for the contaminated site - area of contamination and concentration. These were the same for each of the example compounds. Second are the components of the erosion algorithm - quantities of erosion, enrichment ratio, and distance from the site of contamination. Again these were the same for all example compounds. Finally, there are the key parameters determining exposure site concentration - the depth of mixing layers and the contaminant dissipation rate. For all three compounds, a dissipation rate corresponding to a 10-year half-life was assumed, and 5 and 20 cm mixing depths were used in all cases.

Scenarios 4 and 5

Chapter 3 described the application of the COMPDEP model to estimate air-borne concentrations and deposition rates of the contaminants in the vicinity of the hypothetical incinerator, given contaminant emission rates in units of g/sec. Table 5-3 shows the emission rates of 2,3,7,8-TCDD and TEQs. As discussed in Chapter 3, the emission factors (mass compound emitted per mass feed material combusted) were typical of incinerators with a high level of air pollution control, e.g., scrubbers with fabric filters. The TEQ emission factor for the hypothetical incinerator, 4.5 ng TEQ/kg material combusted, was within a range of 0.3 ng TEQ/kg municipal solid waste incinerated, to 200 ng TEQ/kg hospital waste incinerated. This range was developed from representative test data for source-specific incinerators with a similar high level of pollution control technology. Two hundred metric tons per day of material was assumed to be incinerated at the hypothetical incinerator in order to arrive at emissions in appropriate units of g/sec. Wet and dry particle deposition rates, in units of g/m^2-yr, were determined for all dioxins and furans, at various distances from the stack and in the prevailing wind direction. The exposure sites of Scenarios 4 and 5 are located 500 and 5000 meters, respectively, from the emission source. Although the deposition rate for a site whose midpoint is 500 meters away can be precisely calculated as the average of several rates between, say 300 and

700 meters, the deposition rates at 500 meters as listed in Tables 3-15 and 3-16 were used. The same was done for the site at 5000 meters. Other deposition rates needed for the stack emission source category were those used to estimate average watershed soil concentrations and direct deposition onto the impacted water body. For both the central and high end scenarios, rates of deposition at 500 meters were used for these purposes. This might translate to an assumption that the stack was located near the impacted water body. The soil concentrations at the sites of exposure and within the watershed resulting from these depositions are listed in Table 5-3. It is noted that the soil mixing depth for the untilled circumstance is not the same as in the off-site soil category, demonstrated in Scenario #3. The mixing depth for untilled conditions is assumed to be 1 cm, instead of 5 cm. The reasoning is that particle deposition is a less turbulent process of transport as compared to soil erosion - soil erosion was assumed to transport residues from a site of off-site contamination to a site of exposure. The tilled mixing depth was 20 cm, as in the off-site soil category. Finally, the mixing depth assumed to characterize watershed soils on the average was 10 cm. This might assume, for example, that the watershed soils include tilled (agricultural fields) and untilled (residential) soils.

Scenario 6

All key parameters used in Scenario 6 demonstrating the effluent discharge source category were developed using data associated with the 104 pulp and paper mill study (EPA, 1990). Derivation of the physical parameters including the flow rate of the receiving water body, flow rate of the effluent stream, suspended solids concentrations of the receiving water body and the effluent stream, and so on, are described in Section 4.6 of Chapter 4. An exercise evaluating the simple dilution model for predicting impacts to suspended solids in water body and subsequently to fish tissue concentrations resulting from discharges from these mills is described in Section 7.2.3.6, Chapter 7. The bottom line conclusion from that exercise was that the simple dilution model appears to work satisfactorily for a screening model: predicted whole fish tissue concentrations for the majority of mills were half as much as measured fish tissue concentrations. For the minority of mills, those with the highest volumes of receiving water, the model did not work as well. Predicted fish tissue concentrations were around an order of magnitude lower than measured concentrations. The precise reason for this discrepancy is not

known, but the most likely explanation that larger water bodies have more uses and more sources of dioxin-like input - assuming that the fish tissue concentrations result singly from the mill discharge and a few proximate mills may be inappropriate.

Parameters for Scenario 6 were derived from the mills for which the model best performed. The average discharge rate from these mills was 0.197 mg 2,3,7,8-TCDD/hr. However, this data was valid for the time of sampling, which was 1988. Since then, pulp and paper mills have reduced the discharge of dioxin-like compounds in their effluents by altering the pulp bleaching processes. Gillespie (1992) reports that data on effluent quality from all 104 mills demonstrate reductions in discharges of 2,3,7,8-TCDD of 84% overall. On this basis, the discharge rate assumed for 2,3,7,8-TCDD was 0.0315 mg/hr (16% of 0.197 mg/hr). This same rate was assumed for the other two example compounds.

It is important to note that these discharge assignments are not intended to reflect current discharges of dioxin-like compounds from pulp and paper mills, even for 2,3,7,8-TCDD, but particularly for the other two example compounds. Data from the 104-mill study did allow for development of a "composite" effluent discharger in certainly a plausible setting (receiving water body and discharge flow rates, suspended solids, etc.) for pulp and paper mills. Assigning what might be evaluated as a reasonable discharge rate of 2,3,7,8-TCDD from pulp and paper mills for current conditions allows for the example scenario to placed in some context, which was a primary objective of crafting all example scenarios. Individual sources must be evaluated on an individual basis.

5.6. RESULTS

The results of this exercise include the exposure media concentrations for all exposure pathways and scenarios, and the LADD exposure estimates. These two categories of results are summarized in Tables 5-4 and 5-5. Following now are several observations from this exercise. As a reminder for the TEQ demonstration for the stack emission demonstration scenarios, #4 and #5, individual dioxin and furan congeners with non-zero toxic equivalency factors (TEFs) were modeled with unique fate and transport parameters until estimates of exposure media concentration were made. At that point, the TEQ exposure media concentrations were estimated as: $\Sigma C_j * TEF_j$, where C_j are exposure media concentrations for the individual congeners and TEF_j are the TEF for the individual congeners.

Table 5-4. Exposure media concentrations estimated for all scenarios and pathways.

Exposure pathway/ scenario	Scenarios #1,2,3,6: Scenarios #4,5:	2378-TCDD 2378-TCDD	23478-PCDF TEQ	233'44'55'-HPCB
1. Concentration of contaminants in soil for soil ingestion and dermal contact pathways, μg/kg (ppb)				
#1 On-site soil, central		0.001	0.001	0.001
#2 On-site soil, high end		0.001	0.001	0.001
#3 Off-site soil, high end		0.279	0.279	0.279
#4 Stack emissions, central		$1*10^{-7}$	$3*10^{-6}$	
#5 Stack emissions, high end		$1*10^{-6}$	$2*10^{-5}$	
2. Concentration of contaminants in air in vapor phase for vapor inhalation pathway, μg/m^3				
#1 On-site soil, central		$4*10^{-11}$	$2*10^{-11}$	$9*10^{-11}$
#2 On-site soil, high end		$4*10^{-11}$	$2*10^{-11}$	$9*10^{-11}$
#3 Off-site soil, high end		$4*10^{-9}$	$2*10^{-9}$	$2*10^{-8}$
#4 Stack emissions, central		$5*10^{-12}$	$8*10^{-11}$	
#5 Stack emissions, high end		$1*10^{-11}$	$2*10^{-10}$	
(note: for stack emission scenarios, #4 and #5, air concentrations are total, including vapor + particle phases)				
3. Concentration of contaminants in air in particulate phase for particulate inhalation pathway, μg/m^3				
#1 On-site soil, central		$6*10^{-13}$	$6*10^{-13}$	$6*10^{-13}$
#2 On-site soil, high end		$5*10^{-12}$	$5*10^{-12}$	$5*10^{-12}$
#3 Off-site soil, high end		$2*10^{-10}$	$2*10^{-10}$	$2*10^{-10}$
4. Concentration of contaminants in water for water ingestion pathway, mg/L				
#1 On-site soil, central		$3*10^{-11}$	$2*10^{-11}$	$3*10^{-12}$
#2 On-site soil, high end		$3*10^{-11}$	$2*10^{-11}$	$3*10^{-12}$
#3 Off-site soil, high end		$2*10^{-10}$	$1*10^{-10}$	$2*10^{-11}$
#4 Stack emissions, central		$4*10^{-15}$	$5*10^{-14}$	
#5 Stack emissions, high end		$4*10^{-15}$	$5*10^{-14}$	
#6 Effluent discharge, central		$2*10^{-11}$	$1*10^{-11}$	$3*10^{-12}$

(continued on the following page)

Table 5-4. (continued)

Exposure pathway/ scenario	Scenarios #1,2,3,6: Scenarios #4,5:	2378-TCDD 2378-TCDD	23478-PCDF TEQ	233'44'55'-HPCB
5. Concentration of contaminants in fish for fish ingestion pathway, mg/kg				
#1 On-site soil, central		$6*10^{-7}$	$6*10^{-7}$	$1*10^{-5}$
#2 On-site soil, high end		$6*10^{-7}$	$6*10^{-7}$	$1*10^{-5}$
#3 Off-site soil, high end		$3*10^{-6}$	$3*10^{-6}$	$8*10^{-5}$
#4 Stack emissions, central		$6*10^{-11}$	$1*10^{-9}$	
#5 Stack emissions, high end		$6*10^{-11}$	$1*10^{-9}$	
#6 Effluent discharge, central		$4*10^{-7}$	$5*10^{-7}$	$1*10^{-5}$
6. Concentration of contaminants in below ground vegetables (no below ground fruit was assumed) for their respective pathways, mg/kg fresh weight				
#1 On-site soil, central		$1*10^{-9}$	$1*10^{-9}$	$8*10^{-10}$
#2 On-site soil, high end		$1*10^{-9}$	$1*10^{-9}$	$8*10^{-10}$
#3 Off-site soil, high end		$1*10^{-7}$	$1*10^{-7}$	$6*10^{-8}$
#4 Stack emissions, central		$1*10^{-14}$	$2*10^{-13}$	
#5 Stack emissions, high end		$8*10^{-14}$	$1*10^{-12}$	
7. Concentration of contaminants in above ground fruit and vegetables for their respective pathways, mg/kg fresh weight				
#1 On-site soil, central		$6*10^{-12}$	$1*10^{-11}$	$3*10^{-12}$
#2 On-site soil, high end		$1*10^{-11}$	$2*10^{-11}$	$1*10^{-11}$
#3 Off-site soil, high end		$8*10^{-10}$	$1*10^{-9}$	$7*10^{-10}$
#4 Stack emissions, central		$5*10^{-13}$	$3*10^{-11}$	
#5 Stack emissions, high end		$3*10^{-12}$	$1*10^{-10}$	
8. Concentration of contaminants in beef fat for beef ingestion pathway, mg/kg dry weight				
#2 On-site soil, high end		$1*10^{-7}$	$1*10^{-7}$	$6*10^{-8}$
#3 Off-site soil, high end		$3*10^{-5}$	$2*10^{-5}$	$2*10^{-5}$
#5 Stack emissions, high end		$2*10^{-9}$	$4*10^{-8}$	

(continued on the following page)

Table 5-4. (continued)

Exposure pathway/ scenario	Scenarios #1,2,3,6: Scenarios #4,5:	2378-TCDD 2378-TCDD	23478-PCDF TEQ	233'44'55'-HPCB
9. Concentration of contaminants in milk fat for milk ingestion pathway, mg/kg dry weight				
#2 On-site soil, high end		$6*10^{-8}$	$5*10^{-8}$	$3*10^{-8}$
#3 Off-site soil, high end		$2*10^{-5}$	$1*10^{-5}$	$9*10^{-6}$
#5 Stack emissions, high end		$2*10^{-9}$	$3*10^{-8}$	

It is important to understand that all observations made below are not generalizable comments. Different results would arise from different source strength characteristics, proximity considerations, model parameter values, different models altogether, and so on. Chapters 6 and 7 on User Considerations and Uncertainty describes many areas of this assessment which should be considered when evaluating the methodology or viewing the results.

5.6.1. Observations Concerning Exposure Media Concentrations

- ***Soil Concentrations***:

The lowest soil concentrations resulted from deposition of particles from the example stack emission source. Concentrations for the stack emission central and high end scenario were 4 and 3 orders of magnitude lower than the central and high end scenarios demonstrating the on-site source category, respectively. This implies that the example stack emission source would have little impact to nearby soils, since the on-site source category was demonstrated with soil concentrations evaluated as typical of background conditions. The order of magnitude difference in distance from the stack between the central (5000 meters away) and high end (500 meters) scenarios is matched by the same order of magnitude difference in soil concentrations. TEQ soil concentrations were over an order of magnitude higher than 2,3,7,8-TCDD concentrations. The

Table 5-5. Lifetime average daily dose, LADD, estimates for all scenarios and exposure pathways (all results in mg/kg-day)

Exposure scenario/ pathway	Scenarios #1,2,3,6: Scenarios #4,5:	2378-TCDD 2378-TCDD	23478-PCDF TEQ	233'44'55'-HPCB
#1 On-site soil contamination Central exposure scenario				
a. Soil ingestion		$8*10^{-13}$	$8*10^{-13}$	$8*10^{-13}$
b. Soil dermal contact		$4*10^{-14}$	$4*10^{-14}$	$4*10^{-14}$
c. Inhalation-vapor		$1*10^{-15}$	$5*10^{-16}$	$3*10^{-15}$
d. Inhalation-particle		$2*10^{-17}$	$2*10^{-17}$	$2*10^{-17}$
e. Water ingestion		$7*10^{-14}$	$4*10^{-14}$	$6*10^{-15}$
f. Fish ingestion		$1*10^{-12}$	$1*10^{-12}$	$3*10^{-11}$
g. Fruit ingestion		$2*10^{-16}$	$4*10^{-16}$	$1*10^{-16}$
h. Vegetable ingestion		$2*10^{-14}$	$2*10^{-14}$	$1*10^{-14}$
#2 On-site soil contamination High end exposure scenario				
a. Soil ingestion		$3*10^{-12}$	$3*10^{-12}$	$3*10^{-12}$
b. Soil dermal contact		$9*10^{-13}$	$9*10^{-13}$	$9*10^{-13}$
c. Inhalation-vapor		$3*10^{-15}$	$1*10^{-15}$	$7*10^{-15}$
d. Inhalation-particle		$3*10^{-16}$	$3*10^{-16}$	$3*10^{-16}$
e. Water ingestion		$3*10^{-13}$	$1*10^{-13}$	$2*10^{-14}$
f. Fish ingestion		$1*10^{-11}$	$1*10^{-11}$	$2*10^{-10}$
g. Fruit ingestion		$1*10^{-15}$	$2*10^{-15}$	$1*10^{-15}$
h. Vegetable ingestion		$7*10^{-14}$	$6*10^{-14}$	$4*10^{-14}$
i. Beef ingestion		$6*10^{-12}$	$4*10^{-12}$	$2*10^{-12}$
j. Milk ingestion		$1*10^{-12}$	$9*10^{-13}$	$6*10^{-13}$
#3 Off-site soil contamination High end exposure scenario				
a. Soil ingestion		$9*10^{-10}$	$9*10^{-10}$	$9*10^{-10}$
b. Soil dermal contact		$7*10^{-11}$	$7*10^{-11}$	$7*10^{-11}$
c. Inhalation-vapor		$3*10^{-13}$	$1*10^{-13}$	$1*10^{-12}$
d. Inhalation-particle		$2*10^{-14}$	$2*10^{-14}$	$2*10^{-14}$
e. Water ingestion		$1*10^{-12}$	$8*10^{-13}$	$1*10^{-13}$
f. Fish ingestion		$6*10^{-11}$	$6*10^{-11}$	$1*10^{-9}$
g. Fruit ingestion		$9*10^{-14}$	$2*10^{-13}$	$8*10^{-14}$
h. Vegetable ingestion		$5*10^{-12}$	$5*10^{-12}$	$3*10^{-12}$

(continued on the following page)

Table 5-5. (continued)

Exposure scenario/ pathway	Scenarios #1,2,3,6: Scenarios #4,5:	2378-TCDD 2378-TCDD	23478-PCDF TEQ	233'44'55'-HPCB
#3 Off-site soil contamination High end exposure scenario (continued)				
i. Beef ingestion		$1*10^{-9}$	$9*10^{-10}$	$7*10^{-10}$
j. Milk ingestion		$3*10^{-10}$	$2*10^{-10}$	$1*10^{-10}$
#4 Stack emissions Central exposure scenario				
a. Soil ingestion		$1*10^{-16}$	$3*10^{-15}$	
b. Soil dermal contact		$3*10^{-19}$	$7*10^{-18}$	
c. Inhalation-total		$1*10^{-16}$	$2*10^{-15}$	
d. Water ingestion		$7*10^{-18}$	$1*10^{-16}$	
e. Fish ingestion		$1*10^{-16}$	$2*10^{-15}$	
f. Fruit ingestion		$2*10^{-17}$	$1*10^{-15}$	
g. Vegetable ingestion		$3*10^{-17}$	$1*10^{-15}$	
#5 Stack emissions High end exposure scenario				
a. Soil ingestion		$4*10^{-15}$	$8*10^{-14}$	
b. Soil dermal contact		$5*10^{-17}$	$1*10^{-15}$	
c. Inhalation-total		$1*10^{-15}$	$2*10^{-14}$	
d. Water ingestion		$3*10^{-17}$	$4*10^{-16}$	
e. Fish ingestion		$1*10^{-15}$	$2*10^{-14}$	
f. Fruit ingestion		$3*10^{-16}$	$1*10^{-14}$	
g. Vegetable ingestion		$4*10^{-16}$	$1*10^{-14}$	
h. Beef ingestion		$9*10^{-14}$	$2*10^{-12}$	
i. Milk ingestion		$3*10^{-14}$	$6*10^{-13}$	
#6 Effluent discharge Central exposure scenario				
a. Water ingestion		$5*10^{-14}$	$3*10^{-14}$	$6*10^{-15}$
b. Fish ingestion		$9*10^{-13}$	$1*10^{-12}$	$3*10^{-11}$

difference in 2,3,7,8-TCDD and TEQ impacts to all media mirrors the difference in stack emissions of 2,3,7,8-TCDD and stack emissions of TEQ. As seen Table 5-3, 2,3,7,8-TCDD emissions are 6% of TEQ emissions, and soil concentrations of 2,3,7,8-TCDD are 6% of TEQ soil concentrations. This trend in differences between 2,3,7,8-TCDD and TEQ impacts occurs in all exposure media estimations. The highest soil concentrations at the site of exposure resulted from erosion of contaminated soil originating at the 10-acre contaminated site of Scenario 3. Concentrations at the sites of exposure were 0.279 μg/kg (279 ppt) for the no-till algorithm which mixed delivered residues to a depth of 5 cm and 0.070 (70 ppt) for the till algorithm which had a mixing depth of 20 cm. The soil at the site of contamination 150 meters away was 1 μg/kg (1000 ppt or 1 ppb). Exposure site soil concentrations resulting from erosion were the same for all three compounds. This is because the same initial soil concentration was assumed at the site of contamination, and the erosion algorithm contains only one chemical specific parameter. This is the rate of dissipation for eroding contaminants. It was assigned a value of 0.0693 yr^{-1} (10-year half life) for all three example compounds.

- ***Vapor and Particle-Phase Air Concentrations***:

One statement to make up front about vapor-phase air concentrations is that using the descriptor "vapor-phase" does not necessarily mean that the contaminants are expected to remain in a pure vapor state while air-borne. Residues which volatilize from the soil are expected to initially be a vapor phase. However, it is possible that dioxin-like compounds released into the air this way would not remain in vapor phase, but would partly sorb to air-borne particulates. The assumption is made is this assessment that contaminants released from the soil remain in the vapor phase for further modeling. This assumption influences air-to-leaf transfers of vapors for estimating impacts to vegetations.

It also impacts the relative magnitudes of predicted concentrations in the vapor as compared to the particulate phase for the soil source categories. As seen in Table 5-4, the vapor phase concentrations of 2,3,7,8-TCDD are 1 to 2 orders of magnitude higher than the particle phase concentrations for the soil contamination source demonstrations - Scenarios 1, 2, and 3. In contrast, the reservoirs in the vapor and particle phases for 2,3,7,8-TCDD are comparable for the demonstration of the stack emission source category, Scenarios 4 and 5. In that case, partitioning of 2,3,7,8-TCDD as released and

transported is assumed to be 45% in the particle phase and 55% in the vapor phase. This close partitioning results in comparable reservoirs at sites of exposure.

Concentrations of contaminants in the vapor phase range from 10^{-11} to 10^{-8} $\mu g/m^3$. Similar and lower concentrations, in the 10^{-11} $\mu g/m^3$ range, resulted from the volatilization of background soil concentrations of 0.001 $\mu g/kg$ of the three example compounds, Scenarios 1 and 2. When the soil concentration of these compounds were three orders of magnitude higher at a site 150 meters away, air concentrations at the exposure site were about two orders of magnitude higher.

One interesting trend of note is that the vapor-phase concentrations for the central and high end scenarios of Scenarios 1 and 2 are similar for each compound; i.e., the 2,3,7,8-TCDD concentration for Scenario 1 is the same as the 2,3,7,8-TCDD concentration of Scenario 2 (although they are different within a Scenario for different compounds; that will be discussed shortly). This is, in fact, the result of two inverse trends of the solution algorithm. First, the average volatilization flux (mass/area-time) will always be lower for the high end scenario as compared to the central scenario. This is due to the solution algorithm assumption that residues available for volatilization originate from deeper in the soil profile over time, so that the average flux is lower for longer periods of volatilization. This is seen in the volatilization flux equation - Equation (4-13), Chapter 4 - which has a time term (ED, or exposure duration) in the denominator. The high end scenarios assume 20 years exposure duration compared to 9 years for the central scenarios. This alone would have resulted in lower air concentrations in the high end as compared to the central scenario. However, the dispersion of volatilized residues is a direct function of the area over which volatilization occurs. This is expressed in terms of a side length, parameter "a" in Equation (4-16), Chapter 4, as well as a dispersion term, S_z. It is easy to show that increasing the area alone would have resulted in higher air concentrations at the larger farm site of the high end scenario, 10 acres, as compared to the smaller residence of the central scenario, 1 acre. The two trends cancel each other and vapor phase concentrations for a given compound are similar for both scenarios. However, for different compounds within the same scenario, vapor phase concentrations are different. This difference is due to chemical parameters, principally the Henry's Constant, H. 2,3,3',4,4',5,5'-HPCB had the highest value for H, and it was 2 orders of magnitude higher than the value for 2,3,7,8-TCDD and 3 orders of magnitude higher than

the value for 2,3,4,7,8-PCDF. This drove the trend for air concentrations, as 2,3,3',4,4',5,5'-HPCB had the highest air concentrations, followed by 2,3,7,8-TCDD at a concentration 1 order of magnitude lower and 2,3,4,7,8-PCDF at slightly lower than 2,3,7,8-TCDD.

Total air concentrations of 2,3,7,8-TCDD predicted to occur at exposure sites at 500 meters and 5,000 meters from a stack emission were in the 10^{-12} to 10^{-11} $\mu g/m^3$ range. The air concentration estimated to result from a background soil concentration of 1 ppt (example Scenarios 1 and 2) was dominated by the vapor phase and equalled $4*10^{-11}$ $\mu g/m^3$. The TEQ vapor and particle concentrations exceeded the analogous concentrations of 2,3,7,8-TCDD by about a factor of 20. As in the soil concentration discussion above, this difference is driven by the difference in emission rates of 2,3,7,8-TCDD and TEQs. Even though air concentrations of 2,3,7,8-TCDD are the similar for Scenarios 4 and 5, the stack emission source category, and Scenarios 1 and 2, the soil contamination source category demonstrated at background soil concentrations, the soil concentrations are much different, as noted above in the discussion on soil concentrations. Chapter 6, Sections 6.3.3.9 and 6.3.3.11 discuss this dichotomy in performance between the soil contamination source categories and the stack emission source categories - the dichotomy being that while air concentrations from the stack emission demonstration and background soils appear similar, the soil concentrations are much different.

Particulate-phase concentrations at the exposure sites of Scenarios 1 and 2 were 2 to 3 orders of magnitude lower than exposure site concentrations predicted to occur from emissions at a contaminated site which is 150 meters away at the off-site location of contaminated soil, Scenario 3. This was due principally to the 3 orders of magnitude higher soil concentrations at these off-site soil contamination locations. Another trend is that the particle-phase concentrations are the same for all three compounds within Scenarios 1-3. This is because the algorithm to estimate particle-phase concentrations is independent of chemical properties. The trend discussion above concerning vapor phase concentrations resulting from volatilization and dispersion is not true for particulate phase estimation. In this case, a steady flux is estimated which is not a function of time. The same dispersion algorithm is used, however, so that the high end concentrations in Scenario 2 are higher than the central concentrations in Scenario 1.

- ***Drinking Water and Fish***:

Concentrations of the example contaminants in water were 10^{-15} to 10^{-10} mg/L (ppm; or equivalently 10^{-6} to 10^{-1} pg/L or ppq). Concentrations in fish ranged from 10^{-11} to 10^{-5} mg/kg, or in parts per trillion terms, which are common units used in expressing fish concentrations in the literature, 10^{-5} to 1 ppt. The concentrations resulting from the stack emissions were 4 to 5 orders of magnitude lower than the concentrations resulting from the soil and effluent source discharge source categories. The concentrations resulting from the effluent discharge were nearly identical to the concentrations resulting from basinwide background soil concentrations of 1 ppt, which were used to demonstrate the on-site soil source category. The fish concentrations resulting from the bounded area of high soil contamination, where 10 hectares within the watershed had soil concentrations of 1 ppb, were about an order of magnitude higher than the effluent discharge or on-site soil sources.

The PCB concentrations were 1-2 orders of magnitude higher than the dioxin and furan because the key bioaccumulation variables estimating fish tissue concentrations, the Biota Sediment Accumulation Factor, BSAF, and the Biota Suspended Solids Accumulation Factor, BSSAF (used only for the effluent discharge source category), is 2.0 for the example PCB while it is 0.09 for the example dioxin and furan.

Concentrations of 2,3,7,8-TCDD are about an order of magnitude lower than concentrations for TEQs. This mirrors the results for the air and soil, and reflects about an order of magnitude higher stack emissions of TEQs than 2,3,7,8-TCDD. Also, there is no difference between the central and high end scenarios for the stack emission source category. The exposure sites are located at different points with respect to the stack - the site for the central scenario is 5000 meters away from the stack, and the site for the high end scenario is 500 meters from the stack. This impacts all exposure media estimations except the fish and water estimates. Those two are a function of average watershed impact to the stack emissions, not impact to the site of exposure.

- ***Fruit and Vegetable Concentrations***:

Concentrations in these foods ranged from 10^{-14} to 10^{-7} mg/kg (ppm) expressed on a fresh weight basis. Concentrations in below ground vegetables are found to exceed those in above ground vegetables when the source of contamination is soil - the on-site

and off-site examples scenarios, #1 - #3. When the source of contamination is stack emissions, however, above ground concentrations exceed those of below ground. The causes for this trend follow from the trend discussions on soil and air concentrations above. First, the air concentrations for the stack emission demonstrations, 4 and 5, were comparable to the air concentrations for the background soil scenarios, 1 and 2. This in itself would lead to roughly similar above ground vegetation concentrations, and that in fact is what happened. On the other hand, the soil concentrations were 3 to 4 orders of magnitude lower for the stack emission demonstrations as compared to the background soil demonstrations. This is the reason why above ground vegetation concentrations exceeded below ground concentrations for the stack emission source category, while the reverse was true for the soil contamination source category. Trends regarding vapor phase transfers and particle depositions to vegetations are discussed more extensively in Chapter 6, Section 6.3.3.8.

As in the air and soil trends discussed above, off-site soil contamination in the range of 1 μg/kg (1 ppb; example Scenario #3) results in higher concentrations than on-site background soil concentrations of 0.001 μg/kg (1 ppt; example Scenarios #1 and #2). Another trend noted for Scenarios 1-3, where the initial soil concentrations were the same among the three compounds, is that transfers from soil to plant are driven by chemical parameters, particularly the octanol water partition coefficient, Kow. 2,3,3',4,4',5,5'-HPCB had the highest Kow, with 2,3,4,7,8-PCDF and 2,3,7,8-TCDD at lower but similar Kow. Higher Kow translates to tighter sorption to soil, and less transfer to plant, either through root uptake or air-to-leaf transfer. This trend translated to the lowest fruit/vegetable concentrations for 2,3,3',4,4',5,5'-HPCB. 2,3,7,8-TCDD and 2,3,4,7,8-PCDF had similar fruit/vegetable concentrations for Scenarios 1-3.

The results for the stack emission source category indicate once again that TEQ fruit and vegetable concentrations exceed those of 2,3,7,8-TCDD by about an order of magnitude.

- ***Beef and Milk Fat Concentrations***:

These concentrations ranged from 10^{-9} to 10^{-5} mg/kg, or equivalently, 0.001 to 10 ppt. These results were in terms of fat concentrations, which assumes that all the compound bioconcentrates in the fat of beef and milk. To convert to a whole product

basis, beef fat concentrations should be multiplied by approximately 0.18-0.22 (beef is roughly 18-22% fat) and milk fat by approximately 0.02-0.04 (2-4% fat). Milk fat concentrations were lower than beef fat concentrations in all cases, but within a factor of two. This was due to assumptions concerning apportioning of total dry matter intake between contaminated soil, contaminated pasture grass, and home-grown contaminated feeds. Beef cattle were assumed to take in twice as much soil as lactating cattle, 4% of their dry matter intake versus 2%, and much more leafy vegetations than lactating cattle, 48% pasture grass versus 8% pasture grass. Another observation that can be made is similar to the observation concerning the key bioaccumulation parameters for fish, the BSAF and the BSSAF. In those cases, it was noted that the factors for the PCB example compound was much higher than those of either the dioxin or the furan - hence higher fish concentrations result. In this case, however, the PCB example compound had the lowest beef/milk biotransfer factor, BCF. The BCFs for the dioxin and furan example compound were both 4.3 and 3.1 respectively, while the PCB BCF was 2.3. This resulted in uniformly lower PCB beef and milk concentrations. Another noteworthy trend concerns the comparison of off-site soil impacts (4 hectares at 1 ppb) to on-site soil impacts (a basin-wide 1 ppt), with regard to fish and beef/milk. Specifically, there is only an order of magnitude difference between fish concentrations in the on-site scenarios (1 & 2) versus the off-site contamination scenario (3). Said another way, a basin-wide concentration of 1 ppt has nearly the same impact to fish as a small land area of 1 ppb. However, the same is not true for beef/milk. The 1 ppt basin-wide soil concentration resulted in beef/milk concentration 2 orders of magnitude lower than the 1 ppb small area of contamination impact to beef/milk. An examination of model performance explains this pattern. The pertinent trend is discussed further in Chapter 7, Sections 7.2.3.1, 7.2.3.2, and 7.2.4.1, but briefly has to do with dilution of soil concentrations associated with transport modeling. The ratio of surface water sediment concentration to on-site soil concentration is termed the "sediment dilution ratio", and the ratio of exposure site soil concentration to contaminated site soil concentration is called the "soil dilution ratio". The sediment dilution ratios for example Scenarios 1 and 2 demonstrating basin-wide low concentrations was 2.8, meaning that surface water sediments were in fact enriched compared to basin-wide soil concentrations; the 1 ppt basin-wide soil concentrations translated to bottom sediment concentrations of 2.8 ppt. For Scenario #3, demonstrating the impact of a

smaller area of high soil concentration, the sediment dilution ratio was 0.016, meaning that the 1 ppb soil concentration resulted in a bottom sediment concentration of 16 ppt. Note the one order of magnitude difference in bottom sediments between Scenarios 1 & 2 (2.8 ppt) and 3 (16 ppt); this explains the one order of magnitude difference in fish concentration results. However, the soil dilution ratio of Scenario 3 was 0.279, meaning that the 1 ppb contaminated site concentration translated to 0.279 ppb concentrations to which cattle are exposed. This compares to the 0.001 concentration to which cattle were exposed in Scenarios 1 and 2. Note that the orders of magnitude difference here explains the differences in estimated beef and milk concentrations between Scenarios 1 & 2 and 3.

For the stack emission high end scenario, TEQ concentrations continue to be higher than 2,3,7,8-TCDD concentrations by about an order of magnitude.

5.6.2. Observations Concerning LADD Exposure Estimates

Much of the differences between exposure pathways and scenarios is due to differences in exposure media estimation. Therefore, much of the above discussion is also appropriate for trend analysis of Lifetime Average Daily Dose, LADD, estimates. What will be noted below are unique observations. Unless otherwise noted, these observations pertain to 2,3,7,8-TCDD:

- ***General***:

LADDs over all example compounds ranged from 10^{-19} mg/kg-day to 10^{-8} mg/kg-day. The highest exposures were associated with the off-site soil contamination scenario, Scenarios #3. As discussed above, these scenarios had the highest exposure media concentrations for all exposure media. LADDs for Scenario 3 ranged from 10^{-14} to 10^{-9} mg/kg-day. Fish and water ingestion exposures were very similar for Scenarios #1 (background soil concentrations, central exposures), #2 (background soil concentrations, high end exposures), and #6 (effluent discharges, central exposures). Fish ingestion LADDs for these three scenarios were in the 10^{-10} to 10^{-12} mg/kg-day range. Water ingestion LADDs ranged from 10^{-15} to 10^{-13} mg/kg-day. However, fish and water ingestion exposures were roughly 3 orders of magnitude lower for the stack emission scenarios, #4 and #5, as compared to these three. Fish and water ingestion LADDs, on

the other hand, were about 5 times higher for the off-site scenario, #3, as compared to Scenarios 1, 2, and 6. Inhalation exposures were similar for the stack emission scenarios (#4 and #5) and the on-site soil scenarios (#1 and #2), in the 10^{-15} mg/kg-day range. LADDs for the soil related exposures - soil ingestion and soil dermal contact - were 3 to 4 orders of magnitude higher for the on-site soil scenarios as compared to the stack emission scenarios. Soil ingestion for the on-site soil scenarios, #1 and #2, ranged from 10^{-13} to 10^{-12} mg/kg-day, and for soil dermal contact the impact was lower with LADDs ranging from 10^{-14} to 10^{-13} mg/kg-day. Like other trends, the soil ingestion and soil dermal contact impacts from a nearby site of high soil concentrations, Scenario 3, were the highest at $9*10^{-10}$ mg/kg-day for soil ingestion and $7*10^{-11}$ mg/kg-day for soil dermal contact. The stack emission scenario had lower exposures associated with beef and milk ingestion as compared to the on-site scenarios, over an order of magnitude lower. The range for Scenarios #2 and #5 was 10^{-14} to 10^{-10} mg/kg-day. The beef and milk ingestion pathways for the off-site scenario, #3, were generally the highest of all example pathways at 10^{-10} and 10^{-9} mg/kg-day. For the stack emission scenarios which evaluated 2,3,7,8-TCDD and TEQ exposures, 2,3,7,8-TCDD exposures were about 5% of what TEQ exposures were. This follows from the trends in exposure media concentration estimation as discussed above.

- ***"Central" versus "High End"***:

Differences between analogous "central" and "high end" exposures for the on-site soil source demonstration scenarios were near or less than an order of magnitude (inhalation exposure for the central on-site scenario and the inhalation exposure for high end on-site scenario are analogous exposures). This is because the exposure parameters used to distinguish typical and high end exposures, the contact rates, contact fractions, and exposure durations, themselves did not differ significantly, and these were the only distinguishing features for the on-site soil source category. In the stack emission scenario, placing exposed individuals either 500 or 5000 meters away from the incinerator did significantly impact the results. In this case, the difference was closer to 2 orders of magnitude for all exposures except water and fish exposures, which were not a function of distance from the stack. The order of magnitude difference in distance added about an order of magnitude difference in exposure media concentrations and hence LADD

estimates. The high end scenarios were modeled after a rural farm and did have exposures from home grown beef and milk food products. The central scenarios were modeled after a non-farming rural residence, and did not have beef and milk exposure pathways. Since beef and milk exposure pathways were noted as the highest exposures, along with ingestion of fish (see next bullet), it would be appropriate to conclude that farming families ingesting a portion of their home produced beef and milk are more exposed than non-farming families without these exposures.

- ***Exposure pathway analyses***:

It is inappropriate to compare and rank exposure pathways across all scenarios because the source terms are different. However, relationships between different pathways within each scenario can be discussed. Table 5-6 was constructed by summing the LADDs for all pathways, and then determining the percent contribution by each pathway. Before the summation, LADDs were corrected to account for absorption - all ingestion LADDs assumed 50% absorption and inhalation LADDs assumed 75% (data on bioavailability from animal feeding studies, suggests that the absorption of 2,3,7,8-TCDD is around 50%; 75% for inhalation reflects a general assumption of greater absorption for this pathways; both simple assumptions made only for the purpose of this comparative exercise). The dermal contact LADD was the only one where absorption was already considered in its estimation: absorbed dose was estimated as 3% of dose contacting the body. Also, this exercise assumes all pathways occur simultaneously, and so on. Table 5-6 was generated only for the 2,3,7,8-TCDD example compound, and the rows are listed generally from the highest to lowest percentage contribution. The following observations are made from that table:

- In high end scenarios which assumed exposure to home grown beef, milk, and fish, Scenarios 2, 3, and 5, exposures to these three foods dominated the results. In Scenarios where beef and milk were not considered, but fish was considered, Scenarios 1, 4, and 6, fish exposures dominated. The general dominance of beef, fish, and milk exposures underscores the importance of food chain exposures.

- Milk exposures were lower than beef exposures because of less milk fat ingestion (10.5 g/day milk fat vs. 22 g/day beef fat) and lower concentrations in milk as compared to beef (this was discussed above).

Table 5-6. Percent contribution of the different exposure pathways within each exposure scenario.*

Exposure Pathway	Scenario # 1	2	3	4	5	6
Meat Ingestion	NA	26	50	NA	72	NA
Fish Ingestion	56	44	2	27	1	95
Soil Ingestion	36	15	32	23	3	NA
Milk Ingestion	NA	6	11	NA	23	NA
Soil Dermal	4	8	4	0	0	NA
Vegetable Ingestion	1	0	0	5	0	NA
Fruit Ingestion	0	0	0	5	0	NA
Water Ingestion	3	1	0	1	0	5
Vapor Inhalation	0	0	0	39	1	NA
Particle Inhalation	0	0	0	NA	NA	NA

* Assumes exposed individual experiences all relevant pathways and exposures are additive; see text for further explanation.

- Fish was the principal impacted media for the effluent discharge source category, with fish ingestion 19 times higher than water ingestion, the only two pathways considered for the effluent discharge category. Fish was an important route of exposure in Scenarios #1 and #2 evaluating basin-wide low soil concentrations. It explains over half of all exposures when beef and milk are not considered and still dominate when they are. It is also important for the stack emission central scenario, #4. However, fish is much less important than beef or milk for the high end stack emission scenario which had a beef and a milk pathway, and when a small site of contamination is near a site of exposure (which would be a farm raising a portion of the farming families beef and milk ingestions). The dilution effect of a small site in a basin with regard to surface water impacts as compared to a much less dilution effect of a small site near an exposure site was discussed in Section 5.6.1 above, under the beef and milk bullet.

- Soil ingestion exposures were also noteworthy, particularly in scenarios that did not consider beef and milk, the central on-site scenario, #1, and the central stack emission scenario, #4. Soil ingestion was also the second highest pathway in the scenario evaluating the impact of nearby soil contamination, #3, ranking higher than milk or fish ingestion. Dermal exposures were non-trivial, but ranked behind the four ingestion

pathways previously discussed, beef, milk, fish, and soil.

- Inhalation was the highest impact for the stack emission scenario when farm animal products were not considered, in Scenario #4. Fruit and vegetable exposures were noteworthy only in this same scenario. These trends imply that, where farm animal products are not being produced near a stack emission source, fish and vegetative food products still may dominate the overall exposure, but inhalation exposure can become critical.
- Water ingestion exposures were very low in comparison to the other exposures in these scenarios.

The LADD estimates of all example scenarios were derived assuming a limited duration of exposure to the dioxin-like compounds, and also limited contact with exposure media. A pattern of childhood soil ingestion was assumed to occur over a five-year period. The central scenarios assumed a nine-year duration of exposure to the contamination, and the high end scenarios assumed a twenty-year exposure period. The contact with impacted media was only assumed to occur in the home environment - only a portion of an individual's meat, milk, water, and fruit and vegetable ingestion was evaluated. This is only one approach to scenario development; other approaches might consider the quality of exposure media not associated with the home environment. For example, if the bulk of an individual's ingestion of produce comes from local farms, and local farms may be impacted by an incinerator, then perhaps 90-100% of an individual's fruit and vegetable ingestion, rather than the 20-40% assumed in this assessment, should be considered impacted.

Another issue to consider while interpreting these scenarios is their relation to background exposures. Dioxin-like compounds are commonly found throughout the environment, leading to "background" exposures even in situations where known sources are not present. Since these scenarios are developed around defined sources, they should be interpreted as incremental exposures beyond "background" levels. This interpretation is clearly less satisfying for Scenarios 1 and 2 where soils within a watershed are assumed to be contaminated at 1 ng/kg (ppt) level which, as discussed earlier in Section 5.5, may be close to a background level. In this sense, Scenarios 1 and 2 are more representative of background exposures than incremental exposures. However, diet fractions were applied indicating that only a portion of the food supply was contaminated.

Also, the exposure duration was defined as less than a lifetime. For purposes of a true background exposure analysis, it might be more appropriate to assume 100% for diet fractions and lifetime exposures for example Scenarios 1 and 2.

An exercise was undertaken making the following changes in example Scenarios 1 and 2: 70 years exposure duration was assumed for all pathways except the childhood pattern of soil ingestion (which remained at 5 years), and all contact fractions were set equal to 1.00. All contact rates were unchanged for this exercise. The one contact rate which might be changed is the rate of fish ingestion. For that pathway, the 1.2 (central) and 4.1 (high end) g/day rates were estimated assuming a number of meals and meal sizes that a rural individual would recreationally obtain from a nearby impacted water body. For background impacts, it may be more appropriate to have an average ingestion rate, and assume that the 0.6 pg/g fish concentration estimated for example Scenarios #1 and #2 is typical of all fish ingested. That was not done for the results of this exercise that are displayed in Table 5-7, but was done separately and will be discussed in the last bullet below. Table 5-7 includes LADDs and the percent contribution from each pathway for the original and the amended example Scenarios #1 and #2, and only for 2,3,7,8-TCDD. Observations from this exercise are:

- All exposures increased except soil ingestion. Mostly the increase in LADD were within an order of magnitude. The LADDs are still about an order of magnitude lower than limited exposures estimated to occur from living near an area of high soil contamination, as can be seen from comparing these lifetime results with those in Table 5-5 for example Scenario #3 (off-site source category).

- The increases to vapor phase inhalation exposures were small relative to other increases. This occurs because average volatilization flux decreases as a function of time - average fluxes over long periods of time are lower than average fluxes over short periods of time (see Section 4.3.2, Chapter 4, for further explanation). This has a rippling effect on fruit and vegetable concentrations as well as beef and milk concentrations. A trend of decreasing volatilization flux is realistic when highly contaminated soils become depleted over time. This was a key principal of the volatilization flux algorithm. However, this may not be a realistic trend for ubiquitous concentrations which are likely to be replenished in soil over time. Sensitivity analysis in Chapter 6, Section 6.3.3.1 shows that increasing exposure duration from 20 to 70 years decreases average flux by a factor of 2. By

Table 5-7. Exposures to low soil concentrations of 2,3,7,8-TCDD assuming lifetime exposure durations and unlimited contact with impacted media, compared with exposures assuming limited durations and limited contact.

Pathway	Limited Exposures LADD, mg/kg-day	Percent	Lifetime Exposures LADD, mg/kg-day	Percent
Example Scenario #1 On-site soil contamination Concentration = 1 ng/kg (ppt) Central exposure scenario				
Soil ingestion	$8*10^{-13}$	36	$8*10^{-13}$	7
Soil dermal contact	$4*10^{-14}$	4	$3*10^{-13}$	5
Inhalation-vapor	$1*10^{-15}$	0	$4*10^{-15}$	0
Inhalation-particle	$2*10^{-17}$	0	$2*10^{-16}$	0
Water ingestion	$7*10^{-14}$	3	$7*10^{-13}$	5
Fish ingestion	$1*10^{-12}$	56	$1*10^{-11}$	78
Fruit ingestion	$2*10^{-16}$	0	$3*10^{-15}$	0
Vegetable ingestion	$2*10^{-14}$	1	$6*10^{-13}$	5
Example Scenario #2 On-site soil contamination Concentration = 1 ng/kg High end exposure scenario				
Soil ingestion	$3*10^{-12}$	15	$3*10^{-12}$	3
Soil dermal contact	$9*10^{-13}$	8	$3*10^{-12}$	6
Inhalation-vapor	$3*10^{-15}$	0	$6*10^{-15}$	0
Inhalation-particle	$3*10^{-16}$	0	$1*10^{-15}$	0
Water ingestion	$3*10^{-13}$	1	$1*10^{-12}$	1
Fish ingestion	$1*10^{-11}$	44	$3*10^{-11}$	35
Fruit ingestion	$1*10^{-15}$	0	$1*10^{-14}$	0
Vegetable ingestion	$7*10^{-14}$	0	$6*10^{-13}$	0
Beef ingestion	$6*10^{-11}$	26	$4*10^{-11}$	44
Milk ingestion	$1*10^{-12}$	6	$1*10^{-11}$	11

implication, vapor inhalation, fruit and vegetable ingestion, and beef and milk ingestion, are all underestimated for a lifetime of exposure for example Scenario #2, by around the same factor of 2. On the other hand, the discussion on sources in Volume II, Chapter 3, does indicate that sources of release have been reduced over time. If so, an assumption of ongoing replenishment to similar levels may not be warranted.

- The relative impact of soil ingestion dropped when assuming lifetime exposures. It is interesting that direct soil impacts, a childhood pattern of soil ingestion and a lifetime of soil dermal contact, still are noteworthy impacts, particularly when not considering beef or milk exposures.

- Fish ingestion exposures were the predominant exposures when beef and milk were not considered and became even more so for a lifetime of exposure in Scenario #1. The same was not true for Scenario #2, where fish dropped in prominence when going from a limited to a lifetime of exposures. The main reason for this trend was that only the increase in exposure duration came into play for Scenario #2 and fish exposures - the rate of fish ingestion was not changed for this exercise. However, both the exposure duration and beef and milk ingestion rates increased for the lifetime exercise for Scenario #2.

- Different ingestion rates of fish were evaluated for example Scenario #2 and a lifetime of exposure (2nd column on Table 5-7). The rate of 4.1 g/day used for the results in Table 5-7 was increased to 6.5, 30, and 140 g/day. The 6.5 g/day was used in the Ambient Water Quality Criteria document for 2,3,7,8-TCDD, and was described as an average daily per capita consumption of freshwater and estuarine fish and shellfish (EPA, 1984). The 30 and 140 g/day were recommended as 50th and 90th ingestion rates in EPA (1989) for recreational fisherman in an area where there is a large water body present and widespread contamination is evident, and where site-specific information is unavailable. Increasing to 6.5, 30, and 140 g/day increased the percent of impact for Scenario #2, 70-year impacts, to 46, 79, and 95%, respectively. This does indicate that, even when beef and milk are considered in a lifetime assessment in background settings, ingestion of fish in such settings can be equally if not more critical.

An evaluation of total human exposure, and the relative impact of different exposure pathways for 2,3,7,8-TCDD, was also undertaken by Travis and Hattemer-Frey (1991). Their approach was based on modeling, using their Fugacity Food Chain model. This model requires as input emission rates into air, soil, and water; these emission rates

are then transformed into concentrations. Those concentrations are used to estimate food crop concentrations, beef, milk, and fish concentrations. In the application of this model by Travis and Hattemer-Frey (1991), emission rates were calibrated to arrive at air, soil, and water concentrations that were supported by the literature. Resulting concentrations in these three media were: 0.02 pg/m^3 in air partitioned as 0.016 pg/m^3 in particulate form and 0.004 pg/m^3 in vapor form, 0.96 pg/g in soil, and 0.003 pg/L in water. Using the model to estimate exposure media concentrations, they then assumed contact rates as given by Yang and Nelson (1986) to estimate human exposure. Assuming 100% absorption, they concluded that typical human exposure is on the order of 35 pg/day 2,3,7,8-TCDD.

Their analysis will be compared to the analysis of this methodology. The example scenario most like their's was example Scenario #2, which estimated exposures to soil levels of 1.0 pg/g. The assumption used in the above sensitivity exercise of 100% contact fractions rather than partial contact is also the appropriate assumption for comparison. A key difference to keep in mind is that air and water impacts are estimated given soil concentrations in this methodology, whereas air and water impacts are specified with their model. This comparison is given in Table 5-8 below.

While the exposure of 6.3 pg/day estimated in Scenario 2 (assuming 100% contact fractions) is within an order of magnitude of the 34.3 pg/day estimated by Travis and Hattemer-Frey, there are a few critical differences in the two approaches. One was in the contact rates. However, replacing the contact rates used by Travis and Hattemer-Frey with the contact rates used in this methodology would not particularly change the total exposure estimate - it would increase to 11.3 pg/day using the concentrations estimated in this methodology. The second and more important difference is that air concentrations are derived from soil concentrations in this methodology whereas they are input for the Fugacity Food Chain model. Air concentrations are used for inhalation exposures, to estimate fruit and vegetable concentrations, but most importantly, beef and milk concentrations in a food chain model. The air concentrations used by Travis and Hattemer-Frey, 0.02 pg/m^3, is nearly three orders of magnitude higher than predicted by the volatilization/dispersion modeling used in this methodology. Section 7.2.3.9 of Chapter 7 examines air concentrations found in urban and rural environments. It is noted that the compilation of air monitoring data conducted in Volume II of this assessment

Table 5-8. Comparison of exposure pathway contributions to total daily exposure as estimated in example Scenario #2 and in Travis and Hattemer-Frey (1991).

Quantity	Travis & Hattemer-Frey (1991)	Scenario #2[1]
Inhalation		
concentration, pg/m^3	0.02	0.000027
contact rate, m^3/day	20	20
intake, pg/day	0.40	0.0005
Water Ingestion		
concentration, pg/L	0.003	0.035
contact rate, L/day	1.4	2.0
intake, pg/day	0.004	0.07
Soil Ingestion		
concentration, pg/g	0.96	1.0
contact rate, g/day	0.02	0.06
intake, pg/day	0.02	0.06
Fruit and Vegetables		
concentration, pg/g	0.06	0.001 & 0.00001[2]
contact rate, g/day	20	192
intake, pg/day	1.2	0.032
Milk		
concentration, pg/g	0.03	0.0025
contact rate, g/day	267	300
intake, pg/day	8.0	0.75
Beef		
concentration, pg/g	0.2	0.03
contact rate, g/day	90	100
intake, pg/day	18.2	3.0
Fish		
concentration, pg/g	0.38	0.59
contact rate, g/day	17.6	4.1
intake, pg/day	6.7	2.42
TOTAL INTAKE, pg/day	34.3	6.3

[1] Quantities in this column were transformed from what is otherwise displayed in this document to be analogous to the quantities given in Travis and Hattemer-Frey (1991). Specifically, the following was done: 1) all contact rates are the ones that have been used in this document - however, all contact fractions are set at 1.00; 2) rate of child soil ingestion for this scenario, 0.8 g/day, was normalized over a lifetime to obtain 0.06 g/day ingestion, and 3) beef and milk ingestion were expressed in total ingestion rather than in fat ingestion; also beef and milk concentrations were expressed in whole product rather than in terms of fat.

[2] below and above ground vegetative concentrations, respectively, displayed; also, 192 g/day is the total above+below ground consumption of fruits and vegetables; intake estimation breaks out above/below and fruit/vegetable. Finally, Travis and Hattemer-Frey listed their concentration on a dry matter basis, while the above for Scenario #2 is fresh weight.

indicated an average 2,3,7,8-TCDD concentration in urban air of 0.01 pg/m^3, half as much as the 0.02 pg/m^3 used by Travis and Hattemer-Frey. These authors do note that their air concentration originates from monitoring of urban air in Germany. Section 7.2.3.7, Chapter 7, discusses the fact that had the models of this methodology predicted urban air concentrations given low soil concentrations perhaps typical of rural environments, the model should be questioned. On the other hand, the comparison of limited rural air concentrations and the air concentrations predicted by a background soil concentration of 1 ppt is not favorable. In one literature article measuring concentrations in an area described as a "remote countryside" in Sweden (Broman, et al. 1991), air concentrations of 2,3,7,8-TCDD were measured at 0.0002 pg/m^3. This remote countryside air concentration is hypothesized to be lower than what is likely to occur in rural environments where at least some sources of dioxin release relatively nearby are expected to occur. The air concentration of 2,3,7,8-TCDD modeled in this assessment from background soil concentrations of 1 ppt is nearly an order of magnitude lower than that at 0.000032 pg/m^3. This suggests that the models of this assessment underestimate air concentrations resulting from releases from soils - however, this is not a definitive conclusion. As discussed in Volume II, the principal source of dioxin release into the environment which affects the food chain and associated soils are emissions from combustion sources. These sources provide a steady and ongoing input into the soil and food chains. The true test of the soil release and dispersion algorithms of this assessment would be to measure air concentrations of dioxin-like compounds released from soil into residue-free air, and compare that with modeled concentrations. Such data could not be found in the literature. Most importantly, the fact that air concentrations estimated to result from background soil concentrations are much lower than air concentrations surmised to occur in a rural environment does suggest that the on-site soil source category is an inadequate framework to be estimating background exposures.

The air concentration of 2,3,7,8-TCDD of 0.02 pg/m^3 was run through the food chain algorithms of this assessment using the procedures outlined in Chapter 7, Section 7.2.3.9 of this volume, the air-to-beef food chain validation exercise. It was found that the model predicted a whole beef concentration of 0.32 ppt (19% beef fat) and a whole milk concentration of 0.10 ppt (4% milk fat), which is actually fairly similar to the 0.20 ppt whole beef and 0.03 ppt dairy concentrations as predicted by Travis and Hattemer-

Frey. However, this is more by chance than deliberate, as there are substantial differences in the specifics of the modeling approach and parameter values of this assessment and that of Travis and Hattemer-Frey. Following is a summary of such differences in modeling and 2,3,7,8-TCDD parameterization:

1) Travis and Hattemer-Frey assumed a vapor/particle split of 20%/80%, whereas the models of this assessment assumed a 55%/45%. The air-to-leaf transfer factor, defined identically for both modeling efforts, nonetheless came up with a different value. The B_{vpa} of this assessment was 100,000, whereas for Travis and Hattemer-Frey, the B_{vpa} was 9883. The reason for this difference was that they assumed different values for 2,3,7,8-TCDD log octanol water partition coefficient, Kow, 6.85 versus the 6.64 of this assessment, and Henry's Constant, H, $3.6*10^{-3}$ atm-m^3/mole versus the $1.65*10^{-5}$ atm-m^3/mole of this assessment.

2) They used a "biotransfer" factor for estimating whole beef concentrations as a function of mass ingestion of 2,3,7,8-TCDD, whereas this model used a "bioconcentration" algorithm which only depends on the concentration in the dietary intake and predicts the concentration in beef fat.

3) The key factors in the Travis and Hattemer-Frey approach are the mass ingestion rates of dry matter in the diets of beef and dairy cattle, whereas the important factors for this approach are the proportions in the dry matter categories. Travis and Hattemer-Frey made different assumptions regarding proportions in vegetative and soil as compared to this assessment. For the beef cattle, they assumed that 35% of their ingestion was in unprotected forages, while 64% was in protected grains and 1% in soil. This assessment assumed equal proportions in pasture grass - the analogy to unprotected forage - and 48% in partially protected vegetations (hay, silage, grains), and 4% in soils. This assessment also assumed a 50% reduction in beef concentrations due to feedlot fattening. While not explicitly stating it, Travis and Hattemer-Frey also appeared to be modeling the feedlot fattening diet, as the majority of beef cattle diet was in protected grains, and their article did describe the diet as representing, "beef cattle destined for slaughter".

Although both modeling approaches appear to perform quite similarly, this simple comparison shows how important the assignment of parameters can become in estimating exposures. If any of the assumptions and/or parameters used by Travis and Hattemer-

Frey used were instead used for this assessment (and vica versa), results would be substantially different. Chapter 7 on Uncertainty critically evaluates the modeling approaches and parameters used in this assessment. Chapter 6 contains additional information pertaining to these models, including sensitivity analysis exercises, discussions of model parameters, and discussions on other modeling approaches. Information in both these Chapters should be reviewed when evaluating the validity of the approaches demonstrated in this Chapter.

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6. USER CONSIDERATIONS

6.1. INTRODUCTION

The methodology in this document has been earlier described as screening level in terms of theoretical sophistication, but site specific in its application. Chapter 2 described concepts of exposure and assigned values to exposure parameters which define, for purposes of demonstration, a central and a high end exposure pattern. Chapters 3 and 4 described algorithms for the fate, transport, and transfer of dioxin-like compounds, and also assigned parameter values for purposes of demonstration. The methodology was demonstrated in Chapter 5, using exposure and fate and transport parameters which had been laid out in earlier chapters. Those who wish to use the methodology for further analysis of incremental exposures to sources of dioxin-like compounds are now in a position to use the same algorithms, perhaps many of the same parameter values. The purpose of this chapter is to provide guidance on some key issues for potential users.

Section 6.2 discusses the use of the parameter values selected for the demonstration scenarios in Chapter 5 for other applications. Section 6.3 is a sensitivity analysis exercise on the parameters required for algorithms estimating exposure media concentrations. Section 6.4 addresses the issue of mass balance with regard to the source strength terms of the four source categories.

6.2. CATEGORIZATION OF METHODOLOGY PARAMETERS

Table 6-1 lists all the parameters, including names, definitions, and units, that are required for the methodologies of this assessment except the exposure parameters. Exposure parameters are given in Table 2-1 of Chapter 2. Table 6-1 also gives four additional pieces of information for each parameter listed. Three are numerical values which were used in the sensitivity analysis exercises that are described in Section 6.3. below. The parameter values labeled "selected" were the ones used in the demonstration of the methodologies in Chapter 5. Section 6.3. below justifies the high and low values of parameters selected for sensitivity analysis. Other users of this methodology may wish to view these high and low values as reasonable high and low possible values for their applications; note however that the chemical specific parameters are those only for 2,3,7,8-TCDD. The fourth piece of information is a qualitative judgement on the part of

Table 6-1. Parameters used to estimate exposure media concentrations for this assessment.

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
1. Contaminated and Exposure Site Characteristics					
A. Site of Exposure					
AES	area of exposure site, m^2	4,000	40,000	400,000	SS
E_{slp}	soil porosity, unitless	0.35	0.50	0.60	SS
P_{soil}	particle bulk density, g/cm^3	2.55	2.65	2.75	FOD
B_{soil}	soil bulk density, g/cm^3	1.20	1.50	2.00	SS
OC_{sl}	soil organic carbon fraction	0.005	0.01	0.05	SS
d_t	tillage mixing depth, m	0.10	0.20	0.30	SOD
d_{not}	no-till mixing depth, soil source categories, m	0.01	0.05	0.10	SOD
B. Site of Contamination, Off-site Soil Source Category					
ASC	area of off-site contamination, m^2	4,000	40,000	400,000	SS
E_{slp}	soil porosity, unitless	0.35	0.50	0.60	SS
P_{soil}	particle bulk den, g/cm^3	2.55	2.65	2.75	FOD
OC_{sl}	soil organic carbon fraction	0.005	0.01	0.05	SS
2. Soil and Sediment Delivery Parameters					
SL_s	contaminated site soil loss, kg/ha-yr	2100	21520	42000	SS
SL_{ec}	soil loss between exp. and cont. site, kg/ha-yr	0	2152	21000	SS

(cont'd on next page)

Table 6-1. (cont'd)

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
2. Soil and Sediment Delivery Parameters (cont'd)					
SL_w	watershed soil loss, kg/ha-yr	2100	6455	21500	SS
ER	enrichment ratio, unitless	1	3	5	SOD
C_w	watershed contaminant conc, mg/kg	0	0	$1x10^{-6}$	SS
OC_{ssed}	suspended sediment organic carbon fraction	0.02	0.05	0.10	SS
OC_{sed}	bottom sediment organic carbon fraction	0.01	0.03	0.05	SS
A_w	watershed drainage area, ha	400	4,000	400,000	SS
SD_w	watershed sediment delivery ratio, unitless	0.25	0.15	0.04	SS
TSS	total suspended sediment, mg/L	2	10	70	SS
DL_e	distance to exposure site, m	50	150	1000	SS
DL_w	distance to water body, m	50	150	1000	SS
V_{wat}:	volume of water body, L/yr	$1.5x10^9$	$1.5x10^{10}$	$1.5x10^{12}$	SS
3. Volatilization and Dust Suspension Parameters					
ED	exposure duration, yrs	1	20	70	SS
V	fraction of vegetative cover, onsite, unitless	0.0	0.5	0.9	SS
V	fraction of vegetative cover, offsite, unitless	0.0	0.0	0.9	SS
U_m	average windspeed, m/sec	2.8	4.0	6.3	SS
U_t	threshold wind speed, onsite, m/sec	2.5	6.5	11.3	SS

(cont'd on next page)

Table 6-1. (cont'd)

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
3. Volatilization and Dust Suspension Parameters (cont'd)					
F(x)	model-specific parameter, onsite	0.87	1.05	0.05	SS
U_t	threshold wind speed, offsite, m/sec	2.5	8.25	11.3	SS
F(x)	model-specific parameter, offsite	0.87	0.50	0.05	SS
FREQ	frequency wind blows to site, unitless	0.05	0.15	0.50	SS
4. Bioconcentration and Biotransfer Parameters					
- FISH:					
f_{lipid}	fish lipid fraction	0.03	0.07	0.20	SS
- VEGETATION					
FDW	dry to fresh weight conversion	0.05	0.15	0.30	SS
V_p	particle deposition vel, m/yr	1.5×10^5	3.2×10^5	7.0×10^5	SOD
R	annual rainfall, m/yr	0.3	1.0	2.0	SS
W_p	washout factor, unitless	2×10^3	5×10^4	1×10^6	SOD
R_w	retention of wet deposition, unitless	0.00	0.30	1.00	SOD
Y_{gr}	yield of grass, kg/m^2 dry	0.05	0.15	0.35	SS
INT_{gr}	grass intercept fraction, unitless	0.13	0.35	0.64	SS
Y_{feed}	cattle feed yield, kg/m^2 dry	0.25	0.63	1.30	SS

(cont'd on next page)

Table 6-1. (cont'd)

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
4. Bioconcentration and Biotransfer Parameters (cont'd)					
INT_{feed}	feed intercept fraction	0.20	0.62	0.93	SS
Y_{veg}	vegetable yield, kg/m^2 fresh	2.7	7.8	8.6	SS
INT_{veg}	vegetable intercept fraction, unitless	0.18	0.48	0.72	SS
VG_{bg}	below ground veg. correction factor, unitless	0.001	0.01	0.10	SOD
VG_{veg}	veg/fruit air-to-leaf correction factor, unitless	0.001	0.01	0.10	SOD
VG_{gr}	grass air-to-leaf correction factor, unitless	0.50	1.00	1.00	SOD
VG_{feed}	feed air-to-leaf correction factor, unitless	0.25	0.50	0.75	SOD
- BEEF & MILK					
BCSDF	beef cattle soil diet fraction, unitless	0.01	0.04	0.15	SOD,SS[3]
DCSDF	dairy cattle soil diet fraction, unitless	----	0.02	----	SOD,SS[3]
BCFDF	beef cattle feed diet fraction, unitless	0.02	0.48	0.90	SS
DCFDF	dairy cattle feed diet fraction, unitless	----	0.90	----	SS
BCGDF	beef cattle grass diet fraction, unitless	0.02	0.48	0.90	SS
DCGDF	dairy cattle grass diet fraction, unitless	----	0.08	----	SS
BCGRA	beef cattle fraction of cont. grazing land	0.25	1.00	1.00	FOD,SS[4]
DCGRA	dairy cattle fraction of cont. grazing land	----	1.00	----	FOD,SS[4]
BCFOD	beef cattle fraction of cont. feed	0.25	1.00	1.00	FOD,SS[4]
DCFOD	dairy cattle fraction of cont. feed	----	1.00	----	FOD,SS[4]
B_s	bioavailability of cont. on soil relative to vegetation	0.30	0.65	0.90	SOD

(cont'd on next page)

Table 6-1. (cont'd)

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
5. Effluent Discharge Source Category					
LD	loading to surface water body, mg/hr	0.00315	0.0315	0.315	SS
Q_e	effluent flow rate, L/hr	10^5	$4.1x10^6$	10^7	SS
Q_u	upstream receiving water flow, L/hr	10^7	$4.7x10^8$	10^9	SS
OC_e	effluent organic carbon content, unitless	0.15	0.36	0.50	SS
OC_u	upstream organic carbon content, unitless	0.02	0.05	0.10	SS
TSS_e	effluent total suspended solids, mg/L	10	70	250	SS
TSS_u	upstream total suspended solids, mg/L	2	9.5	50	SS
6. Stack Emission Source Category					
$RDEP_e$	wet+dry deposition onto exposure site, $\mu g/m^2$-yr	$2.2*10^{-6}$	$1.2*10^{-6}$	$1.5*10^{-7}$	SS
$RDEP_{wat}$	wet+dry deposition onto watershed, $\mu g/m^2$-yr	$2.2*10^{-6}$	$1.2*10^{-6}$	$1.5*10^{-7}$	SS
$RDEP_{sw}$	wet+dry deposition onto water body, $\mu g/m^2$-yr	$2.2*10^{-6}$	$1.2*10^{-6}$	$1.5*10^{-7}$	SS
C_{va}	vapor phase air concentration at exp. site, $\mu g/m^3$	$4.7*10^{-13}$	$7.6*10^{-12}$	$2.6*10^{-12}$	SS
$RDEP_p$	deposition of particles onto water body, g/m^2-yr	0.003	0.03	3.00	SS
d_{not}	no-till mixing depth, stack emission source, m	0.01	0.01	0.05	SOD
d_{wmx}	average mixing depth of deposition over watershed, m	0.01	0.10	0.20	SOD
f_{sd}	fraction of particles depositing onto water which remain in suspension	0.00	1.00	1.00	FOD

(cont'd on following page)

Table 6-1. (cont'd)

Parameter Name	Definition	Low	Selected[1]	High	Rating[2]
7. Contaminant Physical, Chemical, and Bioconcentration/Biotransfer Parameters					
H	Henry's Constant, atm-m^3/$mole^{-5}$	$1.65x10^{-6}$	$1.65x10^{-5}$	$1.65x10^{-4}$	FOD
D_a	molecular diffusivity in air, cm^2/s	0.005	0.047	0.10	FOD
Koc	organic carbon partition coefficient, L/kg	$2.7x10^5$	$2.69x10^6$	$2.7x10^7$	FOD
ϕ	fraction of airborne reservoir sorbed, unitless	0.80	0.45	0.20	FOD
B_{vpa}	air-to-leaf transfer factor, unitless	$1.0x10^4$	$1.00x10^5$	$1.00x10^6$	SOD
BCF	beef/milk bioconcentration factor, unitless	1.00	4.32	10.00	SOD
BSAF	biota sediment accumulation factor, unitless	0.03	0.09	0.30	SOD
BSSAF	biota suspended solids acc. factor, unitless	0.03	0.09	0.30	SOD
k	dissipation rate for eroding/depositing cont., yr^{-1}	0.00693	0.0693	0.693	SOD
kw	plant weathering rate constant, yr^{-1}	51	18	8.4	FOD
RCF	root bioconcentration factor, unitless	1,600	3,916	106,000	SOD

[1] "Selected" values are those used in the demonstrations scenarios in Chapter 5, and high and low values are those used in sensitivity analysis exercises in Section 6.3. below;

[2] "Ratings" are qualitative judgements pertaining to the use of the selected values for use in other assessments - see text for more discussion

[3] Note here that high and low values for dairy exposure, DCSDF for example, are not offered. This is because the bioconcentration tests were limited to beef. This was done since general trends will be the same. The sum of all diet fractions must add to 1.00. Strictly speaking, the soil diet fractions vary from site to site depending on the extent to which cattle are grazed, and the lushness of grazing land, etc.. However, there is not good data on soil ingestion by cattle. It is recommended that users first evaluate cattle diet with regard to grass (i.e., pasturing) versus feed (wheat, hay, corn grain, etc.). If they are pastured, then soil ingestion should be considered, with the fractions used here considered as reasonable defaults.

[4] These fractions of grazing land and feed land as contaminated were assigned values of 1.00 which assumed that all grazing land was contaminated to a concentration initially assumed, for the on-site soil source category, and the concentration solved for, for the off-site soil and stack emission source categories. Similarly, all the grass and feed were impacted, meaning that all vegetative consumption by the cattle was from the farm. Users should similarly consider all the grass and feed impacted unless some feed is imported, or grazing land is far from a point of soil contamination.

the authors of this document as to the appropriateness of using the "selected" parameter values for other assessments. This judgement is categorized in three ways:

1) **First Order Defaults, or FOD:** As defaults, these parameters are independent of site specific characteristics and can be used for any assessment. Also, as first order defaults, it is felt that the values selected for the demonstration scenarios carry a sufficient weight of evidence from current literature such that these values are recommended for other assessments. Several of the chemical specific parameters, such as the Henry's Constant, H, and the organic carbon partition coefficient, Koc, fall into this category. The qualifier above, "current literature", indicates that new information could lead to changes in these values.

2) **Second Order Defaults, or SOD:** Like the above category, these parameters are judged to be independent of site specific characteristics. However, unlike the above category, the current scientific weight of evidence is judged insufficient to describe values selected for demonstration purposes as first order defaults. SOD parameters of principal note are the bioconcentration parameters specific to the chemicals, such the Biota Sediment Accumulation Factor, or BSAF. This parameter translates a bottom sediment concentration to a fish tissue concentration. The science is evolving for this parameter, including thought on the extent to which BSAFs generated for one species at one site can be generalized to other sites and/or species, the differences in BSAF between column and bottom feeders, the differences between past and ongoing contamination, and so on. Users should carefully review the justification for the SOD values selected for the demonstration scenarios before using the same values.

3) **Site Specific, or SS:** These parameters should or can be assigned values based on site-specific information. The information provided on their assignment for the demonstration scenarios, and for selection of high and low values for sensitivity analysis testing, is useful for determining alternate values for a specific site. A key class of SS parameters which were not fully included in Table 6-1 above are the source strength terms - the soil concentrations, effluent discharge rates, and stack emission rates. There are likely to be site-specific applications of this methodology for which detailed information is unavailable.

Often the midrange values selected for the demonstration scenarios are suitable for site specific applications when data is unavailable.

The exposure parameters have not been categorized as have the contaminant fate and transport/transfer parameters. Assignment of these values are critical as LADD estimates are linearly related to parameter assignments - doubling exposure duration assumptions double LADDs, and so on. All exposure parameters were developed based on information and recommendations in EPA's *Exposure Factors Handbook* (EPA, 1989) and *Dermal Exposure Assessment: Principals and Applications* (EPA, 1992). Some of the exposure parameters of Table 2-1, Chapter 2, are appropriately described as FOD. These include: lifetime, body weights, water ingestion rates, inhalation rates, and an exposure duration for a childhood pattern of soil ingestion. All of the other exposure parameters are better described as either SOD or SS. Attaining site-specific information is recommended for them. However, this is often difficult for site specific assessments and impractical if the procedures in this assessment are used in general assessments. In the absence of site specific information, the following parameters can be considered SOD: adult exposure durations of 9 years for central scenarios (whether they be modeled after "residential" settings or not) and 20 years for high end scenarios (whether "farming" be the model for high end exposures or not), childhood soil ingestion rates, the fruit/vegetable food ingestion rates, the fraction of fruit/vegetable consumption that comes from a home garden, and the fractions of time spent at home (which are applied to inhalation and water ingestion pathways). The remaining exposure parameters pertain to the exposure pathways evaluated as most critical to dioxin exposures. For this reason, users should either pursue site specific information or carefully justify parameter selections in the absence of site specific information. These include the rate of beef, milk, and fish ingestion and the fraction of these food products which are impacted by the source. Fish ingestion rates for the demonstration of methodologies in this assessment were 1.2 g/day for central scenarios and 4.1 g/day for high end scenarios. These were developed using an approach recommended in the *Handbook* when site specific data was unavailable. Specifically, a meals per year of fish recreationally caught from the impacted water body was assumed, and then this was translated to a grams per day consumed. These rates

are both less than a national average estimate of fish consumption that was published in an water quality criteria document for 2,3,7,8-TCDD, 6.5 g/day (EPA, 1984). The setting for the demonstration scenarios was a rural setting which contained farm and non-farm residences, but which did not contain a major water body for frequent recreational or subsistence fishing purposes. Rather, a smaller size water body which allowed for more occasional recreational fishing was assumed. In a setting where more substantial water bodies exist which do supply fish for commercial and recreational use, fish ingestion rates from these water bodies would be higher. The other parameters are the ingestion rates and contact fractions for beef and milk ingestion. The ingestion rates for these food products were 50% ingestion rates given in the *Handbook*. The contact fractions assigned for the high end scenarios were developed from a USDA survey (USDA, 1966) of rural farm households, some of which home produced. For home producers only, the percent of their total ingestion of beef and milk which was homegrown was 44% and 40%, respectively.

In addition to the above qualifications, the parameters of this methodology have been categorized in terms of their role in the methodology. The following is a brief description of three principal categories.

Category 1. Human behavior exposure parameters

These are the contact rates, contact fractions, exposure durations, lifetime and body weights used in the following equation for lifetime average daily dose:

$$\text{Lifetime Average Daily Dose (LADD)} = (\text{exposure media concentration} \times \text{contact rate} \times \text{contact fraction} \times \text{exposure duration}) / (\text{body weight} \times \text{lifetime}) \quad (6\text{-}1)$$

Category 2. Fate, transport, and transfer parameters

These parameters are all the parameters required to estimate exposure media concentrations, except those specifically associated with a contaminant - chemical-specific parameters are included in Category 3 below. All fate, transport, and transfer parameters are listed, defined, and further subcategorized in Table 6-1. Not included in the

discussions in Section 6.3 are perhaps the most important terms in this category, and these are critical source strength terms: the concentrations of dioxin-like compounds for the soil source categories (onsite and offsite source categories), and the release quantities of dioxin-like compounds into the air for the stack emission source category and into the surface water for the effluent discharge source category. A general comment that can be made for fate and transport parameters is that values for the demonstration scenarios were selected to be midrange and plausible, and that this document provides information on selecting alternate values for site-specific applications. Most of the parameters in this category fall under the SS qualification. Subcategories within the fate and transport category include:

- Contaminated and exposure site characteristics: These are areas, soil properties, and depths of tillage (which are depths to which residues transported by erosion or deposition are mixed in conditions of tillage such as agriculture or gardening, and no tillage). Like the soil concentration term, the area of contamination is a site-specific and critical parameter. Soil properties were assigned to be midrange and typical of agricultural soils. Depths of mixing for tilled and untilled circumstances are not known with certainty, and these two parameters were characterized as SOD.

- Soil and sediment delivery parameters: These include parameters associated the erosion of contaminated soil from a site of contamination to a nearby site of exposure and/or to a nearby surface water body. All but one of the parameters in this subcategory are physical, site-specific parameters which should be evaluated for site specific applications. The one parameter not of this description is the enrichment ratio, which describes the enrichment of eroded soil with dioxin-like compounds, and was assigned a rating of SOD. Geometric parameters include watershed drainage area, water body volumes, and distances. Physical parameters include soil loss estimates, organic carbon contents, water body suspended solids, and background watershed contaminant concentrations.

- Volatilization and dust suspension parameters: These parameters are associated with suspension, dispersion, and transport of contaminants from contaminated soils. One parameter included in this category is the exposure duration, which appears to be

misplaced. In fact, the exposure duration is used to determine the average vapor phase air concentration - this is further discussed in Section 6.3 below. Parameters in this category are site-specific and should be evaluated for specific methodology applications.

- Bioconcentration and biotransfer parameters: These include parameters describing the biota and the media surrounding the biota which influence the transfer of dioxin-like compounds from the media to the biota. Some of these parameters are site-specific, although obtaining values may be difficult. Included here are annual rainfall, fish lipid contents, a fresh to dry vegetable weight conversion factor, and yields and intercept fractions for vegetation categories. Others are theoretical; values for these were determined from the literature and can be used for other assessments if better information is unavailable. Included here are atmospheric deposition velocities of particles, washout of wind-suspended particles from the atmospheric, the retention of wet particle depositions on vegetations, empirical correction factors for atmospheric to plant and soil to plant transfers, and the bioavailability of soil as compared to vegetation as a vehicle of transfer of dioxin-like compounds to cattle. These were given a rating of SOD. A third group describes exposure of cattle to dioxin-like compounds through their diet. These include fractions of cattle diet which are soil, pasture grass, and cattle feed, and the extent to which these three are impacted by the source of contaminant. Sensitivity analysis below shows how beef concentrations are impacted by changes in assumptions of how cattle are exposed to dioxin-like compounds through their diet. Since beef and milk dietary exposures are most critical for human exposure, the cattle exposure assumptions made for demonstrating the methodologies of this assessment should be carefully considered before using them for other assessments.

- Effluent discharge source category: These are three physical parameters that can be determined on a site-specific basis, and include flow rates of the effluent and receiving water body, organic carbon contents of suspended solids in the effluent and the receiving water body, and suspended solids content of the effluent and the receiving water body.

- Stack emission source category: In fact, most of the parameters required to evaluate the impact of stack emissions to a nearby site of exposure have been included in other categories. Sensitivity analysis only focuses on parameters and issues unique to this

category. One set of input values are contaminant wet and dry deposition rates. Three depositions are required: one for the site of exposure, one to represent depositions on watershed soils which drain into the water body, and one to represent direct deposition onto the water body. These were all generated using the COMPDEP model, as described in Chapter 3. Two other key inputs generated by the COMPDEP model are the ambient air vapor phase and particle phase concentrations of contaminant at the site of exposure. All such quantities are a function of that model's algorithms and parameter input requirements, particularly the release rate from the stack. Information on the COMPDEP model and its application is given in Chapter 3 and not discussed further in this chapter. Users can determine air concentrations and contaminant deposition rates in other ways, and use those in the methodologies to determine impacts and exposures. The no-till depth of mixing at the site of exposure, d_{not}, is required for the off-site soil source algorithm as well. It's selected value for the stack emission source category was 1 cm in contrast to 5 cm assumed for the off-site soil source category; hence its impact is examined twice in Section 6.3. below. The only other unique parameters not included in other subcategories are the average watershed mixing depth (used for determining watershed soil concentrations, which are then used to determine impacts to water bodies) and the fraction of particles depositing on water bodies which remain in suspension. These are both theoretical values and can be used in other assessments lacking better information.

Category 3. Chemical properties of dioxin-like compounds

The ten chemical-specific parameters required for the algorithms of this assessment fall under two categories, FOD and SOD. As such, they are all independent of the specifics of the site. The parameters deemed FOD are chemical fate and transport parameters, some of which are common and often determined in laboratory conditions. These include the Henry's Constant, the organic carbon partition coefficient, molecular diffusivity in air, a plant weathering rate constant for contaminated particles, and the soil dissipation rate for eroding or depositing contaminants. The selected values for these parameters are, in the authors' opinion, the best values derivable from current data. A second set of chemical specific parameters are associated with

bioconcentration/biotransfer algorithms. Some of them are determined from field data (data on dioxin-like compounds or other compounds), and others are determined by experimentation and with that experimentation, development of empirical relationships between a critical transfer factor and the chemical's octanol water partition coefficient. The authors cannot be definitive in a judgement that values given to these parameters be considered default, hence the SOD rating. For these compounds, field/experimental data is conflicting or there simply is a lack of appropriate data. Parameters included in this category are a soil to below ground vegetation transfer factor, two air to plant factors: the air-to-leaf vapor phase transfer coefficient and the plant washoff rate constant, two water body to fish parameters: the biota to sediment accumulation factor and the related biota to suspended solids accumulation factor, and a beef/milk bioconcentration factor.

6.3. SENSITIVITY ANALYSIS

Sensitivity analysis was undertaken in order to evaluate the impact of model results with changes in model parameters. The following sections describe the limitations, methodology and parameter selections, and results.

6.3.1. Limitations of the Sensitivity Analysis Exercises

The exercises were not comprehensive and/or definitive. Following are some key limiters:

- **The COMPDEP model was not evaluated in this section.** Chapter 3 describes the COMPDEP model. No sensitivity analysis runs were performed on COMPDEP model output for this chapter. This section does evaluate the impact of different deposition rates and modeled ambient air concentrations on exposure sites soils, surface water, and biota.
- **Sensitivity to changes in exposure parameters was not evaluated.** The basic equation for evaluating lifetime average daily dose was given above as Equation (6-1). Chapter 2 described all terms in this equation except the exposure media concentration, which was the focus of Chapter 4. Because LADD estimates are a linear function of all exposure parameters, sensitivity analysis was not performed on LADD exposure estimates. The focus of this section instead is on the fate, transport, and bioconcentration/biotransfer

algorithms used to estimate the exposure media concentration term in Equation (6-1).

- **The analysis was not exhaustive in its coverage.** Principal algorithms in the fate, transport, and transfer of dioxin-like compounds were evaluated, and all parameters required for algorithms were tested at least once. However, not all possible tests were conducted. Before noting those, following is a list of algorithms which were tested:

  - Volatilization/suspension and transport of vapor/particle phase airborne residues from a site of soil contamination to a nearby site of exposure (using algorithms developed for the off-site soil source category);

  - Volatilization/suspension and dispersion of vapor/particle phase contaminants for the circumstance where soil contamination is at the site of exposure (on-site soil source category);

  - Transport via erosion of contaminants at a site of soil contamination to a nearby site of exposure to impact exposure site soils (off-site soil source category);

  - Transport via erosion of contaminants at a site of soil contamination to a nearby surface water body, to impact bottom sediments, water, and fish (off-site soil source category);

  - Transfers of contaminants from soils to below ground vegetables and from air to above ground vegetations (on-site soil source category);

  - Transfers of contaminants from soils and vegetation to beef (on-site soil source category);

  - Direct discharges of dioxin-like compounds into surface water bodies, and the effect of surface water and effluent parameters on fish and water concentration estimation (effluent discharge source category); and

  - Particle depositions and ambient air concentrations, which result from stack emissions, onto exposure site soils, watershed soils, surface water bodies, and biota (stack emission source category);

The exercise was purposefully limited since several possible exercises would have been duplicative. For example, impacts to beef and milk in the off-site soil source category are, of course, modeled within this assessment, but specific sensitivities to beef and milk concentration predictions with parameter changes within the off-site soil source

category are not explicitly evaluated below. Parameters required for the beef bioconcentration algorithm are evaluated in the context of the on-site source category, and these are the same ones required for all three source categories which include beef impacts (the effluent discharge source category does not include beef and milk impacts). Further, only impacts to the beef algorithms were tested. The milk bioconcentration algorithm was not tested because principal conclusions from the beef exercise are generally true for the milk algorithm. Any generalizations from the on-site source category exercises are transferable to the other two source categories.

A related limitation has to do with the cascading effect of certain parameters. For example, a key contaminant parameter is the organic partition coefficient, Koc, which impacts (among other concentrations) vapor phase air concentrations. Air concentrations are used to estimate above ground vegetation concentrations, including those of grass and cattle feed. Beef concentrations are a function of concentrations in grass and cattle feed. What is not done for this example (and many others like it) is to evaluate the impact of changes in Koc to beef concentrations. What is done, however, is as follows. The sensitivity of air concentration predictions to changes in the partition coefficient are evaluated. Then, the sensitivity to grass and cattle feed concentrations to plus and minus one order of magnitude differences in estimated vapor phase air concentrations are evaluated. In this way, any possible parameter change(s) which influences air concentrations within a plus/minus order of magnitude range is evaluated for grass and feed concentrations. Finally, beef concentration estimations are evaluated within a similar plus/minus order of magnitude change for grass and feed concentrations. With some examination, therefore, the effect of cascading impacts can be determined.

The impact of changing soil concentrations to estimates of exposure media concentrations (air, water, biota) is linear and direct in all cases - i.e, increasing soil concentrations by a factor of five increases all impacted exposure media by the same factor of five. For this reason, soil concentrations are not displayed in the sensitivity graphs displayed in the next section, with one exception. This was in the estimation of beef concentrations from soil contamination. Beef concentrations are a function of concentrations in the dry matter diet of the cattle, including soil, grass, and cattle feed.

Therefore, if soil concentrations were to change and concentrations on the other intakes were to not change, than beef concentrations would not be a linear and direct function of soil concentrations. However, and in the context of this sensitivity analysis, when changing only soil concentrations, vegetative concentrations are linearly and directly impacted by the same order of magnitude change. Therefore, beef and milk concentrations turn out to be linearly related to soil concentrations.

A final limitation to note is that this exercise does not evaluate the multiple effects of changing more than one independent parameter simultaneously. Other numerical methods, particularly Monte Carlo, can be used to evaluate the impact of simultaneous changes to model parameters. Applications of this technique to dioxin exposure assessments are discussed in Chapter 7 of this volume.

There are instances where parameters were evaluated as dependent and changes were made simultaneously. One example is in three parameters which are related to the size of a watershed (also termed the "effective drainage area" since such an area might be smaller than a surrounding river system watershed), and which are important in determining the impact of a bounded area of soil contamination to a nearby surface water body. These three include the watershed size, the watershed sediment delivery ratio (which decreases as watershed size increases), and the surface water body volume (which increases as watershed size increases, assuming sources of water - surface runoff, interflow, and groundwater recharge - remain the same on a per unit area basis). To test the impact of watershed size to surface water and sediment concentrations, all three parameters were changed simultaneously in modeling a small and a large watershed. One set of parameters which might not be independent, but which were treated as such in the sensitivity testing, are the chemical specific parameters. For example, a higher organic carbon partition coefficient might be associated with a lower Henry's Constant - tighter binding to soils means less of a tendency to volatilize. Empirical relationships between such chemical specific parameters have not been established, and since there is uncertainty in precise values selected for the dioxin-like compounds, chemical specific parameters were treated as independent parameters.

- **Only a high and a low value for model parameters were tested; no discussions of**

likelihood for parameter values or distributions of parameter values are included. Certainly the identification of all model parameters and the justification for assignment of high and low values will be helpful to others using the methodology. Assignment of parameter values for purposes of demonstrating the methodologies in Chapter 5 should be carefully considered when users apply this methodology for specific purposes or specific sites.

6.3.2. Methodology Description and Parameter Assignments

Four of the six example scenarios of Chapter 5 served as "baselines" in the sensitivity analysis exercises. The single scenario for the off-site soil source category, example scenario #3 in Chapter 5, served as the basis for testing on these algorithms: 1) transport of vapor and particulate phase airborne contaminants from a site of contamination to a nearby site of exposure, and 2) transport of soils via erosion to nearby sites of exposure and to surface water bodies to impact bottom sediments, fish, and water. The source strength for this scenario, in summary, was a 40,000 m^2 (4 ha, 10 ac) area of soil concentrations of 1 μg/kg (ppb) within a watershed of size 4,000 ha (40,000,000 m^2; 10,000 ac; 15.5 mi^2) with soils otherwise at 0.0 ppb. The high end scenario for the on-site soil source category, example scenario #2 in Chapter 5, served as the baseline for testing on these algorithms: 1) suspension and dispersion of vapor and particle-phase contaminants at a contaminated site, which was also the exposure site for the on-site source category, 2) impacts of soil concentrations and other parameters to below ground vegetations, and air concentrations and other parameters to above ground vegetations, and 3) impacts of soil, grass, and feed concentrations, and other parameters, to beef concentrations. The source strength for this scenario, in summary, were soil concentrations within a 4,000 ha small farm of 1 ng/kg (ppt). The high end example scenario for the stack emission source category, example scenario #5, served as the basis for the testing the impact of particle depositions and ambient air concentrations on soils and biota. The ambient air concentrations and deposition rates at the site of exposure 500 meters from the stack served as the baseline source strength terms. The single scenario for the effluent discharge source category, example scenario #6, was used to evaluate the impact of parameters required for that source category on fish and water concentrations.

The source strength in that case was a discharge of 0.0315 mg/hr into a surface water body with a harmonic mean flow rate of 4.7×10^8 L/hr. Assignment of that baseline discharge was based on data from the 104 pulp and paper mill study, and then considering reductions is discharges which have occurred in these pulp and paper mills since the 104 mill study in 1988.

The baseline chemical for all these sensitivity runs was 2,3,7,8-TCDD; i.e., all the chemical specific parameters were those assigned to this example compound. The high and low values for parameter testings were determined starting with the 2,3,7,8-TCDD assignments. Care was not taken to encompass a range of possible values for all dioxin-like compounds. However, the ranges that were tested are mostly inclusive of the dioxin-like compounds. What will be noted and discussed below is that mostly the model response to chemical-specific parameters is linear or nearly linear, so that model responses to values outside the ranges tested can be evaluated easily.

All the initial parameter values required for all four source categories, and the values selected for high and low sensitivity analysis were listed above in Table 6-1. Following are brief discussions on the selection of these high and low values. Longer discussions on all parameter values can be found in Chapter 4, which included justifications for all parameter values selected for the demonstration of the methodologies in Chapter 5. Often, ranges of possible values were discussed in Chapter 4; those ranges were the basis of high and low parameter values selected below. Discussions in Chapter 4 are not repeated here, but are referenced below. The summaries below are organized in the same order as the parameter listings in Table 6-1.

• Contaminated and exposure site characteristics: These are the area and distance parameters, and the soil characteristic parameters of the site of contamination and the site of exposure. The "site of contamination" refers to the bounded area of high soil concentration for the off-site source category. The "site of exposure" for these sensitivity runs is the small farm which was the basis for the definition of the "high end" example scenarios demonstrated in Chapter 5. The area of the site of exposure, **AES**, and site of contamination, **ASC**, are both 40,000 m^2 in the demonstration scenarios, which is

equal to 4 ha or 10 ac. Low and high values tested were 4,000 m^2 (0.4 ha, 1 ac) and 400,000 m^2 (40 ha, 100 ac). The soil description parameters include soil porosity, **ESLP**, particle bulk density, **Psoil**, soil bulk density, **Bsoil**, and the organic carbon fraction, **OCsl**. The assignment of high/low values to these parameters were developed from Brady (1984) and cover a reasonable range of agricultural field soils. The no-till and tillage depths, d_{not} **and** d_t, refer to the depth to which eroded soil or depositing particulates mix at the site of exposure. The no-till depth was set at 5 cm and was varied between 1 and 20 cm, and the tilled depth was varied between 10 and 30 cm. The no-till concentrations were used to estimate soil concentrations for soil related exposures: soil ingestion and soil dermal contact, and also for the beef and milk bioconcentration algorithm. The tilled concentrations were used only to estimate the concentration in below ground vegetations.

• Soil and Sediment Delivery Parameters: Contaminated soil erodes from a site of contamination, a 4 ha site in the demonstration scenarios, to a nearby site of exposure and also to a nearby stream. The distance to the site of exposure from a site of contamination, DL_e, was set at 150 meters for the example scenarios, and varied between 50 and 1000 meters in this exercise. The same initial distance of 150 meters was the distance to the nearby stream, DL_w, and it was also varied between 50 and 1000 meters. The unit amount of soil eroding off the site of contamination, SL_s, was initialized at 21520 kg/ha-yr, equal to 9.6 Eng. ton/ac-yr (abbreviated t/ac-yr hereafter). Assumptions inherent in this estimate include: midcontinent range of annual rainfall erosivity (which is also the middle of the range of rainfall intensities of the US), midrange agricultural soil erosivity, a gentle 2% slope, no man-made erosion protection (ditches, etc.), and bare soil conditions. A doubling of this amount to 42,000 kg/ha-yr (19 t/ac-yr) was used as a high erosion estimate off the site of contamination. This could reflect any number of different assumptions, such as more erosive soil, more erosive rainfall, steeper slopes, and so on. A low estimate of one-tenth the default value, at 2100 kg/ha-yr (1 t/ac-yr), could reflect all the same assumptions except a dense cover of grass or weeds, which changes the bare soil assumption leading to a "C" (cropping management factor) of 1.0 to a C of 0.1. The erosion amount of 2152 kg/ha-yr was the initial amount assumed for a second unit erosion

term needed in this assessment, a unit erosion typical of land area between the contaminated and the exposure site, $\mathbf{SL_{ec}}$. The critical assumption in this initialization was that all conditions for this land area were similar to the contaminated site, except that the ground was densely covered with grass or weeds. The value of SL_{ec} was reduced to 0 kg/ha-yr for the low, which is unrealistically low but might give a sense of how the algorithm would perform if mixing with soil between the contaminated and exposure site were not considered. The high value was 21,000 kg/ha-yr, which is similar to the initial assumption for the contaminated site, could reflect similar erosion conditions between the contaminated site and the exposure site. The third unit soil loss parameter required is one which reflects average erosion conditions within the watershed draining into the water body, $\mathbf{SL_w}$. This was initialized at 6455 kg/ha-yr (2.88 t/ac-yr) which reflects similar erosion conditions as the contaminated site (soil erosivity, rainfall intensity, average slopes, lack of support practices) except some erosion protection due to vegetation - C equal to 0.3 instead of 1.0. It was reduced to 2100 kg/ha-yr, which might translate to C equal to 0.1, and increased to 21,000, which was equal to the initial higher erosion from the contaminated site. The range of the enrichment ratio, ER, was noted at between 1 and 5 for its application in agricultural runoff field data and model simulations (Chapter 4, Section 4.3.1), and was given an initial value of 3 in this application. High and low values tested were 5 and 1. An average watershed concentration of contaminant was set at 0 for the off-site demonstration scenarios, where the soil concentration of 2,3,7,8-TCDD (and the other example compounds) was set at 1 ppb. This was selected so that the off-site impact to surface water bodies could be demonstrated as an incremental impact. A concentration of 2,3,7,8-TCDD of 1 ppt was, however, justified as a "background" concentration for demonstrating the on-site source category. The value was used to evaluate the impact of a bounded site at 1 ppb when a background concentration of 1 ppt is also assumed to exist. Three parameters reflect watershed size. These include the effective drainage area, $\mathbf{A_w}$, the watershed sediment delivery ratio, $\mathbf{SD_w}$, and the volume of the receiving water body, $\mathbf{VOL_w}$. These are related and should therefore be changed in tandem. The initial watershed size of 4000 ha (15.4 mi^2) was reduced to 400 ha (1.5 m^2) and increased to 400,000 ha (1540 mi^2). Since the water body volume was estimated

using a in/yr runoff times an area, it was concurrently reduced 1 order of magnitude for the small watershed test and increased two orders of magnitude for the large watershed. The values of SD_w were estimated using Figure 4-5 (Chapter 4), which shows watershed delivery ratios as a function of watershed area. The remaining three parameters further described the water body, and were the total suspended solids, **TSS**, and the organic carbon contents of suspended and bottom sediments, $\mathbf{OC_{ssed}}$ and $\mathbf{OC_{sed}}$. The initial value of TSS of 10 mg/L is typical of a moving water body (stream, river) supportive of fish and other aquatic life. It was reduced to 2 mg/L, which is typical of a stationary water body (pond, lake, reservoir) and increased to 50 mg/L, which begins to be high for a water body expected to be supportive of fish. The organic carbon contents were initialized at 0.05 for OC_{ssed} and 0.03 for OC_{sed}. The premise was that they were related - that sediments in suspension were lighter and likely to be higher in organic carbon content than bottom sediments. They were also changed in tandem to 0.02 (OC_{ssed}) and 0.01 (OC_{sed}) for a low organic carbon sensitivity test and 0.10 and 0.05 for a high organic carbon test.

• Volatilization and Dust Suspension Parameters: Distances and areas are pertinent to estimating vapor-phase and particulate-phase air concentrations, and these have been discussed above in the first two categories. One parameter included for sensitivity testing in this category is the exposure duration, **ED**. It is included in these exercises because the estimation of average volatilization flux over a period of time is a function of that period of time. The derivation of the flux model assumed contamination originates at the soil surface at time zero, and over time, originates from deeper within the soil profile. Therefore, the flux decreases over time (because residues have to migrate from deeper in the profile), and the average flux over a period of time will decrease as that period of time increases. This is further discussed in Chapter 4, Section 4.3.2., and in the original citation for the volatilization flux algorithm, Hwang, et al. (1986). The exposure duration assumed in the high end scenarios was 20 years, this was changed to 1 and 70 years in sensitivity tests. A range of average windspeeds, U_m, around the U.S. was noted at 2.8 and 6.3 m/sec, and these two values were used around the selected value of 4.0 m/sec. The frequency with which wind blows from a site of contamination to a site of

exposure, **FREQ**, was set at 0.15, which is appropriate if one assumes that wind blows in all directions roughly equally. It was changed to 0.05 and 0.50, which might translate to an assumption of a prevailing wind direction, either away from or towards a site of exposure. The remaining parameters, fraction of vegetative cover, **V**, threshold wind speed, $\mathbf{U_t}$, and model specific function, **F(x)**, all refer to the wind erosion algorithm which suspends contaminated particulates into the air. Sensitivity tests were applied to this trio for the on-site and the off-site source categories. V for the off-site scenario was initialized at zero, implying bare ground cover; it was increased to 0.9 reflecting dense ground cover in the single sensitivity test here. It was set at 0.5 for the on-site small farm demonstration scenario, reflecting some bare ground conditions (in the agricultural fields, e.g.) as well as some dense vegetation (in other grassed areas of the farm property). It was decreased to 0 and increased to 0.9. The parameters U_t and F(x) reflect intrinsic erodibility of the soil and were varied together. Values were selected to reflect a high and low wind erodibility soil, following guidance in EPA (1985), the primary reference for the wind erosion algorithm.

• Bioconcentration and Biotransfer Parameters: The only such factor for fish concentration estimation was the fraction of fish lipid, $\mathbf{f_{lipid}}$. The brief discussion on this parameter in Chapter 4 (Section 4.3.4.1) indicated a range of around 5 to over 20%. Considering that the lipid content of edible portions of fish are less than whole fish lipid contents, a value less than 5%, 3% (0.03), was chosen as the low value, and also considering edible lipid content considerations, an upper value of 20% (0.20) was selected.

Several parameters are required for the vegetation concentration algorithm, most of which were associated with the algorithm for dry plus wet deposition of particulates. One parameter not associated with fate and transport was the dry to fresh weight conversion factor, **FDW**. The algorithm calculates vegetative matter concentrations on a dry weight basis, which is appropriate for the role of vegetation in the beef/milk bioconcentration algorithm. However, ingestion rates of fruits and vegetables are on a fresh weight basis, so dry weight concentrations have to be converted to a fresh weight basis. The initial

value of 0.15 assumes that fruits and vegetables are 85% liquid. The high and low values tested for this parameter were 0.30 (70% liquid) and 0.05 (95% liquid). Four parameters are described as empirical correction factors for the air-to-leaf algorithm adopted for vapor phase transfers to vegetation (three of the parameters), and for the soil-water-to-root algorithm adopted for below ground vegetation. There is one each for the four principal vegetations considered: below ground vegetables/fruits - $\mathbf{VG_{bg}}$, above ground vegetables/fruits - $\mathbf{VG_{veg}}$, grass - $\mathbf{VG_{gr}}$, and feed - $\mathbf{VG_{feed}}$. The concept for assignment of values to these parameters was the same, and briefly is as follows. The principal biotransfer factors (air-to-leaf and soil-water-to-root) were developed in laboratory experiments where relatively thin vegetations (azalea leaves for air-to-leaf transfers and barley roots for soil-water-to-root transfers) were used. Concurrently, there is evidence that the strongly hydrophobic/lipophilic dioxin-like compounds are found only in outer portions of vegetations and not inner portions of bulky vegetation; there is very little translocation of dioxin-like compounds into and within vegetation. Therefore, the full vegetation concentrations of thin vegetations measured in the laboratory experiments (and the laboratory experiments did use dioxin-like compounds among the several used) would most likely mirror only the outer surface concentrations found for dioxin-like compounds in bulky vegetations, and not full vegetation concentrations of bulky vegetations. As such, an empirical correction factor, based on a surface area to volume calculation, was introduced to arrive at full vegetation concentrations for bulky vegetations. These were principally the fruits and vegetables and the surface area to volume calculations led to assignments of VG_{bg} and VG_{veg} of 0.01. These were reduced to 0.001 and increased to 0.10 in sensitivity testing. The VG_{gr} was set at 1.00 since grass was thought to be analogous to the azalea leaves. Although there is insufficient justification to change VG_{gr}, a lower value of 0.50 was chosen. The VG_{feed} was set at 0.5, recognizing that some cattle feed is unprotected and thin vegetation such as hay, while others are protected grains such as corn grain. That value was changed to 0.25 and 0.75 in sensitivity testing. There is one required parameter for the dry deposition algorithm, and this is the particle deposition velocity by gravity settling, V_p, in m/yr. The initial value of 3.2×10^5 m/yr, from a velocity assumption of 1 cm/sec, was given by Seinfeld (1986) as the gravitational

settling velocity for 10 μm particles. This is the appropriate size to consider since the wind erosion algorithm was developed only for inhalable size particulates, those less than 10 μm (EPA, 1985). This was reduced to 0.5 cm/sec and 2 cm/sec (transformed to m/yr) for sensitivity testing. Three of the vegetation bioconcentration parameters are associated with the particulate wet deposition algorithm. These are the atmospheric washout ratio, $\mathbf{W_p}$, the retention of particles on vegetation, $\mathbf{R_w}$, and the annual rainfall amount, **R**. The definition, derivation, and ranges for these values are described in Chapter 4, Section 4.3.4.2, and are not repeated here (the ranges are given in Table 6.1). The remaining bioconcentration parameters are the yield and crop intercept values for the three above ground vegetations: vegetables/fruits ($\mathbf{Y_{veg}}$, $\mathbf{INT_{veg}}$), grass ($\mathbf{Y_{gr}}$, $\mathbf{INT_{gr}}$), and cattle feed ($\mathbf{Y_{feed}}$, $\mathbf{INT_{feed}}$). Again, discussions of chosen, and high and low, values for these quantities are given in Chapter 4, Section 4.3.4.2 (and displayed in Table 6.1). It is noted that these two terms are correlated - high yields are correlated with high interception amounts. In sensitivity testing, therefore, these parameters were changed in tandem.

The remaining bioconcentration/biotransfer parameters are for the beef/milk bioconcentration algorithm. One of the parameters relates the bioavailability of soil relative to the bioavailability of vegetation, where bioavailability refers to the efficiency of transfer of a contaminant attached to a vehicle. Fries and Paustenbach (1990) developed the bioconcentration factor, BCF, from studies where cattle were given contaminated feed. The studies of McLachlan, et al. (1990), from which BCFs for dioxin congeners were derived and used for this assessment, also used standard cattle feeds. This feed is assumed to be analogous to the vegetation in cattle diet; therefore, the experimental BCFs can be directly applied to vegetation in cattle diets. However, Fries and Paustenbach also hypothesized that soil is less bioavailable than feed, based on some rat feeding studies, and therefore the BCF developed from feed cannot directly be used on a soil concentration - it should be reduced. Information in Fries and Paustenbach led to an assignment of 0.65 for the soil bioavailability factor, $\mathbf{B_s}$. This was reduced to 0.30 and increased to 0.90 in sensitivity testing. Three parameters describe the proportion of the dry matter in the diet of beef cattle that is soil, **BCSDF**, grass, **BCGDF**, and feed, **BCFDF**. The sum of these three terms, by definition, equals 1.00. Beef cattle are principally

pastured (where incidental soil ingestion occurs), with supplemental feeds including hay, silages, and grain, particularly in cooler climates where they are housed during the winter. Values of 0.04 for BCSDF, 0.48 for BCGDF, and 0.48 for BCFDF were used in the demonstration scenarios. The same three parameters are required for cattle raised for dairy products: **DCSDF** for soil, **DCGDF** for grass, and **DCFDF** for feed. The dairy cattle model was one of very little pasturing, principally being fed high-quality grain indoors while they were in lactation: DCSDF of 0.02, BCGDF of 0.08, and DCFDF of 0.90. A final set of four parameters describes the proportion of these dietary intakes that are contaminated. Two are defined as the fraction of grazing land that is contaminated - **BCGRA** for beef cattle and **DCGRA** for dairy cattle. The initial assumption of 1.00 for both these parameters meant that all the vegetations as well as all the soil in the cattle diets was contaminated (since soil was assumed to be ingested during grazing). The last two similarly are defined as the proportion of feed that is contaminated - **BCFOD** for beef cattle and **DCFOD** for dairy cattle. They were also set at 1.00, perhaps indicating that feed was grown on-site. Rather than change these diet fraction assumptions and extent of contamination assumptions individually or in tandem (if necessary), what is done instead is to model four different scenarios relating to cattle exposures. Also, what is done here is to model only the beef cattle exposure. Generally, the trends that result from changes in the diet pattern will be analogous between the beef and dairy cattle. These four scenarios and the parameter changes made are:

1) *High and low soil ingestion*	Low: BCSDF = 0.01 BCGDF = 0.50 BCFDF = 0.49
No changes to BCGRA or BCFOD; diet assumptions changed to reflect high and low soil ingestion patterns	High: BCSDF = 0.15 BCGDF = 0.43 BCFDF = 0.42
2) *Low exposure conditions* Grazing is under lush conditions, so soil ingestion and diet pattern is modeled as "low" soil ingestion above; also, most feed is purchased externally	BCSDF = 0.01 BCGDF = 0.50 BCFDF = 0.49 BCFOD = 0.25

and uncontaminated; BCFOD reduced from 1.00 to 0.25

3) *Low extent of contamination* Diet assumptions are unchanged from initial assumptions; only it is assumed that 25% instead of 100% of dry matter in cattle diet is contaminated	BCGRA = 0.25 BCFOD = 0.25
4) *High/low lifetime pasturing* Tests for beef cattle only assuming heavy lifetime pasturing, 90% grass, and light lifetime pasturing, 08% grass	Low: BCSDF = 0.02 BCGDF = 0.08 BCFDF = 0.90 High: BCSDF = 0.08 BCGDF = 0.90 BCFDF = 0.02

• Effluent Discharge Source Category: Section 4.6, Chapter 4, discusses briefly how data from the 104-mill pulp and paper mill study (EPA, 1990b) were used to develop initial parameters required for this source category in its demonstration in Chapter 5. The use of the 104-mill data in a model evaluation exercise is expanded upon in Chapter 7, Section 7.2.3.6. The data is also used here to assign high and low values for four of the seven required parameters for this source category. Two have to do with flow rates: $\mathbf{Q_e}$ which is the effluent flow rate, and $\mathbf{Q_u}$ which is the receiving water flow rate. The range of Q_e is from 10^5 to 10^7 L/hr, which are the low and high surrounding the 4.1×10^6 rate used in the demonstration scenario in Chapter 5. The range of Q_u is 10^7 to 10^9 L/hr (excluding the top ten receiving water bodies, which were in the 10^{10} L/hr range and for which model did not appear to perform adequately), and these were the low and high around the 4.7×10^9 L/hr rate used in Chapter 5. Two parameters describe the suspended solids content of the effluent, $\mathbf{TSS_e}$, and the suspended solids content of the receiving water body, $\mathbf{TSS_u}$. TSS_e ranged from 10 to 250 mg/L in the 104-mill study, so this was the range around the 70 mg/L used as the initial value. Data from STORET used to develop TSS_u led to an average of 9.5 mg/L and a range of less than 1 to 50 mg/L; a range of 2 (a reasonable value for a stationary water body such as a pond or lake) to 50 mg/L was tested. One required parameter was, of course, the rate of contaminant

discharge, **LD**, in units of mg/hr. The assumed value was 0.0315 mg/hr, and this decreased and increased an order of magnitude for low and high testing. The remaining two parameters are the organic carbon contents of effluent solids, $\mathbf{OC_e}$, and upstream river suspended solids, $\mathbf{OC_u}$. A range based on data was not available for these parameters. OC_e was assigned a value of 0.36 based on the fact that solids in effluent discharges are primarily biosolids, and this value was one cited for surface water algae; values of 0.15 and 0.50 were tested. The value of 0.05 for OC_u was the value assumed for demonstration of other source categories, where the parameter was called OC_{ssed}. The same range of 0.02 to 0.10 for OC_{ssed} was used for OC_u.

• Stack Emission Source Category: The parameters in this category listed in Table 6-1 are the only ones which are unique to this source category (one parameter, the no-till mixing depth at the exposure site, d_{not}, is also used for the off-site soil source category, but its assigned value was 5.0 cm for that source category, and 1.0 cm for the stack emission source category; that is why it is listed for both source categories). As seen, there are only a very few unique parameters. Most of these are associated with surface water impact, and one series of tests evaluated the impact of parameter changes to surface water concentrations and fish concentrations. These include the contaminant deposition rates, $\mathbf{RDEP_{wat}}$ and $\mathbf{RDEP_{sw}}$, which are depositions onto the watershed draining into the surface water body and the surface water body itself (units are $\mu g/m^2$-yr). The initial values for these were those modeled to occur 500 meters from the stack. This assignment for the stack emission demonstration scenarios, #4 and #5 in Chapter 5, assumes that the stack is located essentially next to the water body. These depositions rates are specific to 2,3,7,8-TCDD. Rates of 2,3,7,8-TCDD deposition at 200 meters and at 5000 meters were used as high and low values, respectively. It should be noted that depositions are higher at 200 meters and lower at 5000 meters as compared to 500 meters, but air concentrations are lower at 200 meters as compared to 500 meters. This trend occurs because wet deposition is highest nearest the stack. Total depositions are driven by these high wet deposition totals; hence total depositions at 200 meters exceed those at 500 meters. However, dispersion modeling shows that ambient air

concentrations of contaminants in the vapor phase (given the wind data and all other parameters and assumptions in using the COMPDEP model for the demonstration scenarios) are highest 500-1000 meters from the stack. For sensitivity testing, differences in model performance as a function of distance from the stack will be evaluated. $RDEP_p$ is the deposition of particles themselves and was supplied in order to maintain a mass balance of solid materials entering the water body. The default value of 0.03 g/m^2-yr was taken from Goeden and Smith (1989) for a study on the impacts of a resource recovery facility on a lake. They estimated a total deposition of particles to the lake from all sources was 74.4 g/m^2-yr. Assuming the stack is unlikely to contribute all sources of particles to a water body, a high value was chosen as 3 g/m^2-yr, and a low value was given as 0.003. The fraction of depositing particles remaining in suspension, f_{sd}, was initialized as 1.00 (meaning that all directly depositing particles remain in suspension) based on an argument that the small particles emitted from the stack and transported directly to the surface water body would settle to surface water bottoms much more slowly than other solids entering water bodies. A low value of 0.00 was tested (meaning that all solids directly depositing within a year settle quickly to become bottom sediments). The average watershed mixing zone depth, d_{wmx}, was initialized at 0.10 m (10 cm) which is midway between the 1 cm assumed for non-tilled conditions and 20 cm assumed for tilled conditions. This assumption might translate to a rural watershed comprised equally of farmed and unfarmed land. It was reduced to 1 cm and increased to 20 cm in sensitivity testing. A second series of tests evaluated biota impacts at the site of exposure, vegetables/fruits and beef/milk. Parameter inputs for these tests include the ambient air concentration and depositions at the site of exposure, C_{va} and $RDEP_e$, and the no-till depth of mixing, d_{not}. The no-till depth of mixing was increased from 1 to 5 cm. Concentrations and depositions of 2,3,7,8-TCDD at 200 and 5000 meters were tested. The baseline quantities at 500 meters were varied to reflect different vapor/particle partitioning assumptions. Currently, the assumption is that 2,3,7,8-TCDD emissions are 55% in the vapor phase and 45% in the particle phase. Linear adjustments to the emissions in vapor and in particle form can be made to stack emissions. Concentrations and depositions at specific locations are then adjusted in the same linear manner to reflect

different vapor/particle partitioning assumptions. Two assumptions tested include 10% vapor/90% particle and 90% vapor/10% particle.

• Contaminant Physical and Chemical Properties: The initial values for testing of this category of parameters were the ones used for 2,3,7,8-TCDD. Generally, the high and low values tested are those which may represent a range for this contaminant only, not all dioxin-like compounds. However, several of the ranges also encompass values that could be pertinent to other compounds. It should be remembered that this is simply a model performance exercise and nothing else. Also, it could be argued that some of the parameters should be changed in tandem - that there may be a relationship between soil/water adsorption, as modeled by Koc, and bioconcentration. Such relationships were not explored in these exercises. Notes on the parameters are as follows:

1. **Henry's Constant, H** - The value of 1.65×10^{-5} atm-m^3/mole was used for 2,3,7,8-TCDD. Except for a heptachloro-PCB, Henry's Constants for the dioxin-like compounds ranged from 10^{-6} to 10^{-4}. Because of this, the initial value was reduced and then increased an order of magnitude for this test.

2. **Molecular Diffusivity in Air, D_a** - This parameter is needed for the volatilization flux algorithm. Because no values were available for the dioxin-like compounds, values were estimated based on the ratios of molecular between a dioxin-like compound of interest and a compound for which a D_a was available - in this case, diphenyl. The range of values tested are 0.005 cm^2/s as a low and 0.10 cm^2/s around the initial value of 0.047 cm^2/sec.

3. **Organic Carbon Partition Coefficient, Koc**: The Koc is perhaps the single most influential parameter in this assessment, impacting surface water concentrations, vapor phase air concentrations, and directly or indirectly, all biomass concentrations (fish, vegetations, beef/milk). The literature for 2,3,7,8-TCDD shows a range of Koc under 10^6 (from Schroy, et al., 1985) to over 2×10^7 L/kg (Jackson, et al., 1986). The value selected for 2,3,7,8-TCDD was 2.69×10^6 based on an empirical relationship between Koc and Kow developed by Karickhoff, et al. (1979) (see Section 4.3.1., Chapter 4). The values tested were one order of magnitude less (2.7×10^5) and one order of magnitude more (2.7×10^7)

than the value initially assumed for 2,3,7,8-TCDD.

4. **Air-to-Leaf Vapor Phase Transfer Factor, B_{vpa}**: The initial value for 2,3,7,8-TCDD was estimated as a function of a contaminant's octanol water partition coefficient, Kow, and Henry's Constant, H (Equation 4-30, Chapter 4). This arrives at the volume-based transfer factor, B_{vol}, which is then transformed to a mass based B_{vpa} (Equation 4-31). The empirical formulation for B_{vpa} was developed in a series of experiments by Bacci, et al. (1990, 1992). A second experiment by McCrady and Maggard (1993) demonstrated that the Bacci experiments would overestimate the transfer of 2,3,7,8-TCDD to grass leaves by approximately a factor of 40. An air-to-beef food chain validation exercise described in Chapter 7, Section 7.2.3.9, describes the rationale and model results which led to the approach taken in this assessment for assignment of B_{vpa} for all congeners: determine a value of B_{vol} based on Bacci's empirical algorithm, reduce it by a factor of 40 based on the McCrady and Maggard experiments, and transform it to a B_{vpa} considering the plant density and liquid content of vegetation as given in McCrady and Maggard. For 2,3,7,8-TCDD, the resulting B_{vpa} is 1.0×10^5. Plus or minus an order of magnitude will be tested as a high and low value for B_{vpa}.

5. **Particle-Phase Fraction, ϕ**: This fraction was used in the stack emission source category for determining the portion of emitted contaminant that was and remained in the particle phase from stack to exposure site. Details on the measured and theoretical partitioning is given in Chapter 3 of this Volume. As discussed there, measured partitioning of 2,3,7,8-TCDD in ambient showed a very small amount in the particle phase, 13%. However, speculation was that the monitoring method itself could lead to an underestimate in the particle phase, and for that reason, a theoretical approach was used to partition the dioxin. This led to a ϕ of 0.45 for 2,3,7,8-TCDD. The stack emission demonstration will be used to evaluate the impact of instead assuming 0.20 or 0.80 for 2,3,7,8-TCDD ϕ.

6. **Root Bioconcentration Factor, RCF**: The initial value for 2,3,7,8-TCDD was estimated as a function of octanol water partition coefficient, Kow. Assuming a log Kow of 6.64, RCF was solved as 3916. Different assumptions for log Kow were used to estimate high and low values of RCF for this exercise. Examining literature Kow for the dioxin-like compounds, no log Kow are less than 6.0 (the lowest at 6.2) and only one value estimated to exceed log Kow equal 8.5. A high and low RCF were estimated,

therefore, using log Kow of 6 and 8.5. This led to tested values of RCF of 1260 and 106,000.

7. **Beef/milk Bioconcentration Factor, BCF:** Unlike the RCF, B_{vpa}, and Koc (but like the BSAF and BSSAF as noted blow), there are no empirical formulas developed for BCF as a function of more common parameters such as Kow. The literature summary and interpretation of 2,3,7,8-TCDD cattle feeding studies by Fries and Paustenbach (1990) led them to assign a value of 5.0 for 2,3,7,8-TCDD. The study by McLachlin, et al. (1990) allowed for generation of BCF values for 16 of the 17 congeners of dioxin toxicitiy equivalency, and the results from that study are used for this assessment. The 2,3,7,8-TCDD BCF was 4.3, which is close to the value of 5.0 promoted by Fries and Paustenbach (1990). Their summary, duplicated as Table 4-3 in Chapter 4, showed BCF less than 1.0 for higher chlorinated dioxin-like compounds. For sensitivity testing, values of 1.0 and 10.0 were used as low and high values for BCF.

8. **Biota Sediment and Biota Suspended Solids Accumulation Factors, BSAF and BSSAF:** EPA (1993) summarizes several water column based and sediment (both suspended and bottom) based empirical parameters used to estimate fish concentrations given a water or sediment concentration. Two of these are the BSAF and BSSAF, which are used in this assessment. Although no data exists to determine values of the suspended solids factor, BSSAF, EPA (1993) suggests that BSAF values could be used. The range of BSAF values for 2,3,7,8-TCDD discussed in EPA (1993) is 0.03 to 0.30, and this was the low and high values selected for both BSAF and BSSAF. The literature summary on BSAF included in Chapter 4 of this assessment does include studies which imply higher BSAF for 2,3,7,8-TCDD. One study, which focused on bottom feeders (carp, catfish, etc.), found a BSAF for 2,3,7,8-TCDD (CDEP, 1992) of 0.86, whereas the range of 0.03 to 0.30 focused on column feeders. A high value of 2.94 (Kjeller, et al., 1990) was found in a lake in Sweden speculated to be impacted by an active pulp and paper mill. This high value appears to be an outlier not found in other field data sets.

9. **First-order Plant Weathering Factor, kw:** This is used to simulate the weathering of contaminated particulates which have settled on plant matter via dry and wet deposition. Several modeling efforts have used the same kw as used in this effort; that kw is 18.01 yr^{-1}, which corresponds to a half-life of 14 days (see Section 4.3.4.2, Chapter 4). Values of 51 (half-life of 5 days) and 8.4 (half-life of 60 days) yr^{-1} were used

to test the impact of this parameter.

10. **Dissipation Rate Constant for Eroding or Depositing Contaminants, k**: Evidence for soil degradation of the dioxin-like compounds indicates that residues even millimeters below the soil surface degrade at a very slow rate, if at all (see Chapter 2, Volume 2 of this assessment). This was the basis for not considering degradation of soil sources of dioxin-like compounds in this assessment. However, when residues migrate to impact only a thin layer of soil at a distant site, the processes of volatilization or photolysis (the one degradation process which appears to transform dioxin-like compounds in the environment) are likely to impact delivered residues. A rate constant of 0.0693, which corresponds to a 10-year half-life, was used in two instances for this methodology - for erosion of off-site soils onto exposure site soils, and for deposition of stack emissions onto exposure site soils (see Section 4.4.1 for a further discussion on this parameter). This value was changed to 0.693 (half-life of 1 year) and 0.00693 (half-life of 100 years) yr^{-1} in sensitivity testing.

6.3.3. Results

The results of the sensitivity analysis are principally described in a series of 14 bar graphs. The Y-axis is on a log scale and shows changes in media concentration estimation when the high and low parameter substitutions are made. The Y = 1 line is the value of the media concentration with all baseline parameter selections; the precise value of that media concentration is noted on each graph. Other y-axis values are arrived at as the ratio of the pertinent media concentration estimated with the altered parameter over the baseline concentration; a y-axis value of 0.1, for example, means that the concentration with the parameter substitution was one-tenth the concentration under baseline conditions. Also noted on each graph is the pertinent source strength term - for air concentration sensitivities, soil concentrations are noted, and so on. The parameters tested are named on the x-axis, and these names correspond to the names in Table 6.1. The definition and baseline value of these key parameters are noted below each graph. The high and low values tested are appropriately placed either above (when the concentration increases with the parameter change) or below the bar graphs. These parameters are the only ones which impact the tested media concentration. Of course, the soil concentration also impacts the media concentration, but as noted in the previous

section, soil concentrations have a direct and linear impact in all cases, and so are not displayed on the figures. Observations from each figure now follow.

6.3.3.1. ***Estimation of off-site air concentrations in the vapor phase*** Results for this test are shown in Figure 6-1. No single change resulted in estimations over an order of magnitude different from that made with baseline parameters. The model is insensitive to porosity and particle bulk density parameters, E_{slp} and P_{soil}. The results are also reasonably insensitive to ranges for organic carbon content of soil, OC_{sl}, and windspeed, U_m. For all other parameters, there appears to be roughly an order of magnitude spread over the range of parameters tested. Increasing the exposure duration to 70 years would decrease prediction by roughly one-half and decreasing the duration to 1 year would roughly double concentrations. As discussed earlier in Section 6.2., the volatilization algorithm assumes that contamination begins at the soil surface at time zero, and residues available for volatilization originate from deeper in the profile over time. The result of this assumption is that the flux decreases as time increases. This is the only algorithm of this assessment where an assumption of a decreasing source strength over time is made. The impact does not appear too critical, however, as estimated air concentrations only increase by a factor of 3 when assuming a 1 year duration or decrease by 45% when assuming 70 years duration.

6.3.3.2. ***Estimation of off-site air concentrations in the particulate phase*** Results from this test are shown in Figure 6-2. The y-axis in this test spans two orders of magnitude since changes in the parameters describing the inherent wind erodibility of the soil, U_t and F(x), results in over an order of magnitude higher and lower than concentration estimations as compared to estimations using the selected values of U_t and F(x). The assumption of bare soil conditions at the site of contamination led to a value of 0.0 for V, the vegetative cover parameter. If the contaminated site had a reasonably dense vegetative cover leading to a V of 0.9, air concentrations at the nearby site of exposure would be about an order of magnitude less. The impact of area (ASC), distance (DL_e), and frequency (FREQ) on exposure site concentrations mirror those for vapor-phase air concentrations. That is because these three are used in the same far-field dispersion algorithm. Another parameter used for the far-field dispersion algorithm is windspeed, U_m.

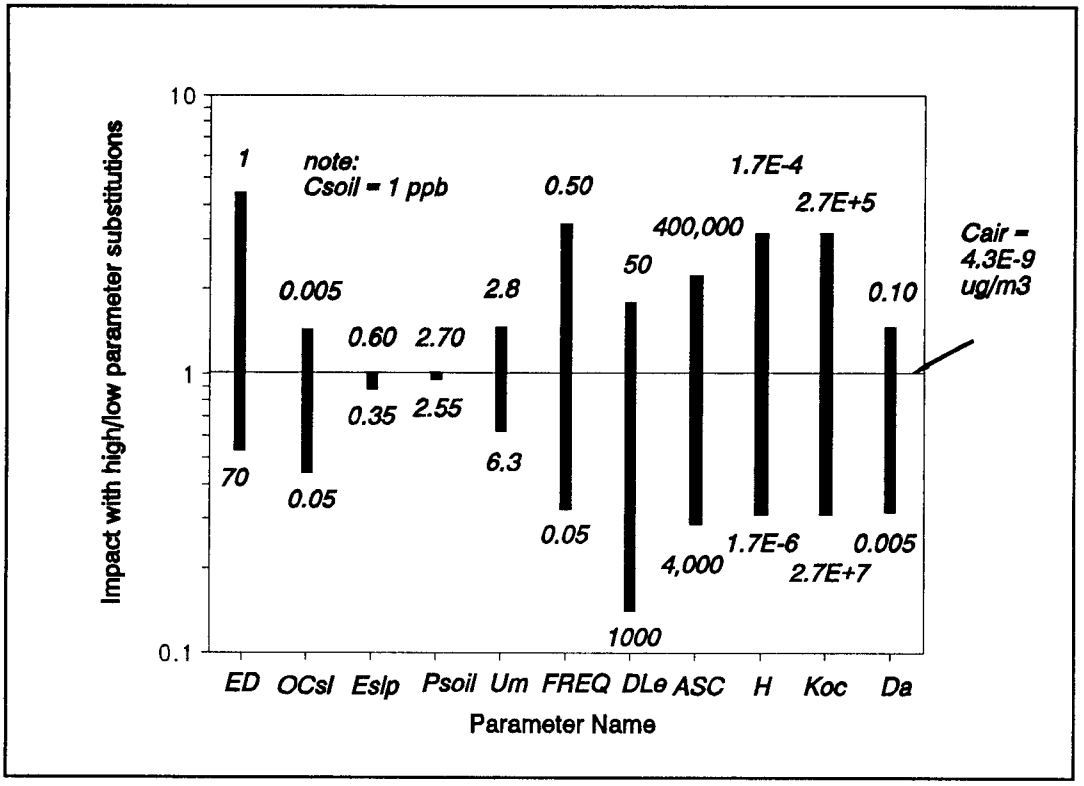

Figure 6-1. Results of sensitivity analysis of algorithms estimating exposure site vapor phase air concentrations resulting from off-site soil contamination.

Parameter Name	Definition	Selected
C_{soil}	soil concentration at off-site area, ng/kg (ppb)	1.00
C_{air}	air concentration at exposure site, $\mu g/m^3$	4.3×10^{-9}
ED	exposure duration, yrs	20
OC_{sl}	soil organic carbon fraction	0.01
E_{slp}	soil porosity, unitless	0.50
P_{soil}	particle bulk den, g/cm^3	2.65
U_m	average windspeed, m/sec	4.0
FREQ	frequency wind blows to site, unitless	0.15
DL_e	distance to exposure site, m	150
ASC	area of off-site contamination, m^2	40,000
H	Henry's Constant, atm-m^3/mole	1.65×10^{-5}
Koc	organic carbon partition coefficient, L/kg	2.69×10^{6}
D_a	molecular diffusivity in air, cm^2/s	0.047

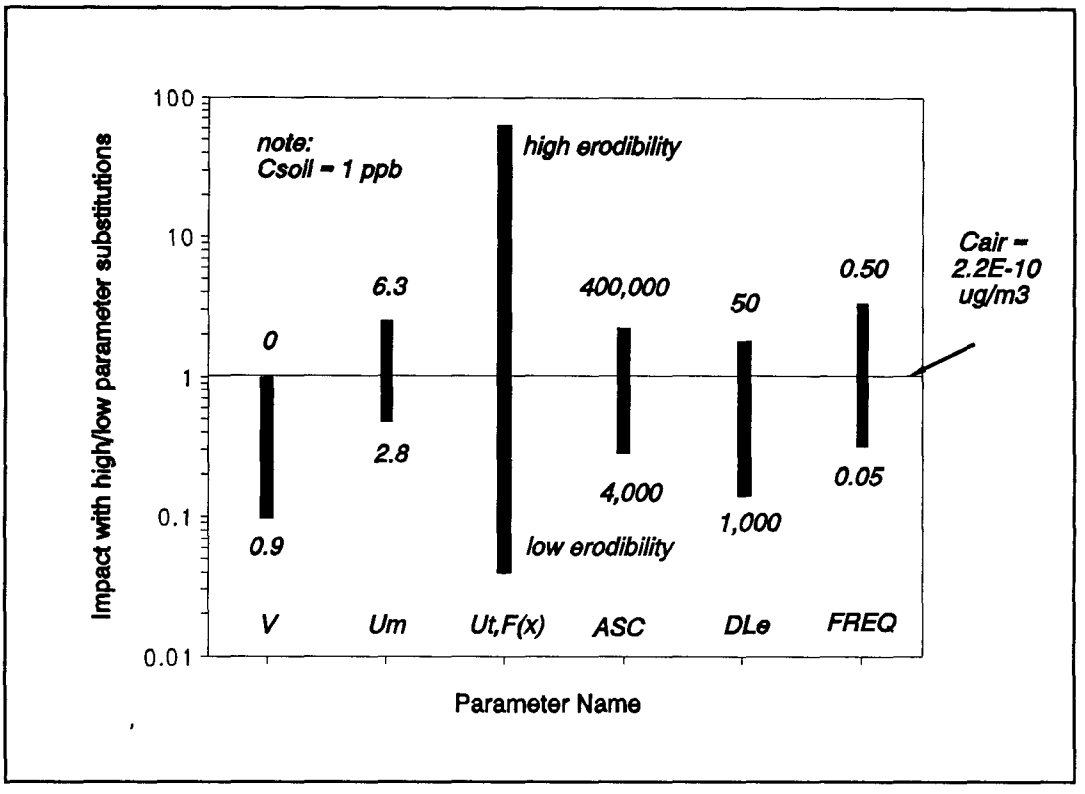

Figure 6-2. Results of sensitivity analysis of algorithms estimating exposure site particle phase air concentration resulting from off-site soil contamination.

Parameter Name	Definition	Selected
C_{soil}	contaminated site soil concentration, μg/kg (ppb)	1.00
C_{air}	exposure site air concentration, μg/m^3	2.2×10^{-10}
V	fraction of vegetative cover, offsite, unitless	0.0
U_m	average windspeed, m/sec	4.0
U_t	threshold wind speed, offsite, m/sec	8.25
F(x)	model-specific parameter, offsite	0.50
ASC	area of off-site contamination, m^2	40,000
DL_e	distance to exposure site, m	150
FREQ	frequency wind blows to site, unitless	0.15

However, interestingly, the impact of that parameter is reversed between the vapor and particulate phase algorithms. For the particulate phase, the windspeed has more of an impact in increasing wind erosion and hence the reservoir of airborne contaminant - increasing windspeed increases air concentrations. For the vapor phase, windspeed does not playa role in estimating volatilization flux, but only a role in the far-field dispersion model. In that role, increasing wind speed increases dispersion and decreases

concentrations. Noteworthy for the particle phase algorithm is that estimated concentrations are independent of any chemical-specific parameters; wind erosion suspending the particles is only a function of climate, ground cover, and soil erodibility. Also noteworthy is that the baseline air concentration of contaminants on particles is over an order of magnitude lower than the baseline air concentration of contaminants in the vapor phase. Besides having implications for particle phase and vapor phase inhalation exposures, this difference also has implications for impacts to vegetation concentrations and subsequently to beef and milk concentrations.

6.3.3.3. ***Estimation of soil erosion impacts to nearby sites of exposure*** Results from this test are shown in Figure 6-3. This model shows little sensitivity to two parameters, the bulk density of soil at the site of exposure, B_{soil}, and the amount of "clean" soil (that which is between the contaminated and exposure site) which erodes onto the exposure site, SL_{ec}, along with the contaminated soil. These will not be discussed further. In contrast to SL_{ec}, the model has a direct linear impact with the amount of soil eroding from the contaminated site, SL_s. Decreasing that amount by a factor of 10 decreases exposure site soil concentrations by the same amount, and doubling contaminated site erosion also doubles exposure site soil concentrations.

The model appears to show insensitivity to the distance between the exposure and contaminated site, DL_e. However, this result should be viewed cautiously. The sediment delivery ratio equation, described in Chapter 4, Section 4.3.1., was developed to estimate sediment loads from construction sites to nearby surface water bodies, and from distances up to 250 m. Its application to distances beyond that are questionable, and applications from one land area to another land area rather than from one land area to surface water, should also be questioned. At the model baseline distance of 150 m, the SD_s (sediment delivery ratio) is 0.26. At 1000 m, it is 0.17, which is a marginal dropoff for what appears to be a significant increase in distance. The distance becomes increasingly important when there are obstructions between the contaminated and the exposure site such as ditches, roads, and so on. When using this methodology, one should consider not relying on the sediment delivery ratio equation for: 1) transport of soils beyond 250 meters, 2) when the exposure site is upgradient from the site of contamination (in its development for construction sites, the assumption that a water body is downgradient

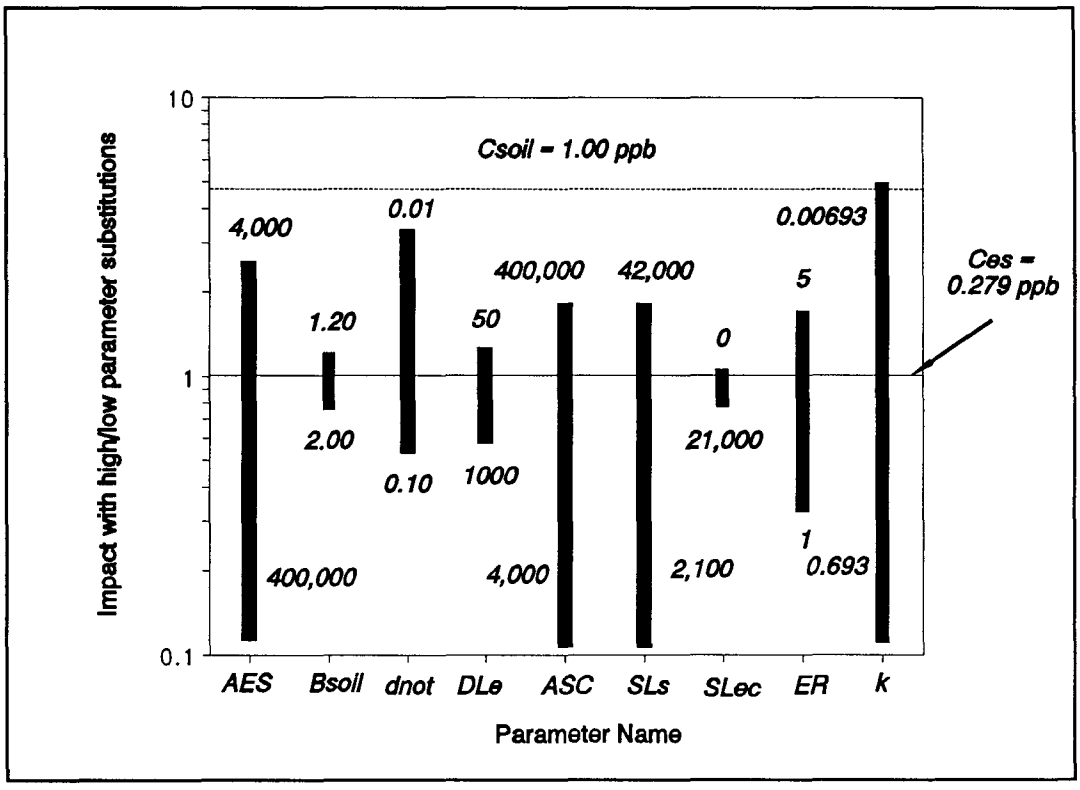

Figure 6-3. Results of sensitivity analysis of algorithms estimating exposure site soil concentrations resulting from erosion from off-site soil contamination.

Parameter Name	Definition	Selected
C_{soil}	contaminated site soil concentration, ng/kg (ppb)	1.00
C_{es}	exposure site soil concentration, ng/kg (ppb)	0.279
AES	area of exposure site, m^2	40,000
B_{soil}	soil bulk density, g/cm^3	1.50
d_{not}	no-till mixing depth, m	0.05
DL_e	distance to exposure site, m	150
ASC	area of off-site contamination, m^2	40,000
SL_s	contaminated site soil loss, kg/ha-yr	21520
SL_{ec}	soil loss between exp. and cont. site, kg/ha-yr	2152
ER	enrichment ratio, unitless	3
k	dissipation rate for eroding/depositing cont., yr^{-1}	0.0693

from the site seems reasonable), and 3) when there are obvious land features which would retard erosion. At the model's baseline value of 150 meters to a nearby site of exposure and to a nearby water body, use of the sediment delivery equation is expected to yield

reasonable results.

One noteworthy trend from Figure 6-3 is that exposure site soil concentrations are not a direct linear function of areas of the exposure and contaminated sites, which they shouldn't be. It is assumed in the erosion algorithm that contaminated soil delivered to the exposure site mixes evenly throughout the exposure site to a depth defined by the tillage depth. The algorithm corrected the amount of contaminated soil delivered to an exposure site when the exposure site was smaller than the contaminated site; it reduced the amount of contaminated soil delivered according to an appropriate size ratio. The baseline scenario had the contaminated and exposure site the same size at 40,000 m^2. For this situation, all contaminated eroded soil from the site reaches and mixes with soil at the exposure site. When the contaminated site increased an order of magnitude to 400,000 m^2, the soil concentration at the exposure site only doubled; it did not increase by an order of magnitude. It is unreasonable to assume that all the eroded soil would crowd into the smaller exposure site. When the contaminated site decreased an order of magnitude to 4,000 m^2, the exposure site soil concentration likewise decreased by an order of magnitude. In this case, like the case when the contaminated and exposure site were of the same size, all the contaminated soil eroding in the direction of the exposure site mixes into exposure site soil, so the resulting average soil concentration at the exposure site is linearly related to the concentration at the contaminated site. A similar trend is noted with changes in the exposure site area term.

The impact to changes in depth of tillage is nearly, but not quite, linear. Decreasing the no till depth of mixing, d_{not}, from 0.05 m to 0.01 m increased soil concentrations by a factor of 3.5 roughly, while increasing d_{not} to 0.10 decreased concentrations by 45%. A similar, nearly linear, impact is noted with the changes tested for tillage depth, d_t. For figure clarity, these results were left off Figure 6-3, but decreasing the depth from an initial 0.20 m to 0.10 m increased concentrations by just under a factor 2, and decreasing it to 0.30 m decreased concentrations by just under 33%.

The model has a linear impact with the enrichment ratio, ER. Its baseline value is 3.0; decreasing it to 1.0 decreases exposure site soil concentrations by 67%, and so on. The most interesting result from this sensitivity analysis exercise, however, was the test with the dissipation rate constant for eroding contaminants, k. This parameter was introduced in the equation since it was hypothesized that dioxin-like contaminants at and

near the surface might be subject to dissipation processes such as photolysis or volatilization. Dioxin-like contaminants would reside near the soil surface for eroding or depositing (the stack emission source category) contaminants. This contrasts the assumption that soil concentrations at a site of soil contamination are steady over time - no dissipation or degradation constant is applied. The baseline value for k is 0.0693 yr^{-1}, which is equivalent to a ten-year half-life. With that and all other baseline parameters, exposure site non-tilled soil concentrations are 0.279 ppb, or 28% of the contaminated site concentration of 1.00 ppb. When the dissipation half-life is increased to 100 years, essentially no dissipation, the exposure site soil concentration increases to over 1.00 ppb, or over that of the contaminated site. This is an improbable, if not impossible, result. Of all the parameters which have an incorrect value to have led to this result, the most likely one is the enrichment ratio. This multiplier increases the concentration on eroded soil from that which was on the site. It has a direct linear impact on exposure site soils - increasing it from its baseline of 3.0 to 5.0 increased exposure site soils by 67%. It is reasonable to assume that soil which erodes from a site is finer and more rich in organic matter in comparison to in-situ soils on the average, and that the eroded soils are "enriched" in comparison to in-situ soils for organic contaminants whose binding to soils is a function of organic carbon content of soils. This concept of enrichment has been used and demonstrated with field data, although not with field data of dioxin-like compounds. This exercise may have demonstrated that the assumed enrichment ratio of 3.00 is too high. Further, it may be reasonable to conclude that since dioxin-like compounds are so tightly sorbed to soils in general that the enrichment effect is not as pronounced as a 3.00 enrichment ratio implies.

A final issue evaluated for the soil erosion algorithm is the assumption of a steady state. As discussed in Section 5.4.1, Chapter 5, the solution did have a time term, which at time t = 0, erosion from a contaminated to an exposure site begins. Assuming long periods of time results in this exponential term approaching 1.0. The term was, therefore, dropped, to arrive at the steady state algorithm for soil erosion impacts. To test the impact of this assumption, tests were run including the exponential term with t equal to 1, 2, 3, 4, 5, 10, and 15 yrs. Expressing results in terms of the percent of steady state concentration reached at the end of each year, the results for these time intervals are 28, 49, 63, 74, 81, 96, and 99%, respectively. As seen, 81% of steady state is reached

after 5 years, and 96% is reached after 10 years. Therefore, if off-site contamination has existed for 5-10 years or more, estimates of exposure site concentration (and related exposures) with a steady state assumption should be reasonable. However, if an assessment is to be done for a site to be newly impacted, such as a planned landfill, than the steady state approach would lead to some overprediction of concentrations and exposures. For the first five years, concentrations would average about 60% of steady state, and for the first 10 years, concentrations would average about 75% of steady state. This would be of most concern for a childhood pattern of soil ingestion, which would be 40% lower for the first five years of a landfill operation as compared to a steady state assumption. Otherwise, it is seen that the steady state assumption does not greatly impact exposure site concentrations.

6.3.3.4. *Estimation of soil erosion impacts to nearby surface water bodies*

Results from this test are shown in Figure 6-4. One immediate point to make about this bar graph is that the same magnitude and direction of change is noted for both water concentrations and bottom sediment concentrations. This is actually true for all but two of the parameters in Figure 6-4. These two are the organic carbon content parameters, OC_{ssed} and OC_{sed}, and the organic carbon partition coefficient. First, the direction of the change is not the same. Increasing the sorption of dioxin-like compounds onto sediments increases the concentration on sediments (of course), but decreases the concentration in water. For the "low organics" test, water concentration increases by a factor of 2.7 rather than slightly decreases as in Figure 6-4, which for this case, displays only the impact to bottom sediments. For the "high organics" test, water concentrations decrease to 0.60 of what they were in baseline conditions. The high Koc decreases water concentrations to 0.1, and the low Koc increases water concentrations 7 times. Both these trends are distinctly different than the sediment trends; they were left out of the graph in order not to crowd the graph (or require another one be drafted), and also because water concentrations in the sub-ppq range are of minimal concern for exposure.

The comments in the above section concerning the enrichment ratio are pertinent for this algorithm. The comments in the above section concerning the sediment delivery ratio equation, which for this algorithm is used to determine a value for SD_w, also pertains to this algorithm. However, if a site is near a surface water body, it seems that the origins

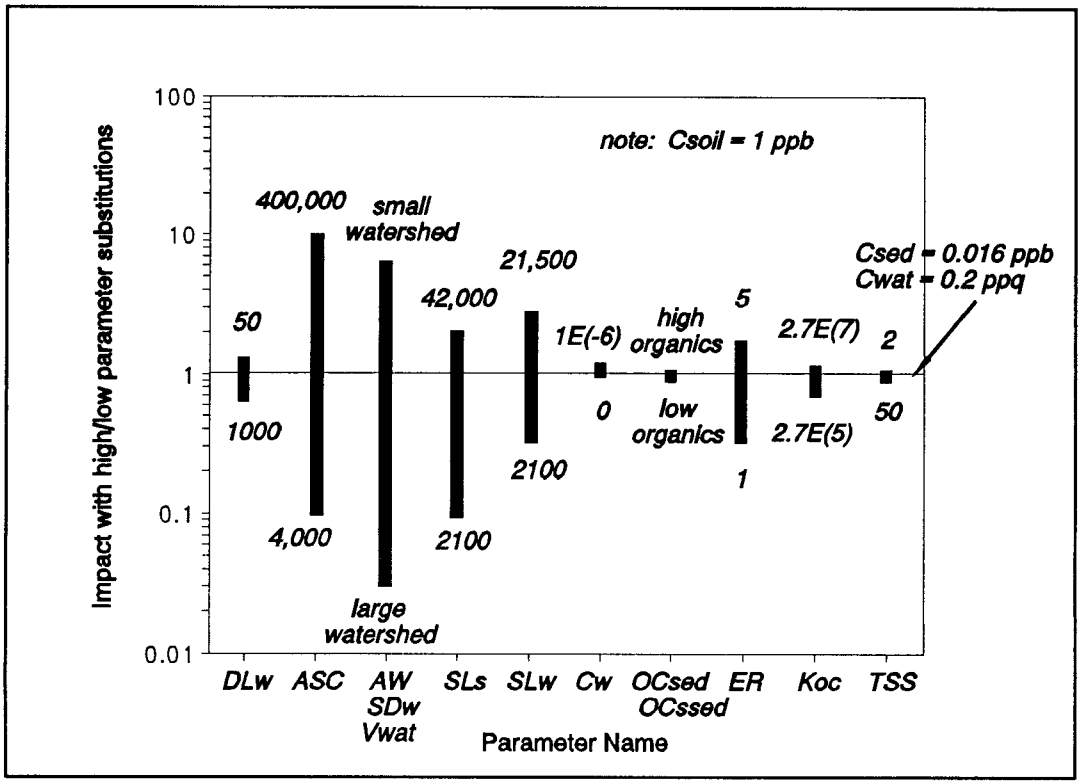

Figure 6-4. Results of sensitivity analysis of algorithms estimating surface water and bottom sediment concentrations resulting from a site of soil contamination.

Parameter Name	Definition	Selected
C_{soil}	concentration in off-site area, μg/kg (ppb)	1.00
C_{sed}	concentration in bottom sediment, μg/kg (ppb)	0.016
C_{wat}	concentration in water, pg/L (ppq)	0.2
DL_w	distance to water body, m	150
ASC	area of off-site contamination, m^2	40,000
A_w	watershed drainage area, ha	4,000
SD_w	watershed sediment delivery ratio, unitless	0.15
V_{wat}	volume of water body, L/yr	$1.5x10^{10}$
SL_s	contaminated site soil loss, kg/ha-yr	21,520
SL_w	watershed soil loss, kg/ha-yr	6,455
C_w	watershed contaminant conc, mg/kg	0
OC_{sed}	bottom sediment organic carbon fraction	0.03
OC_{ssed}	suspended sediment organic carbon fraction	0.05
ER	enrichment ratio, unitless	3
Koc	organic carbon partition coefficient, L/kg	$2.69x10^6$
TSS	total suspended sediment, mg/L	10

of the sediment delivery ratio equation - developed from data on construction sites near surface water bodies - are more appropriate. The key source strength terms tested, the area of contamination, ASC, and the soil loss rate from the site of contamination, SL_s, both have a direct linear impact on the both sediment and surface water concentrations. The other soil loss term, the erosion rate for the watershed, SL_w, also has a direct linear impact. What also appears to be critical in this algorithm is the size of the watershed. The reduction of impacts seen with the "large" watershed necessitated a y-axis spanning two orders of magnitude.

The algorithm seemed fairly insensitive to the remaining four parameters tested. The average watershed concentration, initialized at 0.0 in order to just show the incremental impact from the contaminated site, was increased to 1 ppt. This was also the concentration used to demonstrate the on-site source category, and was identified as a possible background concentration of dioxin-like compounds. If this is a reasonable selection for a background soil concentration, it is seen in Figure 6-4 that background soils have a marginal impact on a water body which is impacted from a site of elevated soil concentrations. The impact of the organic carbon partition coefficient, Koc, on bottom sediments appears small despite the fact that the Koc range spans two orders of magnitude. This is an indication that it is so high for the dioxin-like compounds, that (at least in the algorithm of this assessment), its assignment is not critical for sediment concentration estimations. The same lack of impact appears to be the case for the organic carbon content of water body sediments, and the level of suspended solids in the water column.

6.3.3.5. ***Estimation of fish tissue concentrations*** Fish tissue concentrations for three of the four source categories of this assessment are a direct function of bottom sediment concentrations; the one source category where this is not true is the effluent discharge source category, where fish tissue concentrations are a function of suspended sediment concentrations. As laid out in Section 4.3.4.1, Chapter 4, whole fish tissue concentrations are estimated as: (C_{sed}/OC_{sed}) * BSAF * f(lipid). Therefore, any parameters which impact bottom sediments for the three pertinent source categories impact fish tissue concentrations. All the sensitivities to bottom sediment concentrations displayed in Figure 6-4 and discussed in the above section follow through with fish tissue

concentrations. In Figure 6-5 and from the formulation above, it is seen that fish tissue concentrations are a direct linear function of bottom sediment concentrations. There is the same linear relationship between whole fish tissue concentrations and the other three parameters displayed on Figure 6-5. The linear relationship is direct for C_{oc}, BSAF, and f(lipid), and inverse for OC_{sed}. It is noted that the concentration on bottom sediments, C_{sed}, is impacted by the value assigned to OC_{sed}. However, as described in the previous section, the impact to C_{sed} with changes to OC_{sed} is marginal and in the same direction. For example, reducing OC_{sed} from its baseline of 0.03 to 0.01, reduces C_{sed} by a small amount. The impact to fish tissue from changes in OC_{sed} is more pronounced and essentially in an inverse linear manner, as shown by the formulation above and in Figure 6-5.

6.3.3.6. ***Estimation of on-site air concentrations in the vapor phase*** The impacts of parameter changes for this algorithm are shown in Figure 6-6. These impacts are very similar to those for the algorithm estimating exposure site concentrations from an off-site area of soil contamination, which is shown in Figure 6-1. The principal difference in the algorithms is that the on-site algorithm has a near-field dispersion algorithm, whereas the off-site algorithm has a far-field dispersion algorithm. For all those parameters which only impact the volatilization flux only, the impacts are the same in the on-site and off-site categories. These include the exposure duration, ED, the organic carbon content, OC_{sl}, soil porosity, E_{slp}, particle bulk density, P_{soil}, and the three chemical-specific parameters, Henry's Constant, H, organic carbon partition coefficient, Koc, and molecular diffusivity, D_a. The impact of area is interestingly different in the onsite as compared to the off-site algorithm. For the off-site algorithms, the area term, ASC, impacts the source strength, with an order of magnitude increase in ASC increasing exposure site air concentrations by a little over 2 times (>200%). For the on-site algorithms, the area term, AES, impacts the dispersion algorithm, and the same order of magnitude increase in area only increases concentrations by around 30%.

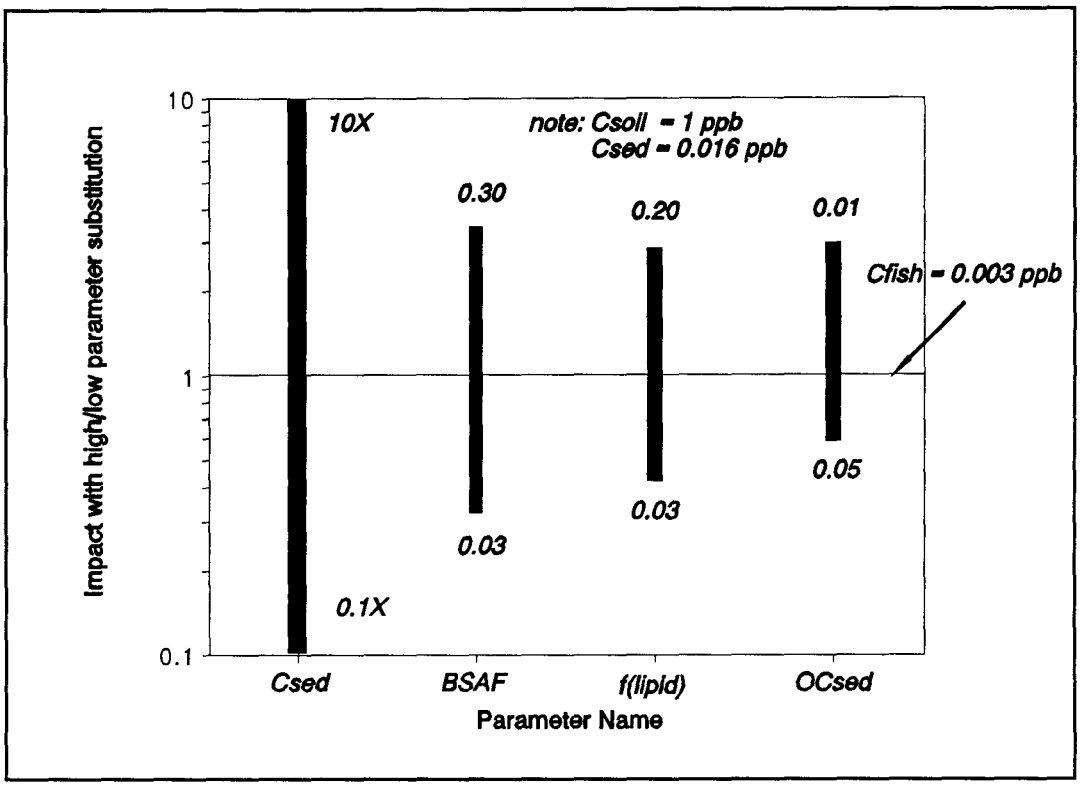

Figure 6-5. Results of sensitivity analysis of algorithms estimating fish tissue concentrations given bottom sediment concentrations.

Parameter Name	Definition	Selected
C_{soil}	soil concentration at off-site area, ng/kg (ppb)	1.00
C_{sed}	bottom sediment concentration, μg/kg (ppt)	0.016
C_{fish}	whole fish concentration, ng/kg (ppb)	0.003
BSAF	biota sediment accumulation factor, unitless	0.09
OC_{sed}	bottom sediment organic carbon fraction	0.03
f_{lipid}	fish lipid fraction	0.07

6.3.3.7. ***Estimation of on-site air concentrations in the particulate phase*** The impacts of parameter changes to this algorithm are shown in Figure 6-7. Like the similarity between on-site and off-site impacts for concentrations in the vapor phase, these

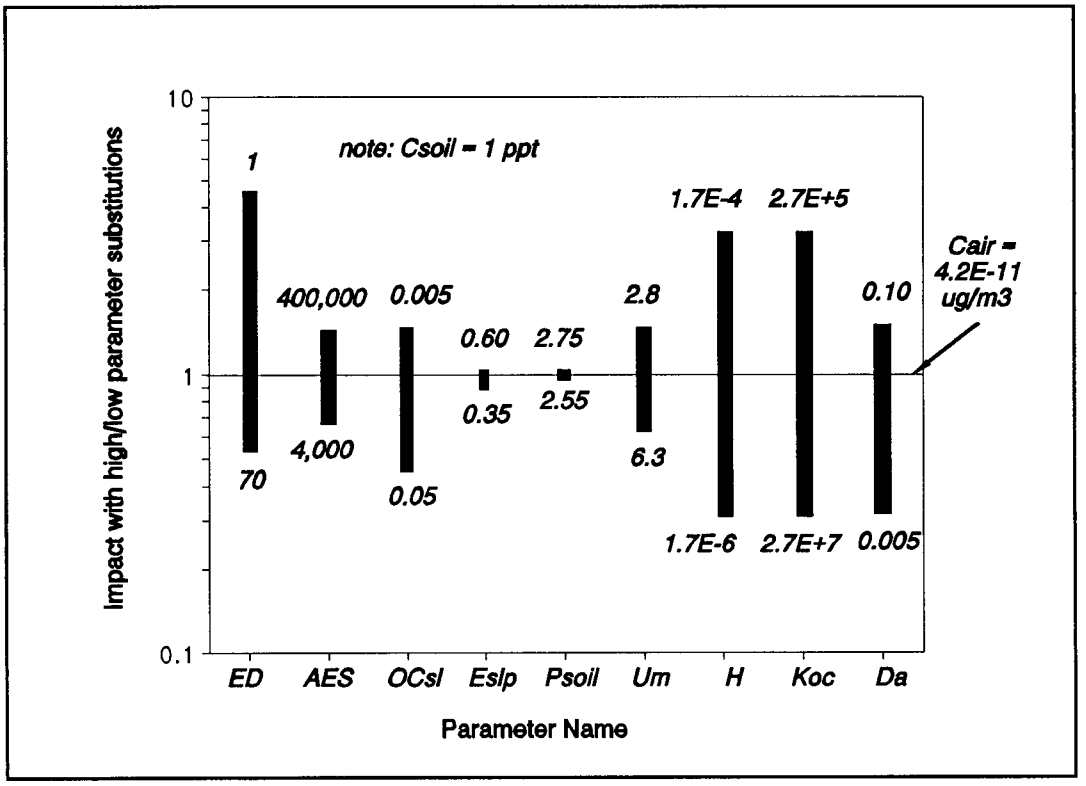

Figure 6-6. Results of sensitivity analysis of algorithms estimating on-site vapor phase air concentrations from on-site soil contamination.

Parameter Name	Definition	Selected
C_{soil}	exposure site soil concentration, ng/kg (ppt)	1.00
C_{air}	exposure site air concentration, $\mu g/m^3$	4.2×10^{-11}
ED	exposure duration, yrs	20
AES	area of exposure site, m^2	40,000
OC_{sl}	soil organic carbon fraction	0.01
E_{slp}	soil porosity, unitless	0.50
P_{soil}	particle bulk den, g/cm^3	2.65
U_m	average windspeed, m/sec	4.0
H	Henry's Constant, atm-m^3/mole	1.65×10^{-5}
Koc	organic carbon partition coefficient, L/kg	2.69×10^6
D_a	molecular diffusivity in air, cm^2/s	0.047

impacts are also similar to those for the algorithm estimating exposure site particle phase concentrations from an off-site area of soil contamination, which is shown in Figure 6-2. And also similar is the difference in the role of the area terms for the off-site versus the

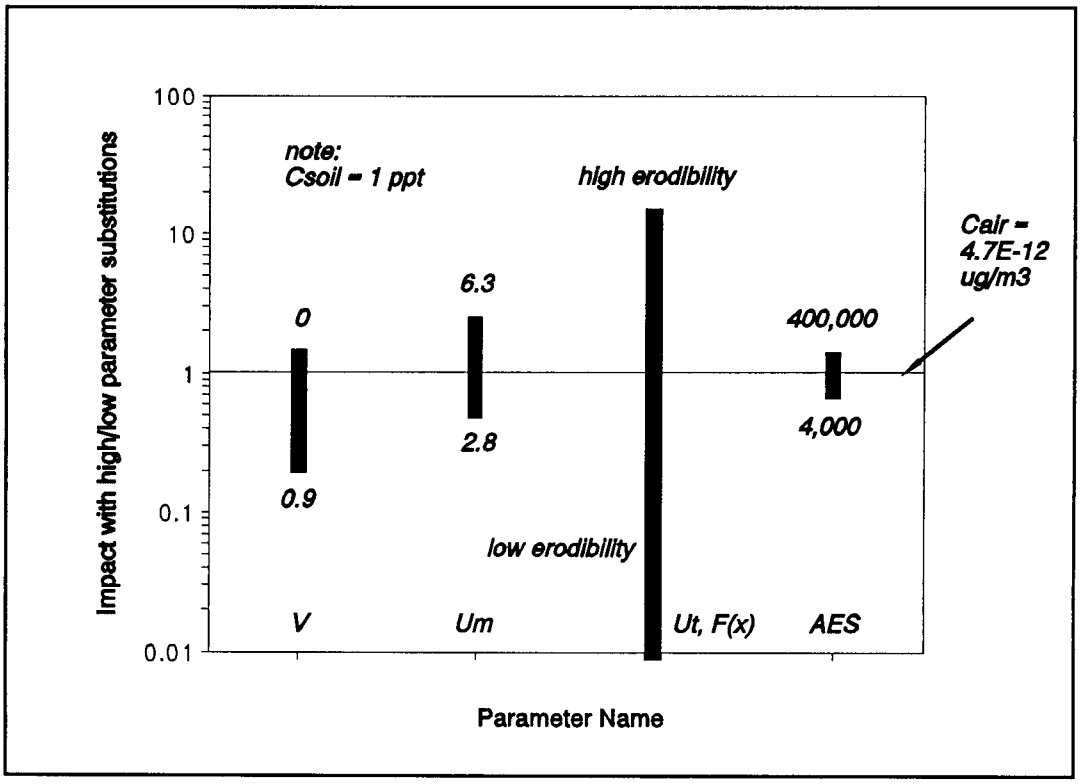

Figure 6-7. Results of sensitivity analysis of algorithms estimating on-site particle phase air concentrations from on-site soil contamination.

Parameter Name	Definition	Selected
C_{soil}	exposure site soil concentration, ng/kg (ppt)	1.00
C_{air}	exposure site air concentration, $\mu g/m^3$	4.7×10^{-12}
V	fraction of vegetative cover, onsite, unitless	0.5
U_m	average windspeed, m/sec	4.0
U_t	threshold wind speed, onsite, m/sec	6.5
F(x)	model-specific parameter, offsite	1.05
AES	area of exposure site, m^2	40,000

on-site particulate algorithms; the area term in the off-site algorithms impacts the source strength and in the on-site algorithm, it impacts the dispersion.

6.3.3.8. ***Vapor-phase transfers and particle phase depositions to above ground vegetations*** Concentrations in above ground vegetations are a function of vapor-phase transfers and particle phase depositions. Vapor and particle reservoirs originate from

contaminated soils as volatilization and wind erosion, respectively. Atmospheric dispersion and deposition modeling delivers concentrations and depositions, respectively, from a stack to a site of exposure. This section focuses on the sensitivities of the transfer algorithms for the contaminated soils source categories. The same general trends would occur for the off-site soil and the stack emission source categories. The principal difference is in the relative proportions of the contaminant which are in the vapor and particle phases. As discussed below, more contaminant is delivered via particle depositions for the stack emission source category as compared to the soil contamination source categories.

Vapor transfers and particle depositions are evaluated in Figures 6-8 and 6-9. Three vegetations are modeled for this assessment, including vegetables/fruit, grass, and cattle fodder. The latter two are for the beef/milk bioconcentration algorithm, the first for human exposure via consumption of unprotected fruits or vegetables.

For vapor-phase impacts shown in Figure 6-8, it would appear that changes to total vegetation concentrations are critically a function of parameters specific to the vapor transfer algorithm. There is between one and two orders of magnitude range of plant concentrations predicted over the range of the vapor phase transfer coefficient, B_{vpa}, tested. This parameter is uncertain as well as very influential in this methodology. Also influential and uncertain is the empirical parameter introduced to model the difference between the leaves of the experiment for which B_{vpa} was developed and the bulky vegetation to which the B_{vpa} is applied, the VG parameters (VG_{veg}, VG_{gr}, and VG_{fod}). The need for such a correction factor is justified given the evidence that dioxin-like compounds to do not translocate into vegetations. The leaf concentrations in the experiments for which B_{vpa} was derived are likely to be analogous only to the outer layer concentrations in bulky vegetations, not the whole plant (or whole fruit/vegetable) concentrations. This empirical parameter was set to 0.01 for bulky fruits/vegetables, but was set at 1.00 for grass, under the assumption that grass is similar to leaves, and 0.50 for cattle fodder, which is assumed to contain some bulky (grains) and leafy (hay) vegetations. In any case, the impact to vegetation concentrations with changes to the VG parameters is significant and displayed on Figure 6-8.

A dry weight to fresh weight conversion factor, FDW, is required for estimating above ground concentrations of vegetable/fruits. This is because the algorithms estimate

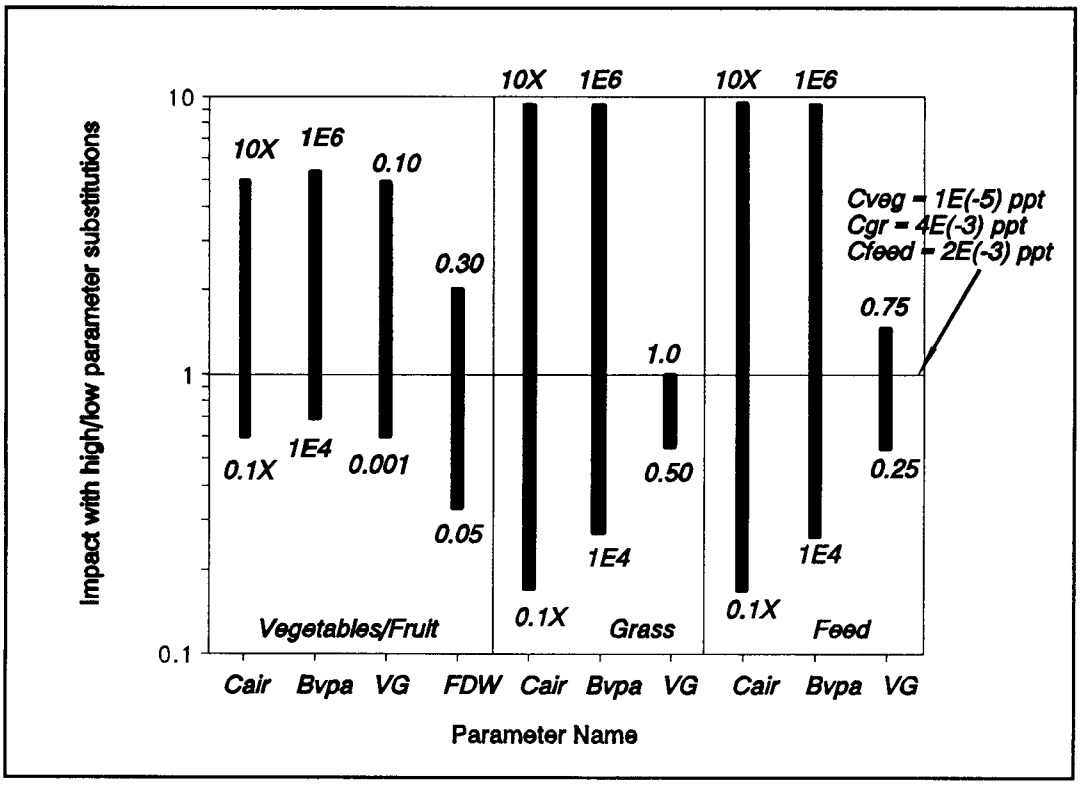

Figure 6-8. Results of sensitivity analysis of algorithms estimating above ground vegetation concentrations due to vapor phase transfers.

Parameter Name	Definition	Selected
C_s	soil concentration, ng/kg (ppt)	1.00
C_{air}	vapor-phase air concentration, $\mu g/m^3$	$4x10^{-11}$
C_{veg}	vegetable/fruit concentration, ng/kg fresh wt	0.00001
C_{gr}	grass concentration, ng/kg dry wt	0.004
C_{fod}	fodder concentration, ng/kg dry wt	0.002
B_{vpa}	air-to-leaf transfer factor, unitless	$1.00x10^5$
VG_{veg}	veg/fruit air-to-leaf correction factor, unitless	0.01
VG_{gr}	grass air-to-leaf correction factor, unitless	1.00
VG_{feed}	feed air-to-leaf correction factor, unitless	0.50
FDW	dry to fresh weight conversion	0.15

above ground vegetative concentrations on a dry weight basis, and the concentrations need to be diluted since fruit and vegetable consumption are given in this assessment on a fresh weight basis. The impact to concentrations is direct and linear, and since the range of likely FDW is small, the impact is small as well. This parameter is also required for

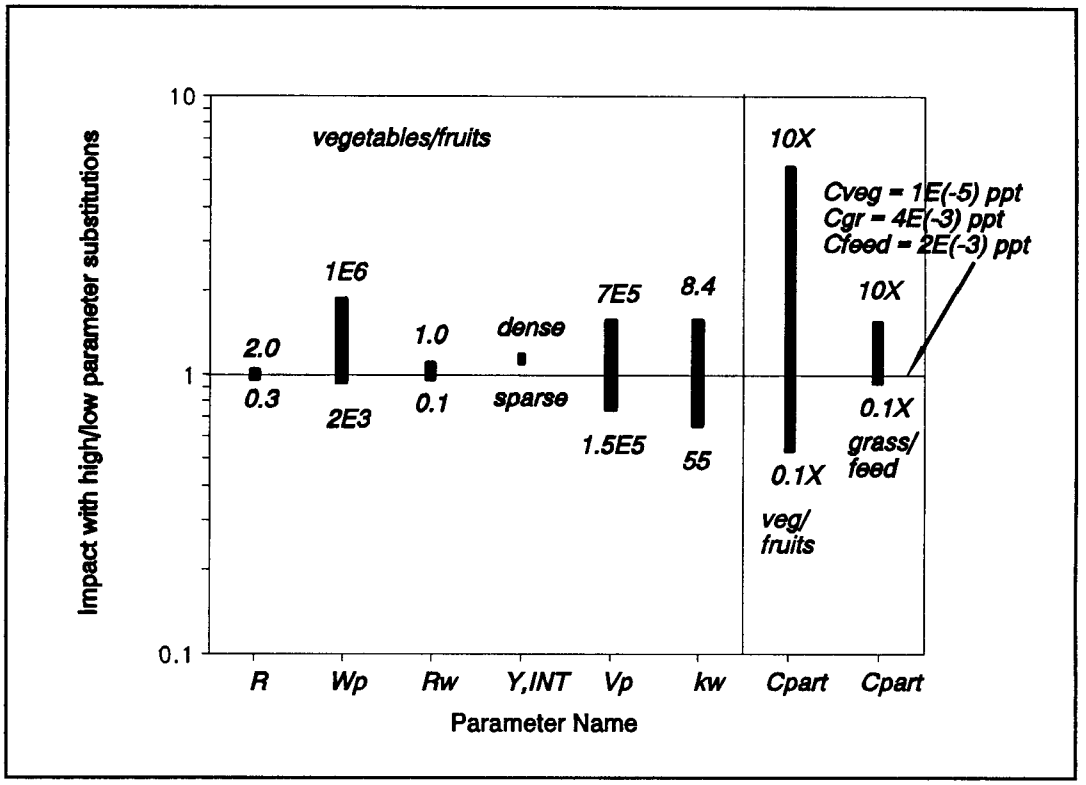

Figure 6-9. Results of sensitivity analysis of algorithms estimating above ground vegetation concentrations resulting from particle phase depositions.

Parameter Name	Definition	Selected
C_s	soil concentration, ng/kg (ppt)	1.00
C_{part}	particle-phase air concentration, $\mu g/m^3$	$5x10^{-12}$
C_{veg}	vegetable/fruit concentration, ng/kg fresh wt	0.00001
C_{gr}	grass concentration, ng/kg dry wt	0.004
C_{fod}	fodder concentration, ng/kg dry wt	0.002
R	annual rainfall, m/yr	1.0
W_p	washout factor, unitless	$5x10^4$
R_w	rainfall retention factor, unitless	0.3
Y_{veg}	vegetable yield, kg/m^2 fresh	7.8
INT_{veg}	vegetable intercept fraction, unitless	0.48
V_p	particle deposition velocity, m/yr	$3.2x10^5$
kw	plant wash-off rate constant, yr^{-1}	18.01

the particle deposition algorithm, but is left out of Figure 6-9 for clarity. In fact, FDW is applied once vapor phase and particulate phase contributions to vegetable/fruit

concentrations are already summed; in other words, it is not tied to either the vapor or particle phase algorithms.

The impact of all the particle phase parameters to overall plant concentrations is less than that of vapor transfers, as seen in a comparison between Figures 6-8 and 6-9. For the parameters including rainfall amount (R), washout factor (W_p), denseness of vegetation (as modeled by yield, Y, and intercept fraction, INT), velocity of particle deposition (V_p), and plant weather dissipation rate, kw, results in Figure 6-9 are for vegetable/fruits and not grass or fodder. Vegetables/fruits are more impacted by particle depositions than grass/fodder, and as seen, there is less than half an order of magnitude impact from the range of values for these parameters tested. The impact of depositions on vegetable/fruit concentrations occurs because the correction factor for vegetables, VG_{veg}, is equal to 0.01, which minimizes the vapor-phase contributions to vegetable concentrations in comparison to the contributions of the vapor phase concentrations for grass and fodder concentrations, which have correction factors of 1.00 (for grass) and 0.50 (for fodder).

Model results on the proportion of above ground plant concentrations that are due to air-to-leaf transfer and particulate deposition were examined for the soil contamination and stack emission source categories for 2,3,7,8-TCDD, and results are summarized in Table 6-2. Results show that vapor phase transfers tend to dominate vegetative concentrations, although particle phase concentrations are important for bulky fruits and vegetables. Again, the critical difference in the two plant types is the use of an empirical VG which reduces the magnitude of vapor phase impact for bulky vegetations. Results also show that the relative impact of vapors and particles is a function of distance for the stack emission source category. For the central stack emission Scenario, #4, where the site of exposure is 5000 meters from the stack, vapor transfers generally have more of an impact to vegetation as compared to the high end Scenario, #5, where the site of exposure is 500 meters away.

It is possible that the impact of particle depositions is being underestimated, for at least four reasons:

- The wind erosion algorithm estimating air-borne contaminant concentrations for soil contamination source category only estimates concentrations of PM-10, or inhalable size particulates, those 10 μm size diameter and less, while the COMPDEP

Table 6-2. Contribution of above ground vegetation concentrations of 2,3,7,8-TCDD from air-to-leaf transfers and particulate depositions.[1]

Description[2]	Air-to-leaf Transfers	Particulate Deposition
Scenarios 2: On-site Soil Source Category		
vegetables/fruit	49	51
pasture grass	94	6
fodder	95	5
Scenarios 3: Off-site Soil Source Category		
vegetables/fruit	68	32
pasture grass	97	3
fodder	98	2
Scenarios 4: Stack Emission Source Category		
vegetables/fruit	55	45
pasture grass	94	6
fodder	95	5
Scenarios 5: Stack Emission Source Category		
vegetables/fruit	32	68
pasture grass	89	11
fodder	88	12

[1] Results are in percent of total contribution.

[2] Scenario 2 demonstrated the "on-site" source category, where soil at the exposed individuals home was contaminated at a level of 1 ng/kg (ppt) 2,2,7,8-TCDD; Scenario 3 demonstrated the "off-site" source category, where soil at a contaminated site 150 meters away was initialized at 1 μg/kg (ppb) 2,3,7,8-TCDD; Scenarios 4 and 5 demonstrated the stack emission source category - in Scenario 4, the exposure site was 5000 meters from the emitting stack, and in Scenario 5, the exposure site was 500 meters from the stack.

model considers all size particulates emitted from stacks. Larger size air-borne particulates, while not inhalable, would deposit onto vegetation.

- For the off-site soil source category which involves soil contamination distant

from the site of exposure, only the off-site locations provide the source of air-borne particulates. Meanwhile, algorithms are in place estimating exposure site contamination, albeit to thin surface levels. Certainly, the reservoir of air-borne particulates depositing onto vegetation would also include contributions from where the vegetation is located and the surrounding land, not only from the area of soil contamination.

- For the stack emission source category, resuspension of deposited particles and deposition onto plants is not considered. This omission is similar to the omission noted in the bullet above.
- The modeling does not consider the splash effect of rainfall, which would deposit soil onto the lower parts of plants. This would make the most impact for grass and for vegetables near the ground surface such as lettuce.

The precise impact of these factors might be investigated more fully in a later assessment with additional models. Tests were run for this sensitivity analysis by increasing the amount of particulate phase contaminants depositing onto vegetation by an order of magnitude to the on-site demonstration scenarios, without changing the vapor phase contributions. The vapor phase/particulate phase contributions to above ground fruits and vegetables, originally 49%/51% (from Table 6-2 above), changed to 9%/91% with an order of magnitude increase in particulate phase contributions. Vegetable concentrations increased by a factor of 6. The impact was less for grass and fodder, with concentrations increasing by a factor of 1.7. The impact was comparable for the off-site soil contamination source category.

One possible theoretical shortcoming of the plant concentration algorithm for the soil source categories is that contaminants which volatilize from soil are assumed to remain in the vapor phase. Given the affinity of the dioxin-like compounds to soil, it seems possible, if not likely, that a portion of the volatilized flux will sorb to airborne particles and become part of the particulate reservoir. As discussed in Chapter 3, Section 3.4.5.5, Bidleman (1988) provides an algorithm to estimate what fraction of a total "available" reservoir of airborne contaminant would sorb to airborne particles. Assuming that volatilized residues would comprise an available reservoir, this sorbed fraction ranges from 10 to 70% (roughly), depending on the density of particles in the air. A test was conducted to see what impact partitioning of the vapor phase reservoir partly into the

particulate reservoir would have on vegetative concentrations. First, 25% of the volatilized vapor phase reservoir was transferred to the particulate reservoir, and then 50%was transferred. The results of this test are shown in Table 6-3.

Vapor phase transfers still explain more of the grass and fodder concentration than particle depositions, with 60-65% of the plant concentration explained by vapor transfers when 50% of the reservoir is transferred to the particle phase reservoir. The overall impact to grass and fodder concentrations, however, is small, with only an 21-26% reduction when 50% of the vapors are transferred. As has been discussed, particle depositions are important for vegetable/fruit concentrations. Therefore, increasing the particle phase reservoir while decreasing the vapor phase reservoir greatly increases the dominance of particle impacts to vegetations - 92% of vegetable/fruit concentrations are due to particle impacts when 50% of the vapor phase reservoir is transferred, and the vegetable/fruit concentrations increase by about a factor of 3 with this transfer.

It might be concluded from this test that modeling the sorption of volatilized vapor-phase dioxin-like contaminants would: 1) mostly impact the inhalation exposures, with vapor phase exposures being reduced equal to the amount modeled to move into the particulate reservoir and particulate inhalations increase by the additional amount added to the particulate reservoir - total vapor plus particle phase inhalation exposure would not change, 2) tend to increase the concentrations in vegetables/fruits with the subsequent impact on exposures from consumption of fruit and vegetables, and 3) apparently have little overall effect for grass and fodder concentrations, and hence little effect on beef and milk concentrations.

6.3.3.9. *Estimation of below ground vegetation concentrations*

One important factor to note up front about below ground vegetable concentrations as compared to above ground vegetable concentrations (no underground fruits are assumed in this assessment) is that below ground vegetable concentrations are about two orders of magnitude higher than above ground vegetable concentrations for the soil contamination demonstration scenarios. Since no fruit is assumed to be grown underground, this difference does not affect fruit ingestion exposures. However, 28 g/day of a total of 106 g/day vegetable ingestion is assumed to be underground vegetables. Given the difference in concentration estimations, below ground vegetables explain 97%

Table 6-3. Results of the sensitivity test of modeling vapor/particle partitioning for volatilized residues (note: soil concentration equals 1 ppt in tests below).

Vegetation	Percent contribution of vegetative concentration due to: Vapor transfers	Particle depositions	Vegetative Conc., ppt	Percent Change from Baseline
I. Baseline				
Veg/fruit	49	51	0.0000109	
Grass	94	6	0.0038	
Fodder	95	5	0.0019	
II. 25% transfer of vapor phase to particulate reservoir				
Veg/fruit	18	82	0.0000221	+103
Grass	79	21	0.0033	-13
Fodder	83	17	0.0016	-16
III. 50% transfer of vapor phase to particulate reservoir				
Veg/fruit	8	92	0.0000333	+206
Grass	60	40	0.0030	-21
Fodder	65	35	0.0014	-26

of the total exposure via ingestion of impacted vegetables. Sensitivity of underground vegetable concentrations to parameter changes for the soil contamination source category becomes important from this perspective.

On the other hand, the trend for the stack emission source category is exactly the opposite - above ground vegetable concentrations exceed below ground vegetable concentrations by two orders of magnitude. If air and soil concentrations were equal (or proportional) for the demonstration of both source categories, than the impact to vegetations would be equal (or proportional). Obviously, that was not the case. The soil concentration of 2,3,7,8-TCDD of 1 ppt (ng/kg) for the on-site soil source demonstration scenarios translated to a total airborne reservoir of 5E(-11) $\mu g/m^3$ (vapor plus particle phase reservoirs). For the stack emission demonstration scenario 5, where the exposure

site was 500 meters from the stack emission source, the vapor plus particle phase concentration of 2,3,7,8-TCDD was 1.4E(-12) $\mu g/m^3$, which is reasonably similar to the air concentration of 5E(-11) $\mu g/m^3$ modeled from a soil concentration of 1 ppt. However, the soil concentration for the stack emission demonstration scenario for the 20-cm mixing zone depth used for underground vegetation concentration was 0.00005 ppt, more than 4 orders of magnitude lower than the 1 ppt level for the soil contamination source categories. Therefore, below ground vegetables for the stack emission source category will be more than 4 orders of magnitude lower for the stack emission source category as compared to the soil source category.

This question now is whether this is a reasonable outcome. Should deposition from an airborne reservoir in the range of 10^{-11} $\mu g/m^3$ 2,3,7,8-TCDD result in a soil concentration closer to 1 ppt than 0.00005 ppt? Is the algorithm estimating soil impacts from depositions inherently underestimating soil concentrations? Likewise, should emissions from soils at 1 ppt result in air concentrations higher than 10^{-11} $\mu g/m^3$? Is the soil emission/dispersion algorithms inherently underestimating air concentrations? If air to soil impacts were being underestimated, and/or if soil to air impacts were being underestimated, than more correct model performance would lead to more equivalent outcomes with regard to vegetation impacts. As stated above, if soil and air concentrations for each demonstration scenario were equal (or proportional), then impacts to vegetation would be equal (or proportional). Air-to-soil and soil-to-air model performances are now examined briefly.

In Section 7.2.3.1 in Chapter 7, the capability of the deposition algorithm to estimate soil concentrations is examined. The hypothesis examined is that air concentrations of 2,3,7,8-TCDD in a rural setting should correlate to untilled soil concentrations in a rural setting, and that hypothesis can be evaluated using the deposition algorithms of the stack emission source category. The conclusion from that section was that it would appear that the deposition algorithm may, in fact, be underestimating soil concentrations. The amount of underestimation was speculated to be about one order of magnitude. Uncertain model parameters identified in that section were the untilled mixing zone depth, the velocity of deposition, and the dissipation half-life for depositing residues. It is also noted that the algorithms of this assessment do not consider detritus production as an input to the soil reservoir. If the deposition algorithm is indeed underestimating soil

concentrations, than in fact an airborne reservoir on the order of 10^{-11} $\mu g/m^3$ might translate to a concentration higher than 0.00005 ppt, although a one order of magnitude increase to 0.0005 ppt is still much less than 1 ppt.

One could also even question the use of a contaminant dissipation rate which is applied to depositing residues which are assumed to be tilled in a home garden or an agricultural field. Routes of dissipation for dioxin-like compounds are physical transport, such as wind or soil erosion, or volatilization, or chemical, such as photolysis, which is the only degradation route shown to be relevant to these compounds. These are phenomena relevant to surface residues, not buried residues. The use of a 10-year dissipation rate for both tilled (a mixing zone depth of 20 cm) and untilled (a mixing zone depth of 1 cm) settings could be a fundamental flaw in the approach - perhaps a dissipation rate should only be applied to untilled soil impacts. In addition to the argument presented above, this is another reason suggesting tilled soil concentrations resulting from stack emissions should be higher than are estimated in this assessment, and hence underground vegetable concentrations should be higher than are estimated in this assessment.

The other hypothesis is that the soil to air algorithms of the soil source categories are underestimating air concentrations. In fact, evidence developed in other parts of this document suggest that air concentrations resulting from soil concentrations may be underestimated. One piece of evidence discussed in different sections of this Volume is that air concentrations modeled to result from background soil concentrations are lower than air concentrations measured in pristine settings. In one literature article measuring concentrations in an area described as a "remote countryside" in Sweden (Broman, et al. 1991), air concentrations of 2,3,7,8-TCDD were measured at $2*10^{-10}$ $\mu g/m^3$. The air concentration of 2,3,7,8-TCDD modeled in this assessment from a 1 ppt background soil concentration of 2,3,7,8-TCDD is nearly an order of magnitude lower than that at $4*10^{-11}$ $\mu g/m^3$. This suggests that the models of this assessment underestimate air concentrations resulting from releases from soils. Another piece of evidence is developed in Section 7.2.3.8, which compares plant:soil ratios as determined by the model with those developed in experimental and field conditions. The soil contamination models of this assessment appear to be leading to above ground plant:soil ratios that are 1-2 orders of magnitude lower (i.e., plant concentrations may be 1-2 orders of magnitude underestimated) than analogous ratios for experiments where soil can be surmised to be

the only source of dioxin. One possible explanation offered is that the air concentrations are being underestimated.

If air concentrations resulting from soil concentration would be modeled to be higher than they are currently, then the dichotomy identified above would be narrowed. If soil concentrations resulting from air depositions are modeled to be higher than they are currently, then the dichotomy identified would be even further narrowed. Evidence summarized above suggests that both are plausible. Clearly, more evaluation of the soil to air algorithms of the soil contamination source categories and the air to soil algorithms of the stack emission source category, is warranted.

Given a soil concentration, in any case, the impacts of parameter changes for the algorithm predicting concentrations in underground vegetables are shown in Figure 6-10. The two orders of magnitude range for the root concentration factor, RCF, translates to a two order of magnitude range of concentration estimation. The same is true for the empirical correction factor applied to below ground vegetables, VG_{bg}, and the organic carbon partition coefficient, Koc. A smaller impact is noted for the organic carbon fraction of soil, OC_{sl}. Koc and OC_{sl} are required for this algorithm because vegetable concentrations are a function of soluble phase concentrations, not soil concentrations. Increasing Koc and/or increasing OC_{sl} results in decreasing the water concentrations, explaining why the high values for these parameters reduce vegetable concentrations.

One final note is that the dry to fresh weight ratio, FDW, is not on this figure, while it does appear on Figure 6-8. This is because the RCF was developed on fresh weight basis already, so no conversion to a fresh weight is required.

6.3.3.10. ***Beef fat concentration estimation*** The impacts of parameter changes to beef fat concentration estimation for the soil source category is shown in Figures 6-11.

First, it is noted that changes in soil concentration result in linear changes in beef concentrations - a ten-fold increase in soil concentration results in the same ten-fold increase in beef concentration. This is because changes to soil concentration alone result in the same proportional change in the concentrations estimated to be in grass and cattle feed. Changes to grass and feed concentrations with no change in soil concentrations (which could result from different parameter selections in estimating grass and feed concentrations) do not result in as substantial a change - a tenfold increase in vegetation

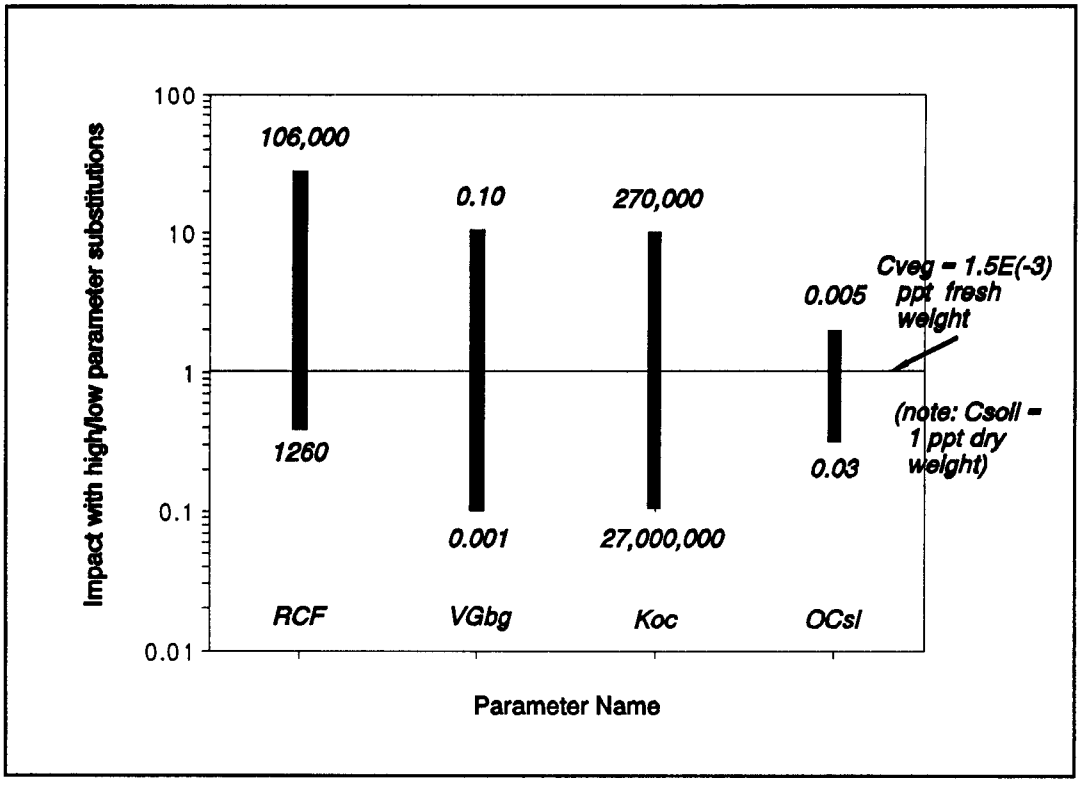

Figure 6-10. Results of sensitivity analysis of algorithms estimating below ground vegetation concentrations resulting from soil to root transfers.

Parameter Name	Definition	Selected
C_{veg}	vegetable concentration, ng/kg (ppt) fresh wt.	0.0015
C_{soil}	soil concentration, ng/kg (ppt)	1.00
VG_{bg}	below ground veg. correction factor, unitless	0.01
OC_{sl}	soil organic carbon fraction	0.01
RCF	root bioconcentration factor, unitless	3,916
Koc	organic carbon partition coefficient, L/kg	2.69×10^6

concentrations only increases beef concentration by a factor of two; a tenfold decrease in vegetation concentration only reduces beef fat concentrations by about 20%.

This is a key and insightful result. If the models and their parameterization are valid, it indicates that the bulk of impact to beef and milk fat is from ingestion of soil for the soil source categories. With a closer look at the results for the demonstration of the on-site soil category, demonstration scenario #2, it is found that soil ingestion explains 90% of the beef fat concentration, despite being only 4% of their diet. Grass (48% of

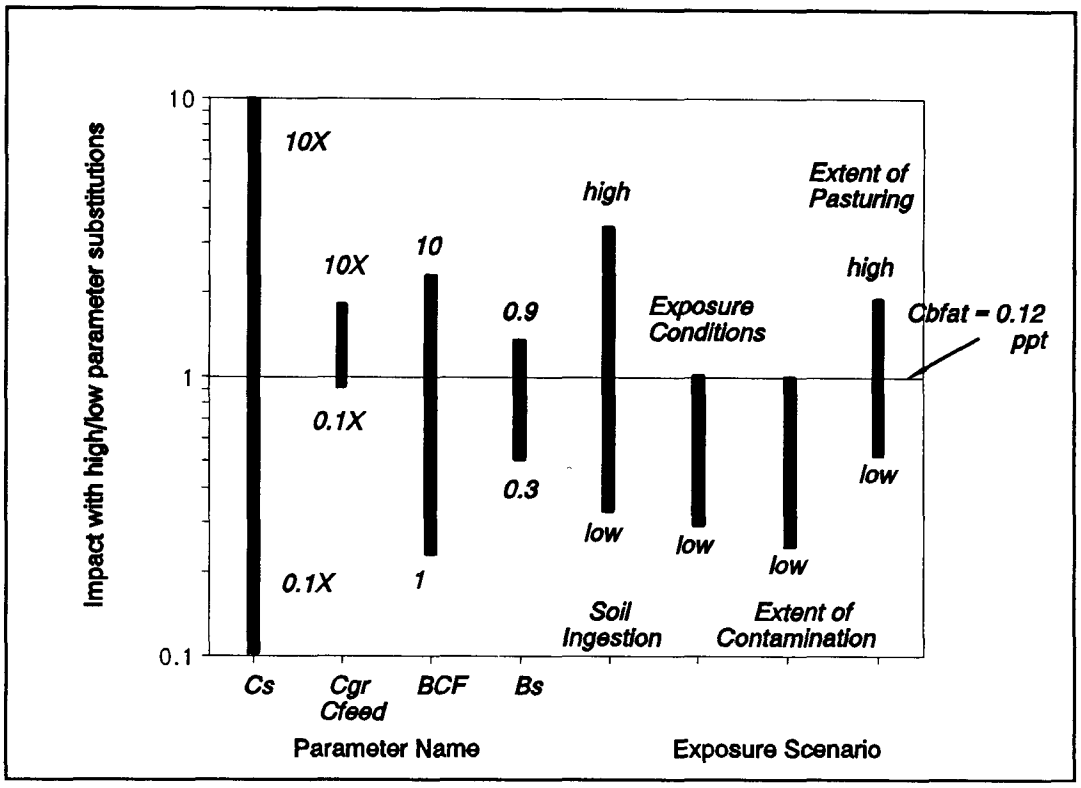

Figure 6-11. Results of sensitivity analysis of algorithms estimating beef fat concentrations resulting from soil contamination.

Parameter Name	Definition	Selected
C_s	soil concentration, ng/kg	1.00
C_{gr}	grass concentration, ng/kg dry wt.	0.04
C_{feed}	feed concentration, ng/kg dry wt.	0.02
C_{bfat}	beef fat concentration, ng/kg	0.12
BCF	beef/milk bioconcentration factor, unitless	4.32
B_s	bioavail. of cont. on soil relative to vegetation	0.65
BCSDF	beef cattle soil diet fraction, unitless	0.04
BCFDF	beef cattle feed diet fraction, unitless	0.48
BCGDF	beef cattle grass diet fraction, unitless	0.48
BCGRA	beef cattle fraction of cont. grazing land	1.00
BCFOD	beef cattle fraction of cont. feed	1.00

their diet) and feed (48%) of their diet explain 7 and 3% of beef fat concentrations. The story is the same for milk fat concentrations. Soil explains 87% of the milk fat concentrations, despite being only 2% of the dairy cattle's diet. Feed (90% of their diet)

and grass (8%) explain 11 and 2% of milk fat concentrations.

Changes to other parameters, or groups of parameters, result in expected changes to beef fat concentrations. A doubling (roughly) of the assigned beef bioconcentration factor, BCF, from 4.3 to 10 doubles beef concentrations; reducing it to 1 reduces concentrations by a factor of 5. The soil bioavailability factor, B_s, has a rather small impact around its 0.3 to 0.9 range. The other tests run on the beef and milk algorithm looked at cattle dietary exposures as modeled by the diet fraction parameters, and the parameters describing the fractions of intake that are contaminated. In one test, patterns of soil ingestion were examined. As noted above, soil ingestion is critical for both beef and milk concentration estimation. In the high and low soil ingestion tests, diet fractions were altered to reflect high (15% of the beef cattle diet) and low (1%) soil ingestion patterns. The impact is nearly linear, with an increase from 4 to 15% nearly quadrupling beef fat concentrations, and a reduction from 4 to 1% reducing concentrations by almost 75%. The same trend is seen with changes in dietary exposures to reflect a lifetime of pasturing versus minimal lifetime pasturing. A lifetime of pasturing translated to an assumption of 90% pasture grass intake, and a greater proportion of incidental soil ingestion, from 4 to 8%. With this rise in soil ingestion mainly, the beef fat concentration doubled. Similarly, with minimal pasturing and half as much soil ingestion at 2%, beef fat concentrations halved. A different test described a condition where exposure to contaminated dry matter was minimized. This was modeled with two modifications: 1) the soil ingestion patterns were low as modeled in the previous test and 2) only 25% of the feed was assumed to be impacted by the soil contamination - i.e., 75% of it was residue free perhaps from being externally purchased and not impacted by soil contamination. The impact of the feed assumption was insignificant, and the fact that beef concentration were reduced by about 75% was due mainly to the reduced soil ingestion assumed - 1%, down from the initially assumed 4%. The final test was termed, low extent of contamination. In this test, 75% of the grazing land was residue free, which reduced both soil and pasture grass concentrations by 75%, and 75% of the feed was also assumed to be residue free. With 75% reductions in concentrations in dry matter intake, beef concentrations both were reduced by the same 75%. These tests demonstrate the importance of assumptions on cattle dietary exposures on estimated beef concentrations, and by analogy, milk concentrations.

6.3.3.11. *Vegetable and beef fat concentrations resulting from stack emissions*

Results of sensitivity analysis of algorithms estimating above and below ground vegetables and beef fat concentrations resulting from stack emissions are shown in Figure 6-15. This examination only looks at impacts that are specific to the stack emission source category; earlier sections described impacts with the several other parameters required for these biota impact algorithms.

First, it should be noted that the trends for soil impacts are the same as those for below ground vegetables. This is because underground vegetable concentrations are a direct linear function of soil concentrations. Second, trends for milk fat concentration are not exactly the same, but very similar to those of beef fat. The only difference in the algorithms estimating beef and milk fat concentrations are the assumptions concerning cattle exposure. The general trends discussed below regarding the impact of soil, the distance from the stack, and the vapor/particle partitioning also occur with milk fat concentration estimation.

One trend to easily spot and explain is the impact of the assumption on the no-till mixing depth. This impacts beef concentrations because soil ingestion by cattle is assumed to occur on untilled soil. This test indicates that the increment of beef concentration due to soil ingestion by cattle is small; that diluting depositing residues into either 1 or 5 cm mixing depth does not impact results. This trend is different then that of the soil source categories, where soil ingestion is critical to beef/milk concentrations. The following shows the percent of beef and milk concentrations that are due to soil, pasture grass, and feed ingestion in example scenarios for on-site soil contamination (Scenario #2) and the stack emissions (Scenario #5):

	Percent impact due to ingestion of:		
Description	Soil	Grass	Feed
Soil contamination, beef	90	7	3
Soil contamination, milk	87	2	11
Stack emission, beef	5	59	32
Stack emission, milk	3	15	82

As seen here, soil only accounts for 5 and 3% of beef and milk concentration impacts from stack emissions in the example scenario. The principal cause for this difference in

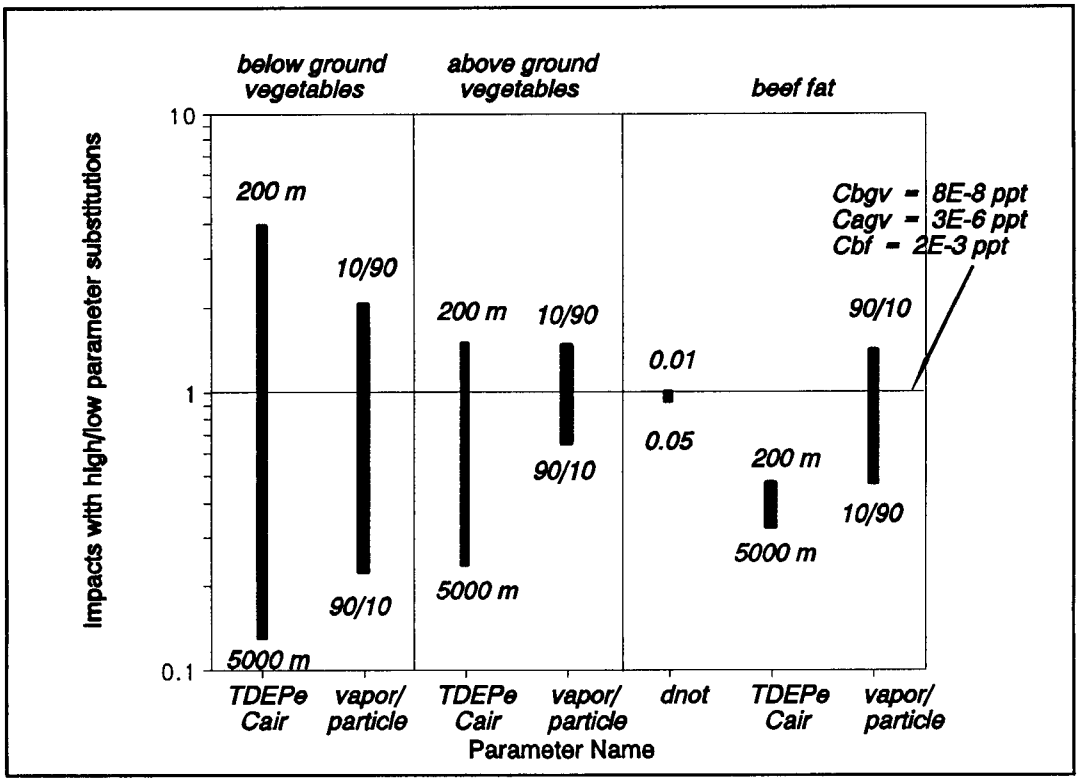

Figure 6-12. Results of sensitivity analysis of algorithms estimating above and below ground vegetation, and beef fat concentrations resulting from stack emissions.

Parameter Name	Definition	Selected
C_{bgv}	below grd. veg. conc., fresh wt, ng/kg (ppt)	$8*10^{-8}$
C_{bgv}	above grd. veg. conc., fresh wt, ng/kg (ppt)	$3*10^{-6}$
C_{bf}	beef fat concentration, ng/kg (ppt)	0.002
$TDEP_e$	total dep, dry + wet, on exp. site, $\mu g/m^2$-yr	$1.2*10^{-6}$
C_{air}	vapor phase concentration at exp. site, $\mu g/m^3$ (note: 200 and 5000 m refers to use of $TDEP_e$ and C_{air} at these distances in sensitivity testing)	$7.6*10^{-12}$
vapor/particle	percent of contaminant arriving at exposure site assumed to be in vapor and particle phases	55%/45%
d_{not}	no-till depth at exposure site, m	0.01

trends between the soil source and stack emission source is the differences in the soil to air trends for the soil source category versus the air to soil trends for the stack emission source category. The dichotomy in these model performances was discussed in Section

6.3.3.9 above. Briefly, emissions from the soil source starting with a 1 ng/kg (ppt) soil concentrations resulted in air concentrations in the order of 10^{-11} $\mu g/m^3$. The demonstration of the stack emission source also led to total air concentrations on the order of 10^{-11} $\mu g/m^3$ at the farm site of exposure. However, depositions onto soils for the stack emission demonstration scenario led to no-till (1 cm mixing depth) soil concentrations on the order of 10^{-3} ng/kg. Since the soil source demonstration had much higher soil concentrations, its contribution to beef and milk concentration was higher as compared to the stack emission source category.

The other two model trends evaluated included impacts of different distances away from the stack emission, and the vapor/particle partitioning at the stack. The farm was assumed to be 500 meters from the stack for the high end demonstration of the stack emission source category. Nearer to the stack at 200 meters, ambient air concentrations and dry deposition amounts were lower, but wet deposition was at its maximum. One effect of this was that vegetable concentrations increased. Below ground vegetables increased by about a factor of 4, due to the same increase in soil concentration as a result of much higher wet deposition. Above ground vegetation increased by about 50%. As seen on Table 6-2, particle depositions dominated above ground vegetable/fruit concentrations. Therefore, an increase in overall particle depositions due to an increase in wet depositions led to increased above ground vegetable/fruit concentrations. However, the trend was not the same for beef and milk fat. As seen on Table 6-2, vapor contributions dominated grass and feed concentrations. Therefore, a drop in ambient air vapor phase concentrations at 200 meters as compared to 500 meters dominated the result, and the net impact was to reduce beef fat concentrations. From Figure 6-12, it is seen that beef fat concentrations were reduced by about one-half when using COMPDEP output from 200 m instead of 500 m. Further from the stack at 5000 meters, all biota concentrations were lower. Vapor phase air concentrations were roughly halved, and dry and wet deposition were lower by 60 and 80% respectively. This led to substantial reductions in vegetable concentrations. Interestingly, beef fat concentrations were lower at 5000 meters than at 200 meters, but not by much. This is because vapor phase concentrations at 5000 meters were in fact greater than they were at 200 m. The net results, according to the modeled depositions and air concentrations, is that beef and milk fat impacts are ironically fairly similar at 200 and 5000 meters.

The baseline vapor/particle partitioning for 2,3,7,8-TCDD was 55% vapor/45% particle. When decreasing the vapor to 10% and increasing the particle to 90%, both vegetations increased. Below ground vegetables increased because below ground vegetables were not a function of vapor phase concentrations, only of soil concentrations, which were a function of particle depositions. Above ground vegetable concentrations increased as well. As seen on Table 6-2, above ground vegetables were more impacted by particle depositions than vapor transfers for the stack emission high end scenario, #5. Increasing the particle depositions would increase their overall dominance and lead to increases in vegetable concentrations.

Interestingly, the trend was different for beef fat impacts. In this case, beef fat concentrations increased when the vapor reservoir was increased, although the increase was small. The reason beef fat concentrations increased can be seen in Table 6-2. Grass and feed were more impacted by vapor phase transfers than particle depositions, the opposite trend noted for vegetables. Therefore, a rise in vapor phase concentrations will even further dominate grass and feed concentrations, the major components of beef cattle diet. With an increase in grass and feed concentrations, beef fat concentrations increase.

6.3.3.12. ***Water and fish concentrations resulting from effluent discharges*** The impacts of parameter changes for algorithms estimating water and fish concentrations are shown in Figure 6-13. First, it should be noted that fish and water impacts are included in the same graph because the impacts to both concentrations are exactly the same with the noted changes in parameters, with one exception. This exception is the partition coefficient, Koc. Increases in Koc result in higher suspended sediment concentrations, which lead to higher fish tissue concentration estimations, but lower water concentration estimations. Increasing Koc by an order of magnitude actually decreases water concentrations to 14% of its baseline value, or 0.14 on the y-axis of Figure 6-13. Decreasing Koc by an order of magnitude increases water concentrations by a factor of 2.4. Roughly, the location of the high and low Koc points on Figure 6-13 should be reversed for water concentration impacts. Also, the biota to suspended solids accumulation factor, BSSAF, and the fish lipid content, f_{lipid}, are specific to fish tissue estimations.

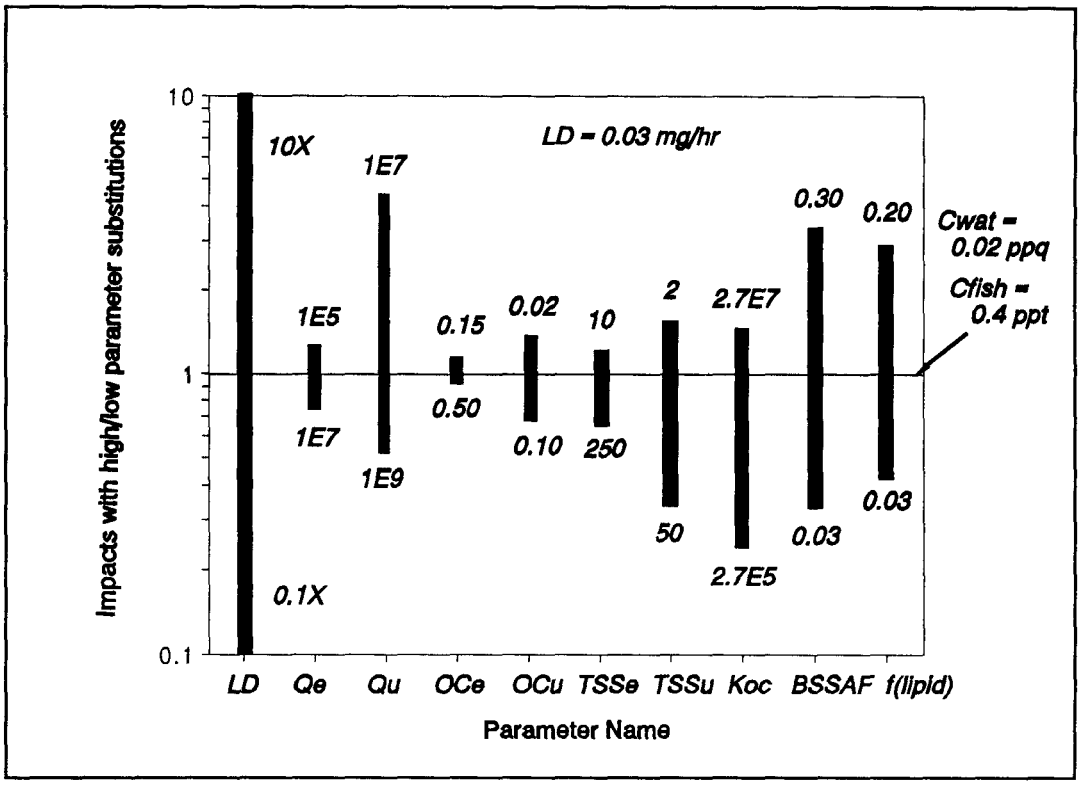

Figure 6-13. Results of sensitivity analysis of algorithms estimating surface water and fish concentrations resulting from effluent discharges.

Parameter Name	Definition	Selected
C_{wat}	water concentration, pg/L (ppq)	0.02
C_{fish}	whole fish concentration, ng/kg (ppt)	0.4
LD	loading to surface water body, mg/hr	0.0315
Q_e	effluent flow rate, L/hr	4.1×10^6
Q_u	upstream receiving water flow, L/hr	4.7×10^8
OC_e	effluent organic carbon content, unitless	0.36
OC_u	upstream organic carbon content, unitless	0.05
TSS_e	effluent total suspended solids, mg/L	70
TSS_u	upstream total suspended solids, mg/L	9.5
Koc	organic carbon partition coefficient, L/kg	2.69×10^6
BSSAF	biota suspended solids acc. factor, unitless	0.09
f_{lipid}	fish lipid fraction	0.07

Clearly, both concentrations are mostly impacted by the loading rate - the impact is linear and direct. Of all the parameters describing the effluent stream and the receiving water body, only the two order of magnitude change in receiving water body flow rate seems to have about an order of magnitude range of predictions. The effluent flow rate is

ultimately low in comparison to the receiving water body, so its impact is limited. The range of organic carbon contents of the effluent and of the suspended solids in the receiving water are reasonably assigned and appear to have a small impact.

Higher suspended solids content in the receiving water body can result in lower fish and water concentrations. This might be termed a "solids dilution effect". Few studies are available in the literature which support this result, but two studies were found which are consistent with a solids dilution effect. One "simulated field experiment" conducted by Isensee and Jones (1975) maintained a constant water concentration of 239 ppb, but reported a decrease in 2,3,7,8-TCDD concentrations in both mosquite fish (2200 ppb to 90 ppb) and catfish (720 to 90 ppb) as the amount of sediment increased from 20 to 440 g. Sherman (1992), in a review of this and other simulated field experiments and laboratory flow through experiments, points out that a bioconcentration factor for these simulated field experiments would decrease as the sediment increases. He speculates that, in comparing water flow through experiments with field simulated data, the bioconcentration factors tend to be less in field simulated experiments because 2,3,7,8-TCDD may sorb to sediments and be less bioavailable. A second study supporting a solids dilution effect was conducted by Larsson, et al. (1992). They studied uptake of PCBs and p,p'-DDE in 341 northern pike in 61 lakes in southern Scandanavia. They found that the levels of these persistent pollutants in the fish decreased as productivity increased. Productivity was measured by total phosphorus, chlorophyll a, and lake water transparency, which was mainly influenced by phytoplankton biomass. Their hypothesis was that the levels decreased because humus adsorbs persistent pollutants, rendering them less available for uptake in fish.

The two order of magnitude range in Koc translates to about a one order of magnitude range in estimated fish and water concentration estimations. Fish tissue concentrations are linearly and directly related to the BSSAF and f_{lipid}. About an order of magnitude of concentration estimation is noted with about the same order of magnitude in likely values.

6.3.3.13. ***Water and fish concentrations resulting from stack emissions*** Results of sensitivity analysis of algorithms estimating surface water and fish concentrations resulting from stack emissions are shown in Figure 6-14. First, it is noted that the impact

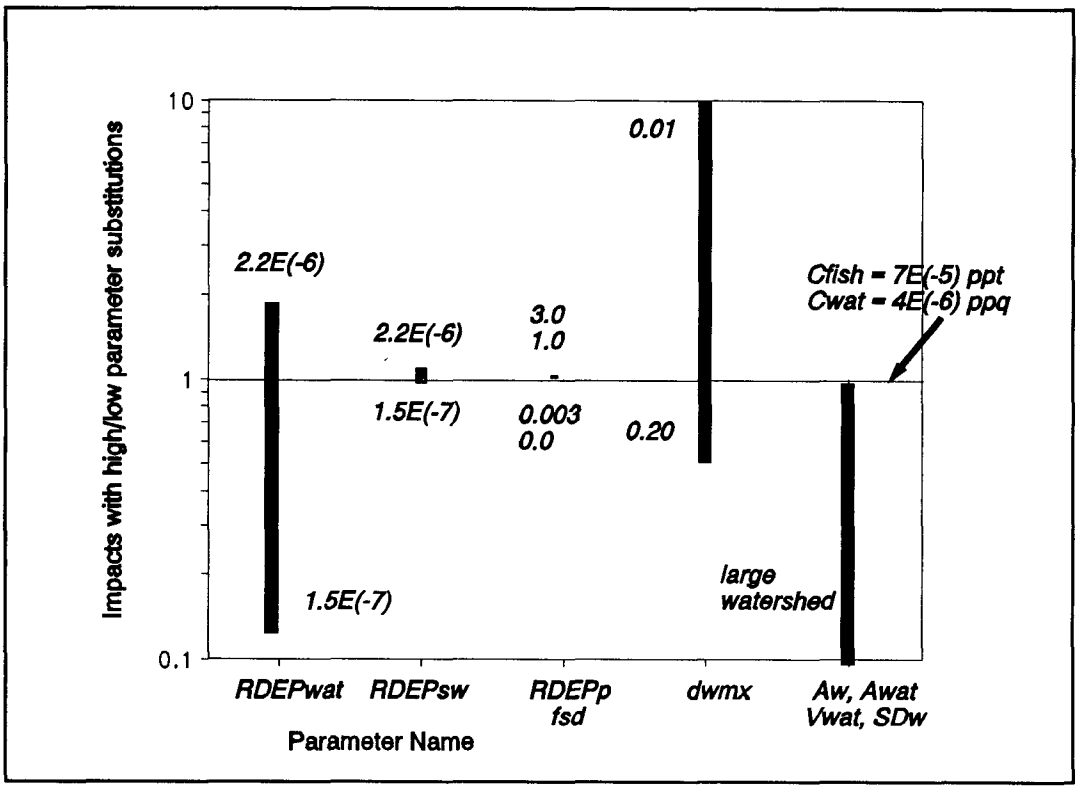

Figure 6-14. Results of sensitivity analysis of algorithms estimating surface water and fish concentrations resulting from stack emissions.

Parameter Name	Definition	Selected
C_{fish}	whole fish concentration, ng/kg (ppt)	0.00007
C_{wat}	surface water concentration, pg/L (ppq)	0.000004
$RDEP_{wat}$	contaminant dep. rate on watershed, $\mu g/m^2$-yr	$1.2*10^{-6}$
$RDEP_{sw}$	contaminant dep. rate on surface water, $\mu g/m^2$-yr	$1.2*10^{-6}$
$RDEP_p$	particle dep. onto surface water, g/m^2-yr	0.03
d_{wmx}	watershed soil mixing depth, m	0.10
f_{sd}	fraction of deposited particles remaining in suspension	1.00
A_w	area of watershed, ha	4000
A_{wat}	surface area of water body, m^2	32200
V_{wat}	water body annual volume, L/yr	$1.52*10^{10}$
SD_w	watershed sediment delivery ratio	0.15

to both these media is the same with impacts to all parameters. The impact with changes in the deposition of particles onto the water body, $RDEP_p$, and with the fraction of deposited particles remaining in suspension, f_{sd}, is negligible. The assigned values to

these parameters for the demonstration are, therefore, sufficient for any purpose. It is importantly noted the COMPDEP model (or other atmospheric transport models) do not need to estimate the concentration of contaminants on emitted particles - all that is required are mass emissions of contaminants (in g/sec units) and the delineation of size fractions of particles emitted. The COMPDEP model does not require a particle emission rate. An assumption of a greater deposition of particles directly into surface waters might translate back to an assumption of particle emissions. The $RDEP_p$ is only required to maintain a mass balance of solids entering the surface water body, and as it turns out, particles entering surface waters by this route are only a miniscule part of the total solids entering the body. There are no impacts to water or fish concentration estimations with reasonable values for this parameter. The same appears true for f_{sd}, which determines the extent to which directly depositing contaminants remain in suspension. The assigned value of 1.00 (meaning that all directly depositing contaminants remain in suspension), based on the argument that particles emitted from stack are likely to be lighter than eroding soil particles, appears sufficient for general purposes.

Water body impacts are linearly related to the average watershed depth of mixing. The value assigned for the demonstration scenario was 0.1 m, which is midway between the value assumed for non-tilled conditions, 0.01 m, and tilled conditions, 0.20. The value of 0.10 m suggests that half the watershed is tilled. The linear relationship underscores the importance of this uncertain parameter, and also suggests that erosion drives water body impacts rather than direct deposition. This trend is also apparent for the tests on depositions to the watershed, the $RDEP_{wat}$ input, versus depositions directly onto the surface of the water body, the $RDEP_{sw}$ input. The impact to changes in $RDEP_{wat}$ are roughly linear - doubling the watershed depositions doubles the water body impacts, and so on. Only a marginal impact was noted for the same change to $RDEP_{sw}$. To further evaluate this trend, another test was undertaken. In this test, it was assumed that the water body was much larger and so was the amount of land draining into the water body. Further, the stack emitter was next to the water body. Two groups of changes were made in this test. First were physical changes to the water body and the watershed - water body volume, V_{wat}, was increased from $1.52*10^{12}$ to $1.52*10^{14}$, the water surface area, A_{wat}, was increased from 32200 to 322000 (a 100-fold increase in water body volume might assume, for example, water body surface area increasing by a factor of

ten and depth increasing by a factor of ten), the land area draining into the water body was increased 2 orders of magnitude from 4000 ha to 400000 ha, and the sediment delivery ratio, SD_w, was decreased from 0.15 to 0.04. The second group was on contaminant deposition rates. The deposition rate onto watershed was that modeled to occur at 5000 meters, $1.5*10^{-7}$ $\mu g/m^2$-yr, instead of 500 meters, $1.2*10^{-6}$ $\mu g/m^2$-yr, and the deposition rate onto the water body was modeled for 200 meters, $2.2*10^{-6}$ $\mu g/m^2$-yr, instead of that at 500 meters. The result in Figure 6-14, labeled "large watershed" indicates that these changes dropped water impacts by about an order of magnitude, with lower unit inputs from erosion contaminant delivered per hectare of land combined with the larger water body driving the result. However, direct depositions were proportionally more important to impacts. For the base conditions, direct depositions only accounted for 3% of the to the water body. For this large watershed test, direct depositions accounted for 25% the impact. Other changes could minimize the impact from the watershed, such as erosion rates or lower sediment delivery ratios. Still, the implication from these tests that direct deposition is of, possibly, much less importance to water body compared to depositions onto soils followed by soil to surface water transport.

6.3.4. Key Trends from the Sensitivity Analysis Testing

These are as follows:

1) Source terms are the most critical for exposure media impacts. Source terms include soil concentrations, stack emission rates, and effluent discharge rates. In nearly all cases, the impact to exposure media is linear with changes to source terms. Proximity to the source term can be important as well, as demonstrated with differences in distance from the stack emission source.

2) Chemical-specific parameters, particularly the bioconcentration/biotransfer parameters, are the second most critical model inputs. Some of these have lesser impacts, such as the organic carbon partition coefficient, Koc, for surface water impacts. Generally, at least an order of magnitude in range in possible media concentrations is noted with the range of chemical-specific parameter ranges tested. The impact of changes to bioconcentration/biotransfer parameters is mostly linear. This is because these transfer factors estimate media concentrations as a linear transfer from one media to another - fish lipid concentrations are a linear function of the concentration of contaminants in

sediments. These transfer parameters are also identified as uncertain parameters. Tested ranges sometimes spanned over an order of magnitude for 2,3,7,8-TCDD.

3) All other parameters had less of an impact as compared to source strength and chemical specific parameters; nearly all impacts were within an order of magnitude for the range of tested values. Part of the reason for this trend is that there is a reasonably narrow range for many of the parameters in this range - soil properties, wind speeds, vegetation yields, and others. It is important, nonetheless, to carefully consider all the model parameters. While impacts were generally within an order of magnitude of the values selected for the demonstration scenarios, there was often an order of magnitude or more difference between plausible high and low values for individual parameters.

4) A principal trend of note concerns the air to soil algorithm for the stack emission source category compared to the soil to air algorithm of the soil source category. With a 1 ppt soil concentration of 2,3,7,8-TCDD, air concentrations are estimated to be in the 10^{-11} $\mu g/m^3$ range. Atmospheric transport modeling in the demonstration stack emission source resulted in a delivery of 2,3,7,8-TCDD to result in an air concentration of the same magnitude, 10^{-11} $\mu g/m^3$. Both models would have predicted similar impacts to vegetations and beef/milk had the deposition rates from the atmospheric transport modeling led to soil concentrations around 1 ppt. However, the tilled and untilled soil concentrations estimated for the stack emission source were $5*10^{-5}$ and 10^{-3} ppt, respectively. This had several primary and secondary impacts, such as below ground vegetables had much higher concentrations for the soil source demonstration scenario, soil was significantly more critical in predicting beef and milk fat concentrations in the soil source category as compared to the stack emission source category, and so on. Exercises described earlier in Section 6.3.3.9 suggest two model performance trends which would narrow the gap in the air-to-soil algorithm of the stack emission source category and the soil-to-air algorithms of the soil contamination source category: 1) evidence suggests that the volatilization/dispersion algorithms of the soil source category are underestimating air concentrations, and 2) the deposition algorithms of the stack emission source category are underestimating soil concentrations. Lack of data allows for definitive conclusions for either of the hypotheses; further analysis of model performance is called for.

6.4. MASS BALANCE CONSIDERATIONS

As has been discussed in this document more than once is the characterization of this methodology as a screening level methodology. Steady state, equilibrium partitioning, and assumptions of nondegradation of source strengths are key assumptions which lead to this qualification. Stacks are assumed to emit a constant amount of contaminant over a duration of exposure for the stack emission source category. Effluent discharges are assumed to continue unabated over a duration of exposure. These are both reasonable assumptions for evaluating the long-term impacts of these sources where no change in practices occur. Any violation of mass balance principals will, therefore, not be examined for these sources. The same assumption of unabated and constant releases might be questioned, however, for the soil contamination source categories, the on-site and the off-site source categories. Soil concentrations are assumed to remain constant, despite mechanisms which would dissipate concentrations over time. Volatilization and transport off-site, and wind erosion and transport off-site, are two mechanisms which dissipate residues into the air and deplete the source strength. Soil erosion off the site to a nearby exposure site and to nearby water bodies also is a mechanism of release. A key dissipation mechanism is soil degradation. There is evidence that photolysis is a mechanism of degradation of dioxin-like compounds, as discussed in Chapter 2 of Volume II of this assessment. However, this would only apply to those residues directly on the soil surface and, as such, it may be reasonable to make an assumption of nondegradation if a concurrent assumption is that residues exist below the soil surface. In any case, releases for a bounded area of soil contamination including volatilization, wind erosion, and soil erosion, which are estimated for purposes of estimating off-site impacts, are not also used to estimate dissipation of the reservoir of contaminant in the soil. Said another way, the amount lost via these pathways is not a function of a soil reservoir which decreases over time.

The purpose of this section is to examine this assumption for the case of a bounded area of high soil concentration. The demonstration of the off-site soil source category will be the focus of discussions below, although the same principals are relevant for the onsite soil source category. First, an estimate of the "reservoir" of 2,3,7,8-TCDD that is implied with the default parameters will be made. Then, an estimate of the rate at which this reservoir dissipates using the solution algorithms for dissipation: volatilization and wind

erosion flux from soils, and soil erosion, will be made. Other routes of dissipation that will be examined are the soil ingestion by cattle and children, the loss via dermal contact, and the removal via harvest of below ground vegetation. These will be shown to be minuscule in comparison to air and soil erosion. The loss of soluble residues via surface runoff or leaching will be evaluated. Surface water bodies and above ground vegetations are sinks for dioxin-like compounds and therefore are not mechanisms of soil dissipation. If it can be shown, for example, that it takes several hundred years to dissipate a given reservoir, then it may be fair to conclude that exposures assuming non-dissipation over a 20 or even a 70 year exposure period are not significant overestimates. On the other hand, complete dissipation within a time period less than or even near to the period of exposure would mean that exposures and risks are being overestimated.

As will be shown, the rates of reservoir dissipation are very important considerations for soil contamination. Users of this methodology should consider dissipation of available residues and the discussions below when determining the duration of exposure for site-specific assessments. A recommended rule of thumb for users of this methodology is to evaluate the time to dissipation using the methodology below, and if it is less than or even near the assumed period of exposure (2 years to dissipate versus 20 years of assumed exposure, e.g.), then it may be appropriate to assign a duration of exposure equal or less than the calculated time to residue dissipation.

One of the key parameters in determining how rapidly residues will dissipate is one which is not required for this methodology. This is the depth of contamination. This depth, plus the initial concentration and the areal extent of contamination, describe the full extent of the source strength. The exercises below have assumed a shallow depth of 0.15 meters, or 6 inches, in soil. The impact of this assumption is demonstrated below. Also, the exercises below are specific to 2,3,7,8-TCDD.

The demonstration of the off-site soil contamination source category were as follows: 40,000 m^2 soil contaminated with an initial concentration of 1 μg/kg (ppb). It is assumed that the contamination extends to 0.15 meters (6 inches).

Step 1. Estimate the amount bound to soil:

(total volume of contaminated site =	40,000 m^2 * 10,000 cm^2/m^2 * 15 cm = 6×10^9 cm^3	
(soil bulk density)	x	1.5 gm/cm^3
(unitless 2,3,7,8-TCDD soil con., g/g)	x	$(1/10^9)$
= grams 2,3,7,8-TCDD in soil		9 gms

Note: at a soil concentration of 1 μg/kg, there will also be some 2,3,7,8-TCDD in soil pore water. This amount is insignificant in comparison to the amount bound to soil, and will be neglected.

Step 2. Now estimate the amounts lost by various routes of dissipation

- Volatilization: Volatilization flux is a function of exposure duration, with less average flux calculated over longer durations - this is, in fact, the only model algorithm which accounts for reservoir depletion over time. The durations of exposure for the high end scenarios was 20 years. The release rate via volatilization is given as the term FLUX and is shown in Equation (4-13) in Chapter 4. Plugging in baseline parameter values for 2,3,7,8-TCDD and a duration of 20 years results in a calculated flux of 1.12×10^{-18} g/cm^2-sec. Over a year and over the 40,000 m^2 contaminated area, this translates to an annual dissipation rate of 0.014 g/yr of 2,3,7,8-TCDD.

- Wind erosion: Unlike the volatilization algorithm, the flux due to wind erosion is not dependent on the duration of exposure. The wind erosion algorithm is described in Section 4.3.3 in Chapter 4. Plugging in baseline parameter values results in a flux of 2,3,7,8-TCDD of 5.74×10^{-20} g/cm^2-sec, or an annual flux over the 40,000 m^2 contaminated area of 0.0007 g/yr.

- Soil erosion: The annual erosion rate off the contaminated site was 21515 kg/ha-yr. This rate was assumed to erode towards the exposure site as well as towards the impacted surface water body. However, it would not be appropriate to double that quantity since it is used in two different algorithms - the exposure site could be in the direction of the water body, for example. Or, if applied to a specific site, one could ascertain that the exposure site is upgradient from the contaminated site, and so on. In

any case, 21515 kg/ha-yr can be translated to a cm/yr of soil erosion as follows:

volume per 1-cm hectare slice	=	10,000 m^2/ha * 10,000 cm^2/m^2 * 1 cm = 1×10^8 cm^3
soil bulk density	x	0.015 kg/cm^3
kilograms per 1-cm hectare slice	=	150,000 kg/cm-hectare

Therefore, 21515 kg/ha-yr translates to a loss of soil equal to 0.14 cm/yr. Given that 9 g 2,3,7,8-TCDD are estimated to occur in 15 cm, the annual loss of 2,3,7,8-TCDD is 0.084 g/yr.

- Runoff and Leaching: Transport via water are not considered in this methodology since the dioxin-like compounds are so tightly sorbed that these are expected to be negligible. An estimate of loss via water will nonetheless be made for this exercise. Surface water body volume was estimated assuming a runoff rate of 15 in/yr, which was defined as all surface water contributions (surface runoff, interflow, and ground water recharge). This is a reasonable estimate for water-borne losses for this exercise. The annual amount of 2,3,7,8-TCDD lost in this water can be estimated using the soil partition coefficient, Kd_s, relationship, which is C_s/C_w. Kd_s is equal to 27,000 for 2,3,7,8-TCDD (organic carbon partition coefficient, Koc * soil organic carbon, OC_{sl}), so the concentration in water, C_w, given a soil concentration, C_s, of 1 μg/kg, is 3.7×10^{-5} μg/L, or 3.7×10^{-11} g/L. Translated to a 40,000 m^2 area, 15 in/yr equals 1.524×10^7 L, so the total annual loss in water equals 0.00056 g/yr 2,3,7,8-TCDD.

Except for soil degradation, these are the dissipation routes that would be considered for a site of soil contamination that is not used for any purpose - residence, agriculture, and so on. For the sake of completeness, other routes that will be looked at now include soil ingestion, soil dermal contact, and harvesting of underground vegetations.

- Soil Ingestion: Soil ingestion by children in the high end scenario is 800 mg/day, or 0.29 kg/yr. Soil ingestion by cattle will also be considered. First, an assumption of how many cattle would be feeding on a 40,000 m^2 area should be made. A daily cattle dry matter ingestion rate is 19 kg/day. For beef cattle that are assumed to principally graze, for 90% of their dry matter intake, the daily ingestion of grass would be 17.1 kg/day, and their daily intake of soil while grazing, 8% of total dry matter intake, is 1.52

kg/day. With this daily ingestion of grass, their annual need for grass would be 6200+ kg/yr. The yield of grass assumed for other purposes in this assessment was 0.15 kg/m^2-yr dry weight, or 6000 kg/40,000 m^2-yr. Therefore, it appears that one grazing cow requires the 40,000 m^2 to himself (as a rough approximation). The annual intake of soil by this cow equals 555 kg/yr, which as expected, is much higher than child soil ingestion. The annual removal of 2,3,7,8-TCDD by cattle soil ingestion is 555 μg/yr, or 0.0006 g/yr.

- Dermal Contact: The dissipation of 2,3,7,8-TCDD residues via dermal contact is estimated as, NE*CA*CR*C_s, where NE = number of dermal contact events per year, which equals 350 in the high end scenario, CA = contact area, which equals 1000 cm^2 in the high end scenario, CR = contact rate, which equals 1 mg/cm^2-event, and Cs = 2,3,7,8-TCDD concentration, which is 1 μg/kg, or in more convenient units, 10^{-12} g/mg. The annual loss via dermal contact is negligible at 3.5×10^{-7} g/yr.

- Underground Vegetation Harvest: The yield of vegetables required for other algorithms of this assessment, is 7.8 kg/m^2 fresh weight. The concentration in underground vegetables that would occur, given the algorithms of this assessment, is 0.0015 μg/kg fresh weight. Therefore, the removal per m^2 is 0.0117 μg/m^2, and the removal over 40,000 m^2 in g/yr is 0.0005 g/yr if all the 40,000 m^2 were devoted to underground vegetables.

This exercise has shown that the principal mechanism of removal is soil erosion at 0.084 g/yr 2,3,7,8-TCDD, with volatilization explaining 0.014 g/yr removal. The sum of these two routes is 0.098 g/yr, and the sum of all the other routes examined briefly above 0.002 g/yr, leading to a round total estimate of 0.1 g/yr. With an initial reservoir of 9 g/yr, it would take 90 years to dissipate the available reservoir, not including degradation and assuming that surface concentrations remain constant. These two latter considerations are screening level considerations in the sense that attempting to model both (i.e., degradation leading to lower soil concentrations, volatilization from deeper depths as surface concentrations decline, etc.) would lead to lower releases and lower off-site impacts. Modeling them both would also, however, lead to a conclusion that the reservoir modeled in the exercise above would take more than 90 years to dissipate.

This was not a definitive exercise, by any means, but it does lend some confidence that a principal of mass balance may not have been violated for the soil source categories, and for the assumption of 20 years exposure duration. As this section began, the algorithms of this assessment are characterized as screening level methodologies. Users of this methodology should be cognizant, nonetheless, of the possibility of depleting a reservoir of soil contamination prior to an assumed duration of exposure.

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7. UNCERTAINTY

7.1. INTRODUCTION

This chapter addresses uncertainty in dioxin exposure assessment performed with the methodologies presented in this document. Some discussion of the issues commonly lumped into the term "uncertainty" is needed at the outset. The following questions capture the range of issues typically involved in uncertainty evaluations:

(1) How certain are site specific exposure predictions that can be made with the methods?
(2) How variable are the levels of exposure among different members of an exposed local population?
(3) How variable are exposures associated with different sources of contamination?

The emphasis in this document is in providing the technical tools needed to perform site-specific exposure assessments. For the assessor focusing on a particular site, question (1) will be of preeminent importance. Therefore the emphasis of this Chapter is to elucidate those uncertainties inherent to the exposure assessment tools presented in this document. This chapter examines the capabilities and uncertainties associated with estimating exposure media concentrations of the dioxin-like compounds using the fate, transport, and transfer algorithms, and also identifies and discusses uncertain parameters associated with human exposure patterns (contact rates and fractions, exposure durations, etc.).

Section 7.2 focuses on the fate, transport, and transfer algorithms of this assessment, which has the following subsections:

1. the variability and uncertainty with chemical-specific parameters (Section 7.2.1);
2. uncertainty issues associated with the use of the COMPDEP model for air transport modeling for the stack emission source category (Section 7.2.2); discussions of the COMPDEP model and its application in this assessment is discussed in detail in Chapter 3;
3. the reliability of the models to predict exposure media concentrations, looked at by comparing estimated exposure media concentrations with those found in the

literature (Section 7.2.3);

4. the similarity and differences for other modeling approaches (Section 7.2.4);

Section 7.3. discusses uncertainties and variabilities with key exposure parameters, and is organized on a pathway-by-pathway basis. This section also provides a general overview of all key uncertainties with each pathway.

A site specific assessment will also need to address the variability of risks among different members of the exposed population, the second key question above. The level of detail with which this can be done depends on the assessors knowledge about the actual or likely activities of these residents. In this document, one approach to evaluating this variability is demonstrated. Separate "central" and "high end" scenario calculations are presented to reflect different patterns of human activities within an exposed population. "Central" scenarios are constructed to represent typical behavior patterns for residential exposures in a hypothetical rural setting. "High end" calculations focus on a farming scenario where individuals raise much food for their own consumption, in the same rural area. It should be emphasized that high end calculations could also have been developed for residential exposures by making, for example, higher range assumptions about duration of residence or contact rates with the contaminated media. Indeed, this would be recommended for an assessment where considerable emphasis was placed on residential exposures. The key issue with regard to intra-population variability is that it is best (if not only) addressed within the context of a specifically identified population. If such information is available, a powerful tool that can be used to evaluate the variability within a population is Monte Carlo Analysis. Section 7.4. reviews 3 recent Monte Carlo studies which have done for exposure to 2,3,7,8-TCDD. Assumptions on distributions of exposure patterns and fate and transport parameter distributions are described, as are the results of their analyses. Aside from this review, this chapter does not address question (2) in any further manner.

With regard to question (3), this document does not present a detailed evaluation of how exposure levels will vary between different sources of release of dioxin-like compounds into the environment. Chapter 2 of Volume II of this assessment does examine sources of release of dioxin-like compounds into the environment. This document, Volume III, does present methodologies for three types of sources - soil, stack emissions, and effluent discharges into surface water bodies. While this document does

demonstrate the methodologies developed for these sources with source strengths and environments crafted to be plausible and meaningful, there is still a great deal of variability on both the source strengths and on the environments into which the releases occur. For example, the frequency with which farms and rural residences are near stack emissions of dioxin-like compounds is not addressed. The scenario calculations in Chapter 5 are intended to be illustrative; the exposure levels that are obtained there are not intended to be typical of actual exposures for the sources and pathways assessed.

Nonetheless, some readers might ideally wish information on both the magnitude of actual exposures and the variability of these exposures associated with different sources of dioxin-like compound release into the environment. However, the analysis presented in this chapter cannot support so broad a goal. Representative data to address the variation of dioxin exposures are becoming available for sources as well as exposure media. The compilation of environmental and exposure media concentrations presented in Chapter 3 of Volume II of this assessment displays the range of measured concentrations in the environment. The careful selection of certain literature reports to represent concentrations of dioxin-like compounds in background conditions, described in Chapter 5 of Volume II, is one way such environmental measurements can be used. More detailed examinations for specific sources was done in Volume II of this assessment. References to EPA and other assessments on dioxin-like compounds have been made throughout this document, such as those related to soil exposures (Paustenbach, et al., 1992), exposures to contaminated fish (EPA, 1991a), exposures resulting from land disposal of sludges from pulp and paper mills (EPA, 1990b), just to name a few. Still, studies comparing and ranking different sources and exposure patterns, and elaborations on ranges of source strengths and exposures, are generally not available. Information in Volume II of this assessment and procedures for source specific evaluations in Volume III can provide others with information and tools to begin such analysis.

7.2. AN EVALUATION OF THE ALGORITHMS USED TO ESTIMATE EXPOSURE MEDIA CONCENTRATIONS

This section examines issues pertinent to the certainty with which exposure media concentrations can be estimated using the fate, transport, and transfer algorithms of this assessment. Section 7.2.1. gives a brief overview of the variability and uncertainty

associated with model parameters specific to the compounds themselves. Section 7.2.2. discusses uncertainty issues associated with the COMPDEP model, which was used in the stack emission source category. Section 7.2.3 evaluates the capabilities of the fate, transport, and transfer algorithms estimating exposure media concentrations by making comparisons of modeled and measured concentrations. Section 7.2.4. reviews other modeling approaches for estimating environmental and exposure media concentrations, and compares their performance with that of the models used in this assessment.

7.2.1. Uncertainties and Variabilities with Chemical-Specific Model Parameters and Assumptions

This assessment assumed that levels of dioxin-like compounds in soil and sediment were constant over the period of exposure, with two exceptions. One circumstance was when contaminated soil eroded from one site and deposited on a site of exposure nearby - the off-site source category. The other was when stack emitted particulates deposited onto a site of exposure - the stack emission source category. In both these instances, it is assumed that only a relatively thin layer of surface soil would be impacted, and that this thin layer is subject to dissipation processes - erosion, volatilization, possibly degradation. Data in Young (1983) implied a soil half-life of 10 years for surficial 2,3,7,8-TCDD residues, although the circumstances of the soil contamination were not analogous. Specifically, a 37 ha test area at the site had received an estimated 2.6 kg of 2,3,7,8-TCDD over a two year period. Soil sampling which occurred over 9 years from the last application suggested that less than 1 percent remained at the test area. Although Young hypothesized that photodegradation at the time of application was principally responsible for the dissipation of residues, other mechanisms of dissipation including volatilization, erosion, and biological removal may also have contributed to the loss of residues. Soil sampling over time after application implied a dissipation half-life of 10 years for soil residues of 2,3,7,8-TCDD. This value was assumed to apply to the other dioxin-like compounds, introducing further uncertainty.

Section 2.6.1, Chapter 2 in Volume II of this assessment, reviewed the literature on degradation of dioxin-like compounds. As discussed, biological transformations as well as chemical processes (oxidation, hydrolysis, and reduction) do not appear to result in substantial degradation of these compounds. There is evidence of photolysis, particularly

when dissolved in solution and when organic solvents are present. Most of these data are specific to 2,3,7,8-TCDD, introducing further uncertainty when applied to the other dioxin-like compounds.

Dissipation of surficial residues could translate to lower soil-related exposures including particulate inhalations, soil ingestion, and soil dermal contact. However, it is not clear that reductions in exposure would, in fact, occur, particularly if the soil is contaminated below the surface. Processes such as wind erosion, soil erosion, or volatilization originating from deeper in the soil profile, could serve, in a sense, to replenish reservoirs at the soil surface. Depositions back onto soils from other soils, or depositions from distant sources, also replenish soils. Given very low rates of degradation (for all degradation processes except photolysis), the assumption of no degradation is reasonable with moderate, but unquantifiable uncertainty.

In evaluating an assumption of no degradation, another issue to consider is the depletion of the original source of contamination. For the stack emission and effluent discharge source categories, the assumption is made that steady releases occur throughout the period of evaluation - the exposure duration. Therefore, depletion of the original source is not an issue. For the soil source category, it is assumed that the reservoir of contaminant is constant throughout the duration of exposure. If such a duration is assumed to be very long, then degradation or dissipation of soil residues would be more critical than if the duration were relatively short. Uncertainties associated with the duration of exposure are discussed in Section 7.3.1. below. Also, Section 6.4 in Chapter 6 evaluated the assumption of a constant soil concentration by estimating the time it would take for a 6-inch reservoir of soil contamination to be depleted, using the dissipation algorithms of this assessment. These algorithms include volatilization, soil erosion, and wind erosion, with lesser releases due to biological uptake, and leaching and runoff. It was found that it would take over 90 years to deplete a 6-inch reservoir, lending some credibility to a non-degradation assumption if the exposure duration were in the range assumed for the demonstration scenarios of this assessment, 20 years.

A critical contaminant parameter required for the procedures in this assessment is the octanol water partition coefficient, Kow, although none of the fate and transport algorithms directly require a Kow. Two empirical biota transfer parameters are, however, a function of Kow. These are the RCF, or Root Concentration Factor, which estimates the

transfer of contaminant from soil water to root, and the B_{vpa}, the air-to-leaf vapor phase transfer coefficient which estimates the transfer of vapor phase contaminants to vegetations. Log Kow estimates for dioxin-like compounds range from 6.00 to 8.5, with higher log Kow associated with higher chlorination. However, this is not a certain parameter. Estimates in literature for 2,3,7,8-TCDD, for example, range from 6.15 to 8.5.

Two biota transfer coefficients are used to estimate fish tissue concentrations based on water body sediment concentrations: the Biota Sediment Accumulation Factor, BSAF, and the Biota Suspended Solids Accumulation Factor, BSSAF. There are no empirical relationships which estimate these as a function of the more common Kow for dioxin-like compounds. Rather, values were assigned based only on experimental and field data. Needless to say, most of the data available was for 2,3,7,8-TCDD, leaving large gaps for other compounds. Also, there is no data available for estimating the BSSAF, a parameter proposed in EPA (1993) which was used in the effluent discharge source category. The BSSAF was set equal to the BSAF for this assessment. Field data including bottom sediment concentrations and concurrent fish concentrations were used to determine values for BSAF. The limited field data available for BSAF suggests values in the range of 0.03 to 0.30 for 2,3,7,8-TCDD, with higher values approaching 1.00 indicated for bottom feeders (catfish, carp, etc.), and decreasing values as the degree of chlorination increases - limited information suggests values in the 10^{-3} to 10^{-2} range for hexa- through octa- CDDs and CDFs. Data on PCBs suggest that BSAFs are higher than those of CDDs and CDFs by an order of magnitude and more, and that the trend with increasing degrees of chlorination is not the same. The data indicates that BSAFs for PCBs increase from dichloro- through hexa- or perhaps hepta-chloro PCBs, and decrease thereafter.

A bioconcentration factor, BCF, translates the average contaminant in the diet of the cattle into a beef or milk fat concentration. Experimental rather than field data was available for estimates of BCF for dioxin-like compounds. Farm animals were fed known quantities of these compounds and their body tissues and milk were monitored over time to arrive at BCFs. Data showed that the BCF decreased to below 1.0 as the degree of chlorination increased. A experimental data set, including analysis of 16 of the 17 dioxin-like congeners, described in McLachlin, et al (1990), was used to assign BCF values for this assessment. Limited data showed PCB BCFs to be the same order of magnitude,

although trend data for increasing degrees of chlorination was not available.

Obviously, a degree of uncertainty is introduced when relying on these empirical bioconcentration or biotransfer coefficients to estimate concentrations in fish, beef, and milk. The variability in the data suggests an order of magnitude range of variation may results from use of these parameters.

Another important chemical-specific parameter that can be estimated from Kow or estimated experimentally is the organic carbon partition coefficient, Koc. Koc describes the steady state partitioning between soil or sediment organic carbon and water; it impacts the volatilization flux from soils, and the partitioning between suspended sediment and water in the water column. Koc is used to estimate in-situ partitioning using a fraction organic carbon in the soil or sediment, OC_{sl}, OC_{sed}, and OC_{ssed}, as $Koc*OC_{sl}$, etc. The resulting chemical-specific parameter is termed the soil (or sediment) partition coefficient, Kd_s (or Kd_{sed}, Kd_{ssed}). The empirical equation used to estimate Koc from Kow in this assessment was derived by Karickhoff (1979). This equation was chosen over others available (Lyman, 1982) because it was derived from laboratory testing of 10 hydrophobic contaminants. Others available would have led to lower estimates of Koc. For example, using a relationship developed by Kenaga and Goring (1980) would estimate a 2,3,7,8-TCDD Koc (given log Kow for 2,3,7,8-TCDD of 6.64) of 97,500. The Koc for 2,3,7,8-TCDD estimated for this assessment using Karickhoff's relationship was 2,700,000. Some data implies that this estimate itself may be low for 2,3,7,8-TCDD. Studies reviewed in Section 2.4.5., Chapter 2 of Volume II of this assessment, particularly those Jackson, et al. (1986) and Lodge (1989), indicate 2,3,7,8-TCDD Koc estimates in the range of 20,000,000 to greater than 30,000,000.

Another critical contaminant parameter is the Henry's Constant. Table A-1, Appendix A of Volume II of this assessment, provides estimates of Henry's Constants, H, for dioxin-like compounds, most of which were estimated given vapor pressure and water solubility data. As seen, the PCDDs and PCDFs were in the 10^{-6} to 10^{-5} atm-m^3/mol range, while coplanar PCBs were in the 10^{-5} to 10^{-4} range, with one high value at $3x10^{-3}$ atm-m^3/mol.

Finally, the contaminant molecular diffusivity in air is required for estimates of volatilization flux from soils. The molecular diffusivity in air is set at 0.05 cm^2/sec for all dioxin-like compounds. Molecular diffusivity is a property of both the chemical and the

medium. It represents the propensity of a chemical to move through a medium. It is recognized to be largely a function of molecular weight. The values selected are evaluated as reasonable for all dioxin-like compounds, since the molecular weight for these compounds are similar.

7.2.2. A Discussion of Uncertainty Issues Associated With Use of COMPDEP for Transport and Dispersion of Stack Emitted Contaminants

Air dispersion and deposition analysis was performed using the COMPDEP Model. The model is intended to give approximate estimations of atmospheric dispersion and wet and dry deposition flux, and does not give absolute values. The model is used in the context of predicting future states based on known characteristics of geographical location, local meteorological conditions, temporal rates of emissions, and the physical description of the facility.

Atmospheric dispersion in COMPDEP is modeled using the common Gaussian plume model. Downwind concentrations of the dioxin-like chemicals are calculated as a function of stack height, the mass emission rate, the wind speed, and general atmospheric conditions. The Gaussian model assumes that the emission concentrations predicted by the model will fit a normal distribution. The principal assumptions in the Gaussian model are (Kapahi, 1991):

- The air concentration of the chemical at a fixed distance from the source is directly proportional to the emission rate from the source;
- The air concentration of a given chemical is inversely proportional to the wind speed corresponding to the effective height of release of the chemical into the air;
- The predicted ground-level concentration of the chemical approaches zero at large distances from the initial point of release.
- The model is steady-state.
- The model assumes constant wind speed, wind direction, and atmospheric stability over time and space for a given time period.

In general the stochastic features of the Gaussian plume model have been shown to predict annual average ambient air concentrations of a chemical emission from an industrial source to within a factor of one-order of magnitude of measured values, and in some cases, within a factor of 3 to 4-fold of field measurements (Cohrssen and Covello, 1989).

This modeling error spans both sides of the predicted concentration, that is, the actual concentration may be plus or minus this amount of the predicted value. The most sensitive aspects to variability in modeled predictions of ambient air impacts, if emissions are held constant, are stack height (height of the release), and terrain (flat verses complex topography).

To investigate modeling variability, EPA placed a prototype hypothetical hazardous waste incinerator in flat terrain and elevated terrain in geographical areas around the U.S. (EPA, 1991b; analysis conducted with the Industrial Source Complex, or ISC, model, which is coded into the COMPDEP model). Then the stack height was varied at these particular locations. Numerous runs were made at twelve specific sites to compare and contrast the influence of stack height and terrain on predicted ambient air concentrations of various mass emission rates of specific inorganic pollutants. A series of tables were developed from this sensitivity analysis from which the numerical estimation of the variability as a function of stack height and terrain can be inferred. When the hypothetical hazardous waste incinerator was modeled in flat terrain, e.g., topography within a distance of 5 km is not above the height of the stack, and the stack height was varied from 4 meters to 120 meters, the variability in the predicted ambient air concentration spanned two orders of magnitude (100). The lower stack height resulted in a predicted ambient air concentration that was 100 times greater than the concentration predicted using the tallest stack height. When the hypothetical hazardous waste incinerator was located in complex terrain over the same range of physical stack heights, the variability in estimated groundlevel concentration of the subject pollutant spanned two orders of magnitude (100-fold). In the latter case the stack height was computed as the terrain-adjusted stack height by subtracting from the physical stack height the influence of terrain on plume rise. From the limited sensitivity analysis of hazardous waste incinerators, it can be assumed that the predictions of spacial ground-level ambient air concentrations of dioxin-like compounds could differ from values in Table 3-14 by two-orders of magnitude in consideration of changes in stack height or changes in terrain. For example, Table 3-14 shows that the maximum annual average ambient air concentration of 2,3,7,8-TCDD predicted near the hypothetical incinerator is approximately 10^{-11} $\mu g/m^3$ for the stack height of 30.5 meters, and assuming flat terrain. If only the stack height is varied from 20 meters to 120 meters, and all other modelling parameters are held constant, then the

predicted ambient air concentration would be approximately 10 times greater and 10 times less than the estimated concentration, respectively. The uncertainty is broader when considering the influence of topography on predictability of the ground-level concentrations from the model. If only terrain elevation is varied at a distance of 5 km from the hypothetical incinerator from zero elevation to 30.5 meters, e.g., the height of the stack, then the predicted ambient air concentration of 2,3,7,8-TCDD would be approximately ten times greater. The tables derived in the hazardous waste incineration analysis have a limitation of elevation of terrain to the height of the stack.

The most uncertain aspect to the modeling is the estimation of dry and wet deposition flux of dioxin-like compounds on the vicinity of the hypothetical incinerator. Contributing most to this uncertainty seems to be the settling velocities and scavenging coefficients estimated for specific particle size diameters (Cohrssen and Covello, 1989; Doran and Horst, 1985). Seinfeld (1986) found that particles over 20 microns in diameter settle primarily by gravity, whereas smaller particles deposit primarily by atmospheric turbulence and molecular diffusion. Considerable, but non-quantifiable, uncertainty exists with respect to deposition velocities of particles 0.1 to 1.0 microns in diameter (Seinfeld,1986). The uncertainty is difficult to define. The wide variation of predicted deposition velocities as a function of particle size, atmospheric turbulence and terrain adds to this uncertainty (Sehmel, 1980). However, Gaussian plume dispersion models have been field validated for their ability to spatially predict dry deposition flux over some specified distance (Doran and Horst, 1985). In a series of field experiments conducted by Pacific Northwest Laboratory (Doran and Horst, 1985), zinc sulfide was used as a depositing tracer gas, and sulfur hexafluoride was used as a non-depositing tracer gas to compare and contrast modeling results with field measurements of dry deposition and atmospheric diffusion of the gases. The tracer was released from a height of 2 meters, and all releases were made under relatively stable atmospheric conditions. Five sampling stations were located downwind of the release from 100 to 3200 meters. The results of these experiments showed good agreement with the predicted verses the measured deposition of the tracer ZnS. The overall correlation coefficient between predicted and measured deposition concentration was found to be 0.82 (Doran and Horst, 1985), but the models marginally over-predicted deposition flux near the source of release, and under-predicted deposition flux at 3200 meters.

Travis and Yambert (1991) have evaluated the uncertainty in modeling the dry deposition flux of particulates using four standard Gaussian plume dispersion models. Since deposition flux is dependent on deposition velocity for a given particle mass and diameter, comparisons were made between model-generated deposition velocities and measured values found in the open literature for particles ranging from 0.01 to 30 microns in diameter. It was found that measured deposition velocities for a given particle size in the scientific literature exhibit variability spanning roughly two orders of magnitude. The analysis of the mean predicted deposition velocities to mean measured values showed that most measured data exceeded the predicted data for all four models. Moreover, the models underestimated the mean deposition velocities for particles in the range of diameters from 0.05 to 1.0 microns.

Similar uncertainty probably exists with regard to scavenging of various diameter particles by various intensity of rainfall. Seinfeld (1986) has calculated scavenging coefficients in terms of the removal efficiency of particles of a given size by rain droplets having a given momentum. Seinfeld (1986) found that the scavenging coefficient of a given particle diameter corresponding to a given rainfall intensity can be calculated based on physical laws, but there is a complete absence of research data to verify these calculations. Hence it is not possible to address the accuracy nor uncertainty of the wet deposition flux estimated in Tables 3-19 and 3-20.

7.2.3. Comparing Model Estimations of Exposure and Environmental Media With Those Found in the Literature

The fate, transport, and transfer models presented in this document may attain a measure of credibility (beyond that due to the integrity of their formulation and careful assignment of model parameters) if it can be shown that estimations of environmental and exposure media concentrations are consistent with those found in the literature. Some of those comparisons can use the exposure media concentrations generated in the demonstration scenarios because the source strength terms of the demonstrations were crafted to be meaningful. Specifically, the on-site source category was demonstrated with basin-wide soil concentrations of 1 ppt, which are characterized as background soil concentrations. The off-site source category was demonstrated with a bounded area of high soil concentrations of 1 ppb. This was also supported by literature showing this that

sites of high soil contamination contained dioxin-like compounds in the ppb range. The effluent discharge source category had substantial data from the 104 pulp and paper mill to both assign model parameters (effluent and receiving water body flow rates, etc.) and source strengths (mg/hr release of 2,3,7,8-TCDD). Other tests are conducted below which do not use results from the demonstration scenarios. It is clearly stated up front that discussions below are not described as validation exercises. Validation exercises would require specific data sets on source strengths, environmental characteristics, and environmental impacts. None of the tests contain complete and accurate site-specific information which would be required for validation testing. The one exception might be the exercises undertaken to evaluate the effluent discharge source category; details on that exercise can be found in Section 7.2.3.6 below.

7.2.3.1. *The impact to soils of point source releases of dioxin-like compounds*

For the stack emission source category, emitted contaminants settle onto exposure and watershed soils and a resulting soil concentration is estimated. For the off-site soil source category, contaminated soils from a bounded area of soil contamination are assumed to migrate via erosion and impact the soils of a nearby exposure site. This section examines the model algorithms for estimating impacts to nearby soils from these two sources.

No data could be found which linked stack emissions to an incremental impact to nearby soils. However, it may be possible to evaluate the algorithm estimating steady state soil concentrations of dioxin-like compounds given a rate of deposition - the deposition rate is determined in this methodology using atmospheric dispersion/deposition modeling. The soil impact algorithm mixes the modeled deposition rate, in mass/area-time units or $\mu g/m^2$-yr, into a defined zone of mixing, in units of length or cm, and assigns a rate of dissipation to the depositing residues, in units if $time^{-1}$ or yr^{-1}, to estimate a steady state soil concentration. The zone of mixing for untilled soils in this assessment is 1 cm and the dissipation rate for dioxin-like compounds is assumed to be 0.0693 yr^{-1}, which corresponds to a half-life of 10 years.

In evaluating the beef bioconcentration algorithm below in Section 7.2.3.9, a side evaluation looked at the algorithm for estimating soil concentration from deposition of dioxin-like compounds. Starting with an air profile crafted to be characteristic of rural

environments, this evaluation showed model predictions of soil concentrations ranged from a factor of 2 to about a factor of 10 lower than observed soil concentrations typical of a rural environment (i.e., observed concentrations are twice as high to about ten times higher than predicted concentrations). This would imply that the model and/or the parameter assignments are in error for the algorithm for estimating depositional impacts to soils. Section 7.2.3.9 below offered three most likely areas which would explain this shortfall: 1) the dissipation rate of 0.0693 yr^{-1}, corresponding to a half-life of 10 years, was developed from field data of 2,3,7,8-TCDD applied to soils in the herbicide 2,4,5-T (Young, 1983). This implies that such a half-life may be appropriate for dissipation of residues from a bounded area of contamination, but perhaps not appropriate for background evaluation as was done in Section 7.2.3.9 below. In that case, dissipation mechanisms such as volatilization, wind or soil erosion, and so on, may not be losses from the background setting, while they would be losses from a bounded area. Therefore, the algorithm may not be in error, but rather the half-life of 10 years might be too short for estimating background depositional impacts, 2) the soil impact algorithms do not consider dry deposition of vapor-phase dioxins. No information could be found on such depositions, and the impact of not considering this loading could not be made, and 3) detritus recycling is not considered. A simple exercise in Section 7.2.3.9 showed that this loading might be equal to about 20% of background deposition loadings.

For the off-site soil source algorithm, contaminated soils erode onto a nearby site of exposure site and mix into a depth of either 5 cm for untilled conditions or 20 cm for tilled conditions. The 5-cm depth was chosen for this source category based on the hypothesis that erosion is more turbulent process than atmospheric deposition, and that there may be mixing of contaminated soil from the site with clean soil between the contaminated and the exposure site. A *contaminant concentration ratio* is defined for purposes of this discussion as the ratio of soil concentration at the site of exposure to the soil concentration at the site of contamination. For example Scenario 3, soil eroded from a 40,000 m^2 (10-acre) contaminated site was assumed to partially deposit onto a 40,000 m^2 exposure site. The contaminant concentration ratio was 0.28 for the 5-cm depth of mixing at the site of exposure and 0.08 for the 20-cm mixing depth.

Data to rigorously validate the approach taken in this assessment is unavailable. However, there have been documented evidence of migration of 2,3,7,8-TCDD away from

industrial sites with soil contamination of 2,3,7,8-TCDD, resulting in off-site soil contamination. Off-site soil concentrations of concern were identified in 7 of 100 Tier 1 and Tier 2 sites of the National Dioxin Study (EPA, 1987). The study noted that in most cases, 2,3,7,8-TCDD had not migrated off-site. Most, but not all, Tier 1 and 2 sites did have some off-site soil sampling without detection. It should be noted, however, that soil detection limits for most of these 100 Tier 1 and 2 sites were at 1 ppb; this would have precluded finding concentrations less than 1 ppb in some of the off-site soil sampling, particularly important for many of the sites where on-site detections were in the low ppb range. Summary data from the 7 sites noted above is provided in Table 7-1. Contaminant concentration ratios cannot be evaluated by this summary because of lack of detail provided in the National Dioxin Study.

Further detail on the 1984 sampling at the Dow Chemical site in Midland is provided in Nestrick, et al. (1986). An evaluation of the information in that reference is more informative than the Dow Chemical summary in Table 7-1. The entire site is 607 hectares. On-site sampling included areas identified as chlorophenolic production areas, a waste incinerator area, and "background" areas. Background areas were within the 607 ha site but away from production areas. Two of the on-site areas were further identified as areas with Localized Elevated Levels (LELs). These two areas comprise less than 0.5% of the total site area, but had the three highest occurrences of 2,3,7,8-TCDD at 25, 34, and 52 ppb. Including these three high occurrences in the total of 33 samples taken on-site at sites of concern (i.e., not including the background sites) leads to an average concentration of 4.3 ppb; excluding them leads to an average of 1.0 ppb. The average of 11 background samples (including two ND assumed to be 0.0) was 0.15 ppb. A contaminant concentration ratio of 0.035 is calculated assuming an average concentration for contaminated soil of 4.3 ppb (0.15/4.3 = 0.035), and a ratio of 0.15 is calculated if the average soil contamination concentration is more like 1.0 ppb rather than 4.3 ppb.

This ratio of 0.035 is about 1/8 as much as the 0.28 ratio estimated assuming the shallow 5-cm depth of contamination, although the ratio of 0.15 is only about half as much as this 0.28 ratio. The depth of 20 cm led to a modeled ratio of 0.08, which is more in line with the Dow contaminant ratios of 0.035 or 0.15. The 5-cm depth ratios are probably more pertinent for comparison, however, since it is unlikely that there were tillage operations (or other soil practices which would distribute residues) in background areas of

Table 7-1. Summary of off-site soil contamination from Tier 1 and 2 sites of the National Dioxin Study.

Site name	On-site # samples/range (ppb)	Off-site # samples/range (ppb)	Comments
Diamond Alkali Newark, NJ	9/60-51,000	537/ND-725	Facility involved in the manufacture of 2,4,5-T; off-site sampling covered a 4000-ft radius including public areas such as a public housing unit, park, streets, and river. Two of 11 samples from a park were positive at 1-3.1 ppb; detection limit was 1 ppb. Other off-site positives were from streets and river sediments.
Brady Metals Newark, NJ	10/1.9-3500	30/1.7-1156	Site directly associated with the Diamond Alkali site summarized above; text did not provide any further detail on off-site soil sampling.
Love Canal Niagara, NY	NA/NA-6.7	20/3-263	Love Canal contamination well documented elsewhere; few details provided in reference for soil sampling programs; it was noted that 3,000 cubic yards of fly ash and BHC cake were taken from Love Canal in 1954 and used as fill at the nearby 93rd Street School, a subsurface sample 3 + ft deep showed a concentration of 6.7 ppb. The off-site summary provided here was from an area identified as Hyde Park.
Vertac Jacksonville, AR	45/<1-1,200	320/<1-33.4	A site manufacturing 2,4,5-T; it is not clear than any of the off-site sampling was for surface soil - summary tables identified it as "various"; text description did not mention off-site soil contamination and indicated that solid and liquid waste were buried on-site in a series of landfills. 2,3,7,8-TCDD was found in fish as far away as 100 miles.
Hooker Chemical Niagara, NY	17/ND-18,600	4/ND-1.1	A site manufacturing 2,4,5-TCP; subsurface soil sampling ranged from ND to 18.6 parts per million; one off-site surface soil detection noted at 1.1 ppb.
Bliss Tank Property Rosati, MO	NA/ND-430	NA/ND-430	No summary text provided in primary reference; tabular summary identified soil sampling as on/off-site soil; non-detects were noted in 13 off-site dust sampling.
Dow Chemical Property Midland, MI	#1: 43/.041-52.0 #2: 106/ND-1500	11/.0006-.45 42/.003-2.03	Site most extensively studied of those in National Dioxin Study; Data identified as #1 was a summary of 1984 data supplied in NDS; #2 was a summary of 1985 data; the 1984 data was further detailed in Nestrick, et al. 1986; see text for further discussions on this site.

Source: EPA, 1987.

the 607 ha Dow site.

It appears reasonable that the no-till contaminant ratio of 0.28 is higher than the Dow ratios for several reasons. First, the contaminated areas sampled were those likely to be of concern and comprising only a small percentage of the total 607 hectare site. That might question the representativeness of 4.3 ppb as average soil contamination in impacted areas; the three highest concentrations came from specifically identified LELs comprising only 0.5% of the 607 ha site area. Second, a map provided in Nestrick, et al. (1986) including a distance scale clearly shows that all of the background samples were much further than 150 meters from the contaminated sample points, with several sample points hundreds to over a thousand meters from the contaminated sample points. The contaminant concentration ratio of example Scenario 3, 0.28, was estimated with a distance of 150 meters. Third, the example scenarios had specific assumptions about erosion which may or may not have been appropriate for application to the Dow site.

Ideally validation of the soil erosion model would involve direct application at the DOW site and comparison of predicted values to measured values. This was not feasible due to lack of information regarding the DOW site. Instead, this analysis has shown that the model predictions of contaminant concentration ratios differ logically from observed ratios at the DOW site.

7.2.3.2. *Soil concentrations and concurrent concentrations in bottom sediments and fish*

The Connecticut Department of Environmental Protection (CDEP, 1992) established a program in 1986 for monitoring TCDD, TCDF, and other dioxin-like isomers of comparable toxicity in several environmental matrices near resource recovery facilities (RRFs). Matrices monitored include ambient air, residues and leachate from the ash disposal sites, surficial soils, surface water surficial bottom sediments, and whole fish. The purpose of the program is to evaluate the impact of RRFs. Eight locations were evaluated through 1990, with one location serving as a baseline or reference site. Of the seven remaining locations, RRFs began operation in 1983 (1 RRF), 1987 (3), 1988 (1), and 1990 (2). This section will examine the soil, sediment, and fish data from that program.

The soil concentrations throughout all eight sites might be characterized as typical of background concentrations mainly because the concentrations of 2,3,7,8-TCDD

measured through 1990 averaged 0.56 ppt (n = 77; assuming non-detects were 1/2 detection limit), with roughly a 50% non-detect rate (at a detection limit which has varied by data set, but has been around 0.1 ppt). In studies measuring soil concentrations of 2,3,7,8-TCDD in background or rural settings, either none was found, or concentrations were found in the low ppt range - this seems to also characterize the Connecticut data. In a statistical analysis of the data collected through 1988, the average soil concentration for 2,3,7,8-TCDD as 0.44 ppt (n = 42; CDEP, 1992; same procedures for estimating average concentrations), which is lower than the 0.56 ppt concentration for all samples through 1990. Concentrations of 2,3,7,8-TCDF taken after 1988, however, are lower than those taken in 1987 and 1988: the average including samples through 1988 was 8.20 ppt (n = 41; CDEP, 1992); while through 1990 was 6.77 (n = 77; CDEP, 1992). This simple examination of averages over time does not seem to indicate statistically significant change, if any. As well, in a statistical analysis of the data (principal component analysis of the concentration levels of all isomers in soil, fish, and sediment to attempt to identify stratification of the data by year) for four of the RRFs through 1990, MRI (1992) concluded that the RRFs had no apparent effect on the levels of the dioxin-like compounds in the three matrices.

The purpose of developing the argument that levels in soil are low and perhaps typical of background conditions is to be able to compare the soil to sediment, and sediment to fish ratios that arise from this data with those that were generated in example Scenarios 1 and 2 in Chapter 5. Those scenarios demonstrated the on-site scenario, with basin-wide soil concentrations of 2,3,7,8-TCDD of 1 ppt. As in all the comparison of literature data with model results in this section, this is not a validation exercise.

Information and results from the CDEP program for the soil, sediment, and fish matrices are presented in Tables 7-2 through 7-4. The data and supporting documentation was supplied by CDEP (1992). Table 7-2 provides a summary of the eight sites currently in the CDEP program. One "reference" or "control" site includes two areas, which for 1988 was at Union, Connecticut, and for 1990 was at Stafford, Connecticut. No nearby potential sources of dioxin release (industrial, commercial) were identified for these two reference sites. One of the sites, the Hartford site, is near the Connecticut River. All water bodies sampled were coves with direct links to the river. Industrial and commercial enterprises which use the river are speculated to have resulted in the generally higher fish

concentrations noted in the Hartford site, as compared to the other sites. Twenty-one water bodies have been sampled, including harbors, channels, impoundments, reservoirs, coves, ponds, rivers, and lakes. Six species of fish have been sampled, including carp, channel and white catfish, white sucker, brown bullhead, and yellow perch. All but the yellow perch are bottom feeders. The yellow perch was sampled mostly when a sufficient sample of bottom feeder could not be obtained. Samples of bottom feeders were sought because it was felt that they would have the highest tissue concentrations due to their association with bottom sediments, and therefore be the best markers for impact and change over time (C. Fredette, CDEP, personal communication). The soil sampling program was not extensive; samples were only taken near ambient air monitoring stations, and only 77 samples were taken through 1990. It certainly cannot be claimed that the samples are statistically representative of soils which drain into the water bodies. However, given the consistency in concentrations noted and their low values, the supposition is made that concentrations are adequately representative of soils which impact the water bodies. Maps of the sites were obtained from CDEP to evaluate the distance from the soil sampling sites to the nearest water bodies. Nearly all soil sampling sites were within 3 miles of the nearest water body, and most were near to and less than one mile away.

Table 7-3 lists the frequency of non-detects for all data through 1990, and incomplete information on detection limits. For determining average concentrations in sampled matrices, non-detects were assumed to equal 1/2 the detection limit. The detection limits for these matrices varied over time with different data sets. The detection limits noted were those cited for 1987 and 1988 data (from a draft Monitoring Progress Report supplied by CDEP). That report did not list detection limits for three matrices noted. In parenthesis is noted the lowest concentration in the data sets, which would correspond to 1/2 the detection limit at the time the non-detect was measured. The purpose of presenting this data is simply to argue that assuming 1/2 the detection limit for computing averages will not greatly impact the averages. This can be demonstrated for the one matrix where this is most likely to be a concern - soil concentrations of 2,3,7,8-TCDD where a 50% non-detect rate was noted. If half the samples were assigned a value of 0.0 instead of perhaps 0.07 ppt (half the noted detection limit of 0.13 ppt), than the overall average would drop from 0.56 ppt to 0.52 ppt.

Table 7-2. Description of soil, sediment, and fish sampling program of dioxin-like compounds undertaken by the Connecticut Department of Environmental Protection.

Site/Sampling Media	Description	Data
1. Bridgeport	Year RRF began operation	1987
Soil	Years of Collection	1987, 1988, 1990
	Number of sampling sites	7
	Total number of samples	21
Sediment	Years of collection	1987, 1988, 1990
	Number of water bodies sampled	6
	Water body descriptions	harbor (2), channel (1; off harbor), river (1), pond (2)
	Total number of sediment samples	66
	Range, samples per water body	4 - 22
Fish	No fish sampling at this site	
2. Bristol	Year RRF began operation	1987
Soil	Years of collection	1987, 1988, 1990
	Number of sampling sites	4
	Total number of samples	12
Sediment	Years of collection	1987, 1988, 1990
	Number of water bodies sampled	2
	Water body descriptions	pond (2)
	Total number of sediment samples	60
	Range, samples per water body	29 and 30
Fish	Years of collection	1987, 1988, 1989, 1990
	Number of water bodies sampled	2
	Water body descriptions	pond (2)
	Total number of fish samples	140
	Range, samples per water body	68 and 72
	Fish species	brown bullhead, white sucker, yellow perch

(continued on following page)

Table 7-2. (cont'd)

Site/Sampling Media	Description	Data
3. Hartford	Year RRF began operation	1987
Soil	Years of collection	1987, 1988, 1990
	Number of sampling sites	4
	Total number of samples	12
Sediment	Years of collection	1987, 1988, 1990
	Number of water bodies sampled	3
	Water body descriptions	impoundment (1), cove (2)
	Total number of sediment samples	90
	Range, samples per water body	30 from each water body
Fish	Years of collection	1987, 1988, 1989, 1990
	Number of water bodies sampled	2
	Water body descriptions	cove (2)
	Total number of fish samples	159
	Range, samples per water body	81 and 78
	Fish species	carp, channel catfish, white catfish, white sucker
4. Preston	Year RRF began operation	1990
Soil	Years of Collection	1990
	Number of sampling sites	4
	Total number of samples	4
Sediment	Years of collection	1990
	Number of water bodies sampled	3
	Water body descriptions	2 ponds, 1 reservoir
	Total number of sediment samples	30
	Range, samples per water body	10 each water body
Fish	No fish sampling at this site	

(continued on following page)

Table 7-2. (cont'd)

Site/Sampling Media	Description	Data
5. Sterling	Year RRF began operation	1990
Soil	Years of collection	1990
	Number of sampling sites	4
	Total number of samples	4
Sediment	Years of collection	1990
	Number of water bodies sampled	2
	Water body descriptions	pond (2)
	Total number of sediment samples	20
	Range, samples per water body	10 each pond
Fish	Years of collection	1990
	Number of water bodies sampled	2
	Water body descriptions	pond (2)
	Total number of fish samples	40
	Range, samples per water body	20 each pond
	Fish species	white sucker, yellow perch
6. Union/Stafford	No associated Resource Recovery Facility, used as "control" or "reference" site	
Soil	Years of collection	1988 (Un), 1990 (St)
	Number of sampling sites	4 (Un), 4 (St)
	Total number of samples	4 (Un), 4 (St)
Sediment	Years of collection	1988 (Un), 1990 (St)
	Number of water bodies sampled	2
	Water body descriptions	pond (Un), reservoir (St)
	Total number of sediment samples	20
	Range, samples per water body	10 each water body
Fish	Years of collection	1988, 1990
	Number of water bodies sampled	2
	Water body descriptions	pond and reservoir
	Total number of fish samples	48
	Range, samples per water body	27 (reservoir), 20 (pond)
	Fish species	brown bullhead, white sucker, yellow perch

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Table 7-2. (cont'd)

Site/Sampling Media	Description	Data
7. Windham	Year RRF began operation	1983
Soil	Years of collection	1988, 1990
	Number of sampling sites	4
	Total number of samples	8
Sediment	Years of collection	1988, 1990
	Number of water bodies sampled	1
	Water body descriptions	reservoir
	Total number of sediment samples	20
	Range, samples per water body	20
Fish	Years of collection	1988, 1989, 1990
	Number of water bodies sampled	1
	Water body descriptions	reservoir
	Total number of fish samples	59
	Range, samples per water body	59
	Fish species	brown bullhead, white sucker, yellow perch
8. Wallingford	Year RRF began operation	1988
Soil	Years of collection	1988, 1990
	Number of sampling sites	4
	Total number of samples	8
Sediment	Years of collection	1988, 1990
	Number of water bodies sampled	2
	Water body descriptions	impoundments
	Total number of sediment samples	40
	Range, samples per water body	20 each water body
Fish	Years of collection	1988, 1989, 1990
	Number of water bodies sampled	2
	Water body descriptions	impoundments
	Total number of fish samples	75
	Range, samples per water body	59
	Fish species	brown bullhead, carp, white sucker

Source: CDEP, 1992.

Table 7-3. Frequency of nondetects and detection limits for soil, sediment, and fish, for three congeners in the Connecticut Department of Environmental Protection data set.

Congener	Soil	Sediment	Fish
2,3,7,8-TCDD			
Percent of non-detects	50	27	3
Detection limit, ppt	0.13	0.25	0.05
2,3,7,8-TCDF			
Percent of non-detects	3	2	0.2
Detection limit, ppt	NDA (0.09)	0.17	NDA (0.09)
2,3,4,7,8-PCDF			
Percent of non-detects	1	5	7
Detection limit, ppt	NDA (0.09)	0.26	0.04

Source: for percent non-detects: MRI, 1992; for detection limits, draft Monitoring Progress Report for 1988, supplied by CDEP (1992) specific to MRI laboratories; NDA = no data available; number of parenthesis is 1/2 detection limit for time when non-detect was noted, see text for further information and interpretation

Table 7-4 summarizes the key results from the CDEP data. The C_{sed}:C_{soil} ratio is the ratio of sediment concentration to soil concentration for the eight sites for 2,3,7,8-TCDD - these are not organic carbon normalized concentration ratios. The second ratio noted is called the BSAF ratio, because it is defined in the same way that the Biota Sediment Accumulation Factor is defined: the ratio of the lipid-normalized whole fish tissue concentration over the organic carbon normalized bottom sediment concentration. The BSAF is used to estimate fish tissue concentrations from bottom sediment concentrations in this assessment. The fish lipid contents and organic carbon contents for each site were supplied by CDEP (1992). The BSAFs for the entire data set and the four concentrations are based on averages of fish lipid and organic carbon contents from the entire data set.

Key observations from the demonstration scenarios and the results of the CDEP program are:

1) Demonstration scenarios 1 and 2 in Chapter 5 estimated the impact from basin-

Table 7-4. Results for Connecticut Department of Environmental Protection sampling, including soil, sediment and fish concentrations, and the key concentration ratios of sediment to soil and the Biota Sediment Accumulation Factor (BSAF) ratio.

Site/Description	Soil	Sediment	Fish
A. 2,3,7,8-TCDD			
1. Bridgeport			
Number of samples	21	66	
Range of concentration, ppt	0.07-4.62	0.10-51.50	No data
Mean concentration, ppt	0.59	4.53	
C_{sed}:C_{soil} Ratio		**7.6**	
2. Bristol			
Number of samples	12	59	140
Range of concentration, ppt	0.01-0.61	0.16-6.50	0.03-0.83
Mean concentration, ppt	0.17	1.67	0.26
C_{sed}:C_{soil} Ratio		**9.8**	
fish lipid/sediment organic carbon		**0.038/0.190**	
BSAF Ratio		**0.78**	
3. Hartford			
Number of samples	12	90	159
Range of concentration, ppt	0.07-0.32	0.04-23.10	0.03-10.90
Mean concentration, ppt	0.16	1.96	2.41
C_{sed}:C_{soil} Ratio		**12.3**	
fish lipid/sediment organic carbon		**0.071/0.056**	
BSAF Ratio		**0.97**	
4. Preston			
Number of samples	4	30	
Range of concentration, ppt	0.14-0.80	0.08-17.9	No data
Mean concentration, ppt	0.39	2.75	
C_{sed}:C_{soil} Ratio		**7.1**	

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Table 7-4. (cont'd)

Site/Description	Soil	Sediment	Fish
5. Sterling			
Number of samples	4	20	40
Range of concentration, ppt	0.01-7.96	0.07-3.08	0.03-0.37
Mean concentration, ppt	2.12	0.90	0.11
C_{sed}:C_{soil} Ratio		**0.42**	
fish lipid/sediment organic carbon		**0.053/0.067**	
BSAF Ratio		**0.15**	
6. Union/Stafford			
Number of samples	8	20	48
Range of concentration, ppt	0.02-1.56	0.23-3.69	0.07-0.85
Mean concentration, ppt	0.28	1.58	0.26
C_{sed}:C_{soil} Ratio		**5.64**	
fish lipid/sediment organic carbon		**0.041/0.178**	
BSAF Ratio		**0.71**	
7. Windham			
Number of samples	8	20	59
Range of concentration, ppt	0.15-0.54	0.18-1.97	0.07-0.60
Mean concentration, ppt	0.25	0.97	0.25
C_{sed}:C_{soil} Ratio		**3.88**	
fish lipid/sediment organic carbon		**0.044/0.129**	
BSAF Ratio		**0.76**	
8. Wallingford			
Number of samples	8	40	75
Range of concentration, ppt	0.07-6.00	0.03-3.10	0.03-8.92
Mean concentration, ppt	1.61	0.54	1.37
C_{sed}:C_{soil} Ratio		**0.33**	
fish lipid/sediment organic carbon		**0.071/0.019**	
BSAF Ratio		**0.68**	

(continued on following page)

Table 7-4. (cont'd)

Site/Description	Soil	Sediment	Fish
B. TOTALS			
2,3,7,8-TCDD			
Number of samples	**77**	**346**	**521**
Mean concentration, ppt	**0.56**	**2.16**	**1.06**
C_{sed}:C_{soil} Ratio	**3.86**		
BSAF Ratio	**0.86**		
2,3,7,8-TCDF			
Number of samples	**77**	**346**	**521**
Mean concentration, ppt	**6.77**	**17.52**	**2.53**
C_{sed}:C_{soil} Ratio	**2.59**		
BSAF Ratio	**0.25**		
2,3,4,7,8-PCDF			
Number of samples	**77**	**346**	**521**
Mean concentration, ppt	**3.56**	**5.62**	**1.49**
C_{sed}:C_{soil} Ratio	**1.58**		
BSAF Ratio	**0.47**		
TEQ			
Number of samples	**77**	**346**	**521**
Mean concentration, ppt	**8.42**	**22.69**	**3.10**
C_{sed}:C_{soil} Ratio	**2.69**		
BSAF Ratio	**0.24**		

(Note: for all total results above, fish lipid content = 0.0557, and the fraction organic carbon content = 0.0982; these are averages for the CDEP data set; CDEP, 1992)

wide soil concentrations of 1 ppt of the example compounds. The difference in the scenarios was in exposure patterns and exposure site characteristics - the impacts to surface water sediments and fish were the same in both scenarios. The estimated concentration of 2,3,7,8-TCDD and 2,3,4,7,8-TCDF in bottom sediments was 2.79 and 2.85 ppt, respectively. The small difference was due to a larger organic carbon partition coefficient assumed for 2,3,4,7,8-TCDF. Sediment to soil ratios for these two compounds are, therefore, 2.79 and 2.85. These compare to the overall 3.86 and 1.58 estimated in the Connecticut data set for these two compounds. The ratios for 2,3,7,8-TCDF and for total toxic equivalents were 2.58 and 2.69. The average of these TCDD and TCDF ratios is 2.68. This tends to support but does not validate the model's approach.

One of the key model parameters in the soil to sediment algorithm which is uncertain and has been questioned is the soil enrichment ratio. It was assigned a value of 3.0, which means that concentrations in soil eroding from the field are three times higher than concentrations on the field. This value was questioned in Section 6.3.3.3, Chapter 6, where it was shown that its assigned value of 3.0 could lead to unrealistically high off-site soil concentrations. However, if it is assigned a lower value, that the sediment:soil ratios would also be lower - an enrichment ratio of 1.0 would lead to sediment:soil ratios less than 1.0. The close match of sediment:soil ratios with an enrichment ratio of 3.0 does not validate the model's approach to evaluating surface water impacts from low basin-wide soil concentrations, however. The model assumes that all surface water impacts are from erosion of basin soils. In fact, sediment concentrations in water bodies are also a function of direct atmospheric depositions onto water bodies and other direct, industrial related, discharges into water bodies. Such depositions may originate from sources other than soil contamination - such as air emissions from cars or industry. The impact of industrial sources to the sediments in the CDEP data is unclear. As noted, evidence collected so far does not indicate an impact from incinerator emissions. The Hartford site has been cited as being impacted with industrial use of the nearby Connecticut River. However, the sediment concentrations of the water bodies at this site are not higher than other sites - in fact, the sediment concentrations from the Bridgeport, Bristol, Preston, and even the background Union/Stafford sites are comparable or higher. In any case, deposition of air-borne contaminants are likely to impact bottom sediments to some degree, and the soil contamination models of this assessment do not include such an impact (the stack

emission source category does include this impact for emissions reaching water bodies). Because the soil contamination models do not include air-borne depositions, it is possible that the enrichment ratio of 3.0 serves to artificially increase modeled bottom sediment concentration. In any case, the CDEP data does appear to indicate that bottom sediment concentrations exceed surface soil concentrations by more than a factor of 2.0 in environmental settings that mostly do not appear to be impacted by industrial activities.

2) The overall BSAF ratios for the three dioxin compounds and the TEQ ratio, ranging from 0.24-0.86, are higher than the BSAF used in the demonstration scenario of 0.09 for 2,3,7,8-TCDD and 2,3,4,7,8-PCDF. Higher BSAF in the CDEP data are expected because the fish species sampled were bottom feeders, except for the yellow perch. The selected BSAF of 0.09 is mainly supported by Lake Ontario data (EPA, 1990a), which was on brown and lake trout, smallmouth bass, and white and yellow perch, all column feeders. Bottom feeders are expected to have more exposure to the contaminants because of their direct contact with sediments. This implies that use of the BSAF for site-specific assessments should consider the dietary pattern of exposed individuals. If a significant portion of local fish consumption includes bottom feeders (such as catfish), then perhaps a BSAF greater the 0.09 used for the demonstration scenarios is warranted.

3) Of the six sites for which BSAFs were individually determined for 2,3,7,8-TCDD, the highest BSAF was from the Hartford site at 0.97. The claim is not made that it is substantially or significantly different from BSAFs at the other sites - it is simply a point of interest for comment. The Hartford site has been previously identified as likely to have been impacted by activity on Connecticut River - all the fish are taken from coves directly connected to the river. Although the bottom sediment concentrations at this site are not different from other sites, one hypothesis is that the water column is more impacted for this site as compared to other sites.

In Chapter 4, Section 4.3.4.1, a key issue identified for the validity of the BSAF approach is the issue of past versus ongoing contamination. The same issue was discussed in Section 4.6. of Chapter 4, on the effluent discharge source category. Generally, the hypothesis offered was that fish are likely to be more exposed with ongoing impacts to the water body as compared to a situation where impacts were principally historical. The effluent discharge source category is a case of ongoing impacts. The argument presented in Section 4.6. of Chapter was that the BSSAF (biota suspended

sediment accumulation factor) should be greater in numerical value than a BSAF whose value is derived from data on a water body whose impacts have been primarily historical. This was the case for the assignment of a 0.09 for the BSAF, which was based on data on column feeders in Lake Ontario, a lake whose impact has been speculated as primarily historical. Although the numerical difference between the Hartford BSAF, at 0.97, and the next largest BSAF at Bristol, at 0.78, is not that large, perhaps that difference is due to the fact that the fish are more exposed at Hartford due to ongoing impacts from the Connecticut River.

In summary, this section has evaluated data supplied by the Connecticut Department of Environmental Protection on fish, sediment, and soil data. It is the only data set that could be found where soil and sediment data were concurrently taken in areas evaluated as (mostly) not impacted by industrial activity. An examination of the sediment to surface soil concentration ratios, showing them generally to be above 2.0 with an average for all data points and dioxin-like congeners of 2.68, supports the soil contamination model of this assessment for estimating sediment impacts from uniform basin-wide soil concentrations, which showed sediment to surface soil concentration ratios of 2.8 for 2,3,7,8-TCDD and 2,3,4,7,8-PCDF. The BSAFs determined from the CDEP data are higher than the BSAFs used in the demonstration scenarios of this assessment. This was likely due to use of bottom feeders for fish concentration of the CDEP - bottom feeders are likely to have more exposure to dioxin-like compounds in water bodies than column feeders due to their association with contaminated bottom sediments.

7.2.3.3. *Other bottom sediment concentration data*

Assuming elevated sediment concentrations are a function of elevated surface soil concentrations is reasonable when the only source of water body contamination is soil contamination. However, comparing soil and sediment concentrations would not be appropriate if sediments and water were impacted by industrial discharges, which has often been cited as the cause for sediment and water impacts (see Bopp, et al., 1991; Norwood, et al., 1989; e.g.). Sediment concentrations of note have also been found in surface water bodies near urban settings, with car and industrial stack emissions cited as likely causes (Gotz and Schumacher, 1990; Rappe and Kjeller, 1987). Rappe, et al. (1989) collected samples from the Baltic Sea, which were described as background samples.

They note that the pattern of tetra-CDF congener concentrations found in the Baltic Sea were typical of what they termed the "incineration patterns" - air and air particulate concentrations that were attributed to sources such as incineration, car exhausts, steel mills, etc. On the other hand, sediment samples collected between 4 and 30 km downstream from a pulp mill revealed a congener pattern typical of bleaching mills. The stack emission and effluent discharge source categories provide separate models for water body impacts. The capability of the effluent discharge model is estimating fish tissue concentrations is examined in Section 7.2.3.6 below. The remainder of this section examines some of the data available which is not attributed to industrial or urban sources.

Except for the CDEP data described in Section 7.2.3.2 above, data was not found linking sediment concentrations to soil concentrations, in an urban or more pertinent to this assessment, a rural setting. Some sampling has occurred in areas described as rural or background. Sediment sampling in Lake Orono in Central Minnesota in such a setting found no tetra- and penta-CDDs, although occurrences of total hexa-CDDs were found in the low ng/kg (ppt) level, occurrences of hepta-CDDs to a high of 110 ppt, and total OCDD concentrations ranged from 490-600 ppt for three samples (Reed, et al., 1990). A report on sampling of several estuaries in Eastern United States included a "reference" or relatively clean site, central Long Island Sound. There were no occurrences of 2,3,7,8-TCDD, although 2,3,7,8-TCDF was found at 15 ppt in this clean site. Other sites had identified industrial source inputs and higher noted concentrations (Norwood, et al., 1990). 2,3,7,8-TCDD was extensively found in sediments of Lake Ontario (EPA, 1990a). The average of samples from all depths of sediment collection from 49 stations including 55 samples was 68 ppt. The average of 30 surficial sediment samples was 110 ppt. A modeling exercise implied that an annual load of 2.1 kg/year into Lake Ontario corresponds to a concentration of 110 ppt. One identified source was the Hyde Park Landfill, located about 2000 feet from the Niagara River, which drains into Lake Ontario. Between 1954 and 1975, an estimated 0.7 to 1.6 tons of 2,3,7,8-TCDD were deposited in the landfill. A principal conclusion from the modeling exercise, however, was that a characterization of historical loadings of 2,3,7,8-TCDD into the lake was not available and would be necessary to evaluate the contributions by the Hyde Park Landfill.

7.2.3.4. *Data on water concentrations of dioxin-like compounds*

Tables B-3 and B-4, Appendix B of Volume II, summarize available data on surface water concentrations of the PCDDs and PCDFs. The results on this table are not directly amenable to comparison because the sources of contamination were unspecified except to note that, in some studies, a portion of the sampling occurred for water bodies known to be impacted by industrial discharges. The 104-mill pulp and paper mill study, which measured discharges into of 2,3,7,8-TCDD and 2,3,7,8-TCDF into surface water bodies, was the only such study currently available which measured impacts to surface water bodies. Section 7.2.3.6 below discusses the use of this data to evaluate the effluent discharge source category. This study did not measure water concentrations, and no other studies could be found which measured both source strength and resulting surface water concentrations.

Nonetheless, the data on water concentrations of dioxin-like compounds does indicate that occurrences of PCDDs and PCDFs are generally not-detected or in the low pg/L (ppq) range; detection limits were generally at or near 1 pg/L. The one exception to this is occurrences in tens to hundreds of pg/L range for PCDFs in one of twenty community water systems sampled in New York (Meyer, et al., 1989). Concentrations exceeding 200 pg/L were found in the hepta- and octa-CDFs; concentrations between 2 and 85 pg/L were found in the tetra to hexa-CDFs for this impacted water system.

The highest water concentration estimated in the demonstration scenarios in this assessment was 0.2 pg/L for the off-site soil demonstration scenario #6, for 2,3,7,8-TCDD. Soil concentrations were 1 ppb in the bounded area of soil contamination in this scenarios. Water concentrations for 2,3,4,7,8-PCDF and 2,3,3',4,4',5,5'-HPCB were both 0.1 and 0.02 pg/L for this scenario, respectively. For Scenarios 1 and 2, where watershed soil concentrations were set at 1 ng/kg (ppt), surface water concentrations were roughly one order of magnitude lower at 10^{-2} pg/L (ppq) range for the example TCDD and PCDF, and 10^{-3} ppq for the example PCB. For Scenarios 4 and 5 demonstrating stack emission depositions and where watershed soil concentrations were estimated to be in the 10^{-4} ppt range, surface water concentrations were the in the 10^{-6} ppq range. For Scenario 6, which demonstrated the effluent discharge source category, surface water concentrations were comparable to the on-site soil demonstration scenarios.

7.2.3.5. *Data on fish concentrations in the literature*

This assessment estimated fish concentrations of 2,3,7,8-TCDD for the various source categories to be: 1) on-site soil source category - 0.6 ppt, 2) off-site soil contamination - 3 ppt, 3) stack emission source category - 0.0004 ppt, and 4) effluent discharge source category - 0.4 ppt. Data was not found to appropriately compare the stack emission source category results, and data on the effluent discharge source category is examined in the next section below. This section will examine some available data on fish concentrations in order to compare results from the first two categories with measured results.

The most appropriate study with which to make comparisons is the National Study of Chemical Residues in Fish (EPA, 1992b; hereafter abbreviated NSCRF, see Chapter 4, Section 4.5 of Volume II for more detail). Fish tissue data on a variety of species and contaminants of concern in aquatic environments and fish from around the country were developed. Most important for current purposes, the sites were carefully characterized in terms of potential sources of fish contamination. There were 353 sites from which fish tissue data was available, of which 347 had data on 2,3,7,8-TCDD. Results from four site categories might be appropriate for comparison with concentrations estimated to occur from low, possibly background, soil concentrations of 2,3,7,8-TCDD. The four categories and number of sites per category were: the USGS water quality network NASQAN - 40 sites; Background (B) - 34 sites, Agricultural (A) - 17 sites, and Publicly Owned Treatment Works (POTW) - 8 sites. The average 2,3,7,8-TCDD concentrations measured for these four categories were: NASQAN - 1.02 ppt; B - 0.56 ppt; A - 0.75 ppt, and POTW - 0.90 ppt. The "on-site" source category was demonstrated in Chapter 5 using a soil concentration of 2,3,7,8-TCDD that might be typical of background conditions - 1 ng/kg (ppt). The resulting fish tissue concentrations estimated for this soil concentration was 0.6 ppt. Four of the site categories of the NSCRF might be considered representative of sources characterized as land areas of high soil concentrations of 2,3,7,8-TCDD. These were: Industrial/Urban site (IND/URB) - 105 sites, Refinery/Other Industry (R/I) - 20 sites, Wood Preservers (WP) - 11 sites, and Superfund Sites (NPL) - 7 sites. Average fish tissue concentrations measured for these site categories were: IND/URB - 4.04 ppt, R/I - 4.38 ppt, WP - 1.40 ppt, and NPL - 30.02 ppt. The source category of this assessment most similarly characterized to these would the category of off-site soil contamination, where a

bounded area of contaminated soil had 2,3,7,8-TCDD at 1 ppb. As noted above, the fish tissue concentration estimated with this source category was 3 ppt. The two remaining site categories of the NSCRF were Paper Mills Using Chlorine (PPC), and Other Paper Mills (PPNC). These data served as the basis for the comparison discussed below in the effluent discharge source category.

In general, the range of fish tissue concentrations measured for (perhaps) background conditions, 0.56 - 1.02 ppt, were comparable to the fish tissue concentration estimated assuming the low (perhaps) background soil concentration of 1 ppt soil concentration, 0.6 ppt. It may also be appropriate to make the same observation for the source categories assuming higher soil concentrations as compared to measured concentrations noted above. In this case, the range of average measured concentrations - 1.4 - 30.02 ppt compares with the modeled 3 ppt. This does not constitute a validation exercise, strictly speaking, since specific field data were not input and compared. However, a few key points can be made. One, the magnitude of concentrations appears to have been captured, and the approximate order of magnitude difference between background and higher source strength categories of the NSCRF also appears to have been duplicated. One data point from that study of interest is the 30.02 ppt concentration found for the NPL site. This is an order of magnitude higher than the 3.0 ppt estimated for the off-site soil source category. No insights can be gained from this difference because information was unavailable on the seven sites which were characterized as Superfund sites and which were expected to have been the cause of the 30.02 ppt fish concentration. However, one exercise contained in Chapter 6 of this volume, the mass balance exercise (Section 6.4), does contain one interesting result. Assuming the 1 ppb concentration of 2,3,7,8-TCDD extended 15 cm (6 in) deep on the 40,000 m^2 contaminated area, the mass of 2,3,7,8-TCDD that would be at this site would be 9 grams. This appears to be a small amount (and in fact the models of this assessment do not require depths of contamination - the fish and all other concentrations would be estimated if the contamination extended 15 cm or 15 m deep), and it would be interesting to know the source strengths of the 7 NPL sites, at least the soil surface concentrations.

Another comprehensive data base of fish concentrations of 2,3,7,8-TCDD is from EPA's National Dioxin Study (EPA, 1987; abbreviated NDS), which actually provided the motivation for the NSCRF when significant residues of 2,3,7,8-TCDD were found in fish in

the NDS. Fish concentrations from the NDS are also listed and discussed in Kuehl, et al. (1989). Travis and Hattemer-Frey (1991) summarized the fish data from the NDS. Their summary is as follows. Data collected from 304 urban sites in the vicinity of population centers or areas with known commercial fishing activity, including the Great Lakes Region, showed concentrations to range from non-detected to 85 ng/kg (ppt). The geometric mean concentration was 0.3 ppt, and only 29% had detectable levels of 2,3,7,8-TCDD. The Great Lakes data had more contamination, with 80% detection rate and a geometric mean concentration of 3.8 ppt. Recall from above that the fish tissue concentrations estimated for 2,3,7,8-TCDD for the off-site soil contamination source category was 3.0 ppt.

The NSCRF also collected data on 2,3,4,7,8-PCDF, the second example compound demonstrated. Briefly, the range of average fish tissue concentrations noted for the site categories evaluated as background above is 0.42-0.78 ppt, very similar to the 2,3,7,8-TCDD range of 0.56-1.02 ppt. The modeled fish tissue concentration of 2,3,4,7,8-PCDF for background conditions was the same as that for 2,3,7,8-TCDD at 0.6 ppt. Actually, 2,3,5,7,8-PCDF concentrations were slightly higher due to slightly higher Koc values for 2,3,4,7,8-PCDF - which translates to less partitioning to water and more in sediments. The key parameter leading to the similar result is the assignment of the bioaccumulation parameter, the biota to sediment accumulation factor (BSAF) the same value for both compounds. The range of 2,3,4,7,8-PCDF average fish concentrations for the sites of elevated soil concentration was 1.86-5.44 ppt, which compares to the modeled 2,3,4,7,8-PCDF concentrations of 3.0 for the off-site source category with initial soil concentrations of 1.0 ppt.

The NSCRF also collected data on PCB concentrations in fish, although the results were expressed in terms of total tetra-, hepta-, and so on. The data indicates concentrations well into the part per billion range for this breakout, and even higher considering total PCBs. The average concentration of total heptachlorobiphenyls over all study sites was 96.7 μg/kg (ppb). The average concentration of total PCBs over all sites was estimated as 1897.88 ppb, and the average concentration of total PCBs for background sites was 46.9 ppb. The modeled concentration of the example heptachlorobiphenyl, 2,3,3',4,4',5,5'-HPCB, for the background scenario (soil concentration = 1.0 ppt) was 10 ppt. The modeled concentration of 2,3,3',4,4',5,5'-

HPCB for the off-site soil source scenario, where soil concentration were 1 ppb, was 80 ppt.

Data from the Great Lakes region indicate that PCB concentrations are significantly higher than PCDD/PCDF concentrations in this area. PCB concentrations from fish in Lake Ontario are in the tens to hundreds of ppb level (Niimi and Oliver, 1989), while 2,3,7,8-TCDD contamination in Lake Ontario was in the tens of ppt level (EPA, 1990a) - a three order of magnitude difference. Other data in Table B.10, Appendix B, Volume II, where concentrations were similarly in the tens to hundreds of ppb level were from Lake Michigan (Smith, et al. 1990) and Waukegan Harbor in Illinois (Huckins, et al., 1988). The single data point from that table for 2,3,3',4,4',5,5'-HPCB, the example PCB congener in Chapter 5, was for carp in Lake Michigan, and was 29 ppb (29,000 ppt).

While the modeled PCDD/PCDF fish concentrations seem reasonably in line with measured concentrations, this assessment may have underestimated concentrations of 2,3,3',4,4',5,5'-HPCB. As noted, concentrations for fish in the Great Lakes Region were in the tens to hundreds of ppb range, while this assessment derived estimates all under 1 ppb. It is inappropriate to make direct comparisons without also comparing source strengths. Concentrations of PCBs in bottom sediments ranged from the low ppb for the tri-PCBs, to the tens of ppb for the tetra through hexa-PCBs, back to the low ppb for the hepta and octa-PCBs, in Lake Ontario (Oliver and Niimi, 1988). Another literature source showing fish concentrations in Waukegan Harbor, IL, in the hundreds of ppb range, had sediment concentrations of specific congeners as low as 5 ppb to as high as 131 ppm. The concentration of 2,3,3',4,4',5,5'-HPCB in bottom sediments was estimated to be only 40 ppt in the off-site soil scenario. Therefore, one reason PCB concentrations in fish estimated in this assessment are as much as three orders of magnitude lower than noted in the literature is because sediment concentrations estimated for the source categories in this assessment are three orders of magnitude lower. The BSAF for PCBs also was noted to be variable, with values below 1.0 to values over 20.0 (see Section 4.3.4.1, Chapter 4 of this volume). The BSAF for the example PCB congener in this assessment was 2.0. Higher BSAFs would also increase PCB concentrations estimated for fish.

The fish concentration of 2,3,7,8-TCDD estimated for the stack emission source category was lowest at 0.00007 ppt. Data was unavailable to place this in any comparative framework. It was noted that the watershed soil concentration estimated

was 0.0001 ppt 2,3,7,8-TCDD. The fish-to-soil ratio of 0.7 compares favorably to the fish-to-soil ratio of 0.6 (0.6 ppt/1.0 ppt) for the on-site soil demonstration which assumed basin-wide 1.0 ppt soil concentrations.

7.2.3.6. *Impact of pulp and paper mill effluent discharges on fish tissue concentrations*

a. Description of Exercise and Model Parameters

This section describes a validation exercise of the effluent discharge algorithm. Validation is a cautious description of the exercise, since much of the data used is of uncertain quality. Discharge rates of 2,3,7,8-TCDD (mass/time units) into surface water bodies from a subset of 104 pulp and paper mills, which were sampled on a one-time basis in 1988 for such discharges and other parameters (EPA, 1990d; hereafter referred to as the 104-mill study), represent the key observed source term for this exercise. Fish concentrations of 2,3,7,8-TCDD for fish sampled downstream of these sources as part of the National Study of Chemical Residues in Fish (EPA, 1992b; abbreviated NSCRF hereafter) represent the key predicted model result for this exercise.

The National Council of the Paper Industry for Air and Stream Improvement (abbreviated NCASI hereafter) has already performed this exercise, and a brief description of their efforts and results can be found in Sherman, et al. (1992). NCASI carefully matched NSCRF data to appropriate mills of the 104-mill study. In many cases, they found more than one fish sample to correspond to a given discharge. Also, they considered circumstances where more than one mill effluent discharge can be considered to have impacted the environment where fish were sampled. In these cases, discharge rates from the contributing mills were fed into the model as source terms.

In NCASI's careful examination of the available data, they only considered 47 of the 104 mills as appropriate for this type of model testing. From these 47 mills, 95 fish samples with detectable residues of 2,3,7,8-TCDD were identified. Some mills had only one fish sample corresponding to it while others had up to four fish samples. The following explains why 57 of the remaining mills were not considered for this exercise:

1. Downstream of 10 pulp and paper mills was an estuary. NCASI considered the model appropriate for riverine situations only and did not calculate fish concentrations for estuarine settings.

2. The measurement for 2,3,7,8-TCDD in the effluent was listed as non-detect, and no further data examination and modeling occurred. There were 13 mills in this category.

3. NCASI could not identify appropriate fish measurements in the NCSRF downstream of the mill, and did not model further. Seven mills were in this category.

4. Some of the mills in NCASI's exercise were only considered "proximate" mills adding to the source term associated with another mill and one or more fish concentrations. Five mills were described in this manner.

5. For the remaining 22 mills, no explanation was provided for their lack of inclusion in the validation exercise.

Details of the NCASI modeling assumptions were supplied to EPA by NCASI (personal communication, Steven Hinton, PhD., P.E., NCASI, Inc.; Department of Civil Engineering, Tufts University, Medford, MA, 02155) and adopted for this exercise. Several other source materials were used to develop the parameters for this exercise. First, Figure 7-1 shows the effluent discharge model and all the numerical quantities required, including the source term and the observed fish concentration, and model parameters associated with the mill discharge and the aquatic environment. Further description of the effluent discharge model can be found in Chapter 4, Section 4.6. The model parameters and their source materials are now listed.

1) **Mill parameters including the 2,3,7,8-TCDD discharge rate, the effluent flow rate, the suspended solids content of the effluent flow, and the organic carbon content of the suspended solids in the effluent flow:** The 104-mill pulp and paper mill study (EPA, 1990d), a cooperative study between EPA and the paper industry, measured mass releases of 2,3,7,8-TCDD (actually effluent flow and concentrations, from which mass releases can be estimated), effluent flow, and total suspended solids content of the effluent flow (and other information such as releases of 2,3,7,8-TCDF, which were not needed for this exercise). For purposes of this validation exercise, actually only the total suspended solids content of effluent discharges was used from the primary reference of this study (EPA, 1990d). Data from the 104-mill study was also used in a modeling study, described more fully below, and in that reference, it was more conveniently organized and compiled. As such, effluent flow and 2,3,7,8-TCDD discharge rates came from a

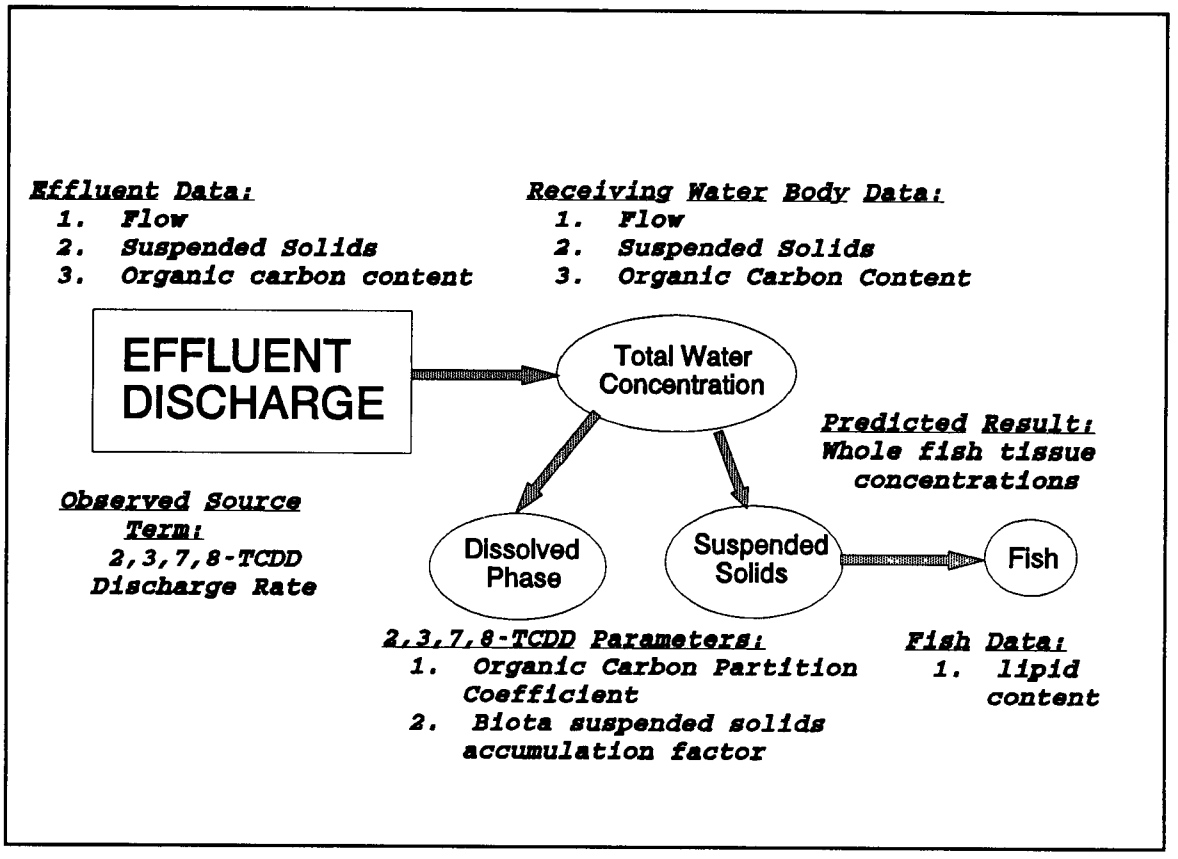

Figure 7-1. Schematic of effluent discharge model showing all parameter inputs and observed fish concentrations.

secondary reference. The organic carbon content of the solids in the effluent was assumed to be 0.36. This was the value used in the example scenario of Chapter 5, and was based on the fact that effluent solids are principally biosolids).

2) Receiving water body parameters including flow rate, suspended solids content, and organic carbon content of suspended solids. A modeling study conducted by EPA (EPA, 1990e) used a simple dilution and the EXAMS model to evaluate the impact from discharges of 2,3,7,8-TCDD and 2,3,7,8-TCDF from chlorine bleaching mills. Mills from the 104-mill study were the ones evaluated in this report. This study developed key receiving water parameters for these mills which are pertinent to the dilution model of this assessment, including harmonic mean flows at the point of effluent discharges, which were based on the nearest STORET sampling point, and suspended solids concentration of

the receiving water body at this point. Details on how these key quantities were developed are included in that report and will not be discussed here. The organic carbon content of the suspended solids was assumed to be 0.05, which was also the content assumed for the example scenarios in Chapter 5.

3) Parameters associated with 2,3,7,8-TCDD, including the organic carbon partition coefficient, Koc, and the biota suspended sediment accumulation factor (abbreviated BSSAF). The Koc for 2,3,7,8-TCDD was the same 2.69×10^6 otherwise assumed in this assessment, and the BSSAF value was assumed to be 0.09, which is the same value as the BSAF, Biota (bottom) Sediment Accumulation Factor. Sections in Chapter 4 further discuss the Koc, BSAF, and BSSAF.

4) Fish data including the fraction lipid and the observed fish concentrations: The core reference for this information is the National Study of Chemical Residues in Fish (EPA, 1992b), as noted above. NCASI compiled the fish concentrations and associated lipid content of the samples as part of their modeling exercise, and these were used here as well.

Table 7-5 lists the parameters used for each identified mill and receiving water body, as well as the modeled and observed fish concentrations. Not included in this table are the parameters assumed for all model runs, including the organic carbon contents of the suspended solids terms, and the 2,3,7,-TCDD Koc and BSSAF.

b. Results and Discussion

One important point to discuss up front is that 38 of the 47 eligible mills discharged into surface water bodies that were characterized as "low", while the remaining 9 mills discharged into "high" receiving water bodies. This characterization refers to the flow rates of the receiving water bodies. The average flow rate of the 38 low water bodies was $5.4 * 10^8$ L/hr, with a range of 10^7 to 10^9 L/hr, while for the other nine, the average flow was $2.8 * 10^{10}$ L/hr, with a narrow range of 1 to $4 * 10^{10}$ L/hr.

This distinction appears to be non-trivial for a few reasons. One, model predictions appear to more closely match observations for the smaller water bodies. The average of 38 mills and 74 fish for modeled and observed fish concentrations is 7 ppt and 15 ppt, respectively. The average of 7 mills and 21 fish associated with large receiving water bodies for modeled and observed fish concentrations is 0.7 and 5.3 ppt, respectively. As

Table 7-5. Model parameters and results for effluent discharge model validation testing.

Number	Company, City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River Flow L/hr*10^8	TSSu mg/L	Lipid	Fish Concentrations Predicted ppt whole wt basis	Fish Concentrations Observed ppt whole wt basis	Multiple Discharges Mill #s
I. Low Receiving water; suitable for testing										
1	James R. Corp, Old Town	2.52	0.098	127	8.57	2	10.9	2.9	8.0	49
2	International Paper Co, Jay	6.31	0.560	89	3.21	2	6.2	8.9	41.0	
	Second fish listing	----	-----	---	----	---	0.6	0.9	3.6	
	Third fish listing	----	-----	---	----	---	0.9	1.3	2.9	
	Fourth fish listing	----	-----	---	----	---	6.3	9.0	16.1	
	Fifth fish listing	----	-----	---	----	---	2.1	3.0	23.1	
3	James R. Corp, Berlin	2.74	0.104	47	5.13	4	3.7	2.0	7.8	
4	Westvaco Corp, Luke	3.12	0.050	57	0.30	13	4.9	2.3	58.2	
	Second fish listing	----	-----	---	----	---	4.7	2.2	35.5	
5	Penntech Pap, Johnsonburg	0.87	0.007	44	0.39	17	1.6	0.2	3.6	
	Second fish listing	----	-----	---	----	---	2.5	0.3	5.8	
6	Chesap. Corp, West Point	2.35	0.038	94	0.41	13	2.1	0.6	0.8	
	Second fish listing	----	-----	---	----	---	2.1	0.6	1.1	
	Third fish listing	----	-----	---	----	---	6.2	1.7	2.5	
	Fourth fish listing	----	-----	---	----	---	4.1	1.1	1.9	
7	Westvaco Corp, Covington	4.18	0.227	46	0.31	13	1.2	2.4	5.9	
	Second fish listing	----	-----	---	----	---	9.7	19.2	54.1	
8	Union Camp Corp, Franklin	19.7	1.343	60	0.35	0.3	1.9	5.1	1.8	
9	Champion Int, Courtland	9.30	0.716	23	43.3	10	11.1	1.9	3.4	26
10	Cont. Corp Amer, Brewton	5.63	0.037	13	1.01	6	2.2	0.8	0.6	
11	Boise Casc Corp, Jackson	3.08	0.332	19	8.25	10	5.3	8.7	8.8	57,56,58,12,13
12	Kimb-Clark Corp, C. Pines	6.91	0.242	19	6.41	18	1.4	1.1	8.8	13,57
	Second fish listing	----	-----	---	----	---	5.8	4.4	30.0	
13	Alab River Pulp, Claiborne	3.53	0.148	87	15.2	12	3.8	1.6	16.8	12, 57
	Second fish listing	----	-----	---	----	---	15.5	6.4	28.7	
14	Buckeye Cellulose, Perry	8.71	0.235	39	0.003	2	8.4	14.1	13.2	
15	Geo-Pac Corp, Palatka	5.84	0.093	8	0.04	2	20.3	81.8	1.4	

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Table 7-5. (cont'd).

Number	Company, City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River Flow L/hr*10^8	TSSu mg/L	Lipid	Fish Concentrations Predicted ppt whole wt basis	Fish Concentrations Observed ppt whole wt basis	Multiple Discharges Mill #s
16	Fed Pap Bd Co., Augusta	4.73	0.076	101	6.56	8	4.1	0.4	4.5	
17	ITT-Rayonier, Inc., Jesup	9.42	0.226	26	7.12	8	2.0	0.6	0.9	
	Second fish listing	----	-----	---	----	---	5.9	1.8	4.6	
18	Int. Paper Co., Moss Point	2.71	0.434	57	0.25	12	0.7	3.4	7.8	
	Second fish listing	----	-----	---	----	---	7.7	37.6	34.4	
19	L. R. For Prod., New Aug	2.76	0.552	46	1.62	12	0.9	1.6	3.8	
	Second fish listing	----	-----	---	----	---	8.8	15.2	98.9	
20	Champion Int., Canton	6.94	0.104	22	0.30	3	3.4	4.3	12.0	
	Second fish listing	----	-----	---	----	---	6.9	8.8	75.7	
21	Wayerhauser Co., Plymouth	6.15	1.968	15	0.56	8	0.9	20.6	18.2	
	Second fish listing	----	-----	---	----	---	3.9	89.2	143.3	
22	Wayerhauser Co, New Bern	3.77	0.166	14	1.22	4	0.8	1.3	5.5	
	Second fish listing	----	-----	---	----	---	8.2	13.2	49.2	
23	Fed. Pap B Co., Riegelwood	4.42	0.124	241	2.32	7	0.9	0.2	0.9	
	Second fish listing	----	-----	---	----	---	8.2	1.7	22.3	
24	Bowater Corp, Catawba	5.30	0.127	13	2.89	5	1.4	0.8	3.2	
	Second fish listing	----	-----	---	----	---	6.1	3.4	15.3	
25	Union Camp Corp, Eastover	1.40	0.028	2	3.95	15	1.5	0.1	1.2	
	Second fish listing	----	-----	---	----	---	8.5	0.5	9.1	
26	Mead Corp, Kingsport	1.53	0.009	88	1.53	6	6.4	0.4	1.0	
	Second fish listing	----	-----	---	----	---	10.7	0.6	6.6	
27	Champion Int., Quinnesec	2.02	0.018	32	1.92	3	1.4	0.2	1.4	
	Second fish listing	----	-----	---	----	---	1.6	0.2	1.4	
	Third fish listing	----	-----	---	----	---	16.8	2.2	21.0	
28	Badger P M, Inc., Peshtigo	0.24	0.001	124	0.64	4	24.4	0.5	8.5	
	Second fish listing	----	-----	---	----	---	1.9	0.04	0.3	
29	James R Corp, Green Bay	1.57	0.017	177	3.02	14	8.0	0.3	5.6	
30	Nekoosa Papers, Inc., Nek	4.78	0.191	36	3.18	6	1.7	1.0	7.1	
	Second fish listing	----	-----	---	----	---	21.5	13.1	67.2	
31	Wayerhauser Co, Rothchild	0.99	0.012	27	2.54	5	1.3	0.1	0.2	
	Second fish listing	----	-----	---	----	---	16.3	1.0	4.6	

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Table 7-5. (cont'd).

Number	Company, City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River Flow L/hr*10^8	TSSu mg/L	Lipid	Fish Concentrations Predicted ppt whole wt basis	Fish Concentrations Observed ppt whole wt basis	Multiple Discharges Mill #s
32	Int. Paper - Bastrop	4.44	1.47	82	10.7	13	1.0	1.1	1.0	
	Second fish listing	----	-----	---	----	---	12.3	13.3	3.6	
	Third fish listing	----	-----	---	1.0	---	3.0	16.4	5.5	
	Fourth fish listing	----	-----	---	----	---	6.2	33.9	5.2	
33	Int. Paper Co., Pine Bluff	4.34	0.478	71	9.97	7	5.2	2.8	8.9	
	Second fish listing	----	-----	---	----	---	10.4	5.5	33.9	
34	Nek Pap, Inc., Ashdown	6.07	0.249	21	4.02	42	3.5	0.8	4.2	
	Second fish listing	----	-----	---	----	---	1.8	0.4	1.7	
35	Boise Casc Corp, Deridder	3.66	0.034	59	0.12	10	8.2	2.8	13.7	
	Second fish listing	----	-----	---	----	---	1.4	0.5	1.4	
36	Temple-East Inc., Evadale	8.67	0.763	26	1.50	7	1.0	3.5	0.7	
	Second fish listing	----	-----	---	----	---	8.0	28.0	0.4	
37	Potlatch Corp, Lewiston	5.43	0.407	126	36.4	19	4.4	0.3	0.7	
	Second fish listing	----	-----	---	----	---	6.4	0.5	0.5	
38	Pope & Talbot, Inc., Halsey	1.83	0.055	14	7.75	7	8.8	0.8	4.6	
	Second fish listing	----	-----	---	----	---	9.6	0.8	0.8	
	Simple Means	4.60	0.31	58	5.40	9	5.8	7.0	15.0	38 mills/74 fish
II. High receiving water; Suitable for testing										
39	Westvaco Corp, Wickliffe	3.53	0.124	34	321.3	129	1.9	0.01	1.4	9, 67
	Second fish listing	----	-----	---	----	---	7.4	0.03	4.8	
40	Int. Paper Co., Natchez	5.99	0.228	115	407.2	221	22.6	0.1	3.1	9,26,33,39,41,67
41	Potlatch Corp, Mcghee	1.92	0.077	21	375.2	130	3.5	0.02	1.4	9,26,33,39,40,67
	Second fish listing	----	-----	---	----	---	5.8	0.03	4.7	
42	James Riv C., St. Francis	4.460	0.366	36	355.3	107	2.3	0.03	1.8	9,31,33,34,39,40,
	Second fish listing	----	-----	---	----	---	2.3	0.03	0.8	41,59,67,91
	Third fish listing	----	-----	---	----	---	10.8	0.1	6.0	

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Table 7-5. (cont'd).

Number	Company, City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River Flow L/hr*10^8	TSSu mg/L	Lipid	Fish Concentrations Predicted ppt whole wt basis	Fish Concentrations Observed ppt whole wt basis	Multiple Discharges Mill #s
43	Georgia Pac., Zachery	4.10	0.718	130	355.3	13	2.0	0.02	1.4	9,26,33,34,39,40,
	Second fish listing	----	-----	---	----	---	8.7	0.1	1.8	41,59,67,91
44	Boise Casc C, St. Helens	5.54	0.122	59	183.5	22	2.0	0.1	1.3	37,38,46
	Second fish listing	----	-----	---	----	---	9.6	0.5	2.6	
	Third fish listing	----	-----	---	----	---	3.2	0.2	1.1	
45	Wayerh Co, Longview	8.36	0.071	46	191.6	22	3.0	0.2	1.5	37,38,44,46
	Second fish listing	----	-----	---	----	---	11.4	0.6	5.2	
46	Boise Casc, Wallula	3.15	1.10	157	145.8	14	3.6	0.7	5.2	37
	Second fish listing	----	-----	---	----	---	10.9	2.2	7.9	
	Third fish listing	----	-----	---	----	---	25.1	5.1	56.0	
	Fourth fish listing	----	-----	---	----	---	0.7	0.1	0.4	
47	James River, Clat	6.43	0.097	40	191.6	46	7.0	1.0	2.8	37,38,44,45,46
	Second fish listing	----	-----	---	----	---	2.9	0.4	1.73	
	Simple Means	4.83	0.32	71	280.8	78	7.0	0.73	5.3	9 mills, 21 fish

III. No fish in NCSRF according to NCASI

48	Georgia-Pac., Woodland	51	Scott Paper, Hinckley	53	Scott Paper Co. Mobile
49	Lincoln Pulp & Pap, Lincoln	52	Int. Paper Co., Mobile	54	Potlatch Corp., Cloquet
50	Scott Paper, Westbrook				

IV. Mill already considered as multiple source

55	Boise Cas. Corp, Rumford	57	Internat. Paper Co, Selma	59	Georgia-Pac Corp, Crosset
56	Gulf St Pap C., Demopolis	58	James River Corp, Butler		

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Table 7-5. (cont'd).

Number	Company, City	Plant flow L/hr*10^6	TCDD mg/hr	TSSe mg/L	River Flow L/hr*10^8	TSSu mg/L	Lipid	Fish Concentrations Predicted	Fish Concentrations Observed	Multiple Discharges Mill #s
								ppt whole wt basis		
V. Effluent discharge at ND										
60	Finch & P. & Co, Glen F.		65	Gilman Paper Co, St. Marys				69	Mead Corp, Escanaba	
61	Appleton Pap, Roaring Sp.		66	Buckeye Cell, Oglethorpe				70	Pentair, Inc., Park Falls	
62	P.H. Glat. Co, Spring Gr.		67	Wilamette Ind, Hawesville				71	Wausau P Mills Co, Brokaw	
63	Proc & Gam, Mehoopany		68	Bowater Corp., Calhoun				72	Longv. Fiber C, Longview	
64	Champion Int., Cantonment									
VI. Mill discharges into estuary, not suitable for model testing										
73	ITT-Ray, Inc., Fernandina B.		77	Alaska Pulp Corp, Sitka				80	Wayerh Co., Cosmopolis	
74	Stone Cont Corp, Pan C.		78	Ketch Pulp & Pap 1,Ketch				81	Wayerh Co., Everett	
75	Bruns P. & Paper, Bruns		79	ITT-Ray, Inc., Port Angeles				82	ITT-Rayonier, Inc., Hoquiam	
76	Int. Paper Co, Georgetown									
VII. Not in NCASI data base, no explanation given										
83	Boise Cascade Corp, Int. Falls		91	Int. Paper Co, Texarkana				99	Simpson Paper Co, Fairhaven	
84	Mead Corp, Chillicothe		92	Louisiana Pacific Corp, Samoa				100	Simpson Paper Co, Pasadena	
85	Champion Int, Lufkin		93	Nekoosa Papers, Port Edwards				101	Simpson Paper Co, Tacoma	
86	Scott Paper, Everett		94	Champion Int, Houston				102	St. Joe Paper Co, Port St. Joe	
87	Int. Paper. Co, Erie		95	Georgia Pacific, Bellingham				103	Stone Container Corp, Missoula	
88	James River Corp, Camas		96	Cons. Paper, Wisc. Rapids				104	Stone Container Corp, Snowflake	
89	Gaylord Container, Antioch		97	Scott Paper, Muskegon						
90	Int. Pap. Co, Ticonderoga		98	Simpson Paper Co., Anderson						

Table Headings:

Number:	mill number, established for this table only	River flow:	receiving water body flow rate
Company, city:	abbreviated name and city location	TSSe,u:	effluent, upstream suspended solids concentration
Plant flow:	effluent flow rate	Fish concentrations:	concentrations as measured in NCSRF
TCDD:	2,3,7,8-TCDD discharge rate	Multiple discharges:	other mills assumed to influence fish concentrations

evaluated by NCASI, another important feature of the larger receiving water bodies is that they were the ones principally considered to have multiple discharges.

A final observation concerning the large receiving water bodies is that the suspended solids data is also significantly different than the low receiving water bodies. For the 38 water bodies associated with the small water bodies, the receiving water body solids content averaged 9 mg/L, while for the nine high receiving water bodies, the suspended solids content averaged 78 mg/L. This importance of the suspended solids content is principally seen for mills 39-42. The solids content of these water bodies ranged from 107 to 221 mg/L. The average modeled fish concentration for these mills was 0.04 ppt, while the average observed fish concentrations was 3.0 ppt. The impact is one of "dilution": discharged 2,3,7,8-TCDD mixes into a larger reservoir of suspended particles, leading to a low 2,3,7,8-TCDD concentration on suspended solids concentration and lower predicted fish tissue concentrations. This dilution effect may also be real, as the average observed fish concentrations for these circumstances of 3.0 ppt may indicate a significant difference with the average 15.0 ppt observed for the smaller receiving water bodies. Nonetheless, these high suspended solids data must be considered suspect.

Considering all 47 mills and 95 fish observations, it was found that 73 and 87% of predictions within a factor of 10 and 20 of observed concentrations, respectively. The predicted and observed results of this exercise for these 47 mills is shown graphically in Figure 7-2. As seen here, a best-fit simple linear regression (using the least squares method) has a slope of 0.86 and an intercept of 8.06. The positive intercept indicates that the model, with all current parameter assignments, has a tendency to underpredict fish concentrations. Also of note and perhaps not ironically, the highest observed fish concentration of 143.3 ppt is matched by the highest predicted fish concentration of 89.2 ppt.

Although the variance, r^2, of 0.27 is not compelling evidence that the model is valid, one must consider the usefulness of this measure. It would certainly be more meaningful if several discharge measurements per mill were made and several fish measurements were made downstream of the discharge. In fact, only one discharge measurement was made per mill and a very limited number of fish samples were taken per mill. To be more rigorous, the several measurements of discharge would have to have been made over time to best reflect an average discharge. Likewise, other mill-specific

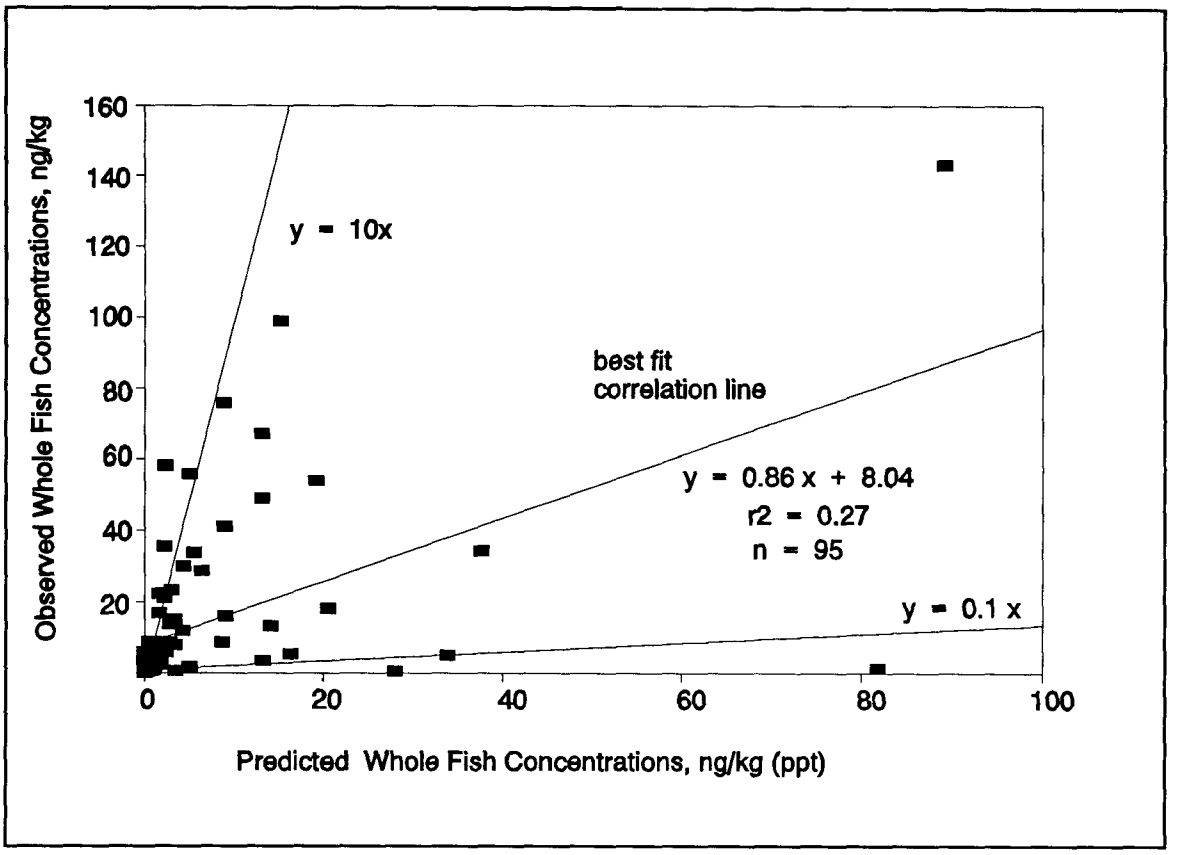

Figure 7-2. Comparison of predicted and observed fish tissue concentrations for validation of the effluent discharge model.

parameters are uncertain, such as receiving water body flow, suspended solids in the water body, and so on. Finally, and perhaps most importantly, the assumption of this exercise is that the mill discharges of 2,3,7,8-TCDD represent the only sources impacting the fish. This is most unlikely to be the case for the large receiving water bodies, which may be receiving other industrial point discharges or non-point sources (runoff, atmospheric deposition). Given the factor of 2 difference in average predicted and observed fish concentrations for the low receiving water bodies, and the factor of 10 difference between predicted and observed for 73% of the fish results over all mills, one might cautiously conclude that the effluent discharge model of this assessment is generally valid for purposes of general discharge assessment.

Given this last cautious statement, one can continue this exercise by attempting a

calibration on an appropriate parameter(s) so that predictions better match observations. The appropriate parameter for calibration is the BSSAF. The choice of 0.09 for the 2,3,7,8-TCDD BSSAF was based on data from Lake Ontario (EPA, 1990d). Specifically, 0.09 was the BSAF - lake bottom sediment to fish lipid accumulation factor - for measured fish and bottom sediments of Lake Ontario. As this is a lake and not a riverine situation, and inasmuch as 2,3,7,8-TCDD contamination of Lake Ontario sediments have been attributed to historical impacts and not ongoing causes, the 0.09 may be inappropriate. As well, a range of BSAFs for 2,3,7,8-TCDD were noted in the literature in Chapter 4 of this assessment, ranging from less than 0.05 to greater than 1.00. EPA (1993) suggests that data collection methods limit the usefulness of some of the available literature, particularly those showing very high BSAF, and in a similar examination of BSAF data, suggests a range of 2,3,7,8-TCDD BSAF from 0.03 to 0.3. In any case, this suggests that the BSSAF is a reasonable candidate for calibration in this exercise.

A different selection for BSSAF significantly improves model performance. If the BSSAF is increased to 0.20 (up from 0.09), the average predicted fish tissue concentration for the 38 mills discharging into the smaller water bodies increases as expected from 7.0 to 15.6 ppt, comparing better now to the average observed concentration of 15.0 ppt. Also, the factor of 10 and 20 test including all mills now improves to 84% of predictions within a factor of 10 of observations, and 87% of predictions within a factor of 20.

Conclusions from this exercise include:

1. For at least smaller receiving water bodies, those with harmonic mean flows on the order of 10^7 to 10^9 L/hr, the effluent discharge model is appropriate for assessing effluent discharge impacts to fish for 2,3,7,8-TCDD and perhaps other dioxin-like compounds.

2. There appears to be a distinction in model performance for the large and small receiving water bodies. The high suspended solids concentrations generated in an earlier modeling exercise for the larger water bodies is one cause for model underprediction; these solids concentrations should be further reviewed. Also, these water bodies were evaluated by NCASI as ones with multiple sources. Other sources not identified by NCASI could also have been the cause for higher measured fish concentrations as compared to model predictions. The NSCRF report (EPA, 1992b) contains an appendix giving a matrix indicating point source categories of discharges which may have affected fish

concentration results. Pulp and paper mills with and without chlorine were listed as point sources for 125 episodes (an episode is a fish sampling site). In 37 of these episodes, other point sources were identified, including one or more of the following: refinery (refinery using the catalytic reforming process), NPL site (a Superfund site), or other industry (an industrial discharge other than a paper mill or refinery). Given other sources, it is in fact a benefit to the exercise that predictions were lower than observations.

3. The model more closely predicts fish concentrations for the smaller receiving water bodies when the BSSAF is calibrated from 0.09 to 0.20. Considering that 0.09 was a value for 2,3,7,8-TCDD developed with data from Lake Ontario, a standing water body with principally historic and not ongoing 2,3,7,8-TCDD impacts, this setting is probably an inappropriate surrogate for ongoing discharges to a riverine situation. This would argue that a calibration is warranted.

7.2.3.7. *Examination of observed air concentrations*

The volatilization and near-field dispersion models of the soil source category were developed from well established theoretical principals, and were developed as part of an effort to assess the impact of soils contaminated with PCBs (Hwang, et al., 1986). The virtual point source dispersion model for far-field dispersion estimates is also based on well established theory (Turner, 1970). However, these models have not been field validated for soils contaminated with dioxin-like compounds. Ideally, the algorithms for estimating air concentrations would be validated using data on soil concentrations of dioxin-like compounds and concurrently measured concentrations in air above and downwind of the contaminated soil. A discussion of the Gaussian plume dispersion theories used in the COMPDEP model is given in Chapter 3, Section 3.4.1.

Some sense of the reasonableness of model values can be made by comparing predictions to measured concentrations in ambient air in urban environments. Reports of such concentrations are summarized in Section 4.7, Chapter 4 of Volume II, and Tables B.14-B.16, Appendix B of Volume II. Sources other than soil are likely to be the cause of levels measured in urban air environments. Also, the dispersion model is designed for situations where the contaminated soil is surrounded by relatively clean soil. As discussed in Section 7.2.3.1 above, off-site impacts have been noted in several sites of 2,3,7,8-TCDD contamination. These two points are made in order to establish a basis for

comparing urban air concentration to concentrations predicted to occur from soils: one would expect urban air concentrations to be at least higher, if not higher by orders of magnitude, than soil emissions.

Tables B.14 and B.15 (Appendix B, Volume II) summarize average PCDD/PCDF congener-specific concentrations in urban air in the United States and in Europe. Results for two example compounds demonstrated in Chapter 5, 2,3,7,8-TCDD and 2,3,4,7,8-PCDF, are examined in this section. Observed concentrations of 2,3,7,8-TCDD were mostly non-detects with detection limits ranging from 0.01 to as high as 0.82 pg/m^3. Occurrences were noted as high as 0.05 pg/m^3 in Bridgeport, CT, and 0.004 pg/m^3 in Wallingford, CT (both measurements as part of a study evaluating the impact of resource recovery facilities) and 0.06-0.08 pg/m^3 in urban settings in Hamburg, Germany. In Stockholm, Sweden, occurrences in suburban, remote countryside, and coastal settings were listed at 0.0007, 0.0002, and 0.0001 pg/m^3 respectively. Concentrations of 2,3,4,7,8-PCDF were detected in several reported studies. The range of 2,3,4,7,8-PCDF detections was 0.001-1.92 pg/m^3. In the few reports where both compounds were detected, 2,3,4,7,8-PCDF was detected at 3 to 10 times higher concentration than 2,3,7,8-TCDD.

Eight air monitoring studies in the United States were used to arrive at a profile of air concentrations used for estimating background exposures to dioxin-like compounds through inhalation. These references were characterized as mostly urban and suburban, not background or rural. A summary of this compilation is in Volume II, Chapter 4, Section 4.7. and in Volume II Appendix Tables B-28 and B-29. The arithmetic mean concentrations (used for background exposure estimation) for 2,3,7,8-TCDD and 2,3,4,7,8-PCDF were 0.01 and 0.03 pg/m^3, respectively. Section 7.2.3.9. below discusses the use of this compilation to craft a profile of air concentrations that might be typical of rural, background settings where cattle are raised. Evidence suggests that urban air concentrations are 4-6 times higher than rural air concentrations. If so, than 2,3,7,8-TCDD and 2,3,4,7,8-PCDF concentrations in a rural environment might 0.002 and 0.006 pg/m^3.

The on-site source category was demonstrated using concentrations of 1.0 ng/kg (ppt) for each example compound. This low concentration was assigned based on reports by researchers who measured concentrations of dioxin-like compounds in what they

described as "background" and "rural" soils - they found non-detects to concentrations in the low ppt level. Modeled air concentrations of the example compounds 2,3,7,8-TCDD and 2,3,4,7,8-PCDF resulting from this level in soil were in the 10^{-5} pg/m^3 range. For the stack emission source category demonstration, total (vapor + particle phases) concentrations of 2,3,7,8-TCDD simulated to arrive at points between 0.2 and 50 km were between 10^{-7} to 10^{-6} pg/m^3. The off-site soil source category evaluated the impact of elevated soil concentrations to exposure sites that were located distant from the site of contamination. The example scenario demonstrating this source category had concentrations of this dioxin and furan congener set at 1 ppb, three orders of magnitude higher than the 1 ppt of the on-site source category demonstration scenarios. Air concentrations predicted in these example scenarios were in the 10^{-3} pg/m^3 range.

Only this air concentration from the off-site soil contamination is generally in line with urban air concentrations of 2,3,7,8-TCDD, and/or a hypothesized rural air environment. It is at least plausible that elevated concentrations in soil would result in air concentrations that are in the same range as found in urban environments. A model result that would have questioned the model validity would have been, for example, that air concentrations resulting from soils of high concentrations would greatly exceed, or be very much lower, than urban air concentrations. In the same vein, it is certainly reasonable that air concentrations resulting from a single stack emission with generally a low release rate of 2,3,7,8-TCDD should be much lower than urban air concentrations.

It is not that clear that emissions and resulting air concentrations above soils at background levels should be lower by up to 2 orders of magnitude lower than what is hypothesized to occur in background setting. The argument has been made in Volumes I and II of this assessment that emissions from tall industrial stacks, followed by long range transport, are the ultimate source of these compounds in rural environments where the food supply is produced. The question remains as to how much of the contaminant in rural air is due to annual emissions and long range transport versus emissions from the soil reservoir source. If the modeling of this assessment is correct, than soils contribute very little to rural air concentrations. However, other evidence developed in this assessment suggests that the soil release and dispersion algorithms of this assessment may be underestimating air concentrations. One piece of that evidence is discussed in the next section below. Plant/soil ratios, defined as the ratio of 2,3,7,8-TCDD concentration in

plants divided by that in the soil, were found to be lower in model predictions as compared to literature values. Two possible hypotheses were offered below: 1) the model is underpredicting air concentrations resulting soil releases, and/or 2) plant:soil ratios derived in experiments are not only the result of soil related impacts, but also from distant sources of air-borne release and long range transport - i.e., the air reservoir is not solely explained by soil releases. One other possibility would be that the algorithms estimating air to plant transfers are not valid and estimating too low a transfer rate. However, the air to plant transfers algorithms were examined in the section further below, Section 7.2.3.9, describing an air-to-beef food chain validation exercise. There, air to plant transfers onto a leafy hay crop were examined with data and model was predicting hay concentrations right in line with observations.

In summary, three pieces of evidence suggest that the soil to air models, and/or the parameters values selected for this model, may be underestimating air concentrations. One is the comparison of predicted air concentrations for a background soil compared against air concentration data described above. The second is developed below where plant:soil ratios predicted by the model appear lower than measured under experimental conditions. Third, air-to-plant transfers appear to test well, leaving the soil-to-air algorithms questionable for predicting low plant:soil ratios.

7.2.3.8. *Impacts of contaminated soils to vegetations*

There have been several studies which have measured plant concentrations of 2,3,7,8-TCDD for plants grown in soils with known concentrations of 2,3,7,8-TCDD, and more recently, studies with plant and soil concentrations for dioxin toxic equivalents or dioxin congener groups. One quantity that can be estimated from these studies is a *plant:soil contaminant concentration ratio*. The plant:soil ratio equals the concentration in the plant divided by the concentration in soil in which the plant is growing. Concentration ratios predicted to have occurred can be compared against those that have been measured in the various studies.

These ratio comparisons can be considered model validations, although none of the experimental or field conditions for the literature studies were duplicated in this exercise. The literature articles measuring soil and resulting plant concentrations of dioxin-like compounds are summarized in Table 7-6. This table also includes concentration ratios,

Table 7-6. Summary of plant concentration versus soil concentration data for 2,3,7,8-TCDD.

Plant/Soil Concentrations	Contaminant Ratio	Reference and Comments
I. Below-Ground Vegetations		
54-167 ppt/ 1-5 ppb	.01-.17	Wipf, et al., 1982; results are for 2,3,7,8-TCDD and greenhouse carrots grown in Seveso contaminated soil; the 54 ppt concentration listed was for carrot peels and inner portions; the 167 ppt listed includes the 54 ppt plus additional residues found in wash water and can be described as "unwashed" concentration; 96% of 167 ppt unwashed concentration includes that found in wash water (67%) and peels (29%).
0.8-9.2 ppb/ 2.7-8.3 ppb	.24-1.73	Coccusi, et al., 1979; results are for 2,3,7,8-TCDD and carrots, potatoes, narcissus, and onions grown on contaminated soil the spring following the Seveso contamination; aerial plant part ratios were 0.25-0.40 - underground part ratios were 0.23-1.73; residues in contaminated plants were found to dissipate when contaminated plants transplanted to unpolluted soils; results show higher ratios than the Wipf, et al. (1982) noted above; results were expressed in fresh plant weight and fresh soil basis; very high ratios and plant impacts render these data suspect.
156-1807 ppt/ 160-752 ppt	1.00-2.40	Facchetti, et al., 1986; results are for 2,3,7,8-TCDD and bean and maize roots grown in indoor greenhouse pots and outdoor pots; unclear whether plant concentrations are fresh or dry weights. Data considered highly suspect due to very high ratios found and also reporting 16 and 37 ppt in roots when "blank" soil had 1.5 ppt (ratios of 10.7 and 24.7).
735 ppt/ 411 ppt	1.8	Young, 1983; results are for 2,3,7,8-TCDD and roots of grass and broadleaf plants at Eglin Air Force Base; unclear whether root concentrations are fresh or dry weight.
0.5-40.2 ppt/ 2-6000 ppt	.001-.3	Hulster and Marschner, 1991; results at right are for unpeeled potato tubers, in TEQ and dry weight basis. Plant:soil ratio decreased as soil concentrations increased; highest ratios were at the 2.4 ppt low soil concentration. Peeled tuber concentration stayed below 0.5 ppt over all soil concentrations, indicating insignificant within plant translocation. Plant concentrations given in dry weight basis.

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Table 7-6. (cont'd)

Plant/Soil Concentrations	Contaminant Ratio	Reference and Comments
0.2-6.0 ppt/ 328-12,800 ppt	.00001-.009	Hulster and Marschner, 1993a. Results are for potato tubers, peeled and unpeeled, and for potato shoots, results for TEQ and in dry matter terms. Concentrations for peeled potato tubers stayed consistently less than 0.5 ppt, despite soil concentrations, while shoots and unpeeled tubers increased as concentration increased. Plant:soil ratios remained relatively constant for tubers and shoots with soil concentration increases, leading authors to conclude that a soil/plant relationship exists for plants growing in the soil. Less transfer was noted for higher chlorination.
0.35, 0.96/ 5, 56 ppt	0.02-0.07	Muller, et al., 1993a. Two plant/soil concentrations are for carrots in soil concentrations of 5 and 56 ppt TEQ; carrot concentrations in dry matter and TEQ terms. Ratios decrease as concentrations increase; most of the concentration was in the peels.
II. Above-Ground Vegetations		
(9-42 ppt)/ 10 ppb	.0009-.0042	Wipf, et al., 1982; analysis of apples, pears, plums, figs, peaches, and apricots grown in Seveso, Italy year following contamination; apples, pears, and peaches showed >95% of whole fruit concentrations listed here was in the peels; analysis of vegetative samples in less contaminated areas showed non-detections at 1 ppt detection limit; reference was unclear as to whether reported concentrations in fruit was based on fresh or dry weight.
(8-9 ppt)/ 10 ppb	.0008	Wipf, et al., 1982; concentrations listed were those found in sheaths of corn grown year following following Seveso contamination; none found in cobs and kernels at 1 ppt detection limit.

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Table 7-6. (cont'd)

Plant/Soil Concentrations	Contaminant Ratio	Reference and Comments
(1-63 ppt)/ (12-3300 ppt)	0.003-0.35	Sacchi, et al., 1986; data was for: "aerial parts" of bean and maize plants, tritiated TCDD TCDD amended soil with concentrations ranging as noted, taken at different intervals including 7, 34 and 57 days (one test), 17, 34, and 57 days (another test), 8 and 77 days, and 8 and 49 days, and in tests where soil was and was not amended with peat. Results showed increasing plant concentrations with increasing soil concentrations, but the ratio of plant to soil concentrations was inversely related to increasing soil concentrations (lowest ratios at highest soil concentrations). Soils without peat had higher ratios than soils with peat. Plant concentrations were fresh weight basis; high plant impact and trend for increasing impact over time renders these results suspect.
ND (DL = 1 ppb)/ 60 ppb	<0.017	Isensee and Jones, 1971; results are for mature oat and soybean tops, and oat grain and the bean of soybean, in soil treated with [^{14}C]TCDD to achieve a concentration of 60 ppb - no residues of TCDD were found; ratios of 0.14 and 0.28 were found for 2,4,-dichlorophenol (DCP) in oat and soybean tops, and 0.20 for 2,7-dichlorodibenzo-p-dioxin (DCDD) in oat tops; trace amounts of DCP and DCDD were found in the bean of soybean.
(10-270 ppt)/ 411 ppt	.02-0.66	Young, 1983; data was for 2,3,7,8-TCDD and above ground plant parts of perennial grasses and broadleaf plants grown on 2,4,5,-T treated soils. Unclear whether plant concentrations are fresh or dry weight basis. Soil concentration was average over 3 depth increments to 15 cm. Crown near soil surface at 270 ppt and 0.66 ratio was highest; plant tops had ratios of 0.02-0.17.
0.3, 0.1 ppt/ 8750, 5215 ppt	0.00003, 0.00002	Muller, et al, 1993a. Result at right are for whole pear (0.3) and whole apple (0.1) dry weight concentrations (article presented TEQs for two pears from one tree which were averaged, and one apple, and for fresh weight; dry weight was estimated assuming 12% dry matter in pears/apples) and the average concentration over 70 cm (article supplied concentrations for the 0-30 and 30-70 cm depths). Article also provided peel and pulp results and results for congener groups. Article concluded: soil levels were not correlated to fruit concentrations and therefore fruits were impacted by airborne contamination, and that concentrations were higher in peel than in pulp.

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Table 7-6. (cont'd)

Plant/Soil Concentrations	Contaminant Ratio	Reference and Comments
0.1-0.6 ppt/ 326-5752 ppt	0.00002-0.0008	Hulster and Marschner (1993a). Results are for inner and outer leaves of lettuce, expressed as dry matter, and in TEQs. Results indicate a drop in ratio as soil concentration increases, and unexpected small differences between inner and outer leaves.
4-38 ppt/ 326-12,800 ppt	.001-.01	Hulster and Marschner (1993a). Results are for hay, dry matter, and TEQs. Results indicate a drop in ratio as soil concentrations increase.
<1 ppt/ 326-5752 ppt	.0001-.0003	Hulster and Marschner (1993a). Results are for grass and herbs, dry matter, and TEQs. Results indicate a drop in ratio as soil concentrations increase. For above three entries, results are also given for congener groups. Authors conclude that: little correlation between soil and above ground plant concentrations, and that contamination is by atmospheric deposition.
<.01, .04/ 5, 56 ppt	<0.002	Muller, et al., 1993b. Results are for peas at soil concentrations of 5 and 56 ppt; pea concentrations in TEQ and dry weight. Results for pods indicated more impact with ratios at 0.002-0.026. Ratios decreased as soil concentration increased.
0.32, 0.21 ppt/ 5, 56 ppt	.004-.064	Muller, et al., 1993b. Results are for lettuce at soil concentrations of 5 and 56 ppt; lettuce concentrations in TEQ and dry weight. Little difference seen between inner and outer leaves, which was unexpected - outer leaves expected to be more impacted. Ratios decreased as soil concentration increased.
0.5-22.6 ppt/ 0.4, 148 ppt	.14-2.5	Hulster and Marschner, 1993b. Results are for zucchini fruit at two soil concentrations of 0.4 and 148 ppt TEQ, fruit results are TEQ and dry weight. Results contradict conventional wisdom that above ground vegetation impact is from air only and mainly an outer surface phenomena; zucchini contamination was uniform throughout plant and plant:soil ratios highest ever found for above ground bulky fruits.

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Table 7-6. (cont'd)

Plant/Soil Concentrations	Contaminant Ratio	Reference and Comments
0.6 ppt/148 ppt	.004	Hulster and Marschner, 1993b. Results are for cucumber grown in soil at 147 ppt TEQ; cucumber results in TEQ and dry weight. Results are more in line with most other studies for above ground bulky fruit plant:soil ratios.
7.5 ppt/148 ppt	.05	Hulster and Marschner, 1993b. Results are for pumpkin grown in soil at 148 ppt TEQ; pumpkin results in TEQ and dry weight. Results not as dramatic as for zucchini, but plant concentrations are ratio are still high.
0.4-1.9 ppt/ 2.4-6000 ppt	.0003-.3	Hulster and Marschner, 1991. Results are for lettuce, in TEQ and dry weight. Experiments were conducted outdoors with soil covered by a water permeable polypropylene fleece. Plant concentrations showed little variation with large increases in soil concentration, and given the soil covering, this would strongly indicate little root to shoot translocation and that lettuce concentrations were the result of air to plant transfer.s

and separates sections for above and below ground vegetations.

In measuring both the soil and the plant concentration, several of the early literature articles, particularly those from Seveso (Wipf, et al., 1982; and Coccusi, et al., 1979) presumed that the soil in which the plant was growing was the ultimate source for the 2,3,7,8-TCDD contamination of above ground plant parts, if not from direct uptake than from deposition of suspended particles. However, recent research has concluded that the contamination of above ground plant parts is due principally to air-to-plant transfers (Hulster and Marschner, 1993a; Muller, et al, 1993a; Muller, et al., 1993b; Welsh-Paush, et al (1993); and others). These cited research efforts have concluded that there is no consistent relationship between soil concentrations of dioxin-like compounds and above ground vegetative concentrations of these compounds, which has led the researchers to conclude that air-to-plant transfers explain plant concentrations (a recent report did strongly imply a direct soil/plant for dioxin-like compounds for at least one family of above ground vegetables, the cucumber family (Hulster and Marschner, 1993b); this will be discussed below). This fact, coupled with the fact that sources of airborne contamination by dioxins include both distant sources and soil releases, make it difficult to compare literature reports of plant:soil contamination concentrations with those predicted by the soil contamination modeling of this assessment.

Recall that the "on-site" soil source modeling presumes that air concentrations and depositions to which the plant are exposed originate only from the soil in which the plant is growing. One would expect that the modeled plant:soil ratio for above ground plant parts would be lower than plant:soil ratios measured in field settings, since the field measured ratios are influenced by more than just the soil releases into the air.

On the other hand, the literature is consistent in concluding that soil provides the source for underground soil to root transfers. For this reason, Table 7-6 and the following discussions distinguish between above and below-ground vegetations.

The following plant:soil contaminant concentration ratios were estimated for the two scenarios demonstrating the on-site source category in Chapter 5, Scenarios 1 and 2: below ground vegetables - 7×10^{-3} (dry weight basis, assuming vegetables are 15% dry matter), above ground vegetables/fruit - 7×10^{-5} (dry weight basis, assuming vegetables/fruits are 15% dry matter), grass - 6×10^{-3} (dry weight), and feed 3×10^{-3} (dry weight). Some observations from experimental results found in the literature, and

comparison with the results of the model, are:

1) The largest body of consistently developed experimental data on soil-plant relationships of dioxin-like compounds comes from a research group in Germany who have published numerous articles for different vegetations and experimental conditions in the 1990s (Hulster and Marschner, 1991; Hulster and Marschner, 1993a,b; Muller, et al., 1993a,b). Some of the earlier literature showed much higher impacts to vegetations than measured by these German researchers (Coccusi, et al., 1979; Facchetti, et al., 1986; Young, 1983), which in the judgement of the authors of this EPA assessment, renders them suspect. One early report, that of Wipf, et al. (1982), does show results consistent with the German research. The observations following will focus mainly on this research from Germany.

2) Experimental results for both above and below ground vegetations suggest that plant:soil ratios decrease as soil concentration increases. For below ground vegetations, this suggests that the movement into plants is not a passive and unimpeded process occurring with transpiration water, for if it were, plant:soil ratios would be constant as concentration increases. For above ground vegetations, the observations given above that air-to-plant transfers and not soil-to-plant transfers better explain plant concentrations, and that air concentrations include soil releases as well as long term transport, leads one to conclude that a consistent relationship between soil concentrations and plant concentrations is not to be expected. An explanation for this trend for below ground vegetative trends could not be found.

The models of this assessment - soil to below ground vegetation, soil to air to above ground vegetation, and air to above ground vegetation - cannot duplicate these observed trends, that is, the models will not show a decrease in plant:soil ratios as soil concentration increases. Above and below ground vegetation concentrations are a linear function of a biotransfer factor and an appropriate media concentration - air, soil water. For particle depositions, no transfer parameters are used, but plant concentrations are a linear function of model inputs, including deposition rates, plant interceptions and yield, and a plant washoff factor. Therefore, plant concentrations will be a linear function of soil concentrations for the soil source categories.

3) Plant:soil ratios for below ground vegetables for soil concentrations in the low ppt range would appear to be in the 10^{-1} to 10^{-2} range (Muller, et al, 1993; Hulster and

Marschner, 1991), in contrast to the 0.007 predicted by the model. Much higher ratios were found in the earlier studies (Coccusi, et al., 1979; Facchetti, et al., 1986; Yount, 1983), which earlier had been speculated as being questionable. One earlier study, that of Wipf, et al. (1982), does report ratios similar to these later studies, as noted above. At higher soil concentrations in the sub to low ppb range, plant soil ratios are more in the 10^{-4} to 10^{-3} range (Hulster and Marschner, 1993a; Hulster and Marschner, 1991), even lower than the modeled 0.007 ratio.

4) The results for above ground bulky vegetations, fruits and vegetables, indicate plant:soil ratios that are lower than plant:soil ratios for bulky below ground vegetations, for comparable soil concentrations. The evidence for this observation is best found in the Hulster and Marschner (1993a) concurrent experiments for potatoes and pears/apples, as well as the earlier work of Wipf, et al. (1982) for several fruits and carrots. The same trend is also found for the grass results for 2,3,7,8-TCDD given in Young (1983). This trend is also duplicated by the models, which showed two orders of magnitude difference in below ground as compared to above ground vegetations. The plant:soil modeled ratio of $7*10^{-5}$ is similar to ratios found when the soil concentration was in the hundreds to thousands of ppt (Hulster and Marschner, 1993a). However, other data, particularly for leafy vegetations such as hay, grass, and lettuce, and for lower soil concentrations, indicate a soil:plant ratio of 10^{-3} to 10^{-2}. Two possible explanations are offered for this trend: 1) above ground vegetations in experiments are likely to be impacted by not only soil releases, but distant sources of release, and/or 2) the models could be underpredicting air concentrations resulting from soil releases.

4) Several of the articles, both from the German work and the earlier work, noted that most of the concentration was in the outer portions of the below and above-ground vegetations, and not the inner portions. Despite significant increases in soil concentration from the ppt to the ppb range, inner potato tuber concentrations remained constant (Hulster and Marschner, 1991, 1993a). This evidence was the principal justification for the use of the empirical adjustment factors termed VG for soil to below ground transfers, VG_{bg}, and vapor-phase air transfers to bulky above ground vegetations, VG_{ag}. The chemical-specific empirical transfers factors for both of these transfers were developed in laboratory experiments with several chemicals using thin vegetations - solution phase transfers to barley roots for below ground vegetation concentrations, and vapor phase

transfers to azalea leaves for vapor phase transfers. For the dioxin-like compounds, direct use of these transfer factors would be most appropriate for the outer few millimeters, perhaps, of below and above ground bulky vegetations. The assignment of a VG of 0.01 for bulky above and below ground vegetations was based on an outer surface volume to whole plant volume ratio for a common vegetation such as a carrot or an apple. A VG of 1.00 was used for grass, since that is a thin vegetation.

Further evidence for the above ground VG came from a recent study by McCrady (1994), who measured the uptake rate constants of vapor-phase 2,3,7,8-TCDD to several vegetations including grass and azalea leaves, kale, pepper, spruce needles, apple, and tomato. The uptake rate for the apple divided by the uptake rate for the grass leaf was 0.02 (where uptake rates were from air to whole vegetation on a dry weight basis). For the tomato and pepper, the same ratios were 0.03 and 0.08. The VG_{ag} was 0.01 for fruits and vegetables in this assessment. McCrady (1994) then went on to normalize his uptake rates on a surface area basis instead of a mass basis; i.e., air to vegetative surface area uptake rate instead of an air to vegetative mass uptake rate. Then, the uptake rates were substantially more similar, with the ratio of the apple uptake rate to the grass being 1.6 instead of 0.02; i.e., the apple uptake rate was 1.6 times higher than that of grass, instead of 1/50 as much when estimated on an air to dry weight mass basis. The ratios for tomato and pepper were 1.2 and 2.2, respectively. Therefore, since the B_{vpa} in this assessment is an air to plant mass transfer, the McCrady experiments would appear to justify the use of an above-ground VG of a magnitude less than 0.10.

5) A recent experiment by the Hulster and Marschner (1993b) on vegetations of the cucumber family contradicted the conventional wisdom that direct soil to root to above ground plant impact would not occur for the dioxin-like compounds. Their results were most striking for zucchini, which showed uniform plant concentrations from inner to outer portions of the zucchini fruit, and the highest whole fruit concentrations and plant:soil ratios they had ever measured, despite careful experimental conditions which physically isolated the fruit from the soil. Pumpkins also showed high plant contamination and plant:soil ratios, with more expected plant concentrations measured for the cucumber. No explanation was offered for these results. It was assumed for this exposure assessment that the fruits and vegetables for human consumption, and the grasses, hay, and other vegetations animals consume, would not follow this pattern.

A principal conclusion that can be drawn from this examination is that the plant:soil contaminant concentration ratios developed by the soil contamination models of this assessment may be lower by perhaps an order of magnitude or more than measured ratios at lower soil concentrations, in the low ppt range, whereas they may be more in line and even higher when soil concentrations are the hundreds of ppt to the ppb range. This trend appears to hold for both above and below ground vegetations. This difference in the comparison of modeled and observed ratios as the concentration changes is because the data shows that plant:soil ratios decrease as soil concentrations increase. This cannot be duplicated by the model since the plant concentrations are a linear function of the source strength terms - the soil, soil water, or air concentrations and deposition. An explanation for this observed trend could not be found. The observation that plant:soil ratios for above ground vegetations are higher in the literature at lower soil concentrations (and more typical of background rather than heavily contaminated soils) as compared to the modeled ratios, has to be carefully considered. Two explanations are offered. For experiments conducted outdoors, the source of air reservoirs of dioxin-like compounds are the soil in which the plant is growing as well as from distant sources and long-term transport. Also, it is possible that the model is underpredicting air concentrations and hence underpredicting air to plant transfers.

7.2.3.9. A validation exercise for the beef bioconcentration algorithm

The premise of this modeling exercise to test the beef food chain model for dioxin-like compounds is that air-borne reservoirs of these compounds in rural environments are the "source term" explaining concentrations found in beef. Further, this exercise probably would not qualify as a validation exercise in the traditional sense. Most environmental model validation exercises rely on data obtained from a single site. This exercise instead develops a representative rural air concentration profile and attempts to model a profile of average beef concentrations.

The model structure, from air to beef, is shown in Figure 7-3. The algorithms for these components, and assignment of model parameters, were described in Chapter 4, and are very briefly summarized here. The "observed" source, or independent, term in this modeling exercise are the air-borne concentrations of dioxin-like compounds shown at the top of Figure 7-3, and the "predicted", or dependent, results are the concentrations in

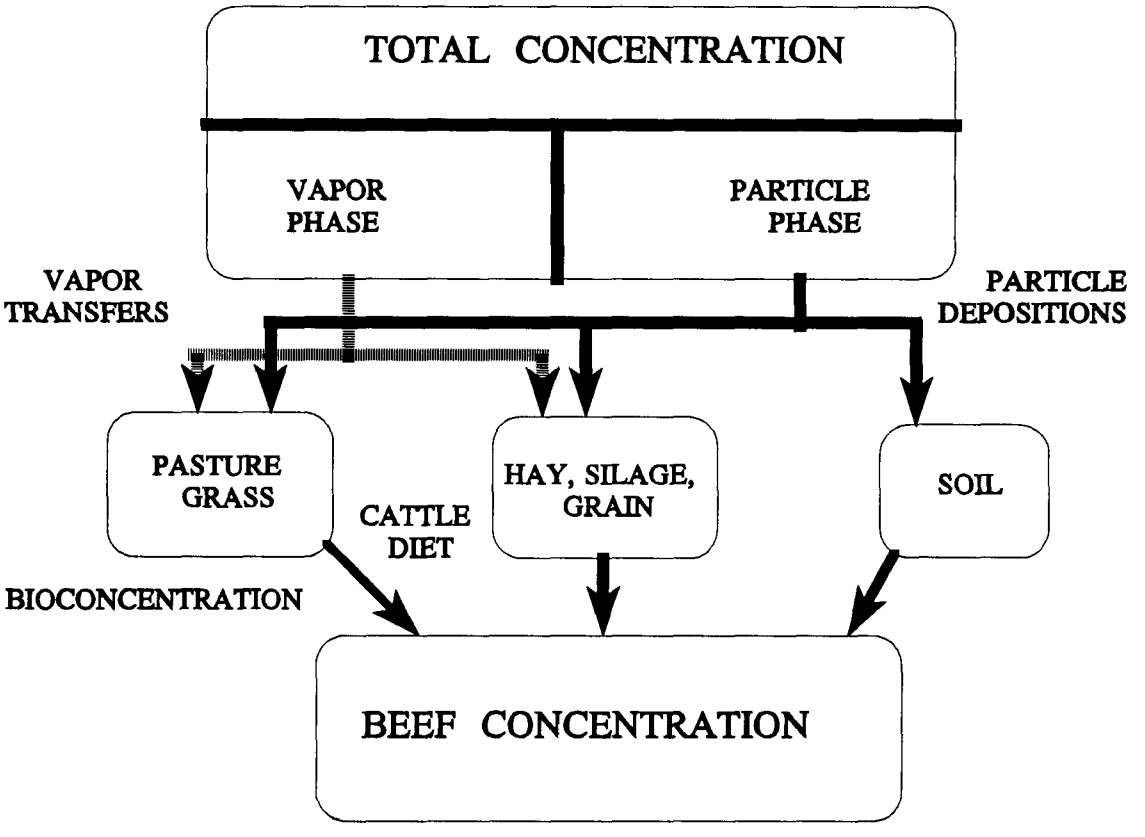

Figure 7-3. Overview of model to predict beef concentrations from air concentrations.

whole beef shown at the bottom of this figure. Both these quantities are developed from reported United States measurements. Section 7.2.3.9.1 below describes the generation of these concentration profiles. Section 7.2.3.9.2 summarizes model algorithms and parameter assignments. Section 7.2.3.9.3. presents the results and discussions from this exercise.

7.2.3.9.1. Air and beef concentrations

Very little data are available worldwide on air concentrations of individual dioxin-like congeners in a rural setting. This is the kind of air concentration data that would be

needed for this exercise. An evaluation of ambient air monitoring studies in the United States conducted for Volume II of this assessment showed that nearly all of the data was from urban or suburban settings. The purpose of this compilation was to determine an ambient air concentration suitable for estimating inhalation exposures to dioxin-like compounds. Measurements which were attributed to a nearby identifiable source, such as an incinerator, were not considered for this effort. From several studies around the country, a total of 84 air samples were available, from which a mean TEQ level of 0.095 pg/m^3 was determined. Further detail on this compilation can be found in Chapter 4 of Volume II.

There are a few references which do have congener-specific data which might be characterized as rural. One is outside of United States in Sweden (Broman, et al., 1991). Air samples were taken in four areas, ranging from the Stockholm urban area to the open coastal area of the Baltic Sea. Results indicate lower TEQs when going from the urbanized area to the remote areas. The Stockholm city center was 0.024 pg TEQ/m^3, a "suburb" was 0.013 pg TEQ/m^3, a "countryside remote" area was 0.0044 pg TEQ/m^3, and an "open coastal" area was 0.0026 pg TEQ/m^3. Twenty-five PCDD/F concentrations were listed at the fg/m^3 level (i.e., 0.001 pg/m^3).

The only reference found for the United States with congener specific data for an area described as rural was from Ohio (Edgarton, et al., 1989). Six sites were tested, one of which might be considered rural. The data contained many non-detects, with detection limits between 0.033 to 0.82 pg/m^3, although most non-detects had detection limits less than 0.3 pg/m^3. The following TEQ concentrations were derived only from the positive listings: two sites in Akron - 0.077 and 0.079 pg TEQ/m^3, two sites in Columbus - 0.092 and 0.179 pg TEQ/m^3, a site near a highway - 0.065 pg TEQ/m^3, and a rural site in a town called Waldo - 0.045 pg TEQ/m^3. Like the data from Sweden, one can see a trend for lower concentrations in the Waldo site as compared to the sites in Columbus and Akron.

Other references did contain other pertinent data, such as total concentrations, TEQ concentrations, or congener group concentrations, in rural and urban settings. Eitzer and Hites (1989) took data from Bloomington, Indiana and a remote area in Wisconsin known as Trout Lake. TEQ concentrations were not given, but total congener group concentrations were reported. The sum of congener group concentrations, or total

concentrations of dioxins and furans, equaled 2.2 pg/m^3 for Bloomington, and 0.51 pg/m^3 for Trout Lake. This 0.51 pg/m^3 total concentration is similar to the total concentration found in the "countryside remote" area in Sweden discussed above, which is 0.41 pg/m^3 (TEQ concentration was 0.0044 pg/m^3, as noted above).

In an evaluation of air, soil, sediment, and fish in Elk River, Minnesota, a rural setting, again total congener concentrations in the air were reported (Reed, et al., 1990). Concentrations for three sites and for two sampling dates, one in the winter and one in the summer, were available. Two of the three sites were in rural settings and the third was near a refuse derived fuel incinerator. Total concentrations for the two rural sites in winter and in summer were 2.29 and 2.91 pg/m^3 in winter, and 0.58 and 0.38 pg/m^3 in summer. For the third site near the incinerator, winter and summer concentrations were 15.2 and 0.35 pg/m^3, respectively. The average of the four data points for rural settings was 1.54 pg/m^3, while the average of the two data points near the incinerator was 7.78 pg/m^3.

Finally, Maisel and Hunt (1990) list TEQ concentrations only for monitoring networks including: a Connecticut coastal location described as urban (measurements described as "wintertime"), a southern California urban setting ("annualized"), and a central Minnesota rural setting ("annualized"). While not identifying it as such, this central Minnesota setting could be the one described above in Elk River, Minnesota. The TEQ concentrations for the two urban and one rural setting were: 0.092, 0.091, and 0.021 pg TEQ/m^3.

Key points from this literature summary are:

1. Congener specific profiles for rural settings in the United States are generally not available. Based on several studies encompassing 84 data points with specific congener concentrations which best represent urban/suburban settings, but are not near identified emission sources, a mean TEQ air concentration of 0.095 pg/m^3 is estimated.
2. Studies are available which do provide side by side data on urban and rural settings, although the literature references only list congener group concentrations or total TEQ concentrations (with the exception of the Edgarton, et al. (1989) described above). What this summary shows is that rural air concentrations of dioxin-like compounds appear to be 4-6 times lower than in urban settings, and that a TEQ concentration for rural settings appear to range from 0.004 to 0.04 pg/m^3.

In order to develop a profile of air concentrations that will be considered

representative of rural settings, what will be done, therefore, is to take the profile of congener-specific air concentrations for urban/suburban settings leading to a TEQ concentration of 0.095 pg/m^3, and divide each concentration by 5. The resulting TEQ concentration is 0.019 pg/m^3. The total concentration of PCDD/Fs in this rural profile equals 1.09 pg/m^3. A uniform division by five for all congeners essentially assumes that the ultimate sources for an urban and a rural profile of air concentrations are the same. The specific concentrations used are shown in Table 7-7.

A review of data on concentrations of dioxin-like compounds in beef showed that very limited data was available worldwide, much less United States. Only three studies contained congener-specific data of dioxins and furans in beef in United States. In one study beef samples were composited with veal and the results described as beef/veal. The three studies only encompassed 14 samples. These studies include one conducted by the California Air Resources Board (CARB; Stanley and Bauer, 1989), the results of background analysis from a study conducted by the National Coalition for Air and Stream Improvement (NCASI; the study described in Lafleur, et al., 1990) and a survey of foods conducted in New York by Schecter et al. (1993).

These were the data used to estimate background exposures to dioxins in beef in Chapter 5 of Volume II. The total TEQ for beef and veal was calculated by using one-half the detection limits reported by the researchers to represent the concentration of nondetectable CDD/F congeners in the samples. Using this methodology, the TEQ concentration was estimated to be 0.48 ng/kg (ppt) for beef and veal on a wet weight basis. If nondetectable concentrations are assumed to be zero, the estimated TEQ for beef and veal is 0.29 ppt. The average whole beef congener-specific concentrations assuming non-detects were one-half the detection limit are to be used to represent beef concentrations, and they are shown in Table 7-7. All studies reported concentrations as lipid-based concentrations. Where lipid fractions were not supplied, 19% lipid content for beef was assumed to estimate whole beef concentrations.

It is important to note that the United States samples came from commercial food outlets (grocery stores, e.g.). This fact will be used to imply that the data represents beef cattle that went through a feedlot fattening process prior to slaughter. As will be discussed below, this has implications regarding final concentrations.

Table 7-7. Observed air and beef concentrations, and fate parameters for individual dioxin and furan congeners.

	Parameters for B_{vpa}			Parameters for Vapor/Particle Partitioning				Observed Data	
Compound	H	log Kow	B_{vpa}	T_m, K	VP_s, atm	Vapor/Particle	BCF	air, pg/m^3	beef, ppt
2378-TCDD	$1.6*10^{-5}$	6.64	$1.0*10^{5}$	578	$9.7*10^{-13}$	0.55/0.45	4.32	0.002	0.03
12378-PeCDD	$2.6*10^{-6}$	6.64	$6.3*10^{5}$	513	$1.3*10^{-12}$	0.26/0.74	4.16	0.006	0.22
123478-HxCDD	$1.2*10^{-5}$	7.79	$2.3*10^{6}$	547	$1.3*10^{-13}$	0.07/0.93	2.02	0.005	0.26
123789-HxCDD	$1.2*10^{-5}$	7.79	$6.9*10^{5}$	516	$6.5*10^{-14}$	0.02/0.98	2.24	0.007	0.84
123678-HxCDD	$1.2*10^{-5}$	7.30	$6.9*10^{5}$	558	$4.7*10^{-14}$	0.04/0.96	1.74	0.010	0.21
1234678-HpCDD	$7.5*10^{-6}$	8.20	$1.0*10^{7}$	538	$4.2*10^{-14}$	0.02/0.98	0.36	0.116	1.92
OctaCDD	$7.0*10^{-9}$	7.59	$2.4*10^{9}$	598	$1.1*10^{-15}$	0.00/1.00	0.52	0.586	2.91
2378-TCDF	$8.6*10^{-6}$	6.53	$1.5*10^{5}$	500	$1.2*10^{-11}$	0.71/0.29	0.94	0.023	0.06
23478-PeCDF	$6.2*10^{-6}$	6.92	$5.3*10^{5}$	469	$4.3*10^{-12}$	0.30/0.70	3.10	0.010	0.04
12378-PeCDF	$6.2*10^{-6}$	6.79	$3.8*10^{5}$	499	$3.6*10^{-12}$	0.42/0.58	0.73	0.006	0.21
123478-HxCDF	$1.4*10^{-5}$	7.30	$5.9*10^{5}$	499	$3.2*10^{-13}$	0.06/0.94	2.34	0.012	0.51
123678-HxCDF	$6.1*10^{-6}$	7.30	$1.4*10^{6}$	506	$2.9*10^{-13}$	0.06/0.94	2.00	0.012	0.06
123789-HxCDF	$1.0*10^{-5}$	7.30	$8.3*10^{5}$	520	$3.7*10^{-13}$	0.11/0.89	2.00*	0.003	0.06
234678-HxCDF	$1.0*10^{-5}$	7.30	$8.3*10^{5}$	512	$2.6*10^{-13}$	0.07/0.93	1.78	0.009	0.07
1234678-HpCDF	$5.3*10^{-5}$	7.90	$6.8*10^{5}$	509	$1.8*10^{-13}$	0.04/0.96	0.41	0.042	0.40
1234789-HpCDF	$5.3*10^{-5}$	7.90	$6.8*10^{5}$	495	$1.4*10^{-13}$	0.03/0.98	0.99	0.006	0.13
OctaCDF	$1.9*10^{-6}$	8.80	$1.7*10^{8}$	532	$4.9*10^{-15}$	0.00/1.00	0.20	0.034	0.22

Column headings are:

H:	Henry's Constant, atm-m^3-mole	T_m:	Melting point temperature, K
log Kow:	log octanol water partition coefficient	Ps:	Crystalline solid vapor pressure, atm^{-1}
B_{vpa}:	air-to-leaf transfer factor, unitless	Vapor/Particle:	fraction of total reservoir in vapor and particle phases
BCF:	beef biotransfer factor, unitless	air:	total reservoir of congener in air, pg/m^3
beef:	whole beef observed concentrations, ng/kg		

* McLachlan, et al. (1990) did not provide data on 123789-HxCDF; the value for 123678-HxCDF was used instead.

7.2.3.9.2. Summary of algorithms, key assumptions, and parameter values

All parameters associated with individual congeners are shown in Table 7-7, and all parameters not specific to the congeners are shown in Table 7-8. Following now are summaries of the algorithms and key assumptions of this exercise. Many of them have been described in earlier chapters of this Volume and Volume II, and are not repeated here.

1. Partitioning total concentrations into a vapor and a particle phase

As shown in Figure 7-3, this is the first key step in this modeling exercise. Chapter 3 of this volume described air monitoring studies which reported the partitioning of dioxins into a particle and a vapor phase. Arguments were presented as to why these studies would likely overestimate the portion in the vapor phase. Because of this, a theoretical model for estimating the fraction of total concentration in the particulate and vapor phases was recommended for use in this assessment. The model of Bidleman (1988) was presented and discussed in Chapter 3, and will be used here as well. Table 7-7 presents the vapor and particle fractions assumed in this assessment, based on the Bidleman model.

2. Particle Depositions to Vegetations and Soils

Chapter 4 described the wet and dry particle deposition algorithm used for this assessment. The dry deposition algorithm and the key parameter assignment of a dry deposition velocity of 0.2 cm/sec will be used for this exercise without change. However, the wet deposition algorithm described in that chapter includes assignment of an annual rainfall amount with a washout factor. This is more appropriate for a site-specific application, and because this exercise is based on a "representative" rural profile of air concentrations and an average beef concentration profile derived from three locations in the United States, a simplification of the wet deposition algorithm is used in this exercise. This simplifications is based on the measurements made by Koester and Hites (1992). They measured wet deposition of total dioxins at two sites in Indianapolis and Bloomington, Indiana, and generally found wet deposition to be comparable to dry deposition. Specifically, the estimated annual wet deposition of dioxins at Indianapolis was equal to 0.7 times dry deposition, while at Bloomington, wet deposition was 1.3 times dry deposition. Therefore, it will be assumed that wet deposition equals dry deposition in this exercise. Crop yields and interceptions which were used for the demonstration scenarios of Chapter 5 are used for the deposition algorithms here as well.

Table 7-8. Model parameters used for all dioxin-like congeners.

Parameter	Description	Value
I. For Vapor/Particle Partitioning		
C	constant to estimate sorbed fraction in Equation *(?)*, atm-cm	$1.7*10^{-4}$
T	ambient air temperature, o K	298.1
$\Delta S_f/R$	entropy of fusion/universal gas constant, unitless	6.79
S_T	average total surface area of aerosol particles relative to average total volume of air, cm^2/cm^3	$3.5*10^{-6}$
V_T	average total volume of aerosol particles per volume of air, cm^3/cm^3	$3*10^{-11}$
II. Particle Depositions		
k_w	first-order plant weathering constant, yr^{-1}	18.01
k_s	first-order soil dissipation constant, yr^{-1}	0.0693
Y_g	yield of grass, kg/m^2	0.15
I_g	interception fraction of grass	0.35
$Y_{h/s}$	yield of hay/silage/grain	0.63
$I_{h/s}$	interception fraction of hay/silage/grain	0.62
V_d	velocity of particle deposition, m/sec	0.002
M	mass of mixing soil, kg/m^2	10
R_w	retention of wet deposition on vegetations, fraction	0.30
III. Vapor Transfers		
VG_{gr}	empirical correction factor for grass, unitless	1.00
$VG_{h/s}$	empirical correction factor for hay/silage/grain, unitless	0.50
IV. Bioconcentration		
B_s	bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless	0.65
DF_s	cattle soil diet fraction	0.04
DF_g	cattle grass diet fraction	0.48
$DF_{h/s}$	cattle hay/silage/grain diet fraction	0.48
V. Other		
	fat content of beef	0.19
	concentration reduction due to feedlot fattening	0.50
	assumption: wet deposition equals dry deposition	

The soil deposition algorithm remains unchanged from the structure and parameter assignments described in Chapter 4 and demonstrated in Chapter 5.

3. Vapor Phase Transfers to Vegetations

The key parameters for this algorithm include the air-to-leaf transfer factor, the B_{vpa}, and the empirical adjustment parameter, VG, which reduces vapor transfers considering the difference in the thin azalea and grass leaves used in experiments to derive the B_{vpa} and the bulky and protected vegetations of the cattle diet, such as silages as grains. The values of these parameters are the same ones used in Chapter 5.

4. Bioconcentration Model

The bioconcentration model includes assignment of the congener-specific bioconcentration factor, BCF, and the soil bioavailability parameter, B_s. The parameter assignments for these parameters are the ones which were developed in Chapter 4, used for the demonstration scenarios of Chapter 5, and shown on Tables 7-7 and 7-8.

5. Dietary Exposure of Cattle to Dioxins

The final key areas in this model are the assumptions concerning cattle exposure to dioxin-like compounds through their diet. A related key issue is the impact of feedlot fattening on final beef concentrations. The general diet profile used for the demonstration scenarios for beef concentration estimations in Chapter 5 is used here as well. This included an assumption of equal proportions of pasture grass and non-grass feed such as hay, silage, or grain, and a small amount of incidental soil. As discussed in Chapter 4, a 4% soil ingestion rate was assumed, leaving 48% each for pasture grass and the second category of cattle vegetation intake, abbreviated hay/silage/grain. Chapter 4 also discussed the impact of feedlot fattening. The demonstration scenario of Chapter 5 did not include feedlot fattening since the scenario was one of a farmer home slaughtering for personal consumption. For this exercise, however, it is likely that the commercial beef samples from which the "observed" concentration profile was derived came from cattle which had undergone a period of feedlot fattening. Chapter 4 summarized modeling efforts which attempted to characterize the impact of a period of fattening assuming residue-free intake for a period of 120 days. Based on their results, these modeling efforts hypothesized that such a diet regime would reduce fat concentrations by one-half. This will be the assumption used here as well; beef concentrations estimated using all the modeling described above will be halved as a final step in the modeling process.

7.2.3.9.3. Results and discussion

A final comparison of predicted versus observed whole beef concentrations is shown in Table 7-9. Total TEQ concentrations compare favorably, with observed total TEQ at 0.48 ppt and predicted TEQ at 0.36 ppt. The congeners of most toxicity also had the best match of predicted and observed concentrations: 2,3,7,8-TCDD - 0.03 ppt observed and 0.03 ppt predicted; 1,2,3,7,8-PCDD - 0.22 observed and 0.27 ppt predicted; 2,3,4,7,8-PCDF - 0.21 ppt observed and 0.17 ppt predicted. The largest discrepancies, an order of magnitude and more, were for two of the HxCDDs and for all HpCDD/Fs and OCDD/Fs. The total concentrations did not compare as well as the TEQ concentrations, with observed total whole beef concentration of 8.15 ppt and predicted at 2.13 ppt.

As a way of further examining these results, limited examinations are now presented on the two key components of this food chain model - the air to vegetation algorithm, and the air to soil algorithms.

One data set in the literature allows some limited comparisons between model predictions and observations of vegetation concentrations. This data was from a rural setting in Elk River, Minnesota (Reed, et al., 1990). This site was mentioned in the section above describing the derivation of the rural air concentration profile. The reference listed air concentrations by congener grouping for a rural setting (2 air sampling sites) and near an incinerator (1 site). It was noted that the average annual air concentrations near the incinerator was about 5 times higher than the average annual air concentration at the two rural sampling stations. The total PCDD/F air concentration in the rural setting was estimated at 1.54 pg/m^3. The corresponding TEQ concentration cannot be estimated without knowing the concentration of the congeners with non-zero toxicity. Therefore, a comparison to the crafted 0.019 pg/m^3 concentration for the rural setting in this paper cannot be made. However, a data set earlier described from Sweden (Broman, et al., 1990), listed a total concentration of 0.42 pg/m^3 and a corresponding TEQ concentration of 0.004 pg/m^3 for a rural Swedish countryside. This ratio of 100 between total and TEQ concentrations indicates that the Elk River total concentration of 1.54 pg/m^3 may translate to a TEQ concentration around 0.015 pg/m^3, which would be consistent with the 0.019 pg TEQ/m^3 developed in this paper.

This study also took samples of vegetations in this rural setting, including two hay and two corn samples. The limits of detection for these vegetation samples varied

Table 7-9. Results of validation exercise showing observed and predicted concentrations of dioxin-like compounds in whole beef.

Compound	Observed whole beef concentrations, ng/kg[1]	Predicted whole beef concentrations, ng/kg
2378-TCDD	0.03	0.03
12378-PCDD	0.22	0.27
123478-HxCDD	0.26	0.10
123678-HxCDD	0.84	0.03
123789-HxCDD	0.21	0.04
1234678-HpCDD	1.92	0.29
OCDD	2.91	0.29
2378-TCDF	0.06	0.46
12378-PCDF	0.04	0.07
23478-PCDF	0.21	0.17
123478-HxCDF	0.51	0.08
123678-HxCDF	0.06	0.13
123789-HxCDF	0.06	0.04
234678-HxCDF	0.07	0.07
1234678-HpCDF	0.4	0.04
1234789-HpCDF	0.13	0.01
OCDF	0.22	0.01
TOTAL CONCENTRATION	8.15	2.13
TEQ CONCENTRATION	0.48	0.36

between 0.31 and 6.5 ppt on a congener-specific and site-specific basis. With vegetation concentrations predicted to be in this range generally, the data therefore cannot be rigorously informative. The congener found with the highest concentration is OCDD, found at 72 (site 1) and 170 (site 2) ppt in two corn samples, and 270 (site 1) and 300 (site 2) ppt in two hay samples. In addition to this higher finding in the hay samples, generally more positives were detected in hay rather in corn. This is consistent with discussions in this paper indicating that vegetation concentrations of dioxin-like compounds is a surface phenomena with little within plant translocation. Hay, in this

observation, is considered a leafy vegetation, whereas corn is considered a bulky vegetation.

Table 7-10 lists the average congener specific hay concentrations observed in Elk River (the average of two hay samples, with non-detects counted as 0.0 when one of the two samples had a positive, and just listed as ND when both hay samples showed non-detects) compared against the model's predicted concentrations in grass. This is felt to be a valid comparison. It assumes that hay alone is reasonably similar to grass in that both are "leafy" vegetations and would be modeled similarly in the framework of this paper.

What is now available to interpret and analyze are the predicted and observed beef concentrations, the predicted and observed leafy vegetation concentrations, and further model trends. Several observations are now summarized based on these analyses:

1) Given the range of the detection limit, 0.31-6.5 ppt for the hay sampling, the model's predictions of grass concentrations are generally consistent with observations, with the exception of the OCDD and OCDF concentrations. It is noted that the second highest congener observation of 30 ppt of 1,2,3,4,6,7,8-HpCDD is matched by the model's prediction of 20.7 ppt for 1,2,3,4,6,7,8-HpCDD.

2) The analysis of the OCDD and OCDF results for hay is very telling. First, it is noted that the crafted rural air concentrations of these two congeners matches very well with the observed air concentrations at this Elk River site: OCDD observed at 0.5 pg/m^3 and crafted at 0.57 pg/m^3; and OCDF observed at 0.09 pg/m^3 and crafted at 0.034 pg/m^3 (note: the observed concentrations for OCDD/F congeners is the average of four listed concentrations of OCDD/F congeners in Reed, et al. (1990) - rural sites 1 and 2 and winter and summer listings). Since the crafted air concentrations match well with the observed air concentrations, one would hope that the vegetative concentrations also match. An analysis of why they did not indicates the importance of vapor phase contributions to vegetative concentrations. According to the application of the Bidleman (1988) approach for estimating the bound fraction, ϕ, in the air, both these congeners were assigned a ϕ of 1.00. In fact, using the OCDD/F vapor pressures and melting points, these ϕ values were both 0.998. If one allows for the possibility that ϕ for OCDD/F could be less than one, and calibrates ϕ for OCDD/F for this exercise, one can show that small reductions in ϕ result in better predictions of both grass and beef concentrations. Recall that the observed "grass" concentrations are, in fact, the hay concentrations found at Elk River, Minnesota,

Table 7-10. Comparison of concentrations of dioxin-like compounds found in hay in a rural setting with model predictions of grass concentrations.

Compound	Observed hay concentration, ng/kg[1]	Predicted grass concentrations, ng/kg
2378-TCDD	ND	0.1
12378-PCDD	ND	0.9
123478-HxCDD	ND	0.7
123678-HxCDD	1.2	0.2
123789-HxCDD	ND	0.2
1234678-HpCDD	30	21.0
OCDD	285	6.0
2378-TCDF	ND	7.2
12378-PCDF	ND	1.4
23478-PCDF	ND	0.8
123478-HxCDF	ND	0.5
123678-HxCDF	ND	0.9
123789-HxCDF	ND	0.3
234678-HxCDF	ND	0.5
1234678-HpCDF	5.4	1.4
1234789-HpCDF	ND	0.1
OCDF	7.5	0.4

[1] Observed data from Reed, et al. (1990). Concentrations listed are the mean of two observations for hay grown in rural settings. ND assumed to be zero for calculation of means. Limits of detection described in Reed, et al. (1990) as ranging between 0.31 and 6.5 ppt, on a congener-specific and site-specific basis.

and that the observed beef concentrations are those which were generated using available data from around the country. Table 7-11 shows the results of a calibration, where ϕ is first 1.00 as initially assumed, and then calibrated so that grass/hay and subsequently beef are more in line. As seen, the calibrated ϕ are 0.9998 for OCDD and 0.998 for OCDF, and the grass and beef concentrations predicted are now much closer to observations.

The main reason for these very large differences in model predictions of hay

Table 7-11. Calibration exercise showing improvements in grass and beef concentrations when the fraction sorbed parameter, ϕ, drops minutely below 1.00 for OCDD and OCDF.

I. Uncalibrated: ϕ = 1.00 for OCDD and OCDF

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
OCDD	6.0	285	0.29	2.91
OCDF	0.4	7.5	0.01	0.22

II. Calibrated: ϕ = 0.9998 for OCDD and 0.998 for OCDF

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
OCDD	237	285	8.51	2.91
OCDF	10.2	7.5	0.14	0.22

concentrations with seemingly small differences in the amount assumed to be in the particle phase is that the air-to-leaf transfer factor, the B_{vpa}, is 2 to 4 orders of magnitude higher for OCDD and OCDF as compared to all other transfer factors. For OCDD, it is also noteworthy that the total air concentration is 1 to 2 orders of magnitude higher than the concentrations for all other congeners.

3) The one congener whose air concentration is within an order of magnitude of OCDD is that of 1,2,3,4,6,7,8-HpCDD, at 0.116 pg/m^3. Also, the calculated B_{vpa} for this congener is second in magnitude behind the OCDD/F congeners. Since 2% of this air concentration is, in fact, predicted to be in vapor phase according to the Bidleman model, vapor transfers are considered and the model predicted 21.0 ppt grass concentration, which compared favorably with the observed 30 ppt concentration.

4) Calibrations for some of the other congeners for which a discrepancy exists between hay/grass predictions and beef predictions were not attempted. However, one

can see with the following how the trend between predicted grass to beef concentrations followed the observed grass to beef trend. That is, when the model underpredicted grass, it also underpredicted beef, and likewise for overpredicting:

	grass/hay, ng/kg (ppt)		whole beef, ng/kg (ppt)	
	Pred.	Obs.	Pred.	Obs.
1,2,3,6,7,8-HxCDD	0.2	1.2	0.029	0.84
2,3,7,8-TCDF	7.1	ND*	0.46	0.06
1,2,3,4,6,7,8-HpCDF	1.4	5.4	0.04	0.40

* the detection limits for hay sampling ranged from 0.30 to 6.5 ppt.

5) A simple analysis of model performance indicates that vegetation concentrations explain beef concentrations. Looking only at 2,3,7,8-TCDD, it is seen that cattle soil ingestion, 4% of total diet, explains only 8.5% of final beef concentration, with grass explaining 60.6% and hay/silage/grain 30.9%. The main difference in grass and hay/silage/grain, as discussed above, is that vapor transfers are halved for hay/silage/grain with the use of the empirical VG parameter. Further, grass and hay/silage/grain concentrations are overwhelmingly dominated by vapor transfers for 2,3,7,8-TCDD, explaining 93% (grass) and 94% (hay/silage/grain) of final plant concentration. Since grass and hay/silage/grain explain over 90% of beef concentration, vapor transfers onto vegetations cattle consume are predicted to explain about 85% of final 2,3,7,8-TCDD beef concentrations in this exercise. Very similar predictions occur for all congeners, with the exception of OCDD/F where 100% was initially assumed to be in the particle phase. Allowing for the calibration described above, now the OCDD/F beef concentrations are dominated by vapor transfers. Further discussion of the importance of vapor-phase dioxins to vegetations and to beef/milk can be found in Section 6.3.3.11 in Chapter 6.

An air to soil examination begins with a comparison of predicted soil concentrations of the dioxin-like compounds and an observed concentration in soils, which is shown in Table 7-12. The observed data originated from four studies in the United States where soils were characterized as "rural" or "background". As seen in Table 7-13, there is clearly an underprediction trend for air to soil impacts. For the nine congeners where the literature allowed for a non-zero average soil concentration, the model appears to

Table 7-12. Comparison of concentrations of dioxin-like compounds found in soils described as "rural" or "background" with model predictions of soil concentrations.

Compound	Observed soil concentration, ng/kg[1]	Predicted soil concentrations, ng/kg
2378-TCDD	0.88	0.12
12378-PCDD	ND	0.57
123478-HxCDD	ND	0.56
123678-HxCDD	4.0	0.87
123789-HxCDD	9.0	1.17
1234678-HpCDD	194	13.9
OCDD	237[2]	69.3
2378-TCDF	1.59	0.8
12378-PCDF	ND	0.7
23478-PCDF	ND	0.5
123478-HxCDF	ND	1.4
123678-HxCDF	ND	1.3
123789-HxCDF	ND	0.3
234678-HxCDF	2.0	1.0
1234678-HpCDF	47	4.9
1234789-HpCDF	ND	0.7
OCDF	30.2	4.1

[1] Observed data from Reed, et al. (1990), Pearson, et al. (1990), EPA (1985), and Birmingham (1990). Concentrations listed are the arithmetic mean of all observations available, counting non-detects as 1/2 detection limit. Only one study of the four noted had measurements for the eight congeners above with Non-Detects. This study, Reed, et al. (1990) listed soil detection limits as varying between 0.79 and 2.9 ppt, depending on site and congener.

[2] Geometric means were also determined for this data set. A wide range of concentrations of OCDD, ND to 10,600 ppt, led to a geometric mean of 60 ppt for this congener. For all other congeners, geometric means were within a factor of about 50% of arithmetic means.

underpredict soil concentrations by a range of about 2 to 10 times (i.e., observed concentrations are twice as high to about ten times higher than predicted concentrations). While this is a non-trivial result, in fact the model would not predict a substantially different beef concentration if soil concentrations were more in line with observations. If the soil concentrations were artificially increased by a factor of 10, than whole beef concentrations of total dioxins increase from 2.13 ppt to 3.62 ppt, and TEQ concentrations increase from 0.36 ppt to 0.45 ppt. The reason for this trend is that soil is only 4% of the beef cattle diet prior to feedlot fattening.

The observation made is that the current formulation and/or parameter assignments for an air to soil impact will underpredict soil concentrations of dioxins by about 2-10 times. If this observation is, in fact, a statement of truth, then the following is offered as the most likely causes for model underprediction:

1. The soil dissipation rate: The dissipation rate of 0.0693 yr^{-1}, corresponding to a half-life of 10 years, was developed from field data of 2,3,7,8-TCDD applied to soils in the herbicide 2,4,5-T (Young, 1983). This may be appropriate for a limited loading onto a bounded area of soil. However, mechanisms for dissipation from this bounded area, such as dust suspension and volatilization, may not directly apply for background settings where such losses may be redeposited downwind. According to the steady state algorithm for soil impacts from depositions, the estimated soil concentration is an inverse function of the dissipation rate. If the dissipation rate is reduced to 0.00693 yr^{-1}, corresponding to a half-life of 100 years, than the soil concentrations are increased by an order of magnitude.

2. Depositions of vapors: Koester and Hites (1992) developed the argument that their collection apparatus for dry deposition of dioxins would not scavenge vapor phase dioxins from the air; that they would only be measuring dry deposition of particle bound dioxins. Since the dry deposition velocities used in this paper originate from their work, and if their arguments are valid, then the algorithms of this paper do not consider the dry deposition of vapors. Their methods for measurement of wet deposition did not preclude the scavenging of vapors, although they do argue that rainfall is more effective at scavenging particle-bound dioxins compared to vapor-phase dioxins. Therefore, the assumption made that total annual wet deposition equals dry deposition made in this paper, based on the

results of Koester and Hites, means that wet deposition of vapor phase dioxins are considered. In any case, algorithms to estimate the additional dry deposition loadings of vapor-phase dioxins to soil could not be found, so the impact of including them cannot be estimated.

3. Detritus recycling: This is another loading not considered, and also a loading tied directly to vapor-phase dioxins. As discussed above, vegetation concentrations are dominated by vapor transfers. Barbour, et al. (1980) list a detritus production rate for a setting described as "tallgrass prairie" as 520 g/m^2-yr. Given the concentrations predicted to occur in grass, one can estimate the loadings of dioxin corresponding to a detritus production of this magnitude. This was done and compared against the estimated total deposition rates from the air to soil of individual congeners. It was found that detritus loadings varied by congener, and was equal to a range of 2% of atmospheric deposition to 100% (equal to) of deposition. Summing the depositions and the detritus loadings of all congeners, it was found that detritus loadings are equal to about 20% of atmospheric deposition loadings of dioxins.

7.2.3.9.4. Conclusions

The beef bioconcentration algorithm of this assessment was tested in this section. A profile of air concentrations was crafted to be typical of rural environments where cattle are raised for production of beef. This profile was routed through the model to predict concentrations of dioxin-like compounds in beef. These predictions were compared with a profile of measured concentrations. An "observed" TEQ concentration of 0.48 ng/kg in whole beef was compared with a "predicted" 0.36 ng/kg. An observed total concentration PCDD/Fs of 8.15 ppt in beef was compared against the predicted 2.13 ppt. Further evaluations of the air to vegetation algorithm indicate the model appears to predict vegetation concentrations consistent with one set of literature observations, with the exception of the octa congeners, OCDD and OCDF. However, when assuming only a minute amount of the airborne reservoirs of these congeners is in the vapor phase, model predictions of both vegetations and subsequently beef concentrations fall in line. A final evaluation of the air to soil model indicates that the model and/or the parameter assignments tend to underpredict soil concentration by as much as an order of magnitude. Refinements to the model which would bring soil concentrations more in line with

observations were offered. It was observed that while the model appears to be underpredicting soil concentrations, a more appropriate prediction would not change beef predictions significantly since soil is only a small part of the cattle diet. A major conclusion of this work is the overwhelming dominance of the vapor phase transfers to vegetations which cattle consume, which in turn implies that the appearance of these chemicals in beef and milk is due to vapor transfers.

Another and more broad conclusion offered is that the validation exercise in general demonstrates the validity of the air-to-beef model framework and parameter assignments. This is a cautious conclusion, obviously, given the uncertainty in the many parameter assignments and real world observations. This exercise would need refinement in several areas before ascribing any finality to the model structure and results. Following is a summary of the key uncertainties of this exercise:

1. A characteristic rural air environment: A profile of air concentrations of dioxin-like congeners in a rural environment in the United States could not be found for this exercise, and instead one was crafted given a representative profile for urban/suburban areas and a simple proportional reduction.

2. A characteristic profile of dioxin-like congeners in beef: Only 14 samples from three literature references, one of which only reported on 2,3,7,8-TCDD and 2,3,7,8-TCDF, were found for this exercise.

3. Vapor/particle partitioning: A theoretical modeling approach was used to partition the total reservoir of congeners into particle and vapor phase. A carefully designed monitoring experiment could shed some light on vapor/particle partitioning for dioxin-like compounds. This is obviously critical given the major conclusion of the dominance of vapor phase concentrations in explaining beef concentrations.

4. Vapor transfers to vegetations: Like the partitioning issue, the quantification of transfers onto vegetations is critical. The generalized model of Bacci (1990, 1992) was used with an empirical refinement suggested by McCrady and Maggard (1993). To highlight the importance of this empirical reduction, consider the following which describes what predictions would be without the benefit of the McCrady adjustments. A factor of 40 difference was noted in the measured transfer of 2,3,7,8-TCDD, on a volumetric basis, to grass leaves in the McCrady experiments compared to the transfer which would be estimated using the empirical algorithm developed by Bacci and coworkers. This factor of

40 was applied to the transfer factor of all dioxin-like compounds. The volumetric transfer factor was transformed to a mass-based transfer factor using plant densities and percent dry matter suggested by McCrady rather than those used by Bacci and coworkers for the azalea leaf. Together, the final mass-based B_{vpa} of this exercise, and this assessment otherwise, is about a factor of 20 lower than that which would be estimated using the Bacci mass-based algorithm. Said another way, the model would have predicted a whole beef concentration greater than 7 ppt, instead of 0.36 ppt. Also, a second empirical refinement reduced the transfer into bulky vegetations. While the need for both refinements is argued to be justified for dioxin-like compounds, the precise numerical adjustments used in the exercises above cannot be rigorously defended without further data.

5. Particle depositions onto vegetations: The impact of wet deposition needs to be further investigated. A literature article suggesting that about 30% of particles depositing in rain are retained on the canopy after the rainfall justified the assignment of 0.30 to the parameter, R_w (fraction retained on vegetation from wet deposition). The weathering half-life of 14 days, while often used for dioxins, is also identified as uncertain. Finally, the deposition velocity of 0.2 cm/sec should be considered further.

6. Air-to-soil impacts: The trend here is that the model appears to underpredict soil concentrations by an order of magnitude or less. Three aspects of the model were offered above as possible candidates for refinement and further research. These included: vapor impacts to soils, dissipation rate in soils, and detritus loadings to soils.

7. The bioconcentration factor: Only one study was found from which congener-specific bioconcentration factors for the suite of congeners could be developed, and this was for one cow, for one lactating period, and was for milk and not beef. The differences in bioconcentration between beef and milk need to be further investigated and quantified.

8. Cattle diet and the impact of feedlot fattening: A cattle diet was simplistically assumed to consist of 4% soil and equal parts of grass and non-grass feeds. Perhaps a more representative diet could be crafted, which would lead to a different exposure pattern by the beef cow prior to feedlot fattening. Equally if not more important is the impact of this feedlot fattening. It is clear that commercial beef cattle in the United States undergo a period of feedlot fattening. However, before and after monitoring quantifying the impact of this practice could not be found. Two modeling studies, which assumed

that dilution and depuration were occurring during feedlot fattening, estimated that concentrations were halved due to this process. This was the assumption also made in this paper, and it needs to be further evaluated.

7.2.3.10. *Comparison of modeled beef and milk concentrations with concentrations found*

The example scenario in Chapter 5 demonstrating the on-site source category (where the soil at the place of residence/farming/exposure is the source of contamination) had soil concentrations initialized at 1 ng/kg (ppt) 2,3,7,8-TCDD. This concentration was chosen because it was similar to concentrations of 2,3,7,8-TCDD found in studies where researchers had measured what they characterized as "rural" or "background" soils. Beef and milk fat concentrations of 2,3,7,8-TCDD estimated with this soil concentration were 0.12 and 0.06 ppt 2,3,7,8-TCDD, respectively. Assuming fat contents for beef and milk of 0.22 and 0.035, respectively, whole beef and milk concentrations are estimated as 0.03 and 0.002 ppt. Beef and milk fat concentrations for an exposure site located 500 meters from a hypothetical incinerator, another of the example scenarios in Chapter 9, were 0.0024 and 0.0017 ppt. Corresponding whole beef and milk concentrations were 0.0005 and 0.00006 ppt. The other source category was a site of higher soil concentration located near a site of exposure. It was termed the off-site source category, and the demonstration scenario had a 4 hectare site contaminated with 2,3,7,8-TCDD at 1 μg/kg (ppb) located 150 meters from an exposure site. This concentration was selected based on similar 2,3,7,8-TCDD concentrations found in sites of elevated contamination, such as Superfund sites. No-till soil concentrations at the site of exposure, the concentrations which beef and dairy cattle were exposed to, were estimated to be 0.28 ppb, or 280 ppt. Concentrations in beef and milk fat were 38 and 19 ppt, respectively, which corresponds to whole product concentrations of 17 and 0.7 ppt.

A limited number of studies were available to estimate concentrations of dioxin-like compounds in beef suitable for background exposure estimations. Data from these studies is summarized in the previous section, Section 7.2.3.9. From this limited data, the concentration of 2,3,7,8-TCDD in beef/veal fat was estimated at 0.134 ppt when non-detects were assumed to equal one-half the detection limit and 0.060 ppt when non-detects were assumed equal to 0.0. A single report containing milk concentrations

(Lafleur, et al., 1990) indicated a concentration of 0.054 ppt in milk fat. This compares to the 0.12 ppt estimated for beef fat and 0.06 ppt estimated for milk fat for the demonstration scenario based on a background soil concentration of 1 ppt.

The example scenario results from the stack emission source estimated beef and milk concentrations over a factor of ten lower than for the background soil concentration scenarios. In interpreting this result, it is important to note that the emission rates assumed in this example scenario were characterized as typical of incinerators with a high level of air pollution control, e.g., scrubbers with fabric filters. The TEQ emission factor (mass TEQs emitted per mass feed material combusted) for the demonstration scenario was 4.5 ng/kg, which was compared to a crafted range of 0.3 ng/kg (for a municipal solid waste incinerator) to 200 ng/kg (for a medical waste incinerator) which had similar high levels of air pollution control. Also, the 200 metric tons per day feed material assumed for the example scenario is considered midrange (see Chapter 3 for more details). Some articles in the public literature suggest a greater impact to milk when the milk is produced near incinerators or urban centers, although a direct comparison obviously is not warranted without a careful evaluation of source strengths from these literature articles, which is not done here. A study sampling remote farms in England also sampled two farms near incinerators and two farms near industrial centers. Whereas samples from remote farms averaged 0.009 ppt for whole milk, two concentrations near the incinerators were 0.034 and 0.036 ppt 2,3,7,8-TCDD, and the samples near the industrial centers were 0.043 and 0.081 ppt (Startin, et al., 1990). A study from Switzerland which sampled milk from locations remote from 2,3,7,8-TCDD sources, and did not find detectable residues, also sampled three locations that were within 1000 meters of incinerators (Rappe, et al., 1987). Whole milk concentrations near the incinerators were 0.021, 0.038, and 0.049 ppt.

Sampling of beef and milk near areas of elevated soil concentrations, or where cattle were raised on soils with known high concentrations of 2,3,7,8-TCDD, were not found in the literature. Therefore, the beef fat concentration of 38 ppt (whole beef equal to 8 ppt) estimated to occur near an area where soil concentrations of 2,3,7,8-TCDD were 1 ppb cannot easily be evaluated. There are some studies on other animals indicating high tissue concentrations in areas of high soil contamination of 2,3,7,8-TCDD. Lower, et al. (1989) studied animal tissues for wild animals in the abandoned town of Times Beach,

Missouri, and compared their results for similar wild animals tissue concentrations found in Eglin Air Force Base in Florida; Seveso, Italy; and Volgermeerpolder, Holland. With 2,3,7,8-TCDD soil levels in these areas in the hundreds to thousands of ppt, tissue levels for earthworm, mouse, prairie vole, rabbit, snake, and liver samples from some of these animals, were in the tens to thousands of ppt.

There is an episode of beef and dairy cows being raised on lots where the soil was heavily contaminated with polybrominated biphenyls (PBB; details can be found in Fries and Jacobs, 1986; and Fries, 1985). Soil concentrations to which dairy and beef cows were exposed were 830 and 350 μg/kg (ppb), respectively. Body fat of the dairy cows had PBB concentrations of 305, 222, and 79 ppt (dairy heifers, primiparous dairy, and multiparous dairy, respectively). Body fat for the beef cows exposed to 350 ppb soil levels were 95 (cows) and 137 ppt (calves). Milk fat concentrations from the primiparous dairy and multiparous dairy cows exposed to 830 ppb soil levels were 48 and 18 ppt.

Fries estimated a quantity which is also useful for purposes of comparison - this quantity is the ratio of concentration in animal fat to concentration in soil to which the animal is exposed. His justification for deriving this ratio is that soil was speculated as the principal source of body burdens of PBB in the data listed above. For the source categories where contaminated soil is the source of dioxin-like compounds, the on-site and off-site source categories, a similar assumption is warranted. Ratios he derived for body fat of dairy heifers ranged from 0.10 to 0.37, while it was 0.02 and 0.06 for milk fat. For body fat of beef cows, these ratios were 0.27 and 0.39. Fries also measured a ratio of 1.86 for sows and gilts. He attributes much higher sow ratios to their tendencies to ingest more soil. Analogous ratios can be derived for the contaminated soil source categories, and for beef and milk fat. For the onsite source category with low soil concentrations, beef fat to soil and milk fat to soil ratios were 0.12 and 0.06, respectively. For the off-site source category, ratios were similar at 0.14 for beef fat and 0.07 for milk fat. The milk fat ratios compare favorably with PBB ratios derived by Fries (1985), although the beef fat ratios appear generally lower.

This is, once again, some indirect evidence that the soil to air models may be underestimating air concentrations. This had been discussed earlier in Section 7.2.3.7 on air concentrations and 7.2.3.8. on soil to plant relationships. For the current discussion, a higher beef fat:soil ratio would result if air concentrations were increased and hence the

cattle vegetation concentrations would increase.

7.2.4. Alternate Modeling Approaches for Estimating Environmental and Exposure Media Concentrations

This section examines alternate modeling approaches for estimating environmental and exposure media concentrations. This is by no means a comprehensive examination, nor is its purpose to justify the models selected. If the models examined can be shown to be similar or to arrive at similar results as the models of this assessment, perhaps some validity for modeling and/or the models selected for this assessment can be gained.

7.2.4.1. *An alternate approach for estimating bottom sediment concentrations from watershed soil concentrations*

The dilution of contaminated sediments entering a river system can be estimated using an alternate approach. The average runoff rate for the midwestern U.S. is about 15 inches/year (Linsley, et al., 1982), the value used in this assessment for determining the flow rate of the receiving water body. For a 10,000-acre watershed (4,000 hectares; the watershed size and effective drainage area for the example scenarios in Chapter 5), this yielded a stream flow of about 17.2 ft^3/sec. The sediment yield can be estimated from the stream flow as follows (Linsley, et al., 1982): $Q_s = aQ^n$, where Q_s = sediment flow rate (Eng. T/yr); Q = stream flow rate (ft^3/sec); and a and n are empirical constants, reflecting the vegetative cover in the watershed. Linsley, et al., (1982) recommend using a = 3,500 and n = 0.82 for coniferous forest and tall grass, and a = 19,000 and n = 0.65 for scrub and short grass. Substituting these into the equation above (and Q = 17.2 ft^3/sec) gives an annual sediment flow rate of 36,000 to 121,000 T/yr. Annual sediment flows will be assumed to consist only of soils which have eroded during the year. As such, sediments will be comprised of contaminated as well as uncontaminated watershed soils. A "contaminant concentration ratio" can be calculated by estimating the sediment contributed by the contaminated areas and dividing by this sediment flow rate range; this assumes all other sediment contributions are uncontaminated. The annual soil loss for Scenario 3 demonstrating the off-site scenario was 9.6 T/ac-yr. The contaminated site area for Scenario 3 was 10 acres (4 ha). The total soil erosion contributed by this site equals: the unit soil loss * area * soil delivery ratio; for Scenario 3, this equals

9.6*10*0.26, or 25 T/yr. The contaminant concentration ratio is (25 T/yr)/(36,000 to 121,000 T/yr), or a range of 0.0002-0.0007.

This can be compared to a contaminant ratio estimated using current methodologies. The example Scenario 3 which had soil concentrations at 1 ppb resulted in a bottom sediment concentration in the nearby water body of 0.0016 ppb, which leads to a contaminant concentration ratio of 0.0016. This is higher than the ratio range noted above. It does incorporate an "enrichment ratio", however, which is the ratio of contaminant concentration on soils eroding from a field to soils within the field. It is given a value of 3 for the demonstration scenario. The ratio range noted above did not consider enrichment; if it had, the range would instead by 0.0006-0.0021. Now the modeled 0.0016 and this range are comparable.

7.2.4.2. *An alternate modeling approach for estimating water concentrations given a steady input load from overland sources*

A study to evaluate the bioaccumulation of 2,3,7,8-TCDD in fish in Lake Ontario included an extensive modeling exercise (EPA, 1990a). The model used was WASP4 (Ambrose, et al., 1988). This is a substantially more complicated model than used in this assessment. The underlying principal for the WASP4 model is a conservation of mass. Contaminant source terms, described in mass/time units, enter what are termed control volumes, or segments. The contaminant partitions between sorbed, bound, and dissolved phases; it is not required to specify whether the contaminant enters via soil erosion, water runoff, surface deposition, or otherwise. Contaminants are, however, assumed to enter via the surface or as part of inflows to the water body, in contrast to ground water recharge. The mass transported into a segment is either transported out of the segment, accumulates in the segment, or is transformed by chemical or biological reactions.

As noted, 2,3,7,8-TCDD input into the Lake Ontario application partitions within the water column into a sorbed compartment, a dissolved compartment, and a bound compartment. This bound compartment is further described as non-settling organic matter. Three analogous compartments receive 2,3,7,8-TCDD in the bottom sediment layer. Several exchanges between the six compartments and contaminant losses within each compartment are modeled. For example, losses from water column compartments include downstream transport, volatilization and photolysis; the loss mechanism from the

bottom sediment layer is sedimentation. Exchanges between compartments consider partitioning, diffusion, and sediment settling and resuspension.

This model requires substantial parameterization. Once values were selected for the Lake Ontario application, an evaluation was made on the impact of different levels of 2,3,7,8-TCDD input. Dynamic and steady state results were discussed. Principally examined for the steady state results were the concentrations of bottom sediment sorbed 2,3,7,8-TCDD and water column dissolved (soluble) phase 2,3,7,8-TCDD. A given level of steady 2,3,7,8-TCDD input, in kg/yr, resulted in a steady state concentration sorbed to bottom sediment and dissolved in the water column.

The premise in both the Lake Ontario steady state application of WASP4 and the water concentration algorithms in this assessment is that contaminants continue to enter water bodies over time unabated. Ground water entry of contaminants is not considered in either approach. Although a direct modeling comparison cannot be done, it is possible to slightly adjust the algorithms of this assessment to evaluate how results from a simple partitioning approach would compare with results from the complex fate and transport approach of the WASP4 steady state application.

Assume a surface water body is initially free of contaminant and at time t equals 1 day, a strongly hydrophobic contaminant, such as the dioxin-like compounds of this assessment, begins to enter a lake. Assuming the contaminant enters via soil particles, as in the approach of this assessment, it will then partition between those soil particles and surrounding water. The soil particles will slowly move toward the bottom of the lake at a rate described by a particle settling velocity. A settling velocity of 1 m/day is assumed in the Lake Ontario simulations. The amount of time it takes to settle to the bottom once entering from the surface equals the lake depth divided by this settling time. The Lake Ontario depth was 86 m. Therefore, it might take 86 days to settle. This, of course, neglects resuspension of settled particulates. With this simplistic framework, a steady state amount coming into the lake after 86 days is matched by an amount depositing onto the lake bottom; the amount of contaminant within the water column has reached steady state. Water concentrations can then be estimated assuming equilibrium partitioning.

Results of sediment and water column steady state concentrations are described for any loading of 2,3,7,8-TCDD in the WASP4 steady state application; those loadings are described in kg/yr. Loadings in kg/yr are easily correlated to a steady state water column

amount, given the above analysis. For example, a loading of 1.0 kg/yr could translate to a within water column steady state amount of 0.24 kg (1.0 kg/yr * (86 d)/(365 d/yr)).

This steady water column amount partitions between suspended sediment and surrounding water. First, the total concentration (sorbed + soluble) simply equals:

$$C_{tot} = 1000 \frac{LD}{VOL} \qquad (7\text{-}1)$$

where:

C_{tot} = total concentration, mg/L
LD = water column steady state amount of contaminant, kg
VOL = lake volume, m^3
1000 = converts kg to mg and m^3 to L

The dissolved phase portion of total is given by:

$$C_{wat} = \frac{C_{tot}}{1 + (Kd_{ssed}\ TSS\ 10^{-6})} \qquad (7\text{-}2)$$

where:

C_{wat} = soluble phase water concentration, mg/L
C_{tot} = total concentration, mg/L
Kd_{ssed} = partition coefficient between suspended sediment and surrounding water, L/kg
= $Koc * OC_{ssed}$
Koc = organic carbon partition coefficient, L/kg
OC_{ssed} = fraction organic carbon of suspended sediments
TSS = total suspended sediments, mg/L
10^{-6} = converts mg/kg to mg/mg

Parameters in this equation for the Lake Ontario WASP4 application include VOL, Koc, OC_{ssed}, and TSS. Lake Ontario volume was given as 1.68×10^{12} m^3, Koc was

estimated for the WASP4 application as 3,162,000, OC_{ssed} was estimated at 0.03, and TSS was estimated 1.2 mg/L. For a steady load of 1 kg/yr and a resulting LD of 0.24 kg, the steady state water column 2,3,7,8-TCDD concentration, using the simplistic approach described above, is estimated as 0.13 pg/L (ppq). The steady state water column concentration estimated by WASP4 given the same parameters and a load of 1 kg/yr is roughly 0.20 pg/L. An uncertainty analysis done with these WASP4 results concluded that 95% confidence limits around this prediction are 0.03 and 0.40 pg/L.

This would seem to imply that the simple partitioning approach used in this assessment compares favorably with the more complex fate and transport modeling assessment using WASP4, for Lake Ontario.

7.2.4.3. *Estimating fish tissue concentrations based on water column concentrations rather than bottom sediment concentrations*

EPA has prepared a document titled, "Interim Report on Data and Methods for Assessment of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin Risks to Aquatic Life and Associated Wildlife" (EPA, 1993). That document provides details on the two key bioaccumulation parameters used for the methodologies of this document, the Biota Sediment Accumulation Factor, BSAF, used for the soil and stack emission source categories, and the Biota Suspended Solids Accumulation Factor, BSSAF, used for the effluent discharge source category. That document also discussed several water column based bioaccumulation factors, which are the focus of this section.

Before discussing these factors, it is noted that food chain modeling is a well developed alternate approach for estimating fish tissue concentrations of bioaccumulating contaminants (Thomann, 1989), which has also been applied to 2,3,7,8-TCDD (Parkerton, 1991). This approach is significantly more complex than the bioaccumulation/biotransfer approach of this methodology. It involves detailed site-specific characterizations, specifically the identification and transfer modeling between trophic levels of a food chain in a water body. Food chain modeling is a mechanistic approach, while the transfer approaches of this methodology are empirical. No judgement is rendered as to the relative merit of food chain models versus use of bioaccumulation coefficients. If detailed site-specific data is available, and given time and resources, assessors should consider food chain modeling for estimating fish tissue concentrations.

One water column measure which has been classically used is termed the Bioconcentration Factor, or BCF. Bioconcentration refers to the net accumulation of a chemical from exposure via water only, and BCFs are most often obtained in laboratory conditions. BCFs are defined as the ratio of the chemical concentration in organism (mass of chemical divided by wet weight of organism tissue) to that in water.

Another water column measure of the potential for a contaminant to accumulate in fish tissue is termed the Bioaccumulation Factor, or BAF. Bioaccumulation refers to the net accumulation of a chemical from exposure via food and sediments as well as water. Similar to the BCF, BAFs are defined as the ratio of the chemical concentration in the organism to that in the water.

For chemicals that are not strongly hydrophobic (unlike the dioxin-like compounds), the distinction between bioconcentration and bioaccumulation is small. Whereas food intake is generally a few percent of body weight per day, water passing over gills will equal hundreds to thousands times the organism weight per day, depending on species, activity, temperature, and other factors. Given this, the concentration of chemical in food must be 3 or more orders of magnitude greater than that in water before food can substantially contribute to uptake. EPA (1993) estimates that food intake becomes a critical contributor to the accumulation of contaminants in fish tissue for contaminants with log Kow of 5 and greater.

Since the dioxin-like compounds fall into this category, the remainder of this section will focus on the Bioaccumulation Factor. EPA (1993) defines steady-state lipid-based BAFs for total chemical in water and freely dissolved chemical in water (i.e., chemical which is truly in a dissolved phase and not bound to dissolved or suspended particulate organic materials) as:

$$ssBAF_l^t = \frac{C_{lipid}}{C_w^t} \qquad (7\text{-}3a)$$

$$ssBAF_l^d = \frac{C_{lipid}}{C_w^d} \qquad (7\text{-}3b)$$

where:

$ssBAF_l^t$ = steady-state lipid-based BAF for total chemical in water, unitless

C_{lipid} = the mass of contaminant in fish lipid tissue divided by the mass of fish lipid tissue, mg/kg

C_w^t = the mass of total contaminant in water divided by the mass of water in the water body, mg/kg (note: 1 L water nearly equals 1 kg, therefore, 1 mg/L can be assumed to equal 1 mg/kg)

$ssBAF_l^d$ = steady-state lipid-based BAF for freely dissolved chemical in water, unitless

C_w^d = the mass of freely dissolved contaminant in water divided by the mass of water in the water body, mg/kg

EPA (1993) then develops relationships between $ssBAF_l^d$ and $ssBAF_l^t$, based on dissolved and particulate organic carbon reservoirs in the water column, and partition coefficients for these reservoirs. This is meaningful in complex modeling where these two reservoirs of organic carbon can be accounted for, such as in the WASP4 model. Alternately, EPA (1993) defines the TBF_{oc}, a total binding factor to organic carbon, which empirically considers the reservoir of dissolved organic material (i.e., increases total binding and reduces truly dissolved phase concentrations) when such a reservoir is not explicitly modeled. The modeling frameworks in this assessment have only one compartment of suspended material to which contaminants sorb, with one associated organic carbon content. A second reservoir to which contaminants bind, the reservoir of dissolved organic material, is not modeled.

EPA (1993) developed a $ssBAF_l^t$ and a $ssBAF_l^d$ for lake trout, 2,3,7,8-TCDD, and for Lake Ontario 1987 contamination conditions. The WASP4 model was used to model three hypothetical loading conditions that might have resulted in fish tissue concentrations observed in 1987: steady state loading, a steady state loading followed by a 90% reduction in annual loads for 20 years (i.e., 1968-1987), a steady state loading followed by a 100% reduction (i.e., no loading) for 20 years. The BSAF for lake trout estimated for 1987 data is given in EPA (1990a) as 0.07. The BSAF is determined from measured bottom sediment concentrations and fish tissue concentrations; an assumption of historical loading is not necessary for BSAF development. Details of the Lake Ontario study, including initial modeling efforts with the WASP4 model can be found in EPA (1990a). Slight refinements to the WASP4 runs were later made (cited in EPA, 1993 as an

unpublished report: Endicott, D.D., W.L. Richardson, T.F. Parkerton, and D.M. DiToro. 1990. A steady-state mass balance and bioaccumulation model for toxic chemicals in Lake Ontario: Report to the Lake Ontario Fate of Toxics Committee. U.S. EPA, Environmental Research Laboratory, Duluth, MN: 121 pp). The BAFs determined in these later runs will be tested using the models of this assessment.

In order to do this exercise, all critical model parameters used to develop the BAFs for this WASP4 modeling exercise will be used in the model framework of this assessment. The most critical parameter is the organic carbon partition coefficients, Koc, assumed for 2,3,7,8-TCDD. BAFs were determined assuming Koc of 10^7 and 10^8. Since the models of this assessment assume steady loading into water bodies, only the BAFs developed under "steady state" loading conditions will be used. As noted, the WASP4 model considers binding to more than one suspended compartment. The increased binding can be modeled using a TBF_{oc}, which was assumed to be 1.5 for Lake Ontario by Cook. For the models of this assessment, this factor will be applied to Koc - it effectively increases Koc by 50%. The concentration of suspended solids in Lake Ontario and used in the WASP4 modeling exercise was 1.2 mg/L. The other critical parameters are the fraction organic carbon contents of the suspended solids and the bottom sediments, OC_{ssed} and OC_{sed}, respectively. Assigned values to these parameters, based on Lake Ontario data, in the WASP4 exercise and in this exercise were 0.15 (15%) and 0.03 (3%), respectively.

Since the purpose of this exercise is to evaluate how the modeling approaches of this document perform using the BSAF or the alternate BAF approach, duplicating the source strength terms used in the WASP4 modeling exercise is not necessary. The pertinent question is, with a given source strength, how would both approaches predict fish tissue concentrations. For simplicity, the on-site source category as demonstrated in Chapter 5 will be used. In this scenario, the soil within the watershed is assumed to uniformly be 1.0 ppt, and the loadings are via soil erosion.

In summary, the parameters for this exercise including the steady state BAFs are:
Test 1: Koc = $1.5*10^7$; $ssBAF_l^d$ = $1.9x10^6$; $ssBAF_l^t$ = $5.16x10^5$; BSAF = 0.07
Test 2: Koc = $1.5*10^8$; $ssBAF_l^d$ = $1.9x10^7$; $ssBAF_l^t$ = $6.78x10^5$; BSAF = 0.07
The 1.5 in the Kocs was the TBF_{oc} noted above. The BAFs specific to each Koc were the ones developed also specific to those Koc in the WASP4 modeling exercises. For both

tests: soil concentration of 2,3,7,8-TCDD = 1.0 ng/kg (ppt), total suspended solids (TSS) = 1.2 mg/L, the organic carbon content of suspended sediments (OC_{ssed}) = 0.15, and the organic carbon content of bottom sediments (OC_{sed}) = 0.03. Whole fish tissue concentrations are estimated as $C_{lipid} * f_{lipid}$, where f_{lipid} is 0.07.

The whole fish tissue concentration for the BSAF approach in Test 1 was estimated to be 0.61 ppt. Using the $ssBAF_l^t$ and $ssBAF_l^d$, the whole fish tissue concentrations were estimated very nearly to be the same at 0.867 ppt for $ssBAF_l^t$ and 0.863 ppt for $ssBAF_l^d$. The test results did not change substantially for Test 2. The BSAF approach led to a fish tissue concentration of 0.62 ppt, and the concentration was identical for BAFs at 0.869 ppt.

While it appears that the water column based approaches estimate fish tissue concentrations identical to each other and very close to estimates made based on bottom sediment concentrations, in fact the performance of the models differ when parameters are changed in these tests. More incoming 2,3,7,8-TCDD can be modeled to remain in the water column with an increase in the reservoir of total suspended solids, the TSS parameter initialized in above tests at 1.2 mg/L. Continuing with Test 1 parameters above, increasing TSS from 1.2 mg/L to 10 mg/L has the following changes to fish tissue concentrations: 0.54 ppt for the BSAF test, 4.85 ppt for the $ssBAF_{lt}$ test and 0.76 ppt for the $ssBAF_l^d$ test. Decreasing the organic carbon content of the suspended solids will have the effect of reducing the amount of incoming 2,3,7,8-TCDD simulated to remain in the water column, while increasing the amount modeled to reside in bottom sediments (because a mass balance of 2,3,7,8-TCDD is maintained), and also increases the dissolved phase concentration. Changing the TSS back to 1.2 mg/L and reducing the organic carbon content of suspended solids from 0.15 to 0.05 results in the following changes to fish concentrations: 0.62 ppt for the BSAF test, 0.45 ppt for the $ssBAF_l^t$ test and 0.88 ppt for the $ssBAF_l^d$ test. These two tests have demonstrated the variability in fish tissue concentrations when key water column parameters are altered. Fish concentrations would also differ if the key bottom sediment parameter, the organic carbon content of bottom sediments, was different. Returning to original Test 1 parameters and reducing the organic carbon content of bottom sediments from 0.03 to 0.01 results in the following changes to fish concentrations: 1.73 ppt for the BSAF test, 2.45 ppt for the $ssBAF_l^t$ test and 2.44 ppt for the $ssBAF_l^d$ test.

The predictions for all tests might be considered reasonably close, given the uncertainties in the bioaccumulation and water modeling parameters. The one test described above where the BSAF and BAF approaches led to the most differences was the one which increased suspended material contents from 1.2 mg/L to 10 mg/L. In that case, nearly a ten-fold difference was noted in fish concentrations with the $ssBAF_l^t$ as compared to the BSAF or the $ssBAF_l^d$.

An important consideration in using the water column based approaches is that the BAFs developed by Cook (or that could be developed otherwise) are based on modeled rather than measured water column concentrations, and measured lake trout tissue concentrations. In that sense, the BAFs were calibrated for Lake Ontario conditions and specific to the WASP4 modeling exercise. Therefore, using these BAFs in the modeling framework of this assessment is, strictly speaking, invalid. Further, the values of the BAFs varied depending on the assumptions on historical loadings into Lake Ontario. As noted above, three loading conditions were tested. The steady state BAFs were given above. For the 20 year - 90% reduction tests, the following BAFs were determined: BAF_l^d was 3.03×10^6 for Koc = 10^7 and 2.86×10^7 for Koc = 10^8, and BAF_l^t was 8.26×10^5 for Koc = 10^7 and 1.02×10^6 for Koc = 10^8. For the 20 year - 100% reduction tests, the following BAFs were determined: BAF_l^d was 3.86×10^6 for Koc = 10^7 and 3.40×10^7 for Koc = 10^8, and BAF_l^t was 1.05×10^6 for Koc = 10^7 and 1.21×10^6 for Koc = 10^8. The BSAF developed for lake trout for Lake Ontario was developed using measurements of both fish tissue and bottom sediment concentrations.

Both the BSAF and BAF are most appropriately developed using site specific data (coupled with a modeling exercise for BAF). Inasmuch as that can be impractical or difficult for many sites, efforts are underway to determine the general applicability of BSAFs and BAFs determined for one site to other sites. EPA (1993) proposes that BAF_ls for different congeners can be roughly estimated as the BAF_l for 2,3,7,8-TCDD multiplied by the ratio of the BSAF for the congener and the BSAF for 2,3,7,8-TCDD. Such an estimate will incorporate differences in uptake, metabolism and chemical partitioning but not differences caused by chemical loss processes such as volatilization and photolysis. This approach for estimating BAF_ls for other congeners does allow for some generality since sediment and fish tissue data for other congeners and water bodies is available.

Another bioaccumulation term discussed in one literature article for dioxin is termed

the Regulatory Bioaccumulation Multiplier, or RBM (Sherman, et al., 1992). Multiplication of this term and a "nominal water concentration" estimates a 3% lipid fish concentration. A nominal water concentration equals an amount of a contaminant, 2,3,7,8-TCDD in this application, added or entering a water body over time, divided by a flow volume over that same time. Assuming a fish lipid content of 3%, an RBM of 5000 was recommended based on examination of laboratory flow through data, simulated field data, and actual field data (EPA's Lake Ontario study and data downstream of pulp and paper mills). Dividing the 5000 by 0.03 gives $1.67*10^5$, and this number is now analogous to the $ssBAF_l^t$ developed by EPA (1993) described above, and in the same range as the 5.2-$6.8*10^5$ range for $ssBAF_l^t$.

7.2.4.4. *Other modeling approaches and considerations for air concentrations resulting from soil volatilization*

Volatilization flux was modeled using an approach given in Hwang, et al. (1986), developed for PCB flux from soils. Principal assumptions for their derivation were that contamination extended indefinitely, biodegradation or other degradation processes were not considered, residues were in equilibrium between soil and soil air, and vertical movement was through vapor phase diffusion. Their analytical solution was integrated over time and a solution was presented which gave average unit flux as a function of time during which volatilization occurs. PCBs and other dioxin-like compounds resist degradation, although there is evidence of photodegradation, which may influence surficial residues. These compounds sorb tightly to soil, so that an assumption of vertical movement primarily through vapor phase diffusion (rather than in a soluble phase with leaching, runoff, or evaporating water) is a tenable one. Also, presentation of an average flux rate solution made Hwang's approach amenable to spreadsheet analysis, the computer software tool used in this assessment.

An alternate model for estimating volatilization flux was presented in Jury, et al. (1983). It is a generalized analytical solution which assumes equilibrium between the sorbed, soluble, and vapor phases. It incorporates considerations of steady state water fluxes and degradation mechanisms. A depth over which contamination occurs is specified. A computer code of this model was obtained from the author (William A. Jury, Professor and Chair, Department of Soil and Environmental Sciences, University of

California, Riverside, 92521-0424). Tests were run holding all pertinent quantities the same with both models including initial concentrations, organic carbon partition coefficients, Henry's Constant, molecular diffusivity, fraction organic carbon in soil, soil bulk density, porosity, and an assumption of contaminant non-degradation. All of these parameters, the contaminant as well as the physical parameters, were the ones assumed for 2,3,7,8-TCDD and the surface soils of this assessment. In applying Jury's model, the depth of contamination was assumed to be 10 cm. Also, Jury's model allowed for a selection of water flux to be 0.5 cm/day (heavy leaching), -0.5 cm/day (heavy evapotranspiration), or 0.0 cm/day (no water flux). The latter selection of no water flux was chosen. This model comparison test showed that the Hwang model predicted an average flux over 10 years roughly three times higher than the average flux predicted by the Jury model over the same time period. Running both models over 50 years showed similar results. The average flux over that time dropped by about 50% for both models and there was still a three-fold difference in predicted volatilization fluxes. The exact reason for this three-fold difference was not investigated, and could lie in differences in assumed boundary conditions (Hwang, et al. (1986) discusses differences in boundary conditions between his and Jury's models). In any case, it is judged that both models predict comparable volatilization fluxes. The Hwang model might be considered conservative in that it predicts 3 times higher volatilization flux (with 2,3,7,8-TCDD parameters, etc.).

The Jury model also provides other informative results. It provides a mass balance which, for the 50-year test, showed that only 2.6% percent of the original mass within the 10-cm layer had volatilized. By implication, the Hwang model predicts a 7.3% loss by volatilization over that time period. With the other parameters and assumptions - no degradation and tight sorption to soil - the Jury model showed that 97.4% remained in the profile and that only a minute quantity diffused below 10 cm. Also, the Jury model gives a concentration profile over time. After 50 years, it showed that all volatilization loss was contained within the upper 2 cm of soil profile. This implies that the boundary condition assumption for the Hwang model, that contamination extends indefinitely, is not consequential for the dioxin-like compounds.

A near-field dispersion model is used to estimate air concentrations resulting from soil volatilization, for the on-site source category (where contamination and exposure occur

at the same site). An alternate approach to estimating on-site dispersion given a volatilization flux is the "box-model" approach. This simple approach can be visualized as follows: air above soil is contained within a structure which has two walls, say a north and south wall, and a ceiling - wind blows through the building in an east-west direction mixing the volatilized flux. This is expressed mathematically as:

$$C_{va} = \frac{FLUX\ AREA\ 10^6}{b\ U_{mix}\ Z} \qquad (7-4)$$

where:

C_{va} = vapor-phase concentration of contaminant in air, $\mu g/m^3$

FLUX = average volatilization flux rate of contaminant from soil, g/cm^2-sec

AREA = area over which flux occurs, cm^2

b = side length perpendicular to wind direction, m

U_{mix} = mean annual wind speed corresponding to mixing zone height, m/sec; estimated as 1/2*Um, where Um is average wind speed

z = mixing zone height, m

10^6 = converts g to μg

Before testing the box-model equation, results for the approach used in this assessment are summarized. The key factors impacting air concentration calculations in Scenarios 1 and 2 is the duration of exposure and area over which contamination occurs. In the central scenario, Scenario 1, the area was 4,000 m^2 (1 acre) and in the high end scenario, Scenario 3, the area was 40,000 m^2 (10 acres). The exposure duration was 9 years in Scenario 1 and 20 years in Scenario 2. The volatilization flux was different for both scenarios, but not because of area considerations, but because of exposure duration assumptions; the average flux of 2,3,7,8-TCDD for the high end scenario was 1.1×10^{-21} g/cm^2-sec, whereas the average flux for the central scenario was 1.7×10^{-21} g/cm^2-sec. The air concentration estimated for both the central and high end scenario was the same at 4.4×10^{-11} $\mu g/m^3$. Larger areas tend to increase air concentration prediction; the larger area of the high end scenario countered the effect of having a lower average volatilization flux; hence similar air concentrations were predicted for the central and high end

scenarios.

The values used to evaluate the box model approach were the fluxes, as given above, the mixing zone wind speed, 2 m/sec, which is half the average wind speed assumed in this assessment, the areas noted above, the side length, estimated as the square root of the area, and a mixing zone height estimated initially at 2 m. The box-model air concentration for the central scenario with these parameters is 2.7×10^{-10} $\mu g/m^3$. This is 6 times higher than the concentrations predicted in this assessment. The box-model concentration estimation for the high end scenario, given slightly lower flux as noted above and the larger land area, was 5.5×10^{-10} $\mu g/m^3$, which is over an order of magnitude higher than the concentration estimated for this assessment.

These box-model estimations are higher than the ones made for this assessment. An uncertain parameter for both modeling approaches is the area of soil contamination. The mixing zone height for the box model is also a parameter of uncertainty. Users of the box model approach have often assumed a conservative 2 m height approximating the height of exposed individuals. However, others have claimed this is far too low a mixing height, suggesting 10 meters or even an atmospheric height closer to 100 meters. Higher mixing zone heights would have brought the box model estimations more in line with estimations made in this assessment. The closest analogous parameter in the dispersion model to the mixing zone height is the height of exposed individual, which is more unambiguously the breathing zone height of 2 m.

One key assumption concerning the exposure site air concentrations resulting from an off-site area of soil contamination should be questioned. The current approach assumes that air-borne contaminates originate at the site of contamination and are transported to the site of exposure. On the other hand, this assessment also assumes that exposure site soil becomes contaminated over time due to erosion. Also, some of the example scenarios have tested the impact of very low, perhaps "background", levels of dioxin-like compounds, which would occur surrounding a site of exposure. It is at least plausible that volatilization from soils other than the area of elevated contamination would contribute to air-borne contamination, and concentrations to which individuals are exposed to at sites of exposure near sites of contamination.

This was tested by using the on-site algorithms and developing soil concentrations for these algorithms based on soil concentrations predicted to occur in the off-site

scenario. Specifically, the off-site demonstration scenarios included a 10 ha field at 1 ppb 150 m from the exposure site, also at 10 ha. The soil concentrations estimated to occur at the exposure site were 0.28 ppb for a 5-cm no-till depth and 0.08 ppb for a 20 cm tilled depth. The on-site algorithms for volatilization and dispersion were run starting with these concentrations, and resulting concentrations were compared with those estimated to occur only from volatilization from the contaminated site and transport to the exposure site. The air concentration estimated to occur from untilled soil is 2.5 times higher than that estimated to occur from the off-site area and transported; the air concentration estimated to occur from tilled soil is 25% less than estimated to occur from volatilization and transport.

This might imply that exposure site air concentrations are being underestimated if air concentrations at the site of exposure are assumed to only originate at the site of contamination, and not also at the site of exposure, or even from other areas. Lower estimated air concentrations also would result in lower estimates of impact to above ground vegetations, including fruits and vegetables for consumption, and grass and cattle feed, whose concentrations partially determine beef and milk concentrations. This exercise implies that the underestimation might be less than a factor of 5.0. Of course, this conclusion is contingent on the off-site impact algorithms which have estimated that a 0.28 or a 0.08 ppb soil concentration will result 150 meters from an area whose concentration is 1.00 ppb.

7.2.4.5. *Alternate models for estimating plant concentrations from soil concentrations*

The models of this assessment separate above and below ground vegetations for estimating concentrations. Root concentrations, which in this assessment translates to below ground vegetations, are a function of soil water concentrations and a Root Concentration Factor, RCF. Above ground vegetations, which in this assessment include above ground fruits and vegetables, pasture grass, and cattle feed, are modeled as a function of vapor phase transfers and wet plus dry particle depositions. This section examines one alternate approach for above ground vegetations; alternate approaches for below ground vegetations could not be found.

One approach to modeling plant concentrations would be with passive uptake via

evapotranspiration. The assumption here is that soluble phase contaminants move passively with transpiring water. This approach has been applied for contaminants which are soluble in water. However, nearly all the evidence suggests that this would not be appropriate for the dioxin-like compounds. Specifically, the evidence suggests that residues do not translocate to within portions of either above or below ground vegetations. Such would be case for soluble contaminants moving passively with transpiring water. This conventional wisdom was, however, challenged with a recent experiment by Hulster and Marschner (1993b) on vegetations of the cucumber family. Their results were most striking for zucchini, which showed uniform plant concentrations from inner to outer portions of the zucchini fruit, and the highest whole fruit concentrations they had ever measured, despite careful experimental conditions which physically isolated the fruit from the soil. Pumpkins also showed high plant contamination, with more expected plant concentrations measured for the cucumber. Assuming the vegetations of this assessment - fruit/vegetables for human consumption and vegetations of the beef/dairy food chain - do not behave as in Hulster and Marschner's (1993b) experiment, than translocation to inner plant parts is not expected.

The specific issue of uptake and translocation via transpiration was investigated using soybean and corn plants grown hydroponically in carefully constructed growth chambers (McCrady, et al., 1990). Roots and the hydroponic growth solution were separated from the shoots and leaves of these plants using two separate chambers, one inverted over the other. Separate air-flow systems for each chamber included traps for volatile organics. Mass balance on the tritiated TCDD experiments was able to recover 98% in the soybean experiment and 86% for the corn experiment. Most of the recovered material was found in the roots; 75% for soybeans and 67% for corn, with the second highest recovery was on the inside surface of the root chamber, around 15% for both experiments. Recovered TCDD was also found, in order of decreasing percentage, in the growth solution, root chamber air, shoot chamber air, and shoots. The recovery from the shoots was negligible at 0.004% and 0.001% of the total TCDD for the soybean and corn, respectively. McCrady, et al. (1990) concluded that transpiration stream transport of 2,3,7,8-TCDD to plant shoots is an insignificant mechanism of plant contamination, and that volatilization of TCDD is an important transport mechanism that can result in significant quantities of airborne TCDD being absorbed by plant shoots.

Briggs, et al. (1982) provide another way to evaluate the translocation of contaminants from roots to above ground vegetation. Experiments with barley roots in growth solution led to the development of an empirical parameter describing the efficiency of transport of organic chemicals to plant shoots from root uptake. This parameter is called the Transpiration Stream Concentration Factor (TSCF) and is defined as (concentration in transpiration stream)/(concentration in external solution). The empirical formula presented for this factor is:

$$TSCF = 0.784\ e^{-[\log Kow - 1.78]^2 / 2.44} \qquad (7\text{-}5)$$

Given a log Kow for 2,3,7,8-TCDD of 6.64, TSCF is solved for as roughly $5 * 10^{-5}$. Assuming that the concentration of external solution concentration for the experimental conditions of Briggs' experiments is equivalent to the concentration in soil water in a field situation, then the TSCF for 2,3,7,8-TCDD implies that the transpiration stream water of a plant is over 5 orders of magnitude lower than the soil water concentration. Like McCrady's experiments, this also shows the insignificance of translocation of residues from roots to shoots.

The one approach that was found that might have been used in the place of the algorithms for above ground vegetation, is simpler and more general in nature. It was developed from field data on above ground vegetation concentrations correlated to soil concentrations of contaminants and the octanol water partition coefficient (Travis and Arms, 1988). This correlation led to an empirical bioconcentration factor for vegetation, B_v, regressed against the contaminant log Kow, and defined by the authors as the concentration in above ground plant parts divided by the concentration in soil:

$$\log B_v = 1.588 - 0.578 \log K_{ow} \quad n = 29,\ r = 0.73 \qquad (7\text{-}6)$$

With 2,3,7,8-TCDD log Kow equal to 6.64, the B_v translates to a value of 0.0056. Note that this B_v is defined identically to the plant:soil contaminant concentration ratios that were discussed in Section 7.2.3.8 which compared the model's estimations of these

ratios with those found under experimental. As discussed in that section, contaminant concentration ratios were estimated for the two scenarios demonstrating the on-site source category in Chapter 5, Scenarios 1 and 2: above ground vegetables/fruit - $7*10^{-5}$, grass - $6*10^{-3}$, and feed - $3*10^{-3}$. It is not clear how to compare the B_v of 0.0056 to these ratios without retrieving the studies which Travis and Arms (1988) used, although this value is clearly higher than the fruit/vegetable ratio and consistent with the grass/feed ratio estimated for Scenarios 1 and 2. The studies used by Travis and Arms were not retrieved. An examination of the chemicals used by Travis and Arms show that 25 of 29 used are pesticides, which suggests that plant concentrations may be those of agricultural crops. If so, a comparison of the above-ground $1*10^{-5}$ ratio with this 0.0056 ratio would be appropriate. An examination of the chemicals also reveals that 10 of the 29 are moderately to very soluble (log Kow less than 4.00), while others are similarly insoluble as the dioxin-like compounds (including DDT, TCDD, Aroclor 1254, and others; 15 with log Kow greater than 5.0). Developing such an empirical relationship which mixes chemicals whose mode of action is passively with water (which would be the case with aldicarb and simazine, among others on the list) with those whose mode is through vapor transfers or particle depositions (TCDD, and so on) does not appear to be technically valid. Nonetheless, the fact that the Travis and Arms B_v is much higher than the plant:soil ratio generated for the on-site soil contamination source category demonstration is noteworthy. First, it was noted in Section 7.2.3.8 that the plant:soil ratios generated by the models were lower than had been measured in the literature, and this is an additional piece of evidence in that direction. Second, other evidence in this assessment suggests that the air concentrations resulting from soil contamination may be underestimated by over an order of magnitude. This was discussed in Section 7.2.3.7 above.

7.2.4.6. Alternate modeling approaches for estimating beef and milk concentrations

Webster and Connett (1990) compared five models which estimated the 2,3,7,8-TCDD content of cow's milk from 2,3,7,8-TCDD air contamination. The five models were described in Michaels (1989), Connett and Webster (1987), Stevens and Gerbec (1988), Travis and Hattemer-Frey (1987), and McKone and Ryan (1989). Ironically, a sixth model by Fries and Paustenbach (1990), noted by Webster and Connett as available but received

too late for inclusion in their article, formed the basis for the approach taken in this assessment.

All five models compared by Webster and Connett have the same basic framework. Particulate-bound 2,3,7,8-TCDD deposits onto the ground and vegetation (cattle feed and pasture grass). Algorithms to estimate resulting vegetation and soil concentrations in these models are the same ones used in this approach, although parameter assignments are different. A daily dosage of 2,3,7,8-TCDD to the cattle is calculated and converted to a concentration in whole milk using a "biotransfer factor". This same structure was used to estimate concentrations in beef, using a beef biotransfer factor different than the milk biotransfer factor. Mathematically, this is expressed as:

$$C_{m,b} = F_{m,b} \; Dose \qquad (7-7)$$

where:

$C_{m,b}$ = concentration in whole milk/beef, mg/kg

$F_{m,b}$ = milk/beef biotransfer factor, day/kg

= $(BCF_{mf,bf} * f_{m,b})/Q$

$BCF_{mf,bf}$ = experimentally-derived unitless bioconcentration factor defined as the concentration in milk fat/beef fat divided by the concentration in the experimental vehicle (cattle feed, e.g.); similar to BCF of this assessment

$f_{m,b}$ = fat content of milk/beef, unitless

Q = daily mass intake of cattle in experiment, kg

Dose = total daily dose of 2,3,7,8-TCDD, mg/day

= $\Sigma (a_j * c_j * Q_j)$

a_j = relative bioavailability on intake vehicle j (soil, air, vegetation, etc)

c_j = concentration of 2,3,7,8-TCDD in vehicle j, mg/kg (or equivalent units)

Q_j = mass of vehicle j intake, kg (or equivalent units)

Further details on the models can be found in their primary references and in Webster and Connett's comparison. Some highlights, including comparisons of the five approaches to

the approach taken in this assessment, are:

1) Two of the approaches, that of Stevens and Gerbec (1988), and McKone and Ryan (1989), consider inhalation of contaminated air by cattle to contribute to their daily dose of 2,3,7,8-TCDD. One of the approaches, that of Travis and Hattemer-Frey (1987), considers ingestion of contaminated water by cattle. A later assessment by Travis and Hattemer-Frey (1991) has all the components of their earlier assessment, and adds cattle inhalation exposures. This assessment does not consider cattle inhalation of contaminated air nor ingestion of contaminated water in estimating beef and milk concentrations. However, these intakes were shown to be insignificant when estimated by these researchers. Stevens and Gerbec estimate inhalation contributions to be less than 0.05% (0.0005 in fractional terms) of total daily dose, or an essentially insignificant amount. Travis and Hattemer-Frey (1991) estimate inhalation to contribute between 0.3 and 1.0% to milk and beef concentrations, respectively. McKone and Ryan (1989) did not provide sufficient information to easily determine the relative contribution of inhalation on estimation of cattle beef and milk concentrations by their estimations. Travis and Hattemer-Frey (1987, 1991) estimate water contributions to be less than 0.01% (0.0001) of total daily cattle dose of 2,3,7,8-TCDD.

2) None of the approaches considered vapor phase transfers from air to plant, although Webster and Connett recommended its inclusion in their article. The later assessment by Travis and Hattemer-Frey (1991) on 2,3,7,8-TCDD did include vapor phase transfers into vegetation consumed by cattle. According to results of the example scenarios in this assessment, these transfers appear to be particularly critical, and this was also the conclusion of Travis and Hattemer-Frey based on their modeling results.

3) Two of the assessments, that of Stevens and Gerbec (1988) and Fries and Paustenbach (1990) considered a period of residue-free grain only diet for a period of time before slaughter for purposes of fattening the cattle. Stevens and Gerbec (1988) assumed that the residues in cattle would depurate during the last 130 days of their lives on this regime. Assuming a half-life of 2,3,7,8-TCDD in cattle of 115 days, they showed a 54% reduction in beef concentrations due to this practice. Fries and Paustenbach (1990) note that cattle can gain as much as 60-70% in body weight, so dilution can also result in lower beef concentrations at slaughter. Procedures are not described in this assessment to estimate the reduction of concentrations in beef and milk fat due to depuration or

dilution periods. However, the modeling result that residue concentrations in the beef are reduced by about 50% was used in the air-to-beef model validation exercise that was described in Section 7.2.3.9. The procedures to estimate a reduction in concentration used by these researchers is straightforward. Assuming first order kinetics sufficiently describes reduction in concentrations during a period prior to slaughter, the fractional reduction during such a period is given as, $1 - \exp(-k_d t)$, where k_d is the depuration rate constant, in $days^{-1}$, and t is the depuration period, in days. The rate constant can be estimated from the depuration half-life, HL, as 0.693/HL. The 115 day half-life assumed by Stevens and Gerbec (1988) corresponds to a rate constant of 0.006 day^{-1}, and assuming a 130 day depuration period, the fractional reduction is easily calculated as 0.54 (i.e., $1 - \exp(-k_d t)$). The amount remaining after 130 days is estimated as the initial amount multiplied by 0.46 (i.e., $\exp(-k_d t)$).

4) Two of the assessments did not assume any cattle ingestion of contaminated soil, and two of the assessments estimated the contribution to milk concentrations due to ingestion of contaminated soil was minor at 1 and 2%. Only one of the assessments, Travis and Hattemer-Frey (1987), estimated any significant impact due to soil ingestion, attributing 19% of the concentration due to ingestion of contaminated soil. Their later assessment (Travis and Hattemer-Frey (1991)) estimated soil to contribute 29 and 20% of beef and milk concentration estimations, respectively. They estimated this high a contribution by contaminated soil even though they assumed that contaminated soil comprised 1% of the total dry matter intake by cattle. Fries and Paustenbach (1990) recognized the importance of cattle soil ingestion, evaluating scenarios where cattle soil ingestion ranged from 1 to 8% of total cattle dry matter intake.

The example scenarios in Chapter 5 assumed that beef cattle ingestion of contaminated soil was 4% of their total dry matter intake, and 2% of a dairy cattle's intake was contaminated soil. The percentage of beef and milk concentrations of 2,3,7,8-TCDD attributed to soil, feed, and pasture grass, when soil contamination is the source and when stack emissions are the source, was examined in Section 6.3.3.13 in Chapter 6. It is noted there that soil ingestion appears significantly more critical for soil contamination as compared to stack emissions. Soil ingestion by beef and dairy cattle explain around 90% of final beef and milk concentration for soil sources. On the other hand, soil ingestion explained only around 5% of final beef and milk concentration for the stack

emission source.

The earlier literature noting only 1-2% impact by soil ingestion were more analogous to the stack emission source category than the soil source category, in that impacts were estimated starting from air-borne contaminants depositing onto soils and vegetations. One difference in the assessments estimating the 1-2% impact with this assessment indicating about 5% impact was that the other assessments assumed less soil ingestion, 0.5% in Stevens and Gerbec (1988) and 1-3% in Travis and Hattemer-Frey (1987) and McKone and Ryan (1989).

The critical focus of the Webster and Connett (1990) comparison, is the milk fat bioconcentration factor, BCF_{mf}. As shown in Equation (7-7), the biotransfer factor, F_m, is estimated using experimental data which yields a milk fat bioconcentration factor, BCF_{mf}. Experiments most relied upon by these modelers are those described in Jensen, et al. (1981), and Jensen and Hummel (1982). A key difference in the early modeling approaches is the interpretation of these two and other studies and the resulting assignment of BCF_{mf}, with values ranging from 5 to 25. Webster and Connett (1990) discuss issues of experimental interpretation.

Parameter assignments and assumptions (cattle soil ingestion versus no ingestion, etc.) obviously all impact estimations and can be a critical source of variation and uncertainty in estimates of beef and milk concentrations. The uncertainty associated with the modeling framework described above was explored by McKone and Ryan (1989) using Monte Carlo techniques. They found that the 90% confidence range for human exposure to 2,3,7,8-TCDD, where the source was air contamination and the human exposure route was through milk, spanned two to three orders of magnitude.

The approach taken by all five researchers centers on the milk biotransfer factor, abbreviated F_m in Webster and Connett (1990) and in units of day/kg. Beef bioaccumulation was modeled in the same way using a beef biotransfer factor, F_b. Travis and Arms (1988) developed this concept to the fullest, taking several data sets from the literature on a variety of contaminants and animals, to derive empirical formulas for F_b and F_m, which they termed B_b and B_m, as a function of contaminant octanol water partition coefficient, Kow:

$$\log B_b = \log Kow - 7.6 \quad (7\text{-}8a)$$

$$\log B_m = \log Kow - 8.1 \quad (7\text{-}8b)$$

Given a log Kow of 6.64 for 2,3,7,8-TCDD (assumed in this assessment), B_b is solved for as 0.110 and B_m is solved for as 0.034. Travis and Hattemer-Frey (1991) used 0.80 and 0.03 for 2,3,7,8-TCDD B_b and B_m.

Simple transformations can show how the earlier approaches, summarized above in Equation (7-7), and the approach of Fries and Paustenbach (1990), the one used in this assessment, are the same. First, the concentration of dioxin-like compounds in the fat of beef and milk is given in this assessment by (also see Chapter 4):

$$C_{fat} = BCF\ DF_s\ B_s\ AC_s + BCF\ DF_g\ AC_g + BCF\ DF_f\ AC_f \quad (7\text{-}9)$$

where:

C_{fat} = concentration in beef fat or milk fat, mg/kg

BCF = bioconcentration ratio of contaminant as determined from cattle vegetative intake (pasture grass or feed), unitless

DF_s = fraction of cattle diet that is soil, unitless

B_s = bioavailability of contaminant on the soil vehicle relative to the vegetative vehicle, unitless

AC_s = average contaminant soil concentration, mg/kg

DF_g = fraction of cattle diet that is pasture grass, unitless

AC_g = average concentration of contaminant on pasture grass, mg/kg

DF_f = fraction of cattle diet that is feed, unitless

AC_f = average concentration of contaminant in feed, mg/kg.

Transformation steps are: 1) factor out the BCF from Equation (7-9) , 2) multiply Equation (7-9) by unity expressed as Q/Q, where Q equals total dry matter intake by cattle; 3) the multiplication of Q by the diet fraction terms, DF_s, DF_g, and DF_f, gives the values for soil dry matter intake, Q_s, grass - Q_g, and feed - Q_f, 4) with BCF factored out, and Q*DFs

replaced by Q_s, etc., the parenthetical now reads, (Qs*Bs*ACs + Qg*ACg + Qf*ACf) - this is the "Dose" term defined earlier in Equation (7-7), 5) finally, multiply the right hand side of Equation (7-9) by fat content, say f_m for milk, which would transform the right and hence left hand side of that equation to whole product concentration. Transformed Equation (7-9) is analogous to Equation (7-7):

$$C = \frac{BCF\ f_m}{Q} \left[Q_s\ B_s\ AC_s + Q_g\ AC_g + Q_f\ AC_f \right] \qquad (7\text{-}10)$$

One critical theoretical assumption not explored in the earlier literature is whether 2,3,7,8-TCDD bioaccumulates equally in beef fat and milk fat - are the BCF_m and BCF_{bf} equal? Fries and Paustenbach (1990) emphasize that differences in observed concentrations in beef and milk are critically a function of the differences in the diets of cattle raised for beef versus those raised for milk. They assumed that the beef and milk bioconcentration factor was equal for their example calculations. The key difference Fries and Paustenbach cite is the tendency for beef cattle to graze while lactating cattle are more often barn fed. Grazing cattle intake more contaminated soil than barn fed cattle. Fries and Paustenbach derived F for higher chlorinated dioxin-like compounds from experimental data, noting that the F value is less with higher chlorination. Webster and Connett (1990) made the analogous observation, saying that 2,3,7,8-TCDD equivalents transferred from air to milk less efficiently than 2,3,7,8-TCDD. This is also consistent with the data of McLachlan, et al (1990), which is used in this assessment for assignment of BCFs to dioxin-like compounds.

Some conclusions from this analysis of earlier efforts for estimating bioconcentration in beef and milk are:

- Although the framework of the earlier approaches looks different than the framework used in this assessment, they are actually the same with a simple mathematical transformation;
- The possible dosage to cattle of 2,3,7,8-TCDD via contaminated air or water was considered in earlier assessments, but was not found to be a significant

pathway, and was not considered in this assessment;

- Earlier assessments did not consider vapor phase transfers to vegetation consumed by cattle; the results of the demonstration scenarios suggest that this transfer is particularly critical;
- Even though the structure of the analysis has been consistent from the earlier to the current approaches, different assumptions on parameter values greatly impacts modeling results. The critical bioconcentration factor, earlier termed BCF_m (for milk) and termed simply BCF in this assessment, has been estimated to be between 5 and 25 for 2,3,7,8-TCDD in different assessments. This assessment uses a BCF value of 4.3 for 2,3,7,8-TCDD. Using Monte Carlo techniques on this model structure for estimating human exposure to milk resulting from air contamination of 2,3,7,8-TCDD, McKone and Ryan (1989) showed a 90% confidence interval spanning 2 to 3 orders of magnitude.

7.3. UNCERTAINTIES ASSOCIATED WITH EXPOSURE PATHWAYS

The purpose of this section is to qualitatively describe the uncertainties associated with exposure estimates for the exposure pathways that are included in this methodology. The principal focus is on the exposure parameters - the contact rates and fractions, exposure durations, and so on. A brief summary is also presented on some of the findings pertaining to the fate, transport, and transfer algorithms used to estimate the exposure media concentrations. This summary will highlight findings that have been included in other sections of this chapter as well as a section in Chapter 6 on User Considerations. Sections 7.2.3 and 7.2.4 above make comparisons between estimated exposure media concentrations and observed concentrations, and discuss alternate models to use for estimation of exposure media concentrations, respectively. Section 6.3 of Chapter 6 discusses the sensitivity of model estimations of exposure media concentrations with changes in required model parameters. Each section below includes a table summarizing key points of uncertainty. Section 7.3.1 looks at three key exposure parameters which are common among all pathways - lifetime, body weights, and exposure durations. Sections 7.3.2. to 7.3.11 are pathway-by-pathway discussions.

7.3.1. Lifetime, Body Weights, and Exposure Durations

As discussed in EPA (1989), values for lifetime of 70 years and adult body weight of 70 kg are derived from large national studies and are not expected to introduce significant uncertainty into exposure estimates. The assumed child body weight of 17 kg (for ages 2-6) is similarly well founded and not expected to introduce much uncertainty into soil ingestion exposure estimates.

Assumptions on exposure durations are the most uncertain of the three parameters discussed here. A value of 9 years assumed for central exposure scenarios was an average derived from census survey data (EPA, 1989) which only asked of respondents the amount of time they lived in their current residences. It is likely to therefore be an underestimate as an average amount of time spent in one residence (i.e., respondents are expected to continue to live at their residence). The estimate of 20 years for the average residence time of farming families (used to define high end exposure scenarios) was not based on data but rather on judgement that farming families live at their farm site longer than non-farming families.

Exposure durations are also tied to assumptions about source strength over time. Assuming 20 years of exposure to stack emissions, for example, assumes that the source of stack emissions will be (or has been) in operation for this length of time with the same stack emission controls in place. The same is noted for the effluent discharge source category. If the source is contaminated soil, assumptions include whether or not the soil will be removed, the site will be capped, and so on. Another consideration is the dissipation of soil residues. Section 7.2.1. discussed uncertainties with the assumption of non-degradation of dioxin-like compounds in soil when the soil itself is contaminated. A ten-year dissipation half-life is assumed for circumstances where residues migrate to an exposure site to impact only a thin layer of surface soil. This is relevant for the erosion from an off-site soil contamination site to an exposure site and the deposition of residues emitted from a stack. An assumption of non-degradation is appropriate given: 1) evidence that suggests little if any degradation of 2,3,7,8-TCDD (and by extrapolation, other dioxin-like compounds) except via photolysis, which would not impact residues below the soil surface, 2) a mass balance exercise conducted in Section 6.4., Chapter 6, which evaluated the possibility that routes of dissipation considered would deplete an available reservoir of 2,3,7,8-TCDD prior to or near an assumed duration, showed that it would take 90 years to

deplete a reservoir of 2,3,7,8-TCDD extending only 6 inches into the soil, and 3) simply that the fate, transport, and transfer algorithms of this assessment have been characterized as screening level in their theoretical sophistication although site specific in their application. In site specific assessments, which are either based on past or projected exposures, more precise statements to address the strength of the contamination source over time should be considered.

Exposure estimates are linearly related to all three exposure parameters - increasing body weight and lifetime decreases exposures in an inverse linear fashion, while increasing exposure durations increase estimates in a direct linear fashion.

Uncertainties associated with body weight, lifetime, and exposure durations are summarized in Table 7-13.

7.3.2. Soil Ingestion Exposure

This exposure is directly a function of the concentration of contaminants in surface soil layers. For example Scenarios 1 and 2, demonstrating the on-site soil source category, soil at the site of exposure was contaminated to a specified level. For example Scenario 3, demonstrating the off-site source categories, erosion onto the site of exposure deposited residues into a thin, no-till, surface layer of 5 cm, and a thicker, 20-cm, till layer of soil. Soil ingestion exposures were based on concentrations in the 5-cm layer. In Scenarios 4 and 5 demonstrating the stack emission source category, contaminated particles deposited onto the exposure site, also creating a till and a no-till concentration. The no-till depth for this category was 1 cm instead of 5 cm, based on hypothesized differences in fate of contaminated particles when they were transported as eroded soil versus particle deposition from the air.

Discussions on the methodology to estimate exposure site soil concentrations resulting from erosion of contaminated soil from a nearby site are contained in Section 6.3.2, Chapter 6, which was on sensitivity analysis and the impact of different parameter values on estimated exposure site soil concentrations, and in Section 7.2.3.1. above discussing literature reports of off-site impacts from soil contamination. While off-site impacts were noted in the literature, no data could be found that was directly amenable to comparison with the scenarios of Chapter 5. The closest site for which data was available was the Dow Site in Midland, Michigan. The ratio of soil concentrations of 2,3,7,8-TCDD

Table 7-13. Uncertainties associated with the lifetime, body weight, and exposure duration parameters.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Lifetime	70 yrs	Standard EPA assumption and based on data	Actuary data indicate that lifetime may may be increasing	Not a major source of uncertainty
Body Weight	70 kg adult	Standard EPA assumption and based on data	Not much uncertainty	Not a major source of uncertainty
Exposure duration	9 & 20 yrs	Based on assumptions for central and high end exposure scenarios. 9 years based on data for time spent in one residence; rural farming families assumed to live in one location longer than non-farming families in rural settings	Can vary for populations in rural settings; also important to consider how long exposure has been occurring for retrospective site-specific assessments or how long exposure may occur for prospective assessments. Source strength dissipation not a consideration for effluent discharge or stack emission sources assuming emissions occur unabated over duration; data and mass balances exercises indicate soil concentrations remain constant for a 9-20 year time frame.	Assuming non-farming families are more transient than farming families is probably reasonable, although data is unavailable to verify that assumption. Considering exposure durations to be in the range of 10-20 yrs rather than 70 years is felt to be more appropriate. Consideration should be given to source strength dissipation over time.

Overall: Of these three parameters, the exposure duration is the most uncertain. The estimates of 9 and 20 years were made in this assessment for non-farming residents in rural settings, and farming residents in rural settings. These values were based on assumptions of time living at one residence. A critical assumption of a constant soil concentration for contaminated soil sites should be carefully considered for site-specific assessments. Data on degradation indicates very slow rates of degradation, and only photolysis as a possible degradation mechanism, which would not impact residues below the surface. Dissipation other than degradation should be considered, but a mass balance exercise indicates that it would take 90 years to dissipate a reservoir of contaminants extending 6 inches into the soil.

in areas described as "background" in the 600 ha site to soil concentrations in the contaminated areas was 1/8 to 1/2 as much (depending on how the contaminated area soil concentration was interpreted) as the ratio modeled in the off-site demonstration scenario. This might imply that the model overpredicts off-site soil impacts, except that the "background" areas in the Dow Site appear substantially further away than the 150 meters in the off-site demonstration scenario. Also, data was unavailable to determine the

erodibility of soil at the Dow Site, which along with other site-specific information, may have allowed for a more precise test of the algorithms of this assessment. Still, a key finding in the sensitivity analysis exercises was that the erosion algorithms may be overestimating off-site impacts. If so, the overestimation is most likely the result of assuming an "enrichment ratio" of 3 for soil erosion (the concentration on eroded soil divided by the concentration of in-situ soil). No information is available on estimating how much of an overestimation may have resulted, and this finding is not a definite conclusion. If the algorithm overestimated the impact from soil erosion, it is unlikely that overestimation exceeded the factor of 3 attributed to the enrichment ratio. Other sensitivity analyses exercises indicated that different parameters values for individual parameters result in roughly an order of magnitude difference in soil concentration estimation around the concentration which was estimated using all parameters assumed for the demonstration scenarios in Chapter 5.

In addition to the enrichment ratio, the depth of mixing is an uncertain parameter. This is a theoretical parameter for which little data is available. Others have also assumed depths of mixing of 1 cm for analogous applications. Evidence from radioactive fallout suggests depths no deeper than 5 cm. Sensitivity analysis on the erosion algorithms showed that assuming a depth of 1 cm instead of 5 cm would have increased soil concentrations by a factor of 2.5, while decreasing the mixing depth to 10 cm decreases soil concentrations by 60%.

No information could be found in the literature which could be used to evaluate the algorithm for soil concentrations resulting from particulate depositions from stack emissions as modeled by the COMPDEP model. However, evaluation of the air-to-soil algorithm of the stack emission source category suggests that the model may be underpredicting soil concentrations, possibly by about an order of magnitude. Soil concentrations are, of course, not an issue for the on-site soil source category, where that concentration is a principal input and not an estimated value.

Another issue is whether children should be assumed to be exposed to tilled soils, tilled by home gardening, farming, etc., or untilled soils. It is feasible that children would be exposed to tilled soils in farming or home garden settings. If the soil was impacted by stack emission depositions or erosion from a nearby site of soil contamination, then tilling would reduce soil concentrations. However, it is more reasonable to assume that they

generally play outside in areas that are not mechanically tilled.

The estimated soil ingestion quantity is based on field measurements, using trace elements, of soil ingested by relatively small groups of children over brief periods. Methodological issues in these studies remain to be addressed. In particular, ingestion estimates may have been lower if dietary intake of the trace elements was taken into account. Research is underway to refine soil ingestion estimates obtained through trace element measurements. Given the available data, 0.2 g/day is used as a typical value for soil ingestion in young children. Due to the behavior known as pica, some children are known to be high ingesters of various non-food materials. Estimates of pica ingestion of soil by children have ranged as high as 5 g/day. Although no quantitative data on soil ingestion are available for children known to exhibit pica, the use of the high-end estimate of 0.8 g/day may better reflect such behavior.

Soil ingestion exposure estimates also depend on the duration of the period over which children are assumed to ingest soil. Data on soil ingestion by age are not available, and the estimate that significant ingestion occurs between ages 2 and 6 is broadly supportable on behavioral grounds.

No measurement data are available on soil ingestion in infants (0-2 yrs. old) or in older children or adults, and no ingestion is assumed for these groups. While some soil ingestion will occur in these groups, e.g., through contact of soiled hands with food, it is plausible that such ingestion is of a lesser degree than occurs in early childhood. If Hawley's (1985) estimate that an adult ingests an average 0.060 g/d of soil is used, after accounting for differences in exposure duration (9-20 yrs versus 5 yr) and body weight (70 kg versus 17 kg), the adult soil ingestion exposure is close to the estimated exposure for children (at 0.2 g/d). The high end example scenarios in Chapter 9 assumed that the exposed family was involved in farming operations. One implication is that individuals on the farm would be working closely with the soil, which may result in some soil or dust ingestion (dust ingestion is distinct from the particulate inhalation exposure pathway). The other implication is that, should this be the case, they would be in contact with tilled soil, whose concentration is 20 times less than the no-till soil for which children are assumed to be exposed.

Considering these uncertainties, the soil ingestion exposure estimates presented for children are plausible. Further consideration may be warranted for considering adult soil

ingestion, particularly in farming situations. Uncertainties associated with the soil ingestion pathway are summarized in Table 7-14.

7.3.3. Soil Dermal Contact Pathway

Estimates of dermal exposure to soil rely largely on four factors unique to this pathway: exposed skin area, soil adherence, frequency of soil contact and fraction of contaminant absorbed. The uncertainty in these three terms are discussed below.

Before that discussion, a brief note is made on uncertainties associated with soil concentrations. Discussions above on the soil ingestion pathway addressed uncertainties associated with soil concentrations which result from migration of residues from a distant source to the site of exposure. Distant sources in this assessment include off-site soil contamination and stack emissions. Discussions in the soil ingestion pathway section above pertain to this exposure pathway and are not repeated here. However, there is one key difference in the soil dermal and soil ingestion pathways. Soil ingestion exposures are assumed to occur only from surficial soil layers and from untilled soils, which translates to the 5-cm (soil contamination source categories) and 1-cm (stack emission source category) mixing depth for both the "central" (residential) and "high end" (farming properties) scenarios. Soil dermal contact for the high end scenario assumes many dermal contact events, 350 per year, that is based on farming activities; the soil concentrations pertinent for this behavior, therefore, are tilled soil concentrations. On the other hand, only 40 dermal contact events per year, which may correspond to some gardening or other contact, is assumed for the central scenario. The soil concentration used in these scenarios is the untilled soil concentrations.

The uncertainty in the assumed value for exposed skin area reflects primarily population variability. As reported in EPA (1992a), relatively accurate measurements have yielded a good data base on total skin area. Thus the uncertainty in this factor is derived more from the assumptions of how much of the total skin area is exposed. EPA (1992a) recommends approaching this issue by determining the coverage of normal apparel in the exposed population and assuming exposure is limited to the uncovered skin. As discussed in EPA (1992a), this assumption could lead to underestimates of exposure since studies have shown that some exposure can occur under clothing, especially in the case of vapors or fine particulates. A default assumption of 25% uncovered is recommended

Table 7-14. Uncertainties associated with the soil ingestion pathway.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Erosion/deposition results in a 1 & 5-cm contaminated layer to which children are exposed	The 1 & 5-cm depths are "no-till" depths; 20 cm is assumed as the tilled depth; children are exposed to no-till concentrations	There is no research to refine the mixing depth parameter; others have assumed similar depths for analogous applications;	Exercises suggest use of an enrichment ratio for eroding contaminants may lead to higher concentrations at exposure sites than are warranted, although by no more than a factor of 3; exercises on the stack emission source suggest that the impact of depositing particles may be underestimated by an order of magnitude or more.	No data could be found to more fully evaluate the erosion algorithm; the result of 0.28 ppb concentration resulting from 1 ppb nearby contamination may be high; the use of an enrichment ratio of 3 was speculated as being the parameter of most uncertainty. For stack emissions, the dissipation half-life of 10 yrs. was speculated as the model parameter most likely to be leading to underpredictions.
Child's ingestion rate (2-6 years old).	Ingestion rate assumed to vary from 0.2-0.8 g/d.	The range selected was primarily based on the results of two field studies of soil ingestion in children.	Field study methodology not fully validated. Data from several sources indicate this range of values for small children.	Pica children have been estimated to ingest higher quantities (5 g/d).
Ingestion rate for other ages	Ingestion assumed to occur only during ages 2-6.	Mouthing tendencies strongest and understanding of personal hygiene low during childhood	Hawley estimates inadvertent ingestion may be 60 µg/d for adults, which would lead to an exposure pattern similar to that of children	Adults may inadvertently ingest soil during gardening and yard work; farmers may have a non-trivial soil ingestion pattern

Overall: Soil ingestion for older children and adults were not considered, which may have underestimated lifetime soil ingestion exposures by a factor of two. The other major area of uncertainty for this pathway is for the scenarios where the source of contamination is located distant from the site of exposure, including areas of high soil contamination, the off-site soil source category, and the stack emission source category. Analysis of results from demonstration of the off-site soil source category suggests that the 0.28 ppb soil concentration (within a 5-cm layer) to which children are exposed, and which resulted from the 1 ppb nearby (150 m) soil contaminated site, may be high. On the other hand, analysis suggests that the soil concentration in a 1-cm layer resulting from depositing particles, the air-to-soil algorithm of the stack emission source category, may be underestimating soil concentrations by an order of magnitude or more. The uncertain parameters in these algorithms are the enrichment ratio (for the erosion algorithm only) the depth of mixing (for both the erosion and deposition algorithms), and the mixing zone depths. The mixing zone depth for untilled situation is particularly uncertain - the assumed depths of 1 and 5 cms for the stack emission and off-site soil contamination sources are supported by data on radioactive fallout, and is similar to 1 to 5 cm depths others have assumed. Pica soil ingestion patterns were not evaluated in this assessment; the ingestion rates considering this appear reasonable.

corresponding to short sleeved shirt, short pants, shoes, and socks. Thus the key uncertainty issue concerns the variability in clothing behavior of the exposed population. In this document the 25% assumption was adopted for residents and 5% was judged more reasonable for farmers who are more likely to wear long pants and long sleeved

shirts for field work. Although clothing coverage is likely to vary over the year and with personal habits, these assumptions are judged to be reasonable averages and unlikely to introduce more than a factor of two uncertainty.

The potential for soil adherence probably varies little across the population, but few actual measurements have been made. Thus the uncertainty in these estimates reflect primarily the lack of measurement data rather than population variability. Site variability is probably important as well since soil properties such as moisture content, clay content and particle size distribution are likely to affect adherence. EPA (1992a) reports four studies which estimated soil adherence on hands under both laboratory and field conditions. Data from these studies were analyzed to obtain a central estimate of 0.2 mg/cm^2 and a high end estimate of 1.0 mg/cm^2. The uncertainty in these estimates are derived from unknown efficiencies in the collection methods, relatively small number of subjects, assumption that hand measurements apply to other parts of the body and assumption that child measurements apply to adults as well. The central default value 0.2 mg/cm^2 was adopted here for the residents and the high end value of 1.0 mg/cm^2 was adopted for farmers. The uncertainties in this estimate could combine to produce either under or over estimates and may vary by as much as a factor of 5 on the basis of the ratio of the high end to central estimates.

Exposure frequency to soil reflects largely personal habits and thus the uncertainty is primarily based on population variability. Seasonal and climate conditions can also affect this behavior introducing site variability as well. EPA (1992a) suggests a central frequency of 40 days/yr corresponding to someone who does yard work, gardens or plays outdoors on most weekends and a high end estimate of 350 days/yr corresponding to a farmer or serious gardener in a warm climate. These recommendations were based on judgement rather than actual survey data. In this document, 40 days/year was selected for the residential scenarios and 350 days/yr for the farmer. The lack of survey data to support these estimates introduces uncertainty, but the values are judged to be reasonable and to create relatively little uncertainty.

The dermal absorption fraction of compounds varies widely across chemicals, whereas skin properties that affect absorption, i.e. thickness and composition vary little across the population. Thus the uncertainty in this factor is derived primarily from measurement error rather than population variability. Soil properties, such as organic

carbon content, can also affect the extent of dermal absorption and thus create site variability as well. EPA (1992a) reports two studies which measured dermal absorption of 2,3,7,8-TCDD from soil. Testing included human skin in vitro, rat skin in vitro and rat skin in vivo. On the basis of these tests, a range of 0.1 - 3.0% was recommended in EPA (1992a). Dermal absorption testing, especially for soils, is a relatively new field and many uncertainty issues are involved. These include extrapolation of animal tests to humans, extrapolation of in vitro to in vivo conditions, and extrapolation of experimental conditions to expected exposure conditions. Extrapolation of the tests on 2,3,7,8-TCDD to the other dioxin like compounds (which have not been tested) introduces further uncertainties. A dermal absorption fraction of 3.0% was adopted here for application to all the dioxin like compounds. Based on the observed range of values for 2,3,7,8-TCDD this assumption may lead to overestimates of a factor of 30. Considering all possible uncertainties, under estimates are also possible, though judged less likely.

In summary, dermal exposure estimations rely on a number of parameters whose values are not well established. Although it is difficult to estimate the overall uncertainty with this pathway, it is judged to be plus or minus one to two orders of magnitude. A summary of the uncertainties associated with the dermal absorption pathway is given in Table 7-15.

7.3.4 Water Ingestion

The strong sorptive tendencies of the dioxin-like compounds result in very low water concentrations. Monitoring for PCDDs and PCDFs mostly have not found these compounds at a detection limit around 1 pg/L (ppq), and when found, have generally been very near this concentration. The one exception is an upstate New York community water system, where tetra through octa-CDFs were found at concentrations ranging from 2 pg/L (tetra) to over 200 pg/L (octa). The surface water concentrations predicted by the algorithms of this assessment for all source categories are 10^{-2} pg/L and lower, which is consistent with the sparse monitoring data. Although there was no data found that could be directly applicable to the source categories, it does not appear that the models estimating water concentrations will introduce significant uncertainty into water ingestion exposure estimates.

The classically assumed water ingestion rate of 2.0 L/day was examined in EPA

Table 7-15. Uncertainties associated with the dermal exposure pathway.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Soil Concentrations	Same issues as soil ingestion pathway for migration of residues from a distant source to site of exposure; see discussions in Section 7.3.2 and Table 7-14 above			
Use of tilled vs. untilled soil concentrations	only one conc. for on-site category; used "tilled" conc. for high end farming scenarios, "non-tilled" for non-farmers in central scenarios for all other sources	behavior parameters for farmers assume dermal exposure results from farming in tilled for non-farmers, yard work during summer assumes dermal contact occurs in non-tilled soils	tilled concentrations are lower than non-tilled concentrations; much uncertainty associated with difference between tilled and untilled mixing zone depths; non-farmers working in home gardens also are exposed to tilled concentrations	For real sites, monitoring is best way to resolve this uncertainty.
Contact rate 1 mg/cm^2-event for farmers	0.2 mg/cm^2-event for non-farming residents;	corresponds to central and high end values of measurement data; supported by EPA, 1992a	measurement data may have experimental error or not be representative; uncertain $\pm$ factor of 5	soil properties could affect adherence
Contact frequency	40 for residents; 350 for farm families	Based on judgement; supported by EPA (1992a)	personal behavior patterns could differ but uncertainty judged to be small	climatic conditions introduce site variability
Surface area	5% (1000 cm^2) for farming adults and 25% (5000 cm^2) for non-farming adults	Based on total body surface area data and clothing assumptions; supported by EPA(1992a)	Clothing assumptions based on judgement rather than survey data; uncertainty judged to be plus or minus factor of 2.	Studies have shown that fine particulates can deposit under clothing
Absorption fraction	0.03 for all dioxin-like compounds	Based on EPA (1992a) which gave a range of 0.001 to 0.03; range supported by 2 different studies in rat and human	Experimental procedures very uncertain, may over estimate by factor of 30	Soil properties may also affect absorption

Overall: The high uncertainty in estimates of soil adherence and absorption fraction make the overall uncertainty in the exposure estimates highly uncertain, judged to be plus or minus 1 to 2 orders of magnitude.

(1989). The conclusion was that this estimate is more appropriately described as an upper percentile consumption rate for adults, and recommended 1.4 L/day for use as an average. This value was used for water ingestion in the central scenarios. EPA (1989) cautions that data on consumption rate for sensitive subpopulations such as manual laborers are unavailable. As such, the 1.4 L/day rate for individuals in farming families who work the

field may be low. For this reason, a 2.0 L/day was assumed in the high end, farming, scenarios.

The contact fraction is defined as the fraction of total contact with an exposure media that is contact with contaminated media. For drinking water, this translates to the fraction of water ingestion that comes from the contaminated water source. In the example scenarios, it was assumed that the impacted water was a river which supplied water to the exposed individuals, perhaps through a public water system. The contact fraction of 0.75 for central scenarios is based on time use surveys which showed roughly this fraction of time spent in and around the home environment on the average. The upper recommended limit in EPA (1989) was 1.00; this was felt to be unrealistic for the example scenarios which involved relatively small sources and consequently the likelihood that contamination would not be widespread. Thus, a farmer would likely obtain some water from outside his home where the water supply was not contaminated. An assumption of 0.90 for farming familes was selected for the high end scenarios of this assessment.

The uncertaintainties associated with the water ingestion pathway are summarized in Table 7-16.

7.3.5. Fish Ingestion Exposure

Sections 7.2.3.5 and 7.2.3.6 earlier addressed the capabilities of the models of this assessment to estimate fish tissue concentrations, by looking at measured fish concentrations and comparing them with modeled concentrations. In general, it was concluded that fish tissue concentrations estimated are consistent with those found in the literature, and differences in concentrations with differences in source strength (i.e., higher soil concentrations, higher effluent discharges) also appear to have been captured.

Section 7.2.3.2. looked at a comprehensive data set developed and supplied by the Connecticut Department of Environmental Protection which included soil concentrations, sediment concentrations of water bodies near where soil samples were taken, and fish concentrations from the same water bodies. Data on 2,3,7,8-TCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PCDF, and total TEQ were examined. Soil concentrations of 2,3,7,8-TCDD were found to be in the low ppt range, which has been described in various places in this document as a range for "background" soil conditions. Sediment concentrations of the three congeners and total TEQ were generally in range of 2-3 times higher than soil concentrations, which was

Table 7-16. Uncertainties associated with the water ingestion pathway.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Water Concentrations	See modeling approaches for the soil, stack emission, and effluent discharge source categories in Chapter 4.		literature data show few occurrences of dioxin-like compounds at 1 pg/L detection; models estimate 10^{-2} pg/L range and lower; cannot therefore easily ascertain uncertainty due to modeling, although little uncertainty expected due low concentrations both found and predicted.	No major uncertainty expected due to modeling of water concentrations
Water ingestion rate	1.4 L/day	The classically assumed 2.0 L/day was evaluated in EPA (1989) and found to be high as an average; 1.4 L/day recommended in general assessments, so it was used for central while 2.0 L/d used for high end	EPA (1989) also noted that information on sensitive subpopulations such as laborers was unavailable; still, their analysis indicated that 2 L/day corresponds to a 90% value; hence it is appropriate for high end settings	Not expected to be a critical factor for uncertainty
Contact rate	0.75 & 0.90	0.75 recommended in EPA (1989) for general uses based on time spent at home; recommended value of 1.00 was felt to be too high for high end scenarios; chose 0.90 instead	Not expected to be widely variable for rural settings.	Same comment as above

Overall: Data in the literature suggests concentrations mostly below 1 pg/L, which is consistent with modeling of concentrations 10^{-2} pg/L and lower in demonstration of all source categories. With this evidence, little uncertainty is expected due to modeling techniques. There also does not appear to be a wide range of possible values for ingestion and contact rate, and these are not expected to introduce significant uncertainty into water ingestion exposure estimates.

consistent with the demonstration of the on-site source category. This demonstration scenario had a basin-wide soil concentration of 1 ppt, and the sediment concentration was estimated at 2.8 ppt. The Biota Sediment Accumulation Factor, BSAF, from this field data was estimated to be 0.86 for 2,3,7,8-TCDD. This was higher than the assumed 0.09 in the demonstration scenarios. Two explanations were offered for this difference. One was that the fish sampled were bottom feeders, which would put them in more contact with contaminated sediments compared to column feeders, and the 0.09 was justified based on

data from column feeders; higher impact from contaminated sediments is expected from bottom feeders as compared to column feeders. Two, the 0.86 may have been skewed from two (of seven) sites in the Connecticut data which had high BSAFs at greater than 1 and 3. Although the soil sampling in this data set was generally sparse, the result that bottom sediment concentrations exceeded surface soil concentrations by 1.6-3.9 times generally supports the model's algorithms for estimating sediment concentrations in areas with low basin-wide concentrations.

Section 7.2.3.5 looked at fish concentrations in background areas and where point source impacts to water bodies were identified. A principal source of information was EPA's National Study of Chemical Residues in Fish (EPA, 1992b; abbreviated NSCRF). The range of fish tissue concentrations measured for (perhaps) background conditions in this study, 0.56 - 1.02 ppt, were comparable to the fish tissue concentration estimated assuming the low (perhaps) background soil concentration of 1 ppt soil concentration, 0.6 ppt. It may also be appropriate to make the same observation for the source categories assuming higher soil concentrations as compared to measured concentrations. In this case, the range of measured concentrations, 1.4 - 30.02 ppt, compares with the modeled 3 ppt. Specific field data were not available for more direct model validation. However, the magnitude of concentrations appears to have been captured, and the approximate order of magnitude difference between background and higher source strength categories of the NSCRF also appears to have been duplicated.

While the modeled PCDD/PCDF fish concentrations seem reasonably in line with measured concentrations, this assessment may have underestimated concentrations of 2,3,3',4,4',5,5'-HPCB in the demonstration scenarios. Concentrations for fish in the Great Lakes Region were in the tens to hundreds of ppb range, while this assessment derived estimates all under 1 ppb. However, an examination of bottom sediment concentrations of PCBs in the literature showed them to be roughly three orders of magnitude higher than estimated with the algorithms of this assessment. This mirrors the difference in observed vs. estimated fish tissue concentrations. The Biota Sediment Accumulation Factors, BSAFs, for PCBs also was noted to be variable, with values below 1.0 to values over 20.0 (see Section 4.3.4.1, Chapter 4). The BSAF for the example PCB congener in this assessment was 2.0. Higher BSAFs would also increase PCB concentrations estimated for fish.

Section 7.2.3.6 evaluated the model for estimating fish tissue concentrations for the effluent discharge source category, using data from the 104-mill study. Comparing model predictions of fish tissue concentrations with observed concentrations, it was found that there was generally an underprediction of observed fish tissue concentrations, although the average predicted concentration 7 ppt cannot be considered significantly different then the observed concentration of 15 ppt. An important qualifier is that this exercise assumed that the effluent discharges were the sole source of contaminants which may have impacted the water bodies. Also, the maximum "observed" fish tissue concentration of 143 ppt was matched by a predicted concentration of 89 ppt. Finally, there was discussion that the BSSAF (biota suspended sediment accumulation factor) assigned value of 0.09 for 2,3,7,8-TCDD, the same value used for the BSAF, might be low for the effluent discharge source category. The justification for this hypothesis concerns the differences between past and ongoing water body impacts, and the fact that the 0.09 value was based on field data for a water body where impacts are speculated as principally occurring in the past (see Section 7.2.3.6 for a further discussion of this issue). When the BSSAF was "calibrated" to 0.20, the average predicted fish concentration of 15 ppt for 2,3,7,8-TCDD now matched the observed fish tissue concentration.

The model did not perform as well for pulp and paper mills discharging into the largest receiving water bodies. The average fish tissue concentration observed for 21 fish was about 7 times higher than predicted concentration. No precise conclusion can be reached with this result. However, it may be true that large water bodies are likely to be ones having multiple sources rather than small water bodies. Therefore, the assumption that one or more proximate mills are solely responsible for observed fish concentrations is most likely to be flawed for large water bodies.

In summary, the evaluations for model performance regarding fish tissue concentration estimation seem to lend credibility to the approaches taken. The sensitivity analyses exercises on the algorithms to estimate fish tissue concentration discussed the variability and uncertainty with the parameters required for the algorithms. Generally the most sensitive input was the source strength characteristics - soil concentrations, contaminant discharge rates in effluents, and so on. A single order of magnitude or less range in predicted concentrations would result with singular changes in all other model parameters.

An exposure parameter of paramount importance in estimating exposure to contaminated fish is the fish ingestion rate. Although fish consumption surveys are available and are discussed in EPA (1989), this assessment uses a different approach to estimate the consumption of fish from an impacted water body. The approach is recommended for use when site-specific survey or other information is unavailable (EPA, 1989). Briefly, assume a meal size of between 100 and 200 g/meal - this assessment assumed 150 g/meals - and estimate the number of fish meals that may be recreationally caught from the impacted water body. An estimate of 3 meals/year was made for central exposure scenarios, and 10 meals/year was made for high end exposures. Ingestion of contaminated fish is therefore, estimated as 1.2 and 4.1 g/day, respectively (150 g/meal * 3 meals/yr * 1/(365 d/yr) = 1.2 g/d).

Surveys of recreational fisherman near large water indicates that these estimates are low for this subgroup. As noted in Chapter 2, EPA (1989) estimates that a typical rate of ingestion of recreationally caught fish for this subgroup is 30 g/day, with a 90% estimate of 140 g/day. Chapter 2 also summarizes the USDA 1977-78 National Fod Consumption Survey (USDA, 1983), a three-day total diet survey which showed a range of 0.00 g/day ingested (i.e., survey respondants reported no fish consumption for the three-day period) up to 146 g/day fish including shellfish. The range of 30-140 g/day may be more appropriate, therefore, if estimating fish ingestion exposure for recreational fisherman near a large, impacted water body. If using any of these estimates in exposure exercises, assumptions on percent of total consumption which is recreationally caught and/or impacted by dioxin-like compounds needs to be made.

A key trend noted for the example scenarios in Chapter 5 is that fish, along with beef and milk ingestion, led to the highest exposure estimates for the dioxin-like compounds. Obtaining site-specific information for fish ingestion is critical for this pathway. The ingestion rates made in this assessment are very likely low by an order of magnitude or more for use to a subgroup of recreational fisherman obtaining fish from a nearby large water body.

A summary of the uncertainties associated with the fish ingestion pathway is given in Table 7-17.

Table 7-17. Uncertainties associated with the fish ingestion pathway.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Bioaccumulation approaches for fish tissue concentration estimation	Modeled bottom and suspended concentrations, multiplied them by BSAF or BSSAF	Bioaccumulation approaches rather than bioconcentration are appropriate for lipophilic persistent organic contaminants; water-based rather than sediment-based approaches could be used.	It is not clear whether BSAFs developed from one set of field data are transportable to other water bodies; uncertainty/variability associated with sediment concentration modeling.	Evaluations of literature reports in Sections 7.2.3.2, 7.2.3.5, and 7.2.3.6 speak well for the algorithms estimating fish tissue concentrations; predicted and observed conc. range from less than 1.0 ppt for background sources to the single to two digit ppt concentrations for more substantial point sources.
Fish ingestion rate	1.2 and 4.1 g/day	Based on 3 and 10 meals per year caught from the impacted water, and 150 g/meal	A low estimate compared to surveys of recreational or subsistence fisherman near large water bodies	Example scenarios were for "rural", agricultural settings; higher rates of ingestion appropriate for other purposes was not deemed appropriate for such settings.

EVALUATION: Comparison of fish concentrations generated in the demonstration scenarios with literature values of fish concentrations of dioxin-like compounds shows them to be comparable. The test run with the effluent discharge source category suggests that fish tissue concentration predictions may be low, but not by a significant amount. It would appear that procedures to estimate fish tissue concentrations, while still obviously containing uncertainties and variabilities, obtain results that are consistent with source strengths and in the same order of magnitude as measured in field settings. Much higher sediment concentrations of PCBs were noted in actual water bodies than were modeled in the demonstration scenarios - hence much lower fish tissue concentrations of PCBs were estimated. The BSAFs were assigned based on field measurements for dioxins, furans, and PCBs. PCB BSAFs were an order of magnitude and more higher than dioxin and furan BSAFs. Alternate modeling approaches based on water column concentrations show comparable fish concentration estimations. Fish concentrations estimations vary by less than an order of magnitude with changes in model parameters, except for source strength terms. The fish ingestion rates assumed were low in comparison to estimates given for subsistence fisherman or others who live near large water bodies where fish are commercially caught. A lower ingestion rate is appropriate for settings where large water bodies containing edible fish are not present.

7.3.6. Vapor and Particle Phase Inhalation Exposures

This section will address the uncertainty associated with vapor and particulate phase inhalation exposures. Sources addressed in this assessment include stack emissions and contaminated soils; this section will only address contaminated soils. The fate and transport of dioxin-like compounds from stack emissions to exposure sites, and the resulting air concentrations, are discussed in Chapter 3.

The respiration rate of 20 m^3/day used for inhalation exposures is within the standard range of 20-23 m^3/day (EPA, 1989). The contact fraction is 0.75 for central scenarios and 0.90 for high end scenarios. Like the water ingestion contact fractions, these were based on time at home surveys. The inhalation rate and contact fractions are not expected to introduce much uncertainty into inhalation exposure estimates.

Another exposure parameter critical for the inhalation pathway is exposure durations, which is 9 years for central and 20 years for high end exposures. The uncertainties associated with this parameter in its use as an exposure parameter are discussed above in Section 7.3.1. However, exposure duration is additionally critical for the inhalation pathway, as estimated volatilization flux is a function of the time during which volatilization is occurring. Essentially, the model assumes that contamination is at the soil surface at time zero, and over time, residues which volatilize originate from deeper in the profile leading to lower volatilization fluxes after time, and also lower average volatilization flux as the averaging time increases. The sensitivity analyses exercises in Chapter 6, Section 6.3.3.1., evaluated the sensitivity of air concentration predictions to changes in exposure duration. It was shown that there is roughly a factor of four difference between concentrations predicted over one year duration to a seventy year duration. Therefore, there is both a direct and an indirect impact from changing the exposure duration in these procedures. The direct impact from changing exposure duration is in the exposure equation - increasing the exposure duration increases the exposure estimate. What is seen also with increases in exposure, however, is a decrease in the estimated average air concentrations to which individuals are exposed. The impact in the exposure estimates is more driven by having more years of exposure rather than being exposed to a lower average air concentration, as expected.

Vapor-phase emissions are estimated with a volatilization flux algorithm. The procedures were developed in Hwang, et al. (1986). A near-field dispersion model estimates air concentrations for the on-site source category - the category addressing soil contamination at the site of exposure. For the off-site source category, where the site of contamination is located distant from the site of exposure, the same volatilization flux model is used. Exposure site concentrations for these sources are estimated using a far-field dispersion model.

Sensitivity analyses in Chapter 6 showed that the air concentration varied roughly over an order of magnitude with testing of key contaminant parameters, the organic carbon partition coefficient, Koc, and the Henry's Constant, H. Air concentration predictions are also sensitive to other key parameters, including those associated with source strength (area of contamination, concentration), geometry, (distance to receptor in off-site source category), and climate (average windspeed). However, these might be

expected to be known with a reasonable degree of certainty for a site-specific application. If they are, it can be concluded that the most uncertainty associated with the vapor phase algorithm is in the contaminant parameters, and it would appear that a range of about an order of magnitude difference in predicted air concentrations might be expected with different pairs of these parameters.

The model's predictions of vapor phase air concentrations in the demonstration scenarios, with all parameters as selected, were compared with air concentrations that were found in the literature earlier in Section 7.2.3.7. This was clearly not a validation test, but might be called a reality test. It was found that air concentrations resulting from low, background levels of 2,3,7,8-TCDD, 1 ppt, were orders of magnitude lower than levels of 2,3,7,8-TCDD found in urban air samples, when 2,3,7,8-TCDD was measured in such samples. It was also found that air concentrations found with elevated soil concentrations of 2,3,7,8-TCDD, 1 ppb, soil concentrations which are more typical of Superfund and related sites, are comparable to noted urban air samples. The claim made was that this leant some credibility to model predictions - other possible outcomes such as air concentrations from low background soil concentrations being equal to urban air concentrations or concentrations from contaminated soil being higher than urban air concentrations, would appear to be inconsistent, and so on.

However, this examination also suggests that air concentration estimated with the volatilization/dispersion algorithms of the soil source categories may be underestimating air concentrations by an order of magnitude. Evidence here came in a few different forms. First, air concentrations of 2,3,7,8-TCDD taken in a "remote countryside" in Sweden showed concentrations an order of magnitude higher than are predicted for the on-site demonstration scenario, where soil concentrations were set at 1 ppt. This soil concentration was developed from literature data where researchers sampled soils in areas described as "background" or "rural". The soil concentration corresponding to the Swedish remote countryside data was unavailable, but it should be at least equal to these background or rural settings, if not lower. Another piece of evidence came in an examination of above ground plant:soil ratios as generated by the models and found in experimental testing. The models underestimated these ratios by 1 to 2 orders of magnitude as compared to the literature when vegetations in the literature were grown in soils with concentrations in the ppt range, a range typical of background settings. Since

the models operate by estimating air concentrations, both particle and vapor concentrations, followed by air-to-plant impacts, this would be further evidence that the models are underestimating air concentrations, perhaps by the same 1-2 orders of magnitude difference.

While these pieces of evidence would seem to indicate that the model is underpredicting air concentrations resulting from soil contamination, the exact amount of this shortfall cannot be quantified. Arguments presented in Volume II and summarized in Volume I of this assessment indicate that the ultimate source of dioxins in soil, vegetations, and food products are air emissions from industrial sources, followed by long-range transport. If this is true, than the measured air concentrations and the vegetations in the experiments discussed above, are impacted not only by soil releases, but by long range transport from other sources. This assessment only models the incremental additions due to soil releases. The difference between the incremental addition from soil releases and the amount attributable to long range source cannot be ascertained at this time.

An alternate model for volatilization flux and an alternate model for air dispersion were evaluated in Section 7.2.4.4 above. It was found that the alternate volatilization model predicted about a third as much volatilization as the Hwang model, but that the alternate dispersion model predicted air concentration that may by 8 times higher than the models predicted in this assessment.

There was no data on concentrations of air-borne contaminants in the particle phase only. The procedures used to estimate the suspension of particles were developed from information on highly erodible soils. As such, fluxes and hence concentrations are expected to be higher than might be seen on the average. Still, inhalation exposures to contaminants sorbed to air-borne particulates were 1 to 2 orders of magnitude lower than exposures to contaminants in the vapor phase, and along with water ingestion exposures, were the lowest exposures estimated for the on-site and off-site soil source categories. In this regard, certainty with regard to estimating exposures due to inhalation of airborne contaminated particulates may be a small concern.

However, the sensitivity analysis exercises in Chapter 6 did indicate a two order of magnitude range in estimated concentrations depending on the assumptions concerning wind erodibility of the soil. Also, several issues of uncertainty concerning the suspension

of contaminated particles and relationship between air-borne vapor and particle phases were examined. It was noted that the total reservoir of suspended contaminated particulates was likely to be underestimated because the algorithm for wind erosion was developed only for inhalable size, < 10 μm, particles, which is appropriate for inhalation exposures but would lead to an underestimate of the depositions onto vegetation, including fruits/vegetables for consumption and grass/feed for the beef/milk bioconcentration algorithm. Vegetation concentrations might also be low because the impact of rainsplash on transferring soil to the lower parts of vegetation was not considered.

A critical assumption made was that volatilized residues remained in the vapor phase and did not sorb to airborne particles. This led to a dominance of vapor phase contaminants - 90% and more of the total airborne reservoirs (vapor + particle phases) estimated for the on-site and off-site soil source categories were in the vapor phase. A model by Bidleman (1988) suggested that the fraction of 2,3,7,8-TCDD that would exist in the particulate phase in background settings (i.e., rural, non-urban) might range from 26% (average background) to 45% (average background with local sources), and in urban settings, would be as high as 72%. Transferring portions of the vapor phase contaminants to the particulate reservoir to get balances suggested by Bidleman's model would not change total inhalation exposures, but would impact concentrations in above ground vegetations. Currently and even with transfers such as these, vapor phase transfers dominate plant concentrations. Because vapor phase reservoirs would be reduced after transferring a portion to the particle phase, such transfers translate to reductions in plant concentrations, and for grass and feed, subsequent reductions in beef and milk estimations.

Perhaps the most critical assumption which could be questioned is that airborne vapor and particle phase contaminants at the site of exposure originate only from the site of contamination in the off-site soil source category. Meanwhile, soils at the exposure site are impacted - concentrations in the air at the exposure site do not consider possible fluxes from exposure site soils, or from soils between the contaminated and exposure sites. A test was conducted for this assumption using the demonstration scenario for the off-site soil source category, which had a 4-ha site at 1 ppb 2,3,7,8-TCDD 150 meters from an exposure site of the same size. The soil concentrations at the exposure site were 0.28

ppb for a 5-cm notill mixing depth and 0.08 ppb for a 20-cm tilled mixing depth. These concentrations were then input as soil concentrations for the on-site soil source algorithms to determine what air concentrations would results. These exposure site air concentrations were compared with exposure site air concentrations generated with the off-site algorithms. It was found that on-site air concentrations with soil concentrations at 0.28 ppb exceeded exposure site vapor and particle air concentrations estimated for a 1 ppb contaminated site 150 meters away by a factor of 3-5. When the same test was run using a tilled concentration of 0.08 ppb, concentrations predicted using the on-site algorithm and this concentration were similar to the concentrations predicted using off-site algorithms and a starting concentration of 1 ppb.

Several uncertainties were discussed, but a lack of data and a complete understanding of atmospheric processes for dioxin-like compounds precludes any final quantitative judgements on uncertainties in the air concentration algorithms. Some of the uncertainties imply that procedures and assumptions adopted overestimate pertinent environmental media, and others imply that such media concentrations were underestimated. The assumption that air-borne reservoirs of contaminant originate only at an off-site area of contamination and not from other soils should be examined further.

A summary of the uncertainties associated with the vapor and particle inhalation routes is given in Table 7-18.

7.3.7. Fruit and Vegetable Ingestion

Consumption rates of 200 g/day for vegetables and 140 g/day for fruit were derived in EPA (1989) and recommended for general assessment purposes. They include all fruits and vegetables and were derived from two principal sources: Foods Commonly Eaten by Individuals: Amount Per Day and Per Eating Occasion (Pao, et al. 1982), and 2) Food Consumption: Households in the United States, Seasons and Year 1977-1978 (USDA, 1983). Pao, et al. (1982) used the data from the USDA survey, which included interview responses from 37,874 individuals, to estimate total consumption and percentiles of home-grown fruits and vegetables. EPA (1989) identifies two principal sources of uncertainty with Pao's estimates:

- These data are from all consumers, only a small percentage of whom are also home gardeners. Those who home garden may have higher total rates of consumption.

Table 7-18. Uncertainties and sensitivities associated with estimating vapor and particle-phase air concentrations from contaminated soils.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Exposure parameters	inhalation rate of 23 m^3/day; contact fraction 0.75 in central and 0.90 in high end parameters	range of inhalation rates typically given as 20-23 m^3/day; confactions based on time at home surveys	not much uncertainty expected due to these choices	uncertainty introduced by exposure durations of 9 and 20 years because of their their role in volatilization algorithm; otherwise uncertainty more due to methodologies estimating air concentrations
Volatilization followed by near or far-field dispersion for vapor phase contaminants	Used model developed by Hwang (1986) for volatilization of PCBs; standard area-source dispersion algorithms for concentration	Like PCBs, dioxin-like are highly sorbed and persistent	Chemical parameters H and Koc are most uncertain with an order of magnitude range in estimated concentrations; estimations also sensitive to area, distance, and frequency wind blows to receptor.	An analysis of model performance suggests that the soil to air algorithms may be underestimating air concentrations by a factor of 10. The amount of underestimation cannot be known, since measurements would include soil emissions and long-range transport from other sources.
Wind erosion followed by same near or far-field dispersion algorithms for particle phase contaminants	Used model based on highly erodible soils for dust flux to estimate fluxes for particle sizes < 10 μm	Assuming highly erodible soils may tend to overestimate flux, but not considering particles of size > 10 μm would underestimate total airborne reservoir	Parameters associated the erodibility of soils can lead to a 2 order magnitude range for estimated concentrations; much less sensitivity noted for other parameters	No data to evaluate model results; however, particle inhalation exposures were 1-2 orders of magnitude lower than vapor phase exposures - certainty may be less of an issue
Volatilization or resuspension of eroded contaminants not considered	contaminants eroding to exposure site assumed not to volatilize or resuspend to contribute to exp. site air concentrations	if delivered contaminants volatilize or resuspend at site of exposure, then exposure site air would increase by a factor of 2 to over a factor of 10.	As noted, the key uncertainty is in the fate of delivered residues	More consideration of of the fate of delivered contaminants is warranted.

Evaluation: Model estimations of vapor-phase 2,3,7,8-TCDD and 2,3,4,7,8-PCDF in a rural setting resulting from emissions from low, background soil concentrations are orders of magnitude lower than observed urban air concentrations of these contaminants. The fact that they are lower is to be expected. However, an analysis of other available data suggests that, in fact, the models predicting air concentrations over soils may be underestimating such concentrations by an order of magnitude or more. This is only a speculation on the degree of underestimation, and in fact that underestimation is occurring. No data could be found on air concentrations over soils where it is definitely known that the soil is the only source of the dioxin-like compounds. The hypothesis put forth in this assessment is that the ultimate source of dioxin-like compounds in soils, vegetations, and food products are emissions into the air from industrial sources. Therefore, literature reports on air and vegetation concentrations are not only impacted by soil emissions, but by industrial emissions and long-range transport. Sensitivity analysis showed estimations to be sensitive to Koc and H, and also to key source strength and delivery terms such as areas of contamination and wind speed. Assuming these non-chemical specific parameters can be known with reasonable certainty for site-specific applications, the most uncertainty lies with chemical specific data. Alternate approaches for volatilization and air dispersion generally estimate comparable air concentrations. Approaches to estimate particulate phase concentrations are empirical and based on field data. They are based on highly erodible soils but are specific to inhalable size particles, those less than 10 μm. As such, they may overestimate inhalation exposures, but may underestimate the total reservoir of particulates, which becomes critical for the particle deposition to vegetation algorithms. Another area of uncertainty is the assumption that volatilized contaminants do not become sorbed to airbone particles - this is also critical because vapor phase transfers dominate plant concentration estimation. A final key area of uncertainty is that transported contaminants from a contaminated to an exposure site via erosion are assumed not to volatilize or resuspend at the exposure site - air borne exposure site concentrations may be underestimated as a result.

- USDA's survey only included information for 3 days from each respondent: products eaten the day before, the day of, and the day after the interview. Therefore, the results on a per day basis only include information for three days from respondents; what is required for long term exposure assessments is an amount eaten per average day over the course of a long time period, such as a year or a duration of exposure. EPA (1989) did not discuss whether this aspect of uncertainty might render the 200 and 140 g/day estimates over- or underestimates.

These total consumption rates were reduced considering fruit and vegetables which are "protected" and "unprotected". Protected fruit, for example, included citrus and cantaloupe, whereas unprotected fruit included peaches or apples. This distinction was made because evidence indicates very little translocation or residues to within the plant. It was assumed that there would be no exposure when the produce was protected. Again using data from Pao, et al. (1982) as summarized in EPA (1989), it was estimated that 44% of total fruit ingestion was ingestion of unprotected fruit and 74% of total vegetable ingestion was unprotected vegetables.

A final distinction was required which divided unprotected fruit/vegetables to those which grow underground and those which grow above ground. Different algorithms were used to transfer soil residues to plants depending on whether they were above or below ground. Using the same data once again, it was estimated that no fruits were grown underground (unprotected or protected), and that 37% of unprotected vegetables were grown underground.

The result of these two distinctions was to estimate total consumptions rates of unprotected fruit as no below ground and 88 g/day above ground consumption; for unprotected vegetables, total consumption included 76 g/day above ground and 28 g/day below ground.

The overall average fraction of total vegetable and fruit consumption which is homegrown is estimated as 0.25 and 0.20, respectively (EPA, 1989). EPA (1989) recommends 90th percentile assumptions for these parameters of 0.40 (vegetables) and 0.30 (fruit), which were assumed in the high end scenarios of this assessment. EPA (1989) notes a wide range of fraction homegrown for individual vegetables, 0.04-0.75, and fruits, 0.09-0.33.

All these assumptions discussed: total consumption rates, protected or

unprotected, above or below ground, and fraction home grown, are probably reasonable for general assessment purposes as long as exposures are to the broad categories of fruits or vegetables, and not for individual fruits or vegetables. For a site specific assessment, there will likely be wide variability on the types of produce grown at home, what percentage of that is unprotected, and so on. Finally, and as is also true for beef and milk exposures, this assessment only considers the impact of home-grown fruits and vegetables. In rural settings, it is plausible that a large percentage of an individual's total fruit and vegetable intake comes from nearby and impacted sources, more than the 20-40% assumed in this assessment. If that is the case, than contact fractions should be set at 1.0, and exposures would increase 2-5 times from what they are estimated as in this assessment.

Several issues of uncertainty pertinent to the estimation of concentrations in below and above ground vegetation have been examined in other parts of this document and are not repeated here. Key issues include: 1) the uncertainty associated with empirical parameters, VG_{ag} and VG_{bg}, 2) the assumption that residues which volatilize from contaminated soils remain in the vapor phase and not partially partition into the vapor phase, 3) the possible underestimation of total particle reservoirs of contaminant in the air resulting from wind erosion of contaminated soils because the wind erosion algorithm only estimated suspension of inhalable size and not all particulates, and also because the possible effect of rainsplash onto vegetables low to the ground such as lettuce, was not considered, 4) for the stack emission source, uncertainties associated with air dispersion and deposition modeling using the COMPDEP model as discussed in Section 7.2.2., and therefore the subsequent impacts of soil-to-plant transfers, 5) for the stack emission and off-site soil source categories, air borne concentrations in the vapor and particle phases at the exposure site are assumed to only originate at the source of contamination (the off-site contaminated soil and stack emissions) and not on impacted soil at the exposure site - considering additional fluxes from impacted soils could lead to up to an order of magnitude higher concentrations in the vapor and particle phases.

Quantitative judgements as the uncertainties associated with these issues are difficult to make. An examination of experimental data in Section 7.2.3.8, where most of the vegetations were grown in well characterized conditions implied that the soil contamination models may be underestimating concentrations in both above and below

ground vegetations. For above-ground vegetations, other evidence suggests that the models estimating air concentrations over contaminated soils may be underestimating such concentrations, which would explain the underestimation of above ground vegetations. On the other hand, the air-to-beef validation exercise described in Section 7.2.3.9 does lend quantitative credibility for the air-to-plant algorithms. While the soil contamination model may be underestimating vegetation concentrations, the literature evidence suggesting that below ground vegetations have higher plant:soil ratios than above ground vegetations, and that perennials have higher concentrations than annuals, was duplicated by the modeling approaches.

A summary of uncertainties associated with the fruit and vegetable ingestion exposure pathway is provided in Table 7-19.

7.3.8. Beef and Milk Ingestion

Concentrations in beef and milk are a function of cattle ingestion of contaminated soil, pasture grass, and cattle feed. Therefore, previous sections on soil contamination, soil transport algorithms, and plant concentration estimation, are relevant to estimating beef and milk concentrations. Section 7.2.3.9 above is particularly relevant. This section described an exercise where air concentrations of dioxin-like compounds were routed through the food chain model to estimate concentrations in beef. Generally, that section showed that an air concentration of 0.019 pg TEQ/m^3, speculated to be an appropriate air concentration for rural environments where cattle are raised for beef, translates to a whole beef TEQ concentration of 0.36 ppt, using the models and parameters of this assessment. The observed whole beef concentration, from three studies in the United States where TEQ concentrations in beef were taken from grocery store beef samples, averaging 0.48 ppt (when non-detects in the sample set were estimated as 1/2 detection limit; 0.28 ppt when they were estimated as 0.0). Section 7.2.3.1. on off-site soil impacts, including erosion from a site of contamination to another site and deposition of stack emitted particulates onto a site, describes uncertainties with estimating soil impacts from a distant source of contamination. Section 7.3.7. above summarizes uncertainties associated with estimating grass and feed concentrations, with further information on vegetation concentration uncertainty in Section 7.2.3.8.

For the bioconcentration algorithm itself, there is uncertainty with the parameters

Table 7-19. Uncertainties associated with vegetable and fruit ingestion exposure algorithms.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Rates of ingestion	fruits: 88 g/day above ground unprotected, 0 g/day below ground unp., 0.20-0.30 home grown; veg: 76 g/day abv grd unp. 28 g/day bel. grd. unp.; 0.25-0.40 home grown.	Protected/unprotected distinction because residues not expected to translocate; above/below ground because procedures for soil transfers are different	Much variability expected when using approach for a specific site when actual home gardening can be ascertained.	All parameters assumed are evaluated as reasonable for general exposure to broad categories of fruits and vegetables.
Below ground vegetable concentration	Uses empirical Root Concentration Factor which is function of Kow, VG_{bg}, an empirical correction factor, and soil water concentrations	Separating below ground with above ground vegeta- was critical and supported by the literature; approach based on laboratory experiments with barley roots.	The VG_{bg} empirically describes the difference in barley roots and bulky underground vegetables; although assignment of 0.01 is rationally based, arguments presented could estimate it instead at 0.10 or 0.001; algorithm also a function of Kow, which is uncertain by 2 orders of magnitude; most likely change in Kow decreases concentration by up to an order of magnitude	Comparison with the literature suggests estimates of below ground vegetables may be low by an order of magnitude; however, the trend that below ground vegetables have higher transfers from soil to plant as compared to above ground vegetables was correctly captured.
Vapor Phase Transfer for Above Ground Vegetation	Uses air-to-leaf factor developed in laboratory conditions for 14 compounds transferred to azalea leaves; empirically corrects for plants like fruit/veg. that have much less transfer to inner parts as compared to leaves; also empirically corrects for the demonstrated high rate of transfer of the 14-compound experiments.	transfer factor is a function of Kow and H as experimentally derived for 14-compound experiment; air-to-beef exercise in Sec. 7.2.3.9 shows that the empirical adjustments by the match of predicted and observed concentrations; results show that vapor transfers dominate plant concentrations	Empirical correction factor, VG_{ag}, is necessary, but values could also be low or high, as above; like algorithm above, transfers critically a function of Kow; most likely alternate Kow would increase concentration estimates by up to an order of magnitude.	Limited literature data suggests that above ground vegetation impacts from contaminated soil may be underestimated. The hypothesized cause is soil to air impacts, not air to plant impacts. The air-to-leaf transfer factors are the most critical since vapor transfers dominate above ground impacts. Experimental evidence recently developed by McCrady (1994) justifies use of VG_{ag} and numerical value of 0.01 used for bulky fruits/vegetables.

(continued on next page)

Table 7-19. (cont'd)

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Particulate Phase Deposition for Above Ground Vegetation	Model for soil contamination solves for airborne particulate phase concentration and applies deposition rate; COMPDEP estimates deposition rate for stack emission source source category; plant concentrations based on wet + dry deposition rates, plant mixing volumes, canopy cover, retention of wet deposition, and washoff.	Algorithm developed for radionuclide impact to agriculture (Baes, et al., 1984) but applied to other contaminants sorbed to airborne particulates; particulate deposition as mechanism of plant contamination speculated to be of concern for 2,3,7,8-TCDD in early literature. Model results show particulate deposition less critical than vapor transfers for plant impact.	Wind erosion algorithm developed for particle sizes < 10 μm and might therefore underestimate total depositions - not the case for COMPDEP modeling which simulates the range of particles; also does not consider rainsplash.	The basic approach given contaminant deposition rates is defensible; model results imply particulate deposition is much less an important process than vapor transfers for impacts to above ground vegetations.

Overall: All ingestion parameters assumed are evaluated as reasonable for general exposure to broad categories of fruits and vegetables. However, great variability is expected if using these procedures on a specific site where home gardening practices can be more precisely ascertained. A contaminant concentration ratio was defined as the concentration of contaminant in vegetation divided by the concentration in the soil. A comparison of the modeled ratios with those found in the literature showed that the modeled ratios tended to be lower for all vegetation (above and below ground fruit and vegetation, grass and cattle feed) by 1-2 orders of magnitude, although the literature data was not consistent. For example, the literature data showed different ratios as a function of soil concentration - lower soil concentrations had higher ratios, while higher soil concentrations had lower plant:soil ratios. Trends noted in the literature which were duplicated by the model include higher below ground vegetable ratios as compared to above ground vegetable ratios, and higher ratios for perennials (grasses, e.g.) as compared to vegetables. A key assumption in the vegetation algorithm, that dioxin-like compounds do not translocate from root to shoot, was verified by two experiments, although a third recently completed experiment (Huelster and Marschner, 1993) contracticted this conventional wisdom for zucchinis and squash. Vapor-phase transfers dominate vegetation concentrations. Evidence suggests that the methodologies and/or parameters used in this assessment may have underestimated the vegetative concentrations that result from contaminated soils. Further, the evidence suggests that the models underestimate air concentrations above soils by an order of magnitude, which leads to lower vegetation impacts. Other evidence suggests that the air to plant transfer algorithms do, in fact, estimate above ground vegetation concentrations appropriately. A critical empirical parameter was the above and below ground correction factors, VG_{ag} and VG_{bg}, both set at 0.01 for fruits/vegetables. These factors are justified for dioxins based on the fact that the experiments for derivation of the below ground empirical transfer factor and the above ground empirical transfer factor were conducted with thin barley roots and azalea leafs, respectively. Whole plant concentrations for these vegetations are likely to be much less than whole plant concentrations of bulky fruits and vegetables; hence the introduction of the VG parameters. Recent experimental evidence by McCrady (1994), where the uptake rates of vapor-phase 2,3,7,8-TCDD into different vegetations including grass, azalea, kale, tomato, pepper, and apple, did in fact show a much lower uptake rate for these bulky vegetations. The ratio of uptakes between the bulky fruit/vegetables and grass leaves was between 0.02 and 0.08, justifying the use of the VG_{ag} of 0.01 for fruits/vegetables in this assesment. A different assumption for VG, such as 0.10, would increase estimated concentrations and perhaps make concentration ratios more in line with literature values. Other experimentally derived empirical factors describing the transfer of compounds from soil to below ground vegetables and vapor-phase air to above ground vegetation were a function of contaminant Kow and H (H for above ground transfers). An alternate value of log Kow for 2,3,7,8-TCDD would more likely be higher than lower, given a literature range of 6.15 to 8.5, and a selected value of 6.64. Increasing log Kow tends to decrease below ground vegetation, by as much as an order of magnitude, while increasing above ground vegetation by as much as an order of magnitude.

estimating beef and milk concentrations: the beef/milk bioconcentration factor BCF, the soil bioavailability factor, B_s, and the parameters describing the cattle diet which include dietary fractions in soil, grass, and feed (the sum of the three adding to 1.00), and the

degree to which these three are impacted by on-site soil and deposition conditions. Section 6.2.3., Chapter 6, described the results of sensitivity analysis of these parameters on beef and milk concentrations. It was shown that there is a small range of possible values for B_s and a small impact on results. Data indicates that range of values for BCF for 2,3,7,8-TCDD is 1 to 10, with a concurrent order of magnitude difference between the upper and lower values. The parameters describing cattle exposure to soils and vegetation at the site are also critical, with up to an order of magnitude difference in concentrations for the example exposure situations examined in Section 6.2.3. It is expected that cattle exposure assumptions can be reasonably described for a specific site. Therefore, the most uncertainty in the bioconcentration algorithm itself lies with the bioconcentration factor, BCF.

The whole beef and milk concentrations of 2,3,7,8-TCDD estimated with the stack emission source were lower than the other sources at 0.0005 ppt and 0.00006 ppt, respectively. The on-site demonstration scenario, where soil concentrations were set at background levels of 1 ppt, estimated beef and milk concentrations in 10^{-2} and 10^{-3} range, respectively. This is consistent with literature data on the concentrations of 2,3,7,8-TCDD in whole beef and milk. There was some literature data showing beef and milk concentrations near incinerators to be higher than concentrations where no incinerators or other known sources were present. Comparisons between impacts as noted in these references with the results of the demonstration scenarios cannot be done because information on the source strength in these references is not available. What can be stated, however, is that the emission factors (mass contaminant emitted per mass contaminant incinerated) from the hypothetical incinerator are comparable to emissions from incinerators having a high level of air pollution control, e.g., scrubbers with fabric filters, and that the feed rate of 200 metric tons per day is a midrange value (for more detail on the example emissions, see Section 3.3.3, Chapter 3). The literature articles noting more impact in the vicinity of incinerators were from the 1980s from Europe, and it is certainly plausible that the incinerators did not have a comparable level of air pollution control. Also, it should be remembered that actually measured concentrations of these compounds are the result of multiple sources impacting the cattle; the methodologies of this assessment such as the stack emission source category evaluate only the incremental impact for that source.

One other literature comparison that was made was comparing beef fat:soil and milk fat:soil concentration ratios developed for PBBs with those estimated for 2,3,7,8-TCDD in the demonstration scenarios. Such a comparison is thought to be valid since PBBs are similar in fate and bioconcentration tendencies to the dioxin-like compounds. In this comparison, differences in beef and milk bioconcentration tendencies appear to be captured. Fries (1985) found body fat:soil PPB and milk fat:soil PBB concentration ratios for dairy heifers to range from 0.10 to 0.37, and from 0.02 and 0.06, respectively. For body fat of beef cows, these ratios were 0.27 and 0.39. Analogous ratios were derived for the contaminated soil scenarios, and for beef and milk fat. For the contaminated soil demonstration scenarios, Scenarios 1-3, beef fat:soil and milk fat:soil ratios were 0.12 and 0.06, respectively. These appear a bit lower than the PBB ratios derived by Fries (1985). The interpretation of this result was that, again here was some evidence that models may be underestimating the impacts of soil contamination to air, and hence air to plants and plants to animals.

Section 7.2.4.6 evaluated other beef and milk bioconcentration models. It was found that most earlier efforts are quite similar to the model of this assessment, with simple mathematical transformations. Other efforts had considered cattle inhalation exposures and cattle ingestion of impacted water, and found them to be of minimal importance in estimating beef and milk concentrations. They were not considered in this assessment. Two efforts, that of Stevens and Gerbec (1988) and Fries and Paustenbach (1990), evaluated the practice of placing beef cattle on a grain-only diet for fattening prior to slaughter. Both assumed that the reduction in beef concentrations could be modeled as a first-order process with a half-life of around 115 days. With grain only diet periods of 120-130 days, they showed beef concentrations to be reduced by about 50%. A similar approach could be adopted for the models of this assessment. The general result that the fattening regime was estimated to reduce body fat concentrations by 50% was used in the air-to-beef validation exercise described in Section 7.2.3.9.

The air-to-soil algorithms of the stack emission source category, and the soil-to-air algorithms of the soil contamination source categories have both been highlighted as algorithms which may have uncertainties. These uncertainties are detailed in Chapter 6, Sections 6.3.3.7, 6.3.3.8, and 6.3.3.10. They uncertainty with regard to soil to air impacts is also discussed in this Chapter in Sections 7.2.3.7 and 7.2.3.8. Generally, it

was found that the air-to-soil algorithms may be underestimating soil concentrations, while the soil-to-air algorithms may be underestimating air concentrations. As a result, an examination of model trends show a key dichotomy in the way the stack emission source category performed as compared to the soil contamination source categories. Specifically, soil alone accounted for about 90% of the milk and beef impacts for the soil source category, whereas soil accounted for only about 5% of the milk and beef impacts for the stack emission source category. Refinements to the model algorithms or the model parameters which would increase air concentrations resulting from soils, and increase soil concentrations resulting from depositions would narrow this gap.

Data on rates of milk and beef consumption were taken from surveys summarized in EPA (1989). Whereas the survey data may lead to adequate estimates for per capita consumption of these products, EPA (1989) cautions that farm families who home slaughter or who home produce dairy products may have higher consumption rates. Data is unavailable for these situations. Another consideration for application to real world rural situations is that farming and non-farming families may be obtaining cattle food products from local farms which may also be impacted by dioxin-like compounds. This possibility was not addressed in this assessment.

The fractions of meat or milk intake coming from the farmer's home supplies was determined in a survey of 900 rural farm households (USDA, 1966). The 0.44 (44%) of meat and 0.40 of dairy contact fractions from this survey were, appropriately, proportions of total dietary intake that is home-produced and consumed by farming families. Therefore, more certainty is expected for these contact fractions as compared to ingestion rates.

The trend analysis for the example scenarios in Chapter 9 indicated that the greatest exposures occur for beef, milk, and fish. Therefore, the rate of consumption of impacted beef and milk is critical. The range of beef fat consumption noted in surveys summarized in EPA (1989) is 14.9 to 26.0 g/day, but a single high consumption rate of 30.6 g/day was noted. If this high rate is more typical of home-producing farm families, then the value of 22 g/day selected for this assessment may be 28% low. The single high rate of 35 g/day of milk fat is significantly higher than the 8.9-10.7 g/day range noted in EPA (1989) and the 10 g/day ingestion rate for milk fat may be low.

A summary of uncertainties associated with the beef and milk ingestion pathways

is given in Table 7-20.

7.4. USE OF MONTE CARLO TECHNIQUES FOR ASSESSING EXPOSURE TO DIOXIN-LIKE COMPOUNDS

The purpose of this discussion is to 1) briefly discuss how Monte Carlo procedures work and could be applied in exposure assessments and 2) summarize recent efforts by three investigators to apply Monte Carlo procedures to assessments involving dioxin-like compounds.

Basically, Monte Carlo is a generic statistical method which generates a distribution for an analytical output of a mathematical model using the distributions of the input variables. Computer simulations are used to repeatedly generate outputs based on parameter inputs, where values for parameters are selected from their distributions. The outputs are compiled and expressed as a frequency distribution. In the context of exposure assessment, a Monte Carlo application could involve developing distributions for each of the parameters in the exposure equation and generating a distribution showing how the exposure levels vary in the exposed population. The final distribution can be interpreted as the probabilities of one individual (randomly selected from the exposed population) experiencing various exposures. Since exposure levels are not only a function of the exposure parameters but also of the concentration in exposure media, another application of the Monte Carlo method would be to estimate the distribution of exposure media concentrations using mathematical models for fate and transport.

Monte Carlo techniques can be a powerful tool for expressing variability and evaluating scenarios in exposure assessments. However, its use requires detailed input data which is frequently unavailable. Although the procedure may make an analysis look more elegant, it may actually yield misleading results if based on poor data. Accordingly, exposure assessors should be very cautious when trying to apply Monte Carlo techniques or interpreting the results.

Generally, Monte Carlo procedures should be applied only when credible distribution data are available for most of the key variables. Distribution data refers to empirical information on the statistical variation of the variable that is relevant to the site assessed. Usually this data should be obtained from surveys conducted at the site of interest. However, data on human behavioral characteristics could be obtained from survey

Table 7-20. Uncertainties associated with beef and milk ingestion exposure algorithms.

Assumption/ Method	Approach	Rationale	Uncertainty	Comments
Ingestion rates	22 g/day beef fat 10 g/day milk fat	Literature showed 14.9-26.0 g/day beef fat, and 18.8-43 g/day milk fat; ranges developed from 3 surveys	Shape of distribution of consumption not well defined; study and survey showing 43 g/day milk fat less well documented than other 2 surveys.	Beef and milk home producers may tend to ingest more than average families.
Contact rates	0.44 for beef fat 0.40 for milk fat	Data from USDA survey including percent of annual consumption of beef and milk homegrown.	Likely to be substantial differences between families; some may not home slaughter.	Again, home producers may obtain more than 44 or 40% of of beef and milk from their own supplies.
Beef and milk fat concentration model	Model of Fries and Paustenbach (1990) used; bioconcentration factor multiplied by proportionally weighted concentration in cattle diet, which is composed of soil, grass, feed.	A key premise was that 2,3,7,8-TCDD bioconcentrates equally in beef and milk fat; Fries and Paustenbach also developed key parameters used here as well.	Uncertainties associated with soil, pasture grass, and feed carry over into beef and milk fat concentrations; other uncertainties with parameters as noted below.	Section 7.2.4.6 shows how current approach is the same as earlier approaches which used whole beef and milk biotransfer factors and similar models for particle deposition impact to soil and vegetation. Also, air-to-beef validation exercise lends important credibility to approach (Section 7.2.3.9)
Key parameters and assumptions	Bioconcentration factor, BCF for dioxin-like compounds; soil bioavailability Bs of 0.65; and cattle diet fractions in soil, grass, and feed	BCFs developed from data in Mclachlin, et al. (1990); Bs from Fries and Paustenbach (1990); diet fractions generalized from infor- on lactating and grazing cattle.	Of three noted, BCF most uncertain; cattle diet assumptions also critical; but site-specific information could reduce uncertainty due to cattle exposures.	Fattening of beef cattle prior to slaughter could result in 50% or more reductions in fat concentrations; considered in air-to-beef validation, but not in general assessment.
Key associated models	For soil source categories, these are the soil-to-air, and air-to-plant algorithms; for stack emissions, these are air-to-soil and air-to-plant	the BCF is applied to a weighted average concentration of dioxin-like compound in cattle diet, which consists of soil, grass, feed	for soil models, uncertainties in air concentration of vapors and particles; for stack emission source, soil concentrations may be underestimated.	A key dichotomy which arises from these key associated models is the role of soil in the beef concentration; for the soil source category, cattle soil ingestion explains about 90% of beef fat concentrations; for the stack emission source, it explained only about 5% of the concentration.

Table 7-20 (cont'd).

Overall: The air-to-beef validation exercise described in Section 7.2.3.9 lends credibility to the algorithms estimating transfers of airborne dioxin-like compounds to vegetations cattle consume, and also to the bioconcentration model taking vegetation and soil concentrations and translating them to beef concentrations. However, uncertainties appear to exist for the soil source categories in modeling the soil to air transfers of dioxin-like compounds leading to an underestimation of air concentrations. This might lead to a requisite underestimation of beef/milk concentrations for the soil source category. Section 7.2.3.9 also shows that the air to soil deposition algorithms may be underestimating soil concentrations. Since beef concentrations are dominated by vegetation contributions to their diet - soil diet fractions are less than 10% - an underprediction of soil impacts for the stack emission source category may not have a great effect on beef/milk concentrations. Another literature comparison was with beef fat:soil and milk fat:soil concentration ratios, where Fries (1985) had developed such ratios for a farm known to be contaminated with PBBs, compounds similar in fate and persistence, and bioaccumulation tendencies, as the dioxin-like compounds. Field data showed ratios of 0.10-0.39 for beef and dairy cow body fat:soil, and 0.02-0.06 for milk fat:soil. In contrast, modeled ratios in the example soil contamination scenarios for 2,3,7,8-TCDD were 0.12 for beef fat:soil and 0.06 for milk fat:soil. Comparison with earlier modeling approaches showed that the current approach is the same as earlier approaches, although mathematically formulated differently. Earlier approaches also estimated cattle dose of 2,3,7,8-TCDD from contaminated air (directly) and contaminated ground water - these earlier estimations showed these contributions to be minimal, and they were not considered in this assessment. Early efforts in the literature did not consider vapor transfers to vegetations; one later assessment did include vapor transfers, and a key result in that assessment, as well as this one, is that vapor transfers are critical for beef/milk impacts. Finally, earlier assessments considered the practice of fattening beef cattle prior to slaughter by feeding them residue-free grains. These efforts estimated over a 50% reduction in beef concentration due to residue degradation or elimination and/or dilution with increases in body fat. The demonstrations scenarios in this assessment did not consider this practice.

information based on populations distant from the site, if comparability can be established.

Paustenbach et. al. (1992a) used Monte Carlo procedures to develop soil cleanup levels for 2,3,7,8-TCDD at residential and industrial sites. The following exposure pathways were included: dermal contact, soil ingestion, dust inhalation and fish ingestion. For each parameter a range of values was identified (on the basis of reported values in the literature) and a uniform distribution assumed. These assumptions are summarized in Table 7-21. For the residential scenario, the soil level corresponding to the 50th percentile (defined as 50% of the population being exposed below a risk of 10^{-5}) was 17 ppb and the 95th percentile was 7 ppb. For the industrial scenario (outdoors), the soil level corresponding to the 50th percentile was 160 ppb and the 95th percentile was 50 ppb.

Anderson et. al. (1992) used Monte Carlo procedures to describe the distribution of exposures to 2,3,7,8-TCDD occurring in various U.S. population segments as a result of ingesting fish caught near pulp and paper mills. The populations considered were all U.S. residents, all sportfishermen, U.S. residents living near (within 50 km) mills, and sportfishermen living near mills. The distributions for the various parameters were derived by either fitting idealized curves to empirical data or using personal judgement. These distributions are summarized in Table 7-22. The distribution of 2,3,7,8-TCDD concentrations in fish was derived from data collected in EPA's National Study of Chemical

Table 7-21. Distributions for a Monte Carlo exercise which developed soil cleanup levels at residential and industrial sites.

Parameter	Range (Residential)	Range (Industrial)
Soil Contact $\mu g/cm^2/d$	200 - 1800	same
Dermal Bioavailability Fraction	0.01 - 0.025	same
Fraction soil from site	0-5 yr: 0.1 - 1.0 6-30 yr: 0.1 - 0.5	0.1 - 1.0
Fraction indoor dust contaminated	(not considered)	0.25 - 1.0
Indoor exposure duration	0-1.5 yr: 182-365 d/yr 1.5-30 yr: 200-365 d/yr	0 - 8 hr/d 220 - 260 d/yr
Outdoor exposure duration	0-1.5 yr: 60-120 d/yr 1.5-30 yr: 60-240 d/yr	0 - 8 hr/d 220 - 260 d/yr
Soil ingestion rate, $\mu g/d$	0-1.5 yr: 100 - 10000 1.5-5 yr: 9000 - 50000 6-12 yr: 5000 - 50000 13-30 yr: 100 - 50000	100 - 50000 (indoors) 100 - 10000 (outdoors)
Oral Bioavailability	0.38, 0.40, 0.47, 0.49	same
Air particulate concen., $\mu g/m^3$	25 - 45	same
Fraction outdoor dust contaminated	0.1 - 0.5	same
Inhalation rate m^3/hr	0-1.5 yr: 0.03 - 0.07 1.5-5 yr: 0.3 - 0.9 6-12 yr: 0.75 - 1.5 13-30 yr: 0.5 - 1.5	9 - 14.6 m^3/d
Lipid Content of Fish	0.01 - 0.05	
Fish Bioavailability Index	0.01 - 0.5	
Organic Carbon content of sediment	0.01 - 0.5	
Fish Consumption g/d	0-1.5 yr: 0 1.5-5 yr: 0.38 - 0.62 6-12 yr: 0.63 - 1.0 13-30 yr: 1.1 - 1.8	
Fraction remaining after cooking	0.3 - 0.75	

Source: Paustenbach et. al. (1992a); uniform distributions assumed over ranges shown.

Table 7-22. Summary of Monte Carlo distributions used in a fish consumption assessment.

Exposure Parameter	Distribu-tion Type	Mean	Stand.Dev.	Min./Max.
Dioxin Conc. (ppt of TEq)	truncated lognormal	3.3	8.7	0.0002/ 16,000
Fraction caught in affected waters	triangular	0.09 (all US) 0.4 (near mill)	0.2 0.2	0/1.0 0/1.0
Consumption (g/d)	truncated lognormal	2.5 (all US) 19.1 (sport - fishermen)	7.3 27.9	0/240 0.2/403
Duration (yr)	truncated lognormal	13.3	12.3	0.1/70
Cooking Loss Fraction	uniform	0.1	0.3	0.25/0.75
Body Weight (kg)	normal	71	18.1	29.9/143.2

Source: Anderson et. al. (1992).

as exposure parameters. Distributions were developed for input factors and Monte Carlo Residues in Fish (EPA, 1992b). The following 50th and 95th percentile risks were estimated (using EPA cancer potency values):

all US residents - 1×10^{-9} & 3×10^{-7}
near mill residents - 4×10^{-8} & 2×10^{-6}
all sportfishermen - 2×10^{-8} & 3×10^{-6}
near mill sportfishermen - 6×10^{-7} & 2×10^{-5}

McKone and Ryan (1989) developed an exposure assessment procedure based on

simple steady state transfer factors called PEFs or pathway exposure factors. These factors were applied to two paths: air/plant/food and soil/plant/food. This is an example of Monte Carlo techniques being applied to estimate exposure media concentrations as well techniques were used to estimate the distribution of exposures. The procedure was demonstrated using 2,3,7,8-TCDD and four pathways: ingestion of fruit/vegetables, grains, meat and dairy products. The distributions used for the various input parameters are summarized in Table 7-23.

The three articles discussed above differ widely in how they have applied Monte Carlo methods, particularly in the selection of input parameter distributions. In some cases, it appears that uniform distributions were assumed due to the lack of data needed to support more complex distributions. The central values in these ranges probably occur more often than those near the ends, so the uniform distribution assumption probably underestimates the occurrence of central values and overestimates the occurrence of values near the ends of the distribution. Clearly more data are needed to better support input parameter distributions.

These three articles are just a small set of the growing body of literature on the topic of applying Monte Carlo methods to exposure and risk assessments. For example, the application of Monte Carlo methods to problems involving contaminated groundwater and related exposure pathways such as ingestion, indoor air inhalation and dermal contact with water has recently been examined (McKone and Bogen, 1991). Although this work does not deal specifically with dioxin, it may be informative to readers generally interested in Monte Carlo procedures. Similarly, Paustenbach has published additional articles dealing with the application of Monte Carlo methods to exposure problems involving other chemicals (Pasutenbach et al. 1991; Paustenbach, et al., 1992a). Burmaster has also published numerous articles on this topic which may be of general interest to readers (ie. Burmaster and Stackelberg, 1991).

Table 7-23. Summary of Monte Carlo distributions used in food chain study.

Parameter	Geo. Mean	GSD[1]	Distrib.
Milk Ingestion 0-15 yr: kg/kg/d 15-70 yr:	0.014 0.0033	1.2 1.1	log normal
Meat Ingestion 0-15 yr: kg/kg/d 15-70 yr:	0.0044 0.0029	1.1 1.2	log normal
Fruit/Veg Ing. 0-15 yr: kg/kg/d 15-70 yr:	0.0081 0.0045	1.4 1.3	log normal
Grain Ing. 0-15 yr: kg/kg/d 15-70 yr:	0.0074 0.0030	1.2 1.2	log normal
Particle to Food Dep-osition Factor, m/d	300	3	log normal
Plant/Soil Part. Factor	0.013	4.0	log normal
Biotransfer Fac. Cattle Intake to Meat, d/kg	0.055	3.0	log normal
Biotransfer Fac. Cattle Intake to Milk, d/kg	0.01	3.0	log normal
	Lower Bound	Upper Bound	
Annual Inventory Food Crops, kg/m^2	1.0	10.0	log uniform
Annual Inventory Pasture Crops, kg/m^2	0.1	1.0	log uniform
Weathering Rate Constant, 1/d	0.01	0.1	log uniform
Cattle Inhalation Rate m^3/d	63	177	uniform
Beef Cattle Ingestion of Pasture Grass, kg/d	4.0	20	uniform
Dairy Cattle Ingestion of Pasture Grass, kg/d	11	23	uniform
Cattle Soil Ingestion kg/d	0.1	0.83	uniform

1. Geometric Standard Deviation
Source: McKone and Ryan, 1989.

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