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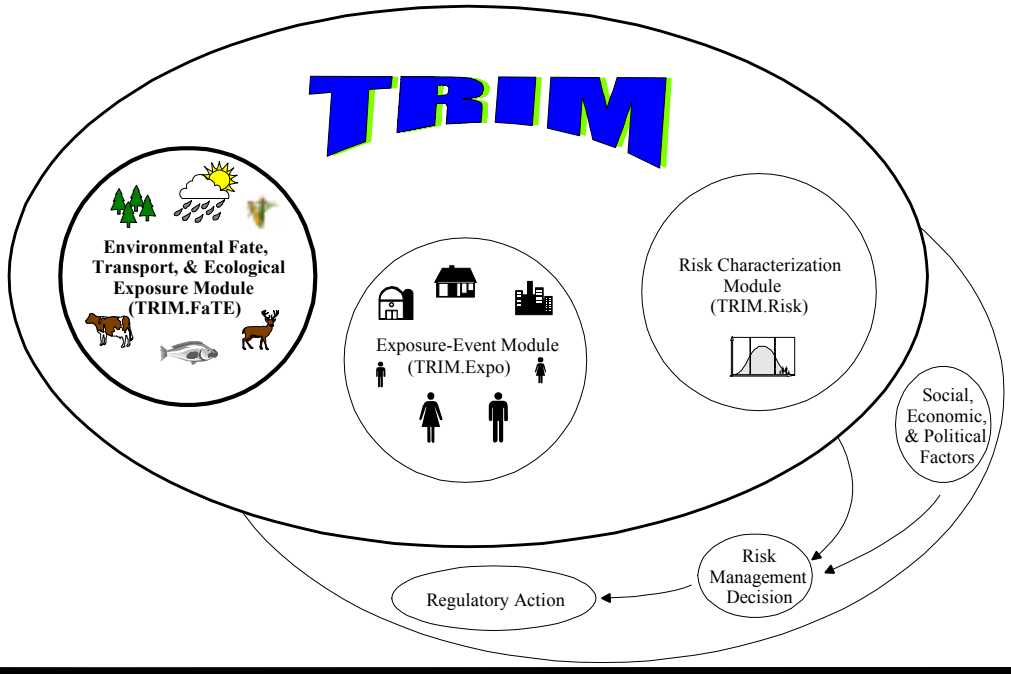
Air

TRIM
Total Risk Integrated Methodology

TRIM.FaTE
TECHNICAL SUPPORT DOCUMENT
Volume II: Description of Chemical Transport and Transformation Algorithms

EXTERNAL REVIEW DRAFT



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Volume II: Description of Chemical Transport and Transformation Algorithms

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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PREFACE

This draft document, the *TRIM.FaTE Technical Support Document*, is part of a series of documentation for the overall Total Risk Integrated Methodology (TRIM) modeling system. The detailed documentation of TRIM's logic, assumptions, algorithms, equations, and input parameters is provided in comprehensive Technical Support Documents (TSDs) for each of the TRIM modules. The purpose of the TSDs is to provide full documentation of how TRIM works and of the rationale for key development decisions that were made. This report, which supersedes an earlier version (U.S. EPA 1998a), documents the Environmental Fate, Transport, and Ecological Exposure module of TRIM (TRIM.FaTE) and is divided into two volumes. The first volume provides a description of terminology, model framework, and functionality of TRIM.FaTE, and the second volume presents a detailed description of the algorithms used in the module.

To date, EPA has issued draft TSDs for TRIM.FaTE (this report) and the Exposure-Event module (*TRIM.Expo TSD*, U.S. EPA 1999a). When the Risk Characterization module (TRIM.Risk) is developed, EPA plans to issue a TSD for it. The TSDs will be updated as needed to reflect future changes to the TRIM modules.

The EPA has also issued the 1999 *Total Risk Integrated Methodology (TRIM) Status Report* (U.S. EPA 1999b). The purpose of that report is to provide a summary of the status of TRIM and all of its major components, with particular focus on the progress in TRIM development since the 1998 *TRIM Status Report* (U.S. EPA 1998b). The EPA plans to issue status reports on an annual basis while TRIM is under development.

In addition to status reports and TSDs, EPA intends to develop detailed user guidance for the TRIM computer system. The purpose of such guidance will be to define appropriate (and inappropriate) uses of TRIM and to assist users in applying TRIM to assess exposures and risks in a variety of air quality situations.

Comments and suggestions are welcomed. The OAQPS TRIM team members, with their individual roles and addresses, are provided below.

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ACRONYMS

B(a)P	Benzo(a)pyrene
BW	Body weight
DOC	Dissolved organic carbon
EPA	United States Environmental Protection Agency
GI	Gastrointestinal
GIS	Geographic Information Systems
HAP	Hazardous air pollutant
IEM	Indirect Exposure Methodology
LSODE	Livermore Solver for Ordinary Differential Equations
NERL	National Exposure Research Laboratory
OAQPS	EPA Office of Air Quality Planning and Standards
OPPT	Office of Pollution Prevention and Toxics
ORD	Office of Research and Development
OW	Office of Water
PAH	Polycyclic aromatic hydrocarbon
R-MCM	Regional Mercury Cycling Model
SAB	Science Advisory Board
TOC	Total organic carbon
TRIM	Total Risk Integrated Methodology
TRIM.Expo	TRIM Exposure-Event module
TRIM.FaTE	TRIM Environmental Fate, Transport, and Ecological Exposure module
TRIM.Risk	TRIM Risk Characterization module
TSD	Technical Support Document
WASP	Water Quality Analysis Simulation Program

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1. INTRODUCTION

This volume presents the algorithms used to describe the transport and transformation of chemicals in the TRIM.FaTE module. These algorithms are used to estimate the physical and chemical processes that drive chemical transport and transformation in the environment. As explained in Volume I of this report, the TRIM.FaTE framework can incorporate first-order and higher order algorithms. At the present time, however, only first-order algorithms have been implemented in the model.

First-order transfer between compartments in TRIM.FaTE is described by ***transfer factors***, referred to as T-factors. This volume documents all of the T-factors currently implemented in TRIM.FaTE. A T-factor is approximately the instantaneous flux of the chemical in the receiving compartment normalized by the amount of chemical in the sending compartment (see Section 4.2 in Volume I of this report for more discussion about the units of T-factors and related issues). That is, $T * N(t)$ is the instantaneous flux in units of chemical mass/time, where $N(t)$ is the chemical mass in the sending compartment at time t. The compartment that receives the mass lost from the sending compartment is referred to as the receiving compartment.

The **transfer factor**, or T-factor, is the instantaneous chemical flux normalized by the current chemical mass in the sending compartment. That is, T-factors are time-dependent.

Because it is a normalized flux, a large T-factor in itself does not imply that the flux is large; the actual flux also depends on the amount of chemical in the sending compartment. The T-factor is not the same as the fraction of mass lost in a given time interval, although the two quantities are related. When the fraction of mass lost is small, these two quantities are generally approximately the same, but they differ significantly when the fraction of mass lost is larger. In particular, $T = -\ln(1-p)$, where p is the fraction of mass lost in one simulation time step, and the units of time are the same as T.

Chapter 2 presents a general description of how each of the different transport and transformation processes are modeled in TRIM.FaTE. Chapters 3 through 6 present the abiotic algorithms for air (Chapter 3), surface water and sediment (Chapter 4), soil (Chapter 5), and ground water (Chapter 6). For simplicity, the algorithms used to describe intermedia transport are only presented in one of the chapters and referenced in the other.

Chapter 7 presents the algorithms used to describe transport of chemical mass between biotic compartment types and between biotic and abiotic compartment types. Chapters 3 through 7 begin with a brief summary of the algorithms described in the chapter and then explain each algorithm in greater detail. While Chapters 2 through 7 focus on the general algorithms used in TRIM.FaTE, Appendix A presents the chemical-specific algorithms for mercury and PAHs.

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2. ALGORITHM OVERVIEW

In this chapter, algorithms that generally apply across a range of compartment types are discussed. Algorithms specific to compartment types are presented in subsequent chapters.

2.1 MULTIPLE-PHASE CALCULATIONS

This section describes how multiple phases within a compartment are currently modeled. The most common phases considered in the prototype are liquid, gas, and solid, which are assumed to be at chemical equilibrium. Other phases may include biotic phases (*e.g.*, algae in surface water). Because chemical equilibrium among phases in a compartment is assumed, the ratios of the concentrations in the individual phases are constant, and mass balance need only be tracked for the total amount of the chemical in all phases in a compartment. The amount of chemical in the compartment in a particular phase can be determined from the total amount in the compartment (described in the following text). It is possible that, in future versions of TRIM.FaTE, chemical equilibrium will not be assumed, in which case the amount of chemical in different phases will need to be tracked as separate compartments.

In any compartment, the total amount of chemical in a given compartment is made up of the sum of the amounts in the different phases:

$$\begin{aligned} N^{Total} &= Amount\ in\ gas\ phase\ +\ Amount\ in\ \ aqueous\ phase\ +\ Amount\ in\ solid\ phase \\ &= C^{gas}V^{gas}\ +\ C^{water}V^{water}\ C^{solid}V^{solid} \end{aligned} \quad (2\text{-}1)$$

where:

N^{Total}	=	total amount of chemical in compartment (g [chemical])
C^{gas}	=	concentration of chemical in gas phase in compartment (g [chemical]/m^3 [gas in compartment])
V^{gas}	=	volume of gas in compartment (m^3 [gas in compartment])
C^{water}	=	concentration of chemical in aqueous phase in compartment (g [chemical]/m^3 [water in compartment])
V^{water}	=	volume of aqueous matter in compartment (m^3 [water in compartment])
C^{solid}	=	concentration of chemical in solid phase in compartment (g [chemical]/m^3 [solid in compartment])
V^{solid}	=	volume of solid in compartment (m^3 [solid in compartment]).

If it is desired that the units of N^{Total} be in units of moles (chemical), then the preceding equation must be multiplied by the molecular weight of the chemical (which has units of moles [chemical]/g [chemical]).

Because chemical equilibrium is assumed, the ratios of the concentrations are constant. However, care must be used in specifying the units of the concentration. This is because, in

practice, it is more common to define notation for ratios of concentrations on a mass by mass basis rather than that of mass by volume basis.

2.1.1 NORMALIZATION TO LIQUID PHASE

This section describes the relevant formulas when the concentrations in other phases are normalized to the concentration in the liquid phase. This normalization is used for all soil, surface water, and sediment compartments (including the cases where additional phases are considered). Using the equilibrium assumptions:

$$C^{solid} = (\rho_{solid} K_d C_f) C^{water} \tag{2-2}$$

$$C^{gas} = (H/RT) C^{water} \tag{2-3}$$

where:

ρ_{solid}	=	density of solid phase in compartment (kg [solid phase]/m^3 [solid phase])
K_d	=	equilibrium partition coefficient; ratio of concentration in solid phase (kg [chemical]/kg [solid phase]) to that in liquid phase (kg [chemical]/liters [L][liquid phase])
C_f	=	10^{-3} m^3/L, conversion factor to convert m^3 (liquid phase) to L (liquid phase)
H	=	Henry's law constant for chemical (Pa-m^3/mol)
R	=	ideal gas constant (8.314 m^3-Pa/mol-K)
T	=	temperature (K)

Applying these relationships to the general equation in the beginning of this section yields:

$$N^{Total} = C^{water} \left(\frac{H}{RT} V^{gas} + V^{water} + \rho_{solid} K_d C_f V^{solid} \right) \tag{2-4}$$

The volumes of each phase in the compartment can be expressed as fractions of the total volume of the compartment, in which case the previous equation yields:

$$N^{Total} = C^{water} V^{Total} \left(\frac{H}{RT} \frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right) \tag{2-5}$$

where:

$$V^{Total} = V^{gas} + V^{water} + V^{solid}$$

The term $C^{Total} = N^{Total}/V^{Total}$ is the total concentration of the chemical in the compartment. Using the assumed equilibrium relationships, the concentrations in the individual phases can be recovered from the total amount of mass in the compartment, as follows:

$$C^{water} = \frac{N^{Total}/V^{Total}}{\left(\frac{H}{RT}\frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \tag{2-6}$$

$$C^{gas} = \frac{H}{RT} C^{water} = \frac{(H/RT) N^{Total}/V^{Total}}{\left(\frac{H}{RT}\frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \tag{2-7}$$

$$C^{solid} = \rho_{solid} K_d C_f C^{water} = \frac{(\rho_{solid} K_d C_f) N^{Total}/V^{Total}}{\left(\frac{H}{RT}\frac{V^{gas}}{V^{Total}} + \frac{V^{water}}{V^{Total}} + \rho_{solid} K_d C_f \frac{V^{solid}}{V^{Total}} \right)} \tag{2-8}$$

For cases in which the concentration in the water phase is negligible (*e.g.*, when compartment is air, or the chemical has a very low solubility), the concentrations must be normalized to another phase.

2.1.2 FRACTION OF CHEMICAL IN EACH PHASE WHEN PHASES ARE IN EQUILIBRIUM

2.1.2.1 General Form

If a chemical is in equilibrium among several phases within a compartment, it is straightforward to calculate the fraction of the chemical that is in each phase. In particular, if there are *n* phases in equilibrium, with:

$$\begin{aligned} C_1 &= \kappa_1 C_{norm} \\ C_2 &= \kappa_2 C_{norm} \\ C_3 &= \kappa_3 C_{norm} \\ &\vdots \\ C_n &= \kappa_n C_{norm} \end{aligned} \tag{2-9}$$

where C_j is the concentration of the chemical in phase j (units of mass [chemical]/volume [phase j]), C_{norm} is the concentration in the phase to which one is normalizing, and κ_j is the equilibrium ratio between the concentration in phase j and the phase to which one is normalizing, with units of (mass [chemical]/volume [phase j])/(mass [chemical]/volume [phase to which one is normalizing]). These ratios κ_j are generally expressed in terms of other environmental and/or chemical parameters. The total mass of chemical in the compartment, denoted by N^{Total}, is:

$$\begin{aligned} N^{Total} &= \sum_{j=1}^{n} V_j C_j \\ &= \sum_{j=1}^{n} V_j \kappa_j C_{norm} \\ &= C_{norm} \sum_{j=1}^{n} V_j \kappa_j \end{aligned} \tag{2-10}$$

where V_j is the volume of phase j in the compartment, and $\sum_{j=1}^{n} V_j = V_{total}$. The fraction of mass of chemical in phase j is then given by:

$$\begin{aligned} \frac{\textit{Mass of chemical in phase j in compartment}}{\textit{Total mass of chemical in compartment}} &= V_j C_j / N^{Total} \\ &= \frac{V_j \kappa_j C_{norm}}{C_{norm} \sum_{j'=1}^{n} V_{j'} \kappa_{j'}} \\ &= \frac{V_j \kappa_j}{\sum_{j'=1}^{n} V_{j'} \kappa_{j'}} \end{aligned} \tag{2-11}$$

When applied to the previous section (and using the notation introduced there), we have that $C_{norm}=C_{water}$, and the terms κ are given by:

$$\kappa_{water} = 1 \tag{2-12}$$

$$\kappa_{gas} = H/(RT) \tag{2-13}$$

$$\kappa_{solid} = \rho_{solid} K_d C_f \tag{2-14}$$

2.1.2.2 Form When Fugacity Concept Is Applicable

It is sometimes convenient to apply the concept of fugacity (Mackay 1991) when presenting the equations. For the chemicals modeled to date (PAH, B(a)P, elemental mercury, divalent mercury, and methylmercury), the algorithms are presented using the fugacity notation. Fugacity has units of pressure and can be linearly or non-linearly related to concentration through the relationship fugacity (f) = (fugacity capacity [Z]) · (concentrations). The fugacity capacities for the pure phases of water, air, and solid are:

$$Z_{water} = 1/H \tag{2-15}$$

$$Z_{air} = 1/(RT) \tag{2-16}$$

$$Z_{solid} = \rho_{solid} K_d C_f Z_{water} \tag{2-17}$$

defined by:

ρ_{solid}	=	density of solid phase in compartment (kg [solid phase]/m^3 [solid phase])
K_d	=	equilibrium partition coefficient; ratio of concentration in solid phase (kg [chemical]/kg [solid phase]) to that in liquid phase (kg [chemical]/liters [L][liquid phase])
C_f	=	10^{-3} m^3/L, conversion factor to convert m^3 (liquid phase) to L (liquid phase)
H	=	Henry's law constant for chemical (Pa-m^3/mol)
R	=	ideal gas constant (8.314 m^3-Pa/mol-K)
T	=	temperature (K)

The total fugacity capacity Z^{Total} for a given compartment is defined as:

$$Z^{Total} = Z_{air}\frac{V^{gas}}{V^{Total}} + Z_{water}\frac{V^{water}}{V^{Total}} + Z_{solid}\frac{V^{solid}}{V^{Total}} \tag{2-18}$$

where phase is either the solid, liquid, gas, or other phase.

It is fundamental to the concept of partition modeling that the concentration ratio between two phases is equal to the ratios of the fugacity capacities of the two phases (Mackay 1991). That is,

$$\frac{C^{phase_1}}{C^{phase_2}} = \frac{Z_{phase_1}}{Z_{phase_2}} \tag{2-19}$$

Applying these relationships shows that:

$$C^{water} = \frac{Z_{water}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{water}}{Z^{total}} C^{total} \quad (2\text{-}20)$$

$$C^{gas} = \frac{Z_{air}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{gas}}{Z^{total}} C^{total} \quad (2\text{-}21)$$

$$C^{solid} = \frac{Z_{solid}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = \frac{Z_{solid}}{Z^{total}} C^{total} \quad (2\text{-}22)$$

where C^{Total} is the total concentration of the chemical in the compartment (units of g [chemical]/m^3[total compartment]). From these relationships, in general, the amount of mass in the different phases is given by:

$$N^{water} = V^{water} C^{water} = V^{water} \frac{Z_{water}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{water} \frac{Z_{water}}{Z^{total}} C^{total} \quad (2\text{-}23)$$

$$N^{gas} = C^{gas} V^{gas} = V^{gas} \frac{Z_{air}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{gas} \frac{Z_{gas}}{Z^{total}} C^{total} \quad (2\text{-}24)$$

$$N^{solid} = C^{solid} V^{solid} = V^{solid} \frac{Z_{solid}}{Z^{total}} \frac{N^{Total}}{V^{Total}} = V^{solid} \frac{Z_{solid}}{Z^{total}} C^{total} \quad (2\text{-}25)$$

where N^{water}, N^{gas}, and N^{solid} are the mass in the water, gas, and solid phases, respectively.

If there are other phases in equilibrium with the chemical dissolved in the water phase, then the fugacity capacities of that phase can be defined in a manner consistent with that above. For example, if $C_{other} = \kappa_{other} C_{water}$, where C_{other} has units of g[chemical]/m^3[*other* phase], then the fugacity capacity of the other phase is defined by:

$$Z_{other} = \kappa_{other} Z_{water} \quad (2\text{-}26)$$

and the total fugacity capacity of the compartment is given by:

$$Z^{Total} = Z_{air} \frac{V^{gas}}{V^{Total}} + Z_{water} \frac{V^{water}}{V^{Total}} + Z_{solid} \frac{V^{solid}}{V^{Total}} + Z_{other} \frac{V^{other}}{V^{Total}} \quad (2\text{-}27)$$

where V^{other} is the volume of the other phase, in units of m^3[*other* phase].

In the following sections, the general equations presented in this section for multiple phase calculations are applied to specific compartment types. The use of these equations in the

following sections primarily involves only adhering to notation commonly used in the literature for the different media.

2.1.3 APPLICATION TO SOIL, SURFACE WATER, AND SEDIMENT COMPARTMENT TYPES

For soil, surface water, and sediment compartment types, the concentrations are normalized to the concentration in the liquid phase, and the same notation is used to represent the relevant parameters. In a soil compartment, the solid phase consists of the soil particles. In a surface water compartment, the solid phase consists of the sediment suspended in the water column. In a sediment compartment, the solid phase consists of clay, silt, or sand particles as opposed to the water phase that fills the interstitial space between the sediment solid particles. Following common practice, the volume fractions of each phase are denoted as follows:

$$\frac{V^{water}}{V^{total}} = \theta \tag{2-28}$$

$$\frac{V^{gas}}{V^{total}} = \epsilon \tag{2-29}$$

$$\frac{V^{solid}}{V^{total}} = 1 - \theta - \epsilon = 1 - \phi \tag{2-30}$$

where:

θ	=	water volume fraction
ϵ	=	gas volume fraction
$1-\theta-\epsilon$	=	$1-\phi$ = solid volume fraction

where ϕ is the total porosity of the compartment ($= \theta + \epsilon$). The equations for the total mass of chemical in the compartment and in the different phases are then given by:

$$N^{Total} = C^{water} V^{Total} \left(\frac{H}{RT}\epsilon + \theta + \rho_{solid} K_d C_f (1-\phi) \right) \tag{2-31}$$

If there are other phases in equilibrium with the chemical in the water phase, then the previous equation is augmented as follows:

$$N^{Total} = C^{water} V^{Total} \left(\frac{H}{RT}\epsilon + \theta + \rho_{solid} K_d C_f \left(1 - \phi - \sum_{j=1}^{m} \psi_j \right) + \sum_{j=1}^{m} K_j \psi_j \right) \tag{2-32}$$

where:

K_j = equilibrium ratio of concentration of chemical in phase *j* and concentration dissolved in water phase (g [chemical]/m^3 [phase *j*])/(g [chemical]/ m^3 [water])

ψ_j = volume fraction of compartment composed of phase *j* (m^3[phase *j*]/m^3[total])

Fugacity-based Notation

If fugacity-based notation is to be used, then the total fugacity for the compartment is given by:

$$Z^{total} = Z_{air}\epsilon + Z_{water}\theta + Z_{solid}(1-\phi) \quad (2\text{-}33)$$

In the general case when there are additional equilibrium phases considered:

$$Z^{total} = Z_{air}\epsilon + Z_{water}\theta + Z_{solid}\left(1-\phi-\sum_{j=1}^{m}\psi_j\right) + \sum_{j=1}^{m} Z_j\psi_j \quad (2\text{-}34)$$

where Z_j is the fugacity of phase *j*.

Note that for the ground water, surface water, and sediment compartment types, the volume fractions of the gas phase (ϵ) are assumed to be zero.

The soil-water partition coefficients (K_d) in each compartment (soil, surface water, and sediment) may be either input or calculated. At present, they are input for mercury species, and calculated for nonionic organic chemicals (Karickhoff 1981) by:

$$K_d = K_{oc} f_{oc} \quad (2\text{-}35)$$

where:

K_{oc} = organic-carbon partition coefficient

f_{oc} = fraction of organic carbon in the compartment.

2.1.4 MULTIPHASE PARTITIONING IN THE AIR COMPARTMENT TYPE

Because the volume of water in an air compartment is so small relative to the volume of the solid and the gas phase, there has not been a historical development of K_d's (*i.e.*, ratio of concentration in solid phase to that in dissolved phase) for the atmosphere, although the concept still applies. Instead, only the solid and gas phases are usually addressed. If chemical equilibrium is assumed between the phases, then a normalization other than to the liquid

concentration is required. In an air compartment, the solid phase consists of the particulate matter in the atmosphere.

At present, the volume fractions of solids in each phase in an air compartment are given by:

$$\frac{V^{water}}{V^{total}} = 0 \tag{2-36}$$

$$\frac{V^{solid}}{V^{total}} = D_L/\rho_{dust} \tag{2-37}$$

$$\frac{V^{gas}}{V^{total}} = 1 - D_L/\rho_{dust} \tag{2-38}$$

where:

D_L = atmospheric dust load in air compartment (kg [aerosol]/m^3 [air compartment])

ρ_{dust} = density of aerosols (kg [aerosol]/m^3 [aerosol]).

The dust load and aerosol density are specified properties of each air compartment. To normalize to either the gas or solid phase, the equilibrium ratio of the concentrations in the two phases must be estimated. In the prototype, the fraction of the contaminant bound to particles, denoted by φ, is estimated using a method developed in Junge (1977) for organics, and a more recent method developed by Harner and Bidleman (1998) that is applied for mercury, both of which are discussed in the subsequent sections. Use of this term in the current notation is:

$$V^{solid}\, C^{solid} = \varphi \tag{2-39}$$

$$V^{gas}\, C^{gas} = 1 - \varphi \tag{2-40}$$

From this, the equilibrium ratio of the concentration in the solid phase to that in the gas phase in an air compartment is given by:

$$\frac{C^{solid}}{C^{gas}} = \frac{\varphi/V^{solid}}{(1-\varphi)/V^{gas}}$$

$$= \frac{\varphi/(DL/\rho_{dust})}{(1-\varphi)/(1-DL/\rho_{dust})} \tag{2-41}$$

$$= \frac{\varphi(1-DL/\rho_{dust})}{(1-\varphi)(DL/\rho_{dust})}$$

The total mass of chemical in the air compartment is then:

$$\begin{aligned} N^{Total} &= C^{gas} V^{Total} \left((1 - DL/\rho_{dust}) + \frac{C^{solid}}{C^{gas}} (DL/\rho_{dust}) \right) \\ &= C^{gas} V^{Total} \left((1 - DL/\rho_{dust}) + \frac{\varphi(1 - DL/\rho_{dust})}{(1-\varphi)(DL/\rho_{dust})} (DL/\rho_{dust}) \right) \\ &= C^{gas} V^{Total} \left((1 - DL/\rho_{dust}) + \frac{\varphi(1 - DL/\rho_{dust})}{(1-\varphi)} \right) \\ &= C^{gas} V^{Total} (1 - DL/\rho_{dust}) \left(1 + \frac{\varphi}{1-\varphi} \right) \end{aligned} \tag{2-42}$$

Fugacity-based Notation

For the air compartment, the fugacity capacity in the solid phase can be determined by use of the relationship as follows.

$$\begin{aligned} Z_{solid} &= Z_{air} \frac{C^{solid}}{C^{gas}} \\ &= Z_{air} \frac{\varphi(1 - DL/\rho_{dust})}{(1-\varphi)(DL/\rho_{dust})} \end{aligned} \tag{2-43}$$

where $Z_{air}=1/(RT)$, R is the ideal gas constant (8.314 m^3-Pa/mol-K), and T is temperature (K).

The total fugacity in the air compartment is then given by:

$$\begin{aligned} Z^{total} &= Z_{air} \frac{V^{gas}}{V^{Total}} + Z_{solid} \frac{V^{solid}}{V^{Total}} \\ &= Z_{air}(1 - D_L/\rho_{ust}) + Z_{solid} D_L/\rho_{dust} \end{aligned} \tag{2-44}$$

2.1.5 CALCULATION OF THE FRACTION OF CONTAMINANT BOUND TO AEROSOL

In the prototype, the fraction of chemical bound to particulate in the air compartment, denoted by φ_i, is calculated using one of two methods. The first method discussed here is discussed in Harner and Bidleman (1998), while the second is due to Junge (1977). The current TRIM.FaTE model relies on the method of Harner and Bidleman. Note that in each of these

methods, any chemical with extremely low or essentially zero vapor pressure is assumed to be 100 percent bound to particulate matter in the air (*e.g.,* cadmium, lead).

2.1.5.1 K_{OA}-based Method

In Harner and Bidleman (1998), a "K_{OA} absorption model" is shown to fit to PCB data better than a Junge-Pankow model similar to that discussed in the previous section. Further, the parameters needed are considered to be more easily measurable than the parameters for the Junge-Pankow model. Using the notation of that paper, this model first estimates the particle/gas partition coefficient (K_P) in terms of the octanol-air partition coefficient and the fraction of organic matter attached to particles, and then one calculates the fraction of compound in the particle phase via the relationship:

$$\varphi = \frac{K_P\,(TSP)}{1 + K_P\,(TSP)} \tag{2-45}$$

where:

K_P = particle/gas partition coefficient for compound (ng[chemical]/µg[particles])/(ng[chemical]/m^3[air])
TSP = total suspended particle concentration (µg[particles]/m^3[air])

Using the notation of this section, the following relationship exists:

$$TSP = 10^9\, D_L \tag{2-46}$$

where D_L is the dust load for the air compartment (kg[particle]/m3[air]).

The particle/gas partition coefficient K_P is calculated via the regression:

$$\log K_P = \log K_{OA} + \log f_{om} - 11.91 \tag{2-47}$$

where:

K_{OA} = octanol-air partition coefficient
f_{om} = organic fraction of the aerosol

If the octanol-air partition coefficient is not available, it can be calculated from the octanol-water partition coefficient K_{ow} via the relationship:

$$K_{OA} = K_{OW}\,(RT/H) \tag{2-48}$$

where the units of R, T, and H are such that the quantity RT/H is unitless.

2.1.5.2 Junge's Method

This method has been used in existing multimedia models and is available as an alternative. This discussion is based on that presented in CalTOX (McKone 1993a,McKone 1993b, McKone 1993c). With this method, the fraction of chemical bound to aerosol is calculated via the formula:

$$\varphi = \frac{c\,\theta}{VP + c\,\theta} \tag{2-49}$$

where:

VP	=	vapor pressure or subcooled vapor pressure of the chemical (Pa)
c	=	empirical constant set to 0.173 as in Junge (1977) (m-Pa)
θ	=	total surface of aerosols per volume of aerosol (m^2/m^3).

There is a range of values for θ, with Whitby (1978) reporting a range of values of 4.2 x 10^{-5} m^2/m^3 for a "clean" continental site to $1.1x10^{-5}$ m^2/m^3 for urban sites. The average of these values is used as the default for θ.

Following CalTOX (McKone 1993a,McKone 1993b, McKone 1993c), the subcooled vapor pressure (vapor pressure of subcooled liquid) is used if the temperature is below the melting point (T_m) of the chemical. In particular:

$$VP = \begin{cases} VP & if\ T > T_m \\ \exp[6.79(T_m/T - 1)] & if\ T \le T_m \end{cases} \tag{2-50}$$

where:

VP	=	vapor pressure or subcooled vapor pressure of the chemical (Pa)
T	=	temperature (K)
T_m	=	melting point (K)

2.2 CONVERTING EQUATIONS WITH EQUILIBRIUM RELATIONSHIPS TO DYNAMIC FORM

In the course of converting equations to a form that is suitable for use within the intended framework, it is possible to convert some algorithms that represent steady-state equilibrium relationships into time-dependent ones. This can be performed if an estimate of the time required for the concentration to reach some fraction of the steady-state value is available. In particular, if the concentration in one compartment C_1 is related to the concentration in another compartment C_2 by an equilibrium relationship of the form $C_1 = K\,C_2$, where K is known and it is known that it

takes time t_α in order to reach 100α percent of the steady-state value when C_2 is approximately constant, then:

$$\frac{dC_1(t)}{dt} = k_2 C_2 - k_1 C_1 \tag{2-51}$$

where k_1 and k_2 are defined as:

$$k_1 = -\ln(1-\alpha)/t_\alpha \tag{2-52}$$
$$k_2 = K\, k_1 \tag{2-53}$$

The solution of the previous differential equation with initial condition $C_1(0) = 0$ is given by:

$$C_1(t) = \frac{k_2}{k_1} C_2 \left(1 - e^{-k_1 t}\right) \tag{2-54}$$

The steady-state solution is $C_1(t) = (k_2/k_1)\, C_2$, and so $K = k_2/k_1$. This assumption that 100α percent of the steady-state value is reached at time t_α means that:

$$1 - e^{-k_1 t_\alpha} = \alpha \tag{2-55}$$

Solving for k_1 yields:

$$k_1 = -\ln(1-\alpha)/t_\alpha \tag{2-56}$$

When k_1 is determined, $k_2 = k_1 K$, from which the general result (*i.e.,* Equations 2-52 and 2-53) follows.

2.3 GENERAL FATE AND TRANSPORT PROCESSES

2.3.1 ADVECTIVE PROCESSES

In general, the advective flux in a given phase (*e.g.*, attached to particles, or dissolved in water) from compartment *i* to compartment *j* is given by:

Advective flux from compartment i to compartment j = (Volume of phase that moves from compartment i to compartment j per unit time) x (Amount of chemical in phase per volume of phase in compartment i) (2-57)

or

$$\begin{aligned} \textit{Advective flux Compartment } i \rightarrow \textit{Compartment } j &= Q(phase) \times \frac{N_i(t) \times f_i(phase)}{V_i(phase)} \\ &= T_{i \rightarrow j}^{adv}(phase) \times N_i(t) \end{aligned} \quad (2\text{-}58)$$

where:

$Q\ (phase)$	=	volumetric flux of phase from compartment *i* to compartment *j* (m^3[phase]/day)
$N_i(t)$	=	amount of chemical in compartment *i* at time (moles [chemical])
$f_i(phase)$	=	fraction of chemical in compartment *i* that is in the moving phase (moles [chemical in phase]/moles [chemical in compartment *i*])
$V_i(phase)$	=	volume of phase that is in compartment *i* (m^3[phase])
$T_{i \rightarrow j}^{adv}(phase)$	=	phase transfer factor for advective flux from compartment *i* to receiving compartment *j* (1/day), given by:

$$T_{i \rightarrow j}^{adv}(phase) = \frac{Q(phase) \times f_i(phase)}{V_i(phase)} \quad (2\text{-}59)$$

This formula for the transfer factor is valid for all advective processes from one compartment to another, and does not rely on the fugacity concept. Application of the concept of fugacity (as presented in Section 2.1.2.2) shows that:

$$f_i(phase) = \frac{Z_i(phase)}{Z_i(Total)} \times \frac{V_i(phase)}{V_i(Total)} \quad (2\text{-}60)$$

where:

$Z_i(phase)$	=	fugacity capacity for moving phase (mol/m^3[phase]-Pa)
$Z_i(Total)$	=	total fugacity capacity for compartment *i* (mol/m^3[sending compartment *i*]-Pa)
$V_i(Total)$	=	total volume of compartment *i* (sum of volumes of each phase in compartment) (m^3[compartment *i*]).

Applying this shows that the fugacity-based form for the transfer factor for advective flux is:

$$T_{i \to j}^{adv}(phase) = \frac{Q\ (phase) \times Z_i(phase)}{V_i(Total) \times Z_i(Total)} = \frac{v\ (phase)\ \times\ A_{ij} \times Z_i(phase)}{V_i(Total) \times Z_i(Total)} \quad (2\text{-}61)$$

In most applications, the volumetric flow rate *Q(phase)* of the phase is calculated as the product of a relevant area (A_{ij}) and the volumetric flow rate per unit area, or a flow velocity (v_{ij}). Usually the relevant area is the interfacial area between the sending and receiving compartments, but this is not always the case; *e.g.*, erosion from surface soil to surface water is usually reported in units of mass (soil)/area (soil layer)-time, in which case the relevant area is the area of the surface soil layer. Table 2-1 summarizes the velocities included for compartment types in the prototype. These flows are discussed in more detail in the sections describing the specific compartment types.

2.3.2 REACTION AND TRANSFORMATION PROCESSES

At present, all reaction and transformation processes are modeled using a first-order rate constant *k* (units of 1/day). The reaction/transformation flux within a compartment is then given by *k N(t)*, where *N(t)* is the mass of chemical in the compartment. There are a variety of ways in which the rate constant is determined, with the details depending on the compartment types and chemicals involved. The simplest is the case where the rate constant is an input (*e.g.*, for the current mercury species transformation algorithms). In other cases, the rate constant may be calculated from other environmental and/or chemical parameters (*e.g.*, from a half-life input by the user).

2.3.3 BIOTIC PROCESSES

The biotic processes in TRIM.FaTE are well characterized by the descriptions of abiotic processes and conversions. Diffusive processes and advective processes are both included. The primary instance of advection is dietary uptake. Another prominent example is litterfall. Fugacity is used as a descriptor in algorithms where it is convenient (*e.g.*, in the uptake of contaminants by foliage from air). Because mechanisms of uptake of contaminants by some organisms are not well understood or are difficult to parameterize, some partitioning processes are assumed to be equilibrium relationships according to the form described in Section 2.2. These processes may be combinations of diffusion, active transport, and/or advection (*e.g.*, transport of contaminants into the plant root), and it is not necessary for the user to specify the mechanistic process, only the empirical relationship (bioconcentration factor or partition coefficient and time to equilibrium).

As with abiotic processes (Section 2.3.2), biotic transformation rates are also described as first-order processes with respect to the average chemical concentration in the particular compartment of concern.

Table 2-1
Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V[a]

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Soil	Soil	Liquid	Precipitation driven percolation	m^3(water)/day	= $A*V_{liquid}$ where: A = Area of soil-soil interface, m^2 V_{liquid} = Darcy velocity of water in sending soil compartment, m^3[water]/m^2[area]-day.
		Gas	Gas discharge	m^3(gas)/day	= $A\ V_{gas}$ where: A = Area of soil-soil interface, m^2 V_{gas} = Darcy velocity of gas in sending soil compartment, m^3(gas)/m^2(area)-day.
	Air	Solid	Resuspension	m^3(soil)/day	It is assumed that volumetric flow of particles from soil is the same as that to soil. Volumetric resuspension rate is then = Vol. Flow TO soil = $A*v_d * \rho_A/ \rho_P$ where: A = Area of soil-soil interface, m^2(area) vd = Dry deposition velocity of particles, m/day ρ_A = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m^3(atmosphere) ρ_P = Density of air particles, kg[particles]/m^3[particles]
	Surface Water	Solid	Erosion	m^3(soil)/day	Calculated from mass-based areal erosion rate and soil density: = $A*E /\rho_s$ where: A = Area of soil layer, m^2 E = erosion rate to surface water, kg (soil)/m^2(area)-day ρ_s = density of eroding soil, kg(soil)/m^3(soil)

Table 2-1 (continued)
Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V[a]

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Soil	Surface Water	Liquid	Runoff	m^3(water)/day	= A*Runoff where: A = Area of soil layer, m^2 Runoff =Amount of runoff that reaches waterbody per unit area of watershed, m^3(water)/m^2(area)-day
Ground Water	Surface Water	Liquid	Recharge	m^3(water)/day	=A*Recharge where: A = Area of soil-surface water interface, m^2 Recharge = Volume of water flow per unit area of interface, m^3(water)/m^2(area)-day
Air	Soil and Surface Water	Solid	Wet & Dry deposition of particles	m^3(particles)/day	= A*v_d * ρ_A/ ρ_P where: A = Area of soil layer, m^2 v_d = Dry deposition velocity of particles, m/day ρ_A = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m^3(atmosphere) ρ_P = Density of air particles, kg(particles)/m^3(particles)
		Liquid	Wet deposition of liquid		Not implemented
	Air or Air Advection Sink	All phases	Wind advection	m^3(air)/day	= A*u where: A = Area of air-air interface, m^2 u = Wind velocity from sending to receiving air compartment, m/day

Table 2-1 (continued)
Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V[a]

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Air	Plant Leaf	Solid	Wet deposition of particles	m^3(particles)/day	$=A*I*(wa_d * \rho_A/\rho_P) * f_L$ where: A = Area of soil layer containing plant I = Interception fraction (see Chapter 7.0 for description of algorithm) v_d = Deposition velocity of particles, m/day ρ_A = Atmospheric dust load in air compartment type (concentration of dust in air), kg(particles)/m^3(atmosphere) ρ_P = Density of air particles, kg(particles)/m^3(particles) f_L = Fraction of deposition adhering that is taken up by plant
Surface Water	Sediment	Solid	Sediment deposition	m^3(suspended sediment)/day	$= A*S_{dep} / \rho_{ss}$ where A = Area of surface water-sediment interface, m^2 S_{dep} = Deposition rate of suspended sediment to sediment bed, kg(suspended sediment)/m^2(area)-day ρ_{ss} = Density of suspended sediment, kg(suspended sediment)/m^3(suspended sediment)
	Surface Water	All phases	River flow	m^3(air)/day	=A*ur where: A = Area of river parcel interface, m^2 ur = River velocity from sending to receiving river compartment, m/day

Table 2-1 (continued)
Summary of Volumetric Advective Flow Velocities Included in TRIM.FaTE Prototype V[a]

Source/ Sending Compartment	Receiving Compartment	Moving Phase	Description of Advective Process	Units	Method for Calculation
Sediment	Surface Water	Solid	Sediment resuspension	m^3(benthic sediment)/day	= $A*S_{resusp} / \rho_{bs}$ where: A = Area of sediment-surface water interface, m^2 S_{resusp} = Resuspension rate of benthic sediment to water column, kg(benthic sediment)/m^2(area)-day ρ_{bs} = Density of benthic sediment, kg(benthic sediment)/m^3(benthic sediment)
	Sediment burial sink	Solid	Sediment burial	m^3(sediment)/day	Calculated so that amount of sediment buried is equal to maximum of 0 and amount deposited minus amount resuspended: = $A*\max\{ 0, S_{dep}/\rho_{ss} - S_{resusp}/\rho_{bs}\}$ where: A = Area of sediment-surface water interface, m^2 S_{dep} = Deposition rate of suspended sediment to sediment bed, kg(suspended sediment)/m^2(area)-day ρ_{ss} = Density of suspended sediment, kg(suspended sediment)/m^3(suspended sediment) S_{resusp} = Resuspension rate of benthic sediment to water column, kg(benthic sediment)/m^2(area)-day ρ_{bs} = Density of benthic sediment, kg(benthic sediment)/m^3(benthic sediment)

[a] Advection of chemicals to and from plants in particles and rain water and advection of chemicals to and from wildlife in dietary and excretory materials are not included. See Chapter 7.

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3. AIR ALGORITHMS

In this chapter the algorithms for the transport of chemical species within and among air compartments and diffusion/volatilization between air compartments and surface water are presented. A description of deposition from air compartments to surface water can be found in Chapter 4 and a description of the transport processes between the air compartments and soil can be found in Chapter 5. The text box on the next page provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used.

3.1 AIR TO AIR ALGORITHMS

For a given wind speed and direction, there are two types of transfer considered from one air compartment to another:

- Advective transfer (bulk) due to the component of the wind vector normal to the boundary between the compartments; and

- Dispersive transfer (bulk) calculated from the component of the wind vector parallel to the boundary between the compartments.

The total transfer factor from one compartment to the other is the sum of these two transfer coefficients.

Let A_R and A_S denote the receiving and sending air compartments. If the boundary between the two air compartments is composed of n distinct line segments, then the transfer factor from the sending to the receiving air compartment is calculated as

$$T_{A_S \rightarrow A_R} = \frac{1}{V_S} \sum_{i=1}^{n} Area_i \left(u_i^{(D)} + u_i^{(L)} \right) \tag{3-1}$$

where:

V_S = volume of the sending air compartment (m^3)
$Area_i$ = interfacial area across ith boundary (m^2)
$u_i^{(D)}$ = direct advective wind velocity across the ith boundary (m/day)
$u_i^{(L)}$ = lateral/dispersive wind velocity across the ith boundary (m/day)

Summary of Transport Algorithms Developed in this Chapter

Air compartment to air compartment:

$$T_{A_S \rightarrow A_R} = \frac{1}{V_S} \sum_{i=1}^{n} Area_i \left(u_i^{(D)} \right)$$

Diffusion/volatilization from air compartment to surface water compartment:

$$T_{air \rightarrow water} = \frac{A}{V_a} K_v \frac{f_a(vapor)}{H / RT_k}$$

Diffusion/volatilization from surface water compartment to air compartment:

$$T_{water \rightarrow air} = \frac{A}{V_w} K_v f_w(liquid)$$

where:

V_S	=	volume of the sending air compartment (m^3)
$Area_i$	=	interfacial area across *i*th boundary (m^2)
$u_i^{(D)}$	=	direct advective wind velocity across the *i*th boundary (m/time)
A	=	interfacial area between the surface water and air compartments (m^2)
$f_w(liquid)$	=	fraction of chemical in the water compartment that is dissolved (unitless)
V_w	=	volume of water compartment (m^3)
$f_a(vapor)$	=	fraction of chemical in the air compartment that is in the vapor phase (unitless)
V_a	=	volume of air compartment (m^3)
K_v	=	volatilization transfer rate, m/day
R	=	universal gas constant (8.206×10^{-5} atm-m^3/mole ^oK)
T_K	=	water temperature (^oK)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m^3/mole)

3.1.1 Direct Advective Transfer

The direct wind flow across an air compartment boundary (notation $u^{(D)}$ is used above) is calculated by finding the projection of the wind vector onto the normal vector to the boundary between the air compartments.

Let $P_1=(x_1,y_1)$ and $P_2=(x_2,y_2)$ be the points defining the line that is the projection of the boundary onto the *xy*-plane (*i.e.*, the view from above of the vertical plane defining the boundary). It is assumed that the points P_1 and P_2 are ordered so that the receiving compartment is on the right side of the directed line segment starting at P_1 and ending at P_2. The unit vector $\vec{v}$ perpendicular to this line segment that is in the direction of the receiving compartment is given by:

$$\vec{v} = \frac{1}{\sqrt{(y_2-y_1)^2+(x_2-x_1)^2}} \left\langle y_2-y_1,\ -(x_2-x_1) \right\rangle = \left\langle \sin\varphi,\ \cos\varphi \right\rangle \tag{3-2}$$

where φ is the angle measured clockwise from due north. If the wind is blowing with speed u towards the direction ϑ (measured clockwise from due north), then the wind vector, denoted by $\vec{w}$, can be written:

$$\begin{aligned} \vec{w} &= \left\langle u\cos(\pi/2-\vartheta),\ u\sin(\pi/2-\vartheta) \right\rangle \\ &= u\left\langle \sin\vartheta,\ \cos\vartheta \right\rangle \end{aligned} \tag{3-3}$$

The projection of the wind vector $\vec{w}$ onto v is just the dot product $\vec{w}\cdot\vec{v}$ of the two vectors, which is given by:

$$\begin{aligned} \vec{w}\cdot\vec{v} &= \frac{u}{\sqrt{(y_2-y_1)^2+(x_2-x_1)^2}} \left[(y_2-y_1)\sin\vartheta - (x_2-x_1)\cos\vartheta\right] \\ &= u\left[\sin\vartheta\sin\varphi + \cos\vartheta\cos\varphi\right] \\ &= u\cos(\vartheta-\varphi) \end{aligned} \tag{3-4}$$

Since $\vec{v}$ is a unit vector, the dot product in this case is the component of the vector $\vec{w}$ in the direction of $\vec{v}$. The wind flow rate from the sending compartment to the receiving compartment is defined to be the dot product if it is positive, otherwise it is zero; *i.e.*,

$$\textit{Wind speed perpendicular to compartment boundary} = u_\perp = max\{0, u\cos(\vartheta-\varphi)\} \tag{3-5}$$

If the wind is blowing perpendicular to the boundary (*i.e.*, $\varphi = \vartheta$), then the wind flow rate across the boundary is just the wind speed; otherwise it is flowing with a velocity less than the wind speed, the magnitude of which depends on the difference in the angles of the wind speed and the boundary.

3.2 AIR TO SOIL ALGORITHMS

The algorithms describing the transfer of chemical mass between air and soil are presented in Section 5.4.3.

3.3 AIR TO SURFACE WATER ALGORITHMS

3.3.1 DEPOSITION

The algorithms describing the deposition of chemical mass from air to surface water are presented in Section 4.2.1.

3.3.2 DIFFUSION

3.3.2.1 Volatilization Transfer Between Surface Water and Air

The following describes the method used for estimating volatilization transfer between air and surface water for any chemical that has a nonzero Henry's law constant. The method is a two-layer resistance model first presented by Whitman (1923) and incorporated into the U.S. EPA WASP water quality model (Ambrose 1995). The proceeding discussion is based primarily on the WASP model documentation.

Volatilization is the movement of chemical across the air-water interface as the dissolved neutral concentration attempts to equilibrate with the gas phase concentration. Equilibrium occurs when the partial pressure exerted by the chemical in solution equals the partial pressure of the chemical in the overlying atmosphere. The rate of exchange is proportional to the gradient between the dissolved concentration and the concentration in air.

With the approach described in Whitman (1923), the dissolved concentration in the surface water is assumed to attempt to equilibrate with the gas phase concentration in the atmosphere, via the general equation:

$$\left(\frac{\partial C_{dissolved}}{\partial t} \right)_{volat} = \frac{K_v}{D} \left(C_{dissolved} - C_a/(H/R T_K) \right) \tag{3-6}$$

where:

$C_{dissolved}$	=	dissolved concentration of chemical (mass [chemical]/volume[water])
C_a	=	vapor phase concentration of chemical in air (mass [chemical]/volume [air])
K_v	=	volatilization transfer rate (m/day)
D	=	water depth (m)
R	=	universal gas constant (8.206×10^{-5} atm-m^3/mole ^oK)
T_K	=	water temperature (^oK)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m^3/mole).

The transfer rate can range from near 0 to 25 m/day, depending on conditions (Ambrose 1995). Multiplying the above equation by the volume of the water compartment, denoted here by V_w, yields:

$$Net\ Flux\ air\ to\ water\ (mass[chemical]/time) = V_w \frac{K_v}{D} \left(C_{dissolved} - C_a/(H/R\,T_K) \right) \quad (3\text{-}7)$$

The term V_w/D will be equal to the area of the water compartment, if the depth of the water compartment is approximately constant. This area is also the interfacial area between the air and water compartments, and so that:

$$Net\ Flux\ air\ to\ water = A\,K_v \left(f_w(liquid) \frac{N_w}{V_w} - f_a(vapor) \frac{N_a}{V_a} \,/\, (H/R\,T_K) \right) \quad (3\text{-}8)$$

or, using the notation of transfer factors,

$$T_{air \rightarrow water}(diffusion/volatilization) = \frac{A}{V_a} K_v \frac{f_a(vapor)}{(H/R\,T_K)} \quad (3\text{-}9)$$

$$T_{water \rightarrow air}(diffusion/volatilization) = \frac{A}{V_w} K_v\, f_w(liquid) \quad (3\text{-}10)$$

where:

A	=	interfacial area between the surface water and air compartments (m^2)
$f_w(liquid)$	=	fraction of chemical in the water compartment that is dissolved (unitless)
N_w	=	total mass of chemical in the water compartment (g)

V_w	=	volume of water compartment (m^3)
$f_a(vapor)$	=	fraction of chemical in the air compartment that is in the vapor phase (unitless)
N_a	=	total mass of chemical in the air compartment (g)
V_a	=	volume of air compartment (m^3)
K_v	=	volatilization transfer rate (m/day) [see below for details]
R	=	universal gas constant (8.206×10^{-5} atm-m^3/mole ^oK)
T_K	=	water temperature (^oK)
H	=	Henry's law coefficient for the air-water partitioning of the chemical (atm-m^3/mole).

The two-resistance method assumes that two "stagnant films" are bounded on either side by well mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From mass balance considerations, it is obvious that the same mass must pass through both films, thus the two resistances combine in series, so that the conductivity is the reciprocal of the total resistance:

$$K_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{R T_K} \right)^{-1} \right]^{-1} \quad (3\text{-}11)$$

where:

R_L	=	liquid phase resistance, day/m
K_L	=	liquid phase transfer coefficient, m/day
R_G	=	gas phase resistance, day/m
K_G	=	gas phase transfer coefficient, m/day.

There is actually yet another resistance involved, the transport resistance between the two interfaces, but it is assumed to be negligible (this may not be true in two cases: very turbulent conditions and in the presence of surface active contaminants).

The value of K_v, the conductivity, depends on the intensity of turbulence in a water body and in the overlying atmosphere. Mackay and Leinonen (1975) have discussed conditions under which the value of K_v is primarily determined by the intensity of turbulence in the water. As the Henry's Law coefficient increases, the conductivity tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's Law coefficient decreases, the value of the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

Because Henry's Law coefficient generally increases with increasing vapor pressure of a compound and generally decreases with increasing solubility of a compound, highly volatile low solubility compounds are most likely to exhibit mass transfer limitations in water and relatively nonvolatile high solubility compounds are more likely to exhibit mass transfer limitations in the

air. Volatilization is usually of relatively less magnitude in lakes and reservoirs than in rivers and streams.

In cases where it is likely that the volatilization rate is regulated by turbulence level in the water phase, estimates of volatilization can be obtained from results of laboratory experiments. As discussed by Mill et al. (1982), small flasks containing a solution of a pesticide dissolved in water that have been stripped of oxygen can be shaken for specified periods of time. The amount of pollutant lost and oxygen gained through volatilization can be measured and the ratio of conductivities (KVOG) for pollutants and oxygen can be calculated. As shown by Tsivoglou and Wallace (1972), this ratio should be constant irrespective of the turbulence in a water body. Thus, if the reaeration coefficient for a receiving water body is known or can be estimated and the ratio of the conductivity for the pollutant to reaeration coefficient has been measured, the pollutant conductivity can be estimated.

The input computed volatilization rate constant is for a temperature of 20°C. It is adjusted for segment temperature using the equation:

$$K_{v,T} = K_{20}\ \Theta_v^{T-20} \tag{3-12}$$

where:

K_{20} = calculated volatilization transfer rate (m/day)
Θ_v = temperature correction factor
T = water temperature (°C).

3.3.2.2 Calculation of Volatilization Transfer Rates for the Whitman Two-Resistance Model

There are a variety of options available for how the transfer rates K_G and K_L are obtained, each of which will be implemented in TRIM.FaTE. These options are summarized in Tables 3-1 and 3-2.

Table 3-1
Methods for Determining Gas Phase Transfer Coefficient K_G[a] for the Whitman Two-Resistance Volatilization Model Between Air and Surface Water

	Method	K_G, Gas phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	1.	$K_G = u^* (\kappa^{0.33}/\lambda_2) S_{ca}^{-0.67}$ where: u^* = the shear velocity (m/s) computed from $u^* = C_d^{0.5} W_{10}$ where: C_d = drag coefficient (0.0011) W_{10} = wind velocity 10 m above water surface (m/sec) κ = von Karmen's constant (0.74) λ_2 = dimensionless viscous sublayer thickness (4) where Sc_a and Sc_w are air and water Schmidt Numbers, computed from $Sc_a = \frac{\mu_a}{\rho_a D_a}$ $Sc_w = \frac{\mu_w}{\rho_w D_w}$ D_a = diffusivity of chemical in air (m^2/sec), = 1.9E-4 / $M_W^{2/3}$ D_w = diffusivity of chemical in water (m^2/sec) = 22E-9 / $M_W^{2/3}$ μ_a = viscosity of air, internally calculated from air temperature, kg/m-sec = (1.32 + 0.009 T_{aC})/10, T_{aC}=air temperature (C) μ_w = viscosity of water, internally calculated from water temperature, kg/m-sec = 10^(-3.0233 + 1301/(998.333+8.1855(T_w-20) + 0.00585 8.1855(T_w-20)^2), T_W=water temperature (C) M_w = molecular weight of compound	O'Connor (1983), Ambrose (1995)
Stagnant Pond or Lake	2.	See Method (1) for definition of terms. $K_G = 10^{-3} + 0.0462\ u^*\ Sc_a^{-0.67}$	Mackay and Yeun (1983), Ambrose (1995)
Flowing stream, River, or Estuary	1.	Same as Method (1) for stagnant water body.	
Flowing stream, River, or Estuary	2.	Same as Method (2) for stagnant water body.	
Flowing stream, River, or Estuary	3.	Input value of 100 m/day	Ambrose (1995)

[a] Used in the calculation of the volatilization transfer rate K_v: $K_v = \left(R_L + R_G\right)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT_K}\right)^{-1}\right]^{-1}$

Table 3-2
Methods for Determining Liquid Phase Transfer Coefficient K_L [a] for the Whitman Two-Resistance Volatilization Model Between Air and Surface Water

	Method	K_L, Liquid phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	1.	K_a * K_{vo}, where K_a=input=reaeration velocity (m/day) K_{vo}=input=ratio of volatilization rate to reaeration rate	Ambrose (1995)
Stagnant Pond or Lake	2.	K_a * $(32/M_w)^{0.5}$, where K_a=input=reaeration velocity (m/day) M_w=molecular weight of chemical (g/mole)	Ambrose (1995)
Stagnant Pond or Lake	3.	$K_L = u^* (\rho_a/\rho_w)^{0.5} (\kappa^{0.33}/\lambda_2) S_{cw}^{-0.67}$ where: u^* = the shear velocity (m/s) computed from $u^* = C_d^{0.5} W_{10}$ where: C_d = drag coefficient (0.0011) W_{10} = wind velocity 10 m above water surface (m/sec) ρ_a = density of air, internally calculated from air temperature (kg/m^3) ρ_w = density of water, internally calculated from water temperature (kg/m^3) κ = von Karmen's constant (0.74) λ_2 = dimensionless viscous sublayer thickness (4) Sc_a and Sc_w are air and water Schmidt Numbers, computed from $Sc_a = \frac{\mu_a}{\rho_a D_a}$ $Sc_w = \frac{\mu_w}{\rho_w D_w}$ where: D_a = diffusivity of chemical in air (m^2/sec), = 1.9E-4 / $M_W^{2/3}$ D_w = diffusivity of chemical in water (m^2/sec) = 22E-9 / $M_W^{2/3}$ μ_a = viscosity of air, internally calculated from air temperature (kg/m-sec) = $(1.32 + 0.009 T_{aC})/10$, T_{aC}=air temperature (C) μ_w = viscosity of water, internally calculated from water temperature (kg/m-sec) = 10^(-3.0233 + 1301/(998.333+8.1855(T_w-20) + 0.00585 8.1855(T_w-20)^2), T_W=water temperature (C)	O'Connor (1983), Ambrose (1995)

Table 3-2 (continued)
Methods for Determining Liquid Phase Transfer Coefficient K_L for the Whitman Two-Resistance Volatilization Model Between Air and Surface Water

	Method	K_L, Liquid phase transfer coefficient (m/day)	Reference/Comment
Stagnant Pond or Lake	4.	$K_L = \begin{cases} 10^{-6} + 0.00341\ u^{*}\ S_{cw}^{-0.5} & if\ u^{*} > .3\ m/s \\ 10^{-6} + 0.0144\ u^{*0.22}\ S_{cw}^{-0.5} & if\ u^{*} < .3\ m/s \end{cases}$ See Method (4) for definition of terms.	Mackay and Yeun (1983), Ambrose (1995)
Flowing stream, River, or Estuary	1.	Same as Method (1) for stagnant water body.	
Flowing stream, River, or Estuary	2.	Same as Method (2) for stagnant water body.	
Flowing stream, River, or Estuary	3.	Same as Method (3) for stagnant water body.	
Flowing stream, River, or Estuary	4.	$K_L = \begin{cases} K_a K_{vo}, where\ K_a = 5.349\ \frac{u^{0.67}}{D^{0.85}}, K_{vo} = input\ or \sqrt{32/M_W} & if\ D < 0.61m \\ (D_w\ u/D)^{0.5} 8.64 \times 10^4 & if\ D \geq 0.61m\ and\ (u < 0.518\ m/s\ or\ D > 13.584\ u^{0.29135}) \\ 5.049\ \frac{u^{0.969}}{D^{0.673}} & else \end{cases}$ where: u = velocity of water (m/s) D = water compartment depth (m) D_w = diffusivity of chemical in water (m^2/sec) =22E-9 / $M_W^{2/3}$	Covar (1976), Ambrose (1995)

[a] Used in the calculation of the volatilization transfer rate K_v: $K_v = \left(R_L + R_G\right)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT_K}\right)^{-1}\right]^{-1}$

4. SURFACE WATER AND SEDIMENT ALGORITHMS

The surface water compartment is assumed to be well-mixed and composed of two phases: pure water and suspended sediment material that contains the sorbed contaminants. Similarly, the sediment is modeled as a well-mixed compartment consisting of a phase sorbed to the benthic solids and a phase dissolved in the benthic pore water or interstitial water. The gas phase of the surface water compartment is considered to be negligible in terms of its impact on the movement of chemicals. The text box beginning on the next page provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used.

4.1 CONCEPTUALIZATION OF THE SURFACE WATER AND SEDIMENT COMPARTMENTS

The behavior of chemicals in surface waters is determined by three factors: the rate of input, the rate of physical transport in the water system, and chemical reactivity. Physical transport processes are dependent to a large extent on the type of water body under consideration *i.e.*, oceans, seas, estuaries, lakes, rivers, or wetlands. Schnoor (1981) and Schnoor and MacAvoy (1981) have summarized important issues relating to surface-water transport. Fugacity models have been developed for lakes and rivers by Mackay et al. (1983a,1983b).

At low concentrations, contaminants in natural waters exist in both a dissolved and a sorbed phase. In slow-moving surface waters (*e.g.*, lakes), both advection and dispersion are important. In rapidly moving water systems (*e.g.*, rivers), advection controls mass transport, and dissolved substances move at essentially the same velocity as the bulk water in the system. A water balance is the first step in assessing surface-water transport. A water balance is established by equating gains and losses in a water system with storage. Water can be stored within estuaries, lakes, rivers, and wetlands by a change in elevation. Water gains include inflows (both runoff and stream input) and direct precipitation. Water losses include outflows and evaporation.

The accuracy of modeling fresh water systems depends on the ability to accurately simulate the movement of water and sediment to and from the system (Schnoor 1981). There are two primary categories for fresh water: rivers and lakes. This model is based on that described in Mackay et al. (1983a,1983b). Table 4-1 summarizes the gains and losses considered from the surface water compartment considered in the TRIM.FaTE prototype. Losses from the sediment due to colloidal diffusion, bioturbation, or reaction/transformation are not considered at this stage of the TRIM.FaTE model.

The general manner in which the model is presented is intended to assist the flexibility of future prototypes and to facilitate implementing different algorithms to describe specific processes. The use of the fugacity terminology is used to describe the advective process for simplicity of notation and consistency.

Summary of Transport Algorithms Developed in this Chapter

Dry deposition of particles to surface water (solid phase):

$$T_{air\rightarrow sw}^{dd} = \frac{A_{airsw}}{V_{air}} \upsilon_d \frac{\rho_a Z_{solid}}{\rho_p Z_{total}}$$

Wet deposition of particles to surface water (solid phase):

$$T_{air\rightarrow sw}^{wd} = \frac{A_{airsw}}{V_{air}} Wet_d \frac{\rho_a Z_{solid}}{\rho_p Z_{total}}$$

Advective flux from rainfall:

$$T_{i\rightarrow j}(rain) = A_{ij} \frac{Rain}{V_{air}} \frac{Z_{water}}{Z_{total}}$$

Deposition of suspended sediment to sediment bed (solid phase):

$$T_{sw\rightarrow sed}^{d} = \frac{A_{swsed}}{V_{sw}} \frac{S_{dep}}{\rho_{ss}} \frac{Z_{solid}}{Z_{total}}$$

Resuspension of sediment to surface water (solid phase):

$$T_{sed\rightarrow sw}^{r} = \frac{A_{sedsw}}{V_{sed}} \frac{S_r}{\rho_{bs}} \frac{Z_{solid}}{Z_{total}}$$

Outflow from surface water to surface water advection sink (total phase):

$$T_{sw\rightarrow s} = Outflow/V_{sw}$$

Resuspension of sediment to surface water (solid phase):

$$T_{sed\rightarrow sw}^{total} = \max\left(0, \frac{A_{sedsw}}{V_{sw}} \frac{S_{dep}}{\rho_{ss}} - \frac{A_{sed\rightarrow sw}}{V_{sed}} \frac{S_r}{\rho_{bs}}\right) \frac{Z_{solid}}{Z_{total}}$$

Advection from one river compartment to another river or lake compartment:

$$T_{i\rightarrow j}^{adv}(total) = \frac{A_{ij}}{V_i} u_{ij}$$

Dispersive exchange flux between two surface water compartments:

$$F_{i\rightarrow j} = \frac{E_{ij} \cdot A_{ij}}{L_{ij}} (C_j - C_i)$$

$$= \frac{E_{ij} \cdot A_{ij}}{L_{i\rightarrow j}} \left(\frac{M_j}{V_j} - \frac{M_i}{V_i}\right)$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

where:

$T^{dd}_{air \rightarrow sw}$	=	advective transfer factor of particles from air to surface water (1/day)
$^{wd}_{air \rightarrow sw}$	=	advective transfer factor of wet particles from air to surface water (1/day)
$^{d}_{sw \rightarrow sed}$	=	advective transfer factor for deposition of suspended sediment to sediment bed (1/day)
$^{r}_{sed \rightarrow sw}$	=	advective transfer factor for resuspension of sediment to surface water (1/day)
$^{total}_{sed \rightarrow sw}$	=	net advective transfer factor for deposition and resuspension of sediment to surface water (1/day)
A_{airsw}	=	area of surface water/air interface (m^2)
V_{air}	=	volume of air compartment (m^3)
υ_d	=	dry deposition velocity of particles (m/day)
ρ_a	=	atmospheric dust load in air compartment (concentration of dust in air) (kg [particles]/m^3 [atmosphere])
ρ_p	=	density of air particles (kg [particles]/m^3 [particles])
Wet_d	=	wet deposition velocity of particles (m/day)
$Rain$	=	rainfall rate (m/day)
A_{swsed}	=	area of surface water/sediment interface (m^2)
V_{sw}	=	volume of surface water compartment (m^3)
S_{dep}	=	deposition rate of suspended sediment to sediment bed (kg [suspended sediment]/m^2 (area)-day)
ρ_{ss}	=	density of suspended sediment (kg [suspended sediment]/m^3 [suspended sediment])
A_{sedsw}	=	area of surface water/sediment interface (m^2)
V_{sed}	=	volume of sediment compartment (m^3)
S_r	=	resuspension rate of benthic sediment to water column (kg [benthic sediment]/m^2 (area)-day)
ρ_{bs}	=	density of benthic sediment (kg [benthic sediment]/m^3 [benthic sediment])
$Outflow$	=	outflow of water from surface water compartment to advection sink (m^3/day)
V_{sw}	=	volume of surface water compartment (m^3)
Z_{solid}	=	fugacity of the solid phase (Pa)
Z_{total}	=	total fugacity (Pa)
Z_{water}	=	fugacity of the water phase (Pa)
u_{ij}	=	averaged river flow between river compartments i and j (m/h)
C_i, C_j	=	concentration of chemical in water compartments *i* and *j* (g/m^3)
$F_{i \rightarrow j}$	=	dispersive flux from water compartment *i* to water compartment *j* (mass [chemical]/day)
M_i, M_j	=	mass of chemical in water compartments *i* and *j* mg/L (g)
E_{ij}	=	dispersion coefficient for exchange between water compartments *i* and *j* (m^2/day)
A_{ij}	=	interfacial area between water compartments *i* and *j* (m^2)
L_{ij}	=	characteristic mixing length between water compartments *i* and *j* (m)

Table 4-1
Summary of the Gains and Losses for Surface Water Compartments Considered in the Prototype

Gains	Type of Process	Relevant Phase	Losses	Type of Process	Relevant Phase
From Surface Soil					
Erosion	Advective	Solid			
Runoff	Advective	Aqueous			
From Air			**To Air**		
Diffusion from air	Diffusive	Vapor	Diffusion to air	Diffusive	Aqueous
Dry deposition of aerosols from air	Advective	Solid			
Wet deposition of aerosols from air	Advective	Solid			
Wet deposition of vapor from air	Advective	Vapor			
From Sediment			**To Sediment**		
Diffusion from sediment	Diffusive	Aqueous	Diffusion to sediment	Diffusive	Aqueous
Resuspension of sediment	Advective	Solid	Deposition to sediment	Advective	Solid
From Rivers			**To Lake**		
Compartment to compartment advective flow	Advective	Total	River to lake advective flow	Advective	Total
From Aquatic Biota			**To Aquatic Biota**		
Elimination from fish	Exchange	Total	Uptake by fish	Exchange	Total
From Surface Water Transformations			**To Sink(s)**		
			Decay/transformation to Reaction/Advection sink	Transformation	Total
			Outflow to Reaction/Advection sink	Advective	Total

4.2 ADVECTIVE PROCESSES

A generalized description of advective processes is provided in Section 2.3.1. This section focuses on the advective processes simulated in the prototype specific to the surface water compartment.

4.2.1 ADVECTIVE PROCESSES BETWEEN AIR AND SURFACE WATER

The advective processes considered between air and surface water are wet and dry deposition of solid phase particles and wet deposition of vapor that is dissolved into the water phase. For all of these processes, the air compartment is the sending compartment and the surface water compartment is the receiving compartment.

Following is a summary of advective processes between air and surface water, and algorithms used to calculate phase flow velocities:

Dry deposition of particles to surface water (solid phase):

$$T_{air \rightarrow sw}^{dd} = \frac{A_{airsw}}{V_{air}} \upsilon_d \frac{\rho_a Z_{solid}}{\rho_p Z_{total}} \tag{4-1}$$

where:

$T_{air \rightarrow sw}^{dd}$	=	advective transfer factor of particles from air to surface water (1/day)
A_{airsw}	=	area of surface water (m^2)
V_{air}	=	volume of air compartment (m^3)
υ_d	=	dry deposition velocity of particles (m/day)
ρ_a	=	atmospheric dust load in air compartment (concentration of dust in air) (kg [particles]/m^3 [atmosphere])
ρ_P	=	density of air particles (kg [particles]/m^3 [particles])
Z_{solid}	=	fugacity of the solid phase (Pa)
Z_{total}	=	total fugacity (Pa).

Wet deposition of particles to surface water (solid phase):

$$T_{air \rightarrow sw}^{wd} = \frac{A_{airsw}}{V_{air}} Wet_d \frac{\rho_a Z_{solid}}{\rho_p Z_{total}} \tag{4-2}$$

where:

$T_{air \rightarrow sw}^{wd}$	=	advective transfer factor of wet particles from air to surface water (1/day)
A_{airsw}	=	area of surface water/air interface (m^2)
V_{air}	=	volume of air compartment (m^3)
Wet_d	=	wet deposition velocity of particles (m/day)
ρ_a	=	atmospheric dust load in air compartment (concentration of dust in air) (kg [particles]/m^3 [atmosphere])
ρ_P	=	density of air particles (kg [particles]/m^3 [particles])
Z_{solid}	=	fugacity of the solid phase (Pa)
Z_{total}	=	total fugacity (Pa).

Additionally, there is advective flux from rainfall. As the rain falls, it gathers chemical from the air, coming into equilibrium with the fugacity of the air compartment.

Advective flux from rainfall:

$$flux(g/day) = A_{ij} \frac{Rain}{V_i} \frac{Z_{water}}{Z_{Total}} N_a$$

$$\Rightarrow \quad T_{i \to j}(rain) = A_{ij} \frac{Rain}{V_i} \frac{Z_{water}}{Z_{Total}} \tag{4-3}$$

where:

$Rain$ = rainfall rate (m/day)
N_a = total mass of chemical in the air compartment (g)
Z_{water} = fugacity of the water phase (Pa)
Z_{total} = total fugacity (Pa).

4.2.2 ADVECTIVE PROCESSES BETWEEN SEDIMENT AND SURFACE WATER

The two advective processes between sediment and surface water involve the transport of the chemical from the surface water to the sediment or from the sediment to the surface water via movement of sediment particles. "Sediment deposition" refers to the transport of the chemical from the surface water to sediment, and "sediment resuspension" refers to the reverse process. Both processes involve only the solid phase.

Following is a summary of advective processes between sediment and surface water, and algorithms used to calculate phase flow velocities:

Deposition of suspended sediment to sediment bed (solid phase):

$$T^d_{sw \to sed} = \frac{A_{swsed}}{V_{sw}} \frac{S_{dep}}{\rho_{ss}} \frac{Z_{solid}}{Z_{total}} \tag{4-4}$$

where:

$T^d_{sw \to sed}$ = advective transfer factor for deposition of suspended sediment to sediment bed (1/day)
A_{swsed} = area of surface water/sediment interface (m^2)
V_{sw} = volume of surface water compartment (m^3)
S_{dep} = deposition rate of suspended sediment to sediment bed (kg [suspended sediment]/m^2 (area)-day)
ρ_{ss} = density of suspended sediment (kg [suspended sediment]/m^3 [suspended sediment])
Z_{solid} = fugacity of the solid phase (Pa)
Z_{total} = total fugacity (Pa).

Resuspension of sediment to surface water (solid phase):

$$T^{r}_{sed \rightarrow sw} = \frac{A_{sedsw}}{V_{sed}} \frac{S_r}{\rho_{bs}} \frac{Z_{olid}}{Z_{total}} \quad (4\text{-}5)$$

where:

$T^{r}_{sed \rightarrow sw}$ = advective transfer factor for resuspension of sediment to surface water (1/day)
A_{sedsw} = area of surface water/sediment interface (m^2)
V_{sed} = volume of sediment compartment (m^3)
S_r = resuspension rate of benthic sediment to water column (kg [benthic sediment]/m^2 (area)-day)
ρ_{bs} = density of benthic sediment (kg [benthic sediment]/m^3 [benthic sediment])

Z_{solid} = fugacity of the solid phase (Pa)
Z_{total} = total fugacity (Pa).

4.2.3 ADVECTIVE PROCESSES BETWEEN SEDIMENT/SURFACE WATER AND ADVECTIVE SINKS

The surface water advection sink represents outflow of the chemical from the study area. For sediment, the advection sink represents the burial of the chemical beneath the sediment layer.

Burial is calculated so that the net flow of sediment into the sediment layer is zero. That is, there is no loss of sediment mass due to burial, only loss of pollutant. This is done by setting the amount of sediment buried equal to the sediment deposition rate minus the sediment resuspension rate, both of which are specified input parameters. If the resuspension rate is larger than the deposition rate, then the burial flow is set to 0. A more sophisticated approach may be implemented in which the sediment layer depth could change, depending on the deposition and resuspension rates. Further, the deposition rates can be calculated to correspond to the suspended sediment concentration, which could change depending on the erosion of soil to the water body and the outflow.

Following is a summary of advective processes between sediment/surface water and advective sinks, and algorithms used to calculate flow velocities:

Outflow from surface water to surface water advection sink (total phase):

$$T_{sw \rightarrow s} = Outflow / V_{sw} \quad (4\text{-}6)$$

where:

$Outflow$	=	outflow of water from surface water compartment to advection sink (m^3/day)
V_{sw}	=	volume of surface water compartment (m^3)

Resuspension of sediment to surface water (solid phase):

$$T_{sedsw}^{total} = \max\left(0, \frac{A_{sedsw}}{V_{sw}}\frac{S_{dep}}{\rho_{ss}} - \frac{A_{sed\rightarrow sw}}{V_{sed}}\frac{S_r}{\rho_{bs}}\right)\frac{Z_{solid}}{Z_{total}} \quad (4\text{-}7)$$

where:

T_{sedsw}^{total}	=	net advective transfer factor for deposition and resuspension of sediment to surface water (1/day)
A_{sedsw}	=	area of surface water/sediment interface (m^2)
V_{sed}	=	volume of sediment compartment (m^3)
S_r	=	resuspension rate of benthic sediment to water column (kg [benthic sediment]/m^2 (area)-day)
ρ_{bs}	=	density of benthic sediment (kg [benthic sediment]/m^3 (benthic sediment])
V_{sw}	=	volume of surface water compartment (m^3)
S_{dep}	=	deposition rate of suspended sediment to sediment bed (kg [suspended sediment]/m^2 (area)-day) (Mackay et al. 1983b; use 0.096 m^3/hr for a lake of volume 7 x 10^{-6} m)
ρ_{ss}	=	density of suspended sediment (kg [suspended sediment]/m^3 [suspended sediment])
Z_{solid}	=	fugacity of the solid phase (Pa)
Z_{total}	=	total fugacity (Pa).

4.3 DERIVATION OF RIVER COMPARTMENT TRANSFER FACTORS

The transfer factor from one river compartment to another, or to a lake compartment, was derived based on advective flow rates of a total pollutant mass between two compartments as developed in Section 2.3.1. By substituting river flow velocity for the total volumetric flow velocity, the following transfer factor is derived.

Advection from one river compartment to another river or lake compartment:

$$T_{ij}^{adv}(total) = \frac{A_{ij}}{V_i}\, u_{ij} \quad (4\text{-}9)$$

where:

u_{ij} = annual averaged river flow between river compartments *i* and *j* (m/day)
A_{ij} = area of interface between compartments *i* and *j* (m^2)
V_i = volume of compartment *i* (m^3).

Because advection is being simulated for the total phase, no phase partitioning is applied in this equation.

4.4 DISPERSIVE PROCESSES

4.4.1 DISPERSIVE TRANSPORT BETWEEN SURFACE WATER COMPARTMENTS

Dispersive transport between water compartments can be approximated as a first order process using the method describe in the WASP water quality simulation program (Ambrose et al.1995). Dispersive water column exchanges significantly influence the transport of dissolved and particulate pollutants in such water bodies as lakes, reservoirs, and estuaries. Even in rivers, longitudinal dispersion can be the most important process diluting peak concentrations that may result from unsteady loads or spills.

Based on the WASP model, the dispersive exchange flux between two surface water compartments *i* and *j* at time is modeled by:

$$F_{i \to j} = \frac{E_{ij} \cdot A_{ij}}{L_{ij}} (C_j - C_i) = \frac{E_{ij} \cdot A_{ij}}{L_{ij}} \left(\frac{M_j}{V_j} - \frac{M_i}{V_i} \right) \quad (4\text{-}10)$$

where:

$F_{i \to j}$ = dispersive flux from water compartment *i* to water compartment *j* (mass [chemical]/day)
C_i, C_j = concentration of chemical in water compartments *i* and *j* (g/m^3)
M_i, M_j = mass of chemical in water compartments *i* and *j* (g/m^3)
E_{ij} = dispersion coefficient for exchange between water compartments *i* and *j* (m^2/day)
A_{ij} = interfacial area between water compartments *i* and *j* (m^2)
L_{ij} = characteristic mixing length between water compartments *i* and *j* (m)
V_i = volume of compartment *i* (m^3)
V_j = volume of compartment *j* (m^3).

The distance between the midpoints of the two water compartments is used for the characteristic mixing length. Values for dispersion coefficients can range from 10^{-10} m^2/sec (8.64x

10^{-6} m^2/day) for molecular diffusion to $5x10^2$ m^2/sec ($4.32x10^7$ m^2/day)for longitudinal mixing in estuaries (Ambrose et al. 1995, p. 35). A value of $2.25x10^{-4}$ m^2/day is chosen as the default value; this is median of the range cited in Ambrose et al. (1995) (p. 112) from a study of Lake Erie conducted by Di Toro and Connolly (1980).

4.4.2 DISPERSIVE TRANSPORT BETWEEN SURFACE WATER AND SEDIMENT COMPARTMENTS

As for dispersive transport between surface water compartments, dispersive transport between surface water and sediment compartments is approximated as a first order process using the method described in the WASP water quality simulation program (Ambrose et al. 1995).

Based on the WASP model, the net dispersive exchange flux between a surface water compartment *i* and sediment compartment *j* is modeled by:

$$F_{j \to i} = \frac{E_{ij} \cdot A_{ij} n_{ij}}{L_{ij}/n_{ij}} \left(\frac{f_{Dj} C_j}{n_j} - \frac{f_{Di} C_i}{n_i} \right) = \frac{E_{ij} \cdot A_{ij} n_{ij}}{L_{ij}/n_{ij}} \left(\frac{f_{Dj} M_j}{V_j n_j} - \frac{f_{Di} M_i}{V_i n_i} \right) \quad (4\text{-}11)$$

where:

$F_{j->i}$ = Net dispersive flux between surface water compartment *i* and sediment compartment *j*, mass[chemical]/day
C_i, C_j = Bulk concentration of chemical in surface water compartment *i* and sediment compartment *j* mg/L (g[chemical]/m^3[compartment])
M_i, M_j = Mass of chemical in surface water compartment *i* and sediment compartment *j* (mass[chemical])
E_{ij} = Dispersion coefficient for exchange between compartments *i* and *j*, m^2/day
A_{ij} = Interfacial area between compartments *i* and *j*, m^2
L_{ij} = Characteristic mixing length between compartments *i* and *j*, m
V_i, V_j = volume of compartments *i* and *j*, m^3
f_{Di}, f_{Dj} = dissolved fraction of chemical in compartments *i* and *j* (calculated)
n_i, n_j = porosity of compartments *i* and *j*
n_{ij} = average porosity at interface ($(n_i + n_j)/2$)

The resulting transfer factors (units of */day*) between the surface water *i* and sediment compartment *j* are given by:

$$T_{i\rightarrow j} = \frac{E_{ij} \cdot A_{ij} n_{ij}}{L_{ij}/n_{ij}} \left(\frac{f_{Di}}{V_i n_i} \right) \quad (4\text{-}12)$$

$$T_{j\rightarrow i} = \frac{E_{ij} \cdot A_{ij} n_{ij}}{L_{ij}/n_{ij}} \left(\frac{f_{Dj}}{V_j n_j} \right) \quad (4\text{-}13)$$

Following the method used in WASP (Amborse et al., p. 25), the sediment compartment height is used as the characteristic mixing length L_{ij}. The porosity of the sediment compartment (n_j) is calculated from the specified benthic solids concentration and solids density. The porosity of the surface water compartment is set to the volume of water compartment that is water. Values for dispersion coefficients can range from 10^{-10} m^2/sec ($8.64x10^{-6}$ m^2/day) for molecular diffusion to $5x10^2$ m^2/sec ($4.32x10^7$ m^2/day)for longitudinal mixing in estuaries (Ambrose et al. 1995, p. 35). A value of 2.25e-4 m^2/day is chosen as the default value; this is median of the range cited in Ambrose et al. 1995 [p. 112] from a study of Lake Erie conducted by DiToro and Connolly (1980).

4.5 DIFFUSIVE PROCESSES

4.5.1 DIFFUSIVE EXCHANGE BETWEEN SURFACE WATER AND AIR

The algorithms describing the diffusive exchange of chemical mass between surface water and air are presented in Section 3.3.2.

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5. SOIL ALGORITHMS

In this chapter the algorithms for the transport and transformation of chemical species within and among soil compartments and between the soil compartments and the lower atmosphere and between the soil compartment and surface water are presented. The text box on the next page and continued on the following pages provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used.

5.1 INTRODUCTION

Two of the primary processes in subsurface soil are exchange by diffusion and advection. These are key components of the overall rate constant. The transport occurs both in the gas and liquid phase for organic chemicals. The predominant transport mechanism in the aqueous phase is advection, and that in the gas phase is diffusion. The advective transport of contaminants in the liquid or gas phase is dependent on the velocity of that phase. In this application, the total contaminant mass is estimated for each soil compartment. Important physicochemical properties include solubility, molecular weight, vapor pressure, and diffusion coefficients in air and water. The important landscape properties include temperatures of air, rainfall rates, soil properties (bulk density, porosity), and depth of each soil compartment.

There are three advective processes considered in the prototype that can potentially transport a chemical from a soil domain to surface water: erosion of surface soil, runoff from surface soil, and recharge from ground water. Erosion applies to the solid phase, while runoff and recharge applies to the dissolved phase.

5.2 SOIL COMPARTMENTS AND TRANSPORT PROCESSES

In the TRIM.FaTE model, soil is modeled as three distinct compartment types — surface soil, rooting-zone soil, and vadose-zone soil above the saturated zone. In TRIM.FaTE these three regions can be sub-divided into one or more compartments for the purpose of assessing mass transfer. Among these compartment types there are two kinds of transport considered — diffusion and advection. In addition, the uppermost surface soil compartment exchanges mass with the lowest compartment of the atmosphere by a combination of diffusion and advection processes.

5.3 TRANSFORMATIONS IN SOIL COMPARTMENTS

The transformation of contaminants in soil layers can have a profound effect on their potential for persistence. Chemical transformations, which may occur as a result of biotic or abiotic processes, can significantly reduce the concentration of a substance. For all chemical reactions, knowledge of a compound's half-life for any given transformation process provides a very useful index of persistence in environmental media. Because these processes determine the persistence and form of a chemical in the environment, they also determine the amount and type of substance to which a human or ecological receptor could be exposed. In the TRIM.FaTE soil

Summary of Transport Algorithms Developed in this Chapter

Lowest air compartment to upper surface soil compartment:

$$T_{a\to i} = \left[\frac{U_{air} \times Area_i \times Z_{air}}{V_a \times Z_a}\right] + \left\{V_d[PC/\rho_p][Z_{ap}/Z_a] + rain[Z_{water}/Z_a]\right\} \times [Area_i/V_a]$$

First soil compartment to lowest air compartment:

$$T_{i\to a} = \left[\frac{U_{air}\gamma_i}{[1-\exp(-\gamma_i d_i]}\right] Z_{air}/Z_i + [Respnd/\rho_{si}][Z_{si}/Z_i] \times [Area_i/V_a]$$

Downward flow from soil compartment *i* to soil compartment *j*:

$$T_{i\to j} = \frac{Y_{ij}}{d_i Z_i} + \frac{ve_i\gamma_i}{\left(e^{+\gamma_i d_i} - 1\right)}$$

Upward flow from soil compartment *j* to soil compartment *i*:

$$T_{j\to i} = \frac{Y_{ij}}{d_j Z_j}$$

Horizontal runoff from compartment *i* to compartment *j*:

$$T_{i\to j}(runoff) = Runoff \times f_{run}(ij) \times Z_i(rain) / (Z_i d_i *)$$

where

U_{air} = mass transfer coefficient on the air side of the air/soil boundary, m/d (It is typical to represent the mass transfer coefficient in air as ratio of the diffusion coefficient in air, D_{air}, divided by the turbulent boundary compartment thickness, δ_{air}. For many compounds, D_{air} is on the order of 0.4 m/d and δ_{air} is on the order of 0.0005 m, so that U_{air} is on the order of 800 m/d.)

$Area_i$ = horizontal area of the soil compartment, m^2 (This is the area assumed to be shared between the top soil compartment and the atmosphere and between any two adjacent soil compartments.)

V_a = volume of the air compartment, m^3.

Z_{air} = fugacity capacity of pure air, = 1/RT, mol/(m^3-Pa).

Z_a = total fugacity capacity of the air compartment (includes gas and particle phase of the atmosphere), mol/(m^3-Pa).

Z_{ap} = fugacity capacity of air particles, mol/(m^3-Pa).

Summary of Transport Algorithms Developed in this Chapter (cont.)

V_d = air-to-soil deposition ratio, mol/m^2/d per mol/m^3 (includes only deposition that is not intercepted by plants, and is calculated as the total deposition velocity times one minus the plant interception fraction), ~ 400 m/d.

PC = particulate matter concentration in air, ~ 6.0 x 10^{-8} kg/m^3.

ρ_p = density of particulate matter in air, ~ 2600 kg/m^3 (Wilson and Spengler 1996).

$rain$ = rate of rainfall, m/d.

Z_{water} = fugacity capacity of the moving phase, water, mol/(m^3-Pa).

$Area_i$ = area of contact between the surface soil compartment and the lowest air compartment, m^2.

Z_i = total fugacity capacity of soil compartment i, mol/(m^3-Pa).

Z_{si} = fugacity capacity of soil compartment i, mol/(m^3-Pa).

d_i = thickness of soil compartment i, m.

Y_{ij} = fugacity-capacity adjusted mass transfer coefficient between compartments i and j, mol/(m^2-Pa-day), and is given by:

$$Y_{ij} = \frac{Z_i De_i \gamma_i + Z_j De_j \gamma_j}{2\left[\frac{\left(e^{+\gamma_i d_i} - 1\right)}{\gamma_i d_i} - \frac{\left(1 - e^{-\gamma_j d_j}\right)}{\gamma_j d_j}\right]}$$

De_i = effective diffusion coefficient in soil compartment i, m^2/d.

ve_i = effective advection velocity of a chemical in the soil compartment i, m/d, and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of soil compartment i; $ve_i = v_i Z_{water}/Z_i$.

v_i = average velocity of the moving phase (assumed to be water) in the soil compartment i, m^{-1}.

γ_i = gradient of soil concentration change in soil compartment i, m^{-1}. Obtained from the inverse of the normalized or characteristic depth X*, that is $\gamma_i = 1/X^*$.
X* is obtained as follows:

If $\lambda_i > 0$ then X* = Minimum (DX_1, DX_2)
Otherwise, if $\lambda_i = 0$, then X* = DX_2.

DX_1 is the Damkoehler distance (the distance at which the soil concentration falls by 1/e based on the competition among diffusion, advection, and reaction) and is given by:

$$DX_1 = \frac{ve_i + \sqrt{ve_i + 4De_i}}{2\lambda_i}$$

DX_2 is the depth that establishes the concentration gradient in soil in the absence of any reaction or transformation processes. It is obtained as follows:

If $ve_i > 0$, then DX_2 = Minimum ($4De_i/ve_i$, DX_{sat})
If $ve_i = 0$, then DX_2 = Minimum ($2d_i$, $\sqrt{(\pi)}$, DX_{sat})

Summary of Transport Algorithms Developed in this Chapter (cont.)

λ_i	=	removal rate constant for a chemical in soil compartment, based on chemical transformation, day^{-1}.
Respnd	=	rate at which dust is resuspended from the soil surface, $kg/m^2/d$.
ρ_{si}	=	density of dust particles, kg/m^3.
α	=	volume fraction of the soil compartment that is gas, unitless.
β	=	volume fraction of the soil compartment that is water, unitless.
ϕ	=	total void fraction in soil compartment, unitless, $\phi = \alpha + \beta$.
Rh	=	hydraulic radius of water flowing over surface soil during a rain event, assumed to be 0.005 m.
d_i	=	depth of surface soil compartment during periods of no rain, m.
d_i^*	=	effective depth of saturated surface soil during a rain event, m, $d_i^* = Rh + d_i$
Runoff	=	flux of water transported away from surface soil compartment *i*, m^3/m^2-day.
$f_{run(ij)}$	=	fraction of water that runs off of surface soil compartment *i* that s transported to compartment *j*, unitless.

layers, all transformation processes are modeled as first-order processes; that is, linear with inventory (*i.e.*, the quantity of chemical substances contained in a compartment). The rate of mass removal in a first-order transformation is calculated as the product of the total inventory and the transformation rate constant. The transformation rate constant is the inverse of the residence time with respect to that reaction.

5.4 VERTICAL TRANSPORT ALGORITHMS

The transfer factors in the subsurface are a function of the advective flux (gas phase plus liquid phase) and the diffusive flux (gas phase plus liquid phase). In the sections below, upward and downward transfer factors are developed for the soil compartments. No provisions are made for preferential flow regions in the vadose zone that could lead to higher concentrations in the ground water because in most cases, the proportion of exposure from ground water is minimal for air pollutants.

5.4.1 THEORETICAL BASIS FOR THE TRANSPORT ALGORITHMS

The algorithms below are developed by assuming that chemical concentration in each compartment decreases exponentially with depth in that compartment. This type of concentration gradient has been demonstrated as the correct analytical solution of the one-dimensional, convective-dispersive, solute-transport equation in a vertical layer with a steady-state concentration maintained at its upper surface (ARS 1982). With the assumption of exponentially decreasing vertical concentration for each soil compartment, *i*, the variation in concentration with depth in that compartment is given by:

$$C_i(x) = C_i(0)\exp(-\gamma_i x) \tag{5-1}$$

where:

x = distance into the soil compartment measured from the top of the soil column (m);

$C_i(0)$ = peak chemical concentration in soil compartment i (mol/m^3), which is related to the total inventory N_i (moles) in this soil compartment (this relationship is provided below);

γ_i = the gradient of soil concentration change in soil compartment i (m^{-1}), and is obtained from the inverse of the normalized or characteristic depth X^*, that is $\gamma_i = 1/X^*$.

X^* is obtained as follows:

If $\lambda_i > 0$ then X^* = Minimum (DX_1, DX_2)
Otherwise, if $\lambda_i = 0$, then $X^* = DX_2$. (5-2)

DX_1 is the Damkoehler distance (the distance at which the soil concentration falls by 1/e based on the competition among diffusion, advection, and reaction) in units of meters and is given by:

$$DX_1 = \frac{ve_i + \sqrt{ve_i + 4De_i}}{2\lambda_i} \quad (5\text{-}3)$$

DX_2 is the depth that establishes the concentration gradient in soil in the absence of any reaction or transformation processes, in units of meters. It is obtained as follows:

If $ve_i > 0$, then DX_2 = Minimum $(4De_i/ve_i, DX_{sat})$
If $ve_i = 0$, then DX_2 = Minimum $(2d_i, \sqrt{(\pi)}, DX_{sat})$ (5-4)

ve_i = the effective advection velocity of a chemical in the soil compartment, i (m/day), and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of the moving phase and divided by the fugacity capacity of soil compartment i;

$$ve_i = v_i Z_{water}/Z_i \quad [5\text{-}5]$$

v_i = the average velocity of the moving liquid phase (assumed to be water) in the soil column i (m/day);
DX_{sat} = depth to saturation in the soil column (m);
d_i = the thickness of soil compartment i (m);
Z_{water} = the fugacity capacity of the moving phase, water (mol/[m^3-Pa]);
Z_i = the total fugacity capacity of soil compartment i (mol/[m^3-Pa]);
λ_i = removal rate constant for a chemical in soil compartment i, based on chemical transformation (day^{-1}); and
De_i = effective diffusion coefficient in soil compartment i (m^2/d), and is derived below.

Compartments such as soils and sediments are neither homogeneous nor single phase. When air and water occupy the tortuous pathways between stationary particles in a porous medium such as a soil or sediment, Millington and Quirk (1961) have shown that the effective diffusivity, D_{eff}, of a chemical in each fluid of the mixture is given by:

$$D_{eff} = (\omega^{10/3} / \phi^2) D_{pure} \quad (5\text{-}6)$$

where ω (α for gas fraction and β for water fraction) is the volume fraction occupied by this fluid, ϕ is the total void fraction in the medium (the volume occupied by all fluids) , and D_{pure} is the diffusion coefficient of the chemical in the pure fluid. Jury et al. (1983) have shown that the effective tortuous diffusivity in the water and air of a soil compartment, such as the root-zone soil(s), is given by:

$$De_i = \frac{Z_{air}}{Z_i}(\alpha_i^{10/3} / \phi_i^2)D_{air} + \frac{Z_{water}}{Z_i}(\beta_i^{10/3} / \phi_i^2)D_{water} \quad (5\text{-}7)$$

where De_i is the effective tortuous, mixed phase diffusion coefficient in the root-zone soil compartment, the Z's are the fugacity capacities derived previously.

5.4.2 RELATIONSHIP BETWEEN INVENTORY, N_i, AND PEAK CONCENTRATION, $C_i(0)$

The assumptions of a peak chemical concentration and an exponential gradient of chemical concentration within a soil compartment makes it possible to define $C_i(0)$ in terms of N_i:

$$N_i = Area_i \int_0^{d_i} C_i(0)\exp(-\gamma_i x)dx \quad (5\text{-}8)$$

$$N_i = Area_i[C_i(0) / \gamma_i][1 - \exp(-\gamma_i d_i)] \quad (5\text{-}9)$$

where:

N_i	=	compartment inventory (mol)
C_i	=	compartment concentration (mol/m^3)
d_i	=	thickness of soil compartment *i* (m); and
$Area_i$	=	horizontal area of the soil compartment (m^2).

Rearranging the right term of Equation 5-9 gives:

$$C_i(0) = \frac{N_i\gamma_i}{Area_i[1 - \exp(-\gamma_i d_i)]} \quad (5\text{-}10)$$

5.4.3 VERTICAL MASS EXCHANGE BETWEEN AIR AND THE UPPER SURFACE SOIL COMPARTMENT

The algorithm for representing diffusion exchange at the air/soil interface is based on defining the flux from air to soil in terms of the concentration gradient at the point of contact between air and soil.

$$Flux = U_{air}\left[C_{air} - C_i(0)\frac{Z_{air}}{Z_i}\right] \quad (5\text{-}11)$$

where:

U_{air} = mass transfer coefficient on the air side of the air/soil boundary (m/d) (It is typical to represent the mass transfer coefficient in air as the ratio of the diffusion coefficient in air, D_{air}, divided by the turbulent boundary compartment thickness, δ_{air}. For many compounds, D_{air} is on the order of 0.4 m/d and δ_{air} is on the order of 0.0005 m, so that U_{air} is on the order of 800 m/d.)

C_{air} = bulk concentration of chemical agent in the lowest compartment of the atmosphere, mol/m^3 and given by $C_{air} = N_a Z_{air}/[V_a Z_a]$, where N_a is the inventory (in mol) of the air compartment above the soil, Z_{air} is the fugacity capacity of pure air, V_a is the volume (in m^3) of this compartment, and Z_a is the total fugacity capacity of the air compartment (includes gas and particle phase of the atmosphere).

$C_i(0)$ = chemical concentration at the top of the uppermost soil compartment in a vertical set of soil compartments, ml/m^3, as given by Equation 5-6. There can be several vertical soil compartment sets in a model run.

Z_{air} = fugacity capacity of pure air, = 1/RT, mol/(m3-Pa).

Making the appropriate substitutions, the net flow of mass between air and soil by diffusion is calculated as:

Net Diffusion Flow ($a \leftrightarrow i$) (mol/day)

$$= Flux \times Area_i = U_{air}\left[\frac{Area_i \times Z_{air}}{V_a \times Z_a} N_a - \frac{\gamma_i}{[1-\exp(-\gamma_i d_i)]}\frac{Z_{air}}{Z_i} N_i\right] \quad (5\text{-}12)$$

It is important to note that the area used to calculate the flux is $Area_i$, the surface area of the soil compartment i that is shared with the lowest atmosphere compartment. This is not necessarily the surface area of the lowest atmosphere compartment.

For dry and wet deposition of particles from air to soil, the rate of mass flow is given by:

Particle Advection Flow (a→i) (mol/d)

$$= V_d[PC/\rho_p][Area_i/V_a][Z_{ap}/Z_a]N_a \quad (5\text{-}13)$$

where:

V_d = air-to-soil deposition ratio (includes only deposition that is not intercepted by plants, and is calculated as the total deposition velocity times one minus the plant interception fraction (mol/m^2/d per mol/m^3) ~ 400 m/d;

PC = particulate matter concentration in air ~ 6.0 x 10^{-8} kg/m^3;

ρ_p = density of the particulate matter in air ~ 2600 kg/m^3;

$Area_i$ = area of contact between the surface soil compartment and the lowest air compartment (m^2); and
V_a = volume of the air compartment (m^3).

For rainfall, the advection flow of chemical from air to the upper surface soil compartment is given by:

Rain Advection Flow ($a \rightarrow i$) (mol/d)

$$= rain[Z_{water} / Z_a][Area_i / V_a]N_a \quad (5\text{-}14)$$

where:

Z_{water} = fugacity capacity of pure water (*i.e.*, no suspended sediments)
Z_a = fugacity capacity of the air compartment (mol/m^3-Pa)
rain = the rate of rainfall (m/d).

For re-suspension of dust from the first surface soil compartment to the lower compartment of the atmosphere, the chemical flow from soil to air is given by:

Advection Flow ($i \rightarrow a$) (mol/d)

$$= [Respnd / \rho_{si}][Z_{si} / Z_i][Area_i / V_a]N_i \quad (5\text{-}15)$$

where:

Respnd = rate at which dust is resuspended from the soil surface ($kg/m^2/d$); and
ρ_{si} = density of the dust particles (kg/m^3).

Combining Equations 5-12 through 5-15 provides the following transfer-rate factors for the exchange of chemical species between the lowest atmosphere compartment and the surface soil compartment:

$$T_{a \rightarrow i} = \left[\frac{U_{air} \times Area_i \times Z_{air}}{V_a \times Z_a}\right] + \left\{V_s\left[\frac{PC}{\rho_p}\right]\left[\frac{Z_{ap}}{Z_a}\right] + rain\left[\frac{Z_{water}}{Z_a}\right]\right\} \times \left[\frac{Area_i}{V_a}\right] \quad (5\text{-}16)$$

$$T_{i \rightarrow a} = \left[\frac{U_{air}\gamma_i}{[1 - \exp(-\gamma_i d_i)]}\right]\left[\frac{Z_{air}}{Z_s}\right] + \left[\frac{Respnd}{\rho_{si}}\right]\left[\frac{Z_{si}}{Z_i}\right] \times \left[\frac{Area_i}{V_a}\right] \quad (5\text{-}17)$$

5.4.4 VERTICAL MASS EXCHANGE BETWEEN TWO VERTICALLY ADJACENT SOIL COMPARTMENTS

The vertical exchange of a chemical substance between two vertically adjacent soil compartments occurs through advection and diffusion. Only the net advection in the downward direction is considered due to long-term infiltration of rainwater. According to Equation 5-1, the concentration in each soil compartment i is given by:

$$C_i(x) = C_i(0)\exp(-\gamma_i x) \qquad \text{(same as 5-1 above)}$$

where x is measured from the top of the soil compartment i. Thus, the diffusion flow at the lower boundary of soil compartment i to compartment j is given by:

$$diffusion\ flow = -Area \times De_i \left.\frac{dC}{dx}\right|_{d_i} = Area \times De_i \times C_i(0) \times \gamma_i e^{-\gamma_i d_i} \qquad (5\text{-}18a)$$

where:

De_i = effective diffusion coefficient in soil compartment i, m2/d
d_i = the thickness of soil compartment i, m;

Conservation of mass requires that flow specified by equation 5-18 out of compartment i must equal the flow into compartment j at the upper boundary of compartment j, that is:

$$diffusion\ flow = -Area \times De_j \left.\frac{dC}{dx}\right|_{0} = Area \times De_j \times C_j(0) \times \gamma_j \qquad (5\text{-}18b)$$

Combining equations 5-18a and 5-18b gives:

$$diffusion\ flow = Area \times \frac{\left[De_i \times C_i(0) \times \gamma_i e^{-\gamma_i d_i} + De_j \times C_j(0) \times \gamma_j\right]}{2} \qquad (5\text{-}19)$$

$C_i(0)$ is found from the condition:

$$N_i = Area \int_0^{d_i} C_i(0) e^{-\gamma_i x} dx = Area \times \frac{C_i(0)}{\gamma_i} \times \left(1 - e^{-\gamma_i d_i}\right) \qquad (5\text{-}20)$$

Rearranging gives:

$$C_i(0) = \frac{N_i \gamma_i}{Area \times \left(1 - e^{-\gamma_i d_i}\right)} \qquad (5\text{-}21)$$

In order to conserve concentration equilibrium at the boundary between two soil compartments, the following condition must hold:

$$C_j(0) = \frac{Z_j}{Z_i} C_i(0) e^{-\gamma_i d_i} = \frac{Z_j}{Z_i} \times \frac{N_i \gamma_i \times e^{-\gamma_i d_i}}{Area \times \left(1 - e^{-\gamma_i d_i}\right)} \tag{5-22}$$

Substituting equations 5-21 and 5-22 into equation 5-19 gives

$$diffusion\ flow = \frac{N_i \gamma_i}{Z_i \left(e^{+\gamma_i d_i} - 1\right)} \times \left(\frac{De_i \gamma_i Z_i + De_j \gamma_j Z_j}{2} \right) \tag{5-23}$$

Then in order to express mass transfer between two compartments, the diffusion flow is represented in the following form:

$$diffusion\ flow = Area \times Y_{ij} \left(\frac{N_i}{Z_i V_i} - \frac{N_j}{Z_j V_j} \right) \tag{5-24}$$

where:

Y_{ij} = fugacity-capacity adjusted mass transfer coefficient between compartments *i* and *j*, mol/(m^2-Pa-day).

N_j, the total inventory in compartment *j* is given by:

$$N_j = Area \int_0^{d_j} C_j(0) e^{-\gamma_j x} dx = Area \times \frac{C_j(0)}{\gamma_j} \times \left(1 - e^{-\gamma_j d_j}\right) \tag{5-25}$$

Substituting equation 5-23 in equation 5-25 gives:

$$N_j = \frac{Z_j N_i \times \gamma_i \times \left(1 - e^{-\gamma_j d_j}\right)}{Z_i \times \gamma_j \times \left(e^{+\gamma_i d_i} - 1\right)} \tag{5-26}$$

An expression for Y_{ij} is obtained by substituting equation 5-26 for N_j in equation 5-24 and then setting equation 5-24 equal to equation 5-23:

$$\frac{N_i \gamma_i}{Z_i \left(e^{+\gamma_i d_i} - 1\right)} \left(\frac{De_i \gamma_i Z_i + De_j \gamma_j Z_j}{2} \right) = Y_{ij} \frac{N_i}{Z_i} \left(\frac{1}{d_i} - \frac{\gamma_i \times \left(1 - e^{-\gamma_j d_j}\right)}{d_j \times \gamma_j \times \left(e^{+\gamma_i d_i} - 1\right)} \right) \tag{5-27}$$

Rearranging gives:

$$Y_{ij} = \frac{Z_i De_i \gamma_i + Z_j De_j \gamma_j}{2\left[\frac{\left(e^{+\gamma_i d_i} - 1\right)}{\gamma_i d_i} - \frac{\left(1 - e^{-\gamma_j d_j}\right)}{\gamma_j d_j}\right]} \quad (5\text{-}28)$$

The definition of Y_{ij} in equation 5-28 completes the definition of all terms in equation 5-24.

The advection flux from soil compartment *i* to *j* at the lower end, d_i, of compartment *i* is given by:

$$advection\ flow(i\ to\ j) = Area \times ve_i \times C_i(0) \exp\left(-\gamma_i d_i\right) \quad (5\text{-}29)$$

where:

ve_i = the effective advection velocity of a chemical in the soil compartment, *i*; m/d, and equal to the rate of soil-solution movement, v_i, multiplied by the fugacity capacity of the moving phase and divided by the fugacity capacity of soil compartment *i*;

$$ve_i = v_i Z_{water} \Big/ Z_i$$

v_i = the average velocity of the moving phase (assumed to be water) in the soil compartment, *i*; m^{-1}.

Substituting Equation 5-21 for $C_i(0)$ in Equation 5-29 gives:

$$advection\ flow(i\ to\ j) = \frac{N_i \gamma_i ve_i}{\left(e^{+\gamma_i d_i} - 1\right)} \quad (5\text{-}30)$$

Combining Equations 5-24 and 5-30 and multiplying by $Area_i$, gives the flow from *i* to *j* as:

net total flow (mol/d) (*i* to *j*) = [*net diffusion flow* + *advection flow*] (*i* to *j*)

$$= Y_{ij}\left(\frac{N_i}{Z_i d_i} - \frac{N_j}{Z_j d_j}\right) + \frac{N_i \gamma_i ve_i}{\left(e^{+\gamma_i d_i} - 1\right)} = T_{i \to j} N_i - T_{j \to i} N_j \quad (5\text{-}31)$$

From this equation, we can derive terms for $T_{i\to j}$ and $T_{j\to i}$:

$$T_{i\to j} = \frac{Y_{ij}}{d_i Z_i} + \frac{ve_i \gamma_i}{\left(e^{+\gamma_i d_i} - 1\right)} \tag{5-32}$$

$$T_{j\to i} = \frac{Y_{ij}}{d_j Z_j} \tag{5-33}$$

5.5 STORM WATER RUNOFF PROCESSES

Horizontal transport processes included in TRIM.FaTE include solution runoff and erosion.

5.5.1 AQUEOUS PHASE TRANSPORT PROCESSES

During a rainfall event, some of the water travels laterally across the soil as runoff. As the water travels over the soil, the concentration of the water approaches that of the soil pore water beneath it. Although the water flowing over the soil does not necessarily reach equilibrium instantaneously, some researchers use an approximation that runoff is in equilibrium with the soil pore water (Wallach et al. 1989). Currently in TRIM.FaTE, a steady-state relationship between the runoff water and the pore water is used. Runoff water is considered a phase of surface soil compartment at each spatial location. A mass-balance approach is used to determine the concentration in run-off water that moves from one soil compartment to a horizontally adjacent compartment.

Runoff transport is assumed to carry chemical from the surface soil compartment of one land unit to the next. During a rain event the surface soil compartment is assumed to be saturated with rain water and this water is assumed to be in equilibrium with the soil solids on the surface. It should be recognized that at times (*e.g.*, short rain events, during very dry periods of the year) the soil will not necessarily be fully saturated with rain water. However, the assumption of saturation by rain is not expected to have a large impact on results for events when the soil is not saturated. Moreover, a lack of information on the extent to which soil is saturated during rain makes this a convenient starting point. The assumption of that chemical equilibrium has more uncertainty and needs further research. During periods of no rain, the fugacity capacity of the surface soil compartment is given by:

$$Z_i = \alpha Z_{air} + \beta Z_{water} + (1-\phi) Z_{si} \tag{5-34}$$

During periods of rain, the fugacity capacity of the surface soil compartment is given by:

$$Z_i(rain) = [(Rh + \phi d_i) Z_{water} + (1 - \phi d_i) Z_{si}] / d_i * \tag{5-35}$$

where:

Z_{water}	=	fugacity capacity of pure water (*i.e.*, no suspended sediments)
Z_{si}	=	fugacity capacity of the solids (or solid phase) in the ith soil layer (mol/m^3-Pa)
α	=	volume fraction of the surface soil that is gas;
β	=	volume fraction of soil that is water;
ϕ	=	total void fraction in surface *soil,* $\phi = \alpha + \beta$;
Rh	=	hydraulic radius of the water flowing over the surface soil during a rain event, assumed to be 0.005 m;
d_i	=	depth of the surface soil compartment during periods of no rain (m); and
d_i*	=	effective depth of the saturated surface soil during a rain event (m), $d_i^* = Rh + d_i$.

The hydraulic radius, *Rh*, for flow of water on top of the soil surface is site specific and depends on the hydraulic gradient (slope of the flow), the rainfall rate, and the recharge rate. It is considered an uncertain variable, but is assigned a default value of 0.005 m. A hydraulic balance is needed to determine the flow of the water and the depth of the runoff stream. From the Geographic Information System (GIS) data, the runoff is estimated.

During a rain event, the horizontal flow of chemical from surface soil compartment *i* to adjacent compartment *j* is given by:

$$Runoff\ flow(i \rightarrow j) = Runoff \times f_{run}(i \rightarrow j) \times Z_i(rain) / Z_i / d_i^* \qquad (5\text{-}36)$$

where:

Runoff	=	flux of water that is transported away from surface soil compartment *i* (m^3/m^2-day); and
$f_{run}(i \rightarrow j)$	=	fraction of water that runs off of surface soil compartment *i* that is transported to compartment *j* (unitless).

From Equation 5-36, the expression for $T_{i \rightarrow j}(runoff)$ can be obtained:

$$T_{i \rightarrow j}(runoff) = Runoff \times f_{run}(i \rightarrow j) \times Z_i(rain) / (Z_i d_i^*) \qquad (5\text{-}37)$$

5.5.2 SOLID PHASE TRANSPORT PROCESSES

The algorithm for erosion runoff is based on knowledge of the erosion factor for the region being modeled. Similar to solution runoff, erosion is also applied only to the surface soil layer. Although erosion is most likely to occur during rain events, erosion can be modeled as a continuous event. The flow of chemical (mol/d) from one surface soil compartment to another by erosion is represented by the following expression:

$$Erosion\ flow\ (i \rightarrow j) = erosion \times f_{ero}\ (i \rightarrow j) \times Z_{si} / Z_i \times N_i / (\rho_{si} d_i) \qquad (5\text{-}38)$$

where:

$erosion$	=	erosion factor (kg of soil solids eroded per day per m^2);
$f_{ero}(i \rightarrow j)$	=	fraction of soil eroded from surface soil compartment *i* that is transported to compartment *j* (unitless);
Z_{si}	=	fugacity capacity of the soil particles in soil compartment *i* (mol/ [m^3-Pa]);
ρ_{si}	=	density of the soil particles, ~ 2600 kg/m^3.

From Equation 5-36, the expression for $T_{i \rightarrow j}(erosion)$ can be obtained:

$$T_{i->j}(erosion) = erosion \times f_{ero}(i \rightarrow j) \times Z_{si} / (Z_i \rho_{si} d_i) \quad [5\text{-}39]$$

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6. GROUND WATER ALGORITHMS

The horizontal flow of pollutants in the saturated zone (ground water) is not expected to be a significant pathway when considering air pollutants. Transport has been simulated because it is a more significant process than diffusion/dispersion. In the prototype, ground water is modeled as a receiving cell from the vadose zone and a sending cell to surface water. The transfer factors for soil to ground water and for ground water to surface water are based on the aqueous phase advection only by substituting recharge for flow velocity:

$$T_{soil \rightarrow groundwater} = \frac{A_{soil\ groundwater}}{V_{soil}} \frac{Z_{water}}{Z_{total}} Recharge \quad (6\text{-}1)$$

and

$$T_{groundwater \rightarrow surfacewater} = \frac{A_{groundwater\ surfacewater}}{V_{groundwater}} \frac{Z_{water}}{Z_{total}} Recharge \quad (6\text{-}2)$$

where:

A	=	cross section area between cells (m^2)
V	=	volume of cell (m^3)
Recharge	=	annual recharge into ground water (m/h).

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7. BIOTIC ALGORITHMS

In this section algorithms for transfers between a biotic compartment type and another biotic or abiotic compartment type are presented. Algorithms are based on diffusive or advective transfer, and most common instances of the latter are transfers via the wildlife diet. Most algorithms apply to all air pollutants, though some that involve octanol-water partition coefficients are only applicable to organic chemicals and mercury species. Some of the equations represent dynamic processes, and others are simple models for which a time-to-equilibrium is calculated. The text box on the next page and continued on the following pages provides a quick summary of the algorithms developed in this chapter and provides a definition of all parameters used. The derivation of chemical-specific algorithms and input parameters is presented in Appendix A.

7.1 SELECTING THE BIOTIC COMPONENTS OF TRIM.FATE

The methodology for determining biotic compartment types is described in Section 3.3 of Volume I of the Technical Support Document for TRIM.FaTE. All major trophic levels in terrestrial and aquatic systems are represented. Default, representative species are chosen based on their prevalence at the test location and/or the availability of parameters for them. Additional species may be chosen based on policy considerations, such as the Endangered Species Act.

General algorithms for plants (Section 7.2.1), soil detritivores (Section 7.2.2), terrestrial mammals and birds (Section 7.2.3) and aquatic biota (Section 7.3) are listed below.

7.2 ALGORITHMS FOR TERRESTRIAL AND SEMI-AQUATIC BIOTA

7.2.1 PLANTS

The plant consists of four compartment types: leaf, stem, root, and the leaf surface (particulate on leaf Lp). Although the leaf surface is not in the plant, it is useful to track because: (1) it is a reservoir of chemical moving to leaves and (2) wildlife diets include particulate matter on leaves.

Several problems arise in modeling uptake and emissions of chemicals by plants.

- Little information is available on the transformations of chemicals within plants.
- The volatilization of chemicals from soils and uptake by plant foliage occurs at a scale that is not easy to model in TRIM.FaTE.
- Little is known about the rate at which chemicals enter plant leaves from particulate matter or rain water on the leaf surface.
- The transport of many chemical species within the plant is not well understood.

Summary of Transport Algorithms Developed in this Chapter

PLANTS

Particulate phase of air to surface of plant leaf (when no rain):

$$T_{Ap \rightarrow Lp} = \frac{v_d I_d A_S}{V_A}$$

Surface of plant leaf to particulate phase of air (when no rain):

$$T_{Lp \rightarrow Ap} = \frac{v_d I_d A_S}{V_A}$$

Vapor phase of air to the leaf surface (during rain):

$$T_{A \rightarrow Lp} = \frac{1}{V_A} \times w_r \times J_{rain} \times A_S \times I_W$$

Particles in air to the leaf surface (during rain):

$$T_{Ap \rightarrow Lp} = \frac{1}{V_A} \times w_r \times J_{rain} \times A_S \times I_W$$

Surface of leaf to surface soil (during rain):

$$T_{LP \rightarrow Ss} = 57.6$$

Leaf surface to leaf:

$$T_{Lp \rightarrow L} = k_{Lp-L}$$

Leaf to leaf surface:

$$T_{L \rightarrow Lp} = 0.01 \times k_{Lp-L}$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

PLANTS (cont.)

Leaf to air (diffusion):

$$T_{L\rightarrow A}^{diff} = (2LAI \times A_S \times g_C + A_S \times g_S) \times \frac{1}{V_L} \times \frac{Z_A}{Z_L}$$

Air to leaf (diffusion):

$$T_{A\rightarrow L}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_A}$$

$$T_{Sr\rightarrow R} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \frac{\rho area_R}{\rho vol_R} \times \frac{K_{R-Sr}}{d_{Sr}}$$

Root-zone soil to root:
Root to root-zone soil:

$$T_{r\rightarrow Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right]$$

Root-zone soil to stem:

$$T_{Sr\rightarrow St} = \frac{Q_{Xy} \times Z_{water}}{Z_{Sr} \times V_{Sr}} \times TSCF$$

Leaf to stem:

$$T_{L\rightarrow St} = Q_P \times \frac{1}{V_L \times K_{Lp-h}}$$

Stem to leaf:

$$T_{St\rightarrow L} = Q_{Xy} \times \frac{1}{V_{St} K_{St-Xy}}$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

PLANTS (cont.)

Leaf to surface soil (litterfall):

$$T_{L \rightarrow Ss} = L$$

Leaf surface (particulate matter) to surface soil (litterfall):

$$T_{Lp \rightarrow Ss} = L$$

where:

V_A = volume of air volume element (m^3)
v_d = dry deposition velocity of particles (m/d)
I_d = fraction of dry-depositing chemical that is intercepted by plant canopy
A_S = soil area (m^2)
J_{rain} = rain rate (m/d)
w_r = washout ratio (mass chemical/volume rain ÷ mass chemical/volume air)
I_W = interception fraction for wet deposition (unitless)
$k_{Lp\text{-}L}$ = first-order rate constant for transfer of chemical from particles on leaf surface to leaf
LAI = 1-sided leaf-area index (m^2 total leaf area / m^2 underlying soil area)
V_L = volume of leaves (m^3)
Z_P = fugacity capacity (Z-factor) of chemicals in plant (mol-$Pa^{-1}m^{-3}$)
Z_L = fugacity capacity (Z-factor) of chemicals in leaf (mol-$Pa^{-1}m^{-3}$)
g_S = conductance of stomatal pathway, including mesophyll (m/d)
g_C = total conductance of the cuticular path, including the air boundary layer (m/d)
Z_A = fugacity capacity of chemicals in the vapor phase of air (mol$Pa^{-1}m^3$)
$K_{R\text{-}Sr}$ = root-soil partition coefficient (wet kg/kg per wet kg/kg)
$\rho area_R$ = areal density of root in root-zone soil (kg root fresh wt/m^2)
ρvol_R = wet density of root (kg/m^3)
d_{Sr} = depth of root-zone soil (m)
Q_{xy} = flow of transpired water in cell area (m^3/d, below)
$TSCF$ = transpiration stream concentration factor (mg/m^3 of xylem per mg/m^3 of soil pore water)
V_{SrW} = volume of water in root-zone soil (m^3)
Z_{water} = fugacity capacity (Z-value) for water
Z_{Sr} = fugacity capacity (Z-value) for root-zone soil
V_{Sr} = volume of root-zone soil volume element (m^3)
Q_P = phloem flux into fruit (m^3/d), due to advection (assume 5 percent of Q_{xy}, Paterson et al. 1991)
$K_{Lp\text{-}h}$ = partition coefficient between leaves and phloem water (mass/vol to mass/vol)
Q_{xy} = flow of transpired water (m^3/d)
V_{St} = volume of stem (m^3)
$K_{St\text{-}Xy}$ = partition coefficient between stem and xylem water (mass/vol to mass/vol)
L = litterfall rate (d^{-1})

Summary of Transport Algorithms Developed in this Chapter (cont.)

SOIL DETRITIVORES

Root-zone soil to earthworm:

$$T_{Sr\rightarrow worm} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \frac{\rho area_{worm}}{\rho vol_{worm}} K_{worm-Sr} \frac{1}{d_{Sr}}$$

Earthworm to root-zone soil:

$$T_{worm\rightarrow Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right]$$

Root-zone soil to soil arthropod:

$$T_{Sr\rightarrow arth} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \rho area_{arth} \times A_S \times \frac{K_{arth-Sr}}{M_{Sr}}$$

Soil arthropod to root-zone soil:

$$T_{arth\rightarrow Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right]$$

where:

$\rho area_{worm}$	=	areal density of earthworm community in root-zone soil (kg worm fresh wt/m^2)
ρvol_{worm}	=	wet density of earthworm (kg/m^3)
$K_{worm-Sr}$	=	earthworm-soil partition coefficient (wet kg/kg per wet kg/kg)
d_{Sr}	=	depth of root-zone soil (v_{sr}/A_S)
A_S	=	soil area (m^2)
$K_{arth-Sr}$	=	arthropod-soil partition coefficient (wet kg/kg per wet kg/kg)
M_{Sr}	=	total mass of root zone soil which contains arthropods (kg)
$\rho area_{arth}$	=	areal density of arthropod community in root-zone soil (kg arthropod fresh wt/m^2)

Summary of Transport Algorithms Developed in this Chapter (cont.)

TERRESTRIAL WILDLIFE

Water to terrestrial vertebrate:

$$T_{w\rightarrow wl} = \rho area_{wl} \times A_S \times \frac{I_w \times A_w}{V_w}$$

Surface soil to terrestrial vertebrate:

$$T_{SS\rightarrow wl} = \rho area_{wl} \times A_S \times \frac{I_{SS} \times A_{SS}}{V_{SS} \times \rho vol_{SS} wet}$$

Plant leaf to terrestrial vertebrate:

$$T_{L\rightarrow wl} = \rho area_{wl} \times \frac{p_P \times I_D \times A_P}{\rho area_L}$$

Surface of plant leaf to terrestrial vertebrate:

$$T_{LP\rightarrow wl} = \rho area_{wl} \times \frac{p_P \times I_D \times A_P}{\rho area_L}$$

Earthworm to terrestrial vertebrate:

$$T_{worm\rightarrow wl} = \rho area_{wl} \times \frac{p_{worm} \times I_D \times A_{worm}}{\rho area_{worm}}$$

Soil arthropod to terrestrial vertebrate:

$$T_{arth\rightarrow wl} = \rho area_{wl} \times \frac{p_{arth} \times I_D \times A_{arth}}{\rho area_{arth}}$$

Terrestrial vertebrate to terrestrial vertebrate:

$$T_{wl\rightarrow wl} = \rho area_{wl} \times \frac{p_{wl} \times I_D \times A_{wl}}{\rho area_{wl}}$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

TERRESTRIAL WILDLIFE (cont.)

Fish to terrestrial vertebrate:

$$T_{f\rightarrow wl} = \rho area_{wl} \times A_S \times \frac{p_f \times I_D \times A_f}{A_{sw} \times \rho area_f}$$

Benthic invertebrate or flying insect to terrestrial vertebrate:

$$T_{bi\rightarrow wl} = \rho area_{wl} \times A_S \times \frac{p_{BI} \times I_D \times A_{BI}}{A_{sw} \times \rho area_{BI}}$$

Air to terrestrial vertebrate:

$$T_{A\rightarrow wl} = \rho area_{wl} \times A_S \times \frac{I_A \times A_A}{V_A}$$

Terrestrial vertebrate to surface soil:

$$T_{wl\rightarrow SS} = f_{uss} E_u$$

Terrestrial vertebrate to water:

$$T_{wl\rightarrow w} = f_{uw} E_u$$

where:

$\rho area_{wl}$	=	wet wildlife biomass density per unit area (kg/m^3, may be calculated as number of animals times average body weight)
A_S	=	area of surface soil (m^2)
I_w	=	water ingestion rate (m^3/kg body weight/d)
V_w	=	volume of water (m^3)
A_w	=	assimilation efficiency of chemical from water (unitless)
I_{SS}	=	surface soil ingestion rate (kg/kg body weight/d)
V_{SS}	=	volume of surface soil (kg)
$\rho vol_{SS}wet$	=	wet bulk density of soil (kg/m^3)
A_{SS}	=	assimilation efficiency of chemical from surface soil (unitless)
p_P	=	proportion of plant matter in diet (unitless)
I_D	=	dietary ingestion rate (kg/kg body weight/d)
A_P	=	assimilation efficiency of chemical from plant in diet (unitless)
$\rho area_L$	=	areal biomass density of foliage (kg/m^2, wet weight)
p_{worm}	=	proportion of earthworm in diet (unitless)
A_{worm}	=	assimilation efficiency of chemical from earthworm in diet (unitless)
$\rho area_{worm}$	=	areal biomass density of earthworms (kg/m^2, wet weight)

Summary of Transport Algorithms Developed in this Chapter (cont.)

TERRESTRIAL WILDLIFE (cont.)

p_{arth}	=	proportion of soil arthropods in diet (unitless)
A_{arth}	=	assimilation efficiency of chemical from soil arthropods in diet (unitless)
p_{wl}	=	proportion of terrestrial wildlife in diet (unitless)
A_{wl}	=	assimilation efficiency of chemical from other wildlife in diet (unitless)
p_f	=	proportion of fish in diet (unitless)
A_f	=	assimilation efficiency of chemical from fish in diet (unitless)
$\rho area_f$	=	areal biomass density of fish (kg/m^2, wet weight, use correct size range for diet)
p_{bi}	=	proportion of benthic invertebrates or emergent flying insects in diet (unitless)
A_{bi}	=	assimilation efficiency of chemical from benthic invertebrates or flying insects in diet (unitless)
A_{sw}	=	area of surface of surface water body (m^2)
$\rho area_{bi}$	=	areal biomass density of benthic invertebrates (kg/m^2, wet weight)
I_A	=	inhalation rate (m^3/kg body weight/d)
V_A	=	volume of air (m^3)
A_A	=	assimilation efficiency of chemical from air (unitless)
E_u	=	chemical elimination through excretory processes (urine and feces) (d^{-1})
f_{uw}	=	fraction of urine and feces excreted to water
f_{uss}	=	fraction of urine and feces excreted to surface soil

AQUATIC BIOTA

Water to macrophytes:

$$T_{w\rightarrow mp} = \frac{V_{mp}\, k_{mp,acc-sw}}{V_w}$$

Macrophytes to water:

$$T_{bi\rightarrow mp} = k_{mp,dep-sw}$$

Water (interstitial or overlying) to benthic invertebrates:

$$T_{w\rightarrow bi} = \frac{n_{bi}\, m_{bi}\, k_{bi,acc-w}}{V_w}$$

Benthic invertebrates to water (interstitial or overlying):

$$T_{bi\rightarrow w} = k_{bi,dep-w}$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

AQUATIC BIOTA (cont.)

Sediment to benthic invertebrates:

$$T_{sed \rightarrow bi} = \frac{n_{bi}\, m_{bi}\, k_{bi,acc-sed}}{V_{sed}\, \rho_{sed}}$$

Benthic invertebrates to sediment:

$$T_{bi \rightarrow sed} = k_{bi,dep-sed}$$

Water to a specific fish domain (*i.e.*, herbivore, omnivore, or carnivore), using the bioenergetic-based kinetic model for nonionic organic chemicals:

$$T_{water \rightarrow fish} = \frac{n_f\, m_f\, k_u}{V_w}$$

A specific fish domain (*i.e.*, herbivore, omnivore, or carnivore) to water, using the bioenergetic-based kinetic model for nonionic organic chemicals:

$$T_{fish \rightarrow water} = k_{eg}$$

A specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore) to the water domain,using the bioenergetic-based kinetic model for mercury:

$$T_{receptor\,(fish) \rightarrow water} = K_E$$

Dietary items to a specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore), using the bioenergetic-based kinetic model:

$$T_{diet \rightarrow receptor\,(fish)} = \frac{n_{receptor}\, m_{receptor}}{n_{diet}\, m_{diet}} \times F_d \times E$$

Dietary items to a specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore), using the time to steady-state-based kinetic model :

$$T_{diet \rightarrow receptor\,(fish)} = \frac{n_{receptor}\, m_{receptor}}{n_{diet}\, m_{diet}} \times \left[\frac{-\ln(1-\alpha)}{t_\alpha} \right] \times K_{receptor-diet}$$

Summary of Transport Algorithms Developed in this Chapter (cont.)

AQUATIC BIOTA (cont.)

A specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore) to the associated dietary items, using the time to steady-state-based kinetic model:

$$T_{receptor\,(fish)\rightarrow diet} = \left[\frac{-\ln(1-\alpha)}{t_{\alpha}}\right]$$

where:

$K_{receptor\text{-}diet}$	=	receptor-diet partition coefficient
$k_{mp,acc\text{-}sw}$	=	accumulation from surface water, for macrophytes (1/day)
$k_{mp,dep\text{-}sw}$	=	depuration to surface water, for macrophytes (1/day)
$k_{bi,acc\text{-}sed}$	=	accumulation from sediment, for benthic infauna (1/day)
$k_{bi,acc\text{-}w}$	=	accumulation from water, for benthic infauna (1/day)
$k_{bi,dep\text{-}sed}$	=	depuration to sediment, for benthic infauna (1/day)
$k_{bi,dep\text{-}w}$	=	depuration to water, for benthic infauna (1/day)
k_{eg}	=	elimination via the gills, for fish (1/day)
k_{u}	=	uptake rate constant for fish from water via the gills (1/kg-day)
n_{bi}	=	number of organisms comprising the benthic invertebrate domain
n_{diet}	=	number of contaminated items comprising the potential diet
n_{f}	=	number of organisms comprising a specific fish domain
$n_{receptor}$	=	number of receptors
m_{bi}	=	mass of individual organisms comprising the benthic invertebrate domain (µg)
m_{diet}	=	mass of individual items comprising the potential diet (µg)
m_{f}	=	mass of individual organisms comprising a specific fish domain (µg)
$m_{receptor}$	=	mass of individual receptors (µg)
t_{α}	=	time required to reach α percent of the steady-state value when the concentration in the source is approximately constant with time (day)
V_{mp}	=	volume of the macrophyte in the cell (L)
V_{sed}	=	volume of sediment in the cell (L)
V_{w}	=	volume of water in the cell (L)
ρ_{sed}	=	bulk density of sediment (g/L)
F_{d}	=	feeding rate constant (kg[prey]/kg[predator]-day)
E	=	efficiency of transfer of chemical

- The accumulation of chemicals by wood is not well understood; therefore, trees in TRIM.FaTE consist of leaves only and not stems or roots, except to the extent that stems are conduits of chemicals from leaves.

7.2.1.1 Transfer of Particles and Rain to Surface of Leaf

The surface of the leaf includes: dry particulate matter deposited to the plant surface, particles deposited to the plant surface in rain water, and rain water containing gaseous chemical. Deposition is defined here as the mass transfer of suspended particulates from air to the plant surface. Elsewhere (*e.g.*, Lindberg et al. 1992), the deposition of chemicals to plants is defined to include the gaseous fraction of the pollutants that come into contact with plants. The uptake of gaseous pollutants in TRIM.FaTE is treated below.

Dry or wet deposition to the surface of the leaf is the deposition velocity times the leaf interception fraction. The leaf interception fraction (I) is the fraction of particles that land on the leaf; thus 1-I is the fraction that lands on soil. It is common for a concentration of a deposited particulate chemical to be estimated with respect to the leaf or above-ground plant mass. However, when that concentration is estimated, it is often forgotten that most of the chemical mass is still *on* the plant rather than *in* it.

Dry Deposition of Particles to Surface of Plant Leaves

Dry deposition is estimated by multiplying the predicted air concentration at ground level by the deposition velocity (U.S. EPA 1997a). Thus, a flux equation that expresses dry deposition to the leaf, from van de Water (1995) follows. Note that the area of soil and that associated with an air volume element may be different.

$$\frac{dN_{Lp}}{dt} = \frac{N_{Ap}}{V_A} v_d I_d A_S \qquad (7\text{-}1)$$

where:

N_{Lp} = mass of chemical depositing on leaf surfaces from particulate matter in air (kg)
N_{Ap} = mass of particle-bound chemical in air (kg)
V_A = volume of air volume element (m^3)
v_d = dry deposition velocity of particles (m/d)
I_d = fraction of dry-depositing chemical that is intercepted by plant canopy (unitless, below)
A_S = soil area (m^2)

The interception fraction for dry deposition (I_d) may be calculated using the following equation (Baes et al. 1984):

$$I_d = 1 - e^{(1-W_L)(-\alpha \times \rho area)} \quad (7\text{-}2)$$

where:

α = vegetation attenuation factor (m^2/kg)
$\rho area$ = wet above-ground non-woody vegetation biomass inventory per unit area (kg/m^2)
W_L = water content of leaf (mass/mass, unitless)

The water content adjusts ρarea to represent dry biomass. The equation was originally derived for pasture grasses and hay and expanded to other crops. For this reason, the biomass should not include wood. The vegetation attenuation factor (sometimes called the foliar interception constant) is sometimes equivalent to the surface area of leaves divided by plant biomass (van de Water 1995) or the leaf biomass if the plant is woody.

Thus,

$$T_{Ap \rightarrow Lp} = \frac{v_d I_d A_S}{V_A} \quad (7\text{-}3)$$

where:

$T_{Ap\text{-}Lp}$ = transfer factor from particulate phase of air to surface of plant leaf (process occurs when it is not raining)

If it is assumed that particles are blown off the plant with wind at a rate that equals the deposition rate to leaves, and all particles are dispersed in air,

$$T_{Lp \rightarrow Ap} = \frac{v_d I_d A_S}{V_A} \quad (7\text{-}4)$$

where:

$T_{Lp \rightarrow Ap}$ = transfer factor from surface of plant leaf to particulate phase of air (process occurs when it is not raining)

Wet Deposition to Plants

Rain scavenges some of the chemical mass from the vapor phase and particulate phase of air. Wet deposition resulting from these processes may be modeled distinctly with the same equation. The rate of mass transfer of vapor-phase or particulate phase mercury from air to rain

water and to the surface of the plant leaf is described by the following equation (modified from van de Water 1995):

$$\frac{dN_{Lp}}{dt} = \frac{N_A}{V_A} \times w_r \times J_{rain} \times A_S \times I_W \quad (7\text{-}5)$$

where:

N_{Lp}	=	mass of chemical on surface of leaf (kg)
N_A	=	mass of chemical in gas phase of air (kg)
V_A	=	volume of air (m^3)
J_{rain}	=	rain rate (m/d)
w_r	=	washout ratio (mass chemical/volume rain ÷ mass chemical/volume air)
A_S	=	area of soil (m^2)
I_W	=	interception fraction for wet deposition (unitless)

The interception fraction may be calculated using the following equation from Muller and Prohl (1993). The fraction is dependent on how much water the leaf can hold, the total amount of rainfall, and the ability of the element or compound to stick to the leaf.

$$I_w = \frac{LAI \times S}{rain}\left[1 - e^{\left(\frac{-\ln 2}{3S} \times rain\right)}\right] \quad (7\text{-}6)$$

where:

LAI	=	1-sided leaf-area index (m^2 total leaf area / m^2 underlying soil area)
S	=	vegetation-dependent leaf-wetting factor (retention coefficient) (m)
$rain$	=	amount of rainfall of a rainfall event (m)

If I_w is calculated to be greater than 1, then the value must be set to 1. Thus,

$$T_{A-Lp} = \frac{1}{V_A} \times w_r \times J_{rain} \times A_S \times I_W \quad (7\text{-}7)$$

where:

$T_{A\text{-}Lp}$	=	the transfer factor from the vapor phase of air to the leaf surface

The rate of mass transfer of particulate-phase mercury from air to rain water and to the surface of the plant leaf may be described by an analogous equation:

$$\frac{dN_{Lp}}{dt} = \frac{N_{Ap}}{V_A} \times w_r \times J_{rain} \times A_S \times I_W \quad (7\text{-}8)$$

where:

N_{Lp} = mass of chemical on surface of leaf (kg)
N_{Ap} = mass of chemical in particulate phase of air (kg/m^3)
V_A = volume of air (m^3)
w_r = washout ratio (mass chemical/volume rain ÷ mass chemical/volume air)
J_{rain} = rate of rainfall (m/d)
A_S = area of soil (m^2)
I_W = interception fraction (unitless, see equation above)

Thus,

$$T_{Ap \rightarrow Lp} = \frac{1}{V_A} \times w_r \times J_{rain} \times A_S \times I_W \tag{7-9}$$

where:

$T_{Ap \rightarrow Lp}$ = the transfer factor from particles in air to the leaf surface

Washoff of Chemical from Plant Surface

It has been observed that particles on the surface of conifer leaves are washed off (during rain events) according to first-order kinetics with a rate constant of 0.04 per min (McCune and Lauver 1986). The rate of 0.04 per min is equivalent to 2.4 per hour or 57.6 per day. It may be assumed that the particles deposited in rain water and the chemical dissolved in rain water is washed off at the same rate. Thus,

$$\frac{dN_{Lp}}{dt} = -57.6 \times N_{Lp} \tag{7-10}$$

and

$$T_{Lp \rightarrow Ss} = 57.6 \tag{7-11}$$

where:

$T_{Lp \rightarrow Ss}$ = transfer factor from surface of leaf to surface soil during rain (d^{-1})

An alternative type of transfer would be an instantaneous transfer at the end of a rain event, where the transfer would also be derived from McCune and Lauver (1986):

$$T_{LP \rightarrow Ss} = 1 - e^{-0.0003 rain} \tag{7-12}$$

where:

$T_{Lp \rightarrow Ss}$ = transfer factor from surface of leaf to surface soil during rain (instantaneous)
rain = cumulative amount of rain during rain event (m)

The implementation of this transfer may be required if the high first-order rate constant above (which is equivalent to 2.4 per hour) causes instability in LSODE, the differential equation solver.

Note that it may not be assumed that the transfer factor for loss to soil is the same as the transfer from the vapor phase of air or particles in air via rain (as is assumed with dry deposition). In order to have this option, the vapor phase and particulate phase of the chemical in rain water on the surface of the leaf would have to be tracked separately, and two transfer factors to surface soil would be required.

Transfer of Chemical to Leaf from Particles on Plant

The fraction of deposited chemical that enters the plant cuticle per day is very uncertain. It depends on the relative concentrations in the plant and particles at equilibrium (which is unknown), as well as the time to equilibrium. It is sometimes assumed that chemicals attached to particles reach instantaneous solution equilibrium with plant tissues when they land on the plant. If that assumption is made for some chemicals (*e.g.*, mercury), TRIM.FaTE is likely to overestimate the contribution of the particles to uptake of the chemical by the plant (Lindberg 1999a). For a chemical that is tightly and chemically bound to particles in air (*e.g.*, Hg), an initial assumption of 0.2 per day may be appropriate. Because particles cover only a small fraction of the surface of the plant, it is assumed that the rate of transfer from leaves to particles is 1 percent of the rate of transfer in the other direction (0.002 per day). The rate may be higher for the transfer of mercury from the plant to a dissolved state in rain water, but no information is available on this. Note that these default values will change if units of time change.

$$T_{Lp \rightarrow L} = k_{LP-L} \tag{7-13}$$

$$T_{L \rightarrow Lp} = 0.01 \times k_{LP-L} \tag{7-14}$$

where:

$T_{Lp \rightarrow L}$ = transfer factor from leaf surface to leaf
$T_{L \rightarrow Lp}$ = transfer factor from leaf to leaf surface

Transformations on the Leaf

Transformations of chemicals in particulate matter on the surface of plant leaves are assumed to occur at the same rate as transformations in air.

7.2.1.2 Uptake of Gaseous Chemical into Foliage

The diffusion pathway is valid for all gaseous forms of chemicals, including organic compounds and mercury species. The diffusion from air to plants is based on two resistances in parallel: a) the series resistance of stomata and mesophyll and b) the series resistance of air and cuticle. It is assumed that a chemical fraction that is in the plant cuticle or mesophyll is inside of the plant, but that the chemical inside of the stoma but outside of the mesophyll is outside of the plant. It should be noted that the resistance is the inverse of the conductance. Damage to the plant (*e.g.*, from insect herbivory) can also contribute significantly to the transport of nutrients from plant leaves (Hargrove 1999). However, the contribution of insect or other sources of damage to the diffusion of Hg into and out of the plant is unknown and not incorporated into TRIM.FaTE.

Stomatal Conductance

The stomatal conductance of gaseous chemicals into the leaf may be determined based on the stomatal conductance of water vapor. The only chemical-specific parameter that is required is the molecular weight of the chemical. One means to estimate the stomatal conductance is the following

$$g_{stomata} = \sqrt{18 / MW} \times g_{water} \tag{7-15}$$

where:

$g_{stomata}$ = conductance of chemical through the stomata (m/s)
g_{water} = conductance of water through the stomata (m/s)
MW = molecular weight of chemical

Conductance of water through the stomata may be calculated using one of the following algorithms. The first is taken from Bennett et al. (1998) and Trapp (1995) and has been implemented in TRIM.FaTE:

$$g_{water} = \frac{461 \times T}{(1 - rh) \times 611 \times 10^{\frac{7.5(T-273)}{(237+(T-273)}}} \times \left(1\,\text{kg} \times \text{d}^{-1} \times \text{m}^2\right) \tag{7-16}$$

where:

g_{water} = conductance through the stomata (m/d)
Z_A = fugacity capacity of chemicals in the vapor phase of air ($\text{molPa}^{-1}\text{m}^3$)
rh = relative humidity (unitless)
T = temperature (degrees Kelvin)

Stomatal conductance of water and chemicals should be adjusted to zero at night.

Alternatively, the stomatal conductance of water may be calculated (Riederer 1995) using the following equation. This option has not yet been implemented in TRIM.FaTE:

$$g_{water} = \frac{D_A^{H_2O} na_S \alpha}{x_S + y_S} \tag{7-17}$$

where:

g_{water}	=	conductance of water through the stomata (m/d)
D_A^{H2O}	=	diffusion coefficient of water in air (m^2/d)
na_S	=	number of stomata in leaf (n) times area of 1 stoma divided by area of leaf (a_S)
α	=	mean degree of opening of stomatal pores, between 0 and 1
x_S	=	depth of elliptical pore (m)
y_S	=	mean pore radius (m)

If this latter algorithm is used, it should be noted that conductance varies with temperature. In the 20° to 40°C temperature range, the vapor flux from leaves has been observed to double with a 10° rise in temperature (Leonard et al. 1998), so variability in temperature could contribute significantly to the uncertainty in this type of transfer.

Mesophyll Conductance

It is suggested that for most organic chemical species and most plant species, the stomatal or cuticular conductance is the rate-limiting pathway (Riederer 1995). Therefore, for most chemicals, there is no need to consider mesophyll (inner tissue) conductance. However, some work with mercury cited in Lindberg et al. (1992) suggests that "resistance on or within mesophyll surfaces dominates the atmosphere-leaf diffusive path of Hg^0." See Section A.1.1 of Appendix A.

Total Conductance of the Stomatal Pathway

Thus, the total conductance of the stomatal pathway is:

$$g_S = \left(\frac{1}{g_{Stomata}} + \frac{1}{g_m} \right)^{-1} \tag{7-18}$$

where:

g_S	=	conductance of stomatal pathway, including mesophyll (m/d)
$g_{Stomata}$	=	conductance of stomata (m/d)
$g_{Stomata}$	=	conductance of mesophyll (m/d)

Boundary-layer Conductance

The boundary-layer conductance is defined by the following equation:

$$g_B = \frac{D_A}{\delta_{AP}} \tag{7-19}$$

where:

g_B = conductance of the boundary layer (m/d)
D_A = diffusion coefficient of chemical through still air (m^2/d)
δ_{AP} = thickness of air boundary layer over plant (m)

The boundary layer thickness (δ_{AP} in m) may be approximated by the following equation (Nobel 1991), or the value may be assumed (*e.g.*, 0.001 m in Riederer 1995, 0.005 m in McKone 1993a,b,c). The constant of 0.004 is the square root of the viscosity of air at 20 degrees Celsius, 1.51 x 10^{-5} m^2 per second (Wilmer and Fricker 1996).

$$\delta_{AP} = 0.004\sqrt{l/v} \tag{7-20}$$

where:

l = length of flat leaf (m)
v = wind velocity (m/s)

Cuticular Conductance

The cuticular conductance (mass transfer coefficient from air outside of the plant to the cuticle) is defined by the following equation (Riederer 1995):

$$g_{cuticle} = \frac{P_C}{K_{AW}} \tag{7-21}$$

where:

$g_{cuticle}$ = conductance of the cuticle (m/s)
P_C = permeance of the cuticle (m/s)
K_{AW} = air-water partition coefficient (unitless)

Cuticular permeance has been measured in *Citrus aurantium* leaves, and the following relationship was derived (Riederer 1995). The variability of this relationship with plant species is unknown.

$$\log P_c = 0.704 \log K_{ow} - 11..2 \quad (r = 0.91) \tag{7-22}$$

In addition, K_{AW} is equivalent to Z_{Air}/Z_W. Thus,

$$g_{cuticle} = \left(\frac{10^{0.704 \log K_{ow} - 11.2}}{Z_{AIR} / Z_w} \right) \times 24 \times 60 \times 60 \quad (7\text{-}23)$$

where:

$g_{cuticle}$ = conductance of the cuticle (m/d, note change in units)
Z_W = capacity (Z-factor) of chemicals in water ($molPa^{-1}m^3$)
Z_{air} = capacity (Z-factor) of chemicals in air, including particulates ($molPa^{-1}m^3$)

The cuticular conductance must be put in series with resistance through the air on the leaf surface to yield the total cuticular conductance (air to plant), adjusted for capacity (Z-factor) of the air and leaf. Thus:

$$g_C = \left(\frac{1}{g_B} + \frac{1}{g_{cuticle}} \right)^{-1} \quad (7\text{-}24)$$

where:

g_B = conductance of the boundary layer (m/d)
$g_{cuticle}$ = conductance of the cuticle (m/d)
g_C = total conductance of the cuticular path, including the air boundary layer (m/d)

Riederer (1995) has derived the flux equation for diffusion in and out of plant leaves.

$$\frac{dN_L}{dt} = A(g_C + g_S)\frac{N_A}{V_A} - A(g_C + g_S)\frac{N_L}{V_L} \times \frac{K_{AW}}{K_{LW}} \quad (7\text{-}25)$$

where:

N_L = mass of chemical in leaf compartment (g)
N_A = mass of chemical in air compartment (g)
V_A = volume of air compartment (m^3)
V_A = volume of leaf compartment (m^3)
K_{LW} = air/leaf partition coefficient (unitless)

Transfer Factors for Diffusion

If the Bennett et al. (1998) equation (which is calculated with respect to soil area) is used for the stomatal conductance, the transfer factor for diffusion from leaf to air is:

$$T_{L-A}^{diff} = (2LAI \times A_S \times g_C + A_S \times g_S) \times \frac{1}{V_L} \times \frac{Z_A}{Z_L} \quad (7\text{-}26)$$

where:

V_L	=	volume of leaves (m^3)
LAI	=	Leaf-area index, the area of one side of a leaf (unitless)
A_S	=	area of soil (m^2)
Z_P	=	capacity (Z-factor) of chemicals in plant (mol-$Pa^{-1}m^{-3}$)
Z_L	=	capacity (Z-factor) of chemicals in leaf (mol-$Pa^{-1}m^{-3}$)

Note that the contact area associated with the cuticular pathway is 2 times the LAI (because cuticles cover the top and bottom of a leaf). If the Riederer (1995) equation (which is calculated with respect to 1-sided leaf area) is used for the stomatal conductance, the transfer factor is:

$$T_{L-A}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_L} \times \frac{Z_A}{Z_P} \quad (7\text{-}27)$$

Z_P may be calculated using the following equation, which represents plants as mixture of air, water and nonpolar organic matter analogous to octanol (Paterson and Mackay 1995). It is assumed that the fugacity capacity of a plant leaf is equivalent to that of a generic plant that is 18 percent air, 80 percent water, and 2 percent nonpolar organic matter.

$$Z_P = 0.18\ Z_A + 0.80\ Z_W + 0.02\ K_{OW}\ \text{x}\ Z_W \quad (7\text{-}28)$$

Similarly, if the Bennett et al. (1998) equation (which is calculated with respect to soil area) is used for the stomatal conductance, the transfer factor for diffusion from air to leaf is:

$$T_{A-L}^{diff} = (2LAI \times A_S \times g_C + A_S \times g_S) \times \frac{1}{V_A} \quad (7\text{-}29)$$

And if the Riederer (1995) equation (which is calculated with respect to 1-sided leaf area) is used for the stomatal conductance, the transfer factor is:

$$T_{A-L}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_A} \quad (7\text{-}30)$$

7.2.1.3 Uptake from Soil by Root

The uptake of chemicals by plant roots is treated as an equilibrium process. Two alternative algorithms may be used to calculate the accumulation of a chemical by plants from

soil: uptake from soil or uptake from soil water. Both algorithms are derived from an equilibrium relationship, an estimated time to equilibrium, and the assumption of a first order rate of uptake. These algorithms do not apply to woody tree roots or tuber crops. Uptake of chemicals by these types of roots is not considered in TRIM.FaTE at this time.

Uptake from Whole Soil

The uptake of chemicals by roots in TRIM.FaTE is described by an equation in the form of a time to equilibrium between the roots and soil. Because of the linear relationships in TRIM.FaTE, uptake is described as proportional to the concentration of the chemical in soil even though some studies suggest that a log-log regression between soil and root concentrations is a more precise model of uptake.

$$C_{R-dry} = K_{RSr-dry} \times C_{Sr-dry} \tag{7-31}$$

where:

$C_{R\text{-}dry}$	=	concentration of chemical in dry root (kg/m^3, dry wt)
$K_{RSr\text{-}dry}$	=	dry root/root-zone-soil partition coefficient (uptake factor, dimensionless)
$C_{Sr\text{-}dry}$	=	concentration of chemical in root-zone soil (kg/m^3, dry wt)

If masses are converted to wet mass, then:

$$C_R = (1\text{-}W_R) \times C_{R\text{-}dry} \tag{7-32}$$

where:

W_R	=	water content of root (kg water/kg worm)
C_R	=	total concentration of chemical in root (kg/m^3)

and

$$C_{Sr} = (1\text{-}W_{Sr}) \times C_{Sr\text{-}dry} \tag{7-33}$$

where:

W_{Sr}	=	water content of soil (kg water/kg root zone soil)
C_{Sr}	=	total concentration of chemical in root zone soil (kg/m^3)

Thus,

$$(1-W_R) \times C_{R-dry} = \frac{(1-W_R) \times K_{R-Sr(dry)}}{1-W_{Sr}} \times (1-W_{Sr}) \times C_{Sr-dry} \tag{7-34}$$

and

$$C_R = K_{R-Sr} \times C_{Sr} \tag{7-35}$$

where:

$K_{R\text{-}Sr}$ = root-soil partition coefficient (wet kg/kg per wet kg/kg), calculated to be:

$$K_{R-Sr} = \frac{(1 - W_R) \times K_{R-Sr-dry}}{1 - W_{Sr}} \tag{7-36}$$

Thus,

$$\frac{dC_R}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times K_{R-Sr} \times C_{Sr} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] C_R \tag{7-37}$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{Sr} is approximately constant with time (d)

If the areal density of roots is approximately constant with time, then:

$$\frac{dN_R}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times V_R \times K_{R-Sr} \times \frac{N_{Sr}}{V_{Sr}} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] N_R \tag{7-38}$$

where:

N_R = mass of chemical in nonwoody roots (kg)
N_{Sr} = total mass of chemical in all phases of bulk root-zone soil (kg)
V_{Sr} = total volume of root-zone soil, which contains roots (m^3)
V_R = total volume of roots (m^3)

and

$$V_R = \frac{\rho area_R \times A_S}{\rho vol_R} \tag{7-39}$$

where:

A_S = area of soil surface (m^2)
$\rho area_R$ = areal density of root in root-zone soil (kg root fresh wt/m^2)

ρvol_R = wet density of root (kg/m^3)

Transfer Factors

$$T_{Sr-R} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \frac{\rho area_R}{\rho vol_R} \times \frac{K_{R-Sr}}{d_{Sr}} \tag{7-40}$$

$$T_{r-Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \tag{7-41}$$

where:

T_{Sr-R} = transfer factor from root-zone soil to root
T_{R-Sr} = transfer factor from root to root-zone soil

Uptake from Soil Water

An alternative method by which to estimate the root concentration of a chemical is an equilibrium between root tissue and soil water concentration. The equilibrium relationship is a generalization of the Briggs et al. (1982) equation developed in Trapp (1995).

$$C_R = K_{R-SrW} \times C_{SrW} \tag{7-42}$$

where:

C_R = concentration in roots (kg [chemical]/m^3 [root fresh weight])
$K_{R\text{-}Sr\,W}$ = root - root zone soil water partition coefficient (kg/m^3 per kg/m^3) (below)
C_{sw} = concentration in soil pore water (kg [chemical]/m^3 [soil pore water])

$$K_{R-SrW} = (W_R + L_R K_{ow}^b)\rho vol_R \rho vol_{SW}^{-1} \tag{7-43}$$

where:

W_R = water content of root (mass/mass wet weight)
L_R = lipid content of root (mass/mass wet weight)
b = correction exponent for the differences between octanol and lipids
ρvol_R = density of fresh root (g [root]/cm^3 [root])
ρvol_{SW} = density of soil pore water (g [soil pore water]/cm^3 [soil pore water])

Thus,

$$\frac{dC_R}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times K_{R-SrW} \times C_{SrW} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] C_R \tag{7-44}$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{Sr} is approximately constant with time (d)

If the areal density of roots is approximately constant with time, then:

$$\frac{dN_R}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times V_R \times K_{R-SrW} \times \frac{N_{SrW}}{V_{SrW}} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] N_R \quad (7\text{-}45)$$

where:

N_R = mass of chemical in nonwoody roots (kg)
N_{SrW} = total mass of chemical in root-zone soil water (kg)
V_{SrW} = volume of root-zone soil water (m^3)
V_R = total volume of fresh roots in parcel (m^3)

$$V_R = \frac{\rho area_R \times A_S}{\rho vol_R} \quad (7\text{-}46)$$

where:

A_S = area of soil surface (m^2)
$\rho area_R$ = areal density of root in root-zone soil (kg root fresh wt/m^2)
ρvol_R = wet density of root (kg/m^3)

The transfer factors are:

$$T_{SrW-R} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \frac{\rho area_R}{\rho vol_R} \times \frac{K_{R-SrW}}{d_{Sr}} \quad (7\text{-}47)$$

$$T_{R-SrW} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \quad (7\text{-}48)$$

where:

$T_{SrW\text{-}R}$ = transfer factor from root-zone soil water to root
$T_{R\text{-}SrW}$ = transfer factor from root to root-zone soil water

7.2.1.4 Uptake by Stem

The algorithms for the uptake of chemicals by the stem are taken from Trapp (1995) who derived them for organic chemicals.

Contribution from Soil Pore Water via Transpiration Stream (Xylem)

$$\frac{dN_{St}}{dt} = Q_{XY} \times TSCF \times \frac{N_{SrW}}{V_{SrW}} \tag{7-49}$$

where:

N_{St} = mass in all stems in volume element (kg)
Q_{XY} = flow of transpired water in cell area (m^3/d, below)
$TSCF$ = transpiration stream concentration factor (mg/m^3 of xylem per mg/m^3 of soil pore water)
N_{SrW} = mass of chemical in root-zone soil water (kg)
V_{SrW} = volume of water in root-zone soil (m^3)

According to Crank et al. (1981),

$$Q_{Xy} = 4.8 \times 10^{-3} \times LAI \times A_S \tag{7-50}$$

where:

4.8×10^{-3} = empirical factor with units of m/d
LAI = leaf-area index
A_S = area of soil (m^2)

Thus,

$$T_{Sr-St} = \frac{Q_{Xy} \times Z_{water}}{Z_{Sr} \times V_{Sr}} \times TSCF \tag{7-51}$$

where:

$T_{Sr\text{-}St}$ = transfer for root-zone soil to stem

Contribution from Leaves via Phloem

Assuming that the chemical concentration in phloem sap is in equilibrium with that in leaves,

$$\frac{dN_{St}}{dt} = Q_P \times \frac{N_L}{V_L \times K_{LPh}} \quad (7\text{-}52)$$

where:

N_{St} = mass of chemical in stems in volume element (kg)
Q_P = phloem flux into fruit (m^3/d), due to advection (assume 5 percent of Q_{xy}, Paterson et al. 1991)
N_L = mass of chemical in leaves (kg)
V_L = volume of leaves (m^3)
K_{LPh} = partition coefficient between leaves and phloem water (mass/vol to mass/vol)

The following equation, adapted from an equation for sorption of contaminants to plant roots (Trapp 1995), may be used to calculate K_{LPh}.

$$K_{LPh} = (W_L + l_L \times K_{ow}^b) \times \rho vol_L \; / \; \rho vol_{Ph} \quad (7\text{-}53)$$

where:

W_L = water content of leaves (mass/mass wet weight)
l_L = lipid content of leaves (mass/mass wet weight)
b = correction exponent for differences between foliage lipids and octanol
ρvol_L = density of leaf (kg/m^3)
ρvol_{Ph} = density of phloem (kg/m^3)

If the chemical in question is ionic, it may be assumed that K_{ow} is close to zero and that the concentration of the ionic species in phloem is the same as that in leaf water.

Thus,

$$T_{L-St} = Q_P \times \frac{1}{V_L \times K_{LPh}} \quad (7\text{-}54)$$

where:

$T_{L\text{-}St}$ = transfer factor for leaf to stem

Loss with Xylem to Leaves

$$\frac{dN_L}{dt} = Q_{Xy} \times \frac{N_{St}}{V_{St} K_{StXy}} \quad (7\text{-}55)$$

where:

N_L = mass of chemical in leaves (kg)
Q_{xy} = flow of transpired water (equation above)
N_{St} = mass of chemical in stem (kg)
V_{St} = volume of stem (m^3)
K_{StXy} = partition coefficient between stem and xylem water (mass/vol to mass/vol)

The following equation, adapted from an equation for sorption of contaminants to plant roots (Trapp 1995), may be used to calculate K_{StXy}.

$$K_{StXy} = (W_{St} + l_{St} \times K_{ow}^{b}) \times \rho vol_{St} \; / \; \rho vol_{Xy} \quad (7\text{-}56)$$

where:

W_{St} = water content of stem (mass/mass wet weight)
l_{St} = lipid content of stem (mass/mass wet weight)
K_{ow} = octanol-water partition coefficient
b = correction exponent for differences between foliage lipids and octanol
ρvol_{St} = density of stem (mass wet weight/volume)
ρvol_{Xy} = density of xylem fluid (mass wet weight/volume)

If the chemical in question is ionic, it may be assumed that K_{ow} is zero and that the concentration of the ionic species in xylem is the same as that in leaf water.

Thus,

$$T_{St-L} = Q_{Xy} \times \frac{1}{V_{St} K_{StXy}} \quad (7\text{-}57)$$

where:

$T_{St\text{-}L}$ = transfer factor for stem to leaf

Loss from Phloem to Fruit

It is not necessary to implement a fruit compartment or this loss term in TRIM.FaTE unless a) moderate to high concentrations of the chemical have been found in fruit and b) fruit constitutes a significant portion of the biomass of the vegetation. This algorithm has not yet been

implemented in any tests of TRIM.FaTE. The concentration of any chemical in the phloem running through the stem is at the same concentration as xylem sap leaving the stem; both are in equilibrium with the stem. Thus,

$$\frac{dN_{PhF}}{dt} = Q_P \times \frac{N_{St}}{V_{St} K_{StXy}} \tag{7-58}$$

where:

N_{PhF}	=	mass of chemical in fruit (kg)
V_F	=	volume of fruit (m^3)
Q_P	=	phloem flux into fruit (m^3/d), due to advection (assume 5 percent of Q_{xy}, Paterson et al. 1991)
N_{st}	=	mass of chemical in stem (kg)
V_{st}	=	volume of stem (m^3)
K_{StXy}	=	partition coefficient between stem and xylem water (mass/vol to mass/vol)

Stem Simplifications for Nonionic Organic Chemicals

The uptake of nonionic organic chemicals by the stem is assumed to originate from the root. Little if any nonionic organic chemical mass is transported from leaves to stems. For that reason, in the PAH test case of TRIM.FaTE, the root and stem were not connected to the leaves. The algorithm for uptake by the stem was an equilibrium relationship taken from Briggs et al. (1983):

$$C_{stem} = SCF \times C_{SrW} \times \rho vol_{stem} \rho vol_{SrW}^{-1} \tag{7-59}$$

where:

C_{stem}	=	concentration of chemical in stem (kg [chemical]/m^3 [stem])
C_{SrW}	=	concentration in soil water (kg/m^3)
SCF	=	stem concentration factor (kg/kg per kg/kg) (below)
ρvol_{stem}	=	density of stem, kg (fresh stem)/m^3 (fresh stem)
ρvol_{SrW}	=	density of soil water, kg (soil water)/m^3 (soil water)

The stem concentration factor may be calculated by the following equation from Briggs et al. (1983):

$$SCF = (10^{0.95 \log K_{ow} - 2.05} + 0.82) \times 0.784 \times e^{-(\log K_{ow} - 1.78)^2 / 2.44} \tag{7-60}$$

Thus,

$$\frac{dC_{stem}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times SCF \times \frac{\rho vol_{stem}}{\rho vol_{SrW}} \times C_{SrW} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] C_{stem} \quad (7\text{-}61)$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{Sr} is approximately constant with time (d)

If the areal density of stems is approximately constant with time, then:

$$\frac{dN_{stem}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times V_{stem} \times SCF \times \frac{\rho vol_{stem}}{\rho vol_{SrW}} \times \frac{N_{SrW}}{V_{SrW}} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] N_{stem} \quad (7\text{-}62)$$

where:

N_{stem} = mass of chemical in fresh stems (kg)
N_{SrW} = total mass of chemical in root-zone soil water (kg)
V_{SrW} = volume of root-zone soil water (m^3)
V_{stem} = total volume of fresh stems in parcel (m^3)

$$V_{stem} = \frac{\rho area_{stem} \times A_S}{\rho vol_{stem}} \quad (7\text{-}63)$$

where:

A_S = area of soil surface (m^2)
$\rho area_{stem}$ = areal density of stem in root-zone soil (kg root fresh wt/m^2)
ρvol_{stem} = wet density of stem (kg/m^3)

The transfer factors are:

$$T_{SrW \rightarrow stem} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \rho area_{stem} \times \frac{SCF}{\rho vol_{SrW} \times d_{Sr}} \quad (7\text{-}64)$$

$$T_{stem \rightarrow SrW} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \quad (7\text{-}65)$$

where:

$T_{SrW \rightarrow stem}$ = transfer factor from root-zone soil water to stem
$T_{stem \rightarrow SrW}$ = transfer factor from stem to root-zone soil water

7.2.1.5 Uptake by Wood and Tree Bark

Wood is of interest in a mass-balanced chemical transport and fate model because of its potential for serving as a large reservoir of chemical mass. The few studies that exist suggest that there is some accumulation of air pollutants in bark and wood. Ralph Turner (1998) has limited data on the accumulation of mercury in wood, but the mechanism of accumulation is not understood. Simonich and Hites (1995) provide data on the accumulation of organochlorine compounds in tree bark; polycyclic aromatic hydrocarbons would be expected to have similar properties. The transfer of chemicals to wood and tree bark is not modeled because of a general lack of information for persistent air pollutants.

7.2.1.6 Chemical Transformations

All transformations are assumed to be first-order processes in TRIM.FaTE. The derivations of these values for particular chemicals (*e.g.*, PAHs and Hg) are described in Appendix A of this volume.

7.2.1.7 Litterfall

The flux of chemical from leaves to surface soil may be expressed by the equation:

$$\frac{dN_{Ss}}{dt} = L \times N_L + L \times N_{Lp} \quad (7\text{-}66)$$

where:

N_{Ss} = mass of chemical in surface soil in cell (kg)
L = litterfall rate (d^{-1})
N_L = mass of chemical in foliage in cell (kg)
N_{Lp} = mass of chemical on surface of leaves in cell (kg)

It is assumed that all leaves of deciduous trees are dropped to surface soil between the day of first frost and a date that is 30 days later. Thus, $L = 1/30\ d^{-1}$.

Conifers drop their leaves at a steady rate, with a complete turnover which lasts 2 to 10 or 11 years (Post 1999). It is assumed for the purpose of TRIM.FaTE that the leaf turnover is 6 years. Thus, $L = 1/2190\ d^{-1}$.

It is assumed that herbaceous plants and grasses become "litter" on the surface of the soil during the 30 day period beginning the day of first frost. Thus, $L = 1/30\ d^{-1.}$

It is assumed that agricultural plants are harvested and do not become "litter." If agriculture were dominant, this assumption would need to be revised, based on harvesting practices (*e.g.*, how much residue is left) for the particular crop. Thus, $L = 0\ d^{-1}$.

Thus,

$$T_{L \rightarrow Ss} = L \tag{7-67}$$

where:

$T_{L \rightarrow Ss}$ = transfer factor from leaf to surface soil

Also,

$$T_{Lp \rightarrow Ss} = L \tag{7-68}$$

where:

$T_{L\text{-}Ss}$ = transfer factor from leaf surface (particulate matter) to surface soil

Note that the transfer of chemical from litter to surface water is not implemented in TRIM.FaTE at this time.

7.2.1.8 Senescence

Senesence is not considered in the current prototype of TRIM.FaTE. Senescence is the aging of plants, a process which affects the uptake of chemicals, growth, and plant parameters such as water content. If a user of TRIM.FaTE wants to include the process of senescence, candidate algorithms for changes in plant biomass may be found in Whicker and Kirchner (1987). Senescence is assumed to be negligible prior to August 1 through most of the United States.

7.2.1.9 Other Seasonal Issues

Plants only take up chemicals during the growing season, *i.e.*, the dates in the spring, summer, and fall between last frost and first frost. Although there may be uptake by conifers outside of the growing season, it is probably negligible for much of the non-growing season in cold environments (*e.g.*, in the Maine case study)" (Lindberg 1999b) and is not considered in TRIM.FaTE modeling purposes. To limit plant uptake only to the growing season, the user must specify the time period considered outside of the growing season.

An additional seasonal issue is deposition to the leaf surface compartment type. Tree foliage and grasses only intercept deposition when they are present. TRIM.FaTE assumes that there is no plant foliage present in the non-growing season, except for conifers. All deposition in deciduous forests, old fields, and agricultural systems in the non-growing season goes directly to

soil. Deposition to conifer foliage may continue in the winter, though accumulation of contaminants from particles or wet deposition is assumed to be negligible.

Chemical transformation within the plant is also assumed to cease in the non-growing season. There is no evidence to support or refute this assumption for most contaminants.

During the non-growing season, herbivores do not eat plants or make up this portion of their diet in any way. For herbivorous or omnivorous animals that do not hibernate or engage in winter sleep, the accumulation of contaminants from alternative, non-plant dietary sources may be underestimated in TRIM.FaTE.

7.2.2 SOIL DETRITIVORES

7.2.2.1 Earthworms

The uptake of chemicals by earthworms in TRIM.FaTE is described by an equation in the form of a time to equilibrium between the earthworms and soil. For simplicity, uptake is described as proportional to the concentration of the chemical in soil even though some studies suggest that a log-log regression between soil and earthworm concentrations is a more precise model of uptake.

$$C_{worm\text{-}dry} = K_{worm\text{-}Sr\text{-}dry} \times C_{Sr\text{-}dry} \quad (7\text{-}69)$$

where:

$C_{worm\text{-}dry}$	=	concentration of Hg in earthworm, kg/kg dry weight
$C_{Sr\text{-}dry}$	=	concentration of Hg in root-zone soil, kg/kg dry weight
$K_{worm\text{-}Sr\text{-}dry}$	=	earthworm-soil partition coefficient

If masses are converted to wet mass, then:

$$C_{worm} = (1\text{-}W_{worm}) \times C_{worm\text{-}dry} \quad (7\text{-}70)$$

where:

W_{worm}	=	water content of worm (kg water/kg worm)

and

$$C_{Sr} = (1\text{-}W_{Sr}) \times C_{Sr\text{-}dry} \quad (7\text{-}71)$$

where:

W_{Sr}	=	water content of soil (kg water/kg root zone soil)

Thus,

$$(1-W_{worm})\times C_{worm-dry} = \frac{(1-W_{worm})\times K_{worm-Sr-dry}}{1-W_{Sr}} \times (1-W_{Sr})\times C_{Sr-dry} \quad (7\text{-}72)$$

and

$$C_{worm} = K_{worm-Sr} \times C_{Sr} \quad (7\text{-}73)$$

where:

$K_{worm\text{-}Sr}$ = earthworm-soil partition coefficient (wet kg/kg per wet kg/kg), calculated to be

$$K_{worm-Sr} = \frac{(1-W_{worm})\times K_{worm-Sr-dry}}{1-W_{Sr}} \quad (7\text{-}74)$$

Thus,

$$\frac{dC_{worm}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times K_{worm-Sr} \times C_{Sr} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] C_{worm} \quad (7\text{-}75)$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{SR} is approximately constant with time (d^{-1})

If the areal density of worms is approximately constant with time, then:

$$\frac{dN_{worm}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times V_{worm} K_{worm-Sr} \times \frac{N_{Sr}}{V_{Sr}} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] N_{worm} \quad (7\text{-}76)$$

where:

N_{worm} = mass of chemical in earthworms (kg)
N_{Sr} = total mass of chemical in all phases of bulk root zone soil (kg)
V_{Sr} = total volume of root zone soil, which contains worms (m^3)

$$V_{worm} = \frac{\rho area_{worm} A_S}{\rho vol_{worm}} \quad (7\text{-}77)$$

where:

A_S = area of soil surface (m^2)
$\rho area_{worm}$ = areal density of earthworm community in root-zone soil (kg worm fresh wt/m^2)
ρvol_{worm} = wet density of earthworm (kg/m^3)

Thus,

$$T_{Sr \rightarrow worm} = \left[\frac{-\ln(1-0.95)}{t_{0.95}} \right] \times \frac{\rho area_{worm}}{\rho vol_{worm}} K_{worm-Sr} \frac{1}{d_{Sr}} \quad (7\text{-}78)$$

$$T_{worm \rightarrow Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}} \right] \quad (7\text{-}79)$$

where:

$T_{Sr \rightarrow worm}$ = transfer factor from root-zone soil to worm
$T_{worm \rightarrow Sr}$ = transfer factor from worm to root-zone soil
d_{Sr} = depth of root-zone soil (V_{Sr}/A_S)

7.2.2.2 Soil Arthropods

An equation for the uptake of chemicals by soil arthropods may be derived similarly to that for earthworms. Much of the available data relates the concentration of a chemical in the fresh (wet weight) arthropod to that in food. The food may be plant matter rather than soil, but for the purpose of TRIM.FaTE, the uptake factors are assumed to apply to soil.

$$C_{arth} = K_{arth-Sr} \times C_{Sr} \quad (7\text{-}80)$$

where:

$K_{arth\text{-}Sr}$ = arthropod-soil partition coefficient (wet kg/kg per wet kg/kg)

Thus,

$$\frac{dC_{worm}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}} \right] \times K_{arth-Sr} \times C_{Sr} - \left[\frac{-\ln(1-0.95)}{t_{0.95}} \right] C_{arth} \quad (7\text{-}81)$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{SR} is approximately constant with time (d^{-1})

Thus,

$$\frac{dC_{arth}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times K_{arth-Sr} \times C_{Sr} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] C_{arth} \quad (7\text{-}82)$$

where:

$t_{0.95}$ = time required to reach 95 percent of the steady-state value when C_{Sr} is approximately constant with time (d^{-1})

If the areal density of arthropods is approximately constant with time, then:

$$\frac{dN_{arth}}{dt} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \rho area_{arth} A_S K_{arth-Sr} \times \frac{N_{Sr}}{M_{Sr}} - \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] N_{arth} \quad (7\text{-}83)$$

where:

N_{arth} = mass of chemical in arthropods (kg)
N_{Sr} = total mass of chemical in all phases of bulk root zone soil (kg)
M_{Sr} = total mass of root zone soil, which contains arthropods (kg)
A_S = area of soil surface (m^2)
$\rho area_{arth}$ = areal density of arthropod community in root-zone soil (kg arthropod fresh wt/m^2)

Thus,

$$T_{Sr \rightarrow arth} = \left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \times \rho area_{arth} \times A_S \times \frac{K_{arth-Sr}}{M_{Sr}} \quad (7\text{-}84)$$

$$T_{arth \rightarrow Sr} = -\left[\frac{-\ln(1-0.95)}{t_{0.95}}\right] \quad (7\text{-}85)$$

where:

$T_{Sr \rightarrow arth}$ = transfer factor from root-zone soil to arthropod
$T_{arth \rightarrow Sr}$ = transfer factor from arthropod to root-zone soil

7.2.2.3 Flying Insects

Flying insects are the food of insectivores (*e.g.*, tree swallows). It may be assumed that the concentration of a chemical in these organisms is equivalent to the concentration in benthic invertebrates such as the mayfly (see Section 7.3.2).

7.2.3 TERRESTRIAL MAMMALS AND BIRDS

Terrestrial wildlife, including mammals and birds, may be exposed to chemicals through food, soil, and water ingestion, and through inhalation of chemicals in air. In addition, chemicals can be taken up dermally, but the rate of sorption to the skin surface is unknown, the rate of uptake into the organism is unknown, and the quantity absorbed by the body (generally less than 3 percent) is low; thus, dermal uptake is not included in TRIM.FaTE. Elimination of chemicals from body tissues may occur through metabolic transformation of the chemical or excretion of the parent compound through urine, feces, milk (female mammals only), eggs (female birds and reptiles only), and excretion to fur, hair, or feathers. To account for these multiple routes of exposure and elimination, the generalized model implemented for all terrestrial wildlife is presented below. In addition, the algorithm applies to semiaquatic populations, such as loons and racoons. If particular rate constants are determined to be insignificant relative to others for a particular implementation of TRIM.FaTE (*e.g.*, excretion via eggs compared to excretion in urine or feces), these may be set to zero. Similarly, if rate constants for excretion and chemical transformation are determined with respect to the mass of a contaminant that is taken up in the diet rather than mass that is assimilated, the dietary assimilation efficiencies may be ignored. However, the assimilation efficiencies for inhalation must always be greater than zero.

$$\frac{dC_{wl}}{dt} = [(I_w \times C_w \times A_w) + (I_{SS} \times C_{SS} \times A_{SS}) + p_P(I_D \times C_L \times A_P) + p_P(I_D \times C_{LP} \times A_P) + p_{worm}(I_D \times C_{worm} \times A_{worm}) + p_{arth}(I_D \times C_{arth} \times A_{arth}) + p_{wl}(I_D \times C_{wl} \times A_{wl}) + p_f(I_D \times C_f \times A_f) + p_{BI}(I_D \times C_{BI} \times A_{BI}) + (I_A \times C_A \times A_A)] - [C_{wl} \times (E_m + E_u + E_l + E_e + E_f)] \quad (7\text{-}86)$$

where:

C_{wl}	=	total, whole body, internal concentration in wildlife (kg [chemical]/kg [body weight])
I_w	=	water ingestion rate (m^3/kg body weight/d)
C_w	=	concentration of chemical in water ingested by animal (kg/m^3)
A_w	=	assimilation efficiency of chemical from water (unitless)
I_{SS}	=	surface soil ingestion rate (kg/kg body weight/d)
C_{SS}	=	concentration of chemical in surface soil (kg/kg)
A_{SS}	=	assimilation efficiency of chemical from surface soil (unitless)
p_P	=	proportion of plant matter in diet (unitless)
I_D	=	dietary ingestion rate (kg/kg body weight/d)
C_L	=	concentration of chemical in leaf component of diet (kg/kg)
A_P	=	assimilation efficiency of chemical from plant in diet (unitless)
C_{LP}	=	mass of chemical on leaf surface with respect to mass of leaf (kg/kg)
p_{worm}	=	proportion of earthworm in diet (unitless)
C_{worm}	=	concentration of chemical in earthworm component of diet (kg/kg)
A_{worm}	=	assimilation efficiency of chemical from earthworm in diet (unitless)
p_{arth}	=	proportion of insect in diet (unitless)

C_{arth}	=	concentration of chemical in insect component of diet (kg/kg)
A_{arth}	=	assimilation efficiency of chemical from insect in diet (unitless)
p_{wl}	=	proportion of other wildlife in diet (unitless)
A_{wl}	=	assimilation efficiency of chemical from other wildlife in diet (unitless)
p_f	=	proportion of fish in diet (unitless)
C_f	=	concentration of chemical in fish component of diet (kg/kg, use correct size range)
A_f	=	assimilation efficiency of chemical from fish in diet (unitless)
p_{BI}	=	proportion of benthic invertebrates or emergent flying insects in diet (unitless)
C_{BI}	=	concentration of chemical in benthic invertebrates or flying insect component of diet (kg/kg)
A_{BI}	=	assimilation efficiency of chemical from benthic invertebrates or emergent flying insects in diet (unitless)
I_A	=	inhalation rate (m^3/kg body weight/d)
C_A	=	concentration of chemical in air, including vapor phase and particles (mg/m^3)
A_A	=	assimilation efficiency of chemical from air (unitless)
E_m	=	chemical transformation (d^{-1})
E_u	=	chemical elimination through excretory processes (urine and feces)(d^{-1})
E_l	=	chemical elimination through lactation (milk production, mammals only) (d^{-1})
E_e	=	chemical elimination through egg production, birds only (d^{-1})
E_f	=	chemical elimination from fur, feathers or hair (d^{-1})

Because the source of drinking water is not usually known and may include puddles, the uptake of the chemical from water may be ignored for all species except the semiaquatic, which are associated with a single water body.

Thus, for a population,

$$\frac{dN_{wl}}{dt} = \rho area_{wl} \times A_S \times [\frac{I_w \times N_w \times A_w}{V_w} + \frac{I_{SS} \times N_{SS} \times A_{SS}}{V_{SS} \times \rho vol_{SS} wet} + \frac{p_P \times I_D \times N_L \times A_P}{A_S \times \rho area_L}$$
$$\frac{p_P \times I_D \times N_{LP} \times A_P}{A_S \times \rho area_L} + \frac{p_{worm} \times I_D \times N_{worm} \times A_{worm}}{A_S \times \rho area_{worm}} + \frac{p_{arth} \times I_D \times N_{arth} \times A_{arth}}{A_S \times \rho area_{arth}} \quad (7\text{-}87)$$
$$+ \frac{p_{wl} \times I_D \times N_{wl} \times A_{wl}}{A_S \times \rho area_{wl}} + \frac{p_f \times I_D \times N_f \times A_f}{A_{sw} \times \rho area_f} + \frac{p_{BI} \times I_D \times N_{BI} \times A_{BI}}{A_{sw} \times \rho area_{BI}} + \frac{I_A \times N_{AIR} \times A_A}{V_A}]$$
$$-[N_{wl} \times (E_m + E_u + E_l + E_e + E_f)]$$

where:

N_{wl}	=	mass of chemical in all wildlife species in parcel (kg)
$\rho area_{wl}$	=	wet wildlife biomass density per unit area (kg/m^3, may be calculated as number of animals times average body weight)

A_S	=	area of surface soil (m^2)
I_w	=	water ingestion rate (m^3/kg body weight/d)
N_w	=	mass of chemical in water source (kg)
V_w	=	volume of water (m^3)
A_w	=	assimilation efficiency of chemical from water (unitless)
I_{SS}	=	surface soil ingestion rate (kg/kg body weight/d)
N_{SS}	=	mass of chemical in surface soil (kg)
V_{SS}	=	volume of surface soil (kg)
$\rho vol_{SS}wet$	=	wet bulk density of soil (kg/m^3)
A_{SS}	=	assimilation efficiency of chemical from surface soil (unitless)
p_P	=	proportion of plant matter in diet (unitless)
I_D	=	dietary ingestion rate (kg/kg body weight/d)
N_L	=	mass of chemical in plant leaves (kg)
A_P	=	assimilation efficiency of chemical from plant in diet (unitless)
$\rho area_L$	=	areal biomass density of foliage (kg/m^2, wet weight)
N_{LP}	=	mass of chemical on surface of all foliage (kg)
p_{worm}	=	proportion of earthworm in diet (unitless)
N_{worm}	=	mass of chemical in earthworms (kg)
A_{worm}	=	assimilation efficiency of chemical from earthworm in diet (unitless)
$\rho area_{worm}$	=	areal biomass density of earthworms (kg/m^2, wet weight)
p_{arth}	=	proportion of soil arthropods in diet (unitless)
N_{arth}	=	mass of chemical in soil arthropods (kg)
A_{arth}	=	assimilation efficiency of chemical from soil arthropods in diet (unitless)
p_{wl}	=	proportion of terrestrial wildlife in diet (unitless)
N_{wl}	=	mass of chemical in wildlife component of diet (kg)
A_{wl}	=	assimilation efficiency of chemical from other wildlife in diet (unitless)
p_f	=	proportion of fish in diet (unitless)
N_f	=	mass of chemical in fish (kg, use correct size range for diet)
A_f	=	assimilation efficiency of chemical from fish in diet (unitless)
$\rho area_f$	=	areal biomass density of fish (kg/m^2, wet weight, use correct size range for diet)
$\rho area_{arth}$	=	areal biomass density of insect (kg/m^2)
p_{BI}	=	proportion of benthic invertebrates or emergent flying insects in diet (unitless)
N_{BI}	=	mass of chemical in benthic invertebrates or emergent flying insects (kg)
A_{BI}	=	assimilation efficiency of chemical from benthic invertebrates or flying insects in diet (unitless)
A_{sw}	=	area of surface of surface water body (m^2)
$\rho area_{bi}$	=	areal biomass density of benthic invertebrates (kg/m^2, wet weight)
I_A	=	inhalation rate (m^3/kg body weight/d)
N_{AIR}	=	mass of chemical in air, including vapor phase and particles (kg)
V_A	=	volume of air (m^3)

A_A = assimilation efficiency of chemical from air (unitless)
E_m = chemical transformation (d^{-1})
E_u = chemical elimination through excretory processes (urine and feces) (d^{-1})
E_l = chemical elimination through lactation (milk production, mammals only) (d^{-1})
E_e = chemical elimination through egg production, birds only (d^{-1})
E_f = chemical elimination from fur, feathers or hair (d^{-1})

The TRIM.FaTE model has been parameterized for many wildlife species. These are listed in Table 7-1. Species-specific parameters, including body weights; water, soil, and food ingestion rates; and inhalation rates are presented as means in Appendix A.

Table 7-1
Terrestrial and Semiaquatic Vertebrate Compartment Types Defined for TRIM.FaTE

Compartment Type (Trophic Functional Group)	Representative Subgroup or Species
Terrestrial Omnivore	White-footed Mouse
Semi-aquatic Piscivore	Bald Eagle Common Loon Mink Belted Kingfisher
Terrestrial Insectivore	Black-capped Chickadee
Semi-aquatic Herbivore	Mallard
Terrestrial Predator/Scavenger	Red-tailed Hawk Long-tailed Weasel
Semi-aquatic Insectivore	Tree Swallow
Terrestrial Vertebrate Herbivore	White-tailed Deer Mule Deer Black-tailed Deer Meadow Vole Long-tailed Vole
Semi-aquatic Omnivore	Raccoon
Terrestrial Ground-invertebrate Feeder	Short-tailed Shrew Trowbridge Shrew

It is advisable for the user to turn on and off wildlife algorithms, to reflect:

- Winter sleep or hibernation;
- Migration;
- Timing of egg laying; and
- Timing of lactation.

These seasonal components of TRIM.FaTE have not yet been implemented.

7.3 ALGORITHMS FOR AQUATIC BIOTA

Aquatic compartment types in TRIM.FaTE are listed in Table 7-2.

Table 7-2
Aquatic Compartment Types in the TRIM.FaTE Prototype

Compartment Type (Trophic Functional Group)	Representative Subgroup or Species
Algae	Generalized Algal Species
Macrophyte	*Elodea densa*
Water Column Herbivore	Bluegill
Water Column Omnivore	Channel Catfish
Water Column Carnivore	Largemouth Bass
Benthic Invertebrate (Herbivore)	Mayfly
Benthic Omnivore	Channel Catfish
Benthic Carnivore	Largemouth Bass

7.3.1 AQUATIC PLANTS

Aquatic vegetation is included as two separate compartment types, algae and macrophytes. Water is assumed to be the primary chemical source for both groups and is the only pathway included in TRIM.FaTE. The algal compartment type is considered to be comprised primarily of phytoplankton, for which water is clearly the primary chemical source. Although rooted macrophytes derive some nutrients and chemicals from the sediment source, direct uptake from water is the primary pathway (Ribeyre and Boudou 1994).

7.3.1.1 Algae

At present, the only available algorithm for the uptake of contaminants by algae is specific to mercury. It is presented in Section A.1.2 of Appendix A.

7.3.1.2 Macrophytes

Uptake by aquatic macrophytes is given by the following concentration-based equation for the chemical flux rate.

$$F_{mp} = k_{mp,acc-sw} V_{mp} C_{sw} - k_{mp,dep-sw} V_{mp} C_{mp} \quad (7\text{-}88)$$

where:

F_{mp}	=	net flux of chemical in the macrophyte, (µg/day)
$k_{mp,acc\text{-}sw}$	=	bioaccumulation rate constant for surface water (day^{-1})
V_{mp}	=	volume of the macrophyte (L)
C_{sw}	=	chemical concentration in water (µg/L)
$k_{mp,dep\text{-}sw}$	=	depuration rate constant for surface water (day^{-1})
C_{mp}	=	chemical concentration in macrophyte (µg/L).

The rate constants $k_{mp,acc\text{-}sw}$ and $k_{mp,dep\text{-}sw}$, for nonionic organic chemicals are estimated using the following equations:

$$1/k_{mp,acc-sw} = 0.0020 + 500/K_{ow} \tag{7-89}$$

$$1/k_{mp,dep-sw} = 1.58 + 0.000015\ K_{ow} \tag{7-90}$$

The rate constants $k_{mp,acc\text{-}sw}$ and $k_{mp,dep\text{-}sw}$ for chemicals other than nonionic organic pollutants were derived from bioconcentration factors using the time-to-steady-state conversion as follows:

$$k_{mp,acc-sw} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{w-mp} \tag{7-91}$$

$$k_{mp,dep-sw} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \tag{7-92}$$

where:

$K_{w\text{-}mp}$	=	water-macrophyte partition coefficient
t_α	=	time required to reach 100α percent of the steady-state value when the concentration in water is approximately constant with time
α	=	fraction of steady-state attained

The transfer of chemical mass from water to the macrophyte is given by:

$$\frac{dN_{mp}}{dt} = k_{mp,acc-sw}\ V_{mp}\ \frac{N_w}{V_w} - k_{mp,dep-sw}\ N_{mp} \tag{7-93}$$

where:

N_{mp}	=	mass of chemical in the macrophyte (ug)
$k_{mp,acc\text{-}sw}$	=	bioaccumulation rate constant for surface water (day^{-1})
V_{mp}	=	volume of the macrophyte (L)

N_w = mass of chemical in water (ug)
V_w = volume of water in the cell (L)
$k_{mp,dep\text{-}sw}$ = depuration rate constant for surface water (day^{-1})

The transfer factors for water to macrophytes and for macrophytes to water are given by:

$$T_{w \rightarrow mp} = \frac{V_{mp}\, k_{mp,acc-sw}}{V_w} \tag{7-94}$$

$$T_{bi \rightarrow mp} = k_{mp,dep-sw} \tag{7-95}$$

7.3.2 BENTHIC INFAUNA

The benthic community is typically comprised of many different classes and species of organisms, including those from the phyla Mollusca (*e.g.*, clams and snails), Annelida (oligochaetes), and Arthropoda (*e.g.*, insects and crustaceans). All trophic levels are represented within this community. This is true even within some families of insects, such as the mayflies and chironomids. Although all trophic transfers within the benthic community could be modeled, that is beyond the scope and needs of TRIM.FaTE. Rather, all benthic infauna are considered to represent the lowest heterotrophic level of the benthic food chain. The current model construct identifies this group as the "Benthic Herbivores."

An explicit dietary uptake component is not practical, given the highly variable diet among benthic infauna. Rather, uptake is modeled based on the extraction of chemical from water (interstitial or overlying) or sediment. It should be noted that at this time only one chemical source (water or sediment) is considered. Selection of the primary source of contamination is chemical dependent. Neutral organic chemicals (*e.g.*, PAHs) are typically evaluated based on uptake from water. If interstitial water is used the results often are considered representative of total sediment exposures. Uptake of metals (*i.e.*, mercury) is based on uptake data from bulk sediments. Sediment chemical concentrations are not apportioned to separate inorganic and organic (living and detrital matter) compartments in TRIM.FaTE. Thus uptake from sediment implicitly includes transfers from algal and detrital matter to the "Benthic Herbivores."

Immature burrowing mayflies (*Hexagenia spp.*) are used as the representative benthic invertebrates for both water and sediment exposures. They are common throughout the United States, represent an important fish forage resource, and are relatively well studied by aquatic ecologists and toxicologists.

7.3.2.1 Water to Benthic Infauna Transfers

Uptake from water is given by the following equation:

$$\frac{dC_{bi}}{dt} = k_{bi,acc-w}\, C_w - k_{bi,dep-w}\, C_{bi} \tag{7-96}$$

where:

C_{bi} = benthic invertebrate concentration (µg/g)
C_w = water (interstitial or overlying) concentration (µg/L)
$k_{bi,acc-w}$ = uptake rate constant for water (day^{-1})
$k_{bi,dep-w}$ = depuration rate constant for water.

The rate constants $k_{bi,acc-w}$ and $k_{bi,dep-w}$ may be derived from the bioconcentration factors using the time-to-steady-state conversion.

$$k_{bi,acc-w} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{w-bi} \tag{7-97}$$

$$k_{bi,dep-w} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \tag{7-98}$$

where:

K_{w-bi} = water-benthic infauna partition coefficient.

Converting to mass units (N) yields the following equation:

$$\frac{dN_{bi}}{dt} = n_{bi}\, m_{bi}\, k_{bi,acc-w}\, \frac{N_w}{V_w} - k_{bi,dep-w}\, N_{bi} \tag{7-99}$$

where:

N_{bi} = mass of chemical in organisms comprising the benthic invertebrate compartment type (µg)
n_{bi} = number of organisms comprising the benthic invertebrate compartment type
m_{bi} = mass of individual organisms comprising the benthic invertebrate compartment type
N_w = mass of chemical in water (µg)
V_w = volume of water in the cell (L)

Thus the transfer factors for water (interstitial or overlying) to benthic invertebrates and for benthic invertebrates to water are given by:

$$T_{w \rightarrow bi} = \frac{n_{bi}\, m_{bi}\, k_{bi,acc-w}}{V_w} \tag{7-100}$$

$$T_{bi \rightarrow w} = k_{bi,dep-w} \tag{7-101}$$

7.3.2.2 Sediment to Benthic Infauna Transfers

Uptake from sediment is given by the following equation:

$$\frac{dC_{bi}}{dt} = k_{bi,acc-sed}\, C_{sed} - k_{bi,dep-sed}\, C_{bi} \tag{7-102}$$

where:

C_{bi}	=	benthic invertebrate concentration (µg/g)
C_{sed}	=	Bulk sediment concentration (µg/g)
$k_{bi,acc-sed}$	=	uptake rate constant for sediment (day^{-1})
$k_{bi,dep-sed}$	=	depuration rate constant for sediment.

The rate constants $k_{bi,acc-sed}$ and $k_{bi,dep-sed}$ may be derived from bioconcentration factors using the time-to-steady-state conversion.

$$k_{bi,acc-sed} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{sed-bi} \tag{7-103}$$

$$k_{bi,dep-sed} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \tag{7-104}$$

where:

K_{sed-bi}	=	sediment-benthic invertebrate partition coefficient
t_α	=	time required to reach 100α percent of the steady-state value when the concentration in water is approximately constant with time
α	=	fraction of steady-state attained

Converting to mass units (N) yields the following equation:

$$\frac{dN_{bi}}{dt} = n_{bi}\, m_{bi}\, k_{bi,acc-sed} \frac{N_{sed}}{V_{sed}\, \rho_{sed}} - k_{bi,dep-sed}\, N_{bi} \tag{7-105}$$

where:

N_{bi}	=	mass of chemical in organisms comprising the benthic invertebrate compartment type (μg)
n_{bi}	=	number of organisms comprising the benthic invertebrate compartment type
m_{bi}	=	mass of individual benthic invertebrates
N_{sed}	=	mass of chemical in sediment (μg)
V_{sed}	=	volume of sediment in the cell (L)
ρ_{sed}	=	bulk density of sediment (g/L)

Thus the transfer factors for sediment to benthic invertebrates and for benthic invertebrates to sediment are given by:

$$T_{sed \rightarrow bi} = \frac{n_{bi}\, m_{bi}\, k_{bi,acc-sed}}{V_{sed}\, \rho_{sed}} \tag{7-106}$$

$$T_{bi \rightarrow sed} = k_{bi,dep-sed} \tag{7-107}$$

7.3.3 FISH

Fish represent five of the trophic compartment types originally included in TRIM.FaTE: the Benthic omnivore and carnivore and the water column herbivore, omnivore, and carnivore. Two alternative approaches are used to estimate chemical uptake by fish in TRIM.FaTE, a bioenergetic-based kinetic model and a time-to-steady-state-based kinetic model. Each type has strengths and weaknesses which make including both appropriate at this time. The bioenergetic-based model is ideal for explicitly incorporating multiple exposure pathways, but parameterization is more difficult, especially for elimination rates. Parameters for the time-to-steady-state-based kinetic model are generally available, but multiple pathways cannot be explicitly incorporated simultaneously and the time required to reach a "steady-state" may be uncertain for strongly bioaccumulated chemicals. Currently, the bioenergetic model is parameterized for PAHs and mercury, whereas the time-to-steady-state model is parameterized for mercury only.

The current structure of TRIM.FaTE has five trophic levels that are represented by fish. They are presented as two separate food chains, one for water column organisms and one for benthic organisms (see blue print). The water column food chain has no linkages to benthic organisms, implying that this is a pelagic food chain. However, most applications of TRIM.FaTE will be better represented by a littoral food chain, which includes linkages between the water column and benthic food chains. The blue print shows the benthic food chain linked to rooted macrophytes and benthic algae, but not to planktonic algae. Thus, neither food chain alone adequately represents a littoral food chain.

To overcome this with minimal modification of the model architecture, each food chain was assumed to be linear but individual species were assumed to reside in more than one food chain or trophic level. That is, water column carnivores consume 100 percent water column omnivores, water column omnivores consume 100 percent water column herbivores (planktivores), benthic carnivores consume 100 percent benthic omnivores, benthic omnivores consume 100 percent benthic invertebrates. However, a given piscivore (e.g., largemouth bass) may consume omnivores from both food chains (e.g., 50 percent water column omnivores and 50 percent benthic omnivores). This is accounted for in the mass transfer formulas by dividing the total biomass of the given piscivorous species into each food chain. In the largemouth bass example, 50 percent of the biomass is counted in each food chain. The mass of fish in each trophic level is derived from studies of the biomass of individual species in various systems and studies of feeding strategies of those species.

7.3.3.1 Bioenergetic-based Kinetic Model

The following model for estimating pollutant concentrations in fish (Thomann 1989) was used as a starting point in the derivation of the transfer probabilities associated with the fish compartment type:

$$\frac{dC_F}{dt} = k_u \times C_{WD} + k_D \times \sum P_i \times C_{D,i} - (R_E + k_{eg} + k_E + k_G) \times C_F \qquad (7\text{-}108)$$

where:

C_F	=	concentration in fish (µg/kg)
k_u	=	uptake rate constant from water via the gills (1/kg-day)
C_{WD}	=	dissolved chemical concentration in water (µg/L)
k_D	=	chemical uptake from food (kg food/kg fish/day)
P_i	=	proportion of the diet consisting of food item I
$C_{D,i}$	=	chemical concentration in food item i (µg/kg)
k_{eg}	=	rate constant for elimination via the gills (1/day)
k_E	=	rate constant for elimination via fecal egestion (1/day)
R_E	=	rate constant for metabolic transformation of chemical (1/day)
k_G	=	rate constant for dilution of chemical concentration from growth (1/day).

For nonionic organic chemicals (PAHs), the chemical uptake rate constant k_u is estimated using the following formula:

$$k_u = 10^3 \left(\omega^{-\gamma} / p\right) E \qquad (7\text{-}109)$$

where:

k_u	=	chemical uptake rate constant (L/day-kg[w])
ω	=	body weight [g(wet)]
γ	=	allometric scaling factor (*e.g.*, 0.2 (Thomann 1989))

p = fraction lipid weight (kg[lipid]/kg[wet])
E = efficiency of transfer of chemical.

There is an apparent increase in assimilation efficiency for smaller organisms; therefore, organisms have been divided into two weight groups: less than 10 to 100 g (wet) and more than 100 g (wet) weight (Thomann 1989). The chemical assimilation efficiency (E) can be approximated for these two size classes of organisms as follows. For smaller organisms, the following equations should be used to estimate E:

For chemicals with log K_{ow} = 2-5, log E = -2.6 + 0.5 log K_{ow}
For chemicals with log K_{ow} = 5-6, log E = 0.8
For chemicals with log K_{ow} = 6-10, log E = 2.9 - 0.5 log K_{ow}

For larger organisms, the following equations should be used to estimate E:

For chemicals with log K_{ow} = 2-5, log E = -1.5 + 0.4 log K_{ow}
For chemicals with log K_{ow} = 5-6, log E = 0.5
For chemicals with log K_{ow} = 6-10, log E = 1.2 - 0.25 log K_{ow}

Thomann (1989) gives the excretion rate from gills using the following equation:

$$k_{eg} = \frac{k_u}{k_{ow}} \tag{7-110}$$

For mercury, the following simplifying assumptions apply: 1) a single elimination rate is used to describe elimination via the gills and egestion ($K_E = k_E + k_{eg}$), and 2) uptake from water is excluded from the mercury transfer equation because it is negligible (Trudel and Rasmussen 1997).

The mercury elimination rate constant (K_E) is given by the following bioenergetic model (Trudel and Rasmussen 1997) :

$$\ln K_E = 0.066\,T - 0.20 \ln W + 0.73E - 6.56 \tag{7-111}$$

where:

T = temperature (°C)
W = weight of fish (g)
E = exposure duration; 0=acute (<90 days), 1=chronic (>90 days)

Only chronic exposures apply to TRIM.FaTE. Therefore, the elimination rate constant is reduced to:

$$\ln K_E = 0.066\,T - 0.20 \ln W - 5.83 \tag{7-112}$$

Trudel and Rasmussen (1997) based the elimination rate on the clearance of methymercury only, because greater than 95 percent of mercury in fish is methymercury and the elimination of methymercury is much slower than that of inorganic mercury (*i.e.*, the overall rate is dominated by the elimination of methymercury).

The bioenergetic-based kinetic model is generally used to estimate concentrations in individual fish of a species. Following is the derivation of the fish model for the entire fish population. Initially the model is derived for a population of two fish and then generalized for the case of *n* fish, where *n* is the fish population. Initially, it is assumed that there is no uptake through other food items, and the elimination via fecal egestion and the metabolic transformation factors were neglected as they were considered second-order rates. Thus, for two fish with concentrations C_{f1}, and C_{f2}, the previous equation can be rewritten as:

$$\frac{dC_{f1}}{dt} = k_{u1} \times C_{WD} - k_{eg1} \times C_{f1} \tag{7-113}$$

$$\frac{dC_{f2}}{dt} = k_{u2} \times C_{WD} - k_{eg2} \times C_{f2} \tag{7-114}$$

To convert the concentrations to masses, it is assumed that:

$$C_{WD} = \frac{N_W}{V_W}, \tag{7-115}$$

$$C_{f1} = \frac{N_1}{m_1}, \tag{7-116}$$

$$C_{f2} = \frac{N_2}{m_2}, \tag{7-117}$$

where:

m_1	=	mass of fish 1 (kg)
m_2	=	mass of fish 2 (kg)
N_1	=	mass of chemical in fish 1 (µg)
N_2	=	mass of chemical in fish 2 (µg)
N_w	=	mass of chemical in surface water cell (µg)
V_w	=	volume of surface water cell (L).

Substituting yields:

$$\frac{d(N_1/m_1)}{dt} = k_{u1}\frac{N_W}{V_W} - k_{eg1}\frac{N_1}{m_1} \tag{7-118}$$

Adding these equations yields the mass transfer equations for the total fish compartment type, as follows:

$$\frac{d(N_2/m_2)}{dt} = k_{u2}\frac{N_W}{V_W} - k_{eg2}\frac{N_2}{m_2} \tag{7-119}$$

Making the simplifying assumptions that individual fish mass is represented by a population average m_f ($m_1 = m_2 = m_f$), and that $ku_1 = ku_2 = k_u$ and $k_{eg1} = k_{eg2} = k_{eg}$, yields:

$$\frac{d(N_1/m_1 + N_2/m_2)}{dt} = (k_{u1} + k_{u2})\frac{N_w}{V_w} - \left(k_{eg1}\frac{N_1}{m_1} + k_{eg2}\frac{N_2}{m_2} \right) \tag{7-120}$$

This equation can be generalized from 2 to n_f fish, with N_f (= N_1+N_2) being the total mass in the fish compartment type to yield the following generalized CMT equation for a fish compartment type:

$$\frac{d\left(\frac{N_1 + N_2}{m_f}\right)}{dt} = 2\ k_u\ \frac{N_W}{V_W} - k_{eg}\frac{N_1 + N_2}{m_f} \tag{7-121}$$

Generalizing this equation to include feeding yields the following food chain mass transfer equations for the individual fish species.

$$\frac{dN_1}{dt} = n_f\ k_u\ m_f\ \frac{N_W}{V_W} - k_{eg}\ N_f \tag{7-122}$$

It is important to note that the equations in their present form exclude dermal uptake as a significant exposure route. The equations include gill uptake (bioconcentration) and food uptake (biomagnification) as the two principal exposure routes. Following are the food web equations:

Aquatic herbivore (f_h ≡ fish herbivores) (100 percent macrophyte diet):

$$\frac{dN_{fh}}{dt} = n_{fh}\ k_u\ m_{fh}\ \frac{N_W}{V_W} - k_{eg}\ N_{fh} + n_{fh}\ m_{fh}\ F_d\ E\ \frac{N_{mp}}{V_{mp}} \tag{7-123}$$

where:

F_d = feeding rate constant (kg[prey]/kg[predator]-day)
E = efficiency of transfer of chemical.

The feeding rate (F_D) is given by the following bioenergetic model presented in Gobas (1993).

$$F_D = 0.022 \times V_F^{0.85} \times e^{(0.06 \times T)} \tag{7-124}$$

where:

V_F = mass of the fish (kg)
T = temperature (°C)

Aquatic omnivore (f_o = fish omnivore):

$$\frac{dN_{fo}}{dt} = n_{fo} k_u m_{fo} \frac{N_W}{V_W} - k_{eg} N_{fo} + n_{fo} m_{fo} F_d E \left(\alpha_{mp} \frac{N_{mp}}{m_{mp}} + \alpha_h \frac{N_h}{m_h} + \alpha_{bi} \frac{N_{bi}}{m_{bi}} \right) \tag{7-125}$$

Aquatic carnivore (f_c = fish carnivore):

$$\frac{dN_{fc}}{dt} = n_{fc} k_u m_{fc} \frac{N_W}{V_W} - k_{eg} N_{fc} + n_{fc} m_{fc} F_d E \left(\alpha_o \frac{N_o}{m_o} + \alpha_h \frac{N_h}{m_h} + \alpha_{bi} \frac{N_{bi}}{m_{bi}} \right) \tag{7-126}$$

Implicit in the previous equation is the assumption that the mass of an individual fish is constant over the time of the simulation. It may be noted that the dilution due to growth factor (k_G) is not included in the equation because k_G is based on concentrations, while the mass transfer equations are in mass units.

The generalized transfer factors for dietary items to a specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore), are given by:

$$T_{diet \rightarrow receptor(fish)} = \frac{n_{receptor} m_{receptor}}{n_{diet} m_{diet}} \times F_d \times E \tag{7-127}$$

Water to a specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore), using the bioenergetic-based kinetic model for nonionic organic chemicals is given by:

$$T_{water \rightarrow fish} = \frac{n_f m_f k_u}{V_w} \tag{7-128}$$

A specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore) to water, using the bioenergetic-based kinetic model for nonionic organic chemicals is given by:

$$T_{fish \rightarrow water} = k_{eg} \tag{7-129}$$

A specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore) to the water domain, using the bioenergetic-based kinetic model for mercury is given by:

$$T_{receptor\,(fish) \rightarrow water} = K_E \tag{7-130}$$

7.3.3.2 Time-to-steady-state-based Kinetic Model

The time-to-steady-state model is based on the assumption that one pathway accounts for the vast majority of the chemical uptake. Thus, only one chemical source is explicitly considered. The model is of the general form:

$$\frac{dC_{receptor}}{dt} = \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{receptor-source} \times C_{source} - \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] C_{receptor} \tag{7-131}$$

where:

$K_{receptor\text{-}source}$	=	receptor-source partition coefficient
$C_{receptor}$	=	concentration in receptor
C_{source}	=	concentration in source
t_α	=	time required to reach 100α percent of the steady-state value when the concentration in the source is approximately constant with time
α	=	fraction of steady-state attained

If the sole chemical source is water, then $K_{receptor\text{-}source}$ is a bioconcentration factor. Bioaccumulation factors (BAFs) implicitly include uptake from food and water, though water is the identified source. This presumes that the concentration in the food item is essentially constant relative to the concentration in the water. An alternative approach is the use of dietary concentrations as the primary source. Thus, empirically derived accumulation data are used to derive factors for each trophic transfer and uptake from water is implicitly, rather than explicitly, included. This alternative is used herein.

Following this approach requires the dietary sources be restricted to one other trophic group. Thus intratrophic group transfers and multitrophic group transfers are not explicitly included. These transfers are implicitly included to the extent that the empirical data used to derive the transfer factors are from systems possessing those transfers. Thus, the "fit" of the model results for any given case study will be partly dependent on how well the food chains at the sites used to derive the transfer factors match the food chains at the case study site (*e.g.*, length of the food chains, number of interconnections, degree of intratrophic group transfer, etc.).

Restriction of the dietary pathway was achieved within TRIM.FaTE by redefining the generic trophic compartment types to represent a straight food chain of three or four segments. As noted in Section 7.3.2, the benthic herbivore compartment type is represented by all benthic invertebrates and the sediment (or interstitial water) is the chemical source. The benthic omnivore compartment type in this approach is the next trophic level up from the benthic invertebrates and the benthic carnivore compartment type contains those fish that consume the benthic omnivores. This is in contrast to the bioenergetic model, which accounts for the fractions of the omnivore diet from plants and herbivores.

A similar approach is used to configure the water column food chain. Three trophic levels are explicitly identified in TRIM.FaTE: the water column herbivore, omnivore, and carnivore. These correspond to the first, second, and third heterotrophic levels of the food chain, respectively. Chemical transfer is unidirectional from lower to higher trophic levels. Thus omnivores are assumed to consume herbivores only, rather than herbivores and algae. It is important to note that zooplankton have been implicitly included in the transfers from algae to herbivores. That is, the biomass and chemical mass associated with zooplankton are not explicitly tracked in TRIM.FaTE, but the dietary transfers are based concentration ratios for planktivorous fish and algae. Some studies provide the intermediate transfer factors for algae to zooplankton, but that compartment type is not currently maintained within TRIM.FaTE.

For each trophic level transfer, the general concentration based equation is converted to the following mass transfer equation:

$$\frac{dN_{receptor}}{dt} = n_{receptor}\, m_{receptor} \times \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{receptor-diet} \times \frac{N_{diet}}{n_{diet}\, m_{diet}} - \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] N_{receptor} \quad (7\text{-}132)$$

where:

$N_{receptor}$	=	mass of chemical in the receptor
$n_{receptor}$	=	number of receptors
$m_{receptor}$	=	mass of individual receptors
N_{diet}	=	mass of chemical in items comprising the potential diet
n_{diet}	=	number of contaminated items comprising the potential diet
m_{diet}	=	mass of individual items comprising the potential diet

For example, the mass transfer equation for water column herbivores is given as:

$$\frac{dN_{f,wco}}{dt} = n_{f,wco}\, m_{f,wco} \times \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] \times K_{f,wco-f,wch} \times \frac{N_{f,wch}}{n_{f,wch}\, m_{f,wch}} - \left[\frac{-\ln(1-\alpha)}{t_\alpha}\right] N_{f,wco} \quad (7\text{-}133)$$

where:

$K_{f,wco\text{-}f,wch}$	=	fish, water column omnivore - fish, water column herbivore partition
$N_{f,wco}$	=	mass of chemical in fish comprising the water column omnivore compartment type
$n_{f,wco}$	=	number of fish comprising the water column omnivore compartment type
$m_{f,wco}$	=	mass of individual in fish comprising the water column omnivore compartment type
$N_{f,wch}$	=	mass of chemical in fish comprising the water column herbivore compartment type
$n_{f,wch}$	=	number of fish comprising the water column herbivore compartment type
$m_{f,wch}$	=	mass of individual fish comprising the water column herbivore compartment type

For each trophic level transfer, the generalized transfer factors for dietary items to a specific fish domain (*i.e.*, benthic omnivore, benthic carnivore, water column herbivore, water column omnivore, or water column carnivore) and for a specific fish domain to dietary items are given by:

$$T_{diet \rightarrow receptor(fish)} = \frac{n_{receptor}\, m_{receptor}}{n_{diet}\, m_{diet}} \times \left[\frac{-\ln(1-\alpha)}{t_{\alpha}} \right] \times K_{receptor-diet} \qquad (7\text{-}134)$$

$$T_{receptor(fish) \rightarrow diet} = \left[\frac{-\ln(1-\alpha)}{t_{\alpha}} \right] \qquad (7\text{-}135)$$

7.3.3.3 Other EPA Models for Bioaccumulation by Fish

Aquatox is a general ecological risk model that estimates the fate and effects of chemical and physical stressors in aquatic ecosystems (U.S. EPA 1998c). The model has been developed by the Office of Pollution Prevention and Toxics (OPPT) and the Office of Water (OW). The Bioaccumulation and Aquatic System Simulator (BASS), developed by the National Exposure Research Laboratory (NERL) of the Office of Research and Development (ORD), also simulates exposure and effects on fish (U.S. EPA 1999c). Aquatox and BASS are designed to predict effects of chemical contaminants and environmental factors on fish populations, whereas TRIM.FaTE is designed to estimate the fate and transport of chemicals throughout aquatic and terrestrial environment, with an emphasis on a collection of identical, individual fish. This difference in purpose results in several differences in structure: (1) Aquatox and BASS include chemical toxicity data; TRIM.FaTE does not (although TRIM.Risk is designed to include such a database); (2) the toxicological data in Aquatox and BASS are used to predict mortality, which is used to modify the structures of the models (*e.g.*, age-class structure and predator-prey

interactions); (3) in Aquatox, decomposition of dead fish and contaminants are linked to the dissolved oxygen levels in water, which affect populations; and (4) growth estimation of fish is fundamental to the population dynamics component of BASS, and growth is not included in the current prototype of TRIM.FaTE.

BASS (U.S. EPA 1999c) and Aquatox (U.S. EPA 1998c) are bioenergetic models of a multiple trophic level aquatic ecosystem. Aquatox, like TRIM.FaTE, provides an explicit steady-state option, whereas BASS does not. Like TRIM.FaTE, Aquatox has a Monte Carlo component to permit probabilistic estimates of exposure or risk. The developers of BASS plan to include metabolism of organic compounds in future versions of the model, but, unlike TRIM.FaTE, these transformations are not a feature of the current version (U.S. EPA 1999c). Components of Aquatox or Bass could be integrated with TRIM.FaTE. The challenge would be to preserve mass balance and to provide adequate links to all TRIM.FaTE compartment types that are connected to surface water and/or fish.

7.4 REVISIONS IN BIOTIC ALGORITHMS

Changes in algorithms since the PAH test case are identified in Table 7-4. It should be noted that PAH-specific parameters for generic algorithms have not been obtained and presented in Appendix A unless the algorithm was used in the 1998 test case.

Table 7-4
Differences Between Algorithms Implemented in the PAH Test Case and New Generic Algorithms that Would be Applicable to PAHs

Process	Algorithm or Assumption Implemented in 1998 PAH Test Case	1999 Generic Algorithm or Assumption
Deposition of particles to plant leaf	Particles deposited to plant leaf; leaf surface and leaf not separate compartment types	Particles deposited to plant leaf; leaf surface and leaf separate compartment types
Particle washoff from plant	Particles washed off leaf at rate equal to deposition rate; 5 percent particulate mass to air and 95 percent to soil	Particles washed off plant at rate in McCune and Lauver (1986), Sect. 7.2.1.1 of this volume; 100 percent of particles to soil
Transfer from surface of leaf to leaf and back	Not implemented because these were part of a single compartment type	First order rate constant, Sect. 7.2.1.1
Mesophyll resistance	Not implemented	Implemented as a generic algorithm, though assumed to be negligible for PAHs
Uptake by root	Uptake from soil water (see below)	Uptake from whole soil
Uptake by stem	Xylem and stem (see below) treated as compartment types; all uptake from soil via root	Stem treated as a compartment type; exchange between stem and leaf, and stem and root
Uptake by earthworm	Uptake from soil water (see below)	Uptake from whole soil
Uptake by soil arthropods	Not included in model	Uptake from whole soil
Uptake by algae	Not included in model	Uptake from surface water
Uptake by fish	Bioenergetic model implemented	Bioenergetic model is one of 2 options (other is time to equilibrium with diet)

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APPENDIX A
DERIVATION OF MERCURY-SPECIFIC ALGORITHMS AND INPUT PARAMETERS

This appendix contains derivations of chemical-specific algorithms, parameters, and information used to derive those parameters. The majority of the appendix focuses on chemical transformations, but information on uptake and distribution of chemicals is also included.

A.1 MERCURY-SPECIFIC ALGORITHMS

A.1.1 PLANT MESOPHYLL RESISTANCE

A general plant algorithm for mesophyll resistance was added to TRIM.FaTE because of the properties of mercury. For most organic chemical species and most plant species, the stomatal or cuticular conductance is the rate-limiting pathway (Riederer 1995). Therefore, for many chemicals, there is no need to consider mesophyll (inner tissue) conductance. However, some work with mercury cited in Lindberg et al. (1992) suggests that "resistance on or within mesophyll surfaces dominates the atmosphere-leaf diffusive path of Hg(0)."

In herbaceous species, it may be assumed that this mesophyll resistance is a factor of 2.5 x stomatal resistance (Lindberg et al. 1992) and that mesophyll conductance is a factor of 1/2.5 or 0.4 x stomatal conductance. It is suggested that the following equation be used for elemental mercury only:

$$g_m = g_{Stomata} \times 0.4$$

where:

g_m = conductance of chemical through mesophyll (m/d)

It should be noted that the high mesophyll resistance of elemental Hg may be due to its assimilation in mesophyll tissue (Lindberg et al. 1992). It has previously been assumed that the mesophyll resistance for divalent mercury is 0 (U.S. EPA 1997a); *i.e.*, that g_m is infinite. It is assumed that mesophyll resistance for methylmercury is also 0, based on a lack of information.

A.1.2 ALGAE

The uptake of pollutants by algae is generally assumed to occur by passive diffusion. The algorithm for chemical uptake by algae in TRIM.FaTE has only been derived for mercury at this time.

Passive uptake of uncharged, lipophilic chloride complexes is the principal accumulation route of both methylmercury and inorganic mercury in phytoplankton and is determined by water chemistry, primarily pH and chloride concentration (Mason et al. 1996). Mason and others

(Mason et al. 1995, Mason et al. 1996) developed an accumulation model for the marine diatom (*Thalassiosira weissflogii*) and modified it for use with "typical" freshwater algae for the purposes of predicting mercury accumulations in fish. It assumes that uptake via passive diffusion is determined by the overall K_{ow} (*i.e.*, the D_{ow}) for the neutral mercury complexes present in solution. The D_{ow} is given as the sum of the individual K_{ow}s for each mercury species by the following equation (Mason et al. 1996):

$$D_{ow} = \sum f_i \left(K_{ow}\right)_i$$

Where f_i = mole fraction of total mercury present as species *i*. The fractional amount of total mercury present as each neutral mercury species was estimated as a function of pH and chloride concentration. The predicted inorganic mercury (divalent) and methylmercury D_{ow} for each of five pH levels (pH 4, pH 5, pH 6, pH 7, and pH 8) and for chloride concentrations ranging approximately from 0.01 mg/l to 10,000 mg/l was presented graphically in (Mason et al. 1996). These D_{ow}s in TRIM.FaTE were estimated based on those curves.

Uptake of inorganic mercury (divalent) and methylmercury by algae is given by the following equation (Mason et al. 1996)

$$Hg_{algae} = \frac{D_{OW} \times U \times 4\pi R^2}{\left(4/3\right)\pi R^3 \times \rho \times \mu} \times Hg_{water}$$

where:

Hg_{algae}	=	concentration in algae (nmol g^{-1})
Hg_{water}	=	concentration in water (nM)
D_{OW}	=	overall K_{OW} for neutral mercury complexes at specified pH and chloride concentrations (unitless)
U	=	algal surface area-specific uptake rate constant (nmol μm^{-2} d^{-1} nM^{-1})
R	=	average radius of algae (μm)
ρ	=	average cell density (g μm^{-3})
μ	=	growth rate constant (d^{-1})

Note that this equation uses moles. Gram weights are derived by multiplying the moles per gram or liter by the chemical-specific molecular weight. Table 7-1 shows the molecular weights of mercury and methylmercury in the units appropriate for converting the above algae (nmol g^{-1}) and water (nM) concentrations.

Table 7-1
Molecular Weights of Mercury and Methylmercury.

Chemical	Molecular Weight		
	g mol^{-1}	µg $nmol^{-1}$	mg $nmol^{-1}$
Hg	200.59	2.0059×10^{-1}	2.0059×10^{-4}
CH_3Hg	215.62	2.1562×10^{-1}	2.1562×10^{-4}

Uptake is assumed to be instantaneous relative to the time steps used in TRIM.FaTE, given that the process occurs in hours rather than days (Mason et al. 1996). Also, uptake of elemental mercury is assumed to be insignificant in TRIM.FaTE, based on the findings of (Mason et al. 1996) that the accumulation rates were less than 1 amol $cell^{-1}$ h^{-1} nM^{-1}, where amol equals 1×10^{-18} moles.

A.1.3 ACCUMULATION OF MERCURY BY FISH

Mercury concentrations in fish are ultimately determined by methylmercury accumulation at the base of the food chain (Mason et al. 1995, Mason et al. 1996). Therefore, one alternative algorithm for the uptake of mercury in fish based on the general equation for the time-to-steady-state food chain model is presented in Section 7.3.3. Intertrophic level concentration ratios ($K_{receptor\text{-}diet}$) were obtained from studies of natural populations of fish, zooplankton, and phytoplankton. Based on studies using MHg/N ratios in whole fish ,the concentration ratio between two trophic levels was found to generally be around 3 to 4 (studies cited in Lindqvist et al. (1991). As noted in Section 7.3.3, mercury transfers from algae to water column herbivores includes the intermediate transfer from algae to zooplankton. Concentration ratios between planktivorous fish and phytoplankton were between 9 and 16 (Lindqvist et al. 1991, Watras and Bloom 1992). That is, zooplankton were an intermediate trophic level and the transfers between each trophic level were approximately equal. Taking the geometric mean results in approximate concentration ratios for methylmercury of 3.5 for one trophic level transfer and 12 for two trophic level transfers (Mason et al. 1996).

Inorganic mercury (divalent) transfer factors between phytoplankton and zooplankton and between zooplankton and planktivorous fish are given by Watras and Bloom (1992). In the absence of similar factors for fish to fish transfers of inorganic mercury, the zooplankton to planktivorous fish transfer factor was used to estimate the concentrations in the water column omnivore, water column carnivore, benthic omnivore, and benthic carnivore compartment types.

A.2 INPUT PARAMETERS SPECIFIC TO MERCURY TRANSFORMATION

Since there are three species of mercury, there are six possible transformation routes from one species to another. All but one of these routes will be considered:

- Reduction $Hg(2) \rightarrow Hg(0)$
- Oxidation $Hg(0) \rightarrow Hg(2)$
- Methylation $Hg(2) \rightarrow CH_3Hg$
- Demethylation $CH_3Hg \rightarrow Hg(2)$
- Mer cleavage demethylation $CH_3Hg \rightarrow Hg(0)$

The route not considered is methylation of Hg(0), for which little information has been reported.

In the case of mercury, the transformation from one chemical species to another is modeled using a first-order rate constant. In particular, the following general equations are used to model transformation.

$$\textit{Reduction}, Hg^{2+} \rightarrow Hg^{0}: \quad \frac{dM_1}{dt} = k_r M_2(t)$$

$$\textit{Oxidation}, Hg^{0} \rightarrow Hg^{2+}: \quad \frac{dM_2}{dt} = k_o M_1(t)$$

$$\textit{Methylation}, Hg^{2+} \rightarrow CH_3Hg: \quad \frac{dM_3}{dt} = k_m M_2(t)$$

$$\textit{Demethylation}, CH_3Hg \rightarrow Hg^{2+}: \quad \frac{dM_2}{dt} = k_{dm} M_3(t)$$

$$\textit{Mer cleavage demethylation}, CH_3Hg \rightarrow Hg^{0}: \quad \frac{dM_1}{dt} = k_{mc} M_3(t)$$

where:

M_1	=	mass of elemental mercury [Hg(0)] in a compartment type
M_2	=	mass of divalent mercury [Hg(2)] in a compartment type
M_3	=	mass of methylmercury (CH_3Hg) in a compartment type
k_r	=	reduction rate in compartment type, 1/day
k_o	=	oxidation rate in compartment type, 1/day
k_m	=	methylation rate in compartment type, 1/day
k_{dm}	=	demethylation rate in compartment type, 1/day
k_{mc}	=	mer cleavage demethylation rate in compartment type, 1/day

The transformation rates may be input directly, or calculated based on other parameters. If both algorithms and input values are available, then the user will be able to choose which method to use.

A.2.1 ABIOTIC MERCURY TRANSFORMATION PARAMETERS

The information in Tables A-2 through A-13 is taken primarily from the 1997 Mercury Report to Congress (U.S. EPA 1997a) and model documentation for EPRI's R-MCM Mercury Cycling Model (Hudson et al. 1994).

Table A-2
Issues Related to Reduction of Hg(2) to Hg(0) in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
Decreases in decreasing sunlight	Decreases with decreasing sunlight and temperatures	Sparse literature on subject
Abiotic reduction (transfer of electrons from humic acid to Hg(2)) is dependent on pH.	Has been observed to increase with decreasing dissolved organic carbon (DOC) conditions (Amyot et al. 1997), and vice versa, due to reduced light penetration and increased complexation of Hg(2)	
Strong stability complex between Hg(2) and humic acid.		

Table A-3
Reduction (k_r) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
5E-1to 3.5	Experimental value using simulated sunlight, after normalizing to sunlight in Stockholm, Sweden	U.S. EPA (1997a), Xiao et al. (1995)
5E-3 to 1E-1	Based on mass balances in Wisconsin seepage lakes	U.S. EPA (1997a), Mason et al. (1994)
2E-2 to 4E-2	Epilimnion	Mason et al. (1995)
1E-2	9 m depth	Mason et al. (1995)
<5E-3	17 m depth	Mason et al. (1995)
1.4E-1	high Arctic lake during 24 hour sunlight period	Amyot et al. (1997)
2E-1 to 4E-1	high Arctic lake, low DOC conditions	Amyot et al. (1997)
2E-2 to 1.4E-1	high Arctic lake, high DOC conditions	Amyot et al. (1997)
1E-1	July-August, upper 3 m	Vandal et al. (1995)
5E-2	July August, upper 6 m	Vandal et al. (1995)

Table A-4
Reduction (k_r) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-6	Inferred value calculated based on presence of Hg(0) in sediment porewater	U.S. EPA (1997a), Vandal et al. (1995)
0.216	Derived from humic acid from farm pool sediment. pH did not appear to affect the rate of reaction, but does seem to influence the amount of mercury reduced.	Alberts et al. (1974)

Table A-5
Reduction (k_r) in Soil: Inputs

Equations Used to Calculate Input Values	Comment	Reference(s)
$k_{norm}\ \theta\ z_{surf} / z_S$' where k_{norm} = reduction rate normalized by soil water content in the surficial 5 mm of soil, L[soil]/L[water]-day; values range from 1E-4 for forest site to 1.3E-3 for field site θ = soil water content, L[water]/L[soil] z_{surf} = depth of soil surface layer to which reduction rate is normalized, 5E-3 m z_S = soil layer depth, m	Formula is derived from evasion flux measurements	U.S. EPA (1997a), Carpi and Lindberg (1997)

Table A-6
Issues Related to Methylation in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
Anaerobic conditions favor higher methylation rates[a]	Anaerobic conditions favor higher methylation rates[a]	Anaerobic conditions favor higher methylation rates[a]
Biotic methylation may occur due to bacteria; abiotic methylation by transmethylation from other organometals or by humic substances[b]	Photodegradation at surface can lower the gross methylation rate[c]	Highest rates may occur at the sediment surface (sulfate-reducing bacteria may be important mediators of the reaction), Gilmour and Henry (1991)
Increases with increasing organic carbon content and BHT[f]	Positively correlated with DOC[d]	Positively correlated with TOC (total organic carbon)[d]
Generally occurs for Hg(2) dissolved in soil porewater	Generally occurs for Hg(2) dissolved in water column[d]	Generally occurs for Hg(2) dissolved in sediment porewater[d]
Abiotic methylation is proportional to temperature and Hg(2) concentration. Also, it is inversely proportional to pH (at pH > 5)[g]	Positively correlated with temperature[d]	Positively correlated with temperature[d]
	Potentially positively correlated with sulfate concentration in water column[e]	Potentially positively correlated with sulfate concentration in sediment porewater[e]

a This is generally due to increased bacterial reactions in anaerobic conditions
b: U.S. EPA (1997a), Gilmour and Henry (1991)
c: Initial reference is Bob Ambrose's discussion of methylation in water column in U.S. EPA (1997a)
d: Hudson et al. (1994)
e: Watras et al. (1995)
f: Nagase et al. (1984); BHT = 2,6, di-tert-butyl-methyl phenol
g: Bodek et al. (1988)

Table A-7
Methylation (k_m) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-4 to 3E-3	reported as maximum potential methylation rate	Gilmour and Henry (1991)
6E-4 to 6E-3	Depth of 3 - 9m	U.S. EPA (1997a), based on Henry et al. (1995a, 1995b) and Jacobs et al. (1995)
5E-4 to 1E-3	Oxic portion of four forest lakes in Finland	Matilainen (1995)
1E-2 to 3E-2	At seasonally-anoxic depth of 15 m	U.S. EPA (1997a), based on Henry et al. (1995a, 1995b) and Jacobs et al., (1995)
4E-3 to 1E-2	Anaerobic layers of hypolimnion	Matilainen (1995)
1E-2 to 4E-2	0.5 - 1.0 m layer of bacterioplankton near the top of the anoxic hypolimnion	Watras et al. (1995)
Equations Used to Calculate Input Values		
$K_{MW}\ Q_{10m}^{(T-Tb)\ 0.1}\ C_{DOC} f_m f_{dissolved}^{II}\ C_s/(C_s+K_s),$ where K_{MW} = methylation rate in the water column, based on DOC (L/mg DOC/day) Q_{10m} = term to adjust methylation rate for temperature (implied suggested value in R-MCM documentation is 2, so that methylation rate doubles for every 10 degree increase in temperature above the base temperature) T = water column temperature, Celsius Tb = base temperature at which methylation rate constant K_{MW} applies, Celsius C_{DOC} = DOC concentration in water column, mg DOC/L f_m = fraction of the dissolved HgII in the water column available for methylation $f^{II}_{dissolved}$ = fraction of the Hg(2) in the water column that is dissolved C_s = concentration of sulfate in the water column, µeq/L K_s = half-saturation constant for the effect of sulfate on methylation, µeq/L	Will need to see what ranges are for K_{MW} and K_s	Hudson et al. (1994)

Table A-8
Methylation (k_m) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-5 to 1E-3	Reported as maximum potential methylation rate	Gilmour and Henry (1991)
8E-4 to 2.5E-2	Above intact sediment cores	Stordal and Gill (1995)
8E-5 to 2E-5	Upper 4 cm of Little Rock Lake sediments	Calculated in U.S. EPA (1997a) from methylation rates in units of ug/m^2/day (Gilmour and Riedel 1995) and assumed dry density of 1.2 g/cm^3
Equations Used to Calculate Input Values		
$K_{MS}\ Q_{10m}^{(T-Tb)\,0.1}\ T_s f_m f_{dissolved}^{II}\ ((p_i - p_b)*0.5)\ C_{ps}/(C_{ps}+K_s),$ where K_{MS} = methylation rate in the sediment, based on TOC (m^2/g TOC/day) Q_{10m} = term to adjust methylation rate for temperature (implied suggested value in R-MCM documentation is 2, so that methylation rate doubles for every 10 degree increase in temperature above the base temperature) T = sediment temperature, Celsius Tb = base temperature at which methylation rate constant K_{MS} applies, Celsius T_s = TOC concentration in water column, g [organisms] C/m^2 f_m = fraction of the dissolved HgII in the sediment porewater available for methylation $f^{II}_{dissolved}$ = fraction of the Hg(2) in the sediment that is dissolved p_i = porosity of the sediment at the sediment/water interface, dimensionless p_b = porosity of the bottom of the sediment, dimensionless C_{ps} = concentration of sulfate in the sediment porewater, µeq/L K_s = half-saturation constant for the effect of sulfate on methylation, µeq/L	Will need to see what ranges are for K_{MS} and K_s. Also make sure porosity dependence is correct (seems odd).	Hudson et al. (1994), p.5-22

Table A-9
Methylation (k_m) in Soil: Inputs

Input Values (1/day)	Comment	Reference(s)
2E-4	average maximum potential methylation rate constant under aerobic conditions for 120-day experiment	Porvari and Verta (1995)
1E-3	average average maximum potential methylation rate constant under anaerobic conditions for 120-day experiment	Porvari and Verta (1995)
7E-5 to 9.7E-4	Range for median aerobic reaction rate (from peat, humus layer, and soil samples, respectively)	Verta et al (1994)
9.2 E-3	Anaerobic median rate of four inundated soil samples (range = 4.2E-3 to 1.2E-2/day)	Verta et al. (1994)

Table A-10
Issues Related to Demethylation in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
May increase with increasing anaerobic conditions	Negatively correlated with light	May depend on bacteria processes
		Has been reported as maximal at the sediment/water interface (Gilmour et al. 1992)

Table A-11
Demethylation (k_m) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-3 to 2.5E-2	Maximum potential demethylation rate constants	Gilmour and Henry (1991)
Equations Used to Calculate Input Values		
$(K_{ds} / K_L) (1 - \exp(-K_L z_W)) / z_W$, where K_{ds} = demethylation rate constant at the lake surface, 1/day K_L = light extinction coefficient for use in demethylation calculations, 1/m z_W = mean depth of water column, m		Hudson et al. (1994)

Table A-12
Demethylation (k_{dm}) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
2E-4 to 1E-1	reported maximum potential demethylation rate constants	Gilmour and Henry (1991)
Equations Used to Calculate Input Values		
$K_{dms}\ T_s f^{MHg}_{dissolved}\ ((p_i + p_b) * 0.5)$, where K_{dms} = demethylation rate in the sediment, based on TOC (m^2/g TOC/day) T_s = TOC concentration in sediment, g [organisms] C/m^2 $f^{MHg}_{dissolved}$ = fraction of the methylmercury in the sediment that is dissolved p_i = porosity of the sediment at the sediment/water interface, dimensionless p_b = porosity of the bottom of the sediment, dimensionless	Will need to see what ranges are for K_{MS} and K_s. Also make sure porosity dependence is correct (seems odd).	Hudson et al. (1994)

Table A-13
Demethylation (k_{dm}) in Soil: Inputs

Input Values (1/day)	Comment	Reference(s)
3E-2	Average of maximum potential demethylation rate constants in aerobic conditions	Porvari and Verta (1995)
6E-2	Average of maximum potential demethylation rate constants in anaerobic conditions	Porvari and Verta (1995)
3.6E-2, 7.6E-2, 1.1E-1	Median aerobic rates for 15 inundated soil samples, 15 humus layer samples, and five peat samples, respectively.	Verta et al. (1994)
8.9E-2	Median anaerobic rate for 15 inundated soil samples.	Verta et al. (1994)

A.2.2 BIOTIC MERCURY TRANSFORMATION PARAMETERS

A.2.2.1 Plants

Fortmann et al. (1978) observed that some plants can change the mercury species accumulated from the environment. However, few studies are available from which to determine transformation rates.

$$Hg(0) \rightarrow Hg(2)$$

This transfer only occurs in leaves; elemental mercury is probably not taken up by the root. This rate is apparently very rapid and may be assumed to be instantaneous (U.S. EPA 1997a). No instances have been found where elemental mercury was measured in plants (*e.g.*, Cappon 1987). Thus, elemental mercury in air or on the surface of the leaf can be directly transferred to divalent mercury in the leaf.

$$Hg(2) \rightarrow \text{methylmercury}$$

It may be assumed that Hg(2) is not transformed. Although the in vivo transformation of inorganic mercury to methylmercury was observed in *Pisum sativum* (peas) in one study (Gay 1975), the chemical was ephemeral and quickly (several hours) decayed to low parts per billion levels. Methylmercury residues were not detected in mature crops following the addition of mercuric chloride to soil (Bache et al. 1973). Indeed, most mercury in plants is usually in inorganic form (Lindberg 1998).

$$\text{methylmercury} \rightarrow Hg(2)$$

This transfer occurs in leaves and stems, and not in roots (since transformations interfere with the equilibrium assumption in roots). It may be assumed that methylmercury is transformed to Hg(2) according to first-order kinetics, where the first-order rate constant is **0.03 per day**, based on the following calculation.

Only one study is available in which methylmercury was added to soil, and forms of mercury (methyl and total) were measured after a defined period of exposure (Bache et al. 1973). In the few other studies of speciation of mercury within plants, either it is not known which species were present in soil (*e.g.*, Heller and Weber 1998), or multiple Hg species were present in soil and it is not known which were initially taken up by the plant (Cappon 1987).

Using data from Bache et al. (1973) Table A-14, it may be assumed that the methylmercury is readily taken up through the roots or foliage, that equilibrium between soil and plant is achieved quickly, that methylmercury is not appreciably transformed in soil during a crop season, that all methylmercury is only transformed to ionic mercury, and that crops were harvested after 40 days. Under these assumptions, 1st order rate constants for the transformation of methylmercury to Hg(2) vary by almost two orders of magnitude in a single study. No mechanistic explanation is available for this high degree of variability.

Table A-14
Concentrations of Methylmercury in Foliage and Stems of Crops from Bache et al. (1973) and Associated First-order Rate Constants, Using Assumptions in Text

Plant Species	Soil	Application to Soil (mg/kg)	Total Mercury in Foliage and Stem	Methylmercury in Foliage and Stem	1st Order Rate Constant (d^{-1})
Bush bean (*Phaseolus vulgaris*)	gravelly loam	1	52	46	0.003
Bush bean (*Phaseolus vulgaris*)	gravelly loam	10	90	28	0.03
Carrot (*Daucus carota*)	gravelly loam	10	214	1	0.1
Potato (*solanum tuberosum*)	silt loam	1	86	27	0.03
Potato (*solanum tuberosum*)	silt loam	10	58	17	0.03
Tomato (*Lycopersicon esculantum*)	gravelly loam	10	341	3	0.1

A.2.2.2 Soil Detritivores

No information is available for transformations of mercury in soil detritivores. In addition, transformation algorithms cannot be implemented if the mercury in these organisms is in equilibrium with mercury in root-zone soil.

A.2.2.3 Terrestrial and Semi-aquatic Wildlife

Little quantitative information is available on the transformation of mercury in mammals and birds. Where information is available, calculations of rate constants assume first order transformations and are calculated on the basis of the total chemical taken up by the organism but not necessarily assimilated. (The exception is the inhalation pathway, where rate constants are derived based on the absorbed fraction.)

$$Hg(0) \rightarrow Hg(2)$$

No information is available from which to derive transformation rate constants for the oxidation of elemental mercury to the mercuric ion. Based on the following information, it may be assumed that the rate is rapid, and 1 day^{-1} is a rough estimate of the first-order rate constant. Elemental mercury is readily oxidized to the inorganic divalent species in most tissues following the hydrogen peroxidase-catalase pathway. This oxidation primarily occurs in the red blood cells

and hydrogen peroxide is probably the rate-determining step (ATSDR 1997, U.S. EPA 1997b). Once it is oxidized to the mercuric ion, it is indistinguishable from Hg(2) from inorganic sources (ATSDR 1997, U.S. EPA 1997b).

$$Hg(2) \rightarrow Hg(0)$$

Mercuric salts primarily remain in their divalent form. However, a small fraction of the inorganic divalent cation can be reduced to elemental mercury and exhaled as a vapor (ATSDR 1997). However, no information is available from which to derive this transformation rate constant. For this reason, the transformation is assumed not to occur.

$$\text{organic mercury} \rightarrow Hg(2)$$

Forms of organic mercury are the most studied species of mercury. The short-chain alkyl mercury compounds (*e.g.* methylmercury) are relatively stable and are more slowly metabolized to the inorganic form (U.S. EPA 1997b) The long-chain compounds may be more readily metabolized to the mercuric ion (U.S. EPA 1997b). Takeda and Ukita (1970) dosed Donryu rats with 20 µg Hg/kg ethyl-mercuric chloride via intravenous injection. After 8 days, 58.1 percent of the mercury excreted in the urine was inorganic mercury and 35 percent of the mercury excreted in feces was inorganic (Table A-15). If it is assumed that 1) the excreted chemicals reflect the transformation rate in the animal (transformation occurred immediately prior to excretion) and 2) the first-order rate reflects a weighted average of the amount of dose excreted in urine (10.52 percent) and that excreted in feces (6.01 percent), then the transformation rate may be estimated to be 0.09 day^{-1}.

Table A-15
Transformation Rate (day^{-1}) of Organic Mercury to the Inorganic Divalent Form (Takeda and Ukita 1970)

Class	Elimination Type	Dose Route	% Organic after 8 days	% Inorganic after 8 days	Transform Rate Constant
Mammalia	urine	injection	41.9	58.1	0.1084
	feces	injection	65.0	35.0	0.0539
	assumed transformation for whole animal				0.09

$$Hg(2) \rightarrow \text{organic mercury}$$

No information is available on this transformation. Therefore it is assumed to be zero.

Miscellaneous Transformations

Miscellaneous transformations in wildlife are presented for the sake of completeness but are not included in TRIM.FaTE at this time. Mercurous salts are transformed to the divalent ion and elemental mercury when in contact with sulfhydryl groups (ATSDR 1997).

A.2.2.4 Aquatic Species

Transformations of mercury in algae, macrophytes, and benthic organisms are assumed not to occur.

$$Hg(2) \rightarrow \text{organic mercury}$$

Very little is known about the rate at which transformation of mercury species occurs in aquatic organisms. A large body of field data suggests that most (> 90 percent) of mercury in fish is in the form of methylmercury and other organic species. For this reason, it is assumed that the first-order rate constant for the conversion is 1 day^{-1}.

$$Hg(0) \rightarrow Hg(2)$$

This transformation is assumed to occur instantaneously in fish.

$$Hg(0) \rightarrow \text{organic mercury}$$

This transformation is assumed not to occur directly in fish.

$$Hg(2) \rightarrow \text{organic mercury}$$

This transformation is assumed not to occur in fish.

$$\text{organic mercury} \rightarrow Hg(2)$$

This transformation is assumed not to occur in fish.

$$\text{organic mercury} \rightarrow Hg(0)$$

This transformation is assumed not to occur in fish.

A.3 INPUT PARAMETERS SPECIFIC TO MERCURY EXCRETION BY BIOTA

First-order rate constants for the elimination of mercury from wildlife are summarized in Table A-16. Supporting information is presented below.

Table A-16
Mean First-order Rate Constants (day^{-1}) for Elimination of Mercury from Birds and Mammals

	Chemical Species	Urine and Feces (E_u)	Lactation (E_l)	Eggs (E_e)	Fur, Feathers, or Hair (E_f)
mammals	Hg(2)	0.48[a]	0.00001	NA	0.00001
	Hg(0)	0.0502[b]	0[b]	NA	0[b]
	organic Hg	0.26[a]	0.00001[c]	NA	0.00014[d]
birds	Hg(2)	0.48[e]	NA	0[f]	0.00011[g]
	Hg(0)	0[b]	NA	0[b]	0[b]
	organic Hg	0.0282[a]	NA	0.0244	0.0559

[a] Averages of elimination rate constants for oral and dietary doses
[b] Rate constant based on inhalation study
[c] Assume same as lactation rate constant for Hg(2)
[d] Averages of elimination rate constants for oral dose and injection
[e] Assume same as elimination rate constant to mammalian urine and feces
[f] No information available
[g] Assume same as elimination rate constant to mammal fur

A.3.1 ELEMENTAL MERCURY

Elemental mercury vapor is rapidly absorbed in the lungs (75 to 85 percent in humans), and to a much lesser extent (three percent), it can be absorbed dermally (ATSDR 1997, U.S. EPA 1997b). Five human subjects inhaled from 107 to 202 $\mu g/m^3$ Hg and retained an average of 74 percent of the dose (Teisinger and Fiserova-Bergerova 1965). The inhaled vapor readily distributes throughout the body and can cross the blood-brain and placental barriers.

Rats exposed for 5 hours to 1.4 mg/m^3 radio-labeled mercury vapor retained an average body burden of 0.256 mg/kg BW (37 µg Hg/rat) and had excreted (urine and feces) 8.5 percent of the initial body burden in 1 day, 24.8 percent in 5 days, and 42.9 percent in 15 days (Hayes and Rothstein 1962). Cherian et al. (1978) exposed 5 human volunteers to approximately 1 µCi of radio-labeled Hg vapor for approximately 19 minutes. Mean cumulative excretion over the first 7 days after exposure was 2.4 percent of the retained dose in urine and 9.2 percent in feces for a total excretion of 11.6 percent of the retained dose (Cherian et al. 1978).

Rates of excretion of elemental mercury by mammals (rats and humans) are summarized in Table A-17. The mean value is presented in Table A-16. No information on excretion by avian species is available.

Table A-17
Excretion of Elemental Mercury (Hg^0) in Mammals.

Test Species	Dose	Dose Route[1]	Elimination Route	Percent of Dose	Days	Rate Constant (Day^{-1})	Source
Rat	0.256 mg/kg	inh	urine + feces	8.5	1	0.08883	Hayes & Rothstein 1962
Rat	0.256 mg/kg	inh	urine + feces	24.8	5	0.05700	Hayes & Rothstein 1962
Rat	0.256 mg/kg	inh	urine + feces	42.9	15	0.03736	Hayes & Rothstein 1962
Human	1 µCi	inh	urine + feces	11.6	7	0.01761	Cherian et al. 1978
				$\bar{x} \pm$ SE		**0.05020 ± 0.01518**	

[1] inh = inhalation

A.3.2 Divalent Mercury

Divalent mercury can be absorbed through oral, dermal, and inhalation routes; however, absorption is inefficient for all pathways. In mice, only 20 percent of the administered dose is absorbed from the GI tract, 2-3 percent of the dose was absorbed dermally in exposed guinea pigs, and limited information on inhalation exposure indicates that 40 percent of the dose was absorbed in the lungs of dogs (U.S. EPA 1997b). Additionally, the absorption of mercuric salts varies with the solubility of the specific salt. For example, the less soluble sulfide salt is more poorly absorbed as mercuric sulfide than the more soluble chloride salt as mercuric chloride (U.S. EPA 1997b). Divalent mercury distributes widely throughout the body, however, it cannot cross the blood-brain or placental barriers.

The metabolism and distribution of mercuric chloride ($HgCl_2$) has been described in dairy cows and rats. Potter et al. (1972) orally administered 344 µCi of radio-labeled mercuric chloride by gelatin capsule using balling gum to 2 Holstein cows. After 6 days, 94.87 percent of the dose was excreted in feces, 0.044 percent in urine, and 0.0097 percent in milk, for a total excretion of 94.924 percent of the dose. The biological half-life was calculated as 28.5 hours. Rats dosed by intravenous injection with 1 mg/kg mercuric chloride excreted 15.2 percent of the dose in feces and 16.3 percent in urine over 4 days for a total excretion (fecal and urinary) of 31.5 percent of the administered dose (Gregus and Klaassen 1986).

The metabolism and distribution of mercuric nitrate [$Hg(NO_3)_2$] has also been described in dairy cows and rats. Four Holstein dairy cows were given an oral dose of 1.7 mCi radio-labeled $Hg(NO_3)_2$ in a gelatin capsule via balling gum. Urine, feces, and milk were collected for 10 days and analyzed. Results indicated that 74.91 percent of the dose was excreted in feces, 0.08 percent in urine, and 0.01 percent in milk with a total excretion of 75 percent of the dose (Mullen et al. 1975). Mullen et al. (1975) also reported a biological half-life for the transfer of

orally ingested mercury to milk of 5 days. Transfer of mercury to feces was slightly more complicated with an initial half-life of 15 hr, then a decrease in elimination time which resulted in a 3 day half-life (Mullen et al. 1975). Rothstein and Hayes (1960) dosed seven Wistar rats with 50 µg (0.2 mg/kg BW) radio-labeled mercury as $Hg(NO_3)_2$ via intravenous injection. After 52 days the cumulative percent excretion was 25 percent of the administered dose in urine and 37 percent in feces for a total excretion of 62 percent of the dose (Rothstein and Hayes 1960). In another study, 6 Holtzman rats were dosed by subcutaneous injection with 20 µCi of radio-labeled $Hg(NO_3)_2$ and 0.018 percent of the dose was recovered in the hair 20 days after administration (Mansour et al. 1973). The maternal clearance half-time of 16.2 days was also reported.

Fitzhugh et al. (1950) exposed rats (n=20/dose group) to mercuric acetate in the diet at doses of 0.5, 2.5, 10, 40, and 160 ppm. The average intake of Hg in a 24 hour period was 7.5, 37.5, 150, 600, and 2,400 µg and the 24 hour excretion was 52, 40, 43, 47, and 43 percent of these doses, respectively, in feces and 4.8, 1.0, 0.5, 0.37, and 1.7 percent, respectively, in urine (Fitzhugh et al. 1950).

Divalent mercury is very poorly absorbed from the GI tract, therefore, rates obtained from oral or dietary exposure may be misleading. Hayes and Rothstein (1962) reported an initial half-life for fecal excretion of inorganic mercury of 0.6 days in Holstein cows. Later, the half-life increased to 3 days. This indicates that a large proportion of the dose is initially excreted via the feces due to lack of absorption. Thus, it may be necessary to correct the oral and dietary fecal elimination rates for inorganic mercury using assimilation factors.

Rates of excretion of divalent mercury by mammals (rats and cows) are summarized in Table A-18. The mean values for excretion to urin and feces, lactation, and excretion to hair are presented in Table A-16. No information on excretion by avian species is available.

A.3.3 ORGANIC MERCURY

Organic mercury was by far the most studied species of mercury. It is rapidly and extensively absorbed through the GI tract (95 percent of the dose in humans) and is distributed throughout the body via carrier-mediated transport (U.S. EPA 1997b). Like elemental mercury, organic mercury can cross the blood-brain and placental barriers.

Radio-labeled methylmercuric chloride was intravenously injected into 6 Holtzman rats at a dose of 10 µCi, and after 20 days 0.21 percent of the administered dose was transferred to hair. The clearance half-life was reported to be 8.4 days (Mansour et al. 1973). Gregus and Klaassen (1986) also administered radio-labeled methylmercuric chloride via intravenous injection to

Table A-18
Excretion of Divalent Mercury in Mammals

Test Species[a]	Form	Dose	Dose[b] Route	Elimination Route	Percent of Dose	Days	Rate (Day^{-1})	Dose Vehicle	Source
Cow-Holstein	$HgCl_2$	344 µCi	oral	urine + feces	94.91	6	0.49632	gel cap	Potter et al. 1972
Cow-Holstein	$Hg(NO_3)_2$	1.7 mCi	oral	urine + feces	74.99	10	0.13859	gel cap	Mullen et al. 1975
					$\bar{x} \pm$ SE		**0.31745 ± 0.17886**		
Rat-SD	$HgCl_2$	1 mg/kg	iv	urine + feces	31.5	4	0.09458	saline sol	Gregus & Klaassen 1986
Rat-Wistar	$Hg(NO_3)_2$	50 µg	iv	urine + feces	62	52	0.01861	sodium chloride	Rothstein & Hayes 1960
					$\bar{x} \pm$ SE		**0.05660 ± 0.03798**		
Rat	mercuric acetate	7.5 µg	diet	urine + feces	56.8	1	0.83933	food	Fitzhugh et al. 1950
Rat	mercuric acetate	37.5 µg	diet	urine + feces	41.0	1	0.52763	food	Fitzhugh et al. 1950
Rat	mercuric acetate	150 µg	diet	urine + feces	43.5	1	0.57093	food	Fitzhugh et al. 1950
Rat	mercuric acetate	600 µg	diet	urine + feces	47.37	1	0.64188	food	Fitzhugh et al. 1950
Rat	mercuric acetate	2400 µg	diet	urine + feces	44.7	1	0.59240	food	Fitzhugh et al. 1950
					$\bar{x} \pm$ SE		**0.63443 ± 0.05443**		
Cow-Holstein	$HgCl_2$	344 µCi	oral	milk	0.0097	6	0.00002	gel cap	Potter et al. 1972
Cow-Holstein	$Hg(NO_3)_2$	1.7 mCi	oral	milk	0.01	10	0.00001	gel cap	Mullen et al. 1975
					$\bar{x} \pm$ SE		**0.00001 ± 0.000003**		
Rat-Holtzman	$Hg(NO_3)_2$	20 µg	sc inj	hair	0.018	20	0.00001	injection	Mansour et al. 1973

[a] Rat-SD = Sprague Dawley rat
[b] iv = Intravenous injection and sc inj = subcutaneous injection.

Sprague-Dawley rats at a dose of 1 mg/kg. Within 4 days, 5.6 percent of the dose was excreted in feces and 0.5 percent in urine for a total excretion of 6.1 percent of the administered dose. Additionally, 2 hr biliary excretion was 0.7, 0.9, 0.7, and 0.5 percent of doses 0.1, 0.3, 1.0, and 3.0 mg/kg, respectively (Gregus and Klaassen 1986). Syrian Golden hamsters (n=9) were given an oral dose of 0.32 mg Hg/kg BW as radio-labeled methylmercury chloride, and the elimination rate was found to follow a first-order rate equation with a half-life of 6.9 days (Nordenhäll et al. 1995). Nordenhäll et al. (1995) estimated that approximately 5 percent of the dose administered to the dams was transferred to pups via milk over 21 days. Four days post-administration of methylmercury chloride, 20 percent of the mercury in milk was inorganic (Nordenhäll et al. 1995). Sell and Davison (1975) dosed via intraruminal injection, 1 Nubian goat and 1 Guernsey cow with 100 and 500 µCi radio-labeled methylmercury chloride, respectively. After 13 days, 0.28, 31.18, and 1.45 percent of the dose administered to the goat were excreted in milk, feces, and urine, respectively. Conversely, none of the dose was excreted in cow milk, 25.32 percent was excreted in cow feces, and 1.28 percent was excreted in cow urine after 7 days.

Takeda and Ukita (1970) exposed Donryu rats to 20 µg Hg/kg BW as radio-labeled ethyl-mercuric chloride dissolved in olive oil by subcutaneous injection. Cumulative excretion during 8 days post-exposure was 10.52 percent of dose in urine and 6.01 percent of dose in feces. In urine, 41.9 percent and 58.1 percent of the total mercury was organic and inorganic, respectively, on day 8. In contrast, 65 percent of fecal mercury was organic and 35 percent was inorganic on day 8 (Takeda and Ukita 1970). Fang and Fallin (1973) orally dosed 14 rats with 3 µmol radio-labeled ethyl-mercuric chloride in corn oil. Mercury content was measured in 1-2 rats on days 0.25, 1, 2, 3, 4, 5, 7, 10, and 14 after dosing. Fourteen days after dosing, 32.5 nmole/g hair had accumulated in the fur. Wistar rats have an estimated 3 g of fur (Talmage 1999), therefore, approximately 3.25 percent of the original dose was excreted in hair.

Fitzhugh et al. (1950) exposed rats (n=20/dose group) to phenyl mercuric acetate in the diet at doses of 0.5, 2.5, 10, 40, and 160 ppm. The average intake of Hg in a 24 hour period was 7.5, 37.5, 150, 600, and 2,400 µg and the 24 hour excretion was 44, 35, 27, 35, and 30 percent of these doses, respectively, in feces and 9.2, 4.5, 6.2, 4.3, and 2.4 percent, respectively, in urine (Fitzhugh et al. 1950).

Humans have also been used as subjects for determining the metabolism of methylmercury. Three subjects were given an oral dose of 2.6 µCi radio-labeled methylmercuric nitrate (Aberg et al. 1969). Mean cumulative mercury excretion 10 days post-exposure were 13.6 percent (13.6, 13, and 14.2 percent) of dose in feces and 0.24 percent (0.18, 0.26, and 0.27 percent) in urine, and after 49 days, 34.1 percent (33.4 and 34.7 percent) of the initial dose was excreted via feces and 3.31 percent (3.29 and 3.33 percent) via urine (Aberg et al. 1969). Aberg et al. (1969) also reported the biological half-life of methylmercuric chloride to be 70.4, 74.2, and 73.7days ($\bar{x}$ = 72.8 days) for the three subjects and measured approximately 0.12 percent of the initial dose in hair approximately 45 days (range 40-50 days) after exposure.

Two papers contained data suitable for use in determining excretion rates for avian species. In the first study, Lewis and Furness (1991) orally dosed black-headed gulls with 200, 100, or 20 µl methylmercuric chloride using gelatin capsules. The cumulative excretion of mercury in the 200 µL group was 26.4 percent of the dose in feces and 51.2 percent in feathers

for a total of 77.5 percent in all excreta over 13 days. At the 100 µL dose, a total of 80.3 percent of the dose was excreted (37.8 and 44.2 percent in feces and feathers, respectively) in 13 days. Finally, only 56.3 percent of the low dose was measured in all excreta with 11 percent of the dose in feces and 52.6 percent in feathers after 13 days (Lewis and Furness 1991).

In the second study, 4 white-leghorn chickens and 4 Japanese quail were dosed with 20 ppm Hg as methylmercuric chloride in the diet for 21 days (Sell 1977). The first 7 days of this dosing period, chickens and quail were also given an oral dose of 2 µCi of radio-labeled methylmercuric chloride (Sell 1977). The rate calculations reported in Table A-17 assume that the author accounted for the total intake of radio-labeled mercury from both sources when reporting percent of dose excreted in feces and eggs. Chickens excreted 64 percent of the dose in feces and 21.88 percent of the dose in eggs produced during the 21 days post-exposure, while quail excreted 41 and 54.08 percent of the dose in feces and eggs, respective, during the same 21 day post-exposure period (Sell 1977).

Rates of excretion of organic mercury by mammals (humans, goats, cows, and rats) are summarized in Table A-19. Rates of excretion by birds are summarized in Table A-20. The mean values for excretion to urine and feces, fur, feathers, and eggs are presented in Table A-16. No information on excretion by avian species is available.

Table A-19
Excretion of Organic Mercury in Mammals

Test Species[1]	Form	Dose	Dose[2] Route	Elimination Route	Percent of Dose	Days	Rate (Day^{-1})	Dose Vehicle	Source
Human	methylmercuric nitrate	2.6 µCi	oral	urine + feces	13.84	10	0.01490	aq sol	Aberg et al. 1969
Human	methylmercuric nitrate	2.6 µCi	oral	urine + feces	37.41	49	0.00956	aq sol	Aberg et al. 1969
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	urine + feces	0.67	1	0.00672	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	urine + feces	17.19	3	0.06287	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	urine + feces	22.62	5	0.05129	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	urine + feces	25.72	7	0.04248	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	urine + feces	31.63	13	0.02925	ethanol	Sell & Davison 1975
Cow-Guernsey	CH_3-HgCl	500 µCi	ir inj	urine + feces	4.80	1	0.04919	ethanol	Sell & Davison 1975
Cow-Guernsey	CH_3-HgCl	500 µCi	ir inj	urine + feces	18.86	3	0.06966	ethanol	Sell & Davison 1975
Cow-Guernsey	CH_3-HgCl	500 µCi	ir inj	urine + feces	23.05	5	0.05240	ethanol	Sell & Davison 1975
Cow-Guernsey	CH_3-HgCl	500 µCi	ir inj	urine + feces	26.60	7	0.04418	ethanol	Sell & Davison 1975
					$\bar{x} \pm$ SE		**0.03932 ± 0.00644**		
Rat-SD	CH_3-HgCl	1 mg/kg	iv	urine + feces	6.1	4	0.01573	saline sol	Gregus & Klaassen 1986
Rat-Donryu	ethyl-$HgCl_2$	20 µg/kg	sc inj	urine + feces	16.53	8	0.02259	olive oil	Takeda & Ukita 1970
					$\bar{x} \pm$ SE		**0.01916 ± 0.00343**		
Rat	phenyl mercuric acetate	7.5 µg	diet	urine + feces	53.2	1	0.75929	food	Fitzhugh et al. 1950
Rat	phenyl mercuric acetate	37.5 µg	diet	urine + feces	39.5	1	0.50253	food	Fitzhugh et al. 1950
Rat	phenyl mercuric acetate	150 µg	diet	urine + feces	33.2	1	0.40347	food	Fitzhugh et al. 1950
Rat	phenyl mercuric acetate	600 µg	diet	urine + feces	39.3	1	0.49923	food	Fitzhugh et al. 1950
Rat	phenyl mercuric acetate	2400 µg	diet	urine + feces	32.4	1	0.39156	food	Fitzhugh et al. 1950
					$\bar{x} \pm$ SE		**0.51121 ± 0.06621**		
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	milk	0.08	3	0.00027	ethanol	Sell & Davison 1975

Table A-19 (cont.)
Excretion of Organic Mercury in Mammals

Test Species[1]	Form	Dose	Dose[2] Route	Elimination Route	Percent of Dose	Days	Rate (Day^{-1})	Dose Vehicle	Source
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	milk	0.14	5	0.00028	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	milk	0.19	7	0.00027	ethanol	Sell & Davison 1975
Goat-Nubian	CH_3-HgCl	100 µCi	ir inj	milk	0.28	13	0.00022	ethanol	Sell & Davison 1975
					$\bar{x} \pm$ SE		**0.00026 ± 0.00001**		
Human	methylmercuric nitrate	2.6 µCi	oral	hair	0.12	45	0.00003	aq sol	Aberg et al. 1969
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.05	0.25	0.00200	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.14	1	0.00140	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.18	2	0.00090	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.52	3	0.00174	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.59	4	0.00148	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	0.67	5	0.00134	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	1.08	7	0.00155	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	2.25	10	0.00228	corn oil	Fang & Fallin 1973
Rat-Wistar	ethyl-$HgCl_2$	3 µmole	oral	hair	5.50	14	0.00404	corn oil	Fang & Fallin 1973
					$\bar{x} \pm$ SE		**0.00168 ± 0.00033**		
Rat-Holtzman	CH_3-HgCl	10 µCi	iv	hair	0.21	20	0.00011		Mansour et al. 1973

[1] Rat-SD = Sprague Dawley rat
[2] ir = Intraruminal injection, iv = intravenous injection and sc inj = subcutaneous injection.

Table A-20
Excretion of Organic Mercury in Birds

Test Species[a]	Form	Dose	Dose Route	Elimination Route	Percent of Dose	Days	Rate (Day^{-1})	Dose Vehicle	Source
Gull-BH	methyl-HgCl	200 µL	oral	feces	26.4	13	0.02358	gel cap	Lewis & Furness 1991
Gull-BH	methyl-HgCl	100 µL	oral	feces	37.7	13	0.03640	gel cap	Lewis & Furness 1991
Gull-BH	methyl-HgCl	20 µL	oral	feces	11	13	0.00896	gel cap	Lewis & Furness 1991
					$\bar{x}$ ± SE		**0.02298 ± 0.00793**		
Chicken-WL	methyl-HgCl	20 ppm + 2 µCi	diet/orl	feces	64	21	0.04865	food	Sell 1977
Quail-Japanese	methyl-HgCl	20 ppm + 2 µCi	diet/orl	feces	32	21	0.01836	food	Sell 1977
					$\bar{x}$ ± SE		**0.03351 ± 0.01514**		
Gull-BH	methyl-HgCl	200 µL	oral	feathers	51.2	13	0.05519	gel cap	Lewis & Furness 1991
Gull-BH	methyl-HgCl	100 µL	oral	feathers	44.2	13	0.04488	gel cap	Lewis & Furness 1991
Gull-BH	methyl-HgCl	20 µL	oral	feathers	52.6	13	0.05743	gel cap	Lewis & Furness 1991
					$\bar{x}$ ± SE		**0.05593 ± 0.00075**		
Chicken-WL	methyl-HgCl	20 ppm + 2 µCi	diet/orl	eggs	21.88	21	0.01176	food	Sell 1977
Quail-Japanese	methyl-HgCl	20 ppm + 2 µCi	diet/orl	eggs	54.08	21	0.03706	food	Sell 1977
					$\bar{x}$ ± SE		**0.02441 ± 0.01265**		

[a] Gull-BH = Black-headed gull, Chicken-WL = White- leghorn chicken.

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