

## 7. TERRESTRIAL BIOTA ALGORITHMS

In this chapter, algorithms for transfers between terrestrial biotic compartment types and other biotic or abiotic compartment types are presented. The terrestrial biotic compartments include terrestrial plants, soil detritivores, and wildlife (*i.e.*, birds and mammals).

The algorithms in this chapter are based on diffusive or advective transfer, and the most common instances of the latter are transfers via wildlife ingestion of chemicals in their diet. Most algorithms apply to all air pollutants, although some apply only to mercury species, and others (*e.g.*, those that involve octanol/water partition coefficients) apply only to nonionic organic chemicals. Some of the equations represent dynamic processes, while others are simple models for which a time-to-equilibrium is calculated and used to estimate relevant transfer factors.

After a brief introduction to the selection of terrestrial biotic compartments for a TRIM.FaTE scenario (Section 7.1), the algorithms used to calculate the transfer factors for chemical transfers in and out of terrestrial biota are developed and presented. General algorithms for terrestrial plants, soil detritivores, and birds and mammals are presented in Sections 7.2, 7.3, and 7.4, respectively. The derivations of chemical-specific algorithms for mercury and polycyclic aromatic hydrocarbons (PAHs) are presented in Appendices A and B, respectively.

### 7.1 TERRESTRIAL BIOTA COMPONENTS

The general approach for selecting biotic compartment types to include in a TRIM.FaTE scenario is noted in Section 3.3 of TSD Volume I and described in more detail in the user guidance document. All major trophic levels in terrestrial systems are represented in the current TRIM.FaTE library. The user can select default, representative species, based on their prevalence at the test location and/or the availability of data to estimate parameter values for them. The user can also create compartments for additional species based on policy considerations, such as the Endangered Species Act. There are some aspects of selecting biotic compartments for the terrestrial environment that we emphasize here. For additional information on these issues and more detailed guidance, see the TRIM.FaTE user guidance.

For terrestrial surface volume elements or parcels, the user can select one of a number of land-use characteristics that influence the type of land cover and/or vegetation. There are four types of plant communities that have already been incorporated into the TRIM.FaTE libraries: deciduous forest, coniferous forest, grasses/herbs, and agricultural (*e.g.*, crop) lands. Each plant community type is represented in TRIM.FaTE by a plant composite compartment, which includes particles on the leaf surface, leaf, stem, and root compartments and associated parameter values for that type of plant community.

For biotic compartments in soil, the current TRIM.FaTE library includes two types of soil organisms: earthworms and soil arthropods. Both types are detritivores (*i.e.*, they feed on the decaying organic materials found in soils). Chemical transformation and degradation

processes that might be mediated by soil bacteria are accounted for in the soil compartment transformation and degradation rates for a chemical.

Finally, the user can populate the vegetated surface volume elements with wildlife species, depending on the goals and objectives of the project as well as considerations of chemical mass distribution across wildlife biomass and trophic levels. Major herbivores at a site should be included to facilitate appropriate partitioning of a chemical within the terrestrial ecosystems. Higher trophic level birds and mammals would affect environmental partitioning to a lesser extent. The current TRIM.FaTE library includes parameterized compartments for several species of birds and mammals as described in Section 7.4.4.

For detailed guidance on how to select and parameterize terrestrial biotic compartments and how to distribute them among surface soil and surface water parcels, see the TRIM.FaTE user guidance.

## 7.2 ALGORITHMS FOR TERRESTRIAL PLANTS

The text box on the next page and continued on the following pages provides a summary of the plant transfer-factor algorithms developed in this section and defines the parameters used in those algorithms.

In TRIM.FaTE, terrestrial plants consist of four compartment types which, taken together, represent an entire plant: leaf, stem, root, and particles on the leaf surface. All four compartments, parameterized for a specific type of plant community (*e.g.*, deciduous forest) are linked together in a single plant composite compartment named for that community. Although the particles on the leaf surface are not in the plant, it is useful to track this compartment type separately from the leaf because: (1) it can provide a reservoir for chemical moving to leaves, (2) herbivorous animals can ingest particulate matter on leaves, (3) particles can wash off leaves during rain, (4) particles can be blown off leaves by wind, and (5) humans can wash most of these particles off of leaves, prior to any consumption (*e.g.*, agricultural plants).

Several attributes of the plant compartments vary with time of day and with season. A logical parameter named *IsDay* in TRIM.FaTE controls whether the plant stomata are open (1 for “yes, it is day”) or closed (0 for “no, it is night”) for a specific simulation run. Diffusion of a vapor-phase chemical between the air and plant leaves through the stomata occurs only during the day when they are open. A logical parameter named *AllowExchange* is used to control whether the plant is actively growing and has leaves (yes) or is dormant and without leaves for the non-growing season (no). Chemical exchanges between the grasses and herbaceous and deciduous plants occur only during the growing season (*AllowExchange* = 1). *AllowExchange* always equals one (yes) for the coniferous plants.

There are, however, several problems that arise in modeling uptake and emissions of chemicals by plants:

- Little information is available on the transformations of chemicals in plants.

Summary of Transfer Factors for Plants in TRIM.FaTE

**ABOVE-GROUND EXCHANGES**

Dry deposition of particulate phase of air to particles-on-leaf compartment: TF 7-1

$$T_{Air \rightarrow LeafP}^{dry\_dep} = \frac{v_{dry} \times I_{dry} \times A_S}{V_{Air}} \times f_{MS}$$

Dry particles on leaf blown off to air: TF 7-2

$$T_{LeafP \rightarrow Air}^{blow\_off} = \frac{v_{dry} \times I_{dry} \times A_S}{V_{LeafP}}$$

Wet deposition of particles in air to the particles-on-leaf compartment: TF 7-3

$$T_{Air \rightarrow LeafP}^{wet\_dep} = \frac{v_{wet} \times I_{wet} \times A_S}{V_{Air}} \times f_{MS}$$

Wash off of particles on leaf to surface soil: TF 7-4a

$$T_{LeafP \rightarrow Ss}^{wash\_off} = \frac{v_{wet} \times I_{wet} \times A_{Ss}}{V_{LeafP}}$$

Particles on leaf to leaf: TF 7-5

$$T_{LeafP \rightarrow Leaf} = k_{LeafP-Leaf}$$

Leaf to particles on leaf: TF 7-6

$$T_{Leaf \rightarrow LeafP} = 0.01 \times k_{LeafP-Leaf}$$

Wet deposition of vapor-phase chemical from air to the leaf (partitioning approach): TF 7-7a

$$T_{Air \rightarrow Leaf}^{Vwet\_dep} = \frac{A_S}{V_{Air}} \times w_{rV} \times rain \times I_{wet} \times f_{MV}$$

Wet deposition of vapor-phase chemical from air to the leaf (fugacity approach): TF 7-7b

$$T_{Air \rightarrow Leaf}^{Vwet\_dep} = \frac{A_S}{V_{Air}} \times rain \times I_{wet} \times \frac{Z_{pure\_water}}{Z_{Total\_Air}}$$

Summary of Transfer Factors for Plants in TRIM.FaTE (cont.)

**ABOVE-GROUND EXCHANGES (cont.)**

Leaf to air (diffusion): TF 7-8a

$$T_{Leaf \rightarrow Air}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_{Leaf}} \times \frac{Z_{pure\_air}}{Z_{Total\_Leaf}}$$

Air to leaf (diffusion): TF 7-9a

$$T_{Air \rightarrow Leaf}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_{Air}}$$

**BELOW-GROUND EXCHANGES**

Bulk root-zone soil to root: TF 7-10a

$$T_{Sr \rightarrow Root} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times \frac{V_{Root}}{V_{Sr}} \times K_{Root-Sr} \quad \text{where } K_{Root-Sr} = \text{input value}$$

Root to bulk root-zone soil: TF 7-11a

$$T_{Root \rightarrow Sr} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}}$$

Root-zone-soil pore water to root: TF 7-10b

$$T_{SrW \rightarrow Root} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times \frac{V_{Root}}{V_{Sr}} \times K_{Root-SrW} \times \frac{Z_{pure\_water}}{Z_{Total\_Sr}} \quad \text{where:}$$

$$K_{Root-SrW} = (fW_{Root} + fL_{Root} \times K_{ow}^b) \times \rho_{Root} \times 0.001$$

Root to root-zone-soil pore water: TF 7-11b

$$T_{Root \rightarrow SrW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}}$$

**PLANT STEM EXCHANGES**

Bulk root-zone soil to stem: TF 7-12a

$$T_{Sr \rightarrow Stem} = \frac{Q_{Xy}}{V_{Sr}} \times f_{ML} \times TSCF$$

Summary of Transfer Factors for Plants in TRIM.FaTE (cont.)

**PLANT STEM EXCHANGES (cont.)**

Root-zone soil pore water to stem (simplification for nonionic organic compounds): TF 7-12b1

$$T_{SrW \rightarrow Stem} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{SrW}} \right] \times \rho_{area\ Stem} \times \frac{SCF}{\rho_{SrW} \times d_{Sr}}$$

Stem to root-zone soil (simplification for nonionic organic compounds): TF 7-12b2

$$T_{Stem \rightarrow SrW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{SrW}}$$

Leaf to stem: TF 7-13

$$T_{Leaf \rightarrow Stem} = Q_{Ph} \times \frac{1}{V_{Leaf} \times K_{LeafPh}}$$

Stem to leaf: TF 7-14

$$T_{Stem \rightarrow Leaf} = Q_{Xy} \times \frac{1}{V_{Stem} \times K_{StemXy}}$$

**LITTER FALL**

Leaf to surface soil: TF 7-15

$$T_{Leaf \rightarrow Ss} = k_L$$

Particles on leaf to surface soil: TF 7-16

$$T_{LeafP \rightarrow Ss} = k_L$$

**LIST OF SYMBOLS USED IN PLANT TRANSFER FACTOR ALGORITHMS**

- $U_{dry}$  = volumetric dry deposition for particle-phase chemical ( $m^3$ [particles]/ $m^2$ [soil]-day).
- $I_{dry}$  = fraction of dry-depositing chemical that is intercepted by plant canopy (unitless).
- $A_S$  = area of associated soil ( $m^2$ ).
- $V_{Air}$  = volume of air compartment ( $m^3$ ).
- $f_{MS}$  = mass fraction of chemical in the air compartment that is sorbed to solid particles divided by the volume fraction of the air compartment that consists of particles (unitless).
- $V_{LeafP}$  = volume of particles-on-leaf compartment ( $m^3$ ).
- $U_{wet}$  = volumetric wet deposition rate of particle-phase chemical ( $m^3$ [particle]/ $m^2$ [soil]-day = m/day),
- $I_{wet}$  = plant interception fraction for wet deposition (unitless).
- $A_{Ss}$  = area of surface soil compartment ( $m^2$ ).
- $k_{LeafP-Leaf}$  = 1<sup>st</sup>-order rate constant for transfer of chemical from particles on leaf to leaf (/day).
- $w_{rV}$  = vapor washout ratio ( $g$ [chemical]/ $m^3$ [rain] per  $g$ [chemical]/ $m^3$ [air]).
- $rain$  = rain rate (m/day).
- $f_{MV}$  = mass fraction of chemical compartment that is in vapor phase divided by the volume fraction of compartment that is gas/vapor phase (unitless).
- $Z_{pure\_water}$  = fugacity capacity of chemical in aqueous phase ( $mol/Pa \cdot m^3$ ).

Summary of Transfer Factors for Plants in TRIM.FaTE (cont.)

LIST OF SYMBOLS USED IN PLANT TRANSFER FACTOR ALGORITHMS (cont.)

$Z_{Total\_Air}$	=	total fugacity capacity of chemical in air compartment (mol/Pa-m <sup>3</sup> ).
$LAI$	=	one-sided leaf-area index (m <sup>2</sup> [total leaf area]/m <sup>2</sup> [soil]).
$g_C$	=	total conductance of the cuticular path, including the air boundary layer (m/day).
$g_S$	=	total conductance of stomatal pathway, including mesophyll and air boundary layer (m/day).
$V_{Leaf}$	=	volume of leaf compartment (m <sup>3</sup> ).
$Z_{pure\_air}$	=	fugacity capacity of chemical in gas phase of air (mol/Pa-m <sup>3</sup> ).
$Z_{Total\_Leaf}$	=	total fugacity capacity of chemical in leaf compartment (mol/Pa-m <sup>3</sup> ).
$\alpha$	=	proportion of equilibrium value achieved (default = 0.95) (unitless).
$t_\alpha$	=	time required to reach 100×α percent of equilibrium value (days) (value depends on the compartments and phases for which time-to-equilibrium is modeled).
$V_{Root}$	=	volume of root compartment (m <sup>3</sup> ).
$V_{Sr}$	=	volume of root-zone soil compartment (m <sup>3</sup> [soil]).
$K_{Root-Sr}$	=	root/bulk-soil partition coefficient (m <sup>3</sup> [soil]/m <sup>3</sup> [root]).
$K_{Root-SrW}$	=	root/soil-pore-water partition coefficient (m <sup>3</sup> [water]/m <sup>3</sup> [root]).
$Z_{Total\_Sr}$	=	total fugacity capacity of root-zone soil compartment (mol/Pa-m <sup>3</sup> ).
$fW_{Root}$	=	fraction water content of root compartment (kg[water]/kg[root wet wt]).
$fL_{Root}$	=	fraction lipid content of root compartment (kg[lipid]/kg[root wet wt]).
$K_{ow}$	=	octanol-water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water]).
$b$	=	correction exponent for the differences between octanol and lipids (unitless).
$\rho_{Root}$	=	density of fresh root (kg[root wet wt]/m <sup>3</sup> [root]).
$Q_{xy}$	=	flow of transpired water (m <sup>3</sup> [xylem]/day).
$f_{ML}$	=	mass fraction dissolved ÷ volume fraction of soil compartment that is liquid (water) (unitless).
$TSCF$	=	transpiration stream concentration factor (g[chemical]/m <sup>3</sup> [xylem] per g[chemical]/m <sup>3</sup> [soil pore water]).
$\rho_{area\_Stem}$	=	areal density of stem on associated soil (kg[stem wet wt]/m <sup>2</sup> [soil]).
$SCF$	=	stem concentration factor (g[chemical]/kg[stem wet wt] per g[chemical]/kg[soil pore water]).
$\rho_{SrW}$	=	density of soil pore water (kg[water]/m <sup>3</sup> [water] = 1 kg/m <sup>3</sup> ).
$d_{Sr}$	=	depth of root-zone soil compartment (m <sup>3</sup> ).
$Q_{Ph}$	=	phloem flux into leaves (m <sup>3</sup> [phloem]/day) due to advection.
$K_{LeafPh}$	=	partition coefficient between leaves and phloem water (g[chemical]/m <sup>3</sup> [leaf] per g[chemical]/m <sup>3</sup> [phloem]).
$V_{Stem}$	=	volume of stem compartment (m <sup>3</sup> [stem]).
$K_{StemXy}$	=	partition coefficient between stem and xylem water (m <sup>3</sup> [xylem]/m <sup>3</sup> [stem]).
$k_L$	=	litter-fall rate constant (/day).

- 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 plants is not well understood.

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

Despite these limitations in understanding and available data, the potentially important transfer processes have been modeled in TRIM.FaTE to the extent possible given the state of the science and modeling efforts to date. The user can assess the importance of the limitations identified above using the sensitivity and uncertainty analysis tools for any given scenario.

## 7.2.1 TRANSFERS BETWEEN THE AIR, PARTICLES, AND PLANT LEAVES

The particles on the leaf surface are represented by the particles-on-leaf compartment type in the current TRIM.FaTE library. This compartment is comprised of particulate matter deposited to the leaf by either wet or dry deposition. 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 described in Section 7.2.2.

Dry or wet deposition of particles to the particles-on-leaf compartment is calculated by multiplying the particle-deposition velocity by the leaf-interception fraction. The leaf-interception fraction ( $I$ ) is the fraction of the depositing chemical mass that is intercepted and initially retained on the leaf. Thus, the quantity  $(1-I)$  is the fraction of depositing chemical mass that is transferred to the surface soil. The chemical mass that is transferred to the leaf surface via particle deposition is assumed to join the particle-phase chemical in the particles-on-leaf compartment. From there, transfers of chemical between the leaf itself and the particles on the surface of the leaf occur via diffusion (see Section 7.2.1.5).

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. This situation is treated explicitly in the current TRIM.FaTE library through the inclusion of a separate compartment for particles on leaf.

In the TRIM.FaTE code, the transfer factors for exchanges between plant leaves and the air or air particles include the variable *AllowExchange*, which must equal one (yes) for the transfer to occur.

### 7.2.1.1 Dry Deposition of Particles to Surface of Plant Leaves

Dry deposition is estimated by multiplying the predicted air concentration of airborne particles at ground level by the dry-particle-deposition velocity (U.S. EPA 1997a). A unidirectional flux equation that expresses dry deposition to the leaf, from van de Water (1995), follows. Note that, as the boundaries of the surface soil and air parcels may not be congruent, that is the area of soil and the area associated with a contiguous air compartment may be different. This algorithm describes the accumulation of chemical mass in the particles on leaves

due to deposition from any air compartment to the area of the associated surface soil compartment that it spatially overlaps.

$$\frac{dN_{LeafP}}{dt} = \frac{N_{Air}}{V_{Air}} \times v_{dry} \times I_{dry} \times \frac{Z_{pure\_solid}}{Z_{Total\_Air}} \times A_S \quad (\text{Eq. 7-1})$$

where:

- $N_{LeafP}$  = mass of chemical in particles-on-leaf compartment (g[chemical]);
- $N_{Air}$  = mass of chemical in the air compartment (g[chemical]);
- $V_{Air}$  = volume of air compartment (m<sup>3</sup>);
- $v_{dry}$  = volumetric dry deposition of particles (m<sup>3</sup>[particles]/m<sup>2</sup>[soil]-day);
- $I_{dry}$  = fraction of dry-depositing chemical that is intercepted and initially retained by the plant canopy (unitless, below);
- $Z_{pure\_solid}$  = fugacity capacity of the chemical in or sorbed to solid particles (mol/m<sup>3</sup>-Pa);
- $Z_{Total\_Air}$  = total fugacity capacity in bulk air, including atmospheric dust particles (mol/m<sup>3</sup>-Pa); and
- $A_S$  = area of associated soil (m<sup>2</sup>).

The volumetric dry deposition of particles is calculated as:

$$v_{dry} = v_{dep} \times \frac{D_L}{\rho_P} \quad (\text{Same as Eq. 4-2})$$

where:

- $v_{dep}$  = dry deposition velocity of air particles (m/day);
- $D_L$  = dust load in air compartment (kg[particles]/m<sup>3</sup>[air]); and
- $\rho_P$  = density of dust particles (kg[particles]/m<sup>3</sup>[particles]).

The interception fraction for dry deposition ( $I_{dry}$ ) of particles is calculated using the following equation (Baes et al. 1984):

$$I_{dry} = 1 - e^{(1-fW_{Leaf})(-\alpha_{VAF} \times \rho_{area})} \quad (\text{Eq. 7-2})$$

where:

- $fW_{Leaf}$  = water content of leaf (kg[water]/kg[leaf wet wt]);
- $\alpha_{VAF}$  = vegetation attenuation factor (m<sup>2</sup>[leaf]/kg[plant dry wt]); and
- $\rho_{area}$  = wet above-ground non-woody vegetation biomass inventory per unit area of the surface soil (kg[plant wet wt]/m<sup>2</sup>[soil]).

Chamberlain (1970) describes the relationship between  $I_{dry}$  and above-ground (dry) biomass, and Prohl and Hoffman (1996) provide an excellent review of interception and loss processes along with values (and ranges) for the constants used to estimate  $I_{dry}$ .

The water content adjusts  $\rho_{area}$  to represent dry biomass. The equation was originally derived for pasture grasses and hay and expanded to other crops. For this reason, the biomass estimate should not include wood biomass in its calculation. 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, TRIM.FaTE estimates the dry deposition of chemical mass associated with airborne particles to the particles-on-leaf compartment as:

$$T_{Air \rightarrow LeafP}^{dry\_dep} = \frac{v_{dry} \times I_{dry} \times A_S}{V_{Air}} \times f_{MS} \quad (TF\ 7-1)$$

where:

$$T_{Air \rightarrow LeafP}^{dry\_dep} = \text{transfer factor for dry deposition of particulate-phase chemical in air to the particles on the surface of plant leaves when it is not raining (/day); and}$$

$$f_{MS} = \frac{Z_{pure\_solid}}{Z_{Total\ Air}} \text{ also the fraction of chemical mass in air compartment that is sorbed to solid dust particles divided by the volume fraction of air that consists of dust particles (see Equations 2-71 and 2-79) (unitless).}$$

The implicit assumption in this algorithm is that depositing particles reach thermodynamic (chemical) equilibrium with the surrounding air before contacting the leaf surface. Accepting this assumption, the transfer to vegetation by dry deposition is related to the total chemical mass in the air compartment (combined gas- and particle-phase) using the particle/gas partition coefficient (normalized on a volume basis),  $K'_p$ , which is the dimensionless particle/gas partition coefficient (g[chemical]/m<sup>3</sup>[particles] per g[chemical]/m<sup>3</sup>[air compartment]). The factor  $f_{MP}$  is equivalent to  $K'_p$ .

### 7.2.1.2 Blow Off of Particles on Leaf to Air

The intent in the conceptual design of the leaf-particle transfer algorithms is to maintain a constant (although unknown) mass of particles on the leaf. The algorithm below is based on three assumptions: (1) particles are blown off the plant by wind at a rate that equals the deposition rate to leaves; (2) the concentration in the particles blown off the leaf is equal to the concentration in particles remaining on the leaf; and (3) all particles are dispersed in air.

$$T_{LeafP \rightarrow Air}^{blow\_off} = \frac{v_{dry} \times I_{dry} \times A_S}{V_{LeafP}} \quad (TF\ 7-2)$$

where:

$$T_{LeafP \rightarrow Air}^{blow\_off} = \text{transfer factor for particle-phase chemical on surface of leaf blown off to air (dry resuspension of particles) when it is not raining (/day); and}$$

$$V_{LeafP} = \text{volume of the particles-on-leaf compartment (m}^3\text{).}$$

The factor  $f_{MP}$  is not needed in the algorithm TF 7-2 because all of the chemical mass inventory in the particles-on-leaf compartment is sorbed to particles, and the compartment consists only of the solid phase. The particles blown off leaves into the air are then available for redeposition to leaves and the surface soil. Note that the algorithm for blow off of particles from leaves includes a meteorological toggle that turns the process off during rain (the analogous process during rain is wash off; see Section 7.2.1.4).

### 7.2.1.3 Wet Deposition of Particles to Surface of Plant Leaves

Rain scavenges some of the particulate-phase chemical from the air, depositing it on the surface of leaves. The concentration in the rain drop is related to the fraction of the chemical in the air that is associated with the particle and the scavenging ratio for particles in rain drops. Thus, wet deposition resulting from this process can be modeled using equations similar to dry deposition of particles. The rate of mass transfer of particle-phase chemicals from air to rain water and to the particles-on-leaf compartment can be described as:

$$\frac{dN_{LeafP}}{dt} = \frac{N_{Air}}{V_{Air}} \times w_r \times rain \times \frac{D_L}{\rho_P} \times I_{wet} \times \frac{Z_{pure\_solid}}{Z_{Total\_Air}} \times A_S \quad (\text{Eq. 7-3})$$

where:

- $N_{LeafP}$  = mass of chemical in particles-on-leaf compartment (g[chemical]);
- $N_{Air}$  = mass of chemical in the air compartment (g[chemical]);
- $V_{Air}$  = volume of air compartment (m<sup>3</sup>);
- $w_r$  = scavenging or washout ratio for particles in air (ranges from 50,000 to 200,000) (m<sup>3</sup>[air]/m<sup>3</sup>[rain]);
- $rain$  = rate of rainfall (m/day);
- $D_L$  = dust load, *i.e.*, density of dust particles in air (kg[particles]/m<sup>3</sup>[air]);
- $\rho_P$  = density of dust particles (kg[particles]/m<sup>3</sup>[particles]);
- $I_{wet}$  = wet interception fraction (unitless);
- $Z_{pure\_solid}$  = fugacity capacity of the chemical in or sorbed to solid particles (mol/m<sup>3</sup>-Pa);
- $Z_{Total\_Air}$  = total fugacity capacity in bulk air, including atmospheric dust particles (mol/m<sup>3</sup>-Pa); and
- $A_S$  = area of associated soil (m<sup>2</sup>).

The washout ratio for particle-bound chemicals typically is restricted to empirical data on particle scavenging ratios (Wania et al. 1998). The expression  $w_r \times J_{rain} \times (D_L/\rho_{dust})$  equals the volumetric particle wet deposition velocity,  $u_{wet}$ :

- $u_{wet}$  = volumetric wet deposition rate of air particles (m<sup>3</sup>[particle]/m<sup>2</sup>[soil]-day = m/day),
- =  $w_r \times rain \times (D_L/\rho_p)$ .

Thus, the transfer factor that describes chemical deposition to the particles-on-leaf compartment from wet deposition of air particles is calculated as:

$$T_{Air \rightarrow LeafP}^{wet\_dep} = \frac{v_{wet} \times I_{wet} \times A_S}{V_{Air}} \times f_{MS} \quad (TF\ 7-3)$$

where:

- $T_{Air \rightarrow LeafP}^{wet\_dep}$  = transfer factor for wet deposition of particulate-phase chemical in air to the particles on plant leaves when it is raining (/day); and  
 $f_{MS}$  = the mass fraction of chemical in the particle-phase divided by the volume fraction of the air compartment that is particulate (unitless).

The wet particle interception fraction in the preceding equations can be calculated using the following equation from Muller and Prohl (1993). The value of the fraction depends on how much water the leaf can hold, the total amount of rainfall during a rainfall event, and the ability of the element or compound to stick to the leaf.

$$I_{wet} = \frac{LAI \times S}{rain} \times \left[ 1 - e^{\left( \frac{-\ln(2)}{3 \times S} \times rain \right)} \right] \quad (Eq.\ 7-4)$$

where:

- $LAI$  = one-sided leaf-area index ( $m^2$ [total leaf area]/ $m^2$ [underlying soil area]);  
 $S$  = vegetation-dependent leaf-wetting factor (retention coefficient) (m); and  
 $rain$  = amount of rainfall during a rainfall event (m).

With the current TRIM.FaTE library, however, the user must specify a value for the wet deposition interception fraction or accept the default value of 0.2, which is based on five years of meteorological data for a site in Maine. Because it is a fraction, the upper bound for  $I_{wet}$  is 1.

#### 7.2.1.4 Wash-off of Chemical from Plant Surface

During rain, the chemical sorbed to particles on the surface of the leaf can be washed off and deposited to the surface soil. In TRIM.FaTE, this transfer is estimated by an equation that is basically the same as TF 7-3, *i.e.*:

$$T_{LeafP \rightarrow Ss}^{wash\_off} = \frac{v_{wet} \times I_{wet} \times A_{Ss}}{V_{LeafP}} \quad (TF\ 7-4a)$$

where:

- $T_{LeafP \rightarrow Ss}^{wash\_off}$  = transfer factor for wash off of particle-phase chemical from particles-on-leaf compartment to surface soil (/day);  
 $v_{wet}$  = volumetric wet deposition rate of air particles ( $m^3$ [particles]/ $m^2$ [soil]-day);

- $I_{wet}$  = fraction of wet-depositing particle-phase chemical that is intercepted by plant canopy (unitless);  
 $A_S$  = area of the associated soil (m<sup>2</sup>[soil]); and  
 $V_{LeafP}$  = volume of particles-on-leaf compartment (m<sup>3</sup>).

This equation has been implemented to ensure that the particle mass on the leaves does not change (*i.e.*, as much is wet-deposited as is washed off). The factor  $f_{MS}$  is not needed in algorithm TF 7-4a because all of the chemical mass inventory in the particles-on-leaf compartment is sorbed to particles, and the compartment consists only of the solid phase. Note that the algorithm for wash off of particles from leaves includes a meteorological toggle that turns the process on during rain (the analogous process when it is not raining is blow off; see Section 7.2.1.2).

There are some data available on wash off of particles from the surface of conifer leaves during rain that indicate first-order kinetics with a rate constant of approximately 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, an alternative equation to estimate wash-off from conifer leaves could be:

$$\frac{dN_{LeafP}}{dt} = -57.6 \times N_{LeafP} \quad (\text{Eq. 7-5})$$

and the associated transfer factor for the chemical wash off to the surface soil compartment is:

$$T_{LeafP \rightarrow Ss}^{wash\_off} = 57.6 \quad (\text{TF 7-4b})$$

This algorithm is not included in the current TRIM.FaTE library, but is included here for users who may prefer this value for coniferous forests.

### 7.2.1.5 Transfer of Chemical to Leaf from Particles on Leaf

The fraction of chemical sorbed to particles on the leaves that enters the leaf 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.*, mercury), an initial assumption of 0.2 per day may be appropriate (*i.e.*, assume a half-life of one week). 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 constant for transfer in the other direction (*i.e.*, 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. Thus, the transfer factors for exchange between the leaf and particles-on-leaf compartments are:

$$T_{LeafP \rightarrow Leaf} = k_{LeafP-Leaf} \quad (TF\ 7-5)$$

$$T_{Leaf \rightarrow LeafP} = 0.01 \times k_{LeafP-Leaf} \quad (TF\ 7-6)$$

where:

$T_{LeafP \rightarrow Leaf}$	=	transfer factor for transfer of chemical from particles-on-leaf compartment to leaf compartment (/day);
$k_{LeafP-Leaf}$	=	first-order rate constant for transfer of chemical from particles on leaf to leaf (/day); and
$T_{Leaf \rightarrow LeafP}$	=	transfer factor for transfer of chemical from leaf to particles-on-leaf compartment (/day).

In the current TRIM.FaTE library, these transfer factors are numeric constants set by the user. Thus, to implement the relationship described here, the value of  $T_{Leaf \rightarrow LeafP}$  should be set to 0.01 times that of  $T_{LeafP \rightarrow Leaf}$ .

### 7.2.1.6 Transfer of Vapor-phase Chemical to Leaf from Air During Rain

The rate of mass transfer of the vapor-phase chemical from air to rain water and to the plant leaf is described by the following equation (modified from van de Water 1995):

$$\frac{dN_{Leaf}}{dt} = \frac{N_{Air}}{V_{Air}} \times w_{rV} \times rain \times A_S \times I_{wet} \times f_{MV} \quad (Eq.\ 7-6)$$

where:

$N_{Leaf}$	=	mass of chemical in the leaf (g[chemical]);
$N_{Air}$	=	mass of chemical in air (g[chemical]);
$V_{Air}$	=	volume of air compartment (m <sup>3</sup> [air]);
$w_{rV}$	=	vapor washout ratio (g[chemical dissolved]/m <sup>3</sup> [rain] per g[chemical vapor-phase]/m <sup>3</sup> [air]);
$rain$	=	rain rate (m/day);
$A_S$	=	area of associated soil (m <sup>2</sup> );
$I_{wet}$	=	interception fraction for wet deposition (unitless); and
$f_{MV}$	=	the fraction of the chemical mass in the air compartment that is in the vapor phase divided by the volume fraction of the air compartment that is gas/vapor ( <i>i.e.</i> , fraction that is not particulate).

It is difficult to know whether vapor-phase chemicals dissolved in rain and deposited to leaves will partition into the particles on the surface of the leaf or into the leaf cuticle. The water droplets on a leaf are small and persist for only a short period of time. The surface area of the leaf that is actually in contact with the water also can be much larger or smaller than the macroscopic surface of the leaf (Riederer 1995). Given the relative surface area of the leaf versus the surface particles, we assume that all wet deposition of vapor that is intercepted and

initially retained by the leaf will interact directly with the leaf compartment. Deposited chemical can subsequently partition between the leaf and particles on the leaf (see Section 7.2.1.5).

The vapor wet interception fraction can be calculated using the same equation from Muller and Prohl (1993) that was used to estimate the particle wet interception fraction (Equation 7-4 above). As before, the value of the fraction depends on how much water the leaf can hold, the total amount of rainfall during a rainfall event, and the ability of the element or compound to stick to the leaf.

$$I_{wet} = \frac{LAI \times S}{rain} \times \left[ 1 - e^{\left( \frac{-\ln(2)}{3 \times S} \times rain \right)} \right] \quad (\text{Same as Eq. 7-4})$$

The vapor washout ratio,  $w_{rV}$ , is the equilibrium partition coefficient for a chemical between rain water and the vapor phase in air; in other words, the chemical concentration in rain divided by the chemical concentration in the gaseous phase. It can also be expressed as a ratio of Z factors (see Chapter 2):

$$w_{rV} = \frac{C_{rain\_water}}{C_{air}} = \frac{Z_{pure\_water}}{Z_{pure\_vapor}} = \frac{1}{K_{AW}} \quad (\text{Eq. 7-7})$$

where:

$C_{rain\_water}$	=	concentration of chemical in rain water (g[chemical]/m <sup>3</sup> [rain]);
$C_{air}$	=	concentration of vapor-phase chemical in gas-phase air (g[chemical]/m <sup>3</sup> [air]);
$Z_{pure\_water}$	=	fugacity capacity of chemical in aqueous phase (mol/m <sup>3</sup> -Pa);
$Z_{pure\_air}$	=	fugacity capacity of vapor-phase chemical in air (excluding dust particles) (mol/m <sup>3</sup> -Pa); and
$K_{AW}$	=	air/water partition coefficient (g[chemical]/m <sup>3</sup> [air] per g[chemical]/m <sup>3</sup> [water], unitless).

For some chemicals (e.g., the mercury species), the user can specify the washout ratio,  $w_{rV}$ , using an empirically derived equilibrium partition coefficient between the water and vapor phases of the chemical,  $K_{WA}$ . Thus, the transfer of vapor-phase chemical from air to plant leaves during a rainfall event is calculated as:

$$T_{Air \rightarrow Leaf}^{Vwet\_dep} = \frac{A_S}{V_{Air}} \times w_{rV} \times rain \times I_{wet} \times f_{MV} \quad (\text{TF 7-7a})$$

where:

$T_{Air \rightarrow Leaf}^{Vwet\_dep}$	=	transfer factor for wet deposition of vapor-phase chemical in air to the leaf when it is raining (/day); and
$w_{rV}$	=	$1/K_{AW}$ as described in Equation 7-7 above.

For other chemicals (e.g., nonionic organic chemicals), the expression  $w_{rV} \times f_{MV}$  can be estimated from the expression  $Z_{\text{pure\_water}}/Z_{\text{Total\_Air}}$  as follows. From Equation 7-7 and the definition of  $f_{MV}$  above:

$$w_{rV} \times f_{MV} = \frac{Z_{\text{pure\_water}}}{Z_{\text{pure\_vapor}}} \times \frac{\text{Mass\_Fraction\_Vapor}}{\text{Volume\_Fraction\_Vapor}} \quad (\text{Eq. 7-8})$$

From Equation 2-73:

$$Z_{\text{Total\_Air}} = Z_{\text{pure\_vapor}} \times \left[ \frac{\text{Volume\_Fraction\_Vapor}}{\text{Mass\_Fraction\_Vapor}} \right] \quad (\text{Eq. 7-9})$$

Therefore:

$$w_{rV} \times f_{MV} = \frac{Z_{\text{pure\_water}}}{Z_{\text{Total\_Air}}} \quad (\text{Eq. 7-10})$$

Thus, an alternative algorithm for wet deposition of vapor-phase chemical to plant leaves is calculated as:

$$T_{\text{Air} \rightarrow \text{Leaf}}^{\text{Vwet\_dep}} = \frac{A_S}{V_{\text{Air}}} \times \text{rain} \times I_{\text{wet}} \times \frac{Z_{\text{pure\_water}}}{Z_{\text{Total\_Air}}} \quad (\text{TF 7-7b})$$

where:

$$\begin{aligned} T_{\text{Air} \rightarrow \text{Leaf}}^{\text{Vwet\_dep}} &= \text{transfer factor for wet deposition of vapor-phase chemical in air to} \\ &\text{the leaf (/day); and} \\ Z_{\text{Total\_Air}} &= \text{total fugacity capacity of chemical in air compartment (mol/m}^3\text{-Pa).} \end{aligned}$$

## 7.2.2 UPTAKE OF GASEOUS CHEMICAL INTO FOLIAGE

The diffusion pathway between air and leaves is relevant 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 air boundary (Section 7.2.2.1), stomata (Section 7.2.2.2), and mesophyll (Section 7.2.2.3), and (b) the series resistance of air boundary (7.2.2.1) and cuticle (Section 7.2.2.5). It is assumed that the chemical fraction that is in the plant cuticle or mesophyll is inside of the plant, but that the chemical inside of the stomata 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 modify the transport of nutrients from plant leaves (Hargrove 1999). However, the contribution of insect or other sources of damage to the diffusion of mercury and other chemicals into and out of the plant is unknown and not currently addressed in TRIM.FaTE.

### 7.2.2.1 Air Boundary-layer Conductance

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

$$g_B = \frac{D_{\text{pure\_air}}}{\delta_{AP}} \quad (\text{Eq. 7-11})$$

where:

- $g_B$  = conductance of the air boundary layer (m/day);
- $D_{\text{pure\_air}}$  = diffusion coefficient of chemical through still, pure air (m<sup>2</sup>[air]/day); and
- $\delta_{AP}$  = thickness of air boundary layer (*i.e.*, still air) over leaf surfaces (m).

The boundary layer thickness ( $\delta_{AP}$  in m) may be approximated by Equation 7-12 below (Nobel 1999), 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 0.00389 in the following equation is the square root of the viscosity of air at 20° Celsius,  $1.51 \times 10^{-5}$  m<sup>2</sup>/sec (Wilmer and Fricker 1996).

$$\delta_{AP} = 0.00389\sqrt{l/v} \quad (\text{Eq. 7-12})$$

where:

- $l$  = length of flat leaf (m); and
- $v$  = wind velocity (m/sec).

### 7.2.2.2 Stomatal Conductance

The stomatal conductance of gaseous chemicals into the leaf is calculated in the TRIM.FaTE library using the following equation (Riederer 1995):

$$g_{\text{stomata}} = \frac{D_{\text{pure\_air}} \times na_S \times IsDay \times \alpha_S}{x_S + y_S} \quad (\text{Eq. 7-13})$$

where:

- $g_{\text{stomata}}$  = conductance of the chemical through the stomata (m/day);
- $D_{\text{pure\_air}}$  = diffusion coefficient of the chemical in pure, still air (m<sup>2</sup>[air]/day);
- $na_S$  = number of stomata in leaf ( $n$ ) times area of 1 stomata divided by area of leaf ( $a_S$ ) (unitless);
- $\alpha_S$  = mean degree of opening of stomatal pores, between 0 and 1 (default = 1) (unitless);
- $IsDay$  = a time-varying parameter that equals 1 during the day and 0 at night, to open and close the stomatal pores (unitless);
- $x_S$  = depth of elliptical pore (m); and
- $y_S$  = mean pore radius (m).

In the field, the degree of opening of stomatal pores tends toward one during the day and zero at night, unless the temperature is high and the humidity low, in which case the value of  $\alpha_s$  will be less than one during the day. The default value in the TRIM.FaTE library for  $\alpha_s$  during the day is one. The stomatal conductance is “turned off” when *IsDay* equals zero.

Analysis of data reported by Wilmer and Fricker (1996, p. 18) indicates that the value for the expression  $(na_s)/(x_s + y_s)$  is relatively similar among plant species (*i.e.*, coefficient of variation  $\sim 0.5$ ). Thus, that expression in Equation 7-13 is replaced in the TRIM.FaTE library by a single parameter:

$$S_N = \frac{na_s}{x_s + y_s} \quad (\text{Eq. 7-14})$$

where:

$S_N$  = stomatal area, normalized for effective diffusion path length (/m).

Thus, in the TRIM.FaTE library:

$$g_{stomata} = D_{pure\_air} \times S_N \times \alpha_s \quad (\text{Eq. 7-15})$$

If this algorithm for  $g_{stomata}$  is used, it should be noted that a model limitation is 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.

If data on the effective diffusivity of the subject chemical in air,  $D_{pure\_air}$  are lacking, the following alternate equation can be used to estimate diffusivity (conductance) of the chemical through stomata based on diffusivity of water through stomata (Trapp 1995). In other words, the stomatal conductance of gaseous chemicals into the leaf may be approximated from the stomatal conductance of water vapor. The only chemical-specific parameter that is required is the molecular weight of the chemical:

$$g_{stomata} = \sqrt{18 / M_W} \times g_{water} \quad (\text{Eq. 7-16})$$

where:

18 = molecular weight of water (g[water]/mol[water]);  
 $M_W$  = molecular weight of chemical (g[chemical]/mol[chemical]); and  
 $g_{water}$  = conductance of water through the stomata (m/day).

Conductance of water through the stomata may be calculated using the following algorithm from Bennett et al. (1998):

$$g_{water} = \frac{461 \times T}{(1 - rh) \times 611 \times 10^{\frac{7.5(T-273)}{(237+(T-273))}}} \times (1 \text{ kg} \times \text{d}^{-1} \times \text{m}^2) \quad (\text{Eq. 7-17})$$

where:

$rh$  = relative humidity (unitless); and  
 $T$  = temperature (°K).

Note that Equation 7-16 for stomatal conductance, with Equation 7-17 substituted for  $g_{water}$ , includes the resistance of the air-side boundary in series with the stomatal resistance. If those equations were to be implemented in TRIM.FaTE instead of Equation 7-15, it would be necessary to remove the air boundary-layer resistance from Equations 7-18 and 7-19 for total conductance of the stomatal pathway (see Section 7.2.2.4 below).

### 7.2.2.3 Conductance of Mesophyll

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 the conductance of mesophyll (inner tissue). However, some work with elemental mercury cited in Lindberg et al. (1992) suggests that “resistance on or within mesophyll surfaces dominates the atmosphere-leaf diffusive path of Hg<sup>0</sup>” (see Section A.1.5 of Appendix A). Thus, conductance of the mesophyll is included when estimating the total conductance of the stomatal pathway for Hg(0), as described in the next subsection.

### 7.2.2.4 Total Conductance of the Stomatal Pathway

The total conductance of the stomatal pathway is:

$$g_s = \left( \frac{1}{g_{stomata}} + \frac{1}{g_m} + \frac{1}{g_B} \right)^{-1} \quad (\text{Eq. 7-18})$$

where:

$g_s$  = total conductance of stomatal pathway, including mesophyll (m/day);  
 $g_{stomata}$  = conductance of stomata (m/day);  
 $g_m$  = conductance of mesophyll (m/day); and  
 $g_B$  = conductance of the air boundary layer (m/day) (see Section 7.2.2.1).

However, of the chemicals evaluated for TRIM.FaTE to date, only elemental mercury encounters significant resistance from the mesophyll (see Section 7.2.2.3). Thus, Equation 7-18 would be used in full for elemental mercury, but the middle term for the resistance of the mesophyll would be dropped from the equation for the two other mercury species (*i.e.*, divalent and methyl). The total conductance of the stomatal pathway for chemicals other than elemental mercury thus far included in the TRIM.FaTE library is:

$$g_s = \left( \frac{1}{g_{Stomata}} + \frac{1}{g_B} \right)^{-1} \quad (\text{Eq. 7-19})$$

### 7.2.2.5 Cuticular Conductance

The cuticular conductance (mass transfer coefficient for chemical transfer across the cuticle side of the air/plant interface) is defined by the following equation (Riederer 1995):

$$g_{cuticle} = \frac{P_{cuticle}}{K_{AW}} \quad (\text{Eq. 7-20})$$

where:

$g_{cuticle}$  = conductance of the cuticle (m/sec);  
 $P_{cuticle}$  = permeance of the cuticle (m/sec); and  
 $K_{AW}$  = air/water partition coefficient, *i.e.*, equilibrium ratio between the chemical in water and in the vapor phase (g[chemical]/m<sup>3</sup>[air] per g[chemical]/m<sup>3</sup>[water]).

Cuticular permeance is an experimentally derived value that describes the mass transfer velocity from water into the leaf. The dimensionless air/water partition coefficient is used to transform the chemical in the sending compartment from water-phase to the vapor-phase in air. Cuticular permeance has been measured in *Citrus aurantium* leaves, and the following relationship in Equation 7-21 (below) was derived from those data (Riederer 1995). The variability of this relationship among plant species is unknown.

$$\log(P_{cuticle}) = 0.704 \times \log(K_{OW}) - 11.2 \quad (r = 0.91) \quad (\text{Eq. 7-21})$$

We extend Equation 7-21 to estimate the conductance from bulk air, using  $Z_{Total\_Air} / Z_{pure\_water}$ . Thus:

$$g_{cuticle} = \left( \frac{10^{0.704 \log K_{ow} - 11.2}}{Z_{Total\_Air} / Z_{pure\_water}} \right) \times 86,400 \quad (\text{Eq. 7-22})$$

where:

$Z_{pure\_water}$  = fugacity capacity of chemical in aqueous phase (mol/Pa-m<sup>3</sup>);  
 $Z_{Total\_Air}$  = total fugacity capacity of chemical in bulk air (mol/Pa-m<sup>3</sup>); and  
 86,400 = units conversion factor (sec/day).

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

$$g_C = \left( \frac{1}{g_B} + \frac{1}{g_{cuticle}} \right)^{-1} \quad (\text{Eq. 7-23})$$

where:

- $g_C$  = total conductance of the cuticular path, including the air boundary layer (m/day);
- $g_B$  = conductance of the boundary layer (m/day); and
- $g_{cuticle}$  = conductance of the cuticle (m/day).

### 7.2.2.6 Transfer Factors for Diffusion

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

$$\frac{dN_{Leaf}}{dt} = \left[ A_{LeafA} \times (g_C + g_S) \times \frac{N_{Air}}{V_{Air}} \right] - \left[ A_{LeafA} \times (g_C + g_S) \times \frac{N_{Leaf}}{V_{Leaf}} \times \frac{K_{AW}}{K_{LeafW}} \right] \quad (\text{Eq. 7-24})$$

where:

- $N_{Leaf}$  = mass of chemical in leaves (g[chemical]);
- $A_{LeafA}$  = effective interfacial area between leaf and air (m<sup>2</sup>);
- $N_{Air}$  = mass of chemical in air (g[chemical]);
- $V_{Air}$  = volume of air (m<sup>3</sup>);
- $V_{Leaf}$  = volume of leaves (m<sup>3</sup>);
- $K_{AW}$  = air/water partition coefficient (g[chemical]/m<sup>3</sup>[air] per g[chemical]/m<sup>3</sup>[water]); and
- $K_{LeafW}$  = leaf/water partition coefficient (g[chemical]/m<sup>3</sup>[leaf] per g[chemical]/m<sup>3</sup>[water]).

If the Riederer (1995) equation (which is calculated with respect to one-sided leaf area; *i.e.*, Eq. 7-4) is used in TRIM.FaTE to estimate stomatal conductance, the following equation is used to estimate diffusion of vapor-phase chemical from the plant leaf into the air:

$$T_{Leaf \rightarrow Air}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_{Leaf}} \times \frac{Z_{pure\_air}}{Z_{Total\_Leaf}} \quad (\text{TF 7-8a})$$

where:

- $T_{Leaf \rightarrow Air}^{diff}$  = transfer factor for diffusion of vapor-phase chemical from leaf to the air (/day);
- $LAI$  = one-sided leaf-area index (for the area of one side of a leaf) (unitless);
- $A_S$  = area of associated soil (m<sup>2</sup>);
- $g_C$  = total conductance of the cuticular pathway, including the air boundary layer (m/day);
- $g_S$  = total conductance of the stomatal pathway, including the air boundary layer (m/day);
- $V_{Leaf}$  = volume of leaf compartment (m<sup>3</sup>);
- $Z_{pure\_air}$  = fugacity capacity of chemical in gas-phase air (mol/m<sup>3</sup>-Pa); and
- $Z_{Total\_Leaf}$  = total fugacity capacity of chemical in the leaf compartment (mol/m<sup>3</sup>-Pa).

The Riederer (1995) equation is the default implemented in the current TRIM.FaTE library.

If the alternative equation for stomatal conductance from Bennett et al. (1998) is used to calculate stomatal conductance (*i.e.*, Equations 7-16 and 7-17), the transfer factor for diffusion from leaf to air would be calculated as:

$$T_{Leaf \rightarrow Air}^{diff} = (2LAI \times A_S \times g_C + A_S \times g_S) \times \frac{1}{V_{Leaf}} \times \frac{Z_{pure\_air}}{Z_{Total\_Leaf}} \quad (TF\ 7-8b)$$

Note that the contact area associated with the cuticular pathway is double the LAI, because cuticles cover the top and bottom of a leaf.

The total fugacity capacity of the chemical in the leaf compartment,  $Z_{Total\_Leaf}$  can be calculated using Equation 7-25 (below), which represents plants as a mixture of air, water, and nonpolar organic matter analogous to octanol (Paterson and Mackay 1995). It is assumed that the fugacity capacity of the chemical in a plant leaf is equivalent to that in a generic plant that is 18 percent air, 80 percent water, and 2 percent nonpolar organic matter.

$$Z_{Total\_Leaf} = 0.18 \times Z_{pure\_air} + 0.80 \times Z_{pure\_water} + 0.02 \times K_{OW} \times Z_{pure\_water} \quad (Eq.\ 7-25)$$

Since the Riederer (1995) equation (which is calculated with respect to one-sided leaf area, *i.e.*, Equation 7-11) is used for the stomatal conductance in the current TRIM.FaTE library, the transfer factor for diffusion of the chemical from the air into the leaf is calculated in the library as:

$$T_{Air \rightarrow Leaf}^{diff} = (2LAI \times A_S \times g_C + LAI \times A_S \times g_S) \times \frac{1}{V_{Air}} \quad (TF\ 7-9a)$$

If the Bennett et al. (1998) equation is used for the stomatal conductance (*i.e.*, Equations 7-16 and 7-17), the transfer factor for diffusion from air to leaf would be calculated as:

$$T_{Air \rightarrow Leaf}^{diff} = (2LAI \times A_S \times g_C + A_S \times g_S) \times \frac{1}{V_{Air}} \quad (TF\ 7-9b)$$

### 7.2.3 UPTAKE FROM SOIL BY ROOT

The uptake of chemicals by plant roots is treated as an equilibrium process in the current library. Two alternative algorithms may be used to calculate the accumulation of a chemical by plants from soil: uptake from bulk soil (Section 7.2.3.1) or uptake from soil pore water (Section 7.2.3.2). Both algorithms are derived from an equilibrium relationship, an estimated time to equilibrium, and the assumption of a first-order rate of uptake. The selection of algorithms for bulk soil or for soil pore water depends on the measured partition coefficient (*i.e.*, whether it was measured relative to bulk soil or estimated relative to soil pore water). Due to uncertainties associated with modeling these root types, initial TRIM.FaTE applications have not applied these algorithms to woody tree roots or tuber crops. Further consideration of compartment

design, parameter values, etc. may lead to some use of these or other algorithms for those root types.

### 7.2.3.1 Uptake from Bulk Soil

The uptake of chemicals from bulk soil by roots is described in TRIM.FaTE by an equation in the form of 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 (Efroymsen et al. 2001).

The change in concentration of the chemical in the root over time can be estimated using a time-to-equilibrium model (see Section 2.5):

$$\frac{dC_{Root}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times K_{Root-Sr} \times C_{Sr} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times C_{Root} \quad (\text{Eq. 7-26})$$

where:

- $C_{Root}$  = concentration of chemical in the root compartment (g[chemical]/m<sup>3</sup>[roots]);
- $\alpha$  = proportion of equilibrium value achieved (default = 0.95);
- $t_{\alpha}^{RSr}$  = time (days) required for the root/bulk-soil interaction to reach 100× $\alpha$  percent (default  $\alpha = 0.95$ ) of equilibrium when  $C_{Sr}$  is approximately constant with time;
- $K_{Root-Sr}$  = user-specified value for the partition coefficient of the chemical between the root and bulk wet soil (or uptake factor, g[chemical]/m<sup>3</sup>[root] per g[chemical]/m<sup>3</sup>[soil wet wt]); and
- $C_{Sr}$  = concentration of the chemical in the root-zone soil (g[chemical]/m<sup>3</sup>[soil]).

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

$$\frac{dN_{Root}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times V_{Root} \times K_{Root-Sr} \times \frac{N_{Sr}}{V_{Sr}} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times N_{Root} \quad (\text{Eq. 7-27})$$

where:

- $N_{Root}$  = mass of chemical in roots (g[chemical]);
- $V_{Root}$  = volume of roots (m<sup>3</sup>[root]);
- $N_{Sr}$  = total mass of chemical in all phases of bulk root-zone soil (g[chemical]);  
and
- $V_{Sr}$  = total volume of root-zone soil, which contains roots (m<sup>3</sup>[soil]).

Thus:

$$T_{Sr \rightarrow Root} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \right] \times \frac{V_{Root}}{V_{Sr}} \times K_{Root-Sr} \quad (\text{TF 7-10a})$$

where:

$T_{Sr \rightarrow Root}$  = transfer factor for transfer of chemical from root-zone soil to root (/day).

The transfer in the other direction, from the root to the bulk root-zone soil is represented as:

$$T_{Root \rightarrow Sr} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSr}} \quad (\text{TF 7-11a})$$

where:

$T_{Root \rightarrow Sr}$  = transfer factor for transfer of chemical from root to root-zone soil (/day).

### 7.2.3.2 Uptake from Soil Pore Water

An alternative method by which to estimate the root concentration of a chemical is as an equilibrium between root-tissue and soil-pore-water concentrations. Selection of the appropriate method (*i.e.*, for bulk soil or for soil pore water) depends on the experimental method used to derive the partition coefficient, *i.e.*, whether the data are reported based on pore water, bulk soil, or dry soil and wet or dry roots. The equilibrium relationship is a generalization of the Briggs et al. (1982) equation developed in Trapp (1995):

$$C_{Root} = K_{Root-SrW} \times C_{SrW} \quad (\text{Eq. 7-28})$$

where:

$C_{Root}$  = concentration in roots (g[chemical]/m<sup>3</sup>[root wet wt]);  
 $K_{Root-SrW}$  = root/root-zone-soil-water partition coefficient (g[chemical]/m<sup>3</sup>[root] per g[chemical]/m<sup>3</sup>[water] or m<sup>3</sup>[water]/m<sup>3</sup>[root]); and  
 $C_{SrW}$  = concentration in root-zone soil pore water (g[chemical]/m<sup>3</sup>[water]).

The root/root-zone-soil-water partition coefficient is determined as:

$$K_{Root-SrW} = (fW_{Root} + fL_{Root} \times K_{ow}^b) \times \rho_{Root} \times 0.001 \quad (\text{Eq. 7-29})$$

where:

$fW_{Root}$  = fraction water content of root (kg[water]/kg[root wet wt]);  
 $fL_{Root}$  = fraction lipid content of root (kg[lipid]/kg[root wet wt]);  
 $K_{ow}$  = octanol/water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water] or L[water]/kg[octanol]);  
 $b$  = correction exponent for the differences between octanol and lipids (unitless);

$\rho_{Root}$  = volumetric density of fresh root (kg[root wet wt]/m<sup>3</sup>[root]); and  
 0.001 = unit conversion factor (m<sup>3</sup>/L).

Thus:

$$\frac{dC_{Root}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times K_{Root-SrW} \times C_{SrW} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times C_{Root} \quad (\text{Eq. 7-30})$$

where:

$t_{\alpha}^{RSrW}$  = time (days) required for the root/soil-pore-water interaction to reach 100×α percent (default α = 0.95) of equilibrium when  $C_{SrW}$  is approximately constant with time.

The value of  $t_{\alpha}$  for the root/soil-pore-water interaction can be determined from empirical studies using roots exposed to the chemical in water. In the absence of any data, this  $t_{\alpha}$  can be estimated from the following equation:

$$t_{\alpha}^{RSrW} = \frac{2 \times (1.62 + e^{\log(Kow)-1.8})}{24} \quad (\text{Eq. 7-31})$$

That equation is based on the equation for the plant-root/soil-water interaction from Hsu et al. (1990), and 24 is the unit conversion factor (hr/day). However, it is a rough estimate, and the proportion of equilibrium that it might represent is not specified.

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

$$\frac{dN_{Root}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times V_{Root} \times K_{Root-SrW} \times \frac{N_{SrW}}{V_{SrW}} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times N_{Root} \quad (\text{Eq. 7-32})$$

where:

$N_{Root}$  = mass of chemical in roots (kg);  
 $V_{Root}$  = total volume of roots (m<sup>3</sup>[root]);  
 $N_{SrW}$  = total mass of chemical in root-zone-soil water (kg), which  
 =  $N_{Sr} \times \text{Fraction\_Mass\_Dissolved}$  (i.e., the total chemical mass in the soil compartment multiplied by the fraction of it that is dissolved in water);  
 and  
 $V_{SrW}$  = volume of root-zone soil water (m<sup>3</sup>[water]), which  
 =  $V_{Sr} \times \text{Volume\_Fraction\_Liquid}$  (i.e., volume of the soil compartment multiplied by  $\theta$ , the fraction of the root-zone soil compartment that is liquid (see Equation 2-37)).

Making the substitutions for  $N_{SrW}$  and  $V_{SrW}$  and using Equation 2-72 (Chapter 2) to substitute  $Z$  factors for the ratio of fractions, the transfer factors are:

$$\begin{aligned}
 T_{SrW \rightarrow Root} &= \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times \frac{V_{Root}}{V_{Sr}} \times K_{Root-SrW} \times \frac{Fraction\_Mass\_Dissolved}{Volume\_Fraction\_Liquid} \\
 &= \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}} \right] \times \frac{V_{Root}}{V_{Sr}} \times K_{Root-SrW} \times \frac{Z_{pure\_water}}{Z_{Total\_Sr}}
 \end{aligned}
 \tag{TF 7-10b}$$

$$T_{Root \rightarrow SrW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{RSrW}}
 \tag{TF 7-11b}$$

where:

- $T_{SrW \rightarrow Root}$  = transfer factor for transfer of chemical from root-zone soil water to root (/day);
- $T_{Root \rightarrow SrW}$  = transfer factor for transfer of chemical from root to root-zone soil water (/day);
- $Z_{pure\_water}$  = fugacity capacity of the chemical in aqueous phase (mol/Pa-m<sup>3</sup>); and
- $Z_{Total\_Sr}$  = total fugacity capacity of the chemical in the root-zone soil compartment (mol/Pa-m<sup>3</sup>); and
- $V_{Sr}$  = volume of the root-zone soil compartment (m<sup>3</sup>[soil]).

Note that the user specifies either equations TF 7-10a and TF 7-11a (for transfers related to bulk soil) or TF 7-10b and TF 7-11b (for transfers related to soil pore water only) for a given chemical.

## 7.2.4 TRANSFERS INVOLVING THE STEM

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

### 7.2.4.1 Contribution from Soil Pore Water via Transpiration Stream (Xylem)

Trapp (1995) derived an equation for the unidirectional flux of chemical from the soil pore water into the stem driven by the plant transpiration stream through its xylem:

where:

$$\frac{dN_{Stem}}{dt} = Q_{xy} \times TSCF \times \frac{N_{SrW}}{V_{SrW}}
 \tag{Eq. 7-33}$$

- $N_{Stem}$  = mass of chemical in stems (g[chemical]);
- $Q_{xy}$  = total flow of transpired water (m<sup>3</sup>[xylem]/day, derived below);
- $TSCF$  = transpiration stream concentration factor (g[chemical]/m<sup>3</sup>[xylem] per g[chemical]/m<sup>3</sup>[soil pore water] or m<sup>3</sup>[water]/m<sup>3</sup>[xylem]);
- $N_{SrW}$  = mass of chemical in root-zone-soil pore water (g[chemical]); and

$V_{SrW}$  = volume of water in root-zone soil ( $m^3$ [water]).

Using the equation of Hsu et al. (1990):

$$TSCF = \left[ 0.7 \times e^{\left( -\left( \log(K_{ow}) - 3.07 \right)^2 / 2.78 \right)} \right] \quad (\text{Eq. 7-34})$$

According to Crank et al. (1981):

$$Q_{xy} = 4.8 \times 10^{-3} \times LAI \times A_s \quad (\text{Eq. 7-35})$$

where:

$4.8 \times 10^{-3}$  = empirical factor ( $m^3$ [water]/ $m^2$ [leaf]-day);  
 $LAI$  = leaf-area index ( $m^2$ [leaf]/ $m^2$ [soil]); and  
 $A_s$  = area of associated soil ( $m^2$ [soil]).

The quantity ( $N_{SrW}/V_{SrW}$ ) in Equation 7-33 equals the concentration of the chemical in the root-zone soil pore water in  $g$ [chemical]/ $m^3$ [water]. That quantity can also be expressed as the fraction of the mass of the chemical in the root-zone soil compartment that is dissolved in water divided by the volume of the root-zone soil compartment that is liquid, which equals  $Z_{pure\_water}/Z_{Total\_Sr}$  (see Section 2.6):

$$\frac{N_{SrW}}{V_{SrW}} = \frac{N_{Sr}}{V_{Sr}} \times \frac{Mass\_Fraction\_Dissolved}{Volume\_Fraction\_Liquid} = \frac{N_{Sr}}{V_{Sr}} \times \frac{Z_{pure\_water}}{Z_{Total\_Sr}} \quad (\text{Eq. 7-36})$$

Thus:

$$\begin{aligned} T_{Sr \rightarrow Stem} &= \frac{Q_{xy} \times Z_{pure\_water}}{V_{Sr} \times Z_{Total\_Sr}} \times TSCF \\ &= \frac{Q_{xy}}{V_{Sr}} \times f_{ML} \times TSCF \end{aligned} \quad (\text{TF 7-12a})$$

where:

$T_{Sr \rightarrow Stem}$  = transfer factor for transfer of chemical from root-zone soil to stem (/day);  
 $Z_{pure\_water}$  = fugacity capacity of chemical in pure water ( $mol/Pa \cdot m^3$ );  
 $V_{Sr}$  = volume of the root-zone soil compartment ( $m^3$ );  
 $Z_{Total\_Sr}$  = total fugacity capacity of chemical in bulk root-zone soil ( $mol/Pa \cdot m^3$ ); and  
 $f_{ML}$  = fraction of chemical mass that is dissolved in water divided by fraction of the volume of the root-zone soil compartment that is water (unitless),  
 which  
 =  $Z_{pure\_water}/Z_{Total\_Sr}$  (see Equations 2-72 and 2-80).

### 7.2.4.2 Alternative Algorithm for Soil/Stem Transfers

An alternative algorithm for uptake of nonionic organic chemicals by the stem from root-zone soil is an equilibrium relationship between the soil pore water and stem taken from Briggs et al. (1983):

$$C_{Stem} = SCF \times C_{SrW} \times \frac{\rho_{Stem}}{\rho_{SrW}} \quad (\text{Eq. 7-37})$$

where:

- $C_{Stem}$  = concentration of chemical in stem (g[chemical]/m<sup>3</sup>[stem]);
- $C_{SrW}$  = concentration in root-zone-soil pore water (g[chemical]/m<sup>3</sup>[water]);
- $SCF$  = stem concentration factor (g[chemical]/kg[stem wet wt] per g[chemical]/kg[water] or kg[water]/kg[stem wet wt]) (see below);
- $\rho_{Stem}$  = density of stem (kg[stem wet wt]/m<sup>3</sup>[stem]); and
- $\rho_{SrW}$  = density of root-zone-soil pore water (kg[water]/m<sup>3</sup>[water]).

The  $SCF$  may be calculated using the following equation from Briggs et al. (1983):

$$SCF = (10^{0.95 \times \log(K_{ow}) - 2.05} + 0.82) \times 0.784 \times e^{-(\log(K_{ow}) - 1.78)^2 / 2.44} \quad (\text{Eq. 7-38})$$

Thus, the change in chemical concentration in the stem is estimated as:

$$\frac{dC_{Stem}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \right] \times SCF \times \frac{\rho_{Stem}}{\rho_{SrW}} \times C_{SrW} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \right] \times C_{Stem} \quad (\text{Eq. 7-39})$$

where:

- $t_{\alpha}^{StSrW}$  = time (days) required for the stem/root-zone-soil-pore-water interaction to reach 100×α percent of the equilibrium value when  $C_{SrW}$  is approximately constant with time.

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

$$\frac{dN_{Stem}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \right] \times V_{Stem} \times SCF \times \frac{\rho_{Stem}}{\rho_{SrW}} \times \frac{N_{SrW}}{V_{SrW}} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \right] \times N_{Stem} \quad (\text{Eq. 7-40})$$

where:

- $N_{Stem}$  = mass of chemical in fresh stems (g[chemical]);
- $V_{Stem}$  = total volume of stem compartment (m<sup>3</sup>[stem]);
- $N_{SrW}$  = total mass of chemical in root-zone soil water (g[chemical]); and
- $V_{SrW}$  = volume of root-zone soil water (m<sup>3</sup>[water]).

The total volume of the stem compartment can be calculated as follows:

$$V_{Stem} = \frac{\rho_{area_{Stem}} \times A_{Sr}}{\rho_{Stem}} \quad (\text{Eq. 7-41})$$

where:

- $\rho_{area_{Stem}}$  = areal density of stem on associated soil (kg[stem wet wt]/m<sup>2</sup>[soil]);
- $A_{Sr}$  = area of associated root-zone-soil compartment (m<sup>2</sup>[soil]); and
- $\rho_{Stem}$  = wet density of stem (kg[stem wet wt]/m<sup>3</sup>[stem]).

Thus, the transfer factors describing the transfer from root-zone-soil pore water to the stem and from the stem to the root-zone-soil pore water are:

$$T_{SrW \rightarrow Stem} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \right] \times \rho_{area_{Stem}} \times \frac{SCF}{\rho_{SrW} \times d_{Sr}} \quad (\text{TF 7-12b1})$$

and:

$$T_{Stem \rightarrow SrW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{StSrW}} \quad (\text{TF 7-12b2})$$

where:

- $T_{SrW \rightarrow Stem}$  = transfer factor for transfer of chemical from root-zone soil water to stem (/day);
- $T_{Stem \rightarrow SrW}$  = transfer factor for transfer of chemical from stem to root-zone soil water (/day); and
- $d_{Sr}$  = depth of root-zone soil compartment (m), which  
 =  $V_{Sr} \text{ (m}^3\text{)} / A_{Sr} \text{ (m}^2\text{)}$ .

Note that this alternative algorithm for nonionic organic chemicals includes transfers in two directions (TF 7-12b1 and TF 7-12b2), whereas the default algorithm in the TRIM.FaTE library (TF 7-12a) is a one-way transfer from root-zone-soil pore water to the stem. Note that TFs 7-12b1 and 7-12b2 are not in the current TRIM.FaTE library. They are provided here for those users who may have data available for the SCF parameter but not one or more of the parameters needed for TF 7-12a (e.g., TSCF,  $Q_{xy}$ ).

### 7.2.4.3 Contribution from Leaves via Phloem

During the growing season, the stem can gain dissolved chemical from the leaves via phloem. Assuming that the chemical concentration in phloem sap is in equilibrium with that in leaves:

$$\frac{dN_{Stem}}{dt} = Q_{Ph} \times \frac{N_{Leaf}}{V_{Leaf} \times K_{LeafPh}} \quad (\text{Eq. 7-42})$$

where:

- $N_{Stem}$  = mass of chemical in stems (g[chemical]);
- $Q_{Ph}$  = phloem flux into leaves (m<sup>3</sup>[phloem]/day), due to advection (assume 5 percent of  $Q_{Xy}$  [defined in Section 7.2.4.4], Paterson et al. 1991);
- $N_{Leaf}$  = mass of chemical in leaves (g[chemical]);
- $V_{Leaf}$  = volume of leaves (m<sup>3</sup>[leaf]); and
- $K_{LeafPh}$  = partition coefficient between leaves and phloem water (g[chemical]/m<sup>3</sup>[leaf] per g[chemical]/m<sup>3</sup>[phloem] or m<sup>3</sup>[phloem]/m<sup>3</sup>[leaf]).

The following equation, adapted from an equation for sorption of contaminants to plant roots (Trapp 1995), can be used to calculate  $K_{LeafPh}$ :

$$K_{LeafPh} = (fW_{Leaf} + fL_{Leaf} \times K_{ow}^b) \times \frac{\rho_{Leaf}}{\rho_{Ph}} \quad (\text{Eq. 7-43})$$

where:

- $fW_{Leaf}$  = fraction of leaves consisting of water (kg[water]/kg[leaf wet wt]);
- $fL_{Leaf}$  = fraction of leaves consisting of lipid (kg[lipid]/kg[leaf wet wt]);
- $K_{ow}$  = octanol/water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water]);
- $b$  = correction exponent for differences between foliage lipids and octanol (unitless);
- $\rho_{Leaf}$  = density of leaf (kg[leaf wet wt]/m<sup>3</sup>[leaf]); and
- $\rho_{Ph}$  = density of phloem (kg[phloem]/m<sup>3</sup>[phloem]).

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 the phloem is the same as that in leaf water. Thus:

$$T_{Leaf \rightarrow Stem} = Q_{Ph} \times \frac{1}{V_{Leaf} \times K_{LeafPh}} \quad (\text{TF 7-13})$$

where:

- $T_{Leaf \rightarrow Stem}$  = transfer factor for leaf to stem (/day).

#### 7.2.4.4 Loss from Stem to Leaf via Xylem

During the growing season, the stem can lose dissolved chemical to the leaves via the xylem:

$$\frac{dN_{Leaf}}{dt} = Q_{Xy} \times \frac{N_{Stem}}{V_{Stem} \times K_{StemXy}} \quad (\text{Eq. 7-44})$$

where:

$N_{Leaf}$  = mass of chemical in leaf compartment (g[chemical]);  
 $Q_{Xy}$  = flow of transpired water (m<sup>3</sup>[xylem]/day);  
 $N_{Stem}$  = mass of chemical in stem compartment (g[chemical]);  
 $V_{Stem}$  = volume of stem (m<sup>3</sup>[stem]); and  
 $K_{StemXy}$  = partition coefficient between stem and xylem water (m<sup>3</sup>[xylem]/m<sup>3</sup>[stem]).

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

$$K_{StemXy} = (fW_{Stem} + fL_{Stem} \times K_{ow}^b) \times \frac{\rho_{Stem}}{\rho_{Xy}} \quad (\text{Eq. 7-45})$$

where:

$fW_{Stem}$  = fraction water content of stem (kg[water]/kg[stem wet wt]);  
 $fL_{Stem}$  = fraction lipid content of stem (kg[lipid]/kg[stem wet wt]);  
 $K_{ow}$  = octanol/water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water] or L[water]/kg[octanol]);  
 $b$  = correction exponent for differences between foliage lipids and octanol (unitless);  
 $\rho_{Stem}$  = density of stem (kg[stem wet wt]/m<sup>3</sup>[stem]); and  
 $\rho_{Xy}$  = density of xylem fluid (kg[xylem]/m<sup>3</sup>[xylem]).

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 the xylem is the same as that in leaf water. Thus:

$$T_{Stem \rightarrow Leaf} = Q_{Xy} \times \frac{1}{V_{Stem} \times K_{StemXy}} \quad (\text{TF-7-14})$$

where:

$T_{Stem \rightarrow Leaf}$  = transfer factor for stem to leaf.

#### 7.2.4.5 Loss from Phloem to Fruit

Depending on the application, it may not be necessary to implement a fruit compartment or this loss term in a TRIM.FaTE simulation. Things to consider may be the concentrations expected in fruit and the portion of the diet (wildlife or human) expected to be comprised of fruit. This algorithm has not yet been implemented in any applications 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:

$$\frac{dN_{Fruit}}{dt} = Q_{PhF} \times \frac{N_{Stem}}{V_{Stem} \times K_{StemXy}} \quad (\text{Eq. 7-46})$$

where:

- $N_{Fruit}$  = mass of chemical in fruit (g[chemical]);  
 $Q_{PhF}$  = phloem flux into fruit (m<sup>3</sup>[phloem]/day), due to advection (assume 5 percent of  $Q_{Xy}$ , Paterson et al. 1991);  
 $N_{Stem}$  = mass of chemical in stem (g[chemical]);  
 $V_{Stem}$  = volume of stem (m<sup>3</sup>[stem]); and  
 $K_{StemXy}$  = partition coefficient between stem and xylem water (m<sup>3</sup>[xylem]/m<sup>3</sup>[stem]).

### 7.2.5 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. Turner (1998) has collected 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; PAHs would be expected to have similar properties. Algorithms for the transfer of chemicals to wood and tree bark are not currently available in the TRIM.FaTE library because of a general lack of information for persistent air pollutants.

### 7.2.6 TRANSFORMATIONS AND DEGRADATION

All transformations are assumed to be first-order processes in TRIM.FaTE. The derivations of these values for mercury and PAHs are described in Appendices A and B of this volume, respectively. Transformations of chemicals associated with particles on the surface of plant leaves are assumed to occur with the same rate constants as transformations of chemicals associated with particles in air.

Transformations of chemicals into other chemicals that are no longer be tracked in TRIM.FaTE are called general degradation processes. In TRIM.FaTE, the degradation of a chemical in particles on leaves and vegetation due to all mechanisms that might apply (*e.g.*, photolysis, and metabolic activity) is reflected by the user input for the half-life of the chemical in the plant leaf, stem, and root, and for the chemical associated with particles on the surface of the leaf.

Transformations of a chemical into another form of the chemical that is tracked in TRIM.FaTE are named for the processes associated with the transformation (*e.g.*, oxidation, methylation, reduction of mercury species). The transformation rate constant is the inverse of the residence time with respect to that reaction.

### 7.2.7 LITTER FALL

The flux of chemical from leaves, including particles on leaves, to surface soil during litter fall at the end of the growing season may be expressed by the equation:

$$\frac{dN_{ss}}{dt} = N_{Leaf} + k_L \times N_{LeafP} \quad (\text{Eq. 7-47})$$

where:

- $N_{Ss}$  = mass of chemical in surface soil in compartment (g[chemical]);
- $k_L$  = litter-fall rate constant (/day);
- $N_{Leaf}$  = mass of chemical in foliage in leaf compartment (g[chemical]); and
- $N_{LeafP}$  = mass of chemical in particles-on-leaf compartment (g[chemical]).

If it is assumed that 99 percent of the leaves of deciduous trees are dropped to surface soil between the day of first frost and a date that is 30 days later,  $k_L$  would be calculated according to the equations:

$$\frac{C}{C_0} = e^{-k_L} \quad (\text{Eq. 7-48a})$$

$$\ln(0.01) = -30k_L \quad (\text{Eq. 7-48b})$$

where:

- $C/C_0$  = ratio of concentration in the leaf compartment after 30 days of litter fall,  $C$ , to the concentration in the leaf compartment at the beginning of litter fall,  $C_0$ , which equals 0.01 if 99 percent of the mass is lost in 30 days (g[chemical]/m<sup>3</sup>[leaf] per g[chemical]/m<sup>3</sup>[leaf]).

Thus,  $k_L$  would equal  $-\ln(0.01)/30$  days which is 0.15 /day.

Litter fall for conifers, on the other hand, usually occurs more gradually, with a complete turnover of leaves taking 2 to 10 or 11 years (Post 1999). Thus, if it is assumed for the purpose of a TRIM.FaTE scenario that the leaf turnover is 6 years,  $k_L$  would equal  $-\ln(0.01)/2190$  days, which is 0.0021/day. Moreover, that litter-fall rate could be set to a constant value for the year.

If 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, again,  $k_L$  would equal 0.15 /day.

If all of the plant material were harvested, the litter-fall rate constant would be set to 0/day and the chemical in the harvested plant compartments would need to be transferred to a chemical sink or to another compartment (e.g., silage) for purposes of balancing mass in TRIM.FaTE. If only a portion of the plant crop (half of the leaves for example) were harvested and the remainder of the plant were allowed to remain in the “field”, the user would need to determine the fraction of the biomass that would be harvested. That fraction of the chemical in the harvested plant biomass could be sent to a harvest sink while the remainder could be sent to the surface soil compartment.

Thus:

$$T_{Leaf \rightarrow Ss} = k_L \quad (\text{TF 7-15})$$

where:

- $T_{Leaf \rightarrow Ss}$  = transfer factor for leaf to surface soil (/day).

Also:

$$T_{LeafP \rightarrow Ss} = k_L \quad (\text{TF 7-16})$$

where:

$T_{LeafP \rightarrow Ss}$  = transfer factor for the particles-on-leaf to surface-soil compartments (/day).

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

### 7.2.8 SENESCENCE

Senescence is not considered in the current version of the TRIM.FaTE library. 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 of plants is assumed to be negligible prior to the date of first frost.

### 7.2.9 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 for 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.

During the 30-day period of litter fall for deciduous trees at the end of the growing season, chemical mass is steadily decreased in the leaf compartment. Because the loss is modeled using a rate constant, at the end of 30 days, a small amount of chemical remains in the leaf compartment, and that amount remains throughout the winter. Note that in the current TRIM.FaTE library, the volume of the leaf compartment goes to zero on the date at which *AllowExchange* goes to zero, which is at the beginning of the 30-day litter-fall period. On that date, the leaf compartment is no longer available as a food source for terrestrial herbivores and omnivores.

An additional seasonal issue is deposition to the particles-on-leaf compartment type. Tree foliage and grasses only intercept deposition when they are present. Like the leaf compartment, the volume of the particles-on-leaf compartment is a function of *AllowExchange*, and so the volume of particles-on-leaf drops abruptly to zero for the winter, starting on the first day of litter fall. TRIM.FaTE assumes that no plant foliage is present in the non-growing season, except for that associated with conifers or other user-created evergreen vegetation types. 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 chemicals 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 chemicals.

During the non-growing season, for herbivorous or omnivorous animals that do not hibernate or engage in winter sleep, the user may want to consider the significance of accumulation from alternative, non-plant dietary sources.

## 7.3 SOIL DETRITIVORES

In this section, the transfer factor algorithms associated with soil detritivores (*i.e.*, earthworms, Section 7.3.1, and soil arthropods, Section 7.3.2) are developed. A list of these algorithms is provided in the table on the next and following page.

### 7.3.1 EARTHWORMS

The uptake of chemicals by earthworms in TRIM.FaTE is described by an equation in the form of time to equilibrium between the earthworms and soil (see Section 2.5). There are two forms of the uptake equation in TRIM.FaTE: one for uptake of chemicals from an interaction with bulk soil (Section 7.3.1.1) and one for uptake of chemicals dissolved in soil pore water (Section 7.3.1.2). The choice of algorithm depends on the data available to derive the partition coefficients. Empirical data on the uptake of chemicals from bulk soil by earthworms are commonly available for inorganic chemicals and some organic compounds. Such empirical ratios are not usually available for earthworm uptake from soil pore water; however, an established relationship exists between octanol-water partition coefficients and earthworm/soil-pore-water partition coefficients.

#### 7.3.1.1 Uptake of Chemicals from Bulk Soil

For simplicity, uptake from bulk soil is described as being 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 (Sample et al. 1999). The concentration of the chemical in the earthworm (dry-weight basis) is equal to the dry worm/soil partition coefficient multiplied by the concentration of the chemical in the soil (dry-weight basis):

$$C_{Worm-dry} = K_{Worm-Sr-dry} \times C_{Sr-dry} \quad (\text{Eq. 7-49})$$

where:

- $C_{worm-dry}$  = dry-weight concentration of chemical in earthworm (g[chemical]/kg[worm dry wt]);
- $K_{Worm-Sr-dry}$  = earthworm/dry-soil partition coefficient (kg[soil dry wt]/kg[worm dry wt]); and
- $C_{Sr-dry}$  = dry-weight concentration of chemical in root-zone soil (g[chemical]/kg[soil dry wt]).

**Summary of Transfer Factors for Soil Detritivores in TRIM.FaTE**

**DIFFUSIVE TRANSFERS**

Bulk root-zone soil to earthworm:

TF 7-17a

$$T_{Sr \rightarrow Worm} = \left[ \frac{-\ln(1 - \alpha)}{t_{\alpha}^{WSr}} \right] \times \frac{M_{Worm}}{M_{Sr}} \times K_{Worm-Sr}$$

Earthworm to bulk root-zone soil:

TF 7-18a

$$T_{Worm \rightarrow Sr} = \frac{-\ln(1 - \alpha)}{t_{\alpha}^{WSr}}$$

Root-zone-soil pore water to earthworm:

TF 7-17b

$$T_{SrW \rightarrow Worm} = \left[ \frac{-\ln(1 - \alpha)}{t_{\alpha}^{WSrW}} \right] \times \frac{M_{Worm}}{V_{Sr} \times \theta \times 1000} \times K_{Worm-SrW}$$

Earthworm to root-zone-soil pore water:

TF 7-18b

$$T_{Worm \rightarrow SrW} = \frac{-\ln(1 - \alpha)}{t_{\alpha}^{WSrW}}$$

Bulk soil to soil arthropod:

TF 7-19

$$T_{S \rightarrow Arth} = \left[ \frac{-\ln(1 - \alpha)}{t_{\alpha}^{AS}} \right] \times \frac{M_{Arth}}{M_S} \times K_{Arth-S}$$

Soil arthropod to bulk soil:

TF 7-20

$$T_{Arth \rightarrow S} = \frac{-\ln(1 - \alpha)}{t_{\alpha}^{AS}}$$

**LIST OF SYMBOLS USED IN SOIL DETRITIVORE TRANSFER FACTOR ALGORITHMS**

- |               |   |   |
|---------------|---|---|
| $\alpha$      | = | fraction of equilibrium value achieved by time $t_{\alpha}$ (default = 0.95 or 95%).  |
| $t_{\alpha}$  | = | time required to reach the fraction $\alpha$ of equilibrium (days) (value depends on the compartments and phases for which time-to-equilibrium is modeled). |
| $M_{Worm}$    | = | total biomass of worms in root-zone soil compartment (kg[worm wet wt]).   |
| $M_{Sr}$      | = | total mass of root-zone soil compartment (kg[soil wet wt]).   |
| $K_{Worm-Sr}$ | = | earthworm/bulk-soil partition coefficient (kg[soil wet wt]/kg[worm wet wt]).  |

**Summary of Transfer Factors for Soil Detritivores in TRIM.FaTE (cont.)**

**LIST OF SYMBOLS USED IN SOIL DETRITIVORE TRANSFER FACTOR ALGORITHMS (cont.)**

$V_{Sr}$	=	volume of root-zone soil compartment (m <sup>3</sup> ).
$\theta$	=	fraction root-zone soil compartment volume that is liquid (unitless).
$K_{Worm-SrW}$	=	earthworm/soil-pore-water partition coefficient ( L[water]/kg[worm wet wt]).
$M_{Arth}$	=	total biomass of arthropods in soil compartment (kg[arthropod wet wt]).
$M_s$	=	total mass of soil compartment (kg[soil wet wt]).
$K_{Arth-S}$	=	arthropod/bulk-soil partition coefficient (kg[soil wet wt]/kg[arthropod wet wt]).

If masses are converted to wet mass, then:

$$C_{Worm} = (1-fW_{Worm}) \times C_{Worm-dry} \quad (\text{Eq. 7-50})$$

where:

- $C_{Worm}$  = concentration of chemical in earthworm (g[chemical]/kg[worm wet wt]);  
 and  
 $fW_{Worm}$  = water content of earthworm (kg[water]/kg[worm wet wt]).

It is also true that:

$$C_{Sr} = (1-fW_{Sr}) \times C_{Sr-dry} \quad (\text{Eq. 7-51})$$

where:

- $C_{Sr}$  = concentration of the chemical in the bulk root-zone soil (g[chemical]/kg[soil]);  
 $fW_{Sr}$  = fraction water content of root-zone soil (kg[water]/kg[root-zone soil wet wt]).

Thus:

$$\frac{C_{Worm}}{(1-fW_{Worm})} = K_{Worm-Sr-dry} \times \frac{C_{Sr}}{(1-fW_{Sr})} \quad (\text{Eq. 7-52a})$$

Rearranging gives:

$$\frac{C_{Worm}}{C_{Sr}} = K_{Worm-Sr-dry} \times \frac{(1-fW_{Worm})}{(1-fW_{Sr})} \quad (\text{Eq. 7-52b})$$

Thus:

$$K_{Worm-Sr} = \frac{(1 - fW_{Worm})}{(1 - fW_{Sr})} \times K_{Worm-Sr\_dry} \quad (\text{Eq. 7-53})$$

where:

$K_{Worm-Sr}$  = earthworm/bulk-soil partition coefficient (g[chemical]/kg[worm wet wt] per g[chemical]/kg[soil wet wt] or kg[soil wet wt]/kg[worm wet wt]).

Using the approach described in Section 2.5, the change in chemical concentration in the earthworm compartment over time can be described as:

$$\frac{dC_{Worm}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \right] \times K_{Worm-Sr} \times C_{Sr} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \right] C_{Worm} \quad (\text{Eq. 7-54})$$

where:

$t_{\alpha}^{WSr}$  = time (days) required for the earthworm/bulk-soil interaction to reach  $100 \times \alpha$  percent (default  $\alpha = 0.95$ ) of equilibrium when  $C_{Sr}$  is approximately constant with time. The value of  $t_{\alpha}$  must be determined from empirical studies reported in the literature.

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

$$\frac{dN_{Worm}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \right] \times \rho_{area_{Worm}} \times A_{Sr} \times K_{Worm-Sr} \times \frac{N_{Sr}}{M_{Sr}} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \right] N_{Worm} \quad (\text{Eq. 7-55})$$

where:

$N_{Worm}$  = mass of chemical in earthworm compartment (g[chemical]);  
 $\rho_{area_{Worm}}$  = areal wet-weight density of earthworms in root-zone soil (kg[worm wet wt]/m<sup>2</sup>[soil]);  
 $A_{Sr}$  = area of root-zone soil compartment (m<sup>2</sup>[soil]);  
 $N_{Sr}$  = total mass of chemical in all phases of bulk root-zone soil (g[chemical]);  
 and  
 $M_{Sr}$  = bulk mass of root-zone soil compartment, including arthropods (kg[soil wet wt]).

Note that the quantity ( $\rho_{area_{Worm}} \times A_{Sr}$ ) is equal to the total biomass of worms (wet wt),  $M_{Worm}$ , in the soil compartment.

Thus, the transfer factors between the bulk root-zone soil and earthworm compartments are estimated as:

$$T_{Sr \rightarrow Worm} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \right] \times \frac{M_{Worm}}{M_{Sr}} \times K_{Worm-Sr} \quad (\text{TF 7-17a})$$

$$T_{Worm \rightarrow Sr} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSr}} \quad (\text{TF 7-18a})$$

where:

- $T_{Sr \rightarrow Worm}$  = transfer factor for transfer of chemical from root-zone soil compartment to earthworm compartment (/day);
- $T_{Worm \rightarrow Sr}$  = transfer factor for transfer of chemical from earthworm to root-zone soil compartments (/day); and
- $M_{Worm}$  = total biomass of worms (kg[worm wet wt]) in the root-zone soil compartment (=  $\rho_{area_{Worm}} \times A_{Sr}$ ).

### 7.3.1.2 Uptake of Chemicals from Soil Pore Water

For simplicity, uptake of chemicals from soil pore water is described as being proportional to the concentration of the chemical in soil pore water. This algorithm is used as an alternative to uptake from bulk soil. All calculations can be done in original wet weights, simplifying the derivation of the transfer factors. These equations are appropriate for any chemicals for which partition coefficients have been reported on a pore-water basis:

$$C_{Worm} = K_{Worm-SrW} \times C_{SrW} \quad (\text{Eq. 7-56})$$

where:

- $C_{Worm}$  = wet-weight concentration of chemical in earthworm (g[chemical]/kg[worm wet wt]);
- $C_{SrW}$  = concentration of chemical in root-zone-soil pore water (g[chemical]/L[water]); and
- $K_{Worm-SrW}$  = earthworm/root-zone-soil-pore-water (or earthworm/water) partition coefficient (L[water]/kg[worm wet wt]).

The partition coefficient for the lipophilic organic chemical between the earthworm and the pore water of the root-zone soil can be calculated as:

$$K_{Worm-SrW} = K_{OW}/3.98 \quad (\text{Eq. 7-57})$$

where:

- $K_{OW}$  = the chemical's octanol-water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water] or L[water]/kg[octanol]).

Equation 7-57 was derived from studies of 32 lipophilic chemicals with  $\log(K_{OW})$  values from 1.0 to 6.5 (Connell and Markwell 1990, Suter et al. 2000). As for uptake calculated with respect to bulk soil, the equilibrium model for uptake from soil pore water can be changed to the following equation to estimate the change in concentration of the chemical in the earthworm over time:

$$\frac{dC_{Worm}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times K_{Worm-SrW} \times C_{SrW} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times C_{Worm} \quad (\text{Eq. 7-58})$$

where:

$t_{\alpha}^{WSrW}$  = time (days) required for the worm/root-zone soil-pore-water interaction to reach  $100 \times \alpha$  percent (default  $\alpha = 0.95$ ) of equilibrium when  $C_{SrW}$  is approximately constant with time.

The value of this  $t_{\alpha}$  can be determined from empirical studies reported in the literature, but these are rare. In the absence of any data, " $t_{\alpha}$ " can be estimated from the following equation if the octanol/ water partition coefficient ( $K_{OW}$ ) is available:

$$t_{\alpha}^{WSrW} = \frac{2 \times 1.62 + e^{(\log(K_{OW})-1.8)}}{24} \quad (\text{Eq. 7-59})$$

This equation is based on the equation for the interaction of plant roots and soil water in Hsu et al. (1990), which is a rough estimate of the time to equilibrium. An empirical relationship derived from plant roots is used for earthworms because a model derived from earthworms is not yet available and the diffusive processes are likely similar. The corresponding proportion of the equilibrium concentration actually reached, however, is uncertain. Thus, the appropriate value to use for  $\alpha$  (e.g., 0.95, 0.99) is uncertain.

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

$$\begin{aligned} \frac{dN_{Worm}}{dt} = & \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times M_{Worm} \times K_{Worm-SrW} \times \frac{N_{SrW}}{M_{SrW}} \\ & - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times N_{Worm} \end{aligned} \quad (\text{Eq. 7-60})$$

where:

$N_{Worm}$  = mass of chemical in earthworms (g[chemical]);  
 $M_{Worm}$  = total biomass of worms (kg[worm wet wt]);  
 $N_{SrW}$  = mass of chemical in root-zone-soil pore water (g[chemical]); and  
 $M_{SrW}$  = mass of root-zone-soil pore water (kg[water]).

It is also true that:

$$\begin{aligned}
 N_{SrW} &= N_{Sr} \times \textit{Fraction\_Mass\_Dissolved} \textit{ (i.e., the total chemical mass in the total soil compartment multiplied by the fraction of the total chemical mass that is dissolved in water); and} \\
 M_{SrW} &= V_{SrW} \textit{ (volume of root-zone soil water in m}^3\text{)} \times 1 \textit{ kg[water]/L[water]} \times 1000 \textit{ L[water]/m}^3\text{[water]}; \textit{ where:} \\
 V_{SrW} &= V_{Sr} \textit{ (m}^3\text{)} \times \textit{Volume\_Fraction\_Liquid (i.e., total volume of the root-zone soil compartment multiplied by the volume fraction of the root-zone soil compartment that is liquid)}.
 \end{aligned}$$

Making the substitutions for  $N_{SrW}$ ,  $M_{SrW}$ , and then  $V_{SrW}$ , and using Equation 2-72 (Chapter 2) to substitute Z factors for the ratio of fractions, the transfer factors are:

$$\begin{aligned}
 T_{SrW \rightarrow Worm} &= \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times K_{Worm-SrW} \times \frac{M_{Worm} \times \textit{Fraction\_Mass\_Dissolved}}{V_{Sr} \times 1000 \times \textit{Volume\_Fraction\_Liquid}} \\
 &= \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \right] \times K_{Worm-SrW} \times \frac{M_{Worm}}{V_{Sr} \times 1000} \times \frac{Z_{\textit{pure\_water}}}{Z_{\textit{Total}}} \quad \text{(TF 7-17b)}
 \end{aligned}$$

and:

$$T_{Worm \rightarrow SrW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{WSrW}} \quad \text{(TF 7-18b)}$$

where:

$$\begin{aligned}
 T_{SrW \rightarrow Worm} &= \textit{transfer factor for transfer of chemical from root-zone-soil pore water to worm (/day);} \\
 T_{Worm \rightarrow SrW} &= \textit{transfer factor for transfer of chemical from worm to root-zone-soil pore water (/day);} \\
 K_{Worm-SrW} &= \textit{worm/soil-pore water partition coefficient (L[water]/kg[worm wet wt]);} \\
 Z_{\textit{pure\_water}} &= \textit{fugacity capacity of chemical in pure water (mol/m}^3\text{-Pa); and} \\
 Z_{\textit{Total\_Sr}} &= \textit{total fugacity capacity of chemical in root-zone soil compartment (mol/m}^3\text{-Pa)}.
 \end{aligned}$$

### 7.3.2 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 its food. The food may be plant matter rather than soil, but for the purposes of TRIM.FaTE, the uptake factor is assumed to apply to bulk soil. Bulk soil includes all phases (*i.e.*, solid, liquid, gas) of the soil compartment.

The user may include the soil arthropods in the root-zone or surface soil compartments or both. In initial applications of TRIM.FaTE, soil arthropods were included in the surface soils.

The concentration of the chemical in the arthropods equals the concentration in the bulk soil multiplied by the arthropod/bulk-soil partition coefficient:

$$C_{Arth} = K_{Arth-S} \times C_S \quad (\text{Eq. 7-61})$$

where:

- $C_{Arth}$  = concentration in arthropods (g[chemical]/kg[arthropod wet wt]);  
 $K_{Arth-S}$  = arthropod/bulk-soil partition coefficient (kg[soil wet wt]/kg[arthropod wet wt]); and  
 $C_S$  = concentration of the chemical in bulk soil (g[chemical]/kg[soil wet wt]).

Thus,

$$\frac{dC_{Arth}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{AS}} \right] \times K_{Arth-S} \times C_S - \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{AS}} \right] \times C_{Arth} \quad (\text{Eq. 7-62})$$

where:

- $t_\alpha^{AS}$  = time (days) required for the arthropod/bulk-soil interaction to reach the fraction  $\alpha$  (default = 0.95) of the equilibrium value when  $C_S$  is approximately constant with time.

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

$$\frac{dN_{Arth}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{AS}} \right] \times \rho_{area\ Arth} \times A_S \times K_{Arth-S} \times \frac{N_S}{M_S} - \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{AS}} \right] \times N_{Arth} \quad (\text{Eq. 7-63})$$

where:

- $N_{Arth}$  = mass of chemical in arthropods (g[chemical]);  
 $\rho_{area\ Arth}$  = areal density of arthropod community in soil (kg[arthropod wet wt]/m<sup>2</sup>[soil]);  
 $A_S$  = area of soil compartment (m<sup>2</sup>);  
 $N_S$  = total mass of chemical in all phases of the soil compartment (g[chemical]);  
 and  
 $M_S$  = bulk mass of soil, including arthropods (kg[soil wet wt]).

Thus:

$$T_{S \rightarrow Arth} = \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{AS}} \right] \times \frac{M_{Arth}}{M_S} \times K_{Arth-S} \quad (\text{TF 7-19})$$

The corresponding algorithm for the release of chemical from the arthropods back to the soil is estimated as:

$$T_{Arth \rightarrow Sr} = \frac{-\ln(1 - \alpha)}{t_{\alpha}^{AS}} \quad (\text{TF 7-20})$$

where:

- $T_{S \rightarrow Arth}$  = transfer factor for transfer of chemical from soil to arthropods (/day);
- $T_{Arth \rightarrow S}$  = transfer factor for transfer of chemical from arthropods to soil (/day); and
- $M_{Arth}$  = total biomass of arthropods (kg[arthropods wet wt]) in the soil compartment; which  
 =  $\rho_{area_{Arth}}$  (kg[arthropods wet wt]/m<sup>2</sup>) ×  $A_S$  (m<sup>2</sup>[soil]).

The transfer factors TF 7-19 and TF 7-20 apply to both organic and inorganic chemicals in TRIM.FaTE at this time. The user must supply empirical data on the time to reach 95 percent (or other selected proportion) of the equilibrium value between the bulk soil and arthropods.

### 7.3.3 FLYING INSECTS

Flying insects are the food of insectivores, particularly aerial feeding insectivores such as tree swallows. In initial applications of TRIM.FaTE, these insects have been assumed to have emerged from benthic aquatic larvae living in the surface water bodies. As a consequence, the concentration of a chemical in flying insects was assumed to be equal to the concentration of that chemical in the benthic invertebrate compartment in the surface water body to which the aerial insectivore is linked in a given scenario (see Section 6.3).

### 7.3.4 TRANSFORMATIONS AND DEGRADATION

Transformations of organic chemicals into metabolic by-products that are no longer tracked in TRIM.FaTE are not included in the current TRIM.FaTE library for soil detritivores. Nor are metabolic transformations among chemicals containing the same core chemical (*e.g.*, transformation among mercury species) included in the current TRIM.FaTE library for soil detritivores. These processes are not included because no information could be found concerning chemical transformations and degradation in soil detritivores.

## 7.4 TERRESTRIAL WILDLIFE

Terrestrial wildlife, including mammals and birds, can 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 via contact with contaminants in surface water, soil, or air. The rate of contact with water and soil, however, generally is unknown. In addition, sorption to the skin surface is unknown, the rate of uptake into the organism is unknown, and the proportion absorbed through the dermis is relatively low compared with the proportion absorbed through the gastrointestinal tract or lungs. Thus, dermal uptake is not included in the current TRIM.FaTE library. 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.