

## 6. AQUATIC BIOTA ALGORITHMS

In this chapter, algorithms for transfers among aquatic biotic compartment types and other biotic or abiotic compartment types are presented. The aquatic biotic components include algae, macrophytes, benthic invertebrates, and several trophic groups of fish. The transfer factor algorithms are based on diffusive or advective transfer.

Most of the algorithms in this chapter apply to all air pollutants, although some are applicable only to mercury species and others that involve octanol-water partition coefficients are only applicable to nonionic organic chemicals. Some of the equations represent dynamic processes, while others are simple models for which a time-to-equilibrium is calculated. The text box on the next page and continued on the following pages provides a summary of the transfer-factor algorithms developed in this chapter and defines all parameters used in those algorithms. The derivation of chemical-specific algorithms and input parameters is presented in Appendix A for mercury and in Appendix B for polyaromatic hydrocarbons (PAHs).

The remainder of this chapter is organized in four sections. Section 6.1 briefly discusses the process of selecting aquatic compartments for use in a TRIM.FaTE scenario. Section 6.2 addresses algorithms associated with aquatic plants. Section 6.3 covers the algorithms for benthic infauna (animals living in sediment), which are represented in the current TRIM.FaTE library by a single compartment type. Section 6.4 develops and describes the transfer factor algorithms associated with the fish compartments.

### 6.1 AQUATIC BIOTA COMPARTMENT TYPES

The aquatic compartments in the current TRIM.FaTE library are listed in the text box to the right. Trophic level 1, the primary producers, are represented by algae<sup>1</sup> and macrophytes. The 2<sup>nd</sup> trophic level is represented by herbivorous fish and benthic infauna, while the 3<sup>rd</sup> and 4<sup>th</sup> levels are represented by two fish trophic levels (omnivores, that might feed on a combination of plant and animal material, and carnivores).

Use of aquatic biotic compartment types in a TRIM.FaTE scenario is described in Section 3.2.2 of TRIM.FaTE TSD Volume I. Additional guidance on how to select aquatic biota for compartments is provided in more detail in the TRIM.FaTE user guidance.

#### AQUATIC BIOTA COMPARTMENT TYPES

Algae (actually represented as a phase of the surface water)  
 Macrophyte  
 Water column herbivore (fish)  
 Water column omnivore (fish)  
 Water column carnivore (fish)  
 Benthic herbivore (invertebrate)  
 Benthic omnivore (fish)  
 Benthic carnivore (fish)

<sup>1</sup>Algae are represented as a phase of the surface water compartment than as a separate compartment.

Summary of Transfer Factors for Aquatic Biota in TRIM.FaTE

**AQUATIC PLANT AND BENTHIC INVERTEBRATE TRANSFERS**

Surface water to macrophytes (nonionic organic chemicals): F 6-1a

$$T_{SW \rightarrow Mp} = \frac{k_{Mp,acc-W} \times V_{Mp}}{V_{SW}} \times f_{ML} \quad \text{where } k_{Mp,acc-W} = \text{Eq. 6-3}$$

Macrophytes to surface water (nonionic organic chemicals): TF 6-2a

$$T_{Mp \rightarrow SW} = k_{Mp,dep-W} \quad \text{where } k_{Mp,dep-W} = \text{Eq. 6-4}$$

Surface water to macrophytes (other chemicals): TF 6-1b

$$T_{SW \rightarrow Mp} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}} \right] \times \frac{K_{Mp-W} \times V_{Mp} \times \rho_{Mp} \times 1}{V_{SW}} \times f_{ML}$$

Macrophytes to surface water (other chemicals): TF 6-2b

$$T_{Mp \rightarrow SW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}}$$

Sediment water (interstitial or overlying) to benthic invertebrates: TF 6-3a

$$T_{SedW \rightarrow BI} = \frac{n_{BI} \times m_{BI} \times k_{BI,acc-SedW}}{V_{Sed}} \times f_{ML}$$

Benthic invertebrates to sediment water (interstitial or overlying): TF 6-4a

$$T_{BI \rightarrow SedW} = k_{BI,dep-SedW}$$

Bulk sediment to benthic invertebrates: TF 6-3b

$$T_{Sed \rightarrow BI} = \frac{n_{BI} \times m_{BI} \times k_{BI,acc-Sed}}{V_{Sed} \times \rho_{Sed}}$$

Benthic invertebrates to bulk sediment: TF 6-4b

$$T_{BI \rightarrow Sed} = k_{BI,dep-Sed}$$

**FISH TRANSFERS**

Gill uptake by fish, bioenergetic-based kinetic model: TF 6-5

$$T_{SW \rightarrow fish}^{gill} = \frac{n_f \times m_f \times k_u}{V_{SW}} \times f_{ML} \times 1000$$

**Summary of Transfer Factors for Aquatic Biota in TRIM.FaTE (cont.)**

**FISH TRANSFERS (cont.)**

Ingestion with food by fish, bioenergetic-based kinetic model: TF 6-6

$$T_{diet \rightarrow fish} = \frac{n_f \times m_f}{n_{diet} \times m_{diet}} \times IN_D \times AE_D$$

Ingestion with algae by water column herbivorous fish, bioenergetic-based kinetic model: TF 6-7

$$T_{Algae \rightarrow Fwch} = \frac{n_{Fwch} \times m_{Fwch}}{(f_{MA} / m_{Algae})} \times IN_D \times P_{Algae} \times AE_D$$

Fish excretion to surface water via gills, feces, and urine, bioenergetic-based kinetic model: TF 6-8

$$T_{fish \rightarrow SW}^{excretion} = k_E$$

Ingestion with food by fish, time-to-equilibrium-based kinetic model : TF 6-9

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

Ingestion with algae by herbivorous water column fish, time-to-equilibrium-based kinetic model: TF 6-10

$$T_{Algae \rightarrow Fwch} = \frac{n_{Fwch} \times m_{Fwch}}{(f_{MA} / m_{Algae})} \times \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{FwchAl}} \right] \times K_{Fwch-Algae}$$

Transfer from fish compartment to diet compartment, time-to-equilibrium-based kinetic model: TF 6-11

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

**LIST OF SYMBOLS USED IN AQUATIC BIOTA TRANSFER FACTORS**

- $V_{Mp}$  = volume of the macrophyte compartment (L).
- $k_{Mp, acc-W}$  = bioaccumulation rate constant for macrophyte in water (/day).
- $V_{SW}$  = volume of the surface water compartment (L).
- $f_{ML}$  = fraction chemical mass dissolved divided by volume fraction of compartment that is liquid *i.e.*, water (unitless).
- $k_{Mp, dep-W}$  = depuration rate constant for macrophyte in water (/day).
- $n_{BI}$  = number of organisms comprising the benthic invertebrate compartment (unitless).
- $m_{BI}$  = average mass per individual benthic invertebrate (kg[invertebrate wet wt]/individual).
- $k_{BI, acc-SedW}$  = benthic invertebrate uptake rate constant from interstitial water in sediment compartment (/day).

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

**LIST OF SYMBOLS USED IN AQUATIC BIOTA TRANSFER FACTORS (cont.)**

$k_{Bl, dep-SedW}$	=	benthic invertebrate depuration rate constant to interstitial water in the sediment compartment (/day).
$k_{Bl, acc-Sed}$	=	benthic invertebrate uptake rate constant from bulk sediment (/day).
$\rho_{Sed}$	=	bulk density of sediment (kg[sediment wet wt]/m <sup>3</sup> [sediment]).
$k_{Bl, dep-Sed}$	=	benthic invertebrate depuration rate constant to bulk sediment (/day).
$n_f$	=	number of fish in fish compartment (unitless).
$m_f$	=	mass per individual fish (kg[fish wet wt]/individual).
$k_u$	=	fish gill uptake rate constant for chemical dissolved in water (/day).
$n^{diet}$	=	number of individuals in diet compartment (unitless).
$m^{diet}$	=	mass per individual in diet compartment (kg[organism]/individual).
$IN_D$	=	food (diet) ingestion rate for fish (kg[food wet wt]/kg[fish wet wt]-day).
$AE_D$	=	assimilation efficiency of chemical from the diet (unitless).
$f_{MA}$	=	fraction of chemical mass in surface water compartment that is in the algal phase (unitless).
$n_{Fwch}$	=	number of water column herbivorous fish in that fish compartment (unitless).
$m_{Fwch}$	=	mass per individual water column herbivorous (kg[fish wet wt]/individual).
$m_{Algae}$	=	total mass of algae in the surface water compartment (kg[algae wet wt]).
$\rho_{Algae}$	=	proportion of total fish diet that consists of algae on a wet-weight basis (unitless).
$k_E$	=	total chemical excretion rate constant (/day).
$\alpha$	=	proportion of equilibrium value reached (default = 0.95).
$t_\alpha$	=	time to reach 100× $\alpha$ percent of equilibrium value (days).
$K^{fish-diet}$	=	fish/diet partition coefficient (kg[diet wet wt]/kg[fish wet wt]).
$K_{Fwch-Algae}$	=	fish(water column herbivore)/algae partition coefficient (kg[algae wet wt]/kg[fish (water column herbivore) wet wt]).

## 6.2 AQUATIC PLANTS

Aquatic vegetation is included as two separate components, algae (modeled as a phase of surface water in the current TRIM.FaTE library) and macrophytes (modeled as a separate compartment). Water is assumed to be the primary source of chemical to both vegetation types, and thus, uptake from water is the only pathway for which algorithms are currently included in the TRIM.FaTE library.

### 6.2.1 ALGAE

As mentioned previously, algae are modeled as a phase of the surface water compartment.<sup>2</sup> For modeling transfer of dissolved chemical from surface water to algae for nonionic organic chemicals or chemicals for which empirically based partition coefficients are available, Equation 4-24 can be used. A more detailed approach has been developed for mercury (see section A.1.2 of Appendix A), and is available in the current TRIM.FaTE library.

<sup>2</sup>The surface water compartment consists of three phases: liquid (dissolved), solid (particles), and algae.

## 6.2.2 MACROPHYTES

Although rooted macrophytes can derive some nutrients and chemicals from sediments, direct uptake from water is the primary pathway (Ribeyre and Boudou 1994). Transfers of chemical between macrophytes and surface water are described in Section 6.2.2.1. Limited chemical transformation by macrophytes is described in Section 6.2.2.2.

### 6.2.2.1 Transfers Between Macrophytes and Surface Water

Net uptake of chemicals dissolved in surface water by aquatic macrophytes (only the dissolved portion of the chemical is available for bioaccumulation by macrophytes) is given by the following concentration-based equation for the chemical flux rate:

$$Flow_{Mp} = \left( k_{Mp, acc-W} \times V_{Mp} \times \rho_{Mp} \times C_{SW} \times f_{ML} \right) - \left( k_{Mp, dep-W} \times V_{Mp} \times \rho_{Mp} \times C_{Mp} \right) \quad (\text{Eq. 6-1})$$

where:

$Flow_{Mp}$	=	net flow of chemical into the macrophyte (g[chemical]/day);
$k_{Mp, acc-W}$	=	macrophyte bioaccumulation rate constant from water (/day);
$V_{Mp}$	=	volume of the macrophyte compartment (L[macrophyte]);
$\rho_{Mp}$	=	density of macrophyte (kg[macrophyte wet wt]/L[macrophyte]);
$C_{SW}$	=	total chemical concentration in surface water (g[chemical]/L[bulk water]);
$f_{ML}$	=	mass fraction of chemical dissolved in surface water (unitless) divided by the volume fraction of the surface water compartment that is liquid, <i>i.e.</i> , water, (unitless, value close to 1.0), <i>i.e.</i> , $Fraction\_Mass\_Dissolved / Volume\_Fraction\_Liquid$ (see Equations 2-72 and 2-80);
$k_{Mp, dep-W}$	=	macrophyte depuration rate constant to water (/day); and
$C_{Mp}$	=	chemical concentration in macrophyte (g[chemical]/L[macrophyte wet wt]).

Note that:

$$Volume\_Fraction\_Liquid = 1 - \left( Vf_{SSed} + Vf_{Algae} \right) \quad (\text{Eq. 6-2})$$

where:

$Vf_{SSed}$	=	volume fraction of the surface water compartment that is suspended solid sediment particles (unitless); and
$Vf_{Algae}$	=	volume fraction of the surface water compartment that is algae (unitless).

The rate constants  $k_{Mp, acc-SW}$  and  $k_{Mp, dep-SW}$  for nonionic organic chemicals are estimated using the following equations (Gobas et al. 1991):

$$\frac{1}{k_{Mp, acc-W}} = 0.0020 + \frac{500}{K_{ow}} \quad (\text{Eq. 6-3})$$

$$1/k_{Mp, dep-W} = 1.58 + 0.000015 K_{ow} \quad (\text{Eq. 6-4})$$

where:

$K_{ow}$  = the octanol-water partitioning coefficient for the chemical (g[chemical]/kg[octanol] per g[chemical]/L[water] = L[water]/kg[octanol] or kg[water]/kg[octanol]).

The rate constants  $k_{Mp, acc-W}$  and  $k_{Mp, dep-W}$  for chemicals other than nonionic organic pollutants were derived from bioconcentration factors using the time-to-equilibrium conversion (see Section 2.5) as follows:

$$k_{Mp, acc-W} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}} \right] \times K_{Mp-W} \quad (\text{Eq. 6-5})$$

$$k_{Mp, dep-W} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}} \quad (\text{Eq. 6-6})$$

where:

$t_{\alpha}^{MpW}$  = time (days) required to reach  $100 \times \alpha$  percent of the macrophyte/water interaction equilibrium when the concentration in water is approximately constant with time;  
 $\alpha$  = fraction of equilibrium value attained (default = 0.95) (unitless); and  
 $K_{Mp-W}$  = macrophyte/water partition coefficient (g[chemical]/kg[macrophyte] per g[chemical]/L[water] = L[water]/kg[macrophyte] or L[water]/L[macrophyte] assuming that the density of macrophytes equals that of water).

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

$$\frac{dN_{Mp}}{dt} = \left( k_{Mp, acc-W} \times f_{ML} \times V_{Mp} \times \rho_{Mp} \times \frac{N_{SW}}{V_{SW}} \right) - \left( k_{Mp, dep-W} \times N_{Mp} \right) \quad (\text{Eq. 6-7})$$

where:

$N_{Mp}$  = mass of chemical in the macrophyte (g[chemical]);  
 $V_{Mp}$  = volume of the macrophyte (L);  
 $N_{SW}$  = mass of chemical in the surface water compartment (g[chemical]); and  
 $V_{SW}$  = volume of the surface water compartment (L[water]).

In the current TRIM.FaTE library, the chemical transfer factors for nonionic organic chemicals from water to macrophytes and for macrophytes to water are given by:

$$T_{SW \rightarrow Mp} = \frac{k_{Mp, acc-W} \times V_{Mp} \times \rho_{Mp}}{V_{SW}} \times 1 \times f_{ML} \quad (\text{TF 6-1a})$$

$$= \frac{k_{Mp, acc-W} \times V_{Mp}}{V_{SW}} \times f_{ML}$$

and:

$$T_{Mp \rightarrow SW} = k_{Mp, dep-W} \quad (\text{TF 6-2a})$$

where:

- $T_{SW \rightarrow Mp}$  = transfer factor from surface water to macrophyte (/day);
- $\rho_{Mp}$  = wet density of macrophyte (kg[macrophyte wet wt]/L[macrophyte] equals same density as water, *i.e.*, 1 kg/L);
- 1 = unit conversion factor (L[water]/kg[water]); and
- $T_{Mp \rightarrow SW}$  = transfer factor from macrophyte to surface water (/day).

The macrophyte/surface water transfer factors for other chemicals, including mercury, use Equations 6-5 and 6-6 to replace the rate constants  $k_{Mp, acc-W}$  and  $k_{Mp, dep-W}$  in TFs 6-1a and 6-2a. Thus, the transfer factors for other chemicals, including mercury, are:

$$T_{SW \rightarrow Mp} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}} \right] \times \frac{K_{Mp-W} \times V_{Mp} \times \rho_{Mp} \times 1}{V_{SW}} \times f_{ML} \quad (\text{TF 6-1b})$$

$$T_{Mp \rightarrow SW} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{MpW}} \quad (\text{TF 6-2b})$$

### 6.2.2.2 Transformation and Degradation

Although the TRIM.FaTE library supports macrophyte transformation of mercury species (see below), it does not currently accommodate biodegradation of any chemicals (*i.e.*, transformation into chemicals that are not tracked in TRIM.FaTE) in macrophytes.

Biotransformation of elemental to divalent mercury in macrophytes is included in the TRIM.FaTE library and is described as a rapid (almost instantaneous) first-order rate constant (*i.e.*,  $10^6$  to  $10^9$ ). This is assumed because elemental mercury can be taken up by macrophytes but is not accumulated in macrophytes in the elemental form (*i.e.*, data showing Hg(0) in

macrophytes were not found). Because data demonstrating methylation of divalent mercury or demethylation of methylmercury in macrophytes were not found, those transformations are not included for macrophytes in the current TRIM.FaTE library.

### 6.3 BENTHIC INFAUNA

The benthic community is typically comprised of many different classes and species of organisms, including those from the phyla Mollusca (*e.g.*, clams and snails), Annelida (*e.g.*, oligochaete worms), and Arthropoda (*e.g.*, crustaceans and larval insects). Several trophic levels are represented within this community. That is true even within some families of insects, such as the mayflies and chironomids. In the current TRIM.FaTE library, benthic infauna are considered to represent the lowest heterotrophic level of the benthic food chain, which includes those species that feed on algae and/or detritus, which is assumed to be derived largely from plant material.

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

Algorithms describing the general case for uptake of chemicals by benthic invertebrates from sediment interstitial (*i.e.*, pore) water are presented in Section 6.3.1. The chemicals to which these algorithms apply are those for which the measured partition coefficient between sediments and benthic invertebrates is based on the chemical concentration in sediment water only, not bulk sediment. An algorithm specific to PAHs that is available in the TRIM.FaTE library is described in Appendix B. Algorithms for chemicals for which the measured partition coefficient is based on bulk sediment rather than sediment pore water (*e.g.*, mercury) are presented in Section 6.3.2.

#### 6.3.1 TRANSFERS BETWEEN SEDIMENT INTERSTITIAL WATER AND BENTHIC INVERTEBRATES

Uptake of chemical by benthic invertebrates from sediment pore water is given by the following equation:

$$\frac{dC_{BI}}{dt} = (k_{BI, acc-W} \times C_{WD}) - (k_{BI, dep-W} \times C_{BI}) \quad (\text{Eq. 6-8})$$



where:

- $C_{BI}$  = chemical concentration in benthic invertebrates (g[chemical]/kg[invertebrates wet wt]);
- $C_{WD}$  = chemical concentration in liquid phase of sediment (*i.e.*, sediment pore water) (g[chemical dissolved]/L[water]);
- $k_{BI, acc-W}$  = uptake rate constant for chemical from water (/day); and
- $k_{BI, dep-W}$  = depuration rate constant for chemical to water (/day).

The rate constants  $k_{BI, acc-W}$  and  $k_{BI, dep-W}$  are derived from the bioconcentration factors using the time-to-equilibrium conversion described in Section 2.5:

$$k_{BI, acc-W} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{BIW}} \right] \times K_{BI-W} \quad (\text{Eq. 6-9})$$

$$k_{BI, dep-W} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{BIW}} \quad (\text{Eq. 6-10})$$

where:

- $t_{\alpha}^{BIW}$  = time (days) required to reach 100×α percent of the benthic invertebrate/water interaction equilibrium when the concentration in water is approximately constant with time;
- $\alpha$  = fraction of equilibrium attained (default = 0.95) (unitless); and
- $K_{BI-W}$  = benthic invertebrate/sediment pore water partition coefficient (L[water]/kg[invertebrates wet wt]).

Converting to mass units (N) yields the following equation:

$$\frac{dN_{BI}}{dt} = \left( n_{BI} \times m_{BI} \times k_{BI, acc-W} \times \frac{N_{WD}}{V_W} \right) - \left( k_{BI, dep-W} \times N_{BI} \right) \quad (\text{Eq. 6-11})$$

where:

- $N_{BI}$  = mass of chemical in organisms comprising the benthic invertebrate compartment (g[chemical]);
- $n_{BI}$  = number of organisms comprising the benthic invertebrate compartment (unitless);
- $m_{BI}$  = average mass per individual benthic invertebrate (kg[invertebrates wet wt]/individual);
- $N_{WD}$  = mass of dissolved chemical in sediment compartment (g[chemical dissolved]);
- $V_W$  = volume of water in the sediment compartment (L) =  $V_{Sed} \times \theta$ , where:
  - $V_{Sed}$  = volume of sediment compartment (L); and
  - $\theta$  = *Volume\_Fraction\_Liquid* (water) (unitless); *i.e.*:

=  $\phi$ , the total porosity of the sediment compartment (unitless) (see Eq. 2-39; volume fraction gas assumed to be zero for sediments).

It is also true that:

$$N_{WD} = N_{Sed} \times Fraction\_Mass\_Dissolved \quad (\text{Eq. 6-12})$$

where:

$N_{Sed}$  = total mass of chemical in sediment compartment (g[chemical]); and  
 $Fraction\_Mass\_Dissolved$  = fraction of chemical mass in sediment compartment that is dissolved in the water phase (unitless).

Thus, the transfer factors for water (interstitial or immediately overlying) to benthic invertebrates and for benthic invertebrates to water are given by:

$$\begin{aligned} T_{SedW \rightarrow BI} &= \frac{n_{BI} \times m_{BI} \times k_{BI, acc-SedW}}{V_{Sed}} \times \frac{Fraction\_Mass\_Dissolved}{\theta} \\ &= \frac{n_{BI} \times m_{BI} \times k_{BI, acc-SedW}}{V_{Sed}} \times f_{ML} \end{aligned} \quad (\text{TF 6-3a})$$

$$T_{BI \rightarrow SedW} = k_{BI, dep-W} \quad (\text{TF 6-4a})$$

where:

$T_{SedW \rightarrow BI}$  = transfer factor for chemical dissolved in sediment pore water to benthic invertebrate (/day);  
 $T_{BI \rightarrow SedW}$  = transfer factor for chemical from benthic invertebrate to the water phase of the sediment compartment (/day); and  
 $f_{ML}$  = mass fraction of chemical dissolved in sediment pore water (unitless) divided by the volume fraction of the surface water compartment that is liquid, *i.e.*, water (unitless); which  
 =  $Fraction\_Mass\_Dissolved/\theta$ , which  
 =  $Fraction\_Mass\_Dissolved/Volume\_Fraction\_Liquid$  (see Equation 2-80).

The designation of these two transfer factors as “a” indicates that they are to be used together for chemicals for which the partitioning coefficient applies to the water phase only of the sediment compartment (*e.g.*, nonionic organic chemicals). The alternative pair of transfer factor algorithms designated as TF 6-3b and TF 6-4b are for use with partitioning coefficients derived from bulk sediments (*e.g.*, for metals), as described in Section 6.3.2.

Note that for organic chemicals categorized as PAHs, specific algorithms for transfers between benthic invertebrates and sediments have been developed as described in Appendix B.

### 6.3.2 TRANSFERS BETWEEN BULK SEDIMENT AND BENTHIC INVERTEBRATES

Uptake of chemicals by benthic invertebrates from bulk sediment (e.g., mercury) is given by the following equation:

$$\frac{dC_{BI}}{dt} = \left( k_{BI, acc-Sed} \times C_{Sed} \right) - \left( k_{BI, dep-Sed} \times C_{BI} \right) \quad (\text{Eq. 6-13})$$

where:

- $C_{BI}$  = chemical concentration in benthic invertebrates (g[chemical]/kg[invertebrates wet wt]);
- $C_{Sed}$  = chemical concentration in bulk sediments (g[chemical]/kg[sediment wet wt]);
- $k_{BI, acc-Sed}$  = benthic invertebrate uptake rate constant from sediment (/day); and
- $k_{BI, dep-Sed}$  = benthic invertebrate depuration rate constant to sediment (/day).

The rate constants  $k_{BI, acc-Sed}$  and  $k_{BI, dep-Sed}$  are derived from bioconcentration factors using the time-to-equilibrium conversion (see Section 2.5):

$$k_{BI, acc-Sed} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{BISed}} \right] \times K_{BI-Sed} \quad (\text{Eq. 6-14})$$

$$k_{BI, dep-Sed} = \frac{-\ln(1-\alpha)}{t_{\alpha}^{BISed}} \quad (\text{Eq. 6-15})$$

where:

- $K_{BI-Sed}$  = benthic invertebrate/bulk sediment partition coefficient (kg[sediment wet wt]/kg[invertebrates wet wt]);
- $t_{\alpha}^{BISed}$  = time (days) required to reach  $100 \times \alpha$  percent of the benthic invertebrate/bulk sediment interaction equilibrium value when the concentration in water is approximately constant with time; and
- $\alpha$  = fraction of equilibrium attained (default = 0.95) (unitless).

Converting to mass units (N) yields the following equation:

$$\frac{dN_{BI}}{dt} = \left( n_{BI} \times m_{BI} \times k_{BI, acc-Sed} \times \frac{N_{Sed}}{V_{Sed} \times \rho_{Sed}} \right) - \left( k_{BI, dep-Sed} \times N_{BI} \right) \quad (\text{Eq. 6-16})$$

where:

- $N_{BI}$  = mass of chemical in organisms comprising the benthic invertebrate compartment (g[chemical]);

$n_{BI}$	=	number of organisms comprising the benthic invertebrate compartment (unitless);
$m_{BI}$	=	average mass per individual benthic invertebrate (kg[invertebrate wet wt]/individual);
$N_{Sed}$	=	total mass of chemical in sediment compartment (g[chemical]);
$V_{Sed}$	=	volume of sediment compartment (L[sediment]); and
$\rho_{Sed}$	=	bulk density of sediment (kg[sediment wet wt]/L[sediment]).

Thus, the transfer factors for bulk sediment to benthic invertebrates and for benthic invertebrates to bulk sediment are given by:

$$T_{Sed \rightarrow BI} = \frac{n_{BI} \times m_{BI} \times k_{BI, acc-Sed}}{V_{Sed} \times \rho_{Sed}} \quad (\text{TF 6-3b})$$

$$T_{BI \rightarrow Sed} = k_{BI, dep-Sed} \quad (\text{TF 6-4b})$$

where:

$T_{Sed \rightarrow BI}$	=	transfer factor for chemical in bulk sediment to benthic invertebrates (/day); and
$T_{BI \rightarrow Sed}$	=	transfer factor for chemical in benthic invertebrates to the bulk sediment (/day).

For a given chemical, the user would specify either algorithms TF 6-3a and TF 6-4a (or, for PAHs, algorithms TF B-1 and TF B-2 from Appendix B) or algorithms TF 6-3b and TF 6-4b, but not both. The most appropriate algorithm depends on whether the available data on the partition coefficients were measured with respect to water only (*e.g.*, sediment pore water) or with respect to bulk sediments.

### 6.3.3 TRANSFORMATIONS AND DEGRADATION

Metabolic transformations of chemicals into different compounds that are tracked in TRIM.FaTE (*e.g.*, mercury species) can be included for biotic compartments. However, biotransformation from one chemical to another that is tracked in TRIM.FaTE is not included for benthic invertebrates in the current TRIM.FaTE library. Appropriate transformation rate data were not identified during initial applications of the model.

Transformations of chemicals into compounds that will no longer be tracked in TRIM.FaTE (*e.g.*, non-toxic degradation products) are called general degradation processes. In TRIM.FaTE, the metabolic degradation of chemicals is determined from the user-input value for the half-life of the chemical in the benthic invertebrate compartment. The algorithm relating the general degradation rate constant to the chemical half-life in a compartment is presented in Chapter 2 (Equation 2-64), and the transfer factor is TF 2-1. The metabolic half-life reflects metabolic degradation only, and not excretion or elimination of the parent chemical to the sediment compartment.

## 6.4 FISH

The current TRIM.FaTE library includes two alternate approaches to estimate chemical uptake by fish: a bioenergetic-based kinetic model or a time-to-equilibrium-based kinetic model. Each model has strengths and weaknesses, which may weigh differently for different chemicals. The bioenergetic-based model is ideal for explicitly incorporating multiple exposure pathways, but finding data to assign values to some of the fish parameters may be difficult (*e.g.*, gill and fecal elimination rates). Data to set parameter values for the time-to-equilibrium-based kinetic model are generally available, but multiple pathways cannot be incorporated explicitly at the same time and the time required to reach equilibrium may be uncertain for strongly bioaccumulated chemicals. In applications to date, the bioenergetic model has been parameterized for PAHs and mercury, whereas the time-to-equilibrium model is parameterized for mercury only.

In comparison to the time-to-equilibrium model, the bioenergetic model provides the user greater flexibility in the specification of the fish compartments and associated diets for a given scenario. For example, the user may employ the five fish compartments currently available in the TRIM.FaTE library, assigning their diets as deemed appropriate to the modeling scenario, or the user may develop a different “set” of trophic compartments and diets to represent the fish community in a particular water body. For each fish compartment, the user can assign more than one diet item (*e.g.*, 20 percent of the diet consists of benthic invertebrates, 70 percent is benthic omnivorous fish, and 10 percent consists of omnivorous fish in the water column), creating a web-like set of trophic relationships, with some fish feeding from more than one trophic level or microenvironment. This approach is essentially the same as that used to model exposure via food ingestion for terrestrial wildlife (see Section 7.4). This approach is described in Subsection 6.4.1 below.

Another approach which has been used in initial TRIM.FaTE applications with both of the two bioaccumulation models, but which is particularly suited to the time-to-equilibrium model (which was developed to use input derived from measured chemical concentrations in fish at different trophic levels in the same water body) involves the adherence to a strict stepwise trophic structure with separate benthic and water column derived food chains. In this design, the existing five fish compartment types are presented as two separate food chains, one for water-column organisms and one for benthic organisms (see the conceptual model in Figure 4-1 of TSD Volume I), with each fish compartment feeding on only the compartment below it in the food chain. That is, water-column carnivores would consume only water-column omnivores, water-column omnivores consume only water-column herbivores (planktivores), water-column herbivores consume only algae (phytoplankton), benthic carnivores consume only benthic omnivores, and benthic omnivores consume only benthic invertebrates. In this type of design, both the benthic invertebrate (*i.e.*, feeding on algae and detritus, which is derived largely from plant material) and the herbivore compartments might be considered equivalent to trophic-level-2 organisms of other models (*e.g.*, Gobas 1993, Ambrose *et al.* 1995). The “omnivore” compartments might be considered equivalent to the trophic-level-3 fish, and the carnivore compartments equivalent to the trophic-level-4 fish of the other models.

In initial TRIM.FaTE applications, a littoral food web (*i.e.*, including linkages between water-column and benthic food chains) was created from the linear benthic and pelagic food

chain design described above by representing individual species as a combination of multiple compartments. For example, a given carnivore (*e.g.*, largemouth bass) may consume omnivores from both the water column and the benthos (*e.g.*, consume 50 percent water-column omnivores and 50 percent benthic omnivores). This diet can be accounted for in the simulation by assigning 50 percent of the bass biomass to each food chain (*i.e.*, 50 percent to the water-column carnivore and 50 percent to benthic carnivore compartments). The mass of fish to be assigned to each trophic level within each food chain may thus be derived from studies of the biomass of individual species in various aquatic ecosystems and studies of feeding strategies of those species. This method is described in detail in Subsection 6.4.2 below. When this approach is employed, interpretation of the model results with regard to individual species requires revisiting these data and calculations.

Regardless of the bioaccumulation model or food chain design employed, the entire fish biomass in the surface water body being modeled should be distributed among the modeled compartments. This will facilitate “realistic” partitioning of the modeled chemical within the biotic and abiotic compartments of the aquatic ecosystem. In addition, the relative distribution of biomass among the different fish compartment types should be as realistic as possible.

### 6.4.1 BIOENERGETIC-BASED KINETIC MODEL

This section describes the bioenergetic-based kinetic model for fish developed for use in TRIM.FaTE. First, the development of the full model is described (Section 6.4.1.1). Next, specific adaptations of the general model for nonionic organic chemicals (Section 6.4.1.2) and mercury (Section 6.4.1.3) are described. Then the equations for the transfer factor algorithms in the TRIM.FaTE library are presented (Section 6.4.1.4). Section 6.4.1.5 describes the TRIM.FaTE algorithms for chemical transformation and degradation by fish.

#### 6.4.1.1 General Model

The following model for estimating chemical concentrations in fish is based on the model developed by Thomann (1989) and used in the derivation of the transfer factors associated with the fish compartment type in the bioenergetic model:

$$\frac{dC_f}{dt} = (U_{gill} \times C_{SWD}) + (AE_D \times \sum p_i \times C_{D,i}) - (E_{met} + E_{eg} + E_{ef} + E_G) \times C_f \quad (\text{Eq. 6-17})$$

where:

$C_f$	=	chemical concentration in fish (g[chemical]/kg[fish wet wt]);
$U_{gill}$	=	uptake from water via the gills (L[water]/kg[fish wet wt]-day);
$C_{SWD}$	=	dissolved chemical concentration in surface water (g[chemical dissolved]/L[water]);
$AE_D$	=	chemical assimilation (absorption) efficiency from diet (unitless);
$p_i$	=	proportion of the diet consisting of diet item <i>i</i> (unitless);
$C_{D,i}$	=	chemical concentration in diet item <i>i</i> (g[chemical]/kg[food <i>i</i> ]);
$E_{met}$	=	metabolic degradation or transformation of the chemical (/day);

$E_{eg}$  = excretion of chemical in the fish (*i.e.*, absorbed chemical) via the gills (/day);  
 $E_{ef}$  = excretion of chemical in the fish via feces and urine (/day); and  
 $E_G$  = dilution of chemical concentration from growth (/day).

Assuming first-order rate constants to express both uptake and elimination, the following relationships hold:

$U_{gill} = k_U$  = rate constant for uptake from water via the gills (L[water]/kg[fish wet wt]-day);  
 $E_{met} = k_{met}$  = rate constant for metabolic transformation of chemical (/day);  
 $E_{eg} = k_{eg}$  = rate constant for excretion of chemical via the gills (/day);  
 $E_{ef} = k_{ef}$  = rate constant for excretion of chemical via feces and urine (/day); and  
 $E_G = k_G$  = rate constant for dilution of chemical concentration from growth (/day).

This comprehensive model can be simplified consistent with the approach used in Thomann (1989) to:

$$\frac{dC_f}{dt} = (k_U \times C_{SWD}) + (AE_D \times \sum p_i \times C_{D,i}) - (k_{ET} + k_G) \times C_f \quad (\text{Eq. 6-18})$$

where:

$k_{ET}$  = rate constant for total elimination via all excretory systems and via metabolic degradation to chemicals no longer tracked (/day);  
 =  $k_{eg} + k_{ef} + k_{met}$  (in Thomann 1989).

This simplification is appropriate in TRIM.FaTE for chemicals that are not lost via metabolic degradation, only transformed among different species or compounds with a conserved element (*e.g.*, mercury) that is tracked individually in TRIM.FaTE. For those chemicals,  $k_{met} = 0$ ; all metabolic reactions are tracked via transformations between species (*e.g.*, between elemental and divalent mercury and methylmercury).

For organic chemicals, that are metabolized to chemicals that are currently not tracked in TRIM.FaTE, such as PAHs, loss of chemical from the modeling system via metabolic degradation should be tracked separately from elimination of the parent chemical from fish back into the surface water compartment. Loss of chemical from the modeling system is simulated in TRIM.FaTE by transfers to a compartment sink, in this case, the fish degradation sink, that accumulates the mass of chemical lost from the system via this pathway. Thus, for use in TRIM.FaTE with organic chemicals that can be degraded, the “elimination” rate constant  $k_{ET}$  in Equation 6-18 would need to be separated into  $k_E$ , for the excretory pathways for transfer of the chemical back to surface water (*i.e.*,  $k_{eg} + k_{ef}$ ), and  $k_{met}$ , for loss (transfer) of chemical to the fish degradation sink.

It is important to note that the equations in their present form exclude dermal uptake as a significant exposure route. Also, growth dilution ( $k_G$ ) is not included in TRIM.FaTE, because a

constant biomass for the entire fish population is assumed and growth of individual fish is not included in the current TRIM.FaTE library.

The bioenergetic-based kinetic model generally is used to estimate concentrations in individual fish of a species. Following is the derivation of the fish model for the entire fish population. Initially the model is derived for a population of two fish and then generalized for the case of  $n$  fish, where  $n$  is the fish population size. Thus, for two fish with concentrations  $C_{f1}$ , and  $C_{f2}$ , Equation 6-18 can be rewritten as:

$$\frac{dC_{f1}}{dt} = (k_{U1} \times C_{SWD}) + (AE_D \times \sum p_i \times C_{Di}) - (k_{ET1} \times C_{f1}) \quad (\text{Eq. 6-19})$$

$$\frac{dC_{f2}}{dt} = (k_{U2} \times C_{SWD}) + (AE_D \times \sum p_i \times C_{Di}) - (k_{ET2} \times C_{f2}) \quad (\text{Eq. 6-20})$$

To convert the concentrations to masses, it is assumed that:

$$C_{SWD} = \frac{N_{WD}}{V_{SW} \times \theta} \quad (\text{Eq. 6-21})$$

$$C_{f1} = \frac{N_1}{m_1} \quad (\text{Eq. 6-22})$$

$$C_{f2} = \frac{N_2}{m_2} \quad (\text{Eq. 6-23})$$

where:

$C_{SWD}$	=	concentration of dissolved chemical in surface water (g[chemical dissolved]/L[water]);
$N_{WD}$	=	mass of chemical dissolved in water (g[chemical dissolved]);
$V_{SW}$	=	volume of surface water compartment (L);
$\theta$	=	volume fraction of surface water compartment that is water (unitless, $\approx 1.0$ );
$m_1$	=	mass of fish 1 (kg[fish wet wt]);
$m_2$	=	mass of fish 2 (kg[fish wet wt]);
$N_1$	=	mass of chemical in fish 1 (g[chemical]); and
$N_2$	=	mass of chemical in fish 2 (g[chemical]).

Note that:

$$\theta = 1 - (Vf_{SSed} + Vf_{Algae}) \quad (\text{Same as Eq. 6-2})$$

where:



$Vf_{SSed}$  = volume fraction of the surface water compartment that is suspended sediment particles (unitless); and  
 $Vf_{Algae}$  = volume fraction of the surface water compartment that is algae (unitless).

Substituting yields:

$$\frac{d(N_1/m_1)}{dt} = k_{U1} \times \frac{N_{WD}}{V_{SW} \times \theta} + (AE_D \times \sum p_i \times C_{Di}) - k_{ET1} \times \frac{N_1}{m_1} \quad (\text{Eq. 6-24})$$

$$\frac{d(N_2/m_2)}{dt} = k_{U2} \times \frac{N_{WD}}{V_{SW} \times \theta} + (AE_D \times \sum p_i \times C_{Di}) - k_{ET2} \times \frac{N_2}{m_2} \quad (\text{Eq. 6-25})$$

Adding Equations 6-24 and 6-25 yields the mass transfer equations for the total fish compartment type, as follows:

$$\begin{aligned} \frac{d(N_1/m_1 + N_2/m_2)}{dt} &= (k_{U1} + k_{U2}) \times \frac{N_{WD}}{V_{SW} \times \theta} + 2 \times (AE_D \times \sum p_i \times C_{Di}) \\ &\quad - \left( k_{ET1} \times \frac{N_1}{m_1} + k_{ET2} \times \frac{N_2}{m_2} \right) \end{aligned} \quad (\text{Eq. 6-26})$$

Making the simplifying assumptions that individual fish mass is represented by a population average  $m_f$  ( $m_1 = m_2 = m_f$ ), and that  $k_{U1} = k_{U2} = k_U$ , and  $k_{ET1} = k_{ET2} = k_{ET}$ , yields:

$$\frac{d\left(\frac{N_1 + N_2}{m_f}\right)}{dt} = 2 \times \left( k_U \times \frac{N_{WD}}{V_{SW} \times \theta} + (AE_D \times \sum p_i \times C_{Di}) \right) - k_{ET} \times \left( \frac{N_1 + N_2}{m_f} \right) \quad (\text{Eq. 6-27})$$

This equation can be generalized from 2 to  $n_f$  fish, with  $N_f (= N_1 + N_2)$  being the total chemical mass in the fish compartment type, to yield the following generalized chemical mass-transfer equation for a fish compartment type:

$$\frac{dN_f}{dt} = \left( n_f \times m_f \times k_U \times \frac{N_{WD}}{V_{SW}} \times f_{ML} \right) + \left( n_f \times m_f \times IN_D \times AE_D \times \frac{N_{diet}}{V_{diet}} \right) - (k_{ET} \times N_f) \quad (\text{Eq. 6-28})$$

where:

$$N_{WD} = N_{SW} \times \text{Fraction\_Mass\_Dissolved} \quad (\text{Eq. 6-29})$$

$$f_{ML} = \frac{\text{Fraction\_Mass\_Dissolved}}{\text{Volume\_Fraction\_Liquid}} \quad (\text{Eq. 6-30})$$

and:

- $n_f$  = total number of fish in surface water compartment;  
 $IN_D$  = food (diet) ingestion rate constant (kg[food wet wt]/kg[fish wet wt]-day);  
 $AE_D$  = assimilation (absorption) efficiency of chemical from the diet (unitless);  
 $N_{SW}$  = total chemical inventory in the surface water compartment (both dissolved and sorbed to suspended sediment particles) (g[chemical]);  
 $f_{ML}$  = fraction of chemical mass in surface water compartment that is dissolved in water divided by the volume fraction of the surface water compartment that is liquid, *i.e.*, water (unitless); and  
 $\theta$  = *Volume\_Fraction\_Liquid* (unitless).

Note that an  $AE_D$  of less than 1.0 implies that the fraction of chemical not absorbed was effectively left in the diet compartment(s). A future enhancement of TRIM.FaTE might be to transfer the unassimilated chemical to the suspended sediment phase of the surface water compartment or directly to the sediment bed to simulate the fecal elimination of unabsorbed chemical implied by the  $AE_D$ .

The food ingestion rate ( $IN_D$ ) of an individual fish is given by the following bioenergetic model presented in Gobas (1993):

$$IN_D = 0.022 \times m_f^{0.85} \times e^{(0.06 \times T)} \quad (\text{Eq. 6-31})$$

where:

- $m_f$  = mass of the fish (kg); and  
 $T$  = temperature (°C).

To illustrate how the dietary transfer calculation would differ between the different fish trophic groups, an equation for a benthic omnivore ( $Fbo$  = fish, benthic omnivore) is illustrated below.

$$\begin{aligned}
 \frac{dN_{Fbo}}{dt} = & \left( n_{Fbo} \times m_{Fbo} \times k_{Fbo} \times \frac{N_W}{V_W} \times f_{ML} \right) \\
 & + \left( n_{Fbo} \times m_{Fbo} \times IN_D \times AE_D \times \left( p_{Mp} \times \frac{N_{Mp}}{m_{Mp}} + p_{Fh} \times \frac{N_{Fh}}{m_{Fh}} + p_{BI} \times \frac{N_{BI}}{m_{BI}} \right) \right) \quad (\text{Eq. 6-32}) \\
 & - \left( k_{ET} \times N_{Fbo} \right)
 \end{aligned}$$

where:

- $n_{Fbo}$  = number of benthic fish omnivores in the surface water compartment (unitless);  
 $m_{Fbo}$  = mass per individual benthic omnivore fish (kg[fish wet wt]/individual);

$N_{Fbo}$	=	chemical inventory in the benthic omnivore fish compartment (g[chemical]);
$P_{Mp}, P_{Fh}, P_{BI}$	=	proportion of the benthic omnivore fish's diet that is comprised of macrophytes, herbivorous fish, and benthic invertebrates, respectively (unitless);
$N_{Mp}, N_{Fh}, N_{BI}$	=	chemical inventory in the macrophyte, herbivorous fish, and benthic invertebrate compartments, respectively (g[chemical]); and
$m_{Mp}, m_{Fh}, m_{BI}$	=	total biomass of the macrophyte, herbivorous fish, and benthic invertebrate compartments, respectively (kg[biomass wet wt]).

Implicit in the previous equation is the assumption that the mass of an individual fish is constant over the time of the simulation. The dilution-due-to-growth factor ( $k_G$ ) is not included in the equation because  $k_G$  is based on concentrations, while the mass transfer equations are in mass units.

### 6.4.1.2 Nonionic Organic Chemicals

For nonionic organic chemicals (e.g., PAHs), the chemical uptake rate constant  $k_U$  for fish gills is estimated using the following formula in TRIM.FaTE if measured values are not available:

$$k_U = 10^3 \times \left( \frac{m_f^{-\gamma_{ASF}}}{f_{lipid}} \right) \times AE_g \quad (\text{Eq. 6-33})$$

where:

$k_U$	=	chemical uptake rate constant (L[water]/kg[fish wet wt]-day);
$m_f$	=	fish body mass (kg[fish wet wt]);
$\gamma_{ASF}$	=	allometric scaling factor (e.g., 0.2 (Thomann 1989)) (unitless);
$f_{lipid}$	=	fraction lipid (kg[lipid]/kg[fish wet wt]); and
$AE_g$	=	chemical assimilation (absorption) efficiency of the gills (unitless).

There is an apparent increase in assimilation efficiency for smaller organisms; therefore, organisms have been divided into two weight groups: 10 to 100 g (wet) and more than 100 g (wet) weight (Thomann 1989). The chemical assimilation efficiency of the gills ( $AE_g$ ) can be approximated for these two size classes of organisms as follows. For smaller organisms, the following equations should be used to estimate  $AE_g$ , where  $K_{ow}$  is the octanol/water partition coefficient (g[chemical]/kg[octanol] per g[chemical]/L[water] = L[water]/kg[octanol]):

For chemicals with $\log(K_{ow}) = 2.00-4.99$ ,	$\log(AE_g) = -2.6 + 0.5 \log(K_{ow})$ ;
For chemicals with $\log(K_{ow}) = 5.00-5.99$ ,	$AE_g = 0.8$ ; and
For chemicals with $\log(K_{ow}) = 6.00-10$ ,	$\log(AE_g) = 2.9 - 0.5 \log(K_{ow})$ .

For larger organisms, the following equations should be used to estimate  $AE_g$ :

$$\begin{aligned} \text{For chemicals with } \log(K_{ow}) = 2.00-2.99, & \quad \log(AE_g) = -1.5 + 0.4 \log(K_{ow}); \\ \text{For chemicals with } \log(K_{ow}) = 3.00-5.99, & \quad AE_g = 0.5; \text{ and} \\ \text{For chemicals with } \log(K_{ow}) = 6.00-10, & \quad \log(AE_g) = 1.2 - 0.25 \log(K_{ow}). \end{aligned}$$

There is a similar relationship between chemical assimilation efficiency from dietary items ( $AE_D$ ) and  $K_{ow}$  (Thomann 1989). However, there does not appear to be an increase in the dietary assimilation efficiency for smaller organisms; therefore, the  $AE_D$  can be approximated for all size classes of organisms as follows:

$$\begin{aligned} \text{For chemicals with } \log(K_{ow}) = 2.00-4.99, & \quad \log(AE_D) = -2.6 + 0.5 \log(K_{ow}); \\ \text{For chemicals with } \log(K_{ow}) = 5.00-5.99, & \quad AE_D = 0.8; \text{ and} \\ \text{For chemicals with } \log(K_{ow}) = 6.00-10, & \quad \log(AE_D) = 2.9 - 0.5 \log(K_{ow}). \end{aligned}$$

Note that this is the same set of equations used to estimate  $AE_g$  for smaller organisms.

Thomann (1989) gives the total excretion rate constant ( $k_{ET}$ ) for nonionic organic chemicals using the following equation:

$$k_{ET} = \frac{k_U}{K_{ow}} \quad (\text{Eq. 6-34})$$

Note that in a subsequent publication, Thomann *et al.* (1992a,b) state that  $k_{ET}$  accounts for elimination via the gills and “other losses...for example, fecal loss and metabolism”. However, those publications (1) indicate that the simplified equation that includes a term for elimination via the gills only is approximately representative of observed excretion data for fish and (2) provide no data or formulas for estimating the values of the other types of losses (which we interpret as meaning fecal loss of biliary secretions and excretion in urine). We interpret the rate constant  $k_{ET}$  in Equation 6-34 as not including losses due to metabolism, because  $k_{ET}$  is set directly proportional to the gill uptake rate divided by  $K_{ow}$ . Therefore, the simplified Equation 6-35 from Thomann (1989) is used here to represent the total excretion rate constant for the absorbed chemical,  $k_E$ , *excluding* losses due to metabolism.

### 6.4.1.3 Mercury

For mercury (all forms), uptake from water is excluded from the transfer equations because accumulation in fish is primarily as methylmercury, for which uptake from water is negligible (Trudel and Rasmussen 1997).

The mercury excretion rate constant ( $k_E$ ) (*i.e.*, transfer of absorbed mercury back to surface water) is given by a bioenergetic model from Trudel and Rasmussen (1997), as described in Appendix A, Section A.1.3. Trudel and Rasmussen (1997) based the excretion rate on the clearance of methylmercury only, because greater than 95 percent of mercury in fish is methylmercury, and the elimination of methylmercury is much slower than that of inorganic mercury (*i.e.*, the overall rate is dominated by the elimination of methylmercury).

### 6.4.1.4 Bioenergetic Model Transfer Factors

Using the bioenergetic model, the transfer factor for uptake of dissolved nonionic organic chemicals from a surface water compartment via gill uptake for a fish compartment (/day) can be expressed as:

$$T_{SW \rightarrow fish}^{gill} = \frac{n_f \times m_f \times k_U}{V_{SW}} \times f_{ML} \times 1000 \quad (\text{TF 6-5})$$

where:

- $n_f$  = total number of fish in surface water compartment;
- $m_f$  = mass per individual fish (kg[fish wet wt]);
- $k_U$  = fish gill uptake rate constant for chemical dissolved in water (/day);
- $V_{SW}$  = volume of the surface water compartment (L[water]);
- $f_{ML}$  = fraction of chemical mass in surface water compartment that is dissolved in water divided by the volume fraction of the surface water compartment that is liquid, *i.e.*, water (unitless); and
- 1000 = unit conversion factor (L/m<sup>3</sup>) to match the units for all TRIM.FaTE compartment volumes.

For mercury, the transfer from surface water to the fish via the gills is set to zero (0) (see Appendix A, Section A.1.3).

The generalized transfer factors for chemical uptake from dietary items to a specific fish compartment are given by:

$$T_{diet \rightarrow fish} = \frac{n_f \times m_f}{n_{diet} \times m_{diet}} \times IN_D \times AE_D \quad (\text{TF 6-6a})$$

$$= \frac{biomass_{fish}}{biomass_{diet}} \times IN_D \times AE_D \quad (\text{TF 6-6b})$$

where:

- $n_{diet}$  = number of individuals in the diet compartment (unitless);
- $m_{diet}$  = mass per individual in the diet compartment (kg[organism]/individual);
- $IN_D$  = total diet (food) ingestion rate (kg[diet wet wt]/kg[fish wet wt]);
- $AE_D$  = assimilation efficiency of chemical from diet (unitless);
- $biomass_{fish}$  = total biomass of the fish compartment (=  $n_f \times m_f$ ); and
- $biomass_{diet}$  = total biomass of the diet compartment (=  $n_{diet} \times m_{diet}$ ).

Because algae is modeled as a phase of the surface water compartment in the current TRIM.FaTE library, consumption of algae by herbivorous fish is represented by a slightly different transfer factor algorithm:

$$T_{Algae \rightarrow Fwch} = \frac{n_{Fwch} \times m_{Fwch}}{\left( f_{MA} / m_{Algae} \right)} \times IN_D \times P_{Algae} \times AE_D \quad (\text{TF 6-7})$$

where:

$T_{Algae \rightarrow Fwch}$	=	transfer factor from algae to water column herbivore (/day);
$n_{Fwch}$	=	number of water column herbivores in surface water compartment (unitless);
$m_{Fwch}$	=	mass per individual water column herbivore (g[fish wet wt]);
$f_{MA}$	=	fraction of chemical mass that is in the algal-phase of the surface water (kg[chemical]/kg[bulk surface water, including suspended sediments and algae]);
$m_{Algae}$	=	total mass of algae in surface water compartment (kg[algae wet wt]); and
$p_{Algae}$	=	proportion of the total diet that consists of algae on a wet-weight basis (unitless).

Using the same bioenergetic model, the transfer of chemicals from the fish population compartment to the surface water compartment can be expressed as:

$$\begin{aligned} T_{fish \rightarrow SW}^{excretion} &= k_{eg} + k_{ef} \\ &= k_E \end{aligned} \quad (\text{TF 6-8})$$

where:

$k_E$	=	rate constant for elimination of chemical from the fish to surface water via the gills and in urine and feces (/day).
-------	---	---

Note that  $k_E$  applies only to the absorbed chemical in the fish compartment. Fecal loss of unabsorbed chemical was accounted for by the  $AE_D$  parameter. As described in Section 6.4.1.4,  $k_E$  does not include losses due to metabolic transformation or degradation.

#### 6.4.1.5 Transformations and Degradation

Transformations of organic chemicals into biodegradation by-products that are no longer tracked in TRIM.FaTE are modeled as transfers to the fish degradation sinks. See the TRIM.FaTE user guidance for recommendations on how to identify rate constants for biodegradation separately from rate constants associated with chemical excretion from fish to surface water. Equation 2-64 (Chapter 2) is used to estimate the metabolic degradation (in TRIM.FaTE, called “general degradation”) rate constant for an organic chemical from its metabolic half-life.

Metabolic transformations of inorganic chemicals into different compounds containing the same core chemical (e.g., mercury) can be included in the TRIM.FaTE fish models. For

example, biotransformation of Hg(0) to Hg(2) in fish is included as a rapid (almost instantaneous) first-order rate constant in the fish compartments. Thus, it is assumed that elemental mercury can be taken up by fish but is not accumulated in the fish (*i.e.*, data showing Hg(0) in fish were not found). It is also assumed that inorganic mercury is not methylated by fish. Demethylation in fish may occur as part of the excretory process, but it is not explicitly modeled here. Rather, it is assumed to be insignificantly small compared to the relative masses of the mercury species in the fish (*i.e.*, receiving compartments).

### 6.4.2 TIME-TO-EQUILIBRIUM-BASED KINETIC MODEL

The time-to-equilibrium model is based on the assumption that one pathway accounts for the vast majority of the chemical uptake. Thus, only one chemical “source” (*e.g.*, food) is explicitly considered for a given “receptor”, (*e.g.*, fish). The general form of the model is:

$$\frac{dC_{receptor}}{dt} = \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{rs}} \right] \times K_{receptor-source} \times C_{source} - \left[ \frac{-\ln(1-\alpha)}{t_{\alpha}^{rs}} \right] \times C_{receptor} \quad (\text{Eq. 6-35})$$

where:

- $K_{receptor-source}$  = receptor/source partition coefficient (*e.g.*, fish/diet partition coefficient) (g[chemical]/kg[receptor wet wt] per g[chemical]/kg[source wet wt]);
- $C_{receptor}$  = concentration in receptor (*e.g.*, fish) (g[chemical]/kg[receptor wet wt]);
- $C_{source}$  = concentration in source (*e.g.*, diet) (g[chemical]/kg[source wet wt]);
- $t_{\alpha}^{rs}$  = time (days) required to reach 100× $\alpha$  percent of the receptor/source equilibrium value when the concentration in the source is approximately constant with time; and
- $\alpha$  = fraction of the equilibrium value attained (default = 0.95; unitless).

If the sole chemical source is surface water, then  $K_{receptor-source}$  is a bioconcentration factor (BCF). Bioaccumulation factors (BAFs) implicitly include uptake from food and water, though water is the identified source. This presumes that the concentration in the food item is essentially constant relative to the concentration in the water. An alternative approach is the use of diet as the primary source. Thus, empirically derived accumulation data are used to derive factors for each trophic transfer, and uptake from water is implicitly, rather than explicitly, included. This latter alternative is used here.

Following this approach requires that the dietary sources for a given fish compartment be restricted to one other trophic group. Thus, intratrophic group transfers and multitrophic group transfers are not explicitly included. These transfers are implicitly included to the extent that the empirical data used to derive the transfer factors are from systems possessing those transfers. Thus, the “fit” of the model results for any given case study will depend partly on how well the food chains at the sites used to derive the transfer factors match the food chains at the case study site (*e.g.*, length of the food chains, number of interconnections, degree of intratrophic group transfer, etc.).

Restriction of the dietary pathway can be achieved within TRIM.FaTE by defining the generic trophic compartment types to represent a straight food chain (*e.g.*, of three or four segments). As noted in Section 6.3, the benthic herbivore compartment type in initial TRIM.FaTE applications has been represented by all benthic invertebrates and in the use of this time-to-equilibrium approach, the bulk sediment (or interstitial water) is the chemical source. The benthic omnivore fish compartment type is the next trophic level up from the benthic invertebrates.

Like the benthic food chain, the chemical transfers in the water column food chain can be set to be unidirectional from lower to higher trophic levels. In initial applications following this design, it is important to note that zooplankton have been implicitly included in the transfers from algae to water column herbivores. That is, the biomass and chemical mass associated with zooplankton have not been explicitly tracked in TRIM.FaTE, but the dietary transfers were based on concentration ratios for planktivorous fish and algae. Some studies provide the intermediate transfer factors for algae to zooplankton, which might be used to include the zooplankton compartment type within future TRIM.FaTE simulations.

For each trophic level transfer, the general concentration-based equation is converted to the following mass-transfer equation:

$$\frac{dN_f}{dt} = n_f \times m_f \times \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{fd}} \right] \times K_{fish-diet} \times \frac{N_{diet}}{n_{diet} \times m_{diet}} - \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{fd}} \right] \times N_f \quad (\text{Eq. 6-36})$$

where:

- $n_f$  = number of fish in the compartment (unitless);
- $m_f$  = mass of individual fish (kg[fish wet wt]/individual);
- $t_\alpha^{fd}$  = time (days) required to reach  $100 \times \alpha$  percent of the fish/diet interaction equilibrium value when the concentration in the source is approximately constant with time;
- $K_{fish-diet}$  = fish/diet partition coefficient (kg[diet wet wt]/kg[receptor wet wt]);
- $N_{diet}$  = mass of chemical in items comprising the potential diet (g[chemical]);
- $n_{diet}$  = number of contaminated items comprising the potential diet (unitless);
- $m_{diet}$  = mass of individual items comprising the potential diet (kg[diet wet wt]/individual); and
- $N_f$  = mass of chemical in the fish (receptor) compartment (g[chemical]).

As an example, the mass transfer equation for water-column omnivores eating water-column herbivores is given as:

$$\begin{aligned} \frac{dN_{Fwco}}{dt} = & n_{Fwco} \times m_{Fwco} \times \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{fd}} \right] \times K_{Fwco-Fwch} \times \frac{N_{Fwch}}{n_{Fwch} \times m_{Fwch}} \\ & - \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{fd}} \right] \times N_{Fwco} \end{aligned} \quad (\text{Eq. 6-37})$$

where:



$N_{Fwco}$	=	mass of chemical in the fish water-column omnivore compartment (g[chemical]);
$n_{Fwco}$	=	number of fish comprising the water-column omnivore compartment (unitless);
$m_{Fwco}$	=	mass per individual fish in the water-column omnivore compartment (kg[fish wet wt]/individual);
$K_{Fwco-Fwch}$	=	fish (water-column omnivore)/fish (water-column herbivore) partition coefficient (kg[ <i>Fwch</i> wet wt]/kg[ <i>Fwco</i> wet wt]);
$N_{Fwch}$	=	mass of chemical in fish water-column herbivore compartment (g[chemical]);
$n_{Fwch}$	=	number of fish comprising the water-column herbivore compartment (unitless); and
$m_{Fwch}$	=	mass per individual fish in the water-column herbivore compartment (kg[fish wet wt]/individual).

For each trophic level transfer, the generalized transfer factors for dietary items to a specific fish compartment type (*i.e.*, benthic omnivore, benthic carnivore, water-column herbivore, water-column omnivore, or water column carnivore) is given by:

$$T_{diet \rightarrow fish} = \frac{n_f \times m_f}{n_{diet} \times m_{diet}} \times \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{fd}} \right] \times K_{fish-diet} \quad (\text{TF 6-9})$$

Because algae is treated as a phase of the surface water compartment, the time-to-equilibrium transfer factor from algae to the water-column herbivore fish compartment is slightly different:

$$T_{Algae \rightarrow Fwch} = \frac{n_{Fwch} \times m_{Fwch}}{(f_{MA} / m_{Algae})} \times \left[ \frac{-\ln(1-\alpha)}{t_\alpha^{FwchAlg}} \right] \times K_{Fwch-Algae} \quad (\text{TF 6-10})$$

where:

$T_{Algae \rightarrow Fwch}$	=	transfer factor from algae to fish (water-column herbivore) (/day);
$f_{MA}$	=	fraction of chemical mass that is in the algal phase of the surface water compartment (unitless);
$m_{Algae}$	=	total mass of algae in surface water compartment (kg[algae wet wt]);
$t_\alpha^{FwchAlg}$	=	time (days) required to reach 100×α percent of the fish/diet interaction equilibrium value when the concentration in the source is approximately constant with time; and
$K_{Fwch-Algae}$	=	fish (water-column herbivore)/algae partition coefficient (kg[algae wet wt]/kg[fish wet wt]).

The generalized transfer factor in the other direction (to allow equilibrium) from a specific fish compartment to its diet compartment is given by:

$$T_{fish \rightarrow diet} = \left[ \frac{-\ln(1 - \alpha)}{t_{\alpha}^{fd}} \right] \quad (\text{TF 6-11})$$

Transformations and degradation are modeled using the same approach as described for the bioenergetic model (see Section 6.4.1.5).

### 6.4.3 OTHER EPA MODELS FOR BIOACCUMULATION BY FISH

Aquatox is a general ecological risk model that estimates the fate and effects of chemical and physical stressors in aquatic ecosystems (U.S. EPA 1998b). The model has been developed by the Office of Pollution Prevention and Toxics (OPPT) and the Office of Water (OW). The Bioaccumulation and Aquatic System Simulator (BASS), developed by the National Exposure Research Laboratory (NERL) of the Office of Research and Development (ORD), also simulates exposure and effects on fish (U.S. EPA 1999c).

Aquatox and BASS are designed to predict effects of chemical contaminants and environmental factors on fish populations, whereas TRIM.FaTE is designed to estimate the fate and transport of chemicals throughout aquatic and terrestrial environments, with an emphasis on a collection of identical, individual fish. This difference in purpose results in several differences in structure: (1) Aquatox and BASS include chemical toxicity data; TRIM.FaTE does not (although TRIM.Risk is designed to include such a database); (2) the toxicological data in Aquatox and BASS are used to predict mortality, which is used to modify the structures of the models (*e.g.*, age-class structure and predator-prey interactions); the biomass in the TRIM.FaTE fish compartments remains constant; (3) in Aquatox, decomposition of dead fish and contaminants are linked to the dissolved oxygen levels in water, which affect populations; in TRIM.FaTE dissolved oxygen levels in surface water are not modeled; and (4) growth estimation of fish is fundamental to the population dynamics component of BASS, whereas growth is not included in the current version of TRIM.FaTE.

BASS (U.S. EPA 1999c) and Aquatox (U.S. EPA 1998b) are bioenergetic models of a multiple-trophic-level aquatic ecosystem. Aquatox, like TRIM.FaTE, provides an explicit time-to-equilibrium model option, whereas BASS does not. Like TRIM.FaTE, Aquatox has a Monte Carlo component to permit probabilistic estimates of exposure or risk. The developers of BASS plan to include metabolism of organic compounds in future versions of the model, but, unlike TRIM.FaTE, these transformations are not a feature of the current version (U.S. EPA 1999c). Components of Aquatox or BASS could be integrated with TRIM.FaTE. The challenge would be to preserve mass balance and to provide adequate links to all TRIM.FaTE compartment types that are connected to surface water and/or fish.