

4. CONCEPTUAL DESIGN AND MASS BALANCE FRAMEWORK FOR TRIM.FaTE

This chapter, building on the definitions and spatial and temporal concepts discussed in Chapter 3, presents the overall logic and mathematical framework implemented in TRIM.FaTE for expressing transport and transformation of chemicals in a multimedia environment. Specifically, this chapter discusses and illustrates the mass balance approach and describes the processes simulated in TRIM.FaTE. The specific algorithms used to implement the approach are documented in Volume II of the TRIM.FaTE TSD.

4.1 CONCEPTUAL DESIGN

TRIM.FaTE calculates, given an initial mass inventory and mass inputs over time from one or more sources and from boundary conditions, the mass of one or more chemicals being modeled in each compartment in the modeled system for each simulation time step. With the estimated chemical mass and total volume or mass for each compartment, TRIM.FaTE can calculate the concentration of each chemical in each compartment for each output time step.

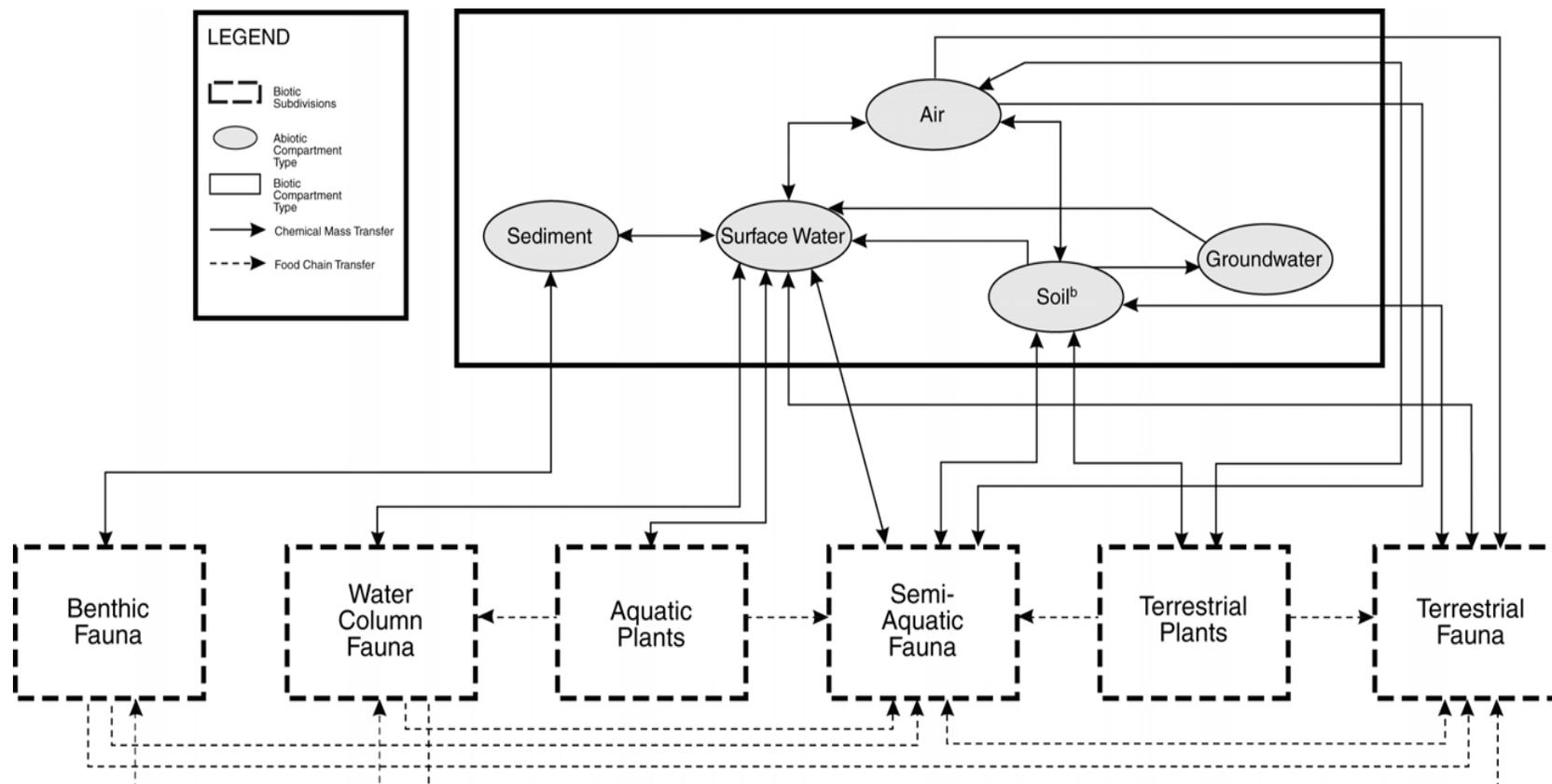
The development of TRIM.FaTE began with a conceptual diagram of the relationships and processes that affect chemical transport within the environment. The current version of this diagram is shown in Figure 4-1. In this figure, biotic compartments are represented by rectangles and abiotic compartments are represented by ovals. The arrows illustrate the potential chemical transfers between each of the components of the ecosystem. Chemical transformations, which may occur within compartments in TRIM.FaTE, are not included in Figure 4-1.

4.2 MASS BALANCE CONCEPTS AND EQUATIONS

TRIM.FaTE has been developed with an emphasis on maintaining a mass balance within the modeling system. That is, all inputs and outputs of the chemical of interest are tracked to ensure that the results are not unrealistic with regard to the relationship between the amount of that chemical being introduced to the system and the amounts predicted to be retained in and lost from the system. More specifically, it means that the amounts of the chemical of interest predicted to be retained in and lost from the system always sum to the amount of chemical introduced into the system. When applied to a specific compartment (*e.g.*, soil, or a mouse population), the mass balance approach implies that, over a given time period, the amount of the chemical of interest in the compartment at the end of the period is equal to the sum of the amount of that chemical in the compartment at the beginning of the period plus the gains of the chemical that occurred during the time period, minus the chemical that was lost from the compartment during the time period.

It should be noted that in order to accommodate transformation of a chemical and modeling of the fate of the transformation product chemicals, the mass balance aspect of TRIM.FaTE is achieved for the chemical entity of interest (*i.e.*, the “core chemical”). Inherent to the application of this approach is that the core chemical, which may be a part of the chemical

Figure 4-1
Simplified Conceptual Diagram for TRIM.FaTE^a



^a Sinks are not shown. Chemical transformation processes are not depicted but may occur in all compartment types. Transformation products may be tracked within compartments in TRIM.FaTE or transferred out of compartments to reaction/degradation sinks.

^b Includes surface soil, root zone soil, and vadose zone soil compartment types.

introduced into the system rather than the whole chemical (*e.g.*, the X molecule of a hypothetical chemical of formula XY_2), is an entity that maintains its chemical integrity throughout the modeling system. To date, certain mercury compounds are the only chemicals for which TRIM.FaTE applications have incorporated transformation among chemicals that are explicitly modeled. In this case, the mercury atom (in elemental or ionic form) is the core chemical for which mass balance is maintained within the system, and the model predicts distribution of that core chemical occurring as elemental, divalent, and methyl mercury within the system. That is, the mass of mercury atoms (regardless of its speciation or the compound of which it may be a part) that is introduced to the system is in balance with the sum of the mass and number of conserved units predicted to remain in and predicted to exit from the system.

To date, TRIM.FaTE has been implemented primarily for first-order linear transfer and transformation processes. Therefore, the following discussion is limited to algorithms of that type. It is important to note that higher order nonlinear methods can also be implemented within the TRIM.FaTE modeling structure.

First-order transfers between compartments are described by transfer factors, referred to as T-factors. T-factors are in units of inverse time and are not dependent on the sending and receiving chemicals or the amount of chemical in the sending compartment. The T-factor is the *instantaneous* flux of chemical normalized to the amount of that chemical in the sending compartment. The actual *instantaneous* flux (*i.e.*, the amount of chemical passing across an interface per unit time) can be calculated using the T-factor and the amount of chemical in the sending compartment.¹

First-order transformation of chemicals is described by a reaction rate, referred to as R. Conceptually similar to (and mathematically identical to) the T-factor, R is measured in units of inverse time. Due to the structure of TRIM.FaTE, a chemical molecule cannot be transferred to a different compartment and transformed simultaneously. Thus, when both a transformation and a transfer occur, two separate processes are modeled in TRIM.FaTE.² Transformations occur for chemicals *within* a compartment, and the reaction products (and remaining parent compound) may subsequently be transferred to another compartment or out of the system. A transformation in which a chemical of interest is converted to a chemical species for which transport and fate are *not* modeled is handled by transferring the chemical moles out of the system of compartments to a degradation/reaction sink. This kind of transformation is treated as an irreversible loss from the system.

¹ T-factors are actually applied to the moles of the chemical in the compartment, rather than mass, to facilitate the modeling of transformation. Although some of the transfer (*e.g.*, advection, diffusion) and degradation algorithms used in TRIM.Fate may be based on mass relationships, there is no mathematical impact of applying the T-factors to moles instead of mass when the sending and receiving chemical are the same. The algorithms involving inter-transformation processes between chemicals are based on mole relationships.

² When there are multiple processes being modeled for a chemical in a given compartment (*e.g.*, multiple transfer processes, simultaneous transfer and transformation), the processes are modeled separately but calculated concurrently based on the same starting number of moles (*i.e.*, the number of moles present in a compartment at the start of the series of calculations for a particular point in time).

A chemical also can be transferred to a sink via advective transport that moves the chemical beyond the physical boundaries of the modeled system (*e.g.*, moles of chemical that are blown out of the modeled area with the air or flushed out with surface water). This kind of sink is referred to as either an advection sink or a flush rate sink depending on the physical processes involved in transferring the chemical. The transfer of chemical to a sink by either advective transport or degradation/reaction is irreversible because after the chemical is transferred to a sink, it can no longer move to any other compartments.

Although TRIM.FaTE models chemical transfers among compartments and chemicals (where transformation is involved) on the basis of moles, it also provides the results in units of mass or concentration by multiplying the resultant moles in each compartment by the molecular weight of each complete chemical being modeled, or the weight of the entity of interest (*e.g.*, methyl mercury mass and concentration results can be provided either in units of methyl mercury or units of methylmercury, as mercury). Figure 4-2 illustrates the mass to moles to mass conversions in TRIM.FaTE.

A simplification of a first-order transfer process involving a single chemical (*i.e.*, no transformation between chemicals) is shown in the top part of Figure 4-3 for a system of one chemical, two compartments, and two degradation/reaction sinks, where degradation is treated as an irreversible loss. For this system, it can be seen that:

$$\text{Chemical gains for compartment A} = S_a + T_{ba} N_b \quad (1)$$

$$\text{Chemical losses for compartment A} = T_{ab} N_a + R_a N_a \quad (2)$$

$$\text{Chemical gains for compartment B} = T_{ab} N_a \quad (3)$$

$$\text{Chemical losses for compartment B} = T_{ba} N_b + R_b N_b \quad (4)$$

where:

- N_a = amount of chemical in compartment A, units of *moles*
- N_b = amount of chemical in compartment B, units of *moles*
- S_a = chemical source outputting to compartment A, units of *moles/time*
- T_{ab} = transfer factor for movement of chemical from compartment A to compartment B, units of */time*
- T_{ba} = transfer factor for movement of chemical from compartment B to compartment A, units of */time*
- R_a = reaction loss of chemical in compartment A, units of */time*
- R_b = reaction loss of chemical in compartment B, units of */time*.

Figure 4-2
Chemical Mass/Mole Conversions in TRIM.FaTE
(Example for a single chemical)

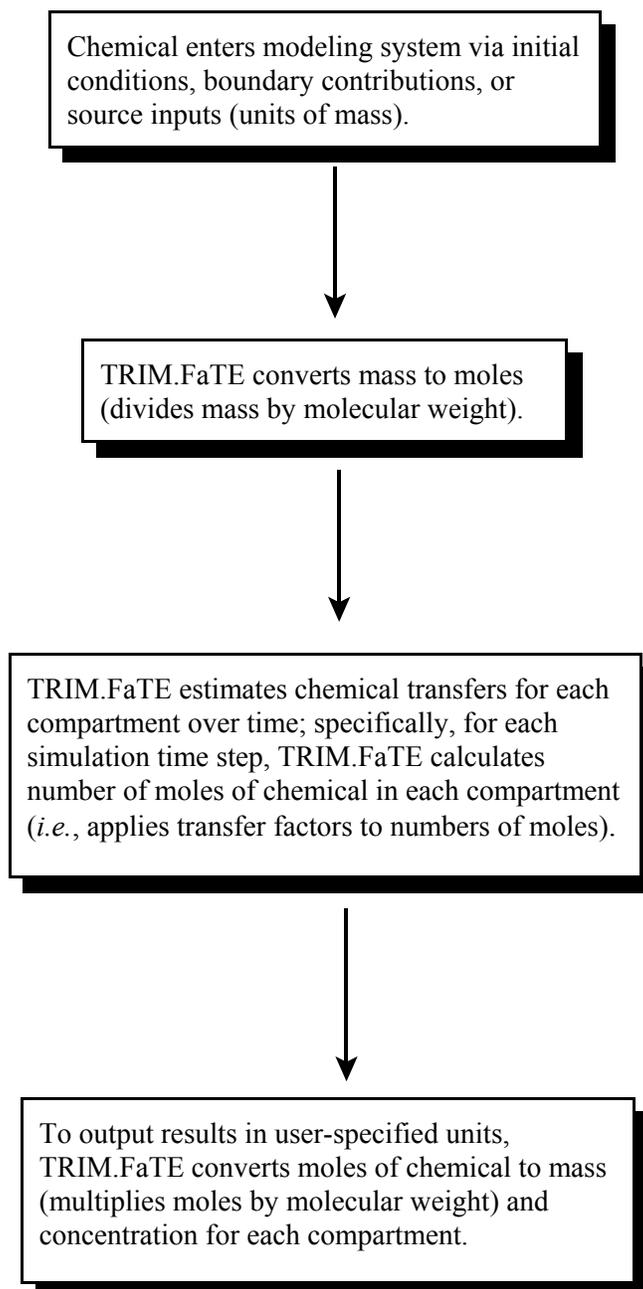
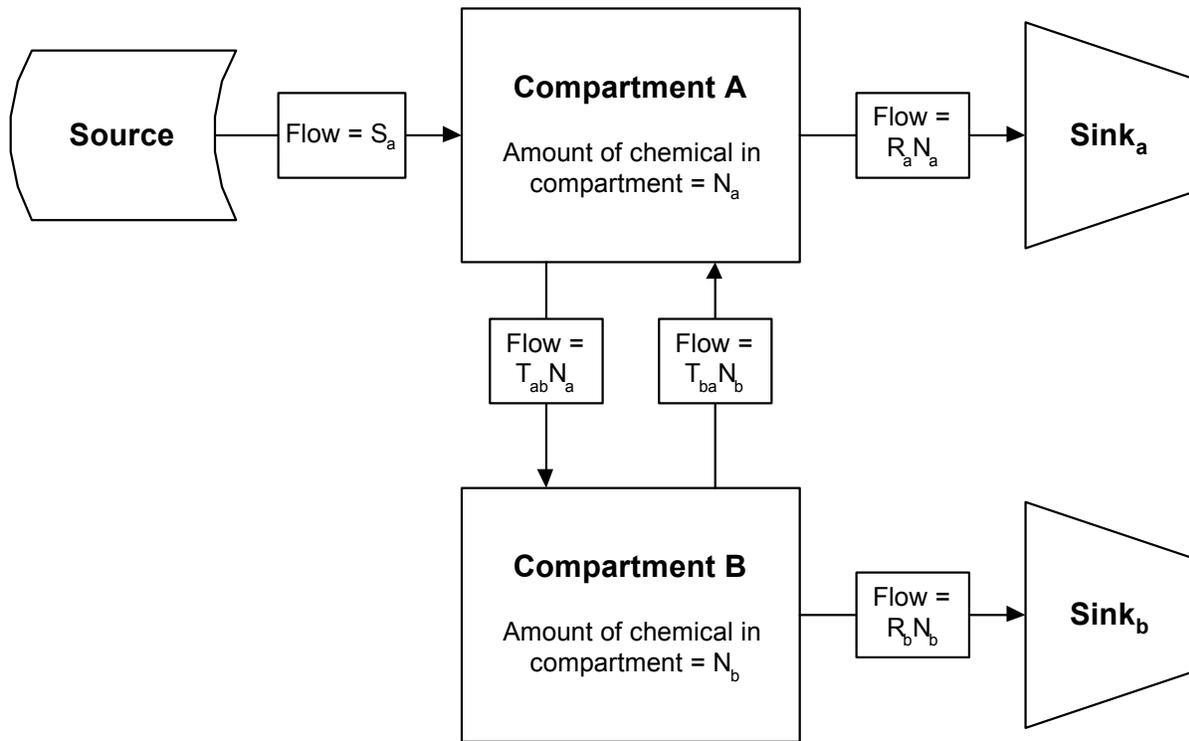


Figure 4-3
Example of First-order Transfer Processes for Two Compartments, One Chemical^a



$$\begin{bmatrix} dN_a/dt \\ dN_b/dt \\ d\text{Sink}_a/dt \\ d\text{Sink}_b/dt \end{bmatrix} = \begin{bmatrix} -(T_{ab} + R_a) & T_{ba} & 0 & 0 \\ T_{ab} & -(T_{ba} + R_b) & 0 & 0 \\ R_a & 0 & 0 & 0 \\ 0 & R_b & 0 & 0 \end{bmatrix} \begin{bmatrix} N_a \\ N_b \\ \text{Sink}_a \\ \text{Sink}_b \end{bmatrix} + \begin{bmatrix} S_a^0 \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (5)$$

^a In this one-chemical example, transformation is treated as an irreversible sink (*i.e.*, a degradation/reaction process). Note that the boxes in this figure labeled *flow* (and similar boxes designating either flow or reaction in subsequent figures) represent the transfer of chemical between compartments A and B as either $(T_{ab} \times N_a)$ or $(T_{ba} \times N_b)$, depending on the direction of the transfer. This “flow” represents the instantaneous change in chemical moles (*i.e.*, mole transfer) with respect to time and is not a constant value. The value for the mole transfer depends on the number of moles (*i.e.*, N_a or N_b) in the sending compartment. Because the number of moles changes continually as transfer process occur, the value for the mole transfer can change continually over time as moles are removed from and added to the sending compartment.

As discussed earlier, the constraint that mass balance must be preserved means that, over any time interval, the change in amount of chemical in a compartment is equal to the gains minus the losses over the time interval. For compartments A and B, this change in amount is the difference in equations (1) and (2), and (3) and (4), respectively. The instantaneous change in amount with respect to time is the derivative with respect to time, denoted by dN/dt . Thus, the mass balance constraint, when applied to the simple system of the two compartments A and B discussed here, yields a system of two linked differential equations:

$$\frac{dN_a}{dt} = S_a + T_{ba} N_b - (R_a + T_{ab}) N_a \quad (6)$$

$$\frac{dN_b}{dt} = T_{ab} N_a - (R_b + T_{ba}) N_b \quad (7)$$

Additional terms are needed to properly account for the mass that is accumulated in the degradation/reaction sinks. Thus, two additional compartments are added to the system as sinks and serve as the repository of the chemicals after a reaction creates a form of the chemical that is no longer modeled in the system. After the chemical is transferred to a sink, it cannot move to any other compartments within the system. $Sink_a$ and $Sink_b$ denote the mass in the degradation/reaction sinks for compartments A and B, respectively. Now the complete system can be described using equations (6) and (7) above along with (8) and (9) presented below:

$$\frac{d Sink_a}{dt} = R_a N_a \quad (8)$$

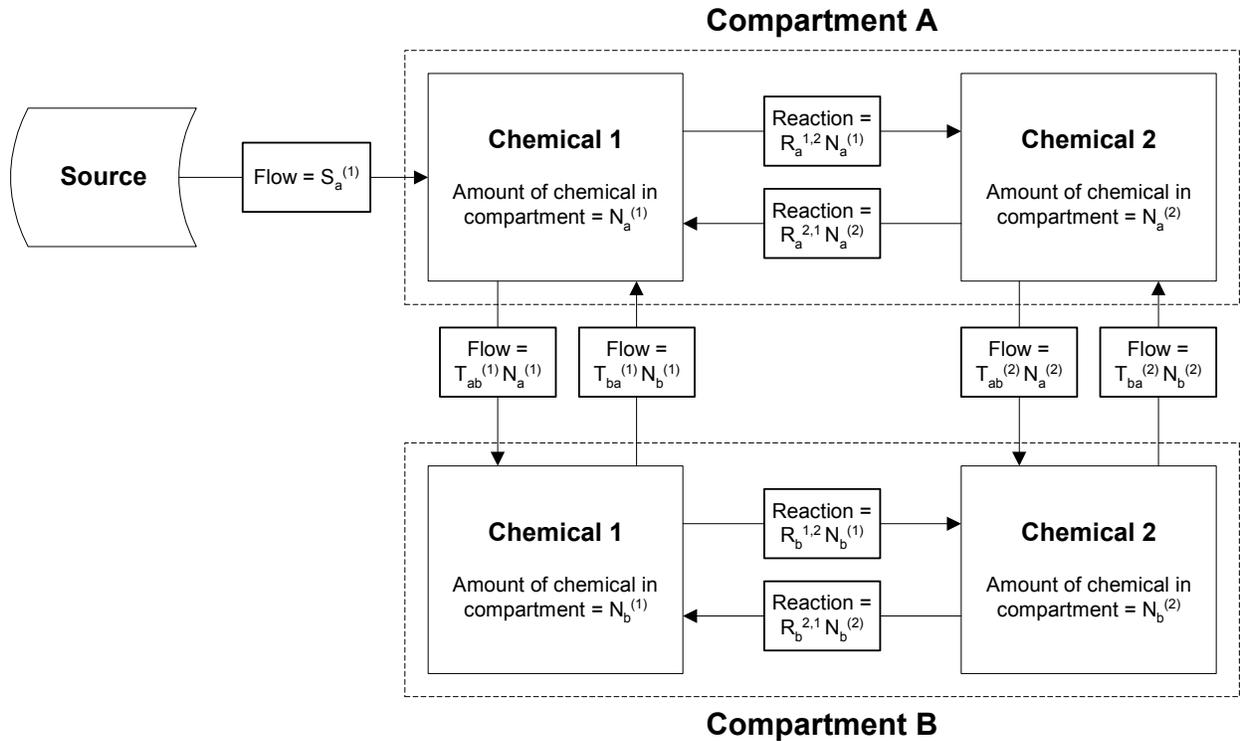
$$\frac{d Sink_b}{dt} = R_b N_b \quad (9)$$

This system of equations (equations (6) through (9)) is shown in matrix form in Equation (5) at the bottom of Figure 4-3.

For TRIM.FaTE, systems of linear ordinary differential equations are solved using the Livermore Solver for Ordinary Differential Equations (LSODE) (Radhakrishnan and Hindmarsh 1993), a Fortran program freely available via several online numerical algorithm repositories. The use of LSODE in TRIM.FaTE is described in more detail in Appendix C of this document.

If the fate of the chemical created by a transformation reaction is to be modeled explicitly, and the necessary algorithms and input data are available for this transformation product, then the mass balance approach described above can be modified accordingly to include this transformation product. Figure 4-4 shows a generalization of the previous example to the case where the transformed chemical is modeled in addition to the parent chemical. In this case, in addition to the reaction rate, T-factors are added for the transformed chemical to account for additional possible transfers between compartments.

Figure 4-4
Example of First-order Transfer Processes for Two Compartments, Two Chemicals^a



^a This example illustrates the transformation and independent physical movement of two chemicals that can transform into each other.

Using the same approach used for the system in Figure 4-3, the more complex system in Figure 4-4 can be expressed as a set of four differential equations, as follows:

$$\frac{dN_a^{(1)}}{dt} = -T_{ab}^{(1)} N_a^{(1)} - R_a^{1,2} N_a^{(1)} + T_{ba}^{(1)} N_b^{(1)} + R_a^{2,1} N_a^{(2)} + S_a^{(1)} \quad (10)$$

$$\frac{dN_b^{(1)}}{dt} = T_{ab}^{(1)} N_a^{(1)} - T_{ba}^{(1)} N_b^{(1)} - R_b^{1,2} N_b^{(1)} + R_b^{2,1} N_b^{(2)} \quad (11)$$

$$\frac{dN_a^{(2)}}{dt} = R_a^{1,2} N_a^{(1)} - T_{ab}^{(2)} N_a^{(2)} - R_a^{2,1} N_a^{(2)} + T_{ba}^{(2)} N_b^{(2)} \quad (12)$$

$$\frac{dN_b^{(2)}}{dt} = R_b^{1,2} N_b^{(1)} + T_{ab}^{(2)} N_a^{(2)} - T_{ba}^{(2)} N_b^{(2)} - R_b^{2,1} N_b^{(2)} \quad (13)$$

where:

- $N_a^{(1)}$ = amount of core chemical 1 in compartment A, units of *moles*
- $N_a^{(2)}$ = amount of core chemical 2 in compartment A, units of *moles*
- $N_b^{(1)}$ = amount of core chemical 1 in compartment B, units of *moles*
- $N_b^{(2)}$ = amount of core chemical 2 in compartment B, units of *moles*
- $T_{ab}^{(1)}$ = transfer factor for movement of chemical 1 in compartment A to compartment B, units of */time*
- $T_{ab}^{(2)}$ = transfer factor for movement of chemical 2 in compartment A to compartment B, units of */time*
- $T_{ba}^{(1)}$ = transfer factor for movement of chemical 1 in compartment B to compartment A, units of */time*
- $T_{ba}^{(2)}$ = transfer factor for movement of chemical 2 in compartment B to compartment A, units of */time*
- $R_a^{(1,2)}$ = reaction/transformation of chemical 1 to chemical 2 in compartment A, units of */time*
- $R_a^{(2,1)}$ = reaction/transformation of chemical 2 to chemical 1 in compartment A, units of */time*
- $R_b^{(1,2)}$ = reaction/transformation of chemical 1 to chemical 2 in compartment B, units of */time*
- $R_b^{(2,1)}$ = reaction/transformation of chemical 2 to chemical 1 in compartment B, units of */time*
- $S_a^{(1)}$ = source for chemical 1 outputting to compartment A, units of *moles/time*

This system of equations can be summarized in matrix form as follows:

$$\begin{bmatrix} dN_a^{(1)}/dt \\ dN_b^{(1)}/dt \\ dN_a^{(2)}/dt \\ dN_b^{(2)}/dt \end{bmatrix} = \begin{bmatrix} -(T_{ab}^{(1)} + R_a^{1,2}) & T_{ba}^{(1)} & R_a^{2,1} & 0 \\ T_{ab}^{(1)} & -(T_{ba}^{(1)} + R_b^{1,2}) & 0 & R_b^{2,1} \\ R_a^{1,2} & 0 & -(T_{ab}^{(2)} + R_a^{2,1}) & T_{ba}^{(2)} \\ 0 & R_b^{1,2} & T_{ab}^{(2)} & -(T_{ba}^{(2)} + R_b^{2,1}) \end{bmatrix} \begin{bmatrix} N_a^{(1)} \\ N_b^{(1)} \\ N_a^{(2)} \\ N_b^{(2)} \end{bmatrix} + \begin{bmatrix} S_a^{(1)} \\ 0 \\ 0 \\ 0 \end{bmatrix} \quad (14)$$

Applying this same approach to a general system with M compartments (including all sinks), and allowing the transfer factors and source terms to depend on time as well, results in a system of linked differential equations of the form:

$$\frac{d\vec{N}}{dt} = A(t)\vec{N}(t) + \vec{s}(t), \quad \vec{N}(t_0) = \vec{N}_0 \quad (15)$$

where:

- $\vec{N}(t)$ = an M -dimensional time-dependent vector whose i th entry is the moles of chemical in the i th compartment
- $A(t)$ = an $M \times M$ -dimensional time-dependent matrix
- $\vec{s}(t)$ = an M -dimensional time-dependent vector accounting for the source terms contributing to each compartment.

The vector \vec{N}_0 is the initial distribution of chemical moles among the compartments. The vector $\vec{N}(t)$ is the distribution of chemical moles among the compartments over time. The matrix $A(t)$ is referred to as the *transition matrix* for the system. This term is borrowed from Markov theory (Schneider and Barker 1989), although the model is not strictly a Markov process. The transition matrix is used in TRIM.FaTE to solve for the T-factors at each time step. The vector $\vec{s}(t)$ accounts for pollutant sources emitting the chemical to specific compartments over time.

4.3 PHASES

Chemicals in the environment can exist in various phases (*e.g.*, liquid, gas, solid). The chemical mass in each phase is tracked in TRIM.FaTE because transfer factors are phase-dependent (*e.g.*, the transfer factor for suspended particulate deposition from air is applied only to the chemical mass in the particulate phase of air). There are multiple environmental phases modeled within the abiotic compartments in TRIM.FaTE. A chemical's phase distribution is generally assumed to be at chemical equilibrium within a compartment (see Volume II of the TSD for exceptions). For example, chemical mass sorbed to suspended particulate matter (solid phase) exists in equilibrium along with chemical mass present as vapor (gas phase) in an air compartment. The adjacent text box lists the phases currently implemented in TRIM.FaTE for each abiotic compartment type.³

PHASES CURRENTLY IMPLEMENTED IN TRIM.FaTE

Air

- vapor/gas
- suspended particulate

Soil^a

- soil pore water
- vapor/gas
- soil solids

Surface water

- water
- suspended solids-algae
- suspended solids-other

Sediment

- sediment pore water
- sediment solids

Groundwater

- soil pore water
- soil solids

^a Includes surface, root zone, and vadose zone soil compartment types.

In any compartment, the total amount of chemical present is made up of the sum of the amounts in the different phases. Because chemical equilibrium among phases is generally assumed, the ratios of the concentrations in the individual phases are constant over time for a given chemical. The fraction of the chemical that is in each phase in a compartment is calculated in TRIM.FaTE using either partitioning or fugacity concepts. Both concepts are mathematical approaches to describe the same physical phenomena. Partitioning coefficients are empirical relationships that show the distribution of a specific chemical between two phases. Fugacity is a measure of a chemical's potential to remain in any particular phase based on its chemical properties. Transfer between two phases is dependent on the fugacity capacity of a chemical, or the tendency for the chemical to "escape," or transfer, to another phase. Details and calculations for the implementation of phases in TRIM.FaTE are presented in Chapter 2 of Volume II of the TRIM.FaTE TSD.

³ Algae are included as a phase within surface water rather than a separate compartment type because of the limited data available to explicitly model chemical movement between algae and surface water at the time TRIM.FaTE was being developed for mercury. Given the available uptake algorithm for algae, uptake was assumed to occur by passive diffusion and could thus be most simply represented by equilibrium partitioning.

4.4 FATE, TRANSFORMATION, AND TRANSPORT PROCESSES

In TRIM.FaTE, the following physical, chemical, and biological processes are implemented as first-order mathematical processes for modeling the transfer and transformation of chemicals:

- Advection;
- Dispersion;
- Diffusion;
- Biotic processes; and
- Reaction and transformation.

Qualitative descriptions of these five types of processes are presented in the subsections below. More detailed explanation of the mathematical representation of these processes and documentation of all of the currently implemented algorithms are presented in Volume II of the TRIM.FaTE TSD.

Fate and transport algorithms developed for early prototypes of TRIM.FaTE were specific to nonionic organic compounds (*i.e.*, phenanthrene and benzo(a)pyrene). Transfer factors used in the algorithms contained in these prototypes relied upon the concept of fugacity for modeling some types of chemical transfers; however, the concept of fugacity cannot generally be applied to metals and other inorganic compounds. In order to address the fate and transport of metals and other inorganic compounds using TRIM.FaTE, non-fugacity-based algorithms can be developed. The current version of TRIM.FaTE includes algorithms specifically developed for mercury and mercury compounds as well as several individual PAHs; it is expected that many of these algorithms can be used for other metals and organic and inorganic compounds as well. The flexibility of the TRIM.FaTE framework allows for the development of additional algorithms specific to other chemicals.

4.4.1 ADVECTION

An advective process is one in which a chemical is transported within a given medium that is moving from one compartment to another. Mackay (1991) refers to this as a “piggyback” process, in which a chemical is “piggybacking” on material that is moving from one place to another for reasons unrelated to the presence of the chemical. Advective processes are modeled using first-order methods in TRIM.FaTE. Mathematically, all that is required to calculate the advective flux (*i.e.*, mass per time traveling across an interface) is the velocity of the moving phase and the amount of the chemical that is in the moving phase. Examples of advective processes included in TRIM.FaTE for transport of a chemical include erosion from a surface soil compartment to a surface water compartment, runoff of water from a surface soil compartment to a surface water compartment, and transport from one air compartment to another due to the wind.

4.4.2 DISPERSION

Dispersion refers to the “spreading out” of a chemical during advective transport and can result in movement in any direction relative to the direction of advective flow (including

perpendicular to the flow). Dispersion can be partially explained by Brownian motion, which is the movement of small particles as they are randomly bombarded by the molecules of the surrounding medium. In the current version of TRIM.FaTE, dispersion is explicitly addressed (as a first-order process) in transfers between surface water compartments using the methods presented in the Water Quality Analysis Simulation Program (WASP) water transport model (Ambrose et al. 1995).

Horizontal dispersion between air compartments is not currently modeled in TRIM.FaTE due to the complexity of accurately modeling this process in a compartment-based model. Currently, vertical dispersion is not modeled either. For a compartment-based model like TRIM.FaTE, however, the assumption that chemicals are instantaneously distributed evenly throughout a compartment volume results in three-dimensional “numerical dispersion” in the air compartments. The effective dilution that results from this assumption is generally much larger than the effects of dispersion in air.

4.4.3 DIFFUSION

In a diffusive process, a chemical is transported from one compartment to another as a result of differences in chemical concentration between the two compartments at their interface. Examples of diffusive processes in TRIM.FaTE include exchange between air compartments and soil or surface water compartments, exchange between adjacent soil compartments, and exchange between sediment compartments and surface water compartments. Models for diffusion frequently use non-first-order methods; however, these can often be approximated with first-order methods. All diffusive processes are currently modeled in TRIM.FaTE using first-order methods. Diffusion rates are based on the chemical concentrations in adjacent compartments at the beginning of each simulation time step.

4.4.4 BIOTIC PROCESSES

The transport of chemicals to biota (*i.e.*, into biotic compartments) consists of advective and diffusive processes, though the former term is rarely used by biologists. For example, chemicals deposit onto plant leaves with particles in air, an advective process; chemicals also diffuse into plant leaves from air and from the plant surface. The uptake of chemicals from soil or water in soil by plant roots or earthworms is treated as diffusion, though water carries the chemical into the plant (advection). Similarly, chemicals are assumed to enter macrophytes and benthic invertebrates by diffusion. The major advective process for the transport of chemicals into animals is food intake by fish, birds, and mammals. The transport of chemicals out of biota and into the surrounding abiotic compartment is also modeled within TRIM.FaTE by the same types of processes (*e.g.*, diffusion by benthic invertebrates, excretion by mammals).

The only transport process within biota (*i.e.*, within the biological system in the biotic compartments) that is included in TRIM.FaTE is advective transport within the composite leaf compartment between the leaves and the plant stem via xylem and phloem fluids. Modeling the distribution of chemicals among organs in fish and wildlife is not currently a feature of TRIM.FaTE; however, this increased complexity could be accommodated within the current TRIM.FaTE framework.

4.4.5 REACTION AND TRANSFORMATION

Reaction and transformation processes in the abiotic media include biodegradation (*i.e.*, the biotically mediated breakdown of the chemical in abiotic compartments), photolysis, hydrolysis, and oxidation/reduction. In biota, metabolic processes can transform the chemical to another chemical of concern tracked in the system or can break down (*i.e.*, degrade) the chemical into metabolites that are not followed in the system. Transformation is modeled in TRIM.FaTE as a reversible reaction using first-order rate equations, as discussed in Section 4.2. In all TRIM.FaTE applications to date, transformation is modeled as a bi-directional process between two inter-transforming chemicals that occurs via a pair of transformation algorithms, whereas degradation is modeled as an irreversible first-order reaction. The first-order transformation and degradation rates may be process-specific, or they may incorporate more than one of the processes involved. First-order rate constants are equivalently described in TRIM.FaTE as transformation half-lives (*i.e.*, a rate constant can be mathematically converted to a half-life and vice-versa). Depending on the algorithm and compartments involved, the mass of chemical transformed may be either lost from the system (*i.e.*, transferred to a sink) or tracked as a different chemical.