APPENDIX A

DERIVATION OF MERCURY-SPECIFIC ALGORITHMS

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APPENDIX A
DERIVATION OF MERCURY-SPECIFIC ALGORITHMS

This appendix contains derivations of mercury-specific transfer algorithms (Section A.1) and transformation algorithms (Section A.2).

A.1 MERCURY-SPECIFIC TRANSFER ALGORITHMS

The algorithms/equations included in the current TRIM.FaTE library that are specific to mercury are described below. These include:

- dry deposition of divalent mercury vapors to surface water, plants, and soil (Section A.1.1);
- exchange of mercury between algae and surface water (Section A.1.2);
- mercury excretion by fish (Section A.1.3);
- time-to-equilibrium-based mercury accumulation by fish (Section A.1.4); and
- resistance of the plant leaf mesophyll to diffusion of elemental mercury (Section A.1.5).

A.1.1 DRY VAPOR DEPOSITION OF DIVALENT MERCURY

Some of the algorithms used to transfer mercury from air to surface water, surface soils, and plants (and the algorithms used for transfers in the opposite direction) depend on the mercury species. The algorithms for diffusion between air and surface water, surface soils, and plant leaves apply only to Hg(0) and CH_3Hg, but not Hg(2). The net diffusion of Hg(2) vapors from air to surface water, surface soils, and plant leaves is described in a single algorithm called dry vapor deposition to distinguish it from the other diffusion algorithms noted above. The dry-vapor algorithm uses an empirical value for net Hg(2) vapor deposition velocity to account for diffusive processes, as described below. Thus, the net dry transfer factors for diffusion of Hg(2) vapors in air to the compartments listed above and are expressed as:

$$T_{Air \rightarrow SW}^{DVdep} = \frac{v_{vapor}^{dry\_dep} \times A_{ASW}}{V_{Air}} \times f_{MV} \qquad \text{(TF A-1)}$$

$$T_{Air \rightarrow Ss}^{DVdep} = \frac{v_{vapor}^{dry\_dep} \times I_{dry} \times A_{ASs}}{V_{Air}} \times f_{MV} \qquad \text{(TF A-2)}$$

$$T_{Air \rightarrow Leaf}^{DVdep} = \frac{v_{vapor}^{dry\_dep} \times (1 - I_{dry}) \times A_{ASs}}{V_{Air}} \times f_{MV} \qquad \text{(TF A-3)}$$

where:

$T_{Air \rightarrow SW}^{DVdep}$ = transfer factor for dry deposition of Hg(2) vapor from air to surface water (/day);

$T_{Air \rightarrow Ss}^{DVdep}$ = transfer factor for dry deposition of Hg(2) vapor from air to surface soil (/day);

$T_{Air \rightarrow Leaf}^{DVdep}$ = transfer factor for dry deposition of Hg(2) vapor from air to plant leaf (/day);

$v_{vapor}^{dry\_dep}$ = dry vapor deposition velocity for Hg(2) based on empirical studies of net diffusion/dry vapor deposition rates (m/day);

A_{ASW} = area of air/surface water interface (m^2);

A_{ASs} = area of air/surface soil interface (m^2);

V_{Air} = volume of air compartment (m^3[air]);

I_{dry} = fraction of dry-depositing chemical that is intercepted and initially retained by the plant canopy (unitless, see Section 7.2.1.1); and

f_{MV} = mass fraction of the chemical that is in the vapor phase divided by the volume fraction of the air compartment that is vapor/gas phase (close to 1.0 of the volume) (unitless).

A.1.2 ALGAE

The uptake of pollutants by algae is generally assumed to occur by passive diffusion. The algorithm for chemical uptake by algae in TRIM.FaTE has only been derived for mercury at this time. Because algae is treated as a phase of the surface water, instead of as a separate compartment, we do not derive a T-factor *per se* for the exchange between algae and surface water.

Passive uptake of uncharged, lipophilic chloride complexes is the principal accumulation route of both methylmercury and inorganic mercury in phytoplankton and is determined by water chemistry, primarily pH and chloride concentration (Mason et al. 1996). Mason and others (Mason et al. 1995, 1996) developed an accumulation model for a marine diatom (*Thalassiosira weissflogii*) and modified it for use with "typical" freshwater algae for the purposes of predicting mercury accumulations in fish. The model assumes that uptake via passive diffusion is determined by the overall octanol/water partition coefficient, K_{ow} (*i.e.*, the D_{ow}) for the neutral mercury complexes present in solution. The D_{ow} is given as the sum of the individual $K_{ow}s$ for each mercury species by the following equation (Mason et al. 1996):

$$D_{ow} = \sum f_i \times \left(K_{ow}\right)_i \qquad \text{(Eq. A-1)}$$

Where f_i = mole fraction of total mercury present as species *i*. The fractional amount of total mercury present as each neutral mercury species was estimated as a function of pH and chloride concentration. The predicted inorganic mercury (divalent) and methylmercury $D_{ow}s$ for each of five pH levels (pH 4, pH 5, pH 6, pH 7, and pH 8) and for chloride concentrations ranging approximately from 0.01 mg/L to 10,000 mg/L were presented graphically in the report by

Mason et al. (1996). The $D_{ow}s$ for divalent mercury and methylmercury in TRIM.FaTE were estimated based on those curves.

Uptake of inorganic mercury (divalent) and methylmercury by algae is given by the following equation (Mason et al. 1996):

$$Hg_{algae} = \frac{D_{ow} \times U \times 4\pi R^2}{\left(4/3\right)\pi R^3 \times \rho \times \mu} \times Hg_{water} \qquad \text{(Eq. A-2)}$$

where:

Hg_{algae}	=	total mercury concentration in algae (nmol[Hg]/g[algae wet wt]);
Hg_{water}	=	total dissolved mercury concentration in water (nM[Hg]);
D_{ow}	=	overall K_{ow} for neutral mercury complexes at specified pH and chloride concentrations (unitless);
U	=	algal surface area-specific uptake rate constant (nmol[Hg]/μm^2[algal surface]-day-nM[Hg]);
R	=	average radius of algae (μm);
ρ	=	average algal cell density (g[algae wet wt]/μm^3[algae]); and
μ	=	algal growth rate constant (/day).

Within TRIM.FaTE, the uptake of mercury by algae is characterized using the ratio of Hg_{algae} to Hg_{water}. To transform the previous equation to this ratio, the units of Hg_{water} should be converted from nM to nmol/g by dividing the right side of the equation by 1000 g/L. If both sides are then divided by Hg_{water}, the equation can be simplified to:

$$\frac{Hg_{algae}}{Hg_{water}} = \frac{D_{ow} \times U \times 3}{R \times \rho \times \mu \times 1000} \qquad \text{(Eq. A-3)}$$

Note that this equation uses moles. Gram weights are derived by multiplying the moles per gram or liter by the chemical-specific molecular weight. Table A-1 shows the molecular weights of mercury and methylmercury in the units appropriate for converting the above algae (nmol/g) and water (nM) concentrations.

Table A-1
Molecular Weights of Mercury and Methylmercury

Chemical	Molecular Weight		
	g/mol	μg/nmol	mg/nmol
Hg	200.59	2.0059×10^{-1}	2.0059×10^{-4}
CH_3Hg	215.62	2.1562×10^{-1}	2.1562×10^{-4}

The uptake process appears to be relatively fast, *i.e.*, hours rather than days (Mason et al. 1996). Also, uptake of elemental mercury by algae is assumed to be insignificant in TRIM.FaTE, based on the findings of (Mason et al. 1996) that the accumulation rates were less than 1 amol/cell-hr-nM, where amol equals 1 x 10^{-18} moles.

A.1.3 MERCURY EXCRETION BY FISH

The mercury excretion rate constant (k_E) (*i.e.*, transfer of absorbed mercury back to surface water) is given by the following bioenergetic model (Trudel and Rasmussen 1997):

$$\ln(k_E) = 0.066 \times T - 0.20 \times \ln(m_f) + 0.73 \times ED - 6.56 \qquad \text{(Eq. A-4)}$$

where:

k_E	=	total mercury excretion rate constant (/day);
T	=	temperature (°C);
m_f	=	body mass fish (**g**[fish wet wt], note units are not kg); and
ED	=	exposure duration; 0 = acute (<90 days), 1 = chronic (>90 days).

For the chronic exposures for which TRIM.FaTE may be most frequently applied, the mercury excretion rate constant is reduced to:

$$\ln(k_E) = 0.066 \times T - 0.20 \times \ln(m_f) - 5.83 \qquad \text{(Eq. A-5)}$$

The transfer factor for mercury from fish to the surface water is simply:

$$T^{Hg}_{fish \rightarrow SW} = k_E \qquad \text{(TF A-4)}$$

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). Trudel and Rasmussen (1997) found the clearance of inorganic mercury by fish to be about three times faster than the clearance of methylmercury. Thus, to estimate k_E for elemental and divalent mercury, the equation to estimate k_E for methylmercury is multiplied by a factor called *HowMuchFasterHgElimination IsThanForMHg*, which is set equal to three in the current TRIM.FaTE library.

A.1.4 ACCUMULATION OF MERCURY BY FISH

Mercury concentrations in fish are ultimately determined by methylmercury accumulation at the base of the food chain (Mason et al. 1995, 1996). Therefore, one algorithm for the uptake of mercury in fish based on the general equation for the time-to-equilibrium food-chain model is presented in Section 6.4.2. Intertrophic level concentration ratios ($K_{receptor\text{-}diet}$) were obtained from studies of natural populations of fish, zooplankton, and phytoplankton. Based on studies using methylmercury/nitrogen ratios in whole fish, the concentration ratio

between two adjacent trophic levels was found generally to be around 3 to 4 (studies cited in Lindqvist et al. (1991)). As noted in Section 6.4.2, mercury transfers from algae to water-column herbivores in TRIM.FaTE implicitly include the intermediate transfer from algae to zooplankton. Concentration ratios between planktivorous fish and phytoplankton were between 9 and 16 (Lindqvist et al. 1991, Watras and Bloom 1992). That is, zooplankton were an intermediate trophic level and the transfers between each trophic level were approximately equal. Taking the geometric mean results in approximate concentration ratios for methylmercury of 3.5 for one trophic-level transfer and 12 for two trophic-level transfers (Mason et al. 1996).

Inorganic mercury (divalent) transfer factors between phytoplankton and zooplankton and between zooplankton and planktivorous fish are given by Watras and Bloom (1992). In the absence of similar factors for fish-to-fish transfers of inorganic mercury, the zooplankton-to-planktivorous-fish transfer factor was used to estimate the concentrations in the water-column omnivore, water-column carnivore, benthic omnivore, and benthic carnivore compartment types. In other words, in the current TRIM.FaTE library, the mercury partition coefficient between adjacent trophic levels in the time-to-equilibrium model for bioaccumulation by fish is set as follows:

$$K_{fish\text{-}diet} = 3.5.$$

A.1.5 PLANT MESOPHYLL RESISTANCE

A general plant algorithm for mesophyll resistance was added to TRIM.FaTE to accommodate the behavior of mercury in plants. For most organic chemicals and most plant species, the stomatal or cuticular conductance is the rate-limiting pathway (Riederer 1995). Therefore, for many chemicals, there is no need to consider mesophyll (inner tissue) conductance. However, some work with mercury cited in Lindberg et al. (1992) suggests that "resistance on or within mesophyll surfaces dominates the atmosphere-leaf diffusive path of Hg(0)."

For herbaceous species, Lindberg et al. (1992) indicate that this mesophyll resistance for elemental mercury is a factor of 2.5 × stomatal resistance and that mesophyll conductance is a factor of 1/2.5 or 0.4 × stomatal conductance. TRIM.FaTE therefore uses the following equation for elemental mercury (only):

$$g_m = g_{stomata} \times 0.4 \qquad \text{(Eq. A-6)}$$

where:

g_m = conductance of chemical through mesophyll (m/day); and
$g_{stomata}$ = conductance of chemical through stomata (m/day).

Note that the high mesophyll resistance of elemental Hg might be due to its assimilation in mesophyll tissue (Lindberg et al. 1992). It has previously been assumed that the mesophyll resistance for divalent mercury is 0.0 (U.S. EPA 1997a); *i.e.*, that g_m is infinite.

A.2 MERCURY TRANSFORMATION ALGORITHMS

Since there are three species of mercury, there are six possible transformation routes from one species to another. All but one of these routes will be considered:

- Reduction Hg(2)→ Hg(0);
- Oxidation Hg(0) → Hg(2);
- Methylation Hg(2)→ CH_3Hg;
- Demethylation CH_3Hg → Hg(2); and
- Mer cleavage demethylation CH_3Hg → Hg(0).

The route not considered is methylation of Hg(0), for which little information has been reported.

In the case of mercury, the transformation from one chemical species to another is modeled using a first-order rate constant. In particular, the following general equations may be used to model transformation:

$$\textit{Reduction}, Hg^{2+} \rightarrow Hg^{0}: \quad \frac{dM_1}{dt} = k_R \times M_2(t) \qquad \text{(Eq. A-7)}$$

$$\textit{Oxidation}, Hg^{0} \rightarrow Hg^{2+}: \quad \frac{dM_2}{dt} = k_O \times M_1(t) \qquad \text{(Eq. A-8)}$$

$$\textit{Methylation}, Hg^{2+} \rightarrow CH_3Hg: \quad \frac{dM_3}{dt} = k_M \times M_2(t) \qquad \text{(Eq. A-9)}$$

$$\textit{Demethylation}, CH_3Hg \rightarrow Hg^{2+}: \quad \frac{dM_2}{dt} = k_{Dm} \times M_3(t) \qquad \text{(Eq. A-10)}$$

$$\textit{Mer cleavage demethylation}, CH_3Hg \rightarrow Hg^{0}: \quad \frac{dM_1}{dt} = k_{MC} \times M_3(t) \qquad \text{(Eq. A-11)}$$

where:

M_1 = mass of elemental mercury in a compartment type (g[Hg(0)]);
M_2 = mass of divalent mercury in a compartment type (g[Hg(2)]);
M_3 = mass of methylmercury in a compartment type (g[CH_3Hg]);
k_R = reduction rate in compartment type (/day);
k_O = oxidation rate in compartment type (/day);
k_M = methylation rate in compartment type (/day);
k_{Dm} = demethylation rate in compartment type (/day); and
k_{MC} = mer cleavage demethylation rate in compartment type (/day).

The transformation rates may be input directly or calculated based on other parameters. If both algorithms and input values are available, then the user will be able to choose which method to use. The corresponding transfer factors for Equations A-7 through A-10, respectively, are listed below:

$$T_{Hg(2)\rightarrow Hg(0)}^{reduction} = k_R \quad \text{(TF A-5)}$$

$$T_{Hg(0)\rightarrow Hg(2)}^{oxidation} = k_O \quad \text{(TF A-6)}$$

$$T_{Hg(2)\rightarrow CH_3Hg}^{methylation} = k_M \quad \text{(TF A-7)}$$

$$T_{CH_3Hg\rightarrow Hg(2)}^{demethylation} = k_{Dm}$$

A.2.1 ABIOTIC MERCURY TRANSFORMATION RATE CONSTANTS

The information in Tables A-2 through A-13 is taken primarily from the 1997 Mercury Report to Congress (U.S. EPA 1997a) and model documentation for EPRI's R-MCM Mercury Cycling Model (Hudson et al. 1994).

Table A-2
Issues Related to Reduction of Hg(2) to Hg(0) in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
Decreases in decreasing sunlight	Decreases with decreasing sunlight and temperatures	Sparse literature on subject
Abiotic reduction (transfer of electrons from humic acid to Hg(2)) is dependent on pH	Has been observed to increase with decreasing dissolved organic carbon (DOC) conditions (Amyot et al. 1997), and vice versa, due to reduced light penetration and increased complexation of Hg(2)	
Strong stability complex between Hg(2) and humic acid		

Table A-3
Reduction (k_R) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
5E-1to 3.5	Experimental value using simulated sunlight, after normalizing to sunlight in Stockholm, Sweden	U.S. EPA (1997a), Xiao et al. (1995)
5E-3 to 1E-1	Based on mass balances in Wisconsin seepage lakes	U.S. EPA (1997a), Mason et al. (1994)
2E-2 to 4E-2	Epilimnion	Mason et al. (1995)
1E-2	9 m depth	Mason et al. (1995)
<5E-3	17 m depth	Mason et al. (1995)
1.4E-1	high Arctic lake during 24 hour sunlight period	Amyot et al. (1997)
2E-1 to 4E-1	high Arctic lake, low DOC conditions	Amyot et al. (1997)
2E-2 to 1.4E-1	high Arctic lake, high DOC conditions	Amyot et al. (1997)
1E-1	July-August, upper 3 m	Vandal et al. (1995)
5E-2	July August, upper 6 m	Vandal et al. (1995)
7.5E-3	Value in current TRIM.FaTE library	U.S. EPA (1997a)

Table A-4
Reduction (k_R) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-6	Inferred value calculated based on presence of Hg(0) in sediment porewater	U.S. EPA (1997a), Vandal et al. (1995)
0.216	Derived from humic acid from farm pool sediment. pH did not appear to affect the rate of reaction, but does seem to influence the amount of mercury reduced	Alberts et al. (1974)
1E-6	Value in current TRIM.FaTE library	U.S. EPA (1997a), Vandal et al. (1995)

Table A-5
Reduction (k_R) in Soil: Inputs

Equations to Calculate Input Values	Comment	Reference(s)
$k_R^{soil} = k_{norm} \times \theta \times d_{Ss} \times d_S$ where k_{norm} = reduction rate constant normalized by soil water content in the surficial 5 mm of soil (L[soil]/L[water]-day); values range from 1E-4 for forest site to 1.3E-3 for field site; θ = soil water content (L[water]/L[soil]); d_{Ss} = depth of soil surface layer to which reduction rate is normalized, 5E-3 (m); and d_S = soil layer depth (m).	Formula is derived from evasion flux measurements	U.S. EPA (1997a), Carpi and Lindberg (1997)

Table A-6
Issues Related to Methylation in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
Anaerobic conditions favor higher methylation rates[a]	Anaerobic conditions favor higher methylation rates[a]	Anaerobic conditions favor higher methylation rates[a]
Biotic methylation may occur due to bacteria; abiotic methylation may occur by transmethylation from other organometals or by humic substances[b]	Photodegradation at surface can lower the gross methylation rate[c]	Highest rates may occur at the sediment surface (sulfate-reducing bacteria may be important mediators of the reaction), Gilmour and Henry (1991)
Increases with increasing organic carbon content and BHT[f]	Positively correlated with DOC[d] (dissolved organic carbon)	Positively correlated with TOC (total organic carbon)[d]
Generally occurs for Hg(2) dissolved in soil pore water	Generally occurs for Hg(2) dissolved in water column[d]	Generally occurs for Hg(2) dissolved in sediment pore water[d]
Abiotic methylation is proportional to temperature and Hg(2) concentration. Also, it is inversely proportional to pH (at pH > 5)[g]	Positively correlated with temperature[d]	Positively correlated with temperature[d]
	Potentially positively correlated with sulfate concentration in water column[e]	Potentially positively correlated with sulfate concentration in sediment pore water[e]

a This is generally due to increased bacterial reactions in anaerobic conditions.
b: U.S. EPA (1997a), Gilmour and Henry (1991).
c: Initial reference is Bob Ambrose's discussion of methylation in water column in U.S. EPA (1997a).
d: Hudson et al. (1994).
e: Watras et al. (1995).
f: Nagase et al. (1984); BHT = 2,6, di-tert-butyl-methyl phenol.
g: Bodek et al. (1988).

Table A-7
Methylation (k_M) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-4 to 3E-3	reported as maximum potential methylation rate	Gilmour and Henry (1991)
6E-4 to 6E-3	Depth of 3 - 9m	U.S. EPA (1997a), based on Henry et al. (1995a, 1995b) and Jacobs et al. (1995)
5E-4 to 1E-3	Oxic portion of four forest lakes in Finland	Matilainen (1995)
1E-2 to 3E-2	At seasonally-anoxic depth of 15 m	U.S. EPA (1997a), based on Henry et al. (1995a, 1995b) and Jacobs et al., (1995)
4E-3 to 1E-2	Anaerobic layers of hypolimnion	Matilainen (1995)
1E-2 to 4E-2	0.5 - 1.0 m layer of bacterioplankton near the top of the anoxic hypolimnion	Watras et al. (1995)
1E-3	Value in current TRIM.FaTE library	U.S. EPA (1997a)

Table A-7
Methylation (k_M) in Surface Water: Inputs (cont.)

Equations to Calculate Input Values	Comment	Reference
$k_M^{SW} = \frac{k_{MW} \times Q_{10m}^{(T-Tb)\times 0.1} \times C_{DOC} \times f_{ma}^{Hg(2)} \times f_{dissolved}^{Hg(2)} \times C_{Su}}{C_{Su} + K_{Su}}$ where: k_{MW} = methylation rate constant in the water column, based on DOC (L/mg[DOC]-day); Q_{10m} = term to adjust methylation rate for temperature (implied value in R-MCM documentation is 2, so that methylation rate doubles for every 10 degree increase in temperature above the base temperature); T = water column temperature (degrees Celsius); Tb = base temperature at which methylation rate constant k_{MW} applies (degrees Celsius); C_{DOC} = DOC concentration in water column (mg[DOC]/L); f_{ma} = fraction of the dissolved Hg(2) in the water column available for methylation (unitless); $f_{dissolved}$ = fraction of the Hg(2) in the water column that is dissolved (unitless); C_{Su} = concentration of sulfate in the water column (µeq[sulfate]/L[water]); and K_{Su} = half-saturation constant for the effect of sulfate on methylation (µeq[sulfate]/L[water[).		Hudson et al. (1994)].

Table A-8
Methylation (k_M) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-5 to 1E-3	Reported as maximum potential methylation rate	Gilmour and Henry (1991)
8E-4 to 2.5E-2	Above intact sediment cores	Stordal and Gill (1995)
8E-5 to 2E-5	Upper 4 cm of Little Rock Lake sediments	Calculated in U.S. EPA (1997a) from methylation rates in units of ug/m^2/day (Gilmour and Riedel 1995) and assumed dry density of 1.2 g/cm^3
1E-4	Value in current TRIM.FaTE library	U.S. EPA (1997a)
Equations To Calculate Input Values	**Comment**	**Reference(s)**
$k_M^{Sed} = k_{MS} \times Q_{10m}^{(T-Tb)\times 0.1} \times C_{TOC} \times f_{ma}^{Hg(2)} \times f_{dissolved}^{Hg(2)} \times ((\theta_i - \theta_b) \times 0.5) \times C_{SPWSu} \div \left(C_{SPWSu} + K_{Su}\right)$ where: k_{MS} = methylation rate constant in the sediment, based on TOC (m^3/g[TOC]-day); Q_{10m} = term to adjust methylation rate for temperature (implied value in R-MCM documentation is 2, so that methylation rate doubles for every 10 degree increase in temperature above the base temperature); T = sediment temperature (degrees Celsius); Tb = base temperature at which methylation rate constant K_{MS} applies (degrees Celsius); C_{TOC} = TOC concentration in water column (g[organic carbon]/m^3); f_{ma} = fraction of the dissolved Hg(2) in the sediment pore water available for methylation (unitless); $f_{dissolved}$ = fraction of the Hg(2) in the sediment that is dissolved (unitless); θ_i = volume fraction water of the sediment at the sediment/water interface (unitless); θ_b = volume fraction water of the bottom of the sediment (unitless); C_{SPWSu} = concentration of sulfate in the sediment pore water (µeq/L); and K_{Su} = half-saturation constant for the effect of sulfate on methylation (µeq/L).		Hudson et al. (1994), p.5-22

Table A-9
Methylation (k_M) in Soil: Inputs

Input Values (1/day)	Comment	Reference(s)
2E-4	minimum value for average maximum potential methylation rate constant under aerobic conditions for 120-day experiment	Porvari and Verta (1995)
1E-3	maximum value for average maximum potential methylation rate constant under anaerobic conditions for 120-day experiment	Porvari and Verta (1995)
7E-5 to 9.7E-4	Range for median aerobic reaction rate (from peat, humus layer, and soil samples, respectively)	Verta et al (1994)
9.2 E-3	Anaerobic median rate of four inundated soil samples (range = 4.2E-3 to 1.2E-2/day)	Verta et al. (1994)
1E-3	Value in current TRIM.FaTE library	Porvari and Verta (1995)

Table A-10
Issues Related to Demethylation in Soil, Surface Water, and Sediment

Soil	Surface Water	Sediment
May increase with increasing anaerobic conditions	Negatively correlated with light	May depend on bacteria processes
		Has been reported as maximal at the sediment/water interface (Gilmour et al. 1992)

Table A-11
Demethylation (k_{Dm}) in Surface Water: Inputs

Input Values (1/day)	Comment	Reference(s)
1E-3 to 2.5E-2 Value in current TRIM.FaTE library = 0.013	Maximum potential demethylation rate constants	Gilmour and Henry (1991)
Equations Used to Calculate Input Values	**Comment**	**Reference(s)**
$k_{Dm}^{SW} = (k_{ds} / L_{ext}) \times \left(1 - e^{-L_{ext} \times d_{SW}}\right) / d_{SW}$ where: k_{ds} = demethylation rate constant at the lake surface (/day) L_{ext} = light extinction coefficient for use in demethylation calculations (/m) d_{SW} = mean depth of water column (m)		Hudson et al. (1994)

Table A-12
Demethylation (k_{Dm}) in Sediment: Inputs

Input Values (1/day)	Comment	Reference(s)
2E-4 to 1E-1 Value in current TRIM.FaTE library = 0.0501	Reported maximum potential demethylation rate constants	Gilmour and Henry (1991)
Equations to Calculate Input Values	**Comment**	**Reference(s)**
$k_{Dm}^{Sed} = k_{DmS} \times C_{TOC} \times f_{dissolved}^{MHg} \times \left((\theta_i + \theta_b) \times 0.5\right)$ where k_{DmS} = demethylation rate in the sediment, based on TOC (m^2/g[TOC]-day) C_{TOC} = TOC concentration in sediment (g[organic carbon]/m^2) $f^{MHg}_{dissolved}$ = fraction of the methylmercury in the sediment that is dissolved (unitless) θ_i = porosity of the sediment at the sediment/water interface (unitless) θ_b = porosity of the bottom of the sediment (unitless)		Hudson et al. (1994)

Table A-13
Demethylation (k_{Dm}) in Soil: Inputs

Input Values (1/day)	Comment	Reference(s)
3E-2	Average of maximum potential demethylation rate constants in aerobic conditions	Porvari and Verta (1995)
6E-2	Average of maximum potential demethylation rate constants in anaerobic conditions	Porvari and Verta (1995)
3.6E-2, 7.6E-2, 1.1E-1	Median aerobic rates for 15 inundated soil samples, 15 humus layer samples, and five peat samples, respectively.	Verta et al. (1994)
8.9E-2	Median anaerobic rate for 15 inundated soil samples.	Verta et al. (1994)
6E-2	Value in current TRIM.FaTE library	Porvari and Verta (1995)

A.2.2 BIOTIC MERCURY TRANSFORMATION RATE CONSTANTS

A.2.2.1 Plants

Fortmann et al. (1978) observed that some plants can change the mercury species accumulated from the environment. However, few studies are available from which to determine transformation rates.

Hg(0) → Hg(2)

The oxidation of elemental mercury to divalent mercury (transformation listed above) occurs in leaves; elemental mercury is probably not taken up by the root. This oxidation rate is apparently very rapid and may be assumed to be instantaneous (U.S. EPA 1997a). No instances have been found where elemental mercury was measured in plants (*e.g.*, Cappon 1987). Thus, elemental mercury in air or on the surface of the leaf can be directly transferred to divalent mercury in the leaf.

Hg(2) → CH_3Hg

It is assumed that the methlyation of Hg(2) to methylmercury (CH_3Hg) does not occur in plants. Although the *in vivo* transformation of inorganic mercury to methylmercury was observed in *Pisum sativum* (peas) in one study (Gay 1975), the chemical was ephemeral and quickly (several hours) decayed to low parts per billion levels. Methylmercury residues were not detected in mature crops following the addition of mercuric chloride to soil (Bache et al. 1973). Indeed, most mercury in plants is usually in inorganic form (Lindberg 1998).

CH_3Hg → Hg(2)

It is assumed that demethylation of methylmercury to Hg(2) (above) occurs in leaves and stems, but not in roots (because transformations interfere with the equilibrium assumption in roots). We assume that methylmercury is transformed to Hg(2) according to first-order kinetics, where the first-order rate constant is 0.03 /day, based on the following information.

Only one study is available in which methylmercury was added to soil and the forms of mercury (methyl and total) were measured after a defined period of exposure (Bache et al. 1973). In the few other studies of speciation of mercury within plants, either it is not known which species were present in soil (*e.g.*, Heller and Weber 1998), or multiple Hg species were present in soil and it is not known which were initially taken up by the plant (Cappon 1987).

Using data from Bache et al. (1973) (see Table A-14 below), we assume that the methylmercury is readily taken up through the roots or foliage, that equilibrium between soil and plant is achieved quickly, that methylmercury is not appreciably transformed in soil during a crop season, that all methylmercury is only transformed to ionic mercury, and that crops were harvested after 40 days. Under these assumptions, 1st-order rate constants for the transformation of methylmercury to Hg(2) vary by almost two orders of magnitude in a single study. No mechanistic explanation is available for

Table A-14
Concentrations of Methylmercury in Foliage and Stems of Crops from Bache et al. (1973) and Associated First-order Rate Constants, Using Assumptions in Text

Plant Species	Soil	Application to Soil (mg/kg)	Total Mercury in Foliage and Stem	Methylmercury in Foliage and Stem	1st Order Rate Constant (d^{-1})
Bush bean (*Phaseolus vulgaris*)	gravelly loam	1	52	46	0.003
Bush bean (*Phaseolus vulgaris*)	gravelly loam	10	90	28	0.03
Carrot (*Daucus carota*)	gravelly loam	10	214	1	0.1
Potato (*solanum tuberosum*)	silt loam	1	86	27	0.03
Potato (*solanum tuberosum*)	silt loam	10	58	17	0.03
Tomato (*Lycopersicon esculantum*)	gravelly loam	10	341	3	0.1

this high degree of variability. The default value of 0.03 /day in the TRIM.FaTE library for demethylation of methylmercury to Hg(2) in plants is one of the mid values in the range.

A.2.2.2 Soil Detritivores

No information is available for transformations of mercury in soil detritivores. In addition, transformation algorithms cannot be implemented if the mercury in these organisms is in equilibrium with mercury in root-zone soil.

A.2.2.3 Terrestrial and Semi-aquatic Wildlife

Little quantitative information is available on the transformation of mercury in mammals and birds. Where information is available, calculations of rate constants assume first-order transformations and are calculated on the basis of the total mercury ingested by the organism but not necessarily absorbed. (The exception is the inhalation pathway, where rate constants are derived based on the absorbed fraction.)

Hg(0) → Hg(2)

No information is available from which to derive transformation rate constants for the oxidation of elemental mercury to the mercuric ion. Based on the following information, we assume that the rate is rapid, and 1.0 /day is a rough estimate of the first-order rate constant. Elemental mercury is readily oxidized to the inorganic divalent species in most tissues via the

hydrogen peroxidase-catalase pathway. This oxidation primarily occurs in the red blood cells, and hydrogen peroxide is probably the rate-limiting reactant (ATSDR 1997, U.S. EPA 1997b).

Hg(2) → Hg(0)

Mercuric salts primarily remain in their divalent form. However, a small fraction of the inorganic divalent cation can be reduced to elemental mercury and exhaled as a vapor (ATSDR 1997). Given the lack of information on the rate of this transformation, the transformation is assumed not to occur.

Organic mercury → Hg(2)

Forms of organic mercury are the most studied species of mercury. The short-chain alkyl mercury compounds (*e.g.* methylmercury) are relatively stable and are more slowly metabolized to the inorganic form than the longer-chain compounds (U.S. EPA 1997b) The longer-chain compounds may be more readily metabolized to the mercuric ion (U.S. EPA 1997b). Takeda and Ukita (1970) dosed Donryu rats with 20 μg Hg/kg body weight as ethyl-mercuric chloride via intravenous injection. After 8 days, 58.1 percent of the mercury excreted in the urine was inorganic mercury and 35 percent of the mercury excreted in feces was inorganic (Table A-15). If it is assumed that (1) the excreted chemicals reflect the transformation rate in the animal (transformation occurred immediately prior to excretion) and (2) the first-order transformation rate reflects a weighted average of the amount of dose excreted in urine (10.52 percent) and that excreted in feces (6.01 percent), then the transformation rate may be estimated to be 0.09 /day.

Table A-15
Transformation Rate (/day) of Organic Mercury to the Inorganic Divalent Form in Mammals (Takeda and Ukita 1970)

Elimination Type	Dose Route	% Organic after 8 days	% Inorganic after 8 days	Transform Rate Constant
urine	injection	41.9	58.1	0.1084
feces	injection	65.0	35.0	0.0539
assumed transformation for whole animal				0.09

Hg(2) → organic mercury

No information is available on this transformation. Therefore it is assumed to be zero.

A.2.2.4 Aquatic Species

Transformations of mercury in algae, macrophytes, and benthic organisms are assumed not to occur with one exception. It is assumed that elemental is transformed to divalent mercury in macrophytes, and the transformation is described as a rapid (almost instantaneous) first-order rate constant (*i.e.*, 10^6 to 10^9). Thus, it is assumed that elemental mercury can be taken up by

macrophytes but is not accumulated in macrophytes (*i.e.*, data showing Hg(0)) in macrophytes were not found). Data demonstrating methylation of divalent mercury or demethylation of methylmercury in macrophytes also were not found.

$Hg(2) \rightarrow CH_3Hg$

Very little is known about the rate at which transformation of mercury species occurs in aquatic organisms. A large body of field data suggests that most (> 90 percent) of mercury in fish is in the form of methylmercury and other organic species (represented here simply as CH_3Hg); however, methylation of inorganic mercury has not been demonstrated in fish. For this reason, it is assumed that methylation of divalent mercury does not to occur in fish.

$Hg(0) \rightarrow Hg(2)$

Oxidation of elemental mercury is assumed to occur instantaneously in fish.

$Hg(0) \rightarrow CH_3Hg$

Methylation of inorganic mercury is assumed not to occur directly in fish.

$Hg(2) \rightarrow Hg(0)$

Reduction of divalent mercury is assumed not to occur in fish.

$CH_3Hg \rightarrow Hg(2)$

Demethylation is assumed not to occur in fish.

$CH_3Hg \rightarrow Hg(0)$

Mer cleavage demethylation is assumed not to occur in fish.

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