Adaptation of Fugacity Models To Treat Speciating Chemicals with Constant Species Concentration Ratios

L I I S A   K .   T O O S E   A N D   D O N A L D   M A C K A Y *

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A "multiplier" method is developed by which multimedia mass balance fugacity models designed to describe the fate of a single chemical species can be applied to chemicals that exist as several interconverting species. The method is applicable only when observed ratios of species concentrations in each phase are relatively constant and there is thus no need to define interspecies conversion rates. It involves the compilation of conventional transformation and intermedia transport rate expressions for a single, selected key species, and then a multiplier, R_i, is deduced for each of the other species. The total rate applicable to all species is calculated as the product of the rate for the single key species and a combined multiplier ($1 + R_2 + R_3 +$ etc.). The theory is developed and illustrated by two examples. Limitations of the method are discussed, especially under conditions when conversion rates are uncertain. The advantage of this approach is that existing fugacity and concentration-based models that describe the fate of single-species chemicals can be readily adapted to estimate the fate of multispecies substances such as mercury which display relatively constant species proportions in each medium.

Introduction

There are several situations in which it is necessary to consider the simultaneous environmental fate of related chemical species. Examples include acids and bases which ionize, chemicals which are subject to chemical conversion such as thions to oxons, dechlorination reactions, and metals which may form ionic and organometallic forms, mercury being the most common example. Multimedia models describing the fate of single chemicals are widely available and are successfully applied, but these models rarely address multispecies substances. It is not feasible to apply a single model to each species independently because of uncertainties about the locations and rates of species-to-species conversions. Thus, there is a need for one or more multispecies, multimedia, mass balance models that can be applied, as needed, to chemicals that are subject to reversible or irreversible conversions.

This issue has been addressed by several groups. Fenner et al. (*1*) used a multimedia model to assess the persistence of a chemical with respect not only to the parent compound but also its transformation products. Overall or "primary"

persistence is calculated for each compound; "secondary" persistence is calculated for all transformation products as they are formed from the parent compound. A "joint" persistence, which combines the two, is also calculated. This approach provides a valuable tool by which environmental contamination by such substances can be predicted and assessed. This approach has been extended by Fenner et al. (*2, 3*) using a matrix inversion method for calculation of concentrations of several species at steady-state or by eigenvalues and eigenvectors for a dynamic approach.

Cahill et al. (*4*) presented a multimedia, multispecies, fugacity-based model to predict the fate of several speciating, organic chemicals. Four interconverting species are defined, and a fifth represents degradation products formed irreversibly from these species. The fifth species, of undefined chemical structure, is included for confirming the mass balance. Not all species need to be defined, nor need all reactions be included, thus this general case can be simplified as required. If there are N compartments and i species, $N \cdot i$ differential equations can be written and solved simultaneously, usually by numerical integration. This rigorous approach is, however, computationally demanding, and the results may be difficult to interpret. Most problematic, however, is the parametrization of the species to species conversion rates.

The Fenner (*1−3*) and Cahill (*4*) approaches can estimate environmental concentrations of interconverting species using measured and estimated reaction rate constants describing the interconversion of one chemical species to another in the various media. These are the only feasible approaches when interconversion rates are comparable to, or slower than, other environmental processes. Reliable estimates of these rate constants are required, but often as in the case of mercury, these interconversion rates are either very fast or are not well quantified.

In an earlier study, Diamond et al. (*5*) developed a fugacity-based "aquivalence" formulation that treats separate species of a chemical in one "pseudo-single component" mass balance equation. This method defines constant concentration ratios of a chemical species within each medium. This avoids the necessity of defining interspecies conversion rates and is most advantageous when these rates are fast and concentration ratios among species are constant or nearly so. The proportion of each species within the "total" quantity of contaminant in each medium is deduced, namely the "aquivalence fraction". These weighted values are combined to describe how the "total" chemical behaves. Because all the partitioning constants are relative to the water phase of the environment, this methodology is suitable for assessing the fate of both volatile and nonvolatile substances. This method only considers the bulk air, water, and sediment compartments and has been applied to describe the behavior of mercury in environments such as a lake typical of the Canadian Shield (*6*) and the Lahontan Reservoir, NV (*7*).

Our objective is to suggest an approach for modeling multispecies substances with constant species concentration ratios based on what we believe to be a simpler approach than that of Diamond et al. (*5*). It is suggested that the new formulation can be readily implemented in existing single species models. Our focus is on fugacity or aquivalence models, but equivalent versions can be written in concentration format. We address in detail the limitations of the approach, especially when species conversion rates are uncertain.

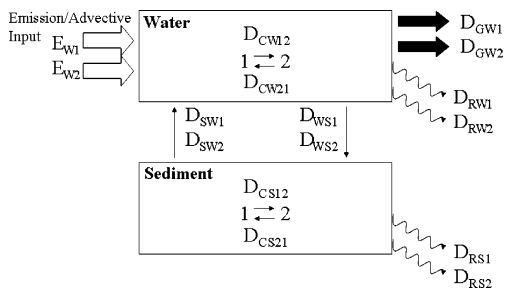* Corresponding author phone: (705)748-1005; fax: (705)748-1080; e-mail: dmackay@trentu.ca.

FIGURE 1. Two-compartment, two-species illustrative environment and processes, including species conversions.

Model Development

Fugacity Modeling. Fugacity may be defined as a "fleeing tendency" and can be viewed as partial pressure (8). It has units of pressure (Pa). In context of multimedia chemical fate modeling it describes the relative tendency of a chemical to either remain in or "flee" from a medium such as air, water, soil, sediment, or biota. Chemical specific air—water and octanol—water partition coefficients along with environmental characteristics (volume, organic matter fraction, etc.) determine the "fugacity capacity" (Z-value, mol/m³Pa) of a medium which relates concentration, C (mol/m³) to fugacity, f(Pa) where C is Zf. Chemical transport parameters (D-values, mol/hPa) are determined by multiplying an effective transport rate, G (m³/h) by the fugacity capacity of the originating environmental compartment (mol/m³Pa) ($D = GZ$). D-values are used to describe all transport mechanisms including advection from the system, transfer between media by diffusion, deposition, or resuspension. They are also used to quantify degrading and interspecies conversion reactions. The rate by which a chemical is transported, Q (mol/h), is calculated by multiplying the transport parameter by the fugacity of the originating compartment ($Q = Df$). Under steady-state conditions (total inputs of a chemical to the system are equal to total outputs) and for a single species substance a set of mass-balance equations (one for each environmental compartment) can be written in the form

$$E + AI + \Sigma f_j(D_{INPUT}) = f_I(D_{LOSS}) \quad (1)$$

Equation 1 describes the mass balance for compartment 1 where E is direct emission (mol/h) to the compartment, AI is advective inputs to the system (mol/h) f_j are the fugacities of external compartments, from which a chemical is transported (D_{INPUT}); on the right-hand side of the equation, f_I is fugacity of compartment 1, and D_{LOSS} is the sum of the D-values describing outputs from this compartment. Equivalent equations can be written for other environmental compartments. The set of equations is solved to determine the fugacity of each compartment. The rates (Q, mol/h) of the transport processes can be determined as well as concentrations (mol/m³) within each compartment. Treatment of interconverting species is addressed below.

General Case Including Interspecies Conversion Rates. For illustrative purposes, we first treat the general case of a simple two-compartment environment (such as a water—sediment system) for two species of a chemical including interspecies conversion rates as shown in Figure 1. This figure uses D-values to characterize the transport pathways available to the chemical. Both species can be emitted into the water compartment by a combination of direct discharge and/or advective inflow ($E_{W1} + E_{W2}$). Conversions occur between species (D_{CW12}, D_{CS21}, etc.), transport is possible between compartments (D_{WS1}, D_{SW2}, etc.), and there are reaction ($D_{RW1} + D_{RW2}$) and advective ($D_{GW1} + D_{GW2}$) losses in the aquatic compartment and only loss by chemical degradation ($D_{RS1} + D_{RS2}$) in the sediment compartment. We consider both

steady-state and unsteady-state or dynamic conditions; however, the primary focus of this paper is on steady-state conditions.

Under dynamic conditions, when predicting the change in mass of a chemical in the system, differential equations are applied to describe the inputs and outputs affecting each compartment. The mass balance differential equation for species 1 in the water compartment is

$$d(V_W Z_{W1} f_{W1})/dt = E_{W1} + D_{SW1}f_{S1} + D_{CW21}f_{W2} - f_{W1}(D_{CW12} + D_{WS1} + D_{RW1} + D_{GW1}) \quad (2)$$

The expression on the left is the rate of inventory change (mol/h) in the water of species 1, calculated as the derivative of the amount of a chemical in the compartment expressed as the product of the compartmental volume, V_W (m³), the fugacity capacity, Z_W (mol/m³ Pa), and the fugacity, f_{W1} (Pa), of the species. The terms on the right include inputs to the system such as emission of species 1 into the water including any advective input, E_{W1} (mol/h), transport of 1 from sediment to water, D_{SW1} (mol/Pa h), and conversion of species 2 to 1 in the water (D_{CW21}). The loss terms are conversion of 1 to 2 in the water (D_{CW12}), transport of 1 from water to sediment (D_{WS1}), degrading reaction of 1 to species other than 2 (D_{RW1}), and finally advective loss of 1 from the water (D_{GW1}). A similar equation can be written for species 2 in the water by substituting 2 for 1 and 1 for 2. Further, an analogous pair of equations can be written for the sediment compartment by substituting water for sediment and sediment for water.

There are thus four equations and four unknowns that can be solved for the four fugacities. The extension to a larger number of compartments and species is obvious. Solution of the differential equations requires an initial condition, knowledge of emission rates as a function of time and all the volumes, Z and D-values. The equations are most easily solved by numerical integration (2−4), but as Fenner et al. (2) have pointed out, analytical solution is possible.

The steady-state versions can be obtained by setting the left side of eq 2 to zero. An analytical solution is straightforward provided the number of unknowns is not excessive. In some cases, it may be more convenient to obtain the steady-state solution by integrating the differential equations until constant fugacities are reached.

Most problematic from the perspective of data input or availability are probably the species interconversion D-values (mol/m³ Pa) for each compartment. When interconversion is fast, as occurs with ionization, the D-values are large necessitating a correspondingly short integration time step. Often an estimate is available in the form of a conversion half-time, $\tau_{1/2}$ (h). This can be converted to a D-value by use of the corresponding rate constant k_{CN12} (h⁻¹) which is $0.693/\tau_{1/2}$, the D-value, designated D_{CN12} (subscript "c" for conversion in compartment "N") being $V_N Z_N k_{CN12}$. When equilibrium is approached between the species with an equilibrium constant K_{12} equal to the ratio of the concentration of species 1 to that of species 2, (C_{N1}/C_{N2}), the forward and backward D-values can be deduced. Since the forward and backward rates are equal, $C_1 k_{CN12} = C_2 k_{CN21}$, therefore $f_1 D_{CN12} = f_2 D_{CN21}$, thus $f_{N1}/f_{N2} = D_{CN21}/D_{CN12} = Z_{N2}k_{CN21}/Z_1 k_{CN12}$ since the volume cancels. Since $K_{12} = C_{N1}/C_{N2} = k_{CN21}/k_{CN12}$, $K_{12} = D_{CN21}Z_{N1}/D_{CN12}Z_{N2}$.

If one D-value is known, then the other can be deduced from it using K_{12} and the ratio of Z-values. Whereas K_{12} is a ratio of concentrations and rate constants, the ratio of D-values is the ratio of fugacities. Conversion between the ratios of concentrations and fugacities requires the corresponding ratio of Z-values.

Constant Ratios of Species Concentrations. If the species conversion rates are fast relative to other processes, or equivalently, the time for species to species conversion is

short relative to the residence time of the substance in a compartment, as described above, then the ratio of concentrations will be approximately constant as dictated by K_{12}. The ratio of species fugacities ($F_{N21} = f_{N2}/f_{N1}$) will also be constant. This constraint increases the number of equations (but reduces the number of unknowns), thus only one fugacity is unknown in each compartment and the solution is similar to that employed in single species calculations, i.e., all of the f_{N2} terms in eq 2 can be replaced by an expression, $F_{N21}f_{N1}$, thus for N compartments there are N unknown fugacities. In eq 2 and its analogue for species 2, the conversion terms $D_{CW21}f_{W2}$ and $D_{CW12}f_{W1}$ cancel since these rates are fast and equal. The conversion D-values are now not needed. It is then immaterial if the emission to the compartment is of species 1 or 2. We believe that this proposed approach may be applicable in an approximate form when the rates of conversion are slow but monitoring demonstrates relatively constant concentration ratios. In some cases species A may dominate in phase 1 and species B in phase 2, an example being elemental mercury in air and ionic mercury in water.

In a previous treatment of this issue (5) the aquivalence formulation was used instead of the fugacity formalism, but the derivation is essentially identical. The use of aquivalence is more convenient and rigorous for substances with zero vapor pressure such as ions. Instead of starting the definition of Z in the air phase it starts in the water phase. In that study a total aquivalence was deduced for all species. An average Z-value is deduced as a weighted mean of the individual values, the weighting being based on aquivalences rather than concentrations and the mass balance is subsequently carried out using the weighted Z-values in the aquivalence formulation.

Derivation of the Multiplier Method. Here we suggest what we believe to be a more transparent and simpler approach which will yield identical results and does not require the introduction of a total aquivalence or an average Z-value. It transpires that all that is required is a series of "multipliers" which are used to increase the D-values of a key species to account for transport or transformations of other species.

First, we select one species as the "key species", preferably one which is present in all media, at least to some, and possibly negligible, but finite, extent. It is designated as species 1.

The total rate Q (mol/h) of each transport and reaction process for species 1 and 2 is then given by an equation of the generic form

$$Q = f_1 D_1 + f_2 D_2 = f_1 D_1(1 + (f_2/f_1)(D_2/D_1)) = f_1 D_1(1 + R_2)$$
$$(3)$$

where the multiplier representing the proportion of species 2 that is involved in the overall process is $R_2 = (f_2/f_1)(D_2/D_1)$. If there are i species, there are i terms, such as R_i, which add to produce a total multiplier (R_T) giving

$$R_T = (1 + R_2 + R_3 + R_4 + \ldots R_i) \quad (4)$$

A corresponding multiplier is applied to each key-species D-value, and the adjusted one-species model is run in the conventional manner. The principal task is to determine the R terms and sum them to obtain the overall multipliers (R_T), for each overall transport process, as above.

Determining Multipliers. The first and obvious approach is to obtain Z- and D-values for each species. To accomplish this, the model must be run for each species independently using species-specific Z-values but only to determine the species-specific D-values, there being no need at this stage to solve the mass balance equations. The concentration ratio for each species to species 1 is defined from empirical data

of species proportions observed in the environment, from which the fugacity ratio (F_{21}) is calculated.

$$F_{21} = f_2/f_1 = (C_2/Z_2)/(C_1/Z_1) = (C_2/C_1)\cdot(Z_1/Z_2) \quad (5)$$

The product of fugacity and D-value ratios, in this case R_2, or ($f_2 D_2)/(f_1 D_1)$, is then calculated. This quantity is constant and independent of the absolute quantities of the species present since it depends only on the ratio of quantities, which is assumed to be unvarying. This is repeated for all D-values.

When inputting empirical concentration ratios care must be taken to avoid overspecifying the system. For a compartment containing a single phase such as pure water, the species concentration ratios are C_2/C_1 and the Z-values are Z_2 and Z_1. The fugacity ratio f_2/f_1 is then simply $(C_2/C_1)\cdot(Z_1/Z_2)$ as above. When the compartment contains multiple phases at an assumed equilibrium such as water and suspended particles a single fugacity applies to both phases. Z-values are defined for each phase, and a bulk Z-value is calculated by weighing all phase Z-values in proportion to the volume fractions. Each species concentration ratio in the bulk phase, i.e., including both phases is defined and used with the bulk Z-value to calculate the fugacity ratio. The concentration ratios in each phase can then be determined. They must not be defined since this would overspecify the system. It is possible, as an alternative, to specify a concentration ratio in one phase, e.g. particles, but since the Z-values are defined, this automatically specifies the concentration ratios in other phases of the compartment. The simplest approach is to specify the species concentration ratios in the bulk phase or compartment and then check that the ratios in each component phase are reasonable and in accord with empirical data. If necessary the Z-values can be adjusted to achieve agreement with such data.

It is noteworthy that, in some cases, the ratio terms R can be determined more simply. For advection processes involving a flow rate G (m³/h), D_{Gi} is GZ_i with G being common to both species. It follows that since each $D_{Gi}f_i$ is also GC_i then R_2 is C_2/C_1, R_i is C_i/C_1, etc.

For degrading reactions D_{Ri} is $VZ_i k_{Ri}$ where k_{Ri} is a rate constant. V is common, thus R_2 is $C_2 k_{R2}/C_1 k_{R1}$, R_i is $C_i k_{Ri}/C_1 k_{R1}$, etc.

For diffusion in a single medium, if it is assumed that the species diffusivities are equal, R_2 is again C_2/C_1. This applies if the diffusion rate is defined by a mass transfer coefficient or by a diffusivity and diffusion path length.

For a diffusive process that occurs in series or parallel as in air−water exchange or air−soil exchange this simplification is not possible, and the overall D-values of each multiresistance process must be calculated for each species and then the ratios calculated. This implies that during the exchange process the species retains its identity during the entire transport process.

The inventory change term in the differential equation, when applied to the sum of all species, becomes

$$Vd(Z_1 f_1 + Z_2 f_2)/dt = VZ_1 df_1(1 + (f_2/f_1)(Z_2/Z_1))/dt =$$
$$VZ_1 df_1(1 + C_2/C_1)/dt = VZ_1 df_1(1+R_2)/dt \quad (6)$$

This term is not required for the steady-state solution.

In summary, all process rates are calculated using the fugacity of the key species, but in the mass balance equation each D-value is increased by a multiplier specific to that process of the form $(1 + R_2 + R_3 + R_4 + \ldots)$ to account for simultaneous transport or transformation of other species. The equations are solved for the fugacity of the key species in each phase. The fugacities of other species and the corresponding concentrations can then be deduced since the ratios of species fugacities and concentrations are known. The result is a consistent mass balance for all species. By

inspecting the total rate of input and output of each species to a phase, the net rate of formation or destruction from other species can be deduced. If there are more than two species it may not be possible to calculate the actual individual species-to-species conversion rates, only the net rate.

Application to Concentration-Based Models. This method can also be applied to mass balance models in which the quantity of a chemical is expressed as a concentration rather than a fugacity. Each flux is expressed as the product of a concentration (mol/m³) and a rate parameter G (m³/h) that is essentially the volume of the compartment cleared of the chemical per hour by the process in question. For reactions the parameter G is usually the product of the volume, V (m³), and a rate constant, k (h⁻¹). For advection it is the actual flow rate (m³/h). For diffusion it is the product of a mass transfer coefficient (m/h) and area (m²) or a diffusivity (m²/h) times an area (m²) divided by a diffusion path-length (m). The multiplier R_i is then the product of the ratio of the transport parameter for species i to that of the key species and the concentration ratio i.e., $(G_i/G_1)(C_i/C_1)$. Since D is GZ and f is C/Z the multipliers expressed as Df- and as GC-ratios are equivalent, as shown in eq 7.

$$R_i = \frac{D_i}{D_1} \cdot \frac{f_i}{f_1} = \frac{G_i Z_i}{G_1 Z_1} \cdot \frac{C_i/Z_i}{C_1/Z_1} = \frac{G_i}{G_1} \cdot \frac{C_i}{C_1} \qquad (7)$$

Conventional concentration based models can thus also be readily adapted to treat multispecies substances by insertion of the appropriately derived multipliers.

The approach is best illustrated by two simple examples using the fugacity formalism.

Model Application

Two-Compartment System. We consider a two-phase, water−sediment system illustrated in Figure 1 in which there are two hypothetical species designated 1 and 2, both of which can degrade to final unidentified products and there is species-to-species conversion but at an unknown rate. It is assumed that 100 mol/h enters the water (75 mol/h of species 1 and 25 mol/h of species 2); there is advective loss and degradation of both species in water and sediment and reversible water−sediment transfer at a rate determined by a mass transfer coefficient-area product $k_{SW} \cdot A$, thus the D-values are $k_{SW} \cdot A \cdot Z_{W1}$ and $k_{SW} \cdot A \cdot Z_{W2}$. In this case diffusion is assumed to be water phase resistance controlled. The phase volumes as well as the advective flow rate are defined. The species-specific rate constants and Z-values are defined for both species in both phases. Finally observed concentration ratios, i.e., C_2/C_1 are defined in both phases from observed data. The species to species conversion rates are not defined since this would overspecify the system. The pseudosingle species steady-state mass balance equations are given in eqs 8−11.

$$E_W + f_{S1} \cdot D_{SW} = f_{W1} \cdot (D_G + D_{RW} + D_{WS}) \qquad (8)$$

$$f_{W2} = f_{W1} \cdot f_{W2}/f_{W1} = f_{W1} \cdot F_{W21} \qquad (9)$$

$$f_{W1} \cdot D_{WS} = f_{S1} \cdot (D_{RS} + D_{SW}) \qquad (10)$$

$$f_{S2} = f_{S1} \cdot F_{S21} \qquad (11)$$

Table 1 illustrates the calculation of the fugacity ratios of the species, the calculation of species D-values, and their combination into single D-values by deducing the multipliers. Eqs 8−11 are solved to give the fugacities of species 1 ($f_{W1} = 21.9$, $f_{S1} = 0.71$), from which those of species 2 can be calculated using the fugacity ratio ($f_{W2} = 109.7$, $f_{S2} = 0.36$),

followed by all concentrations and individual species and total fluxes. The total mass balance is satisfied, but the single-species mass balances are not satisfied because of species-to-species conversions. The rates of conversion of 1 to 2 in water and sediment can be deduced by calculating the surplus (or deficit) of each species not accounted for by other input and removal processes, yielding the correct species balances as shown in Figure 2.

In this case there is conversion of 1 to 2 in the water (8.4 mol/h) and from 1 to 2 in the sediment (6.8 mol/h). The mass balance in air for species 1 shows a total input of 76.5 mol/h consisting of 75.0 mol/h emission, 1.4 mol/h transfer from sediment. This flux is balanced by advective loss (21.9 mol/h), reaction (2.2 mol/h), transfer to sediment (43.9 mol/h) and conversion to species 2 (8.4 mol/h). Of the input of species 1 to the sediment, 35.7 mol/h reacts, 1.4 mol/h returns to the water and 6.8 mol/h is converted to species 2. A similar mass balance can be compiled for species 2. There is net formation of species 1 in both water and sediment.

Note that the conversion rate constants or D-values are not defined. Since the concentration and fugacity ratios are constant, this implies that these processes are fast relative to other loss processes. For example, in the water, reasonable D-values for conversion of species 1 to 2 could be 50 and for 2 to 1 it could be 10 resulting in the observed fugacity ratio, f_2/f_1, of 5, and the absolute rates of conversion would be approximately 1000 mol/h for both cases (actually 1008.4 mol/h from 1 to 2 and 1000 mol/h from 2 to 1), yielding the required net conversion rate of 8.4 mol/h of 1 to 2. The key point is that the constant concentration ratios imply fast, absolute conversion rates, not necessarily large net conversion rates.

The overall mass balance even for this relatively simple system can be difficult to determine from observations of concentrations because of the several complementary and competing processes. The mass balance accounting reveals the relative importance of all processes and enables net conversion rates to be deduced.

The same result could be obtained by writing and solving the four single species mass balance equations which contain four unknowns, namely two selected fugacities and two selected interspecies conversion rates. Note that the two selected fugacities must be of one species, since the other two fugacities are related to them by the defined concentration and fugacity ratios.

The advantage of this new approach is that it can be generalized to more species and more compartments with little increase in mathematical complexity. The second example treats a more complex system of three species in four compartments, each consisting of a bulk phase containing subcompartments at equilibrium.

Four-Compartment System. This example is illustrative of a four-compartment system (air, water, soil, and sediment) contaminated with three species analogous to mercury species (elemental, ionic or reactive and organic) as illustrated in Figure 3. Estimates of the rates of species to species conversion rates for mercury have been compiled from a variety of sources as part of the United States Environmental Protection Agency (U.S.-EPA) TRIM.FaTE mercury case study (9). As shown in Figure 4 the air consists of air plus aerosol particles, water is water plus suspended solids and aquatic biota, soil is solids plus air and water, and sediment is solids plus water, all in defined proportions. There are thus seven phases present, some in more than one compartment. The calculation is steady-state or Level III in nature with emissions into all compartments except sediment. Bulk phase Z-values are calculated for the four compartments for each species. Bulk concentration ratios are defined for the four compartments with elemental mercury being the key species designated number 1, i.e., C_2/C_1 and C_3/C_1 are defined based on

TABLE 1. Example of Two-Species ($i = 2$) Calculations for a Two-Compartment, Water−Sediment ($N = W,S$) System

parameter	symbol/formulas	water	sediment
volumes (m³)	V_N	1000	1
advection rates (m³/h)	G_N	100	
intermedia transfers (m³/h of water)		$G_{WS} = 200$	$G_{SW} = 200$
concentration ratios (dimensionless)	C_{Ni}/C_{N1}	0.5	2

parameter	symbol/formulas	species 1	species 2
Z-values (mol/m³ Pa)			
water	Z_{Wi}	0.01	0.001
sediment	Z_{Si}	10	40
reaction rate constants (h⁻¹)			
water	k_{Wi}	0.01	0.005
sediment	k_{Si}	5	2
D-values (mol/Pa h)			
advection (D_G)	$G_W \cdot Z_{Wi}$	1	0.1
reaction (D_{RW})	$V_W \cdot Z_{Wi} \cdot k_{Wi}$	0.1	0.005
reaction (D_{RS})	$V_S \cdot Z_{Si} \cdot k_{Si}$	50	80
intermedia (D_{WS})	$G_{WS} \cdot Z_{Wi}$	2	0.2
intermedia (D_{SW})	$G_{SW} \cdot Z_{Wi}$	2	0.2

parameter	symbol/formula	water	sediment
Fugacity ratios (dimensionless):	$F_{Ni} = f_{Ni}/f_{N1} = C_{Ni}/C_{N1} \cdot Z_{N1}/Z_{Ni}$	$F_{W21} = 5$	$F_{S21} = 0.5$

R-multipliers (dimensionless)	symbol/formulas	species 1 (R_1)	species 2 (R_2)	total (R_T)
advection (R_G)	$F_{Wi} \cdot D_{Gi}/D_{G1} =$	1	+ 0.5	= 1.5
reaction (R_{RW})	$F_{Wi} \cdot D_{RWi}/D_{RW1} =$	1	+ 0.25	= 1.25
reaction (R_{RS})	$F_{Si} \cdot D_{RSi}/D_{RS1} =$	1	+ 0.8	= 1.8
intermedia (R_{WS})	$F_{Wi} \cdot D_{WSi}/D_{WS1} =$	1	+ 0.5	= 1.5
intermedia (R_{SW})	$F_{Si} \cdot D_{SWi}/D_{SW1} =$	1	+ 0.05	= 1.05

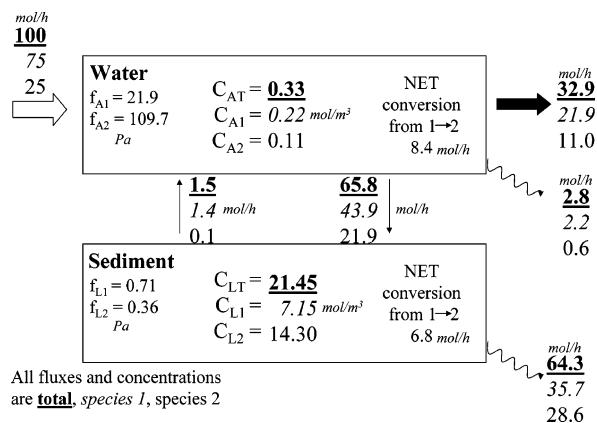| net D-value (mol/Pa h)	symbol/formulas	D_1	R_T	D_T
advection (D_G)	$D_{G1} \cdot R_{TG} =$	1	× 1.5	= 1.5
reaction (D_{RW})	$D_{RW1} \cdot R_{TRW} =$	0.1	× 1.25	= 0.125
reaction (D_{RS})	$D_{RS1} \cdot R_{TRS} =$	50	× 1.8	= 90
intermedia (D_{WS})	$D_{WS1} \cdot R_{TWS} =$	2	× 1.5	= 3
intermedia (D_{SW})	$D_{SW1} \cdot R_{TSW} =$	2	× 1.05	= 2.1

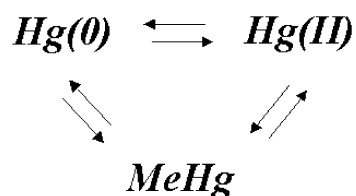FIGURE 2. Mass balance of two-compartment, two-species system.

FIGURE 3. Three interconverting species representing elemental, divalent (inorganic), and methylmercury.

FIGURE 4. Composition and intermedia transport in a four-compartment illustrative system. Percentages are on a volumetric basis.

values compiled for individual media (6, 7). Z-values are defined from equilibrium partition coefficients for all species in all phases. The equilibrium partition coefficients for these chemicals are determined, in part, by values from the literature (6, 7); however, these values are illustrative and do
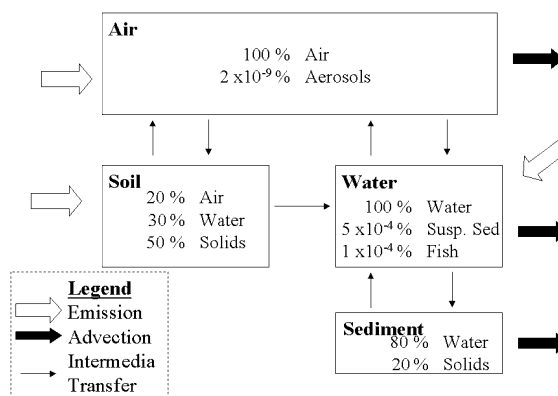
not necessarily accurately represent environmental partitioning behavior. It is emphasized that the concentration ratios and Z-values are illustrative only and should not be regarded as definitive values applicable to mercury species in the environment. The species fugacity ratios in each bulk compartment are calculated, i.e., f_2/f_1 and f_3/f_1. Note that all subcompartments within each compartment are assumed to be at equilibrium. Because of this assumption of equifugacity, concentration ratios for all species within each subcompartment are defined by the ratio of their Z-values, rather than the bulk concentration ratios. For each species 10 overall transport D-values are calculated. In this case no degradation

TABLE 2. Assumed Z-Values for All Media[a]

phase	species 1	species 2	species 3
air (1)	0.1	0.000001	0.0001
water (2)	1	1	1
soil (3)	20	50	30
sediment (4)	30	80	10
susp.sed. (5)	50	50	40
fish (6)	30	80	10000
aerosols (7)	100	10	200

[a] Note that the equilibrium partition coefficients are the ratio of the corresponding Z-values with the Z-value for water ($mol/m^3 \cdot Pa$).

TABLE 3. Bulk Z-Values ($mol/m^3 \cdot Pa$), Bulk Concentration Ratios (C_i/C_1, Dimensionless), and the Corresponding Deduced Fugacity Ratios (F_{i1}, Dimensionless) for the Four Bulk Media

	species	air	water	soil	sediment
concentration ratio	1	1	1	1	1
with respect to	2	2.8×10^{-11}	30.67	2.92	6.37
species 1	3	0.02	1.67	0.08	0.31
fugacity ratio	1	1	1	1	1
with respect to	2	2.1×10^{-11}	30.67	1.19	2.58
species 1	3	20.0	1.65	0.05	0.75
bulk Z-values	1	0.1	1.0	10.3	6.8
	2	1.0×10^{-6}	1.0	25.3	16.8
	3	1.0×10^{-4}	1.0	15.3	2.8

rates are calculated since the element is conserved. Advective losses are included for air, water, and sediment burial.

The model is run for each species in order to estimate all the D-values, and the various multipliers (R_2 and R_3) are deduced. The seven overall intercompartment transport and three advective D-values including the multipliers are then calculated and the equations solved.

Although existing models can be rewritten to treat all species simultaneously, the simplest method involving minimal changes to existing programs is to run the steady-state, single-species program for each species to determine their respective D-values, separately deduce the fugacity ratios, and calculate the individual and total multipliers for each process. These quantities can then be readily inserted into the existing program as multipliers to be applied to calculated D-values of the key species and the equations solved to give the fugacity of the key species. From these fugacities, the concentrations, fugacities, and amounts of other species can be deduced, as can all fluxes and masses.

A convenient method of calculating the fluxes of each species is from their respective multipliers. For example if the multipliers are $R_1 = 1$, $R_2 = 4$, and $R_3 = 5$, the total multiplier (R_T) is 10, and the fractions of each species subject to the process are 1/10, 4/10, and 5/10, i.e., 0.1, 0.4, and 0.5.

Table 2 gives the assumed illustrative Z-values of the three species in the various phases. Note that Z is arbitrarily set at 1.0 for each species in water as in the aquivalence formulation. Table 3 gives the assumed illustrative concentration ratios C_2/C_1 and C_3/C_1 in each compartment the corresponding fugacity ratios and the bulk Z-values. Table 4 gives the advection and transport D-values for species 1, the multipliers R_2 and R_3, the overall multiplier, i.e., ($1 + R_2 + R_3$) and the net D-value which is the product of the D-value for species 1 and the overall multiplier that is used in the determination of the fugacity of the key species.

Figure 5 gives the mass balance for the sum of all mercury species in the system including the intermedia fluxes. Similar diagrams can be compiled for each species, but an exact mass balance is not achieved because of species to species conversions. If we examine the mass balance for all species of individual compartments, important pathways and processes for the accumulation of more toxic substances may be revealed. For example, Figure 6 gives the mass balance for the water compartment indicating that in this case there is net formation of ionic and organic mercury from elemental mercury.

TABLE 4. D-Values for Species 1, Species Multipliers (R_1, R_2, R_3, Dimensionless), Overall Multipliers (R_T), and Total D-Values (D_T)[a]

process	D-value species 1	R_1	R_2	R_3	R_T	D_T
advection in air	1.00×10^{11}	1	2.8×10^{-11}	0.02	1.02	1.02×10^{11}
advection in water	2.00×10^8	1	**30.67**	1.67	33.34	6.67×10^9
advection in soil						
advection in sediment	6.80×10^4	1	**6.37**	0.31	7.68	5.22×10^5
air−water diffusion (air-side)	5.00×10^9					
air−water diffusion (water-side)	5.00×10^8					
air−water diffusion (overall)	4.55×10^8					
rain dissolution to water	1.00×10^6					
aerosol deposition to water	6.00×10^6					
overall air−water transport	4.56×10^8	1	4.79×10^{-9}	0.26	1.26	5.75×10^8
overall water−air transport	4.55×10^8	1	3.37×10^{-3}	0.02	1.02	4.64×10^8
rain dissolution to soil	9.00×10^6					
aerosol deposition to soil	5.40×10^3					
soil−air diffusion (air-phase)	1.80×10^8					
soil−air diffusion (water-phase)	9.00×10^5					
soil−air diffusion (bndry layer)	4.50×10^{10}					
soil−air diffusion (overall)	1.80×10^8					
overall air−soil transport	1.89×10^8	1	1.02×10^{-7}	**1.06**	2.06	3.90×10^8
overall soil−air transport	1.80×10^8	1	1.98×10^{-3}	3.16×10^{-4}	1.00	1.81×10^8
water−sediment diffusion	1.00×10^6					
water−sediment deposition	2.50×10^5					
sediment−water resuspension	6.00×10^4					
overall water−sediment transport	1.25×10^6	1	**30.67**	1.58	33.26	4.16×10^7
overall sediment−water transport	1.06×10^6	1	**2.82**	0.72	4.55	4.82×10^6
soil−water runoff (water)	4.50×10^6					
soil−water runoff (solids)	1.80×10^4					
overall soil−water transport	4.52×10^6	1	**1.20**	0.05	2.25	1.02×10^7

[a] Bold multipliers indicate the dominant species participating in each process.
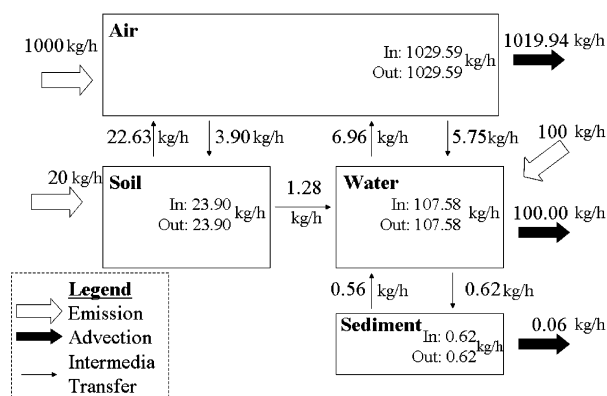
FIGURE 5. Mass balance for total mercury in a four-compartment system.

Mass Balance *(kg/h)*

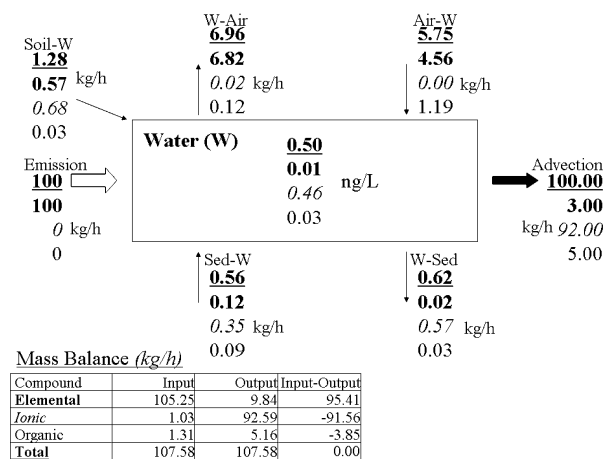| Compound	Input	Output	Input-Output
Elemental	105.25	9.84	95.41
Ionic	1.03	92.59	-91.56
Organic	1.31	5.16	-3.85
Total	107.58	107.58	0.00

FIGURE 6. Mass balance describing all species of mercury for the bulk water compartment within the four-compartment environment. Emissions are assumed to be 100% elemental.

Discussion

The method presented in the two- and four-compartment examples provides a simple, succinct approach for modeling the fate of multispecies chemicals which experience fast species interconversion rates. By examining the output provided by the more complex four-compartment, three-species system, several advantageous properties of the approach become apparent. A valuable feature of this approach is that there are 30 multipliers (i.e. the product of 10 processes and three species) which can be readily inspected to identify the key combinations. Table 4 shows the D-values, multipliers, and dominant species participating in each overall process.

Relatively little error is introduced by ignoring all multipliers which are less than 0.01, thus greatly simplifying the calculation. In this example most multipliers for organic mercury are small, thus this species has little effect on the overall mass balance and could be ignored; however, it remains included because of its toxicological significance. In this example, four atmospheric processes are dominated by elemental mercury, thus there is little error in assigning an overall multiplier of 1.0 for those processes. Four processes have multipliers in the range 2−35 reflecting large fluxes of species 2. These multipliers can be used in existing fugacity- or concentration-based models of the fate of a single chemical species if the species has the properties of elemental mercury (species 1), thus giving the rates of transport of total mercury. It is relatively easy to insert the multipliers into the flux equations as a single number. Because each D-value is
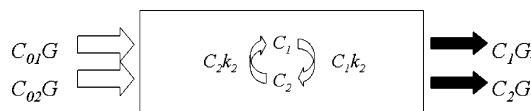

FIGURE 7. One-compartment system used to illustrate the relationship between chemical residence time via advection and conversion residence times. The method is valid if the advective residence time is greater than the interspecies conversion rates.

defined with respect to individual species, the intermedia transfers calculated reflect the proportions of each species transported. There is no need to specify the proportions of the species in any emission quantities because the proportions are defined in the compartments that receive the emissions. Although many emission types are not well defined with respect to emission speciation, coal-fired electrical utility boilers in the United States do have well described speciation, although the proportions may be affected by the type of coal that is being burned (*10*). Typically, this type of emission occurs as 55% elemental mercury, 40% ionic mercury, and less than 5% particulate mercury (*10*). Results from the Mercury Deposition Network (MDN) data show that much of the atmospheric ionic mercury emissions are reduced to elemental mercury, the dominant species occurring in the atmosphere (*10*). This observation supports the assumption made in this approach that the chemical, regardless of its characteristic speciation during emission into the environment, will approach the equilibrium defined by the concentration ratios observed in each medium once received into the environment.

This approach raises the issue of determining when the assumption of constant species proportions is applicable. In other words, how fast must the conversion rate be to ensure validity? More difficult but very relevant is the following question: How can there be assurance that the conversion rate is fast if the rates are highly uncertain? We address this issue below.

The relationship between chemical residence times in a compartment, rates of interspecies conversions, and species concentration ratios is best illustrated by a simple concentration example in which two species are present in one compartment as illustrated in Figure 7. The input rates (mol/h) for each species, i, are $C_{0i}G$ where G is an actual or effective flow rate (m³/h) and C_{0i} is the concentration present in the incoming media (mol/m³). The output rates (mol/h) are C_iG, and the conversion rates (mol/h) are VC_ik_i where V is the volume of the compartment, C_i is the concentration of the species inside the compartment, and k_i is the conversion mass transfer coefficient (h⁻¹). A steady-state mass balance can be written for each species; for example for species $i = 1$:

$$C_{01}G + VC_2k_2 = C_1(G + Vk_1) \qquad (12)$$

The two equations (one for each species) can be solved for C_1 and C_2, and this ratio can be shown to be

$$\frac{C_2}{C_1} = \frac{[k_1(C_{02} + C_{01}) + C_{02}G/V]}{[k_2(C_{02} + C_{01}) + C_{01}G/V]} \qquad (13)$$

If G/V (h⁻¹), the reciprocal of the compartment residence time, exceeds k_1 and k_2, the concentration ratio approaches C_{02}/C_{01}, and the system is flow-dominated with relatively slow conversion. Conversely, if k_1 and k_2 exceed G/V and conversion rates are fast, the ratio approaches k_1/k_2, the condition of chemical equilibrium. When G/V and the rate constants are comparable, an intermediate situation exists, and the

concentration ratio is influenced by both the residence time and the kinetics of conversion.

It is thus enlightening to compare the residence time and the characteristic conversion time or reciprocal rate constants, to determine the likely regime which applies. If all the rate constants for species conversion are known, it is probably preferable to construct a rigorous multispecies model of the types outlined earlier. In many cases the underlying chemistry of the conversion reactions is understood, and an estimate can be made of the conversion times. Ionic reactions are generally fast. Rates of hydrolysis and photolytic reactions can be estimated from the ambient conditions and reported rate data for analogous compounds. Microbial and metabolic rates are most problematic. If the rate constants are unknown or uncertain, a rigorous model cannot be compiled, and the only feasible approach is to apply the constant concentration ratio approach as described here using observed ratios in a tentative model. The resulting tentative model generates data on the rates of species conversion necessary to achieve the observed concentration ratio. These rates can be assessed for reasonableness, and it can be determined if conditions are dominated by flow or kinetics or both. These findings can be used to determine if experimental determination of conversion rates is justified with a view to assembling a rigorous multispecies model.

If sufficient data are available, then the rigorous approach is obviously preferred. In other cases this approach can be applied but with varying degrees of rigor. Even a tentative model may be useful as a stepping stone to a more accurate subsequent analysis of the mass balance.

In conclusion, we hope that this methodology, which is easily adapted to summarize the behavior of speciating chemicals, may be used in conjunction with existing models applicable to various scales to elucidate and predict the environmental fate of speciating chemicals of concern, such as mercury. The aim has been to suggest a simple, nondata-intensive approach which is suitable for use not only for chemicals of known, fast species conversion rates but also as a "first step" toward assessing those speciating chemicals whose conversion rates are not fully understood. In some cases it may prove sufficient for assessment purposes, but in others it will demonstrate the need for a more rigorous approach to be taken. To further this research and validate such models, there is a compelling incentive to measure, interpret, and review concentrations of individual species of a chemical, such as mercury to better define environmental concentration and fugacity ratios. This may require development of novel techniques for measurement of species. Further, when modeling the fate of these chemicals in a real or nonhypothetical system, there is a need for reliable emission rate data. Measured concentrations may then be compared with predictions. We believe that by using this approach in conjunction with existing single species models of real and evaluative or hypothetical systems it will be possible to quantify the often complex environmental behavior of speciating chemicals that tend to display relatively constant species concentration ratios in environmental media.

Supporting Information Available

Two-compartment concentration-flux example (Appendix A) and four-compartment system model parameters (Appendix B). This material is available free of charge via the Internet at http://pubs.acs.org.

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