

**Model Documentation for WASP 8:
META4-WASP
A Metal Exposure and Transformation
Assessment Model
Model Theory and User's Guide**

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WASP 8: META4-WASP, Model Theory and User's Guide

Supplement to Water Quality Analysis Simulation Program (WASP) User Documentation

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Preface

META4-WASP (META4) is a generalized metals transport, speciation, and kinetics model developed for application to a variety of receiving waters experiencing metals contamination, including ponds, streams, rivers, lakes and estuaries. The basis for the transport model is the Water Analysis Simulation Program (WASP). META4 is a kinetic submodel of WASP developed specifically for the simulation of metals contamination in aquatic environmental systems. Since WASP is the basis for META4 it can be applied to one, two or three dimensional systems, and can simulate both water column and benthic layers. Algorithms for the simulation of metals aqueous speciation, sorption, chemical precipitation and kinetics were added to the WASP basic structure, resulting in the META4-WASP model.

DRAFT

The Metal Speciation and Transport Model: META4: Model Documentation

1. Introduction

Contamination by toxic metals occurs in a variety of aquatic habitats. Identification of the specific causes of contamination and factors impacting the fate and transport of those metals is critical to effective resource management.

Based on the 2008 National summary of impaired waters (303(d) list), mercury is the 7th leading cause of U.S. waters not meeting water quality standards (i.e. are impaired) with 3,782 listed waters. USEPA (2009) reported there were 16,808,032 acres of lakes and 1,254,893 miles of river under advisories for consumption of fish due to mercury contamination. The entire near-shore Gulf of Mexico is under mercury fish consumption advisories. The National Research Council (2000) pointed out that the population at highest risk is the offspring of women who consume large amounts of fish and seafood, and that more than 60,000 children are born each year at risk for adverse neuro-developmental effects due to in-utero exposure to methylmercury. In addition, metals other than mercury adversely impact US waters.

Based on the 2008 303(d) list, metals other than mercury were the second leading cause of water quality impairments in the U.S. In some cases the listing was based on “metals (other than mercury)”, but for the listings of specific metals, the top ten leading causes of impairment were contamination by lead, copper, iron, arsenic, zinc, selenium, manganese, cadmium, aluminum, and silver. One common cause of metal contamination, particularly in western states, is acid-mine drainage (AMD). Aquatic life is affected by AMD due to a number of factors, including toxic levels of metals, low pH, and reduction in available oxygen to benthos by armoring and filling of interstitial spaces with settled precipitates (e.g., iron oxyhydroxides) and sediment from erosion of waste rock and/or tailings piles (Butler et al. 2009, Caruso & Ward, 1998; Nimick et al., 2004; USEPA, 1997).

Aquatic resource management strategies, including waste allocation, potential remedial action (restoration) or total maximum daily loading, are best evaluated by an estimation of the impacts of processes affecting metals concentrations in the water, sediments and biota (Willingham and Medine, 1992). These types of analyses are complicated by the fact that metal behavior is non-conservative in aquatic systems and that the transport, transformations, and attenuation depend upon the particular forms of metal present in the system and chemical characteristics of the environmental system. The environmental system behavior and subsequent biological exposure and toxicity of metals is therefore governed by simultaneous and interacting advancement of all possible chemical reactions, each controlled by its individual rate law (Morel, 1983).

Common practice for modeling metals in surface waters has been to treat each metal as an independent state variable subject only to transport and sorption. One approach is to describe sorption reactions using apparent partition coefficients, which reflect the combined effects of the aqueous chemistry. The apparent coefficients are sometimes, but not usually, based upon field measurements. A second approach has been to estimate the apparent partition coefficients for the modeling activity using geochemical equilibrium models, such as MINTEQA2 (Allison et al., 1991), Visual MINTEQ (Gustafsson, 2010), PHREEQC (Parkhurst, 1995, Parkhurst and Appelo, 1999), MINEQL and MINEQL+ (Westall et al., 1986, Schecher and McAvoy, 1994, Environmental Research Software 2007), and incorporating site-specific water chemistry for the range of conditions expected. For example, Allison and Allison (2005) reported partition coefficients for metals based on literature surveys, statistical methods, geochemical speciation modeling, and expert judgment. The former approach completely neglects interactive effects, and the latter approach, while preferable, has limited predictive capability in situations where the modeled chemistry is variable, particularly under future loading and chemical conditions. For example, conditions may vary from complete sorption to complete desorption within as little as one-half a pH unit for some metals, making the range of the apparent partition coefficients large. Sorption is also dependent on the sorbate-sorbent ratio such that considerable error may arise in the estimation of sorption using simple coefficients under varying conditions. (Dzombak and Morel, 1990).

Aquatic system toxicity is not generally governed by the total or total dissolved concentration of metals in water but is believed to be related to the aqueous species, in particular the free ion and possibly simple hydroxide complexes. Rather than to regulate metal concentrations in receiving waters based on the total metal, total recoverable metal or dissolved concentration, as presently implemented, a speciation-based approach may provide the more defensible and fair approach toward managing aquatic resources (Renner, 1997).

Geochemical equilibrium speciation models have been applied widely to compute the aqueous speciation, adsorption-desorption, and precipitation-dissolution of metals in aqueous systems. Equilibrium speciation models, such as those mentioned above, are extremely useful for predictive interactive effects on ionic composition in static systems, including the evaluation of the potential water-sediment interactions and aquatic system toxicity. The equilibrium assumption appears valid for aqueous speciation (acid-base, complexation) and many divalent metal adsorption/desorption reactions relative to hydrologic processes in freshwater environments (Di Toro, 1976; Kimball et al., 1994)

However, a need exists for models that consider the suite of both geochemical and physical processes (e.g. transport) affecting trace metals dynamics in receiving waters, for one, two and three dimensional environments, and, steady as well as non-steady flow situations (Dzombak and Ali, 1993). One such model is the One-Dimensional Transport with Equilibrium Chemistry (OTEQ): A Reactive Transport Model for Streams and Rivers (Runkel 2010). OTEQ couples a solute transport model (OTIS, Runkel 1998) with a chemical equilibrium submodel (MINTEQ, Allison et al., 1991).

This manual describes the coupling of an equilibrium simulation model, based upon MINTEQ and MINEQL, with the generalized Water Analysis Simulation Program (WASP). Coupling of the META4 kinetic and speciation module with the WASP transport framework provides improved capacity to predict trace metal behavior in aquatic systems. The original version of META4 was based on coupling kinetic and speciation module with WASP Version 4 (Medine and Martin 2000). The META4-WASP described in this manual was based on updating the kinetic and speciation module and coupling it with the transport routines of WASP Version 8.0. The history of the development of META4 is summarized in the following section.

Coupling of META4 with the basic transport scheme of WASP allows application to a variety of waterbodies in one, two or three dimensional mode, as well as the simulation of both water column and benthic layers. The basic transport scheme is identical for all of the submodels to WASP (Eutrophication, Organic Toxicants, Heat, Mercury, Simple Toxicant, Non-Ionizing Toxicant, Advanced Eutrophication, and Metals or META4). What distinguishes each of these models are the number of state variables and the reactions and processes included in the kinetic subroutines. In the following discussion, the models described in this report will be referred to as either WASP or META4. WASP will be referred to in the description of processes which are general to all of the WASP submodels, while META4 will be used to refer to characteristics which are unique to that submodel.

The META4 model results from coupling the transport module of WASP with a kinetic module for metals transformations. The metals module is generalized, allowing for the application of META4 to a wide variety of metals and environmental conditions. In addition, other environmental parameters affecting speciation and reactions may be specified. Algorithms are included in META4 for the simulation of metals aqueous speciation, sorption, and chemical precipitation. In addition, algorithms are available allowing simulation of the impact of slow reactions, such as degradation. This manual provides documentation of the basic structure of the META4 model, the model data requirements, and structure of the model input data set. The basic features of the model are described, following by a description of model input requirements and data structure. However, the user should refer to the WASP user's manual for information about the basic implementation of WASP.

2. META4: A Brief History

META4 is a generalized metals transport, speciation, and kinetics model developed for application to a variety of receiving waters experiencing metals contamination, including ponds, streams, rivers, lakes and estuaries. META4 is one of the family of WASP submodels, which include models of heat and coliform bacteria, eutrophication (several subtypes), organic contaminants, mercury and others.

The META4 model was originally based on a submodel developed specifically for the simulation of mercury (MERC4, Martin 1992). The metal speciation and kinetics algorithms included in the MERC4 model were based on approaches utilized in the

Mercury Cycling Model (MCM) model developed by Tetra Tech, Inc. (Hudson et al. 1990, 1991; Porcella et al. 1992) for the Electric Power Research Institute (EPRI) and the MINEQL model equilibrium metal speciation model (Westall et al. 1986). Coupling and enhancing the chemical speciation and kinetics algorithms with the transport capabilities of the WASP modeling system resulted in a generalized dynamic mercury modeling framework applicable to a wide variety of aquatic systems.

Medine and Martin (1995) generalized the modeling framework of MERC4 in order to make it applicable to other metals. The model was subsequently improved such as by adding additional sorption algorithms and applied to a variety of systems (e.g., Medine and Martin, 2000a, 2000b, 2000c, 2002; Butler et al., 2009; and others). This version represents the updating of the model and incorporation into WASP Version 8.0.

3. Overview of WASP

WASP is a box-type, or compartment, model for aquatic systems, including both the water column and the underlying benthos. The time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange are represented in the basic program. The flexibility afforded by WASP is unique. WASP permits the modeler to structure one, two, and three dimensional models; allows the specification of time-variable exchange coefficients, advective flows, waste loads and water quality boundary conditions; and permits tailored structuring of the kinetic processes, all within the larger modeling framework without having to write or rewrite large sections of computer code.

The WASP system simulates the movement and interaction of pollutants within the water. The basic principle of the water-quality program is the conservation of mass. The water volume and water-quality constituent masses being studied are tracked and accounted for over time and space using a series of mass balancing equations.

The principle of the conservation of mass requires that the mass of each water quality constituent being investigated must be accounted for in one way or another. WASP traces each water quality constituent from the point of spatial and temporal input to its final point of export, conserving mass in space and time. To perform these mass balance computations, the user (or through a hydrodynamic linkage) must supply WASP with input data defining seven important characteristics:

- Simulation and output control
- Model segmentation
- Advective and dispersive transport
- Boundary concentrations
- Point and diffuse source waste loads

- Kinetic parameters, constants, and time functions
- Initial concentrations

The above input data, taken together with the general WASP mass balance equations and the specific chemical kinetics equations, uniquely define a special set of water quality equations. The equations are numerically integrated by WASP as the simulation proceeds in time. At user-specified print intervals, WASP saves the values of all display variables for subsequent post-processing.

The basic types of input data required and the structure of the WASP input data set is the same regardless of the kinetic module that is appended to it (e.g., eutrophication, organic chemicals, mercury or metals). What distinguishes the modules are the number of state variables and the reactions and transformations included in the kinetic modules, as specified in the section of the model input for kinetic parameters, constants, and time functions. For example, if there are no kinetic rates assigned to a state variable in any one of the kinetic modules, then that variable becomes nonreactive, or a conservative material such as a chemical tracer, and will be passively transported throughout the water body.

3.1 The General Mass Balance Equation

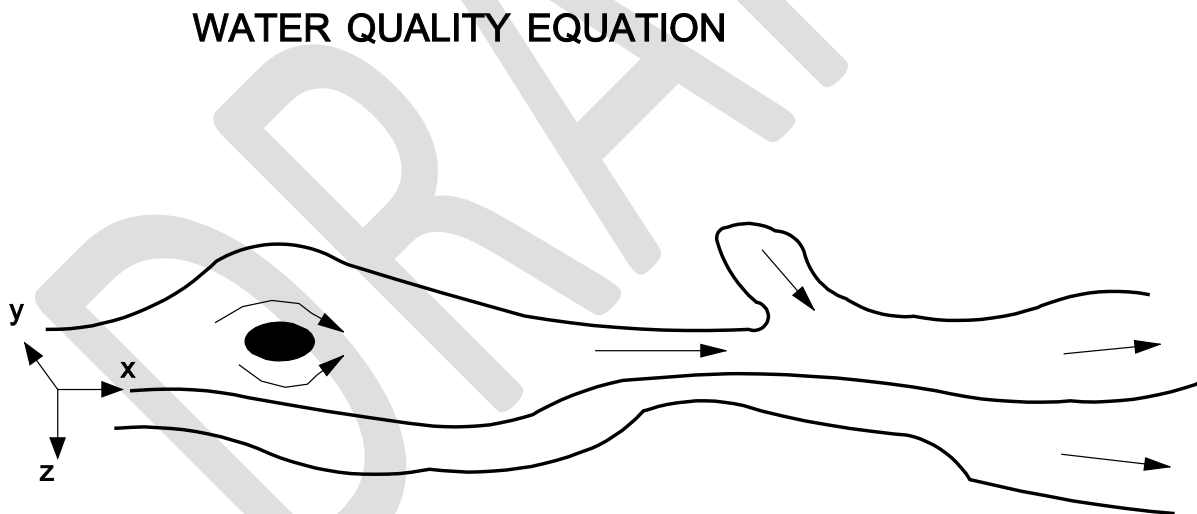


Figure 1. Coordinate system for mass balance equation (Ambrose et al., 1993)

A mass balance equation for dissolved constituents in a body of water must account for all the material entering and leaving through direct and diffuse loading, advective and dispersive transport, and physical, chemical, and biological transformation. Consider the coordinate system shown in Figure 1, where the x- and y-coordinates are in the horizontal plane, and the z-coordinate is in the vertical plane. The mass balance equation around an infinitesimally small fluid volume is:

Equation 1

$$\begin{aligned}\frac{\partial C}{\partial t} = & -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial y}(U_y C) - \frac{\partial}{\partial z}(U_z C) \\ & + \frac{\partial}{\partial x}\left(E_x \frac{\partial C}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial C}{\partial y}\right) + \frac{\partial}{\partial z}\left(E_z \frac{\partial C}{\partial z}\right) \\ & + S_L + S_B + S_K\end{aligned}$$

where:

- C = concentration of the water quality constituent, mg/L or g/m³
 t = time, days
 U_x, U_y, U_z = longitudinal, lateral, and vertical advective velocities, m/day
 E_x, E_y, E_z = longitudinal, lateral, and vertical diffusion coefficients, m²/day
 S_L = direct and diffuse loading rate, g/m³-day
 S_B = boundary loading rate (including upstream, downstream, benthic, and atmospheric), g/m³-day
 S_K = total kinetic transformation rate; positive is source, negative is sink, g/m³-day

By expanding the infinitesimally small control volumes into larger adjoining "segments," and by specifying proper transport, loading, and transformation parameters, WASP implements a finite-difference form of Equation 1. For brevity and clarity, however, the derivation of the finite-difference form of the mass balance equation will be for a one-dimensional reach. Assuming vertical and lateral homogeneity, we can integrate Equation 1 over y and z to obtain

Equation 2

$$\frac{\partial}{\partial t}(A C) = \frac{\partial}{\partial x} \left(-U_x A C + E_x A \frac{\partial C}{\partial x} \right) + A (S_L + S_B) + A S_K$$

This equation represents the three major classes of water quality processes -- transport (term 1), loading (term 2), and transformation (term 3). The model network and the major processes are discussed in the following sections.

3.2 The Model Network

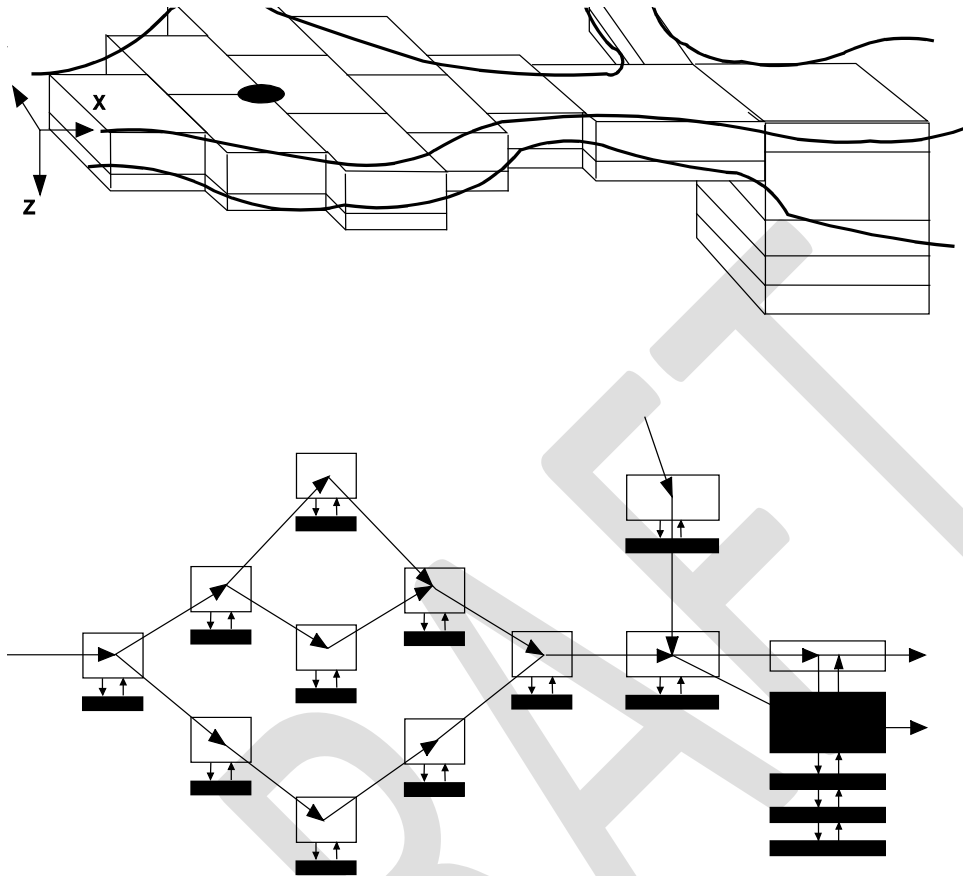


Figure 2. Model segmentation (Ambrose et al., 1993)

The model network is a set of expanded control volumes, or "segments," that together represent the physical configuration of the water body. As Figure 2 illustrates, the network may subdivide the water body laterally and vertically, as well as longitudinally. Benthic segments can be included along with water column segments. If the water quality model is being linked to a hydrodynamic model, then segmentation is based on that of the hydrodynamic model (1 to 1 grid). Concentrations of water quality constituents are calculated within each segment. Transport rates of water quality constituents are calculated across the interface of adjoining segments.

The selection of the number and size of the segments varies with the characteristics of the waterbody and the situation to be analyzed. The segment volumes also influence the simulation time step required to insure stability and numerical accuracy. For example, small segments with short residence times will require the use of small numerical time steps.

3.3 The WASP Model Framework.

The WASP model solves the basic transport equation over the model network for each state variable simulated. The number of state variables (systems), and corresponding reactions and kinetic processes, vary with the particular kinetic model.

The general framework for WASP consists of a generalized transport scheme to which specific kinetics models can be attached. Presently, kinetic models include those for heat and pathogens, eutrophication (two levels of complexity), simple toxicants, mercury, organic chemicals, and now metal speciation (META4). The framework also consists of linkages with other models, such as hydrodynamic and hydrologic models, a graphical user interface (pre-processor/data server) and graphical post-processor (Figure 3).

The reader is referred to the WASP model and interface documentation for a more detailed discussion of the theoretical basis for the model and for guidance on the model interface. This documentation is intended to provide information and guidance on the basic structure and application of META4-WASP.

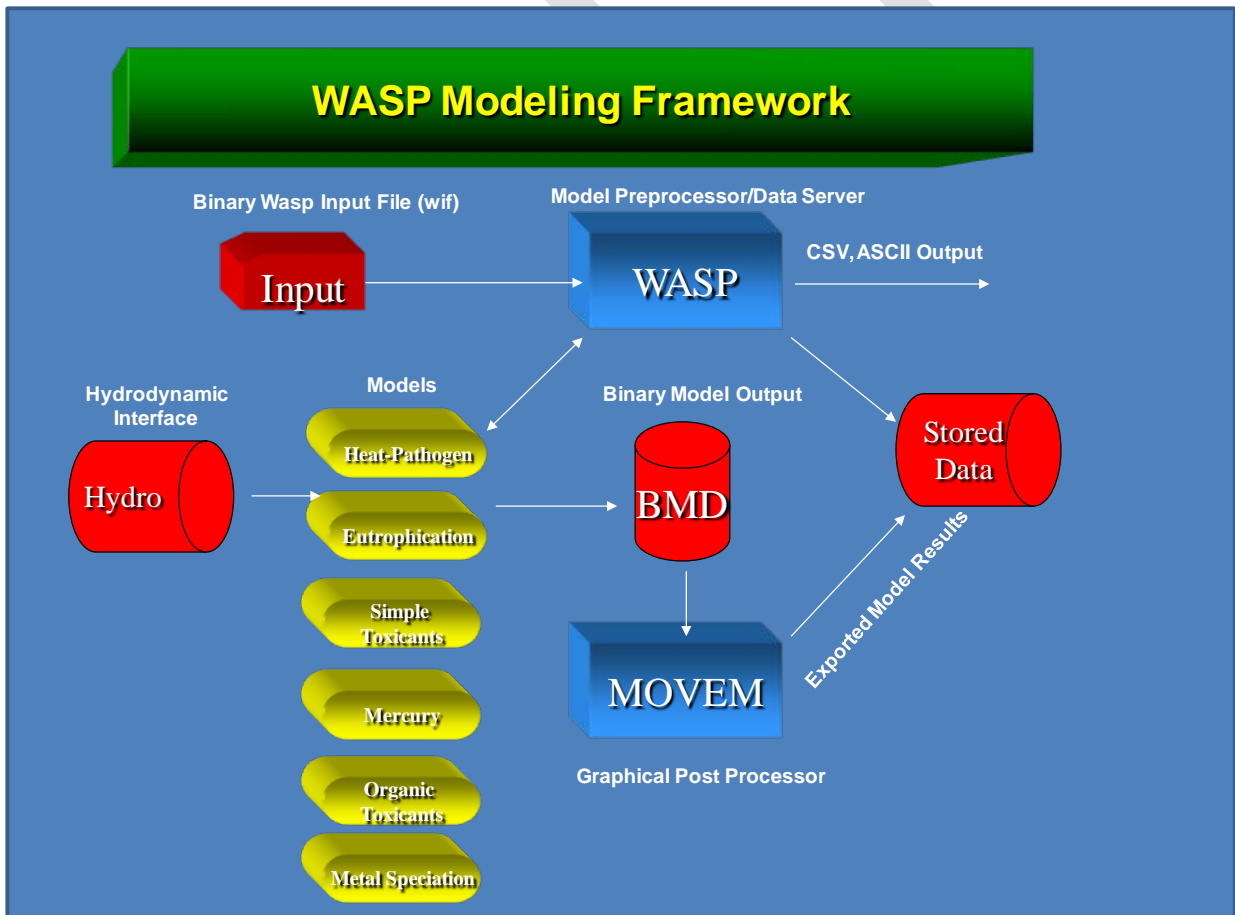


Figure 3. WASP Model Framework

4. Getting Started

In this section, the specific input to the META4 model will be illustrated and a brief discussion of underlying theory provided, where applicable. This section will not discuss the general input requirements for WASP, and the reader is referred to the WASP model documentation for additional details.

4.1 Selecting META4 and basic Input

The first step for using META4 is to either open a new file or create a new file and then select META4 as the WASP submodel. The user selects the general input using the “gears” icon upon which the general parameters input form appears. If the user clicks on model type, META4 will be listed as one of the selectable models. This input form also allows the user to input a description of the input for future reference and to add comments, which is useful in documenting the application.

The screenshot shows the 'Parameters' dialog box for the 'Case 1: Simulation of pH, META4' model. The dialog is divided into several sections:

- Description:** Case 1: Simulation of pH
- Model Type:** META4
- Comments:** This test case demonstrates the META4 computation of H+. In this test the pH is computed based on specified concentrations (molar) of: Al, Ca, H+ and SO4 in a beaker test (single box, CMSTR). The activities are not corrected for temperature or ionic strength.
- Time Range:**
 - Start Date: 1/1/2000
 - Start Time: 12:00
 - End Date: 5/1/2000
 - End Time: 12:00
 - Skip Ahead to Date: 1/1/2000
 - Skip Ahead Time: 12:00
- Non Point Source File:**
 - Use NPS file: ☐
 - NPS File Name: [Browse]
- Hydrodynamics:**
 - Net Flows: ☒
 - Gross Flows: ☐
 - 1-D Network Kinematic wave: ☐
 - Hydrodynamic Linkage: ☐
 - Hydrodynamic Linkage File: [Browse]
- Solution Technique:** EULER
- Solution Options:**
 - Disable WASP to WASP linkage: ☒
 - Enable WASP to WASP linkage: ☐
- Restart Option:**
 - No Restart File: ☒
 - Create Restart File: ☐
 - [Load restart file now]
- Bed Volumes:**
 - Static: ☒
 - Dynamic: ☐
 - Bed Compaction Time Step: 0.00
- Time Step:**
 - Fraction of max time step: 0.90
 - Max time step: 1.0000
 - Min time step: 0.0001
- Solution Options:**
 - Negative Solution Allowed: ☐

Buttons: OK, Cancel

Figure 4. Model general parameter input.

The user would then specify the model print intervals and insert model segments. The model segments would be obtained from the linkage files if the application is linked to a previous application of a hydrodynamic model.

4.2 Selecting META4 State Variables

The META4 state variables represent the series of reaction components (also called systems) important for the particular application. The user selects the specific components used in the application. The user would select the systems icon after which

the user input form shown in Figure 5 would appear. The systems are the model state variables and components available for reactions.

The default option for all of the model systems is “Bypassed” which indicates to WASP that this system will not be simulated. The user selects the systems to be included in simulations by clicking on the option next to the name of that system and changing “Bypassed” to “Simulated.” There are presently 65 selectable systems in META4 (Table 1). Any or all of these may be selected as model state variables.

In addition to the state variables, there are additional components, which while not simulated, impact the selection of the appropriate complexation and sorption reactions. For example, water (H₂O) is automatically added as a component, which is used only in the selection of the complexation reactions. Depending on the selection of the sorption option (such as the HFO model) additional components may automatically be added. However, these are not state variables and only are included in the speciation computations.

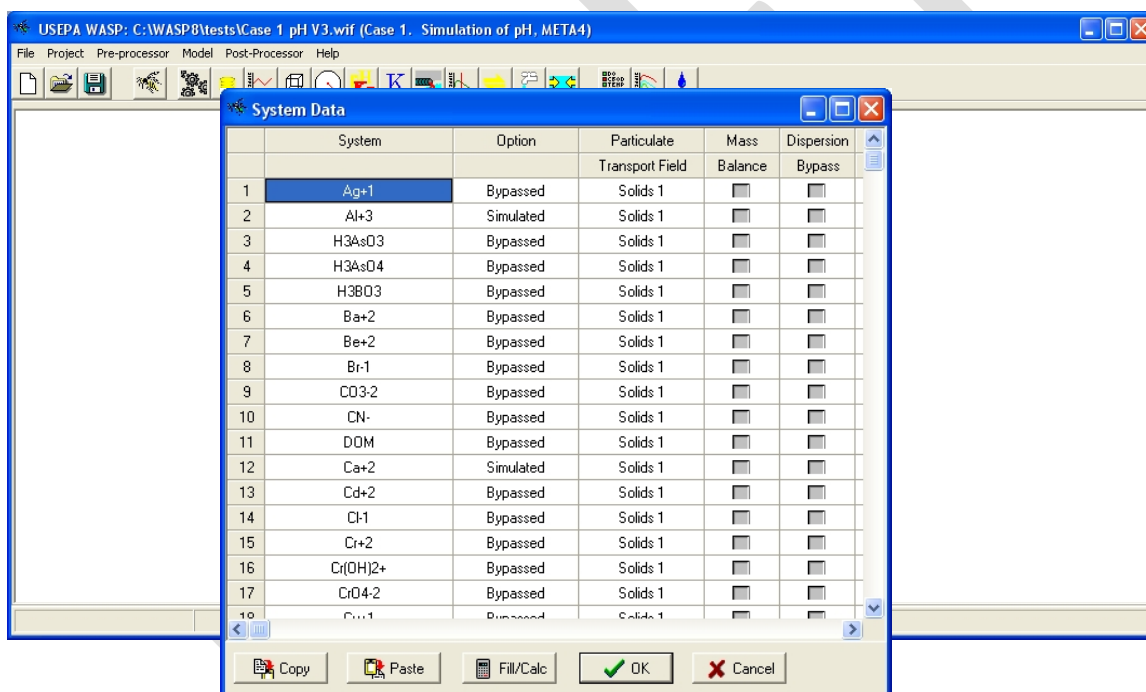


Figure 5. Model systems

Table 1. MET4 Model Systems

No.	Ident. No.	Comp.	No.	Ident. No.	Comp.	No.	Ident. No.	Comp.
1	20	Ag+1	23	330	H+1	45	760	HSe-1
2	30	Al+3	24	360	Hg2+2	46	761	HSeO3-1
3	60	H3AsO3	25	361	Hg(OH)2	47	762	SeO4-2
4	61	H3AsO4	26	380	I-1	48	770	H4SiO4
5	90	H3BO3	27	410	K+1	49	790	Sn(OH)2
6	100	Ba+2	28	440	Li+1	50	791	Sn(OH)6-
7	110	Be+2	29	460	Mg+2	51	800	Sr+2
8	130	Br-1	30	470	Mn+2	52	870	Tl+1
9	140	CO3-2	31	471	Mn+3	53	871	Tl(OH)3
10	143	CN-	32	480	MoO4-2	54	890	U+3
11	145	DOM	33	490	NH4+1	55	891	U+4
12	150	Ca+2	34	491	NO2-1	56	892	UO2+1
13	160	Cd+2	35	492	NO3-1	57	893	UO2+2
14	180	Cl-1	36	500	Na+1	58	900	V+2
15	210	Cr+2	37	540	Ni+2	59	901	V+3
16	211	Cr(OH)2+	38	580	PO4-3	60	902	VO+2
17	212	CrO4-2	39	600	Pb+2	61	903	VO2+1
18	230	Cu+1	40	730	HS-1	62	950	Zn+2
19	231	Cu+2	41	731	S	63	831	Solid 1
20	270	F-1	42	732	SO4-2	64	832	Solid 2
21	280	Fe+2	43	740	Sb(OH)3	65	833	Solid 3
22	281	Fe+3	44	741	Sb(OH)6-			

5. META4 Speciation: Model theory

In META4, a mass balance equation is written for each of the selected systems (Table 1), which are the model **state variables**. As with all WASP state variables, the time and spatially variable concentrations of these state variables are computed using the numerical form of the mass balance or constituent transport equation (Equation 1). The model time step, segmentation, initial conditions, boundary conditions and loads, and advective and diffusive transport each will influence the numeric solution.

In META4, the state variables can exist in soluble, insoluble (precipitates), or sorbed forms. The particular form the state variable can affect its transport, transformation, and reaction kinetics, which vary depending upon the form of the state variable. Therefore, it

is necessary to compute the speciation of metals during each model time step in order to compute changes in total metal concentration.

Two classes of reactions may be specified in META4, fast and slow reactions. The fast reactions include complexation, sorption, and precipitation, which are considered equilibrium processes. That is, each model time step in META4 solves for the distribution of species of the state variables assuming equilibrium conditions. The metals may then be transported and react (slow reactions) at rates which may vary with the form (dissolved, sorbed, or precipitated), and species.

5.1 Equilibrium Speciation Reactions and Model Databases

The state variables make up the **components** in speciation reactions. That is, the components, and chemical combinations of those components, make up particular chemical **species**. The species make up all of the chemical forms included in the equilibrium reactions. Therefore, particular combinations of the state variables (plus water as an added component) make up particular species, so that the total of any of the state variables is the sum of the free species and that which is complexed, sorbed, or precipitated with the other state variables.

The specific reactions included in simulations are not specified directly by the user, but are input through databases supplied with META4 and based on those in MINTEQA2 (Allison et al., 1991). The specific databases are listed in Table 2.

Table 2. META4 Databases

Database	Description
Component.dbs	Includes additional information (molecular weight, etc. for each of the model systems included in Table 1)
Thermo.dbs	Thermodynamic database containing information on over 1000 potential species and their chemical characteristics
FEO_DLM.dbs	Database with speciation information for the diffuse-layer sorption reactions for hydrous ferric oxide (HFO).
MESorb.dbs	Database containing potential sorption reactions
Gaussian.dbs	Database for the Gaussian Model For Dissolved Organic Matter (DOM)
Type6.dbs	Database for precipitates

The chemical species considered by META4 include **dissolved**, **sorbed**, and **precipitated** forms. Dissolved forms include the soluble components (i.e., their simple ions) and complexes (aqueous products of reactions involving components). Sorbed

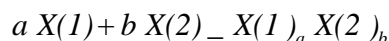
forms are those associated with solids (the three solids types). Precipitated forms are those that form a solid phase.

5.2 Speciation Reactions

5.2.1 Complexation

Complexation refers to the aqueous reactions of a metal with organic and inorganic ligands (e.g. OH⁻, Cl²⁻, S²⁻, Cl⁻, amino acids, humates, fulvates, etc.) in water, to form a third species (the metal-ligand complex) as described by

Equation 3



which, at chemical equilibrium, can be written as

Equation 4

$$\frac{X(1)_a X(2)_b}{X(1)^a X(2)^b} = K(i)$$

or

Equation 5

$$C(i) = K(i) X(1)^a X(2)^b$$

where X are the components of the reaction (in units of activity, or molar concentration if the ionic strength is zero), C(i) is the molar concentration of the ith complex, a and b are stoichiometric coefficients for the complex, and K(i) is a stability constant for the ith complex. The reaction may be written in more general form as

Equation 6

$$C(i) = K(i) \prod_{k=1}^N X(k)^{a(i,k)}$$

where N is the total number of components and a(i,k) the stoichiometric coefficient for the kth component of the ith complex.

Temperature Corrections

As a user option (selectable using the temperature correction constant) the stability constants can be corrected for temperature. When selected, based on specified

temperatures (as model parameters and time functions) the stability constants are temperature corrected using the Van't Hoff Equation:

Equation 7

$$\log(K) = \log(K_T) - \Delta H_i \frac{298.15 - T_K}{298.15 T_K V_{hc} R_j / 1000.0}$$

where T_K is the absolute temperature (oK), ΔH_i is the Enthalpy of Reaction (kJ mol^{-1}) R_j is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and $V_{hc} = \ln(10)$. The enthalpy of reaction is read from the model databases.

Where data are available, an analytical polynomial expression is used to compute the stability constant as a function of temperature.

Equation 8

$$\log(K) = A_t + B_t T_K + \frac{C_t}{T_K} + D_t \log_{10}(T_K) + E_t T_K^2 + \frac{F_t}{T_K^2} + \frac{G_t}{\sqrt{T_K}}$$

Where A_t - G_t are coefficients which, for the specified species, are extracted from the analytical temperature database (see ANALYT.dbs, Section 10.6).

Ionic Strength Corrections

As a user option (selectable using the ionic strength constant) the stability constants can be corrected for ionic strength. When selected, based on specified ionic strength (as model parameters and time functions) the activity coefficients (γ) for charged species are computed using the Davies Equation:

Equation 9

$$\log(\gamma) = A_t z_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right]$$

where z_i is the ionic charge of each reactant or product, read from the model databases, A_t is a function of temperature and ionic strength, and I is the ionic strength. For neutral species activity coefficient is computed from

Equation 10

$$\log(\gamma) = 0.1 I$$

and the stability constant activity corrected by

Equation 11

$$\log(K) = \log(K_T) - \log(\gamma)$$

Note that the activity corrections vary for the Gaussian DOM model and the user is referred to the MINTEQA2 Version 4 user documentation for a detailed description of the corrections.

5.2.2 Gaussian DOM model

META4 includes a Gaussian dissolved organic matter (DOM model based on MINTEQA2 version 4.0 and as described by Dobbs et al. (1989). The Gaussian DOM model is included due to the potential impact of DOM complexation on trace metal mobility and toxicity. Dissolved organic matter strongly complexes many trace metals (e.g., copper and lead).

The Gaussian DOM model is invoked using the DOM model option constant (see model constants). DOM may be specified either as a model component (state variable) or parameter. The Gaussian reactions for the components of interest are then extracted from the Gaussian database (see Gaussian.dbs in Section 10.4).

5.2.3 Sorption

Sorption refers to the association of a component with a solid surface. For example, in META4 may sorb to one or all of the three solids types. There are two sorption models included in META4, each of which is described below.

Modified Exchange Sorption

Sorption is, in general, handled similarly to complexation reactions. The formation of a particular sorbed species, C(i), may be determined as before from

Equation 12

$$C(i) = N_s(i) K_p(i) \prod_{k=1}^N X(k)^{a(i,k)}$$

in comparison to Equation 6 but where the stability constant, K(i), is replaced with the product of a partition coefficient (K_p(i), L/Kg) and a site density (dimensionless).

The sorption option is available for each of the three solids types included in META4 and is invoked using the constant for the model option. One invoked, the sorption constants for the specified components are read from the ME_Sorb database (see Section 10.2).

Hydrous Ferric Oxide Double Layer (HFO DLM) Sorption Model

More complex sediment modeling, as used within META4, requires a delineation of the importance of dominant mechanisms that affect accumulation of metals in sediments and potential releases of metals from sediments. The accumulation of metals in sediments generally includes five major mechanisms:

1. Adsorption onto fine-grained materials, predominantly iron oxides

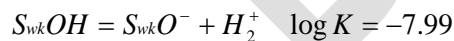
2. Precipitation of trace element compounds
3. Coprecipitation with hydrous Fe, Al and Mn oxides and carbonates
4. Association with organic matter (adsorption or organometallic bonding)
5. Incorporation in crystalline minerals.

In many surface waters, it is generally accepted that sorption of metals to iron oxyhydroxides is the dominant chemical process regulating the dissolved concentrations of metals in waters and sediments (Horowitz, 1991; Dzombak and Morel, 1990). Chemical precipitation of iron is very rapid under neutral pH conditions, and contributes to the sorption properties of suspended and bed sediment components. Desorption of metals from sediments may also be an important process regulating overlying water quality. Desorption depends on several factors including changing pH, metal, sorbent and redox potential of the aqueous microenvironment surrounding the sediment particles. It should be mentioned that while adsorptive processes are very effective at removing metals from the water column, the equilibration of the sediment pore water with the contaminated sediments generally will result in the presence of a significant dissolved concentration of metals in pore waters. Stream flow changes that result in an increase in the sediment re-suspension can lead to significant releases of dissolved metals to the overlying water column.

Due to the importance of iron oxides in regulating metal concentrations, the current approach for mathematically describing the mechanism of metal sorption to iron oxyhydroxides is based on surface complexation theory (Dzombak and Morel, 1990). While the simple, empirical approach described above can be used within META4 (e.g. simple K_p approach), the two-layer surface complexation formulation, as developed by Dzombak and Morel (1990), forms the basis for the description of metal accumulations to hydrous ferric oxides in META4.

The two-layer model is based on a charge balance, analogous to the mass balance equations, with the coulombic factor as a component. Reactions are specified for two different binding sites (e.g. weak and strong surface hydroxyl species) and the coulombic component (Dzombak and Morel 1987, Schecher and McAvoy 1994).

Equation 13



Equation 14



where the subscript “s” represents a site near the surface. The relevant expressions, for this example, are then given by Equations 10, 11, and 12.

Equation 15

$$10^{3.52} = \frac{S_{wk}OH_2^+}{[S_{wk}OH][H^+]} [Coul.]^{\Delta Z}$$

$$10^{-7.99} = \frac{[S_{wk}O^-][H^+]}{[S_{wk}OH]} [Coul.]^{\Delta Z}$$

where the coulombic factor is given by

Equation 16

$$[Coul.] = \exp\left(\frac{-F \Psi_o}{R T}\right)$$

where ψ_o is the surface potential, R the ideal gas constant, T is absolute temperature and ΔZ the change in charge of the surface species due to the adsorption reaction. The relationship between the total surface charge (T_σ) and the surface potential is given by

Equation 17

$$T_\sigma = 0.1174 \quad I^{1/2} \sinh\left(\frac{Z \psi_o}{2RT}\right)$$

where Z is the valency of the electrolyte and I the ionic strength. Presently, in META4 the ionic strength is specified, not computed. In addition to the reactions, the specific surface area of the solids and site density for the two surfaces are specified as well as initial concentrations for the surfaces and the coulombic factor. **The model assumes that the solids type one is the iron oxide and will transport any materials associated with it.**

5.2.4 Precipitation

Precipitation refers to the formation of a solid phase of a particular chemical species. Precipitation differs from sorption in that it removes components from the aqueous phase. The formation of a solid is normally computed based on solubility data, and where the solubility is exceeded the solid will then precipitate.

In equilibrium models such as MINEQL (Westall et al. 1986) or MINTEQA2 (Allison et al 1991), the solubility is checked for each species of interest. If the solubility product is exceeded, the component of the solids is essentially "removed" and the equilibrium solution obtained using a reduced number of components. This process is repeated until all the remaining species are calculated to be soluble.

In META4, solids formations are specified similarly to complexation and sorption reactions. That is, the components of the solid species are specified along with an

equilibrium constant for the solids formation and the formation of the solid phase is described by

Equation 18

$$C_s(i) = K_s(i) \prod_{k=1}^N X(k)^{a(i,k)}$$

in which $K_s(i)$ the solubility constant. In META4 the precipitate species remain in the “soup” unless removed via sediment transport (e.g. settling). That is, the precipitates are transported using the solid transport fields in META4.

5.3 Solution Methods

In order to solve for the form of a metal, solids, or parameter present, two sets of equations are required. First, the concentration of each chemical species is a function of the available concentration of each of the components, so that

Equation 19

$$C(i) = f(X_1, X_2, \dots, X_N) = K(i) \prod_{j=1}^N X(j)^{a(i,j)}$$

where the conditional stability constant for sorbed or precipitated species has been adjusted by the number of sites or geochemical multiplier, respectively. Each of the components may occur in its free ionic form or complexed with other components; however, it is only the free ionic form of the component which is available for reaction, which is an unknown.

A second set of equations may be written based on a mass balance of each of the components over all species. That is, the total concentration of a component distributed among M species is simply the sum of all of those species ($i=1$ to M) multiplied by the stoichiometric coefficient for the particular component, which may be written as

Equation 20

$$X_t(j) = \sum_{i=1}^M a(i, j) C(i) = \sum_{i=1}^M a(i, j) K(i) \prod_{k=1}^N X(k)^{a(i,k)}$$

where X_t is the total concentration (molar). A similar mass balance may be written for each of the N components, resulting in N mass balance equations. The total concentrations are assumed to be known by META4, using information from the previous time step. The unknowns are the free ionic concentrations, or the amount of each component available for chemical reaction (complexation, sorption or precipitation).

There are two solution methods used in META4 to solve for the free ionic concentrations of each of the components. In both approaches the pH specified as a model parameter

(and hydrogen ion concentration) is assumed not to be affected by the speciation reactions (i.e. $[H^+]$ is fixed). Otherwise, H^+ can be simulated as a model state variable. The free ionic concentrations of the remaining species are determined by: (1) assuming that metal concentrations are low, so that the competition between metal species for other components has a negligible impact on the speciation reactions, or (2) solving all the aqueous chemistry equations simultaneously.

Once the free ionic concentrations of each of the components are determined through one of the two solution techniques, the concentration of each of the species may be determined. Since the transport and kinetic reactions depend upon the particular species of metal present, META4 will compute the concentration of each metal species existing in a particular form. For example, only the species sorbed onto solids 1-3 are transported by flow fields 3-5, respectively (e.g. flow field 3 transports solids 1). In addition to the specified forms, there are user defined forms provided by which the user may identify a particular species, or group of species, for kinetic reactions. For example, in addition to the stoichiometry and conditional stability constant, each species may be identified by a species type, called a form number (Table 3). The kinetic reactions then may be limited to only those species with that particular designation.

Table 3. Example forms of the components that can be specified to restrict reactions

Form Number	Chemical Form
1	TOTAL
2	FREE IONIC
3	ALL DISSOLVED
4	BOUND TO SOLID 1
5	BOUND TO SOLID 2
6	BOUND TO SOLID 3
7	ALL BOUND TO SOLIDS (1-3)
8	PRECIPITATE
9	USER DEFINED
10	USER DEFINED
11	USER DEFINED

5.3.1 Non-competitive solution

This solution proceeds in two parts. First, the free ionic concentrations (those available for chemical reactions) for components other than metals (the solids and parameters) are computed. Secondly, the free ionic concentrations of the metal species are computed.

In solving the free ionic concentration for non-metal species, the only type of reactions that may be considered here are those involving H^+ (e.g. HL , HL_2 and HL_3). The hydrogen ion concentration is considered to be fixed (does not vary with the chemical equilibrium

solution) and is specified in the model input. Given the stoichiometric coefficients and stability constants, a mass balance for the total concentration can be written as

Equation 21

$$X_t(j) = \sum_{i=1}^M a(i, j) K(i) \prod_{k=1}^N X(k)^{a(i,k)}$$

which can be solved for the free ionic concentration as

Equation 22

$$[X(j)] = \frac{X_t(j)}{\sum_{i=1}^M a(i, j) K(i) \prod_{k=1}^N X(k)^{a(i,k)}}$$

The solution for the metal species proceeds similarly to that for the non-metal components. The solution is based on the assumption that the concentrations of metal species are low, or conversely that the concentrations of other available components are high, so that competition does not effect the species composition (i.e., ligands are in excess).

5.3.2 Competitive Solution Technique

In the competitive solution technique, the mass balance equations for all components are solved simultaneously following procedures similar to those used to solve the aqueous chemistry in the equilibrium models MINEQL (Westall et al., 1986), MINEQL+ (Schecher and McAvoy, 1994), and MINTEQA2 (Allison et al., 1991). As stated previously, the competitive solution technique used in META4 treats solids similarly to complexation and solids formation. That is solids are not removed from the solution.

The solution technique proceeds the same as the non-competitive technique, with the exception that **initial estimates of the free ionic concentrations are required for all components** (state variables and parameters), as well as **convergence criteria** (typically on the order of 10^{-19} molar concentrations). The solution procedure uses the initial user-input estimate for the activity (or concentration) of each of the components at the start-up time for the model. For subsequent iterations, the final free ionic concentrations from the previous time step are used as the initial estimates.

The solution process is accomplished numerically using the Newton-Raphson method. The function that is solved in the method is

Equation 23

$$[Y(j)] = [X_c(j)] - T(j)$$

where $Y(j)$ is the difference between the computed and known ($T(j)$) totals for the j th component. To solve the j simultaneous equations, the derivative of the function is taken with respect to each component and the derivatives are structured in the Jacobian matrix. The matrix is augmented with the function. An initial guess is made and the matrix is solved iteratively using the Newton Raphson technique for the simultaneous solution of non-linear equations. Solution is achieved when $Y(j)$ is less than some given quantity (the convergence criteria specified in input) for all components. Westall et al. (1986) and Allison et al. (1991) provide a more complete description of the solution technique.

6. META4 Input

6.1 Specifying Initial Conditions and Estimates of Activities

Once the state variables are selected, the user then enters the initial concentrations and estimates of initial activities. Both of these are starting points for the simulation. That is, the initial concentration is the total concentration for each selected state variable and provides a starting place for the time-variable computations. The units may be molar or mass-based depending upon the general constants selected.

Note to Users: The concentration units for input may be either mg/L or molar, **with the default being molar**. The user should select the appropriate option for the input units under the model constants input, model options group, constant 21 (see below). If the units are mg/L in input, they are converted to internal units of molar concentrations based on the molecular or formula weight, which is extracted from the component database supplied with the model.

Constant	Used	Value	Minimum
12 IADS_Solid1 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 1 only, IADS=2 in	<input type="checkbox"/>	0	0.0000
13 S-SA_HFO Specific surface area of solids	<input type="checkbox"/>	0	0.0000
14 SITED1_HFO (Hfo_sOH) Site density for surface 1 (2-layer model,mole sites/mole Fe)	<input type="checkbox"/>	0	0.0000
15 SITED2_HFO (Hfo_wOH) Site density for surface 2 (2 layer model,mole sites/mole Fe)	<input type="checkbox"/>	0	0.0000
16 IADS_Solid2 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 2 only, IADS=2 in	<input type="checkbox"/>	0	0.0000
17 S-SA_HMO Specific surface area of solids	<input type="checkbox"/>	0	0.0000
18 SITED1_HMO (Hmo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Mn)	<input type="checkbox"/>	0	0.0000
19 SITED2_HMO (Hmo_wOH) Site density for surface 2 (2 layer model,mole sites/mole Mn)	<input type="checkbox"/>	0	0.0000
20 IADS_Solid3 Sorption option (IADS=0 for none, 1 for modified exchange option)	<input type="checkbox"/>	0	0.0000
21 ICONC If ICONC=1 then inputs are assumed molar,else assumed inputs are in mg/L and converted to molar using form	<input type="checkbox"/>	0	0.0000
22 IDATAB If IDATAB <=2 then the databases read are those from MINTEQA2 and modified for META4, otherwise the d	<input type="checkbox"/>	0	0.0000

The initial concentrations and activities input forms are subforms under the model segment tab. They are similar in structure and are illustrated below for example Case 1.

The screenshot shows a software window titled "Segments" with a blue title bar and standard Windows window controls. Inside, there are four tabs: "Segments", "Parameters", "Initial Concentrations" (which is selected), "Fraction Dissolved", and "Initial Activity". Below the tabs is a table with five columns: "Segment", "Al+3", "Ca+2", "H+1", and "SO". The first row of the table contains the values "1", "3.1E-5", "4.1E-5", "8.13E-5", and "1.3E-4". Below the table is a large empty rectangular area. At the bottom of the window is a toolbar with several buttons: "Fill/Calc" (with a calculator icon), "Copy" (with a document icon), "Paste" (with a document icon), "+ Insert", "- Delete", "OK" (with a green checkmark), and "Cancel" (with a red X).

Segment	Al+3	Ca+2	H+1	SO
1	3.1E-5	4.1E-5	8.13E-5	1.3E-4

Figure 6. Example of the initial conditions input form

Segment	Al+3	Ca+2	H+1	SO
1	0	0	0	0

Figure 7. Example of the initial activities input form

Note to Users: The initial activities are the initial guesses for the activities (molar) for the iterative speciation computations described above. If these initial guess are not reasonable, the iterative solution in META4 may not converge.

MINTeq (Allison et al., 1999) includes algorithms to aid the user in making initial activity guesses, and solutions for MINTeqA2 may be used to estimate initial activities for META4 if convergence is an issue. Once the simulation starts, the activities from the previous computational time step are used as the activity estimates for the iteration (those input by the user are no longer used).

A reasonable first guess for the activities is the initial total concentrations.

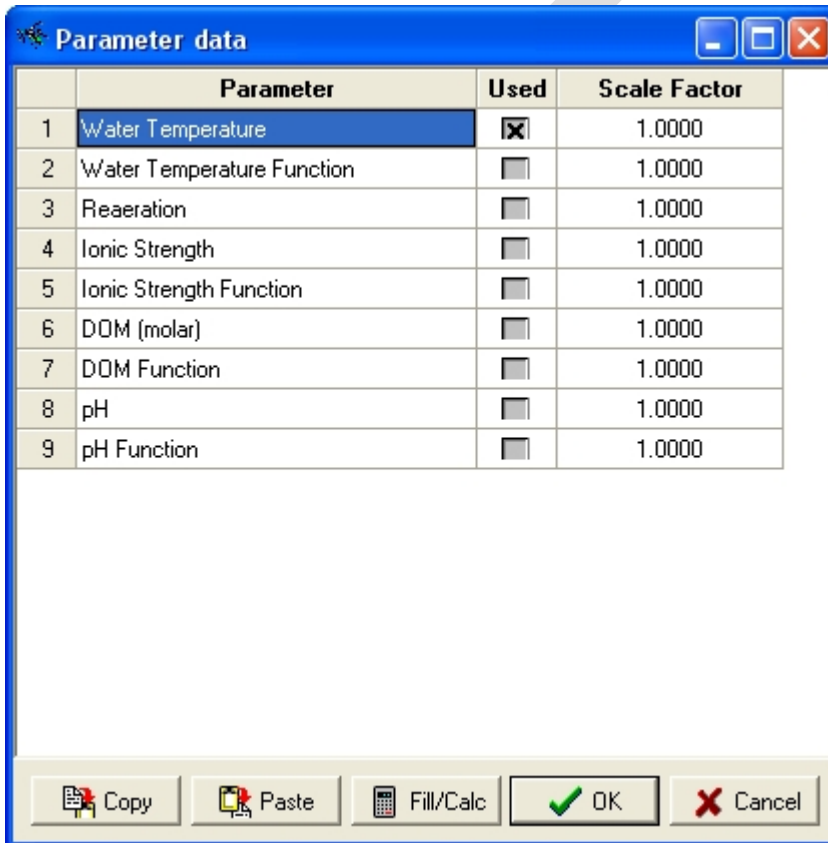
6.2 META4 parameters and Time Functions

Parameters are spatially-variable characteristics of the water body, while time functions vary with time. Parameters are segment specific (may be varied by segment) and, for some parameters, may be varied with time using the time functions. The environmental parameters and time functions allow specification of environmental properties (such as temperature) that effect the META4 computations, but are not predicted by META4. The

reader is referred to the WASP user's manual (Wool et al., 2006) for a more detailed discussion of the role and relationships between model parameters and time functions.

The user selects the specific parameters by clicking on the parameter icon and then selecting the specific parameters from the parameter input form. The checkbox is to specify whether the specific parameter is to be used and a scale factor provided for each. The water temperature and ionic strength are used to correct reaction rates and/or constants (such as speciation).

Note that DOM and pH (e.g. H^+) are included as both parameters and as selectable systems (state variables, Table 1). This is to allow the user to prescribe rather than predict DOM and H^+ concentrations. **If the user selects the model parameter form of this system, the parameter will be used in the computation of speciation reactions and NOT the state variable.**



The screenshot shows a Windows-style dialog box titled "Parameter data". It contains a table with four columns: an index, a parameter name, a "Used" checkbox, and a "Scale Factor". The table lists nine parameters. The first parameter, "Water Temperature", is selected (highlighted in blue) and its "Used" checkbox is checked. All other parameters have unchecked checkboxes. All scale factors are set to 1.0000. At the bottom of the dialog, there are buttons for "Copy", "Paste", "Fill/Calc", "OK", and "Cancel".

	Parameter	Used	Scale Factor
1	Water Temperature	<input checked="" type="checkbox"/>	1.0000
2	Water Temperature Function	<input type="checkbox"/>	1.0000
3	Reaeration	<input type="checkbox"/>	1.0000
4	Ionic Strength	<input type="checkbox"/>	1.0000
5	Ionic Strength Function	<input type="checkbox"/>	1.0000
6	DOM (molar)	<input type="checkbox"/>	1.0000
7	DOM Function	<input type="checkbox"/>	1.0000
8	pH	<input type="checkbox"/>	1.0000
9	pH Function	<input type="checkbox"/>	1.0000

Figure 8. Parameter selection form.

Once the parameters are selected, segment specific values are input in the parameter user form under the model segment input form, as illustrated below.

The 'Segments' dialog box is shown with the 'Parameters' tab selected. The table below contains the following data:

Segment	Water Temperature	Water Temperature Funcl	Reaeration	Ionic
1	2.5E+1	0	0	0

Below the table, there are buttons for 'Fill/Calc', 'Copy', and 'Paste'. At the bottom of the dialog are buttons for '+ Insert', '- Delete', 'OK', and 'Cancel'.

Figure 9. Parameter input form.

Similarly, the model time series are selected using the time-series icon and then selecting the specific time series to be used using the check-box. For each time series, a series of time/dates and values are input or imported.

Time Functions

	Time Function	Used	Interpolation
▶	Water Temperature Function 1(c)	<input checked="" type="checkbox"/>	Linear
	Water Temperature Function 2(c)	<input type="checkbox"/>	Linear
	Water Temperature Function 3(c)	<input type="checkbox"/>	Linear
	Water Temperature Function 4(c)	<input type="checkbox"/>	Linear
	Water Velocity Function 1(m/sec)	<input type="checkbox"/>	Linear
	Water Velocity Function 2(m/sec)	<input type="checkbox"/>	Linear
	Water Velocity Function 3(m/sec)	<input type="checkbox"/>	Linear
	Water Velocity Function 4(m/sec)	<input type="checkbox"/>	Linear
	Wind Speed (m/sec)	<input type="checkbox"/>	Linear
	Reaeration (per day)	<input type="checkbox"/>	Linear
	Air Temperature (c)	<input type="checkbox"/>	Linear
	pH Function 1 (Standard Units)	<input type="checkbox"/>	Linear
	pH Function 2 (Standard Units)	<input type="checkbox"/>	Linear
	pH Function 3 (Standard Units)	<input type="checkbox"/>	Linear
	pH Function 4 (Standard Units)	<input type="checkbox"/>	Linear
	Ionic Strength 1 (molar)	<input type="checkbox"/>	Linear
	Ionic Strength 2 (molar)	<input type="checkbox"/>	Linear
	Ionic Strength 3 (molar)	<input type="checkbox"/>	Linear
	Ionic Strength 4 (molar)	<input type="checkbox"/>	Linear
	DOM Function 1 (mg/l)	<input type="checkbox"/>	Linear
	DOM Function 2 (mg/l)	<input type="checkbox"/>	Linear
	DOM Function 3 (mg/l)	<input type="checkbox"/>	Linear
	DOM Function 4 (mg/l)	<input type="checkbox"/>	Linear

Time/value pairs for Water Temperature Function 1(c)

	Date	Time	Value
1	1/ 1/2000	12:00	2E+1
2	5/ 1/2000	12:00	2E+1

Figure 10. Time series input form

6.3 META4 Constants

6.3.1 General Constants

Chemical constants are global in nature. That is, unlike parameters, they do not vary with space and time. The constants specify the characteristics of each of the chemicals and their reactions. The general identifying constants, as well as those used to characterize speciation and kinetic reactions and volatilization, are described below. The definition of the constants will vary, depending upon the structure and kinetics of the systems simulated. This data group is subdivided into Model Options, constants for volatilization and degradation.

Constants Data

Constant Group: Model Options

Constant	Used	Value	Minimum	Maximum
12 IADS_Solid1 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 1 only, IADS=2 invokes two-layer model DLM for HFD)	<input type="checkbox"/>	0	0.0000	0.0000
13 S-SA_HFD Specific surface area of solids	<input type="checkbox"/>	0	0.0000	0.0000
14 SITED1_HFD (Hfo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Fe)	<input type="checkbox"/>	0	0.0000	0.0000
15 SITED2_HFD (Hfo_wOH) Site density for surface 2 (2-layer model, mole sites/mole Fe)	<input type="checkbox"/>	0	0.0000	0.0000
16 IADS_Solid2 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 2 only, IADS=2 invokes two-layer model DLM for HMD)	<input type="checkbox"/>	0	0.0000	0.0000
17 S-SA_HMD Specific surface area of solids	<input type="checkbox"/>	0	0.0000	0.0000
18 SITED1_HMD (Hmo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Mn)	<input type="checkbox"/>	0	0.0000	0.0000
19 SITED2_HMD (Hmo_wOH) Site density for surface 2 (2-layer model, mole sites/mole Mn)	<input type="checkbox"/>	0	0.0000	0.0000
20 IADS_Solid3 Sorption option (IADS=0 for none, 1 for modified exchange option)	<input type="checkbox"/>	0	0.0000	0.0000
21 ICONC If ICONC=1 then inputs are assumed molar, else assumed inputs are in mg/L and converted to molar using formula weights (molar conc = input/(1000*GPW))	<input type="checkbox"/>	0	0.0000	0.0000
22 IDATAB If IDATAB <=2 then the databases read are those from MINTEQA2 and modified for META4, otherwise the databases are those from Visual MINTEQ	<input type="checkbox"/>	0	0.0000	0.0000

Copy Paste Fill/Calc

OK Cancel

Table 4: META4 General Constants

1	Ionic strength Option (Ionic_Opt)) >1 = yes, reactions will be corrected for ionic strength (Davies equation)
2	Temperature Option >1 = yes, reactions will be temperature corrected
3	ISPEC Speciation Option: ISPEC = 0 No Speciation; ISPEC = 1 Non-competitive Speciation; ISPEC = 2 Competitive Speciation
4	EPS1 Convergence Criteria for Matrix Solver (required only if ISPEC = 2)
5	EPS2 Convergence Criteria for Solution of Non-Linear Speciation Equations (Required only if ISPEC = 2)
6	NMAX Maximum number of iterations allowed in solution of speciation equations (Required only if ISPEC = 2)
7	GFW_Solid1 Gram formula weight for Solids Type 1 (note =HFO or HMO depending on IADS)
8	GFW_Solid2 Gram formula weight for Solids Type 2
9	GFW_Solid3 Gram formula weight for Solids Type 3
10	IDOM Invokes Gaussian DOM model when >=1
11	IPREC Precipitation option (>=1 then include solids)
12	IADS_Solid1 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 1 only, IADS=2 invokes two-layer model DLM for HFO)
13	S-SA_HFO Specific surface area of solids
14	SITED1_HFO (Hfo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Fe)
15	SITED2_HFO (Hfo_wOH) Site density for surface 2 (2 layer model, mole sites/mole Fe)
16	IADS_Solid2 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 2 only, IADS=2 invokes two-layer model DLM for HMO)(<i>not used, under construction</i>)
17	S-SA_HMO Specific surface area of solids (<i>not used, under construction</i>)
18	SITED1_HMO (Hmo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Mn) (<i>not used, under construction</i>)
19	SITED2_HMO (Hmo_wOH) Site density for surface 2 (2 layer model, mole sites/mole Mn) (<i>not used, under construction</i>)
20	IADS_Solid3 Sorption option (IADS=0 for none, 1 for modified echange option)
21	ICONC , If ICONC=1 then inputs are assumed molar, else assumed inputs are in mg/L and converted to molar using formula weights (molar conc. =input/(1000*GFW))
22	IDATAB If IDTAB <=2 then the databases read are those from MINTEQA2 and modified for META4, otherwise the databases are those from Visual MINTEQ

6.3.2 Degradation

Degradation Theory

Each of the state variables in META4, including solids, are allowed to react. The general form of the reactions may be expressed by

Equation 24

$$\frac{\partial [C]}{\partial t} /_{\text{reaction}} = \xi f_{\text{spec}} f_{\text{temp}} f_{\text{geoc}} K [C]$$

where [C] is the total concentration of the state variable in the particular model segment, t is time, ξ is a direction multiplier, K the reaction rate (day^{-1}), and f_{spec} , f_{temp} and f_{geoc} are rate multipliers. The structure of META4 is generalized to provide flexibility in the specification of the kind and number of reactions.

The reactions are specified to META4 first by identifying both the reactant and the product. With respect to Equation 24, for the reactant, the direction multiplier is negative ($\xi=-1$) indicating that this is a loss. For the product, the direction multiplier is positive ($\xi=1$) indicating a gain.

The rate multiplier f_{spec} refers to the fraction of the total concentration that is available for the reaction. For META4, it is assumed that only the dissolved phase reacts.

The reaction rates specified are those at 20°C, which are corrected by a temperature multiplier using a Q_{10} formulation. The water temperatures and a Q_{10} value are specified, and the Q_{10} value is the factor by which the rate changes with a 10°C change in temperature.

Equation 25

$$f_{\text{temp}} = Q_{10}^{\frac{T-20}{10}}$$

The geochemical multiplier (f_{geoc}) accounts for the dependence of the particular reaction on the aquatic chemistry. A maximum of three geochemical multipliers may be used and the value of the rate multiplier is determined by

Equation 26

$$f_{\text{geoc}} = \prod_{i=1}^3 g_{\text{chem},i}$$

The geochemical rate multipliers are computed from a specified variable, dependence, and constant (K). The variable indicates the function to be used, the dependence specifies by chemistry constituent (X). The four functions available are:

Power Law (Variable = 1)

$$g_{chem,i} = [X]^K \quad \text{Equation 27}$$

Saturation Kinetics (Variable = 2)

$$g_{chem,i} = \frac{[X]}{[X] + K} \quad \text{Equation 28}$$

Noncompetitive Inhibition (Variable = 3)

$$g_{chem,i} = \frac{K}{[X] + K} \quad \text{Equation 29}$$

Concentration Limited Function (Variable = 4)

$$g_{chem,i} = 1 \text{ for } [X] \geq K \quad \text{Equation 30}$$

$$g_{chem,i} = 0 \text{ for } [X] < K$$

where the concentration of [X] is molar. Note that the concentration limited function is opposite in meaning to that used in precipitation.

Table 5. Example forms of the components that can be specified to restrict reactions (also see Table 3)

Form Number	Chemical Form
1	TOTAL
2	FREE IONIC
3	ALL DISSOLVED
4	BOUND TO SOLID 1
5	BOUND TO SOLID 2
6	BOUND TO SOLID 3
7	ALL BOUND TO SOLIDS (1-3)
8	USER DEFINED
9	USER DEFINED
10	USER DEFINED
11	USER DEFINED

Implementation Notes

- 1) The default value of Q_{10} is one. If neither temperature (see Parameters) nor Q_{10} values are specified, no temperature correction will be performed. Similarly, the default values of the geochemical multipliers are one.
- 2) It is assumed that only the dissolved phase reacts.
- 3) Constants are only entered for the combination of reactions required. If no constants are specified, no reactions will occur.

Degradation Input

The degradation kinetics are input under the general kinetics input, with a user form specific to degradation. The user would first select the reactant (Figure 11) and product from the drop down-menus (only those systems selected will be included). The user could then specify the Q10, reaction rate, and a product (if needed). The product would allow, for example, simulation of mercury II to methyl-mercury, or any other reaction and product. If the reaction is dependent upon a particular form of those systems or other systems, then the user can specify up to three dependencies for the reaction (see Figure 12. Select product (if applicable))

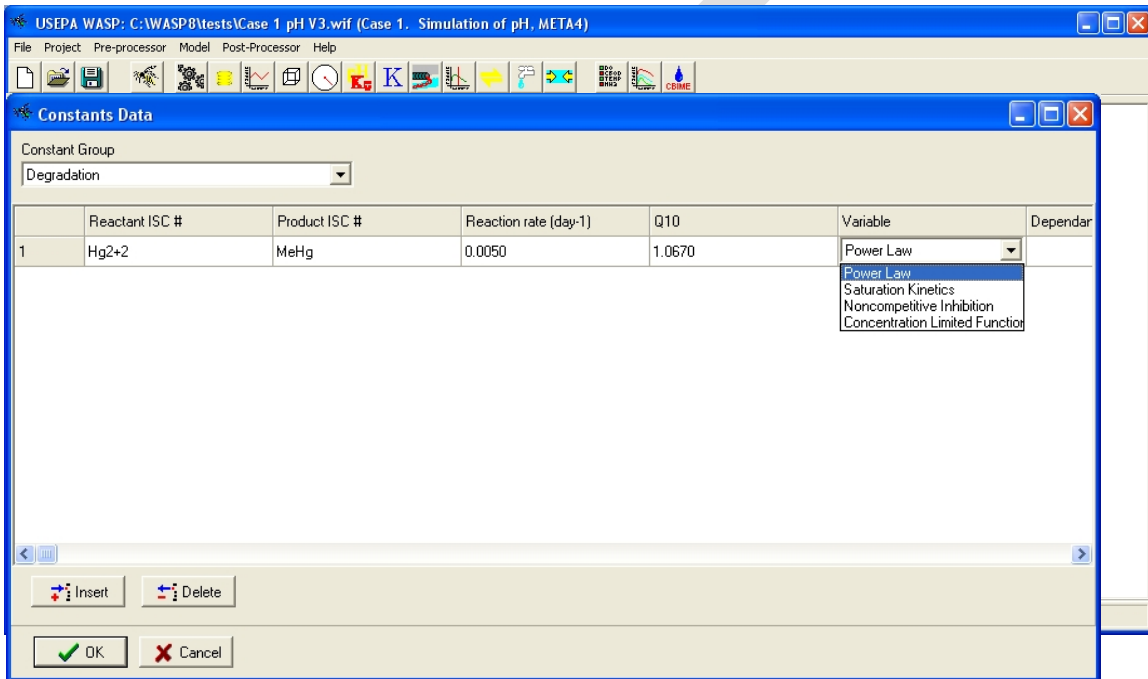


Figure 13. Select variable
and Figure 14).

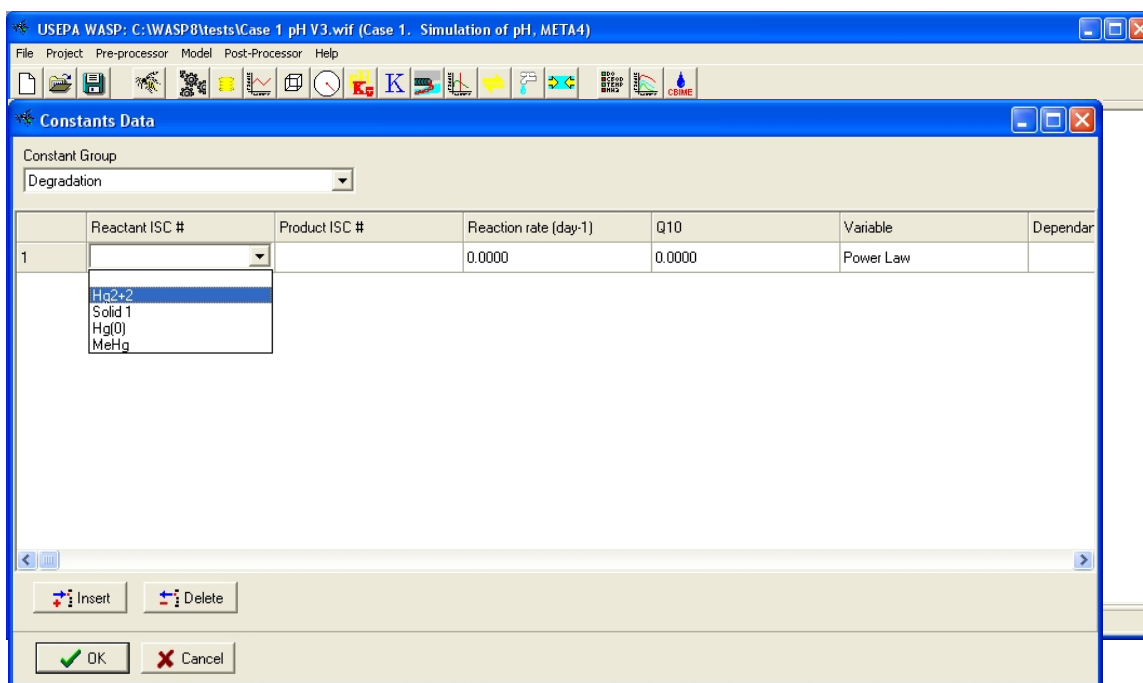


Figure 11. Select reactant

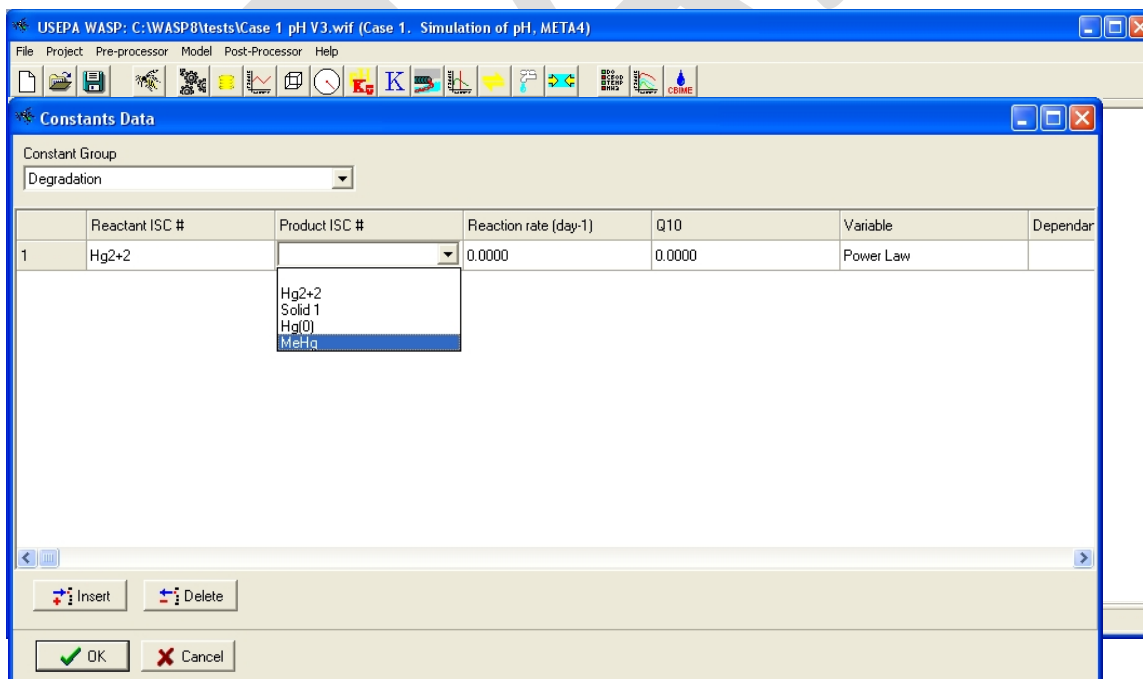


Figure 12. Select product (if applicable)

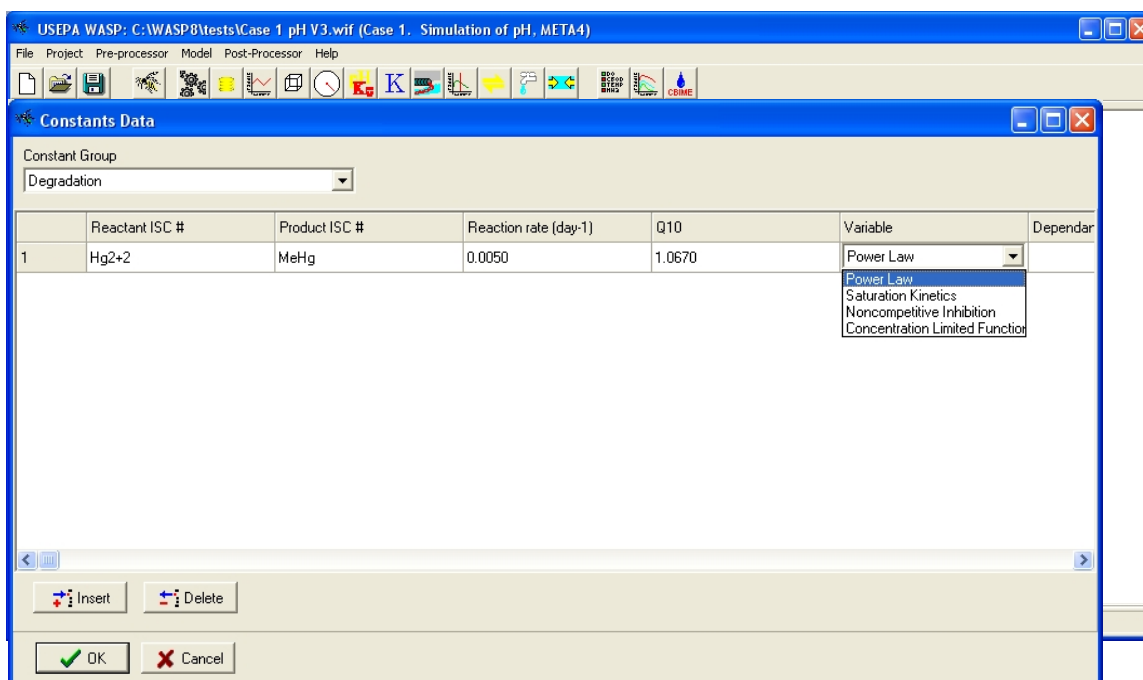


Figure 13. Select variable

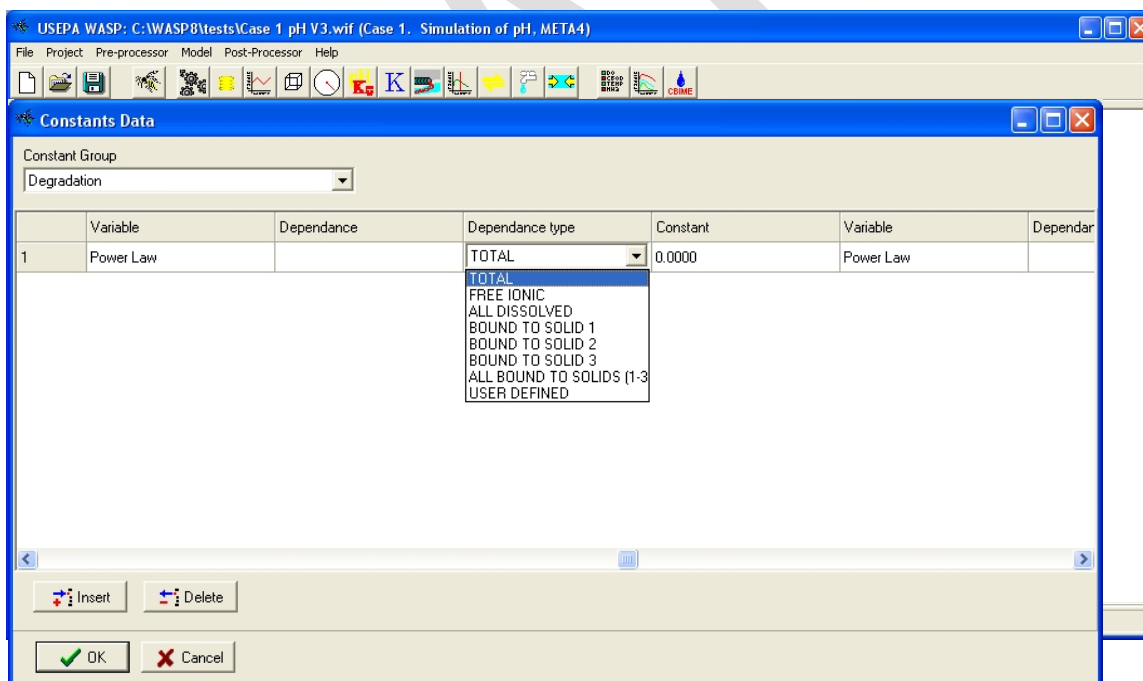


Figure 14. Select form

6.3.3 Volatilization

Volatilization Theory

Volatilization is the movement of a chemical across the air-water interface. The dissolved concentration attempts to equilibrate with the gas phase partial pressure, as given by

Equation 31

$$\frac{\partial C}{\partial t}_{volat} = \frac{K_v}{D} \left(f_{spec} [C] - \frac{[C_a]}{\frac{H}{RT}} \right)$$

where K_v is a transfer rate (m day^{-1}), D is the segment depth (m), C is the total concentration of the form of metal (moles l^{-1}), f_{spec} is the fraction occurring in the form that is subject to volatilized, C_a is the atmospheric concentration (moles l^{-1}), R the universal gas constant ($8.206 \times 10^{-5} \text{ atm mole}^{-1} \text{ } ^\circ\text{K}^{-1}$), T the water temperature ($^\circ\text{K}$), and H the Henry's law coefficient for the air-water partitioning of the metal [atm mole^{-1}]. Equilibrium occurs when the dissolved concentration equals the partial pressure divided by the Henry's Law Constant.

In META4, the dissolved concentration of a metal compound in a surface water segment can volatilize at a rate determined by the two-layer resistance model (Whitman, 1923), where the conductivity is the reciprocal of the total resistance:

Equation 32

$$k_v = (R_L + R_G)^{-1} = \left[K_L^{-1} + \left(K_G \frac{H}{RT} \right)^{-1} \right]^{-1}$$

where R_L is the liquid phase resistance (day/m), K_L the liquid phase transfer coefficient (m/day), R_G the gas phase resistance (day/m), and K_G the gas phase transfer coefficient (m/day).

The two-resistance method assumes that two "stagnant films" are bounded on either side by well-mixed compartments. Concentration differences serve as the driving force for the water layer diffusion. Pressure differences drive the diffusion for the air layer. From mass balance considerations, it is obvious that the same mass must pass through both films, thus the two resistances combine in series. There is another resistance involved, the transport resistance between the two interfaces, but it is assumed to be negligible. This may not be true in two cases: very turbulent conditions and in the presence of surface-active contaminants. Although the Whitman model is rather simplified in its

assumption of uniform layers, it has been shown to be as accurate as models that are more complex.

The value of K_v , the conductivity, depends on the intensity of turbulence in a water body and in the overlying atmosphere. Mackay and Leinonen (1975) have discussed conditions under which the value of K_v is primarily determined by the intensity of turbulence in the water. As the Henry's Law coefficient increases, the conductivity tends to be increasingly influenced by the intensity of turbulence in water. As the Henry's Law coefficient decreases, the value of the conductivity tends to be increasingly influenced by the intensity of atmospheric turbulence.

The input or computed volatilization rate constant is for a temperature of 20°C. It is adjusted for segment temperature using the equation:

Equation 33

$$K_T = K_{20} \Theta^{T-20}$$

where Θ is a user input temperature correction factor and T is the water temperature (°C).

There have been varieties of methods proposed to compute the liquid (K_L) and gas phase (K_g) transfer coefficients, several of which are included in META4. The particular method to be employed is identified by the model through the user's selection of one of six volatilization options, each of which will be briefly described below.

Volatilization Option 1

This option allows the use of measured volatilization rates. The rates (K_L , m day⁻¹) are input as a parameter (it may be varied by segments) and may be time variable.

Volatilization Option 2

This option allows the user to input an oxygen reaeration constant that then is adjusted to represent the liquid film transfer constant for the particular form of the given metal. The adjustment is made in one of two ways. First, the user may input a measured ratio of oxygen to metal exchange so that the rate (K_L) is computed from

Equation 34

$$K_L = K_{L_{O_2}} K_{v_0} = K_{L_{O_2}} \sqrt{32/MW}$$

where $K_{L_{O_2}}$ is the reaeration velocity (m/d) and K_{v_0} the ratio of volatilization rate to reaeration rate. If this ratio is not provided, META4 will compute the ratio based on the molecular weights of O_2 and that of metal as shown below:

Equation 35

$$K_L = K_{L,0} \sqrt{32 / M_w}$$

where M_w is the molecular weight of the chemical, g/mole. Using this option, the gas transfer rate is calculated using O'Conner's method (see Option 5).

Volatilization Option 3

If this option is specified, the liquid film transfer coefficient will be computed as in Option 2. However, the gas film transfer coefficient will be computed using Mackay's method (see Option 6).

Volatilization Option 4

The computation of the liquid and gas film transfer coefficients under this option is based on the simplified method used by Porcella et al (1992) in their MCM model. That method assumes that the gas transfer coefficient increases linearly with wind speed, as given by

Equation 36

$$K_G = K_{G,0} u_w$$

where $K_{G,0}$ is the base coefficient (s day^{-1}) and u_w is the wind speed (m sec^{-1}). The liquid phase transfer coefficient is computed similarly for wind speeds below a threshold value and increased linearly from a base value for higher wind speeds, as given by

Equation 37

for $u_w < u_T$

$$K_L = K_{L,0}$$

for $u_w \geq u_T$

$$K_L = K_{L,0} u_T + K_{L,1} (u_w - u_T)$$

where $K_{L,0}$ and $K_{L,1}$ are base transfer coefficients (sec day^{-1}) and u_T is a threshold wind speed (m sec^{-1}).

Volatilization Option 5

The liquid and gas film transfer coefficients computed under this option vary with the type of water body. The type of water body is specified to the water as one of the volatilization constants and can be a flowing stream, river or estuary or a stagnant pond or lake. The primary difference is that in a flowing water body the turbulence is primarily a function of the stream velocity, while for stagnant water bodies wind shear may be dominant. The formulations used to compute the transfer coefficients vary with the water body type as shown below.

Flowing Stream, River or Estuary.

For a flowing system (type 0) the transfer coefficients are controlled by flow induced turbulence. For flowing systems, the liquid film transfer coefficient (K_L) is computed using the Covar method (Covar, 1976), in which the equation used varies with the velocity and depth of the segment. First, the transfer coefficient for dissolved oxygen is computed using the formulations provided below; then K_L is calculated from Equation 34.

For segments with depths less than 0.61 m the Owens formula is used to calculate the oxygen reaeration rate:

Equation 38

$$K_{L_{O_2}} = 5.349 \frac{u^{0.67}}{D^{0.85}}$$

where u is the velocity of the water (m/s) and D is the segment depth (m). For a segment with a velocity less than 0.518 m/s or a depth (m) greater than $13.584 u^{2.9135}$, the O'Connor-Dobbins formula is used:

Equation 39

$$K_L = \left(\frac{D_w u}{D} \right)^{0.5} 8.64 \times 10^4$$

where D_w is the diffusivity of the chemical in water (m^2/s), computed from

Equation 40

$$D_w = \frac{22 \times 10^{-9}}{M^{\frac{2}{3}}}$$

In all other cases, the Churchill formula is used to calculate the reaeration rate:

Equation 41

$$K_{L_{O_2}} = 5.049 \frac{u^{0.969}}{D^{0.673}}$$

The gas transfer coefficient (K_G) is assumed constant at 100 m/day for flowing systems.

Stagnant Lake or Pond.

For a stagnant system the transfer coefficients are controlled by flow-induced turbulence. For stagnant systems, the liquid film transfer coefficient (K_L) is computed using the

Equation 42

$$K_L = u^* \left(\frac{\rho_a}{\rho_w} \right)^{0.5} \frac{K^{0.33}}{\lambda_2} Sc_w^{-0.67}$$

The O'Connor equations are:

Equation 43

$$K_G = u^* \frac{K^{0.33}}{\lambda_2} Sc_a^{-0.67}$$

where: u^* is the shear velocity (m/s) computed from

Equation 44

$$u^* = C_d^{0.5} W_{10}$$

where C_d is the drag coefficient (assumed to be $C_d = 0.0011$) and W_{10} is the wind velocity 10m above the water surface (m/s), ρ_a , ρ_w are the density of air and water (kg/m^3),

respectively,, κ is von Karmen's constant ($\kappa= 0.74$), λ_2 is a dimensionless viscous sub-layer thickness ($\lambda_2= 4$), and S_{ca} , S_{cw} are air and water Schmidt Numbers, computed from

Equation 45

$$S_{ca} = \frac{\mu_a}{\rho_a D_a}$$

$$S_{cw} = \frac{\mu_w}{\rho_w D_w}$$

where D_a and D_w are the diffusivity of chemical in air and water (m^2/sec), μ_a and μ_w the viscosity of air and water ($kg\ m^{-1}\ sec^{-1}$), where K_G is proportional to wind and inversely proportional to molecular weight to the 2/3 power. The diffusivity of water is computed using Equation 40 while the diffusivity of the chemical in air (D_a , m^2/sec) is computed from

Equation 46

$$D_w = \frac{1.9 \times 10^{-4}}{M_w^{\frac{2}{3}}}$$

Volatilization Option 6

As with Option 5, the liquid and gas film transfer coefficients computed under this option vary with the type of water body. The type of water body is specified to the water as one of the volatilization constants and can either be a flowing stream, river or estuary or a stagnant pond or lake. The primary difference is that in a flowing water body the turbulence is primarily a function of the stream velocity, while for stagnant water body wind shear may dominant. The formulations used to compute the transfer coefficients vary with the water body type as shown below.

Flowing Stream, River or Estuary.

The liquid and gas film transfer coefficients for flowing waterbodies are computed identically to those described under Option 5.

Stagnant Pond or Lake.

Under this option, the liquid and gas film transfer coefficients are computed using formulations described by Mackay (1985). The Mackay equations are:

Equation 47

$$K_L = 10^{-6} + 0.00341 u_- Sc_w^{-0.5} u_- > .3 \text{ m/s}$$

Equation 48

$$K_L = 10^{-6} + 0.0144 u_-^{2.2} Sc_w^{-0.5} u_- < .3 \text{ m/s}$$

Equation 49

$$K_G = 10^{-3} + 0.0462 u_- Sc_w^{-0.67}$$

Implementation Notes

- 1) Volatilization is allowed only for surficial water column segments as identified by the segment type specified in input. The segment types are:
1) Surface water segments (Type 1), subsurface water segments (Type 2), surface sediment segments (Type 3) and subsurface sediment segments (Type 4).
- 2) Volatilization may be allowed only for particular chemical species, or groups of species, as identified using the form number. If a form number is not specified, all of the dissolved species (Species Type = 3) will be allowed to volatilize.
- 3) Input required for each metal state variable includes the Henry's law constant (atm Mole⁻¹) and the option used to compute volatilization may vary between types of metal.

7. META4 Output

META4 simulations produce several files that may be examined by the user. These files use the file name of the input data set with a unique extension. They include:

1. Model output file
2. Graphical simulation results output file
3. Graphical transport results output file
4. Mass balance output file

The model output and mass balance output files are ASCII files which can be viewed using a text editor. The graphical simulation results files can be processed with the post processing programs available with WASP.

8. References

- Allison, J.D., D.S. Brown and K. J. Novo-Gradac. 1991. MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, EPA/600/3-91/021, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA.
- Allison, Jerry D. and Terry L. Allison. 2005. "Partition Coefficients for Metals in Surface Water, Soil, and Waste," U.S. Environmental Protection Agency Office of Research and Development National Exposure Research Laboratory, Athens, GA.
- Ambrose, B, Jr., P.E., T.A. Wool, and J.L. Martin. 1993. The Water Quality Analysis Simulation Program, WASP5; Part A: Model Documentation, U.S. Environmental Protection Agency, Center for Exposure Assessment Modeling, Athens, GA.
- Brown, L.C. and T.O. Barnwell. 1987. The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual. U.S. Environmental Protection Agency, Athens, GA. EPA/600/3-87-007.
- Butler, Barbara A., James F. Ranville, and Philippe E. Ross. 2005. Comparison between Observed and Model Predicted Particulate Metal Transport in a Mining-Impacted Stream (North Fork Clear Creek, Colorado). Presented at 2005 National Meeting of the American Society of Mining and Reclamation, Breckenridge, CO, June 19-23, 2005.

- Butler, Barbara A., Brian S. Caruso and James F. Ranville. 2009. "Reactive Transport Modeling of Remedial Scenarios to Predict Cadmium, Copper, and Zinc in North Fork of Clear Creek, Colorado," *Remediation*, Autumn 2009, 101-119.
- Caruso, B. S., & Ward, R. C. 1998. Assessment of nonpoint source pollution from inactive mines using a watershed-based approach. *Environmental Management*, 22, 225–243.
- Covar, A.P. 1976. Selecting the Proper Reaeration Coefficient for Use in Water Quality Models. Presented at the U.S. EPA Conference on Environmental Simulation Modeling, April 19-22, 1976. Cincinnati, Ohio.
- Dzombak, D.A. and Morel, F.M.M. 1990. *Surface Complexation Modeling Hydrous Ferric Oxides*. John Wiley and Sons Publishers, New York.
- Dzombak, D.A. and F.M.M. Morel. 1987. Adsorption of Inorganic Pollutants in Aquatic Systems, *ASCE J. Hydraulic Eng.* 113, p. 430.
- Dzombak, D.A. and M.A. Ali. 1993. Hydrochemical modeling of metal fate and transport in freshwater environments, *Water Pollut. Res. J. Can.*, 28(1), pp. 7-50.
- Environmental Research Software. 2007. "MINEQL+ version 4.6," Environmental Research Software, Hallowell, ME, August 2007.
- Gustafsson, Jon Petter. 2010. "Visual MINTEQ ver. 3.0," KTH Royal Institute of Technology, Sweden.
- Hudson, R.J.M., S.A. Gherini, and R.K. Munson. 1990. The MTL Mercury Model: A Description of the Model, Discussion of Scientific Issues, and Presentation of Preliminary Results, Section 8 In: Mercury in Temperate Lakes Project Annual Report for 1990 to Electric Power Research Institute, Palo Alto, California.
- Hudson, R.J.M., S. Gherini and D. Porecella. 1991. Instructions for Running the MCM Lake Mercury Cycling Model, Tetra Tech, Inc., Lafayette, CA.
- Horowitz, A.J. 1991. *Sediment-Trace Element Chemistry*, Lewis Publishers, Chelsea, Michigan.
- Leopold, L.B. and T. Maddox. 1953. The Hydraulic Geometry of Stream Channels and Some Physiographic Implications, Professional Paper 252, U.S. Geological Survey, Washington, DC.
- Mackay, D. and P.J. Leinonen. 1975. Rate of Evaporation of Low-Solubility Contaminants from Water Bodies to Atmospheres. *Environ. Sci. Technology*. 7:611-614.
- Mackay, D. and W.Y. Shiu. 1984. Physical-Chemical Phenomena and Molecular Properties, in Gas Transfer at Water Surfaces. Brutsaert, W. and G.H. Jirka, Eds. D. Reidel, Boston.
- Martin, J.L. 1992. "MERC4, A Mercury Transport and Kinetics Model, Beat Test Version 1.0: Model Theory and User's Guide," Prepared for the U.S.

- Environmental Protection Agency, Center for Exposure Assessment Modeling, Athens, GA, July 1992.
- Medine, Allen J. and James L. Martin. 2000a. "Development of a Metal Exposure and Transformation Assessment Model for use in Watershed Management, Restoration and TMDL Analyses," Proceedings of Watershed 2000, Water Environment Federation and British Columbia Water and Waste Association and Western Canada Water and Wastewater Association, July 8-12, 2000.
- Medine, A.J. and J.L. Martin. 2000b. "Development of a Metal Exposure and Transformation Model for Use in Watershed Management, Restoration and TMDL Analysis, Watershed 2000, July 9-12, 2000, Vancouver, BC.
- Medine, A.J. and J.L. Martin. 2000c. "Development of the Speciation-Based Exposure and Transformation Assessment Model (META4): Application to Copper and Zinc Problems in the Alamosa River, Colorado," Presented at the American Chemical Society, Environmental Chemistry Division Symposium, August, 2000, Boulder, CO.
- Medine, Allen J., James L. Martin and Elizabeth Sopher, 2002. Development of the Metal Speciation-based Metal Exposure and Transformation Assessment Model (META4): Application to Copper and Zinc Problems in the Alamosa River, Colorado. In: Fate and Transport of Chemicals in the Environment: Impacts, Monitoring and Remediation. R.L. Lipnick, R.P. Mason, M.L. Phillips, and C.U. Pittman (Eds.) ACS Publications, Washington.
- National Research Council. 2000. National Research Council, Toxicological Effects of Methylmercury, National Academy Press, Washington, DC (2000).
- Nimick, D. A., Church, S. E., & Finger, S. E. (Eds.). (2004). Chapter A, Summary and conclusions from investigation of the effects of historical mining in the Boulder River Watershed, Jefferson County, Montana. In Integrated investigations of environmental effects of historical mining in the Basin and Boulder Mining Districts, Boulder River Watershed, Jefferson County, Montana. Denver, CO: U.S. Geological Survey.
- Parkhurst, David L. and C.A.J. Appelo. 1999. "User's Guide To PHREEQC (Version 2)—A Computer Program For Speciation, Batch-Reaction, One-Dimensional Transport, And Inverse Geochemical Calculations," Water-Resources Investigations Report 99-4259, U.S. Department of the Interior U.S. Geological Survey
- Porcella, D.M., R.M. Hudson and S.Gherini. 1992. The MCM computer Program, Electric Power Research Institute, Palo Alto, Calif.
- Runkel, R.L., 1998, One-Dimensional Transport with Inflow and Storage (OTIS): A Solute Transport Model for Streams and Rivers: U.S. Geological Survey Water-Resources Investigations Report 98-4018, 73 p.
- Runkel, R.L., 2010, One-Dimensional Transport with Equilibrium Chemistry (OTEQ): A Reactive Transport Model for Streams and Rivers: U.S. Geological Survey

Techniques and Methods Book 6, Chapter B6, 101 p.

<http://pubs.usgs.gov/tm/06b06/>

USEPA. 1997. EPA's national hardrock mining framework. EPA 833-B-97-003.

Washington, DC: US EPA Office of Water.

USEPA. 2009. "National Listing of Fish Advisories: Biennial National Listing of Fish Advisories," EPA-823-F-09-007, September 2009

Runkel, Rob. 2000. "Using OTIS to Model Solute Transport in Streams and Rivers," US Geological Survey Fact Sheet FS-138-99, January 2000.

Schecher, W.D. and D.C. McAvoy, 1994. MINEQL+: A Chemical Equilibrium Program for Personal Computers, User's Manual, Version 3.0, The Procter and Gamble Co., Ivorydale Technical Center, Cincinnati, Ohio.

Westall, J.C., J.L. Zachary and F.M.M. Morel. 1986. MINEQL: A Computer Program for the Calculation of the Chemical Equilibrium Composition of Aqueous Systems, Report 86-01, Department of Chemistry, Oregon State University, Corvallis, OR.

Whitman, R.G. 1923. A Preliminary Experimental Confirmation of the Two-Film Theory of Gas Absorption. Chem. Metallurg. Eng. 29:146-148.

Wool, Tim A., Robert B. Ambrose, James L. Martin and Edward A. Comer. 2006. Water Quality Analysis Simulation Program (WASP) Version 6.0 DRAFT: User's Manual. US Environmental Protection Agency – Region 4, Atlanta, GA.

9. Model Input Examples and Test Cases

Examples of META4 model input are provided below, with corresponding input files provided with the model. These examples are not intended to represent realistic case studies. Instead, they are intended only to familiarize the META4 user with the model input and output. The input also is useful to test the model following any changes in the model code or structure.

9.1 Test Case 1. Simulation of pH

9.1.1 General Model Setup

For this test case, the model is configured as one Completely Mixed Stirred Reactor (One WASP “box”) with no inflows or outflows. This test case demonstrates the META4 computation of H^+ . In this test, the pH is computed based on specified concentrations (molar) of:

Component	Concentration (molar)
Al	3.1e-5
Ca	4.1e-5
H+	8.13e-5
SO4	1.3e-4

Three solids types were included in the simulation as well. But, no solids reactions were specified, so their concentrations remained constant.

The above concentrations were specified for both the initial conditions and as guesses for the initial activities. Since there was no transport or slow reactions, the concentrations of the components and computed species were constant over the period of simulation. There was no correction for temperature or ionic strength in this test.

The species considered in this example (extracted from the Thermo Database) include:

SPECIES ID NUMBER	SPECIES NAME	Enthalpy of reaction (kJ/mol)	Log K. Common logarithm of the equilibrium constant
303300	AlOH+2	47.810	-4.997
303301	Al(OH)2+	0.000	-10.094
303303	Al(OH)3 (aq)	0.000	-16.791
303302	Al(OH)4-	173.240	-22.688
1503300	CaOH+	64.110	-12.697
3307320	HSO4-	22.000	1.990
307320	AlSO4+	28.000	3.890
307321	Al(SO4)2-	11.900	4.920
1507320	CaSO4 (aq)	7.100	2.360

9.1.2 Results

The results are tabulated below. Note that these results also correspond exactly to the results from MINTEQA2 (Version 4.03).

Component/Species	Species ID	Predicted Concentration (molar)
Al+3	30	1.5326E-05
Ca+2	150	3.9953E-05
H+1	330	8.2608E-05
SO4-2 -	732	1.1439E-04
Al+3	30	1.5326E-05
Ca+2	150	3.9953E-05
H+1	330	8.2608E-05
SO4-2 -	732	1.1439E-04
AlOH+2	303300	1.8681E-06
Al(OH)2+	303301	1.8087E-07
Al(OH)3 (a	303303	4.3990E-10
Al(OH)4-	303302	6.7505E-12
CaOH+	1503300	9.7169E-14
HSO4-	3307320	9.2343E-07
AlSO4+	307320	1.3608E-05
Al(SO4)2-	307321	1.6679E-08
CaSO4 (aq)	1507320	1.0470E-06

9.2 Test Case 2. Simulation of temperature and ionic strength corrected pH

9.2.1 System

This test case demonstrates the META4 computation for temperature and ionic strength corrections to the equilibrium constants. In META4, options are provided for the user to select whether or not the equilibrium constants are to be corrected for temperature and ionic strength (**ITemp_Corr** and **Ionic_Opt**). If the user elects to correct for temperature and ionic strength, then the corrections are based on specified values (temperature in units of °C and ionic strength in molar units). The temperature and ionic strength are specified as model parameters and time functions by the user, and are not computed in META4. The corrections were based on equations from MINTEQA2 (Version 4.03; Allison et al., 1991).

As with MINTEQA2, there were two schemes incorporated into META4 for temperature corrections. The first is based on those constituents included in the ANALYT database (which includes only 23 species at present). For those species, the logK value at the specified temperature is computed from a power function of the form:

$$\log K_T = A + BT + C/T + D \log(T) + ET^2 + F/T^2 + G/T^{0.5}$$

T = temperature (°K), and A,B,...,G are empirical constants stored in the thermodynamic database (ANALYT.DBS). For any species not included in the database, the equilibrium constant is corrected for temperature variations from 25 °C by the van't Hoff equation (Allison et al. 1991).

The ionic strength is specified in META4 input, corresponding to the fixed option in MINTEQA2. The Davies equation is used to calculate activity coefficients for all charged species. A gamma correction coefficient is computed as a function of temperature, the ionic strength, and the charge on the species (from the appropriate database). With the exception of H₂O, the gamma correction for neutral species in META4 is calculated as a fraction (0.1 as was specified in MINTEQA2 Version 4.03) of the ionic strength (molar).

This test case is identical to the previous test case (Test Case 1) with the exception of the activity corrections being conducted. Three simulations were performed and compared to results from MINTEQA2 as specified below:

- Temperature activity corrections evoked, using a specified temperature of 20°C
- Ionic strength activity corrections evoked, using a specified ionic strength of 0.01 molar
- Temperature and ionic strength activity corrections evoked, using a specified temperature of 20°C and ionic strength of 0.01 molar

As with the previous example, the components included are those tabulated below. The concentrations were specified using the default units (molar) and the initial guesses for activities set equal to the total concentrations.

Component	Concentration (molar)
Al	3.1e-5
Ca	4.1e-5
H+	8.13e-5
SO4	1.3e-4

The species considered in this example (extracted from the Thermo Database) include:

SPECIES ID NUMBER	SPECIES NAME	Enthalpy of reaction (kJ/mol)	Log K. Common logarithm of the equilibrium constant
303300	AlOH+2	47.810	-4.997
303301	Al(OH)2+	0.000	-10.094
303303	Al(OH)3 (aq)	0.000	-16.791
303302	Al(OH)4-	173.240	-22.688
1503300	CaOH+	64.110	-12.697
3307320	HSO4-	22.000	1.990
307320	AlSO4+	28.000	3.890
307321	Al(SO4)2-	11.900	4.920
1507320	CaSO4 (aq)	7.100	2.360

9.2.2 Results

The results are tabulated below for the three cases, with results from META4 compared to results from MINTEQA2.

Table 6. Test case for a specified ionic strength of 0.01 molar

NO.	Species	ID	Predicted Concentration	
			META4	MINTEQA2
			molar	molar
1	Al+3	30	2.28E-05	2.28E-05
2	Ca+2	150	4.05E-05	4.05E-05
3	H+1	330	8.28E-05	8.28E-05
4	SO4-2 -	732	1.23E-04	1.23E-04
5	AlOH+2	303300	1.83E-06	1.83E-06
6	Al(OH)2+	303301	1.44E-07	1.44E-07
7	Al(OH)4-	303302	6.58E-12	6.58E-12
8	Al(OH)3 (a)	303303	3.48E-10	3.48E-10
9	AlSO4+	307320	6.26E-06	6.26E-06
10	Al(SO4)2-	307321	5.44E-09	5.44E-09
11	CaOH+	1503300	8.00E-14	8.00E-14
12	CaSO4 (aq)	1507320	4.96E-07	4.96E-07
13	OH-	3300020	1.50E-10	1.50E-10
14	HSO4-	3307320	6.56E-07	6.51E-07

Table 7. Test case for a specified temperature of 20°C

NO.	Species	ID	Predicted Concentration	
			META4	MINTEQA2
			molar	molar
1	Al+3	30	1.68E-05	1.68E-05
2	Ca+2	150	4.00E-05	4.00E-05
3	H+1	330	8.24E-05	8.24E-05
4	SO4-2	732	1.16E-04	1.16E-04
5	AlOH+2	303300	1.48E-06	1.48E-06
6	Al(OH)2+	303301	2.00E-07	2.00E-07
7	Al(OH)4-	303302	2.28E-12	2.28E-12
8	Al(OH)3	303303	4.87E-10	4.87E-10
9	AlSO4+	307320	1.25E-05	1.25E-05
10	Al(SO4)2-	307321	1.73E-08	1.73E-08
11	CaOH+	1503300	6.27E-14	6.27E-14
12	CaSO4	1507320	1.01E-06	1.01E-06
13	OH-	3300020	8.33E-11	8.33E-11
14	HSO4-	3307320	8.06E-07	8.06E-07

Table 8. Test case for a specified ionic strength of 0.01 molar and temperature of 20°C

NO.	Species	ID	Predicted Concentration	
			META4	MINTEQA2
			molar	molar
1	Al+3	30	2.39E-05	2.39E-05
2	Ca+2	150	4.05E-05	4.05E-05
3	H+1	330	8.24E-05	8.24E-05
4	SO4-2 -	732	1.23E-04	1.23E-04
5	AlOH+2	303300	1.40E-06	1.40E-06
6	Al(OH)2+	303301	1.53E-07	1.53E-07
7	Al(OH)4-	303302	2.14E-12	2.14E-12
8	Al(OH)3 (a)	303303	3.73E-10	3.73E-10
9	AlSO4+	307320	5.52E-06	5.52E-06
10	Al(SO4)2-	307321	5.41E-09	5.41E-09
11	CaOH+	1503300	5.18E-14	5.18E-14
12	CaSO4 (aq)	1507320	4.79E-07	4.79E-07
13	OH-	3300020	1.02E-10	1.02E-10
14	HSO4-	3307320	5.71E-07	5.71E-07

9.3 Test Case 3. Two-Layer Adsorption, the HFO DLM

9.3.1 System

This example demonstrates the use of the double layer model (or DLM) sorption model for HFO (hydrous ferric oxide) sorption model using META4. HFO is the dominant sorbent for metal sorption in some mining-impacted systems (Butler et al., 2005). In this model, hydrous ferric oxide is simulated assuming that two types of binding sites, weak and strong, are available on the oxide surface. Protons and zinc ions compete for the two types of binding sites, and equilibrium is described by mass-action equations. The reader is referred to the MINTEQA2 model documentation and Dzombak and Morel (1990) for a detailed description of the sorption model.

As with the first two examples, this is a “beaker” simulation. That is WASP simulates a single completely mixed stirred reactor (CMSTR, or one “box”) with no inflows or outflows.

- This example predicts adsorption of zinc onto hydrous ferric hydroxide. The system is defined as:
- total ferric iron 1.79×10^{-4} M,
- total zinc of 3.02×10^{-6} M, and aqueous electrolyte solution of 0.01 M NaNO₃.

This example is based upon Example 2F from Schecher and McAvoy (1994).

For this simulation,

- 1) Five state variables are selected (set to simulated): Fe⁺², Zn⁺² and Solids 1-3. **Note that if the HFO model is selected, solids 1 is assumed to represent HFO.** In this test, Solids 2 and 3 are included only to represent conservative tracers. Note that the selection of the HFO DLM model will automatically result in three new components for the reactions, representing the oxide surface and the two binding sites. These will be represented in model output (model ID in parenthesis) as: ADS1TYP1(811), ADS1TYP2(812) and ADS1PSIo(813) for the weak and strong surface hydroxyl species and the coulombic component, respectively.
- 2) Under the general constants, constants were selected in order to correct the results for ionic strength and temperature; indicate the concentration units of all input are molar; set the maximum number of iterations in the solver routines and convergence criteria: and, set the constants for the HFO model.

The HFO Diffuse Layer model is first selected (IADS_Solid1 = 2), and the molecular weight of the HFO specified (=89 g HFO / mol Fe). The specific surface area of the solid (m²/gram) is then specified (typically 600) along with the site density for the two binding surfaces (as shown below). **Note that the units of the site densities are mole sites/mole Fe.**

Ionic strength Option (Ionic_Opt)) >1 = yes, reactions will be corrected for ionic strength (Davies equation)	1
Temperature Option >1 = yes, reactions will be temperature corrected	1
ISPEC Speciation Option: ISPEC = 0 No Speciation; ISPEC = 1 Non-competitive Speciation; ISPEC = 2 Competitive Speciation	2
EPS1 Convergence Criteria for Matrix Solver (required only if ISPEC = 2)	1.00E-16
EPS2 Convergence Criteria for Solution of Non-Linear Speciation Equations (Required only if ISPEC = 2)	1.00E-16
NMAX Maximum number of iterations allowed in solution of speciation equations (Required only if ISPEC = 2)	100
GFW_Solid1 Gram formula weight for Solids Type 1 (note =HFO or HMO depending on IADS)	89
IADS_Solid1 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 1 only, IADS=2 invokes two-layer model DLM for HFO)	2
S-SA_HFO Specific surface area of solids	600
SITED1_HFO (Hfo_sOH) Site density for surface 1 (2-layer model, mole sites/mole Fe)	0.005
SITED2_HFO (Hfo_wOH) Site density for surface 2 (2 layer model, mole sites/mole Fe)	0.2

- 3) Next the model parameters for temperature (=25 °C) and ionic strength (= 0.01 molar) are selected and values specified.
- 4) For this example, based on Example 2F from Schecher and McAvoy (1994), the initial conditions were specified as:
 - $\text{Fe}^{+2} = 1.79 \times 10^{-4} \text{ M}$, $\text{Zn}^{+2} = 3.02 \times 10^{-6} \text{ M}$, and $\text{Fe (Solids 1)} = 1.79 \times 10^{-4} \text{ M}$. The Fe (Solids 1) concentration was based on a concentration of 15.9 mg/L for Fe, and the specified gram formula weight = 89 g HFO/mol Fe.
 - Initial activities were set to the same values as the initial conditions.

9.3.2 Results

The species to be considered in this example, extracted by META4 from the thermodynamic database and the FEO-DLM database include:

Complexation		Sorption	
Species	Log K	Species	Log K
FeOH	-2.19	Fe(st)OHZn	0.99
FeOH ₂	-5.67	Fe(st)OH ₂	7.29
Fe ₂ (OH) ₂	-2.95	Fe(st)OH	-8.93
FeOH ₃ -Aq	-13.6	Fe(wk)OHZn	-1.99
FeOH ₄ ⁻	-21.6	Fe(wk)OH ₂	7.29
Fe ₃ (OH) ₄	-6.3	Fe(wk)OH	-8.93
Zn(OH ₃) ⁻	-28.4		
Zn(OH ₄) ⁺⁵	-41.2		
ZnOH ⁺	-8.96		
Zn(OH) ₂ Aq	-16.9		

The model output can be examined using the model post-processor. Since there are no flows or kinetic reactions, the total concentrations and computed species concentrations do not change with time. The free concentrations computed are shown below with comparison to concentrations predicted by MINTEQA2:

No.	Name	Species ID	META4 Pred. (Molar)	MINTEQA2 Pred. (Molar)	% Difference
1	Fe+2	280	1.78E-04	1.79E-04	-0.01
2	H+1	330	1.11E-07	1.11E-07	-0.01
3	ADS1TYP1	811	7.60E-08	7.60E-08	0.01
4	ADS1TYP2	812	2.72E-05	2.72E-05	-0.01
5	Zn+2	950	1.91E-06	1.91E-06	0.01
6	FeOH+	2803300	5.25E-07	5.25E-07	0.01
7	Fe(OH)3-	2803301	1.34E-12	1.34E-12	0.01
8	Fe(OH)2 (a	2803302	3.78E-11	3.78E-11	0.01
9	OH-	3300020	1.12E-07	1.12E-07	-0.04
10	=FeO-	8113301	1.05E-08	1.05E-08	-0.03
11	=FeOH2+	8113302	1.26E-08	1.26E-08	0.05
12	=FeOZn+	8119500	7.96E-07	7.96E-07	0.02
13	=FeO-	8123301	3.77E-06	3.77E-06	-0.01
14	=FeOH2+	8123302	4.50E-06	4.50E-06	0.01
15	=FeOZn+	8129500	2.99E-07	2.99E-07	0.01
16	ZnOH+	9503300	1.41E-08	1.41E-08	0.01
17	Zn(OH)2 (a	9503301	2.03E-10	2.03E-10	0.00
18	Zn(OH)3-	9503302	1.14E-13	1.14E-13	-0.04
19	Zn(OH)4-2	9503303	6.21E-19	6.21E-19	0.00

9.4 Test Case 4. Solution of Zinc

9.4.1 System

This example compares predictions of META4 and MINTEQ for a solution of Ca, Zn, and SO₄ at a pH of 7.5. As with the previous examples, this is a “beaker” simulation. That is WASP simulates a single completely mixed stirred reactor (CMSTR, or one “box”) with no inflows or outflows. The system is defined as:

- Ca total concentration of 20 mg/L
- SO₄ total concentration of 60 mg/L
- Zn total concentration of 6 mg/L.
- pH = 7.5 (specified as a model parameter)
- no corrections of activities for ionic strength or temperature

9.4.2 Method

1. The model set up for this example is identical to that for the previous examples in terms of segmentation, flows etc.
2. Temperature was selected as a model parameter
3. Constants were specified for the speciation option, maximum number of iterations and convergence criteria as with the previous examples. In this example since the initial concentrations were in mg/L, the concentration option was set to zero so that the concentrations would be converted to internal molar concentrations.
4. Initial activities were specified based on those from the MINTEQA2 output file, as
 - $\text{Ca}^{+2} =$ 5.012E-04 molar
 - $\text{SO}_4^{-2} =$ 6.310E-04 molar
 - $\text{Zn}^{+2} =$ 9.120E-05 molar

Output

The model output can be examined using the model post-processor. Results are presented and compared to MINTEQ predictions in the table below:

Species	ID	Molar Conc.	
		META4	MINTEQ
Ca+2	150	4.42E-04	4.45E-04
H+1	330	3.16E-08	3.16E-08
SO4-2	732	5.58E-04	5.61E-04
Zn+2	950	7.94E-05	8.04E-05
CaOH+	1503300	2.81E-09	1.82E-09
CaSO4 (aq)	1507320	5.66E-05	5.44E-05
OH-	3300020	3.18E-07	2.17E-07
HSO4-	3307320	1.73E-09	1.50E-09
ZnOH+	9503300	2.53E-06	1.74E-06
Zn(OH)2 (a	9503301	1.28E-07	1.29E-07
Zn(OH)3-	9503302	2.04E-10	2.06E-10
Zn(OH)4-2	9503303	2.58E-15	2.61E-15
ZnSO4 (aq)	9507320	9.70E-06	9.45E-06
Zn(SO4)2-2	9507321	4.71E-08	4.82E-08

Note that the predictions are not identical between the two models

9.5 Test Case 5. Gaussian DOM Model Test (Comparison with MINTEQA2)

This example tests the Gaussian DOM model, comparing results from META4 to those from MINTEQA2 Version 4.0. META4 (based on MINTEQA2 Version 4.03) incorporates a competitive Gaussian model for computing the complexation of metals by dissolved organic matter (DOM). Understanding the chemical reactions between DOM and trace metals is important because of the potential impact on trace metal mobility and toxicity.

Notes to Users:

- *For the Gaussian DOM model, in addition to the species extracted from the thermodynamic database (thermo.dbs), additional DOM reactions are extracted from the Gaussian database (Gaussian.dbs), based on the selected components.*

9.5.1 System

Similar to the four previous test cases, the “System” for this test is a single completely mixed stirred reactor with no inflows or outflows. Essentially, this is again a steady-state “beaker” test for comparison with MINTEQA2.

9.5.2 Model State Variables and initial conditions

For this test, the following components were included in the simulation as state variables (selected as Simulated from the Systems input screen). Then under the initial conditions input table (under segments), the concentrations (mg/L) were specified.

Model State Variables for DOM Test

Species ID	Name	Initial Concentration (mg/L)	Molecular Weight*
140	CO3-2 -	10.3725	60.009
145	DOM -	2.267	0.000
150	Ca+2	30.4068	40.080
231	Cu+2	0.0639	63.546
460	Mg+2	9.33	24.312
732	SO4-2 -	98.0118	96.062
330	H+1	8.58E-05	1.008
950	Zn+1	0.40223	65.370

* read from component database

Notes to Users:

- *The concentration units for input may be either mg/L or molar, **with the default being molar**. In this case, under model options, the option was selected so that the units of input were mg/L, which is then converted to internal molar units based on the molecular weight from the component database*
- *Note that the molecular weight of DOM from the database is zero. DOM is assumed to be (if in concentration units) in units of mg C/L. The DOM concentration is converted to molar units in META4 by multiplying by the total acidity and dividing by 10^6 .*

9.5.3 Model Parameters and initial guesses of activities

For this simulation, four parameters were selected and specified:

- DOM (= 2.267E-6 molar)
- pH (=7)
- Temperature (= 15 or 20)
- Ionic Strength (either 0 or 0.05)

Note to Users:

- *In this example, both H and DOM were specified as both state variables and parameters (pH for H). In that case, META4 will assume the parameter is the intended form and rename H and DOM to H_NR and DOM_NR and assign them new ID numbers. These state variables will then be included in simulations (they can be transported and can react) BUT NOT in speciation reactions. Initial guesses for activities were taken from output from MINTEQA2 (molar units). While this was not necessary, it is often convenient, since META4 does not contain the detailed algorithms in MINTEQA2 for computing initial activity guesses.*

9.5.4 Model constants

Constants for this test were similar to the previous test cases with the exception that the option for units of input was set to allow inputs in mg/L and the DOM option was selected.

Description	Value
Ionic strength Option (Ionic_Opt)) >1 = yes, reactions will be corrected for ionic strength (Davies equation)	1
Temperature Option >1 = yes, reactions will be temperature corrected	1
ISPEC Speciation Option: ISPEC = 0 No Speciation; ISPEC = 1 Non-competitive Speciation; ISPEC = 2 Competitive Speciation	2
EPS1 Convergence Criteria for Matrix Solver (required only if ISPEC = 2)	1.00E-16
EPS2 Convergence Criteria for Solution of Non-Linear Speciation Equations (Required only if ISPEC = 2)	1.00E-16
NMAX Maximum number of iterations allowed in solution of speciation equations (Required only if ISPEC = 2)	100
IDOM Invokes Gaussian DOM model when >=1	1
ICONC If ICONC=1 then inputs are assumed molar,else assumed inputs are in mg/L and converted to molar using formula weights (molar conc =input/(1000*GFW)	0

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9.5.5 Model results for the case where ionic Strength = 0 and Temperature =20 °C

Species	Species ID	Concentrations (molar)		% Difference
		META4	MINTEQA2	
CO3-2	140	5.81E-08	5.81E-08	0.01
DOM	145	1.24E-06	1.24E-06	0.02
Ca+2	150	6.38E-04	6.39E-04	0.03
Cu+2	231	5.21E-07	5.21E-07	0.01
H+1	330	1.00E-07	1.00E-07	0.00
Mg+2	460	3.34E-04	3.34E-04	0.05
SO4-2	732	8.51E-04	8.51E-04	0.00
Zn+2	950	5.13E-06	5.13E-06	0.03
Ca DOM	1451500	8.77E-07	8.77E-07	0.01
Cu DOM	1452310	7.16E-08	7.16E-08	0.00
H DOM	1453300	1.28E-09	1.28E-09	0.01
Mg DOM	1454600	4.58E-08	4.58E-08	0.02
Zn DOM	1459500	2.81E-08	2.80E-08	0.05
CaHCO3+	1501400	7.85E-07	7.85E-07	0.02
CaCO3 (aq)	1501401	4.75E-08	4.75E-08	0.03
CaOH+	1503300	8.25E-10	8.25E-10	0.02
CaSO4 (aq)	1507320	1.19E-04	1.19E-04	0.05
CuCO3 (aq)	2311400	1.78E-07	1.78E-07	0.01
Cu(CO3)2-2	2311401	2.79E-11	2.79E-11	0.01
CuHCO3+	2311402	4.08E-09	4.08E-09	0.00
CuOH+	2313300	1.30E-07	1.30E-07	0.02
Cu(OH)2 (a	2313301	3.33E-09	3.34E-09	0.01
Cu(OH)3-	2313302	6.89E-13	6.89E-13	0.01
Cu(OH)4-2	2313303	5.46E-19	5.46E-19	0.00
Cu2(OH)2+2	2313304	7.18E-10	7.18E-10	0.03
CuSO4 (aq)	2317320	9.57E-08	9.58E-08	0.03
OH-	3300020	6.86E-08	6.86E-08	0.01
HCO3-	3301400	1.38E-04	1.38E-04	0.02
H2CO3 (aq)	3301401	3.28E-05	3.28E-05	0.01
HSO4-	3307320	7.20E-09	7.20E-09	0.00
MgCO3 (aq)	4601400	1.71E-08	1.71E-08	0.06

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MgHCO ₃ ⁺	4601401	5.21E-07	5.21E-07	0.03
MgOH ⁺	4603300	3.52E-09	3.52E-09	0.04
MgSO ₄ (aq)	4607320	4.96E-05	4.97E-05	0.05
ZnHCO ₃ ⁺	9501400	2.01E-08	2.01E-08	0.04
ZnCO ₃ (aq)	9501401	1.72E-08	1.72E-08	0.02
ZnOH ⁺	9503300	3.52E-08	3.52E-08	0.03
Zn(OH) ₂ (a	9503301	8.24E-10	8.24E-10	0.03
Zn(OH) ₃ ⁻	9503302	4.16E-13	4.16E-13	0.04
Zn(OH) ₄ ²⁻	9503303	1.67E-18	1.67E-18	0.03
ZnSO ₄ (aq)	9507320	9.15E-07	9.15E-07	0.01
Zn(SO ₄) ₂ ²⁻	9507321	7.08E-09	7.08E-09	0.01

9.5.6 Model results for the case where ionic Strength = 0.05 molar and Temperature =15 °C

Species	Species ID	Concentrations (molar)		% Difference
		META4	MINTEQA2	
CO3-2	140	9.52E-08	9.52E-08	0.01
DOM	145	1.64E-06	1.64E-06	0.01
Ca+2	150	7.27E-04	7.27E-04	0.03
Cu+2	231	7.47E-07	7.47E-07	0.02
H+1	330	1.21E-07	1.21E-07	0.02
Mg+2	460	3.71E-04	3.71E-04	0.04
SO4-2	732	9.77E-04	9.77E-04	0.01
Zn+2	950	5.86E-06	5.86E-06	0.02
Ca DOM	1451500	5.27E-07	5.27E-07	0.01
Cu DOM	1452310	5.41E-08	5.41E-08	0.01
H DOM	1453300	2.44E-09	2.44E-09	0.03
Mg DOM	1454600	2.69E-08	2.69E-08	0.00
Zn DOM	1459500	1.69E-08	1.69E-08	0.07
CaHCO3+	1501400	3.65E-07	3.65E-07	0.01
CaCO3 (aq)	1501401	1.70E-08	1.70E-08	0.01
CaOH+	1503300	3.32E-10	3.33E-10	0.01
CaSO4 (aq)	1507320	3.08E-05	3.08E-05	0.05
CuCO3 (aq)	2311400	8.76E-08	8.76E-08	0.01
Cu(CO3)2-2	2311401	2.27E-11	2.27E-11	0.02
CuHCO3+	2311402	2.46E-09	2.46E-09	0.02
CuOH+	2313300	8.05E-08	8.05E-08	0.02
Cu(OH)2 (a	2313301	2.17E-09	2.17E-09	0.00
Cu(OH)3-	2313302	5.51E-13	5.51E-13	0.01
Cu(OH)4-2	2313303	7.82E-19	7.82E-19	0.00
Cu2(OH)2+2	2313304	4.02E-10	4.02E-10	0.02
CuSO4 (aq)	2317320	3.09E-08	3.10E-08	0.02
OH-	3300020	5.60E-08	5.60E-08	0.01
HCO3-	3301400	1.43E-04	1.43E-04	0.01
H2CO3 (aq)	3301401	2.90E-05	2.90E-05	0.00
HSO4-	3307320	4.03E-09	4.03E-09	0.02

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MgCO ₃ (aq)	4601400	6.04E-09	6.05E-09	0.03
MgHCO ₃ ⁺	4601401	2.68E-07	2.68E-07	0.01
MgOH ⁺	4603300	1.38E-09	1.38E-09	0.01
MgSO ₄ (aq)	4607320	1.27E-05	1.27E-05	0.04
ZnHCO ₃ ⁺	9501400	9.67E-09	9.67E-09	0.04
ZnCO ₃ (aq)	9501401	6.72E-09	6.72E-09	0.04
ZnOH ⁺	9503300	1.51E-08	1.51E-08	0.01
Zn(OH) ₂ (a	9503301	4.28E-10	4.28E-10	0.03
Zn(OH) ₃ ⁻	9503302	2.66E-13	2.65E-13	0.05
Zn(OH) ₄ ²⁻	9503303	1.91E-18	1.91E-18	0.03
ZnSO ₄ (aq)	9507320	2.40E-07	2.40E-07	0.02
Zn(SO ₄) ₂ ²⁻	9507321	2.25E-09	2.25E-09	0.03

9.6 Test Case 6. Modeling Mercury (Comparison with TOXI)

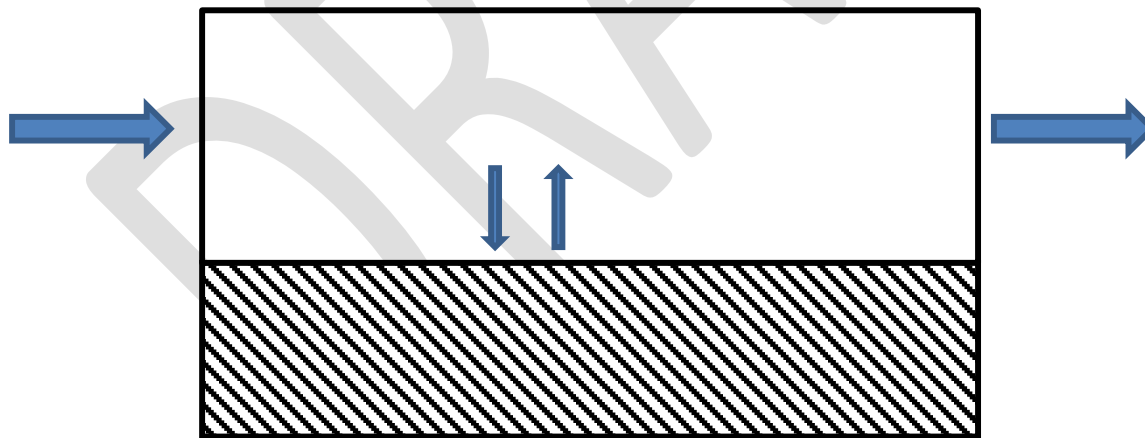
This example tests three model capabilities not included in previous test: simple sorption, degradation and volatilization. The state variables for the simulation are based on combinations of Hg II, Hg(O) and methyl-mercury combined with one or more of the solids types 1-3.

9.6.1 System

There are two systems types of this test case:

System A: Similar to the four previous test cases, the “System” for this test is a single completely mixed stirred reactor. In addition to the water column segment, there is a single sediment layer. For System A, there are no inflows or outflows or exchanges between the water column and sediment layer.

System B: This system is based on System A and in addition includes inflows and outflows to the water column layer as well as settling to and resuspension from the sediment layer, as illustrated below. In System B, a constant and equal flow of $1 \text{ m}^3/\text{s}$ is added to the water column, and resuspension and settling added between the water column and sediments. The rates of resuspension (10^{-5} m/day) and settling (1 m/day) were set so that the net sediment flux is equal to zero.



	Water Column	Sediments
Volume (m^3)	1×10^6	1×10^4

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Depth (m)	10	0.1
Surface Area (m ²)	1 X 10 ⁵	1 X 10 ⁵

9.6.2 Model State Variables, Parameters and Constants

Case 6-1A (Sorption Only).

Systems: For this test, the following components were included in the simulation as state variables (selected as Simulated from the Systems input screen). Then under the initial conditions input table (under segments), the concentrations (mg/L) were specified.

Model State Variables for Case 6-1A

Species ID	Name	Molecular Weight*	Initial Concentration Water Column (mg/L)	Initial Concentration Sediments (mg/L)
360	Hg ₂₊₂	401.18	1.0	1.0
831	Solid 1	-	10.0	1.0E+6
951	Hg(0)	200.59		
952	Methyl-Mercury	230.66	1	1

* read from component database

Parameters: There were no parameters specified for this test case.

Constants: Three constants were specified, first indicating that speciation would be computed, then selecting the Modified Exchange option for partitioning, and finally indicating that the units are specified in mg/L, so will be converted to molar units.

ISPEC Speciation Option: ISPEC = 0 No Speciation; ISPEC = 1 Non-competitive Speciation; ISPEC = 2 Competitive Speciation	2
IADS_Solid1 Sorption option (0 for none, IADS=1 for modified exchange option, and for Solids Type 1 only, IADS=2 invokes two-layer model DLM for HFO)	1
EPS1 Convergence Criteria for Matrix Solver (required only if ISPEC = 2)	1.00E-12
EPS2 Convergence Criteria for Solution of Non-Linear Speciation Equations (Required only if ISPEC = 2)	1.00E-12

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NMAX Maximum number of iterations allowed in solution of speciation equations (Required only if ISPEC = 2)	100
--	-----

Note: For this application, the convergence criteria were relaxed over that from previous examples.

Notes to Users:

- Unless a molecular weight for solids is specified in the model constants, the internal concentration units remain as mg/L, while internal units for all other systems (state variables) are molar.
- If ME sorption is selected, the sorption constants are read from the ME sorption database (see Appendix #).
- Sorption is treated as any other speciation reaction, so is only computed if the speciation option is selected.

Based on the options and state variables selected above, the only reactions for this example are sorption. The sorption coefficients are read from the Modified Exchange sorption database (MESORB) and were $pK_p = 5.6$ and 4.9 L/kg for Hg(II) and Methyl Mercury, respectively.

Results:

The expected results and those predicted by the WASP model for a non-ionizing toxicant for the total and dissolved concentrations are tabulated below for comparisons with META4 predictions. The sorbed fraction can be computed for comparison by difference. Note that for Hg(0), no sorption occurs, so that the total and dissolved concentrations are equal.

Table 9. WASP steady-state predictions for sorbed chemicals

	Hg(II)		Methyl Hg	
	(mg/L)	(molar)	(mg/L)	(molar)
Total	1.0	2.4926E-06	1.0	4.3354E-06
Dissolved, Water	0.333861	8.3220E-07	0.557313	2.4162E-06
Dissolved, Sediment	5.012E-06	1.2493E-11	1.259E-05	5.4579E-11

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Predicted META4 concentrations are tabulated below in terms of the components form for each state variable (system; see Table 3) for comparison to the predictions from TOXI tabulated above.

Form	Concentration (molar)	
	Water Column	Sediments
Hg2+2 Totl	2.49E-06	2.49E-06
Hg2+2 Free	8.32E-07	1.25E-11
Hg2+2Tot.Dis	8.32E-07	1.25E-11
Hg2+2 Sorb1	1.66E-06	2.49E-06
Hg2+2 Sorb2	1.00E-21	1.00E-21
Hg2+2 Sorb3	1.00E-21	1.00E-21
Hg2+2Tot Sor	1.66E-06	2.49E-06
Hg2+2Precip.	0.00E+00	0.00E+00
Hg(0) Totl	4.99E-06	4.99E-06
Hg(0) Free	4.99E-06	4.99E-06
Hg(0)Tot.Diss	4.99E-06	4.99E-06
Hg(0) Sorb1	0.00E+00	0.00E+00
Hg(0) Sorb2	1.00E-21	1.00E-21
Hg(0) Sorb3	1.00E-21	1.00E-21
Hg(0)Tot Sorb	2.00E-21	2.00E-21
Hg(0)Precip.	0.00E+00	0.00E+00
MeHg Totl	4.34E-06	4.34E-06
MeHg Free	2.42E-06	5.46E-11
MeHgTot.Diss	2.42E-06	5.46E-11
MeHg Sorb1	1.92E-06	4.34E-06
MeHg Sorb2	1.00E-21	1.00E-21
MeHg Sorb3	1.00E-21	1.00E-21
MeHgTot Sorb	1.92E-06	4.34E-06
MeHgPrecip.	0.00E+00	0.00E+00
Hg2+2	8.32E-07	1.25E-11
Solid 1	1.00E+01	1.00E+06
Hg(0)	4.99E-06	4.99E-06

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MeHg	2.42E-06	5.46E-11
Hg2+2S1	1.66E-06	2.49E-06
MeHgS1	1.92E-06	4.34E-06

Case 6-2A (Volatilization and Sorption).

For this test case, in addition to sorption, volatilization of Hg(0) was included, based on a Henry's constant of 7.1×10^{-3} , a waterbody type representing a stream or river, and stream velocity of 0.01 m/s. The META4 predicted concentrations of Hg(0) in comparison to those from the WASP organic chemical model are compared below.

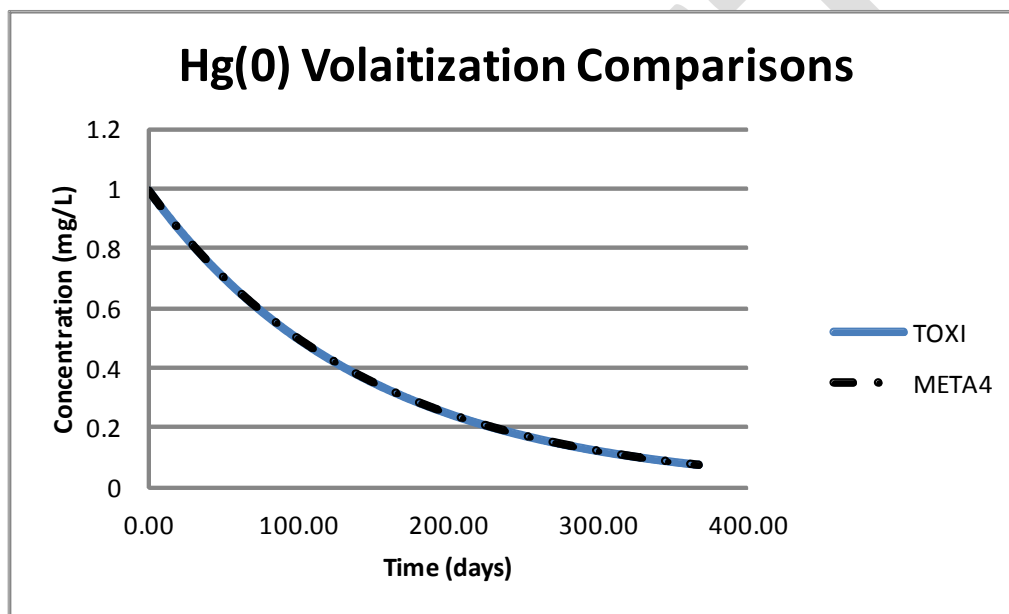


Figure 15. Comparison tests for volatilization of Hg(0)

10. Description of Model Databases

10.1 Thermodynamic database (Thermo.dbs)

The thermodynamic database contains the dissolved chemical species that may potentially be included in simulations. The species are selected based on the components (state variables) for the specific simulation.

The database is a formatted ASCII text file. Each species is represented by three lines of text,

The first line of input includes:

- Species ID

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- Species Name
- Enthalpy of reaction (kJ/mol)
- Log K for formation of the product from the components
- Maximum reported log K (not used in calculations; may not be present)
- Minimum reported log K (not used in calculations; may not be present)
- Charge of species reaction product
- "a" parameter for "WATEQ" Debye-Huckel equations (not used in META4), and
- "b" parameter for "WATEQ" Debye-Huckel equations

Line two (and potentially line 3 if there are more than 5 components in the species) of the input includes:

- Carbonate alkalinity factor (Zero for species not containing carbonate, note used by META4)
- Number of Components
 - Stoichiometric coefficient for the component
 - Component ID number

Line three of the input includes a constant not used in complexation reactions and some alphanumeric documentation of data sources where appropriate.

As an example

```
3307301 S-2          49.4000 -17.3000  0.000  0.000-2.00 5.00 0.00
0.00 2   1.000 730   -1.000 330
32.0651 LMa1987      NIST2.1.1      0.00 25.0
3307601 Se-2         48.1160 -15.0000  0.000  0.000-2.00 0.00 0.00
0.00 2   1.000 760   -1.000 330
78.9521 SCD3.02 (1968 DKa) MTQ3.11      0.00 25.0
```

10.2 Modified Exchange model database (MESorb.dbs)

This database is for the modified exchange sorption model. The database is presently an ASCII formatted and user modifiable file that includes the fields indicated below. The linear pKp values for the partition coefficients (L/Kg) were taken from Table 5 of Allison and Allison (Partition Coefficients for Metals in Surface Water, Soil, and Waste, 2005)

1. Species ID
2. Species Name
3. Site Density
4. Log Kp (L/Kg).

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5. Number of components in species (below are repeated n times)
 - a. Stoichiometry
 - b. Component ID (see component.dbs)

As an example

8300016Hg2+2S1	1.00	5.30	2	1	360	1	831
8300017Hg2+2S2	1.00	5.30	2	1	360	1	832
8300018Hg2+2S3	1.00	5.30	2	1	360	1	833

10.3 FEO_DLM.dbs

The database for the Hydrous Ferric Oxide Double Layer (HFO DLM) Sorption Model is similar in structure to the Thermodynamic database (See Section 10.1), with the exception that each species is represented by 4 lines of input rather than two. As with the thermodynamic input, only constants on the first two lines are used by META4.

As an example

8113302 FeOH2+	0.0000	7.2900	0.000	0.000	1.00	0.00	0.00	0.0000
0.00 3	1.000	811	1.000	330	1.000	813	0.000	0 0.000 0 0.000 0
0.000	0	0.000	0	0.000	0	0.000	0	0.000 0 0.000 0
0 0.000	0	0.000	0	0.000	0			
8113301 FeO-	0.0000	-8.9300	0.000	0.000	-1.00	0.00	0.00	0.0000
0.00 3	1.000	811	-1.000	330	-1.000	813	0.000	0 0.000 0 0.000 0
0.000	0	0.000	0	0.000	0	0.000	0	0.000 0 0.000 0
0 0.000	0	0.000	0	0.000	0			

10.4 Gaussian.dbs

The database for the Gaussian DOM model is similar in structure to the Thermodynamic database (See Section 10.1), but

The first line of input includes the:

- Species ID
- Species Name
- Standard deviation of the log K distribution
- Mean Log K
- Maximum reported log K (not used in calculations; may not be present)

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- Minimum reported log K (not used in calculations; may not be present)
- Charge of the metal (or proton)
- "a" parameter for "WATEQ" Debye-Huckel equations (not used by MWETA4), and
- "b" parameter for "WATEQ" Debye-Huckel equations (not used by META4)

The second line of input contains:

- Carbonate alkalinity factor (Zero for species not containing carbonate, not used by META4))
- Number of Components, and then for each component the
 - mass action stoichiometry
 - Mass balance stoichiometry
 - Component ID number

The third line of input includes the

- Binding site density
- Descriptive alphanumeric information

As an example

```
1443300 H DOM          1.7000  3.8700  0.000  0.000 1.00 0.00 0.00
2 1.000 1.000 144 1.000 1.000 330
0001.0000 Su1991
1440300 Al DOM          0.0000  5.2000  0.000  0.000 3.00 0.00 0.00
2 1.000 1.000 144 1.000 1.000 030
0000.0000 Su1991
```

10.5 Type6.dbs

The Type6 database is a formatted ASCII text file containing information on potential precipitates or solids species. The file is similar in structure to the Thermodynamic database (see Section 10.1), but rather than a Log K for formation of the product from the components, this database includes the Log K_{SP} for formation of the solubility product from the components.

As an example

```
73100 Sulfur          16.3000  2.1449  0.000  0.000 0.00 0.00 0.00
0.00 3  1.000 730 -1.000 330 -2.000 1
32.0651 CODATA89          CODATA89
```

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76000 Se metal (hex,blk) -15.9000 7.7084 0.000 0.000 0.00 0.00 0.00
0.00 3 1.000 760 -1.000 330 -2.000 1
78.9521 NIST2.1.1 NIST2.1.1

10.6 Analytic Database (ANALYT.dbs)

This database contains the coefficients for the analytical polynomial expression used to compute the stability constant as a function of temperature. There are presently 23 species in the database. The structure of the database is one line per species consisting of a species id number followed by the constants A_t - G_t (see Equation 8),

As an example

5015001 -13.543 0.0401 3000.0
4215000 -109.25 -0.0024 3120.98 37.624 4.900E-007 2088.47 298.4
5015000 10.21 -0.0217 0.0 0.0 5.170E-005