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Project Summary

Modeling the Transport, Speciation, and Fate of Heavy Metals in Aquatic Systems

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Concern about environmental exposure to pollutants has increased the need for techniques to predict the behavior of heavy metals entering natural waters as a result of the mining of raw materials and the manufacture, use, and disposal of commercial products. The modeling technique developed in this research study permits the user to examine the equilibrium speciation of heavy metals along with transport and fate in various aquatic systems. Because different species of a metal cause different biological effects, this modeling technique should help users better relate metals discharge and aquatic chemistry data to observed or expected effects.

MEXAMS, the Metals Exposure Analysis Modeling System, allows the user to consider the complex chemistry affecting the behavior of metals in conjunction with the transport processes that affect their migration and fate. This is accomplished by linking MINTEQ, a geochemical model, with EXAMS, an aquatic exposure assessment model.

MINTEQ is a thermodynamic equilibrium model that computes aqueous speciation, adsorption and precipitation/dissolution of solid phases. It has a well-documented thermodynamic data base that contains equilibrium constants and other accessary data for seven priority pollutant metals: arsenic (As), cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), silver (Ag) and zinc (Zn). Six different adsorption algorithms are included: 1) an "activity" partition coefficient, Kd; 2) an "activity" Langmuir equation; 3) an "activity" Freundlich equation; 4) an ion exchange algorithm; 5) a constant capacitance surface complexation model; and 6) the triple layer surface complexation model. In addition, a large number of user-oriented features such as the ability to handle alkalinity inputs, an initial mass of solid, and different analytical input units were incorporated.

EXAMS is designed for the rapid evaluation of synthetic organic pollutants. Given the characteristics of a pollutant and an aquatic system, EXAMS computes steady-state distribution of pollutant concentrations, the fate of the pollutant in the system, and the time required for effective purification of the system (persistence).

To facilitate the use of MEXAMS, a user interactive program was developed. This program queries the user to obtain water quality data for MINTEQ, then controls the operation of MINTEQ and EXAMS, passing simulation results back-and-forth between the models.

As it is currently structured, MEXAMS can be used in a number of ways. It can be used like EXAMS to perform rapid hazard evaluations for priority pollutant metals. MEXAMS also can be used to evaluate the water quality impact of point source discharges and mine drainage as well as to support the interpretation of metals bioassay data. Finally, and perhaps most importantly, MEXAMS can be used as a framework for defining what is and what is not known about the behavior of priority pollutant metals in aquatic systems.

This framework will make it possible to identify the need for and guide the performance of future research.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in two separate reports (see Project Report ordering information at back).

Introduction

One class of pollutants that has received considerable environmental attention is the priority pollutant metals. A reason for this attention is the fact that the current water quality criteria are based on "total recoverable" rather than "dissolved" concentrations. Historically, only total concentrations were reported in the published results of aquatic bioassays for metals, even though it was generally known and accepted that the dissolved fraction is the most bioavailable and toxic, and that certain dissolved species are much more toxic than others. Virtually all modeling studies directed at examining the migration and fate of metals have neglected many of the more important chemical interactions controlling their behavior in aquatic systems. The Metals Exposure Analysis Modeling System (MEXAMS) represents an improvement in metals modeling in that the complex chemistry affecting the behavior of a metal and the transport processes affecting its migration and fate are handled by two separate, but linked, models. The chemical interactions are handled by MINTEQ, a geochemical model that uses fundamental thermodynamic equilibrium relationships and data to calculate dissolved, adsorbed, and precipitated metal concentrations. The migration and fate of a metal is handled by the Exposure Analysis Modeling System (EXAMS), a steady-state transport model developed primarily as a screening-level tool by the Environmental Research Laboratory, USEPA, Athens, Georgia.

User instructions for operating the complete metals exposure model are provided in *MEXAMS—The Metals Exposure Analysis Modeling System.* The mathematical and chemical concepts of the MINTEQ component are described in *MINTEQ—A Computer Program for Calculating Aqueous Geochemical Equilibria.* Although it is not necessary to master these concepts in order to use MEXAMS, it is important that the user be familiar with the basic theory behind MINTEQ. A basic understanding of the MINTEQ program will allow experienced users to solve a broad range of chemical equilibrium problems. *Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation,* EPA-600/3-82-023, was published in 1982.

Conclusions

Using MEXAMS, much of the complex chemistry affecting the behavior of heavy metals in aquatic systems can be explicitly considered, including chemical speciation and its effect on the adsorption and precipitation of metals. MEXAMS, therefore, should provide more accurate predictions of the metal concentrations likely to be found in different aquatic systems. It should also overcome some of the limitations inherent in earlier attempts to model the behavior of metals.

MEXAMS is applicable to a range of problems associated with the impacts of priority pollutant metals on aquatic systems. It can be used to perform both screening-level and site-specific analyses of metals problems such as industrial discharges and mine drainage. It also can be used as a framework for guiding the collection and interpretation of aquatic bioassay data.

There are several limitations that the user must be aware of before applying MEXAMS. First, the thermodynamic data base associated with MINTEQ only contains equilibrium constants and accessary data for seven priority pollutant metals: As, Cd, Cu, Pb, Ni, Ag and Zn. Some data on the other metals exist in the literature. Before they can be included in the data base, however, the data should be carefully evaluated.

The second limitation relates to organic complexation. In many natural waters this phenomenon can have a major impact on the speciation of metals. While MINTEQ is computationally capable of considering organic complexation, the thermodynamic data base does not contain the necessary equilibrium constants and accessary data. Again, the literature does contain some thermodynamic data on organic complexation of selected metals. These data need to be reviewed and evaluated before they are included.

Another limitation of MINTEQ and most other geochemical models is that it treats precipitation/dissolution, oxidation/reduction and adsorption as equilibrium processes when in fact they may not be in equilibrium. In the area of precipitation/dissolution, literature data on the rates of formation and dissolution of selected solids need to be included in the data base and supplemented with experimental work and a kinetic algorithm. The kinetics of oxidation/reduction reactions are not well understood. Because these reactions are frequently biologically mediated and rarely in equilibrium, the equilibrium approach can only provide boundary conditions towards which a system is proceeding. In addition, the importance of the kinetics of adsorption is unclear for metals. Most constituents tend to adsorb quite rapidly (i.e., within hours), but desorb less rapidly. The limited data available on the kinetics of adsorption for selected metals need to be included in the data base and supplemented with experimental work.

A final limitation is the degree of testing MEXAMS has received. Although both MINTEQ and EXAMS have been tested on and applied to a number of problems, the linked system of models has received limited testing. For this reason, users should exercise extreme care in the early stages of applying MEXAMS. MEXAMS is being more rigorously tested on a series of hypothetical and site-specific problems.

Description of MEXAMS

MEXAMS consists of three components: 1) a geochemical model, 2) an aquatic exposure assessment model, and 3) a user interactive program. The geochemical model simulates the complex chemical interactions that affect metal behavior in natural waters. The exposure assessment model simulates the transport processes affecting metal migration and fate in aquatic systems. The user interactive program links the two models and aids in the application of the overall system. Figure 1 shows how these three components are linked, and each component is discussed in greater detail below.

MINTEQ, the geochemical model in MEXAMS, is a thermodynamic equilibrium model that computes aqueous speciation, adsorption and precipitation/dissolution of solids. Speciation is calculated using an equilibrium constant approach wherein a series of mass action expressions are solved subject to mass balance constraints on each chemical component.

In MINTEQ, adsorption is treated as analogous to aqueous speciation. As a result, mass action expressions can be formulated for adsorption reactions. MINTEQ contains six algorithms for calculating adsorption. The first is a single valued partitioning coefficient or Kd that has been corrected for the activity of the metal species binding to the surface. The corrected value is called an "activity Kd." The second algorithm is an "activity" Langmuir isotherm. The third algorithm is an "activity" corrected Freundlich isotherm. The fourth algorithm is for simple ion exchange reactions where the activity ratio of the exchanging species is assumed to remain constant. The constant capacitance model and triple layer model are the other two options. They are more theo-

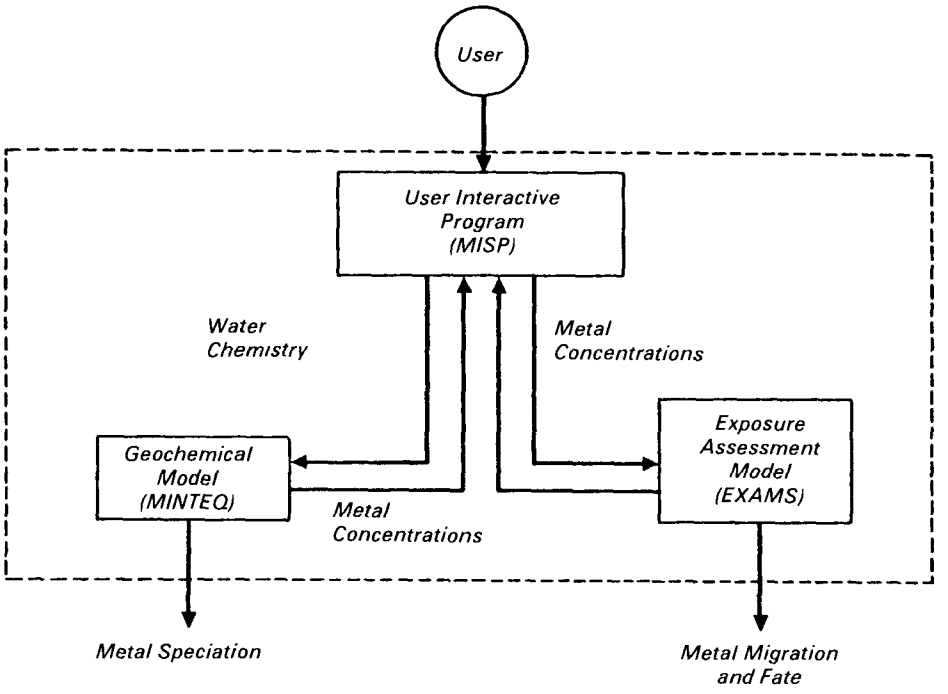

Figure 1. *Structure of MEXAMS.*

retically based approaches that consider the electrostatic potential at the surface of the sorbing media and the effect of pH and ionic strength changes on surface properties.

MINTEQ can compute the mass of metal transferred into or out of solution as a result of the dissolution or precipitation of solid phases. While this calculation is limited by the fact that it is made for equilibrium conditions and precipitation/dissolution reactions may be kinetically controlled, it is possible to obtain reasonable results if the solids considered by MINTEQ as possible equilibrium phases are properly selected. That is, the user must permit MINTEQ to consider only those solids whose formation is not limited by kinetic barriers.

As with any geochemical model, MINTEQ requires both thermodynamic and water quality data. The thermodynamic data are equilibrium constants, enthalpies of reaction, and other basic information required to predict the formation of each species or solid phase. The water quality data are the physical and chemical properties of the water body being analyzed. The user only has to generate the water quality data in order to use MINTEQ. The thermodynamic data are contained in a data base that accompanies the model.

EXAMS is the aquatic exposure assessment model in MEXAMS. It is a steady-state model for screening-level exposure assessments that is applicable to rivers and lakes. The model was developed primarily for use with organic compounds, and it provides estimates of persistence and ambient water quality.

The processes considered by EXAMS can be divided into four categories: 1) ionization and sorption, 2) transformation, 3) transport, and 4) chemical loading. For ionization and sorption, EXAMS can consider up to 15 molecular species of a given pollutant. These include the uncharged parent molecule and its singly- and doubly-charged cations and anions. Each of these can occur in a dissolved, sediment-sorbed or biosorbed form. Equilibrium sorption is calculated using equilibrium distribution coefficients. The second category, transformation processes, includes photolysis, hydrolysis, biolysis and oxidation. Rates of transformation for each process can be assigned to each of the 15 molecular species. The third category, transport processes, includes volatilization and the movement of dissolved, sediment-sorbed, and biosorbed fractions. Since EXAMS does not explicitly compute water and sediment movement, these data must be obtained from field measurements or other models. Volatilization is calculated using the two-resistance or "two-film" model. The final category, chemical loadings, includes external pollutant loadings from point sources, non-point sources, dry fallout or aerial drift, atmospheric washout and groundwater seepage. The user's manual and system documentation report for EXAMS provides extended discussions of how each of the above processes are modeled.

The coupling of EXAMS with MINTEQ required several modifications to the code and the way it is used. Code modifications were designed so that all of the original EXAMS options and capabilities were retained and no additional input data would be required.

MISP, the MEXAMS Interactive Software Program and the third component in MEXAMS, has several important functions. First, it helps the user input data to MINTEQ. (Input data for EXAMS must be prepared separately using the procedure outlined in the EXAMS user's manual.) Second, MISP queries the user to determine simulation and output options. Finally and most importantly, MISP links MINTEQ with EXAMS and controls the operation of each model.

Operation of MEXAMS

MEXAMS can be operated in three modes: 1) the MINTEQ-only mode, 2) the EXAMS-only mode, and 3) the coupled MINTEQ and EXAMS mode. The MINTEQ-only mode allows the user to analyze how changes in water chemistry will affect the behavior of a metal without regard for the effect of transport processes. The EXAMS-only mode functions exactly like the original EXAMS model. The coupled MINTEQ and EXAMS mode allows the user to consider also the effect of transport processes and chemical interactions. MINTEQ offers options that provide flexibility in the way the user defines the chemistry of the system being modeled and make it possible for the user to apply MINTEQ to a large and diverse problem set. Thus, while not all of the options available require the use of MINTEQ to evaluate the behavior of metals, it is important that the user be aware of these options when preparing input data files.

The chemical species in MINTEQ are assigned one of six different species type designations:

- Type I — Components: the chemical species chosen to represent each chemical constituent in the water analysis (e.g., Zn^{2+} is the component for zinc). A complete list of MINTEQ components is given in Table 1.
- Type II — Complexes: all aqueous species that are combinations of two or more components. Examples of complexes are shown in Table 2.
- Type III — Fixed Species: any species with a fixed activity, such as solids of infinite supply or gases at a fixed partial pressure.
- Type IV — Precipitated Solids: solids that have a finite mass and can dissolve completely.

Table 1. *Components in MINTEQ*

Component	I.D. Number	Component	I.D. Number
E	001	NH_4^+	490
H_2O	002	NO_2	491
Ag^+	020	NO_3^-	492
Al^{3+}	030	Na^+	500
H_3AsO_3	060	Ni^{2+}	540
H_3ASO_4	061	PO_4^{3-}	580
H_3BO_3	090	Pb^{2+}	600
Ba^{2+}	100	Rb^+	680
Br^-	130	HS^-	730
CO_3^{2-}	140	S	731
Fulvate	141	SO_4^{2-}	732
Humate	142	H_4SiO_4	770
Ca^{2+}	150	Sr^{2+}	800
Cd^{2+}	160	U^{3+}	890
Cl^-	180	U^{4+}	891
Cs^+	220	UO_2^+	892
Cu^{1+}	230	UO_2^{2+}	893
Cu^{2+}	231		
Fe^{2+}	280		
Fe^{3+}	281		
H^+	330	Zn^{2+}	950
I^-	380	SOH1	990
K^+	410	SOH2	991
Li^+	440	XPSIO	992
Mg^{2+}	460	XPSIB	993
Mn^{2+}	470	XPSID	994
Mn^{3+}	471	SOHB	995

Table 2. *Aqueous Complexes*

Complex	ID
$PbCO_3(AQ)$	6001401
$PbCl^+$	6002800
$CdHCO_3^+$	1601400
$NiSO_4(AQ)$	5407320

- Type V — Dissolved Solids: solid phases that can precipitate if they become oversaturated.
- Type VI — Species Not Considered: species not included in equilibrium computations but checked afterwards.

In summary, MINTEQ is structured to allow the user the flexibility of using as many data as are available. If the system being studied has a relatively constant pH and ionic strength, the metal concentrations are relatively low, and only limited adsorption data for that solid or sediment are available, the "activity" Kd provides an adequate approach to model metal adsorption. If, however, metal concentrations can be relatively high and variable due to changes in metal loading, then one of the "activity" isotherms, either Freundlich or Langmuir, should be used. If the solution pH and ionic strength vary significantly, data for the constant capacitance or triple layer models should be obtained.

Data Requirements

Interpretation of the results predicted by MINTEQ becomes more reliable as the user's knowledge of the system increases. In the case of input data, the more data the user has on the water chemistry of the system, the more accurate will be the predicted results. This does not mean that the user must have data for all of the components listed in Table 2. Many components do not react with other components or are present in such low concentrations that they do not alter the geochemistry of the particular components being studied. Important chemistry data to consider include:

- pH—the most important parameter required by MINTEQ.
- Eh (pE)—an important parameter for elements with oxidation states linked by redox reactions (e.g., Fe, Mn, Cu, As). Seldom measured, Eh must usually be estimated indirectly.
- Temperature—required, but not sensitive.
- Ionic Strength—optional, correctly computed by MINTEQ given dominant cations and anions.
- Major Anions—most important are CO_3^{2-} or alkalinity, and SO_4^{2-}; sometimes important are Cl^- and H_4SiO_4.
- Major Cations—most important are Ca^{2+} and Mg^{2+}; sometimes important are Na^+ and K^+.
- Trace Constituents—hydrogen sulfide, H_2S (for trace metals); orthophosphorus, PO_4^{3-}(for trace metals, Fe, Ca, Mg); iron and manganese (under low pH or Eh conditions); and others.

Applicability

MEXAMS was developed to provide EPA with a predictive tool capable of performing screening-level analyses. The user can examine a broad range of water quality conditions and evaluate how a specific priority pollutant metal will speciate, adsorb, or precipitate. Using a range of generalized environments, the user can also rapidly evaluate fate and persistence of metals, identifying which processes are important in different types of aquatic systems and which types of systems are most likely to be affected by metals.

MEXAMS can also be used on a more site-specific basis to investigate the potential impacts of different metal sources like industrial discharges or mine drainage. Such applications can include the use of MINTEQ alone or in conjunction with EXAMS.

Another application of MEXAMS relates to improving the analysis and interpretation of information derived from bioassays. If the chemistry of the dilution waters is known, MEXAMS, more specifically MINTEQ, can be used to estimate the dissolved concentration of metal present during the bioassay, as well as the species of metal present. The former would provide a means of adjusting the current standards to a dissolved metal basis. This would provide more reasonable standards, because the dissolved fraction is likely to be the most toxic and bioavailable. Estimates of the concentration of aqueous species of metal present during the bioassays would begin to provide a foundation for setting standards based on the toxic species.

A final application involves the use of MEXAMS as a framework for identifying what is and what is not known about the behavior of priority pollutant metals in aquatic systems. One of the overriding objectives in developing MEXAMS was to produce a tool that is not only applicable with existing data sources but also helps guide the collection of data in the future.

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This Project Summary covers two reports, entitled:

"MEXAMS—The Metals Exposure Analysis Modeling System," (Order No. PB 84-157 155; Cost: $17 50)

"MINTEQ—A Computer Program for Calculating Aqueous Geochemical Equilibria," (Order No. PB 84-157 148; Cost: $11.50)

The above reports will be available only from: (cost subject to change)

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