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SIMULATION OF METAL FATE AND TRANSPORT IN THE NAUGATUCK 1/2

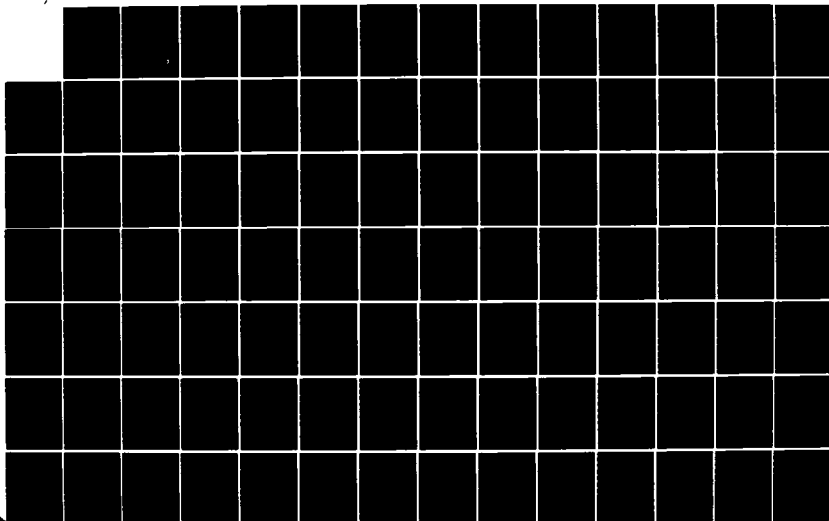
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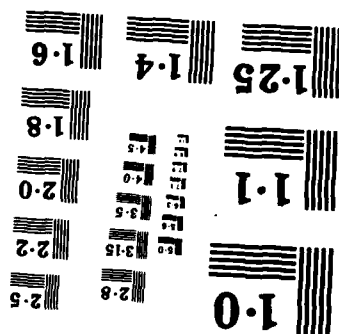
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Streifert, Scott Edward (M.S., Civil Engineering)

Simulation of Metal Fate and Transport in the Naugatuck
River (Connecticut) with MEXAMS

Thesis directed by Dr. Allen J. Medine

Metal transport in the Naugatuck River is currently being investigated to provide important data for waste allocation decisions. The development of suitable metals modeling capability is a necessary part of the management activities. The calibration, testing and evaluation of MEXAMS (Metal Exposure Analysis Modeling System) computer program was performed to meet the above requirement.

Results indicate that the $\log K_d$ and percent groundwater flow into the benthic compartments value were the most sensitive and were used as the major calibration variables. The model very accurately predicted both the particulate concentration of all benthic compartments and the total and aqueous concentration for all water column compartments. Now that the initial calibration has been achieved, the verification procedure will be performed and the initial calibration will be fine tuned.



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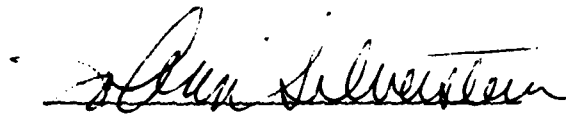
SIMULATION OF METAL FATE AND TRANSPORT
IN THE
NAUGATUCK RIVER (CONNECTICUT) WITH MEXAMS
by
Scott Edward Streifert
B.S.C.E., Norwich University, 1980

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Master of Science
Department of Civil, Environmental,
and Architectural Engineering
1984

This thesis for the Master of Science Degree by
Scott Edward Streifert
has been approved for the
Department of
Civil, Environmental and Architectural Engineering
by



Allen J. Medine



JoAnn Silverstein

Date 11/29/84

DEDICATION

This is dedicated to my parents, Jack and Jane.
Their love, support and encouragement during all of my
endeavors have been invaluable.

ACKNOWLEDGEMENTS

I wish to express my sincere appreciation and thanks to Dr. Allen J. Medine for his continued support throughout my research. His guidance and encouragement were invaluable and helped me over the rough areas. Additional thanks are extended to Arthur H. Hirsch, for his continued positive review of my work. I would also like to thank Dr. Donald D. Runnells and Dr. JoAnn Silverstein for their critiques and recommendations of this report.

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CHAPTER 1

INTRODUCTION

1.1 General

Heavy metals in our aquatic environments, their transport processes, environmental distributions and biological effects have been the focus of increasing concern. Direct toxicity to aquatic organisms and indirect toxicity to higher organisms and man are the center of this concern. Although heavy metals are natural constituents of aquatic environments, additional quantities introduced by man's presence may result in an altered chemical composition of the aqueous and sediment phases, often with detrimental impacts on the environment. In an effort to reduce these impacts, environmental transport/fate models of heavy metals in aquatic ecosystems are being developed.

The purpose of this study was to evaluate the Metal Exposure Assessment Modeling System (MEXAMS). This program is the result of linking MINTEQ, a geochemical model, and the Aquatic Exposure Assessment Model, EXAMS. MEXAMS was developed for the Environmental Protection Agency (EPA) (Felmy et al., 1983) to allow assessment of

the impacts of priority pollutant metals (As, Cd, Cu, Pb, Ni, Ag and Zn). The evaluation consisted of calibrating, testing, and assessing the model response for actual site application on the Naugatuck River located in the Housatonic River Basin in western Connecticut.

1.2 Background Information

The Naugatuck River is located in western Connecticut and has a long history of industrialization along its length. Hydropower generation was responsible for the initial development of the valley, with light metal production soon to follow. Three of the world's largest brass firms were located on its banks and, at the turn of the century, sixty percent of the world's brass products produced annually were manufactured in the valley. As a result of the light metal production industry, the electroplating industry emerged, and approximately 30,300 cubic meters/day of treated electroplating waste is currently being discharged into the Naugatuck River.

Most industrial discharges on the river currently adhere to Best Available Technology (BAT) guidelines. However, both long-term biological monitoring and recent toxicity testing have shown toxic impacts of metals. As a result, the Connecticut Department of Environmental Protection is presently developing allocation guidelines for the discharge of metals into the river. These

guidelines will be based upon results of mathematical modeling being performed by the State Department of Environmental Protection. The data set available was used herein to calibrate MEXAMS to the Naugatuck River and the output will provide a direct comparison of two model formulations for predicting fate and transport of heavy metals in a riverine ecosystem.

CHAPTER 2

MODEL DESCRIPTIONS

2.1 EXAMS General Description

The Exposure Assessment Model System (EXAMS) was developed in response to a need to describe fate, transport and impacts of organic contaminants in aquatic systems. The program is a deterministic, predictive systems model, based on a core of mechanistic process equations derived from fundamental theoretical concepts (Burns et al., 1981).

The model estimates exposure, fate, and persistence following a priority pollutant metal discharge. Exposure is defined as the steady-state pollutant concentration after loadings are balanced with transport and transformation processes. Fate is defined as the distribution of the pollutant in the system, and persistence is the time required for effective purification of the system. The program uses conservation of mass to balance loadings, transport and transformation of the compound.

The chemical loadings can be entered into EXAMS by way of :

- 1., Point Source Loadings

- 2.) Non-Point Source Loadings
- 3.) Aerial Drift
- 4.) Atmospheric Washout
- 5.) Groundwater Seepage

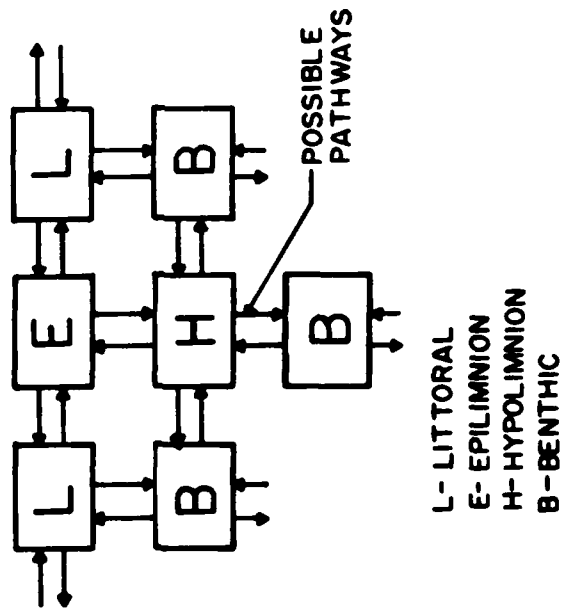
These chemicals can then be transformed by photolysis, hydrolysis, biochemical and oxidation reactions in particular compartments of the environment under simulation. In addition to the above transformation processes, EXAMS is capable of three transport processes: advection (dependent on the hydrologic data input), dispersion (dependent on the description of each dispersive pathway) and volatilization (the air/water interface). Advective and dispersive transport are possible for dissolved species, sediment sorbed material and bio-sorbed materials. Transport through the ecosystem compartments may be represented by whole sediment bed loads, suspended sediment washloads, exchanges with fixed volume sediment beds and ground water infiltration.

EXAMS can also be used to simulate the ionization and sorption of up to fifteen molecular species of an organic chemical. The chemical can be the parent uncharged, singly or doubly charged cations and anions, each of which can occur in the dissolved, sediment-sorbed or bio-sorbed forms. However, EXAMS, like all models, contains important assumptions. These assumptions are listed as follows:

- 1., A first order evaluation can be executed

COMPARTMENTALIZATION EXAMPLES

LENTIC SYSTEM



LOTIC SYSTEM

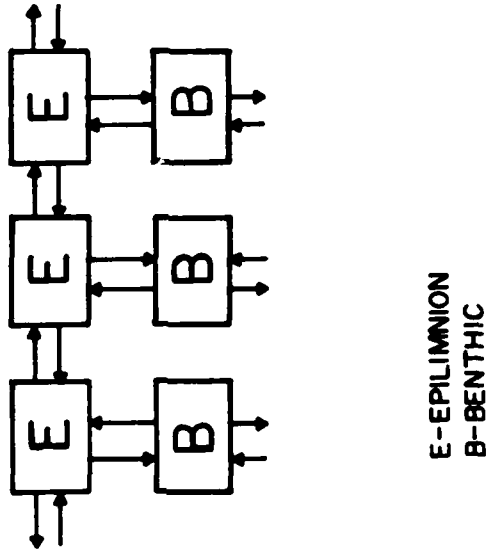


Figure 1.

independently of the chemicals actual effects on the system,

- 2.) Linear sorption isotherms and second order expressions are used, rather than Michaelis-Menten-Monod expressions, for biolysis,
- 3.) EXAMS was developed for long-term or steady-state loadings rather than dynamic transitory (spills) loadings, and
- 4., Sorption is treated as an equilibrium process, that is, sorption/desorption are assumed to be rapid compared to other processes.

EXAMS is capable of simulating both lotic and lentic aquatic systems. These systems are initially compartmentalized and classified as littoral, epilimnion, hypolimnion or benthic (Figure 1 illustrates compartmentalization of a lake system and a river system). Each compartment is assumed to be completely mixed. The computer then develops single differential equations for each compartment. The form of the equation and the variables are defined as:

$$V \left(\frac{dc}{dt} \right) = L_e + L_i - VKC \quad (1)$$

where:

V = volume of water in compartment (l)
 C = total chemical concentration in compartment (mg/l)
 L_e = total external loading (mg hr)
 L_i = total internal loading (mg hr)
 K = overall pseudo-first order loss constant (/hr)
 t = time

EXAMS was not originally designed to describe

metal transport and fate and has been modified so that it can interface with MINTEQ. The first modification involved bypassing calculations that are unnecessary for heavy metal speciation or duplicated by MINTEQ. The second modification included provisions for describing migration and fate of precipitated fractions. Ionization is not utilized in EXAMS, because MINTEQ calculates dissolved species in each compartment. Finally, priority metals are generally unaffected by the transformation and degradation processes that effect the fate of organics in natural waters and these processes are bypassed in the modified EXAMS version.

2.2 MINTEQ General Description

MINTEQ is a computer program for calculating aqueous geochemical equilibria and was developed for incorporation into MEXAMS. The major objective of MINTEQ is the development of a predictive methodology for the assessment of the metal speciation including sorption, precipitation and ion exchange of priority pollutant metals in aquatic environments. This chemical equilibrium problem is described as a set of mass balance equations, one for each component, and a set of mass action equations, one for each specie. The equilibrium constant approach is utilized to solve the equilibrium problem. This method solves nonlinear mass action expressions

using linear mass balance equations. The typical mass action and mass balance equations are as follows:

Mass Action:

$$\gamma_i C_i = K_i \sum_{j=1}^n X_j a(i,j) \quad (2)$$

where:

γ_i = activity coefficient of species i
 C_i = concentration of species i
 K_i = equilibrium constant reaction i
 X_j = activity of component j
 $a(i,j)$ = stoichiometric coefficient of components in species i
 n = number of components

Mass Balance:

$$T_j = \sum_{i=1}^m a(i,j) C_i \quad (3)$$

where:

T_j = total analytical concentration of component j
 m = number of aqueous species

Both of the above equations are definitions for systems with no solid phases. Solid phases are dealt with using the "transformation of basis" method (Felmy et al., 1983). This method reduces the number of independent variables to be determined and allows the solution of a wider range of chemical equilibrium problems.

MINTEQ is also capable of modeling adsorption in

a number of ways. Six different algorithms are accessible through the use of MINTEQ for describing sorption phenomena:

- 1.) "activity" K_d
- 2.) "activity" Langmuir equation
- 3.) "activity" Freundlich equation
- 4.) ion exchange
- 5.) constant capacitance surface complexation model
- 6.) triple layer surface complexation model

The "activity" K_d approach is the ratio of the amount of metal adsorbed to the amount remaining in solution (activity of the free ion). The K_d equation can then be written as follows:

$$K_d = \frac{SCu}{\{Cu\}} \quad (4)$$

where:

K_d = distribution coefficient
 SCu = particulate concentration (molal units)
 $\{Cu\}$ = activity concentration of the free metal (molal units)

The "activity" Langmuir equation has an advantage over the K_d approach, because a mass balance on surface sites is considered. The "activity" Langmuir equation is written as follows:

$$SCu = \frac{K_L S_T \{Cu\}}{1 + K_L \{Cu\}} \quad (5)$$

where:

S_T = maximum quantity that can be adsorbed
 K_L = Langmuir adsorption constant

The third approach, the "activity" Freundlich, is used when laboratory data obtained does not conform to the "activity" Langmuir. The "activity" Freundlich equation is written as follows:

$$S_{Cu} = K_f \{Cu\}^{1/n} \quad (6)$$

where:

K_f = Freundlich adsorption constant
 n = a constant

The above three activity approaches are preferred over their concentration counterparts, due to their ability to deal with a wider range of natural waters. However, the activity approach is not without limitations. The activity approach does not charge balance surface sites and adsorbed species. Secondly, electrostatic interactions between adsorbing ion and charged surfaces are not considered. Finally, the reaction of solid with aqueous constituents other than adsorbate ion is not considered. In order to reduce the above limitations, surface complexation models have been developed which may be more applicable, but also more complex (Felmy et al., 1983).

The constant capacitance model and triple layer models, both based on theoretical approaches, consider charge potential differences and changing properties of the surface with changing pH and ionic strength. Both of these methods require a great deal of detailed laboratory investigation to determine the critical parameters and are primarily research tools.

The ion exchange approach is only useful when the selectivity coefficients for the exchange reactions are known. These coefficients are generally only available for bulk electrolyte ions such as sodium, potassium and calcium. The ion exchange model is inadequate for predicting metal adsorption, because metals usually form covalent bonds with surface sites (Felmy et al., 1983).

Finally, the equilibrium composition of an aquatic environment is determined by minimization of Gibbs free energy of the system within the mass balance constraints. This chemical equilibrium will determine metal speciation in addition to precipitation/dissolution and sorption, and is used in EXAMS to determine the metal fate and migration.

2.3 MEXAMS General Description

The two previous sections described the two individual models that have been linked to form the MEXAMS model (Figure 2). The MEXAMS program can be used

MEXAMS FLOWCHART

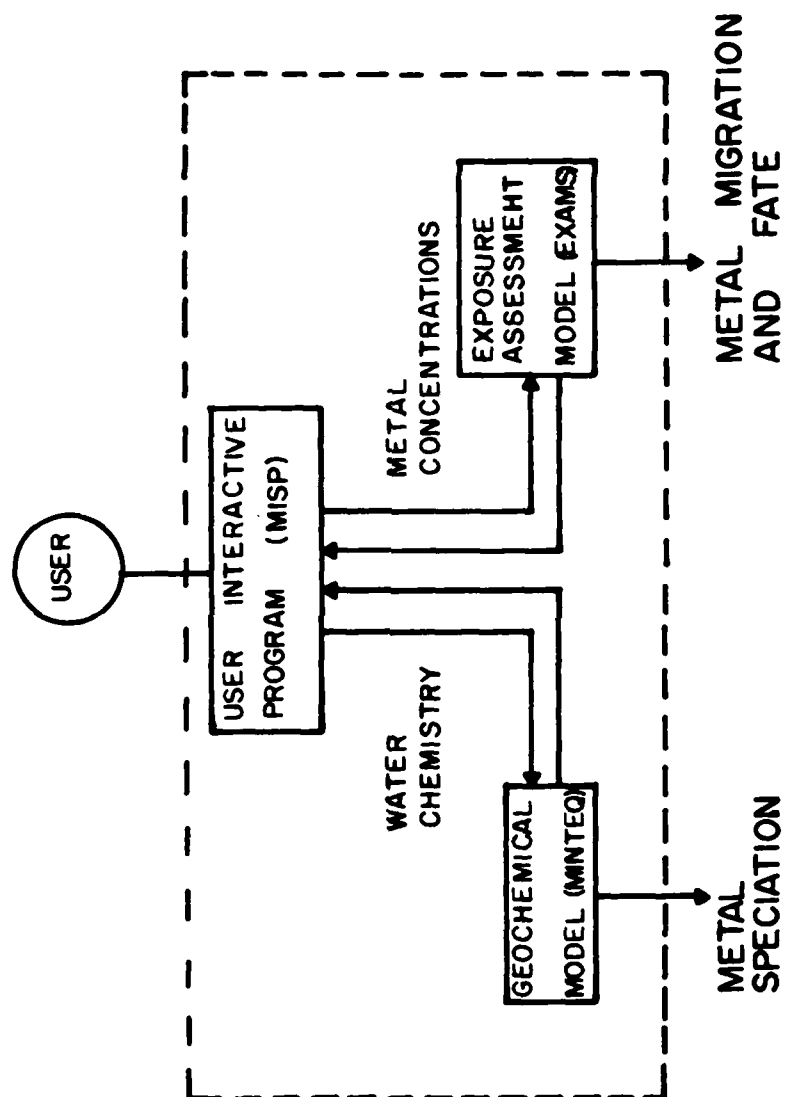


Figure 2.

in both batch and interactive mode with three different modes of operation available. The first mode is the MINTEQ only, which allows the operator to determine how changes in water chemistry will affect metal speciation and solid phase interactions without regard to transport processes. Secondly, the EXAMS only mode, which deals with the ionization, sorption, transport and transformation of a given pollutant. Finally, the third mode, which links EXAMS and MINTEQ together, allows the user to determine the effect of transport processes and chemical interactions on priority pollutant concentration. This section will describe the operation and use of the coupled mode.

The first step is to create an EXAMS input file that describes the characteristics of the aquatic environment being assessed. The user then enters the MEXAMS Interactive Software Package (MISP). MISP will call for a MINTEQ file for each compartment that contains different water quality data. The programmer will also input run-specific information that controls the number of times MINTEQ updates metal concentrations. MEXAMS is now set to simulate metal behavior, migration and fate.

Initial calculations by EXAMS are made assuming no adsorption or precipitation, and the initial distribution of dissolved metals in each compartment is obtained. These concentrations, along with suspended sediment and

biota concentrations, are sent on to MISP. MISP then passes the dissolved metal concentration in the first compartment on to MINTEQ, which simultaneously reads the water quality data for that compartment. MINTEQ then improves the estimate of the concentration of metal in solution, adsorbed to sediments and biota and in a precipitated form. These results are returned to MISP and metal fractions are determined.

MISP then proceeds to the second compartment and, unless the water quality is different and the total metal varies by more than 5%, MINTEQ is not called. MISP utilizes the same fractions from the previous compartment. If total metal varies by more than 5%, MINTEQ is called, but an entire new calculation is only performed when the water quality data differs from one compartment to the next.

After metal fractions have been computed for all compartments, MISP sends the information to EXAMS and the metal transport and transformation are computed. EXAMS then predicts new exposure levels and iterates with MINTEQ again. Calculations of fate and persistence are not performed until all iterations are complete.

EXAMS then sums the flux rate of metal attributable to each transport and transformation process, in which the significance of each process is then obtained by dividing flux rate by the total of the external

loadings. Finally, the persistence is calculated by terminating the external loading and computing the dissipation over two system half lives. In order to reduce computer time the two half lives have been divided into twelve equal time increments. Since metal concentration will change with time, the updating of each compartment metal fraction is possible. The user specifies the number of times the metal fractions are to be updated. The metal fractions will change with each time increment, and thus, after each persistence calculation they should be updated. The EXAMS output provides exposure, fate and persistence estimations, the MINTEQ output provides chemical interaction information and the MISP output provides information on EXAMS-MINTEQ interactions.

The MEXAMS computer program is capable of solving a wide variety of pollution problems. A list of possible uses follows:

- 1.) Rapid evaluation of synthetic organic pollutants
- 2.) Rapid hazard evaluation for priority pollutant metals
- 3.) Assess impact of point source discharge from mine drainage
- 4.) Provide support interpretations of metal bioassays
- 5.) Framework for what is or what is not known about the behavior of priority pollutant metals in aquatic systems
- 6.) Management tool

Now that the three individual programs have been presented, the specific input files used for the

Naugatuck River will be discussed. This discussion will include a description of the compartmentalized system used, and a line by line explanation of the computer inputs. The explanation will state any limitations, the variable names and their computer format code. Some of the parameters were not used in this report due to the fact that the pollutants are priority metals, as opposed to synthetic organic chemical contaminants.

CHAPTER 3

MODEL INPUTS AND OUTPUTS

3.1 Input Description (MINTEQ)

This section will present information regarding the operation of the MINTEQ program. The MINTEQ program has a great deal of flexibility in the way the user defines the chemistry of the ecosystem being modeled. The program is capable of dealing with six different species types, as described in the MINTEQ manual. The Type I species is the component. The component is defined as the chemical species chosen to represent each chemical constituent. Each component corresponds to a MINTEQ identification (ID) number. Table 1 provides a complete list of the components in MINTEQ. Type II complexes are defined as aqueous species which are combinations of two or more components. These complexes are not input by the user, but instead are output by the computer as a result of the Type I species input. Type III species are defined as a species with a fixed activity.

Some examples of Type III species are components at fixed activity such as pH or pE, solid phases present in infinite supply, gases present at a fixed partial

TABLE 1. COMPONENTS IN MINTEQ

Component	I.D. Number	Component	I.D. Number
E	001	NH ₄ ⁺	490
H ₂ O	002	NO ₂ ⁻	491
Ag ⁺	020	NO ₃ ⁻	492
Al ³⁺	030	Na ⁺	500
H ₃ AsO ₃	060	Ni ²⁺	540
H ₃ AsO ₄	061	PO ₄ ³⁻	580
H ₃ BO 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 ₄ SiO ₄	770
Ca ²⁺	150	Si 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	XPS10	992
Mg ²⁺	460	XPS18	993
Mn ²⁺	470	XPS1D	994
Mn ³⁺	471	SOHB	995

(from Felmy et. al., 1983)

pressure, and redox reactions between two components. Type IV species are precipitated solids subject to complete dissolution. The Type III and Type IV solids are similar, except that Type IV solids have a finite mass. Type V species are dissolved solids subject to precipitation. These solid phases will only precipitate when the saturation index is exceeded. Finally, Type VI species are species not considered during equilibrium calculations. Instead, these species are considered after the equilibrium calculations are complete.

An example input file for the Naugatuck River is presented in Table 2, with the numbers on the left corresponding to line numbers, for explanation purposes. The first two lines are descriptive information for the sample site. The third line describes the water temperature (C), analytical units, and fixed ionic strength designation. If ionic strength is not to be fixed, 0.00 is input. Line four contains nine run specific user options, inorganic carbon input, debug print option, charge balance option, considered solids and print option, number of iterations, pH variation option, fixed ionic strength, numerical method selection and output option. The fifth line contains adsorption parameters. Line six through 24 are the component input lines, and the three fields correspond to the specie ID number, total analytical mass and a guess for the log of the

TABLE 2

MINTEQ INPUT

```

1.  NAUGATUCK RIVER CONDITIONS (16-17 AUGUST 1983)
    COMPARTMENT 1 ZN-CU-PB ADSORPTION
2.  KD MODEL: MATRIX OBTAINED FROM BEST AVAILABLE
    DATA PH=7.14
3.  25.00 MG/L      0.00
4.  0 0 1 0 0 0 0 0
5.  1   0.00   0.00   0.00   0.00
6.    150 2.000E+01 -3.80
7.    460 3.500E+00 -3.90
8.    500 1.890E+01 -2.50
9.    140 3.422E+01 -5.50
10.   732 2.500E+01 -2.90
11.   180 3.800E+01 -2.80
12.   090 8.361E-02 -5.10
13.   410 3.090E+00 -4.25
14.   580 4.906E-01 -11.0
15.   770 8.320E+00 -6.50
16.   231 5.450E-02 -9.00
17.   950 1.750E-02 -8.00
18.   492 7.083E+00 -8.00
19.   470 3.550E-02 -7.00
20.   281 2.140E-01 -7.00
21.   600 6.000E-03 -8.00
22.   330 0.000E-00 -7.14
23.   991 0.000E-00  0.00
24.   990 0.000E+00  0.00
25.
26.    3    3
27.   330    7.14
28.   990
29.   991
30.
31.    2    3
32.  9909500 SOH-ZN      -0.24
33.    2      1.00 950    1.00 990
34.
35.  9916000 SOH-PB      1.33
36.    2      1.00 600    1.00 991
37.
38.  9912310 SOH-CU      0.20
39.    2      1.00 231    1.00 991
40.
41.

```

component activity. This section is the water quality data for each compartment of the ecosystem. The water quality data for the Naugatuck River was obtained from three sources (A.J. Medine et al., 1982, Curtis 1982, and USGS Water Resources Data-Connecticut, 1982). The water quality data used is presented in Table 3. The next line is a blank line separating specie Type I from specie Type III. Line 26 corresponds to the specie type and the number of species of that type. The next three lines are for fixed pH and two surface sites for adsorption. After another blank line, the adsorption information is input. This input section consists of nine lines. The first line contains the type of modification and number of these modifications. Then each adsorption input has three corresponding lines of input. The first line is the adsorption description and the $\log K_d$ value for the reaction.

The adsorption routine chosen in this case was the "activity" K_d approach. The $\log K_d$ values were obtained by running the MINTEQ program without adsorption. By using the activity results and the field-observed particulate concentration for each metal in Equation 4, the "activity" K_d was obtained ($\log K_d$ was then utilized as an input to the program). Table 4 presents the data obtained for each compartment, and the respective K_d values. The second line corresponds to the components and

Table 3

Water Quality Data

Component	Concentration (mg/l)	Data Source
150 - Ca	1.50 E+01	U.S.G.S. (1983)
460 - Mg	3.50 E+00	U.S.G.S. (1983)
500 - Na	1.89 E+01	Medine & Conway (1982)
410 - K	3.09 E+00	Medine & Conway (1982)
470 - Mn	*	Conn. - DEP (1982)**
281 - Fe	*	Conn. - DEP (1982)**
770 - SiO ₂	8.32 E+00	U.S.G.S. (1983)
950 - Zn	*	Conn. - DEP (1982)**
090 - B	8.36 E-02	Medine & Conway (1982)
231 - Cu	*	Conn. - DEP (1982)**
732 - SiO ₄	2.50 E+01	U.S.G.S. (1982)
180 - Cl	3.80 E+01	U.S.G.S. (1982)
140 - CO ₃	3.42 E+01	Medine & Conway (1982)
492 - NO ₃	7.08 E+00	U.S.G.S. (1982)
580 - PO ₄	4.91 E-01	U.S.G.S. (1982)
600 - Pb	*	Conn. - DEP**
330 - H	*	Conn. - DEP**

*These inputs are compartment dependent

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Protection

TABLE 4

Compartment Kd Data

Compartment #-Type	Element	Free Ion Activity (M)	Particulate Conc. (M)	Log Kd
1-E	Cu	9.741 E-08	1.50 E-07	.20
	Pb	9.940 E-10	2.17 E-08	1.23
	Zn	1.321 E-07	7.65 E-08	-.24
2-B	Cu	8.467 E-07	4.41 E-03	3.73
	Pb	9.300 E-07	2.79 E-03	3.48
	Zn	5.451 E-05	3.89 E-03	1.85
3-E	Cu	1.634 E-07	1.34 E-07	-.09
	Pb	2.551 E-09	2.17 E-08	.93
	Zn	1.830 E-07	9.94 E-08	-.26
4-B	Cu	1.796 E-06	1.59 E-03	2.95
	Pb	1.834 E-06	3.00 E-04	2.21
	Zn	4.637 E-05	3.49 E-03	1.88
5-E	Cu	4.422 E-08	3.93 E-08	-.05
	Pb	2.234 E-09	2.17 E-08	.99
	Zn	9.065 E-08	5.35 E-08	-.23
6-B	Cu	3.225 E-06	1.51 E-03	2.67
	Pb	2.543 E-06	3.07 E-04	2.08
	Zn	2.177 E-05	3.66 E-03	2.23

E - Eplimnion

B - Benthic

the stoichiometry of the reaction. Finally, the next two lines are blank to signify the end of the input file.

This section described the input file for the Naugatuck River. Also included in the appendices is a copy of the MINTEQ input description (Felmy et al., 1983). This description includes computer format, possible options and a more in-depth description of the MINTEQ input file itself. Following the input of the MINTEQ data file, the next step is the creation of an EXAMS input file.

3.2 Input Description (EXAMS)

The EXAMS input file is generated based on a compartmentalization of the riverine ecosystem. EXAMS, as stated previously, is responsible for the metal fate and migration calculations. Figure 3 displays the initial compartmentalization scheme used for the Naugatuck River system. Once the compartmentalization is selected, the EXAMS input file is generated. The file consists of 67 lines of input, which will be explained next (Table 5).

The first two lines are descriptive lines for the ecosystem, the chemical name and ecosystem name, both a maximum of three characters. The third line corresponds to the number of chemical loadings. In this case, there are five loadings and the next five lines describe the loading as one of five types (units of input for each

COMPARTMENTALIZATION

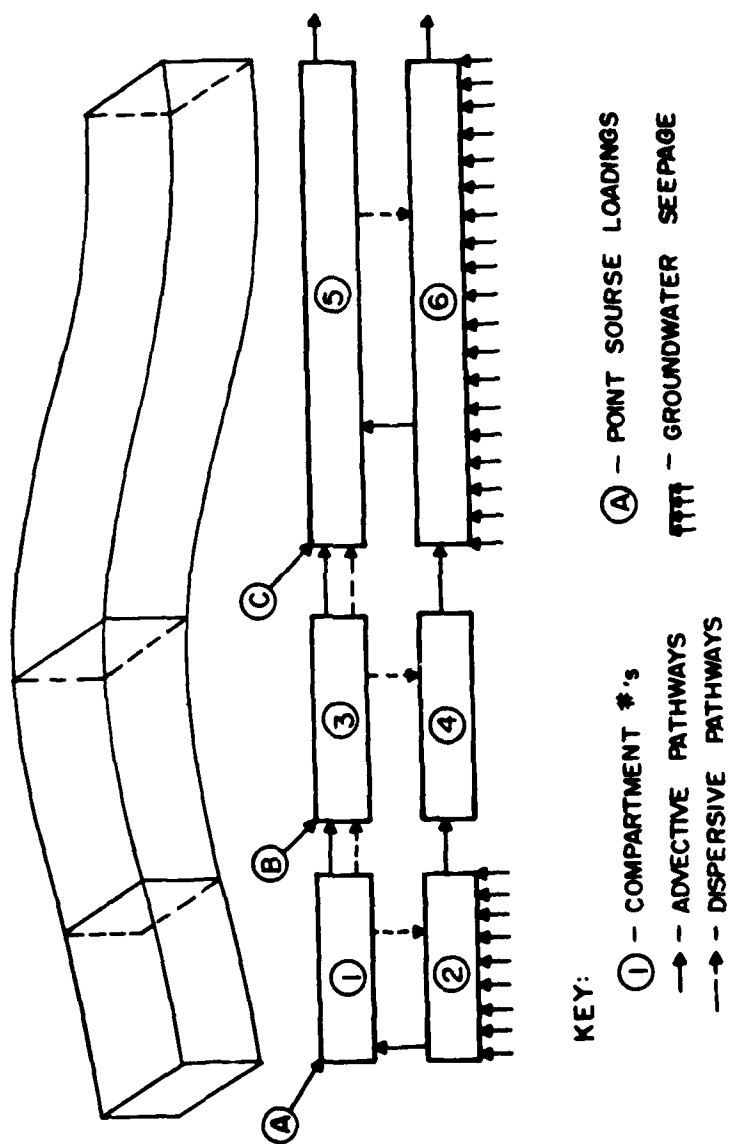


Figure 3.

chemical loading are Kg/hr,. The five types of loadings are point source, non-point source, rainfall, aerial drift and ground water seepage. The loadings are input from left to right for each compartment in the order previously stated. The next two lines are a description of the chemical, followed by a line of flags denoting which species of the organic toxicant can occur. A zero is used for no occurrence and a one for occurrence, and in this case, zeros are input because the pollutant being investigated is a heavy metal. The next two lines are an ecosystem description.

The ecosystem was divided into unequal compartment lengths representing well-defined segments based on actual point loadings. Compartments one and two are 1.3 miles long, compartments three and four are .3 miles long and compartments five and six are 6.7 miles long. Figure 4 displays the four different sample sites (East Albert St., Gulf Stream, Bogue Road, Bridge Abutment) within the stream segment selected for compartmentalization and modeling.

The next seven lines are the number of compartments, and the compartment code for each compartment. The compartments are classified as epilimnion (E), hypolimnion (H), littoral (L) or benthic (B). The compartment classification is then followed by the latitude input in degrees, and the wind velocity at 10 cm above the water

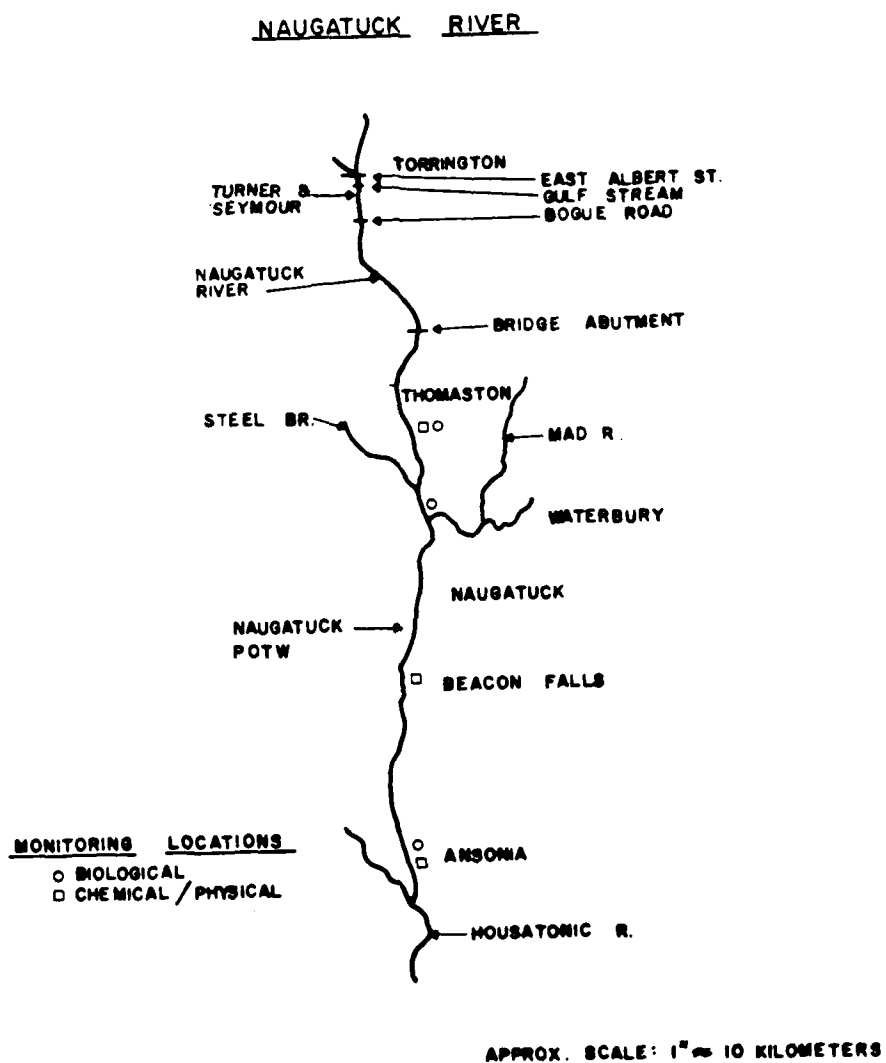


Figure 4.

surface (m/sec, for each compartment. Line 24 is the environmental volume (cubic meters) for each compartment followed by entries of area (square meters, and average depth (m) for each compartment.

The next section, lines 27 through 31, represent flows entering the ecosystem compartments. These flows are of the following type: stream flow (cubic meters/hr), stream-born sediment load (Kg/hr), non-point source water flow (cubic meters/hr), non-point source sediment loads (Kg/hr), and ground water seepage flow (cubic meters/hr). The next input is average rainfall (mm/mo) in the geographic area, then the average cloudiness in tenths of full sky cover is input. From this point on in the data set, many parameters are input as zero because they deal with transformation of organic toxicants and not priority pollutant heavy metals.

The next six lines are inputs for average spectral irradiance immediately below the water surface. These inputs are not required for transformation of heavy metals. Line 40 corresponds to the evaporative water losses (mm/mo) from each compartment. The next line is where suspended sediment concentrations (mg/l) are input if dealing with water column compartments and bulk density (g/cc) for benthic compartments. These inputs are followed by percent water in bottom sediments of benthic compartments. Water column compartments have inputs of

zero for this variable.

The transport mechanisms of advection and dispersion are input in lines 43 - 52. Advection is input first, with the first line corresponding to the number of advective pathways. The next three lines are the source compartment, the receiving compartment and the proportion of the advective flow. The dispersive pathways are then input. The first line equates to the number of dispersive pathways. The source compartments are then entered followed by the receiving compartment and the description of the exchange pathway. The cross-sectional area (square meters), characteristic length (m) and eddy dispersion coefficients (square meters/hr) are the parameters required to describe the dispersive pathway. The characteristic length is defined as the distance from compartment center to compartment center.

The next three lines correspond to the organic carbon content of compartment sediment, cation and anion exchange capacity of the sediments. Line 56 is the average temperature for each compartment. The pH and pOH of each compartment are the next two inputs. Finally, the remaining lines are not required for the modeling of the Naugatuck riverine ecosystem for the migration and fate of priority pollutant metals.

Included in the appendices is a copy of the EXAMS input file description (Burns et al., 1981). The descrip-

tion provides a detailed description of the computer format, and the parameters which were not used, but can be used for organic toxicants.

For each compartment there is a corresponding MINTEQ input file, and it should be re-emphasized that each compartment is assumed to be completely mixed after the priority pollutant enters the compartment. After input files have been created for each compartment (MINTEQ), and the transformation and transport model (EXAMS) input file is complete, the MISP interactive input file is created.

This file encompasses twenty-five lines in this example. These lines allow the interaction of MINTEQ with EXAMS and produce the MEXAMS system model. The first line corresponds to the selection of the computer mode (MINTEQ only, or coupled version). The metal selection is made next from the list of metals (As, Cd, Cu, Pb, Ni, Ag and Zn) and corresponding identification numbers in the MINTEQ components list. The next line corresponds to how many MINTEQ files are needed. The number of required files is dependent on the water quality data for the aquatic system. If the water quality data does not change significantly for each compartment, then one file is sufficient. Water quality fluctuations could be a result of wastewater treatment plant discharges, industrial discharges, overland runoff, etc.

The next group of lines corresponds to the number of compartments that match up with each MINTEQ file, followed by the compartment number that corresponds to each MINTEQ file. The next input is the number of times the programmer wants the steady state metal concentration updated. EXAMS initially assumes all metal is in the dissolved form and by providing MINTEQ with these results, the actual dissolved, sediment sorbed, biosorbed and precipitated metal concentrations are obtained. EXAMS uses these updated calculations in the next simulation for fate and transport of the pollutant. Line seventeen relates to how often MINTEQ is used for persistence calculations. After steady state has been achieved, the pollutant loading is ceased and persistence calculations begin. These calculations are based on two system half-lives, which are divided into twelve equal time increments. This input will continue metal fraction updating throughout the persistence calculations. The next three inputs correspond to the output option, the MINTEQ file names for each compartment, and the EXAMS input file name. There are three output options available: the full MINTEQ output, aqueous species distribution and all mass totals, and all mass totals. This concludes the MISP interactive input file. Table 6 is a sample of the MISP file.

3.3 Output (MINTEQ)

Table 6

MISP Input

3
231
6
1
1
1
2
1
3
1
4
1
5
1
6
3
4
3
NAUG1.DAT
NAUG2.DAT
NAUG3.DAT
NAUG4.DAT
NAUG5.DAT
NAUG6.DAT
EXAMS21.DAT

The MINTEQ output data received when the uncoupled mode is operated can be divided into seven sections. The first section is a duplication of the first five lines of the input file. Section two corresponds to the initial charge balance of the solution being modeled, prior to aqueous speciation. A large percent difference can be indicative that one or more major cations or anions may have been neglected when preparing the water quality input file. However, the water analysis may be entirely correct with the final speciation indicating an acceptable charge balance. Therefore, initial charge imbalance should be evaluated on a case by case basis (section 2 is presented in Table 7).

The third section provides an iterative output displaying the convergence of the first component in the input file to its actual speciated activity (Table 7). Also included in this section is the calculated molality, activity, Log activity, activity coefficient, and new Log K for all input components. The new Log K is the effective equilibrium constant after temperature and ionic strength corrections. This section can be used to enable the user to make a better guess for the activity in the input file.

The fourth section provides the output data for the six different specie types. The output for Type I components and Type II complexes are similar with the

Table 7

MINTEQA Output

CHARGE BALANCE: UNSPECIATED
 SUM OF CATIONS= 2.203E-03 SUM OF ANIONS = 2.863E-03
 PERCENT DIFFERENCE = -13.04 (CATIONS - ANIONS)/(ANIONS + CATIONS)

ITERATIONS DURING SOLVE			
ITER	NAME	TOTAL MOL	LOG ACTVY
1	CA	4.991E-04	-2.910E-04
2	CA	4.991E-04	-3.80000
3	CA	4.991E-04	-6.766E-05
4	CA	4.991E-04	-3.32420
5	CA	4.991E-04	-3.43010
6	CA	4.991E-04	-3.62025
			-3.41555

OUTPUT DATA: ITERATIONS = 6								
ID	NAME	ANAL MOL	CALC MOL	ACTIVITY	LOG ACTVY	GAMMA	NEW LOGK	DIFF FXN
150	CA	4.991E-04	4.815E-04	3.817E-04	-3.41830	.792686	.1009	-3.620E-07
460	MG	1.440E-04	1.393E-04	1.107E-04	-3.95593	.794378	.1000	-1.034E-07
500	NA	8.222E-04	8.211E-04	7.734E-04	-3.11159	.941939	.0260	-1.644E-07
140	CO3	5.703E-04	3.792E-07	2.996E-07	-6.52348	.789951	.1024	-9.605E-08

following headings: calculated molality, activity, Log activity, activity coefficient (GAMMA), new Log K, and the enthalpy of the reaction (DH). Type III fixed solids are of four basic categories, redox reactions, components at fixed activity, solid phases and gases at a fixed partial pressure. The output for these type species consists of calculated molality, Log molality, new Log K and the DH. In our case the Type III species fall into the category of fixed activities, thus any intuitive information from this section cannot be obtained.

However, if solid phases were being dealt with, a positive calculated molality would equal the mass of solid precipitated. On the other hand, a negative calculated molality would equal the dissolved mass or mass added to the solution. No Type IV or Type V species were permitted from the list of solids which were supersaturated as indicated by MINTEQ. Chemical precipitation has not been observed in the Naugatuck River although it cannot be precluded. Type V calculated molality would correspond to saturation index values. Type VI has two different interpretations for the calculated molality. If solid phase, it corresponds to saturation index. If aqueous species, it corresponds to activity of specie. A sample of section four output is displayed in Table 8.

Section five presents the percentage distribution of Type I components and Table 9 is an example. The sixth

Table 8

MINTEQ Output

SPECIES: TYPE I - COMPONENTS							
ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
150	CA	4.815E-04	3.817E-04	-3.41830	.792686	.101	0
460	HG	1.393E-04	1.107E-04	-3.95593	.794378	.100	0
500	NA	8.211E-04	7.734E-04	-3.11159	.941939	.026	0
140	CO3	3.792E-07	2.996E-07	-6.52348	.789951	.102	0
732	SO4	2.408E-04	1.891E-04	-3.72333	.785348	.105	0
180	CL	1.072E-03	1.008E-03	-2.99650	.940572	.027	0
90	H3BO3	1.341E-06	1.342E-06	-5.87224	1.000697	-.000	0
410	K	7.892E-05	7.423E-05	-4.12945	.940572	.027	0
580	PO4	1.940E-11	1.137E-11	-10.94412	.586236	.232	0
770	H4SiO4	8.643E-05	8.649E-05	-4.06305	1.000697	-.000	0
231	CU+2	1.223E-07	9.686E-08	-7.01385	.791776	.101	0
950	ZN	1.671E-07	1.323E-07	-6.87842	.791776	.101	0
492	NO3	1.142E-04	1.074E-04	-3.96888	.940473	.027	0
470	MN+2	6.220E-07	4.925E-07	-6.30758	.791776	.101	0
281	FE+3	1.245E-14	7.545E-15	-14.12233	.606033	.218	0
600	PB	1.286E-09	1.010E-09	-8.99549	.785813	.105	0
SPECIES: TYPE II - COMPLEXES							
ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK	DH
1503300	CAOH +	1.409E-09	1.329E-09	-8.87633	.943302	-12.573	14.535
1501400	CAHCO3 +	1.944E-06	1.834E-06	-5.73669	.943302	11.370	1.790
1501401	CACCO3 AO	1.624E-07	1.625E-07	-6.78917	1.000697	3.152	4.030
1507320	CASO4 AO	1.469E-05	1.470E-05	-4.83263	1.000697	2.309	1.470
1505800	CAHPO4 AO	3.822E-07	3.825E-07	-6.41742	1.000697	15.085	-.230
1505801	CAPO4 -	1.325E-08	1.249E-08	-7.90342	.942758	6.485	3.100
1505802	CAH2PO4 +	2.204E-08	2.078E-08	-7.68242	.942758	20.986	-1.120
5001400	NACCO3 -	4.555E-09	4.295E-09	-8.36707	.942758	1.294	8.911
5001401	NAHCO3 AO	2.017E-07	2.018E-07	-6.69507	1.000697	10.080	0
6001800	PBCL +	4.307E-11	4.055E-11	-10.39199	.941520	1.626	4.380
6001801	PBCL2 AQ	6.475E-14	6.479E-14	-13.18849	1.000697	1.800	1.080
6001802	PBCL3 -	5.498E-17	5.176E-17	-16.28599	.941520	1.725	2.170
6001803	PBCL4 -2	3.186E-20	2.503E-20	-19.60149	.785813	1.485	3.530
6001400	PB(CO3)2-2	5.026E-12	3.959E-12	-11.40245	.785813	10.745	0
6003300	PBOH +	2.888E-10	2.719E-10	-9.56552	.941520	-7.684	0
6003301	PB(OH)2 AQ	1.459E-12	1.460E-12	-11.83554	1.000697	-17.120	0
6003302	PB(OH)3 -	2.458E-16	2.314E-16	-15.63557	.941520	-28.034	0
6003303	PB2OH +3	1.058E-17	6.152E-18	-17.21101	.581390	-8.124	0
6004920	PBNH3 +	1.705E-12	1.606E-12	-11.79437	.941520	1.196	0
6007320	P3SO4 AQ	1.074E-10	1.074E-10	-9.96882	1.000697	2.750	0
6003304	PB3(OH)4+2	6.282E-23	4.937E-23	-22.30658	.785813	-23.775	26.500
6001401	PBCO3 AQ	5.257E-09	5.261E-09	-8.27897	1.000697	7.240	0
6003325	PB(OH)4 -2	9.334E-21	7.335E-21	-20.13460	.785813	-39.594	0
6007321	PB(SO4)2-2	1.357E-13	1.066E-13	-12.97214	.785813	3.575	0
SPECIES: TYPE III - FIXED SOLIDS							
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH		
2	H2O	-9.247E-06	-5.034	.000	0		
991	SOH2	-1.751E-07	-8.757	0	0		
990	SOH1	-7.613E-08	-7.118	0	0		
330	H	-6.425E-04	-3.182	7.140	0		
SPECIES: TYPE VI - SPECIES NOT CONSIDERED							
ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH		
3301403	CO2(GAS)	2.273E-03	-2.643	18.160	-.530		

section presents the amount of each Type I component in solution (aqueous mass), sorbed (sorbed mass) and precipitated (precipitated mass). The final charge balance is also presented, and if the final percent difference after aqueous speciation is less than five percent, the run is acceptable. A sample of section six output is presented in Table 9. The heavy metal under investigation in this case study is copper, and from Table 9 it can be seen that 14.3 percent of the copper is in the free ion form, 16.9% bound to surface sites with the remainder as inorganic complexes.

The final section provides the saturation indices for all minerals and solids in the data base. This section is used to determine if the saturation index of a particular mineral or solid has been exceeded. A positive Log SI means the solid is oversaturated. This also tells you that this solid could precipitate, and thus, if your environment favors this solid, the solid could be input as a Type IV solid and allowed to precipitate. Finally, a line will be printed "NORMAL TERMINATION OF MINTEQ" and the output is complete. The final section is presented in Table 10. An example of the entire MINTEQ output is presented in the appendices.

3.4 Output (EXAMS)

The EXAMS output obtained when the coupled mode

Table 9
MINTEQA Output

PERCENTAGE DISTRIBUTION OF COMPONENTS					
CA	96.5	PERCENT BOUND IN SPECIES	150	CA	
	2.9	PERCENT BOUND IN SPECIES	1507320	CASO4 AQ	
CU+2	14.3	PERCENT BOUND IN SPECIES	231	CU+2	
	17.9	PERCENT BOUND IN SPECIES	9912310	SOH-CU	
	18.2	PERCENT BOUND IN SPECIES	2311400	CUCO3 AQ	
	1.7	PERCENT BOUND IN SPECIES	2313300	CU3H +	
	44.9	PERCENT BOUND IN SPECIES	2313301	CU(OH)2 AQ	
	2.6	PERCENT BOUND IN SPECIES	2311402	CUHCO3 +	
ZN	62.4	PERCENT BOUND IN SPECIES	950	ZN	
	2.2	PERCENT BOUND IN SPECIES	9507320	ZNSO4 AQ	
	2.9	PERCENT BOUND IN SPECIES	9501400	ZNHCO3 +	
	3.0	PERCENT BOUND IN SPECIES	9501401	ZHCO3 AQ	
	28.4	PERCENT BOUND IN SPECIES	9909500	SOH-ZN	

IDX	NAME	AQUEOUS MASS	SORBED MASS	PRECIPITATED MASS
150	CA	4.987E-04	0	0
460	MG	1.430E-04	0	0
500	NA	9.221E-04	0	0
140	CO3	5.702E-04	0	0
732	SO4	2.601E-04	0	0
180	CL	1.072E-03	0	0
90	H3BO3	1.352E-06	0	0
410	K	7.302E-05	0	0
580	PO4	5.164E-06	0	0
770	H4SiO4	8.658E-05	0	0
231	CU+2	7.042E-07	1.535E-07	0
950	ZN	1.915E-07	7.613E-08	0
492	NO3	1.142E-04	0	0
470	MN+2	6.438E-07	0	0
281	FE+3	3.832E-06	0	0
600	PB	7.360E-09	2.160E-08	0
2	H2O	9.247E-06	0	0
330	H	6.425E-04	0	0
CHARGE BALANCE SPECIATED				
SUM OF CATIONS =		2.149E-03	SUM OF ANIONS	2.168E-03
PERCENT DIFFERENCE =		- .43	(CATIONS - ANIONS)/(ANIONS + CATIONS)	
NONCARBONATE ALKALINITY =		0		
IONIC STRENGTH =		3.026E-03		

is selected is dependent upon the MISP file configuration. The parameter which controls the EXAMS output is the number of times EXAMS uses MINTEQ to update steady state metal concentrations. EXAMS utilizes MINTEQ three times to update steady-state metal concentrations in the Naugatuck River test case. The selection of this parameter is based on trial and error; the programmer examines the output obtained while varying the input and determines when system steady state is achieved. System steady state is defined as an equilibrium between the partitioning achieved with EXAMS and MINTEQ.

The EXAMS output file received after each steady state calculation will be divided into three sections. The first section consists of 13 tables, which were obtained from the initial EXAMS calculation. The initial EXAMS calculation assumes the pollutant is in the aqueous form. Tables 2 - 8 (all shown in Table 11) are echoes of the EXAMS input data. Table 1 is not printed because the pollutant in question is a heavy metal and not an organic. If the pollutant had been an organic, Table 1 would have been an echo of the organic input data.

The next section includes Tables 9 - 14 (all shown in Table 12). These five tables are the transport profile, the kinetic profile, the canonical profile, toxicant loadings by system element, the distribution of the chemical at steady state (the water column and

Table 11 (continued)

#	TY	BIOMS (1)	PLRA (2)	BIOTM DEG C.	BACTO (3)	ACBAC (2)	CHL MG/L
1L		.0	.0	23.50	.0	.0	.0
2B		.0	.0	23.50	.0	.0	.0
3L		.0	.0	23.50	.0	.0	.0
4B		.0	.0	23.50	.0	.0	.0
5L		.0	.0	23.50	.0	.0	.0
6B		.0	.0	23.50	.0	.0	.0
7L		.0	.0	23.50	.0	.0	.0
8B		.0	.0	23.50	.0	.0	.0
9L		.0	.0	23.50	.0	.0	.0
10B		.0	.0	23.50	.0	.0	.0

(1) UNITS: MG/L IN WATER COLUMN (L,H,B); G (D.W.)/SQUARE METER IN (B).
 (2) DIMENSIONLESS NUMBERS.
 (3) UNITS: CELLS/ML IN L, E, H; CELLS/100 G D.W. IN B.

Table 11 (continued)

TABLE 4. INPUT DATA DESCRIBING ENVIRONMENT: DEPTHS AND INFLOWS.						
#	TY	DEPTH M	STFLO CU M/HR	STSED KG/HR	NPSFL CU M/HR	INTFL CU M/HR
1L		.1707	988.8	2.967		162.5
2B		9.140E-03				1.626E-02
3L		.1798	46.94	.4890		
4B		9.140E-03				
3048		770.8	5.528			
6B		9.140E-03			117.9	
7L		.3048				1.179E-02
8B		9.140E-03				117.7
9L		.3048				.1179
10B		9.140E-03				117.7
						.1533

Table 11 (continued)

#	TY	K02 CM/HR @20	WIND M/S @10 CM	CMPT /M	DFAC M/M	EVAP MM/MON	AREA SQ M
1L		.0	.0	1.161	.0	.0	5.386E+04
2B							5.386E+04
3L		.0	.0	1.161	.0	.0	1.257E+04
4B							1.257E+04
5L		.0	.0	2.691	.0	.0	8.757E+04
6B							8.757E+04
7L		.0	.0	2.691	.0	.0	8.757E+04
8B							8.757E+04
9L		.0	.0	2.691	.0	.0	8.757E+04
10B							8.757E+04

Table 11 (continued)

TABLE 7. INPUT DATA DESCRIBING ENVIRONMENT: ADVECTIVE INTERCONNECTIONS.			
COMP. NO.	(JFRAD)	3	5
CONNECTED (ITOAD)	3	5	7
ADVECTION (ADVPR)	1.00	1.00	1.00
COMP. NO.	(JFRAD)	4	6
CONNECTED (ITOAD)	1	3	5
ADVECTION (ADVPR)	.900	.900	.240
COMP. NO.	(JFRAD)	4	6
CONNECTED (ITOAD)	4	6	8
ADVECTION (ADVPR)	.100	.100	.760
			.620

TABLE 8. INPUT DATA DESCRIBING ENVIRONMENT: TURBULENT INTERCONNECTIONS.			
COMP. NO.	(JTURB)	3	5
CONNECTED (ITURB)	2	4	6
X-SECTION (XSTUR)	5.39E+04	1.26E+04	8.76E+04
CHAR. LN. (CHARL)	8.99E-02	9.45E-02	.157
EDDY DISP. (DSP)	5.00E-07	5.00E-07	5.00E-07
			8.76E+04
			.157
			5.00E-07
			5.00E-07

Table 12

EXAM'S Output

TABLE 9. TRANSPORT PROFILE OF ECOSYSTEM.

CP Y	T*	VOLUME (CUBIC M)	SEDIMENT MASS (KG)	WATER FLOW (CU. M/DAY)	SED. FLOW (KG/DAY)	FLOW (KG/DAY)	RESIDENCE TIME (DAYS)	WATER SEDIMENTS
1L		9.32E+03	27.9	2.76E+04	313.	.337	8.93E-02	
2B		495.	6.58E+05	1.84	9.80E+03	54.3	67.1	
3L		3.35E+03	10.1	2.88E+04	114.	.117	8.85E-02	
4B		115.	1.53E+05	.361	2.15E+03	64.2	71.1	
5L		2.63E+04	198.	5.01E+04	471.	.526	.420	
6B		801.	1.06E+06	1.64	9.08E+03	98.7	117.	
7L		2.63E+04	198.	5.29E+04	2.69E+03	.498	7.34E-02	
8B		801.	1.06E+06	4.21	2.32E+04	38.4	45.9	
9L		2.63E+04	198.	5.57E+04	1.76E+03	.473	.112	
10B		801.	1.06E+06	7.20	3.28E+04	22.4	32.5	

* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC

Table 12 (continued)

CP	I*	PH	POH	TEMP DEG. C.	REAERATION COEFF. M/HR	COMPOSITE LIGHT AVE % POP.	BACTERIAL SIZE CELLS/**	OXIDANT CONC. (MOLAR)	DISSOLVED PERCENT %
.0			.0		.0	1.00E-09	78.5		
28		7.14	6.86	23.5	.0	.0	.0	.0	6.91E-03
3L		7.01	6.99	23.5	.0	.0	.0	1.00E-09	89.8
4B		7.01	6.99	23.5	.0	.0	.0	5.00E-10	3.11E-02
5L		7.08	6.92	23.5	.0	.0	.0	.0	68.1
6B		7.08	6.92	23.5	.0	.0	.0	1.00E-09	2.28E-02
7L		7.08	6.92	23.5	.0	.0	.0	1.00E-09	87.2
8B		7.08	6.92	23.5	.0	.0	.0	5.00E-10	3.01E-03
9L		7.08	6.92	23.5	.0	.0	.0	1.00E-09	84.3
10B		7.08	6.92	23.5	.0	.0	.0	.0	4.06E-03

* COMP. TYPE: "L"=LITTORAL; "E"=(EPI) AND "H"=(HYPO)LIMNION; "B"=BENTHIC
 ** ACTIVE BACTERIAL POPULATIONS AS CELLS/ML IN WATER COLUMN, -
 CELLS/100 G (DRY WEIGHT) OF SEDIMENTS IN BOTTOM SEDIMENTS.-

Table 12 (continued)

TABLE 12. TOXICANT LOADINGS (KG/HR) BY SYSTEM ELEMENT.				
ELEMENT	STREAM FLOW	RAINFALL	INTERFLOW	DRIFT LOAD
1	1.284E-02			
2			6.505E-04	
3	4.404E-03			
4				
5	3.361E-02		1.179E-04	
6				
7			1.179E-04	
8				
9			1.179E-04	
10				

Table 12 (continued)

TABLE 13. DISTRIBUTION OF CHEMICAL AT STEADY STATE: IN THE WATER COLUMN:

COMP #	STEADY-STATE RESIDENT MASS	***** TOXICANT CONCENTRATIONS *****					*****		
		TOTAL DISSOLVED SORBED BY SORBED BY PRECIP					BIOTA SEDIMENTS SEDIME		
10									
NTS	G/M	KILOS	%	MG/*	MG/L	UG/G	MG/KG	MG/	
L									
1	1.99E-03	.1073	6.87	1.15E-02	9.05E-03	.0	826.	.0	
3	3.98E-03	5.005E-02	3.20	1.49E-02	1.34E-02	.0	507.	.0	
5	7.43E-03	.6504	41.63	2.47E-02	1.68E-02	.0	1.05E+03	.0	
7	4.84E-03	.4235	27.10	1.61E-02	1.40E-02	.0	274.	.0	
9	3.78E-03	.3311	21.19	1.26E-02	1.06E-02	.0	263.	.0	
SUBTOTAL:		1.562	1.90						
AND IN THE BOTTOM SEDIMENTS:									
2	.256	13.79	17.13	21.0	9.53E-03	.0	21.0	.0	
4	.109	1.370	1.70	8.98	1.84E-02	.0	8.98	.0	
6	.137	12.03	14.94	11.3	1.70E-02	.0	11.3	.0	
8	.332	29.10	36.14	27.4	5.42E-03	.0	27.4	.0	
10	.277	24.23	30.10	22.8	6.09E-03	.0	22.8	.0	
SUBTOTAL:		80.53	98.10						
TOTAL MASS (KILOGRAMS) =		82.09							

Table 12 (continued)

TABLE 14. AVERAGE, MAXIMUM, AND MINIMUM CONCENTRATIONS AT STEADY STATE.

1	CP)TOTAL	CP)DISSOLVED	CP)SEDIMENTS	CP)BIOTA	CP)PRECIP	CP)MASS
	MG/*	MG/L	MG/KG	UG/G	MG/L	G/M
WATER COLUMN:						
AV	1.60E-02	1.23E-02	584.	.0	.0	4.4E-03
MA	5) 2.47E-02	5) 1.68E-02	5) 1.05E+03	9) .0	9) .0	5) 7.4E-03
MI	1) 1.15E-02	1) 9.05E-03	9) 263.	9) .0	9) .0	1) 2.0E-03
BOTTOM SEDIMENTS:						
AV	18.3	1.13E-02	18.3	.0	.0	.22
MA	3) 27.4	4) 1.84E-02	8) 27.4	10) .0	10) .0	8) .33
MI	4) 3.98	3) 5.42E-03	4) 8.98	10) .0	10) .0	4) .11

1 NUMBER IN HALF-PARENS CP) INDICATES COMPARTMENT WHERE VALUE WAS FOUND.
 * TOTAL CONCENTRATION AS MG/L IN WATER COLUMN, A* MG/KG IN SEDIMENTS.

sediments), the average, maximum and minimum concentrations at steady state. Table 10, the kinetic profile is for organic toxicants only. These five tables are repeated the number of times EXAMS uses MINTEQ to update steady state metal concentrations. For the Naugatuck River test case, this occurred three times. The most important of the three outputs is the last repetition, because it is the output obtained when system steady state has been achieved for the water column and sediments.

The third section of output is encompassed in Table 15 - 17, the analysis of steady state fate, the simulation of system response after load ceases, and the exposure analysis summary. These three tables contain the persistence calculation performed by EXAMS. These tables are presented in Table 13. The final portion of the program output is the MISP output.

3.5 Output (MISP)

This section as previously stated provides a summary of the EXAMS-MINTEQ interactions. These interactions include steady state calculations made to achieve system steady state, and calculations made during the persistence to update metal fractions. For the Naugatuck River test case, steady state concentrations were updated three times to obtain system equilibrium, and updated

Table 13

EXAMS Output

CHEMICAL: Heavy Metal

ECOSYSTEM: NAUGATUCK RIVER CALIBRATION TEST RUN

TABLE 15. ANALYSIS OF STEADY-STATE FATE OF ORGANIC TOXICANT.

PROCESS	MASS FLUX KG/DAY	% OF LOAD	HALF-LIFE* DAYS
HYDROLYSIS	.0	0.0	---
OXIDATION	.0	0.0	---
PHOTOLYSIS	.0	0.0	---
ALL CHEMICAL PROCESSES	.0	0.0	---
WATER COLUMN (BACTERIA)	.0	0.0	---
BOTTOM SEDIMENTS (BACTERIA)	.0	0.0	---
TOTAL BIOLYSIS	.0	0.0	---
VOLATILIZATION	.0	0.0	---
WATER-BORNE EXPORT	1.245	100.00	45.72
TRANSFORMATION AND TRANSPORT	1.245	100.00	
TOTAL SYSTEM LOAD	1.245		
RESIDUAL ACCUMULATION RATE:	1.341E-06	0.00	

* HALF-LIVES ARE ESTIMATES BASED ON A FIRST-ORDER RATE APPROXIMATION.

Table 13 (continued)

CHEMICAL: Heavy Metal									
ECOSYSTEM: NAUGATUCK RIVER CALIBRATION TEST RUN									
TABLE 16. SIMULATION OF SYSTEM RESPONSE AFTER LOAD CEASES.									
TIME	AVERAGE POLLUTANT CONCENTRATIONS				MASS OF POLLUTANT				
DAYS	WATER COLUMN		BOTTOM SEDIMENTS		WATER COL		SEDIMENTS		
	FREE(MG/L)	SED(MG/KG)	PORE(MG/L)	SED(MG/KG)	TOTAL KG	TOTAL KG	TOTAL KG		
0.	1.28E-02	584.	1.13E-02	18.3	1.562	1.562	80.5		
8.	3.75E-03	165.	1.06E-02	17.0	.4264	.4264	74.5		
16.	3.46E-03	153.	9.91E-03	15.6	.3934	.3934	68.4		
24.	3.20E-03	142.	9.26E-03	14.4	.3630	.3630	62.7		

Table 13 (continued)

TABLE 17. EXPOSURE ANALYSIS SUMMARY.

EXPOSURE:									
A. MAXIMUM CONC. IN WATER COLUMN:		1.7E-02 MG/L DISSOLVED,		2.5E-02 TOT					
MAX. CONC. IN BOTTOM SEDIMENT:		1.8E-02 MG/L DISSOLVED IN PORE WATER							
B. BIOSORPTION - MAX. CONCENTRATION - PLANKTON:		.0		UG/G					
BENTHOS:		.0		UG/G					
C. MAXIMUM TOT. CONC. IN SEDIMENT DEPOSITS:		27.		MG/KG (DRY WEIGHT)					
FAF:									
A. TOTAL STEADY-STATE ACCUMULATION:		82.		KG;		1.90% IN WATER COL.,			
98.10% IN BOTTOM SEDIMENTS.									
B. TOTAL LOAD:		1.2		KG/DAY - DISPOSITION:		0.0 % VIA CHEMICAL			
TRANSFORMATIONS,		0.0 % BIOTRANSFORMED,		0.0 % VOLATILIZED,					
100.00% EXPORTED VIA OTHER PATHWAYS.									
PERSISTENCE:									
A. AT THE END OF A 96.0 DAY RECOVERY PERIOD, THE WATER COLUMN HAD									
LOST 76.77% OF ITS INITIAL TOXICANT BURDEN; THE SEDIMENTS HAD									
LOST 22.16% OF THEIR INITIAL BURDEN (23.20% REMOVAL OVERALL).									
B. SYSTEM SELF-PURIFICATION TIME IS ROUGHLY***** YEARS.									
32.	2.96E-03	131.	8.67E-03	13.2	.3352	57.4			
40.	2.74E-03	122.	8.10E-03	12.2	.3094	52.6			
48.	2.53E-03	113.	7.57E-03	11.2	.2857	48.2			
56.	2.34E-03	105.	7.07E-03	10.3	.2638	44.2			
64.	2.16E-03	97.1	6.60E-03	9.46	.2436	40.5			
72.	2.00E-03	90.0	6.17E-03	8.71	.2252	37.2			
80.	1.85E-03	83.5	5.76E-03	8.02	.2082	34.1			
88.	1.71E-03	77.5	5.38E-03	7.39	.1926	31.3			

again two times during the persistence calculation. This totals five interactions between EXAMS and MINTEQ, and the MISP output file is presented in Table 14.

Table 14

MISP Output

UPDATED CONCENTRATIONS FROM MINTEQ (MG/L)			
UPDATED CONCENTRATIONS FROM MINTEQ (MG/L)			
COMPARTMENT	AQUEOUS	ADSORBED	PRECIPITATED
COMPARTMENT	AQUEOUS	ADSORBED	PRECIPITATED
1	9.024E-03	2.478E-03	0.0
2	9.532E-03	1.379E+02	0.0
3	1.341E-02	1.519E-03	0.0
4	1.836E-02	5.897E+01	0.0
5	1.684E-02	7.880E-03	0.0
6	1.697E-02	7.435E+01	0.0
7	1.404E-02	2.065E-03	0.0
8	5.420E-03	1.798E+02	0.0
9	1.061E-02	1.970E-03	0.0
10	6.094E-03	1.500E+02	0.0
CONCENTRATIONS COMPUTED BY EXAMS IN MG/L			
CONCENTRATIONS COMPUTED BY EXAMS IN MG/L			

CHAPTER 4

MODEL RESULTS

4.1 Calibration Parameters

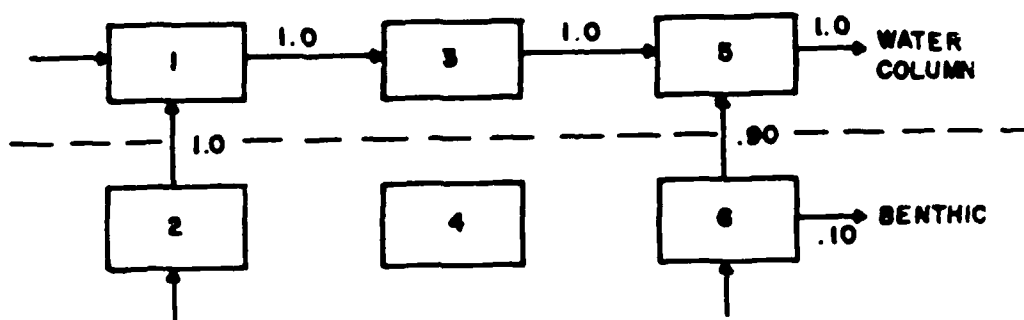
Metal transport in the Naugatuck River is currently being investigated to provide important data for waste allocation decisions. Included within this investigation is the calibration of MEXAMS to a compartmentalized river reach. The reach being calibrated (Figure 3) was originally composed of three water column compartments and three benthic compartments. However, the final model configuration consisted of a ten compartment model; five benthic compartments and five water column compartments. A diagram of the final configuration will be presented herein. This calibration consisted of adjusting certain model inputs to yield results that were the same as the field data obtained on August 16-18, 1983.

The first step in the calibration was to determine which model inputs have the least reliability. These are the parameters that will be adjusted to perform a sensitivity analysis. Any sensitivity analysis is system dependent because certain input parameters may be more or less sensitive depending on the system being modeled.

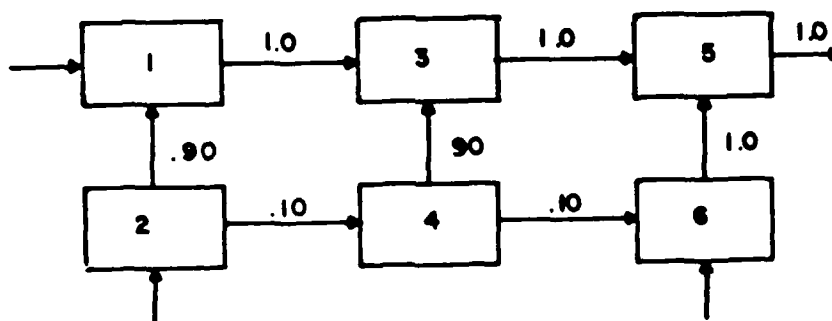
Therefore, the first decision to be made was to select a system configuration. There are many possible configurations due to the possible advective and dispersive pathways. The two initial configurations chosen for this test case are presented in Figure 5. The main difference between configuration one and configuration two is the advective pathways. Configuration one allows flow to exit the system through the sediments via compartment six and has no advective flow through compartment four, configuration two is just the opposite. Originally, both of these configurations had the entire groundflow routed through the benthic compartments (2 & 6). This caused a considerable problem because the sediment residence time within the benthic compartments was so low that the priority pollutant was being flushed out of the system. This problem was corrected by routing a portion of the groundwater into the water column compartments (1 & 5). This increased the sediment residence time and thus, increased the concentration of adsorbed pollutant within the bed sediments. Figure 6 displays the effect of routing various percentages of groundwater through the benthic compartments for both configurations. Compartments two and four were not shown in configuration one because the residence time changed very little. This slight change is a result of no flow being advected through these compartments. On the other hand, compartment six is

CALIBRATION CONFIGURATIONS

CONFIGURATION 1



CONFIGURATION 2



KEY: 1 - COMPARTMENT
1.0 - ADVECTIVE PROPORTION

Figure 5.

EFFECT OF GROUNDWATER ROUTING
ON SEDIMENT RESIDENCE TIMES

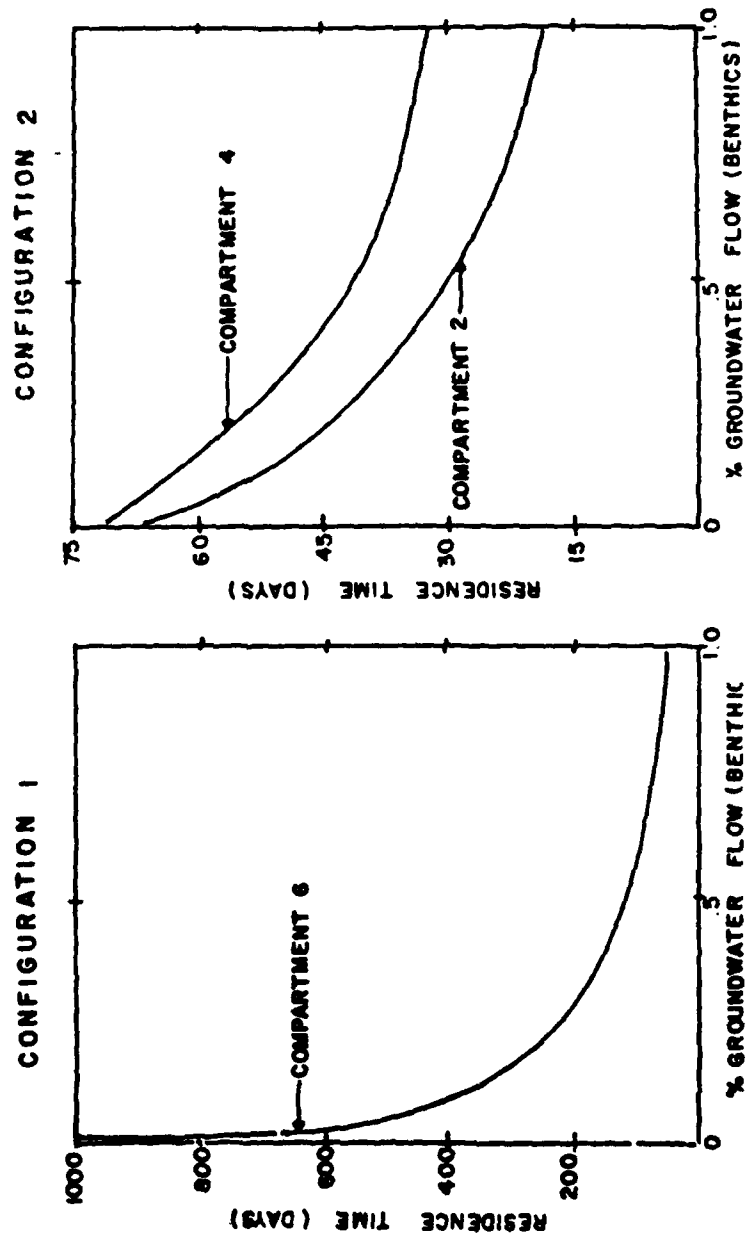


Figure 6.

not shown for configuration two because it also had very little change. Again, this is a result of no flow being advected through compartment six. At this point a decision was made to perform the remaining sensitivity analysis and calibration on configuration two.

The effect of the percent groundwater flow into the benthic compartments for configuration two allowed adjustment of the particulate concentration in the benthic regions (Figure 7). The next parameter adjusted for configuration two was the dispersion coefficient. This parameter was adjusted from 5.00×10^{-5} to 5.00×10^{-8} (meters square/hr) to obtain the relationship between dispersion coefficient and adsorbed concentration in the benthic compartments (Figure 8). The above range for dispersion coefficients did not result from a calculation because the slope of the river bed, the magnitude of the diffusive exchange coefficients for the water column and the interstitial water, and the characteristic length of the gradient were not known. However, a range of possible dispersion coefficients was obtained from Analysis of Fate of Chemicals in Receiving Waters - Phase I (1981, DiToro and St. John).

The trend shown by varying the dispersion coefficient resulted in the sensitivity analysis of a final parameter. This parameter was the K_d and originally it was not to be a calibration variable. The reason behind

EFFECT OF GROUNDWATER ROUTING ON
SEDIMENT CONCENTRATION IN BENTHIC COMPARTMENTS

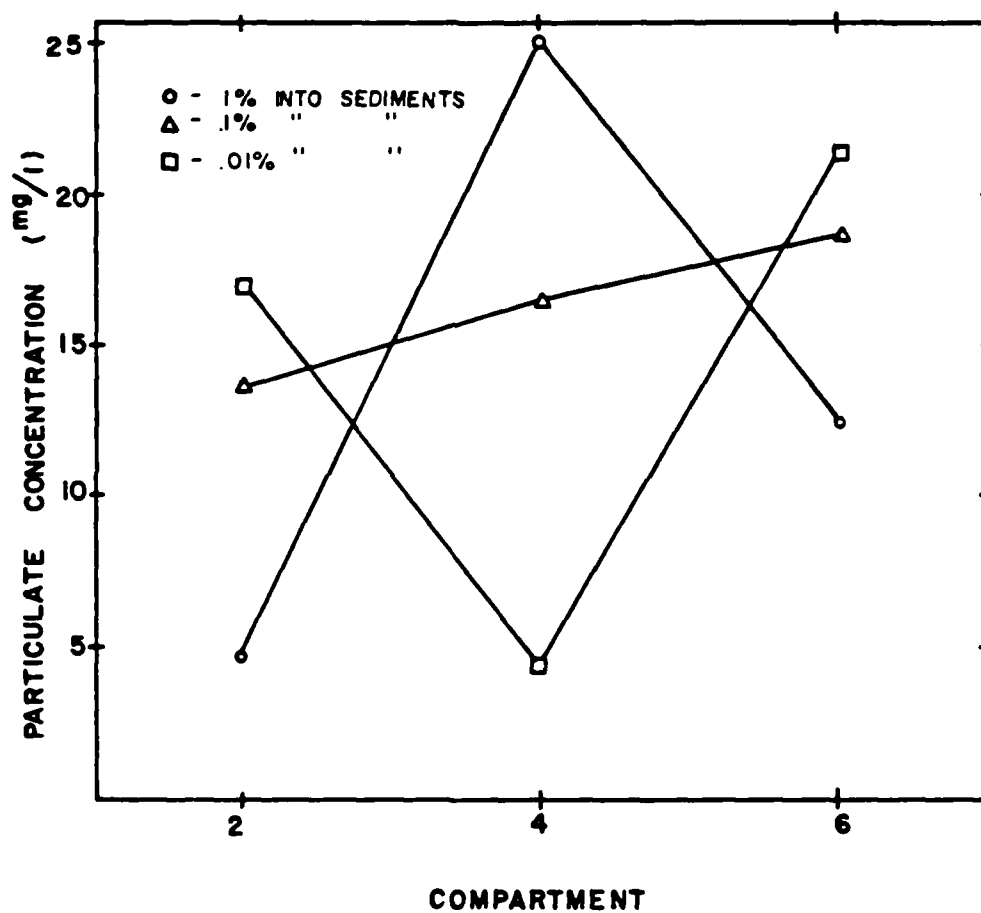


Figure 7.

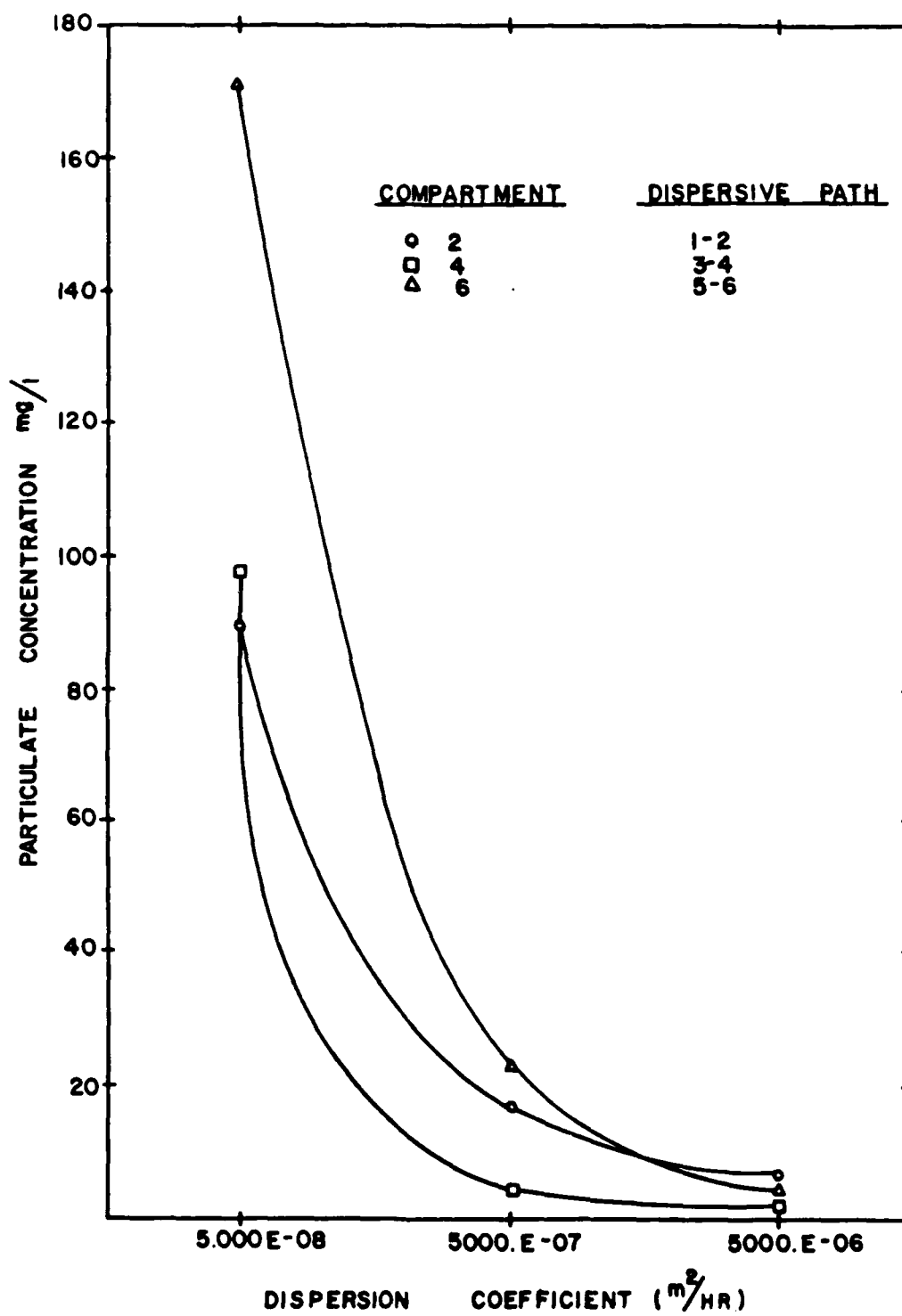
DISPERSION COEFFICIENT VS. CONCENTRATION
IN BENTHIC COMPARTMENTS

Figure 8.

the change stemmed from the inability to achieve the required adsorbed concentration within the benthic compartments. The decision to increase the K_d values from their field-determined values was reasonable considering the accuracy of benthic K_d determinations made in the field. It is very difficult to obtain a sediment sample without entrainment of water from the water column. The aqueous concentration of contaminant within the water column is much lower than that within the bed sediments, and the result would be a dilution. This dilution would result in a K_d value that was too low, and for this reason the K_d parameter has been changed to achieve higher particulate concentrations within the bed sediments. The adjustment of the K_d value and its affect on the benthic compartment adsorbed concentrations are shown in Figure 9.

Another problem was encountered after the calibration of configuration two which resulted in a final adjustment of the advective pathways. The problem was that the total concentration in compartment five was too high, and to reduce this an advective pathway from the benthic compartment (compartment six) was established. The advective flow proportions from compartment six to compartment five were varied in effort to reduce the total concentration in compartment five. The results obtained from varying the advective flow are

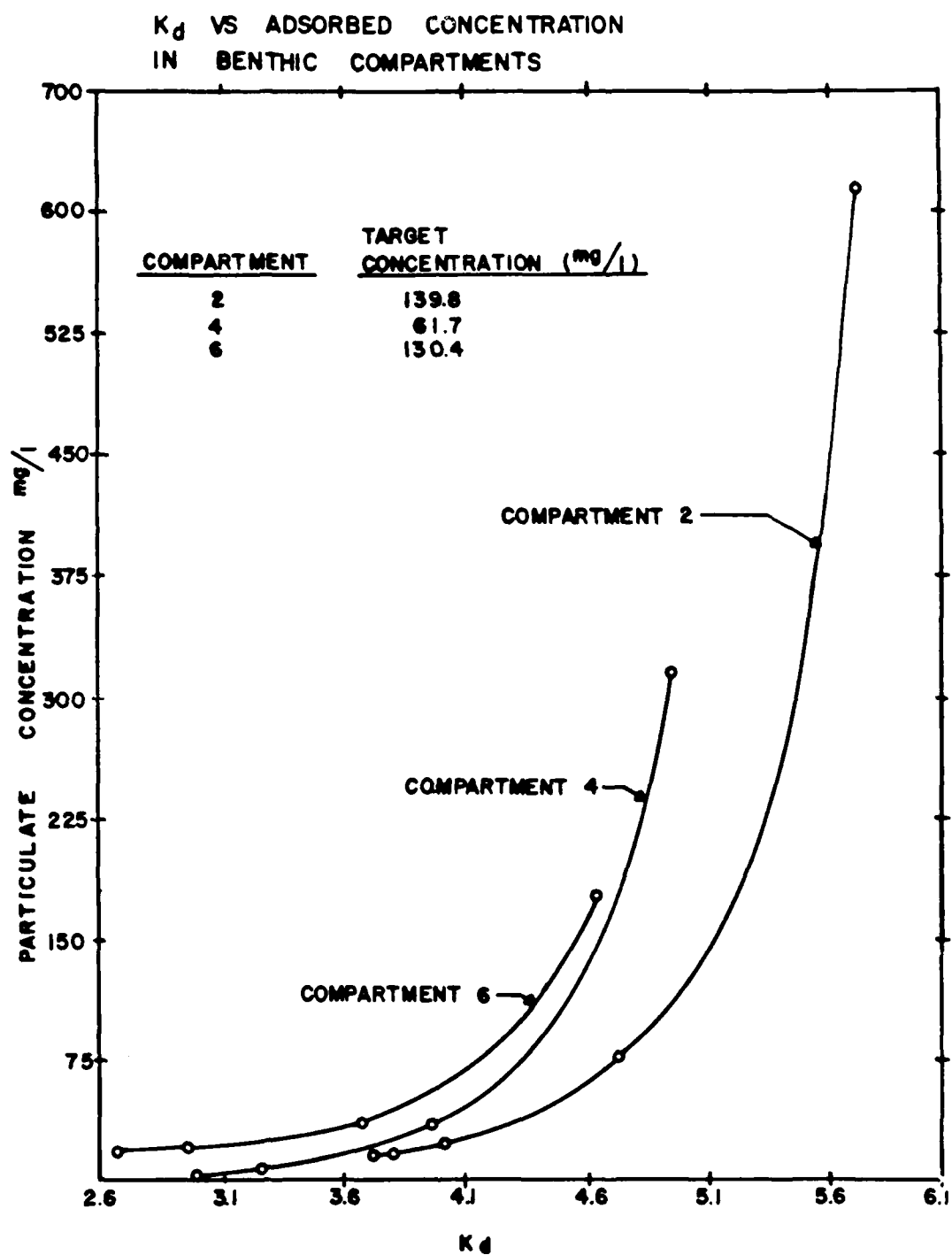


Figure 9.

presented in Figure 10.

The required concentrations for compartment five could not be obtained by varying the advective flow. As a result, a ten compartment configuration was developed. Since the model establishes instantaneous equilibrium, the 6.7 mile compartment was too large and the concentration could not be lowered by adjusting any of the calibration parameters. The final ten compartment configuration is presented in Figure 11. The final configuration was calibrated by adjusting three variables; the percent ground water flow into the benthic compartments (8 & 10), the advective flow between compartments (8 to 7, and 10 to 9), and the K_d value for the benthic compartments.

4.2 Model Results

After a good understanding was achieved for the sensitivity of the calibration parameters, the calibration continued for the ten compartment model. The two models being compared are slightly different, because the incremental flow model utilizes point source loads as incremental loadings to the an existing concentration. This new concentration is then transported downstream. On the other hand, the MEXAMS model establishes instantaneous equilibrium with the point source load, and as a result, the model outputs are mean compartment outputs

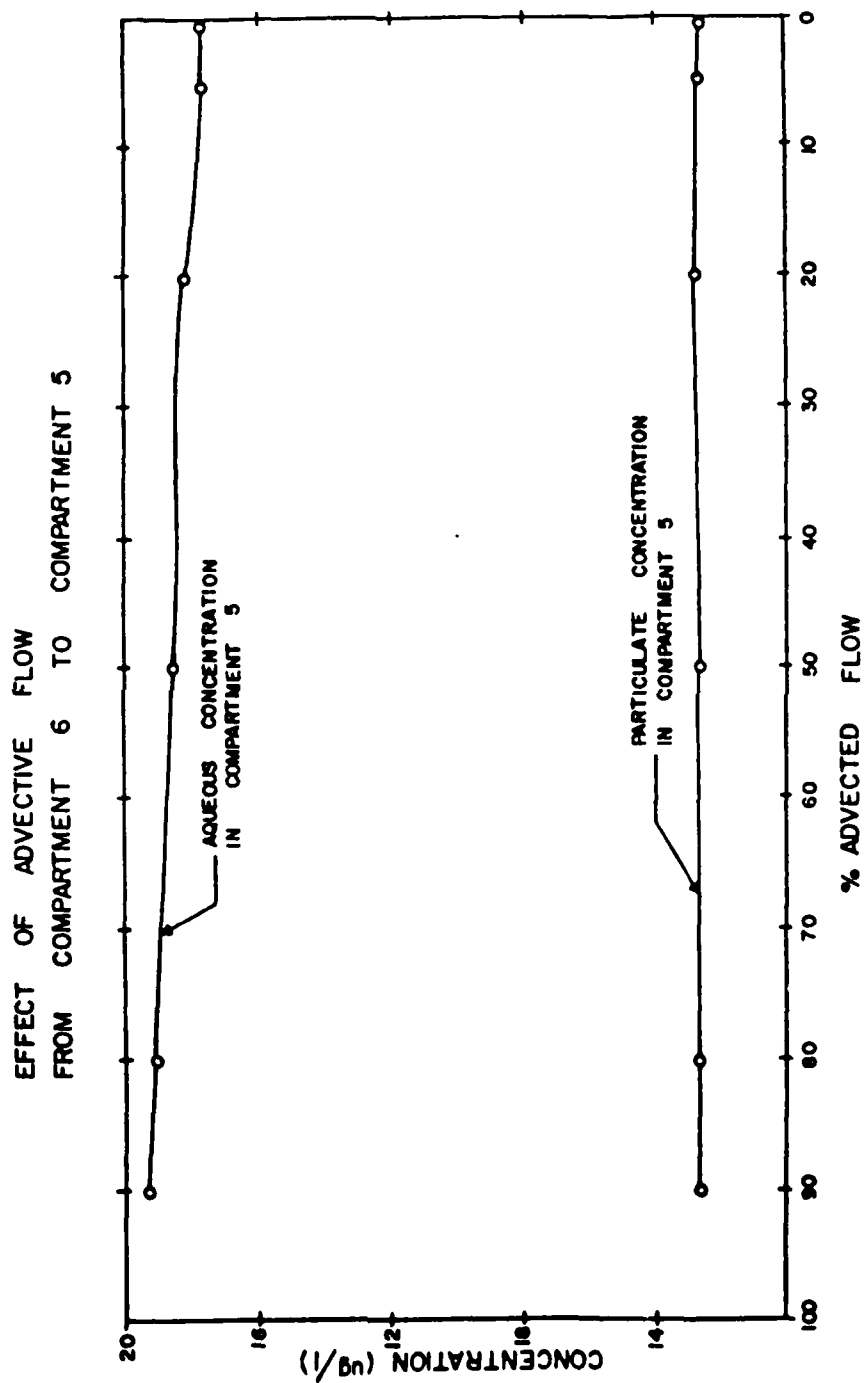
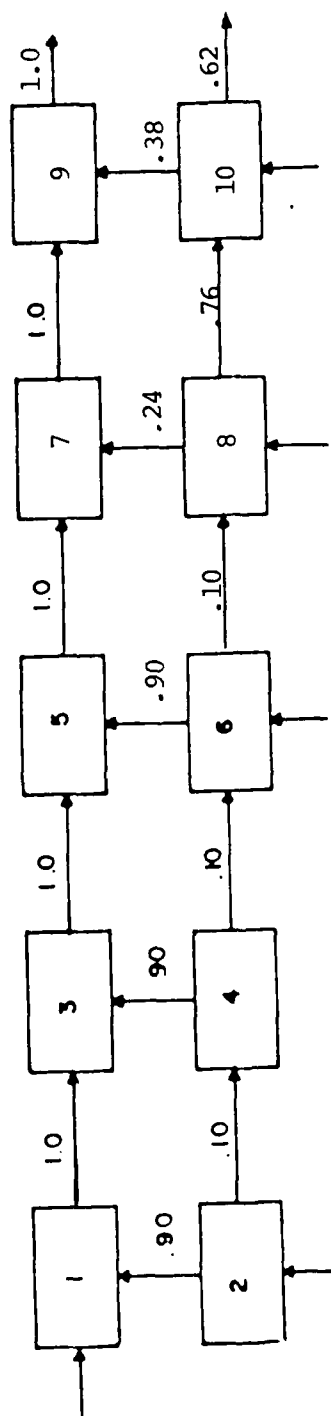


Figure 10.

FINAL CALIBRATION CONFIGURATION



KEY: I - COMPARTMENT #, %
 IO - ADVECTIVE PROPORTION

Figure 11.

and not outputs at various points within the river. Thus, the MEXAMS model will not predict the concentration where a point load enters (Bogue Rd.), and the concentration measured will be higher than predicted. The model calibration was compared to an incremental flow study by Curtis, State of Connecticut, Dept. of Environmental Protection, and laboratory results obtained from samples collected at various sites along the river. The model calibration to particulate concentrations within the benthic compartments was very good. The model calibration to aqueous concentrations in the water column was not as accurate because concentrations in compartments five and six were too high. As a result, compartment five was further divided into smaller compartments. The six compartment model results are presented in Figure 12 and Table 15.

This model was improved by dividing the river segment into smaller compartments. The calibration of compartments five and six into smaller compartments would allow for a greater control of the model calibration. The third segment has been calibrated by splitting compartments five and six into smaller compartments. The calibration results obtained from the final calibration are presented in Figure 13 and Table 16 respectively. As stated previously, three parameters were adjusted to achieve a calibrated model. Table

MODEL CALIBRATION RESULTS

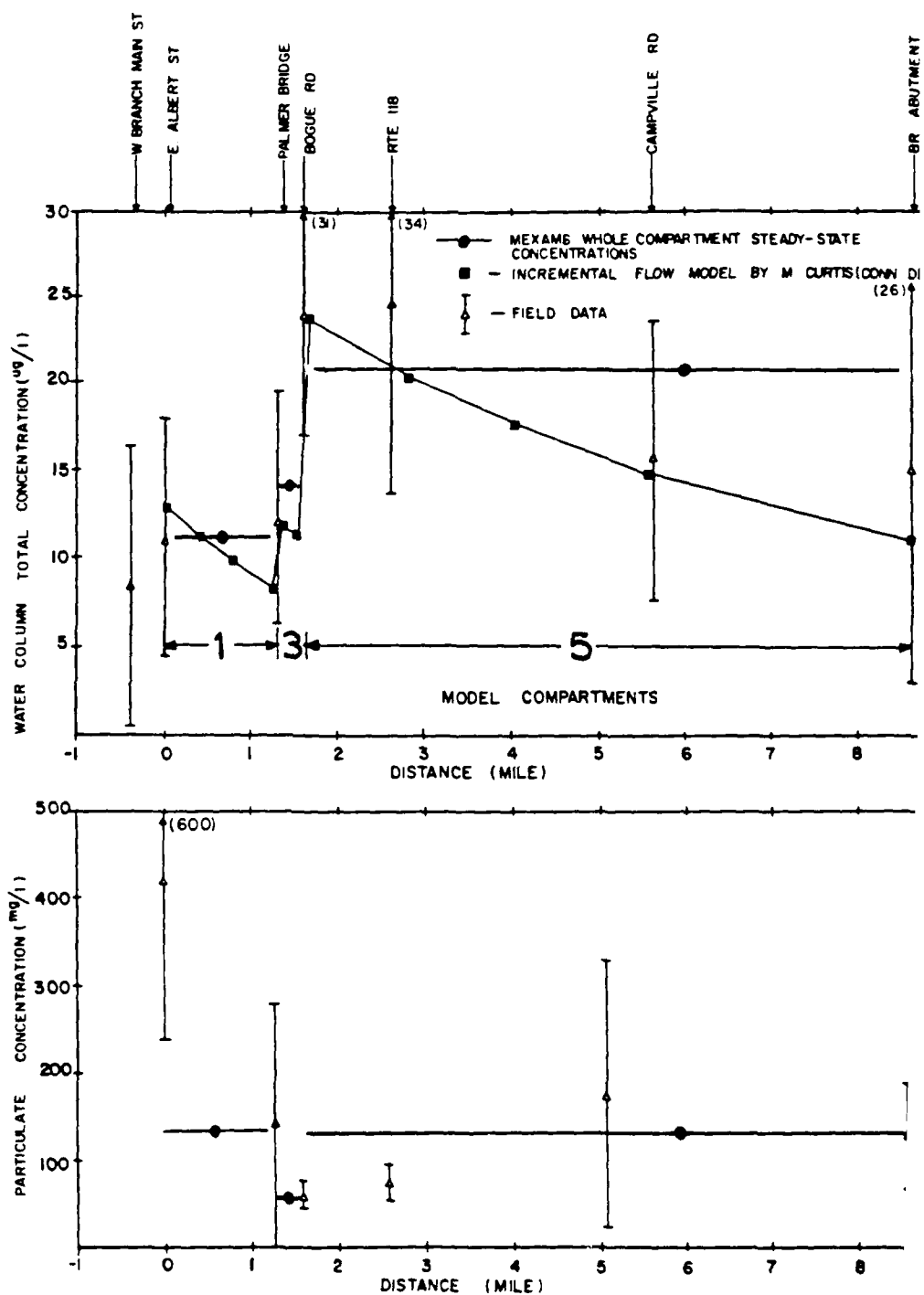


Figure 12.

Table 15
MODEL RESULTS FOR CONFIGURATION 3

Location	Model Compartment	Total		% Diff.	Dissolved *		% Diff.
		Field	Model		Field	Model	
<u>WATER COLUMN ($\mu\text{g/l}$)</u>							
Palmer Br. Rd.	1	12.	11.5	-4.1	9.5	9.1	-4.7
Bogue Rd	3	-----No Segment Data-----			-----No Segment Data-----		
Rte. 118	5	18.3	20.3	+10.9	14.3	17.7	+23.7
Campville Rd.							
Br. Abutment							
<u>BENTHIC REGION (mg/l)</u>							
Palmer Br. Rd.	2	140.	138.	-1.5	140.	138.	-1.5
Bogue Rd.	4	62.	59.	-4.8	62.	59.	-5.0
Rte. 118	6	128.	133.	+3.5	127.	133.	+4.7
Campville Rd.							
Br. Abutment							

* The benthic region is shown as particulate copper in mg/l

MODEL CALIBRATION RESULTS

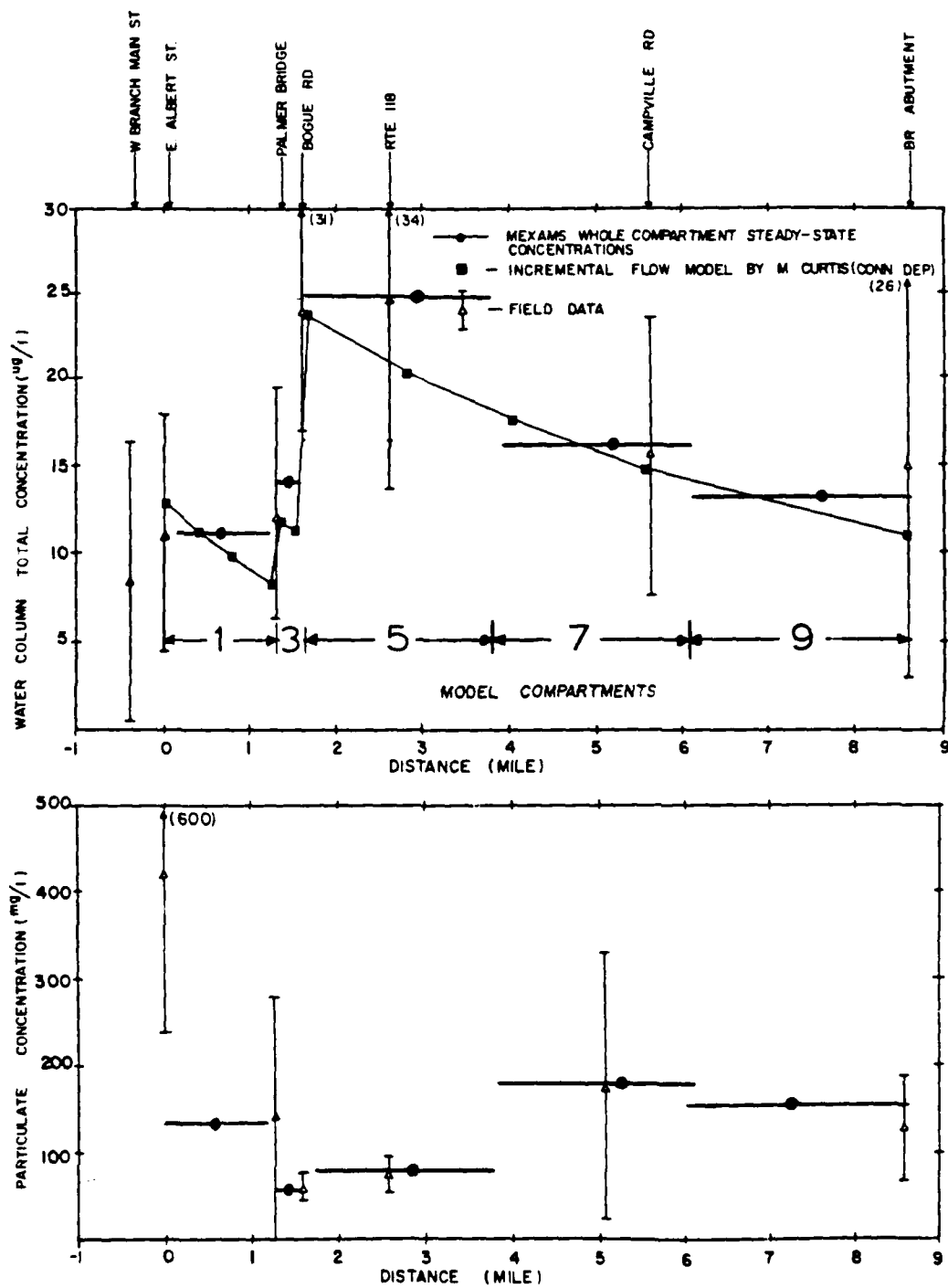


Figure 13.

Table 16
MEXAMS - NAUGATUCK RIVER MODEL RESULTS

LOCATION	MODEL COMPARTMENT	TOTAL COPPER		%	DISSOLVED COPPER		%
		FIELD	MODEL		FIELD	MODEL	
<u>WATER COLUMN (g/l)</u>							
Palmer Br. Rd.	1	12.	11.5	-4.1	9.5	9.1	-4.7
Bogue Rd.	3	-----No Segment Data-----			-----No Segment Data-----		
Rte. 118	5	24.	24.6	+2.5	17.	16.8	-1.2
Campville Rd.	7	16.	16.6	+3.8	14.	14.	0.0
Br. Abutment	9	14.	12.6	-10.0	11.	10.6	3.6
<u>BENTHIC REGION (g/l)</u>							
Palmer Br. Rd.	2	140.	138.	-1.5	140.	138.	-1.5
Bogue Rd.	4	62.	59.	-4.8	62.	59.	-5.0
Rte. 118	6	73.	74.	+1.4	72.	73.	+1.4
Campville Rd.	8	177.	179.	+1.1	176.	178.	+0.6
Br. Abutment and Campville Rd.	10	154.*	150.	-2.6	154.*	150.	-2.6

* The average copper concentration measured at Campville Rd. and the Bridge Abutment was used for comparison (based on model compartmentalization).

Table 17

Comparative Kd Data

Compartment #	Original log Kd	Calibrated log Kd
1	0.30	0.30
2	3.72	5.02
3	-0.25	-0.25
4	2.95	4.20
5	-0.05	-0.05
6	2.67	4.42
7	-0.05	-0.05
8	2.67	5.30
9	-0.05	-0.05
10	2.67	5.17

the original $\log K_d$'s and the final $\log K_d$'s used to obtain the ten compartment calibration. The advective flow paths for the new compartmentalizations were presented in Figure 11, and the percent ground water routed into benthic compartments eight and ten were changed from .01% to .1% and .13%, respectively. The final calibration for the ten compartment model was very accurate, and the concentrations predicted by the model were well within the error bars of the field data.

4.3 Future Loadings

Since the purpose of this report is to illustrate the usefulness of the modeling system, the effect of an increase in metal loading to compartment one was simulated. This increase could be an additional discharger at some point in the future, or an increase in production by an existing discharger. The existing contaminant loading is $1.284 \text{ E-02 } K_d/\text{hr}$ and this was increased to 1.284 E-01 and 1.284 E+00 . The effect of this increased metal loading on both water column and benthic compartments is displayed in Figure 14. This model, however, has some limitations, and they will be discussed next, along with recommendations for solving these drawbacks.

4.4 Limitations and Recommendations

The first limitation encountered dealt with the

EFFECTS OF SIMULATED INCREASED METAL LOADINGS TO COMPARTMENT 1

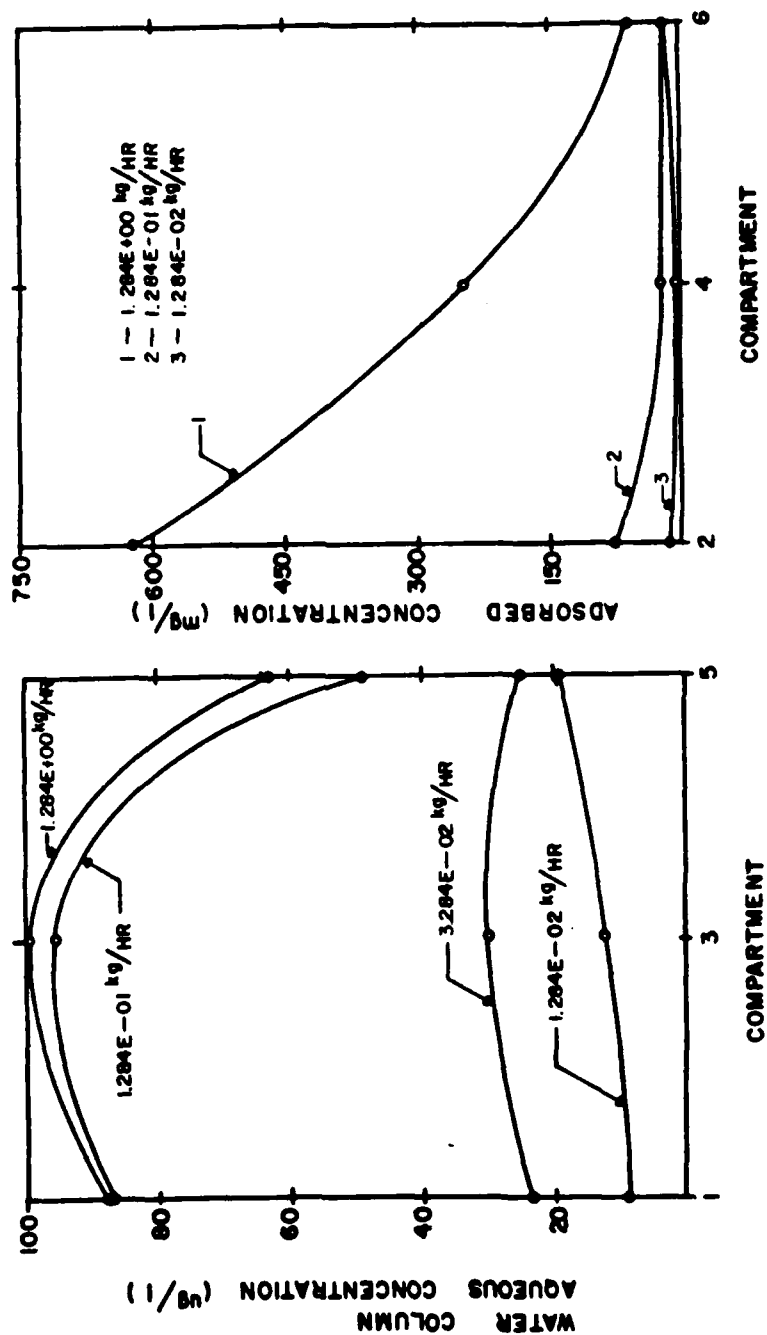


Figure 14.

availability of organic complexes within the thermodynamic data base of MINTEQA2. MINTEQA2 had only a few fulvate and humate complexes. To alleviate this limitation, organic complexes with EDTA were added. A plot was obtained by varying the EDTA concentration. This graph is presented in Figure 15, and the effect of organic complexation with EDTA for three pollutant metals is displayed.

Another limitation to the model occurs during the persistence calculation. The program calculates how long it would take to purify the riverine system, which is incorrect and should instead calculate the time required to achieve a certain concentration. This concentration could correspond to a toxic level for a certain aquatic species, or a desired concentration level, as required by some regulatory agency. This problem can be solved very easily by including an input parameter in the MISP input file. This parameter would correspond to the final concentration desired by the programmer (concentration due to upstream loadings).

To simulate concentrations within the water column prior to pollutant loadings, the point source chemical loads were removed and the model was utilized to obtain concentrations due to upstream loadings only. A comparison of the model results is presented in Figure 16.

EFFECT OF COMPLEXING ORGANIC UPON
ADSORPTION IN COMPARTMENT I.

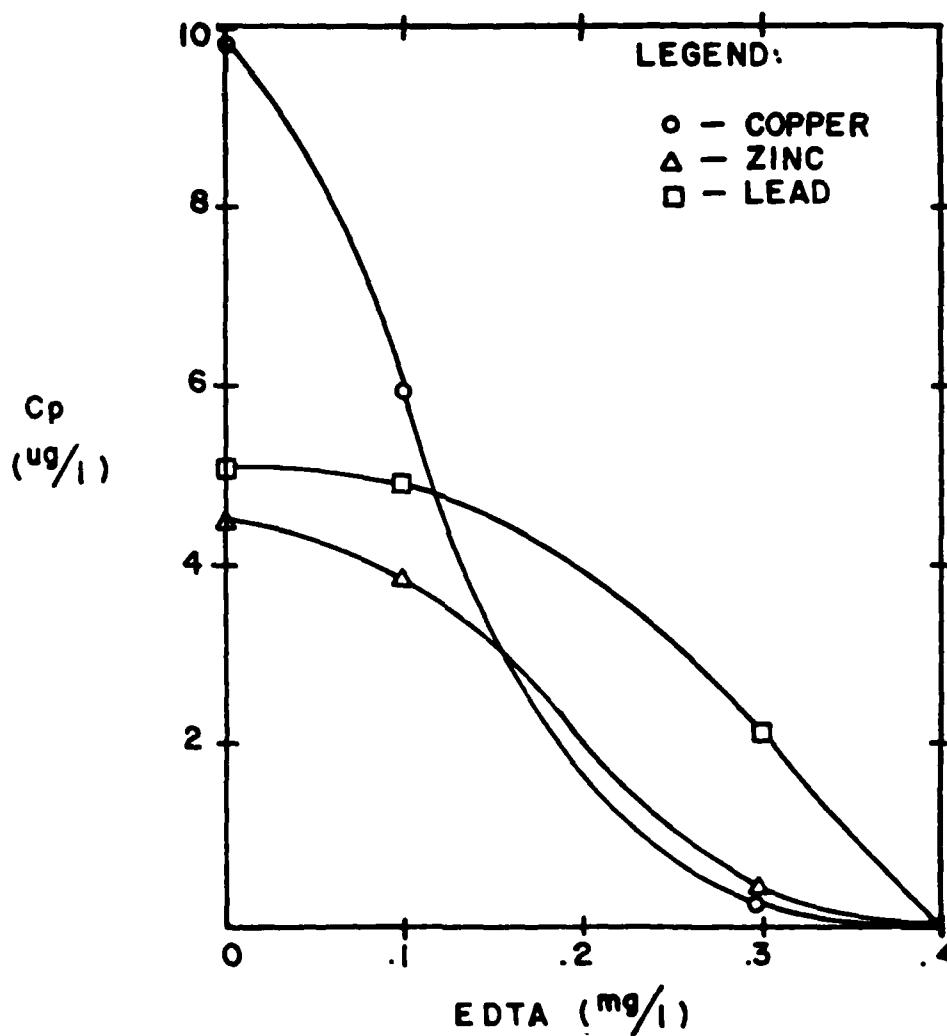


Figure 15

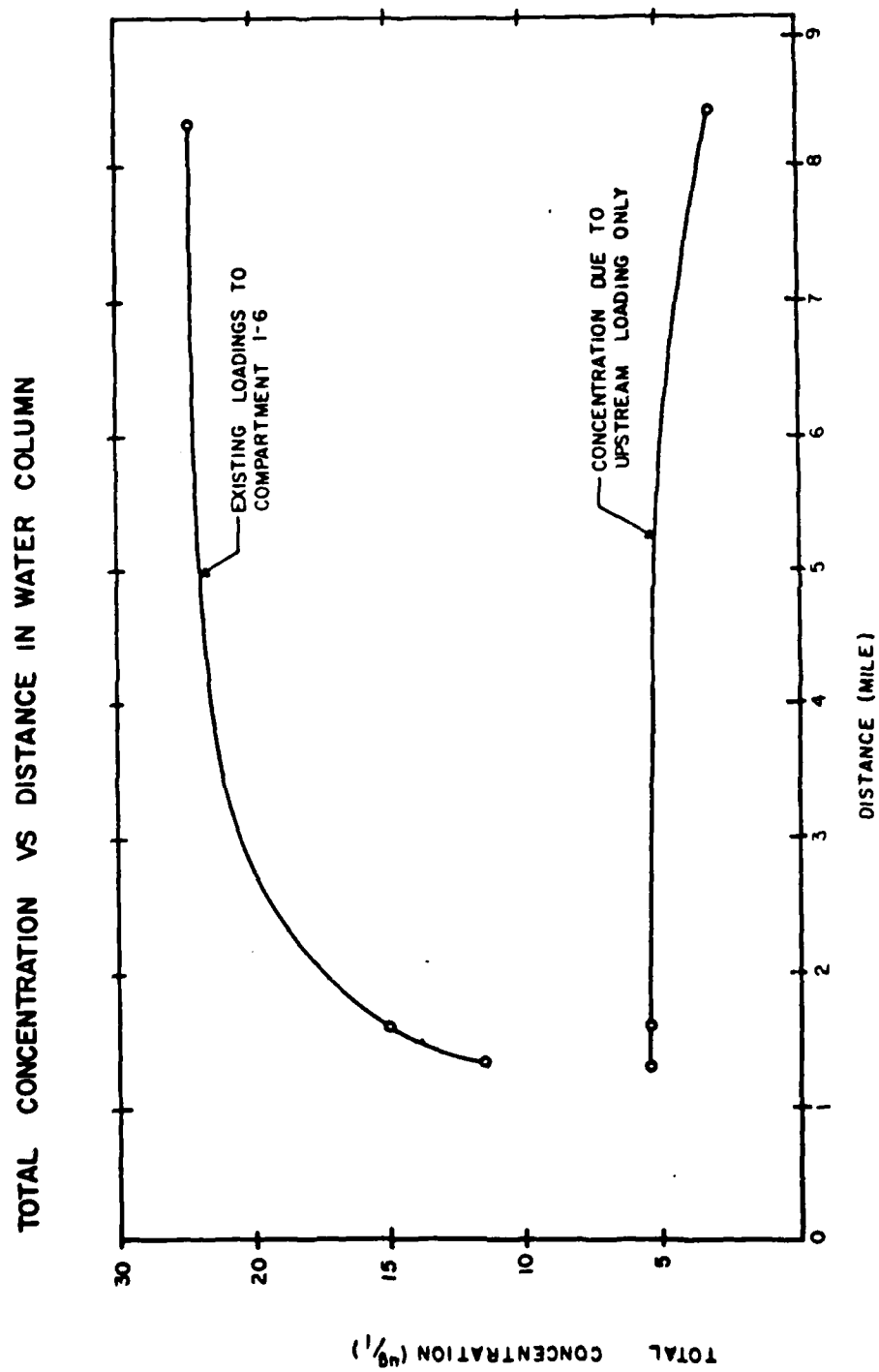


Figure 16

Other limitations include the ability to only run the program with one metal. This allows no competition and is unrealistic for an aquatic ecosystem.. Also, on the subject of competition, when using the K_d "activity" approach, unlimited surface sites are assumed which is unrealistic. It is recommended that an input be established that would limit surface sites and make the model more realistic.

CHAPTER 5

CONCLUSIONS

The behavior of total, dissolved and particulate (adsorbed copper within an 8.3 mile reach of the Naugatuck River (East Albert St. to Thomaston Bridge Abutment) was modeled using the Metals Exposure Assessment Modeling System (MEXAMS). Data provided by the Department of environmental Protection, State of Connecticut concerning mass metal loading, system physical and chemical characteristics was used to calibrate the MEXAMS computer model for this test case.

The most important aspect of this model calibration was the compartmentalization (configuration) of the river reach. The model was initially calibrated for a six compartment configuration. However, the six compartment configuration did not predict adequately (within 10% error) the total and dissolved concentrations in the furthestmost downstream water column compartment (compartment five). The inability for the six compartment model to adequately predict the target (field) concentrations in compartment five was due to the length of the compartment (6.7 miles), and the fact that the model assumes

complete mixing and creates instantaneous equilibrium within each compartment. As a result, a ten compartment configuration was utilized to obtain the final calibration. This configuration was obtained by dividing compartments five (water column) and six (adjacent benthic) into three equal compartments. This division was performed to achieve a greater compartment sensitivity to obtain the target (field measured) concentrations.

This final configuration (based upon the data provided) accurately predicted total, dissolved and particulate concentrations for all water column and benthic compartments. The major parameters adjusted to obtain this final calibration were the percent groundwater routed through the benthic compartments, the percent advected flow from benthic to water column compartments, and the "activity" K_d 's were kept at field determined values. However, the calibration of this model is only the initial phase of accurately modeling this river reach, and model validation to another data set is required.

The validation process could also include a reduction of the following model limitations that were discovered during the calibration process; the need for additional organic complexes within the thermodynamic data base, the ability for the model to simulate more than one priority pollutant metal simultaneously, and the

AD-A152 192

SIMULATION OF METAL FATE AND TRANSPORT IN THE NAUGATUCK 2/2

RIVER (CONNECTICUT) WITH HEXAM5(U) AIR FORCE INST OF
TECH WRIGHT-PATTERSON AFB OH S E STREIFERT 29 NOV 84

UNCLASSIFIED

AFIT/CI/NR-85-21T

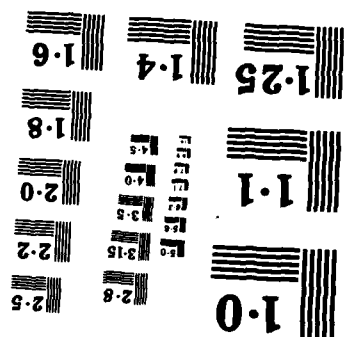
F/G 11/6

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ability for the user to adjust the concentration to be obtained during the system self-purification (persistence calculation). The validation of this model could result in possible future applications and provide additional assistance to the Department of Environmental Protection, State of Connecticut in determining waste discharge allocations for present and future dischargers within this reach of the Naugatuck River.

In conclusion, the results of the study suggest that MEXAMS is a potentially powerful management tool that could be utilized for a variety of environmental problems. Future activity using the model should continue the application to actual field situations so that continued refinement of the model and appropriate modifications are made to promote its use.

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APPENDICES

APPENDIX A

DESCRIPTION OF THE MINTEQ INPUT FILE (Felmy et al., 1983)

This appendix describes how to setup the sample description file for running the VAX and PDP 11/70 versions of MINTEQ. A detailed description of the options available to the user accompanies the file descriptions.

The file is broken into three sections. Each section is separated by a blank line. There should be three and only three blank lines in the sample file. The three sections will be called Basic Input Data, Type Modifications and Insertion of Species. The format field designations for each line are given in parenthesis following the line designation.

Section 1 - Basic Input Data

Line 1 (A80). Alphanumeric description of the sample.

Line 2 (A80). Alphanumeric description of the sample.

Line 3. Water temperature, analytical units and fixed ionic strength designation

The water temperature in degrees Celcius is entered followed by the analytical units. In the VAX free-format version, the temperature and units must be separated by a space and the units enclosed in quote marks. The PDP 11/70 version follows the designated format fields. The analytical unit designations can be either 'PPM', 'MG/l',

'MOL', or 'MEQ/L'. These designations stand for parts per million, milligrams per liter, molality and milli-equivalents per liter, respectively. The fixed ionic strength is entered following the analytical units. In the VAX version there must be a space between the analytical units and the ionic strength. If the ionic strength is not fixed, enter 0.0 following the analytical units.

Line 4[8(I1,IX)]. This line contains the run specific user options.

Option 1. The inorganic carbon input option.

(0) = Total inorganic carbon.

(1) = Total alkalinity.

Option 2. The Debug print option. This is generally used only when modifications have been made to the code and the values of certain arrays must be checked.

(0) = No Debug printout.

(1) = Prints the value of the IDX, C, IDY, GAMMA, C and Y arrays.

(3) = Prints the NNN, NN(1), NN(2) and the IDY, GK, GK1 arrays in subroutine KCORR.

(4) = Prints the IDX, C, IDY, L and GK arrays every iteration in subroutine SOLID and the saturation index for the solid

added to the phase assemblage in sub-routine SOLIDX.

Option 3. The charge balance option.

- (0) = Terminates execution of the program if the initial charge in balance is greater than 30 percent.
- (1) = Does not terminate execution regardless of the initial computed charge imbalance.

Option 4. Considered solids and print option.

- (0) = Do not allow all of the solids in the data base to precipitate or dissolve. The only solids considered will be those entered in the next input section under type changes. Print the problem results after the initial aqueous speciation plus solids problem is solved and after all Type V solids are either in equilibrium or undersaturated.
- (1) = Allow all solids in the data base to precipitate if they become oversaturated. That is, designate all solids in the data base as Type V. Print the problem results only after the entire problem has been solved.
- (2) = Consider all solids in the data base.

Print the problem results after the initial user specified problem has been solved and again after all Type V solids are undersaturated or in equilibrium.

(3) = Consider all solids in the data base.

Print the problem results following the selection of every solid and after all of the solids are in equilibrium or undersaturated.

Option 5. The total number of iterations option.

(0) = Allow 40 iterations.

(1) = Allow 10 iterations.

(2) = Allow 100 iterations.

(3) = Allow 200 iterations.

The 100 or 200 iteration options should be selected if a large number of solids have been designated as considered solids. The ten iteration option is only useful when debugging the program.

Option 6. The pH variation option.

(0) = Do not allow the pH to automatically vary during precipitation/dissolution of solid phases.

(1) = Allow the pH to vary during precipitation/dissolution of solid phases. Not for this option to work all solid phases must

be declared Type V in the initial input.

Option 7. The fixed ionic strength option.

(0) = Allow MINTEQ to compute the ionic strength.

(1) = Fix the ionic strength at the value designated on line 3.

Option 8. The numerical method option.

(0) = Use only Newton-Raphson iteration.

(1) = Use a combination of Newton-Raphson and a modified line search. This option should only be used after consulting the technical manual.

Option 9. Output Option (available only on VAX)

(0) = Do not print on initial listing of the thermodynamic data.

(1) = Print a listing of the thermodynamic data.

Line 5 [I1,1X,4(F6.2,1X)]. This line is for input of adsorption parameters other than the mass total and activity guesses. The first parameter on this line is the adsorption model being used (I1 field). The options are:

0 - No Adsorption

1 - Activity Kd, Langmuir isotherm
Freundlich isotherm

2 - Constant Capacitance Double Layer Model

3 - Triple Layer Site Binding Model.

The next four inputs on this line are:

- Solid Concentration (g/l)
- Specific Surface Area (m²/g)
- Inner Layer Capacitance (F/m²)
- Outer Layer Capacitance (F/m²)

input in this order. None of the last four inputs are required for the activity K_d . The constant capacitance model does not require an outer layer capacitance. The triple layer model requires all four data inputs.

Line 6+ (17,IX,E9.3,IX,F6.2). Component input lines.

There are as many of these lines as there are components. A blank line must follow the last component.

The first specification (17) is the component ID number. Component ID numbers are given in Table 3. The second specification (E9.3 field) is the total analytical mass in the units designated on line 3. The only exception occurs when the constant capacitance of triple layer models are used. In such cases the analytical mass for the surface sites (SOH1 or SOH2 components) must be specified in sites per gram. The third specification on this line is a guess at the log of the component activity. If you leave this field blank the initial estimate of the activity will be the analytical molality divided by 100. Remember you need one line for every

component and a blank line after the last component.

Section 2 - Type Modification

This section is for changing the default species designations. The default type specification have been described in Section 5.

The first line of this section contains the first species type designation and the number of species of this type Format (I3, 1X, I3). The type designations can range from two to six. Then for each species of the entered type, a line is included (I7, 1X, E9.3, 1X, F6.2) designating information for that species. The first field specification is for the species ID number. Species ID numbers for components (Type I) are given in Table 3. All other species ID numbers can be found in the listing of Thermodynamic Data given in the MINTEQ Technical Report. The next two specifications are for the new log K and enthalpy of reaction. These are both optional and if not included the default values in the thermodynamic data base are used. A blank line also ends this section. In the case of Type IV species with an initial mass total (in moles/l) there is an additional input field for the initial mass. This input field follows the input of the enthalpy of reaction resulting in four inputs on one line. The input format for Type IV species is (I7, 1X, E9.3, 1X, F6.2, 1X, E10.3). For examples of necessary species modifications to solve specific problems see

Section 5.

Section 3 - Insertion of Species Not in the Data Base

The first line is for designating the species type and the number of new species of this type (Format I3, 1X, I3). The species type can only range from two to six. The next lines contain the data for the new species of the specified type. There are three lines for each species. The first line of species data is in Format (I7, 1X, A12, 2F10.4, 2F8.3, 3F5.2, F9.4). The format fields correspond to the following data: ID number, name, enthalpy of reaction, log K, minimum log K, maximum log K, charge, Debye-Huckel A parameter, Debye-Huckel B parameter and molecular weight respectively. Only the ID number and log K are absolutely essential. For a description of the Debye-Huckel parameters see the MINTEQ Technical Report. The second line of data is in Format [F5.2, 1X, I1, 1X, 6(F7.3, 1X, I3, 1X)]. The format fields correspond to: carbonate alkalinity factor, number of components in the reaction and the stoichiometry and ID number for up to six components. The carbonate alkalinity factor is only useful if the input inorganic carbon is an alkalinity value. A description of the carbonate alkalinity factor is given in the MINTEQ Technical Report. The third line is in Format [3(F7.3, 1X, I3, 1X)] and is merely a continuation of the component entries for the inserted species. In the VAX version, the third line

is in format [3(F7.3, 1X, I3, 1X), I1, 3(F7.3, 1X, I3, 1X)]. The format field beginning with I1 is for inserting species information into the "B" matrix. Such information is only useful when the component stoichiometries in the mass action expressions are different from the stoichiometries in the mass balance equation. The latter format fields correspond to the number of components in the "B" matrix, stoichiometry of the component and component ID number. This section is also terminated with a blank line.

APPENDIX B

DESCRIPTION OF THE EXAMS INPUT FILE (Burns et al., 1981)

The narrative associated with each database references the format codes listed below.

Code	Format
1	60 characters, left justified. Format: (60A1)
2	Columns 1-5 right justified. Format: (20I5)
3	Column 1, one character/record. The maximum number of records is equal to the number of compartments. Format: (A1)
4	Columns 1-10. Format: (F10.0)
5	Each record contains 8 10-column fields, maximum 2 records per variable. Format: (8F10.0)

	Columns	Compartment
Record 1	1-10	1
	11-20	2
	.	.
	.	.
	.	.
Record 2	1-10	9
(if needed)	11-20	10

6 Five record layout containing 39 values. Four records contain eight 10-column fields; the fifth contains seven. Format: (8F20.0)

	Columns	Value
Record 1	1-10	1
	11-20	2
	.	.
	.	.
	.	.
	71-80	8
Record 2	1-10	9
	.	.
	.	.
	.	.

	71-80	16
.	.	.
.	.	.
Record 5	1-10	33
	.	.
	.	.
	61-70	39

- 7 The number of records is equal to NSPEC1 or NSPEC2 divided by 16. Each record contains 16 five-column fields. For JFRADG and ITOADG use NSPEC1 and for JTURBG and ITURBG use NSPEC2. Each field is right justified. Format: (20I5)

	Columns	<Par>
Record 1	1-5	1
	6-10	2
	.	.
	.	.
	76-80	16
Record 2	1-5	17
	.	.
	.	.
Record n	41-50	29
	51-60	30

- 8 Format: (5(I1,1X))

Column	Flag
1	1
3	2
5	3
7	4
9	5

- 9 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2
21-30	3

10 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2
21-30	3
31-40	4

11 Format: (8F10.0)

Columns	Value
1-10	1
11-20	2

12 The number of records is equal to
NSPEC1 or NSPEC2 divided by eight.
Each record contains eight 10-column
fields. For ADVPRG use NSPEC1 and
for XSTURG, CHARLG, and DSPG use
NSPEC2. Format: (8F10.0)

	Columns	Value
Record 1	1-10	1
	11-20	2
	.	.
	.	.
Record 2	71-80	8
	.	.
	.	.
	.	.
Record n	41-50	29
	51-60	30

Creating or Changing the User Run Information

This sequential file contains chemical name, ecosystem, name, and loads.

Record 1: (CHEM1) Chemical name - three characters maximum. Format: (A3)

Record 2: (EC01) Ecosystem name - three characters maximum. Format: (A3)

Record 3: (NLOAD) Number of Loads. Format: (I5)

Record 4,...,NLOAD+3:(I, STRLDG, NPSLDG, PCPLDG, DRFLDG, IFLLDG) Each of NLOAD records contain the load number and the Ith STRLDG, NPSLDG, PCPLDG, DRFLDG, IFLLDG. Format (I5,5F10.0)

STRLDG - Stream loadings.
NPSLDG - Non-point source loadings.
PCPLDG - Precipitation loadings.
DRFLDG - Drift loadings
IFLLDG - Interflow loadings.

Record 4	Columns	Field
	1-5	I
	6-15	STRLDG(I)
	16-25	NPSLDG(I,
	26-35	PCPLDG(I)
	36-45	DRFLDG(I)
	46-55	IFLLDG(I)

Creating or Changing the Environment Database

The compartment parameter data are located in the following sequential record layout. (The format code list provides detailed format specifications.)

- Record: (SYSTYP) Ecosystem name, maximum 60 characters
Format: 1
- Record: (KOUNT) Number of compartments, maximum number of compartments is NPX, which is fixed for a particular installation.
Format: 2
- Record: (TYPEE) The next KOUNT records each contain a one character compartment code, KOUNT the number of compartments.
Format: 3
- Record: (LATG) Ecosystem latitude, columns 1-10, degrees and seconds as whole number and decimal fraction, e.g. 10.15.
Format: 4
- Record: (WINDG) Wind velocity per compartment, eight per record. Format: 5
- Record: (VOLG) Total environmental volume per compartment. Format: 5
- Record: (AREAG) Area of each ecosystem compartment.
Format: 5
- Record: (DEPTHG) Average depth of each compartment.
Format: 5
- Record: (STDLOG) Stream flow entering ecosystem compartments. Format: 5
- Record: (STSEDG) Stream-born sediment load entering ecosystem compartments. Format: 5
- Record: (NPSFLG) Non-point-source water flow entering ecosystem compartments. Format: 5
- Record: (NPSEDG) Non-point-source sediment loads entering ecosystem compartments. Format: 5
- Record: (INTFLG) Interflow (groundwater seepage) entering each ecosystem compartment.

Format: 5

- Record: (RAING) Average rainfall in geographic area of system. Columns 1-10. Format: 4
- Record: (CLOUDG) Average cloudiness in tenths of full sky cover. Columns 1-10. Format: 4
- Record: (WLAMG) Temporally averaged spectral irradiance immediately below the water surface. This is five record layout containing 39 values, ten columns per value, eight values per record. Format: 6
- Record: (DFACG) Distribution function (optical path) for each compartment. Format: 5
- Record: (EVAPG) Evaporative water losses from ecosystem compartments. Format: 5
- Record: (SDCHRG) For water column compartments the suspended sediment concentration; for benthic sediment compartments the bulk density of the bottom sediment. Format: 5
- Record: (PCTWAG) Percent water in bottom sediments of benthic compartments. Elements corresponding to water column compartments are not used (dummy values). Format: 5
- Record: (NSPEC1) Number of active advective transport pathways. Format: 2
- Record: (JFRADG) Source compartment (J) for advective flow. Format: 7
- Record: (ITOADG) Receiving compartment (I) for advective flow. Format: 7
- Record: (ADVPRG) Proportion of total advective flow from compartment J that flows to compartment I. Format: 12
- Record: (NSPEC2) Number of active dispersive transport pathways. Format: 2
- Record: (JTURBG) Source compartment for dispersive flow. Format: 7
- Record: (ITURBG) Receiving compartment for dispersive flow. Format: 7

Record: (XSTURG) Cross-sectional areas for dispersive exchanges. Format: 12

Record: (CHARLG) Characteristic length of dispersive exchange pairings. Format: 12

Record: (DSPG) Eddy dispersion coefficients for dispersive exchange pairings. Format 12

Record: (FROCG) Organic carbon content of compartment sediments. Format: 5

Record: (CECG) Cation exchange capacity of sediments in each compartment. Format: 5

Record: (AECG) Anion exchange capacity of sediments in each compartment. Format: 5

Record: (TCELG) Average temperature of ecosystem compartments. Format: 5

Record: (PHG) Negative value of log of temporal average of $[H^+]$ concentration for each compartment. Format: 5

Record: (POHG) Negative value of log of temporally averaged $[OH^-]$ concentration for each compartment. Format: 5

Record: (OXRADG) Molar concentration of environmental oxidants in each ecosystem compartment. Format: 5

Record: (BIOMSG) Total actively sorbing biomass in each compartment. Format: 5

Record: (PLRAG) Planktonic fraction of total biomass in each compartment. Format: 5

Record: (BIOTMG) Biotemperature in each compartment. Format: 5

Record: (BACTOG) Bacterial population density in each compartment. Format: 5

Record: (ACBAXG) Proportion of bacterial population that actively degrades toxicant. Format: 5

Record: (K02G) Rearation parameter in each compartment. Format: 5

- Record: (CMPETG) Single-valued zenith light extinction coefficient for water columns, dummy variable for benthic compartments. Format: 5
- Record: (DOCG) Dissolved organic carbon concentration in water column compartments, dummy variable in benthic compartments. Format: 5
- Record: (CHLG) Concentration of chlorophyll and chlorophyll-like pigments in water column compartments, dummy variable in benthic compartments. Format: 5

APPENDIX C

MINTEQ Output

9912310	SON-CU	1.535E-07	1.535E-07	-6.81385	1.000697	200	0
3307320	H504 -	1.412E-09	1.330E-09	-6.87626	941922	2.010	4.910
3305800	H2P04 -	2.317E-06	1.828E-06	-5.73812	788717	12.449	-3.530
3305801	H2P04 -	2.262E-06	2.132E-06	-5.67112	942758	19.579	-4.520
3300020	OH -	1.474E-07	1.387E-07	-6.85803	940954	-13.972	13.345
3307700	H3104 -	1.494E-07	1.407E-07	-6.85183	941447	-9.903	8.935
3307701	H2104 -	5.044E-12	3.984E-12	-11.39986	789951	-21.514	28.714
3300900	H2803 -	1.132E-08	1.064E-08	-7.97305	939974	-9.214	3.224
4603300	PHO3 *	2.661E-09	2.511E-09	-9.60007	943747	-1.739	15.935
4601401	PHO3 *	3.622E-09	3.165E-09	-8.52368	943747	-1.739	15.935
4601401	PHO3 *	3.622E-09	3.165E-09	-8.52368	943747	-1.739	15.935
4605800	PHO4 -	5.715E-06	5.725E-06	-5.24936	941421	-2.456	-1.456
4605801	PHO4 -	5.183E-09	4.866E-09	-8.31105	1.000697	2.250	1.399
4605802	PHO4 *	8.157E-09	7.690E-09	-8.11405	942758	6.615	3.100
1503300	CAH3 *	1.512E-07	1.512E-07	-6.82005	1.000697	21.092	-1.120
1501400	CAH3 *	1.409E-09	1.329E-09	-8.87633	943302	15.220	-2.230
1501401	CAH3 *	1.944E-06	1.834E-06	-5.73669	943302	-12.573	14.535
1507320	CA504 AQ	1.624E-07	1.625E-07	-6.78917	1.000697	11.370	1.780
1505800	CAHPO4 AQ	1.469E-05	1.470E-05	-4.83263	1.000697	3.152	4.030
1505801	CAHPO4 -	3.822E-07	3.825E-07	-6.41742	1.000697	2.309	1.470
1505802	CAH2PO4 *	1.325E-08	1.249E-08	-7.90342	1.000697	15.085	-2.230
3001400	MAHCO3 -	2.504E-08	2.078E-08	-7.08242	942758	0.485	3.100
3001401	MAHCO3 -	4.555E-09	4.235E-09	-6.81607	942758	20.966	-1.120
3005800	MAHPO4 -	7.775E-07	7.330E-07	-6.69597	1.000697	10.086	8.911
3005801	MAHPO4 -	2.923E-09	2.756E-09	-6.13492	942758	10.086	8.911
4107320	VS04 -	1.046E-07	9.654E-08	-8.55971	942758	12.662	1.120
4107800	KHP04 -	2.032E-10	2.670E-10	-7.00596	942758	8.72	2.250
2813300	FEH3 *	8.526E-10	6.724E-10	-9.17236	942758	12.666	0
2815800	FEHPO4 *	3.973E-15	3.746E-15	-14.42645	788717	-2.087	10.399
2817320	FE504 *	1.259E-14	1.187E-14	-13.92566	942758	17.806	-7.300
2811800	FECL2 *	2.912E-16	2.257E-16	-15.63883	942389	3.946	3.910
2811801	FECL2 *	1.098E-16	1.034E-16	-17.98333	788717	1.593	5.600
2811802	FECL3 AQ	1.042E-22	1.034E-22	-21.98183	942389	2.156	0
2813301	FEH2 *	3.260E-06	3.073E-06	-5.51239	1.000697	1.130	0
2813302	FEH3 AQ	7.991E-07	4.984E-07	-5.18441	942758	-3.644	0
2813303	FEHPO4 *	7.244E-08	6.801E-08	-6.18841	942758	-3.644	0
2813304	FEHPO4 *	5.844E-15	5.301E-15	-14.36645	788991	25.082	0
2817321	FE15041.2	7.537E-17	7.096E-17	-16.14899	941520	5.446	4.600
2813304	FE210H12.4	3.192E-17	1.217E-17	-16.91472	381308	-2.531	13.500
2813305	FE310H14.5	3.523E-20	7.814E-21	-20.10710	221689	-5.646	14.300
4701801	HNCL *	5.497E-13	5.501E-13	-12.25558	942389	.633	0
4701802	HNCL3 -	2.653E-16	2.500E-16	-15.60208	1.000697	.041	0
4703300	HNH3 -	1.054E-10	1.747E-10	-5.75760	942389	-10.564	14.399
4703301	HNH313 -1	2.178E-20	2.053E-20	-19.68766	942389	-34.774	0
4707320	HNH504 AQ	1.694E-08	1.689E-08	-7.77090	1.000697	2.260	2.170
4704920	HNH6312AQ	2.201E-14	2.263E-14	-12.94534	1.000697	11.600	-1.396
2311400	CUHCO3	4.515E-08	4.515E-08	-6.80733	1.000697	9.975	0
2311401	CUHCO3AQ	1.537E-07	1.536E-07	-6.80733	1.000697	6.730	0
2311800	CUCL *	7.479E-11	5.877E-11	-10.23081	788913	9.975	0
2311801	CUCL2 AQ	2.792E-10	2.628E-10	-9.58025	941447	4.56	6.650
2311802	CUCL2 AQ	1.422E-13	1.423E-13	-12.84086	1.000697	160	10.560
2311902	CUCL3 -	5.406E-19	5.089E-19	-18.29336	941447	-2.264	13.690
2311003	CUCL4 -	3.360E-24	2.571E-24	-23.58966	788717	-4.487	17.780
2313300	CINH *	1.100E-01	1.117E-08	-7.87188	941117	-7.871	0

9501800	ZNCL *	3	813E-10	3	590E-10	-9.44492	941447	.456	7.790
9501801	ZNCL2 AQ	4	787E-13	3	789E-13	-12.42142	1.000697	.450	6.500
9501802	ZNCL3 -	4	553E-16	4	286E-16	-15.36792	941447	.500	5.500
9501303	ZNCL4 -2	2	739E-19	2	161E-19	-10.66942	787117	.302	10.360
9503300	ZNOM +	2	127E-09	2	002E-09	-8.69845	941520	-6.934	13.399
9503301	ZNOM12 AQ	3	179E-10	3	181E-10	-9.49747	1.000697	-16.899	0
9503302	ZNOM13 -	1	475E-14	1	388E-14	-13.85750	941520	-26.373	0
9503303	ZNOM14 -2	3	865E-20	3	037E-20	-19.51753	941520	-41.094	0
9501804	ZNOMCL AQ	6	092E-11	6	096E-11	-10.21495	1.000697	-7.480	0
9507320	ZNSO4 AQ	5	861E-08	5	863E-08	-8.23175	1.000697	2.370	1.360
9501400	ZNOM12-2	1	147E-11	9	014E-12	-11.04507	785813	3.385	0
9501401	ZNOM13	7	803E-09	7	53E-09	-8.14190	941520	12.426	0
9501402	ZNOM14	6	466E-11	5	055E-11	-10.29536	1.000697	5.300	0
6001800	PRCL *	4	307E-11	4	055E-11	-10.39190	941520	1.232	0
6001801	PRCL2 AQ	6	475E-14	6	479E-14	-13.18849	1.000697	1.630	4.380
6001802	PRCL3 -	5	498E-17	5	176E-17	-16.28599	941520	1.800	1.080
6001400	PRCL4 -2	3	186E-20	2	503E-20	-19.60119	785813	1.225	2.170
6003300	PRCL5 -2	5	038E-12	3	939E-12	-11.40245	785813	1.485	3.530
6003301	PRCL6 -2	2	286E-10	2	719E-10	-9.56552	941520	10.745	0
6003302	PRCL7 -2	1	139E-12	1	460E-12	-11.83534	1.000697	-17.120	0
6003303	PRCL8 -2	2	458E-16	2	314E-16	-15.63557	941520	-26.034	0
6003304	PRCL9 *	1	135E-17	6	52E-18	-17.21101	941520	-6.124	0
6003320	PRCL10	1	705E-12	1	62E-12	-11.78482	941520	1.196	0
6003304	PRCL11	1	074E-10	1	074E-10	-9.06882	941520	2.770	0
6003305	PRCL12	6	282E-23	4	937E-23	-22.30856	785813	-27.740	26.540
6003321	PRCL13	5	257E-09	5	261E-09	-8.27897	1.000697	7.240	0
6003322	PRCL14	9	334E-21	7	335E-21	-20.13460	785813	-39.594	0
6001402	PRCL15	3	691E-13	1	066E-13	-12.97214	941520	3.575	0
3301400	PRCL16	4	917E-04	4	693E-04	-9.45897	941520	13.226	0
3301401	PRCL17	7	500E-05	7	505E-05	-3.33392	941520	10.355	-3.617
9501800	PRCL18	7	613E-08	7	613E-08	-4.12466	1.000697	16.679	-2.247
9501800	PRCL19	2	100E-08	2	160E-08	-7.11042	1.000000	.240	0
9501800	PRCL20	2	100E-08	2	160E-08	-7.60349	1.000000	1.330	0

0 SPECIES TYPE III - FIXED SOLIDS

0 ID NAME CALC MVL LOG MVL NEW LOOK DH

2 H2O -9.247E-06 -5.034 0

991 SOH2 -1.751E-07 -6.757 0

990 SOH1 -7.613E-08 -7.118 0

330 H -6.425E-04 -3.192 7.140 0

0 SPECIES TYPE VI - SPECIES NOT CONSIDERED

0 ID NAME CALC MVL LOG MVL NEW LOOK DH

3301403 CO2(GAS) 2.273E-03 -2.643 13.160

0 PERCENTAGE DISTRIBUTION OF COMPONENTS

OCA

96.5 PERCENT BOUND IN SPECIES 150 CA

2.9 PERCENT BOUND IN SPECIES 1507320 CASO4 AQ

0

0

96.8 PERCENT BOUND IN SPECIES 460 MG

2.6 PERCENT BOUND IN SPECIES 4607320 IN704 AQ

0

OS04	92 6	PERCENT BOUND IN SPECIES	732	S04
	1 4	PERCENT BOUND IN SPECIES	4607320	M0504 AQ
0	5 6	PERCENT BOUND IN SPECIES	1507320	CA504 AQ
OCL	100 0	PERCENT BOUND IN SPECIES	180	CL
0				
OH0803	99 2	PERCENT BOUND IN SPECIES	90	H3803
0				
OK	99 9	PERCENT BOUND IN SPECIES	410	K
0				
OP04	44 9	PERCENT BOUND IN SPECIES	3305800	HP01 -2
	43 8	PERCENT BOUND IN SPECIES	3305801	H2P04 -
	2 9	PERCENT BOUND IN SPECIES	4605802	INHP04 AQ
	7 4	PERCENT BOUND IN SPECIES	1505800	CAHP04 AQ
0				
OH45104	99 8	PERCENT BOUND IN SPECIES	770	H45104
0				
OCU+2	14 3	PERCENT BOUND IN SPECIES	231	CU+2
	17 9	PERCENT BOUND IN SPECIES	9812310	SUH-CU
	18 2	PERCENT BOUND IN SPECIES	2311400	CU03 AQ
	1 7	PERCENT BOUND IN SPECIES	2313300	CU0H *
	44 9	PERCENT BOUND IN SPECIES	2313301	CU0H12 AQ
	2 6	PERCENT BOUND IN SPECIES	2311402	CU1C03 *
0				
OZN	62 4	PERCENT BOUND IN SPECIES	950	ZN
	2 2	PERCENT BOUND IN SPECIES	950740	ZN004 AQ
	2 9	PERCENT BOUND IN SPECIES	950140	ZN003 *
	3 0	PERCENT BOUND IN SPECIES	9501401	ZN003 AQ
	28 4	PERCENT BOUND IN SPECIES	9909500	SUH-ZN
0				
OH03	100 0	PERCENT BOUND IN SPECIES	492	NO3
0				
OHN+2	96 3	PERCENT BOUND IN SPECIES	470	HN+2
	2 6	PERCENT BOUND IN SPECIES	4707320	HN504 AQ
0				
OFE+3	85 1	PERCENT BOUND IN SPECIES	2813301	FE0H2 *
	13 0	PERCENT BOUND IN SPECIES	2813302	FE0H3 AQ
	1 9	PERCENT BOUND IN SPECIES	2813303	FE0H4 *
0				
OPB	4 4	PERCENT BOUND IN SPECIES	600	PB
	16 2	PERCENT BOUND IN SPECIES	6001401	PH003 AQ
	11 3	PERCENT BOUND IN SPECIES	6001402	PH003 *
	74 6	PERCENT BOUND IN SPECIES	9910000	SUH-IN
0				

6028101 JAROSITE H	-2 014	12 100	0	0	0	-14 114	55 150
8450300 MAGADITE	-10 113	-14 300	0	0	0	-24 413	0
3028101 MAGNETITE	8 209	-6 386	0	0	0	14 395	0
5036001 MAGNESITE	-2 430	8 029	8 279	7 779	0	-10 479	6 169
6050001 MIPABILITE	-8 833	1 114	0	0	0	-9 947	-18 987
3050300 NATRON	-11 436	1 311	0	0	0	-12 747	-15 745
5046003 MESUEPHONITE	-4 858	5 021	5 133	4 546	0	-10 479	5 789
2077002 QUARTZ	-0 057	4 006	0	0	0	-4 063	-6 220
8646001 SEMTOLITE (A)	-10 321	-18 780	0	0	0	8 459	0
5050001 SIODIA (B)	-1 045	3 018	0	0	0	-4 063	-4 440
2077003 STRENGITE	-1 351	2 010	0	0	0	-4 063	-3 910
7028100 STRENGITE	1 333	26 400	29 122	26 235	0	-25 030	2 030
8646002 TALC	-8 335	-23 055	-18 988	-23 088	0	15 720	35 505
6050002 THEOPHYTE	-9 768	1 779	0	0	0	-9 947	2 802
3050001 THEOPHYTE	-12 872	1 125	0	0	0	-12 747	2 802
8215001 TREMOLITE	-15 706	-56 346	0	0	0	40 840	96 615
2047003 PYROCHROITE	-7 116	-15 008	0	-15 381	0	7 972	22 590
5047000 RHODOCROSITE	-2 421	10 410	11 019	9 993	0	-12 331	2 079
4147000 RHODOCROSITE	-15 011	2 710	0	0	0	-12 301	-17 380
6047000 RHODOCROSITE	-12 700	2 369	0	0	0	-10 031	15 480
7017000 RHODOCROSITE	-16 944	23 827	0	0	0	-40 311	-2 120
4123100 RHODOCROSITE	-3 730	9 650	0	-4 450	0	-13 537	12 320
2023100 RHODOCROSITE	-3 907	9 610	0	0	0	-13 537	0
4123101 RHODOCROSITE	-2 944	9 840	0	-7 200	0	4 396	15 290
5123101 RHODOCROSITE	-2 944	9 840	0	-7 200	0	4 396	15 290
6023100 RHODOCROSITE	-5 317	-9 240	0	-9 310	0	3 285	17 350
6023101 RHODOCROSITE	-4 495	-8 290	0	-8 900	0	3 285	0
6023102 RHODOCROSITE	-4 279	-15 340	-15 150	-15 500	0	11 061	39 610
2023101 RHODOCROSITE	-5 729	-16 790	0	-17 400	0	11 061	39 610
6023103 RHODOCROSITE	-3 354	-7 520	-7 350	-7 890	0	7 266	15 240
7023100 RHODOCROSITE	-6 080	36 850	0	36 900	0	-3 471	35 575
7023101 RHODOCROSITE	-13 747	-3 010	-2 630	-3 420	0	-42 930	0
6023104 RHODOCROSITE	-8 097	2 640	2 960	2 135	0	-10 737	18 140
6023105 RHODOCROSITE	-13 297	-6 500	0	0	0	-10 737	-1 440
3023100 RHODOCROSITE	-19 901	7 070	-5 350	-7 060	0	3 203	6 960
4195000 RHODOCROSITE	-3 402	10 000	10 810	9 820	0	-12 871	17 480
5050000 RHODOCROSITE	-3 142	10 250	0	-12 480	0	-13 402	4 380
2095000 RHODOCROSITE	-5 048	-12 250	0	0	0	7 402	0
2095001 RHODOCROSITE	-4 798	-12 200	0	0	0	7 402	0
2095002 RHODOCROSITE	-4 348	-11 750	-11 320	-11 890	0	7 402	0
2095003 RHODOCROSITE	-4 308	-11 710	-11 190	-11 840	0	7 402	0
2095004 RHODOCROSITE	-4 098	-11 500	-10 950	-11 620	0	7 402	0
4195001 RHODOCROSITE	-10 533	-15 200	0	0	0	4 667	0
4195002 RHODOCROSITE	-21 703	-36 500	0	0	0	16 735	0
6023100 RHODOCROSITE	-10 700	-7 500	0	0	0	-3 200	0
5195000 RHODOCROSITE	-16 777	26 400	0	0	0	-14 815	0
2095005 RHODOCROSITE	-3 903	-11 310	-11 370	-11 860	0	11 603	-5 910
2095006 RHODOCROSITE	-3 738	-11 140	-10 990	-11 540	0	7 402	21 860
6095002 RHODOCROSITE	-32 822	-19 070	0	0	0	-13 802	62 000
7095000 RHODOCROSITE	-10 404	32 040	0	0	0	-42 521	0
8095000 RHODOCROSITE	-4 409	7 930	0	0	0	3 319	18 270
6095006 RHODOCROSITE	-4 500	15 130	13 150	0	0	10 310	33 330

5060000 CERRUSITE	-2 389	13 130	13 440	12 830	-15 519	-4 860
2050000 MASSICOT	-7 526	-12 910	-12 790	0	5 284	15 780
2060001 LITHARGE	-7 436	-12 920	-12 640	-13 070	5 284	15 380
2060002 PROL 3H20	-7 696	-12 980	0	0	5 284	0
5060001 PR2UCO3	-9 734	500	-780	0	-10 234	11 460
5060000 LARNAKITE	-7 154	280	6 300	0	-7 434	6 440
6060001 PRV2S04	-12 550	-10 400	0	0	-2 150	20 750
6060002 PR403S04	-10 965	-22 100	0	0	3 135	35 070
7060001 CLPYRROMORPH	3 624	84 430	0	34 510	-80 866	0
7060002 NAYPYROMORPH	-7 880	62 790	0	0	-70 670	0
5060002 PR302C03	-15 970	-11 020	0	0	-4 950	26 430
7060005 TSUREBITE	-4 739	9 790	0	0	-14 529	0
8260000 TRS103	-6 099	-7 720	-5 120	-7 640	1 221	9 260
8260001 PR1041	-13 254	-17 700	-19 310	-20 050	12 706	26 000
6060003 ANGLESITE	-2 829	7 790	7 870	-13 630	5 284	13 990
2060004 PR10312 1C1	-2 866	-6 150	0	0	-4 652	0
4150004 LAURUMITE	-5 475	-6 23	-175	0	-4 432	0
4150003 TR21OH13CL	-8 361	-8 793	0	0	-25 753	0
5060003 HYDROCRUSITE	-8 293	17 110	0	0	10 549	0
2060005 PR201OH12	-15 631	-25 200	0	-27 101	3 135	0
5060004 PR41OH15S04	-17 955	-21 169	0	0	-6 271	15 610
5023101 HALACHITE	-1 031	5 180	0	3 940	-19 009	23 770
5023102 AZURITE	-2 289	16 320	0	0	-4 343	0
5295000 INIB0212	-12 573	-8 290	0	0	-6 100	5 800
7060001 PR180212	-14 070	-7 610	0	0	-24 392	0
7060001 PR18041C1	1 008	25 400	0	0	-27 000	0
7060002 PR18041C1	-3 180	55 800	0	0	-46 503	0
7060007 PR1PRM12	-3 578	44 300	0	0	10 862	46 265
2015000 LINE	-21 535	-32 797	0	0	10 321	30 690
2015001 PORTLANDITE	-11 813	-22 675	0	0	24 919	65 639
2046001 PERICLASE	-11 166	-21 510	0	0	6 799	19 498
3016001 MAG-FERRITE	8 154	-16 765	0	0	17 660	54 695
8215002 MOLLASTARITE	-6 197	-12 996	0	0	28 522	106 335
8215003 P-10LLCTAHIT	-7 047	-13 846	0	0	17 123	49 421
8015001 CA-DL IVINE	-19 985	-37 649	0	0	34 783	107 111
8015002 LARNAITE	-21 481	-39 141	0	0	7 298	0
6015007 CASIUS	-45 345	-71 867	0	0	0	0
6015003 MONTICELLITE	-13 149	-50 272	0	0	0	0
8015003 PERICLASE	-23 951	-47 472	0	0	0	0
8015004 MONTICELLITE	-45 345	-71 867	0	0	0	0
3028102 LEPTODERMITE	-45 327	-44 371	0	0	0	0

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