APPENDIX E

PARAMETER SCREENING

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APPENDIX E

PARAMETER SCREENING

Details of the mathematical formulation relating to parameter screening are presented in this appendix. As discussed in Section 4.3.6, the criteria used in parameter screening are:

- Infiltration rate from the waste management unit (WMU)

- Water table elevation due to local recharge and infiltration from the WMU

- Aquifer must be able to support a well with adequate supply for a household

The first criterion is applicable to surface impoundments only.   The second and third criteria are applicable to all types of WMU.

E.1   INFILTRATION RATE CRITERIA

For a surface impoundment (SI) that is outseeping (elevation of waste liquid is greater than the water table elevation) and that is hydraulically separated from the water table, the infiltration rate is limited by the following criteria:

- Saturated hydraulic conductivity of the vadose-zone material

- Maximum feasible infiltration rate that does not cause the groundwater mound to rise to the bottom elevation of the SI unit

The first criterion may be written

$$I \leq K_s$$

(E.1)

where

I	=	Infiltration rate from the SI (m/yr)
K_s	=	Saturated hydraulic conductivity of the vadose-zone material (m/ yr)

According to the second criterion, if the calculated infiltration rate from the SI exceeds the rate at which the saturated zone can transport the groundwater, the groundwater level will rise into the unsaturated zone and the assumption of zero pressure head at the base of the SI is violated. This groundwater "mounding" will reduce the effective infiltration rate. The maximum infiltration rate is estimated as

the rate that does not cause the groundwater mound to rise to the bottom elevation of the SI unit. The maximum allowable infiltration rate may be approximated by:

$$I_{Max} \leq \frac{2K_{aqsat}D_{aqsat}(D_{vadose} - H)}{R_0^2 \ln\frac{R_\infty}{R_0}}$$

(E.2)

where

I_{Max}	=	maximum allowable infiltration rate (m/yr)
K_{aqsat}	=	hydraulic conductivity of the saturated zone (m/yr)
D_{aqsat}	=	depth of the saturated zone (m)
D_{vadose}	=	vadose zone thickness (m)
H	=	hydraulic head (m)
R_0	=	equivalent source radius (m)
R_∞	=	length between the center of the source and the nearest downgradient boundary where the boundary location has no perceptible effects on the heads near the source (m). The nearest downgradient boundary location is normally the nearest surface water body located along one of the streamlines traversing the surface impoundment.

The equivalent source radius may be calculated from:

$$R_0 = \sqrt{\frac{A}{\pi}}$$

(E.3)

where

A	=	source area (m^2)

E.2   WATER-TABLE-ELEVATION CRITERION

Under this criterion, the selected combination of K_{aqsat}, D_{aqsat}, D_{vadose}, and G_{Reg} is rejected when the elevation of water table is above the topographical elevation, i.e.,

$$H\left(x \ at \ \frac{dH}{dx} = 0\right) \geq D_{vadose} + D_{aqsat}$$

(E.4)

where

$$G_{Reg} = \text{regional hydraulic gradient (m/m)}$$
$$= (H_2 - H_1)/x_L$$
$$D_{aqsat} = \text{depth of the saturated zone (m)}$$
$$D_{vadose} = \text{vadose zone thickness (m)}$$
$$H(x) = \text{the hydraulic head elevation at } x \text{ (m)}$$
$$x = \text{the coordinate from the upgradient end of the domain (m)}$$

H(x) is segmentally defined by the following equations:

For $0 \le x \le x_u$

$$H(x) = \frac{-I_r}{2K_xB}x^2 + \left[\frac{I_r-I}{2K_xB}\left(\frac{x_d^2-x_u^2}{x_L}\right) + \frac{I_r-I}{K_xB}(x_u-x_d) + \frac{I_r}{2K_xB}x_L + \frac{H_2-H_1}{x_L}\right]x + H_1$$

(E.5)

For $x_u \le x \le x_d$

$$H(x) = \frac{-I}{2K_xB}x^2 + \left[\frac{I_r-I}{2K_xB}\left(\frac{x_d^2-x_u^2}{x_L}\right) - \frac{I_r-I}{K_xB}x_d + \frac{I_r}{2K_xB}x_L + \frac{H_2-H_1}{x_L}\right]x + \frac{I_r-I}{2K_xB}x_u^2 + H$$

(E.6)

For $x_d \le x \le x_L$

$$H(x) = \frac{-I_r}{2K_xB}x^2 + \left[\frac{I_r-I}{2K_xB}\left(\frac{x_d^2-x_u^2}{x_L}\right) + \frac{I_r}{2K_xB}x_L + \frac{H_2-H_1}{x_L}\right]x - \frac{I_r-I}{2K_xB}(x_d^2-x_u^2) + H_1$$

(E.7)

where:

$$H_1 = \text{the hydraulic head elevation at } x = x_L \text{ (m)}$$
$$H_2 = \text{the hydraulic head elevation at } x = 0 \text{ (m)}$$
$$x_L = \text{the length of the aquifer system (m)}$$
$$B = \text{the saturated thickness of the system (m)}$$
$$x_u = \text{the upgradient coordinates of the strip source area (m)}$$
$$x_d = \text{the downgradient coordinates of the strip source area (m)}$$
$$I_r = \text{the recharge rate outside the strip source area (m/yr)}$$
$$I = \text{the infiltration rate through the rectangular source area (m)}$$
$$K_x = \text{hydraulic conductivity in the longitudinal direction (m/yr)}$$

E.3   AQUIFER TRANSMISSIVITY CRITERION

In order to ensure that the generated set of hydrogeologic parameters do not represent an aquifer with an unrealistically low transmissivity, an option has been added to the EPACMTP code to perform this check. The LTCHK parameter (in the GP01 record in the EPACMTP data input file) controls whether or not this check is performed. When LTCHK is set to TRUE, the EPACMTP code automatically checks to see if the aquifer can support a well with a sustained pumping rate of 0.35 gpm (or 696 m^3/yr) with the maximum drawdown at the well not more than ⅜ of the saturated thickness. The variables that are used to perform this transmissivity check are recharge rate, saturated thickness, and impact radius. Any combination of hydraulic conductivity, saturated thickness, and recharge rate is permissible if it can sustain a continuous pumping rate of 0.35 gpm with drawdown at the well of less than ⅜ of the saturated thickness and with an impact radius not greater than 50 m (164 ft). If the generated set of hydrogeologic parameters fails this transmissivity screening, then that set of input values is rejected and a new data set is generated. The pumping rate of 0.35 gpm was chosen because it is approximately the maxiumum water usage for a four-person household.

APPENDIX F

GROUND-WATER-TO-SURFACE-WATER MASS FLUX

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APPENDIX F

GROUND-WATER-T0-SURFACE-WATER MASS FLUX

A groundwater to surface water pathway is included in the analysis by calculating the total contaminant mass flux at a given downgradient location selected to represent the intersection of the contaminant plume with a surface water body. It is assumed that the surface water body fully penetrates the aquifer and the plume fully intersects the water body. The total contaminant mass flux in mg/year is calculated by multiplying the groundwater flux with the net contaminant mass across the entire plume cross section:

$$M_{flux} \; = \; i \cdot K_H \cdot C_{net} \tag{F.1}$$

where

C_{net} =   net contaminant mass in plume cross-section perpendicular to groundwater flow direction in mg/meter

i =   hydraulic gradient

K_H =   hydraulic conductivity in m/year

       The net contaminant mass is calculated from the plume-center concentration, vertically and transversely integrated. The concentration as a function of transverse distance is approximately given by (Domenico and Schwartz, 1990),

$$C(y) \; = \; \frac{C_{zo}}{2} \left[erf\left(\frac{y + \dfrac{ys}{2}}{2\sqrt{\alpha_T x}} \right) \; - \; erf\left(\frac{y - \dfrac{ys}{2}}{2\sqrt{\alpha_T x}} \right) \right] \tag{F.2}$$

where

C_{zo} =   vertically integrated concentration at plume center in $\dfrac{mg \cdot m}{\ell}$

ys =   source width (m)

α_T =   transverse dispersivity (m)

x =   downgradient distance from source (m)

       The net contaminant mass is determined by integrating C(y) from the plume centerline to the plume boundary:

$$C_{net} = F \cdot C_{zo} \int_{y=0}^{y_{plume}} \left[erf\left(\frac{y + \frac{ys}{2}}{2\sqrt{\alpha_T x}} \right) - erf\left(\frac{y - \frac{ys}{2}}{2\sqrt{\alpha_T x}} \right) \right] dy \qquad (F.3)$$

where

$$y_{plume} = \frac{ys}{2} + 3\sqrt{\alpha_T x}$$

$$F = 1000 \frac{\ell}{m^3} \text{ (conversion factor)}$$

The integral in Equation (F.3) was evaluated numerically using Simpson's 3/8 rule (Burden and Faires, 1989) because a closed form solution is not available:

$$\int_{y_o}^{y_4} f(y)dy \cong \frac{2h}{45} [7f(y_o) + 32f(y_1) + 12f(y_2) + 32f(y_3) + 7f(y_4)] \qquad (F.4)$$

where

h   =   interval between y_o and y_1, y_1 and y_2, etc.

REFERENCES

Burden, R.L. and J.D. Faires, 1989.   *Numerical Analysis*. PWS Publishing Company, Boston. 729 pp.

Domenico, A.J., and F.W. Schwartz, 1990. Physical and Chemical Hydrogeology. John Wiley & Sons, Inc., New York. 820 pp.

APPENDIX G

MINTEQA2-BASED
METALS ISOTHERMS

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APPENDIX G

# MINTEQA2-BASED
METALS ISOTHERMS

G.1   INTRODUCTION

This appendix describes the development of concentration-dependent metal partition coefficients for use in EPACMTP. In the subsurface, metal contaminants undergo reactions with ligands in the pore water and with surface sites on the solid aquifer or soil matrix material. Reactions in which the metal is bound to the solid matrix are referred to as sorption reactions, and metal that is bound to the solid is said to be sorbed. The ratio of the concentration of metal sorbed to the concentration in the mobile aqueous phase at equilibrium is referred to as the partition coefficient (K_d). During contaminant transport, sorption to the solid matrix results in retardation of the contaminant front. Thus, groundwater fate and transport models such as EPACMTP include the contaminant partition coefficient in the calculation of the overall retardation factor (the ratio of the average linear particle velocity to the velocity of that portion of the plume where the contaminant is at 50 percent dilution) for a given chemical constituent. Use of K_d in EPACMTP transport modeling requires the assumption that local equilibrium between the solutes and the sorbents is attained. This implies that the rate of sorption reactions is fast relative to advective-dispersive transport of the contaminant and that the sorption.

Among the options incorporated in EPACMTP for modeling the fate and transport of metals is the option of using non-linear sorption isotherms in the form of tabulated sorption data (see Section 3.3.3.4 for other available options for modeling the sorption of metals). These isotherms reflect the tendency of K_d to decrease as the total metal concentration in the system increases. The non-linear isotherms available for use in EPACMTP are specified in terms of the dissolved metal concentration and the corresponding sorbed concentration at a series of total metal concentrations. The isotherms were calculated using the geochemical speciation model, MINTEQA2. For a particular metal, K_d values in a soil or aquifer are dependent upon the metal concentration and various geochemical characteristics of the soil or aquifer and the associated pore water. Geochemical parameters that have the greatest influence on the magnitude of K_d include the pH of the system and the nature and concentration of sorbents associated with the soil or aquifer matrix. In the subsurface beneath a waste disposal facility, the concentration of leachate constituents may also influence K_d. Although the dependence of metal partitioning on the total metal concentration and on pH and other geochemical characteristics is apparent from partitioning studies reported in the scientific literature, K_d values for many metals are not available for the range of metal concentrations or geochemical conditions needed in risk assessment modeling. For this reason, the U.S. EPA has chosen to use an equilibrium speciation model, MINTEQA2, to estimate partition coefficients in a number of recent risk assessments that required modeling the groundwater fate and transport of metals. The use of a speciation model like MINTEQA2 allows K_d values to be estimated for a range of total metal concentrations in various model systems designed to depict natural variability in those geochemical characteristics that most influence metal partitioning.

G.2   MINTEQA2 MODELING

From input data consisting of total concentrations of inorganic chemicals, MINTEQA2 calculates the fraction of a contaminant metal that is dissolved, adsorbed, and precipitated at equilibrium (see Figure G.1). The total concentrations of major and minor ions, trace metals and other chemicals are specified in terms of key species known as components. MINTEQA2 automatically includes an extensive database of solution species and solid phase species representing reaction products of two or more of the components. The model does not automatically include sorption reactions, but these can be included in the calculations if supplied by the user. When sorption reactions are included, the dimensionless partition coefficient can be calculated from the ratio of the sorbed metal concentration to the dissolved metal concentration at equilibrium. The dimensionless partition coefficient can be converted to K_d with units of liters per kilogram (L/kg) by normalizing by the mass of soil (in kilograms) with which one liter of porewater is equilibrated (the phase ratio). An isotherm is then generated by estimating the equilibrium metal distribution between sorbed and dissolved fractions is estimated for a series of total metal concentrations.

Progress in accounting for sorption in equilibrium calculations over the past decade has resulted in the development of coherent databases of sorption reactions for particular sorbents. These databases include acid-base sorption reactions and reactions for major ions in aquatic systems (Ca, Mg, SO_4, etc.). Including such reactions along with those representing sorption of trace metals makes it possible to estimate sorption in systems of varying pH and composition. Examples of coherent databases of sorption reactions include that for the hydrous ferric oxide surface presented by Dzombak and Morel (1990) and a similar database for goethite presented by Mathur (1995).
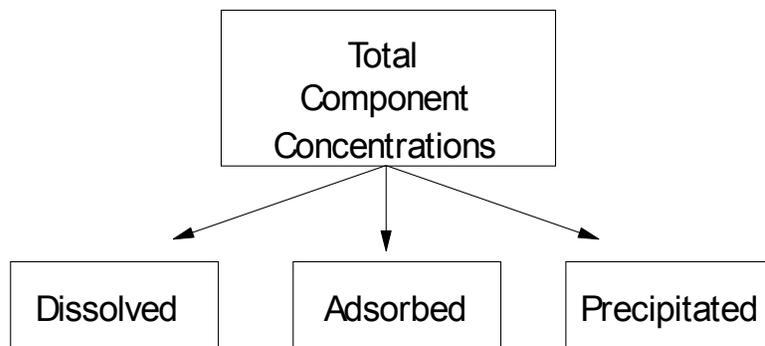
**Figure G.1   MINTEQA2 Computes the Equilibrium
Distribution of Metal**

G.2.1 Input Parameters

We accounted for the expected natural variability in K_d for a particular metal in the MINTEQA2 modeling by including variability in five important input parameters upon which K_d depends. These five input parameters, also called the geochemical master variables, are:

- groundwater compositional-type (carbonate or non-carbonate)

- groundwater pH

- concentration of adsorbents (ferric oxide (geothite) and particulate natural organic matter (POM))

- concentration of dissolved natural organic matter (DOM)

- dissolved concentration of representative anthropogenic (leachate) organic acids (LOA) (derived from leachate infiltrating from the base of the WMU)

Two groundwater compositional types were modeled, one with composition representative of a carbonate-terrain system and one representative of a non-carbonate system. The two groundwater compositional types are correlated with the hydrogeologic environment parameter in EPACMTP (see Section 4.2.3.1 of the *IWEM Technical Background Document*). The carbonate type corresponds to the "solution limestone" hydrogeologic environment setting. The other eleven hydrogeologic settings in EPACMTP are represented by the non-carbonate groundwater type. For each groundwater type, a representative, charge-balanced groundwater chemistry specified in terms of major ion concentrations and natural pH was selected from the literature. The carbonate system was represented by a sample reported in a limestone aquifer. This groundwater had a natural pH of 7.5 and was saturated with respect to calcite. The non-carbonate system was represented by a sample reported from an unconsolidated sand and gravel aquifer with a natural pH of 7.4. An unconsolidated sand and gravel aquifer was selected to represent the non-carbonate compositional type because it is the most frequently occurring of the twelve hydrogeologic environments in HGDB database (see Section 4.2.3.1 of the *IWEM Technical Background Document*). The composition of both the carbonate and non-carbonate representative ground-water samples is shown in Table G.1.

Table G.1   Composition Of Representative Ground Waters

Constituent Chemical	Concentrations (mg/L)	
	Carbonate Ground water	Non-carbonate Ground water
Ca	55	49
Mg	28	13
SO_4	20	27
HCO_3	265	384
Na	3.1	105
Cl	10	34
K	1.5	3.0
NO_3	---	7.8
F	---	0.3
SiO_2	---	21
pH	7.5	7.4
Temp	18 C	14 C
Other	Equilibrium with calcite	---

Two types of adsorbents were represented in modeling the K_d values: ferric oxide (FeOx) and particulate organic matter (POM). Mineralogically, the ferric oxide was assumed to be goethite (FeOOH). A database of sorption reactions for goethite reported by Mathur (1995) was used with the diffuse-layer sorption model in MINTEQA2 to represent the interactions of protons and metals with the goethite surface. The concentration of sorption sites used in the model runs was based on a measurement of ferric iron extractable from soil samples using hydroxylamine hydrochloride as reported in EPRI (1986). This method of Fe extraction is intended to provide a measure of the exposed amorphous hydrous oxide of Fe present as mineral coatings and discrete particles and available for surface reaction with pore water. The variability in FeOx content represented by the variability in extractable Fe from these samples was included in the modeling by selecting low, medium and high FeOx concentrations corresponding to the 17th , 50th and 83rd percentiles of the sample measurements. The specific surface area and site density used in the diffuse-layer model were as prescribed by Mathur. These values along with the molar concentration of FeOx sorbing sites are shown in Table G.3. Although the same distribution of extractable ferric oxide sorbent was used in the saturated and unsaturated zones, the actual concentration of sorbing sites corresponding to the low, medium, and high FeOx settings in MINTEQA2 was different in the two zones because the phase ratio was different (4.57 kg/L in the unsaturated zone; 3.56 kg/L in the saturated zone). The extractable Fe weight percentages used in the modeling are shown in Table G.2.

Table G.2   Concentration Levels For Goethite Sorbent

Concentration Level	Weight Percent Fe (extractable)	FeOOH Sorbent Concentration (g/L)
Unsaturated zone		
Low	0.0182	1.325
Medium	0.0729	5.309
High	0.1190	8.667
Saturated zone		
Low	0.0182	1.032
Medium	0.0729	4.136
High	0.1190	6.751

Table G.3   Model Parameters For The Goethite Sorbent

Parameter	Model Value
Specific surface area (m^2/g)	60
Site density (moles of sites per mole Fe)	0.018
Unsaturated zone: Site concentration (mol/L)	
Low	2.680×10^{-4}
Medium	1.074×10^{-3}
High	1.753×10^{-3}
Saturated zone: Site concentration (mol/L)	
Low	2.087×10^{-4}
Medium	8.365×10^{-4}
High	1.365×10^{-3}

The concentration of the second adsorbent, POM, was obtained from existing organic matter distributions that were developed for use in the EPACMTP model. In the unsaturated zone, low, medium, and high concentrations for components representing particulate organic matter in the MINTEQA2 model runs were based on the distribution of solid organic matter in EPACMTP for the silt loam soil type. (The silt loam soil type is intermediate in weight percent organic matter in comparison with the other two EPACMTP soil types and is also the most frequently occurring soil type among the three.) The low, medium, and high POM concentrations used in the saturated zone MINTEQA2 model runs was obtained from the EPACMTP organic matter distribution for the saturated zone. For both the FeOx and POM adsorbents, the amount of sorbent included in the MINTEQA2 modeling was scaled to

correspond with the phase ratio in the unsaturated zone (4.57 kg/L) and saturated zones (3.56 kg/L).

A dissolved organic matter (DOM) distribution for the saturated zone was obtained from the U.S. EPA STORET database. This distribution was used to provide low, medium, and high DOM concentrations for the MINTEQA2 model runs. The low, medium, and high DOM values were used exclusively with the low, medium, and high values, respectively, of POM. In the unsaturated zone, there was no direct measurement of DOM available. The ratio of POM to DOM in the unsaturated zone was assumed to be the same as that in the saturated zone. This ratio, 194.6, was applied to the low, medium, and high weight percent POM values of the unsaturated zone to obtain DOM concentrations at the low, medium, and high levels. In MINTEQA2 the POM and DOM components were modeled using the Gaussian distribution model. This model includes a database of metal-DOM reactions (Susetyo et al., 1991). Metal reactions with POM were assumed to be identical in their mean binding constants with the DOM reactions. The weight percent POM and concentration (mg/L) of both POM and DOM is shown in Table G.4 for all three concentration levels in both zones.

Table G.4   POM and DOM Concentration Levels

	POM wt%	POM Concentration (mg/L)	DOM Concentration (mg/L)
Unsaturated zone			
Low	0.034	1553.8	6.6
Medium	0.105	4798.5	20.4
High	0.325	14852.5	63.20
Saturated zone			
Low	0.020	712.0	3.00
Medium	0.074	2634.4	14.40
High	0.275	9790.0	69.38

For both POM and DOM, a site density of 1.2×10^{-6} moles of sites per mg organic matter was assumed. The site concentrations for organic matter in both zones are listed in Table G.5

Table G.5   Site Concentrations For POM And DOM Components In MINTEQA2

	POM Site Concentration (mol/L)	DOM Site Concentration (mol/L)
Unsaturated zone		
Low	1.865×10^{-3}	7.896×10^{-6}
Medium	5.758×10^{-3}	2.439×10^{-5}
High	1.782×10^{-2}	7.548×10^{-5}
Saturated zone		
Low	8.544×10^{-4}	3.600×10^{-6}
Medium	3.161×10^{-3}	1.728×10^{-5}
High	1.175×10^{-2}	8.326×10^{-5}

Leachate exiting a WMU may contain elevated concentrations of anthropogenic leachate organic acids. This organic matter may consist of various compounds including organic acids that represent primary disposed waste or that result from the breakdown of more complex organic substances. Many organic acids found in landfill leachate have significant metal-complexing capacity that may influence metal mobility. In an effort to incorporate in the K_d modeling the solubilizing effect of organic acids, representative carboxylic acids were included in the MINTEQA2 modeling at three concentration levels. An analysis of total organic carbon (TOC) in landfill leachate by Gintautas et al. (1993) was used to select and quantify the organic acids. The low, medium, and high values for the representative acids in the modeling were based on the lowest, the average, and the highest measured TOC among the six landfill leachates analyzed; these values are presented below in Table G.6.

Table G.6   Model Concentrations Of Representative Leachate Acids

Concentration Level	Acetic acid (mg/L)	Propionic acid (mg/L)	Butyric acid (mg/L)
Unsaturated zone			
Low	24.80	14.61	15.68
Medium	111.00	64.30	67.94
High	274.60	158.60	169.00
Saturated zone			
Low	3.54	2.09	2.24
Medium	15.86	9.19	9.71
High	39.23	22.66	24.14

G.2.2 Metals of Interest

The metal contaminants whose partition coefficients have been estimated using MINTEQA2 include arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), copper (Cu), chromium (Cr), fluoride (F), mercury (Hg), manganese (Mn), molybdenum (Mo), lead (Pb), nickel (Ni), selenium (Se), silver (Ag), thallium (Tl), vanadium (V), and zinc (Zn).

Several of these metals occur naturally in more than one oxidation state. The modeling described here is restricted to the oxidation states that are most likely to occur in waste systems or most likely to be mobile in ground-water waste systems. For arsenic, chromium, and selenium, partition coefficients were estimated for two oxidation states. These were: As(III) and As(V), Cr(III) and Cr(VI), and Se(IV) and Se(VI). For antimony, molybdenum, thallium, and vanadium, only one oxidation state was modeled although multiple oxidation states occur. For all four of these metals, the choice of which state to model was dictated by practical aspects such as availability of sorption reactions and by subjective assessment of the appropriate oxidation state. The oxidation states modeled were Sb(V) (there were no sorption reactions available for Sb(III)), Mo(VI) (molybdate seems the most relevant form from literature reports), thallium (I) (this form is more frequently cited in the literature as having environmental implications), and V(V) (vanadate; sorption reactions were not available for other forms).

G.2.3 Modeling Methods and Results

The MINTEQA2 modeling was conducted separately for each metal in three steps for the unsaturated zone; these steps were then repeated for the saturated zone:

- ■   Sorbents were pre-equilibrated with groundwaters: Each of nine possible combinations of the two FeOx and POM sorbent concentrations (low FeOx, low POM; low FeOx, medium POM; etc.) were equilibrated with each of the two groundwater types (carbonate and non-carbonate). Because the sorbents adsorb some groundwater constituents (calcium, magnesium, sulfate, fluoride), the input total concentrations of these constituents were adjusted so that their equilibrium dissolved concentrations in the model were equal to their original (reported) groundwater dissolved concentrations. This step was conducted at the natural pH of each groundwater, and calcite was imposed as an equilibrium mineral for the carbonate groundwater type. Small additions of inert ions were added to maintain charge balance.

- ■   The pre-equilibrated systems were titrated to new target pH's: Each of the nine pre-equilibrated systems for each groundwater type were titrated with NaOH to raise the pH or with HNO_3 to lower the pH. Nine target pH's spanning the range 4.5 to 8.2 were used for the non-carbonate groundwater. Three target pH's spanning the range 7.0 to 8.0 were used for the carbonate groundwater. Titration with acid or base to adjust the pH allowed charge balance to be maintained.

- ■   Leachate organic acids and the contaminant metal were added: Each of the eighty-one pre-equilibrated, pH-adjusted systems of the non-carbonate groundwater and the twenty-seven pre-equilibrated, pH-adjusted systems of the carbonate groundwater were equilibrated with three concentrations of leachate organic acids. The equilibrium pH was not imposed in MINTEQA2; pH was calculated and reflected the acid and metal additions. The contaminant metal was added as a metal salt (e.g., $PbNO_3$) at a series of forty-four total concentrations spanning the range 0.001 mg/L to 10,000 mg/L of metal. Equilibrium composition and K_d was calculated at each of the forty-four total metal concentrations to produce an isotherm of sorbed metal versus metal concentration. The isotherm can also be expressed as K_d versus metal concentration.

For each metal, the modeling resulted in 243 isotherms for the non-carbonate ground water for the unsaturated zone and 81 isotherms for the carbonate ground water for the unsaturated zone. The same number of isotherms was produced for each ground water type for the saturated zone. Each isotherm corresponds to a particular setting of FeOx sorbent concentration, POM sorbent (and associated DOM) concentration, leachate acid concentration, and pH. In Monte Carlo or site-specific mode, EPACMTP selects the appropriate isotherm based on the conditions being modeled. As detailed in Section G.2.2, isotherms were produced for Ag, As(III), As(V), Ba, Be, Cd, Co, Cr(III), Cr(VI), Cu, F, Hg, Mn(II), Mo(V), Ni, Pb, Sb(V), Se(IV), Se(VI), Tl(I), V(V), and Zn.

Example isotherms for Cr(VI) are shown in Figure G.2 This figure shows K_d versus total Cr(VI) concentration for the non-carbonate ground water saturated zone at various pH values. The isotherms plotted are for the medium concentration level of FeOx and POM sorbents and the low concentration level of leachate organic matter. Because chromate behaves as an anion in ground water, its adsorption is enhanced at low pH relative to high pH. This behavior is reversed for metals that behave as cations.

Figure G.3 shows the impact of FeOx concentration level on the K_d values of lead. As expected, sorption is enhanced at the higher FeOx concentrations resulting in larger K_d values. The example shown is for the unsaturated zone of the carbonate ground water with the low concentration levels of POM and leachate organic acids. The pH corresponds to the lowest setting for the carbonate systems: 7.0.

The impact of varying the POM concentration level differs among the various metals. The effect of POM concentration level also depends on the pH. The variable impact of POM is due to two factors: the absence of organic matter reactions for anionic metals and the concurrent influence of DOM for those metals for which organic matter reactions are included. In the MINTEQA2 modeling procedure used here, increasing the POM sorbent concentration is always accompanied by a proportional increase in the DOM concentration. The overall impact on the amount of metal sorbed depends on the relative competition among all constituents in the systems for these two substances. The "winner" of this relative competition (POM or DOM) shifts with pH because both substances undergo acid-base reactions. Figure G.4 shows

the impact of varying the POM/DOM concentration level on lead sorption for the non-carbonate ground water unsaturated zone with medium FeOx concentration level and low leachate organic matter concentration level at pH 6.3.

The influence of the leachate organic matter concentration level is illustrated in Figure G.5 for copper sorption. The LOM level is represented in the model by particular concentrations of three representative leachate organic acids. The acids exert two modes of influence on metal sorption: (1) they lower the pH, reducing sorption of cations and enhancing sorption of anions; (2) for those metals that complex these acids, metal sorption is reduced through competition. The latter effect is generally restricted to metals that behave as cations. The results shown in Figure G.5 correspond to high concentration levels of FeOx and POM sorbents in the unsaturated zone for the carbonate ground water. The pH is 7.0.
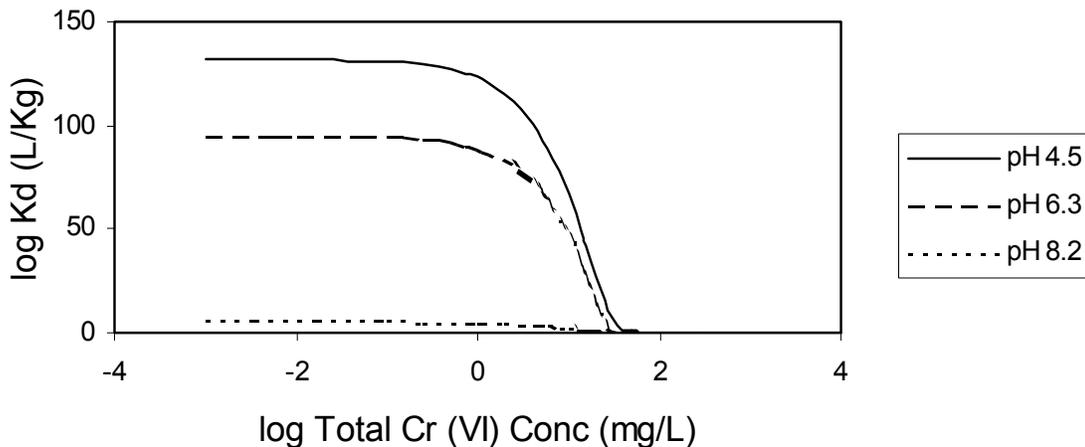
Figure G.2   Cr(VI) Isotherms Illustrating Influence of pH
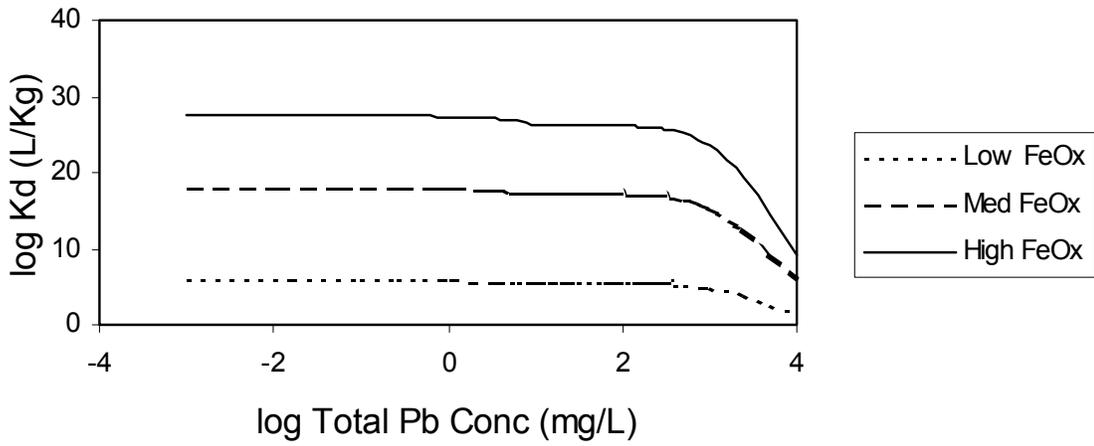
Figure G.3   Pb Isotherms Illustrating Influence of FeOx Sorbent Concentration
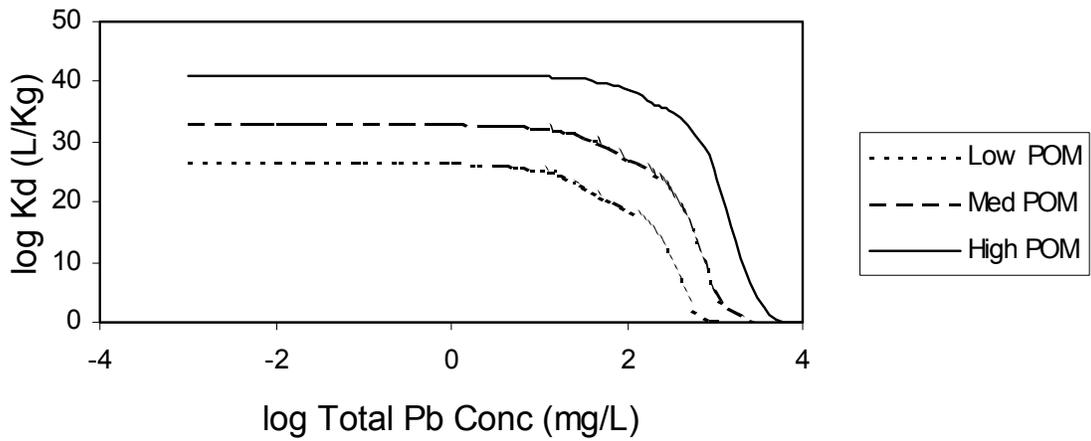
Figure G.4   Pb Isotherms Illustrating Influence of POM/DOM Concentration

Figure G.5   Cu Isotherms Illustrating Influence of LOM Concentration

G.2.4 MINTEQA2 Modeling Assumptions and Limitations
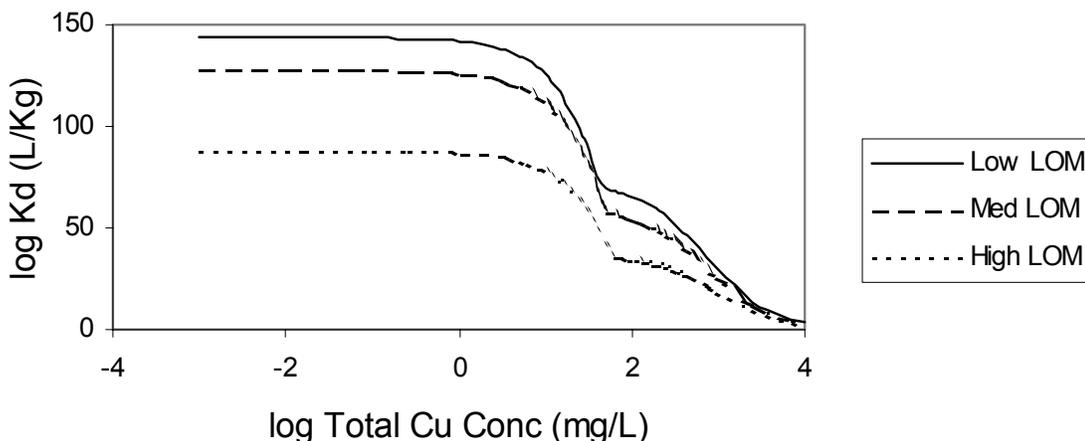
There are many assumptions inherent in the use of a speciation model to estimate partition coefficients. Some of these must be acknowledged to result in limitations on the utility of the model results. Undoubtedly, the modeling results are more accurate for some metals than for others. The assumptions and limitations inherent in using the MINTEQA2 speciation model to estimate sorption isotherms for metals are summarized below. Although the impact of potential error in the estimated K_d values is apparent from some of these limitations, for many issues listed here, it appears impossible to quantify their effect on the modeled K_d values.

Issues concerning the characterization of the groundwater chemistry include:

- The categorization of all ground waters into two types, carbonate and non-carbonate, is quite broad.

- Although the pre-equilibration step is helpful in more realistically establishing appropriate major ion concentrations, it is somewhat artificial in the sense that sorbents are not correlated with ground water.

- Both ground waters were artificially adjusted to different pH's of interest by titrating with an acid or base. The degree to which this procedure can result in model ground-water compositions that adequately represent true variability in factors that impact K_d is unknown.

Issues concerning the characterization of the adsorbent include:

- Only two sorbents are represented in the model systems. Other sorbents are important in some circumstances including clays, hydrous aluminum and manganese oxides, calcite, and silica.

- The ferric oxide was accounted in the modeling as goethite. Other ferric oxides may be important in ground water, including hydrous ferric oxide (HFO).

- The data used to quantify the FeOx and POM sorbents (and the DOM) is sparse. The degree to which the true variability in concentration levels of these sorbents has been captured in the modeling is unknown.

- There is no provision in the modeling to account for occlusion of sorbents (formation of coatings over other surfaces).

- The ferric oxide (goethite) sorbent is included in all model runs, implying that it is ubiquitous. However, there are natural ground-water conditions that preclude the formation of ferric oxide precipitates (low pH and low E_h).

- The Gaussian model for estimating metal interactions with organic matter was developed for dissolved organic matter. It has not been tested for estimating the degree of metal sorption onto POM.

Issues concerning the characterization of the leachate include:

- The concentration levels for leachate organic matter were based on a limited sampling from six municipal landfills.

- Other leachate constituents may be present at elevated concentrations, but these are not accounted for. Some of these (e.g., Ca, Mg, SO_4, Cl, etc.) may reduce the amount of metal sorption by competing for adsorption sites (especially Ca) or by complexing metals so that a greater fraction is retained in solution (especially SO_4 and Cl).

- Leachate from highly alkaline wastes was not included in the modeling. Highly alkaline leachates may result in elevation of the ground-water pH above the upper bound for which isotherms have been computed. Sorption tends to increase with pH for many metals up to about pH 8 to 9. Above this level, formation of metal hydroxy solution species may inhibit sorption for some metals.

- The metal was introduced as a metal salt. The metal species was chosen to avoid impact on the pH, but some pH effect is unavoidable.

■   Methylated forms of metal were not accounted for in this modeling. Mercury and arsenic are known to undergo methylation in the environment.

Other modeling issues include:

■   The system redox potential was not explicitly defined in the modeling. All species that might undergo oxidation-reduction reactions were constrained to remain in the form in which they were entered in the model.

■   All contaminant metals were introduced separately and individually in the modeling. The possible simultaneous presence of multiple metals is unaccounted for.

G.3 INCORPORATION OF MINTEQA2 ADSORPTION ISOTHERMS IN EPACMTP

Monte Carlo modeling of metals transport using the MINTEQA2-derived adsorption isotherms requires, for each Monte Carlo realization, selecting one of the available isotherms for each metal species, for both the unsaturated and saturated zones. The selection of the appropriate adsorption isotherm for each Monte Carlo realization depends on the values of the five geochemical master variables, as discussed in Section G.2.1. These values of the geochemical master variables are generated randomly from given distributions. This section describes how EPACMTP selects and prepares adsorption isotherms for use in the transport simulations and how the option to linearize the nonlinear MINTEQA2-generated isotherms works; additional technical details are provided in Section 3.3.3 of the *EPACMTP Parameters and Data Background Document*.

G.3.1 Incorporation of MINTEQA2 Isotherms

In the Monte Carlo transport simulations, for each realization a value is generated for each of the five geochemical master variables according to the specified distributions. Each generated value is then compared to contiguous ranges of values. This set of rangewise classifications is then used to choose the appropriate adsorption isotherm from the matrix of master variables to be used for that realization. Note that isotherms are selected independently for the unsaturated and saturated zones; that is, this process is performed once for the unsaturated zone and then repeated for the saturated zone.

The isotherm curves generated by running the MINTEQA2 model are provided to EPACMTP in tabular form. The table of values consists of a set of dissolved concentration and associated distribution coefficient (K_d) pairs for each isotherm. For each metal, the modeling resulted in 243 isotherms for the non-carbonate ground water for the unsaturated zone and 81 isotherms for the carbonate ground water for the unsaturated zone. The same number of isotherms was produced for each ground water type for the saturated zone. Each isotherm is indexed to the particular values of the five geochemical variables used in its generation by

MINTEQA2, and to the zone (unsaturated or saturated) to which it applies. Note that the unit of concentration used in MINTEQA2, and hence presented in the isotherms, is mol liter^{-1}, while EPACMTP uses mg liter^{-1}. EPACMTP converts isotherm units to mg liter^{-1} using the atomic weights shown in Table 4.3.

Table G.7   Atomic weight of metals (CRC, 1970)

Metals	Atomic Weight
Ba^{2+}	137.34
Cd^{2+}	112.40
Cr^{3+}	51.995
Hg^{2+}	200.59
Ni^{2+}	58.71
Pb^{2+}	207.19
Ag^{+4}	107.89
Zn^{+2}	16.38
Cu^{+2}	63.55
V^{+4}	50.94

G.3.2 Precipitation Effects

In the EPACMTP Monte Carlo transport simulations, the effect of adsorption is incorporated through a partition coefficient K_d, defined as the ratio of the metal bound on the soil (C_s, expressed in mass of metal per mass soil) to dissolved phase concentration (C_d, expressed in mass of metal per volume of solution). In EPACMTP, K_d has the units liter kg^{-1}. The K_d values computed from the MINTEQA2 output are dimensionless, because in that model, the equilibrium mass of metal in each phase (dissolved, sorbed, and precipitated) is expressed relative to a liter of solution. Here, the sorbed metal should be regarded as the mass of metal that has been *sorbed from the liter of solution*. Hence, dimensionless K_d, called $K_d{}'$, can be expressed:

$$K_d{}' \;=\; \frac{C_s}{C_d} \tag{G.1}$$

where C_s and C_d have, as in MINTEQA2, the same units. (Conversion of K_d' to K_d is discussed in Section G.3.3.) Because the output from the MINTEQA2 model simulations includes the equilibrium mass of metal in each of the three phases: dissolved, adsorbed, and precipitated (C_p), the effect of precipitation can, in principle, be incorporated into the transport simulations by defining K_d' (which becomes K_d after units conversion in the transport model) as the ratio of immobile concentration ($C_s + C_p$) to mobile concentration (C_d). However, if K_d' is defined in this way, rather than as in (4.1), the form of the isotherm relating dissolved concentration and K_d is no longer monotonic. The K_d initially will decrease with increasing metal concentration, but when the solubility product is exceeded and precipitation occurs, K_d will begin to increase. The slope of the K_d curve may change again as total metal

concentration increases if the anion with which the metal is co-precipitating becomes depleted. In the Monte Carlo transport analysis, EPACMTP uses a robust and computationally efficient analytical solution technique for the unsaturated zone simulations (see Section 3.3.5.3). This solution method requires a monotonic isotherm; it cannot accommodate the non-monotonic isotherms that result when precipitation is included. Therefore, precipitation is not included in the EPACMTP transport analysis. This is justified somewhat by the fact that precipitation, when it does occur, is restricted to the high end of the concentration range for the metals simulated using MINTEQA2. At lower concentrations, precipitation does not occur. Also, to include precipitation would require making assumptions about the availability of the anion(s) with which the metal is precipitating. Ignoring precipitation in the transport simulations will, for those cases where it does occur in the MINTEQA2 simulations, lead to a more conservative model outcome.

G.3.3 Variable Soil Moisture Content

The partition coefficient needed in the EPACMTP transport simulations has units of volume per mass (liters kg^{-1}), but the K_d' values provided by MINTEQA2 are dimensionless. As mentioned in the preceding section, this is simply because the sorbed mass in MINTEQA2 is expressed in terms of mass of metal sorbed *from* a liter of the solution rather than mass of metal sorbed *onto* the mass of soil with which one liter is equilibrated. The partition coefficient can be transformed to the units appropriate for the transport model (i.e., liters kg^{-1}) by normalizing the MINTEQA2 sorbed concentration (in mg $liter^{-1}$) by the phase ratio (the mass of soil with which one liter is equilibrated, given in kg $liter^{-1}$). As explained in Chapter 3, the phase ratio was always 4.57 kg $liter^{-1}$ in the unsaturated zone and 3.56 kg $liter^{-1}$ in the saturated zone. These values were determined from the median values of water content (θ) and soil dry bulk density (ρ_b) from EPACMTP distributions for these parameters. The phase ratio (*a*) is used in calculating the concentration of HFO and POM adsorption sites specified in the MINTEQA2 model runs. It follows that the dimensionless K_d' values should be normalized by 4.57 and 3.56 kg $liter^{-1}$, respectively, for the unsaturated and saturated zones to provide the input K_d for EPACMTP:

$$K_d \; = \; \frac{K_d'}{a} \; = \; K_d' \; \frac{\theta^M}{\rho_b^M} \tag{G.2}$$

where θ^M and $\rho_b{}^M$ are the median water content and dry bulk density. In the subsequent EPACMTP calculations, sorption is incorporated through the retardation factor R, defined as:

$$R \; = \; 1 \; + \; \frac{\rho_b}{\theta} \, K_d \tag{G.3}$$

where θ and ρ_b are selected from their corresponding distributions for each particular Monte Carlo realization.

G.3.4   Linearization of MINTEQA2 Adsorption Isotherm

Although EPACMTP can be run using nonlinear adsorption in both the unsaturated and saturated zones in the deterministic case (in other words, for a single set of hydrogeological parameters), the computer processing time required for a Monte Carlo analysis that includes nonlinear adsorption in both zones is prohibitive. For that reason, a technique was developed that calculates a single value of K_d from a nonlinear isotherm. This "linearized" single K_d value can then be used as a linear partition coefficient in the model, which decreases computer processing time dramatically. Obviously, when the original nonlinear isotherm from which the linear K_d is calculated is almost linear to begin with, the impact of reducing it to a linear K_d is small. Conversely, the error associated with using a linear approximation is increased for highly nonlinear isotherms.

In EPACMTP, two methods are provided for approximating a linear isotherm from a nonlinear isotherm. In the first method, a concentration-interval weighted approach is used to compute a single K_d from the nonlinear K_d versus C_d curve. In effect, the technique simply calculates an average K_d over the range of dissolved metal concentration represented by the isotherm. Concentration-interval weighting is used to account for the fact that the dissolved concentration values are not evenly spaced on the isotherm. This option is provided for use in the unsaturated zone. In the second method (for use in the saturated zone), the K_d corresponding to the peak water table metal concentration is used for linear partitioning. The procedure involves the following steps: First, a saturated zone isotherm is specified by Monte Carlo selection of values for the four geochemical master variables. Then, the peak dissolved metal concentration at the water table is determined, and the K_d corresponding to this dissolved concentration is obtained from the isotherm by interpolation. If the peak concentration at the water table is lower than the minimum dissolved concentration given by the isotherm, the K_d value corresponding to the minimum concentration is used. Likewise, if the peak concentration is higher than the maximum concentration on the isotherm, the K_d corresponding to the isotherm maximum is used.

The specific options used in EPACMTP pertaining to linearizing isotherms and further discussion of the implications of linearized isotherms is presented in Section 3.3.3 of the EPACMTP Parameters/Data Background Document.

G.4   IMPLEMENTATION OF EPACMTP FOR METALS

The EPACMTP computer code was modified to include capabilities to simulate fate and transport of metals. Most of the existing algorithms in the EPACMTP model are applicable to the simulation of metals. However, significant modifications were necessary to simulate metals adsorption with nonlinear sorption isotherms. Additional modifications were made to the data input module and the Monte Carlo module for assigning values to each model parameter.

G.4.1   Additional Input Data for Metals

Several input parameters were added to EPACMTP for metal simulations. A control parameter (a FORTRAN logical variable) was added to indicate if the contaminant of interest is a metal species. Additional parameters, specifying the type of adsorption isotherm to be used and the distributions of the geochemical waste variables were also included.

G.4.1.1 <u>Control Parameters</u>

The following parameters were added to the General Parameter (GP01) record.

Table G.8   Additional Control Parameters for Metals Simulation

Variable	Type	Column	Descriptions
IF-METAL	logical	41-45	Enter 'T' for metals simulations and 'F' otherwise.
KDEVAL	integer	46-50	Isotherm type; (required only when IF_METAL='T') =1 for pH-dependent linear isotherm =2 for linearized MINTEQA2 isotherm =3 for nonlinear MINTEQA2 isotherm

Note that the KDEVAL=1 option is available only for the five metals: As^{III}, Cr^{VI}, Se^{VI}, Sb^{V}, T1. The other two options are available for the ten metals: Ag, Ba, Cd, Cr^{III}, Cu, Hg, Ni, Pb, V and Zn. It is possible that certain other metals may be assumed to behave like one of the above metals (e.g., K_d results for Be may be assumed to be the same as for Ba; As^{III} results may be assumed to apply to As^{V}, etc.).

G.4.1.2 <u>Metal Specific Data</u>

A separate data group was added to specify additional parameters for metals simulations. This data group is identified in the input data file with the code 'MT'. The first variable in this group specifies the identification number for the metal species to be simulated. The remaining variables specify the distributions of the geochemical master variables for the unsaturated and saturated zones.

Table G.9   Additional Input Parameters for Metals Specific (MT) Group

Variable No.	Description
1	Metal identification number (1-12, Table 5.3)
2	pH for both unsaturated and saturated zones
3	HFO for both unsaturated and saturated zones
4	Leachate organic acids for unsaturated zone
5	POM for unsaturated zone
6	POM for saturated zone

Each metal species is identified using a numerical code, which is shown in Table 5.3. The table also shows the isotherm selection options available for the different metal species.

Table G.10   METAL_ID and Corresponding Metal Species

METAL_ID	1	2	3	4	5	6	7	8	9	10	13	14	15	16	17
Metal species	Ba	Cd	Cr^{III}	Hg	Ni	Pb	Ag	Zn	Cu	V	As^{III}	Cr^{VI}	Se^{VI}	Tl	Sb^{V}
KDEVAL available	2 and 3										1				

The remaining parameters in the metals group specify distributions of the geochemical master variables for the unsaturated and saturated zones. The distributions of the parameters were presented in Section G.?of the EPACMTP Parameters/Data Background Document. Note that the distributions of pH and natural organic matter (NOM) are also required for degrading chemicals (organics) as part of the unsaturated zone and saturated zone data groups. However, they are duplicated in the metal-specific data input group to emphasize the dependence of metals on these parameters. For the HWIR analyses of industrial waste management units, the leachate organic matter is always assigned a value of <u>low</u>.

G.4.2 Evaluation of Approaches for Handling Metals Isotherms

The partitioning of metals between aqueous and soil components through adsorption is generally a nonlinear function of metal concentration. However, including nonlinear adsorption in metals transport simulations in a Monte Carlo framework places great demands on computer processing resources. In fact, accounting for nonlinear adsorption in both the unsaturated and saturated zone simulations is not feasible. In the unsaturated zone, several different adsorption schemes for metals transport are included in EPACMTP, including a coefficient for linear partitioning calculated by the model by linearizing the MINTEQA2 isotherms as described earlier and a nonlinear partitioning isotherm developed using MINTEQA2. These two options were compared for modeling adsorption in the unsaturated zone and the results were evaluated in terms of model response and computational efficiency, leading to the following conclusions:

- ■   Linearization of the adsorption isotherm to produce a linear partition coefficient and subsequent use of the analytical unsaturated zone transport solution (option 2) is computationally efficient, but produces significantly different water table concentrations than using nonlinear adsorption (option 3). Option 2 should only be used for unsaturated zone transport when the concentration range being modeled corresponds to a segment of the isotherm that is approximately linear (relatively low concentrations).

- ■   The use of nonlinear adsorption with the numerical unsaturated zone transport solution can lead to convergence problems in the model, especially if the isotherm has a high degree of nonlinearity. In that case, the transport time step must be made very small to insure convergence, but this leads to long computer simulation times.

- ■   The use of nonlinear adsorption with the analytical unsaturated zone transport solution is both fast and accurate. Only minor differences were found between this solution technique and the numerical technique, which includes dispersion. The nonlinearity of the isotherm itself creates a contaminant profile with a sharp front and a long (dispersed) tail. For typical MINTEQA2 isotherms, this effect was found to be more pronounced than for cases involving hydrodynamic dispersion alone.

For saturated zone transport, a linear partition coefficient must always be used in EPACMTP, regardless of the unsaturated zone adsorption option selection. Linear partitioning must be used because including nonlinear partitioning in the saturated zone requires a numerical solution, which in turn requires small time steps to insure convergence. This places an insupportable demand on computational resources, given the Monte Carlo framework of the problem to be solved. Further, there is some justification for its use in that, at low concentration ranges, most of the MINTEQA2 adsorption isotherms are linear. Also, the maximum saturated zone metal concentrations are expected to be lower than the leachate concentrations of metal leaving the waste disposal unit due to adsorption in the unsaturated zone and initial dilution in the groundwater. This provides some logical basis for the use of linear partitioning in the saturated zone. EPACMTP determines the K_d value to be used in the saturated zone from the selected MINTEQA2 isotherm after the unsaturated zone simulation has been completed. This permits the saturated zone K_d to be determined as a function of the peak metal concentration exiting the unsaturated zone. The method is described in Section G.4.5.

G.4.3 Determination of Isotherm Monotonicity

A new approach for determining the monotonicity of any tabular metal sorption isotherm utilizes the frequency of upward and downward changes in adjacent tabulated values of the distribution coefficient, Kd, with respect to the dissolved concentration, C, as well as the magnitude of these changes. This approach improves upon the current approach in the EPACMTP which identifies the overall trend of an isotherm as increasing if the frequency of upward changes in tabulated

values of Kd is greater than downward changes in Kd, or visa versa. In addition, all tabulated values of the selected isotherm are used in the current approach regardless of the maximum concentration entering the unsaturated zone, Cmax. Therefore, trends may be establish without regard to the range of constituent concentrations in the media.

The proposed approach calculates the incremental changes in area under the plotted isotherm (the logarithm of Kd plotted as a function of the logarithm of C) for all concentrations less than or equal to Cmax. If the sum of upward changes in area is greater than the sum of downward changes, the isotherm is assumed to be monotonically increasing over the range [Cmin, Cmax], where Cmin in the minimum concentration represented by the isotherm. If the sum of upward changes in area is less than the sum of downward changes, the isotherm is assumed to be monotonically decreasing over the range [Cmin, Cmax].

The sum of incremental upward changes in area, A^+, is expressed as

$$A^+ = \sum \delta C_i \times \delta Kd_i, \quad i \in \delta Kd_i > 0 \tag{G.4}$$

where the ith incremental changes in concentration, δC_i, and distribution coefficient, δKd_i, are calculated as

$$\delta Kd_i = \log(Kd_{i+1}) - \log(Kd_i) = \log\left(\frac{Kd_{i+1}}{Kd_i}\right)$$
$$\delta C_i = \log(C_{i+1}) - \log(C_i) = \log\left(\frac{C_{i+1}}{C_i}\right), \tag{G.5}$$

for all tabulated pairs (C, Kd) for all C less than or equal to Cmax. The sum of incremental downward changes in area, A^-, is expressed as

$$A^- = \sum |\delta C_i \times \delta Kd_i|, \quad i \in \delta Kd_i < 0 \tag{G.6}$$

If A^+ is greater than A^-, the trend of the isotherm is assumed to be monotonically increasing. Conversely, if A^+ is less than A^-, the trend of the isotherm is assumed to be monotonically decreasing.

G.4.4 Application of Isotherm Monotonicity

A modification of the existing approach for enforcing the assumption of monotonicity on tabular metal sorption isotherms in the EPACMTP ensures a more conservative application of these nonlinear isotherms. The approach utilizes enhancements made in the determination of an isotherm's trend to smooth the raw data into a monotonically increasing or decreasing isotherm.

For the case of an isotherm that is determined to have a downward trend over the concentration range [Cmin, Cmax], where Cmin is the minimum dissolved concentration represented in the isotherm and Cmax is the maximum dissolved concentration entering the unsaturated zone, the filtered isotherm is

$$Kd_i = \min(Kd_{i-1}, Kd_i),\ i = 2, N, \tag{G.7}$$

where N is the number of tabulated pairs (C, Kd) for all C less than or equal to Cmax. For the case of an isotherm determined to have an upward trend over the concentration range [Cmin, Cmax], the filtered isotherm is

$$Kd_i = \min(Kd_i, Kd_{i+1}),\ i = N-1, 1. \tag{G.8}$$

G.4.5 Selection of Sorption Coefficient for Saturated Zone

The new search algorithm for a distribution coefficient for the saturated zone (Kd_{SAT}) determines the most conservative value for Kd_{SAT} within the range of Kd's in the tabulated isotherm corresponding to dissolved concentrations that are less than or equal to the diluted maximum observed water table concentration. The resulting value of Kd_{SAT} is independent of the isotherm used, original or monotonic.

Given:

$CMAX_{Dilute}$ Diluted maximum observed concentration at the watertable
C   Array of dissolved concentration in tabular isotherm
Kd   Array of distribution coefficients corresponding to
                          concentrations in C
N   Number of (Kd, C) pairs in tabular isotherm

Result:

Kd_{SAT} Distribution coefficient for saturated zone simulation

Algorithm:

Kd_{SAT} = Kd(1)
i = 1
While C(i) < $CMAX_{Dilute}$ & i <= N
       Kd_{SAT} = min(Kd(i), Kd_{SAT})
       i = i + 1
End

G.4.6   References

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