Appendix B:
Model Development and Configuration

B.1 INTRODUCTION

pH changes in streams and waterbodies result from water chemical and biogeochemical reactions in their different environments—air, soil, and water. These reactions are important to consider in modeling pH levels in streams. This appendix discusses how each chemical was represented in the MDAS model and how the predictions were generated. Model assumptions and the calibration process are also discussed.

To address water chemical and biogeochemical reactions affecting pH, six modules were developed and added to MDAS to better simulate pH levels: (1) the nitrogen soil (subsurface) transformation module, (2) the nitrogen stream (in-stream transformation) module, (3) the sulfate (subsurface) adsorption/desorption module, (4) the sulfate stream (aqueous chemical reaction) module, (5) the soil (subsurface) chemical reaction module, and (6) the stream (in-stream) chemical reaction module. Figures B-1 through B-3 present generalized representations of how the modules interact with each other, the flow of chemical species through the model layers, and the interactions of the species within the modules. With these modules, additional variables (Table B-1) were added to the model.

Chemical species generated in the surface storage layer of the modeling environment by the nitrogen, sulfate, and soil chemical reaction modules are either transported to stream segments as surface runoff loadings or percolate into the upper subsurface and enter the subsurface module. Nitrogen, sulfate, and soil chemical reaction modules are applied to the chemical species in the subsurface storage. Once the chemical species are generated in the upper zone, they are transported to the lower subsurface (groundwater storage) level to undergo nitrogen reactions. The species eventually enter into the corresponding stream segment as interflow and groundwater loadings.
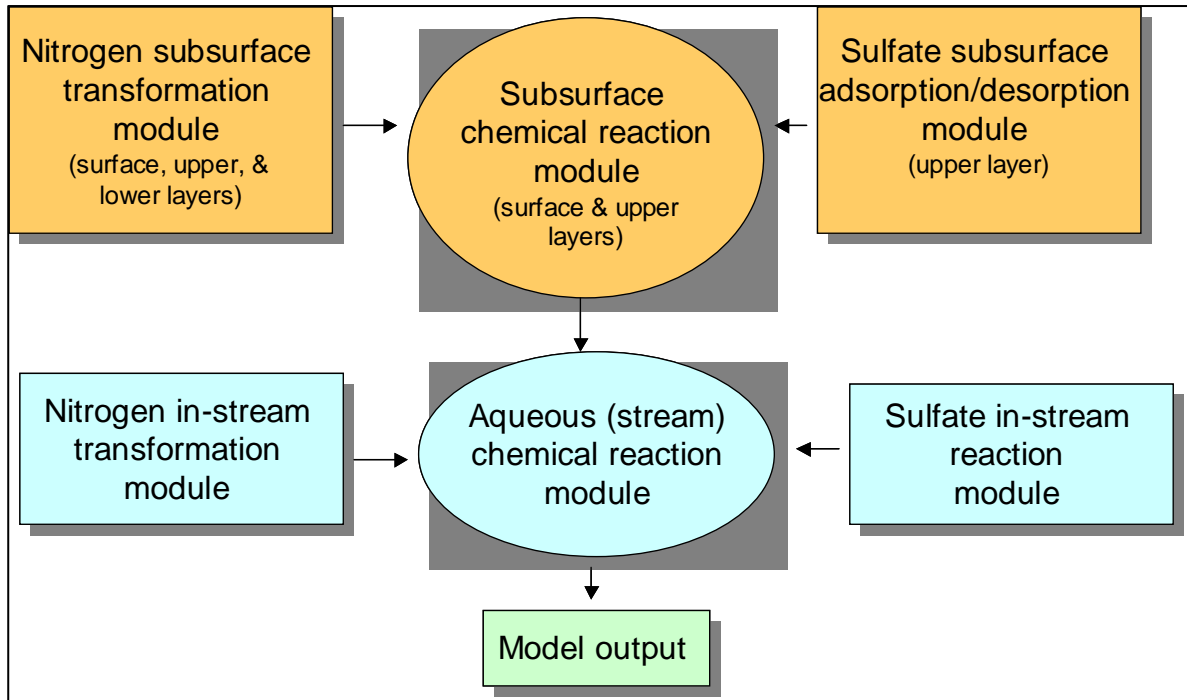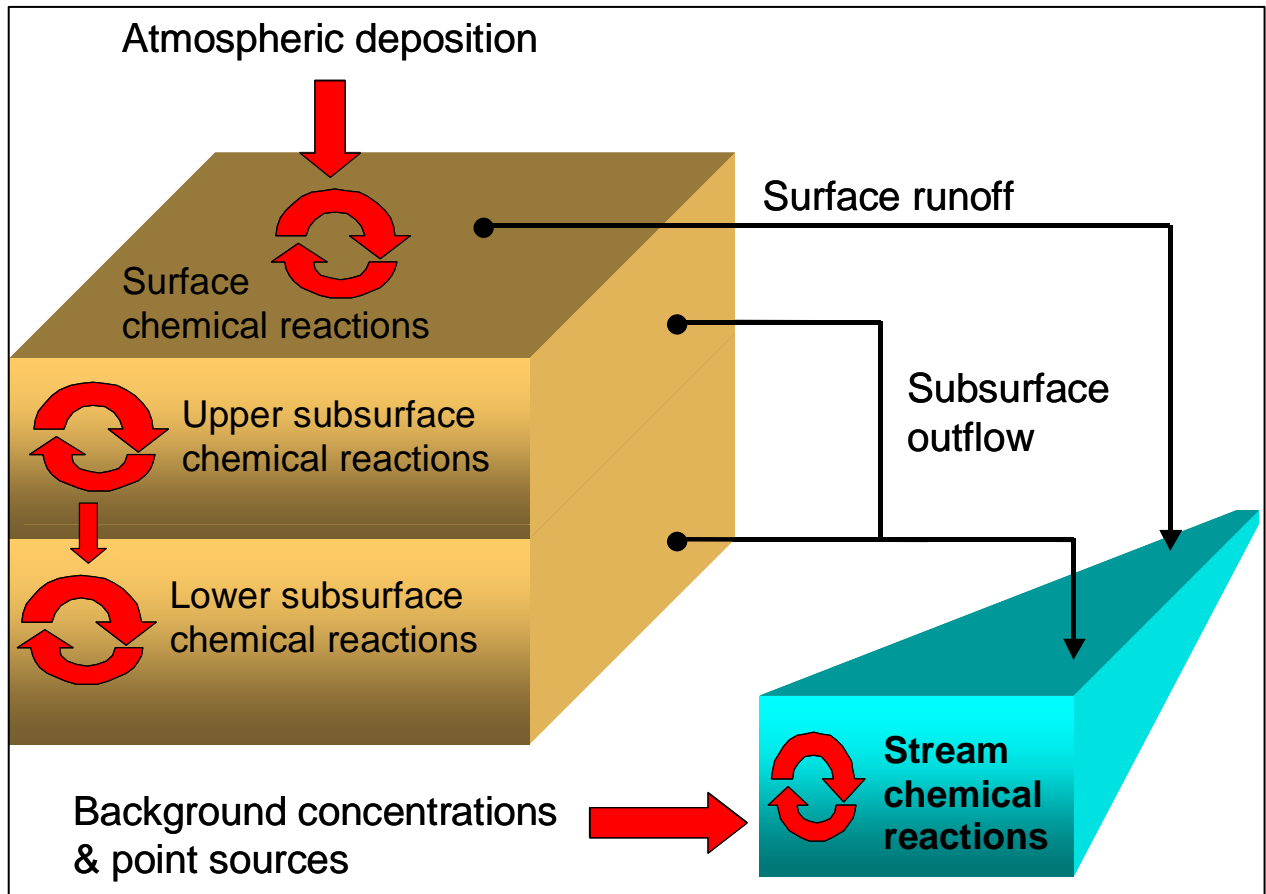
Figure B-1. MDAS overview

Figure B-2. Chemical reaction flow in MDAS

Figure B-3. Chemical species flow in MDAS

Table B-1. Variables added to the MDAS model

Variable	Description	Variable	Description
AlK	Metal (aluminum) dissolution constants	k_3	Nitrogen transformation (plant uptake of NO_3) rate (per day)
CaX	Base saturation percentage (fraction)	k_4	Nitrogen transformation (plant uptake of NH_4S) rate (per day)
DESORP	Ratio of dissolved and adsorbed sulfate	k_6	Nitrogen transformation (OrgN to NH_4S) rate (per day)
FEK	Iron dissolution constants	k_{es}	Nitrogen transformation (NH_4E to NH_4S) rate (per day)
FR_3	Precipitation rate for Ca^{+2} (per day)	kk_1	Sulfate transformation rate (per day)
FR_4	Precipitation rate for CO_3^{-2} (per day)	kk_6	Nitrogen transformation (NH_4S to OrgN) rate (per day)
FR_5	Precipitation rate for dissolved iron (per day)	kk_8	Nitrogen transformation (NO_3 to OrgN) rate (per day)
FR_8	Precipitation rate for dissolved aluminum (per day)	Log Ks	Log of selectivity coefficient
FR_9	Precipitation rate for organic nitrogen (OrgN) (per day)	k_{se}	Nitrogen transformation (NH_4S to NH_4E) rate (per day)

Table B-1. (continued)

Variable	Description	Variable	Description
FRP_5	Precipitation rate for particulate iron (per day)	P_{CO}	CO_2 value (per day)
FRP_8	Precipitation rate for particulate aluminum (per day)	PeakMon	Growing season peak month
k_1	Nitrogen transformation (NH_4S to NO_2) rate (per day)	Theta	Temperature correction coefficient for nitrogen transformation
k_2	Nitrogen transformation (NO_2 to NO_3) rate (per day)		

B.2 NITROGEN

Nitrogen compounds, such as nitrate and ammonium from atmospheric deposition, accumulate and undergo chemical reactions on land surfaces until they infiltrate into soils or run off. The hydrogen ions that are carried with nitrate are a significant contributor to the acidity often observed in rain (Sullivan 2000; Stumm and Morgan 1996) and thus have an impact on pH levels.

Nitrate and ammonium enter the model as atmospheric deposition (wet and dry). These nitrate and ammonium loadings are added directly to land surfaces and stream channels. Loadings from dry deposition are added directly to the stream or to the different land uses and accumulate until they are washed off by precipitation. Loadings due to wet weather are calculated using precipitation data and deposited to different land uses or the stream.

For land surface contributions, the HSPF module MSTLAY transports moisture and chemical species from surface soils through the subsurface soil zones. MDAS processes water quality in the subsurface soils and surface water through the nitrogen soil transformation and nitrogen stream modules, which are described in Sections B.2.1 and B.2.2. In the model, nitrogen assimilation and mineralization reactions are considered first-order reactions.

B.2.1 Nitrogen Soil Transformation Module

Nitrate and ammonium from atmospheric deposition on the land surface percolate through soils, where they are subject to biological transformation. The nitrogen subsurface transformation module performs nitrogen transformations through first-order kinetics and includes uptake of nutrients by plants. Nitrogen species considered in the module are exchangeable ammonium on clays (NH_4E), ammonium (NH_4S), nitrite (NO_2), nitrate (NO_3), and organic nitrogen (OrgN) in solution. Figure B-3, shows the interaction of these different species.

The nitrogen soil transformation module applies to different soil layers: surface, upper layer, and lower layer. Equations in the module are included in Equation Set 1 with rate constants (/day) and nitrogen species (mg/L). This module is based on the concept presented by Mehran and Tanji (1974).

Equation Set 1. Nitrogen soil transformation module

1-1: $\dfrac{\Delta OrgN}{\Delta t} = (-K_6 \times OrgN^n) + (KK_6 \times NH_4S^n) + (KK_8 \times NO_3{}^n)$

1-2: $\dfrac{\Delta NH_4S}{\Delta t} = (-(K_1 + K_{se} + KK_6 + K_4) \times NH_4S^n) + (K_{es} \times NH_4E^n) + (K_6 \times OrgN^n)$

1-3: $\dfrac{\Delta NO_3}{\Delta t} = (-(K_3 + KK_8) \times NO_3{}^n) + (K_2 \times NO_2{}^n)$

1-4: $\dfrac{\Delta NO_2}{\Delta t} = (-K_2 \times NO_2{}^n) + (K_1 \times NH_4S^n)$

1-5: $\dfrac{\Delta NH_4E}{\Delta t} = (-K_{es} \times NH_4E^n) + (K_{se} \times NH_4S^n)$

B.2.2 Nitrogen Stream Module

In the nitrogen stream module, the transformation from ammonium to nitrite to nitrate is considered in the stream using processes similar to those in the subsurface module. The nitrate uptake by aquatic plants is implicitly expressed through first-order kinetic rates. Nitrate and ammonium from background concentrations, atmospheric deposition, and point sources are added to the nitrogen cycle and transformed by this module. Equations in this module are included in Equation Set 2 with rate constants (/day) and nitrogen species (mg/L).

Equation Set 2. Nitrogen stream module

2-1: $\dfrac{\Delta NO_3}{\Delta t} = (-K_3 \times NO_3{}^n) + (K_2 \times NO_2{}^n)$

2-2: $\dfrac{\Delta NO_2}{\Delta t} = (-K_2 \times NO_2{}^n) + (K_1 \times NH_4S^n)$

2-3: $\dfrac{\Delta NH_4S}{\Delta t} = (-K_1 \times NH_4S^n) + (K_6 \times OrgN^n)$

2-4: $\dfrac{\Delta OrgN}{\Delta t} = -K_6 \times OrgN^n$

B.2.3 Nitrogen Calibration

The model was calibrated using observed nitrate and ammonium stream concentrations. Calibration parameters included the nitrogen transformation rates in the different model layers (surface layer, upper subsurface layer, lower subsurface layer, and streams) and precipitation of organic nitrogen in streams. In addition, a temperature correction for nitrogen transformation rates could be calibrated.

B.3 SULFATE

Sulfate is the most significant acid-carrying chemical with potential to decrease the pH of waterbodies in the United States (Sullivan 2000). Sulfate contributions from a variety of sources are represented in the model, including mine seeps (modeled as point sources), background contributions, and atmospheric deposition. Some contributions are direct to the streams while

others accumulate on the land surface and undergo chemical reactions until they ultimately infiltrate into the subsurface or wash off during rainfall events.

Sulfate loading from wet and dry atmospheric deposition is added directly to land surfaces and stream channels in the model. Loadings from dry deposition are added to the different land uses and accumulate until they are washed off by precipitation. Loadings due to wet weather are calculated using precipitation data. Wet and dry deposition are also added directly to the streams. Point source contributions of sulfate are represented as direct stream contributions in the model.

The HSPF module MSTLAY transports moisture and chemicals from surface soils through the subsurface soil zones. Water quality in the subsurface soils (upper zone only) and surface water are processed through the sulfate adsorption/desorption module and sulfate stream modules, which are described in Sections B.3.1 and B.3.2.

B.3.1 Sulfate Adsorption/Desorption Module

This module simulates the amount of sulfate in solution by using the desorption rate (DESORP). The module simulates adsorption/desorption mechanisms of sulfate onto and from soil particles. The model assumes that adsorption and desorption reactions can be explained linearly using DESORP to estimate the sulfate existing in the soil solution.

B.3.2 Sulfate Stream Module

Sulfate loading from the land surface that travels to the stream goes through a first-order reaction in the stream. Equations in this module are included in Equation Set 3 with rate constants (/day) and sulfate (mg/L).

Equation Set 3. Sulfate stream module

$$4\text{-}1:\ \frac{\Delta SO_4}{\Delta t} = (-KK_1 \times SO_4{}^n)$$

B.3.3 Sulfate Calibration

The sulfate subsurface module runs in conjunction with the sulfate module in the stream. The modules were calibrated using observed in-stream sulfate concentrations. The calibration was conducted by adjusting the stream and subsurface variables. Calibration parameters included the desorption ratio (DESORP), sulfate transformation rate (kk_1), and background concentrations.

B.4 CHEMICAL REACTION MODULES

The outputs from the nitrogen and sulfate modules are used as inputs to the chemical reaction modules. These inputs, along with inputs of iron and aluminum, are used to predict pH and acidity levels in the stream segments.

B.4.1 Subsurface Chemical Reaction Module

This module calculates total aluminum, total hydrogen, total calcium, total nitrate, total sulfate, and total carbonate levels and determines loadings that are applied to the aqueous (stream) chemical reaction module. In the subsurface environment, hydrogen generated by acid inputs tends to dissolve aluminosilicate (aluminum hydroxide) if there are insufficient basic cations to

counteract the acidic effect. Subsurface processes associated with this effect are the core part of the module and are based on the model presented by Reuss and Johnson (1985).

This module uses the charge balance principle—any increase of negative charges should be accompanied by an equivalent increase in positive charge—to estimate pH levels and aluminum species. The module uses sulfate, nitrate, ammonium, and CO_2 gas as chemical inputs. It is run for pervious land uses in the surface layer and upper subsurface layer. The convergence of the numerical calculation was assured by the bisection method, which was used only if the Newton-Raphson method (Schnoor 1996; Moreal and Morgan 1972) failed to converge.

The method for estimating available subsurface CO_2 gas was based on methods found in Appelo and Postma (2005). The method uses the mean annual actual evapotranspiration to estimate the mean growing season soil CO_2. The estimated mean annual actual evapotranspiration was estimated for Maryland by Appelo and Postma (2005). The CO_2 daily values in the model were estimated using sine curves to assign the peak CO_2 month and peak CO_2 value because CO_2 levels in soils tend to rise due to microbial and plant activities during warmer months (Brady and Weil 1999). The model allows for a user-defined peak growing season month, and, thus, the peak month of CO_2 usage. The module uses a fixed atmospheric CO_2 gas level of 0.00035 atmospheres (atm) for the surface soil layer. For the upper subsurface soil layer, the CO_2 gas level is derived from equations 5-1 through 5-4 in Equation Set 4.

Equation Set 4. CO_2 peak sine curve calculations

5-1: $\max = 10^{-3.47 + 2.09 \times (1^{-0.00172 \times AET})}$

5-2: $amp = 0.5 \times (max\text{-}min)$

5-3: $up = amp + min$

5-4:

$$CO_2 = up + (amp \times \sin(\frac{Pi \times 360 \times JDay}{180 \times DaysInYear} + \frac{90 \times Pi}{180} - \frac{Pi \times 360 \times PeakJDay}{180 \times DaysInYear}))$$

where:
   AET = annual actual mean evapotranspiration (AET = 800 mm)
   max = maximum height of the sine curve
   min = minimum height of the sine curve (min = 0.00035)
   amp = amplification of the sine curve
   up = vertical movement of the sine curve
   Pi = 3.14159265358979323
   $JDay$ = Julian day

The model also requires an aluminum solubility constant (K_Al), exchange selectivity coefficient (K_s), and base cation saturation ratio (CaX) for basic cations. The selectivity coefficient describes the tendency of soil particles to exchange aluminum with base cations such as calcium, magnesium, and sodium or vise versa, while the base saturation ratio indicates how much base cation is available for the exchanges.

The output from the subsurface chemical reaction module (total aluminum, total hydrogen, total calcium, total nitrate, total sulfate, and total carbonate) is input into the aqueous chemical reaction module. Equation Set 5 describes the main equations used for the soil chemical reaction module. Details and the model concepts can be found in Reuss and Johnson (1985).

Equation Set 5. Chemical reaction module main equations

6-1: $3[Al^{+3}]+2[Ca^{+2}]+2[Al(OH)^{+2}]+[Al(OH)_2^{+}]+[H^{+}]+[NH_4^{+}]=$

$\qquad [HCO_3^{-}]+2[SO_4^{-2}]+[NO^{-3}]+[OH^{-}]+2[CO_3^{-2}]$

6-2: $[Al^{+3}]=K\_Al\times[H^{+}]^3$

6-3: $[Al(OH)^{+2}]=K\_Al\times10^{-5.02}\times[H^{+}]^2$

6-4: $[Al(OH)^{+2}]=K\_Al\times10^{-9.3}\times[H^{+}]$

6-5: $[Ca^{+2}]=\dfrac{K_s(CaX^3)^{2/3}\times K\_Al^{1/3}\times[H^{+}]^2}{(1-CaX)^2}$

6-6: $[HCO_3^{-}]=\dfrac{P_{CO_2}\times10^{-7.81}}{[H^{+}]}$

B.4.2 Aqueous (Stream) Chemical Reaction Module

The chemical concentrations estimated from the subsurface chemical reaction module are used as input for the aqueous chemical reaction module. Main inputs include total aluminum, total hydrogen, total iron, total calcium, total nitrate, total sulfate, total ammonium and total carbonate. The model simulates the concentrations for different chemical species and pH, and if metals become supersaturated, the model precipitates the metals out of solution. The aqueous chemical reaction module is based on a chemical speciation model, MINEQL (Westall et al. 1974). MINEQL uses the same numerical solution method used for EPA's MINTEQA4 (Allison et al.1991). Table B-2 shows chemical species considered in the aqueous model.

Table B-2. Stoichiometric matrix

Name	H^{+}	Ca^{+2}	CO_3^{-2}	Fe^{+3}	NO_3	NH_4	Al	SO_4^{-2}	K (reaction constants)
H^{+}	1	0	0	0	0	0	0	0	0
Ca^{+2}	0	1	0	0	0	0	0	0	0
CO_3^{-2}	0	0	1	0	0	0	0	0	0
Fe^{+3}	0	0	0	1	0	0	0	0	0
NO_3^{-2}	0	0	0	0	1	0	0	0	0
NH_4^{+}	0	0	0	0	0	1	0	0	0
Al^{+3}	0	0	0	0	0	0	1	0	0
SO_4^{-2}	0	0	0	0	0	0	0	1	0
OH^{-}	-1	0	0	0	0	0	0	0	-13.998
NH_3	-1	0	0	0	0	1	0	0	-9.25

Table B-2. (continued)

Name	H^+	Ca^{+2}	CO_3^{-2}	Fe^{+3}	NO_3	NH_4	Al	SO_4^{-2}	K (reaction constants)
$Al(OH)_2^+$	-2	0	0	0	0	0	1	0	-10.1
$Al(OH)_3$	-3	0	0	0	0	0	1	0	-16
$Al(OH)_4^-$	-4	0	0	0	0	0	1	0	-23
$AlOH^{+2}$	-1	0	0	0	0	0	1	0	-4.9
$Al(SO_4)^+$	0	0	0	0	0	0	1	1	3.89
$CaCO_3$	0	1	1	0	0	0	0	0	3.15
$CaHCO_3^+$	1	1	1	0	0	0	0	0	11.33
$CaOH^+$	-1	1	0	0	0	0	0	0	-12.598
$CaSO_4$	0	1	0	0	0	0	0	1	2.309
H_2CO_3	2	0	1	0	0	0	0	0	16.681
HCO_3-	1	0	1	0	0	0	0	0	10.33
$FeOH^{+2}$	-1	0	0	1	0	0	0	0	-2.19
$Fe(OH)_2^+$	-2	0	0	1	0	0	0	0	-5.67
$Fe_2(OH)_2^{+4}$	-2	0	0	2	0	0	0	0	-2.95
$Fe(OH)_3$	-3	0	0	1	0	0	0	0	-13.6
$FeOH_4^-$	-4	0	0	1	0	0	0	0	-21.6
$Fe_3(OH)_4^{+5}$	-4	0	0	3	0	0	0	0	-6.3
$FeSO_4^+$	0	0	0	1	0	0	0	1	3.92
CO_2	2	0	1	0	0	0	0	0	18.16
H_2O	0	0	0	0	0	0	0	0	0
$Fe(OH)_3$ (solid)	-3	0	0	1	0	0	0	0	-4.891
$Al(OH)_3$ (solid)	-3	0	0	0	0	0	1	0	-8.7

B.4.3 Metals, pH, and Acidity Calibration

After nitrogen and sulfate calibrations were completed, metals and pH calibrations were conducted. These calibrations were conducted mainly with the subsurface chemical reaction module (see Section B.4.1) because chemical loadings were largely generated from the contributing watersheds. Calibrations focused on those sources. The model uses the MINTEQA2 database for acidity and dissolved constants.

B.5 REFERENCES

Allison, J.D., D. S. Brown, and K.J. Novo-Gradac. 1991. *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual.* EPA/600/3-91/021. U.S. Environmental Protection Agency, Washington, DC.

Appelo, C.A.J., and D. Postma. 2005. *Geochemistry, Groundwater and Pollution*. 2nd ed. Taylor & Francis.

Brady, N.C., and R.R. Weil. 1999. *Elements of the Nature and Property of Soils*. Prentice Hall, Upper Saddle River, NJ.

Mehran. M., and K.K. Tanji. 1974. Computer Modeling of Nitrogen Transformation in Soils. *Journal of Environmental Quality*. 3(4):391–396.

Morel, F., and J. Morgan. 1972. A Numerical Method for Computing Equilibria in Aqueous Chemical Systems. *Environmental Science & Technology* 6(1):58–67.

Reuss, J.O., and D.W. Johnson. 1986. Acid Deposition and the Acidification of Soils and Waters. *Ecological Studies* 59, Springer-Verlag.

Schnoor, J.L. 1996. *Environmental Modeling: Fate and Transport of Pollutants in Water, Air, and Soil*. Wiley-Interscience, New York, NY.

Sullivan, T.J. 2000. *Aquatic Effects of Acid Deposition 2000*. Lewis Publishers, Boca Raton, FL

Stumm, W., and J.J.Morgan. 1996. *Aquatic Chemistry*. John Wiley, New York.

Westall, J.C., J.L. Zachary, and F.M.M. Morel. 1974. *MINEQL, A computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous Systems*. MIT Technical Note No.18.