

**APPENDIX H**  
**MAGIC MODEL DESCRIPTION AND APPLICATION METHODS**

## **H.1 Introduction**

The major tools available for evaluating the potential response of aquatic resources to changes in atmospheric deposition of sulfur and nitrogen are mathematical models. One of the prominent models developed to estimate acidification of lakes and streams is MAGIC (Model of Acidification of Groundwater In Catchments, Cosby et al., 1985a-c). MAGIC was the principal model used by the National Acid Precipitation Assessment Program (NAPAP) in assessment of potential future damage to lakes and streams in the eastern United States (NAPAP 1991, Thornton et al. 1990). The validity of the model has been confirmed by comparison with estimates of lake acidification inferred from paleolimnological reconstructions of historical lake changes in pH (Sullivan et al. 1991, 1996) and with the results of several catchment-scale experimental acidification and de-acidification experiments (e.g., Cosby et al. 1995, 1996). MAGIC has been used to reconstruct the history of acidification and to simulate future trends on a regional basis and in a large number of individual catchments in both North America and Europe (e.g., Lepisto et al. 1988; Whitehead et al. 1988; Cosby et al. 1989, 1990, 1994, 1996; Hornberger et al. 1989; Jenkins et al. 1990a-c; Wright et al. 1990, 1994; Norton et al. 1992).

## **H.2 Conceptual Basis of the Model**

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry. The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: 1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving sulfate adsorption, cation exchange, dissolution-precipitation- speciation of aluminum and dissolution-speciation of inorganic carbon; and 2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and aluminum. Sulfate adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of aluminum trihydroxide. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with sulfate and fluoride. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. First-order rates are used for retention (uptake) of nitrate and ammonium in the catchment. Weathering rates are assumed to be constant. A set of mass balance equations for base cations and strong acid anions are included. Given a description of the historical deposition at a site, the model equations are solved numerically to give long-term reconstructions of surface water chemistry (for complete details of the model see Cosby et al., 1985 a-c, 1989).

### **H.3 Equilibrium Equations in the Model**

#### *H.3.1 Cation and Anion Exchange in Soil Water*

Cation exchange reactions between the soil matrix and soil solution are assumed to result in an equilibrium partitioning of calcium, magnesium, sodium, potassium and trivalent aluminum between solid and aqueous phases. The equilibrium expressions for cation exchange (Table H-1) are constructed using a Gaines-Thomas expression (Gaines and Thomas, 1953).  $E_i$  represents exchangeable fractions of each base cation on the soil (equivalents of each base cation per total cation exchange capacity of the soil). The sum of all exchangeable fractions must equal 1.0. Base saturation of the soil is defined as the sum of the exchangeable fractions of the base cations (Table H-2). The selectivity coefficients (Table H-3) must be calibrated for each aggregated soil layer in the model. The calibration procedure relies on observations of the exchangeable fractions of base cations in soils and measured base cation concentrations in streamwater (see Cosby et al. 1984, 1985a,b for details).

Anion exchange reactions are assumed to occur only for sulfate ion. The relationship between dissolved and adsorbed sulfate (Table H-1) is assumed to follow a Langmuir isotherm (Couto et al. 1979, Hasan et al. 1970). MAGIC is a catchment-scale model and it is often the case that the effective values of aggregated parameters intended to represent large-scale function cannot be derived by a direct scaling-up of similar parameters measured in a laboratory setting

Table H-1. Equations in the MAGIC model.

Equilibrium Equations

Cation and Anion Exchange in Soil Water

$$E_{Ca} + E_{Mg} + E_{Na} + E_K + E_{Al} = 1.0$$

$$\frac{\{Ca^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{Ca}^3} = S_{AlCa} \quad \frac{\{Mg^{2+}\}^3 E_{Al}^2}{\{Al^{3+}\}^2 E_{Mg}^3} = S_{AlMg} \quad \frac{\{Na^+\}^3 E_{Al}}{\{Al^{3+}\} E_{Na}^3} = S_{AlNa} \quad \frac{\{K^+\}^3 E_{Al}}{\{Al^{3+}\} E_K^3} = S_{AlK} \quad \frac{\{SO_4^{2-}\}}{C_{1/2} + \{SO_4^{2-}\}} * E_{mx} = E_{SO4}$$

Inorganic Aluminum in Soil Water and Surface Water

$$\{Al^{3+}\} = [K_{Al}] * \{H^+\}^{S_{Al}}$$

$$\frac{\{Al(OH)^{2+}\} \{H^+\}}{\{Al^{3+}\}} = K_{Al1} \quad \frac{\{Al(OH)_2^+\} \{H^+\}^2}{\{Al^{3+}\}} = K_{Al2} \quad \frac{\{Al(OH)_3^0\} \{H^+\}^3}{\{Al^{3+}\}} = K_{Al3} \quad \frac{\{Al(OH)_4^-\} \{H^+\}^4}{\{Al^{3+}\}} = K_{Al4}$$

$$\frac{\{AlF_2^+\}}{\{Al^{3+}\} \{F^-\}} = K_{Al5} \quad \frac{\{AlF_3^0\}}{\{Al^{3+}\} \{F^-\}^2} = K_{Al6} \quad \frac{\{AlF_4^-\}}{\{Al^{3+}\} \{F^-\}^3} = K_{Al7} \quad \frac{\{AlF_6^{3-}\}}{\{Al^{3+}\} \{F^-\}^4} = K_{Al8}$$

$$\frac{\{AlF_5^{2-}\}}{\{Al^{3+}\} \{F^-\}^5} = K_{Al9} \quad \frac{\{AlF_6^{3-}\}}{\{Al^{3+}\} \{F^-\}^6} = K_{Al10} \quad \frac{\{Al(SO_4)^+\}}{\{Al^{3+}\} \{SO_4^{2-}\}} = K_{Al11} \quad \frac{\{Al(SO_4)_2^-\}}{\{Al^{3+}\} \{SO_4^{2-}\}^2} = K_{Al12}$$

Inorganic and Organic Carbon in Soil Water and Surface Water; Dissociation of Water

$$\{H^+\} \{OH^-\} = K_w \quad \frac{\{H_2CO_3^0\}}{P_{CO2}} = K_{CO21} \quad \frac{\{HCO_3^-\} \{H^+\}}{\{H_2CO_3^0\}} = K_{CO22} \quad \frac{\{CO_3^{2-}\} \{H^+\}}{\{HCO_3^-\}} = K_{CO23} \quad \frac{\{H_2A^-\} \{H^+\}}{\{H_3A\}} = K_{OA1}$$

$$\frac{\{HA^{2-}\} \{H^+\}}{\{H_2A^-\}} = K_{OA2} \quad \frac{\{A^{3-}\} \{H^+\}}{\{HA^{2-}\}} = K_{OA3} \quad \frac{\{AlA\}}{\{Al^{3+}\} \{A^{3-}\}} = K_{OA4} \quad \frac{\{Al(H)A^+\}}{\{Al^{3+}\} \{H^+\} \{A^{3-}\}} = K_{OA5}$$

Braces denote activities (calculated from concentrations using the extended Debye-Huckel equation)

Mass and Ionic Balance Equations

Ionic Balance in Soil Water and Surface Water (parentheses denote molar concentrations)

$$2(Ca^{2+}) + 2(Mg^{2+}) + (Na^+) + (K^+) + (NH_4^+) + (H^+) + 3(Al^{3+}) + 2(AlOH^{2+}) + (Al(OH)_2^+) + 2(AlF_2^+) + (AlF_3^0) + (AlSO_4^+) + (Al(H)A^+) \\ = 2(SO_4^{2-}) + (Cl^-) + (NO_3^-) + (F^-) + (OH^-) + (HCO_3^-) + 2(CO_3^{2-}) + (H_2A^-) + 2(HA^{2-}) + 3(A^{3-}) + (Al(OH)_4^-) + (AlF_4^-) + 2(AlF_5^{2-}) \\ + 3(AlF_6^{3-}) + (Al(SO_4)_2^-)$$

Mass Balance for Ions in Soil Water and Surface Water (rates of change in eq m<sup>-2</sup> yr<sup>-1</sup>)

$$\frac{dCa_T}{dt} = AD_{Ca} + W_{Ca} + SS_{Ca} - Q * 2(Ca^{2+}) \quad \frac{dNO_3_T}{dt} = AD_{NO3} + W_{NO3} + SS_{NO3} + NIT - IM_{NO3} - UP_{NO3} - DEN - Q * (NO_3^-)$$

$$\frac{dMg_T}{dt} = AD_{Mg} + W_{Mg} + SS_{Mg} - Q * 2(Mg^{2+}) \quad \frac{dNH_4_T}{dt} = AD_{NH4} + W_{NH4} + SS_{NH4} + MIN - IM_{NH4} - UP_{NH4} - NIT - Q * (NH_4^+)$$

$$\frac{dNa_T}{dt} = AD_{Na} + W_{Na} + SS_{Na} - Q * (Na^+) \quad \frac{dSO_4_T}{dt} = AD_{SO4} + W_{SO4} + SS_{SO4} - Q * 2[\{SO_4^{2-}\} + \{AlSO_4^+\} + 2\{Al(SO_4)_2^-\}]$$

$$\frac{dK_T}{dt} = AD_K + W_K + SS_K - Q * (K^+) \quad \frac{dCl_T}{dt} = AD_{Cl} + W_{Cl} + SS_{Cl} - Q * (Cl^-)$$

$$\frac{dF_T}{dt} = AD_F + W_F + SS_F - Q * [\{F^-\} + \{AlF_2^+\} + 2\{AlF_3^0\} + 3\{AlF_4^-\} + 4\{AlF_5^{2-}\} + 5\{AlF_6^{3-}\} + 6\{AlF_6^{3-}\}]$$

Table H-2. Variables in the MAGIC model.

State Variables (functions of time, calculated by model)	
<i>Aqueous Phase - Ionic Concentrations in Soil Water and Surface Water (mol m<sup>-3</sup>)</i>	
Base Cations: (Ca <sup>2+</sup> )(Mg <sup>2+</sup> )(Na <sup>+</sup> )(K <sup>+</sup> )(NH <sub>4</sub> <sup>+</sup> )	Strong Acid Anions: (SO <sub>4</sub> <sup>2-</sup> )(Cl <sup>-</sup> )(NO <sub>3</sub> <sup>-</sup> )(F <sup>-</sup> )
Hydrogen and Hydroxyl Ions: (H <sup>+</sup> )(OH <sup>-</sup> )	Inorganic Carbon: (H <sub>2</sub> CO <sub>3</sub> <sup>*</sup> )(HCO <sub>3</sub> <sup>-</sup> )(CO <sub>3</sub> <sup>2-</sup> )
Aluminum: (Al <sup>3+</sup> )(AlOH <sup>2+</sup> )(Al(OH) <sub>2</sub> <sup>+</sup> )(Al(OH) <sub>3</sub> <sup>0</sup> )(Al(OH) <sub>4</sub> <sup>-</sup> )(AlF <sup>2+</sup> )(AlF <sub>2</sub> <sup>+</sup> )(AlF <sub>3</sub> <sup>0</sup> )(AlF <sub>4</sub> <sup>-</sup> )(AlF <sub>5</sub> <sup>2-</sup> )(AlF <sub>6</sub> <sup>3-</sup> )(AlSO <sub>4</sub> <sup>+</sup> )(Al(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup> )	
Organic Carbon: (H <sub>3</sub> A)(H <sub>2</sub> A <sup>-</sup> )(HA <sup>2-</sup> )(A <sup>3-</sup> )(AlA)(Al(H)A <sup>+</sup> )	
<i>Solid Phase - Exchangeable Ions on Soil Matrix; Soil Organic Matter Constituents</i>	
Exchangeable Cations (fraction): E <sub>Ca</sub> , E <sub>Mg</sub> , E <sub>Na</sub> , E <sub>K</sub> , E <sub>Al</sub>	Exchangeable Sulphate (eq kg <sup>-1</sup> ): E <sub>SO4</sub>
Organic Carbon and Nitrogen (mol m <sup>-2</sup> ): C <sub>Org</sub> , N <sub>Org</sub>	
Defined Variables (derived from state variables)	
<i>Total Ions for Mass Balance (eq m<sup>-2</sup>)</i>	
Ca <sub>T</sub> = SM*CEC*E <sub>Ca</sub> + SV*2(Ca <sup>2+</sup> )	SO <sub>4T</sub> = SM*E <sub>SO4</sub> + SV*TOT <sub>SO4</sub>
Na <sub>T</sub> = SM*CEC*E <sub>Na</sub> + SV*(Na <sup>+</sup> )	NO <sub>3T</sub> = SV*(NO <sub>3</sub> <sup>-</sup> )
Mg <sub>T</sub> = SM*CEC*E <sub>Mg</sub> + SV*2(Mg <sup>2+</sup> )	Cl <sub>T</sub> = SV*(Cl <sup>-</sup> )
K <sub>T</sub> = SM*CEC*E <sub>K</sub> + SV*(K <sup>+</sup> )	NH <sub>4T</sub> = SV*(NH <sub>4</sub> <sup>+</sup> )
	F <sub>T</sub> = SV*TOT <sub>F</sub>
<i>Total Aqueous Concentrations (eq m<sup>-3</sup>)</i>	
SBC = 2(Ca <sup>2+</sup> ) + 2(Mg <sup>2+</sup> ) + (Na <sup>+</sup> ) + (K <sup>+</sup> )	TOT <sub>Al</sub> = 3(Al) <sub>TOT</sub>
TOT <sub>Al</sub> = 3(Al) <sub>TOT</sub>	TOT <sub>F</sub> = (AlF <sup>2+</sup> ) + 2(AlF <sub>2</sub> <sup>+</sup> ) + 3(AlF <sub>3</sub> <sup>0</sup> ) + 4(AlF <sub>4</sub> <sup>-</sup> ) + 5(AlF <sub>5</sub> <sup>2-</sup> ) + 6(AlF <sub>6</sub> <sup>3-</sup> )
SAA = 2(SO <sub>4</sub> <sup>2-</sup> ) + (Cl <sup>-</sup> ) + (NO <sub>3</sub> <sup>-</sup> ) + (F <sup>-</sup> )	DOC <sub>Al</sub> = 3(Al) <sub>DOC</sub>
	TOT <sub>SO4</sub> = 2(SO <sub>4</sub> <sup>2-</sup> ) + 2(AlSO <sub>4</sub> <sup>+</sup> ) + 4(Al(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup> )
<i>Summed Species (mol m<sup>-3</sup>)</i>	
(Al) <sub>OH</sub> = (AlOH <sup>2+</sup> ) + (Al(OH) <sub>2</sub> <sup>+</sup> ) + (Al(OH) <sub>3</sub> <sup>0</sup> ) + (Al(OH) <sub>4</sub> <sup>-</sup> )	(Al) <sub>SO4</sub> = (AlSO <sub>4</sub> <sup>+</sup> ) + (Al(SO <sub>4</sub> ) <sub>2</sub> <sup>-</sup> )
(Al) <sub>TOT</sub> = (Al <sup>3+</sup> ) + (Al) <sub>SO4</sub> + (Al) <sub>OH</sub> + (Al) <sub>F</sub> + (Al) <sub>DOC</sub>	(Al) <sub>DOC</sub> = (AlA) + (Al(H)A <sup>+</sup> )
	(Al) <sub>F</sub> = (AlF <sup>2+</sup> ) + (AlF <sub>2</sub> <sup>+</sup> ) + (AlF <sub>3</sub> <sup>0</sup> ) + (AlF <sub>4</sub> <sup>-</sup> ) + (AlF <sub>5</sub> <sup>2-</sup> ) + (AlF <sub>6</sub> <sup>3-</sup> )
	(OA) <sub>TOT</sub> = (H <sub>3</sub> A) + (H <sub>2</sub> A <sup>-</sup> ) + (HA <sup>2-</sup> ) + (A <sup>3-</sup> ) + (AlA) + (Al(H)A <sup>+</sup> )
<i>Charge Balance Alkalinity (eq m<sup>-3</sup>)</i>	
CALK = SBC + (NH <sub>4</sub> <sup>+</sup> ) - SAA	Soil C/N ratio C/N = $\frac{C_{Org}}{N_{Org}}$
<i>Solution pH, pAl</i>	
pH = -log <sub>10</sub> (H <sup>+</sup> )	Soil Base Saturation BS = E <sub>Ca</sub> + E <sub>Mg</sub> + E <sub>Na</sub> + E <sub>K</sub>
pAl = -log <sub>10</sub> (Al <sup>3+</sup> )	

Table H-3. Parameters in the MAGIC model.

Parameters (constant values that must be specified)		
<i>Soil Physical/Chemical Properties</i>		<i>Surface Water Properties</i>
D = depth (m)	CEC = cation exchange capacity (eq kg <sup>-1</sup> )	RT = retention time (yr)
P = porosity (fraction)	C <sub>1/2</sub> = sulphate adsorption half saturation (eq m <sup>-3</sup> )	RA = relative area of lake/stream (fraction)
BD = bulk density (kg m <sup>-3</sup> )	E <sub>max</sub> = sulphate adsorption maximum (eq kg <sup>-1</sup> )	K <sub>Al</sub> = aluminum solubility constant (log <sub>10</sub> )
SM = soil mass (D*BD)	K <sub>Al</sub> = aluminum solubility constant (log <sub>10</sub> )	S <sub>Al</sub> = slope of pH-pAl relationship
SV = soil pore volume (D*P)	S <sub>Al</sub> = slope of pH-pAl relationship	
<i>Aqueous Phase - Equilibrium Constants (log<sub>10</sub>)</i>		
Organic Acid: pK <sub>1</sub> , pK <sub>2</sub> , pK <sub>3</sub> [ -log <sub>10</sub> (K <sub>OA1</sub> , K <sub>OA2</sub> , K <sub>OA3</sub> ) ]		Organic Aluminum: K <sub>OA4</sub> , K <sub>OA5</sub>
Inorganic Aluminum Speciation: K <sub>Al1</sub> , K <sub>Al2</sub> , K <sub>Al3</sub> , K <sub>Al4</sub> , K <sub>Al5</sub> , K <sub>Al6</sub> , K <sub>Al7</sub> , K <sub>Al8</sub> , K <sub>Al9</sub> , K <sub>Al10</sub> , K <sub>Al11</sub> , K <sub>Al12</sub>		
Inorganic Carbon Speciation and Dissociation of Water: K <sub>CO21</sub> , K <sub>CO22</sub> , K <sub>CO23</sub> , K <sub>w</sub>		
<i>Solid Phase - Weathering and Exchange Constants</i>		
Cation Exchange Selectivity Coefficients (log <sub>10</sub> ): S <sub>AlCa</sub> , S <sub>AlMg</sub> , S <sub>AlNa</sub> , S <sub>AlK</sub>		
Weathering Rates (eq m <sup>-2</sup> yr <sup>-1</sup> ): W <sub>Ca</sub> , W <sub>Mg</sub> , W <sub>Na</sub> , W <sub>K</sub> , W <sub>NH4</sub> , W <sub>SO4</sub> , W <sub>Cl</sub> , W <sub>NO3</sub> , W <sub>F</sub>		(can be pH dependent)

(see Rastetter et al. 1992). The sulfate adsorption parameters (Table H-3) used in MAGIC must, therefore, be calibrated for each site. Cosby et al. (1986) described a method for calibrating sulfate adsorption parameters in whole catchment simulations based on input/output budgets and deposition histories for the site.

### H.3.2 Inorganic Aluminum in Soil Water and Surface Water

Inorganic aluminum speciation consists of one reaction involving the equilibrium dissolution of a solid phase of aluminum trihydroxide and twelve reactions involving formation of aqueous complexes of Al<sup>3+</sup>. These reactions are assumed to occur both in soil solution and in surface waters in the model and can be represented by a series of equilibrium equations (Table H-1). Values of the equilibrium constants for the aqueous phase complexation reactions (Table H-3) can be found in the literature. The aluminum solubility constants for the soils in the model are represented by aggregated values. These values are not, therefore, necessarily associated with a particular crystalline form of Al(OH)<sub>3</sub> and must be selected as part of the calibration process.

### *H.3.3 Inorganic and Organic Carbon in Soil Water and Surface Water; and Dissociation of Water*

Inorganic carbon reactions in MAGIC consist of dissolution of CO<sub>2</sub> to form carbonic acid, followed by dissociation to bicarbonate and carbonate. These reactions are assumed to occur both in soil solution and in surface waters in the model and can be represented by equilibrium equations (Table H-1) whose "constants" are temperature-dependent. Values of the equilibrium constants for the carbonate-bicarbonate system and for the dissociation of water (Table H-3) and their temperature dependencies can be found in the literature.

Organic acids are the dominant form of dissolved organic material in natural waters (e.g., McKnight et al. 1985, David and Vance 1991). Organic acids are effective hydrogen ion buffers and can form complexes with inorganic aluminum. Considerable evidence has accumulated suggesting that organic acids influence the response of surface waters to changes in strong acid inputs, most likely by changes in the protonation of the organic acid anions (see Wright 1989). Organic acids were not included in the original formulation of MAGIC because specification (and calibration) of organic acid analog models was hampered by lack of data on organic acid behavior (e.g., Jenkins and Cosby 1989). In 1994, Driscoll et al. (1994) compared several organic acid analog models (mono-, di-, and triprotic organic acid analogs and the model of Oliver et al. 1983) with respect to their abilities to resolve mass balance discrepancies in measured water samples from Adirondack lakes. They concluded that organic acids were important buffers in surface waters even when dissolved organic carbon was low. They obtained the best agreement between predicted and observed pH values using a triprotic organic acid analog model. The triprotic organic acid analog model can also be used to describe the complexation of Al by organic solutes (Schecher and Driscoll 1993, Driscoll et al. 1994). A triprotic organic acid analog model is currently incorporated into the structure of MAGIC.

## **H.4 Mass and Ionic Balance Equations**

Mass balance is required for the total amounts of base cations and strong acid anions in each compartment of the simulated catchment (Table H-1). That is, input minus output of each mass balance ion must equal the rate of change of the total amount of that ion in each compartment of the model. Total amounts in surface water compartments are calculated from concentrations and the water volume. In soil compartments, total amounts include both dissolved amounts in the pore water and adsorbed amounts (if applicable) on the soil matrix. Process-

related inputs (Table H-4) are by atmospheric deposition, primary mineral weathering (in soil compartments) and biological production (decomposition and mineralization). Process-related outputs are by drainage water discharge or biological removal (uptake or immobilization). Unspecified sources and sinks of each ion are also available in the model. These may be used to simulate processes or perturbations not explicitly represented in the model (such as experimental additions of ions, losses of ions resulting from land use changes, etc.). At each time step during model simulation, inputs and outputs are added or subtracted from each compartment, new total amounts are calculated, and the equilibrium equations are solved subject to the constraint of ionic balance (Table H-1) to derive the concentrations of the state variables (Table H-2) for that time step.

## H.5 Model implementation

Atmospheric deposition and net uptake-release fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. Atmospheric fluxes are calculated from concentrations of the ions in

Table H-4. Inputs to the MAGIC model.

Input Fluxes and Conditions (functions of time that must be specified)
<i>Conditions are annual averages (monthly averages are specified for seasonal simulations)</i>
Temperature (°C), Carbon Dioxide (atm), Organic Acid (mol m <sup>-3</sup> ): TEMP, P <sub>CO2</sub> , (OA) <sub>TOT</sub> <i>[CO<sub>2</sub> partial pressure and Organic Acid concentration control the weak inorganic and organic carbon buffers]</i>
<i>Fluxes are annual values (monthly fractions of annual fluxes are specified for seasonal simulations)</i>
Catchment Discharge (m yr <sup>-1</sup> ) and Flow Fractions: Q, F <sub>1</sub> , F <sub>2</sub> , F <sub>3</sub> <i>[Flow fractions specify the pathway of water flux through the modelled system and can vary seasonally]</i>
Atmospheric Deposition (eq m <sup>-2</sup> yr <sup>-1</sup> ): AD <sub>Ca</sub> , AD <sub>Mg</sub> , AD <sub>Na</sub> , AD <sub>K</sub> , AD <sub>NH4</sub> , AD <sub>SO4</sub> , AD <sub>Cl</sub> , AD <sub>NO3</sub> , AD <sub>F</sub> <i>[Deposition is specified as the product of precipitation concentrations and amount, scaled by a dry deposition factor]</i>
Sources and Sinks of Ions (eq m <sup>-2</sup> yr <sup>-1</sup> ): SS <sub>Ca</sub> , SS <sub>Mg</sub> , SS <sub>Na</sub> , SS <sub>K</sub> , SS <sub>NH4</sub> , SS <sub>SO4</sub> , SS <sub>Cl</sub> , SS <sub>NO3</sub> , SS <sub>F</sub> <i>[Sources and sinks are distinct and represent processes, inputs or outputs not explicitly included in the model]</i>
<i>The flow fractions determine atmospheric deposition fluxes into each soil and surface water compartment. Other fluxes and conditions must be specified separately for each model compartment (if appropriate).</i>
Initial Values
<i>Initial values of these state variables must be specified for each model compartment (if appropriate)</i>
Cation and Anion Concentrations (mol m <sup>-3</sup> ): (Ca <sup>2+</sup> ), (Mg <sup>2+</sup> ), (Na <sup>+</sup> ), (K <sup>+</sup> ), (NH <sub>4</sub> <sup>+</sup> ), (SO <sub>4</sub> <sup>2-</sup> ), (Cl <sup>-</sup> ), (NO <sub>3</sub> <sup>-</sup> ), (F <sup>-</sup> )
Exchangeable Ions (fraction): E <sub>Ca</sub> , E <sub>Mg</sub> , E <sub>Na</sub> , E <sub>K</sub>

precipitation and the rainfall volume into the catchment. The atmospheric fluxes of the ions must be corrected for dry deposition of gas, particulates and aerosols and for inputs in cloud/fog water. An estimate of the streamflow volume of the catchment must also be provided to the model. In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual or seasonal simulations. Mean annual or mean monthly deposition, precipitation and streamflow are used to drive the model. The model is not designed to provide temporal resolution greater than monthly. Most simulations are based on annual average conditions. Values for soil and streamwater temperature, partial pressure of carbon dioxide in the soil and streamwater and organic acid concentrations in soilwater and streamwater must also be provided.

As implemented in this project, the model is a two-compartment representation of a catchment. Atmospheric deposition enters the soil compartment and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate streamwater chemistry.

Once initial conditions (initial values of variables in the equilibrium equations) have been established, the equilibrium equations are solved for soil water and streamwater concentrations of the remaining variables. These concentrations are used to calculate the streamwater output fluxes of the model for the first time step. The mass balance equations are (numerically) integrated over the time step, providing new values for the total amounts of base cations and strong acid anions in the system. These in turn are used to calculate new values of the remaining variables, new streamwater fluxes, and so forth. The output from MAGIC is thus a time trace for all major chemical constituents for the period of time chosen for the integration. Details of the numerical integration and a computer code for implementing the model are given by Cosby et al. [1984a, 2001].

## **H.6 Model Calibration Procedure**

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model which can be directly measured or observed in the system of interest (called “fixed” parameters). The model is then run (using observed atmospheric and hydrologic inputs) and the output (stream water and soil chemical

variables, called “criterion” variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called “optimized” parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated. If new assumptions (or values) for any of the fixed variables or inputs to the model are subsequently adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

Because the estimates of the fixed parameters and deposition inputs are subject to uncertainties, a "fuzzy" optimization procedure can be implemented for calibrating the model. The fuzzy optimization procedure consists of multiple calibrations of each catchment using random values of the fixed parameters drawn from the observed possible range of values, and random values of deposition from the range of model estimates. Each of the multiple calibrations begins with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the adjustable parameters. The adjustable parameters are then optimized using the Rosenbrock (1960) algorithm to achieve a minimum error fit to the target variables. This procedure is undertaken ten times for each stream. The final calibrated model is represented by the ensemble of parameter values and variable values of the successful calibrations.

Calibrations are based on volume-weighted mean annual fluxes for a given period of observation. The length of the period of observation used for calibration is variable, but model output will be more reliable if the annual flux estimates used in calibration are based on a number of years rather than just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an “outlier” year (very dry, etc.) constitutes the primary data on which model forecasts are based. On the other hand, averaging over too long a period may remove important trends in the data that need to be simulated by the model. For the study here, the model was calibrated using five-year average values of deposition and up to three years of streamwater chemistry data, if that length of observation were available.

The results discussed in this report are based on the **median** values of the simulated water quality variables from the multiple calibrations of each site. The use of median values for each

stream helps to assure that the simulated responses are neither over- or underestimates, but approximate the most likely behavior of each stream (given the assumptions inherent in the model and the data used to constrain and calibrate the model). The uncertainty analyses in this report make use of the maximum and minimum simulated values from the multiple calibrations for each site to calculate uncertainty “widths” (or confidence intervals) around the median simulated values.

### **H.7 Coupling atmospheric deposition changes with MAGIC for SAMI applications**

In order for MAGIC to be calibrated, we require data describing: a) the absolute amount of total (wet plus dry and occult) deposition for the year in which surface water data are available at a site, and b) the historical changes in total deposition at the site. These data should be available for each site for which the model will be calibrated. The outputs of the atmospheric deposition models employed in SAMI for the future scenarios do not directly provide the required data for MAGIC calibration for two reasons.

First, the SAMI deposition models give average deposition over a fairly large grid area. Local geographical characteristics, however, can give rise to substantial spatial variation in the amount of deposition within these grids. Elevation especially can produce sharp departures from the “grid average” deposition. The calibration of MAGIC requires as precise an estimate of the absolute amount of total deposition as possible for each site. For this reason we use the spatial extrapolation model of Grimm and Lynch (1997) to provide a geographically-explicit, elevation-corrected estimate of wet deposition at each site. This model is based on observed wet deposition values from the NADP wet collection network, and observed precipitation amounts from climate stations.

Once relatively precise estimates of wet deposition are generated for a site, the dry and cloud component of deposition must be estimated. For this, we must rely on atmospheric models because of the scarcity of empirical observations. We use the ratio of wet to (dry plus cloud) deposition from the atmospheric models to calculate dry and cloud deposition amount for our sites from the spatially-explicit wet deposition estimates. Our reasoning is thus: while the absolute deposition amount within a grid square (for which the atmospheric models provide only an average value) may vary quite a lot in the “real world”, the ratio of wet to dry deposition within the grid may be more uniform. That is, if wet deposition is larger at high elevations

compared to low elevations within the grid, then dry deposition is likely to be larger at high elevations. While absolute amounts vary considerably within grids, relative amounts are more uniform. So using wet to dry ratios from the models along with interpolated empirical observations of absolute wet deposition amounts provides the most accurate and precise estimate of total deposition at a site.

The second limitation of the atmospheric models used in SAMI for future scenarios concerns the years simulated. The future scenario models only simulate deposition for the SAMI Reference Year and future years. In order to calibrate MAGIC, we need deposition information for years prior to the SAMI Reference Year. In part, this is due to the necessity of using historical patterns of deposition in the calibration procedure, and in part it is due to the fact that observed surface water data used for calibration of MAGIC are often only available in years other than the SAMI Reference Year.

To overcome this problem, output from the ASTRAP atmospheric model (Shannon 1998) was used to provide the following data for each site being calibrated: a) the ratio of wet to (dry plus cloud) deposition for the calibration year; and b) the relative changes in wet deposition and the wet to (dry plus cloud) ratio that have occurred historically. These data are based on a number of historical runs made using ASTRAP. The model output (wet, dry, and cloud deposition) was provided by Shannon (1998) for a network of sites within the SAMI region for every 5 years from 1900 to 1990. Each SAMI site calibrated to MAGIC is associated with one of the ASTRAP sites. The paired sites can be used to provide estimates of the wet-to-(dry plus cloud) ratio in the Calibration Year, the relative historical variations in wet deposition, and the relative historical variations in the wet-to-(dry plus cloud) ratio for each particular MAGIC site.

#### *H.7.1 Calibration Year Deposition*

The Calibration Year for a given site may not be the same as the SAMI Reference Year (for instance, the DDRP data are calibrated for 1985). In that case, once a site has been calibrated, the model is run forward from the MAGIC Calibration Year to the SAMI Reference Year using the relative changes in deposition known to have occurred based on the NADP data and Lynch's model. In this way, all sites being modeled are "positioned" at the SAMI Reference Year following calibration, and we can then use the modeled changes in future deposition as described in the next section.

### *H.7.2 Deposition for Future Strategies and Scenarios.*

In order to run simulations into the future using MAGIC, we require data describing the change in total (wet plus dry and cloud) deposition at a particular MAGIC site for every year of the future simulation period. The outputs of the atmospheric deposition models employed in SAMI for the future strategies provide these estimates.

SAMI has defined a Reference Year for atmospheric modeling. All future strategies of change in atmospheric deposition are expressed as the % change in total deposition in any year relative to the Reference Year.

The Reference Year for MAGIC has been defined as the same as the SAMI Reference Year (all MAGIC simulations are “positioned” at the SAMI Reference Year following calibration as described above). Therefore, when the atmospheric modelers provide % change in total deposition relative to the SAMI Reference Year, those % changes are applied directly to the total (wet, dry, and occult) deposition amounts used in MAGIC beginning in the SAMI (MAGIC) Reference Year.

## **H.8 Comments on Model Applicability**

The MAGIC model of acidification is a model that has been extensively subjected to the process of testing and confirmation over a 15-year period and thousands of applications (see references cited in the discussion above and additional citations in the References Section of this appendix that are a partial listing of published research using the MAGIC model). MAGIC has been used in scientific studies, as a tool in establishing management practices, and as an aid in making policy decisions regarding controls on emissions and deposition. Overall the model has proven to be robust, reliable, and useful in all of these activities. The longevity and utility of MAGIC results as much from the philosophical approach to its formulation (empirically-based, compatible with readily available data, technically easy to implement, and capable of being tested), as from the soundness of the hydrobiogeochemical concepts and understanding on which the model is based. The success of this conceptual approach in the qualitative and quantitative description of acidification responses of ecosystems suggests that it is also an appropriate tool for examining the recovery responses as well.

## **H.9 References for Appendix H**

Note: The reference list below contains the citations in Appendix H. Following this list is a second reference list containing references to applications of MAGIC. The extra references are included as a partial bibliography of previous MAGIC applications, intended for the general information of the reader.

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