Table 3. Biogeochemical Models

Model	Description	Critical Assumptions	Citations[1]
MAGIC 5.01	Dynamic watershed acidification model; SOx & NOx deposition, weathering, cation exchange, Al_2O_3 equilibrium & kinetics, CO_2 equilibria, SO_4 adsorption, Al & N speciation; Soil aggregated into 2 soil layers, time scale of 1 mo. or annual, organic acids added.	Lumped hydrology and annual timescale provide adequate basis to estimate dynamics of H+ and Al+++; NH_4 deposition is constant.	Cosby 1985, 1995 Van Sickle & Church 1995 Sullivan et al. 1996 Jenkins et al. 1997 Driscoll et al. 1998 Sullivan et al. 1999 http://dino.wiz.uni_kassel.de/model_db/mdb/magic.html
PnET-BGC/CHESS	Integrated dynamic watershed acidification model; Calculates photosynthesis, transpiration, evapotranspiration, drainage; BGC provides biogeochemistry of forest growth & maturation cycle; Chess includes equilibrium aqueous speciation, dissolution & precipitation equilibria, redox, and adsorption.	Most growth/uptake parameters are similar for different tree species.	Running & Gower 1991 Aber & Federer 1992 Aber et al. 1993 Mitchell et al. 1994 Running 1994 Santore & Driscoll 1994 Aber et al. 1997 Aber et al. 1996 Kram et al. 1999
PHREEQC	A CSTR model of aqueous speciation, dissolution & precipitation, adsorption, generalized kinetics, redox, batch-reaction, one-dimensional transport.	Requires linking to a series of CSTRs to represent watershed.	Parkhurst et al. 1980 Plummer et al. 1988 Parkhurst & Appelo 1999 http://water.usgs.gov/software/phreeqc.html
SAFE	Dynamic soil acidification model with soil biogeochemistry, weathering rates (dynamic version of PROFILE).		Sverdrup et al. 1995 http://dino.wiz.uni-kassel.de/model_db/mdb/safe.html
PROFILE-CL	Steady state soil acidification model that calculates critical load for various pH, ANC and Al endpoints; Accepts deposition input, weathering of specified amounts of individual minerals, nitrification, plant uptake (NO_3, NH_4, Ca, Mg, K), adjustable Ksp for Al oxide, DOC complexation of Al.	Data available for soil layer thickness and mineralogy, gibbsite Ksp values known.	Sverdrup et al. 1990 Janicki et al. 1991 http://www.oekodata.com/eng/html/downloadadress.html
BIOME-BGC	Ecosystem process model that computes water, carbon, and nitrogen cycles at a plot scale. In addition to the major 1-D hydrology fluxes, the model simulates the major biological processes that govern vegetation growth and senescence: photosynthesis, respiration, allocation, litterfall, decomposition, and nitrogen mineralization. Generic vegetation types (e.g. evergreen needleaf) and associated biophysical parameters are defined. BIOME-BGC has been linked with the distributed hydrologic model DHSVM.	Its "point" model structure simulates only vertical 1-D processes, and assumes horizontal homogeneity. Therefore, single plots or grids with individual cells that are larger in scale than hillslopes are the ideal applications. Daily time step. Meteorological input consists of daily minimum and maximum air temperature, short-wave radiation, vapor pressure deficit, and precipitation.	Running and Coughlan 1988; Running and Gower 1991 http://www.forestry.umt.edu/ntsg/

Other Biogeochemical Models

[1] For complete references see: http://inrm.labworks.org/acidrain/notes.htm

Birkenes
A very early acidification model that has been superseded by others. (Sogn 1993.)

Direct Distribution
A statistical relationship between changes in acidic deposition and ANC, which requires calibration via another model. Statistical model must be recalibrated for each geographic region. (Small et al. 1987, Small et al. 1995.)

Extended TrickleDown
A lumped parameter model that is poorly constrained; has an annual time step, accepts deposition, calculates a rate-limited ANC mass balance, SO4 sorption. Assumes that NO3, Al, and organic acids can be disregarded. This model was dropped out of the latter part of the 1990 assessment studies and does not appear to have been published on since. (Nikolaidis 1987, Schnoor et al. 1982.)

ILWAS
Integrated Lake Watershed Acidification Study calculates weathering, cation exchange, Al_2O_3 solubility equilibria, CO_2 equilibria, SO_4 adsorption, numerous reaction rates and accepts SO_x & NO_x deposition inputs. License from Electric Power Research Institute required. (Eary et al. 1989, 1992, 1994; Cook et al. 1992, Sogn 1993, Porcella et al. 1995.)

MAGIC-REGIONAL
A version of MAGIC with single soil layer that was used in Maryland Critical Load study. (Ryan 1990, Janicki et al. 1995.)

Mass Flux
Estimates the extent of calcium loss due to export of mobile anions from soil profile. Does not explicitly deal with acid deposition, mineral weathering, etc. (Driscoll et al. 1998, Sogn 1993.)

MINTEQ
Aqueous equilibrium speciation, dissolution & precipitation equilibria, adsorption, redox. Has less adsorption competence than PHREEQC. (Felmy et al. 1984, Allison et al. 1991, Eary & Jenne 1992.)

NETPATH
Transport model with solubility-based cation release, developed to interpret the origin of groundwaters and calculate extent of the mixing of groundwaters. Does not have components needed for critical load calculation (e.g., acidic deposition input, multilayer capability). (Plummer et al. 1991, Mitchell et al.1994, Plummer et al. 1994.)

NuCM
License from Electric Power Research Institute required.

Reuss and Johnson
Simplified charge balance acidification model that includes chemical equilibria. This is an early model that provided a basis for subsequent models. (Sogn 1993.)

SMART II
Simulation Model for Acidification's Regional Trends is a dynamic model that includes deposition, weathering, cation exchange, mass balance (based on mobility concept), equilibrium solubility, organic acid reactions, SO_4 sorption, denitrification, nitrification, charge balance & equilibrium

equations adequate to calculate H^+ and Al^{3+} concentrations, and weathering rate. Contains lake and stream modules. Not enough information to adequately evaluate. (Iivonen et al.1993, Paschet et al. 1993.)

TAME

Terrestrial Aquatic Model for Ecosystems is spatially lumped, one-dimensional transport of S, N, ANC, NH_4, Cl, and total organic carbon. It calculates cation exchange and adsorption. No reference found to its application beyond original publication. (Rees & Schnoor 1994.)

Conclusions

In developing TMDLs for acid deposition impact on lakes and streams, the representation of the biogeochemical processes is complex. A variety of processes, including ion exchange, mineral weathering, and plant uptake, interact in an extremely nonlinear fashion. Processes occur at time scales ranging from hours to years. The timing and movement of water is further governed by the complex nature of the hydrologic response of the watershed. Spatial variability in soil and vegetation require some spatial discretization. Modeling the response of the watershed in all its complexity (spatial, temporal, and process complexity) would clearly exceed the data available to validate the modeling system. Our review of available biogeochemical models recommends the use of PROFILE-CL for screening and PHREEQC for detailed assessment.

PROFILE-CL is a steady-state version of SAFE. It is specifically developed to estimate critical loads required to acidify multi-layered soil systems. Critical loads can be estimated for various assessment endpoints, including pH and Al. PROFILE-CL also includes some sensitivity analysis capability. Estimating critical loads is useful in screening for TMDLs. Mapping critical loads over large regions based on the limited available soil and vegetation data, helps prioritize and focus efforts. PROFILE-CL has a limited set of reactions that cannot be expanded by the user. The steady state nature of PROFILE makes model validation impossible, since steady state conditions are never observed.

PROFILE-CL has been developed by researchers in Sweden, Germany and the Netherlands, and is the most widely used critical loads model in Europe. It is implemented in MICROSOFT(tm) ACCESS(tm). It is free and publicly available. (Note the PROFILE-CL website has gone offline in the past few weeks and we are trying to ascertain why.) However, the source code is not open. Therefore, understanding the model is limited to the scant documentation. Given the limited documentation, steady state assumption, and lack of sufficient peer review, PROFILE-CL cannot be expected to defend final TMDLs. Further documentation of SAFE/PROFILE process representation is attached.

PHREEQC is a geochemistry code with a long history, extensive peer review and a high level of credibility within the scientific community. This provides it a high level of defensibility in any final TMDL decisionmaking. It was developed by the US Geological Survey. It is publicly available and the source code is open. The code is written in C and therefore can be run on any PC or workstation. PHREEQC was developed as a general purpose geochemistry code with no specific features for acid rain or TMDL assessments. While the code has a flexible input file structure, it is not interactive or intended for those without significant understanding of geochemistry models. PHREEQC's chemistry is robust and complete. PHREEQC's database can be expanded by the user to include any speciation reaction. PHREEQC's application to acid rain TMDLs involves all the issues typical with complex dynamic models (initial conditions, boundary conditions, parameter uncertainty, spatial and temporal discretization). Significant amounts of data (spatial and temporal) are required to validate the model. Additionally, there is no explicit representation for bio (vegetation) process in the model.

The distinct strengths of PROFILE-CL and PHREEQC can be applied together in TMDL development. PROFILE-CL can be used to identify critical loads for each watershed in the entire study domain. The spatial maps of critical loads can be overlain with atmospheric deposition developed from the RADM simulations. At a screening level, watersheds where the RADM deposition levels exceed the critical loads are assumed to be at risk. Numerous RADM scenarios can be considered to assess the number and location of watersheds impacted by each scenario. Priority watersheds assessed to be at risk should be further investigated with PHREEQC. PHREEQC results should be validated with time series water quality data. Any final TMDL will be based on PHREEQC results.