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Research conducted under this grant has included several issues concerning acid-base chemistry modeling of aquatic ecosystems using the Model of Acidification of Groundwater in Catchments (MAGIC). The influence of naturally-occurring organic acids and land use practices within the watershed have been investigated with respect to their effects on model performance. A verison of the MAGIC model was prepared for use in DOE's Tracking and Analysis Framework.

1. INFLUENCE OF ORGANIC ACIDS ON MODEL PERFORMANCE

Sullivan et al. (1991, 1992) recently compared MAGIC model hindcasts and paleolimnological inferences of historical acidification (based on diatom-inferred pH) for a set of 33 statistically-representative Adirondack lakes. This study represented the first regional and statistical model confirmation exercise conducted for a process-based acid-base chemistry model. Both assessment methods suggested that acidification of low-ANC Adirondack lakes had occurred since pre-industrial times. They differed primarily in that MAGIC inferred greater acidification and also that acidification had occurred in all lakes in the comparison. The diatom approach inferred that acidification had been restricted to low-ANC lakes (currently $<$ about 50 μeq L^{-1}).

The lack of organic acid representation in the MAGIC simulations reported by Sullivan et al. (1991, 1992), and similarly by the U.S. EPA's Direct Delayed Response Project (Cosby et al. 1989, Church et al. 1989) and the NAPAP Integrated Assessment analyses (NAPAP 1991), may have been an important factor contributing to the differences in acidification implied by the two approaches. Organic acids commonly exert a large influence on surface water acid-base chemistry, particularly in dilute waters having moderate to high dissolved organic carbon (DOC) concentrations. A project was therefore initiated by E&S Environmental Chemistry, Inc. in March, 1992 to incorporate an organic acid representation into MAGIC (Model of Acidification of Groundwater in Catchments) and test the revised model using independent data sources. Major components of the project included:

1. extending the MAGIC model by incorporating a quantitative organic acid representation, based on empirical data and geochemical considerations, and
2. testing the revised model using data from paleolimnological hindcasts of pre-industrial chemistry for 33 Adirondack Mountain lakes, and the results of whole-catchment artificial acidification projects in Maine and Norway.

The principal objectives of this research were to extend the MAGIC model by incorporating an organic acid analog representation, and test the extended MAGIC model using independent data. Model testing involved evaluation of all major ion responses, and included comparisons between MAGIC hindcasts or forecasts and the results of diatom inferences of lakewater pH in the Adirondack Mountains of New York and also the results of whole-catchment acid addition and exclusion experiments in Maine and Norway.

DISCLAIMER

1.1. Comparison of the Magic and Diatom Models for Adirondack Lakes

The organic acidity of lakewater sampled by the Adirondack Lakes Survey Corporation (ALSC) was modeled by fitting the ALSC data base to mono-, di-, and triprotic organic acid models, and also to the model of Oliver et al. (1983). The calibration procedure consisted of numerical fitting of the pK values and site densities of each model to observed pH, aluminum, dissolved organic carbon, and calculated charge imbalance (i.e. assumed to be organic anion charge) for all of the lakes in the ALSC data base. The object of the fitting routine was to minimize the differences (across all lakes) between the organic charge simulated by the pertinent organic acid model and the calculated charge imbalance (assumed organic anion charge) for the lakes. The triprotic acid model gave the best fit to the ALSC data.

The 33 Adirondack study lakes included in this project were sampled as part of the U.S. EPA's Eastern Lake Survey (ELS-I, Linthurst et al. 1986). They were also included in EPA's Direct Delayed Response Project (DDRP) and the Paleoecological Investigation of Recent Lake Acidification-Phase II study (PIRLA-II).

Three independent data sets (DDRP, PIRLA-II, and ALSC) and three independent interpretive models (MAGIC, paleolimnology, and Driscoll et al.'s [1994] triprotic organic acid analog) were combined to test the consistency of the results between the diatom approach and the extended MAGIC model for estimating pre-industrial lakewater pH. A triprotic organic acid model was incorporated into MAGIC and simulated pH values were then compared with diatom-inferred pH. This comparison yielded considerably closer agreement for pre-industrial pH than did the comparison using MAGIC simulations without the effects of organic acids. The MAGIC estimates of acidification were 0.6 pH units lower than diatom estimates when organic acids were not included in the modeling scenarios, with the greatest discrepancies occurring in the lakes with diatom-inferred current pH < 6.0. This difference was only 0.2 pH units when the triprotic organic acid analog model was included, and the agreement for individual low-pH lakes improved by as much as a full pH unit. The improved agreement between MAGIC and diatom estimates of pre-industrial pH was due, in part, to smaller MAGIC simulations of ΔpH for some lakes and, in part, to lower simulations of current pH for some lakes. The effect of the inclusion of an organic acid representation on model results was largest for lakes with moderately high concentrations of DOC (400-500 μM C).

Results of the hindcast comparisons between paleolimnological inferences of pre-industrial lakewater pH and MAGIC simulations, with and without the inclusion of organic acids, illustrate three important points:

1. There is a systematic departure with decreasing pH between diatom and MAGIC model hindcasts of pre-industrial pH when organic acids are not included in the MAGIC simulations.

2. Inclusion of a reasonable formulation for organic acidity in the MAGIC simulations of pre-industrial pH greatly improves the agreement with diatom reconstructions, particularly for lakes having pH < 6.0.
3. The choice among organic acid analog models (e.g., mono-, di-, triprotic, or Oliver model) does not alter the agreement with diatom reconstructions to an appreciable degree for a regional analysis.

The inclusion of organic acids in the MAGIC model simulations of pre-industrial pH did not alter the agreement between diatom and MAGIC model hindcasts for lakes with pH values greater than about 6.5. Previous hindcast comparisons (Sullivan et al. 1991) that did not include an organic acid representation had obtained good agreement for these high-pH lakes. For low-pH lakes, however, the lack of organic acid representation had resulted in an increasing level of divergence between diatom and MAGIC model hindcasts of pre-industrial pH. Thus, the lakes of greatest relevance with respect to potential biological effects of acidification, especially those having pH less than 5.5, exhibited increasingly larger discrepancies with decreasing pH between diatom and MAGIC model estimates of pre-industrial pH when organic acids were omitted from the analysis. The inclusion of an organic acid representation in the MAGIC simulations conducted in this study resulted in a great improvement in the agreement between these two modeling approaches.

The results of our analyses of Adirondack lakes demonstrate that: 1) organic acids must be considered in modeling the response of lakewaters in the Adirondack Mountains to acidic deposition, and 2) once organic acids are included in the modeling approach, reasonable agreement is obtained in hindcast comparisons with diatom-inferred pH. It should be emphasized, however, that this test included only two points in time, and essentially only pH. MAGIC, and other process models, require further testing and confirmation. Many potentially important geochemical processes are not well represented in the model or often in the input data, and it is not clear how inclusion of such processes might affect model results.

The results of this comparison are important for acidic deposition assessment activities in two respects. This study is the first to show quantitative agreement of changes in pH of natural aquatic systems subjected to acidic deposition, as estimated by two independent and conceptually different approaches over a large geographic region and over a long temporal span. Previous model testing studies have been of relatively short duration (e.g. Norton et al. 1992), site specific (e.g. Renberg and Hultberg 1992), or comparisons among two or more models that share many fundamental assumptions (e.g., Cook et al. 1992). Second, and perhaps more importantly, this demonstrated agreement between MAGIC and paleolimnological model hindcast estimates of lakewater pH is dependent upon inclusion of organic acids in the process model. The latter result was obtained despite the relatively low concentrations of DOC in the study lakes (mean value = 313 μM C).

However, "successful" comparison of MAGIC with diatom hindcasts in one region does not constitute a sufficient verification to impart complete confidence in using MAGIC, or any process model, for predicting the response of surface water chemistry to changes in acidic inputs. Many uncertainties remain in addition to those associated with organic acidity, particularly with respect to basic model assumptions, adequacy of model input data, details of hydrological routing, and algorithms for calculating N and Al dynamics. Additional model confirmation, in the form of comparison of model output with *measured* data, is required. This has been the focus of our modeling efforts at Lake Skjervatjern, Bear Brook, and Risdalsheia, which are discussed in the following *section*.

1.2. Model Evaluation at Whole-Catchment Manipulation Sites

MAGIC was calibrated to the three study areas using measured inputs and outputs for the respective reference catchments. Four-to-seven year mean annual fluxes for the period of observation were averaged to reduce variability in inputs and outputs. Weathering rates and cation-exchange selectivity coefficients for the base cations were determined using input-output budgets and measured soil saturations of base cations in the reference catchments. After calibrating the model to simulate the correct concentrations of strong acid anions and base cations in surface water, the weak acids and bases were calibrated such that the pH and concentrations of Al and organic acid anions matched those observed in the reference catchment. Following the calibrations, model simulations for the treated catchments were conducted using observed inputs, including experimental treatments. The projections were based solely on data from the reference catchments, except that nitrogen uptake dynamics were modified to match those observed in the treatments.

1.2.1. Site Descriptions

Lake Skjervatjern

The Humic Lake Acidification Experiment (HUMEX) was initiated by the Norwegian Institute for Water Research (NIVA) in 1987. The principal goals of HUMEX are to evaluate the role of humic substances in the acidification of surface waters and the effects of sulfur and nitrogen deposition on the properties of humic substances in watershed soils and surface waters (Gjessing 1992). The data generated at Lake Skjervatjern provided an excellent opportunity to test the accuracy of MAGIC forecasts in a catchment where organic acids are an important component of the lakewater acid-base chemistry. MAGIC was applied to project the response of Lake Skjervatjern to whole-ecosystem manipulation. The lake was divided in 1988 by a plastic curtain that effectively separated the lake and its drainage basin into two systems, a manipulated side and control side. Water quality was monitored during a five-year period that included two years of pre-treatment data and three years during which nitrogen and sulfur were applied to one half of the lake and its respective drainage basin.

Bear Brook

The Bear Brook Watershed in Maine was established in 1986 as part of the Environmental Protection Agency's Watershed Manipulation Project (WMP). The goals of the project were to: 1) assess the chemical response of a small upland forested watershed to increased loadings of SO_4^{2-}, 2) determine interactions among biogeochemical mechanisms controlling watershed response to acidic deposition, and 3) test the assumptions of the Direct/Delayed Response Program (DDRP) modeling efforts of watershed acidification. The work we conducted in this project provides an important contribution to Objective #3 above, which was perhaps the major reason EPA initiated the watershed manipulation project. The two Bear Brook watersheds (East and West) are located on the upper slope of Lead Mountain, Maine. The East Bear and West Bear watersheds are similar in most respects including slope, aspect, elevation, area, geology, hydrology, soils, vegetation, and water chemistry. A total of six applications per year of $(NH_4)_2SO_4$ fertilizer was applied in dry form by helicopter to the West Bear Brook watershed since November 1989.

Risdalsheia

The Risdalsheia site in southernmost Norway receives a high loading of acidic deposition (SO_4^{2-} wet + dry loading, 112 meq m^{-2} yr^{-1}), and is characterized by exposed granitic bedrock (30% to 50% of surface) and thin, organic-rich, truncated podzolic soils (Wright et al. 1986a). Acid exclusion at the KIM catchment is accomplished by a 1200 m^2 transparent roof that completely covers the 860 m^2 catchment. Incoming precipitation is collected from the roof and pumped through a filter and ion exchange system. Seawater salts are added back at ambient concentrations and the clean precipitation is automatically applied beneath the roof by a sprinkler system. During winter, artificial snow is applied beneath the roof using commercial snow-making equipment. Controls include a mini-catchment with a roof (EGIL) and one without (ROLF), both of which receive acidic rain and snow. There are eight years of runoff chemistry data available from the manipulation at Risdalsheia as of this report (water years 1985 through 1992). Risdalsheia provides a good parallel to Lake Skjervatjern, except high ambient S and N deposition have been experimentally decreased, whereas at Lake Skjervatjern low ambient deposition has been experimentally increased. Organic acids play a major role in the acid-base chemistry of runoff at the site, with average annual DOC values generally in the range of 800 to 1200 μM C, and in moderating pH change following reduction in acid deposition (Wright 1989).

The organic acid analog representation we developed for the Adirondack region was recalibrated, for modeling at the Norwegian sites, to empirical data collected in Norway in the 1000

Lake Survey (SFT 1987). The organic acid analog calibration procedure involved adjusting the H^+ *dissociation constants and site density of the DOC, which specifies the number of dissociation sites* per mole of organic carbon. The object of the fitting routine was to minimize the observed differences across all lakes between the organic charge simulated by the analog model and the estimated organic anion concentration determined from the charge balance. The fitted pK_a values and site density were very close to those obtained for lakes in the Adirondack Mountains, New York.

1.2.2. Measured Responses in the Experimental Catchments

Lake Skjervatjern

The largest change in lakewater chemistry in response to the treatment at Lake Skjervatjern was for SO_4^{2-}, which increased 15 μeq L^{-1} during the first two years, suggesting that about two-thirds of the sulfur added during the first two years has been retained by the watershed. Other ionic constituents, except organic acid anions, also increased with the experimental treatment, but to a lesser degree. The increase in $[H^+]$, which would approximately equal the corresponding decrease in Gran ANC in this pH range, was about 30% of the SO_4^{2-} increase. The measured annual average F-factor (Δ base cation concentrations ÷ Δ[sulfate + nitrate] concentrations) was 0.5. The remaining 20% of the SO_4^{2-} increase was apparently compensated primarily by changes in DOC, organic acid *anion protonation, and a small (1 μeq L^{-1}) increase in Al concentration.*

Bear Brook

A number of ionic constituents changed in concentration in response to the measured change in volume-weighted $[SO_4^{2-} + NO_3^-]$ at West Bear Brook during the first two years of watershed manipulation. The change in base cation concentrations was largest, and accounted for 54% of the change in $[SO_4^{2-} + NO_3^-]$ after correcting for base cations charge-balanced by Cl^- (marine contribution). Substantial changes also occurred, as proportions of the change in $[SO_4^{2-} + NO_3^-]$, for Al^{n+} (20%) and ANC (14%). DOC decreased slightly in both West Bear (-84 μM C) and East Bear Brooks (-62 μM C). During the first year of treatment, 94% of the added N was retained by the Bear Brook watershed. Percent retention subsequently decreased to 81% in Year 2 and 74% in Year 3 (Kahl et al. 1993). Although the forest ecosystem continued to accumulate added N, the rate of accumulation decreased steadily with the experimental treatment. Both the immediate nature of the nitrogen response and the magnitude of the increase in NO_3^- flux from the treated West Bear catchment were unexpected (Kahl et al. 1993). Nitrate flux increased from 200 to more than 500 eq ha^{-1} yr^{-1} in two years.

Risdalsheia

Major results of the acidic deposition exclusion experiment at Risdalsheia have been discussed in detail by Wright and co-workers (e.g., Wright 1989, Wright et al. 1986a, 1988, 1990). Average streamwater SO_4^{2-} concentrations were reduced from 92 μeq L^{-1} in the 1985 water year to 28 μeq L^{-1} in 1992. This reduction in SO_4^{2-} was compensated primarily by decreased base cation concentrations, from 136 to 104 μeq L^{-1} (F-factor = 0.5). In addition, the average H^+ concentration decreased from 87 to 61 μeq L^{-1} and the Al concentration decreased from 12 to 3 μeq L^{-1}.

1.2.3. Model Results in the Experimental Catchments

Lake Skjervatjern

MAGIC model projections of the response of Lake Skjervatjern to whole-catchment acid additions were close to measured values for SO_4^{2-}, NO_3^-, and NH_4^+. Although the retention of added sulfur within the terrestrial system was considerable, the MAGIC-simulated SO_4^{2-} concentrations at Skjervatjern in 1991 and 1992 were within 3 to 6 μeq L^{-1} of average measured concentrations.

MAGIC simulations of base cation responses were very close to measured values, within 12 μeq L^{-1} for the sum of base cation concentrations (C_B). Lakewater ANC declined by about 5 μeq L^{-1} more than was predicted by MAGIC, whereas MAGIC predicted a more substantial pH decline than was actually observed. Overall, however, the MAGIC projection of acidification responses at Lake Skjervatjern simulated measured values very well.

The percent retention for both NH_4^+ and NO_3^- during the experimental treatment was very similar to the pre-manipulation percent retention of atmospheric inputs (~90%). Therefore, the MAGIC-simulated values of N species were in agreement with measured responses without having to manually change the inputs to match measured values. Such agreement would not routinely be expected, however, as is illustrated for Bear Brook and discussed below, and a process-based approach to modeling N cycling and fluxes would be a desirable addition to the model.

Bear Brook

MAGIC predicted a much larger increase in streamwater SO_4^{2-} concentration than was observed in the Bear Brook treated stream. The trajectory of MAGIC-simulated SO_4^{2-} concentration approached the anticipated steady-state concentration of about 300 μeq L^{-1} projected to occur within the eight-year simulation period; that is, about 200 μeq L^{-1} higher than pre-treatment concentrations. In contrast, the trajectory of measured values appeared to be moving towards a new steady-state concentration that would reflect an increase in streamwater SO_4^{2-} only about half as large. It appears that MAGIC overpredicted the increase in streamwater SO_4^{2-} concentrations at Bear Brook by nearly a factor of two. This overprediction of the increase in streamwater SO_4^{2-} concentration that resulted from the manipulation experiment was attributed to the high value assumed for modeling the half saturation of sulfur adsorption. The adsorptive behavior of the soils was effectively removed because concentrations of SO_4^{2-} never approached the half-saturation value.

As a consequence of the overprediction of streamwater SO_4^{2-} concentration, other key variables (especially ANC and Al) also were predicted to respond to a greater degree to the experimental acidification than was actually observed. As anticipated at the onset of the project and as predicted by MAGIC, the treated stream experienced decreases in ANC and increases in Al compared to the control. However, MAGIC predicted substantially larger changes in each of these parameters than was observed.

MAGIC projected extremely high values of Al^{3+} in response to the manipulation. Although measured Al concentrations did increase substantially in the manipulated stream, MAGIC projected increasingly larger increases each year of the experiment. By Year 3 of the manipulation, the MAGIC estimate of increase in Al^{3+} was about 6 times larger than was observed, and the MAGIC estimate of Al^{3+} concentration was extremely high (~ 90 μeq L^{-1}). The standard method for MAGIC applications is to determine the aluminum solubility product empirically, based on pre-treatment data. For East Bear Brook, the estimated value for this model application was log K_{sp} = 10.7, which is much higher than is normally assumed for acidified waters. Partly as a consequence of using such a high log K_{sp} value from the control stream to predict experimental Al^{3+} concentrations in West Bear Brook, we predicted unrealistically high values of Al^{3+}.

The fundamental problem in the model application is that a single value for gibbsite equilibrium cannot be used to explain variations in streamwater chemistry. This problem has been illustrated previously in several field studies. The MAGIC model forecasts presented here for Bear Brook reconfirm the problematic nature of the commonly-employed assumption of gibbsite equilibrium and a fixed K_{sp}, and illustrate the magnitude of error that can result.

MAGIC overpredicted the sum of mineral acid anions (C_A), largely because of the errors in predicted SO_4^{2-} concentrations. In addition, MAGIC underpredicted the sum of base cations (C_B), mainly Ca^{2+} and Mg^{2+}. This latter bias, however, was due primarily to pre-treatment differences between the control and manipulated stream chemistry. This is a reflection of the extreme difficulty of finding "paired catchments" with identical chemistry. The combined influence of the observed biases in C_B and C_A resulted in relatively large errors in predicted ANC, because ANC is defined in MAGIC for this application as (C_B - C_A). The simulated decrease in (C_B - C_A) was too large, and in order to satisfy charge balance constraints ($\sum$ cations = $\sum$ anions) MAGIC calculated concentrations of acidic cations (H^+, Al^{3+}) sufficient to balance this simulated charge discrepancy. MAGIC partitioned those acidic cations between H^+ and Al^{3+}, based on the assumed solubility product (log K_{sp}) for gibbsite dissolution. Because the log K_{sp} value was assumed to be very high (10.7), MAGIC allocated most of the change in acidic cations into the Al^{3+} component, and relatively little into the H^+ component.

There was an especially large discrepancy between simulated and observed base cation concentrations and ANC in the third year of treatment at Bear Brook (1992). The measured increases in C_B in East and West Bear Brooks were about 30 and 35 μeq L^{-1}, respectively, between 1991 and 1992, while ANC increased about 10 μeq L^{-1}. These increases in measured C_B and ANC were likely attributable in part to lower than normal precipitation during that year. Stream discharge during 1992 was only about 75% of the three previous years. Gross hydrological changes, such as altered contact of drainage waters with soils in response to unusually dry or wet conditions, are difficult to capture in any dynamic model. Thus, the fairly pronounced changes between 1991 and 1992 in measured values for many key variables were not represented by the MAGIC simulation.

In order to assess the degree to which discrepancies between predicted and observed streamwater chemistry at Bear Brook could be improved by correcting sulfur dynamics and *a priori* differences between treatment and control catchments, a revised calibration was conducted. The resulting simulations matched measured values in West Bear Brook to a substantially greater degree than had the forecasts based on the initial calibration. Differences from the initial calibration were primarily related to SO_4^{2-} half-saturation, selectivity coefficients and weathering of base cations. Projected streamwater SO_4^{2-} concentration in the revised model projection agreed closely with measured values in West Bear Brook for the first three years of manipulation. The model simulation also showed much better agreement with measured values for the sum of base cations and ANC than had the initial MAGIC simulation. Although the effects of the drought year (1992) on C_B and ANC were still not captured by the simulation, the overall agreement between predicted and observed C_B and ANC was much improved. Slight underestimation of pH decrease and overestimation of Al^{3+} increase were still evident in the revised projections, although the magnitudes of these biases were reduced dramatically because of the improvement in predicted SO_4^{2-} concentration and ANC.

Risdalsheia

The MAGIC simulations of the responses of the treatment catchment (KIM) at Risdalsheia to reduced acidic deposition matched measured values extremely well. In particular, the observed changes in SO_4^{2-}, base cation concentrations, and ANC closely paralleled the observed trends and interannual variations. Also, despite the importance of organic acids in modifying the pH of drainage waters at this site (Wright 1989), incorporation of the triprotic organic acid analog into MAGIC, calibrated to the Norwegian 1000 Lake Survey, resulted in good agreement between modeled and measured pH. Perhaps the most substantial bias observed at Risdalsheia was the generally-consistent underestimation of Al^{3+} concentrations, particularly for the period between 1988 and 1991 when measured concentrations averaged about 2 to 3 times higher than simulated concentrations.

The results of the MAGIC model evaluation at Risdalsheia are particularly noteworthy in two respects. First, our model simulations of pH matched measured values despite using a regional model representation for organic acids to simulate pH in a system in which organic acids provide a great deal of pH-buffering. Second, we demonstrated agreement between simulated and observed chemistry, for all major variables except perhaps Al, over an eight-year period. This is a very long period of record for a model testing study that has involved substantial change in acidic deposition inputs.

1.3. Influence of Organic Acids on Estimates of pH

We compared MAGIC hindcasts with diatom reconstructions for 33 lakes in the Adirondack Mountains and showed that incorporation of organic acids into MAGIC altered both the calibrated current pH values and simulated ΔpH for some lakes, particularly those inferred to have experienced the greatest amount of historical acidification. In addition, we showed that MAGIC hindcasts agreed much more closely with diatom reconstructions of historical pH when organic acids were considered in the model. Lakes for which the inclusion of organic acids altered model estimates of ΔpH by more than 0.5 pH units had DOC concentrations in the range of 400 to 500 μM C. Such concentrations of DOC are not considered high, but were at the upper end of measured DOC concentrations in the 33 study lakes.

We also found that inclusion of organic acids in the MAGIC simulations for Lake Skjervatjern, Bear Brook, and Risdalsheia had dramatic effects on model simulations of pH. In all cases, MAGIC simulated considerably higher pH values when organic acids were omitted from the model. Even at Bear Brook, where annual average DOC concentrations are very low (< 250 μM C), incorporation of organic acids into the model reduced simulated pH by 0.1 to 0.3 pH units for the years of study. At Lake Skjervatjern and Risdalsheia, where organic acids provide substantial pH buffering, omission of the organic acid analog representation from MAGIC resulted in consistent overprediction of pH by about 0.2 to 0.5 pH units.

1.4. Influence of Acidic Deposition on Dissolved Organic Carbon and Organic Anion Concentrations

Results of the three catchment manipulation experiments that we have examined (Bear Brook, Skjervatjern, Risdalsheia) all show some evidence of changes in organic acid anion concentration in response to the acidification or de-acidification treatment. Changes in DOC also may have occurred. Unfortunately, none of these manipulation experiments provide conclusive quantitative data regarding the effects of acidification on DOC mobilization from catchment to surface waters or changes in the concentration of DOC caused by acidification. There are problems in interpretation of the data regarding changes in the concentration of DOC/TOC in runoff from each of the studies.

In the Watershed Manipulation Project, DOC declined about 50% from 1989 to 1992 in both East and West Bear Brooks. These streams are very low in DOC throughout most of the year (annual average DOC < 300 μM C), and therefore are less than optimal sites for evaluation of this question. In addition, the acidification caused by the manipulation experiment has been fairly modest, because a large percentage of the added sulfur and nitrogen has been retained within the catchment. It is likely that observed decreases in DOC at Bear Brook were mostly related to a pattern of generally decreasing runoff, although a small decrease in DOC in response to the chemical manipulation also seemed to have occurred.

TOC concentration at Skjervatjern was highly variable, thus making it difficult to quantify any changes that may have occurred in response to the experimental treatment. Data from the treatment side of the lake showed no indication of a decline in TOC relative to the control with acidification. The increase in lakewater SO_4^{2-} concentration has been small, because most of the sulfur applied to the terrestrial catchment has been retained in watershed soils. Thus, the possible long-term influence of watershed acidification on TOC mobilization at Skjervatjern is highly uncertain. If sulfur retention in the watershed decreases over time, effects on TOC mobilization may become more evident.

At Risdalsheia, the annual variability in TOC was very large at both the roofed control and manipulated catchments and sufficient pre-treatment data were not collected to allow a rigorous evaluation of the extent to which TOC mobilization may have been affected by the acid exclusion. Thus, none of these three experimental manipulation studies provide the kind of quantitative data on DOC/TOC responses to acidification that would be needed to justify further modifying the MAGIC model to account for hypothesized changes in DOC concentration in response to changes in acidic deposition.

1.5. Model Evaluation

A major objective of the research conducted in this project has been to evaluate the accuracy of MAGIC model projections, using available paleolimnological data from the Adirondack Mountains and results of whole-catchment acidification experiments at Bear Brook, Maine and Lake Skjervatjern and Risdalsheia, Norway. Results of these model evaluation exercises were mixed. The MAGIC triprotic acid model provided projections of lakewater chemistry in the Adirondacks and at Lake Skjervatjern and Risdalsheia that were generally consistent with independent diatom-inferred and measured data, respectively. In all cases, the agreement for pH was dependent upon inclusion of an organic acid representation in the MAGIC model, and in all cases MAGIC projected slightly greater change in pH than was inferred or measured by other means. In general, however, MAGIC performed very well in simulating the major changes that occurred at these sites. In contrast, at Bear Brook, organic acids were less important to annual average estimates of chronic chemistry, but MAGIC projections of streamwater acidification were substantially greater than was measured. The most significant bias was an overprediction of streamwater SO_4^{2-} concentration, attributable to underestimated sulfur adsorption in watershed soils. Other biases were apparently related to Al solubility and hydrology.

The modeling work we have conducted at Bear Brook has been very valuable in terms of assisting in the verification of previously suspected inadequacies in model structure and application, and clarification of remaining research needs. As a direct result of using WMP data for the primary purpose for which the WMP was designed, i.e. model testing, we have been able to reconfirm several aspects of the model that are in need of improvement. The Bear Brook modeling study clearly demonstrated the importance of the following problem areas:

1. lack of incorporation of nitrogen processes in the model,
2. errors in the way Al dissolution is modeled in MAGIC (and other models),
3. uncertainties in simulating hydrological routing and the fundamental importance of hydrology in regulating acid-base chemistry,
4. uncertainties in sulfur retention in watershed soils when sulfur inputs are changed, regardless of apparent "steady-state" input/output conditions prior to the perturbation, and
5. differences that exist *a priori* between paired catchments selected for "treatment" and "control" basins that can introduce bias into the comparison between syn-manipulation measured variables on the treatment versus model projections for the reference site.

Results of our modeling efforts at Bear Brook, as well as measured ionic changes at Bear Brook, and to a lesser extent Lake Skjervatjern and Risdalsheia, illustrate that a remaining major weakness of MAGIC (and other process models) is the failure to include algorithms to simulate nitrogen cycling and nitrogen retention in watershed soils and vegetation. The success of the nitrogen component of the modeling effort at Bear Brook (and Risdalsheia to some extent) was totally dependent on adjusting the nitrogen inputs to the model to match measured outputs in streamwater. Nitrogen dynamics were extremely important at this site (Kahl et al. 1993), although this had not been anticipated at the inception of the Watershed Manipulation Project at Bear Brook. The process of evaluating and improving MAGIC is an iterative one. We have shown here that the inclusion of organic acids in the model is important and that MAGIC often yields acceptable model simulations of past and future change. We have also shown that further improvements are needed, particularly with respect to nitrogen. The model simulations at Bear Brook also revealed important weaknesses and uncertainties in several aspects of the model structure and/or the manner in which the model is applied to a given catchment. Results at Bear Brook verified that key remaining uncertainties relate to the modeling of Al dissolution, sulfur retention in soils, and the dependence of runoff chemistry on hydrological variations that are difficult to simulate.

We have shown here that long-term projections of the effects of acidic deposition on surface water pH are sensitive to the dynamics of organic acids for lakes having only moderate concentrations of DOC. Assessment activities, such as those conducted previously by NAPAP (1991) and those on-going in Europe in conjunction with the critical loads debates and mapping activities (e.g., Bull 1992, Forsius et al. 1992), should consider organic acid effects in the process models used in conducting assessments. Failure to include consideration of organic acids will introduce substantial bias into the assessment results regarding pH and associated biological effects.

2. LAND USE IMPACTS

The impacts of atmospheric deposition of sulfur and nitrogen on aquatic ecosystems have been well recognized. However, the interactions between acidic deposition and concurrent changes in landscape cover have received relatively little attention. A review of recent literature suggests that changes in landscape, or land use, and hydrology can influence the delivery of sulfur, nitrogen, and base cations to drainage waters and consequently modify acid-base chemistry and catchment responses to acidic deposition. Research has focussed heavily on the importance of acidic deposition as an agent of surface water acidification, with less emphasis on other important acidifying or alkalizing processes associated with deforestation, forest regrowth, and other agents of catchment disturbances. This omission can have important effects on model estimates of future acidification or recovery of surface waters in response to various atmospheric deposition scenarios. A case study was conducted, using available paleolimnological data, for the Adirondack Mountain region of New York, USA, the most intensively studied region in the world regarding the aquatic effects of acidic deposition. We found that the onset of acidification for most paleolimnological study lakes in the Adirondacks corresponded temporally with both the onset or increase in acidic deposition and also the occurrence of major landscape disturbances associated with logging and windthrow. Although such landscape changes are unlikely on their own to cause lakes to become acidic, model scenarios have suggested that they can cause decreases in the base saturation of soils, thereby predisposing sensitive watersheds to subsequent acidification from acidic deposition.

Interactions between acidic deposition and landscape/physical watershed characteristics were further evaluated for a group of Adirondack lakes for which sufficient data were available upon which to base an evaluation. Landscape characteristics were compiled and examined relative to paleolimnological inferences of historical acidification. Results of model estimates of acidification using the MAGIC model and paleolimnological analyses were compared to physical, biological, and landscape change data to evaluate if inclusion of additional processes could improve model estimates. Results of bivariate and multivariate analysis confirmed that lakes that have experienced historical acidification tend to be those that receive relatively high amounts of precipitation and have short hydraulic residence times. These variables explained 58% of the diatom-inferred acidification. A combined model of long-term precipitation, hydraulic residence time, and blowdown explained 71% of the historic acidification in the Adirondacks. Lakes that have increased in pH since pre-industrial times tend to be those subject to substantial human disturbance and those that burned during major fires recorded after the turn of the century. The magnitude of the discrepancy between MAGIC model and diatom-inferred hindcasts of acidification was not significantly correlated with any of the landscape change variables, suggesting that additional modifications to the MAGIC model to further take into account landscape change are not likely to appreciably improve model performance.

3. TRACKING AND ANALYSIS FRAMEWORK

The Tracking and Analysis Framework (TAF) project provided an integrated assessment framework for the National Acid Precipitation Assessment Program (NAPAP) with which to evaluate the environmental and economic impacts of acidic deposition. The TAF prototype includes a series of linked reduced-form models intended to provide the foundation for informed decision-making regarding emissions controls and regulations for nitrogen and sulfur. Each of the reduced-form models in TAF is based on a state-of-the art full form model, and provides input and output specifications for one or more components of the acidic deposition effects story (e.g. deposition, aquatic effects, valuation, etc.). The aquatic chemistry and soil solution chemistry modules are each constructed as a reduced-form representation of the MAGIC model. A report was prepared for DOE to provide documentation for the MAGIC model and the manner in which it has been implemented for TAF.

The Aquatics Effects and Soils Effects modules of the TAF prototype include reduced-form modeling capabilities for one region of the United States: the Adirondack Mountains. The TAF prototype includes reduced-form model response surfaces for Adirondack lakes, based on the Direct Distribution Model of Mitchell Small and colleagues, for predicting the output from MAGIC. MAGIC outputs include key elements of surface water chemistry (e.g., pH, Al, Ca concentrations) and soil solution chemistry (e.g., base saturation, Al:Ca molar ratios). Results for surface water chemistry derived from MAGIC are used to estimate fish presence/absence and acid stress indices. The objective of these reduced-form models is to estimate the results that would be simulated by the full-form model, MAGIC, under changing deposition scenarios. These estimates of chemical and biological response are then used as inputs for valuation estimation procedures.

3.1. Basic Description of MAGIC

MAGIC is a lumped-parameter model of intermediate complexity (Cosby et al. 1985) that is calibrated to the watershed of an individual lake or stream and then used to simulate the response of that system to changes in atmospheric deposition. MAGIC includes a section in which the concentration of major ions is governed by simultaneous reactions involving sulfur adsorption, cation weathering and exchange, aluminum dissolution/precipitation/speciation, and dissolution/speciation of inorganic carbon. A mass balance section of MAGIC calculates the flux of major ions to and from the soil in response to atmospheric inputs, chemical weathering inputs, net uptake in biomass and losses to runoff.

Model calibration to a specific catchment is accomplished by specifying deposition and hydrological forcing functions, setting the values of those parameters that can be measured (fixed parameters), and determining the values of the remaining parameters that cannot be measured (adjustable parameters) through an optimization routine. The adjustable parameters are modified to give the best agreement between observed and predicted surface water and soil chemistry (Cosby et al. 1985a,b,c).

3.2. Changes to the Model

3.2.1. Background Sulfate and Subregional Calibration

Subsequent to the MAGIC modeling that was conducted for EPA's Direct Delayed Response Project (DDRP; Church et al. 1989) and for NAPAP (1991), there was concern that Adirondack soils might differ in their chemical properties from similar soils in other areas of the Northeast, and that MAGIC projections for Adirondack watersheds might be biased because they were based on soil attributes that actually reflected conditions elsewhere than the Adirondacks. The DDRP soils data were therefore reaggregated to characterize Adirondack watershed attributes using only soil data collected from pedons in the Adirondacks (Sullivan et al. 1991).

Modeling for the DDRP and Integrated Assessment also assumed that the deposition of sulfur in pre-industrial times was limited to sea salt contributions. Based on analyses presented by Husar et al. (1991), this assumption was modified such that pre-industrial deposition of sulfate was assumed equal to 13% of current values (Sullivan et al. 1991).

Recalibration of MAGIC to the Adirondack lakes database using the regionally corrected soils and background SO_4^{2-} data resulted in approximately 10 μeq L^{-1} lower estimates of current ANC. A substantial downward shift was also observed in predicted pre-industrial and current lakewater pH (~0.25 pH units) for lakes having pH greater than about 5.5. These differences were attributed to lower calibrated values for lakewater SO_4^{2-} concentrations and higher pCO_2 values estimated for Adirondack lakes, compared with the Northeast as a whole (Sullivan et al. 1991).

3.2.2. Organic Acids

Concern was raised subsequent to the IA regarding potential bias from the failure to include organic acids in the MAGIC model formulations used by NAPAP. MAGIC hindcasts of pre-industrial lakewater pH showed poor agreement with diatom-inferences of pre-industrial pH (Sullivan et al. 1991), and preliminary analyses suggested that these differences could be due, at least in part, to the presence of naturally-occurring organic acids in Adirondack lakewaters.

Driscoll et al. (1994) compared output from several organic acid analog models, using data collected by the Adirondack Lakes Survey Corporation (ALSC) (Kretser et al. 1989) for 1400 lakes located in the Adirondack region. The best agreement was obtained ($r^2 = 0.92$) between predicted and observed pH values using the triprotic analog representation, with fitted pK_a values of 2.62, 5.66, and 5.94, and a calibrated site density of 0.055 mol sites per mol C. The fitted values for pK_a and site density obtained by Driscoll et al. (1994) were used in the revised MAGIC applications reported here. Model scenarios using the original version of MAGIC without organic acids are designated $MAGIC_1$, and those that include the triprotic organic acid analog are designated $MAGIC_2$.

Unmodified $MAGIC_1$ hindcasts yielded pre-industrial pH values that were substantially higher than diatom-based estimates, and the discrepancy was greatest for those lakes in the most biologically-sensitive portion of the pH range, (pH 5.0 to 6.0). Furthermore, $MAGIC_1$ hindcast pH estimates were greater than 6.0 for all lakes investigated, whereas diatom estimates of pre-industrial pH ranged from as low as 5.2 to above 7.0. When the organic acid model was incorporated into $MAGIC_2$ and simulated pH values were compared with diatom-inferred pH, the comparison yielded considerably closer agreement between model estimates of pre-industrial pH than did the simulations that did not consider the effects of organic acids (Sullivan et al. in press a). The mean difference in $MAGIC_1$ versus diatom estimates of pre-industrial pH was 0.6 pH units when organic acids were omitted from the modeling scenarios, with the greatest discrepancy being for lakes with diatom-inferred pH < 6.0. This mean difference was reduced to only 0.2 pH units when the triprotic organic acid model was included, and the agreement for individual low-pH lakes improved by as much as a full pH unit (Sullivan et al. in press a).

3.2.3. Aluminum

Al mobilization is now widely believed to be one of the most important ecological effects of surface water acidification. Potential effects of Al mobilization to surface and soil waters include alterations in nutrient cycling, pH buffering effects, toxicity to aquatic biota, and toxicity to terrestrial vegetation. The relationship between $[Al^{3+}]$ and $[H^+]$ in surface waters has generally been modeled with MAGIC and other acid-base chemistry models as being cubic. It is determined by an assumed solubility product for gibbsite (K_{SO}). Model estimates of changes in the concentration of Al^{3+} in surface waters, using this relationship,have shown a consistent pattern of overestimating the change in Al^{3+}

concentration in response to experimental treatment (Sullivan et al. in press b). This overestimate of the change in Al^{3+} concentration calculated by MAGIC is generally due to a combination of the cubic relationship between H^+ and Al^{3+} assumed in the gibbsite model and the model calibration procedure of selecting a gibbsite solubility product based on measured pre-treatment data.

Sullivan and Cosby (in review) examined a large number of data sets for lakes and streams in the northeastern United States that contain appreciable dissolved inorganic Al concentrations (Al_i). For all data sets examined, a consistent relationship was evident between pAl_i and pH for the waters of interest (pH 4 to 6). The slope of this relationship was consistently near 1.0, ranging from 0.77 to 1.28. When plots of pAl^{3+} versus pH were examined, similar results were found. The slopes of the relationships in this case were consistently near 2.0, and ranged from 1.82 to 2.34. These results illustrate that, for the surface waters in the United States that are of interest with respect to potential aluminum mobilization, a gibbsite-type equation to model Al_i concentration directly should use a power term of about 1. For predicting Al^{3+} concentration, a power term of about 2 should be used. None of the data examined suggested a power term close to 3, the value currently used in model formulations.

A version of MAGIC that incorporated this change was applied to the Bear Brook watershed acidification data. The revised MAGIC projections of Al_i concentration at West Bear Brook agreed more closely with measured values than did the previous projections based on the gibbsite solubility assumption (Sullivan and Cosby in review). The results of comparing simulated with measured Al_i concentrations at the Risdalsheia acid exclusion site in Norway were not so consistent. However, the majority of the annual average measured values at Risdalsheia more closely followed the MAGIC trajectory that was constructed assuming an exponent of 2, rather than 3 as in the gibbsite model. Neither formulation was completely satisfactory for predicting streamwater Al_i concentration. This is to be expected given the lumped-parameter nature of the model and the complexity of the Al hydrogeochemical response. In most cases, however, a power term of 2.0 in the model formulation for Al^{3+} provided the most reasonable projections.

A new version of the MAGIC model was produced, called MAGICAL, that allows flexibility in the way surface water Al dynamics are represented. MAGICAL allows user-specification of both the exponent and the constant (K_{so}) in the solubility relationship. In previous versions of MAGIC, the exponent was fixed at a value of 3. After calculating the concentration of Al^{3+}, the model estimates the concentration of other inorganic species of Al using thermodynamic relationships in a manner analogous to ALCHEMI and other models of Al speciation.

3.2.4. Nitrogen

MAGIC contains an extremely simplified representation of nitrogen dynamics within catchment soils. The model simulates net nitrogen retention as a linear process. That is, retention of either

NO_3^- or NH_4^+ is assumed to be linearly proportional to the input fluxes of these ions. There are no processes controlling the details of N cycling in the model. In light of the increasing concern about N saturation in forested ecosystems, this is a serious shortcoming in the model, and is currently being addressed by considering a number of modifications for the model.

The current version of the MAGIC model is not appropriate for simulations of changes in atmospheric deposition of NO_3^-. For TAF modeling efforts, however, it was desired to make projections of lakewater pH responses assuming scenarios of increasing NO_3^- deposition. For TAF, we proposed a modification to the MAGIC model to allow simulation of the effects of changes in NO_3^- deposition. This proposed modification was based on NO_3^- input/output budget calculations.

The majority of the Adirondack lakes in the modeling data set had lakewater NO_3^- concentrations lower than the calculated concentration that would be expected based on direct NO_3^- deposition to the lake surface. For modeling these lakes, we therefore assumed that all NO_3^- deposited on watershed soils is taken up within the terrestrial catchment, in terms of its impact on fall index chemistry. In addition, a component of the NO_3^- deposited directly to the lake surface is taken up by in-lake biota. For those lakes that had higher concentrations of lakewater NO_3^- than would be expected based on direct NO_3^- deposition to the lake surface, we assumed that some amount of chronic watershed leaching of NO_3^- occurs.

From the available data, we estimated an amount of chronic NO_3^- leaching from each watershed, expressed in μeq L^{-1} in lakewater. This value is zero for most lakes and ranges up to 16 μeq L^{-1}. We also estimated an amount of in-lake NO_3^- uptake for each lake, expressed in μeq L^{-1}. For many lakes, we used an estimated "average" value of 4 μeq L^{-1}.

For modeling the response of the lakes to future changes in NO_3^- deposition, we assumed that 1) in-lake NO_3^- uptake will remain unchanged; 2) increased NO_3^- deposition to the lake surface will be directly reflected in increased lakewater NO_3^- concentrations; and 3) the current amount of in-watershed retention of NO_3^- (kg ha^{-1} yr^{-1}) deposited on the watershed will remain constant on a percentage basis over time. In other words, for watersheds that currently do not appear to be chronically leaching NO_3^- from watershed to lake, we assumed that changes in NO_3^- deposition will only change lakewater NO_3^- concentrations by an amount equal to the change in deposition to the lake surface. For watersheds that do appear to be chronically leaching some NO_3^- to the lakes, we assumed that the percent terrestrial retention of incoming NO_3^- will stay constant under changing levels of NO_3^- deposition.

The approach outlined here for modeling NO_3^- was viewed as a first approximation. It allows changes in NO_3^- deposition to be included in MAGIC scenarios, which was not possible using the version of MAGIC applied for the 1990 NAPAP Integrated Assessment. It lacks, however, a process basis for determining at what point watersheds start to leak NO_3^- under increasing N deposition, the dynamics of changing NO_3^- retention in watersheds that are chronically leaching NO_3^- at the present time, and the role of NH_4^+ deposition and subsequent nitrification in the dynamics of NO_3^- leaching. We anticipate including these components in the next iteration of nitrogen modeling for TAF, using the newly developed version of MAGIC with aggregated nitrogen dynamics, MAGIC_WAND.

3.3. Cumulative Impacts of Changes to the MAGIC Model

In order to evaluate the incremental and cumulative impact of the model modifications, a suite of model simulations was conducted by Sullivan and Cosby (in press) for the Adirondack DDRP lakes. The changes were considered cumulatively. The baseline structure was that used in the DDRP and NAPAP IA studies. The changes to the model that were examined included modifying the assumption regarding background sulfur deposition, reaggregating the soils data, recalibrating the model specifically for the Adirondack subregion, adding the triprotic organic acid analog model to the surface water compartment, and changing the aluminum/ hydrogen ion relationship from cubic to quadratic. The analyses of Sullivan and Cosby (in press) did not include examination of the effects on model output of including nitrogen dynamics in the model simulations. That work is currently in progress.

A suite of simulations was conducted based on the application of an assumed deposition scenario to derive a 50 year forecast using each model structure. The deposition scenario assumed constant sulfur deposition from 1984 (the calibration year) to 1994, followed by a 30% decrease in sulfur deposition from 1995 to 2009, with constant deposition thereafter until 2034. The modeled responses of thirty three Adirondack lakes to this deposition scenario were considered. The impacts of the changes were illustrated by tabulating the percentage of lakes predicted to have pH, ANC or Al values in excess of commonly accepted thresholds of potential biological effects.

The overall effect of the various changes to the model structure and application procedures was an increase in the percentage of lakes exceeding various biological thresholds with respect to pH, Al, and ANC subsequent to an hypothesized 30% decrease in sulfur deposition. The largest changes were observed for pH and Al; ANC projections were less affected. The modifications to the model that caused the greatest changes in projected output were the recalibration of the model to the Adirondack subregion, modification of the assumption regarding background SO_4^{2-}, and the incorporation of the triprotic organic acid model into MAGIC. The modification of the Al algorithm caused fewer lakes to be projected to exceed Al threshold values in response to the reduced deposition scenario; this change was quantitatively less important than the previous changes.

The magnitude of effect of the cumulative modifications to the model was considerable. For example, thirty-two percent of the lakes had measured pH less than 5.5 in 1984, whereas only 8% were projected to still have pH less than 5.5 after the reduction in sulfur deposition, using the original MAGIC application. In contrast, the improved version of MAGIC projected that 32% of lakes would still have pH less than 5.5 in the year 2034. Similarly, of the 30% with measured Al_i >

50 μg L^{-1} in 1986, the original model structure projected only 4% would still have $Al_i > 50$ μg L^{-1} in 2034 compared to 30% projected to continue to have high Al_i by the improved version of MAGIC. Based on model projections using the improved version of MAGIC, little recovery of Adirondack lakes would be expected subsequent to a 30% reduction in sulfur deposition. The number of lakes having pH < 6 is actually projected to increase, and the number of lakes projected to have ANC < 0 only decreases slightly in response to lower deposition. These estimates are independent of any possible increases in NO_3^- leaching that might occur. The lack of recovery suggested by these model projections is attributable partly to a decrease in the modeled base saturation of watershed soils. These results may affect expectations of recovery in response to sulfur emission controls mandated by the Clean Air Act Amendments of 1990.

3.4. Magic Model Confirmation

MAGIC has been tested after inclusion of many of the model modifications discussed in the preceding sections. The revised model with Driscoll et al.'s (1994) triprotic organic acid analog yielded reasonable agreement between model hindcast pH and diatom-inferred pH for the data set of 33 Adirondack lakes (Sullivan et al. in press a). Differences between diatom and MAGIC estimates of pre-industrial pH of Adirondack lakes, based on the version of MAGIC that includes a triprotic organic acid representation were well within the range of expected differences due to annual and seasonal variability, uncertainties in the algorithms used to calculate pH from major ion chemistry, and the influence of dissolved CO_2 on air-equilibrated pH measurements that were used to calibrate the diatom model (Sullivan et al. 1994). However, "successful" comparison of MAGIC with diatom hindcasts in one region does not constitute a sufficient verification to impart complete confidence in using MAGIC, or any process model, for predicting the response of surface water chemistry to changes in acidic inputs. Additional model confirmation in the form of comparison of model output with *measured* data, is required. This has been the focus of modeling efforts at Lake Skjervatjern, Bear Brook, and Risdalsheia.

MAGIC model projections of the response of Lake Skjervatjern to whole-catchment acid additions were close to measured values for SO_4^{2-}, NO_3^-, and NH_4^+. Although the retention of added sulfur within the terrestrial system was considerable, the MAGIC-simulated SO_4^{2-} concentrations at Skjervatjern were within 3 to 6 μeq L^{-1} of average measured concentrations (Cosby et al. 1995). The simulated values for NO_3^- and NH_4^+ in Lake Skjervatjern were also very close to measured values for both years, within about 1 μeq L^{-1}. It is important to note, however, that the observed success in modeling the nitrogen fluxes into Lake Skjervatjern lakewater was not a result of nitrogen processing algorithms, which are not part of the current version of MAGIC. Rather, the simulation was run assuming that the percent retention of NH_4^+ and NO_3^- within the treated watershed would equal the calculated percent retention for each ion in the control catchment, based on estimated atmospheric inputs and lakewater concentrations. The actual percent net retention for both NH_4^+ and NO_3^- during the experimental treatment was very similar to the pre-manipulation percent retention of atmospheric inputs. Therefore, the MAGIC-simulated values were in agreement with measured responses without having to manually change the inputs to match measured values. Such agreement would not routinely be expected, however, as is illustrated in the Bear Brook data, and a process-based approach to modeling N cycling and fluxes would be a desirable addition to the model.

The MAGIC model simulations of the responses of the treatment catchment at Risdalsheia to reduced acidic deposition matched measured values extremely well (Cosby et al. 1995). In particular, the observed changes in SO_4^{2-}, base cation concentrations, and ANC closely paralleled the observed trends and interannual variations. Also, despite the importance of organic acids in modifying the pH of drainage waters at this site (Wright 1989), incorporation into MAGIC of the triprotic organic acid analog, calibrated to the Norwegian 1000 Lake Survey, resulted in good agreement between modeled and measured pH.

The results of the MAGIC model testing at Risdalsheia (Cosby et al. 1995) are particularly noteworthy in two respects. First, model simulations of pH matched measured values fairly well despite using a regional model representation for organic acids to simulate pH in a system in which organic acids provide a great deal of pH-buffering. Second, agreement was demonstrated between simulated and observed chemistry, for all major variables except perhaps Al, over an eight-year period. This is a very long period of record for a model evaluation study that involves substantial change in acidic deposition inputs.

Sullivan and Cosby (in press) modified the equations used by MAGIC to simulate Al dissolution. The modified version of MAGIC, incorporating the new equations for Al, was applied to the Risdalsheia data. In general, the revised model predicted Al concentrations that were closer to measured values at this site (Sullivan and Cosby in review).

Modeling efforts at Bear Brook (Sullivan et al. 1994, Cosby et al. in press) provide a continuation of the MAGIC model forecasting efforts presented by Norton et al. (1992). MAGIC predicted a much larger increase in streamwater SO_4^{2-} concentration than was observed in the treated stream. The trajectory of MAGIC-simulated SO_4^{2-} is approaching the anticipated steady-state concentration of about 300 μeq L^{-1} projected to occur within the eight-year simulation period; i.e., about 200 μeq L^{-1} higher than pre-treatment concentrations. In contrast, the trajectory of measured values is substantially lower.

It appears that MAGIC overpredicts the increase in streamwater SO_4^{2-} concentrations at Bear Brook by nearly a factor of two. This overprediction of the increase in streamwater SO_4^{2-} concentration that resulted from the manipulation experiment was due to the high value assumed for the half saturation of sulfur adsorption. The adsorptive behavior of the soils was effectively removed because concentrations of SO_4^{2-} never approached the half saturation value.

As a consequence of the overprediction of streamwater SO_4^{2-} concentration, other key variables (especially ANC and Al) were also predicted to respond to a greater degree to the experimental acidification than was actually observed. MAGIC predicted substantially larger changes in each of these parameters than was observed. The discrepancies between MAGIC predictions and measured values for ANC increased with each year of the treatment, and are attributable mainly to the errors in predicting the responses of SO_4^{2-} and secondarily to errors in predicting the responses of Ca^{2+} and Mg^{2+}. This latter bias, however, was due primarily to pre-treatment differences between the reference and manipulated stream chemistry. This is a reflection of the extreme difficulty of finding "paired catchments" with identical chemistry. The combined influence of the observed biases in C_B and C_A resulted in relatively large errors in predicted ANC, because ANC is defined in MAGIC for this application as $(C_B - C_A)$.

The original calibration of MAGIC for the Bear Brook forecast was based on four years of data from the reference stream, East Bear. In order to assess the degree to which discrepancies between predicted and observed streamwater chemistry at Bear Brook could be improved by correcting sulfur dynamics and *a priori* differences between treatment and control catchments, a revised calibration was conducted. The revised Bear Brook calibration corrected for the obvious large bias in effective sulfur adsorption in watershed soils and also corrected for *a priori* differences between the treatment and reference catchments. The resulting simulations matched measured values in West Bear Brook to a substantially greater degree than had the forecasts based on the initial calibration that was based on the behavior of East Bear.

Projected streamwater SO_4^{2-} concentration agreed closely with measured values in West Bear Brook for the first three years of manipulation (Cosby et al.1996). There was a suggestion, however, in the measured data of a leveling off in the annual increase in streamwater SO_4^{2-} concentration, whereas the model projected a steady increase in concentration throughout the duration of the model projection (1989 through 1994). The model simulation also showed much better agreement with measured values for the sum of base cations and ANC, than had the initial MAGIC simulation. Although the effects of the drought year (1992) on C_B and ANC were still not captured by the simulation, the overall agreement between predicted and observed C_B and ANC was much improved.

Based on the results of extensive model testing using diatom inferences of historical acidification of Adirondack lakes and the results of experimental watershed acidification (Lake Skjervatjern, Bear Brook) and deacidification (Risdalsheia), it appears that the MAGIC model provides reasonably accurate forecasts of changes in surface water acid-base chemistry in response to changing levels of acidic deposition. Although some uncertainties remain, particularly with respect to watershed nitrogen dynamics, we conclude that the MAGIC model provides a generally accurate and well-tested tool for integrated assessment modeling.

References

Bull, K.R. 1992. An introduction to critical loads. Environ. Pollut. 77:173-176.

Church, M.R., K.W. Thorton, P.W. Shaffer, D.L. Stevens, B.P. Rochelle, R.G. Holdren, M.G. Johnson, J.J. Lee, R.S. Turner, D.L. Cassell, D.A. Lammers, W.G. Campbell, C.I. Liff, C.C. Brandt, L.H. Liegel, G.D. Bishop, D.C. Mortenson, and S.M. Pierson. 1989. Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province (Results of the Direct/Delayed Response Project). U.S. Environmental Protection Agency Environmental Research Laboratory Corvallis, OR.

Cook, R.B., K.A. Rose, A.L. Brenkert, and P.F. Ryan. 1992. Systematic comparison of ILWAS, MAGIC, and ETD watershed acidification models: 3. Mass balance budgets for acid neutralizing capacity. Environ. Pollut. 77:235-242.

Cosby, B.J., S.A. Norton, and J.S. Kahl. In press. Using a paired-watershed manipulation experiment to evaluate a catchment-scale biogeochemical model. Sci. Tot. Environ.

Cosby, B.J., R.F. Wright, and E. Gjessing. 1995. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. J. Hydrol. 170:101-122.

Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. Water Resour. Res. 21:51-63.

Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. Water Resour. Res. 21:1591-1601.

Driscoll, C.T., M.D. Lehtinen, and T.J. Sullivan. 1994. Modeling the acid-base chemistry of organic solutes in Adirondack, New York, lakes. Water Resour. Res. 30:297-306.

Forsius, J. Kämäri, and M. Posch. 1992. Critical loads for Finnish lakes: comparison of three steady-state models. Environ. Pollut. 77:185-193.

Gjessing, E. 1992. The HUMEX Project: Experimental acidification of a catchment and its humic lake. Environ. Internat. 18:535-543.

Husar, R.B., T.J. Sullivan, and D.F. Charles. 1991. Historical trends in atmospheric sulfur deposition and methods for assessing long-term trends in surface water chemistry. pp. 65-82, In: Charles, D.F. (ed.). Acidic Deposition and Aquatic Ecosystems. Regional Case Studies. Springer-Verlag, New York.

Kahl, J.S., S.A. Norton, I.J. Fernandez, K.J. Nadelhoffer, C.T. Driscoll, and J.D. Aber. 1993. Experimental inducement of nitrogen saturation at the watershed scale. Environ. Sci. Tech. 27:565-568.

Kretser, W., J. Gallagher, and J. Nicolette. 1989. An Evaluation of Fish Communities and Water Chemistry. Adirondack Lakes Survey Corporation, Ray Brook, New York.

Linthurst, R.A., D.H. Landers, J.M. Eilers, D.F. Brakke, W.S. Overton, E.P Meier, and R.E. Crowe. 1986. Characteristics of Lakes in the Eastern United States. Volume I. Population

Descriptions and Physico-Chemical Relationships. EPA/600/4-86/007a, U.S. Environmental Protection Agency. 275 pp.

NAPAP. 1991. National Acid Precipitation Assessment Program 1990 Integrated Assessment Report. National Acid Precipitation Assessment Program, Washington, DC. 520 pp.

Norton, S.A., R.F. Wright, J.S. Kahl, and J.P. Scofield. 1992. The MAGIC simulation of surface water at, and first year results from, the Bear Brook Watershed Manipulation, Maine, USA. Environ. Pollut. 77:279-286.

Oliver, B.G., E.M. Thurman, and R.L. Malcolm. 1983. The contribution of humic substances to the acidity of colored natural waters. Geochim. Cosmochim. Acta 47:2031-2035.

Renberg, I. and H. Hultberg. 1992. A paleolimnological assessment of acidification and liming effects on diatom assemblages in a Swedish lake. Can. J. Fish. Aquat. Sci. 49:65-72.

SFT. 1987. Thousand Lake Survey. Norwegian State Pollution Control Authority, Norwegian Institute for Water Research (NIVA), Oslo, Norway.

Sullivan, T.J., B.J. Cosby, C.T. Driscoll, H.F. Hemond, D.F. Charles, S.A. Norton, H.M. Seip, and G. Taugbøl. 1994. Confirmation of the MAGIC Model Using Independent Data: Influence of Organic Acids on Model Estimates of Lakewater Acidification. Report No. DOE/ER/30196-4. Final Report prepared for The U.S. Department of Energy, under Agreement No. DE-FG02-92ER30196.

Sullivan, T.J., R.S. Turner, D.F. Charles, B.F. Cumming, J.P. Smol, C.L. Schofield, C.T. Driscoll, B.J. Cosby, H.J.B. Birks, A.J. Uutala, J.C. Kingston, S.S. Dixit, J.A. Bernert, P.F. Ryan, and D.R. Marmorek. 1992. Use of historical assessment for evaluation of process-based model projections of future environmental change: Lake acidification in the Adirondack Mountains, New York, U.S.A. Environ. Pollut. 77:253-262.

Sullivan, T.J., J. A. Bernert, E. A. Jenne, J. M. Eilers, B. J. Cosby, D. F. Charles, and A. R. Selle. 1991. Comparison of MAGIC and diatom paleolimnological model hindcasts of lakewater acidification in the Adirondack region of New York. Prepared for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830. Pacific Northwest Laboratory, Richland, WA.

Wright, R.F. 1989. Rain Project: Role of organic acids in moderating pH change following reduction in acid deposition. Water Air Soil Pollut. 46:251-259.

Wright, R.F., B.J. Cosby, M.B. Flaten, and J.O. Reuss. 1990. Evaluation of an acidification model with data from manipulated catchments in Norway. Nature 343:53-55.

Wright, R.F., E. Lotse, and A. Semb. 1988. Reversibility of acidification shown by whole-catchment experiments. Nature 334:670-675.

Wright, R.F., E.T. Gjessing, N. Christophersen, E. Lotse, H.M. Seip, A. Semb, B. Sletaune, R. Storhaug, and K. Wedum. 1986. Project RAIN: changing acid deposition to whole catchments. The first year of treatment. Water Air Soil Pollut. 30:47-64.