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Progress Report

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Abstract

A project was initiated in March, 1992 to 1) incorporate a rigorous organic acid representation, based on empirical data and geochemical considerations, into the MAGIC model of acidification response, and 2) test the revised model using three sets of independent data. After six months of performance, the project is on schedule and the majority of the tasks outlined for Year 1 have been successfully completed. Major accomplishments to data include development of the organic acid modeling approach, using data from the Adirondack Lakes Survey Corporation (ALSC), and coupling the organic acid model with MAGIC for chemical hindcast comparisons. The incorporation of an organic acid representation into MAGIC can account for much of the discrepancy earlier observed between MAGIC hindcasts and paleolimnological reconstructions of pre-industrial pH and alkalinity for 33 statistically-selected Adirondack lakes. Additional work is on-going for model calibration and testing with data from two whole-catchment artificial acidification projects. Results obtained thus far are being prepared as manuscripts for submission to the peer-reviewed scientific literature.

NOTICE

A. INTRODUCTION AND SCOPE

The project entitled, "Incorporation of an organic acid representation into MAGIC (Model of Acidification of Groundwater in Catchments) and Testing of the Revised Model Using Independent Data Sources" (DOE Grant DE-FG02-92ER30196.A000) was initiated in March, 1992. Major components of the project are:

1. improving the MAGIC model by incorporating a rigorous 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.

MAGIC (Model of Acidification of Groundwater in Catchments) has been the principal model used thus far by the National Acid Precipitation Assessment Program (NAPAP) for making projections of likely future changes in surface water chemistry throughout the United States in response to various levels of acidic deposition. The current version of the model has been described in the NAPAP State of Science/Technology Report on modeling methods (Thornton et al. 1990), and numerous model projections of future scenarios were presented in the Integrated Assessment (NAPAP 1990).

MAGIC, like other processed-based models, is a simplified representation of catchment processes. Although rooted in hydrochemical principles, the model includes major temporal and spatial process aggregation, and some catchment processes are not well represented. Few data sets are available that contain a sufficiently long period of record for validating the approach. In the absence of such validation, however, future scenario projections are subject to large, and unquantifiable, uncertainties.

The most extensive model validation exercise conducted for MAGIC, or any process-based acid-base chemical model, was the recent comparison between model hindcasts and paleolimnological inferences of historical acidification for a set of 33 statistically-representative Adirondack lakes (Sullivan et al. 1990, 1991, 1992). This research effort was sponsored by the U.S. Department of Energy, and represents the only regional and statistical model validation exercise conducted to date for a process-based acid-base chemistry model. Both assessment methods suggested acidification of low-ANC Adirondack lakes 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 (< about 50 μeq L^{-1}).

It was recognized that the lack of organic acid representation in the MAGIC simulations conducted by the U.S. EPA's Direct Delayed Response Project, Sullivan et al. (1991), and the Integrated Assessment analyses may have been an important factor contributing to the observed discrepancy. Organic acids often exert a large influence on surface water acid-base chemistry, particularly in waters having low ionic strength. To investigate the potential role of organic acids in influencing the comparison results, a MAGIC model scenario was conducted by Sullivan et al. (1991) that included a "reasonable" first-approximation organic acid representation (uniform organic acid contribution assumed for all lakes, using 20 μeq L^{-1} of organic anion charge at pH=5, and a diprotic acid with pK=4.0 and 10.0). The results of this scenario suggested that inclusion of a reasonable representation of organic acids in MAGIC can substantially improve the agreement between MAGIC-simulated and diatom-inferred pre-industrial lakewater pH. Quantification of the degree of improvement was uncertain, however, because a rigorous treatment of organic acids, on an individual lake basis, was not performed.

Recently, Driscoll et al. (1991) modeled the organic acidity of lakewater sampled by the Adirondack Lakes Survey Corporation (ALSC) using a triprotic organic acid and calibrating the three pK values. They obtained a good fit between measured ANC and modeled ANC, including organic acids in the modeled ANC expression. This research is important because of the large ALSC data base (> 1600 lakes) and wide range of organic acid contributions to the lakewater chemistries. This, or a similar, approach could be coupled to MAGIC to produce a more rigorous evaluation of organic acid influence on the comparison results. The improved version of MAGIC might be far superior for NAPAP future-scenario projections than the version used thus far within

NAPAP (without organic acid representation), or recent versions that include a monoprotic representation.

MAGIC is a lumped-parameter model that represents catchment processes in a spatially-undifferentiated format. The model is being applied as a representation of each individual watershed. The goal of the watershed version of MAGIC is to calibrate the model to an individual lake or stream and then to forecast the response of that system to future changes in atmospheric deposition. Site-specific information on soils, geology, bathymetry, and deposition is used as input data.

A sense of the uncertainty involved in the model input parameters and calibration procedures is obtained by running the model using what is referred to as "fuzzy optimization" (Cosby et al. 1990). Fuzzy optimization consists of running MAGIC for each watershed many times, varying the watershed and deposition input parameter characteristics within reasonable bounds to reflect the uncertainty in the data. If our knowledge of each lake and watershed was complete, such that there was little uncertainty in the physical or chemical composition of the watershed, there would be no need to vary the input parameters. However, our knowledge of the characteristics of the surface waters and watersheds of interest is incomplete, and it is important to recognize this uncertainty in our approach to generating the model output. This variability in the input parameters is used to explicitly represent the within-catchment variation of soil and water parameters. The types of parameters that vary for the fuzzy optimization include soil depth, soil chemistry, precipitation volume, hydraulic residence time, and lake/stream chemistry. In this manner we construct a suite of calibrated parameter sets for each lake or stream that will produce the observed water chemistry from a variety of soil conditions.

The on-going research will be conducted over a period of two years, and involves development of an organic acid representation to be incorporated into the MAGIC model and testing of the improved model using three independent data sources. This work has been subdivided into four discrete tasks, as follows:

Task 1 - Develop an organic acid model subroutine, based upon empirical data and theoretical considerations, and incorporate it into the MAGIC model.

Task 2 - Conduct MAGIC model hindcasts, using the revised model, for 33 statistically-selected Adirondack Mountain lakes for which diatom-inferred current and pre-industrial lakewater pH and ANC estimates are available; test the revised MAGIC model by comparing hindcast results with the diatom pH and ANC inferences. Task 2 also includes site visits to the two project sites to be studied within Tasks 3 and 4.

Task 3 - Conduct MAGIC model forecasts, using the revised model and pre-acidification baseline chemistry, for the U.S. EPA's watershed manipulation project (WMP) site in Maine, and compare simulated streamwater chemistry with the measured chemistry resulting from chemical manipulation.

Task 4 - Conduct MAGIC model forecasts, using the revised model and pre-acidification baseline chemistry, for the Norwegian whole-catchment manipulation project (HUMEX), and compare simulated lakewater chemistry with the measured chemistry resulting from chemical manipulation.

Research to be completed during Year 1 includes conducting two workshops to agree on an approach for the organic acid modeling, developing the organic subroutine and incorporating it into MAGIC (Task 1), conducting MAGIC hindcasts for Adirondack lakes and comparing the results with paleolimnological reconstructions (Task 2), and conducting site visits to the manipulation project sites in Maine and Norway. The research to be completed in Year 2 will include conducting MAGIC forecasts (based on pre-treatment and dose application data) of catchment responses to experimental acidification and comparing those forecasts with post-treatment measured chemistry (Tasks 3 and 4).

Two workshops were conducted during Year 1, prior to and after development and refinement of the organic acid subroutine. The workshops were attended by internationally-recognized experts in the fields of surface water acid-base chemistry, organic acid chemistry, and process-based modeling. An approach was agreed upon by the workshop participants for the modeling efforts. Detailed acid-base chemical data were examined at the workshops for brown-water systems from the northeastern United States and Scandinavia. These empirical data, and also geochemical theoretical considerations, formed the basis for the modeling approach.

The agreed-upon organic acid modeling approach has been incorporated as a subroutine into the MAGIC model. A series of sensitivity analyses have been and will continue to be conducted to evaluate parameter uncertainty and internal consistency of calibrated and calculated variables. The comparisons between model output results and independent measurements/inferences will provide important information on: (1) the accuracy of the model projections, and (2) the importance of the organic acid modeling effort to the accuracy of those results.

The purpose of this Progress Report is to provide a more detailed summary of the work that has been conducted on this project to date. Many of the components of Tasks 1 and 2 have now been completed, and the remainder will be completed prior to the end of Year 1 (March 15, 1993) of the project. Many analyses are on-going, and the results presented herein should be viewed as preliminary. Several major project deliverables are in the process of being prepared as manuscripts for submission to peer-reviewed scientific journals.

B. SIGNIFICANT RESULTS TO DATE

1. Corvallis Workshop

A workshop was held in Corvallis, Oregon on April 9-10, 1992 at the offices of E&S Environmental Chemistry, Inc. The purpose of this workshop was to initiate research efforts on E&S's grant from the U.S. Department of Energy, "Incorporation of an organic acid representation into MAGIC (Model of Acidification of Groundwater in Catchments) and testing of the revised model using independent data sources". A project outline is shown in Figure 1.

The workshop was attended by a team of internationally-recognized experts in the fields of surface water acid-base chemistry, organic acids, and watershed modeling. The following scientists were in attendance:

T. Sullivan	E&S Environmental Chemistry, Inc.
C. Driscoll	Syracuse University
B. Cosby	University of Virginia
H. Hemond	Massachusetts Institute of Technology
H. Seip	University of Oslo
P. Wigington	U.S. EPA
J. Eilers	E&S Environmental Chemistry, Inc.
G. Taugbøl	University of Oslo
D. Charles	Patrick Center for Environmental Research, Academy of Natural Sciences of Philadelphia

PROJECT OUTLINE

Year 1:

Task 1 - Develop an organic acid model subroutine, based upon empirical data and theoretical considerations, and incorporate it into the MAGIC model.

Task 2 - Conduct MAGIC model hindcasts, using the revised model, for 33 statistically-selected Adirondack Mountain lakes for which diatom-inferred current and pre-industrial lakewater pH and ANC estimates are available; test the revised MAGIC model by comparing hindcast results with the diatom pH and ANC inferences. Task 2 will also include site visits to the two project sites to be studied within Tasks 3 and 4.

Year 2:

Task 3 - Conduct MAGIC model forecasts, using the revised model and pre-acidification baseline chemistry, for the U.S. EPA's watershed manipulation project (WMP) site in Maine, and compare simulated streamwater chemistry with the measured chemistry resulting from chemical manipulation.

Task 4 - Conduct MAGIC model forecasts, using the revised model and pre-acidification baseline chemistry, for the Norwegian whole-catchment manipulation project (HUMEX), and compare simulated lakewater chemistry with the measured chemistry resulting from chemical manipulation.

Figure 1. Project Outline

a. Summary of Previous MAGIC/Paleolimnology Comparison Project

The agenda for the Corvallis workshop is presented in Table 1. The meeting included presentations by selected team members and also considerable time for group discussions. At the beginning of the workshop, Sullivan outlined the major objectives of this research project. They are to develop a rigorous approach for modeling the effects of organic acids on surface water acid-base chemistry, incorporate the organics submodel into MAGIC, test the improved version of MAGIC by comparing model hindcasts with paleolimnological inferences of historical acidification, and test the improved MAGIC model using measured chemistry data from on-going whole-catchment acidification projects in Maine and Norway.

Table 1. Agenda: Corvallis Workshop on Organic Acid Modeling and Model Validation

Dates: April 9, 10, 11

Place: Office of E&S Environmental Chemistry, Inc., located in Business Enterprise Center, 800 NW Starker St., Corvallis, OR (corner of 9th and Starker)

April 9

8:30	Welcome and workshop objectives (Sullivan)
9:00	Summary of previous comparison between MAGIC and paleolimnology and relationship to on-going ILWAS project (Sullivan)
10:00	Break
10:15	Organic model strawman (Driscoll)
11:15	Modeling approach (Cosby)
12:00	Lunch
1:00	Comments on modeling surface water chemistry with emphasis on dissolved organic compounds. Approach and available data (Seip)
1:30	Catchment modeling of DOC and chemical interactions - key processes. A short-term model used on the organic-rich stream at Svartberget, northern Sweden (Taugbøl)
2:00	Discussion of approach(es) to be taken for organic acid modeling (All)
5:00	Adjournment
Evening:	Social activity

April 10

8:30	Summary of organic modeling approach (Sullivan)
9:00	Comparison with Paleolimnology (Charles)
10:00	Validation with watershed manipulation project data, Maine (Driscoll)
11:00	Validation with HUMEX project data, Norway (Seip/Taugbøl)
12:00	Lunch
1:00	Discussion of validation approach (All)
3:00	Schedule, deliverables, and responsibilities (Sullivan)
4:30	Meeting summary and wrap-up
5:00	Adjournment

April 11 - Field Trip

7:00	Depart Corvallis
8:30	Breakfast in Newport
9:30-5:30	Tour Newport to Florence
~9:00	Return to Corvallis

Sullivan spent one hour reviewing the objectives and principal findings of the earlier MAGIC/paleolimnology comparison project (Sullivan et al. 1991), which largely provided the rationale for the current project. Many of the complicating factors that were investigated by Sullivan et al. (1991) will also be important in the new project, mainly for the paleolimnological comparison component. Although several of the project team members (e.g., Cosby, Charles, Jenne) were also involved in the precursor project, other team members were only slightly familiar with the earlier research results.

An analysis was conducted in the previous project to compare paleolimnological estimates of pre-industrial pH and ANC of Adirondack lakes with MAGIC model hindcast estimates of pre-industrial chemistry. Thirty-three lakes that had been statistically selected as part of the U.S. Environmental Protection Agency's (EPA) Eastern Lake Survey, Phase-I and Direct Delayed Response Project (DDRP) were included in the comparison. The study lakes thus represented a well-defined population of Adirondack lakes that are larger than 4 ha in area and have acid neutralizing capacity (ANC) less than 400 μeq L^{-1}. Paleolimnological estimates of pre-industrial chemistry were derived from the Paleoecological Investigation of Recent Lake Acidification-II (PIRLA-II) study.

It was found that direct comparison of pre-industrial and current chemistry estimates, using DDRP protocols for MAGIC and PIRLA-II diatom-inferred chemistry, was inappropriate. A host of inconsistencies in methodologies and problematic assumptions obscured the reasons for differences between the paleolimnological and MAGIC model results. The major potential difficulties included (1) the influence of watershed disturbance and land use on acid-base chemistry, (2) seasonal differences between the paleolimnological study and the EPA survey data, (3) differences in the definition of ANC used as MAGIC model output versus the diatom calibration, (4) uncertainties regarding pre-industrial atmospheric deposition of sulfur and base cations, which must be estimated in order to conduct MAGIC hindcast simulations, and (5) uncertainties regarding the soils aggregation and calibration of MAGIC to the northeastern region, rather than the Adirondack subregion, within the DDRP. In order to evaluate the relative importance of these issues in confounding direct comparison between paleolimnological and MAGIC model reconstructions, several different scenarios and calibrations were conducted for both approaches.

The most reasonable comparison available between the paleolimnological and MAGIC hindcasts included the MAGIC scenario that was based on the subregional reaggregation and recalibration of MAGIC to the Adirondacks (designated Scenario #4) and the paleolimnological inferences of ANC defined as (C_B - C_A) (where C_B is the base cation sum: Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+, and C_A is the mineral acid anion sum: SO_4^{2-} + NO_3^- + Cl^-). This comparison removed the biases associated with different ANC definitions, and the regional (rather than subregional) nature of the other MAGIC scenarios. The recalibration also minimized potential influences of CO_2 oversaturation on data interpretation, which are particularly important for pH comparisons. Results of this comparison showed good agreement for the estimates of current chemistry, thus demonstrating that both approaches can be successfully calibrated to current conditions. Substantial differences were observed, however, between the MAGIC and paleolimnological estimates of pre-industrial chemistry. The MAGIC model estimates of pre-industrial ANC were generally higher than the diatom-inferred estimates, and MAGIC implied that lakewater acid-base chemistry had been more responsive to historical increases in acid deposition than did paleolimnology.

The extent to which the model estimates agreed or disagreed depends largely on one's perspective. A decade ago, most scientists believed that 60% to 100% of the atmospheric sulfate input caused a stoichiometric decrease in ANC. Compared to those earlier estimates, the diatom and MAGIC hindcast estimates of acidification were lower, and implied that the above percentage has been 0% to 50%. Both approaches suggested acidification of low-ANC Adirondack lakes 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. Paleolimnology inferred that acidification had been restricted to low-ANC lakes (< about 50 μeq L^{-1}).

b. Organic Acid Modeling Approach

An approach was agreed upon by the workshop participants for the modeling efforts to be used in this study. The "strawman" approach was developed by C.T. Driscoll. Driscoll presented a series of analyses that he and co-workers conducted for Adirondack lakes, using the 1469-lake Adirondack Lakes Survey Corporation (ALSC) data base (Baker et al. 1990). The ALSC data base was fit to mono-, di-, and triprotic organic acid models, and also to the Oliver et al. (1983) model. The best fit to the data was obtained using a triprotic acid and a site density of 0.043 mol sites per mol C. Calibrated pK values were 1.76, 5.90, and 6.83, with roughly one-third of the charge sites being "strong acid" sites.

It was pointed out by several workshop participants that the lowest pK value (1.76) seems to be extremely low, but that the effect of having a low (highly acid) site is the same regardless of whether the pK value is 1.76, or substantially higher. This is because all of the strong acid sites would be dissociated at existing lakewater pH values. Driscoll indicated that the uncertainty about this pK estimate was high, but also reiterated that it would have no effect on model output if the value was 2.76, for example, instead of 1.76.

Driscoll and co-workers also developed a chemical response surface, illustrating the relationship between organic acid anion (A^-) concentration, dissolved organic carbon (DOC), and pH (Figure 2). A charge balance method was used to estimate organic acid anion concentrations. The total contribution of charge for aluminum, DIC, and free fluoride was estimated using the ALCHEMI chemical equilibrium model (Schecher and Driscoll 1987).

Evidence for the importance of strong organic acidity was provided by regression analyses within discrete sets of lakes having roughly equivalent C_B - C_A. A series of plots of Gran ANC

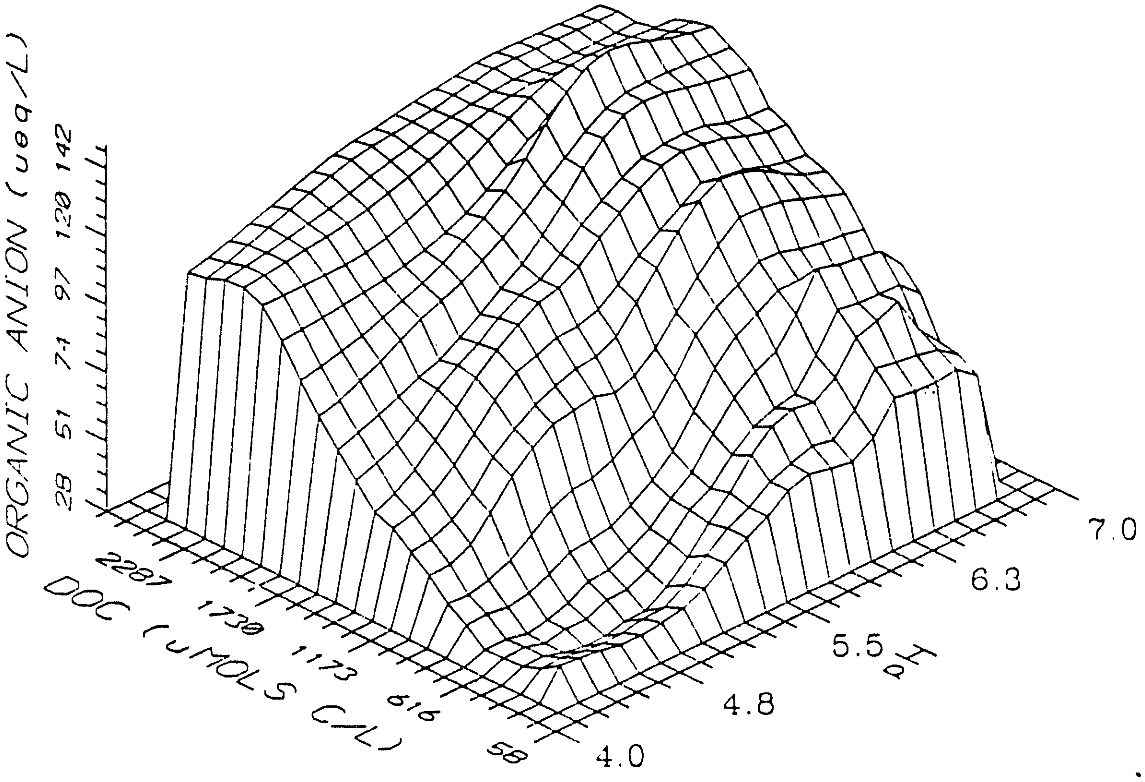

Figure 2. Concentration of organic anions as a function of pH and dissolved organic carbon (DOC) concentration in lakewater. Organic anion concentrations were determined from the charge balance. The response plot is based on 1175 observations of lakes with pH ≤ 7.0 (72 suspected outliers were deleted), collected by the Adirondack Lake Survey Corporation. (Source: Driscoll and Lehtinen, in preparation)

versus DOC showed clear relationships within each of the uniform C_B - C_A data sets (e.g. Figure 3). Gran ANC decreased relative to defined ANC (C_B - C_A) with increasing DOC.

The preferred model, based on the analyses with ALSC data, is a triprotic acid (Figure 4). Although the Oliver et al. (1983) model also provided a reasonable fit, it does not allow for the inclusion of organo-aluminum binding without prior modification. Since aluminum is an important component of watershed response, it is desirable to maintain the ability to account for Al effects in the selected model. Driscoll pointed out that a weakness of this, or any model of organic acidity, is that we do not know to what extent organic acid anion concentrations and/or DOC may have changed in response to changes in acidic deposition inputs. Sullivan indicated that a recent literature review he prepared for Battelle-PNL concluded that, although DOC changes appeared to have occurred in some cases, those changes tended to be small in magnitude. In many cases, changes in the degree of protonation appeared to be much more important than changes in the DOC.

c. Integration of Organic Modeling and MAGIC

Cosby reviewed conceptually the behavior of mineral and organic acids in natural waters (e.g., Figure 5) and the relationships among pH, ANC, and DOC for the Adirondack study lakes (Figure 6). Cosby presented the results of a new set of preliminary MAGIC model hindcast simulations for the 33 Adirondack lakes investigated by Sullivan et al. (1991). In these model simulations, Cosby incorporated a diprotic organic acid representation, with $pK_1 = 4.20$, $pK_2 = 6.04$, and a site density of 0.082 mole sites per mole carbon. This was based on the diprotic acid fit obtained by Driscoll for ALSC data. Adding this diprotic organic acid component greatly increased the agreement between the diatom reconstructions and MAGIC hindcasts.

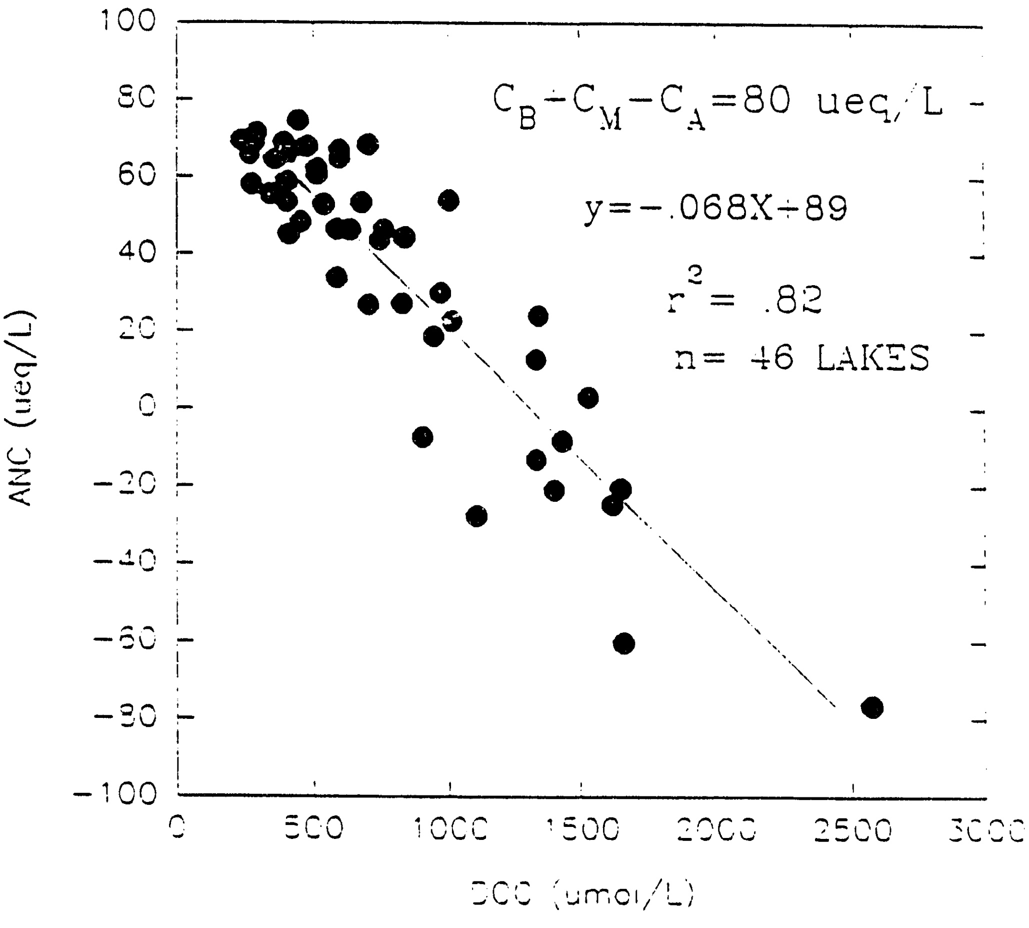

Figure 3. Example regression analysis for values of $C_B + C_M - C_A = 80 \pm 5$ μeq L^{-1} in which the relationship between ANC and DOC is evaluated using data from ALSC lakes. Results show that the ordinant intercept (89 μeq L^{-1}) is close to the nominal value of 80 μeq L^{-1} for this grouping of $C_B + C_M - C_A$. As DOC increases, values of ANC decrease (Lehtinen 1991).

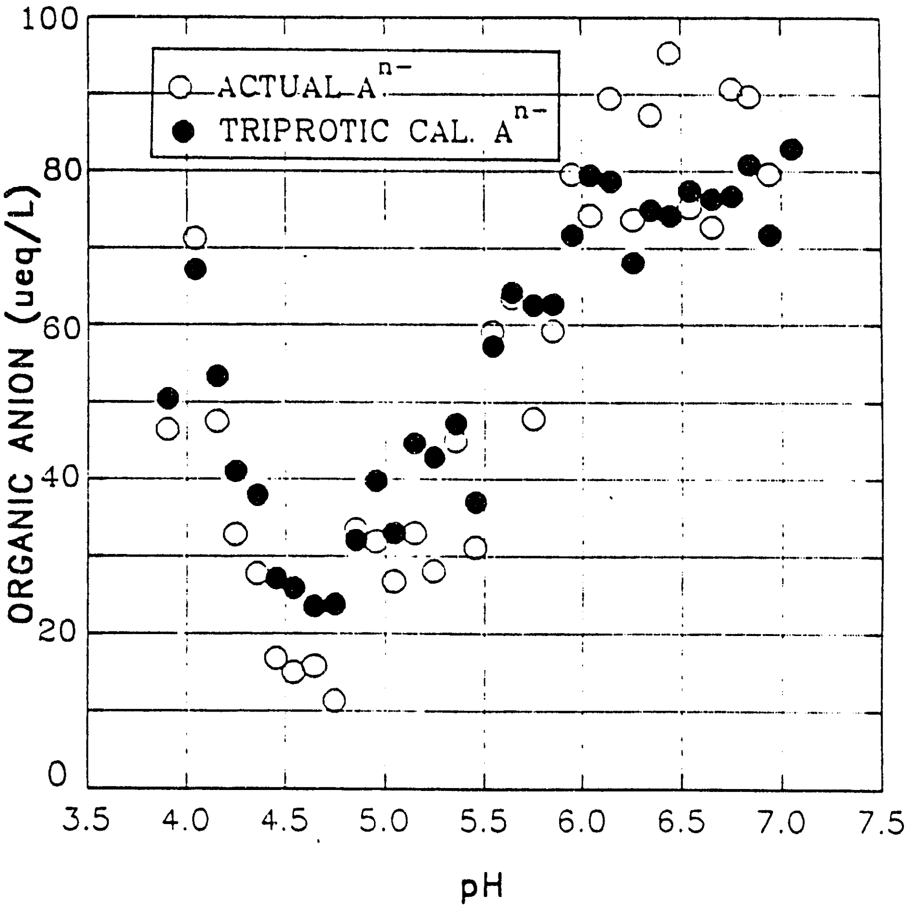

Figure 4. Comparison of the organic acid anion concentration determined from the charge balance (open circles) and the mean organic anion concentration as calculated using the ALSC-calibrated triprotic organic acid model in the chemical equilibrium model ALCHEMI (r^2=0.92) (Lehtinen 1991)

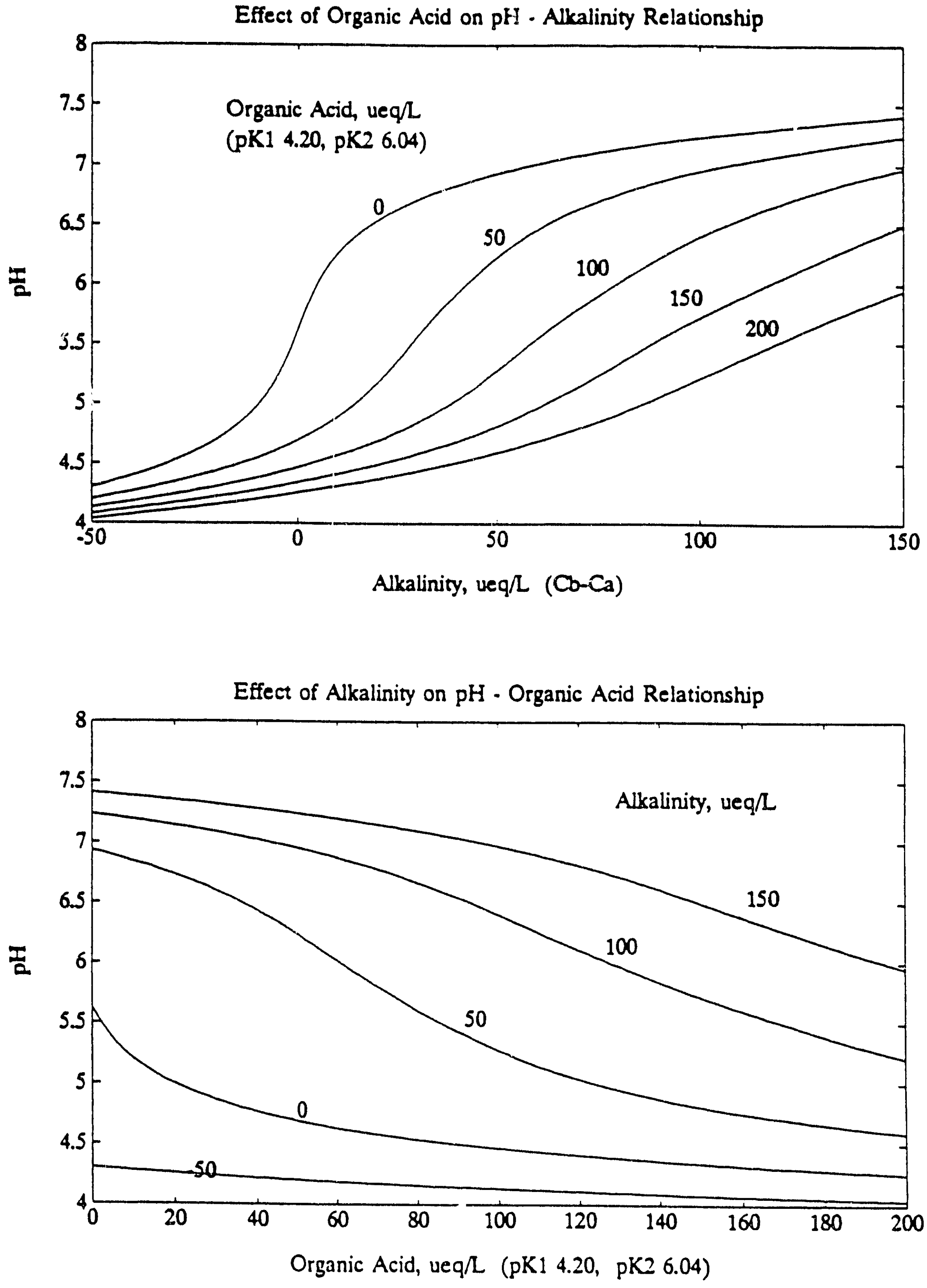

Figure 5. a) Effect of organic acids on the pH/alkalinity relationship; b) Effect of alkalinity on the pH/organic acid relationship.

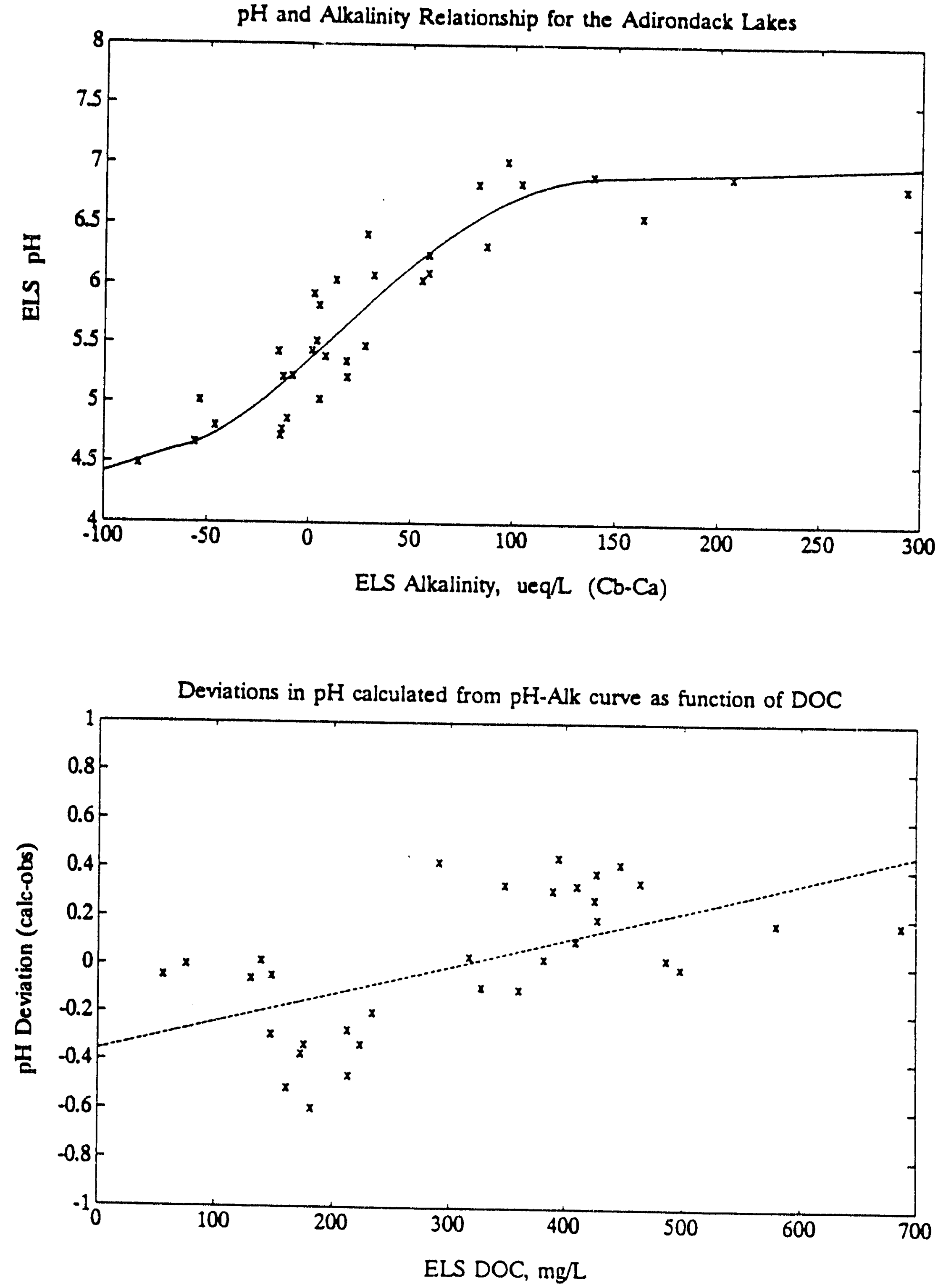

Figure 6. Relationships between pH, alkalinity, and DOC for Adirondack lakes sampled by the Eastern Lake Survey (ELS).

d. Hydrology, Model Complexity, and Time Step

The major uncertainties in hydrological flowpaths and weathering were discussed in some detail. Taugbøl and Seip pointed out, based on the Scandinavian modeling experiences, that detailed hydrology is essential to obtain a reasonable fit of model simulations to streamwater data. Driscoll pointed out a problem with simulating weathering because that assumes that exchange values have remained constant over time. Cosby responded that such an error is minimized by running the model for a long period of time (e.g. > 100 years). Initial errors regarding weathering assumptions disappear in the calibration procedure. It was also pointed out by Cosby that he felt that having organics in the model is much more important for hindcasting than for forecasting. It is not clear at this point, however, to what extent forecasts might also be affected.

Seip presented some of his recent modeling efforts, using the Birkenes model (Figure 7). This model includes substantially more hydrological detail than TOPMODEL (used in MAGIC) and works with a shorter time-step. The model output is typically very sensitive to the hydrological detail. Furthermore, from a biological perspective, it may be more important to simulate the short-term catchment responses which are critical to aquatic biota. Other major issues raised by Seip included the uncertainty in describing alumino-organic binding reactions, the factors controlling organic anion concentrations (e.g., DOC production), and possible changes in the *properties* of organic acid anions (e.g., with season, with precipitation). He also mentioned that, in addition to the data from HUMEX, WMP, and Adirondack paleolimnology that will be investigated in this project, other useful data could be obtained from the RAIN project (Norway), Svartberget (Sweden), Birkenes (Norway), and Langtjern (Norway). He was concerned about the lack of process-level formulations in MAGIC, particularly with respect to hydrology, sulfur mineralization, nitrogen processing, and aluminum chemistry.

Geir Taugbøl presented a discussion of the extended Birkenes model, which now includes watershed production and degradation of DOC. Temperature was found to be the most important

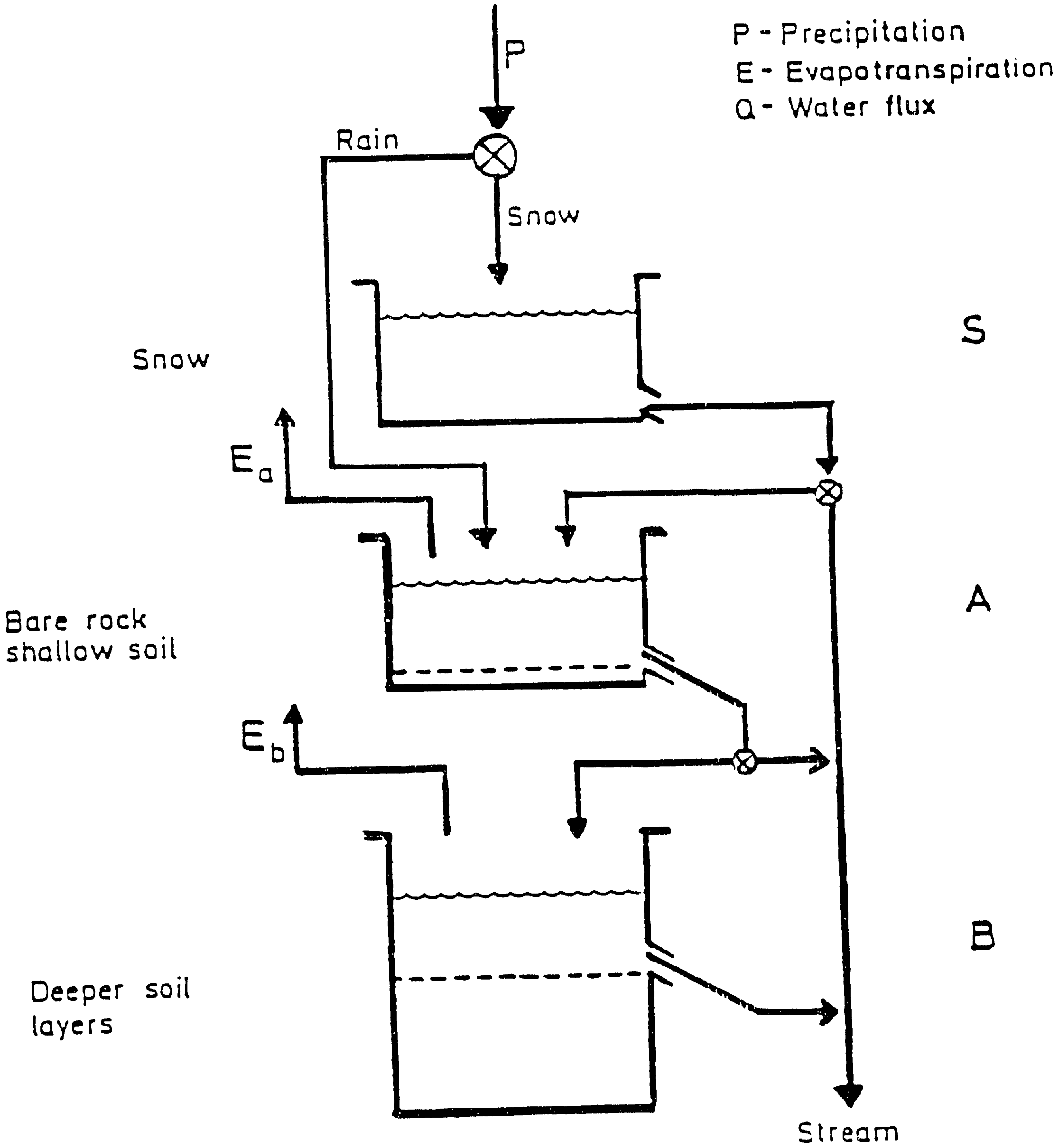

Figure 7. Birkenes model formulation.

factor governing the DOC degradation rate. Streamwater data modeled by Taugbøl and co-workers in Sweden suggested that hydrology was the key factor in controlling the water chemistry. It was extremely important to calibrate the hydrological submodel confidently in order to build a reliable chemical model. A large portion of piston flow (> 90%), routing water to the deeper soil layers, was needed in the model to explain the dampened chemical signals in the streamwater. Either two or three soil layers were needed. An Oliver model approach was used for organic acid chemistry, with a lower pK value of 3.3 to 3.7. Although he felt that a distribution function for pK's seemed more reasonable, replacing that with one or two values did not seem to have a major effect on the simulations. Taugbøl recommended using a short-term model, like Birkenes, to refine the process representation in a long-term model (e.g., MAGIC). Although a more complex model requires more input data and is more difficult to calibrate to a given site, it provides greater theoretical consistency and is more generally applicable. Taugbøl proposed that the short-term modeling efforts would increase knowledge of the processes controlling DOC variations. Short-term variations are often large in magnitude, and data are now available from a number of sites. This information could then be transferred to the long-term modeling efforts (i.e., MAGIC) in terms of DOC-production, complexing features, and hydrological parameters.

In response to the questions raised by Seip and Taugbøl regarding the level of complexity needed to obtain a reasonable model calibration, and the trade-offs between a long-term and a short-term model, a lengthy discussion was held of the major issues and uncertainties. Seip emphasized the importance of episodes, but Sullivan questioned the extent to which we could expect to incorporate either detailed hydrology or episodes into this project. These questions and uncertainties were especially important with respect to the objectives for Year 2 of the project in performing model validation at the watershed manipulation site (WMP) and HUMEX. Concern was raised that it will be difficult to validate MAGIC if there is little or no change in surface water chemistry at these manipulation sites. This could be particularly problematic at HUMEX if the watershed takes up most of the incoming sulfur before it reaches the lake. The other major difficulty pointed out by Sullivan was the lack of available data on which to base any modeled changes in watershed production of DOC and/or DOC precipitation (or co-precipitation with aluminum). Cosby indicated that this type of detail cannot be put into MAGIC at this point, but that we could perform sensitivity analyses to bracket "reasonable" levels of change. Alternatively, detailed sub-models could be interfaced with MAGIC and used to provide MAGIC model input. It was generally agreed that we will put the major uncertainties into perspective primarily via sensitivity analyses and literature review/comparisons. One possible important outcome of this project could be a series of recommendations for future model improvements. Although the current project has been designed to investigate and remedy primarily the previous lack of organic acid representation, all participants agreed that many important problems regarding hydrology, aluminum, nitrogen, and DOC production/degradation (among others) will remain. Hemond pointed out that, although MAGIC may not provide the needed short-term time scale, it *may* be able to deal with the spatial scale issues because it is a lumped-parameter model and can therefore be applied to a large number of watersheds.

Participants agreed that the project team was not constrained to examine *only* manipulation data from HUMEX and WMP. Data from the RAIN project, in particular, might also be useful, especially if little or no sulfur breaks through at HUMEX. Cosby responded, however, that merely trying to calibrate a humic-rich catchment such as HUMEX would be an extremely worth-while exercise and would likely help considerably in the refinement of a reasonable organic module for MAGIC.

Hemond pointed out the difficulty of trying to model DOC movement from soil solution into the stream or lake. The major problem would be devising an appropriate model formulation to deplete DOC in the lower soil compartment. He suggested that it might be better at this point to put the DOC directly into the lake or stream in the modeling effort. Cosby agreed, but also recognized that, for episodes, the soil water concentrations will be critical. Seip suggested using soil lysimeter data as part of the validation. Cosby agreed that this might be a reasonable test, but pointed out that this is not a major focus of the model.

Taugbøl questioned how the hydrology was derived for MAGIC simulations in DDRP. Cosby responded that none of the catchments were gauged, and a two-box model was specified by the DDRP program. Cosby would have preferred using a 1-box model because it was more consistent with the detail of the input data. Seip responded that, in view of the hydrological simplification, he was surprised that MAGIC worked as well as it did.

Although Driscoll indicated that there is a large uncertainty in the fitted pK values derived from his empirical analyses of the ALSC data and also in the formulation of the alumino-organic binding processes, Hemond pointed out that the organic modeling will not be sensitive to the selected pK values (within reason), and that either one of Driscoll's fits or the Oliver approach would probably work fine. The more important problem is how much DOC to put into the system.

e. Modeling Approaches

Subsequent to the lengthy discussion of uncertainties and possible model approaches, a number of decisions were made by the workshop participants for the preliminary modeling work to be conducted in this project.

It was agreed to conduct model runs with all three of Driscoll's approaches (mono-, di-, and triprotic acids) and also the Oliver model. Driscoll obtained close agreement between the triprotic and Oliver approaches for the ALSC data. Although the Oliver approach suffers from an inability to incorporate alumino-organics, it has generally been well-received in the scientific community, and should therefore be included in the comparison. Most likely, the results will be fairly similar, especially at pH greater than about 5.0 because Al becomes less important at higher pH. It was agreed that, in performing the organic acid modeling, the site density (total sites per mole of carbon) will be tuned. Driscoll emphasized that, based on the literature, this seems to be most variable. Hemond cautioned that we should evaluate this parameter carefully, because people express it in different ways. The issue of changes in DOC will be addressed for the paleolimnological comparison by conducting sensitivity analyses, assuming DOC changes of 1 and 2 ppm, and also 25% change (both increases and decreases).

It was also agreed to examine the aluminum solubility controls (Seip thought that this component was very important), although Sullivan emphasized that it was unlikely that we could expect to do much about modeling Al solubility within the scope of this project. It was agreed that a comparison of ANC would be conducted, but that it would not be emphasized because of the substantial uncertainties in the diatom-inferred pre-industrial ANC values. Diatom-inferred values for Al and DOC will be evaluated in the study for lakes included in the paleolimnological investigations. Data from other sites will also be examined (e.g. RAIN, Svartberget) within time and budget constraints.

The discussion of ANC comparisons focussed on two principal issues. First, there is uncertainty in the definition of ANC used in the various studies. Sullivan et al. (1991) corrected for this in the earlier MAGIC/Paleo comparison for Adirondack lakes. The other major problem is that the diatom inferences of ANC are tightly correlated with, and likely controlled by, the pH inferences. Biota are very sensitive to pH, but ANC is a very vague parameter, especially from a biological perspective. The lakes may have changed historically in their pH/ANC relationships, particularly in response to substantial increases in ionic strength (from added SO_4^{2-}, C_B, etc.). Sullivan suggested that we *might* be able to correct for this empirically by examining ANC/pH relationships of ALSC lakes, stratified by C_B class. It was agreed that the best approach would be to down-play the importance of the ANC variable in the paleolimnological comparison, and focus more on pH, Al, and DOC. However, the ANC comparisons will still be conducted.

Seip emphasized the importance of developing a connection between soils and streamwater for aluminum. Cosby responded that, although desirable, this will be difficult; there is especially a problem with modeling Al precipitation. Cosby will examine using a Gaines-Thomas (rather than gibbsite) approach. The assumption of a gibbsite-type equilibrium in MAGIC (and most other models) has been called into question by numerous studies showing major deviations between surface water [Al] and equilibrium concentrations, especially under high-flow conditions.

f. Comparison with Paleolimnology

Charles summarized the paleolimnological inference techniques that are currently being used for the Adirondack lakes data set. The data set used to develop inference equations was based on a calibration set of 80 lakes. In addition, a set of 37 lakes was evaluated that have been studied as part of PIRLA-II, by examining diatom remains in the tops and bottoms of sediment cores (Figure 8). He showed a graphic representation of the output from canonical correspondence analysis to simultaneously show the relationship between independent environmental variables and sediment diatom assemblages (Figure 9). The relationships are strongest for pH, followed by ANC, Al, and DOC (in descending order). Charles indicated that there is a geographical component to the diatom-inferred acidification of Adirondack lakes, unlike the earlier MAGIC hindcasts, which showed a generally uniform distribution for ΔpH. He also discussed the availability of chrysophyte data for the model comparisons, which generally suggest greater acidification than the diatom data. This may be due to the seasonal abundance of these two groups of algae. Chrysophytes are more abundant in spring, and may reflect spring pH depressions. Diatoms are probably more reflective of average conditions. Diatoms generally give more accurate reconstructions, however, because they are typically represented by about an order of magnitude more species than the chrysophytes (more ecological information for reconstruction). The techniques provide generally-reproducible results (Figures 10-12) that have been well-documented.

Driscoll volunteered to classify the 33 Adirondack study lakes (those included in the MAGIC/paleo comparison) into hydrological categories. This will be done in a manner similar to that followed by Driscoll et al. (1991), which used Ca^{2+} as the classification variable. Cosby volunteered to simulate MAGIC Gran titrations and compare them to Hemond's recent nomograph for the 33 Adirondack study lakes.

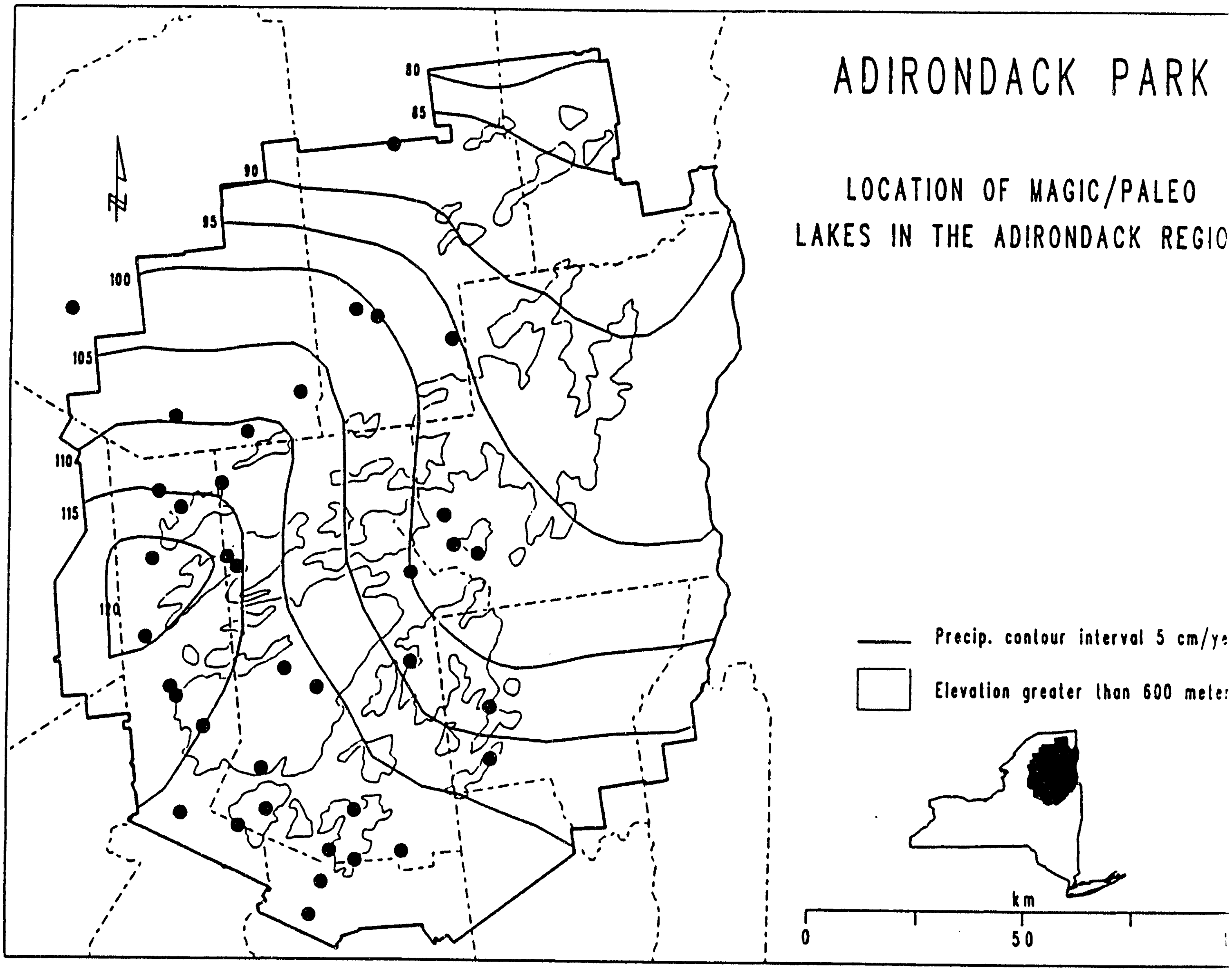

Figure 8. Location of Adirondack lakes involved in the MAGIC/diatom comparison.

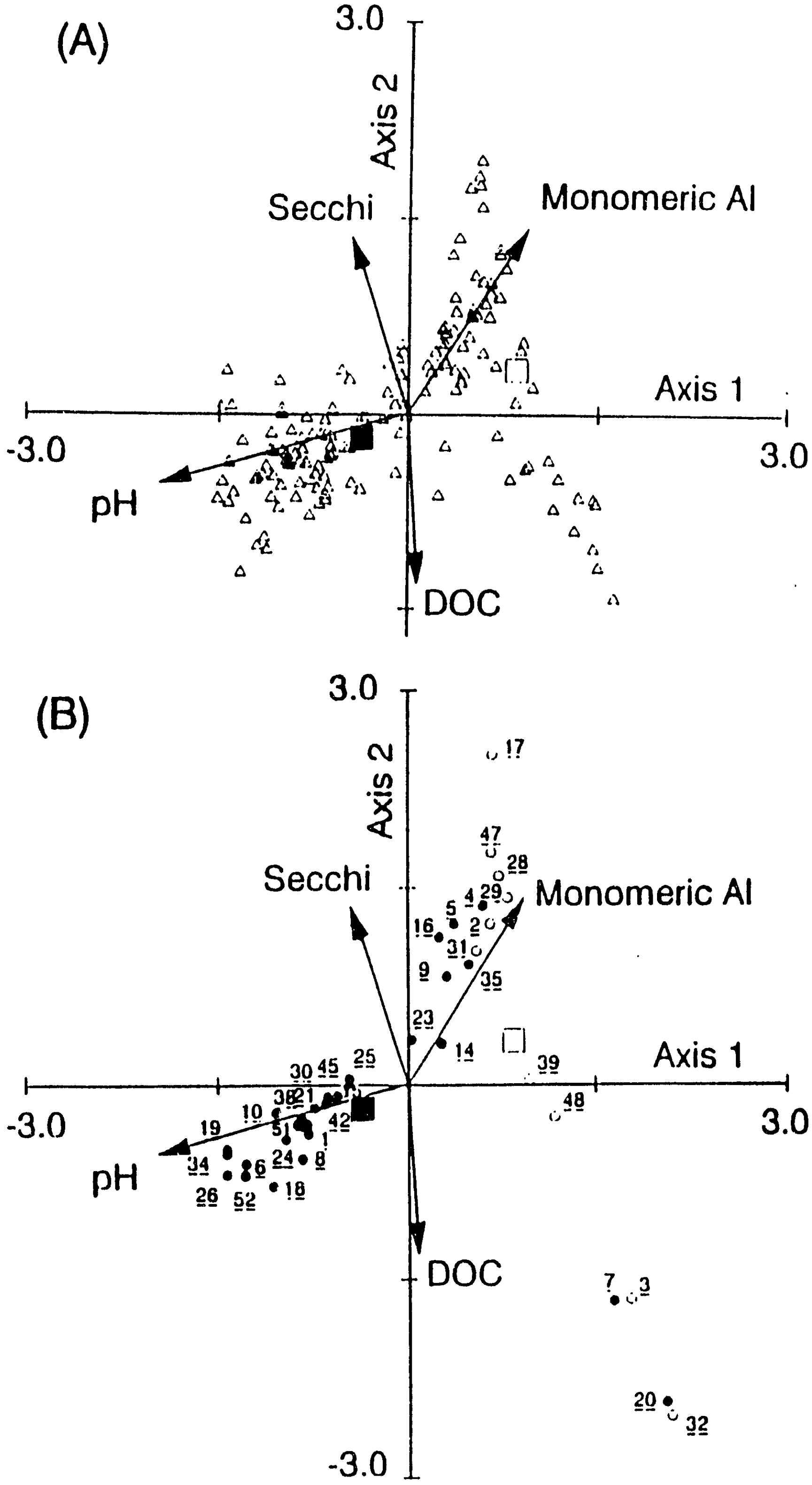

Figure 9. Canonical correspondence analysis ordination plots of (A) 149 diatom species in 37 Adirondack lakes and (B) 37 lake surface-sediment samples, each with environmental biplot arrows for the four significant variables as determined in forward selection. (Dixit et al., in review)

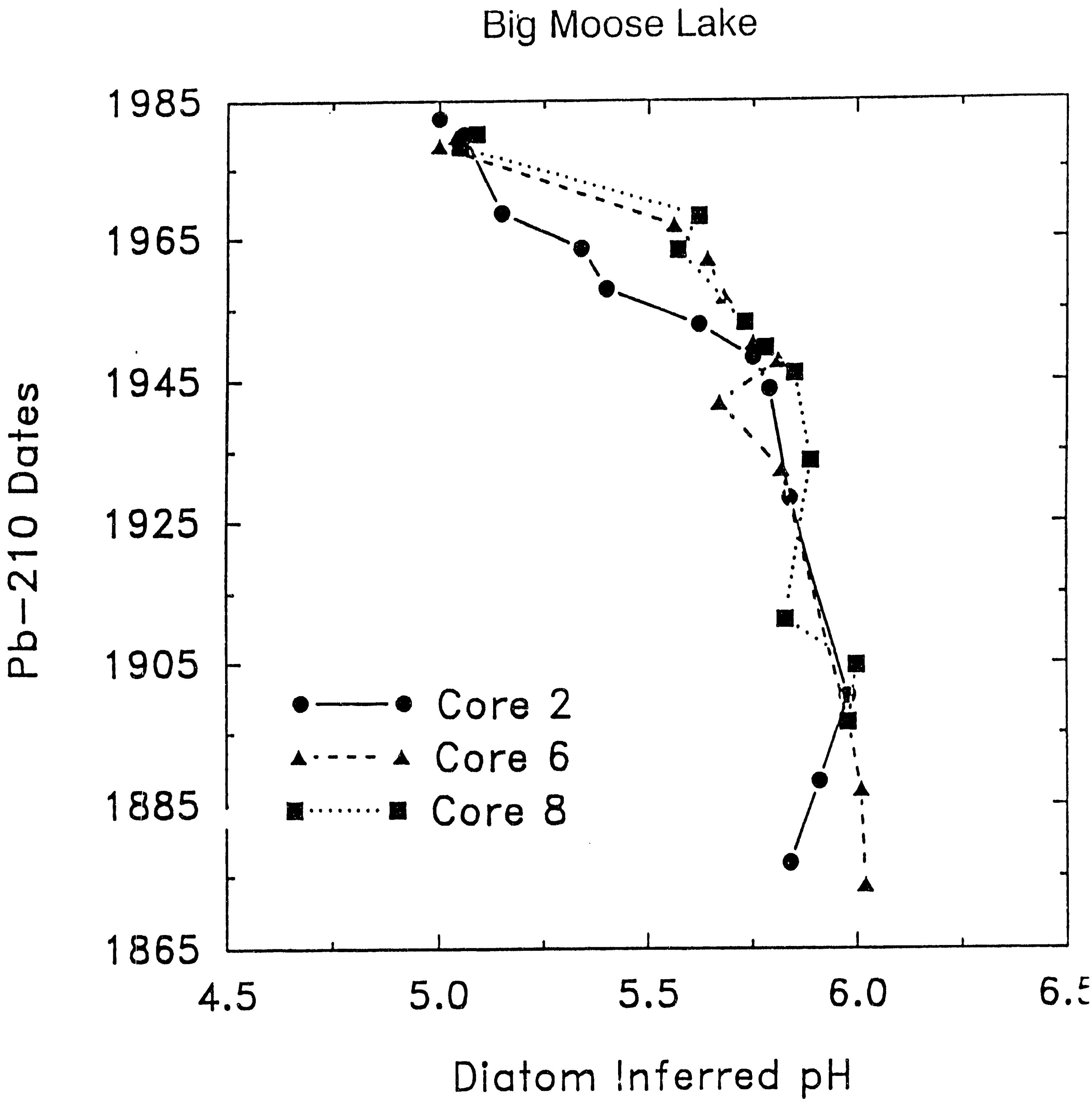

Figure 10. Paleolimnological reconstructions for Big Moose Lake (Charles et al. 1991).

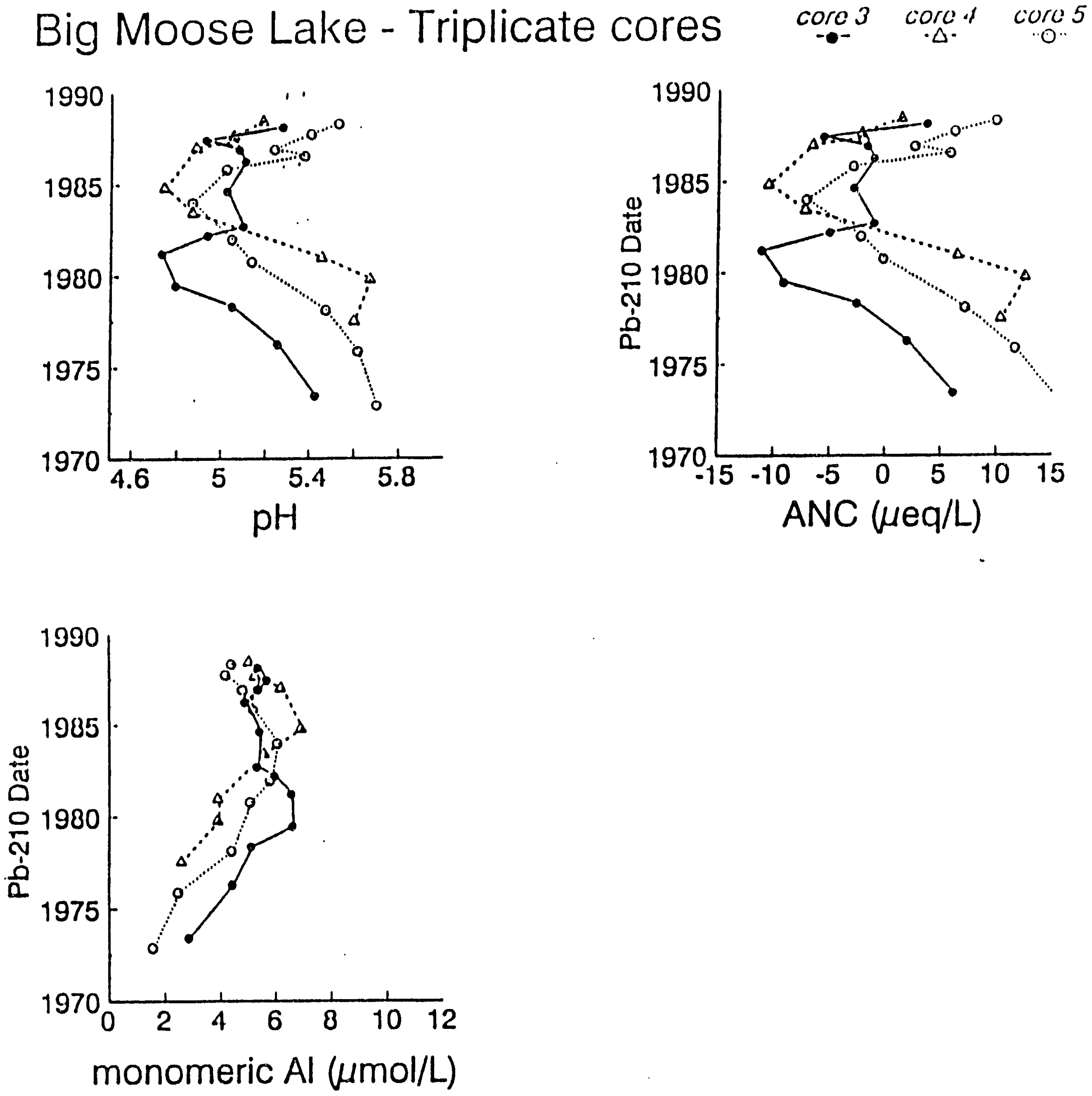

Figure 11. Chrysophyte-inferred reconstructions of recent (1972-1989) lakewater pH, ANC, and monomeric Al concentrations in three separate sediment cores collected from Big Moose Lake (Source: B.F. Cumming).

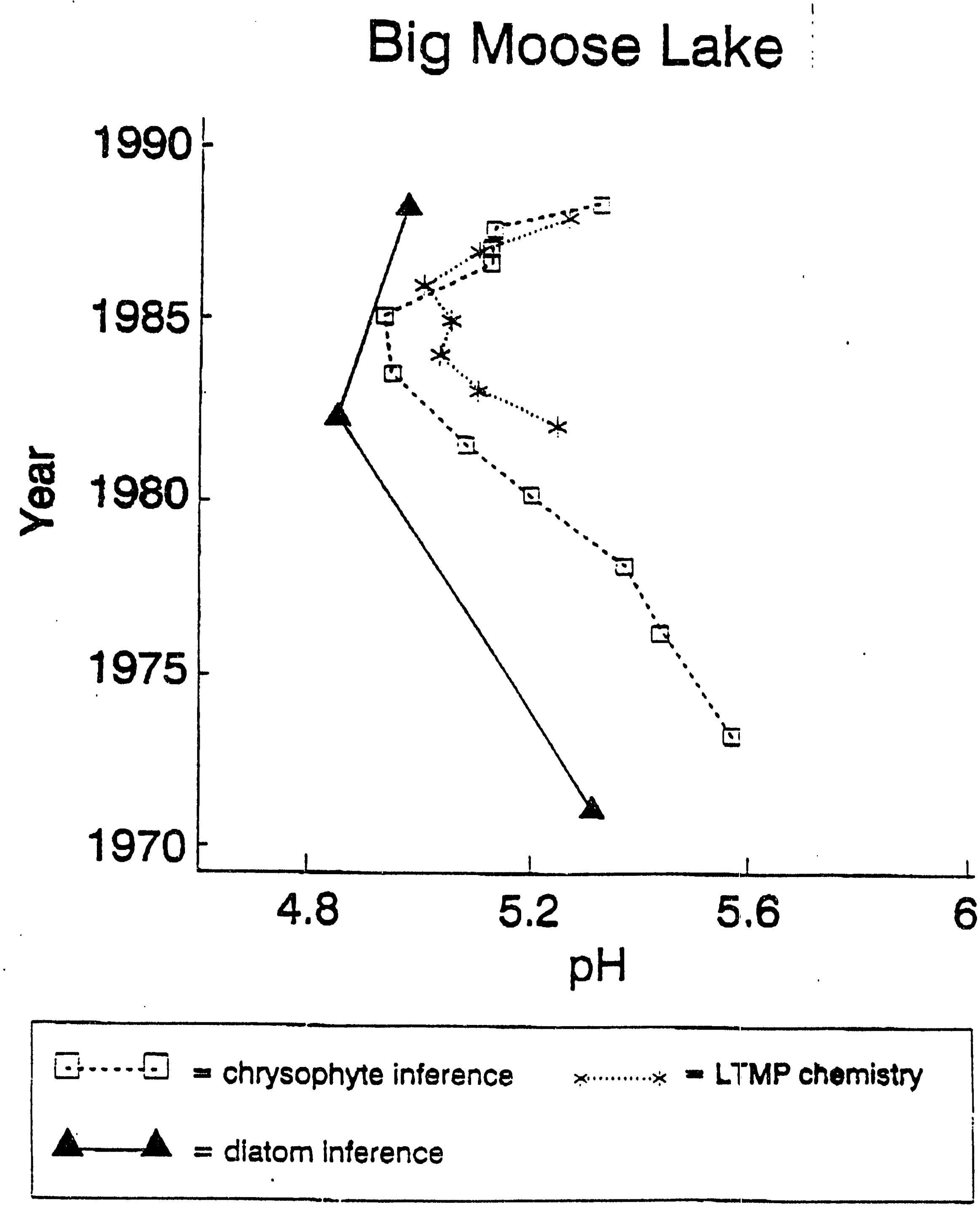

Figure 12. Comparison among chrysophyte inferences, diatom inferences, and measured (Long-term Monitoring Program) data for the recent pH of Big Moose Lake (Source: S.S. Dixit and B.F. Cumming).

g. Comparison with Watershed Manipulations

Driscoll presented a summary (for Norton, who was unable to attend the workshop) of the Watershed Manipulation Project (WMP) at Bear Brook in Maine. It is a large, multi-faceted project, with a number of separate Task Groups (Table 2). The stream site manipulation includes paired watersheds (10-15 ha each). Spodosols predominate, but soils and geologic materials are heterogeneous. The two catchments (treatment and control) seem to be well-paired, but the pre-treatment streamwater sulfate concentration was fairly high ($\sim$ 100 μeq L^{-1}). Cosby suggested that MAGIC could be used to check S and N fluxes in the watersheds as part of the validation. TOPMODEL has already been calibrated to the site.

Seip and Taugbøl emphasized the utility of using a short-term model like Birkenes as part of the WMP validation. Sullivan agreed that this would be a good idea, but that additional funding was not likely to be available to conduct this modeling work. It was also not certain whether the WMP cooperators would want to release the data for additional modeling work. It was agreed that Sullivan would inquire about availability of the data for this purpose[1]

Table 2. Watershed Manipulation Project task groups.

Task Group	Leader
Site	S. Norton, S. Kahl, I. Fernandez
Organic acids	M. David
Sulfur	M. Mitchell
Nitrogen	J. Aber, K. Nadelhoffer
Hydrology	G. Hornberger
Weathering	J. Schnoor, J. Dreaver
Al and cation exchange	C. Driscoll

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[1] Norton subsequently discussed this request with other WMP cooperators, and they do not object to the use of WMP data for this effort.

Taugbøl and Seip agreed to try to perform some preliminary modeling within the currently-available funding. Seip was particularly concerned about the possibility of a substantial pH effect on an episodic basis at the WMP site that the MAGIC model may be unable to simulate.

Cosby also suggested that it might be reasonable to use the control catchment at WMP to determine whether a one-box or a two-box hydrological representation is needed. Wigington stated that there will be a number of scientific papers and reports coming out this fall on the WMP data. These may be helpful in the interpretation of the results of our validation study.

Seip showed a short video tape describing the Norwegian HUMEX manipulation. The humic lake was divided in half with a plastic curtain in 1988. Since 1990 one-half is being acidified with sulfuric and nitric acids. The hydrology appears to be very complex. Investigators have identified (by temperature probes) a number of hydrologic vents that seem to route water through the peat and into the lake. Seip raised two issues that may cause problems for the modeling efforts. First, there is large variability in lakewater TOC (~ 2 to 12 mg L^{-1}) with considerable increases during summer. Second, preliminary data suggest that much of the incoming sulfur is at present being retained in the watershed, and is not entering the lake. Driscoll advocated examining the Norwegian 1000 lake data set to derive organic constants, as was done for the ALSC data base. This analysis could be used to evaluate the applicability to Norwegian data of the approach derived from Adirondack data. It was agreed to proceed with the calibration and modeling effort at HUMEX, and to also consider incorporating RAIN data into the analysis.

h. Schedule and Deliverables

The final portion of the workshop was devoted to a discussion of logistical and contracting issues, schedules, deliverables, and responsibilities. Project team members agreed that other manuscripts, closely tied to the major objectives and deliverables of this project, will also likely be produced in conjunction with the project.

2. Orono Workshop

A second project workshop was held at the University of Maine at Orono on July 17 and 18, 1992. It was attended by Drs. Sullivan, Norton, Cosby, Charles, Driscoll, and Hemond, and by the coordinator of many of the site activities at the watershed manipulation project (WMP) Bear Brook catchment, Steve Kahl. The major objectives of the workshop were to:

1. Review and discuss recent MAGIC modeling results,
2. Resolve any final questions regarding the organic acid modeling approach,
3. Examine the revised MAGIC/diatom hindcast comparisons,
4. Plan model validation exercises for next winter and spring on the data from Lake Skjervatjern and Bear Brook, and
5. Discuss plans and schedules for journal articles and other deliverables.

The itinerary for the workshop is included as Table 3. Dr. Cosby presented the results of a large array of model scenario results and sensitivity analyses. Model outputs were examined for mono-, di-, and tri-protic organic acid models, and also the Oliver model, using different approaches for the aluminum formulations (total dissolved versus total extractable), regional average versus site-specific data for P_{CO_2} and K_{Al}, and assuming varying levels of historical change in dissolved organic carbon (e.g. increases and decreases in absolute concentration and relative concentration). Different levels of goodness-of-fit were also examined (e.g. mean difference versus root mean square difference). The former provides information on bias and the latter gives information on scatter.

Table 3. Agenda

Orono Workshop on Organic Acid Modeling and Model Validation

Dates: July 17, 18

Place: Boardman Hall, University of Maine, Orono, ME

Accommodations: Black Bear Inn, Stillwater Exit off Rt. I-95, North of Bangor (2 mi. from campus)

July 17

8:30	Welcome and workshop objectives (Sullivan)
8:45	Summary of project accomplishments to date (Sullivan)
9:15	Organic modeling approach (Driscoll)
9:45	Model results (Cosby)
10:15	Break
10:30	Comparison with paleolimnological reconstructions (Cosby/Charles)
12:00	Lunch
1:00	Bear Brook modeling approach (Norton/Cosby)
2:00	Short-term modeling of Bear Brook (Sullivan)
2:30	HUMEX modeling approach (Sullivan/Cosby)
3:00	Discussion of approaches and results to date (All)
4:30	Schedule and Deliverables Revisited (Sullivan)
4:45	Meeting summary and wrap-up (Sullivan)
5:00	Adjournment

July 18

8:00	Field trip to Bear Brook watershed
~2:00	Return to Orono

a. Model Comparisons

The improved MAGIC model is being compared, on a lake-by-lake and population basis, with paleolimnological inferences of historical and current lakewater chemistry for the data set of Adirondack lakes studied by Sullivan et al. (1991). This research is also investigating the influence of organic acids and historical changes in lakewater ionic strength on the pH/ANC relationship of diatom-inferred pre-industrial chemistry. Because diatoms respond more strongly to pH than to ANC, differences in the pH/ANC relationship between pre-industrial and current chemistry could influence diatom inferences of historical change in ANC. Agreement between the MAGIC and paleolimnological methods will be assessed, including the degree of improvement in fit obtained by including the inferred organic acids in both assessment methods.

The comparison with paleolimnological hindcasts of Adirondack lakewater chemistry is ongoing. Preliminary results indicate a major improvement in the agreement between diatom-inferred hindcasts and MAGIC hindcasts after inclusion of the organic acid subroutine. This research effort will continue and will be described in a manuscript prepared this fall for submission to the peer-reviewed literature.

Agreement between models (MAGIC and diatom) was slightly better using regional average P_{CO_2} and K_{Al} values, rather than site-specific values, but results were generally similar. Inclusion of an organic acid submodel, based on data from the Adirondack Lakes Survey Corporation (ALSC), greatly improved the agreement between pre-industrial estimates of pH and ANC. Improvement is slightly better using the triprotic organic acid formulation, but all organic acid modeling approaches examined yield similar results. Inclusion of organic acids worsened the agreement between the model approaches for current chemistry in the absence of further calibration. A site density of 0.055 moles of site per mole of C was used, based on the average site density obtained by Driscoll for ALSC data.

Dr. Norton provided a thorough overview of the Bear Brook artificial acidification experiment within the WMP. Streamwater SO_4^{2-} concentration is generally quite stable in the control catchment and well buffered by the soil (~ 105 μeq L^{-1}). West Bear Brook, the manipulated site, now exhibits spikes of streamwater SO_4^{2-} concentration to nearly 200 μeq L^{-1}. Much of the incoming and applied sulfur is still being retained in the soils. Streamwater NO^- pulses up to 20 to 30 μeq L^{-1} have been common during high flow periods at the manipulated site, and elevated streamwater $[NO_3^-]$ is now observed on a chronic basis as well. DOC in West Bear Brook may have decreased by 5 to 10% in response to the manipulation. The pH change has been about 0.4 pH units and concentrations up to 6-8 μM of Al are occurring during high flow periods. A potential problem with the Bear Brook modeling effort is that NO_3^- accounts for about 1/3 of the anion increases in streamwater, yet MAGIC was not designed to incorporate nitrogen dynamics. The current plan for the Bear Brook modeling work is to use one soil layer, use the observed discharge during each month to drive the hydrology, and specify the amount of nitrogen inputs that will be removed in the system. Modeling problems related to nitrogen will be handled in the episodic modeling work (Birkenes model) by using observed NO_3^- output to adjust (increase) Cl^- input. This will avoid complications related to the internal processing of SO_4^{2-} (e.g. mineralization).

Dr. Sullivan summarized the results to date at HUMEX (see Foreign Trip Report, Appendix A). A major focus of the modeling work at HUMEX will be the pH buffering of DOC during variable flow periods, because the catchment may not respond to a large degree to the acid additions and the hydrology will be complex. The MAGIC implementation will likely be a two-layer horizontal application, based on organic soils and podsols.

The research team was treated to a tour of the Bear Brook catchments and the water quality laboratory by Dr. Norton. The catchments appear to be well-chosen, with minimal recent disturbance and a well-developed (for this region) primarily mixed-hardwood forest.

b. Sensitivity Analysis

The objective of the sensitivity analysis was to evaluate the potential importance of several issues to the regional modeling output. The following issues were evaluated:

1. Choice of organic acid formulation (e.g., monoprotic, diprotic, triprotic, Oliver, no organic representation),

2. Use of average values for the Adirondack region versus individual watershed-specific estimates of P_{CO_2} and K_{Al},
3. Use of measured values of total aluminum versus extractable Al

These issues were evaluated for the 33 Adirondack lakes, including examination of both pH and ANC model output and including comparisons for a variety of 1984 estimates and 1844 hindcasts (Table 4). As is illustrated in the table, this involved a total of 5,280 evaluations. The regional analysis was somewhat more manageable, yielding 160 test results (i.e., 5280 ÷ 33 lakes).

The following tasks were performed:

1. Program the three organic acid models derived by Driscoll from ALSC data (monoprotic, diprotic, triprotic), and also the Oliver model,
2. Apply the 4 organic acid models to previously calibrated MAGIC and diatom simulation results,
3. Recompare MAGIC and diatom model output, *without recalibrating MAGIC* subsequent to incorporation of the organic model results, including comparisons of both pH and calculated alkalinity,
4. Determine the sensitivity of the results to hypothesized changes in DOC, and
5. Assess the potential effects of the assumptions regarding aluminum solubility.

Given that the pH of a given lake is a function of the following variables,

- calculated alkalinity (ALK)
- pK values for organic acids (pK's)
- partial pressure of CO_2 (P_{CO_2})
- K_{Al}
- DOC concentration
- site density for organic acids (sd),

pH was calculated from the MAGIC CALK outputs, and diatom-inferred CALK was calculated as a function of diatom-inferred pH.

Table 4. Analysis Design

Monoprotic	Ave P_{CO_2}, K_{Al} (ALT)	1844 Mag/Dia	pH diff	1A1-012
Diprotic	SS P_{CO_2}, K_{Al} (ALT)	1984 Mag/Dia	CALK diff	1A1-012
Triprotic	Ave P_{CO_2}, K_{Al} (ALEX)	1984 Mag/ELS		1A1-014
Oliver	SS P_{CO_2}, K_{Al} (ALEX)	1984 ELS/ELS		...
Model				... (n=33)
(5 models) x	(4 conditions) x	(4 measures) x	(2 criteria) x	(33 lakes)

= 5,280 evaluations

$$\mathrm{CALK} = f(\mathrm{pH}, \mathrm{pK's}, P_{CO_2}, K_{Al}, \mathrm{DOC}, \mathrm{sd})$$

The P_{CO_2} values were calculated from measured values of pH and DIC collected in 1984 by the Eastern Lake Survey (ELS), using pK's of inorganic carbon reactions from the literature. It was assumed that P_{CO_2} was constant historically, even though DIC may have changed. Measurements of pH and aluminum concentration (total and extractable) for ELS were used to calculate K_{Al}, using pK's for aluminum reactions from the literature. It was assumed that K_{Al} remained constant historically. Organic acid concentrations were calculated from measured DOC (ELS) and the four organic acid models, using the pK's and site density estimates obtained by Driscoll for the ALSC data. It was assumed that DOC and site density remained constant historically.

Thus the MAGIC simulated CALK values for 1984 and 1844 that were derived by Sullivan et al. (1991) were used to recalculate MAGIC pH values for both time periods. Similarly, diatom-inferred pH for 1984 and 1844 were used to recalculate diatom CALK values for both time periods. The latter component avoided any potential bias associated with the suspected dependency of diatom-inferences of alkalinity upon the pH/alkalinity relationship. This dependency is potentially problematic because the pH/alkalinity relationships may have changed over time.

The following reactions were used in the calculations.

Ionic charge balance

$$2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] + [NH_4^{+}] \quad - [Cl^{-}] - [NO_3^{-}] - 2[SO_4^{2-}]$$

$$+ [H^{+}] - [OH^{-}] \quad + 3[Al^{3+}] + 2[Al(OH)^{2+}] + [Al(OH)_2^{+}] - [Al(OH)_4^{-}]$$

$$- [HCO_3^{-}] - 2[CO_3^{2-}] \quad - [HA^{-}] - 2[A^{2-}] - 3[A^{3-}] \quad = \quad 0.0$$

Charge balance alkalinity

$$CALK = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] + [NH_4^{+}] - [Cl^{-}] - [NO_3^{-}] - 2[SO_4^{2-}]$$

Rearranging

$$CALK = [HCO_3^{-}] + 2[CO_3^{2-}] \quad + [HA^{-}] + 2[A^{2-}] + 3[A^{3-}] \quad + [OH^{-}] - [H^{+}]$$

$$- 3[Al^{3+}] - 2[Al(OH)^{2+}] - [Al(OH)_2^{+}] + [Al(OH)_4^{-}]$$

$$CALK = f(pH, pK's, P_{CO2}) + f(pH, pK's, sd, DOC) + f(pH, pK's, K_{Al})$$

$$+ f(pH, K_w)$$

Inorganic carbon reactions:

$$CO_2(g) + H_2O = H_2CO_3^{*}$$

$$H_2CO_3^{*} = H^{+} + HCO_3^{-}$$

$$HCO_3^{-} = H^{+} + CO_3^{2-}$$

Equilibrium expressions:

$$\frac{\{H_2CO_3^{*}\}}{P_{CO2}} = K_1 \qquad \frac{\{HCO_3^{-}\}\{H^{+}\}}{\{H_2CO_3^{*}\}} = K_2$$

$$\frac{\{CO_3^{2-}\}\{H^{+}\}}{\{HCO_3^{-}\}} = K_3$$

Aluminum reactions:

$$3H^+ + Al(OH)_3\ (s) = Al^{3+} + 3H_20$$

$$Al^{3+} + H_20 = Al(OH)^{2+} + H^+$$

$$Al^{3+} + 2H_2O = Al(OH)_2{}^+ + 2H^+$$

$$Al^{3+} + 3H_2O = Al(OH)_3{}^\circ + 3H^+$$

$$Al^{3+} + 4H_2O = Al(OH)_4{}^- + 4H^+$$

Equilibrium expressions:

$$\frac{\{Al^{3+}\}}{\{H^+\}^3} = K_{Al}$$

$$\frac{\{Al(OH)^{2+}\}\{H^+\}}{\{Al^{3+}\}} = K_1 \qquad \frac{\{Al(OH)_2{}^+\}\{H^+\}^2}{\{Al^{3+}\}} = K_2$$

$$\frac{\{Al(OH)_3{}^0\}\{H^+\}^3}{\{Al^{3+}\}} = K_3 \qquad \frac{\{Al(OH)_4{}^-\}\{H^+\}^4}{\{Al^{3+}\}} = K_4$$

Total aluminum:

$$Al_{tot} = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2{}^+] + [Al(OH)_3{}^0] + [Al(OH)_4{}^-]$$

Rearranging:

$$Al_{tot} = K_{Al}*[H+]^3 + K_1*K_{Al}*[H+]^2 + K_2*K_{Al}*[H+] + K_3K_{Al} + K_4*K_{Al}/[H+]$$

$$Al_{tot} = K_{Al} * ([H+]^3 + K_1*[H+]^2 + K_2*[H+] + K_3 + K_4/[H+])$$

Net charge on aluminum:

$$Al_{chg} = K_{Al} * (3*[H+]^3 + 2*K_1*[H+]^2 + K_2*[H+] - K_4/[H+])$$

$$Al_{chg} = f(pH, pK's, K_{Al})$$

Net charge on inorganic carbon:

$$DIC_{chg} = P_{CO2} * (K_2*K_1/[H^+] + 2*K_3*K_2*K_1/[H^+]^2)$$

$$DIC_{chg} = f(pH, pK's, P_{CO2})$$

Triprotic acid reactions:

$H_3A = H^+ + H_2A^-$

$H_2A^- = H^+ + HA^{2-}$

$HA^{2-} = H^+ + A^{3-}$

$$\frac{\{H_2A^-\}\{H^+\}}{\{H_3A\}} = K_1 \qquad \frac{\{HA^{2-}\}\{H^+\}}{\{H_2A^-\}} = K_2$$

$$\frac{\{A^{3-}\}\{H^+\}}{\{HA^{2-}\}} = K_3$$

Diprotic acid reactions:

$H_2A = H^+ + HA^-$

$HA^- = H^+ + A^{2-}$

$$\frac{\{HA^-\}\{H^+\}}{\{H_2A\}} = K_1 \qquad \frac{\{A^{2-}\}\{H^+\}}{\{HA^-\}} = K_2$$

Monoprotic acid reactions:

$HA = H^+ + A^-$

$$\frac{\{A^-\}\{H^+\}}{\{HA\}} = K_1$$

Oliver acid reactions:

$HA = H^+ + A^-$

$$\frac{\{A^-\}\{H^+\}}{\{HA\}} = K_1$$

$$pK = a + b(pH) + c(pH)^2$$

Total inorganic carbon:

$$\mathrm{DIC} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{2-}]$$

Rearranging:

$$\mathrm{DIC} = K_1 * P_{CO2} + K_2 * K_1 * P_{CO2}/[H^+] + K_3 * K_2 * K_1 * P_{CO2}/[H^+]^2$$

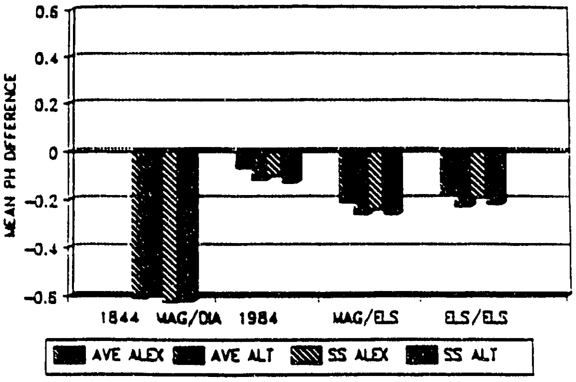
$$\mathrm{DIC} = P_{CO2} * (K_1 + K_2 * K_1/[H^+] + K_3 * K_2 * K_1/[H^+]^2)$$

Results of the principal recomparisons between the MAGIC and diatom models are presented as a series of histograms in Figures 13 and 14 and scatter plots in Figures 15 through 18.

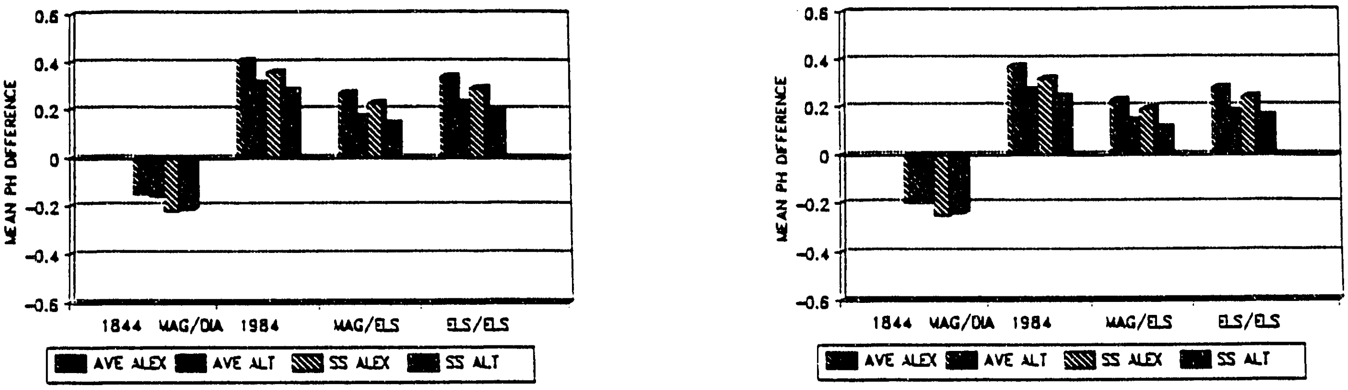
The mean difference in pH model output between the MAGIC and diatom models is presented in Figure 13. Histograms A through E in the figure depict results for no organic acid, and each of the four organic acid models, respectively. Each of the four bars in each group represents a different pairwise comparison based on extractable (ALEX) or total (ALT) aluminum, and site-specific (SS) or regional average (AVE) values for P_{CO_2} and K_{Al}. The four groups of bars represent the four major kinds of pairwise comparisons:

1. 1844 hindcasts for the MAGIC and diatom models
2. 1984 current estimates for the MAGIC and diatom models
3. 1984 estimates for MAGIC and measured ELS values
4. 1984 predicted ELS pH (calculated from measured alkalinity as Gran ANC) and measured ELS pH

Figure 13 shows that there is a large difference in pH between the MAGIC and diatom models for 1844 hindcasts of pH where no organic acid is used (as per Sullivan et al. 1991). The mean pH difference without considering organic acids was approximately 0.6 pH units (Figure 13A). Once

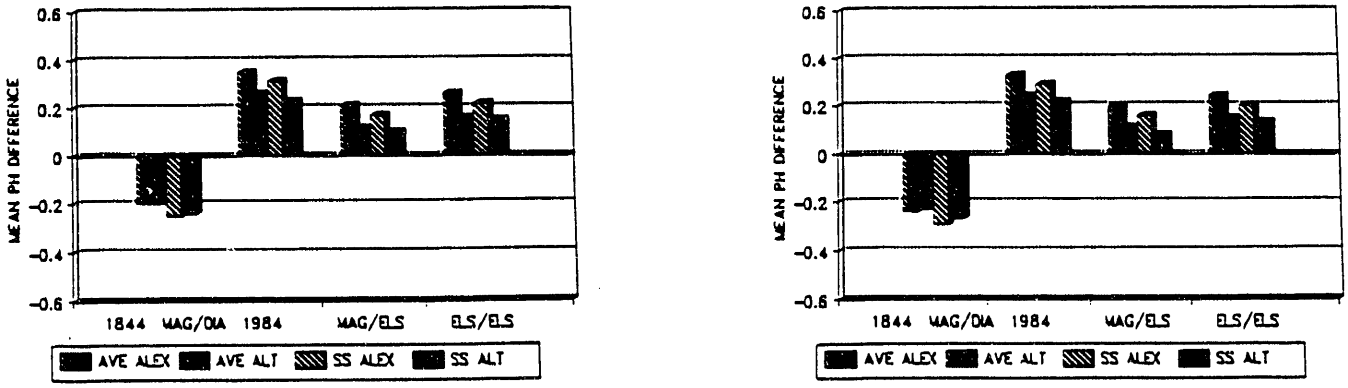


A) NO ACID



B) MONOPROTIC ACID
USING ALSC MODEL PARAMETERS

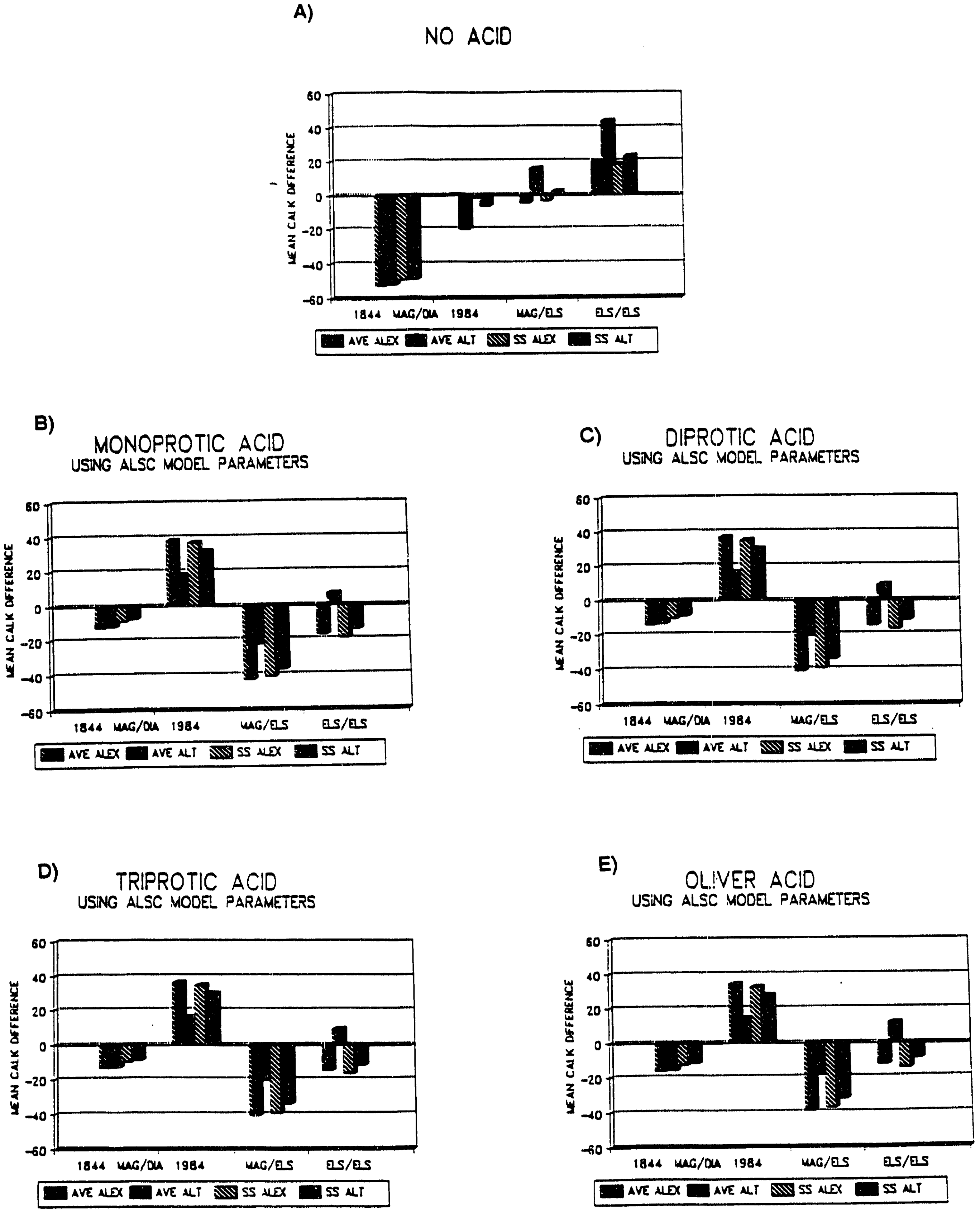
C) DIPROTIC ACID
USING ALSC MODEL PARAMETERS



D) TRIPROTIC ACID
USING ALSC MODEL PARAMETERS

E) OLIVER ACID
USING ALSC MODEL PARAMETERS

Figure 13. Histograms showing the mean value of the differences between various simulations or measurements of pH for 33 Adirondack lakes. Each of the four bars in a group represents one of the four conditions regarding choice of aluminum input variable and site-specific (SS) or regional average P_{CO_2} and K_{Al} (see text). Each group of bars represents a different pairwise comparison, and includes (from left to right): 1844 hindcasts of MAGIC versus diatoms, 1984 reconstructions of MAGIC versus diatoms, 1984 reconstructions of MAGIC versus ELS measured values, and 1984 ELS measured values versus predicted values from the equilibrium equations. The five sets of histograms were based on A) no organic acid representation and B through E, mono-, di-, triprotic, and Oliver, respectively.



A) NO ACID

B) MONOPROTIC ACID
USING ALSC MODEL PARAMETERS

C) DIPROTIC ACID
USING ALSC MODEL PARAMETERS

D) TRIPROTIC ACID
USING ALSC MODEL PARAMETERS

E) OLIVER ACID
USING ALSC MODEL PARAMETERS

Figure 14. Histograms for calculated alkalinity (CALK) comparisons, as described for pH in Figure 13.

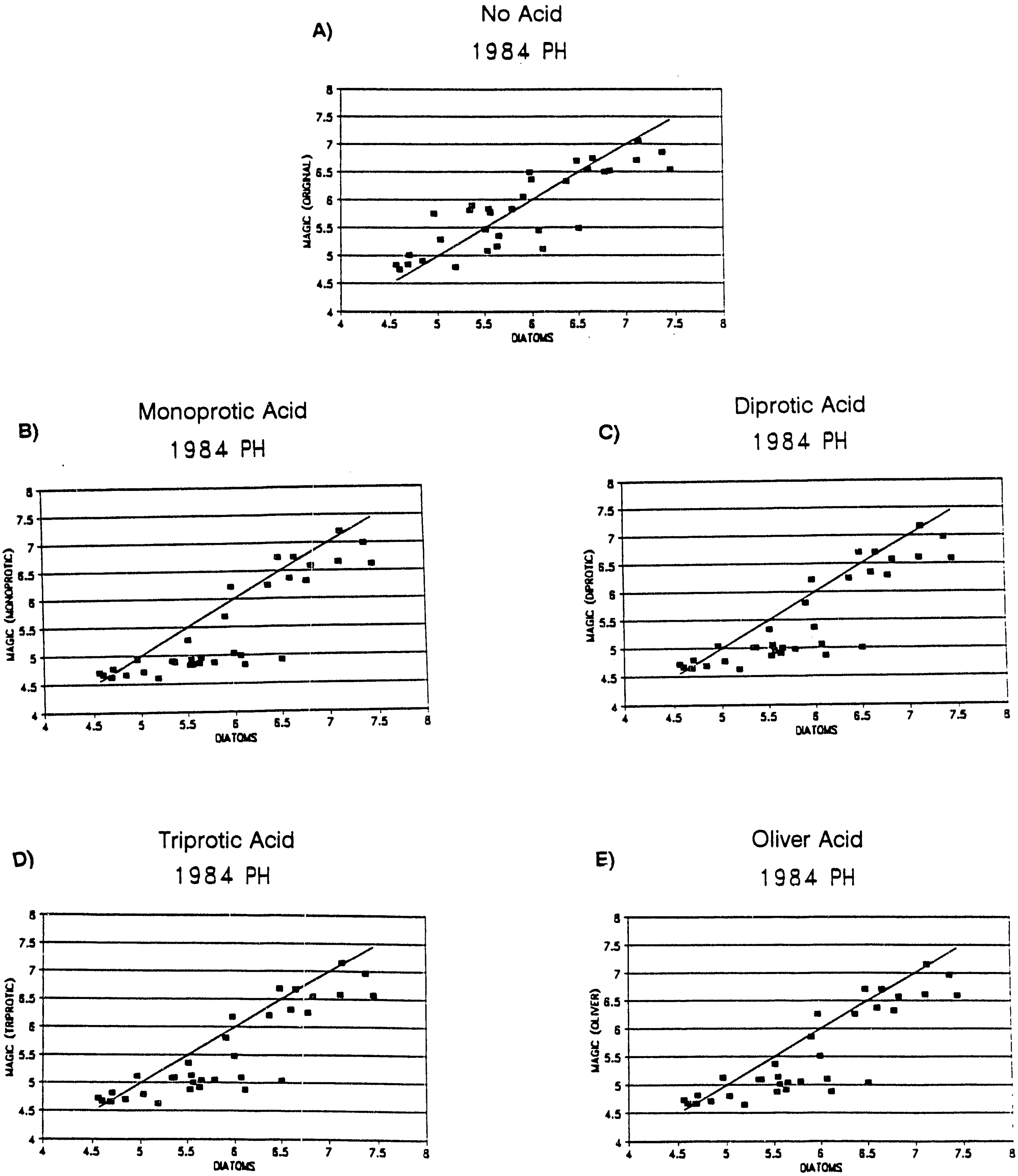


Figure 15. MAGIC estimates of 1984 pH versus diatom-inferred 1984 pH for 33 Adirondack lakes. MAGIC estimates included A) no organic acid, and B through E monoprotic acid through the Oliver models. All model estimates were based on extractable aluminum and regional average values for P_{CO_2} and K_{Al}.

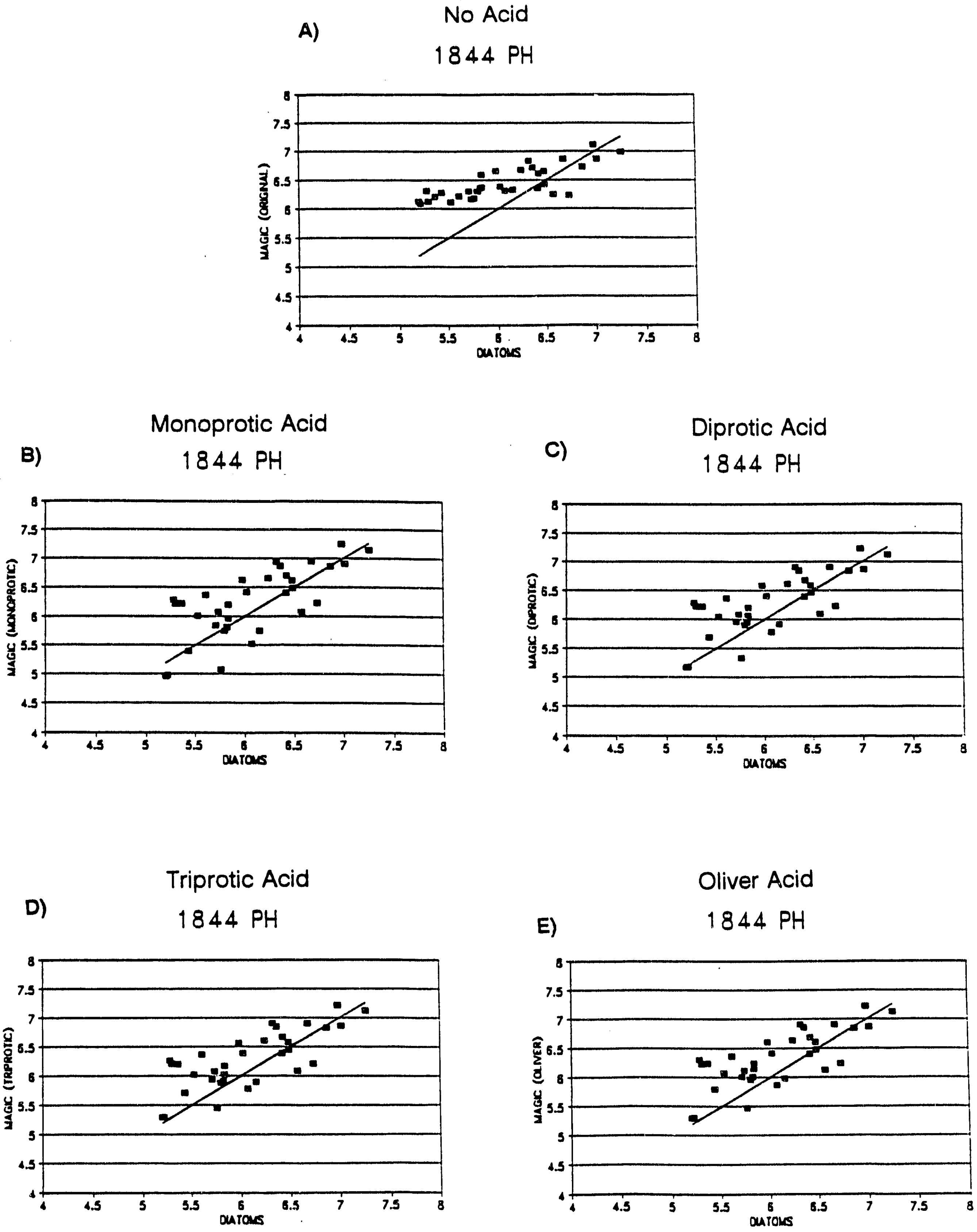


Figure 16. MAGIC estimates of 1844 pH versus diatom-inferred 1844 pH for 33 Adirondack lakes. MAGIC estimates included A) no organic acid, and B through E monoprotic acid through the Oliver models. All model estimates were based on extractable aluminum and regional average values for P_{CO_2} and K_{Al}.

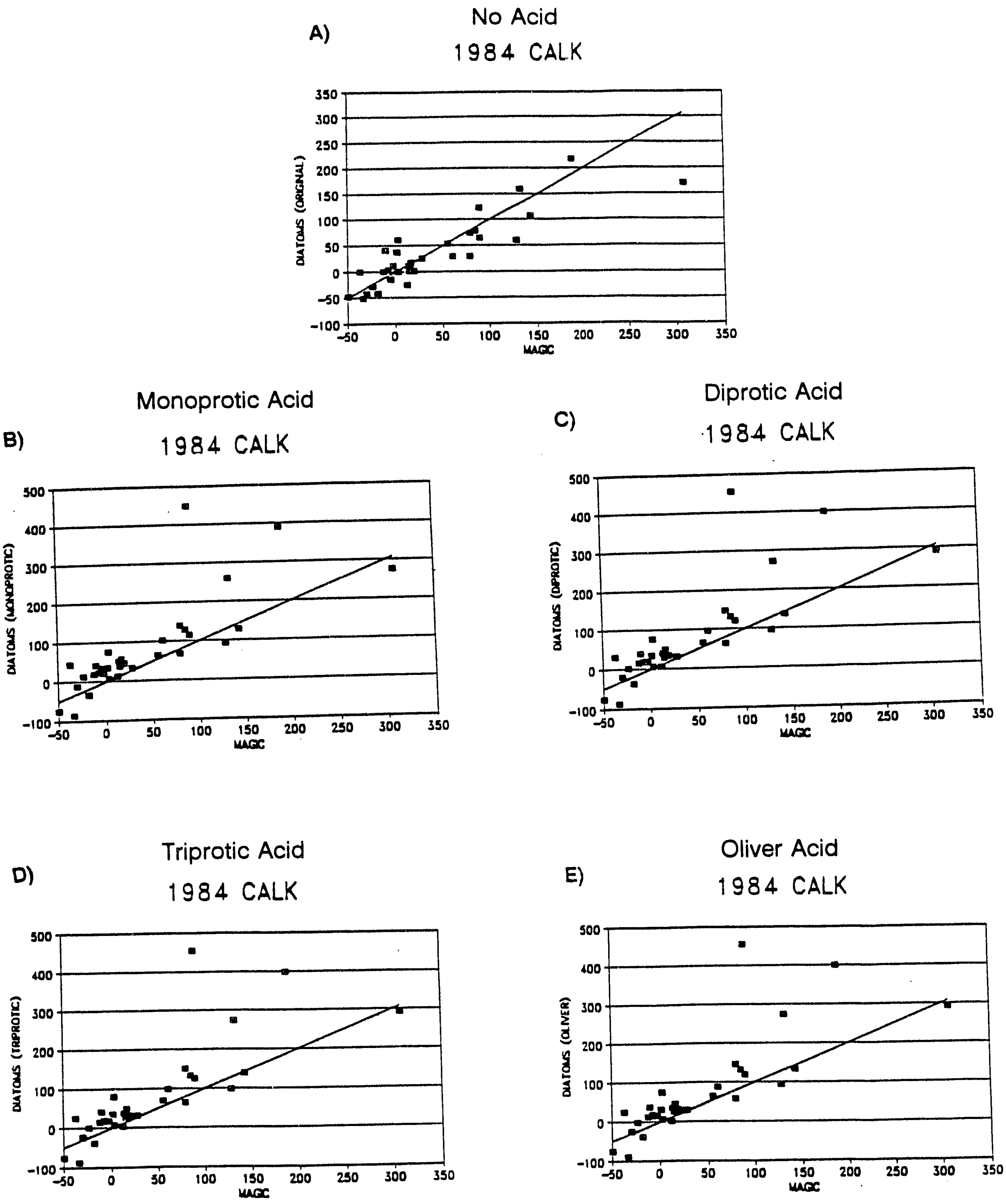


Figure 17. MAGIC estimates of 1984 calculated alkalinity (CALK) versus diatom-inferred 1984 CALK for 33 Adirondack lakes. MAGIC estimates included A) no organic acid, and B through E monoprotic acid through the Oliver models. All model estimates were based on extractable aluminum and regional average values for P_{CO_2} and K_{Al}. Diatom-inferred CALK values were calculated from diatom-inferred pH and the equilibrium expression for pH, CALK, P_{CO_2}, K_{Al}, site density, pK values, and DOC.

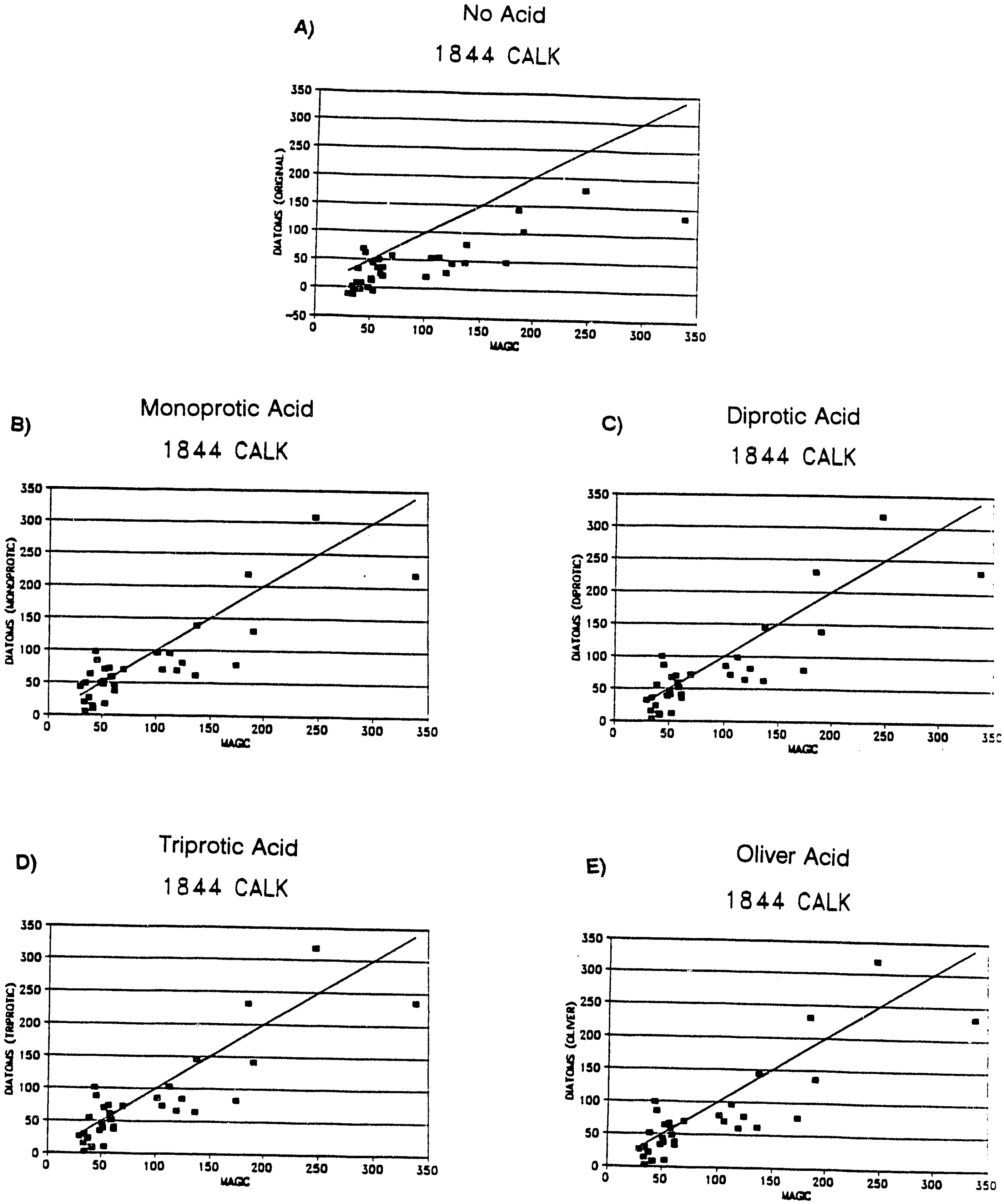


Figure 18. MAGIC estimates of 1844 calculated alkalinity (CALK) versus diatom-inferred 1844 CALK for 33 Adirondack lakes. MAGIC estimates included A) no organic acid, and B through E monoprotic acid through the Oliver models. All model estimates were performed as described for Figure 17.

organic acids were included in the analysis, the mean pH difference was substantially lower (0.2 to 0.3 pH units, Figure 13 B,C,D,E). The mean pH difference was not much affected by the choice of organic acid representation; all four organic acid models yielded generally similar results. The mean pH difference was also not much affected by the choice of aluminum measurement (ALEX versus ALT) or site-specific versus regional average values for P_{CO_2} and K_{Al}. The only dramatic effect on the 1844 hindcast results was obtained merely by including *any* reasonable organic acid representation. It should also be noted that inclusion of the various organic acid models increased the mean pH difference between the MAGIC and diatom estimates of 1984 pH. In other words, inclusion of organics worsened the agreement between the models for current pH. This is due, at least in part, to the fact that the MAGIC model was not recalibrated to the new data. The calculations are based on model calibrations that did not include organics. The degree to which the current chemistry estimates will be improved by further calibration is now under investigation and will be reported in the Annual Technical Report to be completed by March, 1993.

The histograms depicted in Figure 14 show results for calculated alkalinity (CALK) in a similar fashion to the pH presentation in the previous figure. Again, the results indicate that the MAGIC and diatom models give very different 1844 hindcast results (average CALK difference of about 50 μeq L^{-1}) when no organic acid model is used, and much closer agreement (average CALK difference of about 10 to 20 μeq L^{-1}) when any of the four organic models are included. Agreement between models is again worsened for current chemistry estimates, in the absence of further calibration. Agreement is generally somewhat better using regional average values of ALT, as compared with the other options (Figure 14 B,C,D,E).

Individual pH reconstructions for the 33 Adirondack lakes are compared for pre-industrial and current conditions in Figures 15 and 16, respectively. Similarly, alkalinity comparisons for pre-industrial and current conditions are shown in Figures 17 and 18 respectively. For these analyses, regional average values were used for P_{CO_2} and K_{Al}, and ALEX was used as the aluminum input data. The major biases observed between the MAGIC and diatom pre-industrial reconstructions were removed by inclusion of any of the four organic acid models (Figures 15 and 17), although the current chemistry estimates for pH and alkalinity were made worse by the inclusion of organics, *in the absence of further calibration* (Figures 16 and 18). This was partially attributable to a few outlier lakes, especially for the alkalinity comparisons (Figure 18).

c. Preliminary Conclusions and Continuing Work

Important conclusions from the model scenarios and sensitivity analyses are 1) that "reasonable" organic acid representations can account for much of the discrepancy observed earlier between MAGIC and diatom pre-industrial reconstructions, and 2) that from a practical modeling standpoint, the major problems do not lie with the exact organic acid formulation or the exact Al representation utilized. This is particularly true for regional comparisons. Once organic acids are included in a reasonable way in the analyses, additional critical questions lie elsewhere. Inclusion of organic acids in the MAGIC model formulations, however, necessitates additional calibration of the current chemistry data. This is because the earlier calibrations did not include the pH buffering of organic acids. Additional calibration is on-going and will be discussed in the Annual Technical Report to be prepared at the end of Year 1 of the project.

3. Site Visits

During Year 1, Dr. Sullivan conducted a site visit to the two on-going, large watershed manipulation projects. The Maine site is funded by EPA and involves whole-catchment acidification and monitoring of streamwater chemistry. The Norwegian site is operated by the Norwegian Institute for Water Research (NIVA), and involves experimental acidification of one-half of a small lake and its catchment. Drs. Cosby and Charles also visited the Maine site.

4. Planned Journal Articles and Annual Report

Our current schedule for major project deliverables is presented in Table 5. There are currently three manuscripts being prepared for submission to the peer-reviewed scientific literature within this project. The first two papers will be authored by Driscoll et al., and will present the acid/base characteristics of the DOC in Adirondack lakes and describe the organic acid modeling approaches derived on the basis of the ALSC data. Target journals have not yet been selected. The third manuscript will be submitted as a letter to *Nature* by Cosby et al., and will present the major conclusions regarding the consistencies between the MAGIC, diatom, and organic acid models. A tentative title is "Long-term environmental change: Intercomparisons among paleolimnological, organic acid, and process-based models of acidification response." This manuscript will present the major conclusions of the first year of this project. All journal

Table 5. Schedule of major project deliverables.

Deliverable	Principal Author(s)	Date
Workshop summary	Sullivan/Eilers	6/15/92
Organic acid modeling approach manuscript	Driscoll	10/31/92
MAGIC/Paleo comparison manuscript	Cosby/Charles	12/31/92
Annual Report	Sullivan	2/15/93
Financial Report	Sullivan	3/15/93
WMP comparison manuscript	Cosby/Norton	9/30/93
HUMEX comparison manuscript	Sullivan/Cosby	12/31/93
Final Report	Sullivan	3/31/94

articles are scheduled to be drafted this fall. An Annual Technical Report will also be prepared by Sullivan et al. and will be submitted at the end of Year 1. It will include all information contained in the journal articles, and will also present the extensive details of the modeling efforts and sensitivity analyses. Much of this information is not appropriate for the peer-reviewed literature, but will provide important documentation of the approach and the results of the various scenarios and analyses.

The Annual Technical Report will be submitted for external peer review to four independent scientists. The following scientists have tentatively agreed to review the report:

Dr. R. Turner, Oak Ridge National Laboratory, Oak Ridge, TN
Dr. P. Wigington, U.S. EPA, Corvallis, OR
Dr. D. Porcella, Electric Power Research Institute, Palo Alto, CA
Dr. E. Krug, Winona, MN

The manuscripts prepared for this project will receive reviews in conjunction with normal scientific journal procedures and will also be reviewed by Dr. Krug.

C. COMPLIANCE WITH AGREEMENT REQUIREMENTS

The current project is proceeding on schedule and within budget. No major changes to the scope of work have been made thus far, or are proposed for the remainder of the project. The principal investigator and members of the project team are in compliance with all requirements of the agreement with DOE.

D. PRINCIPAL INVESTIGATOR LEVEL OF EFFORT

During the first six months of this project, the Principal Investigator, Dr. Timothy Sullivan, has spent slightly over 3 person months on the project. It is anticipated that Dr. Sullivan will spend an additional 1.5 to 2.0 person months on the project during the remainder of Year 1. This level of effort is in accordance with the level of effort originally proposed.

The level of effort to be spent on the project by Dr. Sullivan during Year 2 is proposed as 6.2 person months. This time commitment will be spent primarily for the preparation of two journal articles, to be submitted to the peer-reviewed scientific literature, and the final report to DOE.

E. PLANS FOR THE CONDUCT OF THE PROJECT DURING YEAR 2

The schedule of activities conducted within the project has not changed since the initial proposal. The originally proposed activities for Year 1 will be completed by the end of the current budget period (March 15, 1993). Year 2 activities will proceed as proposed.

The revised MAGIC model will be applied to the Bear Brook watershed in Maine, which has been included in EPA's Watershed Manipulation Project (WMP). Model simulations will be conducted by calibrating the model to the west Bear catchment, using pre-manipulation data. Ammonium sulfate has been applied (six applications per year) by helicopter to this catchment since November, 1989. The total artificial loading of 1,320 kg of $(NH_4)_2SO_4$ per year quadruples the annual flux of atmospheric SO_4^{2-} to the watershed. Model projections will be conducted by Dr. B.J. Cosby, principal developer of the MAGIC model, in cooperation with Dr. S. Norton, the principal site investigator for the WMP. Model projections of the manipulation results will be compared with measured weekly stream chemistry at the site to determine the accuracy of the MAGIC model projections. This modeling effort will be augmented with additional modeling work using the Birkenes model. The latter modeling effort will be conducted at the University of Oslo, and will permit shorter time-step modeling which will allow investigation of episodic effects related to organic acid enrichment, nitrate enrichment, and base cation dilution.

During Year 2, the project team will also carry out modeling work at the Humic Lake Acidification Experiment (HUMEX) in Norway. Lake Skjervatjern was divided in half in 1988 by a plastic curtain. Artificial acid precipitation is being applied via sprinklers (mounted on trees) to half of the lake and its respective drainage basin. The other half serves as a control. Loadings of H^+, SO_4^{2-}, NO_3^-, and NH_4^+ are similar to those received in the highly impacted areas of southernmost Norway. Model projections, using MAGIC, of the response of Lake Skjervatjern to the artificial acidification will be conducted by Drs. Cosby and Sullivan in Oslo, in cooperation with the HUMEX project Principal Investigator, Dr. Egil Gjessing (NIVA).

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Foreign Trip Report

for Travel to Norway June 29-July 7, 1992

Timothy J. Sullivan

E&S Environmental Chemistry, Inc.
P.O. Box 609
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July, 1992

Prepared for

The U.S. Department of Energy

Grant No. DE-FG02-92ER30196.A000

Foreign Trip Report

Subject:	Report of foreign travel by Timothy J. Sullivan E&S Environmental Chemistry, Inc., P.O. Box 609, Corvallis, OR 97339
Date:	July 10, 1992
Submitted to:	James R. Bieschke, Branch Chief Contracting Officer
Submitted by:	Timothy J. Sullivan

Places Visited:

June 30, 1992	Oslo, Norway
July 1-4	Jølster, Norway
July 4-5	Gårdsjön, Sweden
July 6	Oslo, Norway

Participants in Attendance at the Workshop:

Albretsen, Anne-Louise	Norway	Lien, Leif	Norway
Bangsund, Anne Grete	Norway	Lindstrøm, Eli-Anne	Norway
Brandrud, Tor Erik	Norway	Lynch, Lavia	U.S.A.
Brettum, Pål	Norway	Malcolm, Ronald	U.S.A.
Clair, Tom	Canada	Morgan, Mark	U.S.A.
David, Mark	U.S.A.	Munster, Uwe	Denmark
Gjessing, Egil	Norway	Myklebust	Norway
Gray, Dennis	U.S.A.	Norrstrøm, Ann-Catrin	Sweden
Hargeby, Anders	Sweden	Petersen, Robert	Sweden
Hayes, Michael	U.K.	Rennekleiv, Sissel B.	Norway
Hessen, Dag	Norway	Riise, Gunnhild	Norway
Holsen, Tor	Norway	Schlaepfer, Martin	Switzerland
Johansen, Stein W.	Norway	Salonen, Kalevi	Finland
Johansson, Jan	Sweden	Shaw, Peter	U.K.
Kjørstad, Ole Jakob	Norway	Skopal, Vitek	Norway
Knulst, Johan	Sweden	Stolhandske, Pia	Sweden
Kortelainen, Pirkko	Finland	Sullivan, Tim	U.S.A.
Kramer, James	Canada	Svensson, Marie	Sweden
Kramer, Miriam	Canada	Vähätalo, Anssi	Finland
Kullberg, Anders	Sweden	Vogt, Rolf	Norway

Background and Purpose:

The purpose of this trip to Norway was to attend the summer seminar held by the Norwegian Institute for Water Research (NIVA) in conjunction with the whole-catchment artificial acidification experiment on-going at Lake Skjervatjern in western Norway. The Humic Lake Acidification Experiment (HUMEX) was begun in 1988 by separating Lake Skjervatjern into two basins by means of a plastic curtain installed from the middle of the natural outlet to the opposite shore. Lake water chemistry has been monitored weekly since October 1988. Artificial acidification with sulfuric acid and ammonium nitrate was begun two years after installation of the curtain. Acids are applied to the treatment half of the lake, and its drainage basin, during periods of precipitation by means of a sprinkler system. The target loadings for sulfate and total nitrogen are 6.3-6.6 g/m^2 and 1.7-3.2 g/m^2, respectively.

The data being collected by the HUMEX project will be used by members of the DOE project team for MAGIC model validation. Drs. Cosby and Sullivan will conduct MAGIC model simulations of the responses of Lake Skjervatjern to the artificial acidification during 1993. Model simulations will be compared with measured results of the lake response to the manipulation.

The study of Lake Skjervatjern currently involves more than two dozen scientists from nine countries. Many detailed process-level studies are on-going in conjunction with the catchment manipulation. This international cooperation is conducted under the HUMOR project, also initiated by NIVA. The major questions being addressed by HUMOR/HUMEX are:

> What role do humic substances in soil and water play for problems related to the effects of acid rain on surface waters?
>
> What is the influence of acid rain on the chemical and biological properties of humic substances?

While in Scandinavia, a short trip was made to the Gårdsjön catchment manipulation site in Sweden, July 4-5, 1992. Although data collected from Hans Hultberg at Gårdsjön will be helpful in conjunction with the current DOE project, travel expenses to Sweden were covered by a project with the National Acid Precipitation Assessment Program (NAPAP) to summarize on-going nitrogen research in Europe.

Site Visit

The purpose of the seminar was to share preliminary results among the various research groups working at Lake Skjervatjern. Many field studies were being conducted in conjunction with the meeting, and part of the time was spent touring and investigating the catchment. I spent several hours walking around the site with Mark David (University of Illinois) and Pirko Kortelainen (National Board of Water and the Environment, Finland), both of whom are involved in organic acid characterization at the site. Skjervatjern seems to be a very good choice for this type of humic lake and catchment manipulation. Human disturbance is minimal, although access is good. Lake water from a near-by lake is pumped to a large network of sprinklers that have been installed throughout the treatment side of the catchment. The irrigation water is acidified by addition of H_2SO_4 and NH_4NO_3, and sprayed on the system during precipitation events. Acidified precipitation is applied to both the lake surface and the terrestrial basin of the treatment side of the catchment.

The 6.5 ha catchment is comprised of two sub-basins, 1.8 ha and 4.7 ha in area. The former serves as the treatment side and the latter the control or reference side. Vegetation, topography, and soils are generally similar on the two sides. The site is forested primarily with Scotts pine, with a well-developed understory of *Vaccinium* and other small shrubs. A *Sphagnum* bog area occurs on each side and there are also several small fens dominated by *Sphagnum* moss. Water flow is more pronounced through the fens, whereas water appears to be more stagnant in the bogs. Bog and fen areas are *slightly* more developed on the reference side than on the control side. This difference is also reflected in a slightly lower pH and slightly higher dissolved organic carbon (DOC) on the reference side (Table 1).

Table 1. Selected annual mean water chemistry parameters of Lake Skjervatjern two years before and one year after initiaiton of the whole-catchment acidification experiment.

	Treatment Side			Control Side		
Parameter	Year 1	2	3	Year 1	2	3
pH	4.60	4.59	4.63	4.57	4.55	4.63
TOC (mg/L)	6.4	5.0	6.2	7.2	5.7	7.0
SO_4^{2-} (mg/L)	1.2	1.3	1.5	1.3	1.4	1.1
NO_3^- (μg N/L)	6	10	33	8	13	10
NH_4^+ (μg N/L)	18	14	31	19	14	16
Al_o (μg/L)	42	31	50	52	39	65
Al_i (μg/L)	31	29	24	37	33	21

Hydrology appears to be very complex throughout the basins. Bob Petersen (Sweden) has identified a number of hydraulic vents (now being called "Petersen vents" by a number of the project participants). These vents are hydraulic openings through the side of the *Sphagnum* that forms the lake/shoreline interface. They appear to provide most of the water flow from the terrestrial basins into the lake. They can be identified on the basis of temperature, water flow, and chemistry. Vent water is anoxic, strongly reducing, low in pH (~ 4.0), and high in DOC (~ 20-25 mg/L). At the vent/lakewater interface, redox conditions change abruptly and the water becomes oxygenated very quickly. Petersen has concluded that these vents drain portions of the basins in a dendritic pattern. They occur beneath the small depressions in the topography. In a few places, underground running water can be heard in the fen areas; in one place we could actually see a small underground stream about 30 cm down through a hole in the *Sphagnum*.

The vent water pH is about 0.3 units lower than the pH measured in any of the 30 soil lysimeters that have been previously installed. Rolf Vogt (University of Oslo) was in the process of installing 130 additional lysimeters throughout the site, however, and we discussed with him the installation of some of these just above the bedrock in the fens. These areas might be extremely important in controlling the chemistry of drainage water that flows through the hydraulic vents into the lake. It is possible that soil chemistry throughout the upland areas has relatively little effect on the chemistry of drainage water. This possibility may make our modeling efforts quite difficult.

Overall, I was very impressed with the quality of the work being done at the site. The site is well-chosen. The installations have been done carefully and thoroughly. It is quite obvious that NIVA personnel have done this sort of thing before (i.e. Sogndal, Risdalsheia). The field personnel are all extremely competent. I have little doubt that this project will provide an excellent data set for the assessment of the interactions between acidic deposition and organic materials.

Seminar Presentations

A total of 18 scientists from about seven different countries presented some preliminary results from their various studies at Skjervatjern. The focus was more biological than chemical. Although much high-quality work is being conducted, research is sorely needed on hydrology. Some additional efforts on especially soil chemistry, and also water chemistry, would be desirable. Egil Gjessing told me that Gunnar Jacks will be conducting some hydrological studies, but the scope of these studies is not clear.

Petersen (University of Lund, Sweden) reported on his efforts at thermal and hydraulic mapping of the littoral zone and vent water chemistry. Initially they had thought that most water enters the lake by diffuse permeation since there are no stream inlets (there is an outlet). However, this does not seem to be the case; the organic materials along the shoreline appear to be highly impermeable. The hydraulic head from the catchment has generated cannuli that end in holes. Petersen has identified 71 of these holes, or vents, although some of them may be blind. The vent water is generally 2-4° C colder than the littoral water. DOC is much higher in the vents (20-25 mg/L) than in the littoral water (~ 6 mg/L). Variations in water chemistry throughout the littoral zone are very large. Some areas are sphagnum-dominated and some podzolic soil-dominated. Microbial respiration is about twice as high in the vents as the littoral zone; there is probably much faster turn-over of detritis in the vents.

Uwe Munster, Max Plank Institute, Sweden, reported on initiation of a study on microbial enzyme activity in lakewater. A possible problem in interpreting the results of this project is that the treatment side of the lake is somewhat more organic in nature and the control side is more mineral. Although the differences are small, concern was raised that the treatment may serve mainly to "make the manipulated side more like the control side!"

Leif Lien reported on fish experiments which have just begun. There were previously stocked brown trout in Lake Skjervatjern prior to this study. They were removed by intensive fishing prior to separation of the lake. Lien did not want to introduce fish directly into the lake, so as not to compromise on-going plankton studies. (Even when kept in enclosures, some fish always seem to escape). He has set up fish exposure tanks, into which lakewater from the two sides of the lake is pumped. Three different strains of brown trout are being studied - 10 fish of each strain in each side. Mortality curves to date show fish are dying at about the same rate on both sides. Blood plasma chloride levels are slightly lower so far on the treated side.

Benthic green algae are being studied by Eli-Anne Lindstrøm. A procedure is being used that involves setting out small clay flower pots upside down on the lake bottom at depths of 0.5 and 2 m. These are used to measure benthic algal primary production and respiration.

Ron Malcolm (USGS, Denver) has fractionated and isolated organic solutes in the water from each side of the lake in 1990 (pre-treatment) and 1991 (post-treatment). The technique employs both XAD-4 and XAD-8 columns and fractionates the DOC into humic acids, fulvic acids, hydrophobic neutrals, and hydrophyllics. About 85% of the DOC is recovered, and the various fractions are characterized by nuclear magnetic resonance (NMR). The DOC composition was essentially the same on both sides in 1990. Malcolm believes that there has been a dramatic effect from the acid treatment on the ratio of hydrophobic to hydrophyllic organic substances and also a change in the chemical composition of the humic acids. The limitation with the approach is that it is based on only two samples from each side, thus precluding a statistical evaluation. (Note: it is very expensive to analyze these samples and additional studies seem unlikely.)

On-going studies on phytoplankton, macrophytes, and characterization of the lake surface microlayer were reported by Pål Brettum, Tor Brandrud, and Johan Knulst, respectively. Preliminary results from these studies thus far suggest the following:

- Primary production of phytoplankton may be decreasing in the treatment half.
- Some changes are occurring in phytoplankton species abundances.
- *Sphagnum ariculatum* (submerged mats) are growing more rapidly in the control side.
- The chemical composition of the surface microlayer has been altered. This may influence the transport of heavy metals and organic pollutants from the atmosphere to the lake.

Mark Morgan (Rutgers University) is studying changes in sulfur pools at Skjervatjern using sulfur isotope ratios. He is focussing on a large bog area and two smaller fens (through which drainage water is flowing). He has found a clear and tight relationship between the C:S ratio and the total sulfur concentration. As sulfur is added to the site it is being incorporated into the peat by dissimilatory processes (i.e., peat is not living and cannot therefore assimilate S). Sulfur is being accumulated primarily in the large fen, followed by the smaller fen, and then the bog. Sulfur is incorporated mostly at the bottom of the fen (where water flows) and at the top of the bog (which has little flow). Morgan interprets these data as a reflection of the great importance of hydrology for processing sulfur at this site.

Rolf Vogt (University of Oslo) described his on-going studies of soils and soil solution chemistry. The catchment is comprised of granitic bedrock, covered by histosols in the lower portions and podzols on thin glacial till in the upper portions. Bogs and fens are common in the lower portions. Scotts pine and *Vaccinium* predominate in the uplands. In the summer of 1990, 30 ceramic cup lysimeters were installed throughout the catchment. An additional 130 lysimeters were installed during the week of the conference. The initial 30 lysimeters were sampled on 11 occasions between August 1990 and August 1991. Soil solution is generally highly organic and heavily seasalt influenced, with moderate amounts of organically-bound aluminum (Al_o).

Site-specific and temporal variability was high among the soil solution samples. The data suggest, however, small decreases in DOC and Al_o in the surface layers of the histosols in response to the acid additions, and a slight increase in DOC in the lower (Bg and Bhs) mineral soil horizons. Sulfate concentrations increased in four of ten soil horizons, including the surface of the histosols, subsequent to the initiation of acid additions. Nitrate concentrations remained unchanged.

Jim Kramer (McMaster University, Canada) presented his analyses of organic acid titration data. Lakewater exhibited a large peak in pK distribution at about 4.4. This is also the approximate pH of lakewater, illustrating the strong pH buffering of organic acids in this system.

Egil Gjessing discussed NIVA's weekly water chemistry data. The treatment side of the catchment receives a mixture of H_2SO_4 and NH_4NO_3. From May 1991 to May 1992 the area received 2200 mm of precipitation, slightly more than the long term average of about 2 m. Lake sulfate concentration has increased by about 17 μeq/L during the 1 1/2 years of treatment. This increase is somewhat more than the amount of sulfate applied directly to the lake surface. Thus, although most of the sulfur applied to the catchment is taken up by the terrestrial system, some gets into the lakewater. Ammonium and nitrate are also increasing, but by less than the amount sprinkled directly on the lake surface. Lakewater DOC is highly variable and has not shown a statistically significant change with the treatment. The anion deficit is decreasing in the treated side. The loading to the entire area has been:

6.32 g/m^2 H_2SO_4

4.97 g/m^2 NO_3

Presentations were made by Tom Claire (Canada), Michael Hays (U.K.), and Peter Shaw (U.K.) on pH/ANC empirical modeling, NMR spectra of the humic and fulvic acids, and Fe/PO_4 interactions, respectively. Thereafter, Pirkko Kortelaninen (Finland) presented her work with Mark David (University of Illinois) on the acid-base characteristics of the DOC in Lake Skjervatjern. They noted some discrepancies in the internal consistency of the chemical data set. Specifically, a cation deficit ($\sim$ 10 μg/L) was observed for several low-DOC, high-chloride samples. We discussed some avenues to pursue to investigate this potential problem. Egil Gjessing will follow up on it.

Egil announced that the annual HUMEX meeting next year will be held in conjunction with the Nordic meeting of the International Humic Substances Society (IHSS). It will be held June 7-9, 1993 at Loen in western Norway.

Birkenes Modeling

After returning to Oslo, I met with Geir Taugbøl and Hans Seip, University of Oslo. They will conduct model simulations on the Bear Brook, Maine, data set using the Birkenes model. Taugbøl will model the Bear Brook site using an approach that was followed by Christophersen et al. (1990) at the Birkenes site in the SWAP program. Essentially, the MAGIC and Birkenes models will be coupled to predict short-term changes in streamwater chemistry. Christophersen et al. (1990) used the two-box version of MAGIC, with the boxes defined in the same manner as in the Birkenes model. The amounts of water passing through the boxes were estimated with Birkenes. At selected points in the future, the Birkenes model was fed the soil chemistry parameter values provided by MAGIC and simulations of the short-term episodic chemistry were conducted.

I think there are several potential benefits of doing this. First, we will be able to take advantage of the greater hydrological detail of the Birkenes model. This will be important in a flashy catchment like Bear Brook. Second, we may be able to evaluate episodic effects of the artificial acidification, which are likely more pronounced than the chronic, long-term average effects. Thirdly, a major thrust of this project is to improve MAGIC with respect to organic acid influence. Organic acids are relatively unimportant in the annual average, or baseflow, chemistry of Bear Brook. Episodic changes in DOC are, in contrast, fairly pronounced. Increases in streamwater DOC during high-flow periods are commonly on the order of 2-4 mg/L. It may not be unreasonable to expect that these changes in DOC may account for about one-third of the episodic acidification response. Short-term modeling with the Birkenes model will allow us to evaluate these organic effects.

A significant complication in the Birkenes modeling work at Bear Brook will concern how to handle nitrogen. It is too important, especially during high flow, to ignore, but there are no appropriate formulations in the model to deal with it. The tentative plan at present is to increase the sulfate input by an amount equivalent to nitrate output. This will require some adjustments of the formulations for processing, such as sulfur mineralization. But these uncertainties probably account for much smaller errors than ignoring the nitrate flux.

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June 15, 1992

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Dear Tim:

Enclosed are comments on "ORGANIC ACID MODELING AND MODEL VALIDATION. Workshop Summary, April 9-10, 1992" by Sullivan and Eilers.

COMMENTS

The logical framework of my commentary is principally embodied in the scientific debate on <u>pages 16 and 18</u> of the Summary:

1. - Trade-offs must be made between empirical and exhaustive mechanistic modeling.
2. - Assumptions must be clearly stated and the consequences of these assumptions, their error (sign and range in values) must be "reasonably" bracketed.
3. - Recommendations for future model improvements are to be made.

<u>Pages 3 - 8 Previous MAGIC/Paleolimnology Comparison as Basis of Present Work.</u>

A "rigorous approach" is to be developed to improve upon the earlier MAGIC/Paleolimnology project (Sullivan et al., 1991).

As the Summary states on page 7, the most "reasonable" comparison (best fit) between the two models was obtained by Scenario # 4 using (C_B - C_A) for ANC in both models and assuming elevated concentrations of CO_2 for the Adirondack lakes.

I agree.

Sullivan et al. (1991) indicate that such comparison was between to autonomous, theoretical and independent models. Not totally. For example, paleo cannot measure changes in C_A (SO_4^{2-}, NO^{3-}, Cl^-). Changes in C_A have to be guessed at; and the same way that they are guessed at for MAGIC. So the two models do, in fact, share fundamental identities.

Also, as discussed extensively in my review of the previous MAGIC/Paleolimnology comparison project, the assumption of elevated CO_2 levels for the Adirondack lakes is an exercise in curve fitting.

But all of this is OK. For example, chemists use empirical, semiempirical, and mechanistic adsorption isotherm equations to accurately predict chemical phenomenon. We use the tool which most efficiently (least work/greatest output) does the job.

If it works, fine. Let us develop a tool that can do the job. But let us say what we are doing and state its limitations.

Assumption of Changes in C_B and C_A: The Unstated Assumption About Strong Mineral Acidity.

The natural history of "sensitive" watersheds - biology evolved in excess amounts of SO_4^{2-} ("leaky" not conservative for this essential macronutrient) and that acid aquatic and wetland vegetation have nearly universally acquired characteristics that enable survival in the presence of strong mineral acidity/ monomeric ionic, inorganic aluminum - demands that we, as scientists, rethink our assumptions about pre-industrial levels of SO_4^{2-} and the assumption that strong mineral acidity/monomeric ionic inorganic aluminum was rare or absent from pristine "sensitive" ecosystems before the Industrial Revolution. Such assumptions do not explain the natural history of "sensitive" watersheds; a natural history which can only be explained by a general presence of strong mineral acidity in the acidic waters of the past (Krug, 1991, J. Hydrol. 128:1-27).

If we are to assume that no strong mineral acidity existed in the past, we must state this assumption.

Such an assumption will have a great influence of how we model organic chemistry. The Summary suggests that revisiting our assumptions about the nature of pre-industrial acidity may answer some of the concerns that Dr. Driscoll has about the Oliver model and the problem of dealing with aluminum-organic interactions.

Indeed, the problem of aluminum-organic interactions was stated by Oliver et al. (1983, Geochim. Cosmochim. Acta 47:2031-2035) themselves.

Oliver et al. noted that they were dealing with humic acids which they H-saturated. However, appreciable portions of aquatic humic acids are naturally bound with Al and other metals; such interaction imparts free hydrogen ions to water. Oliver et al. themselves note that this free acidity from humic acids will come from - not only organometals present in surface waters - but also from "ion exchange reactions of organic acids in the watershed's soils and sediments" (Oliver et al., last paragraph of the paper). Rosenqvist was making this very point way back in 1980.

In the presence of C_A, this H^+ released from the humic acid appears as strong mineral acidity.

Dr. Frank Stevenson, one of the world's preeminent soil organic chemists, brought on board Mark David's organic acid research group for Bear Brook (to lend his much-needed credentials in organic chemistry to the project) has written about the creation of strong mineral acidity by metal-organic interaction and, in 1987, told Mark David to his face (and in front of me) that this factor must not continue to be dismissed. Five years later and not much has changed in this regard.

As with the last comment, if we continue to make such an assumption, fine, however embarrassing it is to ignore something the real experts have been telling us about for more than 10 years. But let us say what we are doing, define what type of error and limitation this introduces, and bring it up as a <u>future research need</u> requiring further study.

<u>P. 9 - 21: Complexities of Organic Chemistry</u>

P. 9 "In many cases, changes in the degree of protonation appeared to be much more important than changes in the DOC," Driscoll on ALSC data in Figure 2.

<u>Yes</u>.

Regarding Figure 2, we should state that ALSC Organic anion/DOC/pH relationships may be different now than from the past - dynamic nature of ion exchange brought up by Driscoll for CEC (p. 10) and Seip for organic matter (p. 15-16) and that pH/ANC relationships of lakes may have changed are all consistent with the logic of this suggestion.

Some additional comments regarding anion/DOC/pH relationships:

1. - Interaction of acid deposition with forests has, so far, been treated as acid ion exchange of bases out of above-ground portion of vegetation with ion exchange of that same acid back into the watershed via the below-ground portion of vegetation with no loss of acidity (teflon trees). However, acid deposition necessarily interacts with the organic portion of vegetation and litter, solubilizing some organic material via acid hydrolysis (hydration) to create organic "acids" (form acid functional groups). Some undetermined portion of acid deposition is being converted to organic acid and can go to increase DOC.
2. - Reduced DOC by flocculation of aquatic humic substances and pH-dependent solubility of humic solids and gels.
3. - Solubilization of organmetals by acid hydrolysis to increase DOC.

In summary, acid deposition/organic interactions are complex. Depending upon proportion of various types of interactions, DOC and go down or up. Even with significant acid deposition/organic interaction concentration of DOC and organic anion may even remain the same (+ 's and -'s equal out to give net zero sum change).

A modeling exercise could be run to see what various assumptions mean to organic chemistry.

Such an exercise could be a useful assessment for future research needs.

Regarding these considerations of organic chemistry:

1. - Trade-offs must be made between empirical and exhaustive mechanistic modeling.
2. - Assumptions must be clearly stated and the consequences of these assumptions, their error (sign and range in values) must be "reasonably" bracketed.
3. - Recommendations for future model improvements are to be made.

Thus, while we cannot conduct such organic analyses exhaustively, simple, "back-of-envelop" calculations can be simply done to determine rough sign and magnitude of error, and what is useful to pursue as future research needs.

P. 20 - 24: Paleolimnology

p. 20 "It was agreed that a comparison of ANC would be conducted, but that it would not be emphasized because of substantial uncertainties in the diatom-inferred ANC values. Diatom-inferred values for Al and DOC will be evaluated ... ."

P. 21 "Charles summarized the paleolimnological inference techniques ... . The techniques work best for pH, followed by ANC, Al, and DOC (in descending order)."

Comparing the two statements indicate that we have major problems if ANC reconstructions are considered too inaccurate but we are going to use parameters which are even more inaccurate!!

Indeed, as I noted in my March 28, 1990 review of the original MAGIC/paleo comparison project, MAGIC (without organics and arbitrarily high P_{CO2} values) bottoms out at pH~6 while paleo gets into trouble (even for pH, its "best" parameter) by pH 5.

All else being equal, error margins widen out substantially at the end of a range. This is compounded by decreasing species diversity, total numbers, poorer ecological information on acidic species, and acidophilic species often are not particularly fastidious for acidity (could care less if pH is 4.9 or 4.4) and without bracketing of pH from organisms which require even more acidic conditions (as happens at circumneutral pH's) we have very poor resolution. (Some additional comments on paleo sensitivity to pH and ANC from my March 28, 1990 review are included as an appendix to this letter).

Additional Comments on Future Research Needs

Theoretically one can assign the following categories to the ability of models to predict changes in acidic waters:

WORST - CO_2-H_2O-MINERAL Models (which is why we are attempting to incorporate organic acids into MAGIC so that it can operate in pH ranges too acidic for considerations of carbonate chemistry alone in surface waters).

MODERATE - BIOLOGICAL Models (e.g., paleo models limited by decreasing biological quantity, quality and diversity at acidic pH values).

BEST - BIOGEOCHEMICAL Models.
Theoretically, such models would operate best as acid interaction with metals and acid dissolution of biological materials (e.g., vacuoles in pine pollen) are quite marked at pH values more acidic than 5.0!! Indeed, many such reactions only occur here.

Norwegian scientists associated with the SWAP Project initiated Biogeochemical modeling to validate their Paleolimnological modeling (see references).

Ultimately, any **scientific** validation of an improved MAGIc or improved Paleolimnological model will **require** validation by biogeochemical modeling of acidic aquatic processes.

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APPENDIX

p. 4 - 6 of March 28, 1990 review of MAGIC/paleo comparison.

Problem - The authors should state what this really means is that for waters with pH-5 and lower, and ANC values approaching 0, and lower, paleolimnology is going to have the most problems and be least accurate and predictive. Make information relevant as you did when discussing diatoms and chrysophytes on page 12.

p. 13 - Continuing from where I left off in the last quote, "This problem can be especially important if the distribution of one or more of the dominant taxa is not well characterized in the calibration set (Charles and Smol, 1988)."

Problem - This statement reinforces my argument about paleolimnology having the most problems in the more acidic systems - systems that have been the least studied and have the lowest numbers of species.

Again, you should frankly discuss the strengths and weaknesses of the methodology. Such relevant and honest considerations enables the reader (and the authors) to accurately assess the information.

2.2.2 Methodology

The title not appropriate for this section. Perhaps a more descriptive title would be Calibration Modeling, or some such thing.

I am incapable of evaluating this statistical methodology of calibration modeling at this cursory level of description.

p. 16 - "A curvilinear relationship was observed, however, between inferred and measured ANC for this calibration (Figure 2.2-1). Because the low ANC lakes are of greater interest with respect to the chemical reconstructions, a separate calibration was developed for the lakes having ANC $\leq$ 100 ueq/L. This revised calibration equation produced a substantially reduced error of ANC predictions (from 38 to 12 ueq/L) (Figure 2.2-1). The revised ANC equation was used to infer current and pre-industrial ANC for the low ANC ($\leq$ 100 ueq/L) drainage lakes."

Problem

ANC - The $\leq$ 100 ueq/L ANC lakes still appear to have a curvilinear (asymmetrical S-shape) relationship between observed and inferred (predicted) ANC for values < 15 ueq/L.

The bottom of the observed ANC range (ANC $\leq$ -15 ueq/L) has a 0^{o} slope, not being anywhere near a 1:1 relationship between predicted ANC (Figure 2.2.1). In other words, no matter what the measured ANC value in this 0^{o} slope range is, the predicted value is the same. For example, using values estimated from Figure 2.2.1:

OBSERVED ANC	PREDICTED ANC
-15	-25
-25	-25
-40	-25
-50	-25

Therefore, the paleo appears to be incapable of making predictions for ANC ≤ - 15 ueq/L ADirondack lakes.

I recommend that paleolimnology not be used for ANC < - 15 ueq/L.

Between ANC values - 15 to + 15 ueq/L, the calibration curve has a slope of approximately 2:1, so that at approximately +15 ueq ANC/L, measured ANC - predicted ANC, ± some error.

Thus, for ANC values < 15 ueq/L Adirondack lakes, paleolimnology is totally insensitive or is systematically biased for unknown reasons.

Until we can understand why paleolimnology does not work, or work well, for ANC < 15 ueq/L waters, as well as correct for such problems, we can not scientifically and confidently extrapolate paleolimnological predictions (e.g., to 1850 waters).

pH - Given that pH and ANC are related, I examined the pH calibration curve also represented in Figure 2.2.1.

Like the ANC lake data, there appears to have a curvilinear (asymmetrical S-shape) relationship between observed and inferred (predicted) for pH ≤ 5.4 lakes.

Visually, the curve does not appear to be as great as that of the ANC lakes. However, log-log comparison always compresses deviation and error relative to plotting the same data on a linear, arithmetic scale. Thus, it should be expected that related data and similar magnitudes of associated error made on log-log plots (pH) appears to be better than that plotted on a linear, arithmetic scale (ANC) - and calculated measures of error appear to be smaller numbers when expressed for log-log plots than for linear, arithmetic plots.

The pH data show that for highly acidic pH values (pH < 4.7) the slope between observed and predicted is qualitatively similar to that for ANC ≤ -15 ueq/L waters - it is flat. Predicted pH values are higher than observed values:

OBSERVED pH	PREDICTED pH
4.4	4.7
4.5	4.6
4.6	4.7
4.6	4.9

Around pH 4.7 - 5.0, there is agreement between predicted and observed pH (with some associated ± error). Then, there is systematic overestimation of pH up to pH > 5.5 where, again, predicted approximates observed, ± some error:

OBSERVED pH	PREDICTED pH
5.05	5.20
5.10	5.20
5.20	5.30
5.20	5.60
5.20	5.30
5.30	5.40
5.30	5.50
5.30	5.55
5.30	5.60
5.40	5.50
5.40	5.80
5.45	5.45
5.50	6.05

Like the ANC plot, there is an asymmetrical S-curve (relatively compressed by log-log plotting) for observed versus predicted pH values for below pH 5.5.

Recommendations are the same as for ANC.

Figure 2.2.2 shows similar relationships for pH and ANC.

ORGANIC ACID MODELING AND MODEL VALIDATION

Response to comments offered by Dr. E.C. Krug
on the Draft Workshop Summary
(DOE Report Number DOE/ER/30196-1)

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June 22, 1992

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INTRODUCTION

Critical review comments were submitted by Dr. E.C. Krug in response to the workshop summary report prepared for DOE (Report Number DOE/ER/30196-1). The following is a reconciliation of Dr. Krug's comments. This reconciliation is included as an addendum to the workshop summary report.

In general, we concur with Dr. Krug's principal concerns. He offered the following principal overview comments, which were then followed by more specific concerns.

1. Trade-offs must be made between empirical and mechanistic modeling
2. Assumptions must be clearly stated and errors reasonably bracketed
3. Recommendations for future model improvements are to be made

Members of the research team are in full agreement with Dr. Krug on these points and will strive to accomplish those objectives in the deliverables that follow for this project.

Pages 3-8, Previous MAGIC/Paleolimnology Comparison

Dr. Krug stated that the MAGIC model and paleolimnological approaches do, in fact, share fundamental identities because paleo cannot measure changes in C_A (they have to be guessed at). This is not entirely true. The paleo technique infers changes in pH and other parameters irrespective of cause. There is no a priori assumption of change in C_A input. In contrast, in order to hindcast with MAGIC, we have to first guess at historical inputs of C_A. The paleo technique becomes more ambiguous, however, when we attempt to reconstruct changes in ANC. This is because it is unclear to what extent the tool is responsive to actual changes in ANC (C_B - C_A) or is responsive to pH (which in turn is correlated with ANC). The paleolimnological reconstructions of pH, Al, and DOC appear most reasonable because there likely exist physiological bases for these responses on the part of the algal flora. ANC, however, is an artificially constructed parameter with no known biological basis.

Dr. Krug further stated that the assumption of elevated CO_2 in Adirondack lakes is an exercise in curve fitting (although he did not have a major problem with that). He is essentially correct. It is all part of the MAGIC calibration procedure to force the simulations through the "window" of current chemistry.

Assumption of Changes in C_B and C_A

Dr. Krug was concerned that we would assume in this project that no strong mineral acidity existed historically. If so, we should explicitly state this assumption. We disagree that such an assumption is, or will be, made in this project. The validation aspect of the project involves three components: 1) comparison with paleolimnology, 2) comparison with Bear Brook manipulation results, and 3) comparison with HUMEX manipulation results. In order to conduct the first component it is first necessary to *assume* (i.e., guess at) pre-industrial sulfur input. The model cannot be run without first making this assumption. To do that, however, we do not advocate assuming pre-industrial sulfur input equal to zero (i.e. no strong mineral acidity), as was done in DDRP. Rather, we advocate using Husar's estimate of 13% of current levels. This seems to be the most defensible estimate available at present. For conducting the validation components #2 and #3, assumptions about pre-industrial acidity are far less important because the projections will be conducted forward from known (measured) pre-treatment chemistry. Thus, we share Dr. Krug's concern about assuming zero pre-industrial mineral acidity, but do not think this will have an appreciable effect on this project.

Complexities of Organic Chemistry

We agree with Dr. Krug that the relationship illustrated in Figure 2 may be different now from the past. Actually, Dr. Krug's concern is the major reason why we are skeptical about relying too heavily on paleolimnological reconstructions of ANC. They are likely controlled to a large degree by the pH/ANC relationship, and this relationship has likely changed over time.

Paleolimnology

Dr. Krug was concerned that we stated in the report that the paleolimnological techniques work best for pH, followed by ANC, Al, and DOC (in descending order). Yet we advocated not relying heavily on the ANC reconstructions, whereas Al and DOC are even more inaccurate. Actually, we advocate relying most heavily on pH. It is perhaps the single most important variable in terms of biological response. Also, the paleo tool performs best for pH, and there is a clear physiological basis for the diatom response. We also plan to include evaluation of diatom-inferred ANC, Al, and DOC. Our major concerns with the ANC reconstructions are the following:

1. It is an ambiguous term.
2. It has been over-emphasized as the controlling variable in acidification research.
3. There is no known physiological basis for the diatom response.
4. It is likely, to a large degree, an artifact of the pH reconstructions. If so, historical changes in the pH/ANC relationship will bias the results for ANC.

Dr. Krug was also concerned that error margins for the paleo techniques increase at very low pH. We agree. This will need to be considered in subsequent reports and deliverables.

Additional Comments on Future Research Needs

Dr. Krug apparently feels, and we agree, that the validations conducted in this project will provide only one step in the process of obtaining complete validation of our acidification assessment tools. We feel strongly, however, that this is an important step to take. The lack of consideration of organic acids in previous modeling efforts was a substantial deficiency.

Summary of our Response to Dr. Krug's Comments

In general, we agree with the comments and concerns offered by Dr. Krug on the draft workshop summary report. In some cases, his concerns were largely due to a misunderstanding of what we had intended, or some ambiguity in the draft report. There are no major disagreements, however, between the suggestions offered by Dr. Krug and what we have outlined for this project thus far.

END

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