CONF-9204207--Summary

DOE/ER/30196--1

DE93 001862

ORGANIC ACID MODELING AND MODEL VALIDATION

Workshop Summary

April 9-10, 1992

DOE Report Number DOE/ER/30196-1

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Received OSTI
OCT 2 2 1992

Project Title: Incorporation of an organic acid representation into MAGIC and testing of the revised model using independent data sources

U.S. Department of Energy Grant Number: DE-FG02-92ER30196

Draft Workshop Summary Report Submitted June 9, 1992

Final Workshop Summary Report Submitted August 14, 1992

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A. Background and Introduction

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 recently-acquired 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" (Grant Number DE-FG02-92ER30196.A000). 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 rationale for the proposed research is based on the recent comparison between MAGIC model hindcasts and paleolimnological inferences of historical acidification for a set of 33 statistically-selected Adirondack lakes (Sullivan et al. 1990, 1991, in press). The earlier research was sponsored by DOE and conducted through Battelle-PNL. Agreement between diatom-inferred and MAGIC-hindcast lakewater chemistry in the earlier research had been less than satisfactory. Based on preliminary analyses presented in an appendix to the report by Sullivan et al. (1991), it was concluded that incorporation of a reasonable organic acid representation into the version of MAGIC used for hindcasting was the logical next step toward improving model agreement.[1]

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[1] The version of MAGIC used in the U.S. EPA's Direct Delayed Response Project (DDRP) and by NAPAP for the Integrated Assessment (IA) projections of future change did not include any consideration of organic acid effects.

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

B. List of Attendees

The Corvallis workshop was attended by the following scientists:

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

C. Major Topics of Discussion

1. 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.

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.

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

The remainder of this section includes a brief summary of the major points discussed by Sullivan at the workshop. 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 obscure 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}).

2. 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 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

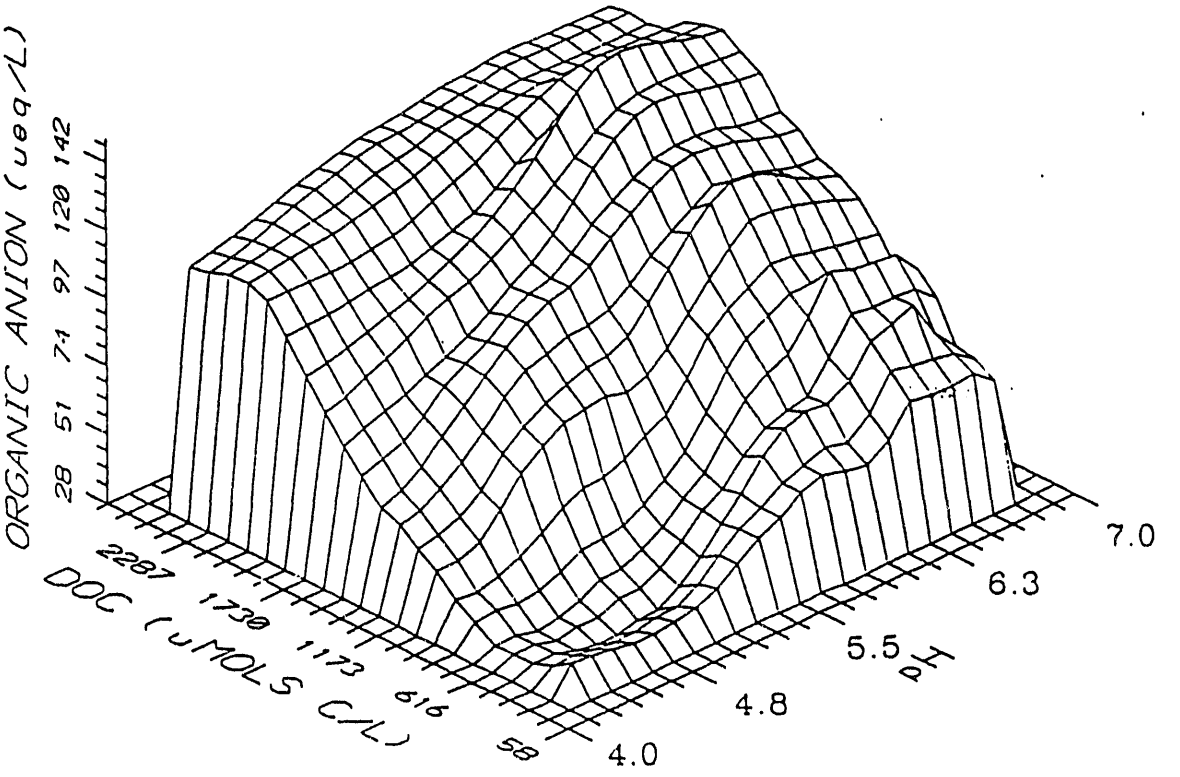


Figure 2. Concentration of organic anions as a function of pH and dissolved organic carbon (DOC) concentration in lakewater. Organic anion concentrations were determined from the charge balance. The response plot is based on 1175 observations of lakes with pH ≤ 7.0 (72 suspected outliers were deleted),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

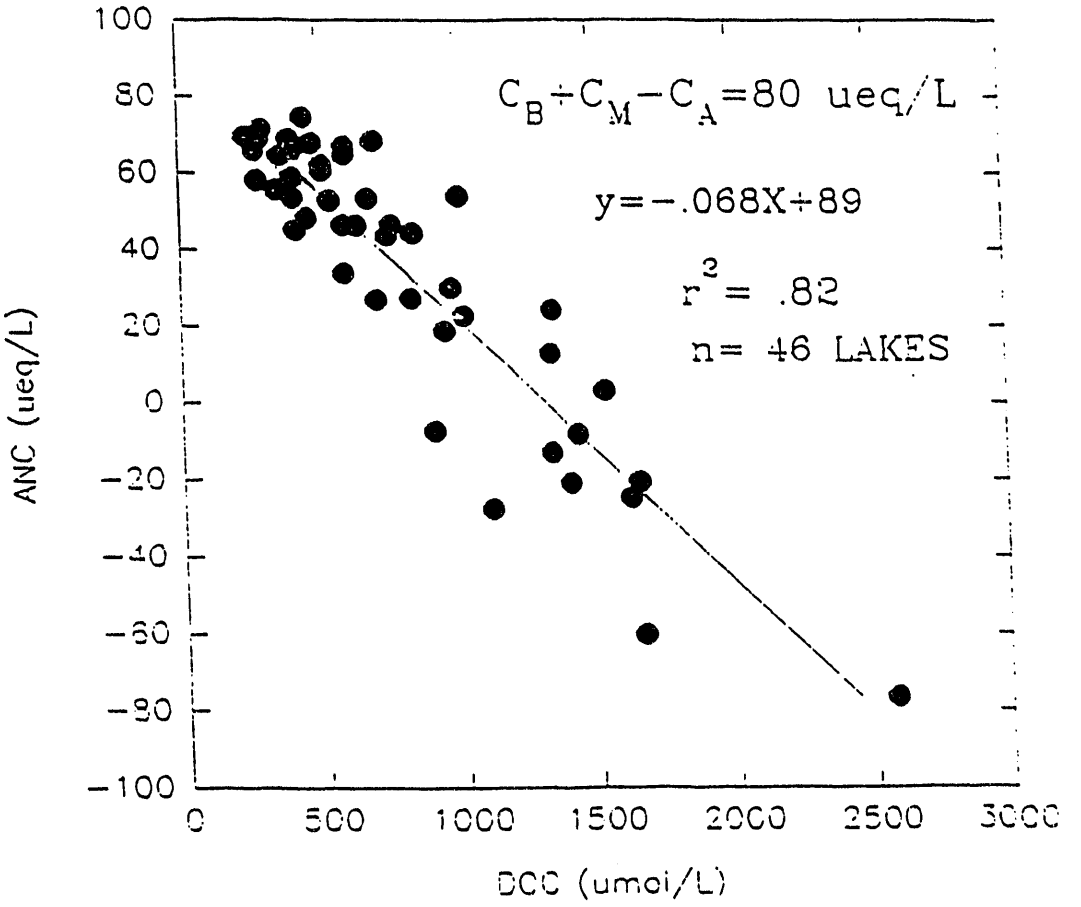


Figure 3. Example regression analysis for values of $C_B + C_M - C_A = 80 \pm 5\ \mu eq\ L^{-1}$ in which the relationship between ANC and DOC is evaluated using data from ALSC lakes. Results show that the ordinant intercept (89 $\mu eq\ L^{-1}$) is close to the nominal value of 80 $\mu eq\ L^{-1}$ for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

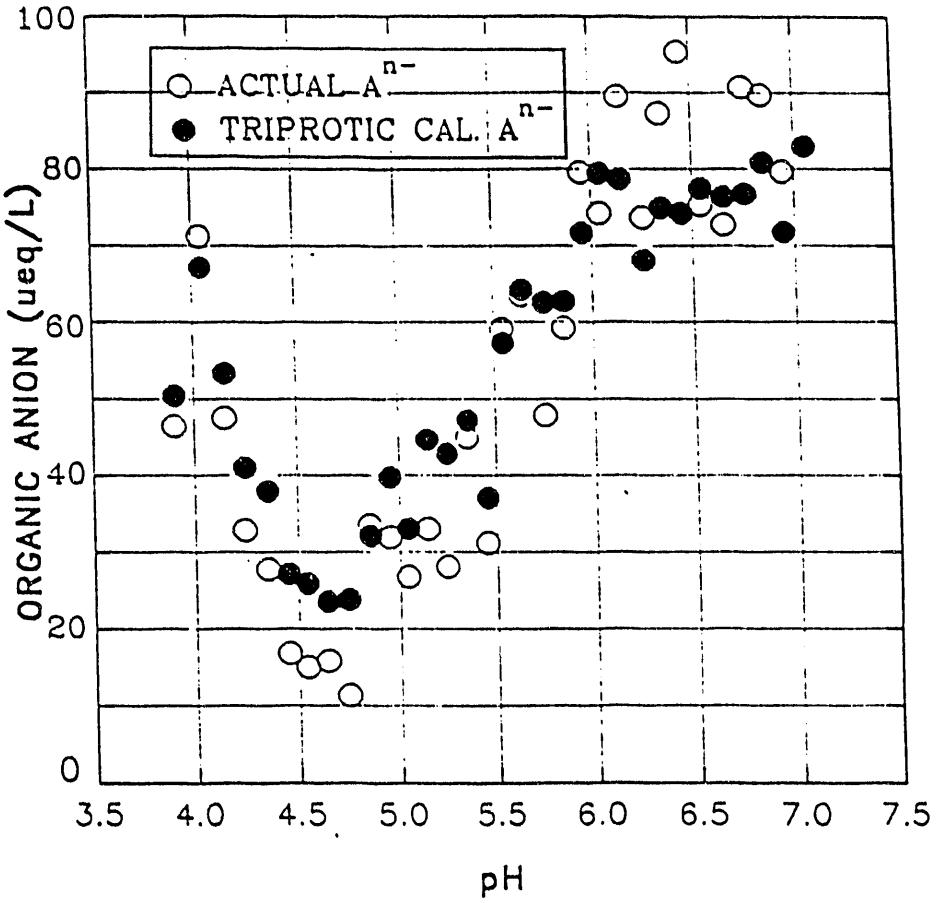


Figure 4. Comparison of the organic acid anion concentration determined from the charge balance (open circles) and the mean organic anion concentration as calculated using the ALSC-calibrated triprotic organic acid model in the chemical equilibrium model ALCHEMI (r^2=0.92) (Lehtinen 1991)

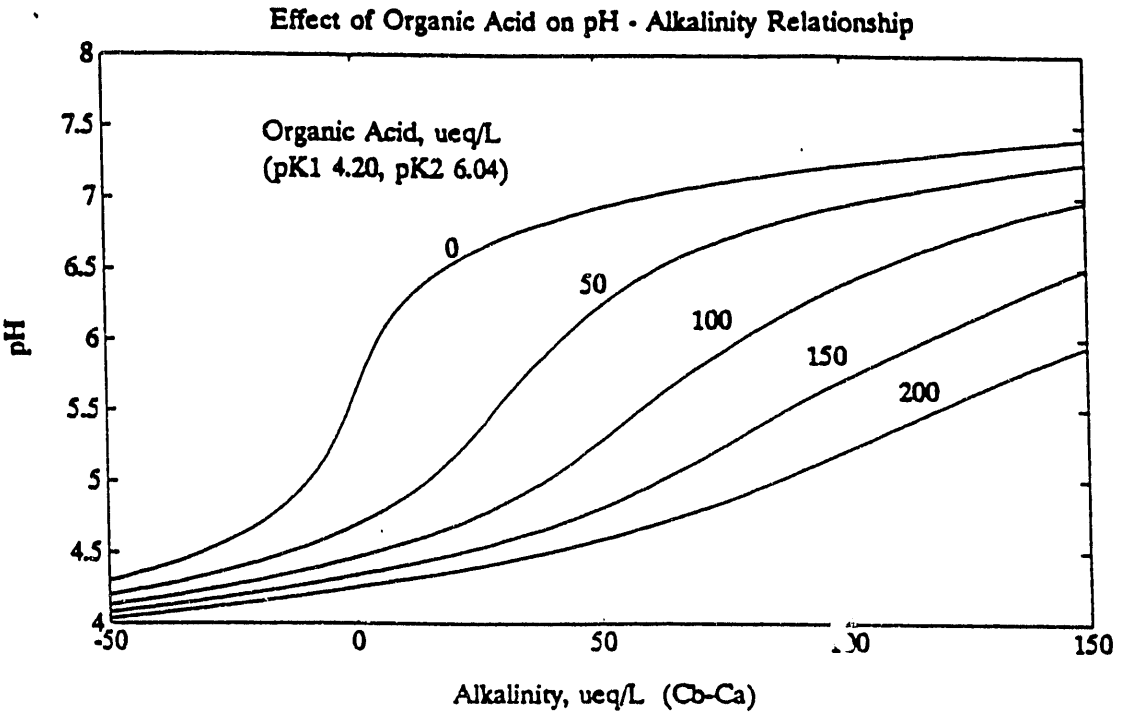
acidity, is that we do not know to what extent organic acid anion concentrations and/or DOC may have changed in response to changes in acidic deposition inputs. Sullivan indicated that a recent literature review he prepared for Battelle-PNL concluded that, although DOC changes appeared to have occurred 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.

3. 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 7).

4. 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



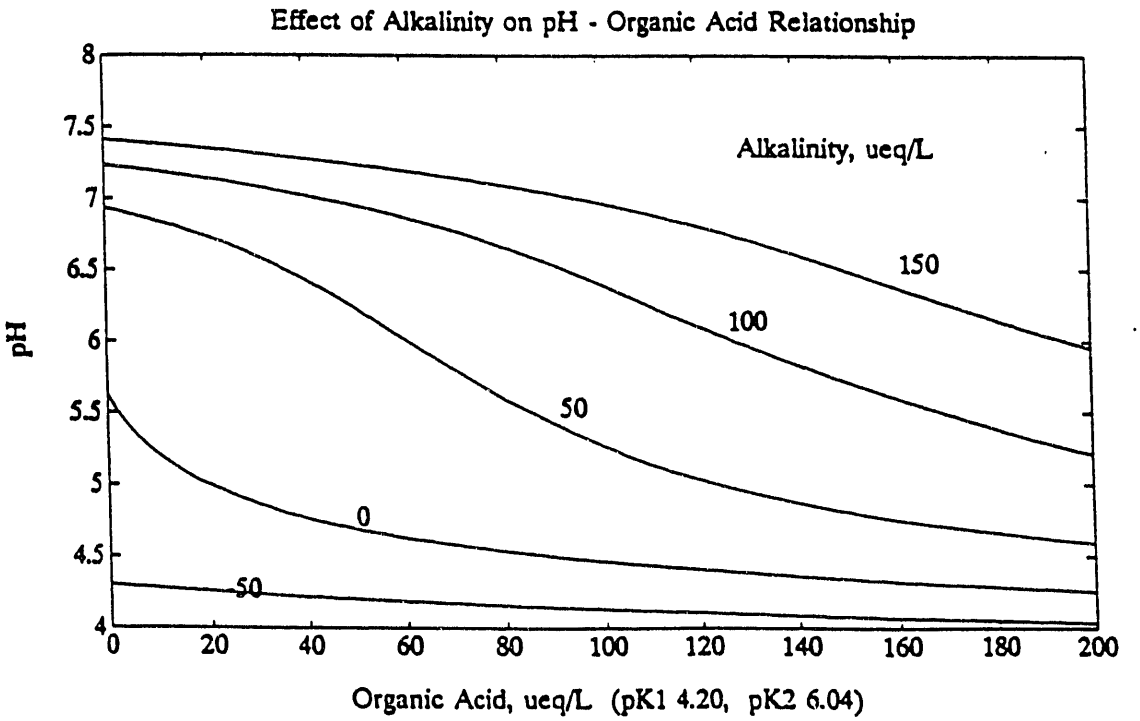
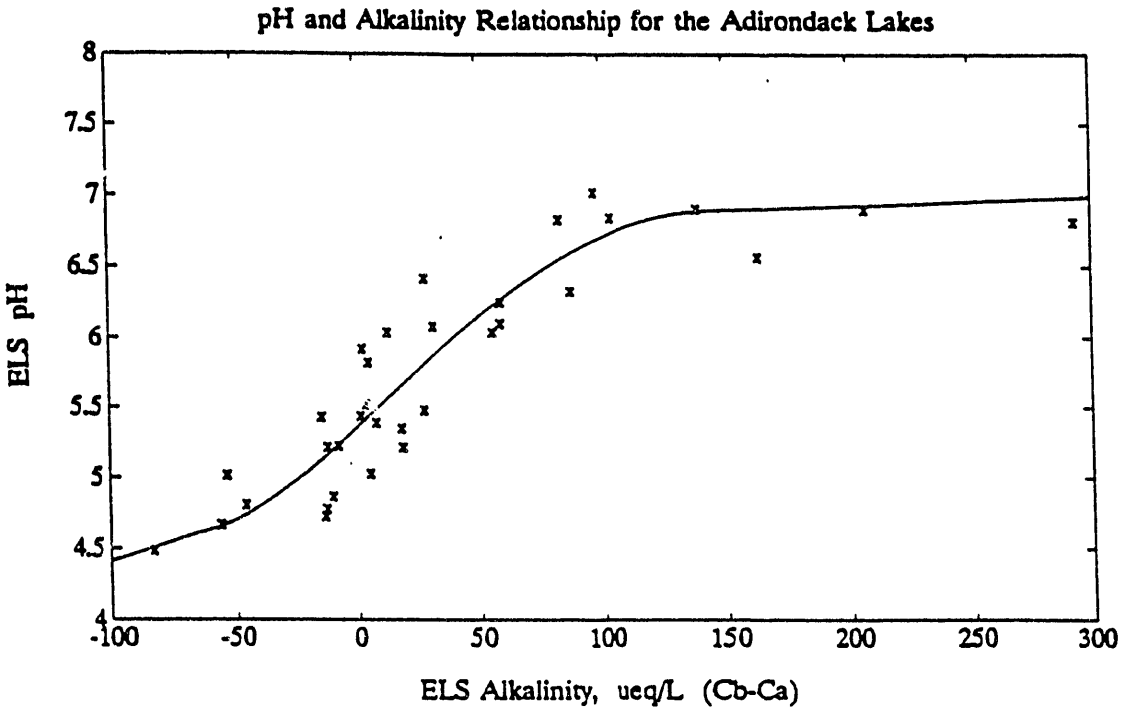


Figure 5. a) Effect of organic acids on the pH/alkalinity relationship; b) Effect of alkalinity on the pH/organic acid relationship.



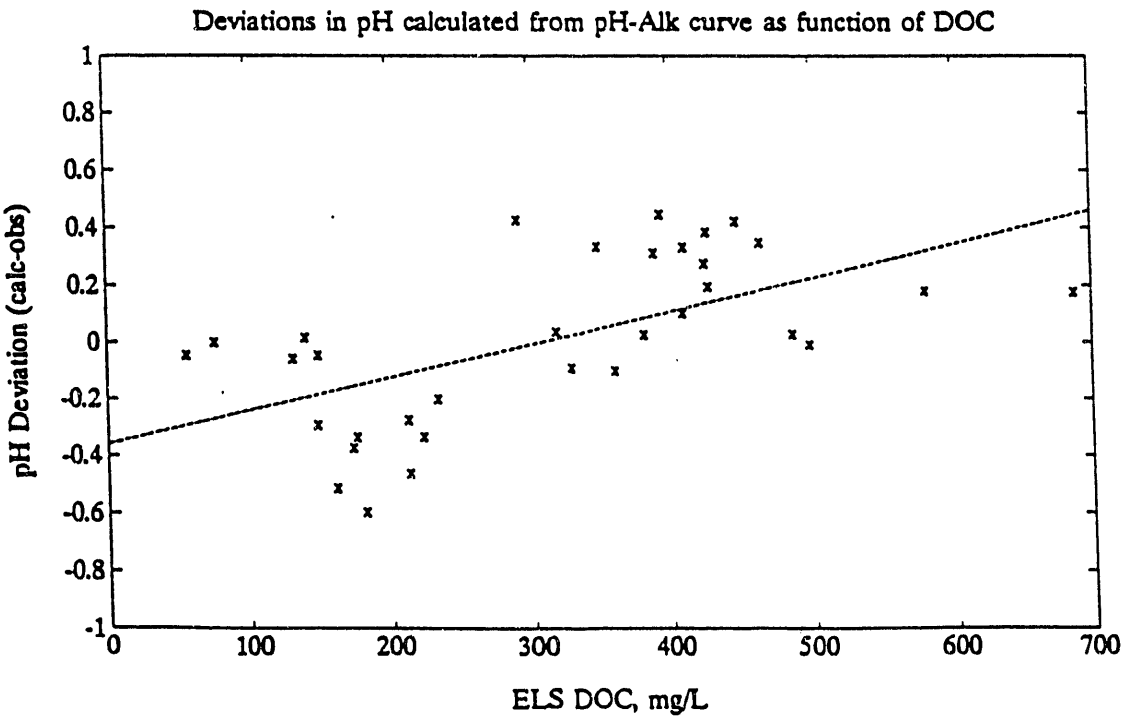


Figure 6. Relationships between pH, alkalinity, and DOC for Adirondack lakes sampled by the Eastern Lake Survey (ELS).

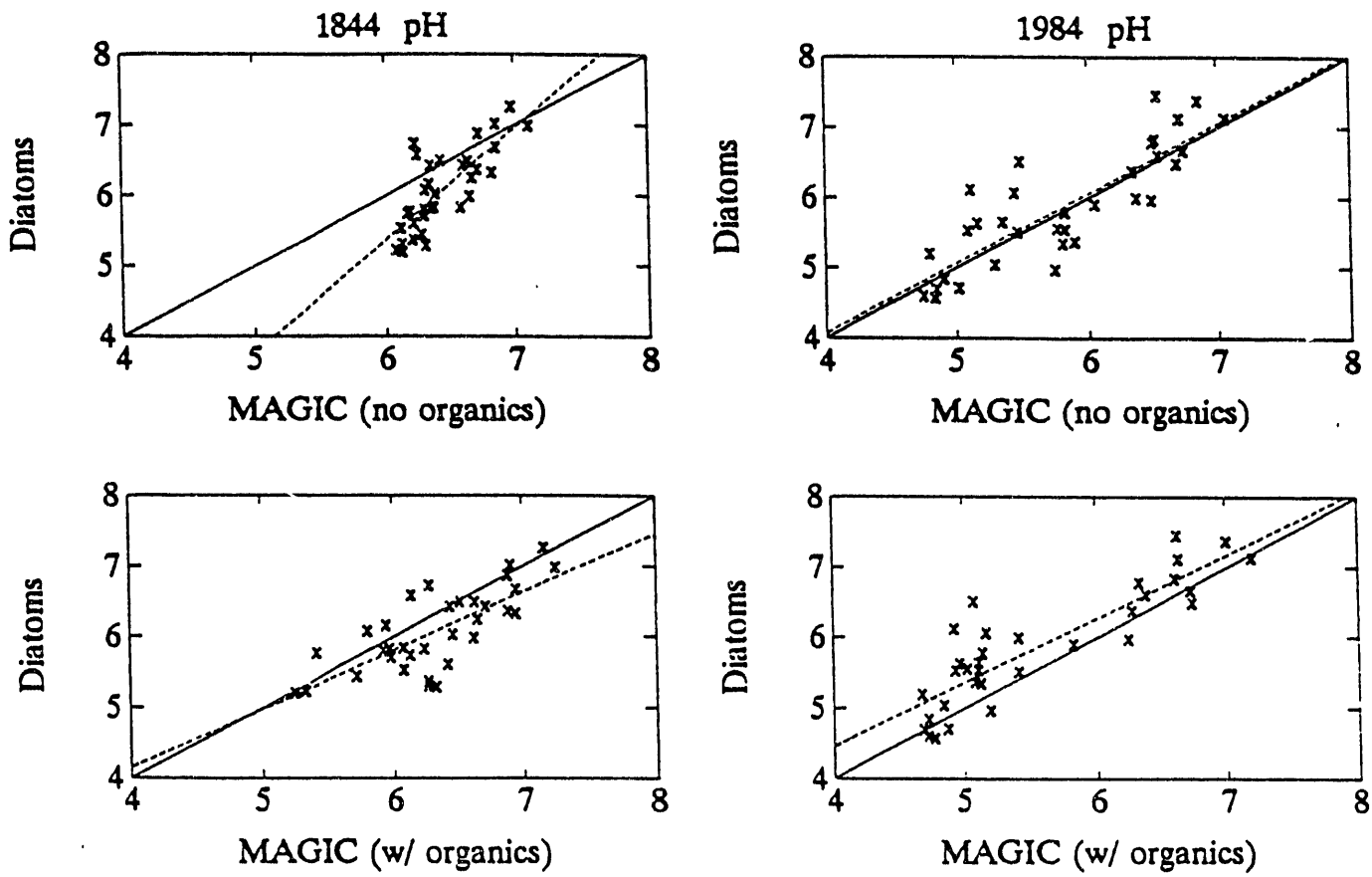


Figure 7. Diatom-inferred pH versus MAGIC hindcast pH for pre-industrial and current lakewater, both with and without an organic representation in the MAGIC simulations. Comparisons are based on the Adirondack lakes data set, using Driscoll's diprotic organic acid representation.

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 8). 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 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

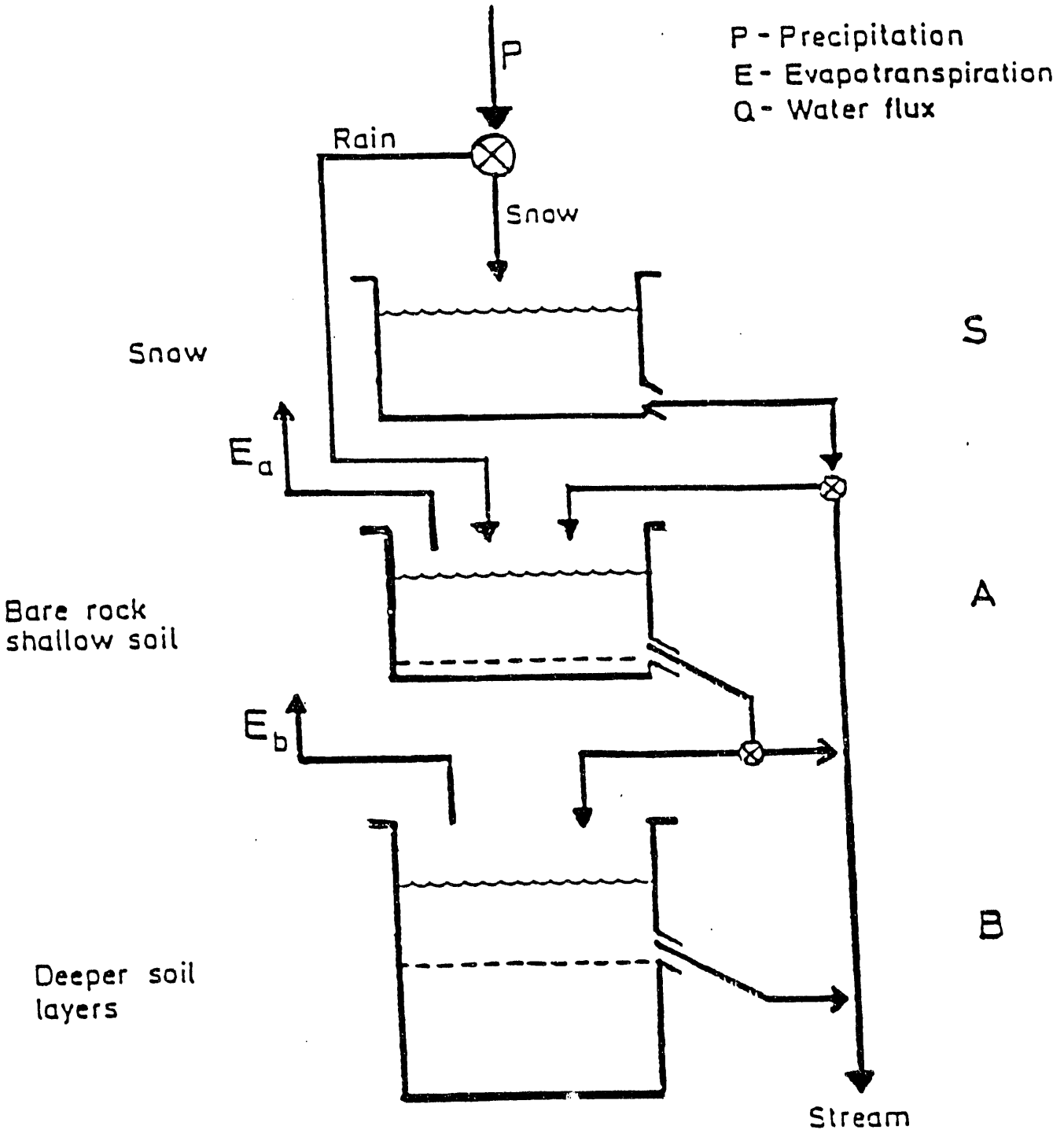


Figure 8. Birkenes model formulation.

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 development 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. 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.

5. 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.

6. 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 9). He showed a graphic representation of the output from canonical

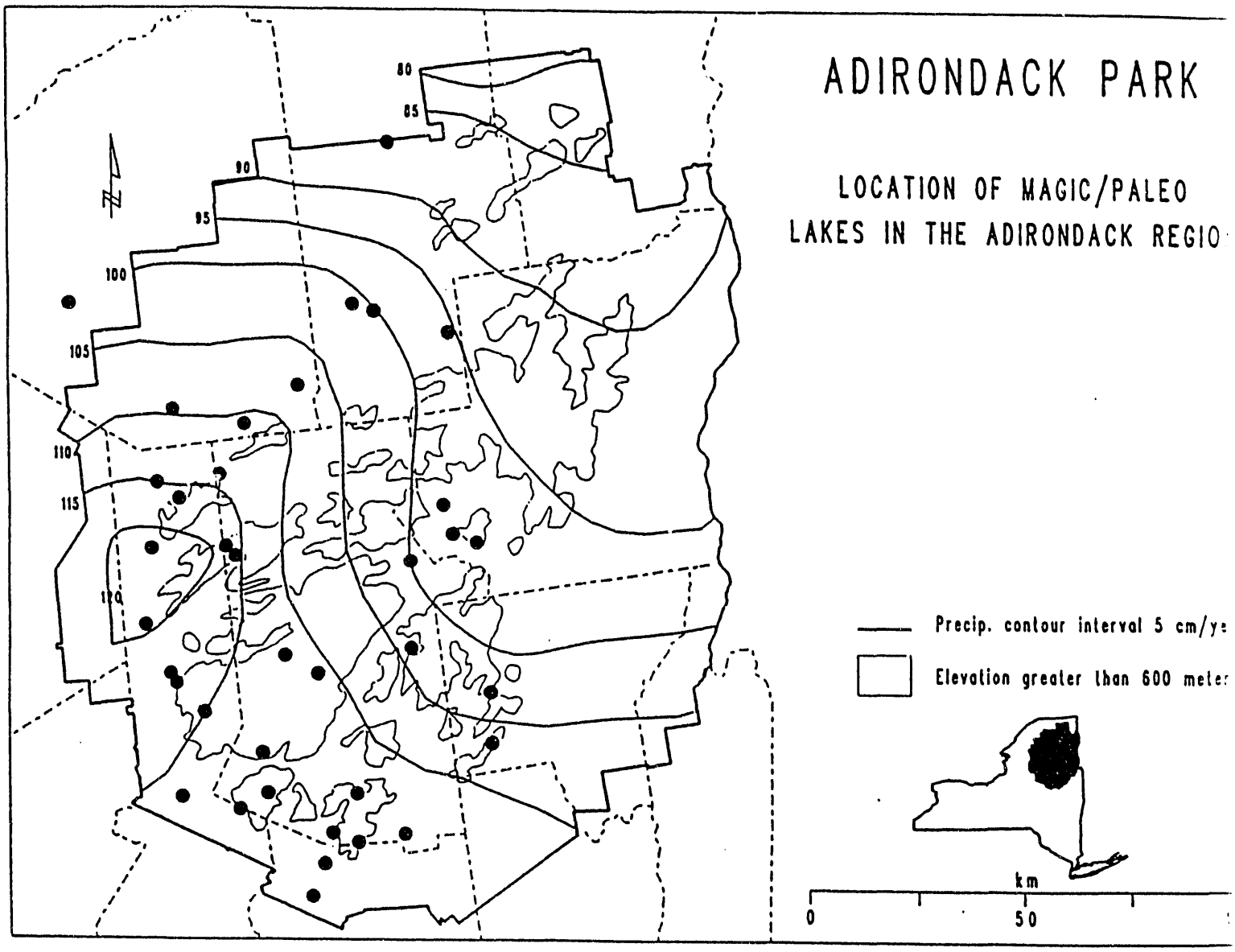


Figure 9. Location of Adirondack lakes involved in the MAGIC/diatom comparison.

correspondence analysis to simultaneously show the relationship between independent environmental variables and sediment diatom assemblages (Figure 10). 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 11-13) 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.

7. 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 (~ 100 μeq L^{-1}). Cosby suggested

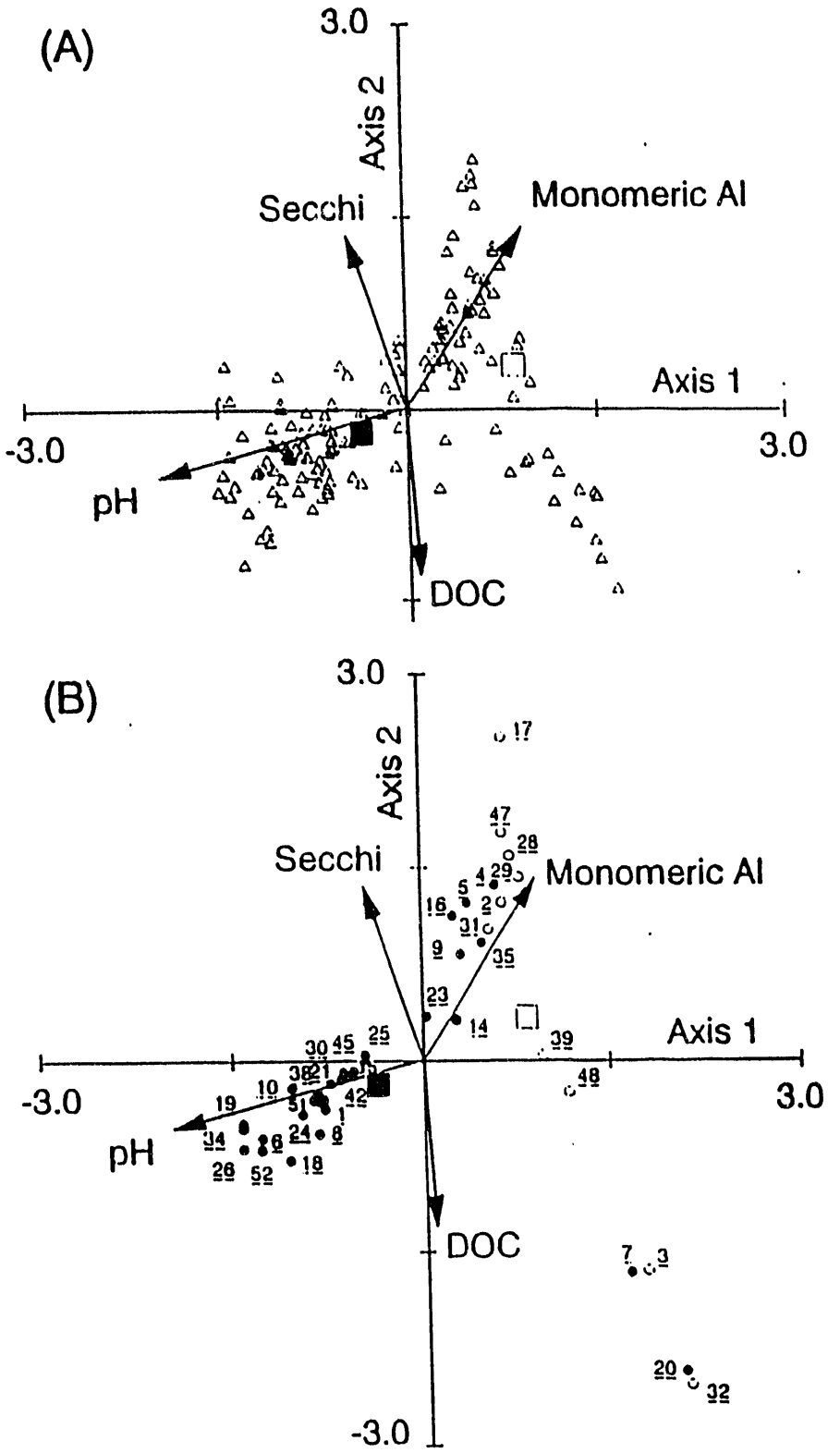


Figure 10. Canonical correspondence analysis ordination plots of (A) 149 diatom species in 37 Adirondack lakes and (B) 37 lake surface-sediment samples, each with environmental biplot arrows for the four significant variables as determined in forward selection. (Dixit et al., in review)

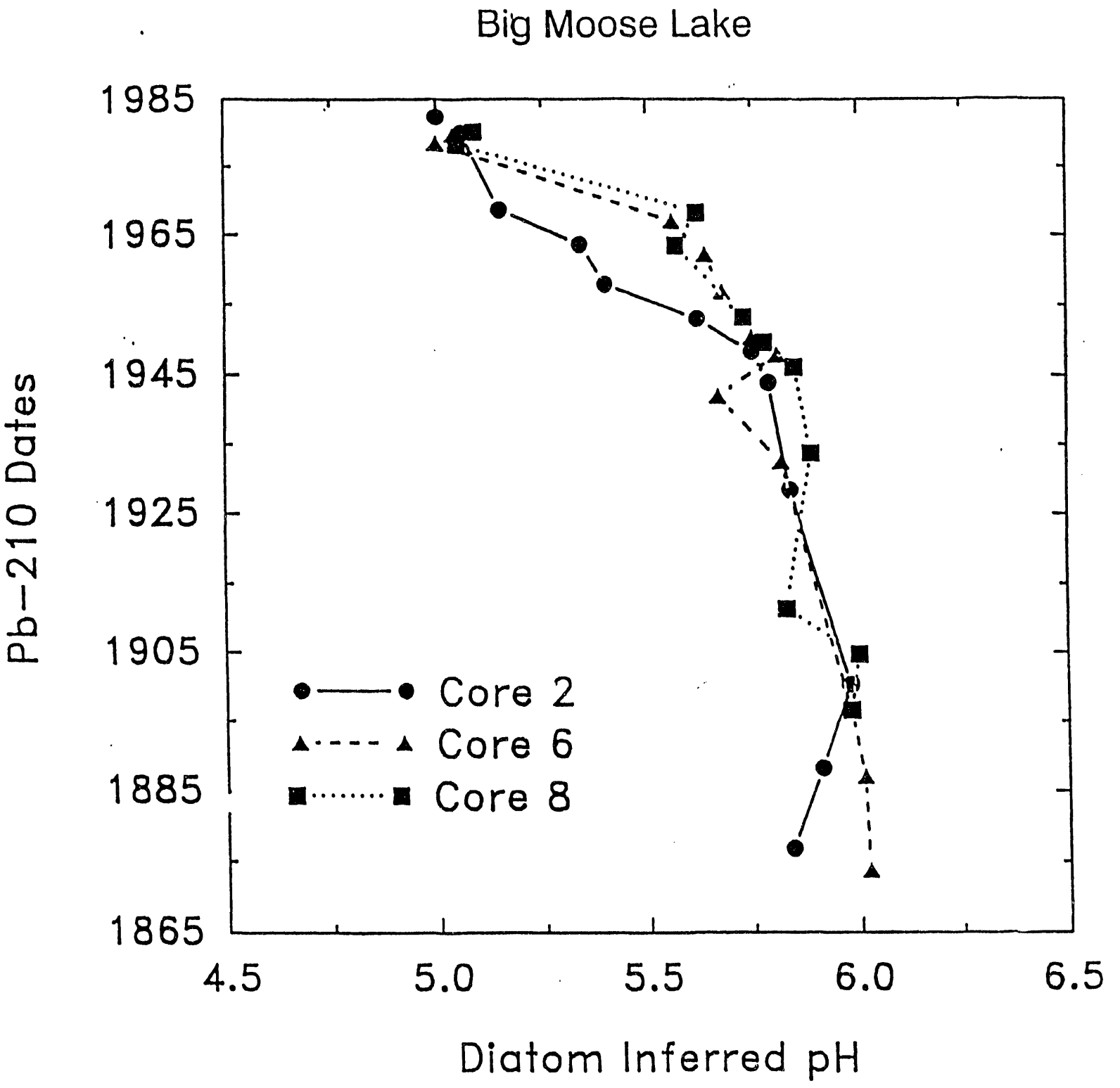


Figure 11. Paleolimnological reconstructions for Big Moose Lake (Charles et al. 1991).

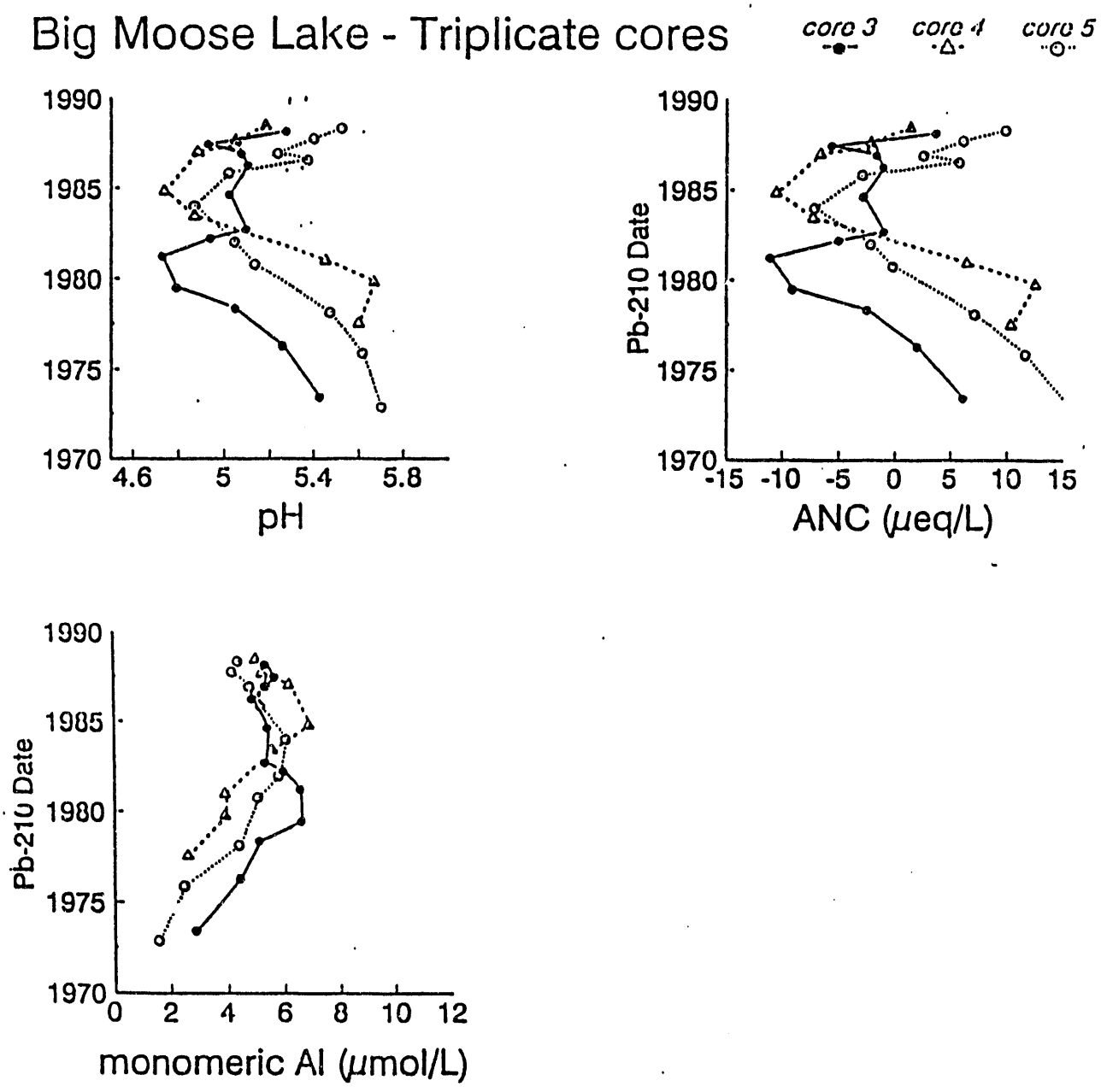


Figure 12. Chrysophyte-inferred reconstructions of recent (1972-1989) lakewater pH, ANC, and monomeric Al concentrations in three separate sediment cores collected from Big Moose Lake (Source: B.F. Cumming).

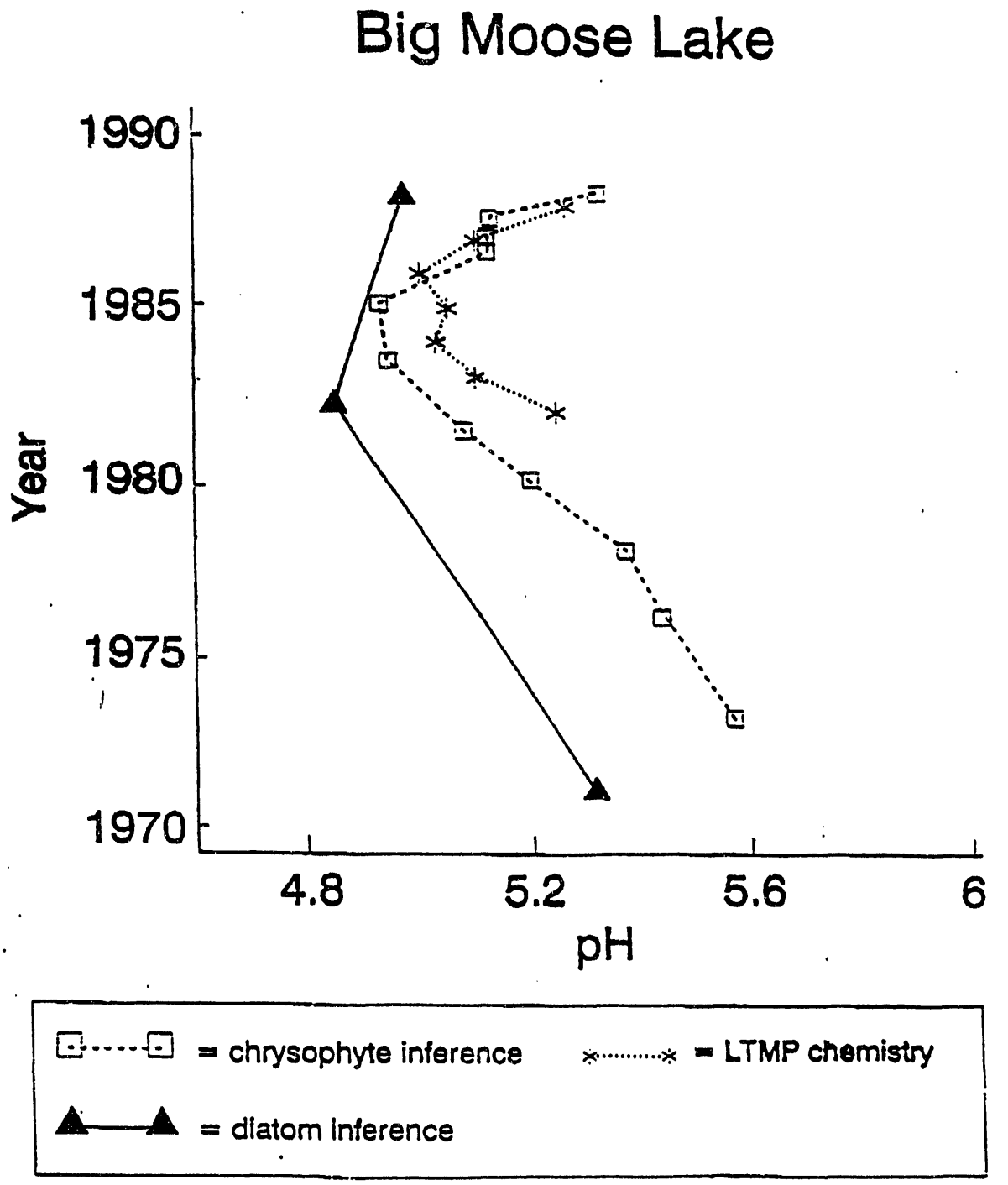


Figure 13. Comparison among chrysophyte inferences, diatom inferences, and measured (Long-term Monitoring Program) data for the recent pH of Big Moose Lake (Source: S.S. Dixit and B.F. Cumming).

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

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[2] 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.

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

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.

D. Schedule and Deliverables

The final portion of the workshop was devoted to a discussion of logistical and contracting issues, schedules, deliverables, and responsibilities. Major project deliverables are outlined in Table 3. 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.

Table 3. Schedule of major project deliverables.

Deliverable	Principal Author(s)	Date
Workshop summary	Sullivan/Eilers	6/15/92
Organic acid modeling approach manuscript	Driscoll	8/31/92
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

E. Literature Cited

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Schecher, W. and C.T. Driscoll. 1987. An evaluation of uncertainty associated with aluminum equilibrium calculations. Water Resour. Res. 23:525-535.

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Appendix 1

Comments on Draft Report Received from Dr. E.C. Krug

June 15, 1992

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Edward C. Krug, Ph.D.
521 Deborah Ave.
Winona, MN 55987

(507) 454-6082

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 pages 16 and 18 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.

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

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.

REFERENCES

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Stabell, B. 1990. Pre-industrial acid-water periods in Norway: diatom analysis. pp. 325-326 in Mason.

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° 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° 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 $\leq$ - 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, $\pm$ 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 $\leq$ 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 $\leq$ -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.

Appendix 2

Response to Dr. Krug's Comments

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)

Prepared by: Timothy J. Sullivan
Joseph M. Eilers

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.

<u>Pages 3-8, Previous MAGIC/Paleolimnology Comparison</u>

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.

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12/23/92