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Comparison of MAGIC and DIATOM Paleolimnological Model Hindcasts of Lakewater Acidification in the Adirondack Region of New York

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March 1991

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
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COMPARISON OF MAGIC AND DIATOM PALEOLIMNOLOGICAL
MODEL HINDCASTS OF LAKEWATER ACIDIFICATION IN THE
ADIRONDACK REGION OF NEW YORK

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those earlier estimates, the Diatom and MAGIC hindcast estimates are in relatively good agreement, and imply that the above percentage has been between 0% and 50%. Both models suggest acidification of low-ANC Adirondack region lakes since pre-industrial times. The models differ primarily in that MAGIC inferred greater acidification and also that acidification has occurred in all lakes in the comparison. The Diatom paleolimnological model inferred that acidification had been restricted to low-ANC lakes (< about 50 $\mu\text{eq L}^{-1}$).

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ACRONYMS

ANC	Acid-neutralizing capacity
CANOCO	Canonical correspondence analysis
CEC	Cation exchange capacity
CERL	Corvallis Environmental Research Laboratory
DDRP	Direct/Delayed Response Project
DCA	Detrended correspondence analysis
DOC	Dissolved organic carbon
DTBR	Depth to bed rock
ELS-I	Eastern Lake Survey, Phase I
ELS-II	Eastern Lake Survey, Phase II
EPA	U.S. Environmental Protection Agency
ETD	Enhanced Trickle Down Model
ILWAS	Integrated Lake-Watershed Acidification Study
MAGIC	Model of Acidification of Groundwater in Catchments
NAPAP	National Acid Precipitation Assessment Program
NCDC	National Climate Data Center
ORNL	Oak Ridge National Laboratory
pCO ₂	Partial pressure of CO ₂
PIRLA	Paleoecological Investigation of Recent Lake Acidification, Phase I
PIRLA-II	Paleoecological Investigation of Recent Lake Acidification, Phase II
PNL	Pacific Northwest Laboratory
PRL	Proton reference level
RMSE	Root mean square error
SSA	Sum of strong acid anions
SSB	Sum of strong base cations

1.0 INTRODUCTION

In 1980, the United States Congress established the interagency National Acid Precipitation Assessment Program (NAPAP) to evaluate acid-deposition causes, effects, and control strategies. This research effort will conclude in 1991 with the publication of a series of 28 State of Science and Technology (SOS/T) Reports and an Integrated Assessment (IA). The SOS/T Reports document the current scientific information on a variety of acid deposition issues. The Aquatic Effects component includes reports on current status, processes, historical change, episodes, biological effects, and future projections. The IA provides a structured synthesis of the policy-relevant technical information contained in the SOS/T Reports.

Two of the major objectives of the Aquatic Effects research of NAPAP have been to evaluate historical changes in surface-water chemistry in response to acidic deposition (e.g., Sullivan in press^(a)) and to construct projections of future change under different scenarios of acidic deposition (e.g., Church et al. 1989; Thornton, Marmorek, and Ryan, in press^(b)).

Largely, these efforts require different approaches, each with its own set of assumptions and limitations. A truly integrated assessment of the effects of acid deposition on aquatic systems in the United States, however, requires a comparison of estimates of past and future change. The discrepancies observed in these two approaches constitute an estimate of the uncertainty associated with our current level of understanding of the aquatic effects of acid deposition.

Evaluations of historical changes in surface-water chemistry in response to acid deposition have been based on a weight-of-evidence approach (Sullivan, in press). To document and quantify, where possible, the historical effects

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- (a) Sullivan, T. J. 1990. "Historical Changes in Surface Water Acid-Base Chemistry in Response to Acidic Deposition." State of the Science, SOS/T 11, National Acid Precipitation Assessment Program. (In press).
 - (b) Thornton, K., D. Marmorek, and P. Ryan. 1990. "Methods for Projecting Future Changes in Surface Water Acid-Base Chemistry." State of the Science, SOS/T 14, National Acid Precipitation Assessment Program. (In press).

of acid deposition on surface-water quality in the United States, various sources of information have been used, including paleolimnological data, historical water-quality measurements, ion ratios, space-for-time substitutions, estimates of recent change, results of catchment and lake-manipulation experiments, and model hindcasts. The uncertainties in the most direct approach of using historical ANC and pH data have rendered its use controversial and problematic (Ashbury et al. 1990; Kramer 1990; Metcalf and Gerlach 1990). Thus, quantification of historical change is based primarily on paleolimnological data, and is possible on a regional basis only for lakes in the Adirondack subregion at this time. Sixty Adirondack lakes have been included in the paleolimnological studies, of which 35 were selected using a statistical basis, so as to allow the results to be projected to the region as a whole.

Projections of future changes in surface water chemistry in response to constant or changing deposition are based primarily on model estimates, as summarized by Thornton, Marmorek, and Ryan (in press). Among the models most commonly used for such projections are several that focus on soil-mediated processes, such as the Birkenes (Christophersen, Seip, and Wright 1982; Rustad et al. 1986), ILWAS (Chen et al. 1983; Goldstein et al. 1984; Gherini et al. 1985), MAGIC (Cosby et al. 1985a, 1985b), and Reuss and Johnson (1985) models. Reuss, Christophersen, and Seip (1986) discussed the differences in scope and structure among these models which contain similar assumptions regarding several key soil chemical processes, in particular the anion mobility concept of Seip (1980), cation exchange, the carbonic-acid system, Al-bearing weathering and Al-hydroxide dissolution and precipitation (Reuss, Christophersen, and Seip 1986). The "Trickle Down" models of Schnoor and coworkers (Stumm, Morgan and Schnoor 1983; Schnoor and Stumm 1985; Schnoor, Nikolaidis, and Glass 1986; Lin and Schnoor, 1986) are based on mass balance for acid-neutralizing capacity (ANC). A variety of steady-state and dynamic models have been utilized within the NAPAP research efforts. Particular emphasis has been placed on the process-based models included in the Direct Delayed Response Project (DDRP): MAGIC, ILWAS, and ETD (Church et al. 1989). All three models yielded results that were generally similar for lakes in the northeastern United States (Thornton, Marmorek, and Ryan, in press).

These dynamic watershed acidification models have proven useful for hypothesis testing and have played an integral role in the effort to understand the net effects of the complicated interacting processes that govern ecosystem response to acid deposition (Stone and Seip 1989). These models may need improvement to varying degrees (Reuss, Christophersen, and Seip 1986; Seip, Christophersen, and Sullivan 1989; Stone and Seip^(a)). They are currently being applied to questions of future change under alternative acidic-deposition scenarios (Thornton, Marmorek, and Ryan, in press). Thus, it is important to test the validity, under a reasonable set of assumptions regarding pre-industrial deposition and water chemistry, of the results of watershed acidification models against independent estimates of historical change. Paleolimnological models and dynamic process modeling approaches are fundamentally different. Paleolimnology provides a direct measure of a surrogate indicator of lake acidity, whereas the process models, although rooted in hydrochemical principles, represent major temporal and spatial process aggregation, and thus constitute a simplification of the catchment system (Jenkins et al. 1990). Few direct measurement data sets are available that contain a sufficiently long period of record for validating either approach. It is therefore important to compare and contrast the results obtained from these approaches in order to assess the level of confidence that should be ascribed to estimates of change in lake acid-base status. In particular, the widespread international debate regarding future acidification of surface waters and the establishment of critical loadings of atmospheric deposition of acidic substances require validation of projections of future change. Verification of the dynamic process models can be achieved via comparison with Diatom paleolimnological model results.

The major objectives of this report are to:

- compare and contrast paleolimnological and MAGIC model hindcast estimates of historical acidification (i.e., decreased ANC and pH) of the statistically (probability) sampled lakes of the Adirondack region

(a) Stone, A., and H. M. Seip. "Are Mathematical Models Useful for Understanding Water Acidification?" *Sci. Total Environ.* (In press).

- evaluate the agreement between the MAGIC and paleolimnological model estimates of historical acidification of Adirondack lakes and discuss the implications of this agreement
- explore alternative explanations for observed discrepancies between the two models
- evaluate the magnitude of the differences between the models relative to error estimates for each.

2.0 APPROACH AND METHODS

2.1 WATERSHED AND LAKE SELECTION

The watersheds and associated lakes that were used are a subset of those used in preceding studies: Phase I of the EPA Eastern Lake Survey (ELS-I), DDRP, and PIRLA-II. Thus, the selection process of those studies is briefly described in the following subsections.

2.1.1 Direct Delayed Response Project (DDRP)

The 145 DDRP lakes in the northeastern United States represent a subsample of the population of lakes included in ELS-I (Linthurst et al. 1986). The ELS-I survey consisted of a probability sample of lakes in regions of the United States containing lakes (as represented on 1:250,000 scale maps) expected to have alkalinity values $\leq 400 \mu\text{eq L}^{-1}$, based on a regional compilation of published and unpublished data on surface-water alkalinity, and in some cases, geology (Linthurst et al. 1986). Within the Northeast, lakes were stratified based on subregions and alkalinity-map classes. Map classes were comprised of three groups of expected alkalinity (< 100 ; $100-200$; $> 200 \mu\text{eq L}^{-1}$), and within each strata approximately 50 lakes were systematically selected from an ordered list following a random start. Thus, each lake was selected with a known inclusion probability (or sample weight), which varied among strata. The sample structure for ELS-I lakes in the Northeast is shown in Table 2.1.

The DDRP lakes in the Northeast were selected from this ELS-I frame, which can generally be described as lakes that are greater than 1.5 m deep represented on 1:250,000 scale USGS topographic maps (typically > 4 ha in surface area). Lakes with gross anthropogenic disturbances were excluded from the DDRP subsampling frame, as were those in several other minor exclusion categories (Linthurst et al. 1986). The lakes were further restricted to exclude those with $\text{ANC} > 400 \mu\text{eq L}^{-1}$, surface area > 2000 ha, or watershed area > 3000 ha (Church et al. 1989). Lakes in the frame selected for the DDRP were grouped into three clusters based on ANC measured in ELS-I: 1) $\leq 25 \mu\text{eq L}^{-1}$; 2) $25-100 \mu\text{eq L}^{-1}$; and 3) $> 100 \mu\text{eq L}^{-1}$. Approximately 50 lakes were selected from each cluster, using a variable-probability

TABLE 2.1. Description of Sample and Target Populations for Eastern Lake Survey I of the Northeastern United States

<u>Stratum</u>	<u>Frame Population</u>	<u>Lakes in Probability Sampling</u>	<u>Lakes Sampled</u>	<u>Expansion Factor</u>	<u>Estimated Target Population Size (TPS)</u>	<u>Standard Error of TPS</u>
1A1(a)	711	75	57	9.633	549.08	33.08
1A2(a)	542	65	51	8.338	425.24	26.13
1A3(a)	431	68	47	6.719	315.79	22.14
1B1	208	70	49	3.192	156.41	9.29
1B2	96	70	48	1.477	70.90	3.00
1B3	1682	68	47	27.209	1278.82	90.37
1C1	631	88	63	7.822	492.79	27.31
1C2	752	70	54	10.743	580.12	36.20
1C3	650	74	47	8.953	420.79	34.59
1D1	443	70	47	6.572	308.88	23.00
1D2	656	95	43	6.905	296.92	31.14
1D3	1568	93	37	19.426	718.76	85.22
1E1	1038	130	89	8.070	718.23	39.71
1E2	606	74	48	8.344	400.51	31.80
1E3	744	72	41	10.333	423.65	41.55

(a) The Adirondacks are represented by Strata 1A1, 1A2, and 1A3 with a total N of 1290.

systematic sampling design that resulted in the selected lakes having nearly equal inclusion probabilities within and among strata. This was accomplished by setting DDRP selection probabilities to be inversely proportional to ELS-I inclusion probabilities. The resulting sample structure for the DDRP is presented in Table 2.2. Additional details of the lake-selection methodology are presented in Linthurst et al. (1986) and Church et al. (1989).

2.1.2 Paleoecological Investigation of Recent Lake Acidification (PIRLA)

Most of the paleolimnological data for lakes in the United States were obtained by two large regional studies, PIRLA-I (Charles and Whitehead 1986a

TABLE 2.2. Structure for the Northeastern Lakes Sampled by the Direct/Delayed Response Project

<u>ANC Cluster^(a)</u>	<u>DDRP Lakes Sampled from ANC Group</u>	<u>Estimated Number of Lakes in DDRP Target Population</u>
1	55	796
2	46	1100
3	44	1772
Total	145	3668

(a) 1 = ANC < 25 $\mu\text{eq L}^{-1}$
 2 = 25-100 $\mu\text{eq L}^{-1}$
 3 = ANC > 100 $\mu\text{eq L}^{-1}$
 based on recalculated ANC values

and b) and the ongoing PIRLA-II (Charles and Smol in press^(a)). PIRLA-I included stratigraphic analysis of approximately 35 lakes in four regions of the United States (Adirondacks, northern parts of New England, Upper Midwest, and Florida). In addition to obtaining biological data (diatoms, chryso-phytes) for inferring water chemistry, sediment measurements also included analyses of metals, sulfur, nitrogen, carbon, polycyclic aromatic hydrocarbons, coal and oil carbonaceous particles, pollen, and ²¹⁰Pb for dating strata. The PIRLA-I project developed standardized protocols, including quality assurance/quality control guidelines, for all aspects of diatom research (Charles and Whitehead 1986a).

The PIRLA-I investigation of Adirondack subregion lakes included many of the same lakes studied in the RILWAS project (Driscoll and Newton 1985; Rudd 1987). Most of the lakes were small to moderately sized, were low in alkalinity, and had forested watersheds with little or no cultural development. Alkalinity and pH inference equations, based on a calibration set of 36 lakes, involved multiple linear regression of percentages of diatoms in pH categories. The standard errors for pH and alkalinity were 0.26 pH units and

(a) Charles, C. F., and J. P. Smol. 1990. "The PIRLA II Project: Regional Assessment of Lake Acidification Trends." *Verh. Internat. Verein. Limnol.* (In press).

21 $\mu\text{eq L}^{-1}$, respectively (Charles et al., in press^(a)). Procedures for developing the inference equations were those of Charles (1985) and Charles and Smol (1988). Eight replicate analyses of a sediment interval from a core taken from Big Moose Lake showed a mean pH of 5.54, with standard deviation of 0.04 pH units, well below that for the predictive equation.

The PIRLA-II research was designed to answer many of the key questions of the NAPAP State-of-Science and Assessment activities. The project was described by Charles and Smol (in press^(b)). The major objectives of the PIRLA-II study are to determine the proportion of low-ANC Adirondack lakes that have become more acidic since pre-industrial times (i.e., about 1850), to quantify the ANC change that occurred, and to determine the percentage of lakes that were naturally acidic. Sediment cores from 35 of the Adirondack lakes that were included in the DDRP (Church et al. 1989) were analyzed. Because these lakes were selected statistically, estimates of historical change can be extrapolated to the population of Adirondack lakes. The "tops" (0-1 cm depth) and "bottoms" (pre-1850, usually > 30 cm) of the sediment cores have been analyzed for diatoms. Major results of PIRLA-II have been presented by Smol et al. (1990)^(c) and Sullivan et al. (1990). The comparison presented here is based on the statistically selected Adirondack lakes that were included in the DDRP and PIRLA-II studies.

2.2 PALEOLIMNOLOGY

In the absence of data from long-term chemical monitoring, inference from diatom fossil assemblages preserved in lake sediments is frequently used for evaluating historical chemical changes (Charles and Norton 1986). Diatoms

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- (a) Charles, D. F., M. W. Binford, E. T. Furlong, R. A. Hites, M. J. Mitchell, S. A. Norton, F. Oldfield, M. J. Paterson, J. P. Smol, A. J. Uutala, J. R. White, D. R. Whitehead, and R. J. Wise. "Paleoecological Investigation of Recent Lake Acidification in the Adirondack Mountains, New York. *J. Paleolimnology* (In press).
 - (b) Charles, D. F., and J. P. Smol. "The PIRLA II Project: Regional Assessment of Lake Acidification Trends". *Verh. Internat. Verein. Limnol.* (In press).
 - (c) Smol, J. P., et al. 1990. Poster Presentation. National Acid Precipitation Assessment Program. International Review, Hilton Head, South Carolina.

(Bacillariophyceae) are single-cell algae composed of siliceous valves. The fossil remains of these organisms are good indicators of past lakewater chemistry because 1) they are common, 2) many taxa have rather narrow ecological (water chemistry) tolerances, 3) the remains are well preserved in sediment, usually in very large numbers, and 4) they can be identified to the species level or below (Smol, Charles, and Whitehead 1984; Charles 1985; Charles and Norton 1986; Smol et al. 1986; Husar, Sullivan, and Charles in press^(a)).

Past lakewater chemistries are reconstructed from transfer functions derived from relationships between present chemistry and diatom remains in surficial lake-bed sediments. From these relationships, predictive equations (i.e., a model) are developed using regional lake data sets to infer water chemistry, especially pH and ANC. Calibration equations have also recently been developed for inferring concentrations of DOC, total Al (Al_t), and monomeric Al (Al_m) (Kingston and Birks 1990; Birks et al. 1990). It is assumed that quantitative relationships observed between lakewater chemistry and the distribution and abundance of diatom taxa have remained constant over time.

Trends within sediment cores can be analyzed to determine whether they are statistically significant (Birks et al. 1990). Inferred water chemistry can be dated using ^{210}Pb activity and compared with stratigraphies of other lake-sediment markers such as pollen, charcoal, coal and oil carbonaceous particles, polycyclic aromatic hydrocarbons, metals (Pb, Zn, Cu, V, Ca, Mg, Ti, Al, Si, S), and others that provide a record either of atmospheric inputs of materials associated with the combustion of fossil fuels or watershed disturbance (Charles and Norton 1986). With these data, knowledge of watershed events, and historical information on regional atmospheric emissions of sulfur and nitrogen, scientists have evaluated whether lakes have likely been affected by acidic deposition and to what extent (e.g., Husar, Sullivan, and Charles, in press^(b) and Charles et al., in press^(c)).

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- (a) Husar, R. B., T. J. Sullivan, and D. F. Charles. "Methods for Assessing Long-Term Trends in Atmospheric Deposition and Surface Water Chemistry." In *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, ed. D. F. Charles. Springer-Verlag, Inc., New York. (In press).
- (b) Husar, R. B., T. J. Sullivan, and D. F. Charles. "Methods for Assessing Long-Term Trends in Atmospheric Deposition and Surface Water Chemistry." In *Acidic Deposition and Aquatic Ecosystems: Regional Case Studies*, ed. D. F. Charles. Springer-Verlag, Inc., New York. (In press).

Diatom studies have documented the rates and magnitudes of acidification for selected lakes in the Adirondack Region (Del Prete and Schofield 1981; Charles 1984; Charles et al. 1986; Charles 1987; Charles et al. 1987; Charles et al. in press; Sullivan et al. 1990), New England (Davis et al. 1983), the Upper Midwest (Kingston et al. in press), Florida (Charles et al. 1986), Ontario (Dixit 1983; Dixit, Dixit, and Evans 1987; Dixit, Dixit, and Smol 1989a, 1989b), Sweden (Renberg and Hellberg 1982; Renberg and Wallin 1985), Finland (Tolonen and Jaakkola 1983), Norway (Davis and Anderson 1985; Davis and Berge 1980), Scotland (Flower and Battarbee 1983; Flower, Battarbee, and Appleby 1987), West Germany (Arzet, Krause-Dellin, and Steinberg 1986) and the Netherlands (van Dam et al. 1988).

In a paleolimnological study at experimentally acidified Lake 223 in the Experimental Lakes Area in Ontario, Davidson (1984) illustrated the rapid response of diatoms to changes in water chemistry. Results from the sediment core closely agreed with the plankton history measured in the water column. Similarly, paleolimnological inferences of recent changes in lakewater chemistry have been shown to correspond closely with measured pH values at three lakes near Sudbury, Ontario (Dixit, Dixit, and Evans 1987; Dixit, Dixit, and Smol 1989a, 1989b). Dixit, Dixit, and Evans (1987) reconstructed the pH of Hannah Lake, near Sudbury, using diatom remains. Between approximately 1880 and 1975, the inferred lakewater pH declined roughly from 6.0 to 4.6. After the lake was limed in 1975, its pH increased from 4.3 to 7.0, and this increase was reflected in the Diatom-inferred values (Dixit, Dixit, and Evans 1987). A recent paleolimnological investigation (Dixit, Dixit, and Smol 1989a) of acidification and subsequent recovery of Swan Lake, near Sudbury, Ontario, indicated that paleolimnological reconstructions of recent chemical change corresponded well with measured values. Also significant were the large declines in trace-metal concentrations in sediments coincident with pH recovery. Changes in metal concentrations do not pose a problem for the diatom models because the large diatom species diversity allows accurate pH reconstruction irrespective of metal concentrations. Dixit, Dixit, and Smol

(c) Charles, D. F., R. W. Battarbee, I. Renberg, H. van Dam, and J. P. Smol. "Paleoecological Analysis of Lake Acidification Trends in North America and Europe Using Diatoms and Chrysophytes." In: *Acid Precipitation*, Springer-Verlag, New York (in press).

(1989a) also used diatoms and chrysophytes to reconstruct the recovery of Baby Lake subsequent to the closure in 1972 of the nearby (1-km distance) Conistan Smelter near Sudbury. Measured lakewater pH increased from 4.2 in 1972 to 6.5 in 1987, and this recovery was closely mirrored by shifts in the diatom and chrysophyte species composition and the inferred pH.

Paleolimnology as a quantitative science has evolved extremely rapidly over the past five years, and improved techniques are often developed before previous research has appeared in the literature. Multiple linear-regression analysis of measured lakewater pH with the percentage of diatoms in each pH category has been used to develop predictive equations (Charles 1985; Huttunen and Meriläinen 1986). Other multiple-regression approaches involve using selected taxa or principal components of taxa (Davis and Anderson 1985; Gasse and Tekaiia 1983). The standard error for inferred pH ranges from 0.25 to 0.4 pH units for any of these approaches and their associated data sets (Battarbee 1984; Charles and Norton 1986). Other techniques include detrended correspondence analysis (DCA) (Huttunen and Meriläinen 1986), canonical correspondence analysis (ter Braak 1986; Stevenson et al. 1989), and a multiple regression technique using both diatoms and chrysophytes (Charles and Smol 1988). ter Braak and Van Dam (1989) developed new methods using maximum-likelihood calibration based on weighted averaging and on Gaussian logit response curves of taxa against pH. Oksanen et al. (1988) used weighted averaging, least squares, and maximum likelihood to calculate pH optima and tolerance of diatom taxa, then used these estimates to predict the pH of other lakes, using weighted averaging. Recently, Birks et al. (1990) suggested using the straightforward but heuristic approach of weighted-averaging regression and calibration as a compromise between ecological realism and computational feasibility. For the 167 lake data set in the joint British-Scandinavian Surface Water Acidification Programme (SWAP), this method actually gave superior results in terms of a lower root mean square error (RMSE) of prediction in cross validation, than did maximum likelihood Gaussian logit regression and calibration.

Diatoms are both planktonic and benthic, but the diatom flora of low-pH (< 5.5) lakes are dominated by benthic forms (Battarbee 1984; Charles 1985; Charles and Smol 1988). Although planktonic diatoms are most abundant in

spring, most littoral species are common throughout spring and summer (DeNicola 1986; Jones and Flower 1986; Charles and Smol 1988). In general, assemblages with the greatest diversity of algal remains will provide the largest amount of ecological information and the best predictive equations. Results must be interpreted with caution where equations are applied to assemblages containing only a few dominant taxa. In such cases, the inferred pH or ANC will be determined largely by the pH category or the abundance-weighted mean of the few dominant taxa. This has sometimes been a problem for highly acidic lakes. 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).

2.2.1 Methodology

During the past several years, category-based, multiple-regression techniques (based on the assignment of diatom taxa to pH categories) have been replaced by theoretically superior 'gradient analysis' techniques. The theory has been developed and summarized primarily by ter Braak (ter Braak 1985; ter Braak and Barendregt 1986; ter Braak and Looman 1986; ter Braak 1986, 1987, 1988; ter Braak and Gremmen 1987; ter Braak and Prentice 1988). Gradient-analysis theory is based on a species-packing model along environmental gradients, assuming a simple normal distribution of each species' abundance in samples along the gradient. In the regression step, curves are fitted to each taxon's distribution, and the properties of the estimated optimum, \hat{Q}_k , and estimated tolerance, \hat{t}_k , can be determined. The calibration step may be split further, into steps treating "active" samples (with associated environmental data) and "passive" samples (without associated environmental data). The algal assemblage in each active surface-sediment sample is used to obtain a single estimated value based on the optima, with or without tolerance down-weighting. The relationship between predicted and observed environmental values emerges for the entire set of active samples. In the next calibration step, that of paleolimnological reconstruction, passive samples (sediment core samples) are used to obtain predicted environmental variable values, based on their taxa having the same characteristics obtained for the "active" taxa in the regression step.

Notation and formulae for weighted averaging follow Birks et al. (1990) and Kingston (in press)^(a):

x is the environmental variable to be reconstructed,
 x_i is the value of x in sample (lake) i ,
 y_{ik} is the abundance of taxon k in sample i ($y_{ik} \geq 0$) ($i = 1 \dots n$ lakes);
 $k = 1 \dots m$ diatom (taxa), and
 \hat{x}_i is the estimated or inferred value of x for sample i .

A reasonable estimate of a taxon's pH optimum is the average of all pH values for lakes in which the taxon occurs, weighted by the taxon's relative abundance. The taxon's optimum (abundance weighted mean), \hat{u}_k , is

$$\hat{u}_k = \left[\sum_{i=1}^n y_{ik} x_i \right] / \left[\sum_{i=1}^n y_{ik} \right] \quad (2.1)$$

and a taxon's tolerance (weighted standard deviation), t_k , is

$$t_k = \left[\sum_{i=1}^n y_{ik} (x_i - \hat{u}_k)^2 \right] / \left[\sum_{i=1}^n y_{ik} \right]^{1/2} \quad (2.2)$$

The estimated optima can be used to infer an environmental variable value from a lake's diatom assemblage by

$$\hat{x}_i = \left[\sum_{k=1}^m y_{ik} \hat{u}_k \right] / \left[\sum_{k=1}^m y_{ik} \right] \quad (2.3)$$

(a) Sullivan, T. J. *Historical Changes in Surface Water Acid-Base Chemistry in Response to Acidic Deposition*, with section by Kingston, J. C., "Recent Paleolimnological Advancements," pp. 3-26 to 3-29. State of the Science, SOS/T 11, National Acid Precipitation Assessment Program (In press).

whereas a tolerance-weighted estimate would be

$$\hat{x}_i = \left[\sum_{k=1}^m y_{ik} (\hat{u}_k / t_k^2) \right] / \left[\sum_{k=1}^m y_{ik} / t_k^2 \right]. \quad (2.4)$$

Averages are taken twice, once in the regression step and once in the calibration steps. The resulting shrinkage of the environmental gradient is corrected by a linear deshinking regression. Deshrinking is discussed by ter Braak and van Dam (1989) and by Birks et al. (1990). Weighted averaging without tolerance correction has proven superior for diatom reconstructions of several environmental variables (Birks et al. 1990; Kingston and Birks 1990), whereas tolerance correction may be superior for chrysophyte data (B. F. Cumming and H. J. B. Birks, personal communication); this may be explained by the higher diversity and greater number of "zero occurrences" in the diatom data.

For the PIRLA-II Project, weighted-averaging calibration (Birks et al. 1990) was used to develop calibration equations. Seventy-one lakes were included in the drainage-lake calibrations, 20 lakes in the seepage-lake calibrations. The Diatom-inferred air-equilibrated versus measured (laboratory) pH and ANC of drainage and seepage lakes from that study are presented in Figures 2.1 and 2.2, respectively. Calibration equations were also developed for drainage lakes to infer pH and ANC from chrysophyte scales (Figure 2.3). The calibration relationships were not as strong for chrysophytes as for diatoms, but the chrysophyte data provide corroborative evidence of chemical change. The initial Diatom calibration equation was developed by Birks et al. (1990) on the basis of all (n=71) Adirondack drainage lakes > 1.5-m depth in the calibration set. A curvilinear relationship was observed, however, between inferred and measured ANC for this calibration (see Figure 2.1C). 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 $\leq 100 \mu\text{eq L}^{-1}$. This revised calibration equation produced a substantially

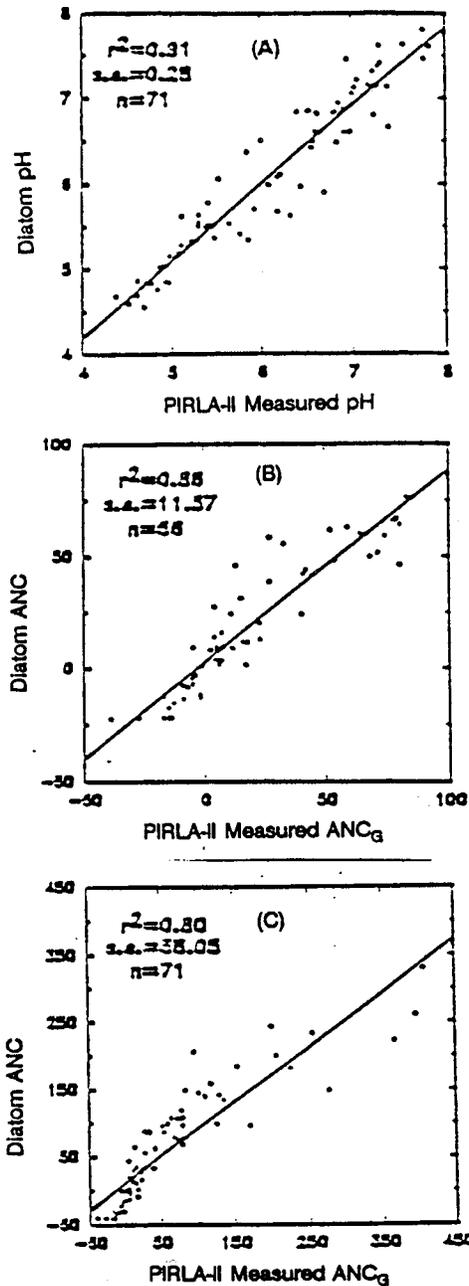


FIGURE 2.1. Calibration Relationships Developed in PIRLA-II Between Measured and Diatom-inferred Values of pH (Figure 2.1A) and ANC for Drainage Lakes in the Adirondacks (Source: S. S. Dixit, personal communication). Note that two calibration equations are presented for ANC. The relationship based on all calibration lakes ($n=71$) was used for inferring ANC of lakes having current $ANC > 100 \mu\text{eq L}^{-1}$ (Figure 2.1B). Because of nonlinearity and bias for acidic lakes, a restricted calibration was developed for low ANC ($\leq 100 \mu\text{eq L}^{-1}$) lakes (Figure 2.1C).

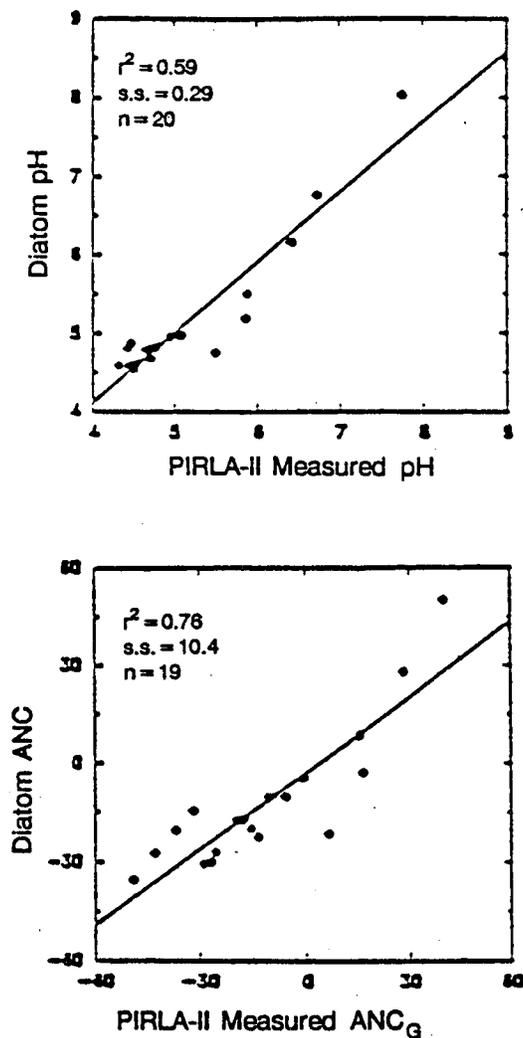


FIGURE 2.2. Calibration Relationships Between Measured and Diatom-inferred Values of pH and ANC for Seepage Lakes in the Adirondacks (Source: S. S. Dixit, personal communication).

reduced standard error for ANC predictions for the low-ANC lakes, from 38 to 12 $\mu\text{eq L}^{-1}$ (see Figure 2.1B). This revised ANC equation was used in the present study to infer current and pre-industrial ANC for the low-ANC ($\leq 100 \mu\text{eq L}^{-1}$) drainage lakes, whereas the full-range calibration was used for inferring ANC of the five high-ANC lakes. For the most acidic lakes in the data set (ANC < about $-20 \mu\text{eq L}^{-1}$), the ANC low-range inference equation had little discriminatory ability (Figure 2.1).

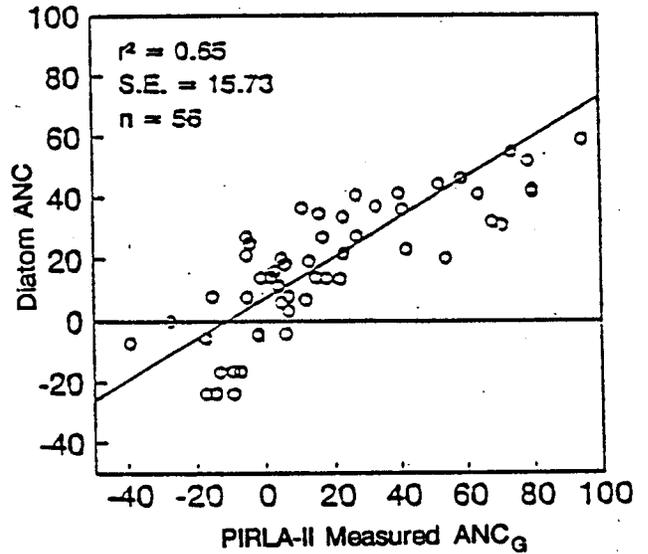
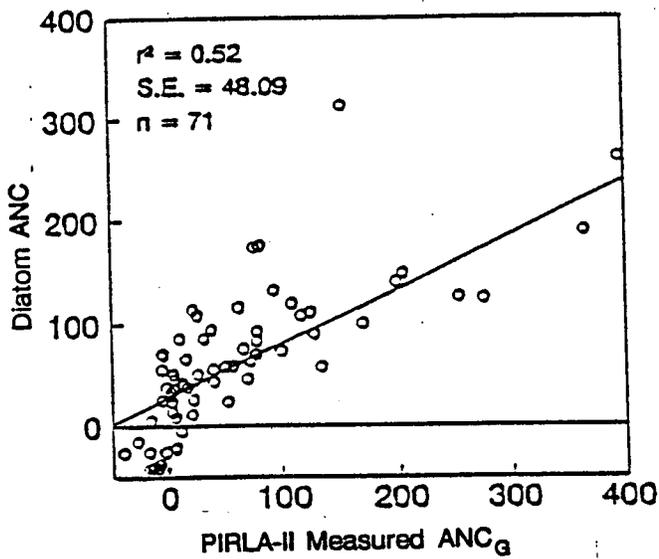
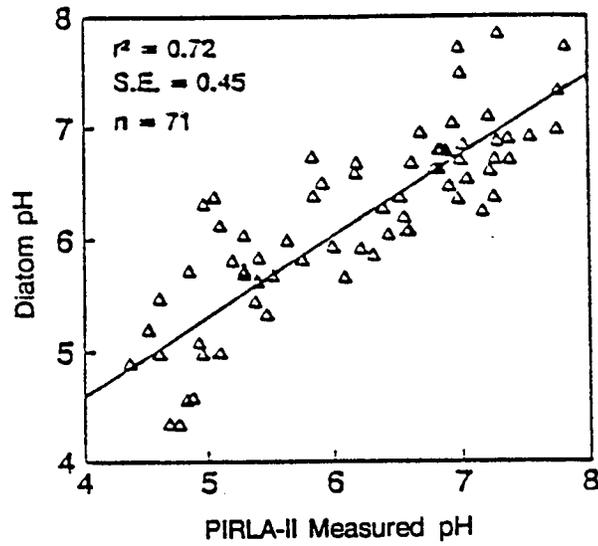


FIGURE 2.3. Calibration Relationships Between Measured and Chrysophyte-inferred pH and ANC for Drainage Lakes in the Adirondack Subregion (Source: B. F. Cumming, manuscript in preparation)

2.2.2 Error Evaluation

The greatest advances in estimating error in paleolimnological reconstructions have come from recent research within the Surface Water Acidification Programme (Birks et al. 1990) and PIRLA-II. The root mean square error (RMSE) is used to compare the predictive abilities of various techniques (Birks et al. 1990). This RMSE is the "apparent error" for a calibration training set and always underestimates "true error" (Oksanen et al. 1988; ter Braak and van Dam 1989). Better estimates of RMSE are obtained by cross-validation, splitting the data into a training set and a test set. This procedure has the undesired effect, however, of decreasing the number of lakes in the calibration. Maximizing the number of lakes in the calibration set is desirable to assure the maximum probability of surface analogs for down-core passive samples.

Error estimates for the PIRLA-II project have been obtained by using bootstrapping, a computer-intensive resampling procedure (Efron 1983; Birks et al. 1990). In bootstrapping, a subset of training samples the same size as the original training set is selected at random with replacement, and the remaining unselected samples are used as a test set. After a large number of bootstrap cycles (e.g., 1000), one obtains a new boot RMSE which is less subject to bias because it uses a larger training set. Another advantage, essential for comparisons with watershed acidification models, is that unique error estimates are obtained for the predicted pH or ANC from each fossil sample. This was not possible before bootstrapping. Furthermore, the bootstrap error can be split into s_{i1} , an estimate of prediction error unique for each sample (bias), and s_2 , a constant error for the entire data set that represents variability (Birks et al. 1990; H. J. B. Birks, personal communication). Note that s_{i1} will become smaller as the training set gets larger, so that it will decrease in the larger PIRLA-II Adirondack data sets. For sediment core samples, the errors down-core are expected to increase above the errors for surface samples if the sampled assemblages diverge from the floristic composition of surface analogs. These errors can be greatly affected by data screening. The removal of outlier samples from the calibration can greatly improve performance of the relationships (Birks et al. 1990). Bootstrap-estimated errors for Diatom-inferred ANC_0 are presented in Figure 2.4.

2.3 MAGIC

The Model of Acidification of Groundwater in Catchments (MAGIC) is a lumped-parameter model of intermediate complexity that was developed to predict the long-term (i.e., decades to centuries) effects of acidic deposition on surface-water chemistry. One of the model's principal assumptions is that a minimum number of critical processes in a watershed influence the long-term response to acidic deposition (Cosby et al. 1985a, 1985b). The MAGIC formulation was parsimonious in the processes selected for inclusion and was intended to be used as a heuristic tool for understanding the influences of the selected processes on surface water acidification. The spatial/temporal scales in the model reflect its intended use in assessment and multiscenario evaluations.

MAGIC represents the horizontal dimension of the watershed as a homogeneous unit with no subcatchments and the vertical dimension as two soil layers. Watershed data for MAGIC (Tables 2.3 and 2.4) were lumped or aggregated to provide average or weighted-average values for each of the soil layers. The top soil compartment represented the mass-weighted-average conditions of the A and B horizons. The lower soil compartment represented the mass-weighted average conditions in the C horizon. Hydrologic flow of water through soil layers to the receiving system is simulated using a separate hydrologic model, TOPMODEL (Hornberger, Cosby, and Galloway 1986). TOPMODEL is a topography-based, variable contributing area, catchment model adapted from the version of Beven and Kirkby (1979). The model considers overland flow, macropore flow, drainage from the upper zone to the lower zone and to the stream, and base flow from the lower zone. Forecasting long-term effects of acidic deposition on surface water chemistry using MAGIC involves coupling MAGIC with TOPMODEL (Cosby et al. 1985a, 1985b, 1985c). Note that the DDRP analyses were constrained by a set of assumptions (Table 2.5) (Church et al. 1989).

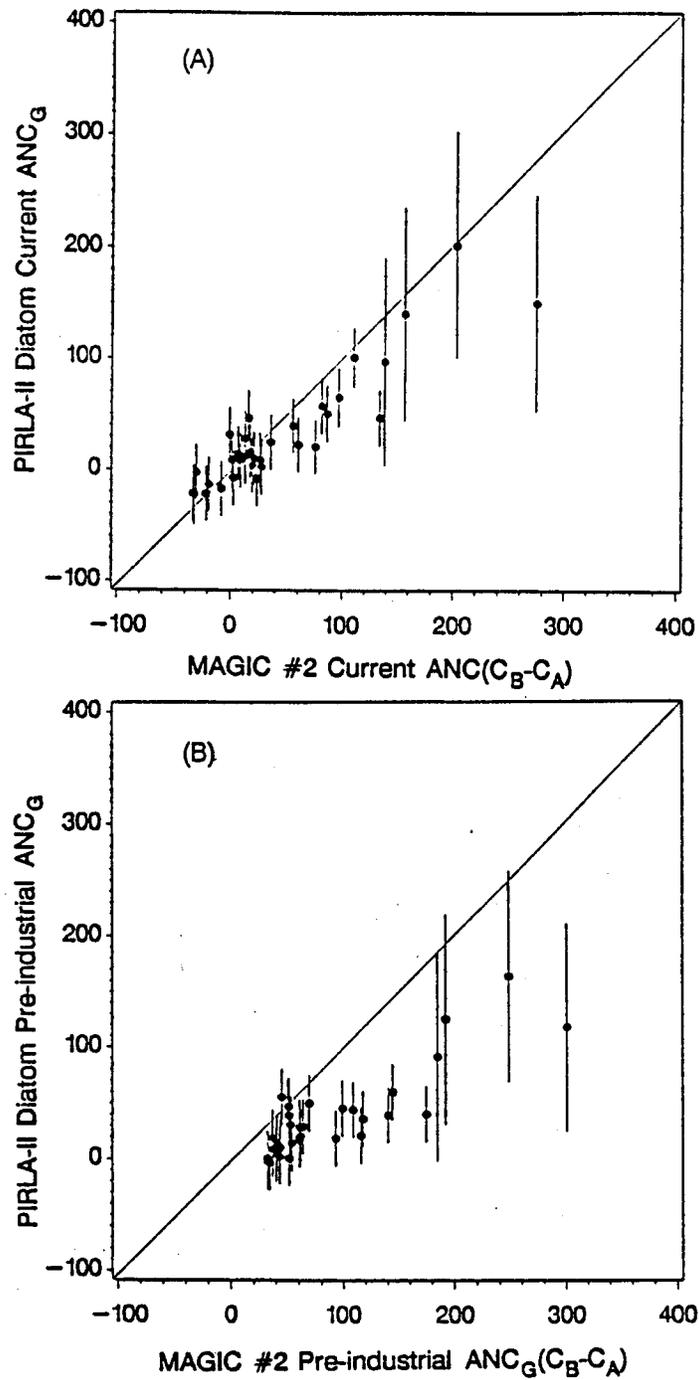


FIGURE 2.4. Plot of Diatom-inferred ANC_G Versus the MAGIC Scenario #2 Estimate of $ANC(C_B-C_A)$, with Error Estimates Placed on the Diatom-inferred Estimates. The error estimates reflect a 90% confidence interval from the bootstrapping procedure. Current chemistry is presented in (A) and pre-industrial chemistry in (B).

TABLE 2.3. Fixed Parameters Used in MAGIC

Parameter Name	Description
DEP1	Depth, soil layer 1, meters
POR1	Porosity, soil layer 1, fraction
BD1	Bulk density, soil layer 1, kg m ³
CEC1	Cation exchange capacity, soil layer 1, meq kg ⁻¹
EMX1	Maximum sulfate adsorption capacity, soil layer 1, meq kg ⁻¹
C1	Sulfate adsorption half saturation, soil layer 1, μeq L ⁻¹
K1 _{AL}	Apparent aluminum solubility product, (log ₁₀) soil layer 1
DEP2	Depth, soil layer 2, meters
POR2	Porosity, soil layer 2, fraction
BD2	Bulk density, soil layer 2, kg/m ³
CEC2	Cation exchange capacity, soil layer 2, meq kg ⁻¹
EMX2	Maximum sulfate adsorption capacity, soil layer 2, meq kg ⁻¹
C2	Sulfate adsorption half saturation, soil layer 2, μeq L ⁻¹
K2 _{AL}	Apparent aluminum solubility product, (log ₁₀) soil layer 2
RA	Lake-area to catchment-area ratio, fraction
QS	Discharge per unit area of catchment, m ³ yr ⁻¹
FR1	Overland-flow fraction (routing), percent
FR2	Macropore-flow fraction (routing), percent
FR3	Interflow-fraction (routing), percent
USOL	Sulfate uptake rate (reduction), lake, meq m ⁻² yr ⁻¹
KL _{AL}	Apparent aluminum solubility product (log ₁₀) lake

The meteorological and deposition input requirements for MAGIC are shown in Tables 2.6 and 2.7. The model uses equilibrium and rate-controlled expressions to represent geochemical processes to simulate both soil solution and surface water chemistry. Mass balances for the major cations and anions and the effects of aqueous Al and organic acid species on ANC are incorporated in the model. These processes are listed in Table 2.8. Annual output is the

TABLE 2.4. Adjustable Parameters Used in MAGIC

Parameter Name	Description
WECACa	Weathering rate, $\text{meq m}^{-2} \text{ yr}^{-1}$
WEMGMg	Weathering rate, $\text{meq m}^{-2} \text{ yr}^{-1}$
WENA	Na^+ weathering rate, $\text{meq m}^{-2} \text{ yr}^{-1}$
WEK	K^+ weathering rate, $\text{meq m}^{-2} \text{ yr}^{-1}$
EC01	Initial Ca^{2+} base saturation, soil layer 1, percent
EM01	Initial Mg^{2+} base saturation, soil layer 1, percent
EN01	Initial Na^+ base saturation, soil layer 1, percent
EK01	Initial K^+ base saturation, soil layer 1, percent
UN01	Initial NO_3^- base saturation, soil layer 1, percent
UNH1	Initial NH_4^+ base saturation, soil layer 1, percent
EC02	Initial Ca^{2+} base saturation, soil layer 2, percent
EM02	Initial Mg^{2+} base saturation, soil layer 2, percent
EN02	Initial Na^+ base saturation, soil layer 2, percent
EK02	Initial K^+ base saturation, soil layer 2, percent
UN02	NO_3^- uptake rate (biological), soil layer 2, yr^{-1}
UNH2	NH_4^+ uptake rate (biological), soil layer 2, yr^{-1}
UNOL	NO_3^- uptake rate (biological), lake, yr^{-1}
UNHL	NH_4^+ uptake rate (biological), lake, yr^{-1}

**TABLE 2.5. Operational Assumptions for MAGIC Modeling
(Modified from Church et al. 1989)**

1. Index soil data from the DDRP Soil Survey adequately characterize geochemical watershed attributes influencing surface-water chemistry.
2. Chemistry of a fall water sample, from ELS-1, provides an index of chronically acidic systems and systems with low ANC that are susceptible to acidic deposition.
3. Only geochemical and hydrologic processes need to be considered in MAGIC modeling.
4. The major geochemical processes are known well enough to be incorporated in MAGIC and used for hindcasting.
5. Sulfur is assumed to be the primary acidifying agent in acidic deposition causing surface-water acidification and sulfur deposition over the last century can be estimated.
6. The watershed processes controlling the effects of sulfur deposition on surface-waters are sulfate adsorption and desorption, base cation depletion and resupply through mineral weathering and exchange, and in-lake uptake (i.e., reduction to sulfide).
7. Hindcasts of historical acidification consider chronic, but not episodic, acidification.
8. Acidification is reversible and the geochemical processes in MAGIC are adequate to describe both geochemical acidification and recovery.
9. Current watershed attributes and conditions (e.g., basin characteristics, climate) have remained relatively constant over the last century and do not influence the results of the hindcasts whereas land use is known to have changed and the magnitude of its effects must be evaluated.
10. The effects of organic acids on acid-base chemistry are constant through time and independent of sulfate.
11. Base cation deposition has not changed significantly since pre-industrial times.
12. "Typical" year precipitation and deposition projections are not intended to predict future water chemistry but rather to provide a common basis for comparisons among deposition scenarios to assess potential changes in surface-water chemistry.
13. Uncertainty calculations provide estimates of relative error for long-term comparisons among models and deposition scenarios but do not estimate absolute error.
14. Lake waters are in equilibrium with aluminum hydroxide.
15. Other than paleolimnological models, dynamic process-based watershed models such as MAGIC, are the only feasible approach for evaluating the long-term effects of sulfur deposition on surface-water chemistry.

TABLE 2.6. Meteorological Data Required by the MAGIC/TOPMODEL Code
(Source: Jenne et al. 1989)

<u>Meteorological Data</u>	<u>Units</u>
Interval for data measurement	Monthly, ^(a) yearly
Precipitation	m
Minimum air temperature	°C
Maximum air temperature	°C
Mean daylight hours	%

(a) TOPMODEL runs with a daily time step.

TABLE 2.7. Chemical Constituents in Wet and Dry Deposition Considered
by the MAGIC Model^(a) (Source: Jenne et al. 1989)

<u>Constituent</u>	<u>MAGIC</u>	
	<u>Wet</u>	<u>Dry^(b)</u>
SO _x (g)	--	(X) ^(c)
NO _x (g)	--	(X) ^(c)
Ca ²⁺	X	X
Mg ²⁺	X	X
K ⁺	X	X
Na ⁺	X	X
NH ₄ ⁺	X	X
SO ₄ ²⁻	X	X
NO ₃ ⁻	X	X
Cl ⁻	X	X
F ⁻	X	X

- (a) Units are for monthly or yearly average.
 (b) The MAGIC code requires that dry deposition be expressed by means of a dry deposition factor.
 (c) SO_x(g) and NO_x(g) are implicitly included by means of the dry deposition factor.

TABLE 2.8. Major Processes Incorporated in the Combined MAGIC/TOPMODEL Code (Jenne et al. 1989)

<u>Processes</u>	<u>MAGIC/TOPMODEL (a)</u>
<u>Atmospheric Processes</u>	
- Dry deposition	X
- Wet deposition	X
<u>Hydrological Processes</u>	
- Evapotranspiration	X
- Interception storage	(X) (b)
- Snowmelt	X
- Overland flow	X
- Macropore flow	X
- Unsaturated subsurface flow	X
- Saturated subsurface flow	X
- Stream flow	X
<u>Geochemical Processes</u>	
- Carbonic acid chemistry	X
- Aluminum chemistry	X
- Organic acid chemistry	X
- Weathering	X
- Anion Retention	X
- Cation exchange	X
<u>Biogeochemical Processes</u>	
- SO ₄ ²⁻ reduction in lake	(X) (c)
- Nitrification in soil	(X) (c)
- Nutrient uptake	(X) (c)
- Canopy interactions	(X) (b)
- Litter decay	(X) (b)
- Root respiration	(X) (b)

- (a) Parentheses indicate limited treatment of process.
- (b) Canopy interactions and root decay and respiration are implicitly included in the MAGIC code by use of dry deposition factor and by designation of CO₂ partial pressure in soils and surface-waters.
- (c) Sulfate reduction, nitrification, and uptake of ions can be simulated with the MAGIC code by specifying uptake rates of SO₄ and NH₄ for various hydrologic compartments.

typical temporal resolution of the model, but monthly output also can be obtained for the constituents listed in Table 2.9. MAGIC does not use a Gran ANC in simulating watershed response. Rather, it uses two definitions of ANC as follows:

$$\text{ANC}_{\text{ALK}} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{HR}^{''-}] + 2[\text{R}^{''2-}] + [\text{Al}(\text{OH})_4^-] - [\text{H}^+] - 3[\text{Al}^{3+}] - 2[\text{Al}(\text{OH})^{2+}] - [\text{Al}(\text{OH})^+]$$
(2.5)

$$\text{ANC}_{\text{CALK}} = \text{SBC} + \text{NH}_4^+ - \text{SSA} = C_B - C_A$$
(2.6)

where $\text{SBC} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+]$, $\text{SSA} = [\text{Cl}^-] + [\text{NO}_3^-] + [\text{SO}_4^{2-}]$, $\text{R}^{''2-}$ is a doubly charged organic ligand, and all units are microequivalents per liter ($\mu\text{eq L}^{-1}$). Equation (2.6), referred to as charge balance ANC, is identical to calculated $\text{ANC}(C_B - C_A)$ as used in this report, unless stated otherwise.

2.3.1 Calibration

Calibration of MAGIC involves selecting a set of initial parameter values that, in conjunction with estimated precipitation and deposition, yield a trajectory from 1844 through a "window" about the 1984 measured lake chemistry values. The hindcast pre-industrial lakewater chemistry used here is the mean of those runs with initial conditions that resulted in a trajectory that passed through a specified window for 1984 chemistry. The calibration exercise was a three-step process. The first step was to specify the model inputs such as precipitation, deposition (both wet and dry), an estimate of historical inputs for the long-term model, and fixed parameters whose values correspond directly to (or can be computed directly from) field measurements, e.g., topographic variables such as slope, aspect, and area. This approach, in effect, assigns all of the uncertainty associated with sampling, aggregation, and intrinsic spatial variability to the "adjustable" parameters. The adjustable parameters are those that are calibrated or scaled to match observed field measurements.

TABLE 2.9. Aqueous Chemical Constituents Included in the MAGIC Code
(Source: Jenne et al. 1989)

ANC	Ca ²⁺	Mg ²⁺
K ⁺	Na ⁺	NH ₄ ⁺
H ⁺	Al ³⁺	Al(OH) _n ³⁻ⁿ (n=1 to 4)
Al(F) _n ³⁻ⁿ (n=1 to 6)	Al(SO ₄) _n ³⁻ⁿ (n=1 to 2)	SO ₄ ²⁻
NO ₃ ⁻	Cl ⁻	F ⁻
CO ₂ (g)	CO ₂ (aq)	H ₂ CO ₃ (aq)
HCO ₃ ⁻	CO ₃ ²⁻	R ²⁻

The second step was to select optimal values for the adjustable parameters, optimizing both MAGIC and TOPMODEL using the method of Rosenbrock (1960). Optimal values were determined by minimizing a loss function defined by the sum of squared errors between simulated and observed values of system state variables. Different loss functions were used for the hydrologic and chemical models. The loss function for the hydrological model was based on measured monthly catchment discharge values. The loss function for the MAGIC model was based on surface water concentrations of Ca²⁺, Mg²⁺, Na⁺, K⁺, SO₄²⁻, Cl⁻, NO₃⁻, NH₄⁺, and F⁻ (taken from the ELS-I fall lake chemistry), and soil exchange fractions of Ca²⁺, Mg²⁺, Na⁺, and K⁺ for the upper and lower soil layers (aggregated by ORNL from DDRP soil survey data).

The final step was to assess 1) the structural adequacy of the model to reproduce the observed behavior of the measured variables and 2) parameter identifiability or the uniqueness of the set of optimized parameters. Structural adequacy was assessed by examining the mean error in simulated values of observed state variables for those variables used in the calibration procedure as well as for an additional state variable not used during calibration. Parameter identifiability was assessed using approximate estimation-error variances for the optimized parameters (Bard 1974). Additional information on the MAGIC calibration process was presented by Cosby, Hornberger, and Wright (1989).

Atmospheric deposition data, supplied by Pacific Northwest Laboratory (PNL), was assumed to be uniform over the individual catchments. Atmospheric

fluxes in the code are calculated from concentrations of the ions in precipitation and from estimated rainfall volume interpolated to each catchment (Church et al. 1989). The wet-deposition data and annual-precipitation volume provided for each DDRP catchment were used to calculate annual average concentrations for each ion in precipitation. Dry deposition of particulates and aerosols was represented as a fraction of wet deposition by a dry-deposition factor, calculated for each mass-balance ion for each catchment (Church et al. 1989).

Discharge data, provided by the Environmental Research Laboratory of EPA (EPA/CERL) for each catchment, was obtained by interpolation from U.S. Geological Survey discharge maps. Relative lake area was determined from data on terrestrial and lake areas provided by EPA/CERL.

Depth, bulk density, cation-exchange capacity, maximum sulfate-adsorption capacity, and the sulfate-adsorption half-saturation constant were from the DDRP data set (EPA/CERL). Oak Ridge National Laboratory (ORNL) aggregated parameters of the A and B soil horizons for MAGIC Layer 1 and those of the C soil horizon for MAGIC Layer 2. The depth used for the soil Layer 2 was derived as one of two possible values in the data base. If the depth to bedrock (DTBR) was less than the sum of the layer depths (DEP1 + DEP2, provided in the soils data base), then the aggregated depth (DEP2) was used for the lower soil layer in MAGIC. If, however, DTBR was greater than DEP1+DEP2, the depth of the lower soil layer was redefined as $DEP2 = DTBR - DEP1$. This procedure assured that a conservative (large) total soil depth was used when ambiguity in the data existed. Soil-layer depths were not corrected for coarse-fragment content in the initial DDRP aggregations, but this correction was made for the MAGIC Scenario #4 (see Section 2.4.5). Porosity was calculated from the bulk-density measurement for each layer, assuming a specific gravity for the soil particles of 2.65 g cm^{-3} .

Soil temperatures were not provided in the DDRP data sets, but daily air temperatures for each catchment were provided. Mean annual soil temperatures were derived from the daily air-temperature data by 1) setting all daily values that were less than -1.5°C to be equal to -1.5°C ; 2) calculating the mean annual air temperature from the modified daily values; and 3) setting the

mean annual soil temperature equal to the modified mean annual air temperature. This procedure was tested by applying it to data from Soil Conservation Service sites for which mean annual air and soil temperatures were both available (Smith et al. 1964). The procedure was found to produce unbiased estimates of soil temperatures. The same soil temperature was used for both soil layers. Mean annual surface-water temperature was assumed to be equal to the mean annual soil temperature.

Cosby et al. (1986) have demonstrated that the calibration of MAGIC is sensitive to the value of soil pCO_2 but soil pCO_2 measurements were not provided in the DDRP data sets. Soil pCO_2 was estimated from a regression on soil temperature constructed from mean growing-season soil pCO_2 data from 19 regions of the world (Brook, Polkoff, and Box 1983):

$$\log_{10}(pCO_2) = 0.03 T - 2.48 \quad (2.7)$$

where pCO_2 is in atmospheres and T is the soil temperature in $^{\circ}C$. Using this expression, a mean annual soil temperature of $10^{\circ}C$ would produce a soil pCO_2 of 0.0066 atm. (approximately 20 times atmospheric pCO_2). However, some of the catchments could not be calibrated using a pCO_2 value derived from the relationship in Equation (2.7). For those catchments, which tend to be in the lower pH range, the pCO_2 was increased by a factor of 10 from the value derived from Equation (2.7). Insufficient primary data on soil partial-pressure of CO_2 exist to evaluate the error in either approach. However, Schecher and Driscoll (1988) noted that the carbonate alkalinity of RILWAS lakes in the Adirondack Region was frequently greater than the value calculated for equilibria with the pCO_2 in the atmosphere.

Because surface-water pCO_2 values were also unavailable, the surface-water chemistry data were used to estimate values of surface-water pCO_2 . Assuming that all titrated ANC results from carbonate buffering, an expression for pCO_2 as a function of surface-water ANC and pH can be derived from the equilibrium equations for the dissociation of inorganic carbon and the dissociation of water, i.e.,

$$ANC = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]. \quad (2.8)$$

Substituting into the equilibrium equations, and solving for $p\text{CO}_2$ yields

$$p\text{CO}_2 = \frac{10^{(-3\text{pH})} + (\text{ANC})10^{(-2\text{pH})} - a_1 10^{(-\text{pH})}}{a_2 10^{(-\text{pH})} + 2a_3} \quad (2.9)$$

where ANC is in equivalents per liter, and the constants a_1 , a_2 , a_3 are functions of thermodynamic equilibrium constants for the dissociation of water, the reaction of CO_2 with water and subsequent deprotonation:

$$a_1 = K_w, \quad a_2 = K1_{\text{CO}_2} K2_{\text{CO}_2}, \quad a_3 = K1_{\text{CO}_2} K2_{\text{CO}_2} K3_{\text{CO}_2}.$$

Equation (2.9) was solved using the measured values of ANC and closed-head-space pH. The mean over all catchments was 0.00066 atmospheres (twice atmospheric $p\text{CO}_2$). This value was lower than the soil $p\text{CO}_2$ values calculated from soil temperature. The use of the mean surface water of $p\text{CO}_2$ values for all catchments removes any bias due to a lack of precision of measurement for individual lakes. However, the results are biased for those lakes wherein Al and DOC contribute significantly to ANC. The results may also be biased by the assumption of equilibrium between lake water and $\text{Al}(\text{OH})_3(\text{s})$.

Apparent Al-hydroxide solubility products for both soil layers ($K1_{\text{Al}}$, $K2_{\text{Al}}$), given as negative logarithms (base 10), were assumed to be equal to 9.05 at 25 C for both soil layers for all catchments. The assumed value represents a solid phase of $\text{Al}(\text{OH})_3$ intermediate in solubility between natural and synthetic gibbsite (see Cosby et al. 1985b). The apparent Al-hydroxide solubility product for surface-waters ($K0_{\text{Al}}$) was estimated from an analysis of surface-water pH and Al concentrations provided in the DDRP lake index data base for the northeast. If the complexation reactions of Al with F^- , SO_4^{2-} and dissolved organic carbon are disregarded, total monomeric Al (Al_m) can be defined as:

$$\text{Al}_m = [\text{Al}^{3+}] + [\text{Al}(\text{OH})^{2+}] + [\text{Al}(\text{OH})_2^+] + [\text{Al}(\text{OH})_3^0] + [\text{Al}(\text{OH})_4^-]. \quad (2.10)$$

An equilibrium expression for Al_{\square} as a function of pH, Al-hydroxide solubility product and the thermodynamic constants for Al-hydrolysis species is given by

$$Al_{\square} = K_{O_{Al}} [10^{(-3pH)} + 10^{(a1-2pH)} + 10^{(a2-pH)} + 10^{(a3)} + 10^{(a4+pH)}] \quad (2.11)$$

where a_1 , a_2 , a_3 , and a_4 are the thermodynamic constants for $K_{1_{Al}}$, $K_{2_{Al}}$, $K_{3_{Al}}$, and $K_{4_{Al}}$, respectively [see Equation (2.9)], and equilibrium between the lake water and Al-hydroxide is assumed.

Given the measurements of closed-head-space pH and total inorganic Al (Al_{\square}), assumed to be equal to Al_{\square} , Equation (2.12) was solved for an Al-hydroxide apparent solubility value ($K_{O_{Al}}$) for each lake. The values of $K_{O_{Al}}$ thus derived for each catchment were arithmetically averaged over all catchments to obtain a regional mean value of 8.06 which was used for all of the northeastern catchments. The use of the mean value for all catchments results in an unbiased estimate of surface-water Al-hydroxide solubility value over the group of catchments as a whole, assuming equilibrium between the lake waters and an Al-hydroxide.

Significant amounts of sulfur can be retained in lakes through dissimilatory reduction of SO_4^{2-} , with H_2S , ester sulfates, or metal sulfides being produced as end products (Rudd, Kelly, and Furutani 1986; Brezonik, Baker, and Perry 1987). Sulfate uptake in the lake sediments was calculated from the Baker and Brezonik (1988) model of lake sulfate retention using hydraulic resident time calculated from lake-area to catchment-area ratio and unit area discharge (see Table 2.3). Reduction rates for $[SO_4^{2-}]$ are approximately first order at concentrations typically encountered in these soft-water lakes. In-lake reduction rates are apparently limited by diffusion into the sediments (Baker, Brezonik, and Pollman 1986; Kelly et al. 1987). Baker, Brezonik, and Pollman (1986) and Kelly et al. (1987) showed that this process can be represented effectively by the following:

$$\% SO_4 \text{ retained} = \frac{100 k_{SO_4}}{(Z/t_w) + k_{SO_4}} \quad (2.12)$$

where k_{SO_4} = sulfate mass-transfer coefficient ($m\ yr^{-1}$)
 Z = mean lake depth (m)
 t_w = hydraulic residence time (yr) (outflow based).

The DDRP modeling of watersheds in the Northeast (Cosby et al. 1989) employed the in-lake sulfate reduction model and used an average k_{SO_4} value of 0.52 which compares with average sulfate mass-transfer coefficients computed by Baker, Brezonik, and Pollman (1986) and Kelly et al. (1987) of 0.54 and 0.46 $m\ yr^{-1}$, respectively. Although sulfur retention can be very high in seepage systems and other lakes with long residence times (Lin and Schnoor 1986; Schindler et al. 1986; Baker, Pollman, and Eilers 1988), computations of in-lake alkalinity generation indicated that the drainage lakes in ELS-I subregion 1A (the Adirondack region) have a median SO_4^{2-} retention of 2.8%. Only approximately 8% of these lakes exhibit sulfur retention > 10% (Shaffer and Church 1989). This low sulfur retention for drainage lakes in the Adirondack region is attributed to their short hydraulic-retention times, which, based on data from Linthurst et al. (1986) and Kanciruk et al. (1986), average 0.23 yr for the estimated population of 1091 drainage lakes.

Biological uptake of NO_3^- and NH_4^+ were simulated as first-order rate processes. That is, the uptake parameters were considered to be rate constants that represent the fraction of nitrogen input to a layer taken up per unit time (units = yr^{-1}). These parameters were calibrated by selecting values for the rate constants that produced the correct surface-water concentrations. Calibration of the weathering fluxes and specification of the initial saturation of the exchange sites with individual base cations (a fixed parameter) specifies the selectivity coefficients for the base cations. These selectivity coefficients (Table 2.10) are calibrated parameters of the model. Weathering was calibrated per unit-area of catchment, i.e., as a flux. Weathering products were distributed between the two soil layers using a weighting scheme based on the total mass of soil per unit area in each layer (the product of depth and bulk density for each layer). Weathering fluxes and selectivity coefficients were chosen in the calibration procedure such that the individual base saturations and the surface-water base-cation concentrations simulated for 1984 matched those provided in the DDRP data base.

TABLE 2.10. Selectivity Coefficients Used in the Calibration of MAGIC (All Log Base 10)

<u>Selectivity Coefficient</u>	<u>Description</u>
SALCA1	Ca/Al selectivity coefficient, soil-layer 1
SALMG1	Mg/Al selectivity coefficient, soil-layer 1
SALNA1	Na/Al selectivity coefficient, soil-layer 1
SALK1	K/Al selectivity coefficient, soil-layer 1
SALCA2	Ca/Al selectivity coefficient, soil-layer 2
SALMG2	Mg/Al selectivity coefficient, soil-layer 2
SALNA2	Na/Al selectivity coefficient, soil-layer 2
SALK2	K/Al selectivity coefficient, soil-layer 2

Results from MAGIC for three lakes in the Northeast have previously been compared with results from ILWAS, another process-based model used in the DDRP (Eary et al. 1989; Jenne et al. 1989). The outputs (discharge and concentrations of cations, anions, Al and H⁺) compared favorably with the observed standard error for the study sites. The similarities in calibration/confirmation RMSEs for MAGIC indicate that parameter values for all processes can be constrained by watershed and lake attributes to achieve calibration within the range of observed values. However, for a few watersheds, no acceptable calibration of MAGIC was obtained, while in others fewer than 10 acceptable calibrations were obtained by the automatic optimization procedure. MAGIC modeling conducted within both DDRP and the present study did not consider potential organic acid influence on acid-base chemistry. Limited sensitivity analyses were subsequently performed to evaluate the potential extent to which this omission may explain discrepancies between Diatom and MAGIC model results, and the results are presented in the Appendix.

2.3.2 Error Evaluation

Because the measurements of the fixed parameters and the target variables used in the calibration procedure are subject to errors, a "fuzzy" optimization procedure was implemented for calibrating MAGIC. The "fuzzy" calibration procedure provided estimates for uncertainty widths for simulated variables; that is, the values represented the width of the interval containing equally viable simulated variable values. The fuzzy optimization procedure consisted

of multiple calibrations of each catchment using perturbations of the values of the fixed parameters. All successful calibrations for a site fall within the ranges specified by the output uncertainty width. The size of the perturbations was based on known measurement errors for the fixed parameters (error estimates provided for the DDRP aggregated-soils data base). Each of the multiple calibrations began with 1) a random selection of perturbed values of fixed parameters and 2) a random selection of the starting values of the adjustable parameters. The adjustable parameters were then optimized using the Rosenbrock algorithm to achieve a minimum error-fit to the target variables. This procedure was undertaken 10 times at each site. The final calibrated model is represented by the median parameter values and median variable values of the successful calibrations, and the (maximum-minimum) values of the multiple simulations were taken as the uncertainty estimates. An average of more than eight successful calibrations was achieved for the DDRP sites. All catchments had at least three successful calibrations.

Using the fuzzy optimization based on multiple calibrations, uncertainty bands for the model simulations can be presented as maximum and minimum values for output variables in any year derived from the group of successful calibrations. These uncertainty bands encompass the range of variable values that were simulated, given the specified uncertainty in the parameter values and measured target variables. The difference between maximum and minimum simulated values derived from the multiple optimizations defines an uncertainty width around the simulated value arising from parametric uncertainty. Using this procedure, a measure of parametric uncertainty for each variable of interest for each of the catchments was derived. These uncertainty widths are available for all years simulated for each catchment. The uncertainty widths are smallest for the calibration year (when the measured data are available). The uncertainty widths for each variable for each catchment increase as the simulations move away from the calibration year; that is, the uncertainty estimates are nonstationary. The uncertainty widths for a given variable in a given year are different for different catchments.

2.4 COMPARISON AND COMPLICATING FACTORS

The three separate intercomparisons used to evaluate the estimates of historical acidification obtained from the Diatom and MAGIC models are estimates of current chemistry, pre-industrial chemistry, and change from pre-industrial to present chemistry. Prior to presenting these comparisons, however, we first establish the comparability of the data used, the ANC definitions, the deposition assumptions, and the region definition. Differences in the manner in which observational data are treated that potentially can introduce bias into the comparison include:

1. **Watershed Disturbance and/or Land Use** - A number of factors, other than acid deposition, particularly those related to disturbance and land use, can influence surface water acid/base status. The dynamic models are not constructed to estimate changes associated with these complicating factors. In contrast, the Diatom model provides estimates of the actual water chemistry and net changes, irrespective of the causes of change. For example, if a given watershed had experienced a loss of $10 \mu\text{eq L}^{-1}$ of ANC in response to acid deposition, and in addition had either gained or lost $15 \mu\text{eq L}^{-1}$ of ANC because of watershed disturbance, the results for paleolimnological versus MAGIC evaluation would be quite different. The former would provide an estimate of the net change in ANC, whereas the latter would provide an estimate of the change associated with acid deposition only, because the model is driven by estimated deposition.
2. **Lake Chemistry Seasonality** - The Diatom model was originally calibrated to average summer lakewater chemistry (air-equilibrated pH; PIRLA-I and -II), whereas the MAGIC model was calibrated to ELS-I fall index chemistry (closed-system pH). Seasonal differences between summer and fall may bias the results.
3. **ANC Definition** - The ANC calculated by MAGIC is a defined $\text{ANC}(C_B - C_A)$ (see Equation [6]), whereas the Diatom estimates of ANC were calibrated to titrated ANC (ANC_0) in the PIRLA study. Unfortunately, ANC_0 and defined $\text{ANC}(C_B - C_A)$ often differ for low-ANC waters, largely due to the influence of aqueous Al and organic acids (Sullivan et al. 1989).
4. **Deposition Assumptions** - Hindcasting pre-industrial surface water chemistry, using a process-based model such as MAGIC, has different requirements than projecting into the future because a single accurate estimate of pre-industrial chemistry is needed. A primary limitation on the reliability of hindcasts is the limited quality of the data available to estimate pre-industrial SO_4^{2-} and base cation-deposition. This uncertainty could have an appreciable effect on the accuracy of the modeled chemistry.

5. Reaggregation of Subregional Soil Data - Scenario #1 of the MAGIC model simulations (Table 2.11) was conducted as part of the DDRP, which was designed to make regional, rather than subregional, projections. Estimates of soil-chemistry data input to MAGIC for Adirondack lake/watershed systems were based on an aggregation of sampled soil classes across the 145 DDRP watersheds in the north-eastern United States. Differences between soil chemistry in the Adirondack subregion and the general soil-chemistry patterns observed throughout the region could bias the simulations for the Adirondack subregion.

Potential bias introduced from any or all of the five issues discussed above complicates a direct comparison between Diatom and MAGIC results. We evaluate the influence of each of these factors in turn in the following sections, in an effort to present an unbiased overview of the differences in results obtained by the two approaches. The various MAGIC scenarios and Diatom calibrations used in the comparisons are outlined in Table 2.11. Finally, methods are described for estimating the errors associated with both the Diatom and MAGIC model estimates of lake chemistry. Evaluation of the potential pre-industrial organic acid influence is presented in the Appendix.

2.4.1 Watershed Disturbance/Land Use

The disturbance classification^(a) was based on a number of currently observable characteristics of the lakes and watersheds. A lake was designated "disturbed" if there was any indication of recent liming or road-salt application, if the number of shoreline structures exceeded 10 (criterion reduced to three structures for lakes smaller than 8 ha), or if paved roads were present in the watershed. These evaluations were made on the basis of input data from 7.5 minute topographic maps, DDRP aerial photos, field sampling reports, Adirondack Lake Survey Corporation and New York Department of Environmental Conservation records, and ELS records. Potential road-salt input was evaluated by identifying lakes having high $[Cl^-]$ ($> 20 \mu eq L^{-1}$), and examining topographic maps for likely road-salt influence. On the basis of the above criteria, a total of three lakes were designated as disturbed and seven lakes as relatively disturbed. This is largely a subjective designation and must be interpreted as a general indication of the lakes in the data set

(a) A. Selle, unpublished data

TABLE 2.11. Description of Various MAGIC and Diatom Model Scenarios

<u>Scenario</u>	<u>Type of Reconstruction</u>	<u>Description</u>
<u>MAGIC Model</u>		
#1	DDRP	Assumed pre-industrial deposition of SO_4^{2-} equal to sea-salt component (near zero) and base cations equal to current base-cation deposition. Used soils data aggregation and calibration to northeast region, Baker-Brezonik lake sulfate "uptake" coefficients, and pCO_2 averaged over 145 watersheds.
#2	Reference simulations	Modified from Scenario #1 using the historical deposition scenario of Husar, Sullivan, and Charles (in press) and its assumption of a pre-industrial SO_4^{2-} value equal to 13% of current value.
#4	Subregional	Modified from Scenario #1 by re-aggregating the soils data (with correction for coarse fragments) for the Adirondack subregion only (rather than the northeast region) and recalibrating the model, use of original Baker-Brezonik lake sulfate "uptake" coefficients, and pCO_2 values specific to Adirondack subregion, assuming pre-industrial $[\text{SO}_4^{2-}]$ equal to 13% of current (Husar, Sullivan, and Charles in press).
<u>Diatom Model</u>		
#1	pH	Calibrated to air-equilibrated pH
#2	ANC_0	Calibrated to titrated ANC_0
#3	$\text{ANC}(C_B - C_A)$	Calibrated to defined $\text{ANC}(C_B - C_A)$

most likely to have experienced anthropogenic disturbances that may have altered their chemistry.

2.4.2 Lake Chemistry Seasonality

Differences between summer and fall lakewater chemistry can potentially bias the results of the comparison because the Diatom model was calibrated to summer chemistry whereas the MAGIC model was calibrated to fall chemistry. This issue was assessed by comparing fall measurements from ELS-I with the average summer chemistry obtained in the PIRLA-II study for the same lakes. An additional set of comparisons was conducted between summer 1986 and fall 1986 measurements for ELS-II Adirondack lakes. The latter comparison involved 36 lakes, 30 of which were also included in the DDRP statistical sampling.

2.4.3 ANC Definition

The pH of water is extremely useful as an H-ion-intensity parameter. However, H⁺ is not conserved as precipitation moves through a watershed because it reacts with a multitude of solutes and soil minerals. Thus, the capacity of the system to neutralize added H⁺ must be calculated in any process-based modeling. In the geochemical literature, the term alkalinity has been extensively used and is generally defined in terms of carbonate alkalinity:

$$\text{Alkalinity} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] - \text{H}^+. \quad (2.13)$$

Acid-base titration results have generally been corrected for the acid consumption by other proton acceptors by use of geochemical models, e.g., WATEQ (Truesdel and Jones 1974) and MINTEQ (Felmy, Girvin, and Jenne 1984). However, in the acid-to-circumneutral waters of most interest in acid rain research, carbonate alkalinity is low to nonexistent and the other acid-titratable species and H⁺ become of primary importance. Acid-neutralizing capacity is the principal variable used to classify the acid-base status of surface waters (Omernik and Powers 1982), those waters with an ANC of ≤ 0 being commonly defined as acidic. The ANC is used qualitatively to evaluate the susceptibility of surface waters to acidic deposition, whereas the change in ANC, by direct measurement (Smith, Alexander, and Wolman 1987) or inference from lake sediment diatom assemblages (Charles and Smol 1988; Sullivan et al.

1990), is used to quantify the extent of prior acidification (Altshuller and Linthurst 1984; Schindler 1988). Acid-neutralizing capacity is a major variable used in dynamic, process-based models that simulate the response of ecosystems to changing atmospheric deposition (Christophersen, Seip, and Wright 1982; Goldstein et al. 1984; Reuss and Johnson 1985; Cosby et al. 1985b; Lin and Schnoor 1986).

The ANC, a measure of the titratable bases in solution to a specified pH endpoint, is measured by quantifying the amount of strong acid that must be added to a solution to neutralize these bases. The endpoint of this strong-acid titration is easily identified, except in low-ANC waters where weak acids and relatively small amounts of strong bases obscure the endpoint. Because of the endpoint problem, the Gran procedure (Gran 1952) for determining the endpoint is commonly used to yield more accurate ANC estimates. Gran-estimated ANC is termed titrated ANC₀ (for Gran analysis of the titration curve).

Alternatively, the ANC can be defined by two distinct methods of calculation without the use of titration data. Using the principles of conservation of charge and conservation of mass, these two techniques have been shown to be mathematically equivalent (Gherini et al. 1985). In one method (Stumm and Morgan 1981), ANC is calculated as the difference between the sum of proton (H⁺) acceptors and the sum of the proton donors, taking into consideration the proton reference level (discussed below):

$$\text{ANC} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] + [\text{other proton acceptors}] - [\text{H}^+] \quad (2.14)$$

where brackets denote molar concentrations. The other method relates ANC to the sum of cation concentrations (excluding H⁺), M_{ti}, minus the sum of the strong acid anions, A_{tj}. Defined ANC is calculated using the relation

$$\text{ANC} = \left[\sum_i^n |z_i| M_{ti} \right] - \left[\sum_j^m |z_j| A_{tj} \right] \quad (2.15)$$

where z_i and z_j are the charges on the individual uncomplexed cations and anions at the equivalence point (i.e., the point during titration where the

concentration of proton donors equals the concentration of proton acceptors) (Church et al. 1984; Gherini et al. 1985; Schofield, Galloway, and Hendry 1985). For aerobic surface-waters the first term on the right-hand side of Equation (2.15) is typically approximated as:

$$\sum_i^n |z_i| M_{ti} \approx 2[Ca_t] + 2[Mg_t] + 2[Mn_t] + [K_t] + [Na_t] + [NH_4] + x[Al_t] \quad (2.16)$$

and the second term is approximated as

$$\sum_j^m |z_j| A_{tj} \approx 2[SO_4_t] + [NO_3_t] + [Cl_t] + [F_t] \quad (2.17)$$

where x , the $[Al_t]$ coefficient, is the mean charge of all dissolved Al species. The charges z_i and z_j (and thus the concentration multipliers in Equations [2.16] and [2.17]) are determined by the predominant charges of the uncomplexed constituents at the equivalence point. However, since very little effort is required to actually calculate the quantities of the various cation-anion complexes with a geochemical speciation model (Felmy et al. 1984; Parkhurst et al. 1980; Mattigod and Sposito 1979), it is generally preferable to do so rather than using an estimated average charge for components such as Al.

Because much of the early research was carried out in a survey mode and by groups with limited analytical support facilities, the minimum number of constituents usually were analyzed. Thus, ANC in many studies is defined:

$$\begin{aligned} \text{ANC} = & 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + [NH_4^+] \\ & - 2[SO_4^{2-}] - [Cl^-] - [NO_3^-]. \end{aligned} \quad (2.18)$$

This definition, the one used in DDRP, omits Al, Fe, Mn, and organic acids and yields variable errors in the resulting calculations. Indeed, numerous studies omit NO_3^- and sometimes K^+ . Below pH 6, where CO_3^{2-} and OH^- make a

negligible contribution to ANC, the charge-balance equation is sometimes written (Reuss, Christophersen, and Seip 1986)

$$\text{ANC} = [\text{HCO}_3^-] - [\text{H}^+] - [\text{Al}_n] \quad (2.19)$$

Equations (2.16-2.17) implicitly assume that all dissolved Fe is complexed with dissolved organic carbon (DOC) (e.g., Perdue, Beck, and Reuter 1976), that the contribution of organic acids and organic-Fe complexes to the titrated ANC₀ is minimal, and that dissolved Mn does contribute significantly to ionic charge.

For strong base cations and acid anions, there is little uncertainty as to the absolute value of the predominant uncomplexed charge at the equivalence point (e.g., Ca = 2, Na = 1, SO₄ = 2, Cl = 1). However, because of complexation with OH⁻, F⁻, and organic ligands, the mean charge of Al [x in Equation (2.16)] is not always obvious. Designation of the mean Al charge, however, establishes the proton reference level (PRL). Both +3 and 0 have been used as the PRL for Al in calculating the defined ANC (Cosby et al. 1985a; Church et al. 1984; Schofield, Galloway, and Hendry 1985).

Data collected during the Regionalized Integrated Lake-Watershed Acidification Study (RILWAS) (Driscoll and Newton 1985; Goldstein et al. 1987) from 25 lake-watershed systems in the Adirondack subregion were used by Sullivan et al. (1989) to estimate the mean Al PRL. The speciation of Al was calculated using the chemical equilibrium model ALCHEMI (Schecher and Driscoll 1987). The ALCHEMI output was used to sum the product of the concentration of an individual inorganic ion (e.g., Al³⁺, AlF₂⁺, Al(OH)²⁺, Al(OH)₂⁺, Al(SO₄)⁺) times its respective charge (neglecting potential contributions of organic-Al to the titrated ANC). Division of this sum by the Al_t concentration gives the mean PRL. This approach yields results that are quantitatively very similar to simply designating a charge of +2 for all Al_n for ELS-II lake-chemistry data (T. Sullivan, unpublished data). Although the mean charge on Al_n decreases with pH, a mean charge of +2 approximates the charge at the equivalence point of acid-sensitive waters (pH 4.8 to 5.2) (Driscoll and Bisogni 1984; Sullivan et al. 1989).

The acid-neutralizing capacities calculated using Equation (2.18) may overestimate the titratable ANC because of the dissociation of organic acids. Titrating to low pH (e.g., pH 3) reduces the concentration of organic anions that remain unprotonated during the titration and minimizes curvature in the Gran function, thus reducing the DOC effects on ANC_0 (Sullivan et al. 1989). This is evident in surface-water data for the Meander Lake basin in northern Minnesota. Values of DOC at the outlet of Meander Lake average only approximately $400 \mu\text{mol L}^{-1}$ (1000 mmol L^{-1} of C = 12 mg L^{-1} DOC), but one of the inlets drains a spruce bog and contains DOC values as high as $2400 \mu\text{mol L}^{-1}$ (Chen et al. 1988). The discrepancy between the calculated and titratable ANC for this lake can be as large as $50 \mu\text{eq L}^{-1}$ at DOC concentrations of $800 \mu\text{mol L}^{-1}$. A single maximum discrepancy of $180 \mu\text{eq L}^{-1}$ was observed for a sample from the bog inlet with $2400 \mu\text{mol L}^{-1}$ of DOC (Figure 2.5). Concentrations of Al in Meander waters are very low (mean $Al_{\text{f}} = 1.3 \mu\text{mol L}^{-1}$) and do not account for the difference between calculated and titrated ANC_0 .

The process-based watershed models include mono- and di-protic organic acids in calculated ANC. The MAGIC model (Cosby et al. 1985a) includes the $HR''COO^-$ and $R'COO^{2-}$ species (where R' , R'' , and R''' are mono-, di- and tri-protic acids). The ILWAS model (Goldstein et al. 1984) includes the two additional organic ligands and four organic-Al complexes. Husar, Sullivan, and Charles (in press) have proposed the inclusion of a single organic term ($RCOO_0^-$) as an acid anion in Equation (2.15) to reflect the influence of organic anions on Gran titration results. The value for organic acids ($RCOO_0^-$) required in Equation (2.15) to make the calculated ANC comparable to titration ANC depends, in part, on the extent of DOC-induced curvature in the Gran function and extent to which the DOC is protonated. These two factors are dependent on the strength of the organic-acid functional groups relative to the end point pH used in the Gran titration. Using data from ELS-II, collected in autumn 1986, Husar, Sullivan, and Charles (in press) estimated that for lakes in the northeastern United States, $RCOO_0^-$ ($\mu\text{eq L}^{-1}$) could be approximated as $7.5 \times \text{DOC}$ (mg L^{-1}) (Figure 2.6). This estimate agrees with that of Eshleman and Hemond (1985), based on one lake in Massachusetts. Data presented by

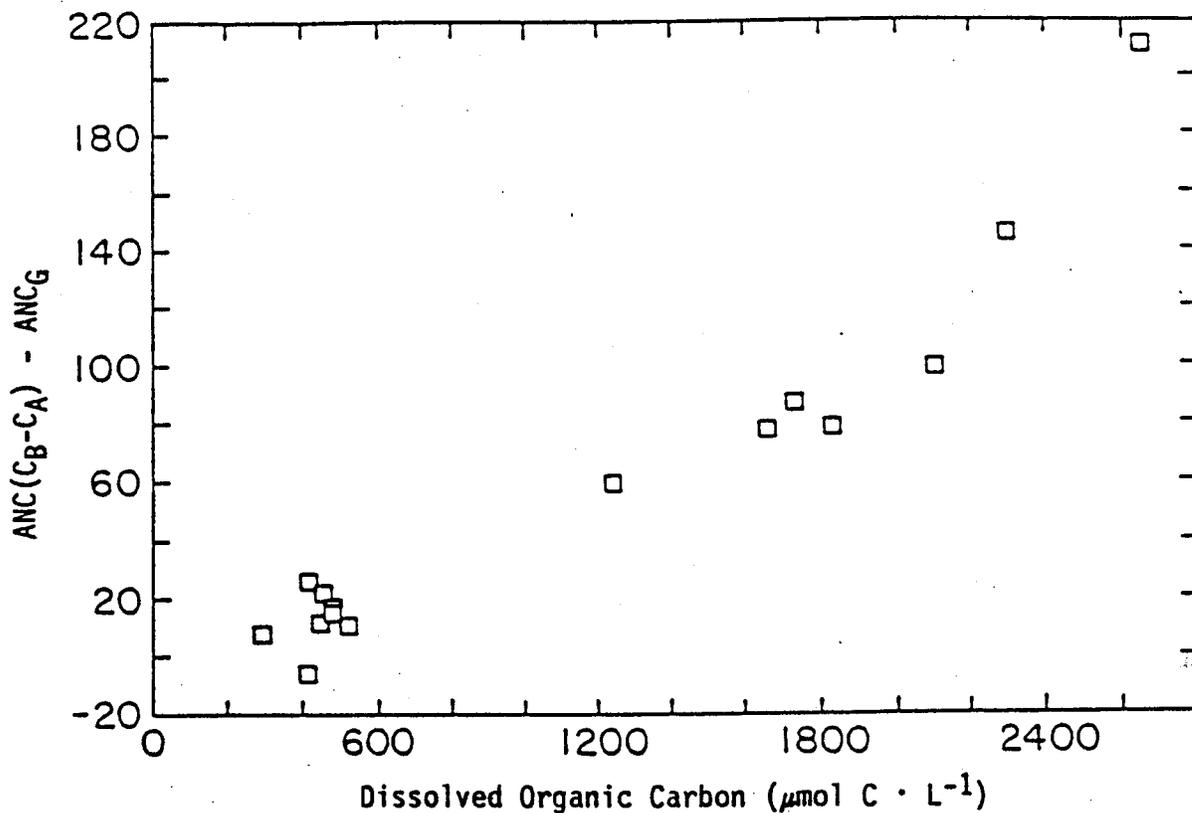


FIGURE 2.5. Difference Between Defined ANC (Equivalence of Base Cations and Mn^{2+} Minus Equivalence of Mineral-Acid Anions Plus Two Times Al_3 in $\mu\text{mol L}^{-1}$) and Titration ANC_G Versus DOC for Waters in the Meander Lake Basin (Source: Sullivan et al. 1989)

Sullivan et al. (1989) for Meander Lake, however, suggest a charge of only $4.0 \mu\text{eq mg}^{-1}$. Estimation of RCOO_0^- defined in such a way is ambiguous. Husar, Sullivan, and Charles (in press) noted, however, that interpretation of the exact cause of the discrepancy between titrated ANC and that calculated according to Equation (2.15) (Figure 2.6) is not important if one is interested in quantifying the influence of organic acids on titration ANC_G . Regardless of the relative importance of curvature in the Gran function (Sullivan et al. 1989), whether due to protonation of adjacent functional groups of polyprotic organic acids (Oliver, Thurman, and Malcolm 1983; Stevenson 1982) or strength of carboxylic acidity (Eshleman and Hemond 1985), the titrated ANC is somewhat lower than the calculated ANC [Equation (2.15)] because of the presence of organic acids. Whether the data points in Figure 2.6 are shifted to the left (e.g., curvature) or upward (e.g., low pK_a),

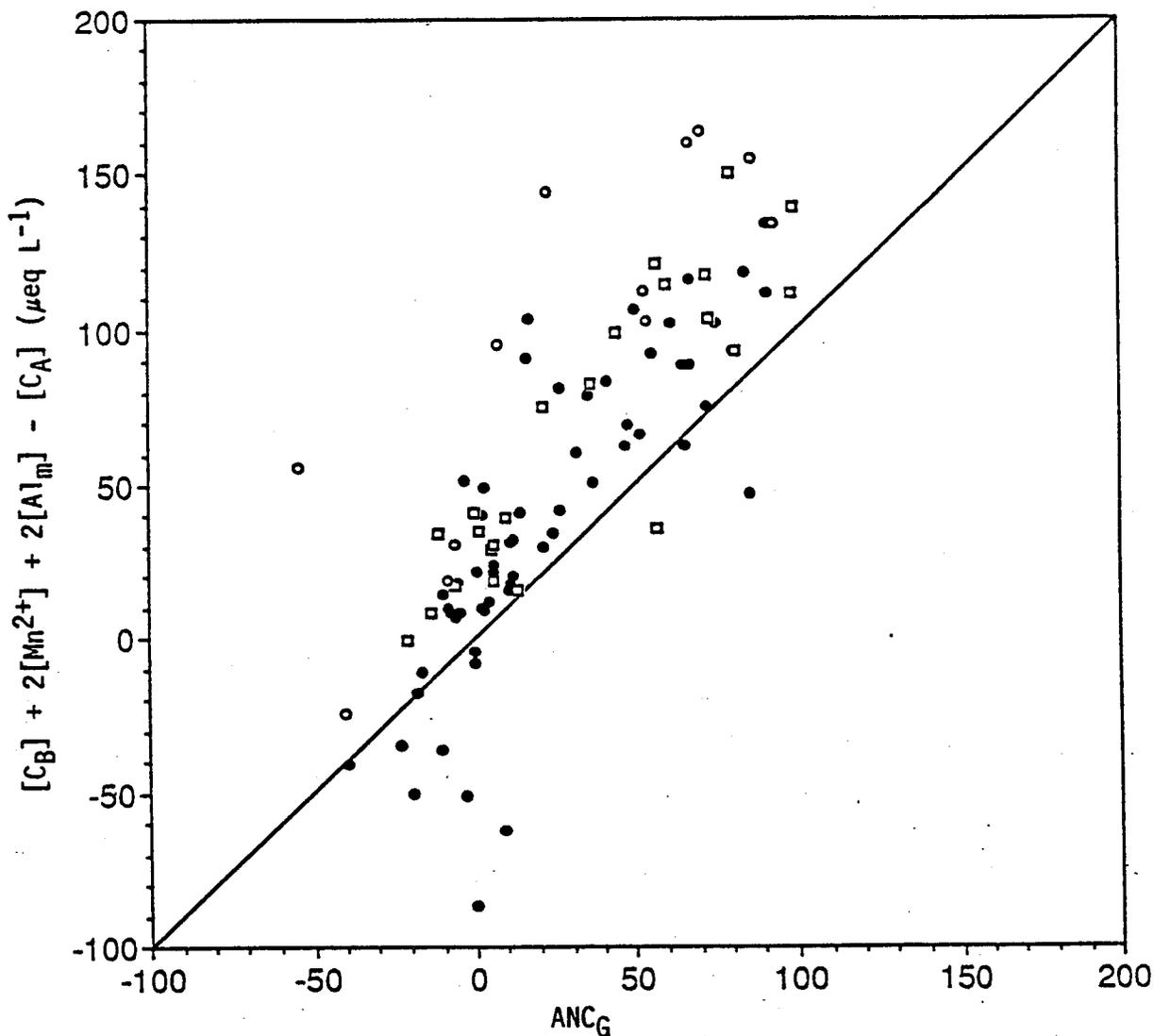


FIGURE 2.6. Acid-Neutralizing Capacity Defined as $[C_B] + 2[Mn^{2+}] + 2[Al_m] - [C_A]$ Versus ANC Determined by Gran Titration. C_B is the equivalent sum of base cations ($Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+$), C_A is the equivalent sum of acid anions ($SO_4^{2-} + NO_3^- + Cl^- + F^-$), and Al_m is total monomeric Al. The multiplier used for Al_m , +2, corresponds to the average valence of monomeric Al near the equivalence of Gran titrations for dilute waters (pH 4.8 to 5.2) (Sullivan et al. 1989). Data are from the Eastern Lake Survey Phase II, collected in autumn 1986 in the northeastern United States. Data points are coded by dissolved organic carbon: \circ is > 6 mg L^{-1} , \square is 4-6 mg L^{-1} , \bullet is ≤ 4 mg/L. The vertical distance from each data point to the 1:1 line is an estimate of organic acid influence on the Gran titration estimation of ANC as compared with defined ANC (Source: Husar, Sullivan, and Charles, in press).

the bias is largely attributable to the presence of organic acids and can be approximated as a function of DOC. Charge for RCOO_3^- in the range of 4 to $7.5 \mu\text{eq mg}^{-1}$ appears reasonable for estimating the influence of organic-acid anions on titration ANC_0 . The total concentration of organic acid anions (RCOO_3^-) as a function of DOC is generally higher and has been estimated to be approximately $10 \mu\text{eq mg}^{-1}$ (Oliver, Thurman and Malcolm 1983).

The discrepancy between calculated and titrated ANC caused by organic-acid influence and/or differences in defining the proton reference level for Al has significant implications for the NAPAP assessment activities. Titration ANC_0 is used primarily for classifying, evaluating current status, monitoring temporal trends, and calibrating paleolimnological transfer functions. Defined ANC (defined in different ways) is used for dynamic-model predictions (see, e.g., Reuss, Christophersen, and Seip 1986) and for interpreting trends in some instances (e.g., Wright, Lotse, and Semb 1988). Unfortunately, the differences between the various definitions of ANC are seldom considered. These differences can drastically affect interpretations of chemical change. For example, Wright, Lotse, and Semb (1988) presented results for 1983-1987 at the Risdalsheia site of the RAIN Project in southernmost Norway, where acidic deposition has been excluded by placing a roof over the minicatchment and applying neutralized rainwater below. Wright, Lotse, and Semb (1988) concluded that 40% of the observed reduction in $[\text{SO}_4^{2-} + \text{NO}_3^-]$ in runoff had resulted in an increase in defined ANC as calculated from the difference of summed base cations and summed acid anions ($C_B - C_A$). This ANC definition treats Al^{3+} as an acidic cation, similar to H^+ , whereas the Gran titration treats Al^{3+} as a base cation, similar to Ca^{2+} . However, if an alternative definition of ANC, such as carbonate alkalinity minus H^+ ($\text{HCO}_3^- - \text{H}^+$), were used, it would be concluded that only 9% of the change in $[\text{SO}_4^{2-} + \text{NO}_3^-]$ resulted in an increase in ANC. An additional 5% of the change in $[\text{SO}_4^{2-} + \text{NO}_3^-]$ was attributable to a decrease in Al. An appreciable proportion of the surface-water response was attributable to deprotonation of organic acids, which are present in very high concentrations at this site. It is apparent that interpretation of acidification and recovery depends on the specific ANC definition used. Any comparison of current and pre-industrial defined $\text{ANC}(C_B - C_A)$ will incorporate any change in RCOO^- as a change in alkalinity, in

based in part on data reported by Goldstein and Gherini (1984). An iterative correction was applied to the monthly deposition to ensure that this sum agreed with the annual total.

The pre-industrial background sulfate deposition in DDRP (Scenario #1) was assumed to be sea-salt-derived and was estimated from 1984 $[Cl^-]$ using the $[SO_4^{2-}]$ to $[Cl^-]$ ratio in seawater. This assumes that sea salt was the only important source of SO_4^{2-} for Adirondack lakes. This resulted in near-zero pre-industrial $[SO_4^{2-}]$ values, with only three exceptions.

Dry deposition of base cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and Cl^- at inland sites (e.g., Adirondack region) was estimated by assuming deposition velocities of 0.8 cm sec^{-1} for fine-particulate deposition ($< 2 \mu\text{m}$). Annual values were partitioned into monthly fluxes. Coarse-particle dry deposition ($> 2 \text{ mm}$) for these ions was estimated by coarse-to-fine ratios of 1.5 for Ca; 1.0 for Mg, Na, and K; and 0.2 for Cl.

Dry depositions of NO_3^- and NH_4^+ were estimated to be equal to 0.5 of wet deposition. (Note that there is an inconsistency in $[NO_3^-]$ between the text and tables in the DDRP report of Church et al. 1989). Dry deposition of H^+ was computed as the charge difference between the sum of dry anions and dry cations, and H^+ was set to zero in cases where cations exceeded anions. The resulting ratios of dry deposition to wet deposition used for the typical-year-deposition data set (Church et al. 1989) are summarized in Table 2.12.

Alternative Pre-industrial Sulfate Deposition

Considerable uncertainties surround the estimates of pre-industrial deposition of SO_4^{2-} and base cations required as input for MAGIC. The potential importance of uncertainties in pre-industrial SO_4^{2-} deposition levels were assessed by comparison of Scenarios #1 and #2 (Table 2.11). Sullivan et al. (1988) concluded that, at distances greater than about 50 to 60 km from the coast, marine contributions of chloride were negligible. Therefore, marine contributions of SO_4^{2-} to lakes in the Adirondacks approach zero. For Scenario #2 in the present study, we assumed that some sulfur is derived from background contributions of entrained soil particles. Sulfate deposition in

TABLE 2.12. Ratios of Dry Deposition to Wet Deposition for DDRP Watersheds for the Typical Year Deposition Data Set

<u>NE</u>	<u>Median</u>	<u>Mean</u>	<u>Standard Deviation</u>
SO ₄ ²⁻	0.44	0.48	0.12
Ca ²⁺	1.13	1.12	0.42
Mg ²⁺	1.92	1.82	0.72
Na ⁺	1.29	1.29	0.61
K ⁺	1.56	1.66	0.71
Cl ⁻	0.38	0.33	0.12
NO ₃ ⁻	1.0 ^(a)	1.0 ^(a)	--
NH ₄ ⁺	0.5 ^(b)	0.5 ^(b)	--
H ⁺	0.47	0.46	0.23

(a) Nitrate set to 1.0.
 (b) Ammonium set to 0.5.

1844, using the deposition scenario of Husar, Sullivan, and Charles (in press), was about 13% of 1984 levels. The deposition scenarios used are shown in Figure 2.7.

Alternative Base-Cation Deposition

The simulations conducted in Scenario #2 assumed that base-cation deposition had not changed from pre-industrial times to the present. Data for the Hubbard Brook Experimental Forest suggested, however, that base-cation deposition there has fallen, coincident with decreased SO₄²⁻ deposition during the past 25 years (Driscoll et al. 1989). The degree to which the changes in SO₄²⁻ and base cation deposition at Hubbard Brook may have been coupled is unclear. To assess the sensitivity of MAGIC output to potential historical changes in base-cation deposition, a sensitivity analysis is needed that involves readjusting pre-industrial base-cation deposition to lower levels and increasing simulated base-cation deposition along the estimated historical SO₄²⁻ trajectory provided by Husar, Sullivan, and Charles (in press).

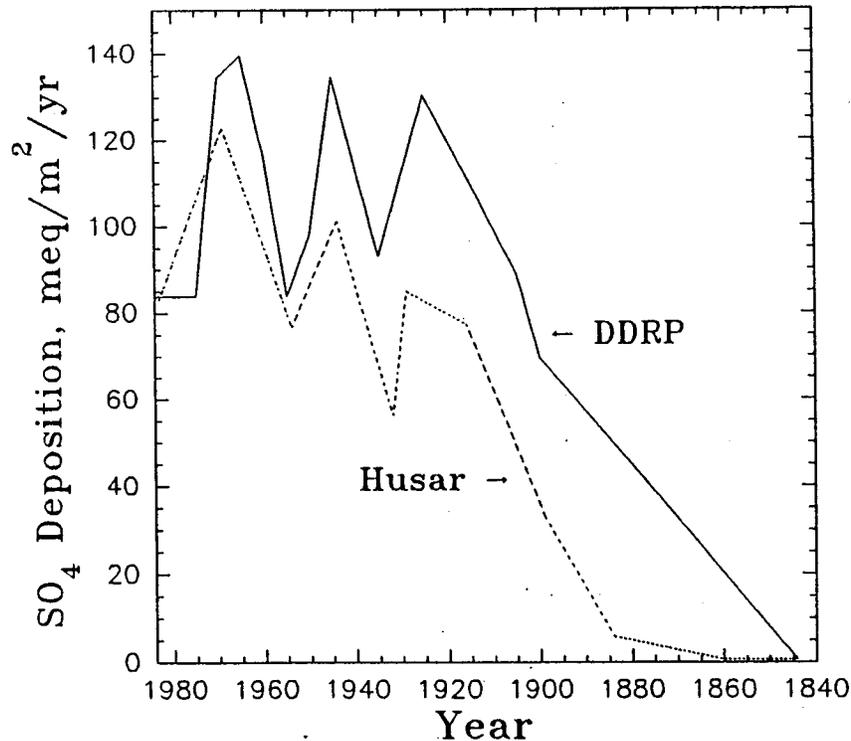


FIGURE 2.7. Depiction of Relative Sulfate Deposition Used in DDRP (MAGIC Scenario #1) Versus that of Husar, Sullivan and Charles (in press) Scenarios #2 and #4

2.4.5 Reaggregation of Subregional Soils Data

The DDRP soil aggregation characterized watershed soils based on attributes of sampling classes estimated from pedons collected across the entire Northeast. In January, 1990, however, ORNL reaggregated the DDRP soils data, based only on data collected from the Adirondack region. The purpose of this reaggregation was to characterize Adirondack watershed soil attributes using only soil data actually collected from pedons in the Adirondacks. The concern was that the Adirondack soils might differ in their chemical properties from similar soils in other areas of the Northeast, and that MAGIC projections for Adirondack watersheds might be in error (i.e., biased) because they were based on soil attributes that actually reflected conditions elsewhere than the Adirondacks. This reaggregation also included a correction for the coarse-fragment content (e.g., rocks) of the various horizons in which the range and mean fragment content of Layer 1 (A+B horizon) were 10.1-24.2% and 18.3%,

respectively, and of Layer 2 (C horizon) were 19.9-40.5% and 24.05%, respectively (C. C. Brandt, written communication, January 18, 1990).

Table 2.13 lists the soil sampling classes mapped in the Adirondacks together with the number of pedons sampled in this subregion and in the entire Northeast. The regional (DDRP) estimates of watershed soil chemistry are based on all Northeast pedons belonging to the sampling classes listed in Table 2.13. The subregional (reaggregated) watershed soil chemistry estimates are based on only the pedons sampled in the Adirondacks.

In the following discussion of the lateral and vertical aggregation method let k denote the subhorizon, j the pedon, i the sampling class, and h the watershed. The method used to create the two sampling class data sets was:

1. Subset the subhorizon chemistry by retaining only those observations with acceptable confidence levels from the mineral horizons of the routine pedons (i.e., discard extreme data).
2. Weight each subhorizon chemistry observation (x_{ijk}) by its mass per unit area (m_{ijk}) to obtain a mass-weighted average for each pedon (x_{ij}) in a sampling class:

$$x_{ij} = \left| \sum_k m_{ijk} x_{ijk} \right| / \left| \sum_k m_{ijk} \right|. \quad (2.20)$$

The mass of subhorizon k is given by

$$m_{ijk} = \text{SOILDEN} \times (\text{THKM} \times [1 - \text{FRAG}/100]) \quad (2.21)$$

where SOILDEN is the bulk density of the soil, THKM is the measured thickness of the subhorizon, and FRAG is the percent of coarse fragments in the soil. The term $(\text{THKM} \times [1 - \text{FRAG}/100])$ is the soil thickness adjusted for rock fragments.

TABLE 2.13. Number of Sampled Pedons for Adirondack Sampling Classes

<u>Sampling Class</u>	<u>Number of Sampled Pedons</u>	
	<u>Adirondack</u>	<u>Northeast</u>
E02	4	8
E05	4	7
E06 ^(a)	1	6
H01	6	8
H02	1	8
H03	4	6
I01	6	10
I02	0	5
I05	0	8
I06	1	8
I09	0	8
I10 ^(b)	0	8
I25	0	9
I37	0	8
I38	0	6
I46 ^(b)	1	7
S01	6	11
S02	4	8
S05 ^(b)	3	3
S09	4	8
S10	1	7
S11	3	8
S12	4	8
S13 ^(b)	1	6
S14	4	8
S15	0	6

(a) Sampling class was sampled but not mapped in the Adirondack region.

(b) Contaminated pedons not included.

3. Weight the pedon values ($x_{ij.}$) by their mass per unit area ($m_{ij.}$) to obtain a sampling class weighted average ($x_{i..}$):

$$x_{i..} = \left| \sum_j m_{ij.} x_{ij.} \right| / \left| \sum_j m_{ij.} \right| \quad (2.22)$$

where the mass of pedon j is given by

$$m_{ij.} = \sum_k m_{ijk} \quad (2.23)$$

For bulk density, the adjusted horizon thickness (THKM x [1 - FRAG/100]) was used instead of the subhorizon mass as the weight in calculating the pedon values. Estimates of measured and adjusted thickness were calculated in the same way as the mass estimate.

The watershed estimates (w_h) based on the Northeast pedons are a weighted average of the sampling classes occurring on a watershed:

$$w_h = \left| \sum_i a_{hi} x_{i..} \right| / \left| \sum_i a_{hi} \right| \quad (2.24)$$

where $x_{i..}$ denotes the sampling class estimate and a_{hi} is the areal fraction of the sampling class on the watershed. A slightly different weight was used in aggregating the Adirondack sampling class estimates to watersheds. The watershed estimates (w_h) are calculated by:

$$w_h = \left| \sum_i a_{hi} m_{i..} x_{i..} \right| / \left| \sum_i a_{hi} m_{i..} \right| \quad (2.25)$$

where $x_{i..}$ denotes the sampling class estimate, $m_{i..}$ is the unit mass of the sampling class, and a_{hi} is the areal fraction of the sampling class on the watershed. In this aggregation, the volume of the soil ($a_{hi} m_{i..}$) is used as the weight. The average pedon mass of sampling class i is given by:

$$m_{i..} = \left[\sum_j m_{ij.} \right] / n_i. \quad (2.26)$$

where n_i is the number of pedons in the i^{th} sampling class. Estimates of measured and adjusted thickness were calculated in the same way as the mass estimate.

The MAGIC model was recalibrated for the Adirondack lakes using these re-aggregated soils data. The calibration procedure was identical to that described in Section 2.3.2, except that the new subregional values of Adirondack soils were used. In addition to the modified soils data, the recalibration included new calculations of $p\text{CO}_2$ in lake water and apparent Al-hydroxide solubility products for lakes. These new calculations were performed as described in Section 2.3.2, except that the lakes were restricted to the Adirondack region.

2.5 SUMMARY OF POSSIBLE COMPARISONS BETWEEN PALEOLIMNOLOGY AND MAGIC

As discussed in the previous sections of this report, a number of factors could potentially bias the comparison between paleolimnological and MAGIC-model hindcast results for the Adirondack lakes. To evaluate and correct potential bias, three separate sets of MAGIC simulations were conducted, as outlined in Table 2.11, and in addition, the diatom assemblages were calibrated to two different ANC definitions (titrated ANC_0 and $\text{ANC}(C_B - C_A)$). The Scenario #2 MAGIC simulations were unchanged from the DDRP program, with the exception that pre-industrial SO_4^{2-} deposition was estimated as suggested by Husar, Sullivan, and Charles (in press) ($\sim 13\%$ of 1984 deposition), rather than assuming sea-salt deposition as the principal source of SO_4^{2-} (nearly zero), as was done in DDRP (Church et al. 1989). Output from Scenario #1 (Table 2.11), in comparison with Scenario #2, evaluates the sensitivity of MAGIC output to assumptions regarding pre-industrial SO_4^{2-} . Scenario #4 represents the most appropriate currently available scenario comparison with the Diatom model. In this scenario, both models use a comparable ANC definition (i.e., $C_B - C_A$) and both are calibrated to the Adirondack subregion only; the MAGIC model used the Husar et al. (in press) estimate of pre-industrial SO_4^{2-} deposition and a revised estimate of $p\text{CO}_2$. Scenario #4A,

presented in the Appendix, provides an approximation of the potential influence of organic acids on the MAGIC estimates of pre-industrial acid-base chemistry.

3.0 RESULTS AND DISCUSSION

3.1 BASIC COMPARISON

Comparisons between the Diatom model and MAGIC model (Scenario #2) results are presented in Figures 3.1 to 3.3. Figure 3.1a shows the MAGIC current-day estimated defined $ANC(C_B - C_A)$ plotted against the Diatom estimates of ANC_G . There is general agreement between the models for the low-ANC lakes, but for lakes having ANC greater than about $25 \mu\text{eq L}^{-1}$, either MAGIC is biased to higher estimates of ANC or the Diatom model is biased to lower ANC values. MAGIC also yielded slightly higher estimates of current pH (Figure 3.1b).

Agreement between the models was considerably poorer for estimates of pre-industrial (pre-1850) chemistry (Figure 3.2). The MAGIC model gave higher estimates for both ANC and pH during the pre-industrial period. The minimum estimated ANC and pH, using MAGIC, were approximately $30 \mu\text{eq L}^{-1}$ of ANC and pH 6.4. In contrast, the Diatom model estimated that some lakes had been slightly acidic ($ANC \leq 0$) and that the minimum pH was about 5.2.

Estimates of change in ANC and pH from pre-industrial time to the present are contrasted in Figure 3.3. The MAGIC model estimated that all lakes had acidified (decreased in both ANC and pH) since pre-1850, whereas the Diatom model estimated that some lakes increased in ANC and pH, while others decreased. The magnitude of estimated acidification was generally greater for the MAGIC than the Diatom model.

3.2 ERROR ESTIMATES

The uncertainty estimates calculated for the Diatom and the MAGIC simulations are not directly comparable, and only approximate the errors associated with the comparison between the Diatom and MAGIC models. It is not possible to quantify the errors associated with the underlying assumptions of the MAGIC and Diatom models, or the assumptions regarding pre-industrial deposition (which must be estimated in order to hindcast with MAGIC). Note that prediction errors cannot be calculated for the pre-industrial chemistry because we do not know what the "true" measured values were. Therefore, the average

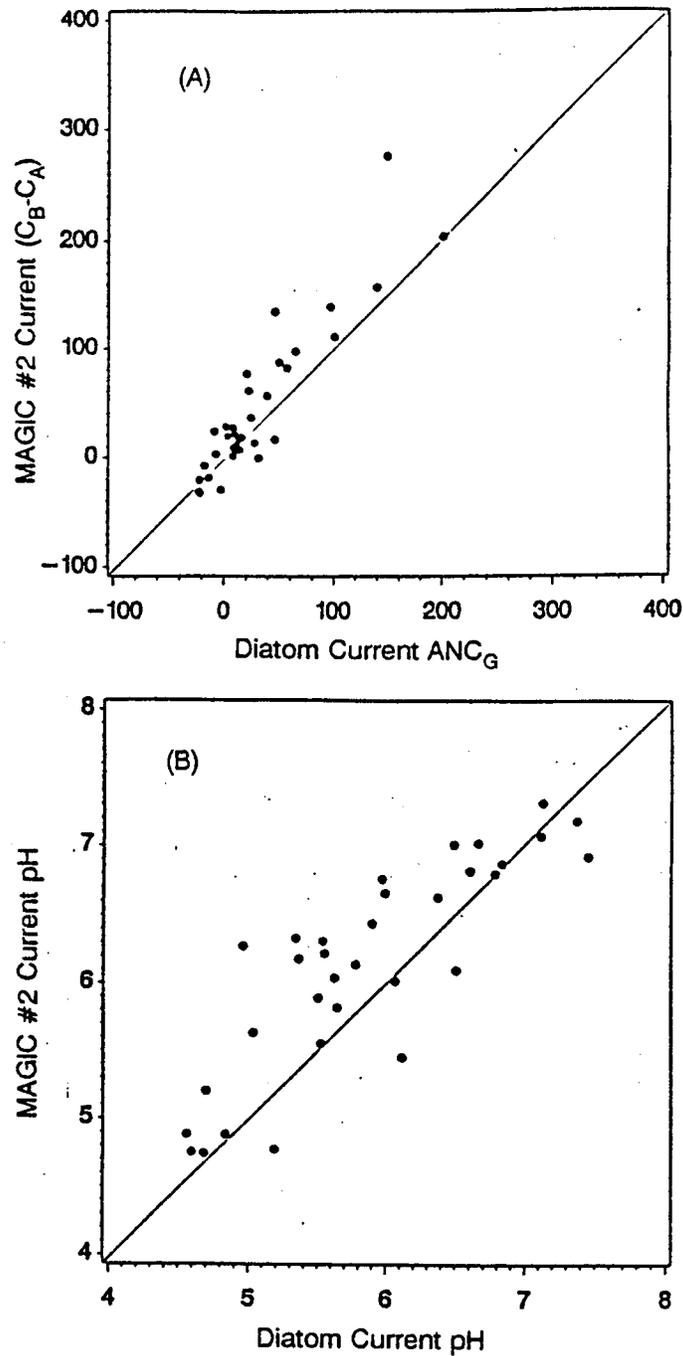


FIGURE 3.1. Comparison Plots of (A) Current ANC Estimates Between the MAGIC Scenario #2 Simulations of Current ANC ($C_B - C_A$) and the Diatom Inferences of Current ANC_G and (B) MAGIC Reference Simulations of Current pH and Diatom-inferred Current pH (Based on Tops of Cores)

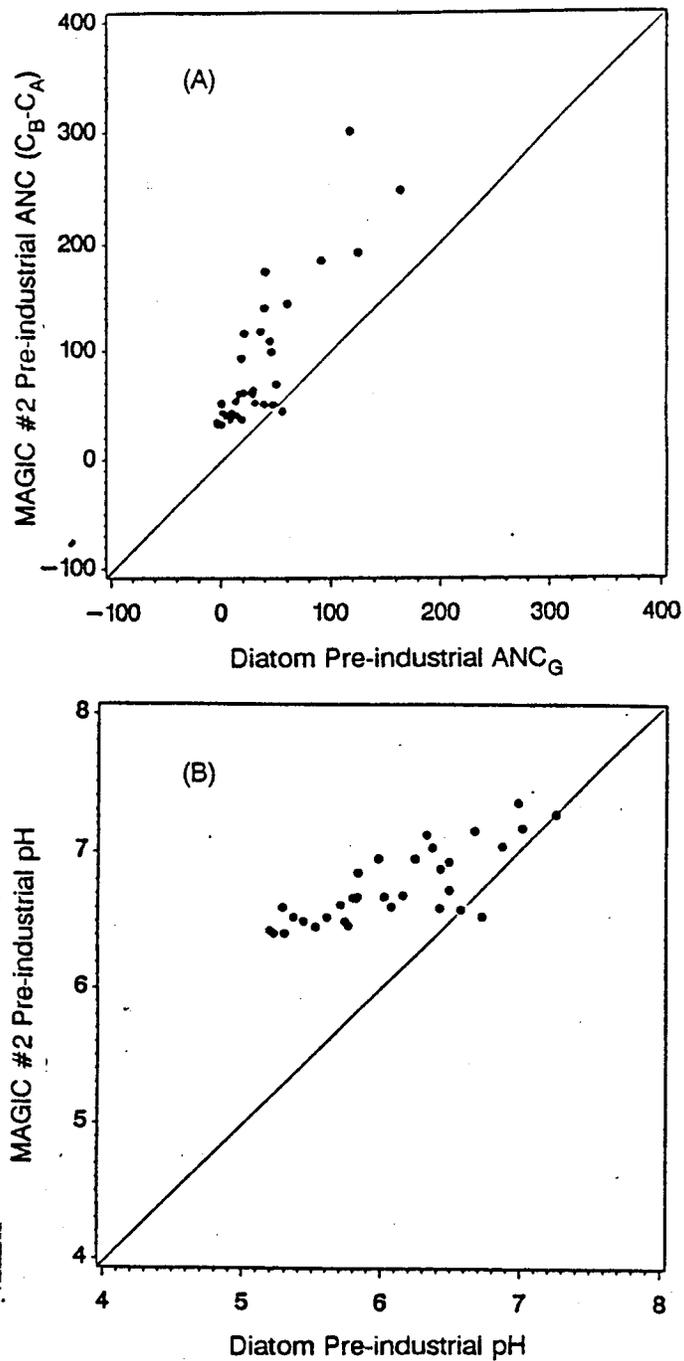


FIGURE 3.2. Comparison Plots of (A) Pre-industrial ANC Estimates from MAGIC Scenario #2 Simulations and Diatom-inferred Pre-industrial ANC_G (Based on Bottom Cores) and (B) Pre-industrial pH Estimates from MAGIC Reference Simulations and Diatom-inferred pH (Based on Bottom Cores)

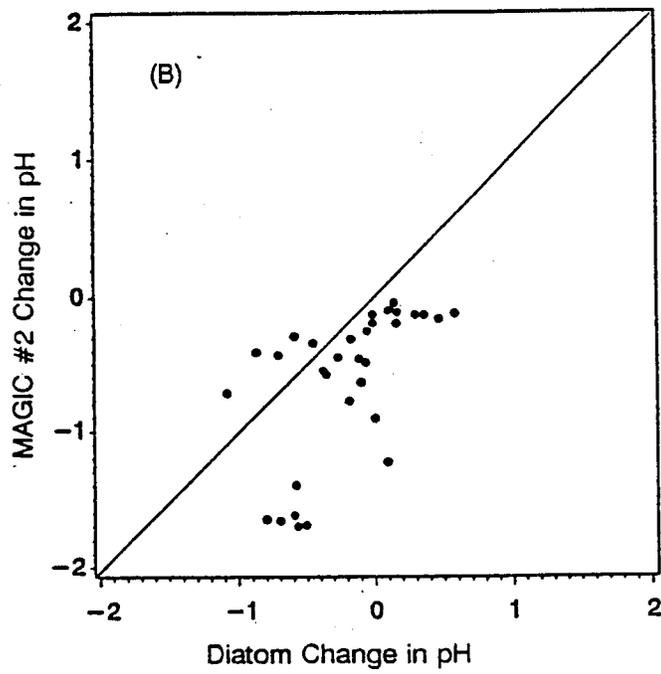
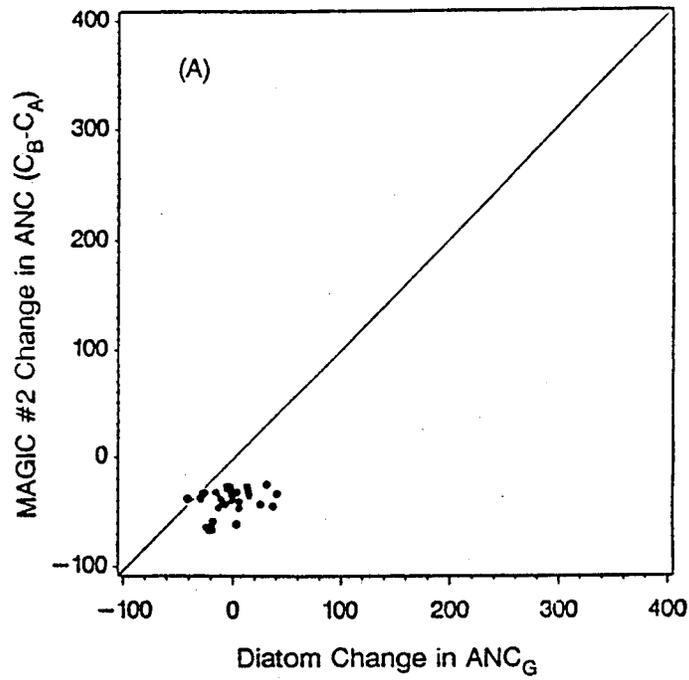


FIGURE 3.3. Estimates of Change in (A) ANC and (B) pH Using the MAGIC Model Scenario #2 Simulations versus Diatom Inferences of Change

Diatom prediction errors for the current chemistry estimates were also applied to the historical-chemistry estimates. The Diatom model error estimates are presented as 90% confidence intervals, which include the variability component of multiple bootstrap calibrations (s_2) and the average prediction error (bias) for the inferences of current chemistry (s_{i1}) (Figure 2.4).

MAGIC error estimates were derived from the "fuzzy" calibration procedure, as described in Section 2.3.3. They represent the width of the interval containing equally viable simulated variable values from up to 10 calibrations. The error bars thus reflect an uncertainty associated with the calibration procedure (Figure 3.5).

3.3 COMPLICATING FACTORS

3.3.1 Watershed Disturbance/Land Use

A rigorous evaluation of the impact of watershed disturbance and land-use activities on estimates of acidification of Adirondack lakes was not part of our analyses. It is clear that disturbance and land use changes can have significant effects on surface water acid-base chemistry (see, e.g., review of Sullivan, in press), and may have played a role in recent changes in the chemistry of Adirondack lakes. However, the lakes investigated here were assigned by A. Selle (unpublished data) to one of three current "disturbance" categories based on road networks, shoreline structures, lakewater $[Cl^-]$, and liming records. As shown in Figure 3.6a, lakes with alkalinity values $> 100 \mu eq L^{-1}$ were generally rated as being disturbed. There is no evidence, however, that disturbance exerted a significant influence on the results of the comparison because undisturbed lakes did not generally exhibit better agreement between methods than did disturbed lakes (Figure 3.6b).

3.3.2 Lake Chemistry Seasonality

The MAGIC model was calibrated to fall index lakewater chemistry using closed-system pH values, whereas the Diatom model was calibrated to an average of lakewater chemistry derived primarily from multiple summer samples using air-equilibrated pH values. It was therefore important to evaluate any potential bias introduced into the comparison from seasonal differences in

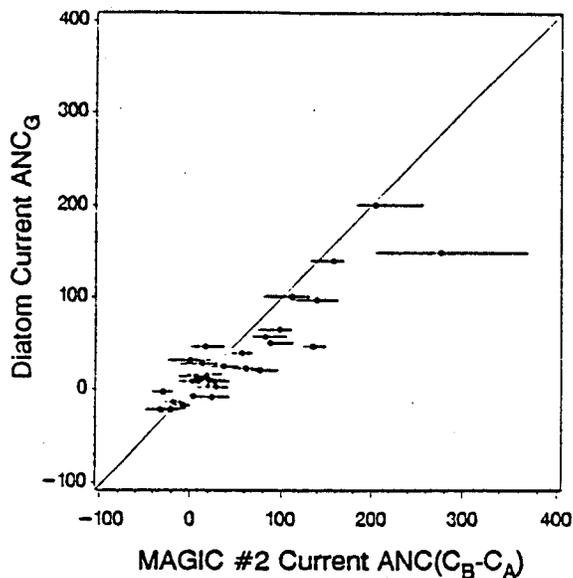


FIGURE 3.4. Plot of Diatom-inferred Current ANC_G Versus MAGIC Scenario #2 Simulation Estimate of Current $ANC(C_B-C_A)$, with Error Estimates Placed on MAGIC Estimates. The error estimates represent a confidence width, derived as the maximum and minimum of up to 10 separate calibrations for each lake.

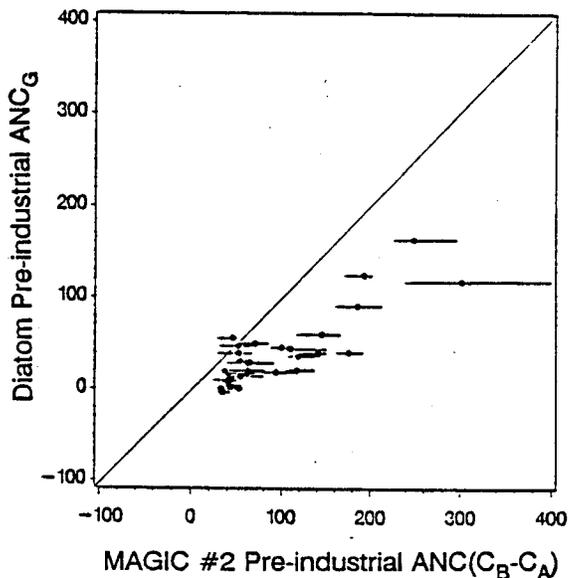


FIGURE 3.5. Plot of Diatom-inferred Pre-industrial ANC_G Versus the MAGIC Scenario #2 Simulation Estimate of Pre-industrial $ANC(C_B-C_A)$, with Error Estimates Placed on the MAGIC Estimates. The error estimates represent a confidence width, derived as the maximum and minimum of up to 10 separate calibrations for each lake.

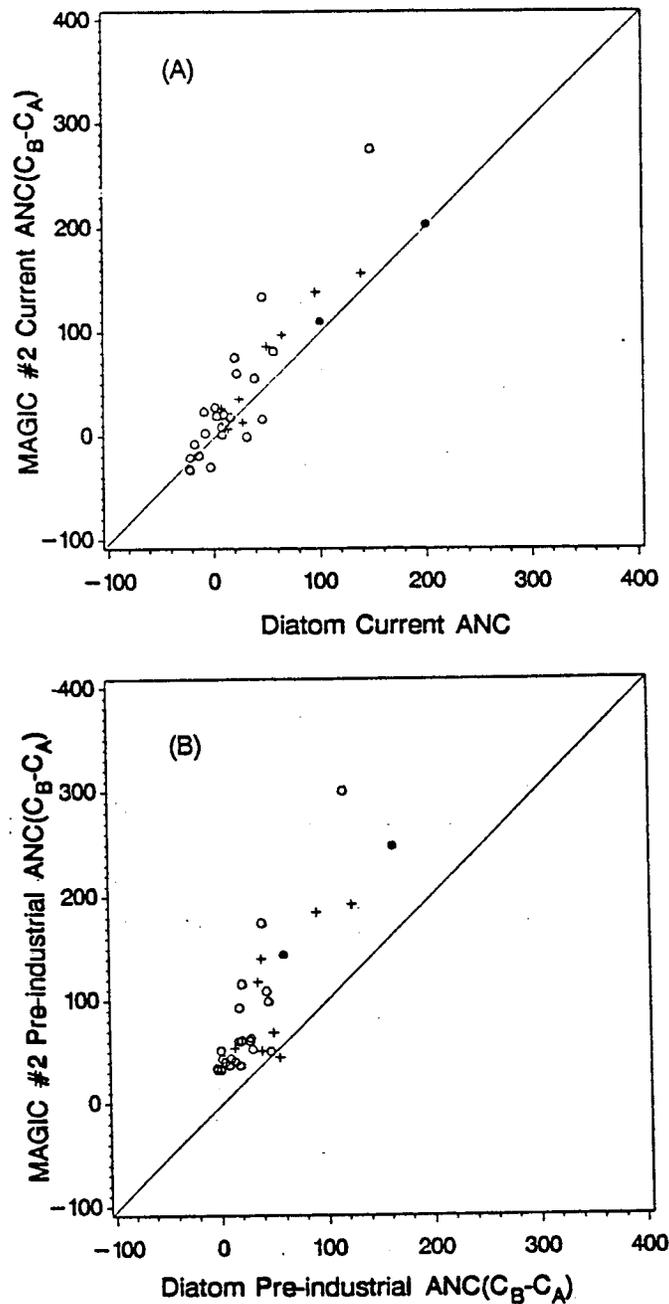


FIGURE 3.6. MAGIC Scenario #2 ANC(C_B-C_A) Versus Diatom-inferred ANC(C_B-C_A) (μeq L⁻¹). Lakes are coded by disturbance classes determined by A. Selle: • is disturbed, + is relatively disturbed, and o is undisturbed. Current chemistry is presented in (A) and pre-industrial chemistry in (B).

lakewater chemistry. The average chemical values for summer samples collected as part of the PIRLA-II research effort are plotted in Figure 3.7 versus ELS-1 fall index values used for the MAGIC simulations. The differences between summer and fall chemistry were very small for ANC and pH, and no major bias was introduced into the comparison because of seasonal differences. In general, ANC tended to be slightly lower during fall than summer as indicated by the following linear regression equation:

$$\text{ANC}_{\text{fall}} = 0.92 \text{ANC}_{\text{summer}} - 3.93 \quad (3.1)$$

(with standard deviations of 0.02 and 1.21, respectively) which yields an r^2 of 0.99 ($n = 33$).

There was a bias in the pH measurements for lakes having pH values greater than approximately 5.5 (Figure 3.7b). These lakes showed slightly higher pH for summer PIRLA-II samples compared with fall ELS-1 samples. This may be attributable to CO_2 degassing effects in water samples from the higher pH lakes, because pH values used in the PIRLA calibrations were air-equilibrated. When the regression was done using PIRLA-II field pH measurements (Figure 3.7c), the bias for the high-pH lakes was removed, i.e.,

$$\text{pH}_{\text{fall}} = 1.05 \text{pH}_{\text{summer}} - 0.26 \quad (3.2)$$

(with standard deviations of 0.04 and 0.25, respectively), yielding an r^2 of 0.95 ($n = 33$). Similarly, lakewater chemistry data collected during summer 1986 were compared with data collected from the same lakes during fall 1986 within the ELS-II project in the Adirondack subregion. No obvious seasonal bias was observed (Figure 3.8). The ELS-II pH values reported for both seasons were field laboratory (non-equilibrated) measurements.

On the basis of the above comparisons, we conclude that seasonal differences do not introduce any substantial bias into the comparison of MAGIC (fall) with Diatom (summer) results. The use of air-equilibrated pH values in the Diatom reconstructions versus the non-equilibrated (i.e., closed system) pH estimates used for MAGIC may, however, bias results for high-pH lakes. The

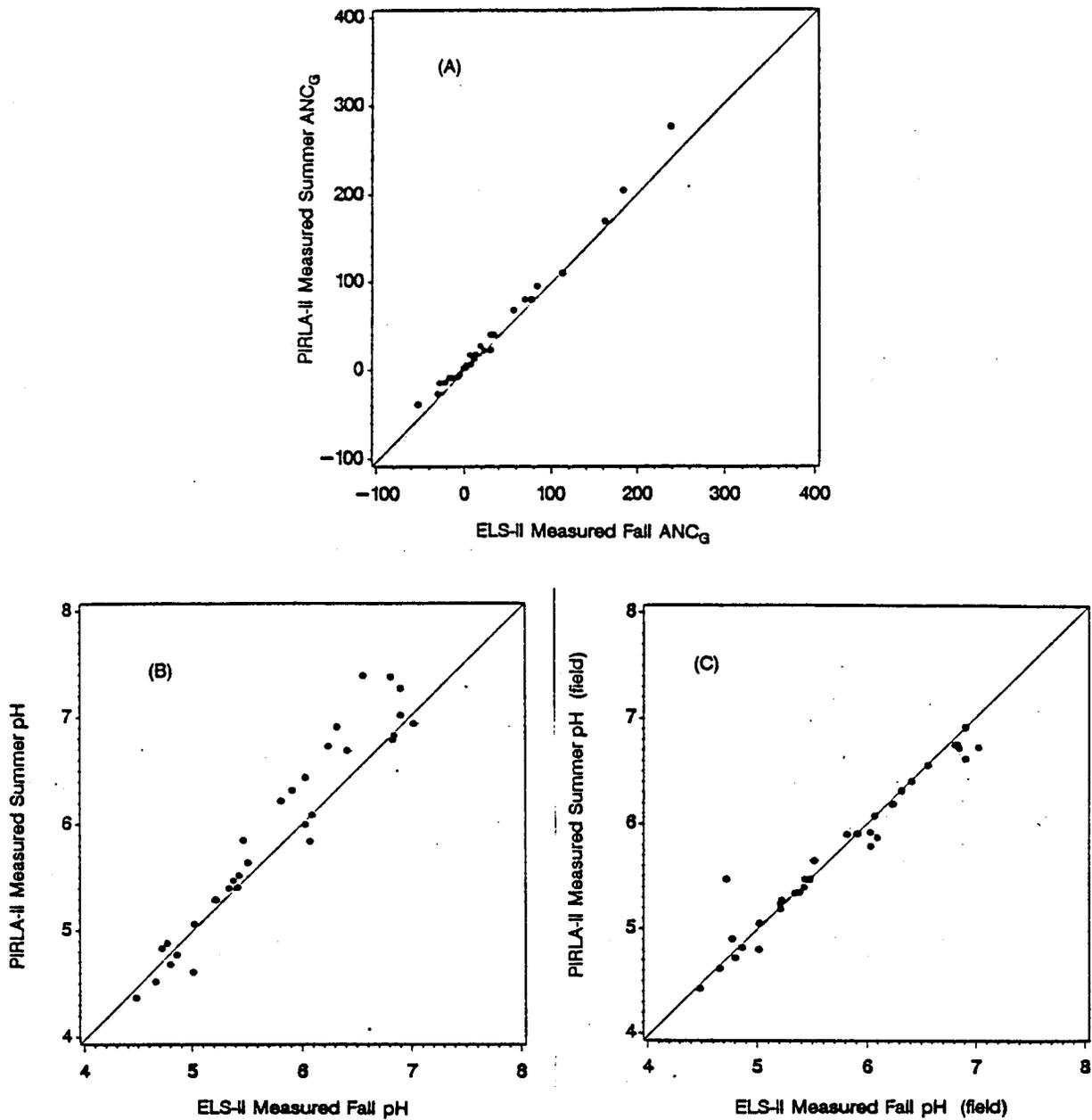


FIGURE 3.7. Comparisons of (A) PIRLA-II measured ANC_G (Average of Summer Samples) and ELS-I-measured ANC_G (Fall Index Samples), (B) Air-equilibrated pH (Average of Summer Samples) and ELS-I-measured Field pH (Fall Index Samples), and (C) Field pH (Average of Summer Samples) and ELS-I-measured Field pH (Fall Index Samples)

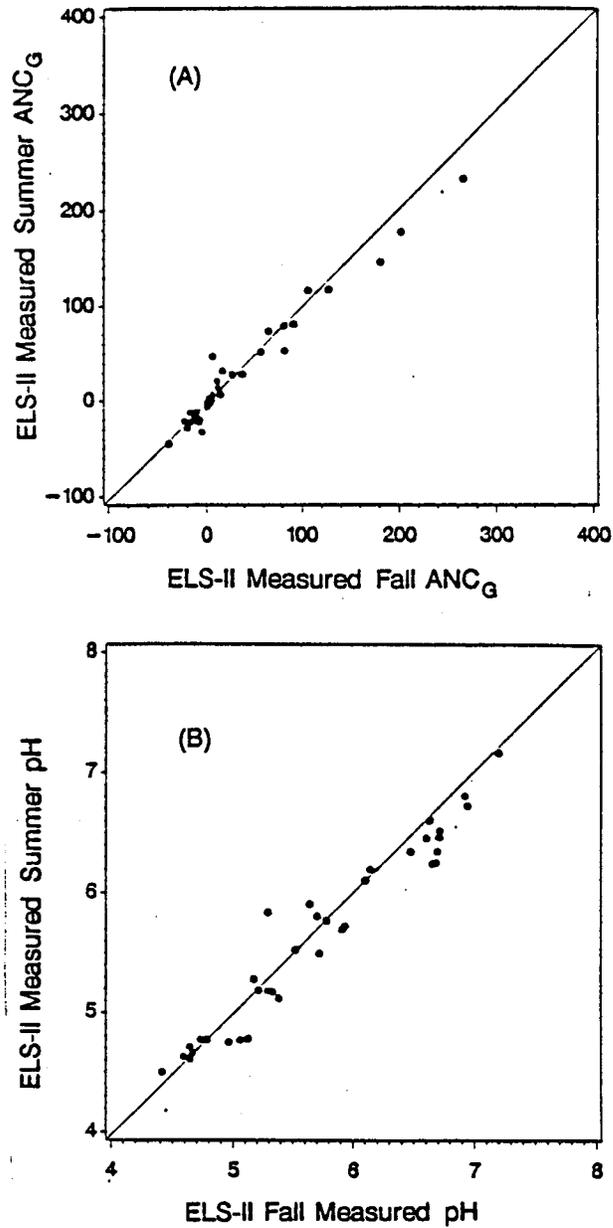


FIGURE 3.8. Comparison of (A) Summer 1986 ANC_G Versus Fall 1986 ANC_G, and (B) Summer 1986 Station pH Versus Fall 1986 Station pH. Interseasonal comparison for 36 lakes in the Adirondack subregion sampled by ELS-II; unofficial and unverified version of the ELS-II 1986.

Diatom model should yield slightly higher estimates of pH for high pH lakes because they were based on air-equilibrated values.

3.3.3 ANC Definition

Because the Diatom model was calibrated to titration ANC (ANC_G) (Diatom Scenario #2) and the MAGIC model used a defined ANC ($C_B - C_A$) (all MAGIC Scenarios), it was necessary to reconcile the differences between these two estimates of ANC. The differences are caused primarily by the partially counteracting influences of Al and organic acids on titration ANC results. Aluminum tends to increase ANC_G relative to defined ANC ($C_B - C_A$) because it acts essentially as a base cation in the titration procedure. Some relatively strong organic acids depress ANC_G relative to ($C_B - C_A$). The difference between titrated and defined ANC for the set of study lakes is depicted in Figure 3.9 using measured values from ELS-I. The Al influence causes a shift to higher ANC_G for acidic lakes, and the organic acids influence causes a shift to lower ANC_G for higher ANC lakes that do not contain appreciable concentrations of Al (Figure 3.9).

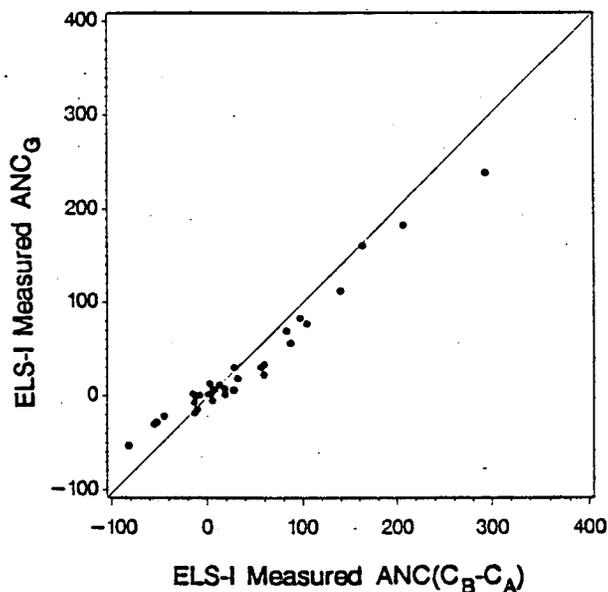


FIGURE 3.9. ELS-I Chemistry Comparison of Calculated Versus Titrated ANC. The x-axis is ELS defined ANC ($C_B - C_A$), where C_B is $Ca^{2+} + Mg^{2+} + Na^+ + K^+ + NH_4^+$ and C_A is $SO_4^{2-} + NO_3^- + Cl^-$. The y-axis is ELS 1984 measured ANC_G .

The difference in ANC definition between models was removed in Diatom Scenario #3 by recalibrating the diatom assemblages in the PIRLA-II lakes to a defined $ANC(C_B-C_A)$. The calibration data for Diatom-inferred $ANC(C_B-C_A)$ are presented in Figure 3.10 for low-ANC ($\leq 100 \mu\text{eq L}^{-1}$) lakes and for the full data set. The equation derived for low-ANC lakes had a standard error of $18 \mu\text{eq L}^{-1}$. A plot of current Diatom-inferred $ANC(C_B-C_A)$ versus measured $ANC(C_B-C_A)$ for the comparison lakes is presented in Figure 3.11. The Diatom-inferred estimates of $ANC(C_B-C_A)$ exhibited similar shifts relative to Diatom-inferred estimates of ANC_G (Figure 3.12), as were found for the measured values (Figure 3.9). For pre-industrial chemistry, the differences between Diatom-inferred $ANC(C_B-C_A)$ and Diatom-inferred ANC_G were less

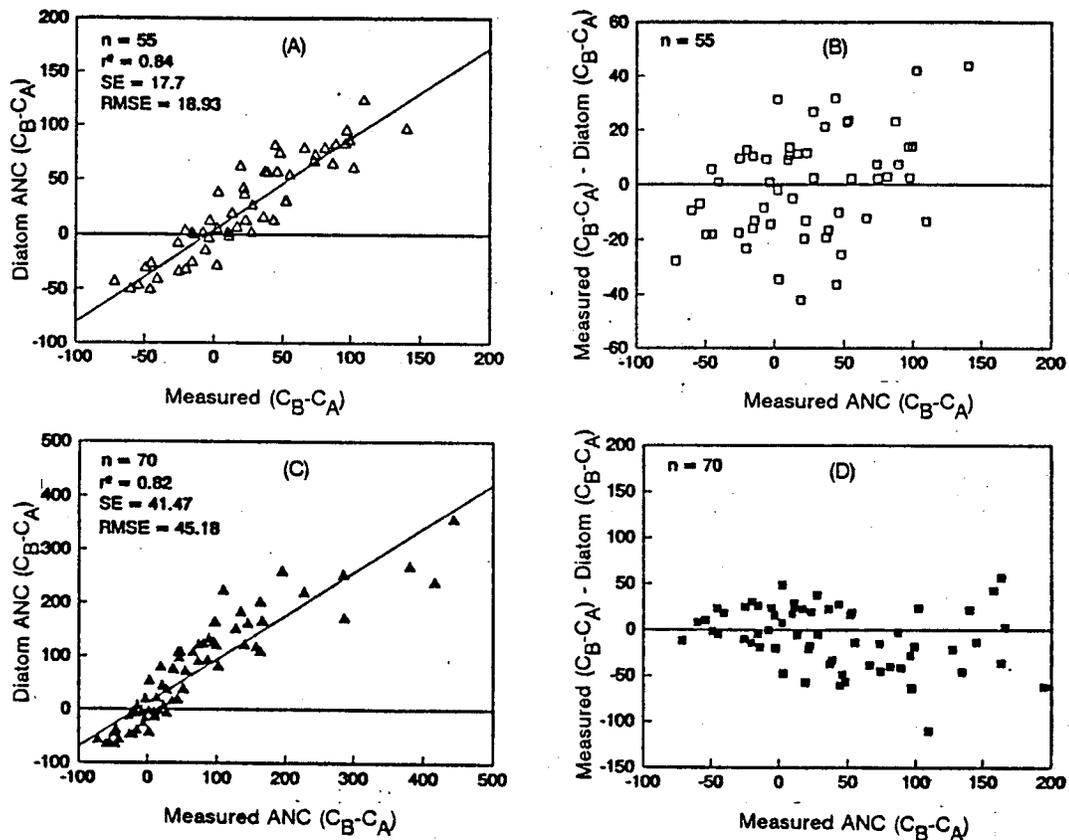


FIGURE 3.10. Paleolimnological Calibration Equations for Diatom-inferred $ANC(C_B-C_A)$ for (A) a restricted data set of lakes having $ANC \leq 100 \mu\text{eq L}^{-1}$, (B) the full data set; and corresponding residual plots. for (C) lakes with $ANC \leq 100 \mu\text{eq L}^{-1}$, and (D) the full data set

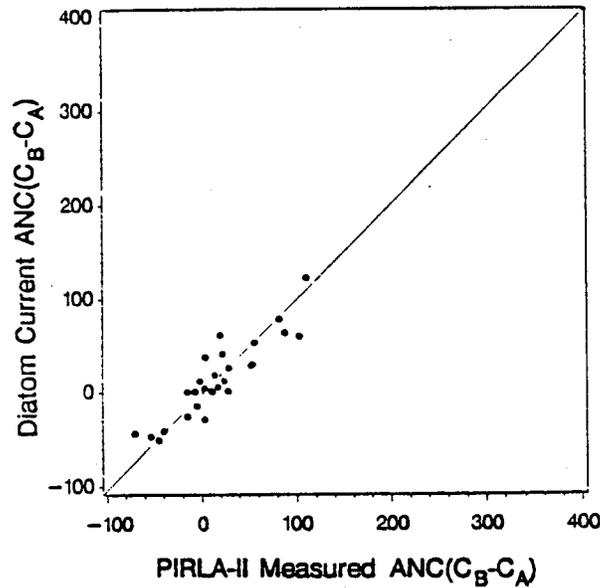


FIGURE 3.11. Diatom-inferred $ANC(C_B-C_A)$ Versus Measured $ANC(C_B-C_A)$ for Lakes Included in This Study

pronounced for the lower-ANC lakes (Figure 3.12b). This is attributed to the lower concentrations of Al_3 in pre-industrial times in those lakes with higher pH values in pre-industrial times.

3.3.4 Deposition Assumptions

Two scenarios were devised to evaluate the general sensitivity of MAGIC to the assumptions regarding pre-industrial deposition of sulfur and base cations. First, the MAGIC Scenario #2 differed from #1 in that pre-industrial sulfur deposition was estimated to be approximately 13% of current deposition (Husar et al. in press) instead of the near-zero value for pre-industrial Adirondack lakewater [SO_4^{2-}] that results from assuming all Cl^- is of seasalt origin.

As expected, the slight difference in the sulfur deposition scenario did not affect the MAGIC simulations for current chemistry (Figure 3.13), because the model is calibrated to current measured chemistry. The pre-industrial estimates of defined $ANC(C_B-C_A)$ and pH were higher, however, for Scenario #1

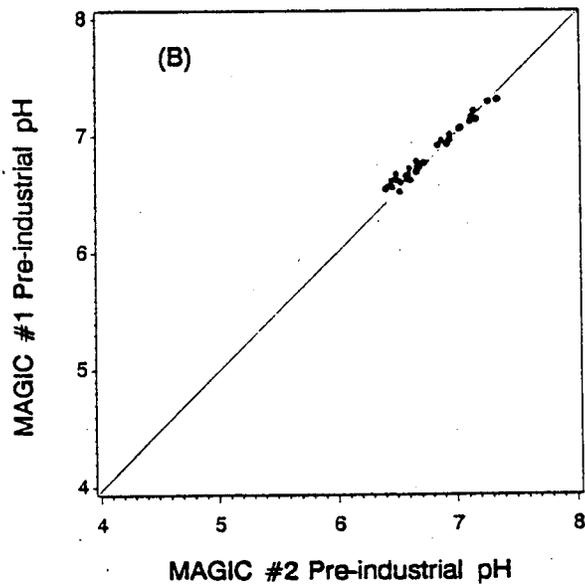
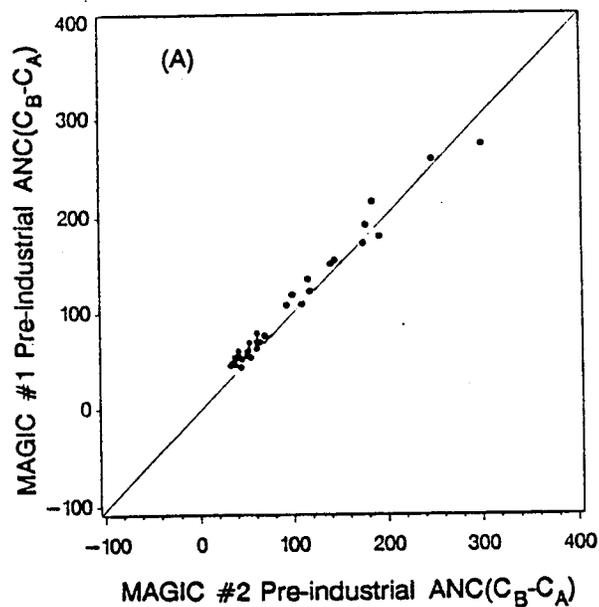


FIGURE 3.14. Comparison Plots of MAGIC Scenarios #1 and #2 for (A) $ANC(C_B-C_A)$ and (B) pH. The y-axis is simulated pre-industrial $ANC(C_B-C_A)$ for (A) and pH for (B) using MAGIC Scenario #1. The x-axis is simulated pre-industrial $ANC(C_B-C_A)$ for (A) and pH for (B) using MAGIC Scenario #2 (Husar-based background SO_4).

than #2 (Figure 3.14). The uncertainty in sulfur deposition assumption is unlikely to introduce bias as large as that found between MAGIC Scenarios #1 and #2 since it is generally accepted that pre-industrial sulfur deposition was low but above zero, i.e., in the range of 10-20 $\mu\text{eq L}^{-1}$ (e.g., Galloway et al. 1984, 1987; Brakke, Henriksen and Norton, 1989; Sullivan, in press).

3.3.5 Reaggregation of Subregional Soils Data

Reaggregation of the DDRP soils data to the Adirondack subregion, rather than to the northeastern region, did not result in major changes in estimated soil characteristics. Means and standard deviations for the Northeast and Adirondack sampling classes are shown in Table 3.1. Also given in Table 3.1 are the results of a paired t-test of the difference between the sampling class estimates based on the Adirondack pedons and the Northeast pedons. The only parameter found to be significantly different between the two aggregation procedures was cation exchange capacity (CEC) in the upper soil horizon. This implies that CEC in the Adirondack A+B horizons is higher than in similar soils in the Northeast as a whole. This difference could bias MAGIC projections because CEC is an important capacity parameter in the model.

Table 3.2 lists the means and standard deviations for the watershed estimates based on the aggregation from the Northeast and Adirondack sampling classes. The results of a paired t-test of the differences in watershed estimates are also shown in this table. Of the sixteen comparisons shown in Table 3.2, nine are significant at the 0.01 level. This was unexpected because most sampling class differences had not been significant. Some of the differences, though statistically significant, probably do not have implications for the modelling results because the differences are so small (e.g., bulk density) or because the parameters are relatively unimportant (e.g., exchangeable Na, K). Differences in important capacity parameters such as CEC and soil thickness could result in differences in model results. However, they may be offsetting; Adirondack soils have higher CEC, but are thinner, so the overall exchangeable base cation pool is probably similar for both aggregations.

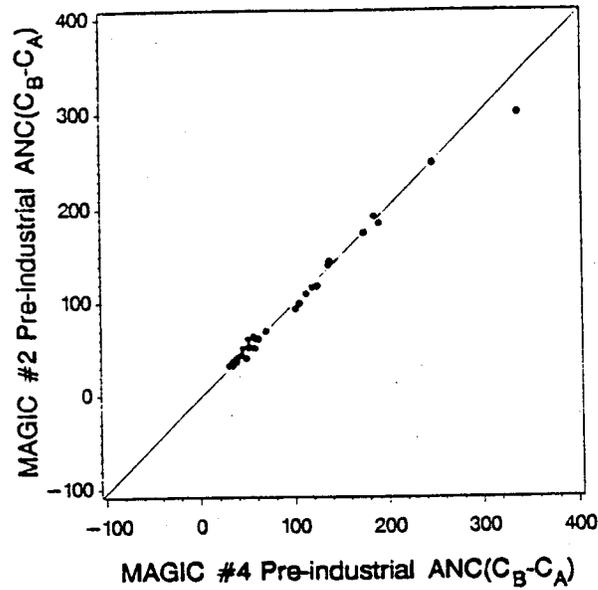


FIGURE 3.15. Comparison Between MAGIC Estimates of Current $ANC(C_B-C_A)$ for MAGIC Scenario #2 (Calibrated to Northeastern Region) and Scenario #4 (Recalibrated to Adirondack Subregion)

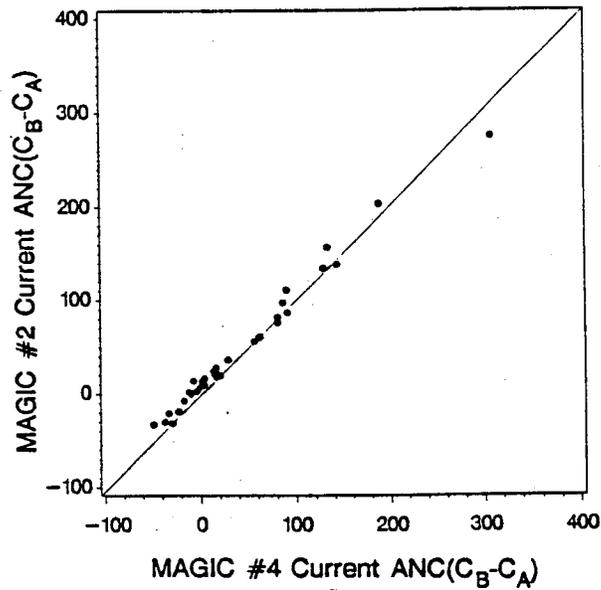


FIGURE 3.16. Comparison of MAGIC Scenario #2 Simulations of Pre-industrial $ANC(C_B-C_A)$ with Simulations Based on Reaggregation of Soils Data and Recalibration of MAGIC to Adirondack Subregion (Rather Than Northeastern Region) (Scenario #4)

following two observations. Although pre-industrial ANC remained essentially the same after the recalibration (Scenario #4) as for the MAGIC Scenario #2 (Figure 3.15), the recalibration produced approximately $10 \mu\text{eq L}^{-1}$ lower estimates of current ANC (Figure 3.16). This shift was probably caused largely by a bias in predicted versus observed lakewater SO_4^{2-} concentration in the Scenario #2 simulations (Figure 3.17a). This bias was removed during the calibration to the Adirondack subregion. Recalculating the in-lake sulfur uptake in the Baker and Brezonik (1988) sulfur retention model to the Adirondack subregion lakes yielded near zero values for this coefficient (Figure 3.17b).

A substantial shift was observed for the pH estimates as a result of the subregional MAGIC recalibration (Figures 3.18, 3.19). The recalibration resulted in consistently lower pre-1850 pH values (by about 0.25 pH units; Figure 3.18). A similar bias was observed for current pH estimates for the lakes having current pH greater than approximately 5.5 (Figure 3.19), whereas the bias decreased at lower pH and was not observed for lakes having pH less than 5.0. This shift is attributable primarily to the higher pCO_2 values estimated for Adirondack lakes, compared with the northeastern ELS-I region as a whole. The reason the shift was not apparent for low-pH (< 5.0) lakes was that lakewater pH is generally insensitive to CO_2 over-pressure at such low pH values.

Thus, the MAGIC calibration (Scenario #1) to the Northeast region did not appear to bias results for the Adirondack subregion as a consequence of differences in soil characteristics within the northeast region. The MAGIC calibration, however, was apparently sensitive to differences between the Adirondack subregion and the Northeast as a whole, particularly in terms of in-lake sulfur uptake and lakewater pCO_2 . The Adirondack lakes tend to be located at higher elevation, are more often headwater lakes, and have shorter retention times than northeastern lakes in general, which results in little in-lake sulfur retention. These subregional characteristics tend to produce smaller effects of in-lake sulfur retention on lakewater ANC and pH and larger pH effects from CO_2 oversaturation. Such expected differences appear to have

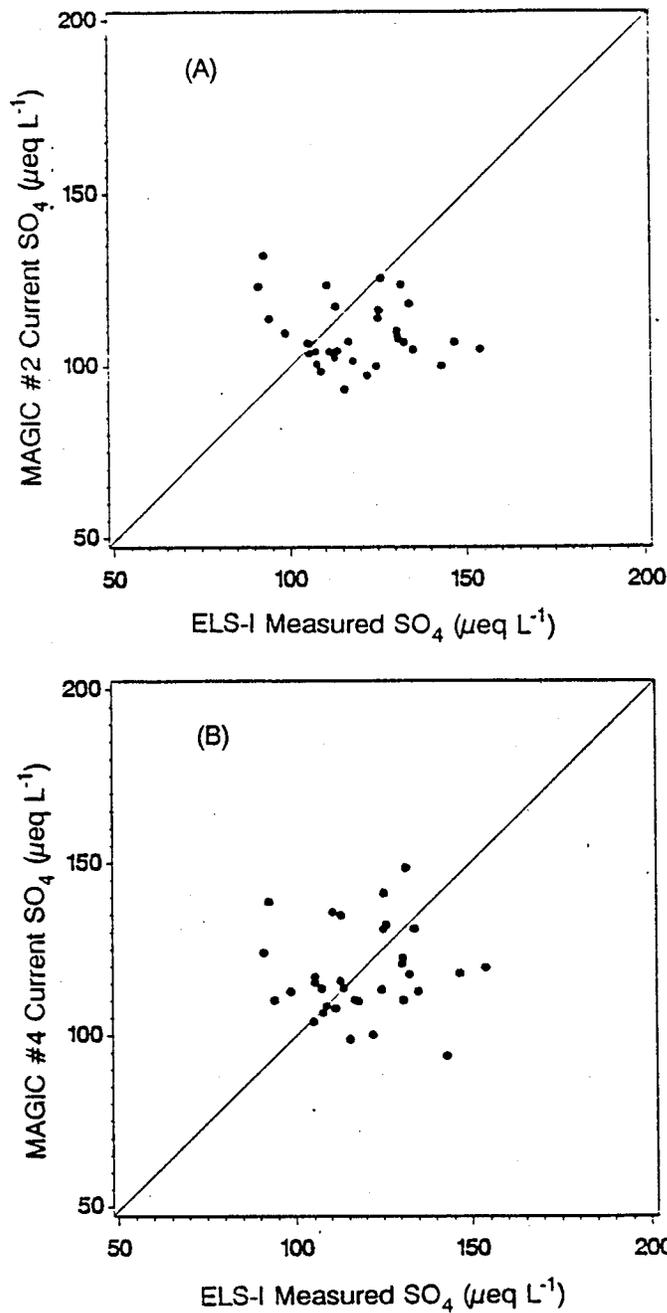


FIGURE 3.17. Sulfate Calibration data for (A) MAGIC Scenario #2 Simulations and (B) Recalibration for Adirondack Subregion (Scenario #4). The recalibration removed the bias associated with SO_4^{2-} simulated values in Scenario #2. The mean and (standard deviation) for simulated minus observed SO_4^{2-} concentration was -9.7 (19.4) $\mu\text{eq L}^{-1}$ for the upper plot and -0.8 (19.7) $\mu\text{eq L}^{-1}$ for the lower plot.

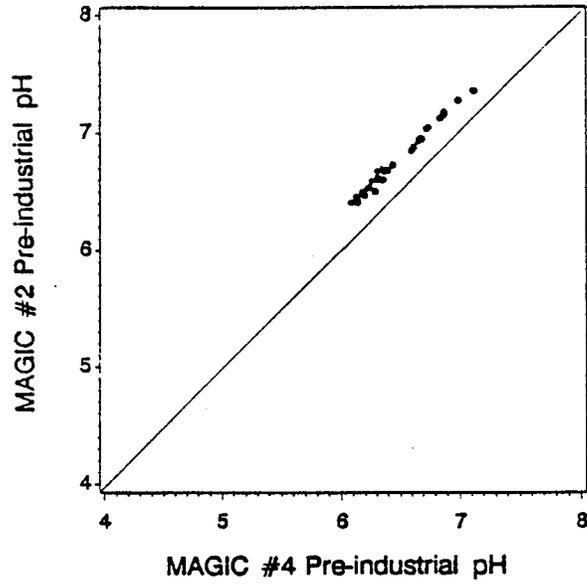


FIGURE 3.18. MAGIC Pre-industrial pH Versus Diatom-inferred Pre-industrial pH. MAGIC simulations were based on reaggregation and recalibration to the Adirondack subregion (Scenario #4).

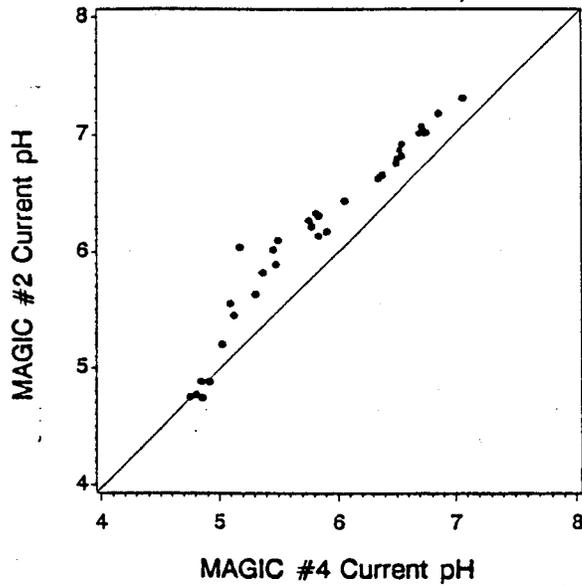


FIGURE 3.19. MAGIC Current pH Versus Diatom-inferred Current pH. MAGIC simulations were based on reaggregation and recalibration to the Adirondack subregion (Scenario #4).

resulted in appreciable differences in MAGIC output, depending on whether the model was calibrated to the region or subregion.

3.4 SYNTHESIS

Comparisons of Diatom and process-based model estimates of historical acidification have previously been conducted for a limited number of aquatic systems. For example, Wright et al. (1986) applied the MAGIC model to four lakes for which paleolimnological reconstructions had been constructed: Big Moose Lake in the Adirondack subregion, Loch Grannoch in Scotland, Lake Gårdsjön in Sweden, and Lake Hovvatn in Norway. All four lakes were inferred by both paleolimnology and MAGIC to have been low in ANC ($< 50 \mu\text{eq L}^{-1}$) prior to the turn of the century, and there was generally good agreement between the two approaches. Paleolimnological and MAGIC reconstructions of the pH history of Round Loch of Glenhead, Scotland, also showed close agreement (Neal, Whitehead, and Jenkins 1988). Both approaches suggested that the lakewater pH in Round Loch of Glenhead decreased roughly from 5.7 to 4.8 since 1800.

Jenkins et al. (1990) applied MAGIC to a range of six catchments in Scotland subject to different levels of acid deposition and land use. Simulated trends in pH were compared with paleolimnological pH reconstructions for the same sites. Both techniques produced similar historical acidification trends, and, with some exceptions, closely matched current measured pH. A comparison of current and pre-industrial pH, as estimated using the two approaches, is presented in Figure 3.20.

Schnoor, Nikolaidis, and Glass (1986) conducted hindcast simulations for three upper Midwestern seepage lakes (Clara, Vandercook, and McNearney Lakes) using time-variable and steady-state versions of the Trickle-Down model. The authors cautioned that the model results should be viewed as indications of the types of changes the lakes may have experienced rather than as firm reconstructions of lake acid-base chemistry because of the large uncertainties in historical deposition and in the response of weathering to increased strong mineral acids. The model reconstructions suggested that Lakes Clara and Vandercook had acidified by approximately $10\text{-}15 \mu\text{eq L}^{-1}$ of ANC. The model-projected acidification of McNearney Lake by $60 \mu\text{eq L}^{-1}$ was inconsistent with

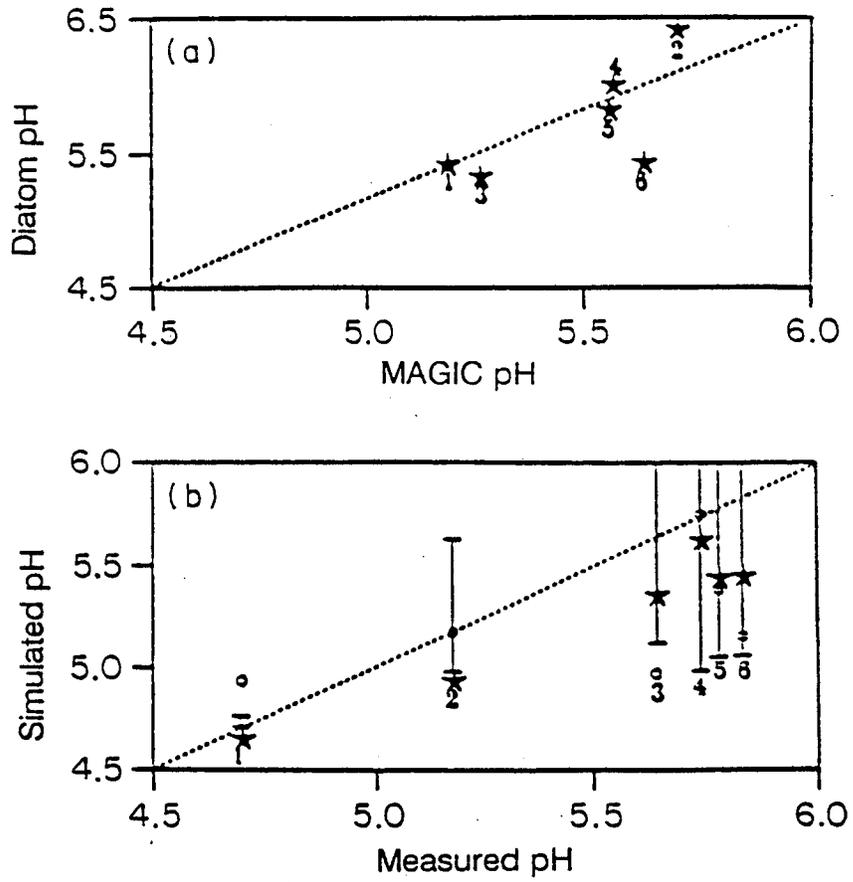


FIGURE 3.20. Comparisons of (A) Diatom Inferences and MAGIC Model Hindcasts of Pre-industrial (ca. 1850) Lakewater pH at Round Loch of Glenhead (1), Loch Chon (2), Loch Dubh (3), Loch Tinker (4), Loch Doilet (5), and Loch Uaine (6) in Scotland and (B) Simulated Present-day pH from Diatom (o) and MAGIC (*) Versus Measured pH. Solid bars represent the range of present-day measured pH values at each site. (Source: Jenkins et al. 1990)

paleolimnological data that suggest this lake (current ANC = $-38 \mu\text{eq L}^{-1}$) has been acidic for at least the last 4000 years (Cook et al. in press). The Trickle-Down model did not account for Al, which is present in high concentrations ($248 \mu\text{g}^{-1}$) in McNearney Lake. This may account, at least in part, for the discrepancy.

Thus, earlier studies that compared process-based model and paleolimnological estimates of historical acidification generally showed good agreement, primarily for comparisons between MAGIC and paleolimnology for lakes that have

Both issues described above are likely to exert some influence on the evaluation of change in pH or ANC_Q , but data are lacking with which to quantify the effect. Diatom-inferred changes in DOC for the Adirondack lakes (Kingston and Birks 1990; B. F. Cumming and J. C. Kingston, personal communication) suggest, however, that the DOC changes have generally been small (less than the standard error of the inference equation, $55 \mu\text{M}$ or $\approx 0.6 \text{ mg L}^{-1}$ DOC) (Table 3.3). Although organic effects on ANC_Q can be substantial (Sullivan et al. 1989), such effects should be minimal on $ANC(C_B-C_A)$, because such a definition excludes organic anions. Data are lacking with which to quantify the extent to which the influence of organic acids on pre-industrial lakewater chemistry may bias the comparison between Diatom-inferred and MAGIC-simulated pre-industrial pH. Analyses presented in the Appendix suggest, however, that failure to include organic acids in the MAGIC simulation presented in this study may have substantially biased the pH comparison results.

The most reasonable comparison available between the MAGIC and paleolimnological hindcasts includes MAGIC Scenario #4 (based on the subregional reaggregation and recalibration) and the paleolimnological inferences of ANC defined as $ANC(C_B-C_A)$. This comparison removed the biases associated with the ANC definition used and the regional (rather than subregional) nature of the other MAGIC scenarios. Results of this comparison showed good agreement for the estimates of current chemistry (Figure 3.21) but substantial differences between the MAGIC and paleolimnological estimates of pre-industrial chemistry (Figure 3.22). The MAGIC model estimates of pre-1850 pH and ANC were generally higher than the Diatom estimates. MAGIC results therefore imply that the lakewater acid-base status had been more responsive to historical increases in acidic deposition (Figure 3.23). The extent to which the model estimates "agree" or "disagree" depends largely on one's perspectives and expectations. A decade ago, most scientists believed that 60-100% of the atmospheric sulfate input caused a stoichiometric decrease in ANC (e.g., Henriksen 1979, 1980; Wright 1983). Compared to these earlier estimates, the Diatom and MAGIC hindcast estimates are in relatively good agreement, and imply that the above percentage has been 0-50%. Nevertheless, the MAGIC estimates of historical

TABLE 3.3. Measured and Diatom-inferred Dissolved Organic Carbon Concentrations for Lakes Included in the Diatom/MAGIC Comparison

Lake	Measured			Current Minus Average Measurement	Diatom-Inferred		
	ELS-I	PIRLA	Average ELS and PIRLA		Pre-1850	Current	Pre-1850 minus Current
----- $\mu\text{eq L}^{-1}$ -----							
1A1-003	131	278	205	-47	331	158	173
1A1-012	213	204	209	22	251	230	21
1A1-014	182	182	182	81	236	263	-27
1A1-017	291	354	323	-118	263	205	58
1A1-020	347	347	347	51	311	398	-87
1A1-028	327	305	316	-74	222	242	-20
1A1-029	497	538	518	50	434	567	-133
1A1-033	317	312	315	5	334	319	15
1A1-039	56	101	79	99	176	177	-1
1A1-046	425	425	425	-112	264	313	-49
1A1-049	75	199	137	94	261	231	30
1A1-057	427	498	463	-55	349	408	-59
1A1-061	486	531	509	-10	350	499	-149
1A1-064	223	212	218	74	215	291	-76
1A1-066	148	155	152	192	325	343	-18
1A1-073	176	278	227	-8	274	219	55
1A2-002	147	143	145	-27	198	118	80
1A2-006	382	339	361	-98	292	263	29
1A2-037	463	463	463	-37	410	426	-16
1A2-041	687	548	618	-245	271	373	-102
1A2-042	409	399	404	-3	328	401	-73
1A2-045	173	170	172	51	240	222	18
1A2-046	161	161	161	-26	46	135	-89
1A2-048	446	446	446	-52	378	394	-16
1A2-052	394	415	405	-55	360	350	10
1A2-054	410	400	405	-105	296	300	-4
1A3-001	360	354	357	-116	211	241	-30
1A3-040	212	205	209	-5	199	204	-5
1A3-042	427	346	387	21	410	407	3
1A3-043	579	537	558	-149	387	409	-22
1A3-046	234	247	241	34	222	274	-52
1A3-048	389	345	367	-34	314	333	-19
1A3-065	139	143	141	84	273	225	48
Mean/100	3.13	3.21	3.17	-0.16	2.86	3.01	-0.15

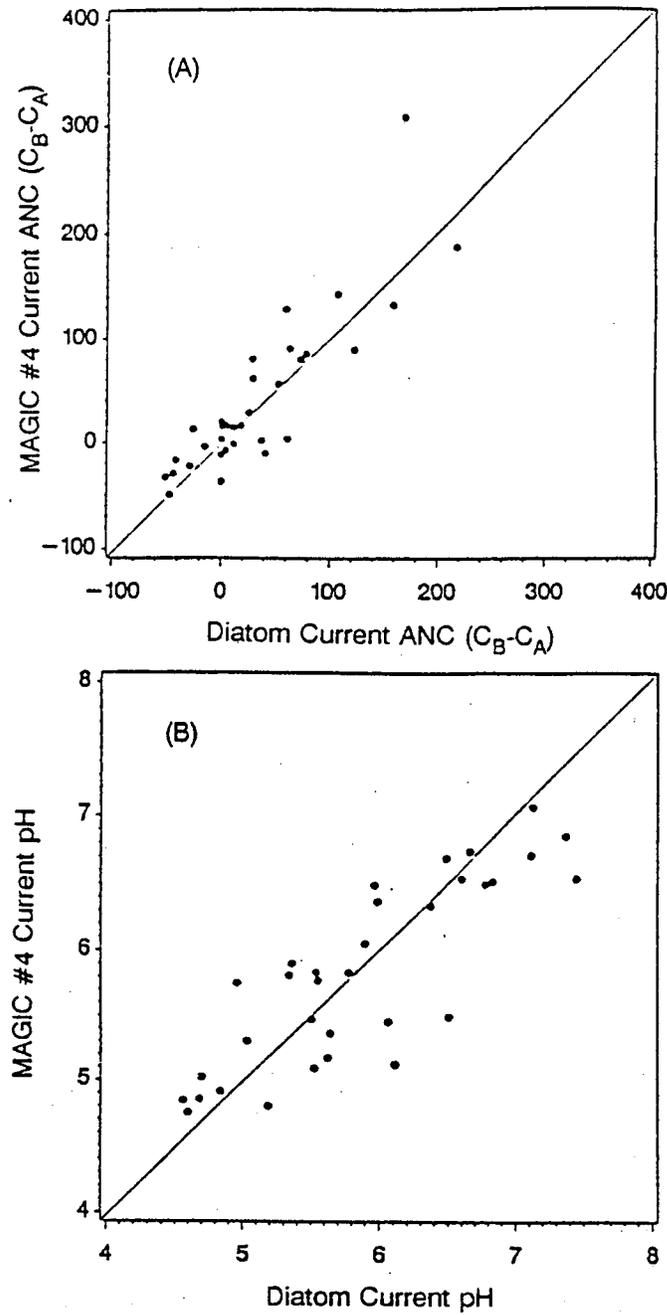
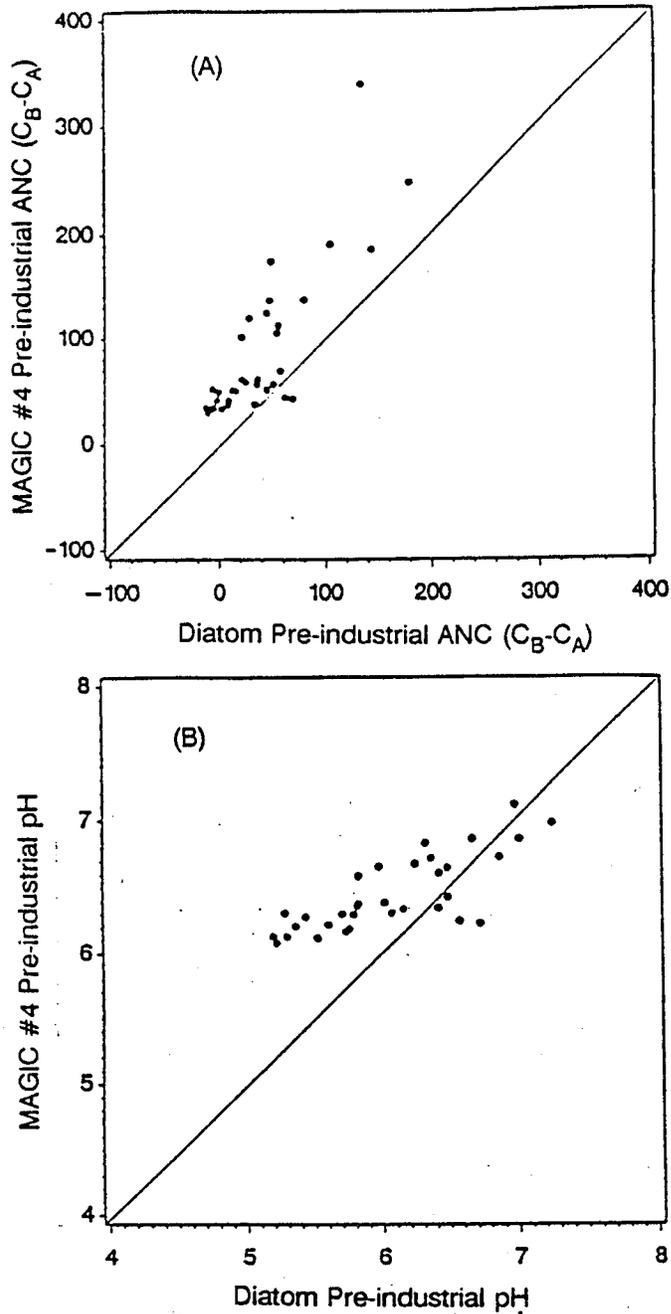


FIGURE 3.21. Comparison Plot of (A) Current ANC Estimates Between the MAGIC Scenario #4 Simulations of $ANC(C_B - C_A)$ and the Diatom Inferences of $ANC(C_B - C_A)$ and (B) Current pH Estimates Between the MAGIC Scenario #4 Simulations and Diatom Inferences



— pre-1850

FIGURE 3.22. Comparison Plot of (A) Pre-industrial ANC Estimates Between the MAGIC Scenario #4 Simulations of $ANC(C_B - C_A)$ and the Diatom Inferences of $ANC(C_B - C_A)$ and (B) Comparison Plot of Pre-industrial pH Estimates Between the MAGIC Scenario #4 Simulations and Diatom Inferences

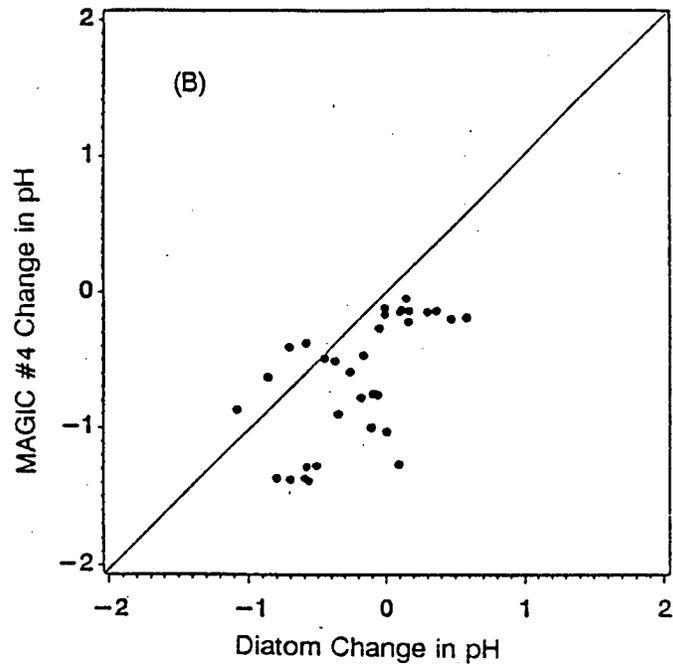
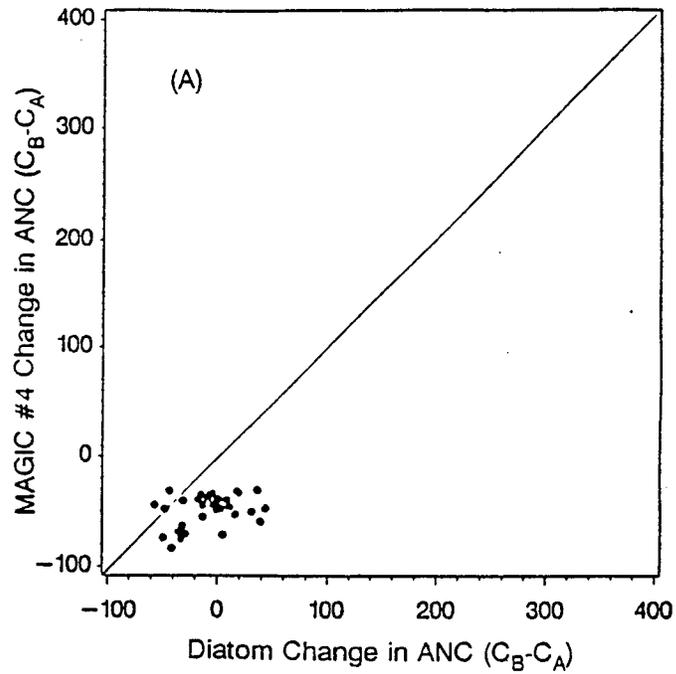


FIGURE 3.23. Estimates of Change From Pre-industrial Time to the Present Using the MAGIC Model Scenario #4 Simulations versus Diatom Inferences of Change in (A) $ANC(C_B - C_A)$ and (B) pH

acidification presented here imply that the acidification since pre-industrial times has been substantially greater than the acidification inferred from the Diatom model.

4.0 CONCLUSIONS

Results of these analyses indicate that differences in ANC definition and deposition assumption between a Diatom model and MAGIC, a process-based watershed model, confound a comparison of estimates of historical acidification made with these models. Nevertheless, the comparisons made suggest that there are both similarities and differences between the two hindcast approaches, as follows:

Similarities

- Both approaches indicate acidification of low-ANC lakes in the Adirondacks since pre-industrial times
- Both approaches suggest that lake acidification has been of lesser magnitude than was generally believed prior to NAPAP and that neutralization of acidic inputs (e.g., via base-cation release) has been substantial

Differences

- Diatom paleolimnological estimates suggest that lake acidification has been restricted to low-ANC ($< 50 \mu\text{eq L}^{-1}$) lakes, whereas MAGIC infers acidification of higher-ANC lakes as well
- Inferred historical changes in pH and ANC are greater using MAGIC than using diatom paleolimnology.

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equations:

$$\begin{aligned} \text{HTOT} &= (\text{HA}^-) 0.00001/0.0001 + (\text{HA}^-) \\ &= 1.1 (\text{HA}^-). \end{aligned} \tag{A.4}$$

Thus, 22 mmol L⁻¹ of total organic acid was added to each lake in the simulations in order to produce 20 µeq L⁻¹ of organic anion charge at pH = 5.0.

The results of the new MAGIC scenario (#4A) are presented in Figures A.1 and A.2 for current and pre-industrial acid-base chemistry, respectively. The MAGIC results for simulated current pH were in slightly poorer agreement with diatom pH estimates (Figure A.1), as compared with MAGIC scenario #4, which did not include an organic acid representation (Figure 3.21). The change in agreement was fairly small and was likely attributable to not recalibrating the model pH/ANC relationship with the added organic acids. The end result of a recalibration of this relationship would be to adjust the calibrated CO₂ overpressure in lakewater. In the calibration procedure for scenario #4, it was assumed that CO₂ overpressure accounted for all of the discrepancy between measured and calculated pH. This relationship was altered by the addition of organic acids in Scenario #4A, but time and resource constraints precluded further calibration for the purposes of the research described in this appendix.

MAGIC results for simulated current ANC(C_B-C_A) were not appreciably different between scenario #4A (Figure A.1) and scenario #4 (Figure 3.21). Inclusion of an organic acid representation in Scenario #4A did not have a major effect on ANC estimates because a defined ANC was used that excludes organic anions (see Section 2.4.3).

The MAGIC results for simulated pre-industrial ANC(C_B-C_A) were also similar between the MAGIC Scenarios #4 and #4A (Figures 3.22 and A.2), again because a defined ANC was used that excluded organic influence. Results for simulated pH were in much better agreement with diatom estimates for the scenario that included an organic representation (Scenario #4A, Figure A.2) than for the otherwise similar scenario that excluded organic acids

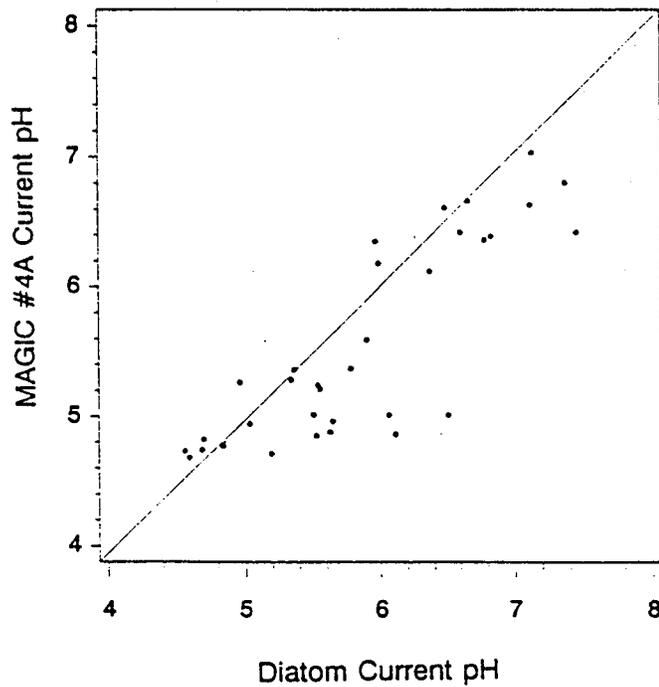
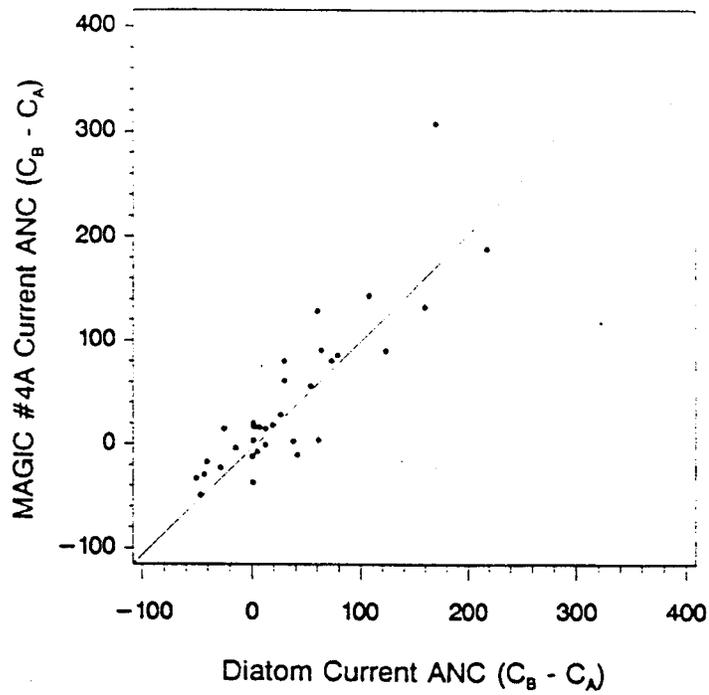


FIGURE A.1. Comparison Plot of (A) Current ANC Estimates Between the MAGIC Scenario #4A Simulations of ANC ($C_B - C_A$) and the Diatom Inferences of ANC ($C_B - C_A$) and (B) Current pH Estimates Between the MAGIC Scenario #4A Simulations and Diatom Inferences

a good fit for Adirondack lakes between measured ANC and modeled ANC, including organic acids in the modeled ANC expression. This, or a similar, approach could be coupled to the MAGIC model to produce a more rigorous evaluation of organic influence on the comparison results of pre-industrial pH between the Diatom and MAGIC models. The results of MAGIC Scenario #4A (Figure A.2) suggest that such an approach would be an appropriate next-step in the attempt to rectify the observed discrepancies between model results.

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