Executive Summary

Calibration of diatom-pH-alkalinity methodology for the interpretation of the sedimentary record in Emerald Lake, Integrated Watershed Study.

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Submitted by

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In 1968 a report by Oden (Smol et al. 1986) drew attention to the probable relationship between acid deposition from the atmosphere and lake acidification in Swedish lakes. In assessing such a relationship it is important to have long-term records of the pH (i.e. hydrogen ion concentration) in lakes of different chemical composition and buffering capacities. Unfortunately, accurate pH measurements spanning the past few decades do not exist for many lakes. Thus limnologists have attempted to develop methods of estimating the pH levels which occurred during the past century or more. One such method which is currently in use is based on the species composition and relative abundance of the siliceous skeletons of a group of unicellular algae, called diatoms, which are preserved in lake sediments. The species found and their relative abundances are indicators of the chemistry of water in which they once lived.

The method relies on observations reported initially in the late 1930's through the 1950's, that diatom assemblages in lakes reflect, among other things, the pH of their environment. Some species thrive only in acidic water, others in water with pH's of about 7 and still others in alkaline waters. This sensitivity has recently been employed to infer pH values of the past through the analysis of diatoms preserved in lake sediments. From cores which reach down into older sediments it has been possible to reconstruct pH trends in lakes which occurred over the past 100 to thousands of years. In a number of lakes in Europe, Scandinavia and North America it has been demonstrated that an appreciable reduction in pH has occurred during the past 30-40 years; this is believed to be the result of acid deposition.

Lake sediment diatom pH reconstruction is a three-step process. First diatoms in the surface sediments are identified and enumerated in a study area. Generally one sample is examined in each lake in a calibration suite of lakes (usually 20 or more) which exhibit a wide range of pH values. These data are then used to establish pH "preference" categories of each of the observed diatom taxa. Generally the categories employed are the five proposed by Hustedt (1939):

alkalibiontic (ALB):	species occurring only at pH values above pH 7
alkaliphilous (ALP):	species occurring at pH values about 7 and with widest distribution at pH greater than 7
indifferent (IND) :	species occurring at about pH 7
acidophilous (ACB) :	species occurring at about pH 7 with widest distribution at pH values below 7
acidobiontic ACB) :	occurring below pH 7 with optimum distribution below pH 5.5

In the present study a slight modification of this classification has been used.

The second step is to calculate the percentage of the diatoms assigned to each pH category on a lake-by-lake basis. The percentages of diatoms in the various pH categories are then employed to calculate an index for each lake which predicts the individual lake pH. An equation is next obtained using regression methods which expresses the relationship between the logarithm of the indices and observed pH in all lakes in the calibration set. In common usage are indices developed by Scandinavian scientists. However, the slope and intercept values of the equations employing these indices vary from lake calibration set to lake calibration set making it necessary to calibrate each area in which diatom-pH relationships and predictions are sought. Such calibration sets from Scandinavia, Canada, Europe, the United Kingdom, and the northeastern United States have provided area-specific but statistically significant equations between such indices and lake pH, permitting pH predictions from lake diatom assemblages within each study area. Multiple linear regression techniques, which have also been applied to estimate lake pH from the frequency of occurrence of diatoms in each pH category, provide coefficients for the independent variables which are also area-specific.

In step three these equations are applied to the diatom occurrence data obtained from samples at a number of depths in a lake sediment core. The calculated pH estimates, together with sediment age data, are then used to reconstruct the pH history of the lake over the time interval represented by the core material. The equations predict pH with an estimated standard error from about ± 0.25 to about ± 0.5 pH units.

Predictive diatom-pH relationships have been developed in the present ARB-funded project. Surface sediment samples, together with water chemistry data, were collected in midsummer 1985 in 30 high elevation Sierra Nevada lakes with an air-equilibrated pH range of 5.84 to 9.53. In one lake diatoms were extremely scarce and could not be enumerated quantitatively. After placing the diatoms in pH preference categories (Appendix A) in the remaining 29, lakes log index B (Renberg and Hellberg 1982) and multiple linear regression equations (Battarbee 1984, Charles 1985) were calculated and the relationship between the predicted and observed air-equilibrated pH examined. In both treatments the pH prediction for the two lakes with the highest pH values (9.07 and 9.53) deviated greatly from the rest of the lakes. These extreme outliers were not used in the following calcualtions:

1) diatom inferred pH = 7.11 - 0.40 log Index B
$F = 117$ Prob. $>F = 0.0001$ $r^2 = 0.82$ $n = 27$

2) diatom inferred pH = 7.08 - 0.0086% ACP + 0.0012% IND + 0.0081% ALP + 0.021% ACB
$F = 37.5$ Prob. $>F = 0.0001$ $r^2 = 0.87$ $n = 27$

Since the multiple linear regression analysis revealed that the relative abundance of the indifferent forms contributed little to the statistical significance of the regression, the equation was recalculated omitting indifferent taxa. The equation omitting the "indifferent" forms is as follows:

3) diatom inferred pH = 7.18 - 0.0097% ACP + 0.0070% ALP + 0.020% ALB

$F = 52 \quad \text{Prob.} > F = 0.0001 \quad r^2 = 0.87 \quad n = 27$

These relationships are significant and have high r^2 values showing that the equations account for 82 to 87% of the observed variability in the relationship. The r^2 values of these equations are similar to those obtained by investigations in other areas.

Diatom occurrence was also examined with respect to lake alkalinity using both log Index B and multiple linear regression. The relationship between alkalinity and diatom preference pH groups was less strong (r^2 for log Index B = 0.60, r^2 for multiple linear regression using ACP, ALP, and ALB categories = 0.77), although remaining statistically significant.

These results reveal that the ARB now has available an effective tool to obtain pH reconstructions from cores in high elevation Sierra Nevada lakes. These pH predictive equations will be employed shortly to construct a diatom inferred pH reconstruction over the past 100-125 years of Emerald Lake (ARB Contract A3-096-32) in Sequoia National Park. Such a reconstruction in Emerald Lake, or other Sierra lakes, will be useful in understanding and documenting long-term trends in pH and its possible relationship to acid deposition loading which is one of ARB's regulatory responsibilities.

In the present study usable surface sediment cores were obtained in 29 lakes. Diatom data from the two highest pH lakes (Bright Dot, pH 9.03 and Barney, pH 9.53) could not be used in developing the equations as they were extreme outliers in the data set. Improvement in the pH predictive equations could be obtained by coring and analyzing surface sediment diatoms in additional lakes. While there is no reason to suspect that the 27 lakes employed in the Sierra lake calibration set are atypical, there is a need to obtain independent estimates of the errors associated with the use of these pH predictive equations. This can best be done by sampling the surface sediments in a number of lakes not used in deriving the predictive equations and comparing the predicted pH values with the observed pH values.

The diatom flora of high elevation Sierra lakes is inadequately known. We have not been able to find valid names for about 40% of the taxa encountered in this study. Since we have good photographic documentation of these unknowns, no serious problems relating to diatom identification and pH category assignment is expected to arise in developing the pH reconstruction of Emerald Lake. However, other scientists who may wish to use our diatom pH assignments will be confronted with a considerable number of undescribed forms. Thus, if additional diatom pH reconstructions are to be undertaken in the future, it would be highly desirable to publish descriptions of those taxa which have proved to be useful pH indicators.

References:

Battarbee, R. W. 1984. Diatom analysis and the acidification of lakes. Phil. Trans. R. Soc. Lond. B:305, 451-477.

Charles, D. 1985. Relationships between surface sediment diatom assemblages and lakewater characteristics in Adirondack lakes. Ecology 66(3):994-1011.

Hustedt, F. 1939. Systematische und okologische Untersuchungen uber die Diatomeen-Flora von Java, Bali, und Sumatra nach dem Material der Deutschen Limnologischen Sunda-Expedition III. Die okologischen Factorin und ihr Einfluss auf die Diatomeen flora. Archiv. fur Hydrobiol. 16:274-394.

Oden, S. 1968. The acidification of air and precipitation and its consequences in the natural environment. Ecological Committee Bull. No. 1. Swedish National Science Research Council, Stockholm.

Renberg, I. and T. Hellberg. 1982. The pH history of lakes in southwestern Sweden, as calculated from the subfossil diatom flora of the sediments. Ambio. 11(1):30-33.