LIMING DOSAGES FOR ACID LAKES AND WATERSHEDS[a]

Discussion by James J. Bisogni Jr.,[2] Member, ASCE

As Walski clearly states, computing liming dosages for acid lakes is not straightforward. Liming as a remedial action for neutralizing acid surface waters requires accurate dose calculations because of the large mass of neutralizing agent required and because of the ecological consequences of overdosing. A majority of lake neutralization projects have been done using limestone as the neutralizing agent. Limestone is a natural choice because of its availability and relatively low cost. One disadvantage of limestone is the relatively slow dissolution kinetics. This low dissolution must be taken into account when calculating the appropriate dosage for limestone, since some of the applied limestone does not have a chance to dissolve before it settles to the bottom of the lake. In some cases the settled limestone will eventually dissolve, and in other cases it will be covered with detritus or become coated with chemical precipitates. In the latter cases little or no acid neutralization is accomplished.

Accurate computation of limestone dosages requires a knowledge of the dissolution kinetics. Therefore, considerable research has been aimed at delineating these kinetics for acid lakes. Of equal importance, but unfortunately of less research interest, is the procedure used to calculate final pH. Olem (1991) provides a summary of these dosage calculation procedures. The most sophisticated of these assume that the lake will be in equilibrium with atmospheric carbon dioxide after the neutralizing agent has been added. For example, the dosing models proposed by Scheffe et al. (1986), DePinto et al. (1989), and Driscoll et al. (1982) used the open-system assumption to calculate the resultant pH. Interestingly, many of the procedures for predicting limestone dissolution assume that dissolving limestone particles are in equilibrium not with an open, but rather with a closed system (Olem 1991).

The purpose of this forum discussion is to suggest that a closed system is a more appropriate assumption for calculating target pH. The basis for this suggestion is a 10-year neutralization study conducted at Wolf Pond, a 21 ha dimictic lake located in the Adirondack region of New York. In this study Wolf Pond was neutralized with $NaHCO_3$. Since $NaHCO_3$ is extremely soluble, dissolution kinetics did not obfuscate the observations. Results of the study showed clearly that most of the lake behaves as a closed system relative to atmospheric carbon dioxide.

This is demonstrated in Figs. 1 and 2 which are plots of in-situ measured pH versus pH calculated using open- and closed-system equilibrium assumptions. Computation of pH was based on:

$$\mathrm{ANC} = \mathrm{TIC}\cdot(\alpha_1 + 2\cdot\alpha_2) + [\mathrm{OH}^-] - [\mathrm{H}^+] + [A_{org}] \qquad (1)$$

where ANC = acid neutralizing capacity as measured by Gran titration; TIC = $[CO_2]$ + $[HCO_3^-]$ + $[CO_3^{2-}]$; α_1, α_2 = ionization fraction for HCO_3^- and CO_3^{2-}, respectively; $[A_{org}]$ = concentration of humic and fulvic acids, equiv/L; and $[A_{org}]$ was determined by the method described by Bisogni and Arroyo (1991). For closed-system calculations TIC values were measured. For open-system calculations TIC values were computed from atmospheric carbon dioxide partial pressure using (2)

$$\mathrm{TIC} = \frac{1}{\alpha_0}\cdot K_H\cdot P_{\mathrm{CO}_2} \qquad (2)$$

where a_0 = ionization fraction for H_2CO_3; P_{CO_2} = partial pressure of atmospheric CO_2, atm; and K_H = Henry's constant for CO_2, mols/L·atm.

Figs. 1 and 2 show results for all depth and surface samples, respectively. Plotted on each of these graphs is a line that represents a 1:1 correspondence between measured and calculated pH. Depth samples are defined as samples taken from depths greater than 0.5 m. The sampling period for these results was July to October 1993. During this period Wolf Pond was thermally stratified. Thermocline was located at 4.5-m depth. Approximately 25% of the depth samples were located in the epilimnion (at depths ranging from 4.5 to 18 m). Differences between measured (closed) and calculated (open) TIC ranged from approximately zero at the surface to 500 μmol/L at 18-m depth. Similar results were obtained from an earlier study by Arroyo and Bisogni (1991) for data collected from Wolf Pond in 1988. Others have also found significant CO_2 disequilibrium in freshwater lakes (Cole et al., unpublished paper, 1993; Kratz et al. 1987).

It is obvious that surface samples are better represented by "open" conditions and depth samples are better represented by "closed" calculations. Since more than 98% of the lake volume

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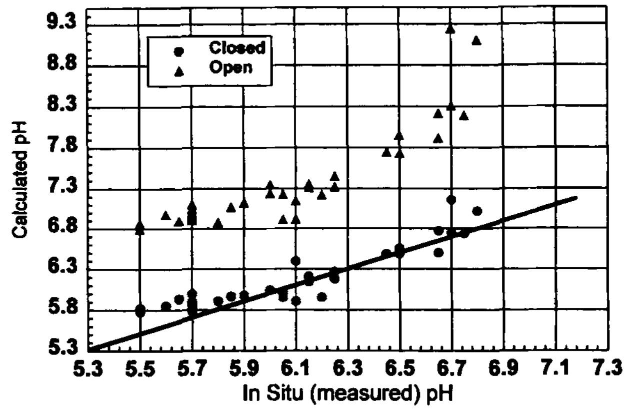

FIG. 1. Measured versus Calculated pH—Depth Samples

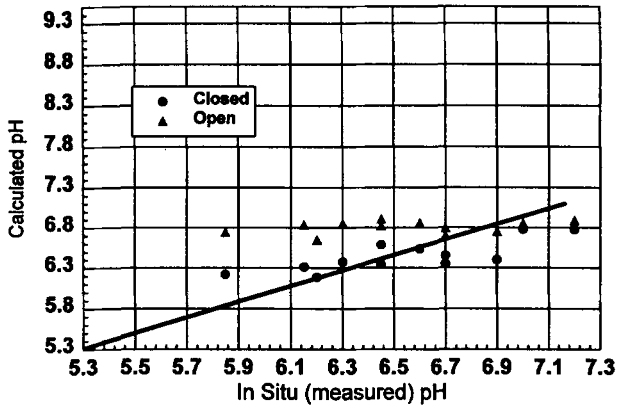

FIG. 2. Measured versus Calculated pH—Surface Samples

in Wolf Pond is located below 0.5 m, closed-system pH calculations seem more appropriate than open-system calculations for estimating the target pH of Wolf Pond and similar neutralized lakes.

Studies from Wolf Pond suggest that calculations used to predict required acid neutralizing capacity to attain a target pH should be based on closed-system equilibrium. Limestone dissolution models (Olem 1991) can then be used to estimate the dosage required to attain the required ANC to meet the target pH. Note that most of the limestone dissolution models do use the closed-system assumption while the limestone is dissolving, so the use of the closed model is consistent.

APPENDIX. REFERENCES

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Closure by Thomas M. Walski,[3] Member, ASCE

I wish to thank the discusser for sharing his observations on lake liming with the Forum readers. He makes two important observations regarding liming dosage calculations.

The first is that steps must be taken to prevent sediment from burying the limestone and coatings from reducing the effectiveness of the limestone. Sedimentation can be minimized by placing the limestone in a portion of the lake or tributary stream where velocities prevent high rates of deposition. The writer has only found coating to be a problem in water bodies with high iron concentrations, such that ferric oxyhydrates coat the limestone. (This is one of the principle problems in using limestone to treat acid mine drainage). As long as iron concentrations are low (as they are in most lakes), the coating problem should be minimized.

The second and more significant finding is that carbon dioxide equilibrium is not reached except for in the most shallow water bodies. Engineers can therefore use closed-system models to determine lime doses, as proposed by Olem (1991).

Because of the many processes occurring in lakes (e.g., mixing, stratification, sedimentation, oxidation), calculating the optimal dosage for liming is still somewhat of an art. Application of limestone needs to be monitored afterward to determine if the desired effect was achieved. The discusser's observations have helped reduce the uncertainty in dosage calculations.

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