Comment on "Dynamic Model of In-Lake Alkalinity Generation" by L. A. Baker and P. L. Brezonik

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INTRODUCTION

A recent paper by *Baker and Brezonik* [1988] presents a predictive model of in-lake alkalinity production in acidified lakes. In their model, they assumed that algae are solely responsible for alkalinity production by nitric acid consumption. They also assumed that algae are solely responsible for consumption of alkalinity by ammonium uptake. These assumptions lead to models with nitrate and ammonium removal coefficients based on lake volume.

We have two comments on the validity of these assumptions. First, in some acidified lakes, algal nitrate consumption predominates. In other lakes, bacterial denitrification is primarily responsible for nitrate consumption. It is possible to predict the predominant removal process from summer epilimnetic nitrate concentrations [*Rudd et al.*, 1986; *Kelly et al.*, 1987; Rudd et al., unpublished manuscript, 1988]. For lakes in which denitrification predominates, a model based on sediment area instead of lake volume should be used because denitrification is mainly a sediment process [*Rudd et al.*, 1986; *Kelly et al.*, 1987]. Second, bacterial nitrification plays an important role in ammonium uptake. At low *pH* this process is inhibited [*Rudd et al.*, 1988], resulting in accumulation of ammonium and increased alkalinity. Modeling of ammonium transformations in acidified lakes requires a more sophisticated approach which could explain why *Baker and Brezonik*'s [1988] proposed algal uptake ammonium model did not give statistically significant agreement with the data.

MODELING ALKALINITY PRODUCTION BY ALGAL NITRATE ASSIMILATION AND BACTERIAL DENITRIFICATION

Nitrate assimilation by either algae or denitrifying bacteria produces one equivalent of alkalinity per mole of nitrate assimilated. The rates of nitrate removal by these two processes, however, must be modeled differently. In lakes where summer nitrate concentrations are less than 2 μmol/L, nitrate removal is rapid and virtually complete (Table 1). Such rapid, complete removal is best explained as algal uptake. In this case, an algal-lake volume model for predicting alkalinity production is appropriate. The nitrate mass transfer coefficients calculated for algal uptake lakes are several times higher than those

calculated for a second category of lakes where there is excess nitrate during summer (>2 μmol/L, Table 1 [*Kelly et al.*, 1987]). In the second category of lakes, nitrate removal is much slower, and less complete, and rates of removal agree well with rates of denitrification measured at the sediment-water interface [*Kelly et al.*, 1987]. This slower removal is because the nitrate must diffuse to the sediments before being denitrified. We have successfully modeled nitrate consumption in such lakes using a sediment area based-model [*Kelly et al.*, 1987].

The basis for the different removal rates and coefficients in the two categories of lakes can be explained by looking at phosphorous availability. In softwater oligotrophic lakes, which are prone to acidification, phytoplankton production and standing crop is limited by the availability of phosphorous [*Schindler*, 1974; *Schindler et al.*, 1978; *Dillon and Rigler*, 1975; *Healey and Henzel*, 1980]. In many regions, acidic precipitation contains elevated levels of nitrate [*Barrie and Hales*, 1984; *Husar*, 1986] but there have not been corresponding increases of phosphorous. Thus in P limited softwater lakes, nitrate inputs from polluted rain are in excess of algal requirements and nitrate accumulates in the surface water. For example, in New Hampshire, the N:P molar ratio of precipitation is 1250:1, and the N:P ratio of runoff from the nitrogen-saturated terrestrial ecosystems is 480:1 [*Likens et al.*, 1977]. This is well above the required N:P ratio of algae (5-10:1 [*Healy and Henzel*, 1980]). This excess has led to elevated concentrations of nitrate (10-30 μEq/L) during summer in lakes located in North America and Europe [e.g., *Driscoll et al.*, 1987; *Rudd et al.*, 1986].

Similar circumstances were deliberately created in Lake 302N at the Experimental Lakes Area (ELA) in northwestern Ontario. The lake was acidified over a 5-year period by additions of 30 meq m^{-2} yr^{-1} of HNO_3 [*Schindler*, 1988; Rudd et al., unpublished manuscript, 1988]. Summer surface water nitrate concentrations increased to about 40 μEq/L, but there was no increase in algal photosynthesis because the lake was P limited. Sedimentation of particulate nitrogen from the epilimnetic waters was lower in Lake 302N than in Lake 302S, which was being concurrently acidified by additions of sulfuric acid (Table 2). These data demonstrate that there was no stimulation of uptake of nitrate by algae following nitric acid additions. Thus algae were not a major source of alkalinity production. In contrast, rates of nitric acid consumption by

TABLE 1. Percent Removal R_n and Mass Transfer Coefficients S_n of Lakes with Very Low and
With Easily Detectable Surface Water Nitrate Concentrations

Lake*	t_w, year	Z, m	$[NO_3^-]$, μeq/L	R_n,† %	S_n,† m/year
		Low NO_3^-			
227 (ELA)	4.1	4.4	1.5	99.7	214
302S (ELA)	8.3	5.1	1.5	98.0	30.1
223 (ELA)	7.1	7.1	1.0	98.0	40.0
Crystal (northern Wisconsin)	10.6	25	0.5	99.0	42.0
		Easily Detectable NO_3^-			
Dart's (Adirondacks)	0.6	7.1	20	7	8.9
302N (ELA)	5.8	5.7	19	70	2.3
239 (ELA)	6.2	10.9	3	88	12.9
Langtjern (Norway)	0.2	2.4	2	36	6.8
Harp (southern Ontario)	2.5	12.4	6.5	58	6.8
Plastic (southern Ontario)	3.0	8.0	1.4	80	10.7

*Data for Crystal, Dart's, Harp, and Plastic lakes are taken from *Kelly et al.* [1987]. Data for
Langtjern are taken from *Wright* [1983].
†$S_n = (R_n(Z/T_w))/(1-R_n)$ from *Kelly et al.* [1987].

bacterial denitrification, measured at the sediment-water inter-
face using $^{15}NO_3^-$, increased from undetectable levels to be-
tween 200 and 1000 μeq m^{-2} d^{-1}. These directly measured
rates of denitrification agreed well with whole lake losses of
nitrate from Lake 302N, indicating that bacterial denitrifica-
tion was the major process removing nitrate from the lake
[*Kelly et al.*, 1987].

We have also successfully used a model based on denitrifi-
cation at the sedimet water interface to predict nitrate removal
from several acidified lakes in the Adirondack Mountains and
in Norway where there is excess nitrate in the water column
during summer [*Rudd et al.*, 1986; *Kelly et al.*, 1987]. Our
model worked equally well if we used a mass balance ap-
proach to calculate the mass transfer coefficient or if we used
directly measured rates of denitrification to predict the mass
transfer coefficient [*Kelly et al.*, 1987]. Measured rates of deni-
trification agreed well with measured mass of nitrate lost in
the lakes.

In summary, both the experiment in Lake 302N and
measurements in lakes acidified by atmospheric deposition
support our contention that denitrification and not algal as-
similation is the most important pathway of nitric acid con-
sumption in lakes where there is detectable nitrate in the sur-
face waters during summer.

The lakes in the work by *Baker and Brezonik* [1988] have
easily detectable nitrate concentrations of between 1.5 and 8.4
μmol/L. The mean coefficient of nitrate removal for these
lakes that they calculated using our denitrification-sediment
area model is 6.8 m/year. This is very close to the two coef-
ficients that we calculated from our set of lakes (9.2 m/year via
mass balance calculation and 7.4 m/year via direct measure-
ment of denitrification rates using $^{15}NO_3^-$ [*Kelly et al.*,
1987]). These "slow" coefficients are typical of lakes with
excess nitrate concentrations where denitrification at the
sediment-water interface is the predominant removal process.
In lakes where nitrate removal is controlled by algal assimi-
lation, much higher mass transfer coefficients are observed
(Table 1).

Even though the nitrate removal coefficients for denitrifica-
tion dominated lakes are much "slower" than for algal domi-

nated lakes, the total amount of nitric acid consumed by deni-
trification can be substantial because the supply of nitrate is
not exhausted during summer when the denitrification rates
are fastest.

Thus in regions where nitric acid inputs are low, and most
of the strong acid input is sulfuric acid, algal assimilation will
predominate over denitrification. In regions where nitric acid
inputs are elevated, and nitrate is in excess in the surface
waters, such as in eastern North America and Europe, the
denitrification process will predominate and nitrate removal
should be modeled by the sediment area–denitrification ap-
proach [*Kelly et al.*, 1987]. In these regions, *Rudd et al.* [1986]
have estimated that nitric acid consumption by denitrification
produces 6 times as much alkalinity as does sulfuric acid con-
sumption by sulfate reducing bacteria.

MODELING ALKALINITY CHANGES ASSOCIATED WITH AMMONIUM TRANSFORMATIONS

Baker and Brezonik [1988] also modeled ammonium uptake
as a single process (algal uptake) based on lake volume. How-
ever, the comparison of their model results to measured values
was not statistically significant ($r^2 = 0.14$). This lack of agree-

TABLE 2. Sedimentation of Particulate Nitrogen in Lake 302S
and Lake 302N

Lake	Year	$[NO_3^-]$,* μmol/L	Sedimentation, mmol m^{-2} d^{-1}
302S	1982	0.5	2.5
302S	1984	0.8	3.0
302N	1982	16.4	1.3
302N	1984	42.4	1.9

At the time of these measurements, Lake 302S was being acidified
by additions of sulfuric acid, while Lake 302N was being acidified by
additions of nitric acid. Sedimentation was measured by suspending
duplicate cylindrical sediment traps with an aspect ration of 0.19 at
depths of 6, 8, 10, 11, and 12 m in the north basin and 6, 7, and 8 m
in the south basin. The traps were removed weekly and the contents
were analyzed by CHN analyzer.
*Mean annual epilimnetic nitrate concentrations.

ment may be due to their oversimplified approach. In the case of ammonium transformations, there are at least three situations all of which must be understood before a model should be constructed: (1) alkalinity consumption by algal ammonium assimilation during summer, which is limited by phosphorous availability; (2) alkalinity consumption during winter by nitrifying bacteria, which produce nitric acid from the excess ammonium not used by the algae; and (3) the effect of inhibition of nitrification by reduced pH, which will shift the ecosystem toward higher alkalinity values [Rudd et al., 1988].

Because algal ammonium assimilation is limited by phosphorous availability, modeling ammonium transformations is in some ways analogous to modeling nitrate removal. However, this modeling is more difficult because of the involvement of the nitrification process which is not well understood. The similarities and differences of nitrate and ammonium transformations were demonstrated by a whole lake experiment at ELA designed to examine the acidifying effect of adding various combinations of ammonium and phosphorous to lakes [Schindler et al., 1985]. When a combination of ammonium chloride, phosphoric acid, and sucrose was added to the lake, algal growth was stimulated and ammonium was assimilated by the algae resulting in acidification of the lake. Under these circumstances the volume related model of Baker and Brezonik [1988], which assumes ammonium assimilation by algae, would be appropriate. During the next phase of the experiment, the phosphoric acid additions were stopped while the ammonium chloride additions continued. This experimental regime was a closer simulation of the acid precipitation situation where ammonium input is elevated but phosphorous is not. Under these circumstances, the ammonium was in excess of algal requirements and it accumulated in the surface waters each summer. During the following winters, the ammonium was nitrified under the ice, causing acidification of the lake. This acidification was not caused by algae, but by nitrifying bacteria. At the present time, it is not known if nitrifiers are more active in the water column or the sediments of lakes. Thus we are unable to suggest whether a volume based model or a sediment-area-based model would be more appropriate. It is also not known what effect the time of year of acid production by ammonia uptake has on our abilities of modeling alkalinity consumption in lakes.

The ammonium model of Baker and Brezonik [1988] assumes that algae are the only organisms that consume alkalinity by ammonium uptake. Alkalinity consumption by nitrifying bacteria must also be considered. However, developing a model that would include nitrification is complicated by an incomplete understanding of the nitrification process in lakes and by our recent finding that the nitrification process was inhibited in two lakes experimentally acidified to pH 5.4–5.7 by sulfuric acid [Rudd et al., 1988]. This blockage of the nitrification process caused year-to-year increases in ammonium accumulation in the lakes, and destroyed one "sink" for alkalinity in the lakes by decreasing the acidification efficiency of incoming ammonium.

With further research on microbial transformations of nitrogen pollutants, it should be possible to build a comprehensive model of biological alkalinity production and consumption in lakes. The model must account for phosphorous limitation of algae in lakes. It should contain submodels for each microbial process responsible for permanently producing or consuming alkalinity. Submodels for alkalinity production by algal assimilation of nitrate and sulfate would follow directly

from the phosphorous model and N:S:P ratios of algae. Submodels for alkalinity production by bacterial processes such as sulfate reduction and denitrification are presently available [Baker et al., 1986; Kelly et al., 1987]. These submodels would be triggered by concentrations of nitrate and sulfate in the surface waters during summer. Because sulfate is always in excess of algal requirements, it would be permanently switched on. The denitrification submodel would only be triggered in lakes where there is excess nitrate during summer. The nitrification submodel requires further research. At the present time, we do not know if it should be sediment or water column based, but we know that it is inhibited at low pH.

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